Recommendation: Publish in JACS after minor revisions.

Comments:
The anion [P(CN)$_2$]($^-$) is a known phosphorus(1+) compound and the authors decided to make it by careful and efficient electrochemical oxidation of P$_4$ using HCN (provided in situ by Me$_3$SiCN/LiOH). The authors go on to show that [P(CN)$_2$]($^-$) is a useful source of phosphorus for the synthesis of various interesting organophosphorus compounds. This is an ingenious piece of work.

1. Figure 2 needs to be re-drawn in order to show clearly the half-reactions that the authors are proposing take place at the anode and at the cathode. Clearly the HCN is proposed to be converted to H$_2$ and cyanide, consistent with the authors characterization of the HCN as the "electrochemical oxidant". Has HCN ever been used in this manner in an electrochemical reaction? If so, the authors should provide some literature references in order to properly contextualize their work. Could another cyanide source, such as cyanogen, be used in place of HCN in this synthesis?

2. The experimental section should say what was the commercial source of the P$_4$. This compound used to be commercially available but is not any more in many parts of the world because it is a controlled substance.

3. The SI section 1.2 mentions observation of HCN. HCN is a highly toxic gas. This section should be updated with an appropriate safety note. Researchers should not be exposed to HCN. The safety issues ought to be mentioned in the manuscript text as well.

4. In SI section 1.2 Sample A, the authors mention use of 15.3 mg of P$_4$ but give the mmol as 0.5. Note, this is the mmol of P atoms, not P4 molecules. The authors should update the experimental section to give the correct mmol for formula units.

5. The authors report that the value of x is 1.1 in the formula reported for Li(dioxane)$_x$P(CN)$_2$. This formula should be confirmed by elemental analysis (CHN combustion analysis) as should be all the new compounds reported in the present work, for completeness of characterization.

6. In the manuscript it states that the Li(dioxane)$_{1.1}$P(CN)$_2$ is obtained "as an analytically pure product" but no elemental analysis (CHN combustion analysis) was reported. This should be corrected. If the value of x is 1.1, why is it shown as 0.8 in Figure 4?

7. In the preparative description, the authors report washing with a mixture of THF and dioxane, and then obtaining the product after evaporating the solvent from the combined filtrates. Why is the product formulated as only containing dioxane solvent and not any THF?

8. The authors report making the Na and K salts of [P(CN)$_2$]($^-$) from P(CN)$_3$. Was this P(CN)$_3$ synthesized from PCl$_3$? If so, this should be clearly stated in the manuscript because it goes against their main point of making the anion by oxidation of P$_4$ and without the intermediacy of PCl$_3$.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation: Moderate (not suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: In Part

Recommendation: Publish in JACS after minor revisions.

Comments:
Liu and coworkers present an impressive and well-written study on the conversion of P4 to the P(CN)2 anion and the synthetic potential of this anion. They finetune and expand the work the group of Smidpeter reported in the late 1970s and early 1980s (ref. 11-13). It is intriguing to see this 'dated' work getting the attention it deserves. It is not surprising to see electrochemistry play a key role in the selective conversion of white phosphorus, but the demonstrated selectivity is. In so doing I feel that the authors are somewhat overselling their finding, all how relevant it may be.

1. Solid points are made to eliminate the use of both PCl3 and PH3 in the conversion of white phosphorus to organophosphorus. However, the proposed use of a HCN surrogate (2Me3SiCN and LiCl) is also a matter of concern for safety and economic reasons to truly scale up the reaction, but the findings are intriguing.

2. The authors should compare their calculated structure of the P(CN)2 anion with the X-ray crystal structure reported by Smidpeter. The paragraph under Figure 5 (“In addition,…apparently inert”) begs for a computational analysis and this should be provided.

3. Ref. 18 should give the proper reference to the work of Kulkarni et al. in Chem. Eur. J. 2021, 27, 200 instead of referring to a frontispiece.

4. The structure analyses given the SI are fine and the NMR spectra are clean, suggesting pure compounds. However, for many if not all IR frequencies, UV maxima, mass spectra, and melting points are missing. Ultimately, such data are or will become relevant not only for experimentalists but also for theoreticians.
Additional Questions:
Significance: Highest (top 5%, 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

Recommendation: Reconsider after major revisions.

