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Phosphorus Heterocycles

Sodium Phosphaethynolate as a Building Block for Heterocycles**

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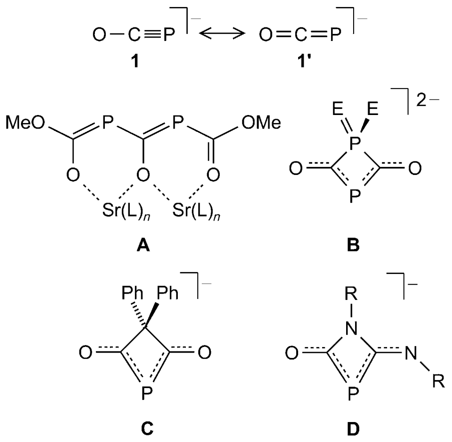
Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

***Abstract:** Phosphorus-containing heterocycles have evolved from laboratory curiosities to functional components, such as ligands in catalytically active metal complexes or molecular constituents in electronic devices. The straightforward synthesis of functionalized heterocycles on a larger scale remains a challenge. Herein, we report the use of the phosphaethynolate (OCP)$^-$ anion as a building block for various sterically unprotected and functionalized hydroxy substituted phosphorus heterocycles. Because the resulting heterocycles are themselves anions, they are building blocks in their own right and allow further facile functionalization. This property may be of interest in coordination chemistry and material science.*



Scheme 1. Resonance structures **1** and **1′** of the OCP$^-$ anion and organophosphorus compounds **A**–**D** obtained with M(OCP). Herein, we report the use of (OCP)$^-$ as reagent in cycloadditions leading to various hydroxy-substituted phosphorus heterocycles.[9,10]

The (OCP)$^-$ anion (**1**) in the alkaline phosphaethynolate salts, M(OCP) (M = Li, Na, K, Cs), is the simplest isolated stable compound containing a phosphorus–carbon triple bond. This anion is best described as a superposition of the resonance structures of phosphaethynolate **1** and phosphaketenide **1′** (Scheme 1). According to natural resonance theory (NRT) calculations, **1** contributes slightly more than **1′** to the electronic ground state of this anion.[1] The synthesis of Li(OCP) from Li[P(SiMe$_3$)$_2$] and dimethylcarbonate, (MeO)$_2$CO[2,8] was complimented by the one of the sodium salt, Na(OCP), which was prepared either from NaPH$_2$ and carbon monoxide[3] or by a bond metathesis reaction from a niobium phosphido complex, (L)$_n$Nb≡P$^-$ and CO$_2$.[4] The reaction between K$_3$P$_7$ and CO in presence of 18-crown-6 in DMF at 150 °C yields [K(18-crown-6)(OCP)].[5] In our hands, the simplest procedure is the reaction of NaPH$_2$ with ethylene carbonate, which gives [Na(OCP)·(dioxane)$_x$] ($x \approx 2.5$) in reproducible yields (70% based on P).[6] The use of the (OCP)$^-$ anion as building block for organophosphorus compounds has been scarcely exploited. Remarkably, whereas the alkali metal salts are rather stable and can even be briefly treated with water, the earth alkaline salts are unstable and must be kept at low temperatures.[7] For the strontium salt, the product of a dimerization reaction in presence of an excess of (MeO)$_2$CO to the [P$_2$C$_3$O$_2$(OMe)$_2$]$^{3-}$ dianion **A** was observed (Scheme 1). In the reaction of Li(OCP) with sulfur or selenium, the formation of the four-membered cycles **B** is suggested,[8] and recently Jupp and Goicoechea reported heterocycles **C** and **D** as products from the reaction of K(OCP) with a ketene or a carbodiimide.[5]

The reaction of Na(OCP) (**1**) in the form of its dioxane adduct, [Na(OCP)·(dioxane)$_{2.5}$], and two equivalents of phenylethynylcarboxylic ethylester (**2a**) in refluxing 1,2-dimethoxyethane (DME) delivers the sodium salt of diethyl 4-hydroxy-2,6-diphenylphosphinine-3,5-dicarboxylate (**4a**) (Scheme 2). An intermediate compound with a ^{31}P chemical shift of 153.2 ppm was observed in the yellow reaction solution, which we assigned to the first [2+2] cycloadduct **3a**.[5,11] Intermediate **3a** likely reacts further with a second equivalent of alkyne **2a** in a subsequent [2+2] cycloaddition

