

Chemoselective Facile Synthesis of the Dicyanophosphide Anion via Electrochemical Activation of White Phosphorus: An Avenue to Organophosphorus Compounds

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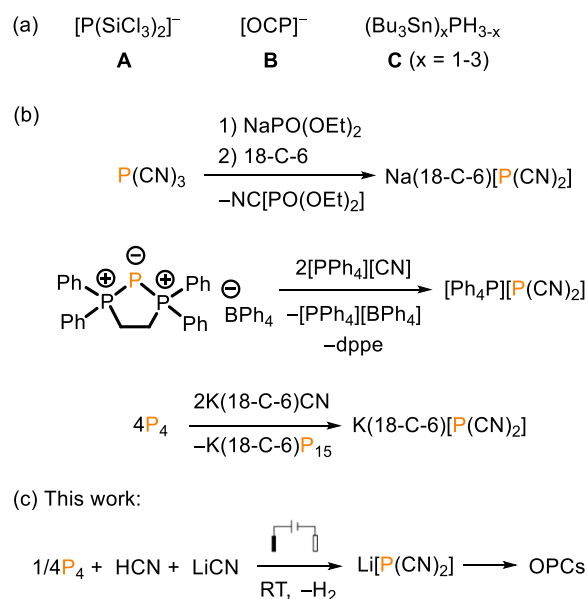
Supporting Information Placeholder

ABSTRACT: Organophosphorus compounds (OPCs) have gained tremendous interest in the past decades due to their wide applications ranging from synthetic chemistry to materials and biological sciences. We describe herein a practical and versatile approach for the transformation of P₄ into useful OPCs with high P atom economy via a key bridging anion [P(CN)₂][−]. This anion can be prepared on a gram scale directly from P₄ through an unprecedented electrochemical process. A variety of OPCs involving phosphinidenes, cyclophosphanes and phospholides have been made readily accessible from P₄ in a two-step manner. Our approach has a significant impact on the future preparation of OPCs in laboratory and industrial settings.

Organophosphorus compounds (OPCs) are widely used as herbicides, flame-retardants, ligands, pharmaceuticals, detergents, and photo-initiators.¹ Currently, their industrial syntheses demand two phosphorus transfer reagents, namely phosphorus trichloride (PCl₃) and phosphine gas (PH₃). PCl₃ is a highly corrosive liquid, which is produced by oxidation of white phosphorus (P₄) with toxic chlorine gas. The preparation of OPCs via PCl₃ involves stepwise displacement of the chloride atoms, and thus inherently has low selectivity and efficiency while concurrently generating chlorine containing waste.² Catalytic transformation of PH₃ into OPCs is less preferred as PH₃ is an extremely toxic gas and its synthesis from P₄ requires harsh reaction conditions.²⁻³ To bypass PCl₃ and PH₃, tremendous efforts have been devoted into investigating direct functionalization of P₄,⁴ whose industrial production is on a scale of more than 10⁶ tons per year. However, preparation of OPCs directly from P₄ remains extremely challenging; they generally suffer from low selectivity and conversion efficiency or only lead to partial breakup of the P₄ tetrahedron.⁵ A recent breakthrough by the group of Wolf disclosed that the direct catalytic transformation of P₄ into arylphosphines and phosphonium salts via photo-redox catalysis.⁶

Development of phosphorus transfer reagents other than PCl₃ and PH₃ is a promising strategy for the syntheses of OPCs and other value-added phosphorus-containing chemicals. To this end, Cummins and co-workers demonstrated that the bis(trichlorosilyl)phosphide anion [P(SiCl₃)₂][−] (A, Figure 1a) derived from phosphates is capable of producing OPCs.⁷ The Grützmacher and Goicoechea groups independently synthesized a large array of unprecedented phosphorus frameworks via the 2-phosphaethynolate anion [OCP][−] (B, Figure 1a).⁸ More recently, Wolf *et al.* reported the synthesis of monophosphines from hydrostannyl phosphines (Bu₃Sn)_xPH_{3-x} (x = 1-3) (C, Figure 1a) resulting from the direct activation of P₄ with stannyl radicals.⁹ Although chemical reactions for P₄

activation have been explored in depth over the past decades, practical electrochemical activation of P₄ is still in its infancy.¹⁰ The electrocatalytic C–P bond formation using transition metal catalysts with sacrificial metal electrodes as reducing reagents have been reported.¹⁰



