

Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish in JACS after minor revisions.

Comments:

In this article, Liu and his colleagues present very interesting results on the synthesis of a stable plumbyne substituted with a phosphino group on its carbon atom. The authors have successfully demonstrated its unique behavior as a carbene source by showing its reactions with chlorotrimethylsilane and chlorostanylene, yielding the corresponding phosphinosilylcarbene and C-phosphino-stanylene, respectively. The article is very well written and all compounds are carefully characterized. The reviewer fully approves the publication of this article in JACS after a few minor revisions.

1) The title “Free Plumbyne” is misleading. It is recommended to use “Base-free C-phosphino plumbyne.”

2) The article by Saito, which reports on the synthesis of dilithiumplumbole featuring aromatic character and therefore a multiple C-Pb bond, should be cited. (Science, 2010, 328, 339-342. DOI: 10.1126/science.1183648)

Additional Questions:

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

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

Broad interest: Highest (top 5%, suitable for JACS)

Scholarly presentation: Highest (top 5%, suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: In Part

Reviewer: 2

Recommendation: Reconsider after major revisions.

Comments:

Liu and co-workers report on novel lead organometallic compounds featuring central alkyne-type structural motifs, which, through multiple-bond character between lead and carbon atoms, are interpreted as “plumbynes.” Establishing such a framework with distinct multiple-bond characteristics between C and Pb is a remarkable achievement, realized through the clever attachment of a phosphine unit to a diazo precursor. The release of N₂ appears to facilitate the clean formation of the “plumbyne”, benefiting from electronic delocalization.

This strategy closely parallels the authors’ previously reported “stannynes” (Nature Chem. 2024, 16, 1673), yet this does not detract from the novelty of the present work. The multiple-bond character is convincingly supported by reactivity studies and computational analysis. Particularly exceptional is the reported “plumbyne → stannyne

conversion”, which is remarkable as it involves the transfer of one tetrylene to another; a transformation that, to my knowledge, represents a unique example of what could be described as a “transtetrelation.”

The work has been carried out thoroughly, is clearly written in most parts, and is supported by a well-prepared Supporting Information section. The motivation for the study is effectively presented throughout the introduction. Overall, this is a solid and well-executed piece of research that will be of broad interest to the main-group and organometallic chemistry communities.

In conclusion, I consider this work potentially suitable for publication in JACS. However, I recommend that the authors carefully revise the manuscript according to the points raised, following a detailed proofread prior to acceptance.

Issues concerning the written manuscript and methodology:

- P.1: Line 34: “dissociation energy”. Do the authors refer to gas phase calculated values here? Or were they measured? Give a brief note.

- Figure 1 (and selected text). Statement of “poor hybridization”: Even though of course correct, it might be better to phrase as “s-p-separation significantly decreases directionality of bonding”. Note that hybridization itself starts failing for elements from third period on.

- Figure 1: Draw bonds to Dipp in grey as well. This just highlights the fragments of interest.

- Figure 1: Use the colors to highlight the modular C coordination towards Pb: Light blue: triplet carbene – yellow: multiply bonded.

- P.2: The first sentence here is too long for my taste containing too much information. Note that this sentence here covers five lines. Please rephrase and make more convenient to the reader.

- P-2 “... the $\nu(\text{CN}_2)$ absorption disappeared, consistent with N_2 extrusion and the formation...” Have the authors done in-situ IR studies here? Or had samples been isolated after a while of irradiation. Here, please be more precise if N_2 extrusion was monitored or rather observed upon isolation of products after irradiation.

- P4.: “...namely plumbyne \rightarrow stannyne” For me, this is a (remarkable) “transtetrelation” akin to for instance, transhalogenation. The consideration as “plumbyne \rightarrow stannyne” is a bit specific. If the authors have indication for further transtetrelation (i.e. to C, Si, Ge) please provide. This would further strengthen the manuscript.

- Figure 3: Add level of theory to the figure caption.

- P4.: “...our calculations indicate that homolytic cleavage of 3a to

[(CH₂)(NDipp)]₂Pb and ·Pb(C₆H₃-2,6-Mes₂) is strongly uphill ($\Delta G \approx +70.9$ kcal mol⁻¹)..." These calculations are a bit deficient. I guess either one expands this section i.e. with EDA to give more information, or one could remove this section without removing crucial information.