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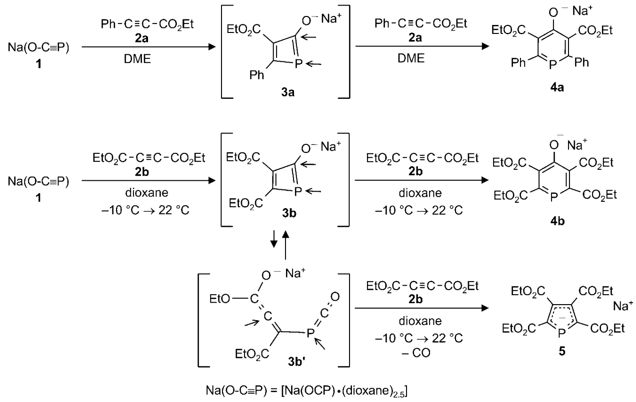


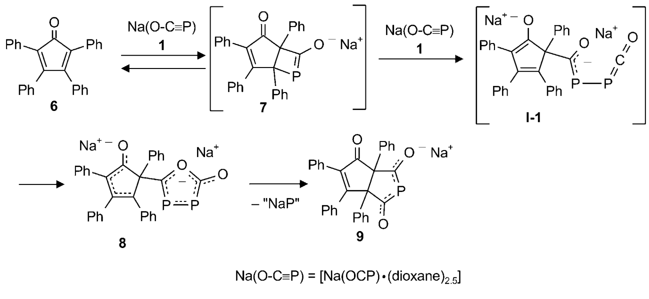
Scheme 2. Synthesis of the phosphinin-4-olates **4a**, **4b**, and the phospholide **5**. In intermediates **3a**, **3b**, and **3b′**, the centers involved in either a [2+2] or a [3+2] cycloaddition are indicated by arrows.

to give a Dewar-benzene analogue (not detected) which rearranges to the final product **4a** in excellent yield as pale yellow crystals. The ^{31}P NMR shifts of this sodium phosphinin-4-olate are strongly solvent dependent, with $\delta\,^{31}\mathrm{P} = 91.9$ ppm in [D$_8$]THF and 66.2 ppm in [D$_6$]DMSO.

In contrast to **2a**, the more-electron-deficient diethyl but-2-ynedioate (**2b**) does not only form the 2,3,5,6-tetracarboxyphosphinin-4-olate (**4b**), but also the phospholide anion **5** in an approximate 1:1 ratio. A detailed reaction mechanism cannot be provided, but we propose that the cyclic intermediate **3b** is in equilibrium with the acyclic phosphaketene **3b′**, which is likely the primary product formed by nucleophilic attack of the (OCP)$^-$ anion on the activated alkyne. This intermediate may then further react with a second equivalent of alkyne **2b** to give the phospholide **5** under loss of CO.

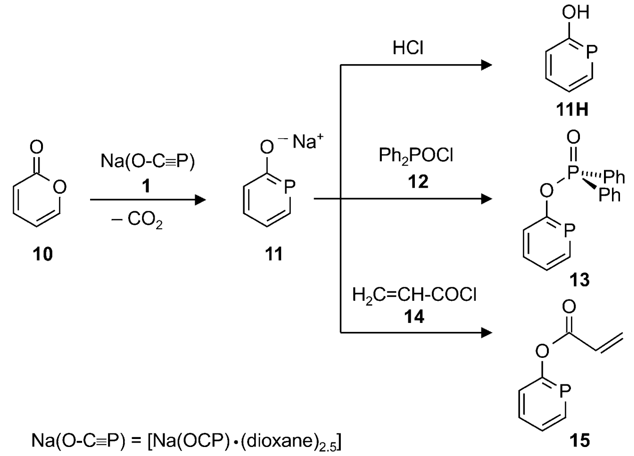
As can be seen in Scheme 3, Na(OCP) **1** was reacted with tetracyclone **6** in THF in an attempt to prepare a phosphinin-2-olate derivative.[12a–e] At room temperature, the reaction mixture turned immediately from deep red to orange, and after several minutes, yellow crystals started to precipitate. A [D$_8$]THF solution of these crystals shows two doublets in the ^{31}P NMR spectrum at $\delta = 159.2$ ppm and -35.5 ppm with a $^1J_{\mathrm{PP}}$ coupling constant of 361 Hz, which is not consistent with the expected phosphinin-2-olate.

