

The chemistry of the 2-phosphaethynolate anion

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Dedicated to the memory of Gerd Becker

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1. PCO^- : Known syntheses and electronic properties

1.1. Historic overview

Over the course of the last six years, the 2-phosphaethynolate anion (PCO^-) has emerged as a versatile chemical reagent for the synthesis of a variety of unprecedented phosphorus-containing molecules and solids. This remarkable anion is valence isoelectronic with the cyanate ion (NCO^-), however while there are some clear similarities in their reactivity, the reactivity of PCO^- is largely dominated by the relative weakness of the P–CO bond and/or the tendency of the P–C multiple bond to oligomerise. Both of these reactivity pathways are highly unusual for the cyanate ion. As with the cyanate ion, two principal tautomeric forms can be invoked for PCO^- : 1) a phosphaethynolate-like resonance structure, exhibiting a formal triple bond between the phosphorus and carbon atom and a negative charge on oxygen (**A**, Figure 1); and 2) a phosphaketene species with a formal double bond between phosphorus and carbon and a negative charge on the phosphorus atom (**B**, Figure 1). A third resonance form, which effectively represents a carbonyl adduct of a monoanionic phosphide, (**C**, Figure 1) can also be invoked, and while this contribution does not weigh in significantly on the electronic structure of PCO^- , it does help rationalize the relative ease with which PCO^- decarbonylates (*vide infra*).

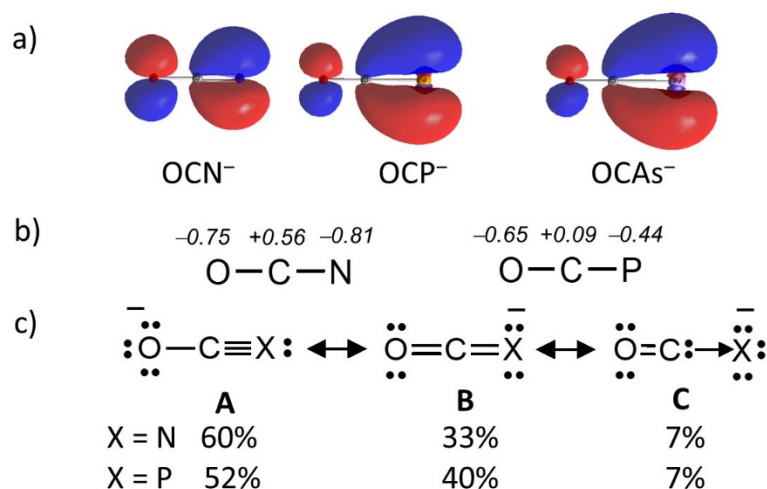


Figure 1. a) Highest occupied molecular orbitals of OCN^- , OCP^- , and OCAs^- showing the different polarizations. b) NPA charges of OCN^- and OCP^- . c) Resonance forms of PCO^- and NCO^- and their weights from a natural resonance theory (NRT) analysis (B3LYP/6-31+G*).

In all likelihood, the first synthesis of the 2-phosphaethynolate anion was achieved in 1894 by Shober and Spanutius at Lehigh University by reaction of sodium phosphanide (NaPH_2) and carbon monoxide, although the authors mistakenly identified this compound as sodium cyaphide ($\text{C}\equiv\text{P}^-$; a heavier analogue of the cyanate ion).¹ In their report, the authors made the following closing statement: “We have been obliged to discontinue this investigation for the present, but in the near

future we shall take it up again". It is unclear what obstacles impeded Shober and Spanutius from following up on their research (we suspect that funding for curiosity-driven science may have been just as difficult to procure in the late XIX century as it is today); it was not until 117 years later that this reaction was repeated and the product correctly identified.

1.2. Known syntheses of the PCO^- ion

In 1992 Becker et al. were able to develop the first rational synthesis of PCO^- and succeeded in characterising this anion for the first time.² In their seminal report, the authors were able to synthesise $\text{Li}(\text{DME})_2(\text{OCP})$ (DME = 1,2-dimethoxyethane) by reaction of lithium bis(trimethylsilyl)phosphide ($\text{LiP}(\text{SiMe}_3)_2$) with dimethyl carbonate (Scheme 1). The compound was structurally authenticated revealing a linear anion ($\text{P}-\text{C}-\text{O}$ $178.5(3)^\circ$), with P–C and C–O bond lengths of 1.555(3) and 1.198(4) Å, respectively. The structure also revealed a relatively short $\text{O}\cdots\text{Li}$ interaction (1.878(5) Å), which is shorter than the sum of the covalent bond radii for lithium and oxygen (1.94–1.96 Å) indicating the presence of a strong ion pair, which serves to increase the triple bond nature of the $\text{P}\equiv\text{C}$, and the weighting of resonance form **A**. This association, which has some degree of covalency, increases the reactivity of PCO^- in two ways. Firstly, the increased contribution of resonance form **A**, gives rise to a species that is comparable to phosphalkynes ($\text{P}\equiv\text{C}-\text{R}$) and, due to the relatively weak nature of the P–C π -bonds relative to σ -bonds, favours oligomerization pathways where the number of σ -bonds can be increased (alternatively additional thermodynamic stability can be achieved by generating aromatic molecules – *vide infra*). In addition, such an interaction diminishes the charge on the anion thereby reducing Coulomb repulsion between anions, an interaction which protects the OCP^- anion from decomposition through oligomerization.

As a consequence of the instability of $\text{Li}(\text{DME})_2(\text{OCP})$ the chemistry of this remarkable species laid dormant for over twenty years. Limited studies were reported in the years following the discovery of this anion until it was observed that heavier alkali metal salts of the 2-phosphaethynolate anion exhibited an enhanced stability, not only to decomposition, but also in solvents such as water, which, on account of its moderately acidic nature, would typically be considered incompatible with such a species.

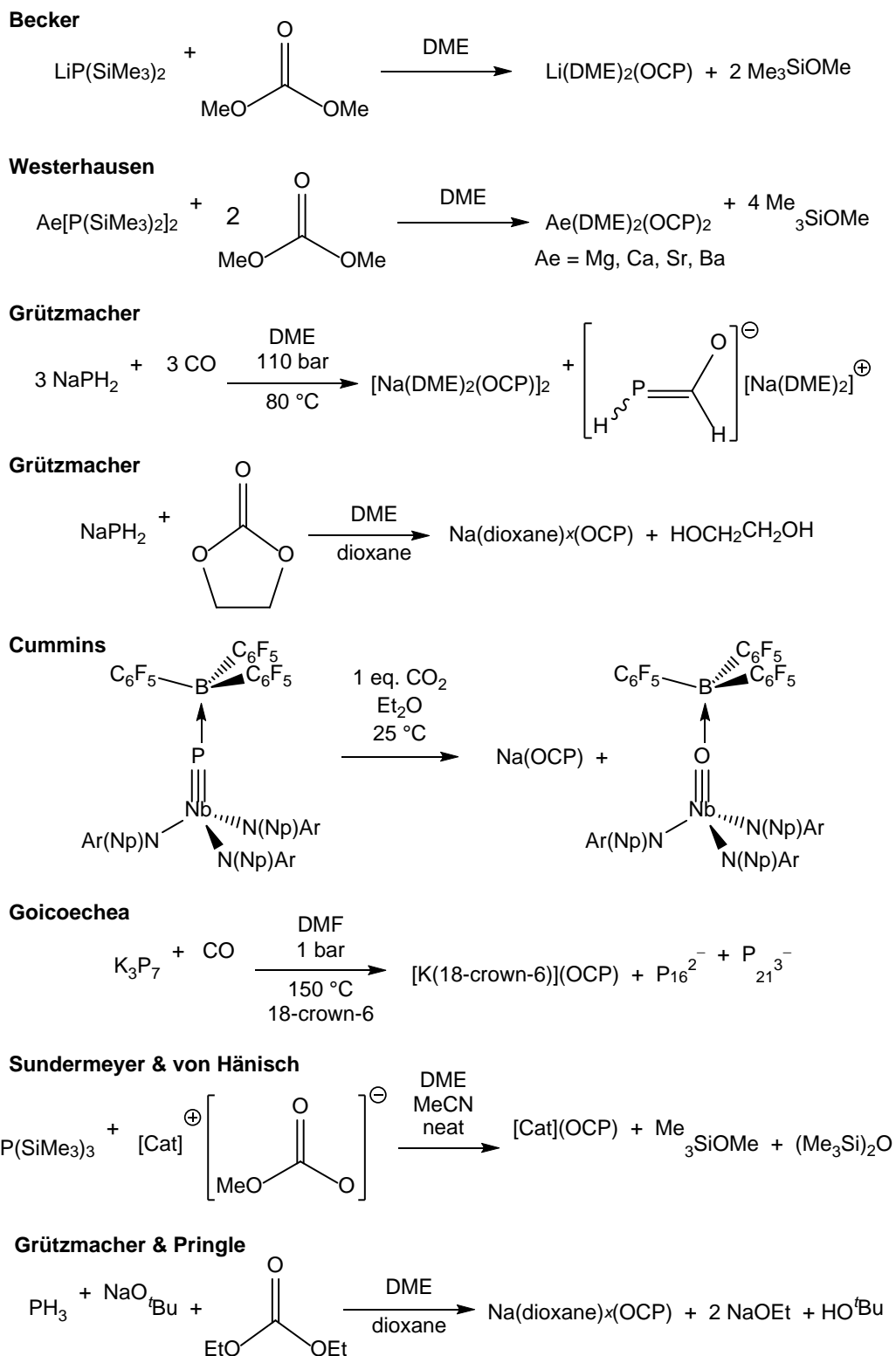
Since 1992, several other salts of PCO^- have been reported. The first family of these, alkaline earth metal bis(2-phosphaethynolates), $\text{Ae}(\text{DME})_3(\text{PCO})_2$ where Ae = Mg, Ca, Sr, Ba, were reported by Westerhausen et al. in 2002, however, these species were found to be of comparable stability to

[Li(DME)₂][PCO].³ The authors reported that such salts “... *decompose upon isolation and have to be stored in an ethereal solution at low temperatures*”.

In 2011 Grützmacher and co-workers reported the synthesis of both Na(DME)₂(OCP) and Na(dioxane)_{2.5}(OCP) by direct carbonylation of sodium phosphanide (NaPH₂) in DME at 80 °C and 110 bar of CO, and by reaction of NaPH₂ with ethylenecarbonate, respectively.⁴ The authors noted that the latter of these compounds “...*is remarkably stable and can be handled in air without decomposition*”. This observation, and the fact that the sodium salts can be handled in water with limited hydrolysis (*t*_{1/2} at 298 K of a 0.5 to 0.7 M solution ca. 2 days), highlight the importance of the associated counter-cation in the stabilization of PCO[−]. In 2012, an alternative synthesis of Na(DME)₂(OCP) was reported by Cummins and co-workers by reaction of the borane-capped niobium phosphide anion [(C₆F₅)₃B:P≡Nb(N[Np]Ar)₃][−] (Ar = 3,5-C₆H₃Me₂; Np = neopentyl) with carbon dioxide.⁵

The synthesis of Na(dioxane)_x(OCP) (where *x* = 1–5) was optimized by Grützmacher and co-workers in 2014, allowing for a multi-gram synthesis of the salt from inexpensive precursors (sodium, red phosphorus, ^tBuOH, ethylenecarbonate) in high yields (typically > 80%).⁶ The nature of the carbonate can be varied and a number of other carbonates are also synthetically viable, e.g. dimethyl- or diethyl-carbonate. The dioxane content of the resulting product strongly depends on how long the solid is treated under vacuum, and can be determined by ³¹P or ¹H NMR spectroscopy relative to an internal standard. This procedure represents the current state-of-the-art in the synthesis of this interesting anion and has led to a veritable deluge of reactivity studies focused on PCO[−] in the past three years.

In 2013 Jupp and Goicoechea described an alternative synthesis of PCO[−] as a [K(18-crown-6)]⁺ salt by direct carbonylation of DMF (DMF = *N,N*-dimethylformamide) solutions of K₃P₇ at 150 °C.⁷ As with the sodium salts reported by Grützmacher, this salt is also very stable to work with and can be handled in water for short periods of time. In fact, aqueous work-up was employed as a way of separating [K(18-crown-6)](OCP) from the P₁₆^{2−} and P₂₁^{3−} side-products generated from such reactions.



Scheme 1. Known syntheses of the 2-phosphaethynolate anion.

A more recent synthesis of PCO^- is the reaction of organic methylcarbonate salts with tris(trimethylsilyl)phosphine (a variation of Becker's original synthesis) reported by Sundermeyer and von Hähnisch.⁸ This method gives rise to a variety of salts, many of which behave as ionic liquids, and

is highly tunable allowing for the synthesis of a number of ammonium and phosphonium salts of the 2-phosphaethynolate anion (at least three of which have been structurally authenticated).

Most recently, an improved synthesis of $\text{Na}(\text{dioxane})_x(\text{OCP})$ has been developed by Grützmacher and co-workers.⁹ The synthesis uses phosphine gas (PH_3) as a feedstock, and a simple deprotonation with NaO^tBu allows for the formation of NaPH_2 . The resulting phosphanide readily reacts with carbonates to afford sodium salts of the 2-phosphaethynolate anion which can be precipitated out of solution using dioxane. While this synthesis will probably not be commonly employed on a small laboratory scale due to the highly pyrophoric nature of PH_3 , it is much more attractive on a larger industrial scale as it circumvents the use of solid reagents such as sodium and red phosphorus which have the potential to foul chemical reactors.

In the span of twenty six years since Becker first correctly identified the 2-phosphaethynolate anion, this species has come of age and is rapidly developing into a multifunctional reagent the chemistry of which we will attempt to comprehensively survey in the coming pages.¹⁰

2. Structural, spectroscopic and electrochemical properties

2.1. Structure and spectroscopic properties

All of the known ionic salts of the 2-phosphaethynolate anion (Table 1) feature similar structural metrics (as determined by single crystal X-ray diffraction). The anions are linear with comparable P–C–O bond angles (these range between $178.5(3)$ and $179.9(3)^\circ$). P–C bond lengths vary somewhat from one structure to another, ranging between $1.555(3)$ and $1.634(3)$ Å, values that are in between the predicted values for P–C double (1.69 Å) and triple (1.54 Å) bonds. The C–O interatomic distances are more narrowly distributed and have values that range from $1.198(4)$ and $1.213(1)$ Å. The similarity of the bond metric data from one structure to another make it difficult to tease out subtle arguments regarding the contribution of different resonance structures to overall structures, although qualitatively it would seem that for structures in which there are no direct cation–anion interactions, the P–C bonds are generally longer, consistent with a greater contribution of the phosphaketene resonance form **B**.

Spectroscopically, the PCO^- ion exhibits a characteristic singlet in the low frequency region of its ^{31}P NMR spectrum, the chemical shift of which is strongly dependant on the nature of the associated counter-cation and solvent. This resonance is typically observed between -367.9 and -396.8 ppm (e.g. $\text{Na}(\text{dioxane})_{2.5}(\text{OCP})$ is observed at -392.0 ppm in $[\text{D}_8]\text{THF}$; THF = tetrahydrofuran). The ^{13}C NMR

spectrum of the anion exhibits a weak doublet between 166.3 and 170.7 ppm with a $^1J(^{31}\text{P}-^{13}\text{C})$ coupling constant that ranges between 41.5 and 62.9 Hz. The magnitude of this coupling constant appears to be very sensitive to the major contributing resonance forms of the anion, with phosphaketenide type ions ($^-\text{P}=\text{C}=\text{O}$) giving rise to a greater coupling constant than those that are best described phosphaehtynolate compounds ($\text{P}\equiv\text{C}-\text{O}^-$). This is due to the greater contribution of the phosphorus 3s orbital to the P–C bond of the former of these two resonance structures. This observation also holds true for compounds exhibiting more covalent interactions between metal centers and the phosphaehtynolate anion (*vide infra*).