- General: "C₆H₃-2,6-Mes₂": potentially shorten to "MesTer"; C₆H₃-2,6-Trip₂: "TipTer" (the central motif is terphenyl).

- General: I was wondering if the authors have tried 207 Pb NMR for the compounds reported herein. It would be nice to have a spectroscopic feature "at lead". I cannot find any information on this in the SI.

- General: The authors have mentioned Munz's and co-workers work on a lead(II) substituted triplet carbene, which contrasts with the title compounds. Hence, it would be interesting to assess what the singlet-triplet gap is (i.e. what distinguishes the herein reported compounds from Munz's apart from the obvious ligand entities?). Please provide (vertical s-t gap is sufficient); I reckon this adds value to the present study.

- General: The title of the manuscript is "Free Plumbynes". Even though I don't see major issues in considering these compounds as plumbynes I would like to discuss a bit. Note that these compounds profit from P-coordination and delocalization. Only as such it was possible to establish the multiple-bonded framework. Hence, is it really fair to state that they are "free"? Maybe it would be more appropriate to be less definite here – such as "En route to an isolable Plumbyne" or alike? From my point of view "free" suggests something different.

Issues concerning cited literature:

- Seminal work by Couret should be introduced to the manuscript. This work is certainly related. DOI: 10.1002/1521-3773(20010302)40:5<952::AID-ANIE952>3.0.CO;2-S

Issues concerning the experimental part and SI:

- Page S3: The authors have performed HRMS: What method was used? Several types of Ionization could be meant here, please clarify.

- I like that the authors address potential hazards due to spontaneous N₂ release (i.e. akin to azides). However, the note on page S3 should be written in bold; as such it gets more attention.

- ¹³C{¹H}: write without space bar (some instances)

- Please indicate whether the ³¹P NMR spectra are coupled or decoupled with ¹H.

- Major issue: X-ray structure of 2a. Even though R-values don't inevitably represent a "good crystal" I am at this point concerned about the quality of the structure. I don't

find any explanation on why the structure appears with higher R-values as usual. It is a common feature to give a brief comment in the X-ray crystallographic section of the SI explaining the reader what the issue is with these crystals. Note that not only Alerts “A” and “B”, but generally issues with the crystal structure refinement should be discussed. Please clarify or ideally provide “better” data. Also note that the temperature given in the .cif is 180K, the one in the SI is 100K. Please clarify as well. If measured at 180K: Why? Furthermore, restraints were employed for refinement. This is perfectly fine, the number of restraints urges for legitimation, though. Also here, “cifcheck” does not urge the authors to do differently, however, I recommend clarifying that.

- Major issue: The atom labelling of compound 3a, 4,: the labelling differs from the one used in the main manuscript. This needs to be changed for the sake of clarity. It is a common practice to have the same labelling for both: Manuscript and CCDC deposition. Please revise the respective .cif files.

- Major issue: The crystal structure of 6 contains bromine. In several instances this compound is only considered as its chlorine derivative throughout the manuscript. Due to the presence of bromine, there is positional disorder between the Cl and Br atoms which required the use of an EXYZ constraint. This needs to be discussed. Also, note that due to the positional disorder only parts of this crystal refers to “6” (the Cl derivative) whereas the other part is (ArPbBr)₂. In this regard, the reviewer is concerned that bromide impurities might be kept throughout the preparation of compounds. Note: No bromide source can be found for the procedure yielding 6! Please have a close look.

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?: In Part

Reviewer: 3

Recommendation: Publish in JACS after minor revisions.

Comments:

This manuscript by Liu and co-workers reports the isolation and characterization of the first free, stable plumbynes. This work represents an impressive extension of the authors’ earlier research on free stannyne chemistry (Nat. Chem. 2024, 16, 1673), further pushing the boundaries of heavy main-group multiple-bond systems. The authors provide convincing crystallographic, spectroscopic, and computational evidence supporting the existence of a multiply bonded P–C–Pb unit, thereby achieving

a Pb–C multiple bond that has long remained elusive in the literature. Notably, the reported species exhibits divergent reactivity, undergoing either saturation or bond cleavage; the former reinforces the multiple-bond character of the title compound. Given the synthetic challenges associated with well-defined Pb–C multiple bonds and the ongoing interest in heavy main-group multiple bonding, I consider this study to be of great importance and recommend publication in JACS after minor revision.