This compound was unequivocally identified as a disodium salt of the 1,3,4-oxadiphospholonide derivative **8**, which is an unknown phosphorus heterocycle (see below for an X-ray diffraction study). When **1** and **6** were reacted in a 1:1 ratio, an intermediate with a ^{31}P NMR resonance at 154.9 ppm was detected, which we assign to **7**, in analogy to the assumed formation of **3**. Heating a solution of **8** to about 80 °C leads to a clean rearrangement reaction. The product, the sodium salt of the 2-phosphapentalene-1,3-dione derivative **9** ($\delta\,^{31}\mathrm{P} = 66.5$ ppm), is obtained in good yield as a slightly yellow crystalline substance under formal extrusion of "NaP".[13]



Scheme 3. Synthesis of oxadiphospholonide **8** and 2-phosphapentalene-1,3-dione **9**.

Finally, the reaction of Na(OCP) (**1**) with α-pyrone **10** in DME at 25 to 60 °C was investigated (Scheme 4). A distinct gas evolution (CO$_2$) is observed and a red precipitate is obtained in almost quantitative yield. NMR spectra and structure determination by single-crystal X-ray diffraction (see below) show that this compound is sodium phosphinin-2-olate (**11**). This salt is remarkably stable, and can be handled in air or dissolved in water without decomposition.



Scheme 4. Synthesis of phosphinin-2-ol **11H** and functionalized phosphinines **13** and **15**.

Simple neutralization of the sodium salt **11** with HCl allowed us to prepare larger quantities of phosphinin-2-ol (**11H**; ^{31}P NMR: $\delta = 149$ ppm) as a slightly yellow oil (Scheme 4).[14] The ^{1}H NMR chemical shift of the hydroxy proton is strongly solvent dependent (5.73 ppm in CDCl$_3$ and $\delta = 9.50$ ppm in THF), which is indicative of hydrogen bonding to THF molecules. Pyridin-2-ol, the nitrogen analogue of **11H**, exists predominantly in its tautomeric form as pyridin-2(1*H*)-one, which has a planar structure. We have no experimental evidence for the presence of a phosphinin-2(1*H*)-one.[15] At the BH&HLYP/6-311+G(3df,2p)//BH&HLYP/6-31+G(d) level of theory,[16] **11H** is more stable by 75.6 kJ mol^{-1} than its tautomer **11P** (see the Supporting Information for details). Moreover, the computed barriers for the monomolecular and bimolecular 1,3-shift between **11H** and phosphinin-2(1*H*)-one are very high (275.7 kJ mol^{-1} and 197.7 kJ mol^{-1}, respectively). The pK_a value of **11H** was determined in a buffered aqueous solution by a UV/Vis-titration to be 8.16 (see the Supporting Information for details). Compared to phenol (p$K_a = 9.99$) and pyridin-2(1*H*)-one (p$K_a = 11.6$),[17] the higher acidity of

11H is attributed to the high stability of the phosphinin-2-olate anion. Sodium phosphinin-2-olate **11** is also a versatile starting material for functionalized phosphinines, and reacts further with chlorodiphenylphosphane oxide (**12**) or acroyl chloride (**14**) to give **13** (δ ^{31}P: 177.6, 30.2 ppm, $^{3}J_{PP} = 10.9$ Hz) and **15** (δ ^{31}P: 177.0 ppm), respectively, which were obtained in almost quantitative yields (Scheme 4).