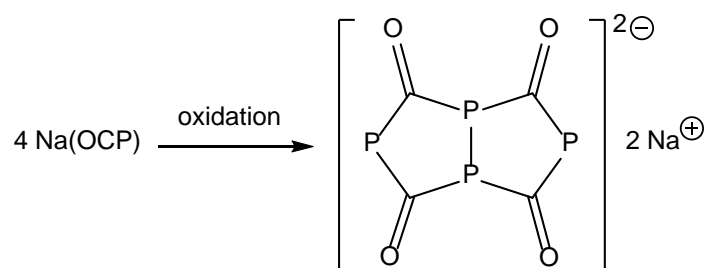
Table 1. Selected structural and spectroscopic properties for known salts of PCO^- .

salt	ref.	P–C–O (°)	P–C (Å)	C–O (Å)	O...M ⁿ⁺ (Å)	³¹ P (ppm)	¹³ C (ppm)	¹ J _{P–C} (Hz)	IR (cm ^{–1})
Li(DME) ₂ (OCP)	2	178.5(3)	1.555(3)	1.198(4)	1.878(5)	–384.2	166.6	41.5	N.A.
Ca(DME) ₃ (OCP) ₂	3	179.2(2)	1.575(2)	1.207(3)	2.358(2) 2.335(2)	–369.6	N.A.	N.A.	N.A.
Mg(THF) ₄ (OCP) ₂	11	179.6(2)	1.572(3)	1.196(3)	2.024(16)	–367.9	N.A.	N.A.	1759
Na(OCP)	12	178.9(11)	1.622(15)	1.16(2)	2.411(9)	N.A.	N.A.	N.A.	N.A.
Na(DME) ₂ (OCP)	4	179.3(3) 179.5(4)	1.589(3) 1.575(3)	1.203(4) 1.213(4)	2.349(3) 2.336(3)	N.A.	N.A.	N.A.	1780, 1262
Na(dioxane) _{2.5} (OCP)	4	N.A.	N.A.	N.A.	N.A.	–392.0	166.3	46.5	1755, 1247
Na(dioxane) ₃ (OCP)	12	178.6(3)	1.634(3)	1.163(4)	N.A.	N.A.	N.A.	N.A.	N.A.
Na(dibenzo-12-c-6)(OCP)	11	179.4(3)	1.582(3)	1.207(4)	2.290(2)	–388	N.A.	N.A.	1765
K(18-crown-6)(OCP)	7	178.9(3)	1.579(3)	1.212(4)	2.901(2)	–396.8	170.3	62	1730
[PMe ₄][OCP]	8	179.9(15)	1.579(1)	1.213(1)	N.A.	–389.2	170.6	62.5	1772, 1243
[C(NMe ₂) ₃][OCP]	8	179.3(4)	1.594(1)	1.188(1)	N.A.	–389.6	170.7	62.9	1771, 1254
[NMe ₄][OCP]	8	179.2(2)	1.601(2)	1.203(2)	N.A.	–387.2	169.2	62.0	1768, 1282

The infrared spectrum of the ion exhibits two bands arising from the asymmetric and symmetric stretches. The former of these has been recorded between 1730 and 1780 cm^{–1}, whereas the latter band is observed between 1243 and 1282 cm^{–1}. The remarkable variations between samples are due to the extent of cation–anion interactions in the lattice and the media in which the spectra were recorded. The observed experimental data differ significantly from computed values, which predict bands at 1838 and 807 cm^{–1} for the asymmetric and symmetric stretches, however it is worth noting that the latter of these is predicted to be very weak (8 km/mol).¹³

2.2. Electrochemistry

The 2-phosphaethynolate anion belongs to the class of pseudo-halogen ligands, and can in principle bond to a variety of transition metal and non-metal centers in an ambiphilic fashion. However, experimentally one of the major limitations towards forming such complexes is that PCO^- is readily oxidized. This was originally observed by Becker and co-workers who reported that on reacting $\text{Li}(\text{DME})_2(\text{OCP})$ with sulfur dioxide (SO_2) an oxidative tetramerization occurs which gives rise to the heterobicyclic dianion, $(\text{P}_4\text{C}_4\text{O}_4)^{2-}$, which contains a central P–P bond.¹⁴ This dianion has a butterfly structure as indicated in Scheme 2 and is easily identified by its characteristic ^{31}P NMR spectrum (^{31}P NMR: $\delta = 36.9$ ppm, 81.4 ppm; $^2J_{\text{P-P}} = 32$ Hz). This compound is frequently observed as an undesired product when an OCP^- salt is reacted with an oxidizing main group or transition metal halide.



Scheme 2. Synthesis of $(\text{P}_4\text{C}_4\text{O}_4)^{2-}$ by oxidation of PCO^- with SO_2 .

Cyclic voltammometric measurements of NaOCP solutions reveal irreversible oxidations at rather low anodic potentials. This observation combined with the fact that “... the oxidation product is insoluble in DMSO...” led Grützmacher and Peruzzini to hypothesise that the resulting product was $\text{Na}_2(\text{P}_4\text{C}_4\text{O}_4)$, in line with Becker’s original report.¹⁵ The high stability of the oxidation product was confirmed by the observation that in the reverse cathodic scans no increase in current was observed up to potentials of -2 V.

In principle, a single electron oxidation of PCO^- should give rise to a neutral radical PCO^\bullet . Such a species is expected to be very short lived, and should couple to form the dimer $\text{P}_2\text{C}_2\text{O}_2$, presumably through formation of a P–P bond. The neutral radical PCO^\bullet has previously been observed by infrared spectroscopy in an argon matrix,¹⁶ and was recently reinvestigated in the gas phase through negative ion photoelectron spectroscopy (NIPES) and photoelectron imaging spectroscopy.¹⁷ These latter studies permitted the determination of the electron affinity (EA), spin–orbit coupling (SOC) and stretching mode vibrational frequencies of PCO^\bullet . These studies reveal that the electron affinity of the radical is 2.670 ± 0.005 eV which is significantly lower than the value determined for the NCO^\bullet radical (3.609 eV), in line with the decreased electronegativity of phosphorus relative to nitrogen.

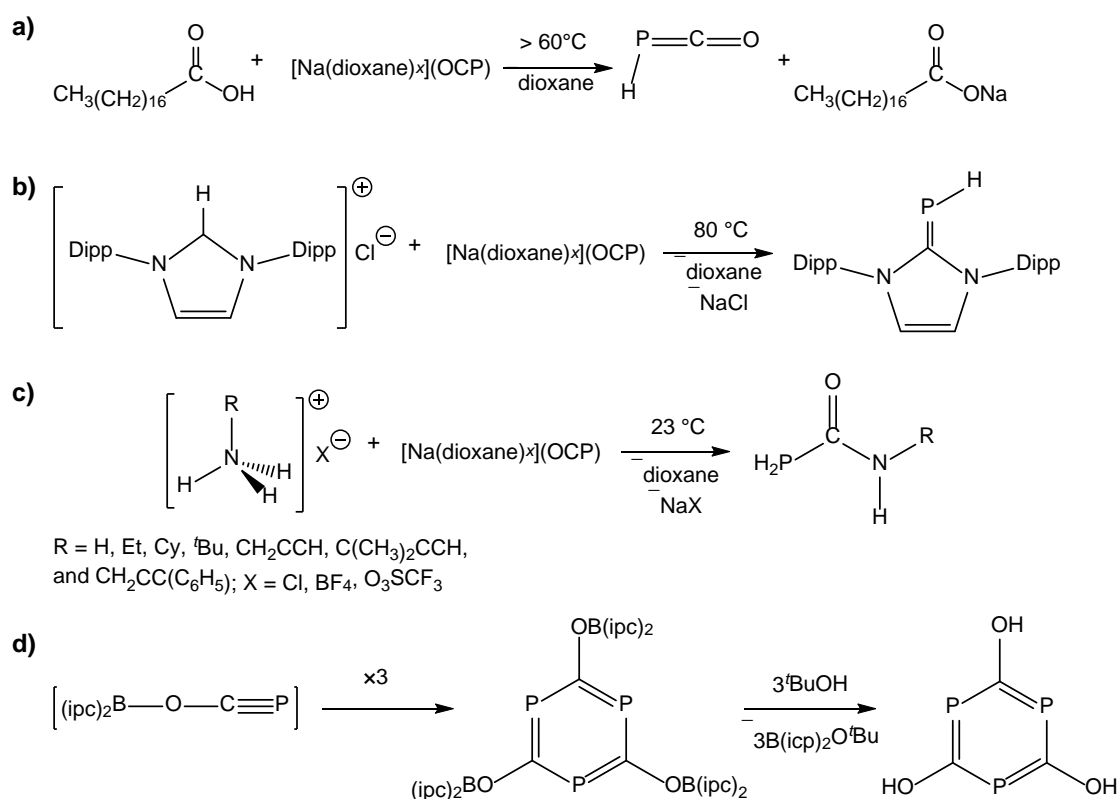
The asymmetric stretching frequency of PCO^* is red-shifted with regard to that of PCO^- ($1895 \pm 20 \text{ cm}^{-1}$) whereas the symmetric stretching frequency of is blue-shifted ($725 \pm 20 \text{ cm}^{-1}$).

The reduction chemistry of PCO^- is less well-explored than the oxidation chemistry of the anion. The reductive dimerization of the PCO^- anion to afford the formally tetra-anionic species $(\text{OCPPCO})^{4-}$ has recently been achieved in the coordination sphere of scandium, by reduction of a phosphaeethynolate-scandium(III) compound with potassium graphite.¹⁸ In principle, such reductions may be used as a method of cleaving the O–C bond to generate the cyaphide ion ($\text{C}\equiv\text{P}^-$) and an oxide (O^{2-}), a reactivity mode that has been explored recently (see section 5.3).

3. Acid-base chemistry and the synthesis of HPCO

The Brønsted acid–base chemistry of the 2-phosphaeethynolate anion is fundamentally very interesting. While the anion is known to have some stability in neutral aqueous solutions, early studies focusing on acidifying these solutions gave rise to insoluble pale yellow precipitates. Interesting correlations can be drawn with the chemistry of the cyanate ion in this regard. Cyanic acid (NCOH) is known to rapidly decompose, but is presumed to be present in about 3% when its tautomer isocyanic acid (HNCO) is generated by protonation of NCO^- . This species rapidly trimerises to give rise to cyanuric acid (HNCO)₃.¹⁹ The phosphorus-containing analogues of such compounds PCOH , HPCO and $(\text{HPCO})_3$ cannot be spectroscopically observed on addition of most common acids to solutions of PCO^- , despite the fact that HPCO has been postulated as an intermediate in a number of transformations. The resulting insoluble precipitates suggest more complex catenation processes than a simple trimerization. Theoretical studies predict that the HPCO tautomer is significantly more stable than the PCOH and HCPO by 98.7 and 259.0 kJ mol^{-1} , respectively.²⁰ This phosphorus-containing analogue of isocyanic acid has even been postulated to exist in space. Matrix isolation studies allowed for the synthesis of HPCO by electric discharge of argon/ PH_3 / CO or argon/ P_4 / CO mixtures which permitted the determination of the infrared spectrum of this highly unstable acid.²¹ Related studies involving mixtures of PH_3 and CO highly diluted in neon have also allowed for the determination of the microwave spectra of HPCO and HP^{13}CO .²² The first evidence for the formation of HPCO by NMR spectroscopy was reported in 2016 by Hinz and Goicoechea.²³ The authors employed a method that has previously been used for the synthesis of HN_3 ,²⁴ HNCO ,²⁵ and HNSO .²⁶ By heating a solid mixture of $[\text{Na}(\text{dioxane})_{1.0}][\text{PCO}]$ and stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) *in vacuo* and condensing all the volatiles into an NMR tube containing a deuterated solvent (toluene, dichloromethane or THF), they were able to record the NMR spectra of this elusive species, and identify several oligomers prior to decomposition (Scheme 3a). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of HPCO

in [D₈]toluene reveals a singlet at –316.7 ppm, which, upon proton coupling transforms to a doublet with $^1J_{\text{P-H}} = 188$ Hz. The ^1H NMR spectrum reveals a doublet centered at 0.25 ppm, while the ^{13}C NMR spectrum also shows a doublet at 201.4 ppm with a $^1J_{\text{P-C}}$ coupling constant of 102 Hz.



Scheme 3. a)–c) Selected reactions involving HPCO; and d) the synthesis of a phosphorus-containing analogue of cyanuric acid.

Despite its relative instability and the difficulties associated with its isolation, the phosphorus containing analogue of isocyanic acid, HPCO, has been postulated as a reactive intermediate in a number of transformations. These include the reaction of Na(OCP) towards [HIPr]Cl (where IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), in which the imidazolium cation is postulated to protonate PCO[–].²⁷ The resulting species rearranges and decarbonylates to afford a carbene-stabilized phosphandiyl (or phosphinidene) IPr=PH (Scheme 3b). Similarly, HPCO has been postulated as an intermediate in the synthesis of phosphinecarboxamides, a family of primary phosphines synthesized from the reaction of PCO[–] salts with ammonium salts (Scheme 3c).²⁸ In this particular case, the chemistry of the 2-phosphaethynolate anion closely mimics that of its lighter congener the cyanate ion, as such transformations are reminiscent of Wöhler’s historic synthesis of urea from the reaction of silver cyanate with ammonium chloride.²⁹ More recently, these reactions have been extended to aminoacids.³⁰

A phosphorus-containing analogue of cyanuric acid, $P_3C_3(OH)_3$ was reported in 2017 from the alcoholysis of the derivatized cyclic compound $P_3C_3[OB(ipc)_2]_3$ (where ipc = diisopinocampheyl; Scheme 3d).³¹ This latter species is prepared from the reaction of the commercially available (–)-B-chlorodiisopinocampheylborane, $(ipc)_2BCl$, with $Na(dioxane)_{2.5}(OCP)$, which is postulated to give a phosphaethynealato-borane, $(ipc)_2B-O-C\equiv P$, that spontaneously trimerises. $P_3C_3(OH)_3$ was characterized by ^{31}P NMR spectroscopy revealing a singlet resonance 133.7 ppm. The presence of a higher order multiplet in the ^{13}C NMR spectrum of this species 231.3 ppm verifies the existence of a cyclic core with magnetically inequivalent carbon atoms.

4. Coordination chemistry and salt metathesis

The Lewis basic nature and ambiphilicity of the 2-phosphaethynolate anion has been extensively studied in the coordination sphere of a number of transition metal and main group element fragments. As stated previously, PCO^- can act as an ambidentate nucleophile, much like its lighter congener NCO^- . Perhaps unsurprisingly, soft, polarisable elements favour coordination through the phosphorus atom, while hard, charge-dense Lewis acids favour binding through the oxygen atom. In selected cases, isomerization between these binding modes has been proposed (as in the case of $^iPr_3Si(PCO)$ and $^iPr_3Si(OCP)$, which has been spectroscopically observed as both isomers in solution).³² A list of the known, structurally authenticated, compounds of PCO^- is provided in Table 2 along with selected structural and spectroscopic data on these compounds.

What is immediately apparent on inspection of the compounds in Table 2 is that bonding through the phosphorus atom is the predominant bonding mode for the 2-phosphaethynolate anion. Such phosphaketene compounds, $M-P=C=O$, can be readily synthesized by salt metathesis reactions with halide precursors, and have been characterized for elements of the transition metal series and the main group. The first transition metal complex of PCO^- to be isolated was $(triphos)Re(PCO)(CO)_2$ ($triphos = MeC(CH_2PPh_2)_3$; Figure 2 A) which was reported in 2012 by reaction of $(triphos)ReCl(CO)_2$ with $Na(dioxane)_{2.5}(OCP)$.¹⁵ In their report, Grützmacher, Peruzzini and co-workers observed that finding an appropriate metal halide precursor for such reactions was challenging and that the reaction mixtures often gave rise to insoluble precipitates, the authors concluded that “*redox reactions may be the reason for this behavior*”. Since then over fifteen phosphaketene type compounds have been isolated and structurally authenticated, and many more postulated as reaction intermediates. The commonality to all of these species is that bulky supporting ligands are often required for their isolation, and that species featuring more than one phosphaketene ligand have yet to be synthesized.