Ambient conditions; High yield; Atom economy; Undivided cell

Figure 1. (a) Selected examples of phosphorus transfer reagents. (b) Known methods to generate [P(CN)₂][−]. (c) Electrochemical synthesis of [P(CN)₂][−] from P₄.

The isolation of the dicyanophosphide anion salt Na(18-C-6)[P(CN)₂] (18-C-6 = 18-crown-6) dates back to 1977 by the group of Schmidpeter but its chemistry has been scarcely investigated likely due to the lack of efficient synthetic routes for large scale syntheses.¹¹ The known procedures include the reduction of P(CN)₃ with NaPO(OEt)₂,^{11a} the ligand exchange of [dppeP][BPh₄] (dppe = bis(diphenylphosphino)ethane) with cyanides and the disproportionation of P₄ with K(18-C-6)CN.¹² These are typically associated with low efficiency and poor atom economy (Figure 1b). A handful of reports described the displacement of the cyano groups of [P(CN)₂][−] by carbon- or/and phosphorus-based anionic nucleophiles and the halide substitution of 2-chloro imidazolium salts and alkyl iodides.¹³

We herein present the unprecedented chemoselective facile synthesis of $[\text{P}(\text{CN})_2]^-$ via electrochemical activation of P_4 at room temperature using hydrogen cyanide (HCN) as the oxidant in an undivided cell (Figure 1c). The electronic structure of $[\text{P}(\text{CN})_2]^-$ is examined by DFT calculations. The utility of $[\text{P}(\text{CN})_2]^-$ towards neutral and anionic carbon-based nucleophiles selectively affords scarcely accessible OPCs, such as cyano-phosphinidenes, cyclophosphanes and phospholides. These pave a straightforward path for facile bridging of OPCs from P_4 .

The nucleophilic disproportionation of P_4 by $\text{K}(\text{18-C-6})\text{CN}$ in boiling MeCN can generate $\text{K}(\text{18-C-6})[\text{P}(\text{CN})_2]$ but at the cost of losing 15 equivalents of phosphorus (Figure 1b).^{12b} We hypothesized that the controlled oxidation of P_4 in the presence of cyanides might selectively afford $[\text{P}(\text{CN})_2]^-$. Specifically, electrochemical methods may be able to delicately control the oxidation from $\text{P}(0)$ to $\text{P}(+1)$ with the proper voltage. Hydrogen cyanide (HCN), which is industrially produced, was postulated to work as the electrochemical oxidant and a cyanide source. However, to avoid the direct handling of HCN gas the combination of Me_3SiCN with LiOH as a HCN surrogate was employed. This reaction also generated LiCN and $(\text{Me}_3\text{Si})_2\text{O}$ (Figure S1) and the former provides another equivalent of cyanide needed for the subsequent electrolysis.

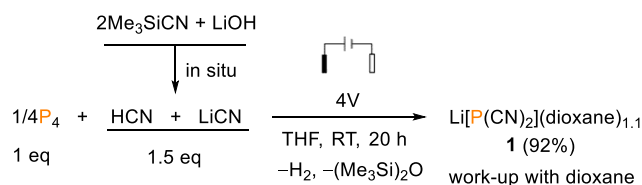


Figure 2. Electro-oxidation of P_4 to $\text{LiP}(\text{CN})_2$.