Single crystals of **4a** (yellow-orange), **5** (yellow), **8** (orange), **9** (yellow), and **13** (colorless) were investigated by X-ray diffraction methods, and the structures of these compounds were determined.[18] The sodium salt **4a** (Figure 1 a) and the disodium salt **8** (Figure 1 b) form dimeric aggregates in the solid state with Na_2O_2 rings as a common structural motif. The sodium salt of 2-phosphapentalene-1,3-dione **9** (Figure 1 c) forms a one-dimensional coordination polymer in which O6 and O10 of one bicyclic butterfly-shaped anion bind to Na1 in a bidentate fashion, while O45 takes a bridging position between the anions. In the sodium salt of 2,3,4,5-tetra(ethylcarboxy)phospholide **5**, the carbonyl oxygen centers O2/O4 and O6/O8 of the four COOEt groups are coordinated to sodium cations to form $\{Na[PC_4(COOEt)_4]\}_\infty$ ribbons, which are then linked by two dioxane molecules bound in a *cis*-fashion to Na1 to form a coordination network. The phosphorus-containing heterocycles in all compounds are flat, and the distances indicate delocalized π-systems in all cases. The phospholide ring in **5** is the only known example in which the PC_4 ring is “free” and not coordinated to a metal center; however, this has no systematic influence on the bond parameters (see the Supporting Information for details).

Pale yellow crystals of the composition $[\{2\text{-}(NaO)\text{-}(PC_5H_4)\}\cdot\{2\text{-}(HO)\text{-}(PC_5H_4)\}\cdot(\text{dioxane})]$ [**11·11H**·(dioxane)] were obtained when **11** was recrystallized from dioxane containing small amounts of water. The result of an X-ray diffraction study is shown in Figure 2 a,b. A two-dimensional coordination polymer is formed containing octahedrally coordinated sodium cations. In one dimension (a axis), the phosphinine moieties take a μ_2-bridging position between two sodium cations, whereby the P center binds to one sodium cation and the O center to the other. An additional hydrogen bond strengthens the network (Figure 2 b) and strands of $[Na\{\mu_2\text{-}\kappa O,\kappa P\text{-}O(PC_5H_4)\}\{\mu_2\text{-}\kappa O,\kappa P\text{-}HO(PC_5H_4)\}]$ are interconnected by μ_2-$\kappa O,\kappa O'$-dioxane molecules along the b axis to form a layered structure.