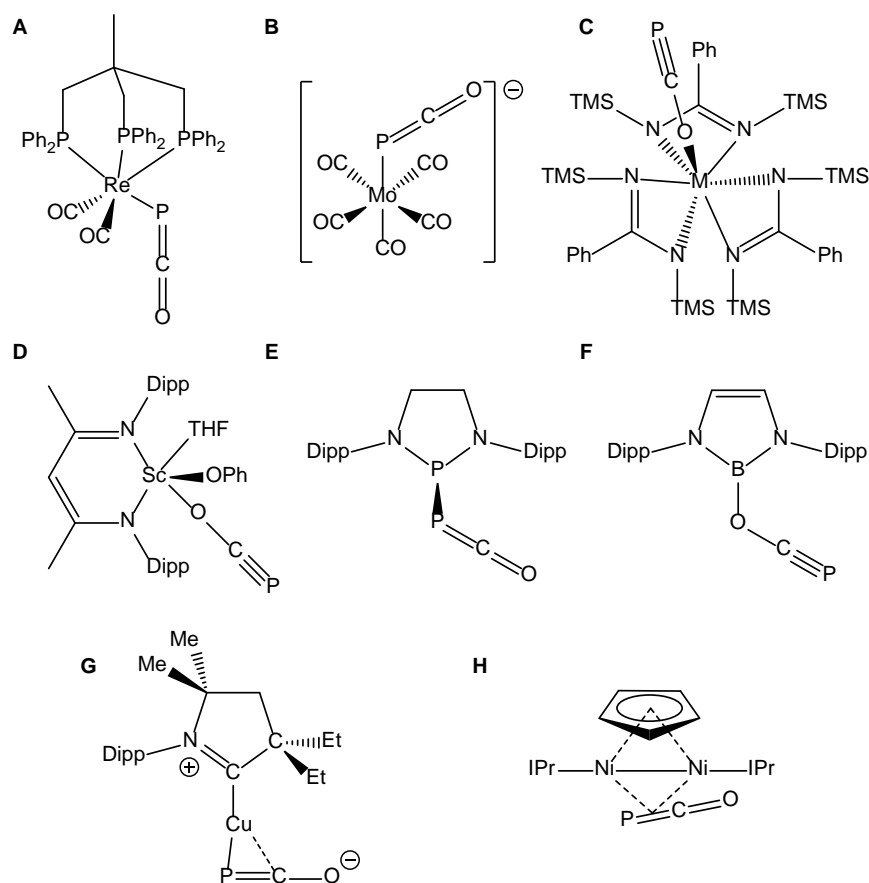


Figure 2. Selected examples of compounds of the PCO^- ion. TMS = trimethylsilyl; Dipp = 2,6-diisopropylphenyl; THF = tetrahydrofuran; IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene.

Simple ligand displacement reactions are also possible with compounds coordinated by relatively weak Lewis bases, thus reaction of $\text{W(CO)}_5(\text{MeCN})$ with PCO^- affords the anionic coordination compound $[\text{W(CO)}_5(\text{PCO})]^-$ (Figure 2 B).³³ In this species, as with all of the other phosphaketanyl compounds synthesized to date, coordination of the $^-\text{P}=\text{C}=\text{O}$ moiety takes place through the phosphorus atom with a bent geometry relative to the metal (or main group element) center. This contrasts with analogous compounds of the cyanate anion in which linear coordination is observed. The E–P–C bond angles for the majority of phosphaketanyl compounds approach 90° (e.g. $94.7(1)^\circ$ for $[\text{W(CO)}_5(\text{PCO})]^-$) which can be rationalized by taking into consideration the frontier molecular orbitals of PCO^- . The HOMO of this anion has a significant degree of phosphorus p-orbital character, implying that on coordination to a Lewis acid, it acts as a two-electron σ -donor, but through a polarized π -bonding orbital. Such bent coordination modes are common to all of the known phosphaketanyl compounds isolated, and can in fact be related to the bent geometry observed for the parent acid HPCO .

By contrast, reactions involving metal centers that are more ionic in character favour formation of oxygen-bonded phosphaehtynolate compounds ($E-O-C\equiv P$). This bonding mode was first structurally authenticated in the coordination sphere of the actinide elements in $(\text{amid})_3M(\text{OCP})$ ($M = \text{U}, \text{Th}$; where $\text{amid} = N,N\text{-bis}-(\text{trimethylsilyl})\text{benzamidinate}$; Figure 2 C).³⁴ In these compounds, and in the two scandium and uranium compounds that have been isolated since, $\{\text{CH}[\text{N}(\text{Dipp})\text{C}(\text{CH}_3)]_2\}\text{Sc}(\text{ODipp})(\text{THF})(\text{OCP})$ ¹⁸ and $[(^{\text{Ad,Me}}\text{ArO})_3\text{N}]\text{U}(\text{DME})(\text{OCP})$, the PCO^- ion binds through the oxygen atom in a linear fashion with $M-O-C$ angles approaching 180° ($170.9(3)^\circ$ for $(\text{amid})_3\text{U}(\text{OCP})$).³⁵ The bonding in these phosphaehtynolato species has much greater ionic character than in phosphaketenyl-type compounds, and results in a significant shortening of the $P-C$ bonds and a concomitant lengthening of the $C-O$ bonds of the anion relative to those observed for phosphorus-bonded species. This allows for subsequent coordination of the formal $P\equiv C$ triple bond to other metal centers, as demonstrated by the formation of an adduct between $(\text{amid})_3\text{Th}(\text{OCP})$ and a $\text{Ni}(\text{COD})$ fragment (where $\text{COD} = 1,5\text{-cyclooctadiene}$);³⁴ or perhaps more remarkably, in the cleavage of the $O-C$ bond to afford the cyaphide ligand ($C\equiv P^-$) as shown by Meyer and co-workers.³⁵ Coordination of the PCO^- anion to a metal center via the oxygen atom also permits for the reductive dimerization of two PCO^- units to afford the formally tetra-anionic $[\text{OCPPCO}]^{4-}$ ligand, which has recently been achieved from the reduction of the scandium complex $\{\text{CH}[\text{N}(\text{Dipp})\text{C}(\text{CH}_3)]_2\}\text{Sc}(\text{ODipp})(\text{THF})(\text{OCP})$ (Figure 2 D).¹⁸

For the main group elements, phosphaketenyl compounds (such as the phosphanyl phosphaketene pictured in Figure 2 E) are also quite numerous and have been shown to readily decarbonylate affording phosphandiyls, the majority of which oligomerise on formation (*vide infra*).³⁶ As with the known transition metal compounds, coordination through the phosphorus atom with acute $E-P-C$ bond angles is observed in all cases. By contrast, there is only one known structurally authenticated example of a phosphaehtynolate compound of a main group element reported to date, $[\text{N}(\text{Dipp})\text{CH}]_2\text{B}(\text{OCP})$ (Figure 2 F).³⁷ A related phosphaehtynolato-borane has been postulated as an intermediate in the formation of the phosphorus-containing analogue of cyanuric acid $\text{P}_3\text{C}_3(\text{OH})_3$.³¹ The high oxophilicity of boron favours formation of phosphaehtynolate-type compounds, however even in the case of $[\text{N}(\text{Dipp})\text{CH}]_2\text{B}(\text{OCP})$, the phosphorus-bonded isomer is predicted to be thermodynamically more stable by computational methods. As with phosphaehtynolate compounds of the actinides and scandium, there is an enhanced reactivity of the formal $P\equiv C$ triple bond, which allows for such species to be rationalized as phosphaehtyne analogues. For example, the cyclic trimerization of $(\text{icp})_2\text{B}-O-C\equiv P$ is closely related to the trimerization of $^t\text{Bu}-C\equiv P$ to afford triphosphabenzene type species.

A close look at the spectroscopic data provided in Table 2 reveals that ^{31}P NMR spectroscopy cannot be used as a reliable tool in the distinction of $\text{E}-\text{P}=\text{C}=\text{O}$ and $\text{E}-\text{O}-\text{C}\equiv\text{P}$ coordination modes, as such compounds often have comparable chemical shifts. However, notable differences are observed in the IR spectra of such species with $\text{E}-\text{P}=\text{C}=\text{O}$ type compounds often exhibiting bands arising from the asymmetric vibrational mode around 1899 cm^{-1} , whereas those of the phosphaeethynolate-type compounds occur at lower wavenumbers, with an average value of 1677 cm^{-1} . There is also a remarkable change in the magnitude of the one-bond $^{31}\text{P}-^{13}\text{C}$ coupling constant for the PCO^- moiety in such species, which changes by almost an order of magnitude from the phosphorus-bonded compounds (94 Hz) to oxygen-bonded species (12 Hz).

In addition to these common η^1 -monodentate binding modes, there are also two literature reported examples of the PCO^- anion binding through the π -manifold in an η^2 mode reminiscent of alkynes and phosphalkynes. The first of these was reported by Bertrand and Grützmacher, and shows a side-on binding of the PCO^- ion to a copper(I) metal center, $(\text{CAAC})\text{Cu}(\text{PCO})$ (where CAAC is the cyclic alkyl amino carbene pictured in Figure 2 G).³⁸ This compound features relatively short Cu–P and Cu–C bonds, 2.2244(5) and 2.501(2) Å, respectively, and differs significantly from a closely related gold(I) compound, $(\text{CAAC})\text{Au}(\text{PCO})$. Theoretical calculations on both compounds revealed that while for the gold complex a Au–P σ bond was present, for the related copper complex no such bond was observed, and that consequently, the PCO^- moiety was less tightly bonded to the copper center. Recently, a closely related silver(I) complex, $(\text{ITr})\text{Ag}(\eta^2\text{-PCO})$, was reported by Rivard and co-workers which exhibits a similar binding mode.³⁹

A related η^2 -bonding mode has also recently been reported for a bimetallic nickel(I) compound, $(\mu^2\text{:}\eta^5, \eta^5\text{-Cp})[\mu^2\text{:}\eta^2, \eta^2\text{-PCO}]\{\text{Ni}(\text{IPr})\}_2$ (Figure 2 H; IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene),⁴⁰ in which the PCO^- ion bridges to metal centers in a unique $\mu^2\text{:}\eta^2, \eta^2$ -binding mode. This species is an intermediate to the bimetallic butterfly compound $(\mu^2\text{:}\eta^2, \eta^2\text{-P}_2)\{\text{Ni}(\text{IPr})(\text{CO})\}_2$ formed via a decarbonylative process discussed herein.

Table 2. Selected structural and spectroscopic properties for known compounds of PCO^- .

Compound	ref.	P–C–O (°)	P–C (Å)	C–O (Å)	E–P/O (Å)	^{31}P (ppm)	^{13}C (ppm)	$^1J_{\text{P-C}}$ (Hz)	IR (cm^{-1})
Phosphorus bonded									
$^i\text{Pr}_3\text{Si}(\text{PCO})$	32	N.A.	N.A.	N.A.	N.A.	–370.1	183.4	91.8	1947
$\text{Ph}_3\text{Si}(\text{PCO})$	32	N.A.	N.A.	N.A.	N.A.	–340.5	184.0	99.8	1962
$\text{Ph}_3\text{Ge}(\text{PCO})$	32	N.A.	N.A.	N.A.	N.A.	–344.0	182.5	105.0	1954
$\text{Ph}_3\text{Sn}(\text{PCO})$	32	N.A.	N.A.	N.A.	N.A.	–378.0	180.6	108.0	1946
$\text{Ph}_3\text{Sn}(\text{PCO})$	32	N.A.	N.A.	N.A.	N.A.	–364.0	181.7	110.0	1923
$\{\text{N}(\text{Dipp})\text{C}_2(\text{C}_5\text{H}_8)\text{P}(\text{N}^t\text{Bu}_2\text{Si}(\text{CH}_3)_2)\text{Ge}(\text{PCO})$	41	178.0(3)	1.670(4)	1.167(4)	2.433(1)	–317.3	183.4	37.1	1920
$\{\text{CH}[\text{N}(\text{Dipp})\text{CH}]_2\text{Ge}(\text{PCO})$	42	178.0(2)/177.8(2)	1.643(2)/1.639(2)	1.166(3)/1.170(3)	2.476(1)/2.478(1)	–298.9	189.7	91.2	1895
$\{\text{CH}[\text{N}(\text{Dipp})\text{C}^t\text{Bu}]_2\text{Ge}(\text{PCO})$	42	178.7(4)	1.625(4)	1.174(5)	2.501(1)	–304.9	192.0	87.0	1888
$\{\text{CH}[\text{N}(\text{Dipp})\text{CMe}]_2\text{Ge}(\text{PCO})$	43	178.7(3)	1.609(4)	1.173(4)	2.514(1)	–301.7	191.6	88.0	1879
$[(p\text{-tolyl})_2\text{B}[1-(1\text{-Ad})\text{-3-yl-2-ylidene}]_2\text{Ge}(\text{PCO})$	44	176.7(2)	1.617(2)	1.162(3)	2.483(1)	–325.8	N.A.	N.A.	1879
$[\text{N}(\text{Dipp})\text{CH}]_2\text{P}(\text{PCO})$	36	179.1(2)	1.642(2)	1.170(2)	2.441(1)	–232.6	198.4	95.6	1881
$[\text{N}(\text{Dipp})(\text{CH}_2)]_2\text{P}(\text{PCO})$	36	179.4(3)	1.635(3)	1.170(3)	2.378(1)	–245.6	194.6	98.2	N.A.
$[\text{N}(\text{Ar}^{**})(\text{CH}_2)]_2\text{P}(\text{PCO})$	36	N.A.	N.A.	N.A.	N.A.	–240.9	194.6	98.0	N.A.
$(\text{triphos})\text{Re}(\text{PCO})(\text{CO})_2$	15	174.1(2)	1.62(2)	1.23(2)	2.561(7)	–397.5	175.4	91	1846
$[\text{W}(\text{PCO})(\text{CO})_5]^-$	33	176.8(4)	1.616(4)	1.176(5)	2.666(1)	–441.0	173.0	94.9	1841
$(\text{PDI})\text{Co}(\text{PCO})$	38	169.9(4)	1.633(4)	1.179(6)	2.263(1)	–225.8	181.2	98.8	1851
$(\text{CAAC})\text{Au}(\text{PCO})$	38	176.5(3)	1.640(3)	1.176(4)	2.354(1)	–359.5	183.0	100.4	1887
$(\text{CAAC}')\text{Au}(\text{PCO})$	38	N.A.	N.A.	N.A.	N.A.	–364.2	182.5	101.1	1889
Oxygen bonded									
$[\text{N}(\text{Dipp})\text{CH}]_2\text{B}(\text{OCP})$	37	175.7(2)	1.545(2)	1.269(2)	1.425(2)	–285.9	140.2	17.6	1649
$^i\text{Pr}_3\text{Si}(\text{OCP})$	32	N.A.	N.A.	N.A.	N.A.	–307.2	145.5	9.8	1656
$\{\text{CH}[\text{N}(\text{Dipp})\text{C}(\text{CH}_3)]_2\}\text{Sc}(\text{ODipp})(\text{THF})(\text{OCP})$	18	179.9(3)	1.558(2)	1.235(3)	2.032(2)	–343.5	154.2	10.0	1702
$(\text{amid})_3\text{U}(\text{OCP})$ (M = U, Th)	34	179.1(4)	1.576(5)	1.219(6)	2.297(3)	–285.2	N.A.	N.A.	1685
$(\text{amid})_3\text{Th}(\text{OCP})$ (M = U, Th)	34	179.7(4)	1.561(4)	1.246(4)	2.318(2)	–334.4	N.A.	N.A.	1683
$[(^{\text{Ad,Me}}\text{ArO})_3\text{N}]\text{U}(\text{DME})(\text{OCP})$	35	177.9(5)	1.559(6)	1.237(6)	2.345(4)	N.A.	N.A.	N.A.	1688
Side-on bonded									
$(\text{CAAC})\text{Cu}(\eta^2\text{-PCO})$	36	176.4(1)	1.636(2)	1.184(2)	2.224(1)	–387.4	175.2	97.8	1849
$(\text{ITr})\text{Ag}(\eta^2\text{-PCO})$	39	174.5(2)	1.588(3)	1.211(4)	2.4015(6)	–304.8	172.8	91.8	N.A.
$(\mu^2\text{-}\eta^5\text{-}\eta^5\text{-Cp})(\mu^2\text{-}\eta^2\text{-}\eta^2\text{-PCO})\{\text{Ni}(\text{IPr})\}_2$	40	158.5(10)	1.80(2)	1.15(2)	N.A.	–290.8	185.8	10.2	1688