Comments:
Liu and co-workers report on the transformation of P₄ into useful organophosphorus compounds (OPCs) with high P atom economy via the anion [P(CN)₂]⁻. This anion is synthesized directly from P₄ through an electrochemical procedure using hydrogen cyanide (HCN, generated in situ from Me₃SiCN and LiOH) as the oxidant in an undivided cell. The isolation of the dicyanophosphide anion salt Na(18-C-6)[P(CN)₂] dates back to 1977, but its chemistry has been hardly investigated likely due to the lack of efficient synthetic routes for large scale syntheses. The authors claim that the reported electrochemical synthesis of Li(dioxane)xx[P(CN)₂] (1) is a practical approach to generate the dicyanophosphide anion on a gram scale. It appears that heavier alkali metal salts M[P(CN)₂] (M = K, Na) cannot be isolated using the electrochemical procedure. Alternatively, M[P(CN)₂] (M = Li, Na, K) were generated by the reduction of P(CN)₃ with the corresponding alkali metals.

Reactivity studies of [P(CN)₂]⁻ towards neutral and anionic carbon-based nucleophiles afforded selectively useful OPCs, such as phosphinidenes, cyclophosphanes and phospholides, which are already know in the literature with other substituents. In contrast to the syntheses known in the literature, the use of 1 avoids multiple steps and harsh conditions.

However, I am not convinced that the reported electrochemical method for P₄ functionalization is as practical and versatile as claimed by the authors. Upon inspection of the experimental section,
it seems obvious that the follow-up reactions were carried out with the material generated from P(CN)$_3$ (i.e. ultimately from PCl$_3$) rather than with the material generated by electrolysis. Material with a 1,4-dioxane content of 0.8 equiv. per Li[P(CN)$_2$] was used for the reactivity studies. This clearly is the material generated from PCl$_3$. The phosphide generated from P$_4$ has a higher 1,4-dioxane content. The purity of the Li[P(CN)$_2$] obtained from the large scale electrochemical reaction should be unequivocally confirmed, and the utility of this material for the synthesis of OPCs (instead of the material obtained from PCl$_3$) needs to be demonstrated. Otherwise, the practicality of the reported method remains in doubt.

Unfortunately, the level of characterization of some of the reported compounds does not meet the standard expected for a JACS paper. Some important data are missing in the SI (see below for details). The purity of the compounds is not sufficiently demonstrated. Specifically, elemental analysis and IR should be reported, because the purity of the compounds cannot be proven only by NMR alone when NMR silent side products such as KCN and LiCN are formed. Furthermore, while compounds 6 and 7 are mentioned in the manuscript, their analytical data are completely missing in the SI! Although the manuscript is generally well-written, some revisions are also necessary to the main text (see my detailed comments below).

In conclusion, this manuscript presents a promising method for converting P$_4$ into the dicyanophosphide anion. However, the practicality and versatility of the method for the synthesis of useful OPCs via [P(CN)$_2$]$^-$ has not been convincingly demonstrated as yet. The authors need to show that the material accessed from P$_4$, LiCN, Me$_3$SiCN, LiOH and electricity can actually be used for the synthesis of OPCs. It is not good enough to use the material obtained from PCl$_3$ for the follow-up chemistry. Unfortunately, the level of characterization of some of the OPCs and technical quality of the supporting information are also lacking. As such, I am currently only able to support publication of this manuscript after major revision.

The following major issues should be addressed upon revision:

1. The authors should demonstrate the purity of Li[P(CN)$_2$] obtained in the large scale electrochemical synthesis (sample E) by multinuclear NMR, IR spectroscopies and elemental analysis. The characterization of the reported compounds is incomplete. Elemental analysis is missing for all synthesized compounds. EA should be given for compounds 1-12. Even though the NMR spectra indicated analytically pure compounds, only the elemental analysis can prove the purity. In most of the reactions side products such as LiCN and KCN would not be seen in the NMR spectra, but the elemental analysis would show these impurities.
2. They need to show that the [LiP(CN)\(_2\)] obtained from P\(_4\) is suitable for the efficient preparation of compounds 2-12 (instead of the material obtained from P(CN)\(_3\), i.e. ultimately from PCl\(_3\)).

3. Please explain how the dioxane content of each compound containing dioxane was determined!

4. IR spectra need to be included for compounds 1-6 due to the presence of a diagnostic CN vibration.

5. What is the mechanism of formation of [P(CN)\(_2\)] from P\(_4\)? The authors seem to suggest that the oxidation of P\(_4\) followed by nucleophilic attack is the general mechanistic scenario. I would argue that the oxidation of cyanide to form cyano radicals or dicyan (NC-CN) is much more likely to occur. These species would then attack P\(_4\) to ultimately form [P(CN)\(_2\)].

In addition, there are a number of more minor, but still significant issues that should be addressed:

Main text
6. I have found several typos and inconsistencies in the manuscript (e.g. Page 2, left column, line 31 and 41: missing brackets in LiP(CN)\(_2\). Please proofread carefully.

7. The word ‘unprecedented’ is overused.

8. Figure 1, section (b) could be more clearly arranged, so the three reactions should be marked or numbered to get a better connection to the main text.