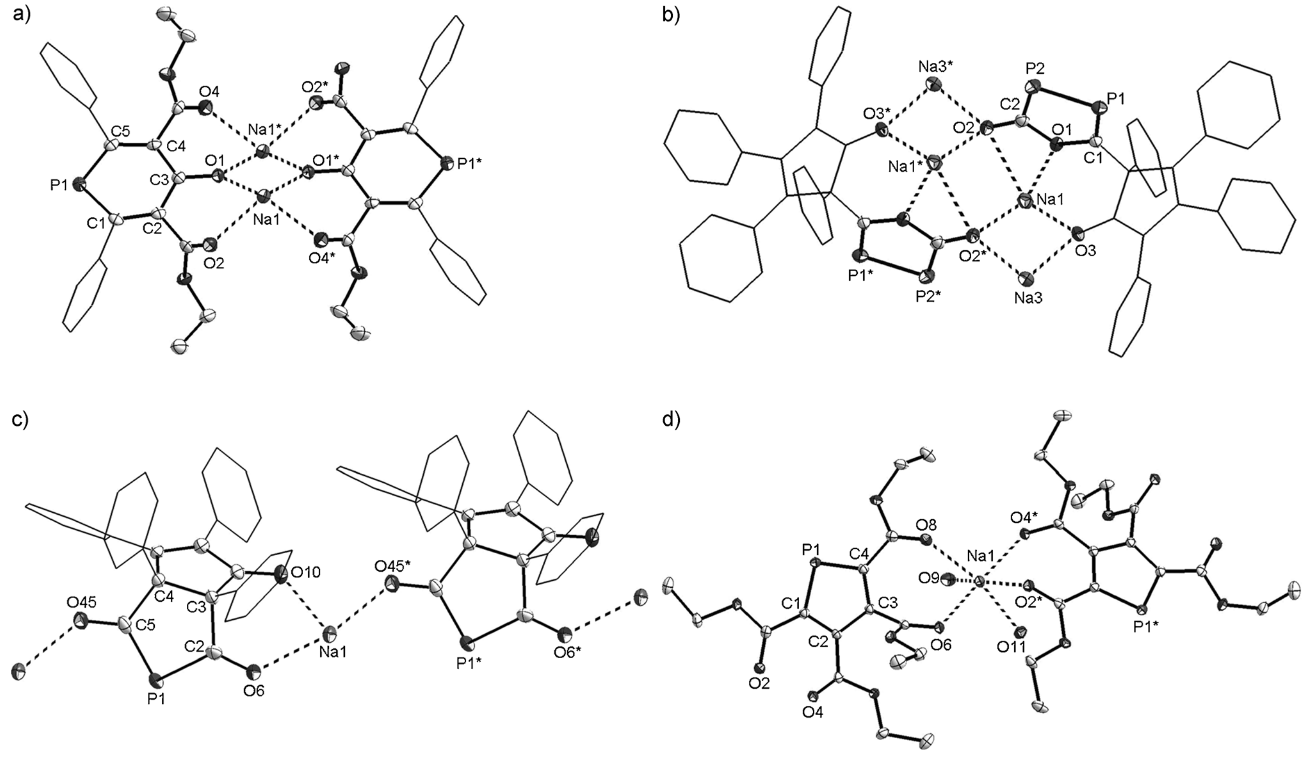


Figure 1. Structures of **4a**, **8**, **9**, and **5**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity. Solvent molecules completing the coordination sphere of the sodium cations are not shown (**4a:** 1 THF at Na1; **8**: 1 THF at Na1, 3 THF at Na3; **9**: 2 THF at Na1, **5**: 2 dioxane at Na1, but the O atoms attached to Na1 are shown). Atoms marked with * are symmetry generated. Selected bond distances [Å] and angles [°]: a) P1–C1 1.749(3), P1–C5 1.750(3), C1–C2 1.378(4), C2–C3 1.428(4), C3–C4 1.434(4), C4–C5 1.391(4), C3–O1 1.284(3), O–Na1 2.275(2)–2.366(2); C5-P1-C1 100.7(1), P1-C1-C2 124.8(2), C1-C2-C3 125.5(3), C2-C3-C4 118.8(2), C3-C4-C5 125.2(3), C4-C5-P1 124.9(2). b) P1–P2 2.1516(1), P1–C1 1.694(3), P2–C2 1.750(3), C1–O1 1.382(3), C2–O1 1.401(3), C2–O2 1.267(3), Na1–O 2.285(2)–2.791(2), Na1–Na3 3.347(2); P2-P1-C1 93.9(1), P1-C1-O1 119.2(2), C1-O1-C2 116.9(2), O1-C2-P2 116.6(2), C2-P2-P1 93.2(1). c) P1–C2 1.783(4), P1–C5 1.783(4), C4–C5 1.554(5), C3–C4 1.553(5), C2–C3 1.576(5), O6–C2 1.224(4), C5–O45 1.220(4), Na1–O 2.295(3)–2.391(2); C5-P1-C2 92.4(2), C3-C2-P1 114.6(3), C4-C5-P1 114.6(2), O6-C2-P1 126.7(3), C3-C4-C5 109.6(3), C4-C3-C2 107.9(3). d) P1–C1 1.747(1), P1–C4 1.754(1), C1–C2 1.417(2), C2–C3 1.401(2), C3–C4 1.414(2), Na1–O 2.249(1)–2.467(1); C1-P1-C4 90.4(1), P1-C1-C2 112.4(1), C1-C2-C3 112.4(1), C2-C3-C4 112.6(1), C3-C4-P1 112.2(1).

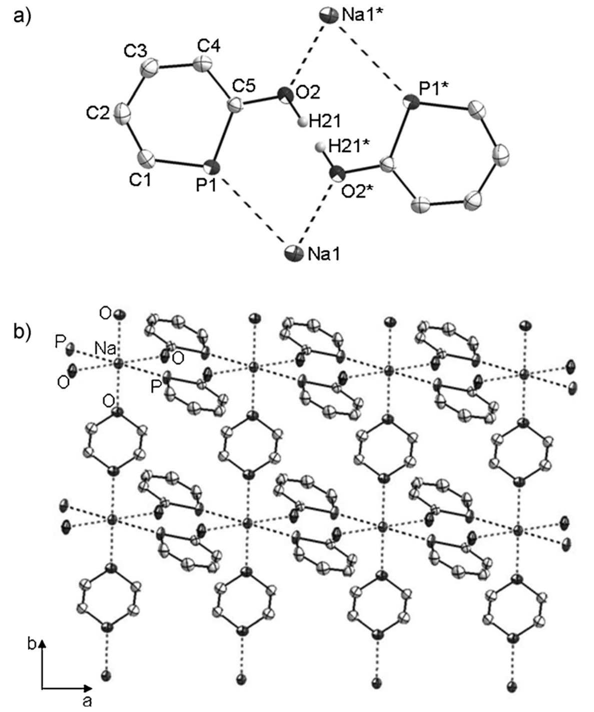
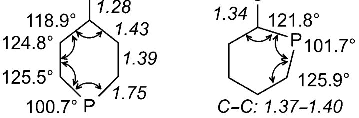