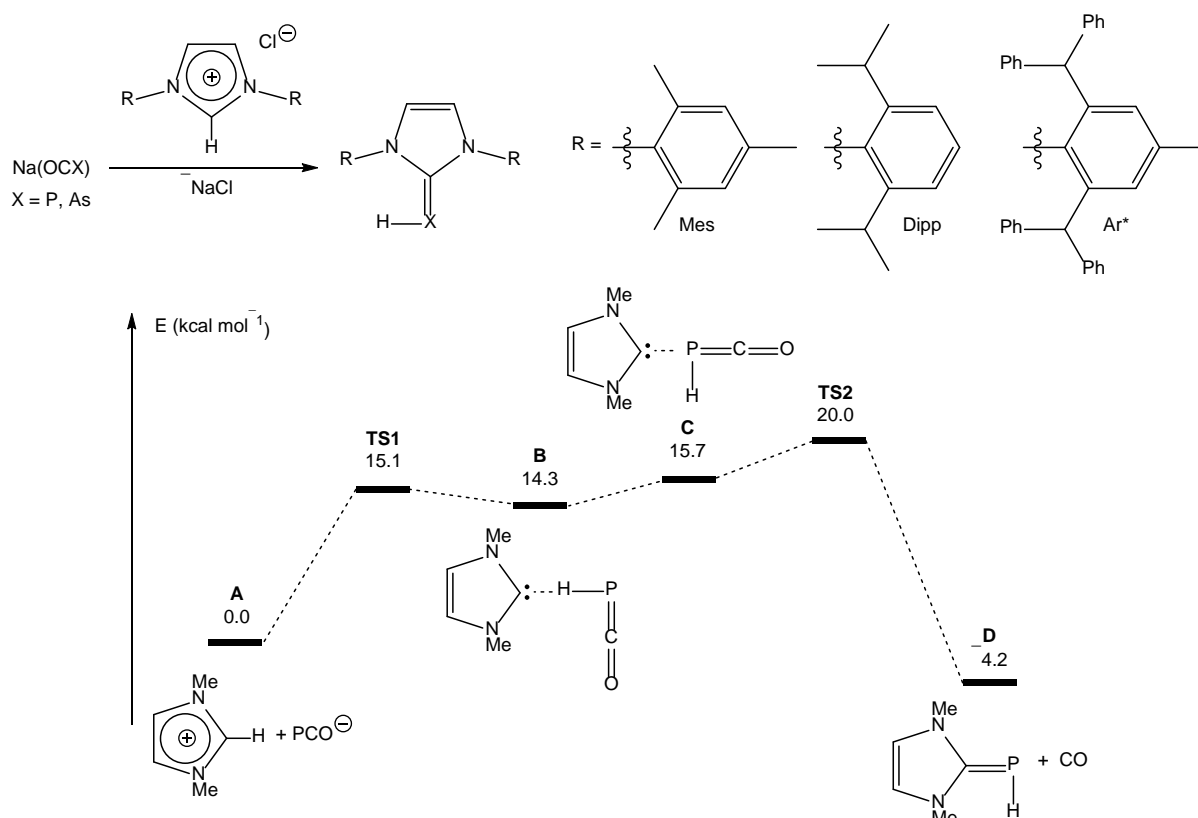
triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$; Ar^{**} = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl; PDI = α,α -diiminato pyridine; CAAC and CAAC' = cyclic alkyl amino carbenes; amid = *N,N'*-bis-(trimethylsilyl)benzamidinate; $(^{\text{Ad,Me}}\text{ArO})_3\text{N}$ = trianion of tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)-amine; ITr = 1,3-bis(2,6-di(trityl)phenyl)-imidazol-2-ylidene; IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene.

5. Decarbonylation and deoxygenation reactions

5.1. Main group element compounds

As the resonance structure **C** in Figure 1 implies, the OCX^- anions can be viewed to a certain extent as CO complexes of a pnictogen monoanion, X^- ($\text{X} = \text{N} - \text{Bi}$). This relates the chemistry of OCX^- to the chemistry of the valence isoelectronic azide anion, N_3^- , which can be regarded as source of N^- . Indeed covalently bonded main group element and transition metal azides readily decompose thermally or photochemically according to $[\text{M}]-\text{N}_2 \rightarrow [\text{M}]\equiv\text{N}$ into terminal nitrides which can be isolated as such or are reactive intermediates. Calculations show that the Wiberg bond indices (WBI's) and X–C dissociation energies for the reaction $\text{XCO}^- \rightarrow \text{X}^- + \text{CO}$ leading to X^- in its triplet ground state (^3P) strongly decrease from $\text{X} = \text{N}$ to Bi and the tendency for losing CO indeed increases in this order (*vide infra*).¹³ As will be shown, decarbonylation reactions do occur quite frequently when OCP^- is employed in the synthesis of phosphorus heterocycles. These are discussed below in section 6. Here we describe reactions first in which a simple decarbonylation leads to terminal pnictogenides.

The first reaction in which OCP^- which was discovered to act as a “P⁻” transfer reagent is the one between imidazolium salts and $\text{Na}(\text{OCP})$ (Scheme 4). Originally only a cation exchange was expected when THF solutions of $[\text{ImdH}]^+\text{X}^-$ salts were mixed with $\text{Na}(\text{OCP})$ which works well with $[\text{tBu}_4\text{N}]\text{Cl}$ to give $[\text{tBu}_4\text{N}](\text{OCP})$ as yellow oil ($\delta^{31\text{P}} = -390.3$ ppm). Instead, the ^{31}P NMR spectrum of the reaction solution shows one peak at -136.7 ppm with a $^1J_{\text{P-H}} = 164$ Hz indicative of the formation of an adduct between an N-heterocyclic carbene (NHC) and the parent phosphandiyl, PH .²⁷ A possible minimum reaction pathway was calculated using DFT and is included in Scheme 4. The whole reaction is weakly exothermic but becomes exergonic by -14.9 kcal mol⁻¹ on inclusion of the entropy factor caused by the formation of CO. The rate determining step is an endothermic proton transfer from the acidic imidazolium cation to the OCP^- anion which results in H-P=C=O . This highly unstable molecule (*vide supra*) remains bonded in adduct **B** via a hydrogen bond to the basic N-heterocyclic carbene. Subsequently, **B** rearranges to adduct **C** which collapses via a low energy barrier (4.3 kcal mol⁻¹) to the observed products.

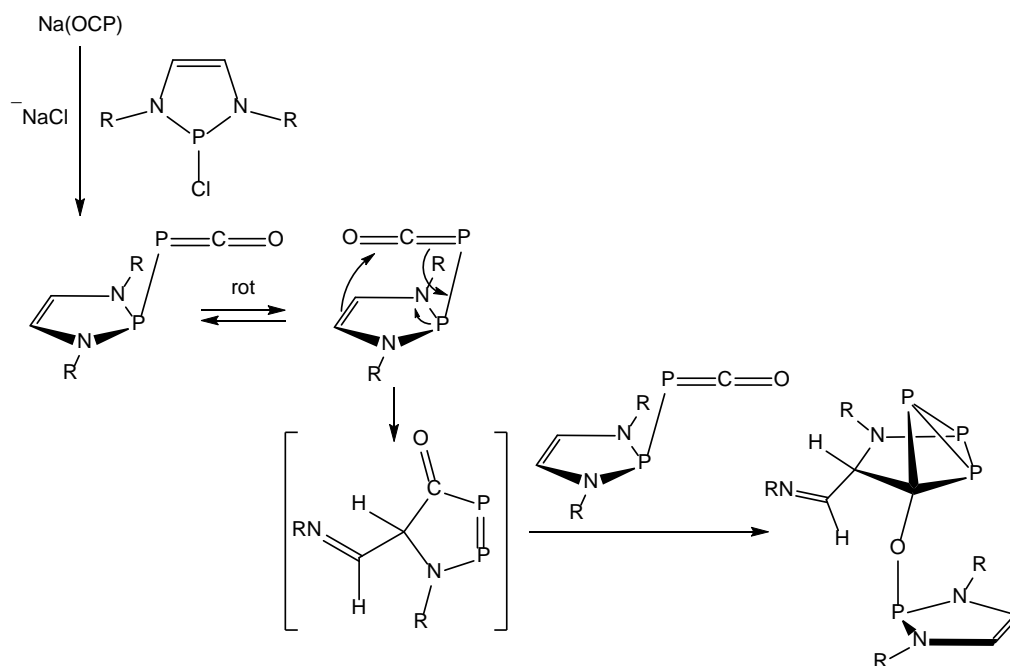


Scheme 4. Synthesis of NHC-stabilized phosphandiyls (P–H) and arsandiyls (As–H) by reaction of imidazolium salts with OCX[−] (X = P, As).

This method allows for the preparation of N-aryl substituted NHC adducts and was recently expanded to the synthesis of NHC adducts of AsH.⁴⁵ Note that imidazolium cations without acidic hydrogen can be used to prepare stable salts with the OCP[−] anion which are low melting solids or ionic liquids (*vide supra*).⁸

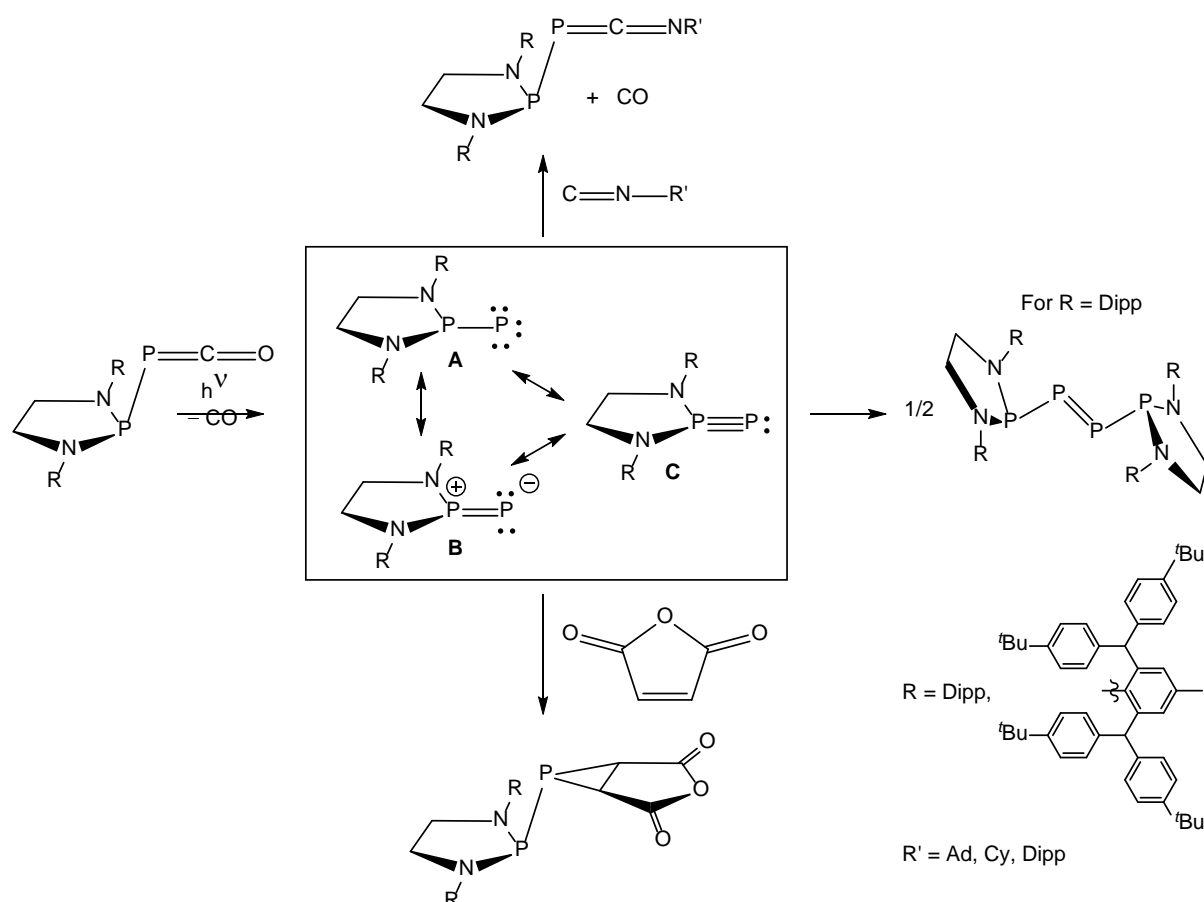
A second – and rather bizarre – example of the decarbonylation of OCP[−] is shown in Scheme 5.⁴⁶ When the 1-P-chloro-diazaphosphole with the bulky substituent R = Dipp is reacted with Na(OCP), the corresponding phosphanyl phosphaketene is obtained as crystalline yellow solid. This class of compounds (*vide infra*) have a very long P–P bond (> 2.4 Å) and are best described as tight ion pairs between a diazaphosphenium cation and OCP[−]. While the phosphaketene can be stored in the solid state, it rearranges cleanly in solution under loss of CO to give a tricyclic cage compound with a P₃ ring as sole product. Initially, it was believed that this reaction involves an intermediate with a central phosphanyl phosphandiyl C₂N₂P–P unit, stabilized by participation of the C₂N₂P≡P resonance structure,⁴⁷ but calculations show that this compound is not only thermodynamically significantly higher in energy (+29 kcal mol^{−1}) but also inaccessible because of a very high activation barrier for

the loss of CO (+49 kcal mol⁻¹). Instead this reaction proceeds via a heterocycle with a reactive P=P bond which is formed in a Hetero-Cope-rearrangement of the starting material.



Scheme 5. Decarbonylation of OCP⁻ on reaction of the anion with a 1-P-chloro-diazaphosphole (R = diisopropylphenyl (Dipp)).

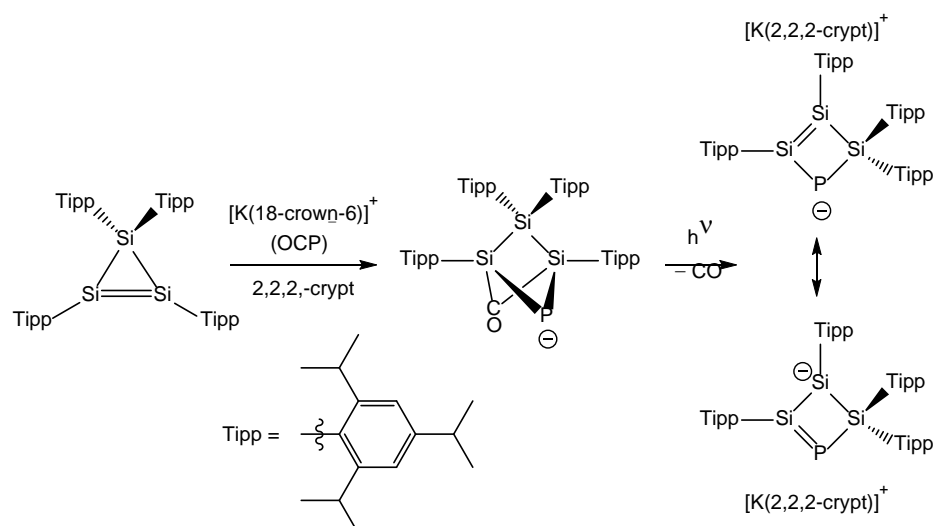
Bertrand and co-workers prepared the phosphanyl ketenes shown in Scheme 6. These compounds differ from those shown in Scheme 5 only by the saturated CH₂–CH₂ bridge in the diazaphospholane P(NR)₂(CH₂)₂ moiety.³⁶ But remarkably, irradiation of these derivatives with a medium pressure Hg lamp (λ = 200 – 400 nm) initiated loss of CO. With smaller R substituents like diisopropylphenyl (Dipp) violet crystals were obtained which contain the P,P-bis(phosphanyl)diphosphene. The assumption that a transient phosphanyl phosphandiyl is formed was bolstered by trapping reactions with isocyanides which cleanly gave phosphanyl ketimines as products. When the “super-bulky” substituent Ar^{**} (where Ar^{**} = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl) was used as protecting group in the diazaphospholane ring, photolysis indeed led to a stable phosphanyl phosphandiyl which was isolated as yellow-orange solid. A very large ¹J_{P–P} coupling constant of 884 Hz indicates a short P–P bond with high s-orbital character. Calculations indicate that this species is best described with three resonance structures **A** – **C** of which **B** and **C** with a P–P multiple bond have significant weight, such that the singlet state of this phosphandiyl is at least 24 kcal mol⁻¹ more stable than the triplet state, which is the usual electronic configuration of phosphandiyls, RP.



