Organophosphorus Compounds

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The 2-Phosphaethynolate Anion: A Convenient Synthesis and [2+2] Cycloaddition Chemistry[**]

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The 2-phosphaethynolate anion (P≡C–O$^-$; **1**), the phosphorus-containing analogue of cyanate (N≡C–O$^-$), was first isolated by Becker and co-workers in the early 1990s by reaction of lithium bis(trimethylsilyl)phosphide and dimethylcarbonate.[1] This procedure was extended to yield other alkali earth metal salts of the anion several years later.[2] The nature of the metal countercation and solvent has been found to have a profound effect on the relative stability of **1**. Very recently, Grützmacher and co-workers described the synthesis of two new salts of this anion, $[Na(dme)_2(\mathbf{1})]_2$ (dme = dimethoxyethane) and $[Na(dioxane)_{2.5}(\mathbf{1})]_\infty$, from sodium phosphide ($NaPH_2$) and carbon monoxide under high-pressure conditions (110 bar).[3] The authors report that the salts are soluble in water and stable to hydrolysis, albeit for short periods of time (several days). An alternative synthesis of $[Na(dme)_2(\mathbf{1})]_2$ was also reported soon after, by a remarkable bond metathesis reaction of a terminal niobium phosphide with carbon dioxide.[4]

Common to all of these reports is the hypothesis that the phosphaethynolate anion is accessed by initial nucleophilic attack of a phosphide vertex at the carbon atom of the CO source. These findings prompted our research group to explore the reactivity of bare (substituent-free) polyphosphides toward carbon monoxide, building on previous studies on the reactivity of P_7^{3-} toward unsaturated substrates.[5] Direct combination of CO with a K_3P_7 solution provides a straightforward route to the 2-phosphaethynolate anion, which can be isolated in moderate yields. Subsequent reactivity studies show that the anion undergoes [2+2] cycloaddition with diphenylketene or bis(2,6-diisopropylphenyl)carbodiimide to yield the unprecedented 4-phospha-[2,2-diphenylcyclobuta-1,3-dione]-yl (**2**; $P[C(O)]_2C(C_6H_5)_2^-$) and 3-phospha-[[4-*N*′-(2,6-diisopropylphenylimino)]-1-*N*-(2,6-diisopropylphenyl)-azetidin-2-one]-yl (**3**; PC(O)(CNDipp)-NDipp$^-$) anions, respectively.

Heating a DMF solution of K_3P_7 and [18]crown-6 to 150 °C under one atmosphere of carbon monoxide for 24 h yielded [K([18]crown-6)]-**1**.[6] The formal transfer of a P^- anion to carbon monoxide results in the formation of oxidized polyphosphide species (P_{16}^{2-} and P_{21}^{3-}, predominantly), which have characteristic ^{31}P NMR spectroscopic signatures.[7] The PCO$^-$ anion can be extracted from these reaction mixtures using degassed and deionized water (which hydrolyses the other reaction side-products). Filtration, followed by removal of water under a dynamic vacuum, affords [K([18]crown-6)]-**1** in moderate yields (38 %). Treating P^- as the stoichiometrically limiting reagent, the maximum yield of PCO$^-$ available from such a transformation is 43 %. The ^{31}P and ^{13}C NMR spectra of **1** exhibit singlet and doublet resonances at $\delta = -396.8$ ppm and $\delta = 170.3$ ppm, respectively ($^1J(PC) = 62$ Hz). These are consistent with other literature reported values. An IR spectrum of the solid in a Nujol mull reveals a band at 1730 cm^{-1} arising from the P≡C stretching mode (the C–O band was obscured by the broad vibrational bands of arising from the [K([18]crown-6)]$^+$).

[K([18]crown-6)]-**1** was crystallized from a THF/hexane solvent mixture, affording X-ray diffraction quality single crystals (Figure 1).[8] The structure of [K([18]crown-6)]-**1** has a single triatomic linear anion in the asymmetric unit alongside a [K([18]crown-6)]$^+$ cation. There is a close electrostatic contact between the K$^+$ cation and the phosphorus atom (3.383(1) Å), while the C–O moiety interacts with an adjacent [K([18]crown-6)]$^+$ moiety with K–C and K–O distances of