An undivided cell at room temperature was equipped with graphite and platinum electrodes as the respective anode and cathode, then a THF solution of P_4 , Me_3SiCN and LiOH was subjected to electrolysis at 4V voltage (Figure 2). ^{31}P NMR analysis of the aliquots of the reaction mixture indicated the selective conversion of P_4 to $[\text{P}(\text{CN})_2]^-$ (-196.7 ppm) and no other phosphorus-containing products or intermediates were observed. The electrolysis was complete within 20 h and subsequent workup with dioxane gave $\text{Li}(\text{dioxane})_{1.1}[\text{P}(\text{CN})_2]$ (**1**) as an analytically pure product in 92% yield. It is important to note that the reaction can be scaled up to make grams of $\text{LiP}(\text{CN})_2$.

No conversion was observed after stirring the same mixture for 10 h without electrolysis. In the presence of 50% mol LiCN , complete conversion of P_4 took a shorter time (10h) and gave a similar yield. Mechanistically, P_4 is oxidized to form $[\text{P}(\text{CN})_2]^-$ on the anode and HCN is reduced to dihydrogen on the cathode. Gas bubbles was observed from the Pt electrode during the electrolysis. An analogous reaction using MeCN as solvent gave the same product and the formation of hydrogen was observed by ^1H NMR spectroscopy (Figure S2). A similar redox reaction occurred via the combination of P_4 with Me_3SiCN under the same conditions and the byproduct $(\text{Me}_3\text{Si})_2$ was observed by ^1H NMR spectroscopy. While we were able to observe the generation of $\text{M}[\text{P}(\text{CN})_2]$ ($\text{M} = \text{K}, \text{Na}$) using KOH or NaOH , instead of LiOH , the lack of appropriate electrolytes to maintain the conductivity obscures the isolation of analytically pure $\text{M}[\text{P}(\text{CN})_2]$.

Alternatively, $\text{M}[\text{P}(\text{CN})_2]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) can be obtained by reduction of $\text{P}(\text{CN})_3$ with the corresponding alkali metals (See SI for details). Stirring a mixture of $\text{P}(\text{CN})_3$ with Li, Na or K in THF at room temperature followed by extraction using dioxane gave the corresponding salts $\text{M}[\text{P}(\text{CN})_2](\text{dioxane})_x$ ($\text{M} = \text{Li}, x = 0.8; \text{M} = \text{Na}, x = 0.5; \text{M} = \text{K}, x = 0$) in good yield (65-90%). The combination of

such salts with 18-crown-6 gave the ensuing $\text{M}(\text{18-C-6})[\text{P}(\text{CN})_2]$ ($\text{M} = \text{Na}, \text{K}$). All these salts can be stored in the solid state under inert atmosphere over a week without noticeable decomposition.

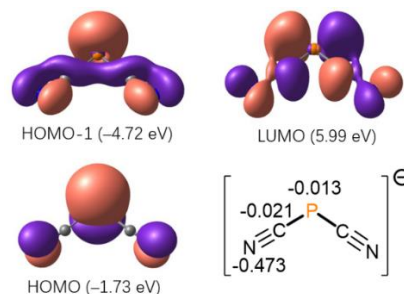


Figure 3. Frontier orbitals and NPA charge distribution of $[\text{P}(\text{CN})_2]^-$.

The electronic structure of the $[\text{P}(\text{CN})_2]^-$ anion was probed by density functional theory (DFT) calculations (M06-2X/def2-TZVP//M06-2X/def2-SVP) (Figure 3). The HOMO-1 (-4.72 eV) and HOMO (-1.73 eV) are predominantly the in-plane and out-of-plane P lone pairs, respectively, while the LUMO exhibits features of π^* orbitals over the anion with the major contribution of P. The natural population analysis (NPA) reveals that the anionic charges are considerably located at two N atoms (-0.47 a.u.) whereas the P atom bears almost no net charge (-0.01 a.u.). The Wiberg bond indices (WBIs) of P-C and C-N bonds are 1.1 and 2.8, respectively. Collectively, these results demonstrate the ambiphilic nature of P.