Scheme 6. Synthesis of a phosphanyl phosphandiyl and subsequent reactivity.

As with the transient $\text{R}_2\text{P}-\text{P}$ compound, the stable phosphanyl phosphandiyl can be reacted with isocyanides and electron deficient alkenes such as maleic anhydride. In subsequent studies, it was demonstrated that the CO group of the phosphanyl phosphaketenes can be easily replaced by a number of donors such as isocyanides, stable carbenes, and phosphanes which led to the notion that these type of phosphandiyls behave to a certain extent like transition metal carbonyl complexes.^{48, 49}

The use of phosphaehtynolate as source of “P⁻” has also been observed in the reaction between an unsaturated three-membered silicon ring (a cyclotrisilene) and $\text{Na}(\text{OCP})$ (Scheme 7).⁵⁰

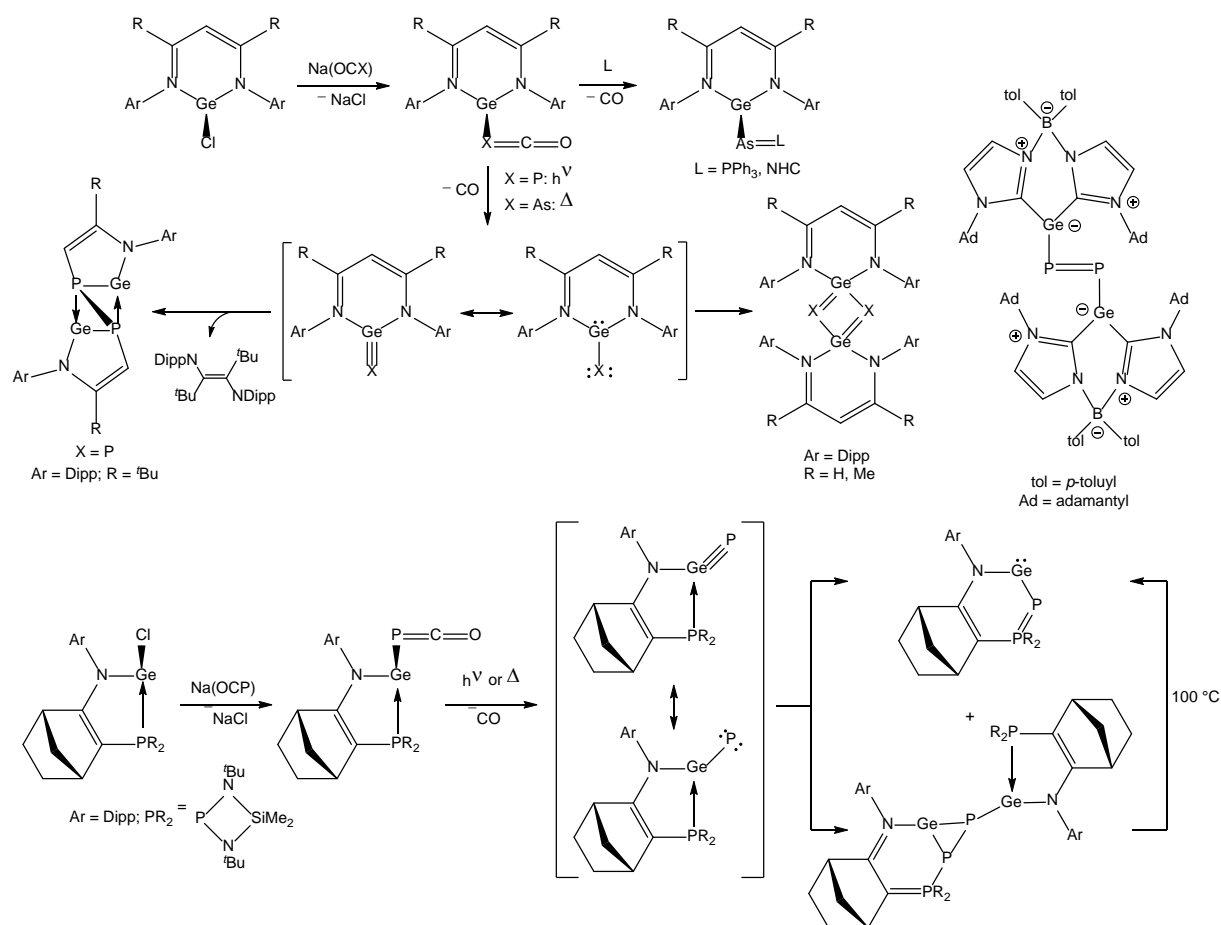


Scheme 7. Reactivity of PCO^- towards a cyclotrisilene and subsequent decarbonylation.

This highly solvent dependent reaction gives bright yellow crystals of a bicyclic compound in moderate yield in which the $\text{P}=\text{C}$ bond of the OCP^- anion has been thermally broken. Subsequent photolysis leads to the blue-green four-membered Si_3P heterocycle. Note that during the photolysis not only CO is extruded but also formally a triisopropylphenyl (Tipp) group migrated from the Si atom *trans* to phosphorus to a *cis*-position. To a certain extent, the whole process can be regarded as a “molecular doping process” by which a P^- center was incorporated into an unsaturated silicon scaffold.

The finding that $\text{Na}(\text{OCP})$ can be used to synthesize a stable singlet phosphanyl phosphandiyl which has an electronic structure to which a resonance form with a $\text{P}=\text{P}$ triple bond largely contributes, inspired the attempts to synthesize compounds with a $\text{Ge}=\text{P}$ or $\text{Ge}=\text{As}$ triple bond.^{41, 42, 43, 44} As starting materials, $\text{Ge}(\text{II})$ halides like the ones shown in Scheme 8 are suitable. Reactions with $\text{Na}(\text{OCP})$ or $\text{Na}(\text{OCAs})$ give first the corresponding germanyl substituted phospho- or arsaketenes. These germynyl substituted phosphaketenes, $\text{R}_3\text{Ge}-\text{PCO}$, are the more stable isomers when compared to derivatives with a $\text{Ge}-\text{O}-\text{C}\equiv\text{X}$ unit ($\text{X} = \text{P}, \text{As}$; *vide supra*). The $\text{Ge}(\text{II})-\text{XCO}$ ($\text{X} = \text{P}, \text{As}$) compounds can be isolated but the arsaketene derivatives are significantly more labile and lose CO at room temperature. The CO group in these can also be easily replaced by other neutral two-electron donor groups such as PPh_3 or N-heterocyclic carbenes (NHC). The decarbonylation of germanyl phosphaketenes required photolysis. In all cases, no stable compound with a $\text{Ge}=\text{P}$ or $\text{Ge}=\text{As}$ could be prepared. But it is highly likely that these are transient intermediates which are best described by the two major resonance structures $\text{Ge}(\text{II})-\text{X} \leftrightarrow \text{Ge}(\text{IV})=\text{P}$. These either dimerize in a head-to-tail fashion to four-membered Ge_2X_2 rings,^{42, 43} or in a head-to-head fashion to give

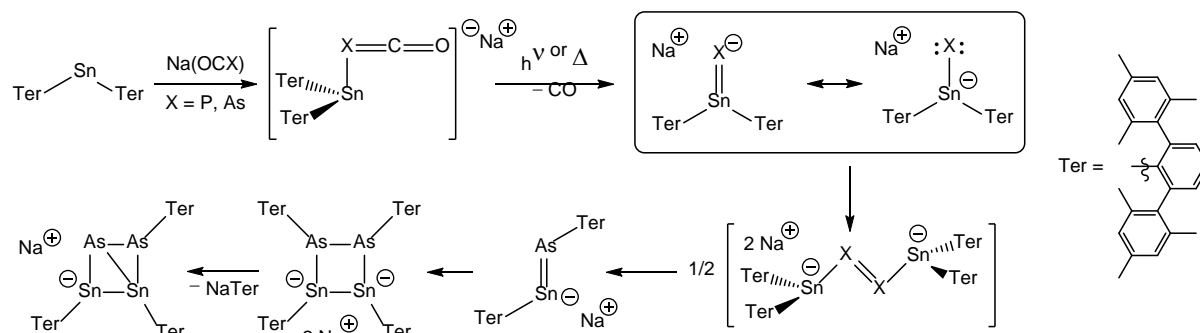
bis(germyl)diphosphenes.⁴⁴ When the amidogermanyl phosphaketene reported by Bacereido and Kato with an additional intramolecular phosphane–germanium interaction is photolyzed, a ring expansion reaction is observed which leads to an unsaturated six-membered C_2NP_2Ge ring which is best represented as a cyclic germylene with a Ge(II) center.⁴¹ A special case is the rearrangement of the diketiminato stabilized germaalkyne with bulky substituents Ar and R which loses an iminyl radical, $ArN=CR^*$, and forms compound $[DippNC(^tBu)C(H)PGe]_2$ in high yield.



Scheme 8. Synthesis and reactivity of germanyl phospho- and arsaketenes.

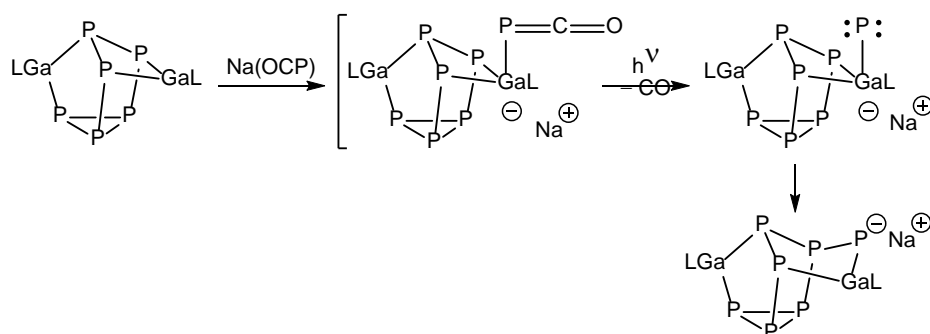
The reaction between the mildly Lewis acidic stannylene $SnTer_2$ and $Na(OCX)$ ($X = P, As$) leads to the anionic adducts $[Na(18\text{-crown-6})][Ter_2Sn-X=C=O]^-$, which in case of $X = As$ could be crystallized from the reaction mixture at low temperature (Scheme 9). These adducts are highly unstable and lose CO either thermally or under radiation with light.⁵¹ The reactive stannyl pnictogenyls $[Ter_2Sn-X]^-$ formed as initial products after loss of CO could nevertheless be isolated for the arseninidine derivative. In case of $X = P$, only the head-to-head dimer, $[Ter_2Sn-P=P-SnTer_2]^{2-}$, could be detected by NMR in low yield. In case of $X = As$, this species is formed as intermediate as well but readily dissociates and

rearranges via a 1,2-Ter-shift to give the anionic stannaarsene $[\text{TerSn}=\text{AsTer}]^-$ which likewise was unambiguously characterized including a structure determination by X-ray diffraction methods. This compound finally dimerizes to afford, under loss of a sodium terphenyl (NaTer), the final product. The 1,2-diarsa-3,4-distannacyclobutandiide is proposed as a transient intermediate in this remarkable transformation.



Scheme 9. Reactivity of OCX^- ($\text{X} = \text{P}, \text{As}$) towards a bulky stannylene.

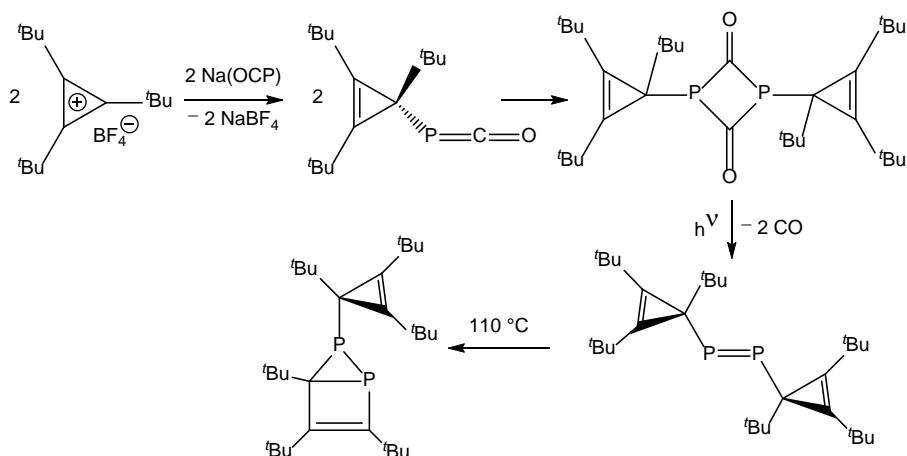
In a systematic study of the chemistry of the $(\text{LGa})_2\text{P}_6$ cluster ($\text{L} = \text{CH}[\text{N}(\text{CMeDipp})]_2$), this compound was also reacted with $\text{Na}(\text{OCP})$.¹² Although the exact reaction mechanism remains unknown, one can assume in light of the results discussed above that one of the Lewis-acidic $\text{Ga}(\text{III})$ center reacts with the OCP^- anion in the initial phase of the reaction (Scheme 10). The resulting adduct again easily loses CO to give a transient species which reacts further by insertion of the phosphandiyl center into the adjacent $\text{Ga}-\text{P}$ bond giving rise to an expansion of the cluster.



Scheme 10. Reaction of the $(\text{LGa})_2\text{P}_6$ cluster ($\text{L} = \text{CH}[\text{N}(\text{CMeDipp})]_2$) with $\text{Na}(\text{OCP})$.

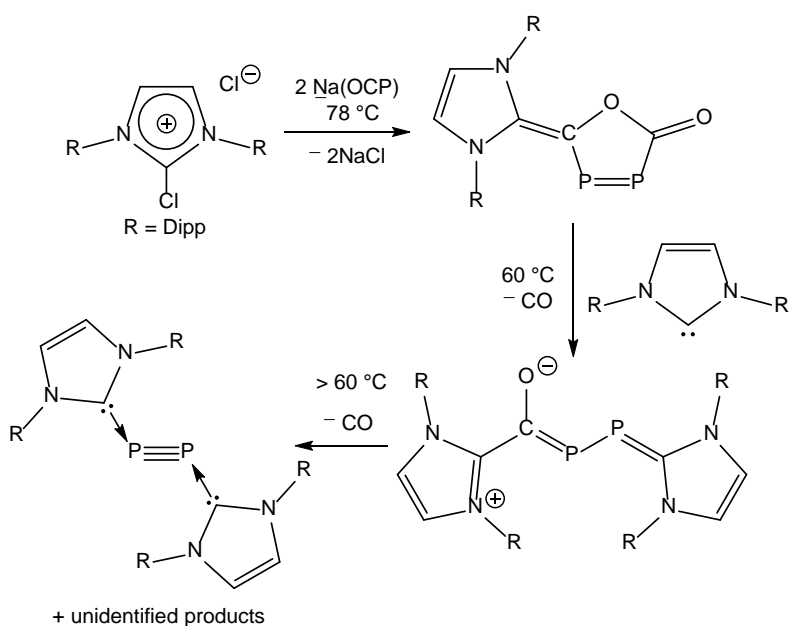
The examples discussed so far, involve phospho- and arsaketenes, $\text{R}-\text{X}=\text{C}=\text{O}$ ($\text{X} = \text{P}, \text{As}$), which are labile and lose CO rather easily. That also dimers formed by $[2+2]$ cycloadditions of these ketenes (*vide infra*) may be light sensitive and lose CO was recently demonstrated. The 1,3-diphosphetane-2,4-dione shown in Scheme 11 is thermally stable but loses CO under irradiation with a Xe lamp to

give quantitatively a diphosphene. This in turn rearranges thermally at 110 °C to a diphosphahousene derivative.⁵²



Scheme 11. Reaction of Na(OCP) with 1,2,3-tris-tert-butylcyclopropenium tetrafluoroborate to afford a 1,3-diphosphetane-2,4-dione, and its subsequent reactivity.