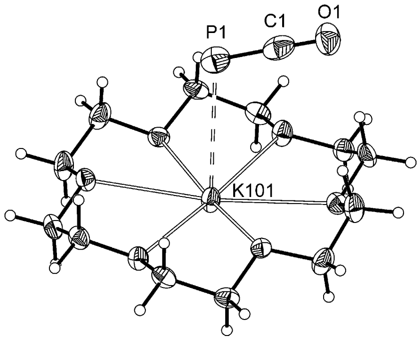

Figure 1. Thermal ellipsoid plot of the atoms in the asymmetric unit of [K([18]crown-6)]-**1**.[8] Ellipsoids are set at 50 % probability. Hydrogen positions were assigned idealized coordinates and are pictured as spheres of arbitrary radii. Selected distances [Å] and angles [°]: P1–C1 1.579(3), C1–O1 1.212(4), P1–K101 3.383(1), C1–K101′ 3.508(3), O1–K101′ 2.901(2); P1-C1-O1 178.9(3). Atoms labeled with a′ are generated by the symmetry operation: *x*-1, *y*, *z*.

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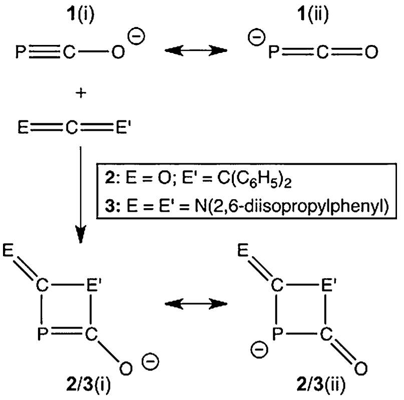
Supporting information for this article, including a full description of experimental methods and spectroscopic data (including single crystal X-ray collection and refinement data), is available on the WWW under http://dx.doi.org/10.1002/anie.201305235.

3.508(3) and 2.901(2) Å, respectively. Bond metric data within the anion are comparable with other reported crystal structures and consistent with a resonance structure exhibiting a formal triple bond between the phosphorus and carbon atom and a negative charge on the oxygen: the P1−C1 and C1−O1 distances are 1.579(3) Å and 1.212(4) Å, respectively (resonance form **1**(i) in Scheme 1).[9] The Supporting Information contains a comparison of bond metric and spectroscopic data for all of the known salts of the phosphaethynolate anion.



Scheme 1. Synthesis of **2** and **3** from **1** and diphenylketene and bis(2,6-diisopropylphenyl)carbodiimide, respectively.

To date only a handful of reactions of the 2-phosphaethynolate anion have been reported. These include metal-mediated dimerizations and oxidative tetramerizations to yield $P_2C_2O_2^{2-}$ and $P_4C_4O_4^{2-}$, respectively.[10] The latter report also details the reaction of the lithium salt of **1** with carbon disulfide to yield the heavier isoelectronic analogue $P{\equiv}C{-}S^-$.[10b] Recently Grützmacher, Peruzzini, and co-workers described the first instance of the PCO^- anion acting as a ligand in a transition-metal complex.[11] Interestingly however, despite the close relationship of the 2-phosphaethynolate anion with phosphaalkynes (the chemistry of which has been extensively studied),[12] the cyclization chemistry of the former remains largely unexplored. To our knowledge there are no reports of the reactivity of this anion towards common unsaturated substrates.

Reaction of [K([18]crown-6)]-**1** with one equivalent of diphenylketene was found to yield the [2+2] cycloaddition product $P[C(O)]_2C(C_6H_5)_2^-$ (**2**), which results from a formal addition of the $P{\equiv}C$ bond in **1** across the $C{=}C$ double bond of the ketene (Scheme 1). This reactivity is consistent with that of other multiply bonded phosphorus systems towards heterocumulenes.[12] The reaction affords **2** in good to high yields, although it involves the formation of other, as of yet identified, phosphorus-containing intermediates (observed as two singlets at $\delta = 21.6$ and 31.4 ppm in the ^{31}P NMR spectrum), which can be readily separated from the final product. The ^{31}P NMR spectrum of **2** reveals a singlet resonance at $\delta = -165.7$ ppm and six resonances in the ^{13}C NMR spectrum (two of which are observed as doublets). The IR spectrum of [K([18]crown-6)]-**1** reveals two strong bands in the carbonyl stretching region at 1598 and 1557 cm^{-1}, which is consistent with the symmetric (A_1) and asymmetric (B_1) bond stretching modes, respectively.[10a,13]