Figure 2. a) Structure of **11·11H**·(dioxane). Ellipsoids are drawn at the 50% probability level. Selected hydrogen atoms and dioxane molecules coordinated to Na have been removed for clarity. Atoms marked with * are symmetry generated. The hydrogen atom H21 (H21*) resides on two disordered positions on the O2⋯O2* axis. Selected bond distances [Å] and angles [°]: P1–C1 1.732(1), P1–C5 1.758(1), C1–C2 1.374(2), C2–C3 1.394(2), C3–C4 1.382(1), C4–C5 1.402(1), C5–O2 1.338(1); P1-Na1 3.116(1), Na1-O2 2.384(1)–2.384(1); C1-P1-C5 101.7(1), C2-C1-P1 126.0(1), C1-C2-C3 121.9(1), C4-C3-C2 124.0(1), C3-C4-C5 124.6(1), C4-C5-P1 121.9(1), O2-C5-C4 118.4(1), O2-C5-P1 119.7(1). b) Packing diagram of **11·11H**·(dioxane) in the solid state.

A comparison of relevant bond lengths and angles in the phosphinin-4-olate anion **4a** and the mixed neutral/anionic phosphinin-4-ol/ate [**11·11H**·(dioxane)] is given in Scheme 5. In **4a**, the six-membered ring is stretched along the O⋯P axis with a short C–O bond [1.284(3) Å] and a long–short sequence of C–C bonds in the ring. Both ipso angles in the *para*-position at C3 [118.8(2)°] and P1 [100.7(1)°] are compressed, indicating a quinonoid-type distortion of the π-system.[19]



Scheme 5. Comparison of selected structure parameters of the phosphinin-4-olate anion in **4a** and the phosphinin-2-olate anion in **11·11H**·(dioxane).

The phosphinine ring in **11·11H**·(dioxane) and also the neutral derivative **13** (not shown, see Figure S1 in the Supporting Information) is less perturbed and shows a less narrow *ipso*-angle at the P atom [101.7(1)°] and a longer CO bond [1.338(1) Å], as typically seen in phenolates.[19a] The C–C distances (1.37–1.40 Å) show no quinoidal distortion. According to the computed nucleus independent chemical shift[20] (NICS) values at 1 Å above the ring plane, the aromaticity of the two phosphininol isomers is practically the same (NICS(1) for phosphinin-4-ol is −9.6 ppm and for phosphinin-2-ol −9.5 ppm) and is very similar to that of phenol (NICS(1): −10.1 ppm). The deprotonated anions are remarkably less aromatic, as indicated by the NICS(1) values of −5.3 ppm for phosphinin-4-olate, −5.1 ppm for phosphinin-2-olate, and −6.4 ppm for phenolate, but again similar. Consequently, the phosphorus atom has no significant effect on the aromaticity, either in the neutral or anionic ring systems. For phenol, the reduction of aromaticity upon deprotonation is due to the predominance of the quinonoid resonance structures.[19c] Thus, the structural differences between the chinonoid anion **4a** and the neutral **13** or the mixed anion-neutral system **11·11H**·(dioxane) are in line with the change in aromaticity.

In summary, Na(OCP) is indeed a valuable building block, which can be obtained in a simple one-pot procedure from sodium, elemental phosphorus, and ethylene carbonate.[6] A variety of phosphorus-containing five- and six-membered heterocycles can be prepared in practically quantitative yields. Unlike its nitrogen analogue, the cyanate salt Na(OCN), which behaves as an ambivalent pseudohalogenide, the C≡P-triple bond in the $(OCP)^-$ anion undergoes [2+2], [3+2], and [4+2] cycloadditions. Our first experimental results, bolstered by computations,[6] indicate that these do not proceed in a concerted fashion, but are stepwise initiated by a nucleophilic attack of the phosphorus atom in $(OCP)^-$.

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