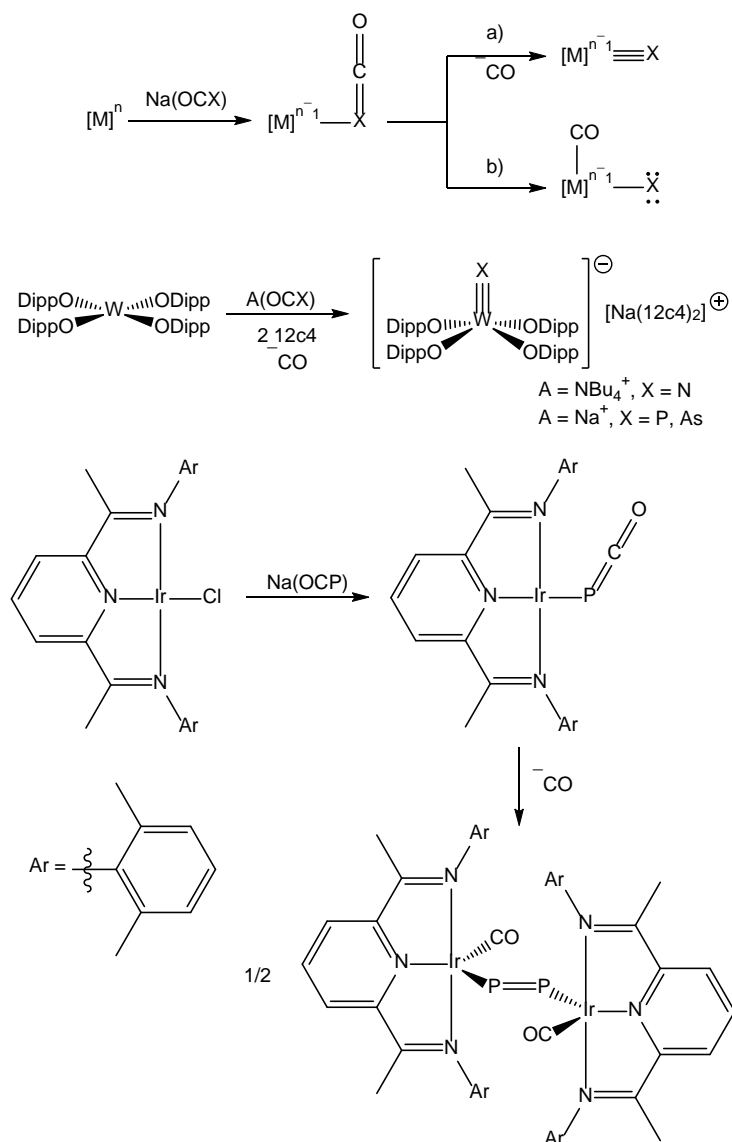
Another interesting case of double decarbonylation was observed when a chloroimidazolium chloride was reacted with two equivalents of Na(OCP) as pictured in Scheme 12.⁵³ When this reaction is performed at low temperature, red crystals can be isolated which consist of a N-heterocyclic carbene (NHC) substituted 1,3,4-oxodiphosphole. When this compound is heated between 55–60 °C in benzene in the presence of free NHC, a quantitative decarbonylation occurs to give the acyclic NHC–CO–P₂–NHC compound as green crystals. Subsequent heating of this compound above 60 °C allows for the loss of the second equivalent CO to give the NHC stabilized P₂ molecule although in low yield. NHC→P₂←NHC was previously synthesized by another route.⁵⁴



Scheme 12. Double decarbonylation on reaction of a chloroimidazolium chloride with two equivalents of Na(OCX).

5.2. Transition metal compounds

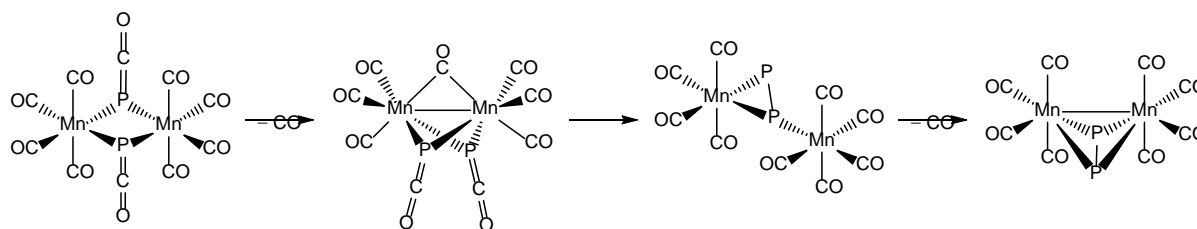
The analogy – based on similar chemical reactivity – between the azide ion as N_2 complex of “N⁻” and OCX^- anions as CO complexes of X^- ($X = N, P, As$) inspired the synthesis of transition metal pnictaethynolate complexes $[M]-X=C=O$ which after decarbonylation may lead to terminal metal pnictides, $[M]X$. Depending on the valence electron count at the metal center, two pathways by which these species form can be imagined. With electron poor metals, terminal pnictides are formed under loss of CO which are best described with $M\equiv X$ bonds (path a in Scheme 13). Electron rich metal pnictoketenes may rearrange as illustrated in path b, in which the strong π -electron acceptor CO group migrates to the metal center while the pnictogen atom is converted into a type of terminal pnictodiandiyl. The proof for the viability of path a) comes from a study, where the d²-valence configured tungsten(IV) alkoxide complex $[W(ODipp)_4]$ was reacted with Na(OCX) ($X = N, P, As$) in DME or in the presence of 12-crown-4 (12c4) (Scheme 13). This almost square planar tungsten complex is ideally suited for forming multiple bonds to a terminal pnictogen center.⁵⁵ Indeed, simply mixing $[W(ODipp)_4]$ with Na(OCX) yields under decarbonylation to the desired salts $[Na(L)_x]^+[W\equiv X(ODipp)_4]^-$ in excellent to moderate yields, whereby the rate of conversion increases in the order $N < P < As$. All species are diamagnetic with slightly distorted square-pyramidal structures. Notably, the scalar $^1J_{W-X}$ coupling constants indicate that the s-orbital contribution in the $W\equiv X$ bond decreases from N to P to As.



Scheme 13. Reactions of transition metal compounds with Na(OCX) (X = N, P, As).

An archetypical example for the reaction sketched in path b) is found in the reaction of the d^8 -Ir(I) complex with a redox non-innocent pyridyl diiminato (pdi) ligand, $[IrCl(pdi)]$.³⁸ The iridiaphosphaketene was detected by ^{31}P NMR spectroscopy ($\delta^{31}P = -317$ ppm) at low temperature. Upon warming to room temperature, the ^{31}P chemical shifts changes by almost 1000 ppm to +682 ppm which is in the range of diphosphenes with organic substituents. Compound $[Ir_2(P_2)(CO)_2(pdi)_2]$ is the first dimetalladiphosphene which could be isolated and fully characterized and although speculative, a d^8 -valence electron configured iridia-phosphadiendiyl $[Ir(dpi)(CO)P]$ can be postulated as intermediate which undergoes a head-to-head dimerization as was also observed for related germanium and tin pnictodiendiyls (*vide supra*).

It is noteworthy, that the formation of metal phosphides obtained by CO migration of metallaphosphaketenes has been predicted by calculations.⁵⁶ In an extensive survey of possible structures of various mononuclear and dinuclear manganese carbonyl complex fragments bound to PCO^- units, the formation of $[\text{Mn}_2(\text{CO})_8(\text{P}_2)]$ phosphides were foreseen by consecutive CO loss and double CO migration steps from the coordinated phosphaketene units to the Mn centers (Scheme 14).

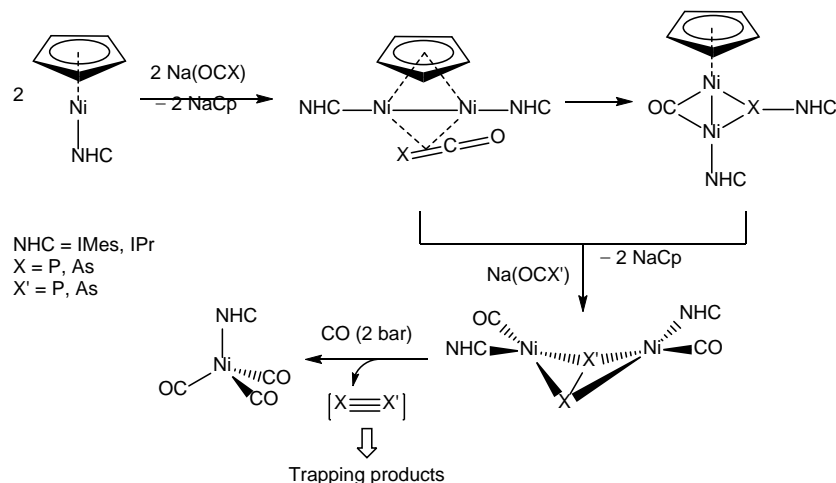


Scheme 14. Computed decarbonylation processes in bimetallic manganese metal carbonyl compounds.

The possible pathways for these reactions involve intermediates with dihapto $\mu^2:\eta^2\text{-PCO}$ ligands comparable to the $[\text{Cu}(\text{PCO})(\text{NHC})]$ complex discussed above (Figure 2).³⁸ Such metal bridging $\mu^2:\eta^2\text{-PCO}$ ligands may serve as six electron donors and hence compensate the electron deficiency at metal centers caused by CO loss. This makes the chemistry of OCP transition metal complexes more versatile than the one of analogous isocyanate compounds.

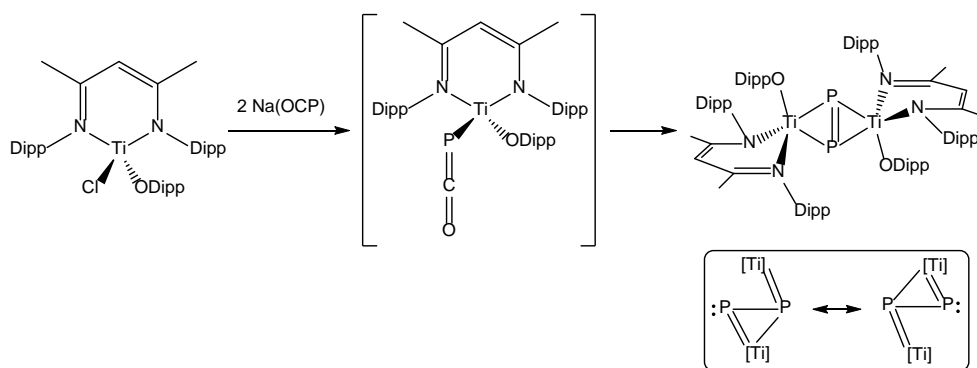
Indeed, such intermediates with $\mu^2:\eta^2\text{-XCO}$ ligands are observed in the formation of dinuclear metal complexes with bridging decarbonylated X_2 units ($\text{X} = \text{P}, \text{As}$). A suitable metal precursor complex is the Ni(I) complex $[\text{Ni}(\text{Cp})(\text{NHC})]$ (Cp = cyclopentadienyl; NHC = N-heterocyclic carbene) in which the Cp^- ligand acts as leaving group.⁴⁰ Its reaction with $\text{Na}(\text{OCX})$ in a 2:1 ratio yields indeed first a dinuclear complex with a $\mu^2:\eta^2, \eta^2\text{-OCX}$ ligand which was isolated and characterized by single crystal X-ray diffraction for $\text{X} = \text{P}$ and $\text{NHC} = \text{IPr}$. These complexes subsequently rearrange under migration of the CO group from the X center to take a bridging position between both Ni atoms while the Ni bound NHC ligand moves to the bridging X center ($\text{X} = \text{P}, \text{As}$). Adding a second equivalent $\text{Na}(\text{OCX}')$ with $\text{X}' = \text{P}, \text{As}$ to either these two primary products with a Ni(I)–Ni(I) bond (2.37–2.42 Å), displaces the remaining Cp^- ligand and yields $[\text{Ni}_2(\text{XX}')(\text{CO})_2(\text{NHC})_2]$. This reaction sequence allows also the synthesis of the complex $\text{X} \neq \text{X}'$, that is with a $\eta^2, \eta^2\text{-}\mu^2\text{-P}\equiv\text{As}$ ligand, although this compound could not be isolated in pure form. This is in contrast to the homoleptic species with $\mu^2:\eta^2, \eta^2\text{-P}_2$ or $\mu^2:\eta^2, \eta^2\text{-As}_2$ ligands which are simply prepared by reacting $[\text{Ni}(\text{Cp})(\text{NHC})]$ with $\text{Na}(\text{OCP})$ or $\text{Na}(\text{OCAs})$ in a 1:1 ratio. The coordination sphere around the Ni centers in $[\text{Ni}_2(\text{XX}')(\text{CO})_2(\text{NHC})_2]$ is best

described as distorted square-planar. The Ni...Ni distance is about 3 Å which excludes any significant interaction between the metal centers. These structural features imply an oxidation state of +2 at each Ni center with a d^8 valence electron configuration. Consequently, the central $[XX']$ unit is best described as $[X-X']^{4-}$ although the relatively short P–P (2.076 Å) and As–As bond lengths (2.301 Å) would suggest double bonds as in the dianions $[X=X']^{2-}$. Remarkably, under CO pressure $[\text{Ni}_2(\text{XX}')(\text{CO})_2(\text{NHC})_2]$ releases the highly reactive diatomic neutral molecules $[XX']$ which can be trapped.



Scheme 15. Reactivity studies of Na(OCX) (X = P, As) with N-heterocyclic carbene-stabilized Ni(I) complexes.

The reaction of the trivalent dark magenta Ti(II) complex $[\text{TiCl}(\text{ODipp})(\text{nacnac})]$ (nacnac = $\text{CH}[\text{N}(\text{CMeDipp})]_2$) with Na(OCP) leads to gas evolution and gives the binuclear dark brown complex $[\text{Ti}_2(\text{ODipp})_2(\text{nacnac})_2(\text{P}_2)]$.⁵⁷ A Ti(III) phosphaketene is the first plausible intermediate which could, however, not be detected. This species is calculated to be about 7 kcal mol⁻¹ more stable than its O-bound phosphalkyne isomer with a $[\text{Ti}]\text{--O--C}\equiv\text{P}$ group.



Scheme 16. Reactivity of Na(OCP) (X = P, As) towards $[\text{TiCl}(\text{ODipp})(\text{nacnac})]$ (nacnac = $\text{CH}[\text{N}(\text{CMeDipp})]_2$).

[Ti₂(ODipp)₂(nacnac)₂(P₂)] is the only structurally characterized group four metal P₂ complex to date. Like the Ge₂P₂ cycles, it shows an almost planar Ti₂P₂ ring but the P–P distance of the μ²:η²,η²-P₂ ligand of 2.11 Å indicates a bond in between a P–P single and P=P double bond. Furthermore, the Ti–P bonds are quite long and pairwise significantly different in lengths (2.42; 2.60 Å) such that the Ti₂P₂ ring has a rhomboidal shape. A careful inspection of the electronic structure suggests that this compound is best described with a zig-zag Ti–P–P–Ti chain and the two resonance structures shown in Scheme 16 are major contributors to the electronic ground state. There is a strong electron donation from each Ti center into the out-of-plane π* orbital of the central P₂ unit.