1. In the Introduction, while the authors list several examples of organolead compounds featuring multiple bonding at Pb—including diplumbenes, diplumbynes, and phosphinidene-plumbylene species—I suggest adding examples of heavier metal carbyne complexes, specifically $\text{ArPb}\equiv\text{Co}(\text{PMe}_3)_3$ (Angew. Chem. Int. Ed. 2023, 62, e202305951) and $\text{ArPb}\equiv\text{Rh}(\text{PPh}_3)(\text{PMe}_3)_2$ (Angew. Chem. Int. Ed. 2021, 60, 5882–5889). These feature formal Pb–metal triple bonds and would provide valuable context.

2. Compared to compound 2a, the compressed bond angles at C(1) and Pb(1) in 3a ($131.4(2)^\circ$ vs. $138.7(7)^\circ$ at C(1); $97.70(12)^\circ$ vs. $107.20(11)^\circ$ at Pb(1)) are notable. Could the authors comment on the origin of this difference? Typically, greater multiple-bond character correlates with more obtuse bond angles, as seen in the trend from ethane to ethene to ethyne.

3. Regarding the reactivity of 2a, bond metathesis yields carbene and stannyne products, and the authors have excluded homolytic C–Pb bond cleavage based on EPR data and the calculated uphill ΔG . Could the authors provide additional data on the bond dissociation energies (BDEs) for both homolytic and heterolytic cleavage pathways of the C–Pb bond?

4. For clarity and completeness, it is recommended to explicitly provide the yields of all newly synthesized compounds in Figures 2 and 4. This information is important for readers to assess the efficiency and cleanliness of the reactions.

5. In Figure 2a, it would improve clarity if the independent structures of 1a and 1b were clearly referenced.

6. In Figure 2b, please verify the thermal ellipsoids of 2a, as the atomic displacement parameters appear significantly larger than those in 3a (Figure 2c).

7. Please ensure that the chemical equations in Figures 2a and 4a are balanced.

8. For resonance weights, using the “approximately equal” symbol (\approx) may be more appropriate than a single wavy line.

9. In the abstract, please revise “single Pb–C bonds” to “Pb–C single bonds” for grammatical accuracy.

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Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: In Part

Reviewer: 4

Recommendation: Publish in JACS after minor revisions.

Comments:

The manuscript by Liu and colleagues describes thermally stable compounds with a PbC unit, which may be viewed as alkyne analogues or plumbynes, because both atoms are strictly dicoordinate and their interaction has considerable bond multiple-bond character. The work presented in the manuscript is in continuation of a previous study of the Liu group, which has resulted in the publication of an analogous tin compound (stannyne), as described in ref. 17. The manuscript is very well written, and the level of scholarly presentation is high. The results are of substantial interest to a broad audience and, in view of their fundamental nature and general significance, will undoubtedly find their way into chemistry textbooks. I support publication in JACS, provided that the authors take care of the following minor issues:

p.1, left column: Lead is certainly not “the heaviest member of group 14”. I suggest replacing this by “the heaviest stable member of group 14”.

p.1, left column: The authors claim that “there are essentially no isolable, molecular Pb=E (E = heteroatoms such as N, O, etc.) double bonds.” This is an oversimplification. JACS 2008, 130, 5648 and Angew. Chem. Int. Ed. 2015, 54, 11283 describe PbO and PbSe containing compounds with partial double bond character. These papers should be referenced and used for a more balanced description of this topic.

p.2, Figure 2(a): hv is very general and should be replaced by UV. The UV light source used should be explicitly mentioned in the SI. It is unclear from the wavelengths given in the SI (“254 nm, 352 nm, 302-313 nm, and 340 nm”), whether a single UV light source has been used or a combination of two or more.

p.3, right column: The longest Pb–C bond reported for carbene–plumbylene adducts is indeed 2.585(5) Å in the CAAC adduct described in ref. 25b. However, the shortest such bond is 2.418(3) Å in an NHC adduct described in Angew. Chem. Int. Ed. 2019, 58, 1387, which should be referenced instead of, or in addition to, ref. 25a.

p4, right column: I think that “chloride abstraction at Pb in 3a” is misleading (no Cl atom present in 3a) and should be replaced by ‘chloride abstraction by Pb in 3a’.

Additional Questions:

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Scholarly presentation: High (suitable for JACS)

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