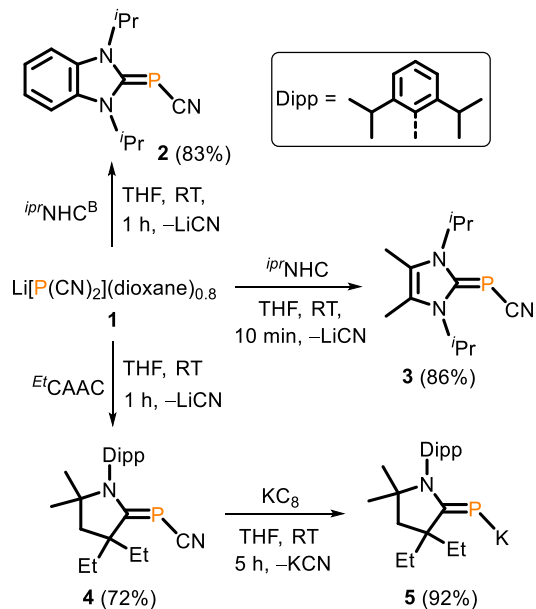


Figure 4. Reaction of $[\text{P}(\text{CN})_2]^-$ with NHC/CAAC and the reduction of **4**.

We then investigated the synthetic potential of $[\text{P}(\text{CN})_2]^-$ for OPCs using carbon-based nucleophiles. Albeit the $[\text{P}(\text{CN})_2]^-$ has an overall anionic nature, treatment of **1** with various neutral carbon nucleophiles (i.e. N-heterocyclic carbene (NHC) and cyclic(alkyl)(amino)carbene (CAAC)) gave rise to base-stabilized phosphinidenes **2-4**, concurrent with the elimination of LiCN . The ^{31}P NMR spectra of **2**, **3** and **4** consist of a singlet at -133.7 , -154.0 and -59.6 ppm, respectively. Further confirmation of structures of **2-4** was carried out with single crystal X-ray diffraction (Figures 5a and S5,6), which reveals that the $\text{C}(1)\text{-P}(1)$ bond length in **4** ($1.748(2)$ Å) is significantly shorter than those of **2** ($1.805(2)$ Å)

and **3** (1.821(3) Å). These are consistent with the enhanced π -accepting ability of CAACs compared to NHCs.¹⁴ The formation of **2-4** indicates the facile replacement of LiCN with nucleophilic carbenes, reminiscent of examples of ligand exchange reactions at a phosphinidene described by Bertrand et al.¹⁵ Notably, while the chemistry of base-stabilized phosphinidenes is quite rich, their syntheses usually require multiple steps and relatively harsh conditions.¹⁶ Our synthetic route represents a two-step procedure accessing rare examples of cyano-substituted phosphinidenes from white phosphorus.

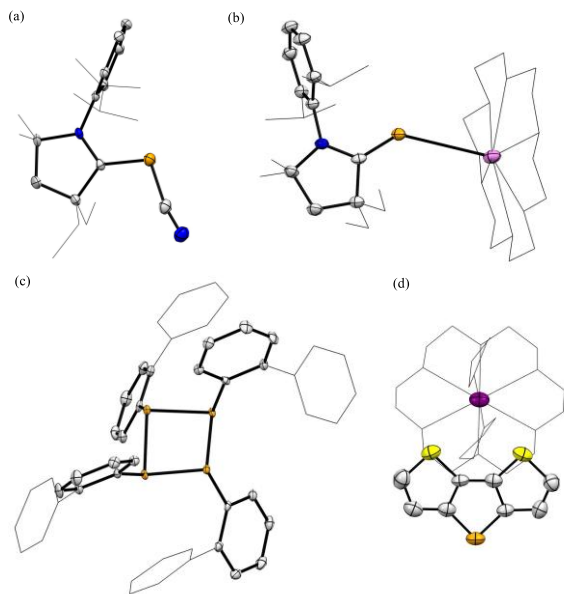


Figure 5. Solid-state structures of **4** (a), **5** (b), **9** (c) and **12** (d). C: grey; N: blue; P: orange; S: yellow; K: violet; Na: purple. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