9. In the abstract it is the first time P\(_4\) is mentioned, so maybe change text to ‘…transformation of white phosphorus (P\(_4\)) into…’.

10. The electrochemical generation of analytically pure M[P(CN)\(_2\)] (M = K, Na) using KOH or NaOH, instead of LiOH was not successful because of the lack of appropriate electrolytes to maintain the conductivity. Which electrolytes were investigated to generate M[P(CN)\(_2\)] (M = K, Na)? I would suggest to add a short section to the SI about the attempts to generate M[P(CN)\(_2\)] (M = K, Na).

11. Page 3, left column, line 2: please mention that these chemical shifts occur in C\(_6\)D\(_6\).

12. Compound 2 is already known with MeNHC. Please mention this in the manuscript and cite citation 13(a) at this point in the text.

13. Page 3, right column, lines 10 – 12: Have the authors actually tried this reaction in the absence of cyanide 200 °C or just cited literature? If this is only cited, please write: “As Baudler et al. reported in 1984, in the absence of cyanide the thermal arrangement of 7 to 8 requires much higher temperatures.”\(^{21}\).

14. The numbering of compound 5 is inconsistent, see Figure 5b: solid state structure of 5 contains (18-C-6), but in the following text the compound is named 5(18-C-6).

15. It should be mentioned in the text that 8 was only identified comparing the \(^{31}\)P NMR of the isolated crystals with the literature.
16. In the formation of 9, can the analogous monomer to 6 (namely Li(Ar)PCN) be observed by NMR? Add the NMR spectrum of the reaction mixture to the SI.

17. Figure 7: synthesis to compound 10. In the SI there is another step adding tBuCl and stirring the mixture at 60°C for 1.5 h. Please add these details to the reaction scheme shown in Figure 7.

18. Section 1.2: Sample A-E: ‘P4 (15.3 mg, 0.50 mmol)’ 15.3 mg of P4 would be 0.12 mmol, not 0.50 mmol. Please define all molar amounts referring either to P4 or per P-atom!

19. Section 1.2: Sample A-E: Were the reaction mixtures of sample A-E also subjected to $^{31}$P NMR studies? Are the different procedures selective and clean reactions or do they show some side products?

20. Please give the molecular weight of the products.

21. Section 1.3: Would be easier for the reader if both organo-dilithium reagents and the 3,3'-dibromo-2,2'-bithiophene would be numbered in the manuscript (Figure 7) and the ESI.

22. Section 1.3: Synthesis of P(CN)$_3$: ‘The light-yellow solid was washed ‘with' hexane…’.

23. Section 1.3: Synthesis and analytical data of compounds 6 and 7 are completely missing. Have there been any attempts to isolate and characterize both compounds? Please record a VT reaction NMR to confirm the formation of species 6 and 7 NMR spectroscopically. Please add missing details to the SI!

24. ‘The combined filtrates and wash solutions was were evaporated to dryness.’ This sentence is repeated in almost every synthetic procedure, so please change the ‘was’ to ‘were’ in all cases.

25. I have found several typos and inconsistencies in the SI. For example, missing spaces for most of the time data. Inconsistence in naming compound 1. Please proofread carefully.

26. The NMR spectra (section 3) could be presented in a better way, most of the spectra extend beyond the given boxes. No temperature of the recorded NMR spectra is given, and the deuterated solvents should be labeled in the NMR spectra (e.g., marked with a * and mentioned in the caption or directly labeled in the spectra).

27. $^{1}J_{HH}$ are only given as $^{1}J$! Please correct this!

28. Inconsistencies concerning the P-C coupling constants: Sometimes they are given as $^{1}J_{PC}$, sometimes as $^{1}J_{PC}$, sometimes as $^{1}J_{PC}$, please proofread carefully!

29. Were the NMR assignments done using 2D techniques? If yes, mention this! If not, record the 2D spectra and assign the unassigned signals!

30. Section 3: In some of the $^{1}$H NMR spectra are some impurities (e.g., Figure S10, S16, S37, S40), but are neither mentioned in the experimental section, nor in the caption. So, if there can be seen some impurities in the NMR the elemental analysis will be probably off. Please check!

31. Section 3: In Figure S44 there is a huge grease peak compared to the tBu signals (38H). Can the grease be removed? Such a large amount of grease is unacceptable for a ‘pure compound’,
and it raises doubts concerning the suitability of the purification procedure. Note that the $^{13}$C NMR spectrum is missing, please add these data!

32. Give the probability level for the thermal ellipsoids for each structure.

33. Mention in the captions that hydrogen atoms and solvent molecules are omitted for clarity.

34. Give selected bond lengths and angles of the structures.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation: Moderate (not suitable for JACS)

Are the conclusions adequately supported by the data?: No

Are the literature references appropriate and correct?: Yes