Crystals of [K([18]crown-6)]-**2** could be grown by slow diffusion of hexane into a THF solution of the product (Figure 2).[8] The crystal structure reveals a single crystallographically unique anion with C_{2v} symmetry and a planar PC_3 central ring (maximum deviation from plane: 0.012 Å). This is consistent with formal sp^2 hybridization at the P1, C1, C2, O1, and O2 positions, as would be anticipated based on the resonance structures depicted in Scheme 1. Bond metric data are in line with a functionalized phospha-[cyclobuta-2,4-dione]-yl anion (**2**(ii) in Scheme 1). P1−C1 and P1−C2 distances are comparable (1.784(2) and 1.799(3) Å, respectively). These distances are in between the sum of single- and double-bond covalent radii for P and C (1.86 and 1.69 Å, respectively).[14] The C−O bond distances (1.237(3) Å and 1.228(3)) are comparable to those of other structurally authenticated ketones.

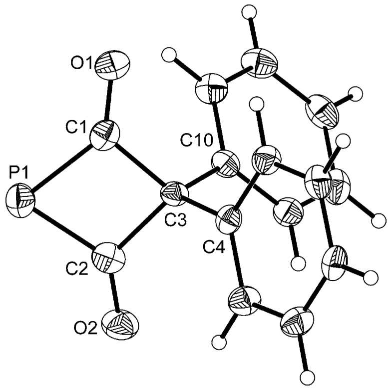


Figure 2. Thermal ellipsoid plot of the anionic moiety present in [K([18]crown-6)]-**2**.[8] Ellipsoids are set at 50% probability. Hydrogen positions were assigned idealized coordinates and are pictured as spheres of arbitrary radii. Selected distances [Å] and angles [°]: P1–C1 1.784(2), P1–C2 1.799(3), C1–C3 1.562(3), C2–C3 1.564(3), C1–O1 1.237(3), C2–O2 1.228(3); C1-P1-C2 75.08(11), P1-C1-C3 98.48(15), C1-C3-C2 88.61(17), P1-C2-C3 97.78(15). O1 displays a short interatomic contact to the potassium cation of 2.667(2) Å.

To our knowledge, **2** is the first example of an isolated monoanionic four-membered phosphorus-containing heterocycle. This species is closely related to the 2-H-isophosphindoline-1,3-dione ion reported in 1984 by Liotta and co-workers (a related species with a central five-membered PC_4 ring that displays similar bond metrics).[15] Monoanionic phosphido ligands in which the phosphorus atom forms part of a four-membered ring are extremely rare, and until now they have exclusively been isolated in the immediate coordination sphere of a metal.[16] Similarly there is only one example of a dianionic four-membered ring.[17] By contrast, phospha- and diphospha-cyclobutadiene species are more common.[18,19] Neutral phosphines in which the phosphorus atom forms part of a four-membered ring, such as phosphetanes, have also been studied extensively owing to their ability to act as supporting ligands in metal-meditated transformations.[20]

An analogous reaction between **1** and bis(2,6-diisopropylphenyl)carbodiimide also gave rise to an anionic four-membered ring, $\mathrm{PC(O)(CNDipp)NDipp^-}$ (**3**). Full conversion of the $\mathrm{PCO^-}$ starting material to a new product with a singlet resonance in the ^{31}P NMR spectrum was observed after approximately 3 h at room temperature. Unlike the reaction that yielded **2**, the synthesis of **3** proceeded quantitatively with no side-product formation. It is worth noting, however, that this [2+2] cycloaddition strongly depends on the nature of the substituents on the carbodiimide. Thus, reaction of **1** with bis(cyclohexyl)carbodiimide showed no evidence of the cycloaddition product being formed even upon prolonged heating. The ^{31}P NMR spectrum of a [D$_8$]THF solution of [K([18]crown-6)]-**3** shows a singlet resonance at $\delta = 18.6$ ppm. Two magnetically inequivalent Dipp groups could be distinguished in the ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectrum showed two doublet resonances at $\delta = 196.6$ ($^1J(\mathrm{PC}) = 42$ Hz) and 178.2 ($^1J(\mathrm{PC}) = 48$ Hz) ppm, corresponding to the carbonyl and imine carbons, respectively. An additional two doublets arising from the *ipso*-carbon atoms of the two Dipp substituents were also observed at $\delta =$ 149.0 and 133.2 ppm. An IR spectrum of the solid reveals two bands at 1599 and 1579 cm^{-1} arising from C=O and C=N stretching modes.