In addition, reduction of **4** with excess KC_8 at ambient temperature in THF for 5 h afforded species **5**, which was after workup isolated as an orange solid in 92% yield. The ^{31}P NMR resonance of **5** (203.9 ppm) is comparable to those observed for $[\text{MeCAAC=PLi}]_2$ (179.3 ppm)¹⁷ and $[\text{CyCAAC=PK}]_2$ (206.9 ppm).¹⁸ X-ray quality single crystals of **5**(18-C-6) were obtained via addition of 18-C-6 to a toluene solution of **5** (Figure 5b). In contrast to the dimeric structures of $[\text{MeCAAC=PLi}]_2$ and $[\text{CyCAAC=PK}]_2$, **5**(18-C-6) represents a rare example of a monomeric carbene-stabilized P[−] anion. The conversion of $[\text{P(CN)}_2]^-$ to $[\text{E}^{\text{t}}\text{CAAC=P}]^-$ can be viewed as a formal “P[−]” anion delivery to carbenes, and thus showcases huge potential of $[\text{P(CN)}_2]^-$ for P atom transfer reactions. However, the formation of **5** is unique as the analogous reaction of **2** or **3** with KC_8 is apparently inert.

Next, attempts to efficiently synthesize cyclophosphanes were undertaken (Figure 6). These species with a small P_n ($n = 2-5$) ring are usually prepared via reduction reactions of mono-substituted phosphorus dichlorides with undesirable reagents (e.g. alkaline-earth reductants), which typically suffer from low chemoselectivity and operational complexity for purification.¹⁹ Dropwise addition of $^t\text{BuLi}$ to a THF solution of $\text{Li[P(CN)}_2]\cdot(\text{dioxane})_x$ at -35°C forms an intermediate **6** (^{31}P NMR: -89.9 ppm) that upon warming up to room temperature smoothly converted into two products (^tBuP)₃ **7** (^{31}P NMR: -70.5 and -109.5 ppm) and (^tBuP)₄ **8** (^{31}P NMR: -57.1 ppm) in a molar ratio of 1:1.²⁰ Heating the reaction mixture at 70°C for 24 h resulted in complete conversion into **8**. As early work by Schmidpeter and co-workers described the reaction of $\text{K[P(CN)}_2]$

with PhLi leading to an equilibrium of M[PhPCN] ($\text{M} = \text{Li}$ or K) and the pentaphenyl pentaphospholane (PhP)₅,^{13c} the cyanide anion in the reaction mixture is proposed to promote the transformation of **7** to **8**. Indeed, in the absence of cyanide the thermal rearrangement of **7** to **8** requires much higher temperature (i.e. 200°C).²¹ In a similar vein, we reacted ArLi ($\text{Ar} = 1,1'$ -biphenyl-2-yl) with **1** at room temperature to give (ArP)₄ **9** in 76% yield (Figures 5c and 6b). In this case, no cyclotriphosphane (ArP)₃ was observed.

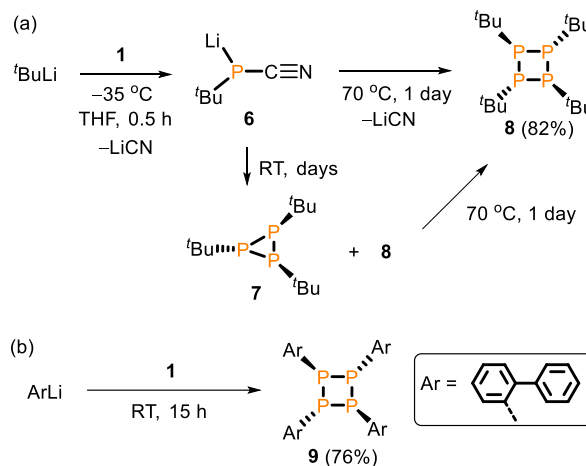


Figure 6. Reaction of organolithium reagents with $[\text{P(CN)}_2]^-$.