5.3. Deoxygenation reactions

The deoxygenation of OCP[−] would lead to the smallest imaginable building block for organophosphorus compounds: C≡P[−].⁵⁸ This analogue of cyanide – named cyaphide, correspondingly – would also allow for the preparation new coordination polymers with highly electronically coupled metal centers. On paper, one can envision a synthetic strategy in which OCP[−] is reacted with an strongly oxophilic electrophile according to, OCP[−] + E⁺ → EO–C≡P, whereby the oxygen center is incorporated in a leaving group EO such that reduction by two electrons, EO–C≡P + 2e[−] → EO[−] + C≡P[−], will give the desired cyaphide ion. While this looks rather straight forward on paper, to date all reactions between OCP[−] and such strong electrophiles such as halosulfonates, X–SO₂R, or related phosphonates, X–POR₂, and phosphates X–PO(OR)₂ (X = halogen) failed. Instead, oxidation of the rather strongly reducing OCP[−] anion to the tetrameric [P₄C₄O₄]^{2−} was observed.⁵⁹ By chance, an alternative but related pathway was found which indeed allows the deoxygenation of OCP[−] to give novel C₂P₂ and C₃P₃ compounds.

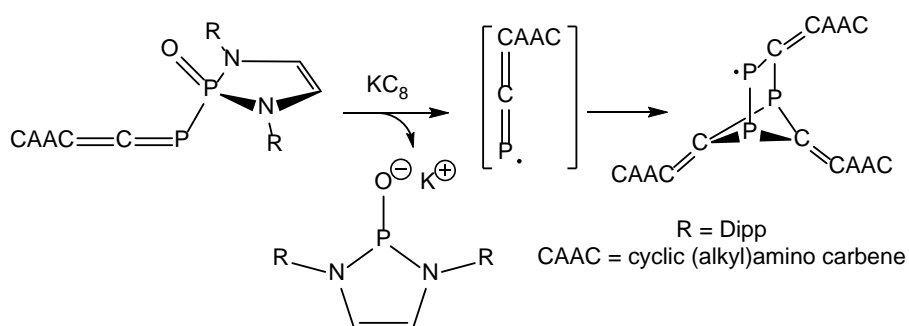
Diazaphospholene and diazaphospholane substituted phosphaketenes react cleanly with a variety of N-heterocyclic carbenes with a saturated or unsaturated C₃N₂ ring.⁶⁰ Primary products are zwitterionic compounds which could be isolated in some cases and which result from the nucleophilic attack of the carbenes on the carbon atom of the P=C=O unit. Subsequently, these compounds rearrange in an intramolecular Wittig-type reaction in which the oxygen center of the carbonyl group is transferred to the terminal phosphorus center. This step is rate determining according to DFT calculations with model compounds. Subsequently, a “phosphorotropic tautomerism” R₂P–P(=O)R₂ → R₂P–O–PR₂,⁶¹ takes places and leads to the final products. Remarkably, in this process the sequence OCP has been converted to CPO and the final products can be viewed as NHC-stabilized isocyaphides, :CP–R. This rearrangement reaction also occurs when

[illegible]

When cyclic diamido carbenes (DACs) are used as carbenes in the reaction with diazaphospholenyl phosphaketenes, again the rearrangement to $(\text{DAC})=\text{C}=\text{P}-\text{PO}(\text{CR})_2(\text{CH})_2$ was observed. But when this compound is reduced with KC_8 not a cyclic but an acyclic dimer is obtained. Formally this can be described as a DAC adduct of the elusive diisocyanide $:\text{C}=\text{P}-\text{P}=\text{C}:$.⁶³ A careful inspection of the electronic structure reveals that this compound contains electron shared bonds and is best represented as $\text{DAC}=\text{C}=\text{P}-\text{P}=\text{C}=\text{DAC}$. In contrast, the cyclic isomer, $\text{NHC} \rightarrow \text{C}_2\text{P}_2 \leftarrow \text{NHC}$, is constructed from two NHC units as donors in their singlet ground state and a C_2P_2 fragment as acceptor in an excited singlet state with a cyclic delocalized 6π electron system. This difference can be explained as follows: In order to achieve a cyclic molecule with electron shared bonds, the C_2P_2 ring has to be lifted into an excited quintet state and the two carbene fragments into a triplet state. Because of the

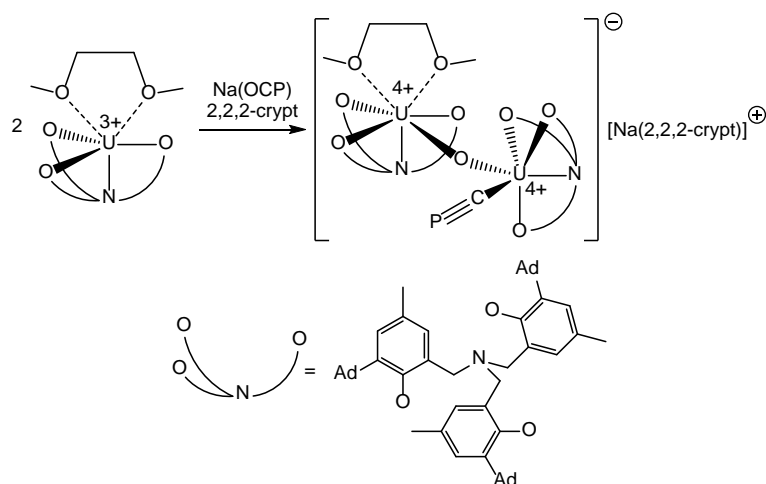
high S→T excitation energy of NHCs (89.9 kcal mol⁻¹) compared to that of DACs (45.5 kcal mol⁻¹) the total energy, E_{prep} , needed to prepare the fragments for forming electron shared bonds is too high for molecules with NHC fragments. But E_{prep} is compensated by the binding energy when DACs are the binding partners to C₂P₂.

It is likely that in the reduction of the NHC=C=P[PO{(NR)₂CR}₂] monomeric radicals NHC=C=P• are formed as transient intermediates. This assumption is bolstered by the isolation of stable tricarbontriphosphide radicals when cyclic (alkyl)amino carbenes (CAAC) were used (Scheme 18). These are the products of a [2+2+2] cycloaddition process in which the primarily formed products, CAAC→C₂P₂←CAAC, obtained by dimerization of CAAC=C=P•, undergo a third cycloaddition to give stable neutral radical (CAAC)₃C₃P₃ with a tricyclic cage structure.⁶⁵ EPR studies combined with DFT calculations show that the unpaired electron is localized in a p-type orbital at the non-bridgehead phosphorus atom ($\rho \approx 0.73$ e).



Scheme 18. PCO⁻ deoxygenation reaction to afford a neutral radical, (CAAC)₃C₃P₃, with a tricyclic cage structure.

A very elegant strategy to achieve the reductive deoxygenation of OCP⁻ according to OCP⁻ + 2e⁻ → O²⁻ + C≡P⁻ was found in the reaction of the strongly reducing trivalent uranium(III) aminoalkoxide complex with Na(OCP) in the presence of 2.2.2-cryptand.³⁵ In this reaction, a dinuclear complex is formed. Formally, the oxygen center of OCP⁻ is captured as O²⁻ between the two U(IV) centers while the cyaphide ion binds as terminal ligand to one U(IV) center (Scheme 19). The C≡P bond length (1.52 Å) is in the expected range, however, the ³¹P chemical shift δ = 266 ppm in the diamagnetic uranium complex is significantly shifted to higher frequencies when compared to the few known [Ru]–C≡P complexes ($\delta \approx 166$ - 160 ppm). Notably, when a non-reducing U(IV)-Cl complex carrying the same ligand is reacted with Na(OCP), a simple salt metathesis reaction occurs and the complex [U(IV)–O–C≡P] is isolated in high yield.

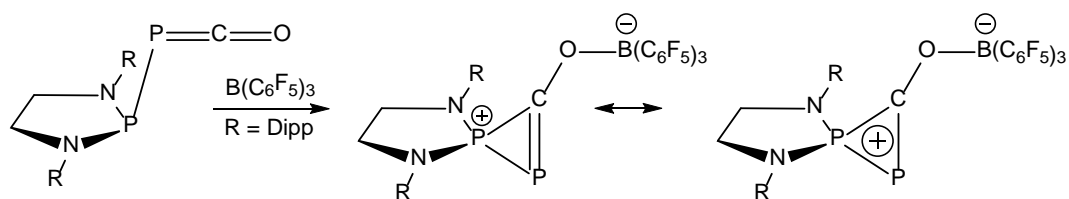


Scheme 19. Deoxygenation of PCO^- in the coordination sphere of a uranium(III) compound to afford the cyaphide anion.

6. Organic cyclizations

6.1 Three membered heterocycles

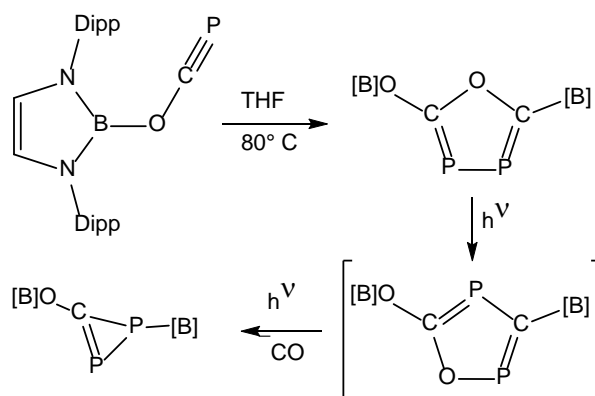
Bertrand et al. discovered that the phosphanyl substituted phosphaketenes are not only suitable precursors to transient and stable phosphanyl phosphandiyls by loss of CO (see Scheme 6),³⁶ but also are building blocks for a range of unusual phosphorus heterocycles. The reaction of the thermally highly stable diazaphospholanyl phosphaketene with BH_3 gives a classical phosphane-borane complex in which the BH_3 coordinated to the P atom of the five-membered heterocycle. But reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ leads to a remarkable cyclization in which a zwitterionic diphosphirenium salt is formed (Scheme 20). Calculations of the Nuclear Independent Chemical Shift (NICS) indicate that the central P_2C ring is best described as a 2π -electron aromatic ring.⁶⁶



Scheme 20. Borane promoted cyclization of a phosphanylphosphaketene to a zwitterionic diphosphirenium ion.

Goicoechea and co-workers described the synthesis a related diphosphirene.³⁷ This involves the formation of a phosphaehtynolato compound by making use of a bulky boryl substituent. In this case, the reaction was found to be strongly solvent dependent. Coordinating solvents such as THF cause a dimerization of this compound (accompanied by boryl group migration to afford a neutral five-membered heterocycle featuring a direct P–P bond ($\delta^{31}\text{P}\{^1\text{H}\} = 223.3$ (d) and 38.3 (d) ppm; $^1J_{\text{P-P}} =$

386 Hz). Interestingly, photolysis of this compound is accompanied by loss of carbon monoxide to give rise to a rare 1*H*-diphosphirene, *cyclo*-P{PO[B]}{C[B]} (where [B] = *N,N'*-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaboryl). This species could be isolated in good yield and was fully characterized including a single-crystal X-ray-diffraction study which indicates the electronic structure drawn for three-membered P₂C heterocycle in Scheme 21. This compound exhibits two doublets in its ³¹P{¹H} NMR spectrum at 284.6 and –71.5 ppm (¹J_{P-P} = 188 Hz). The decarbonylation reaction is believed to take place via an intermediate 1,2,4-oxadiphosphole.



Scheme 21. Reactivity of a phosphaehtynolato-borane. [B] = *N,N'*-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaboryl.

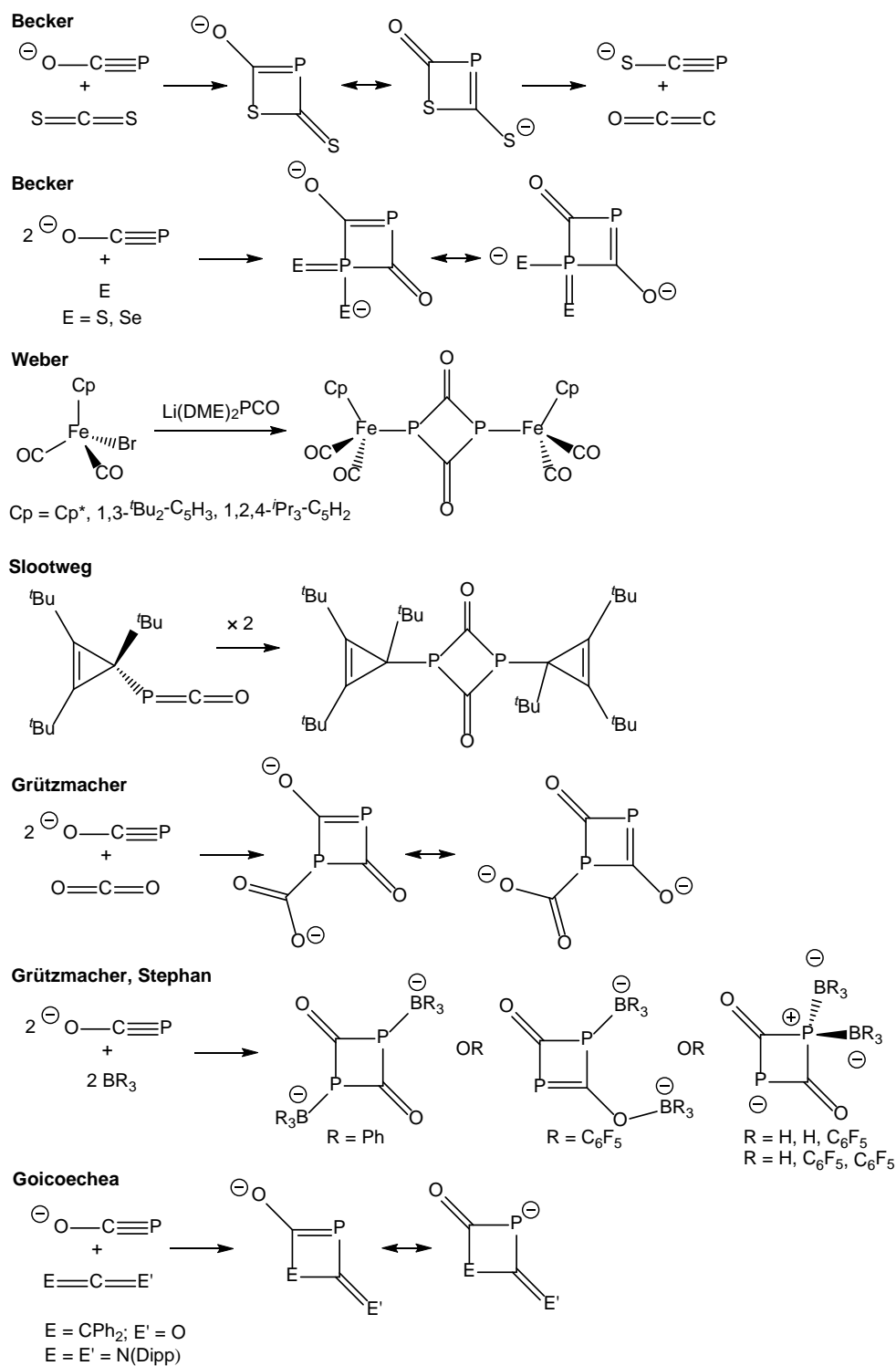
6.2. Four-membered heterocycles

In addition to its reactivity as a pseudo-halide, the PCO^- ion can be employed directly for the generation of a wide variety of phosphorus-containing heterocycles. The ion is valence isoelectronic with heteroallenes such as CO_2 , CS_2 , carbodiimides ($\text{RN}=\text{C}=\text{NR}$), ketenes ($\text{O}=\text{C}=\text{CR}_2$), and isocyanates ($\text{O}=\text{C}=\text{NR}$), amongst others. Given the known propensity of such species to take part in cyclization reactions, the reactivity of PCO^- in a number of organic cyclizations has been extensively explored since the ion was first discovered in 1992.

The first indication that PCO^- can take part in [2+2] cycloaddition reactions was reported by Becker in 1994 when he observed that PCO^- reacts with CS_2 to afford PCS^- and $\text{S}=\text{C}=\text{O}$ (Scheme 22).⁶⁷ In order to rationalise this reactivity, a four-membered cyclic intermediate was proposed, the formation of which involves cyclization of the $\text{P}\equiv\text{C}$ and $\text{C}=\text{S}$ bonds of the reactants, followed by a [2+2] cycloreversion. Related four-membered heterocycles were also observed on oxidation of PCO^- with sulfur or selenium.