Crystals of [K([18]crown-6)]-**3** suitable for X-ray diffraction could be grown by slow diffusion of hexane into a THF solution of **3** (Figure 3). As with **2**, the structure of **3** shows a planar four-membered heterocyclic core (the maximum deviation from planarity for P1, C1, N1, and C2 is 0.015 Å). The P1−C1 and P1−C2 distances (1.837(2) and 1.839(2) Å) are identical within experimental error despite the different substituents on the two carbon atoms. They are, however, approximately 0.04 Å longer than those observed in **2** (1.784(2) and 1.799(3) Å). This presumably arises because of the increased electron density in the π-manifold of the four-membered ring owing to the N1 lone pair. The C1−O1 bond distance is 1.226(2) Å, which is comparable to those observed for **2** (1.237(3) and 1.228(3) Å). The C2−N2 interaction (1.269(2) Å) is consistent with a carbon–nitrogen double bond (1.27 Å),[14] and notably shorter than the other C−N distances (1.406(2)–1.429(2) Å). These data indicate that bonding in **3** can be best described by the resonance structure **3**(ii) in Scheme 1.

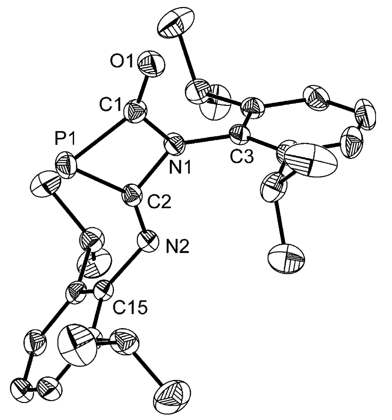


Figure 3. Thermal ellipsoid plot of the anionic moiety present in [K([18]crown-6)]-**3**.[8] Ellipsoids are set at 50% probability. Hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: P1–C1 1.837(2), P1–C2 1.839(2), C1–N1 1.406(2), N1–C2 1.417(2), C1–O1 1.226(2), N1–C3 1.429(2), C2–N2 1.269(2), N2–C15 1.415(2); C1-P1-C2 71.02(7), P1-C1-N1 95.52(10), C1-N1-C2 98.33(12), P1-C2-N1 95.05(10). O1 displays a short interatomic contact to the potassium cation of 2.655(1) Å.

Density functional theory (DFT) calculations on **2** and **3** yielded optimized computed geometries with bond metrics that are in excellent agreement with the crystallographically determined values (see the Supporting Information for full details). As might be expected, the HOMO and HOMO−1 in **2** were found to be predominantly phosphorus based. In the case of **3**, the HOMO and HOMO−2 are orbitals of analogous phosphorus parentage (other frontier orbitals are composed of Dipp group π orbitals or the lone pair from the nitrogen atom of the azetidin-2-one ring). The HOMO in both species is largely of phosphorus p_y orbital character (55.5 and 73.7 % in **2** and **3**, respectively; the *y* axis being orthogonal to the four-membered ring). In **2**, this orbital is moderately extended onto adjacent carbon atoms consistent with some delocalization of the formal negative charge (4.2 and 4.5 % p_y orbital character for C1 and C2, respectively). The HOMO−1 and HOMO−2 orbitals in **2** and **3**, respectively, have significant lone-pair character on the phosphorus atom (33.8 % p_z in **2** and 18.23 % p_z in **3**). These theoretical findings along with bond metric data are consistent with a depiction of **2** and **3** as the **2**/**3**(ii) isomer shown in Figure 1. The computed HOMO–LUMO gaps are 4.73 and 4.08 eV for **2** and **3**, respectively.

In summary, we have developed a novel route to the 2-phosphaethynyl anion by direct carbonylation of bare polyphosphides at atmospheric pressures. This method afforded $\mathrm{PCO^-}$ in moderate to good yields, allowing for subsequent reactivity studies that have demonstrated that cyclizations between the P≡C bond in **1** and unsaturated substrates are possible, yielding novel heterocyclic species such as **2**. Studies are currently underway exploring the reactivity of **1** towards a library of unsaturated compounds. We are also exploring the reactivity of species **2** and **3**.

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