Phospholides featuring an anionic unsaturated five-membered P_1C_4 ring have received tremendous interest in the past decades due to the fundamental significance of the structural and electronic properties as well as their applications in synthetic chemistry.²² We envisioned the likelihood that the simple reaction of $[\text{P(CN)}_2]^-$ with organo-dilithium reagents would furnish phospholides, which are versatile precursors for synthesis of phosphole-based materials.²³ Gratifyingly, addition of $\text{Na(18-C-6)[P(CN)}_2]$ or **1** to the respective dilithium reagents gave rise to the corresponding phospholides **10-12** as a single P-containing product (Figure 7). **10-12** were isolated in moderate to good yield (62%–84%) and their structures were further authenticated by X-ray diffraction (Figures 5d and S7-8). Although the generation and synthetic applications of phospholides **10**,²⁴ **11**²⁵ as well as the studies of derivatives of **12**²⁶ as luminescent materials have been reported, the solid-state structures of these anions are hitherto unknown. The synthetic method presented herein provides access to phospholides from P_4 in a two-step fashion via $[\text{P(CN)}_2]^-$ as a bridge. It is important to note that the current protocols for phospholides generation require multistep synthesis, involving the use of phosphorus trihalides.²⁷ Zhang et. al. reported the direct facile synthesis of phospholides from P_4 but with low P atom economy (theoretically loss of 75% P atoms).^{5g, 5l, 28}

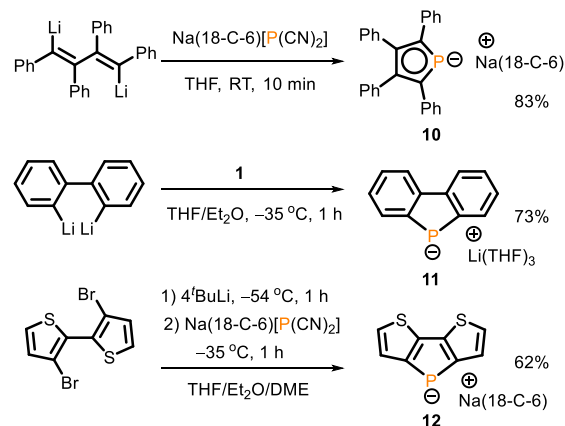


Figure 7. Synthesis of phospholides from $[P(CN)_2]^-$.

To conclude, we have showcased a practical versatile approach for the conversion of P_4 into useful OPCs with high P atom economy via $[P(CN)_2]^-$, exemplified by the effective synthesis of base-stabilized cyano-phosphinidenes **2-4**, cyclophosphanes **7-9**, and phospholides **10-12**. Importantly, this anion is readily available from an unprecedented electrochemical activation of P_4 on a gram scale. The practical simplicity of our strategy may spur considerable interest in development of $[P(CN)_2]^-$ that has been relatively dormant for many years. The utility of this approach directly from P_4 to construct other useful OPCs as well as unusual inorganic/organic phosphorus skeletons are the subject of ongoing work.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We gratefully acknowledge financial support from the National Natural Science Foundation of China (22101114) and SUSTech startup fund (Y01216248). The theoretical work is supported by the Center for Computational Science and Engineering and CHEM High-Performance Supercomputer Cluster located in the Department of Chemistry at SUSTech. We thank Drs. Xiaoyong Chang, Yuhui Hua, Zhe Huang and Rui Wei at SUSTech for helpful discussions and assistance in X-ray diffraction analyses. Prof. Chuan He and Dr. Jie Ke are thanked for assistance in electrolysis experiments. We thank Profs. Yufen Zhao and Guo Tang for providing P_4 . We thank Dr. D. A. Ruiz for valuable discussion.

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SYNOPSIS TOC.