Several years later, Weber and co-workers found that, when attempting to access metallo-phosphaketenes of the type $(\text{Cp})(\text{CO})_2\text{Fe}-\text{P}=\text{C}=\text{O}$ ($\text{Cp} = \text{Cp}^*$, 1,3-*t*Bu₂-C₅H₃, 1,2,4-*i*Pr₃-C₅H₂) via salt

metathesis reactions of $(\text{Cp})(\text{CO})_2\text{FeBr}$ with $\text{Li}(\text{DME})_2(\text{OCP})$, the resulting species spontaneously dimerized to afford 1,3-dimetallo-1,3-diphosphetane-2,4-diones.⁶⁸ The four-membered 1,3-diphosphetane-2,4-dione core of such molecules is the result of a head-to-tail cyclization of two $\text{P}=\text{C}$ bonds. The formation of this type of dimer is characteristic for phosphaketenes, and this Woodward-Hoffmann allowed $[2\pi_s + 2\pi_a]$ dimerization has been shown to follow a synchronous concerted mechanism. Clearly, steric bulk is critically important in isolating such species. The reactivity observed by Becker contrasts with that discussed previously for other metallo-phosphaketenes (*vide supra*), bulky ligand frameworks allow for the stabilization of well-defined phosphaketene precursors, while less sterically encumbered metal centers permit cyclization/oligomerization reactions.



Scheme 22. Known [2+2] cycloaddition reactions involving the PCO[−] ion and phosphaketene compounds.

A related dimerization was recently reported by Slootweg and co-workers who on reacting 1,2,3-tris-*tert*-butylcyclopropenium tetrafluoroborate with sodium salts of PCO[−] observed the transient formation of a phosphaketene intermediate at −78°C ($\delta^{31}\text{P}\{^1\text{H}\} = -231.7$ ppm) which on warming

dimerises to afford a 1,3-diphosphetane-2,4-dione ($\delta^{31}\text{P}\{^1\text{H}\} = 119.0$ ppm).⁵² The ^{31}P NMR chemical shift of this species is closely related to those observed by Weber ($\delta^{31}\text{P}\{^1\text{H}\} = 110.93$ (Cp*), 78.06 (1,3- $t\text{Bu}_2\text{-C}_5\text{H}_3$), 89.25 (1,2,4- $i\text{Pr}_3\text{-C}_5\text{H}_2$) ppm). The resulting 1,3-diphosphetane-2,4-dione is photolytically unstable and readily decarbonylates as discussed above (Scheme 11).

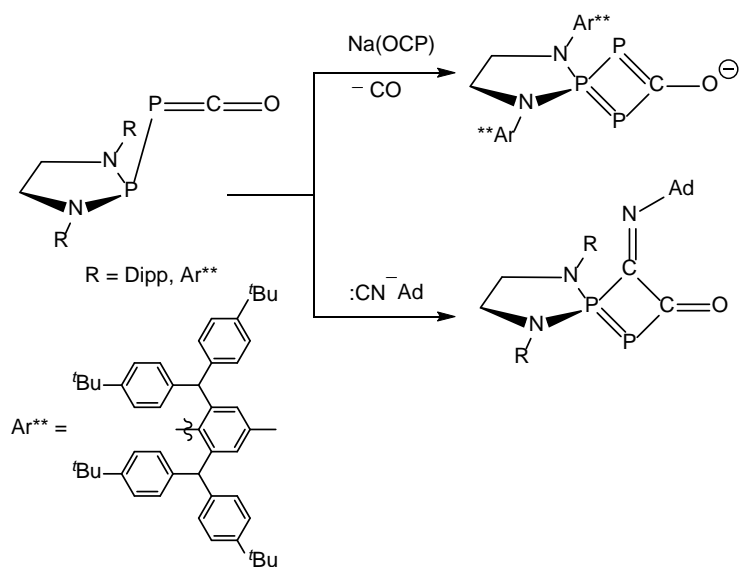
Related 1,3-diphosphetane-2,4-dione cores have been observed on reaction of a PCO^- with carbon dioxide and other neutral Lewis bases such as boranes. In these cases, the resulting products are dianionic. The reaction with carbon dioxide affords a four membered ring with a carboxylate unit attached to one of the phosphorus atoms, $\text{Na}_2(\text{P}_2\text{C}_3\text{O}_4)$.⁶ Two broad resonances are observed in the ^{31}P NMR spectrum of this compound ($\delta^{31}\text{P}\{^1\text{H}\} = 105$ and 270 ppm; $\nu_{1/2} = \text{ca. } 4500$ Hz) which indicate a dynamic process, however such resonances remain broad even at -100 °C. It is possible that such a species remains in equilibrium with CO_2 and $\text{Na}(\text{OCP})$. Functionalization of the dianion is possible with 2-iodopropane and 4,4',4''-trimethoxytriphenylmethyl chloride to afford phosphorus-functionalized heterocycles through a decarboxylative metathesis process.

In the case of the reactivity of PCO^- towards boranes, the reaction outcome is clearly dependant of the steric profile of the Lewis acids involved. In all cases, dimeric dianionic species with a 1,3-diphosphetane-2,4-dione cores were observed, however the atoms bonded to the boranes differ, giving rise to three different constitutional isomers.⁶⁹ When triphenylborane is reacted with PCO^- a symmetric four-membered dianionic heterocycle was isolated and structurally characterized revealing two borane moieties each associated with one of the phosphorus atoms ($\delta^{31}\text{P}\{^1\text{H}\} = 169.9$ ppm). Reactions with the more strongly Lewis acidic borane $\text{B}(\text{C}_6\text{F}_5)_3$ afford an asymmetric dimer in which one of the phosphorus atoms and one of the exocyclic oxygen atoms are stabilized by their interactions with the boranes, as evidenced by the presence of two resonances in the ^{31}P NMR spectrum at 269.1 and 124.7 ppm ($^2J_{\text{P-P}} = 12$ Hz) and two sharp resonances in the ^{11}B NMR spectrum ($\delta^{11}\text{B} = -2.4$ and -4.6 ppm). Finally, reactions involving Piers' borane, $\text{HB}(\text{C}_6\text{F}_5)_2$, or Lancaster's reagent, $\text{H}_2\text{B}(\text{C}_6\text{F}_5)\cdot\text{SMe}_2$, both give rise to similar products with 1,3-diphosphetane-2,4-dione cores. But in both cases, the two boranes are bonded to a single phosphorus atom as corroborated by single crystal X-ray diffraction studies and by the presence of a single resonance in the ^{11}B NMR spectra of the resulting species ($\delta^{11}\text{B} = -25.6$ and -32.4 ppm for reactions involving $\text{HB}(\text{C}_6\text{F}_5)_2$ and $\text{H}_2\text{B}(\text{C}_6\text{F}_5)\cdot\text{SMe}_2$, respectively).

Given the chemistry reported between PCO^- and CO_2 and CS_2 , the reactivity of the 2-phosphaethynolate anion towards more sterically bulky heteroallenes is also of significant interest.

In 2013, Jupp and Goicoechea explored the reactivity of $[K(18\text{-crown-6})]^+$ salts of PCO^- towards diphenylketene and bis(2,6-diisopropylphenyl)carbodiimide.⁷ In both cases, the reactions cleanly give rise to well-defined anionic heterocycles, $P[C(O)]_2C(C_6H_5)_2^-$ and $PC(O)(CNDipp)NDipp^-$, respectively. While on first inspection, both anions are structurally very similar, electronically they are notably different. The product from the reaction with the carbodiimides has a 6π -aromatic core, whereas the CPh_2 moiety of $P[C(O)]_2C(C_6H_5)_2^-$ precludes delocalization of electrons in the four-membered ring. This is evidenced in their contrasting ^{31}P NMR chemical shifts ($\delta^{31}P\{^1H\} = -165.7$ and 18.6 ppm for $P[C(O)]_2C(C_6H_5)_2^-$ and $PC(O)(CNDipp)NDipp^-$, respectively, with the latter being significantly more deshielded). Interestingly, and in contrast with what was observed in the reactivity of CS_2 , no evidence of $[2+2]$ cycloreversion was observed for either product, at least at room temperature. While for the case of $P[C(O)]_2C(C_6H_5)_2^-$ the resulting cycloreversion would be trivial, giving rise to the two precursors, one can envision that a cycloreversion involving $PC(O)(CNDipp)NDipp^-$ might give rise to a 2,6-diisopropyl-isocyanate and the anionic phosphalkyne $P\equiv C-NDipp^-$.

A four-membered heterocycle with three phosphorus centers can be prepared by the reaction between the diazaphospholanyl phosphaketene with the very bulky substituent $R = Ar^{**}$ at the nitrogen centers and a further equivalent of $Na(OCP)$ (Scheme 23).⁶⁶



Scheme 23. Formation of four-membered heterocycles by reaction of a diazaphospholanyl phosphaketene with $Na(OCP)$ and isocyanates.

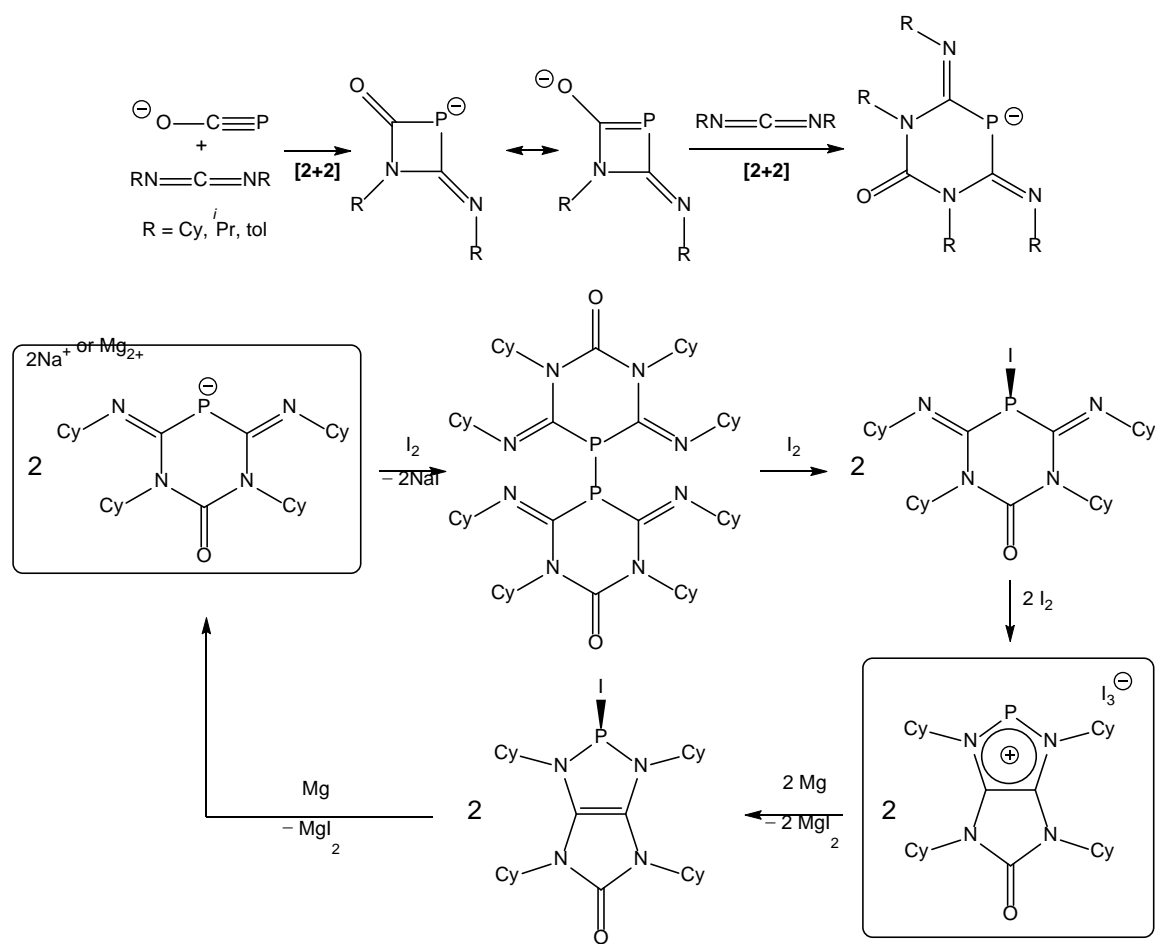
Formally this reaction, which proceeds under loss of CO , can be viewed as a $[3+1]$ cycloaddition of the P^- anion to the $P=C=O$ unit. That these type of reactions may indeed occur is seen in the reaction with a sterically less encumbered phosphanyl ketene and adamantylisonitrile, $Ad-NC:$, which gives

another new unsaturated P_2C_2 heterocycle with a λ^5 -P and a λ^3 -P center.⁶⁶ Note that this reaction does not proceed under substitution of CO by the isonitrile to give $[P]-P=C=NR$ as observed with the bulky derivative with $R = Ar^{**}$.^{48, 49}

6.2. Six-membered heterocycles.

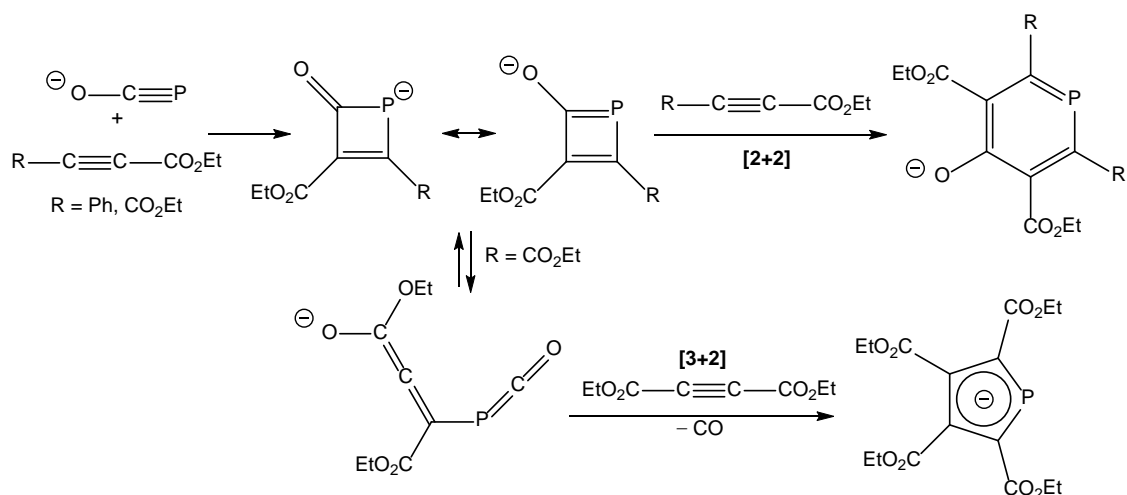
Before we discuss the synthesis of five-membered heterocycles which are mostly formed through more complex reaction pathways involving the loss of CO, we describe here the synthesis of six-membered heterocycles. These are either formed by [2+2+2] cycloadditions, as an extension to the preceding [2+2] cycloaddition chemistry, or by [2+4] cycloaddition processes.

By contrast to the reactivity observed when PCO^- reacts with $DippN=C=NDipp$, reactions with less sterically demanding carbodiimides, specifically bis(cyclohexyl)carbodiimide, bis(isopropyl)carbodiimides and bis(tolyl)carbodiimide, give rise to anionic six-membered 1,3,5-diazaphosphinane rings (Scheme 24).⁷⁰ Such reactions are postulated to go through four-membered cyclic intermediates such as that observed for reactions involving $DippN=C=NDipp$, however the reduced steric bulk of the imide functionalities allows for further reactivity. The phosphorus atoms of the (unobserved) four-membered heterocycles are formally anionic, and have significant nucleophilic character to attack another equivalent of the carbodiimides which insert into the $P-C(O)$ bond. The resulting six-membered rings have characteristic ^{31}P NMR chemical shifts at -44.2 , -49.3 , and -53.7 ppm for the Cy, iPr and tol functionalized ring systems, respectively. The oxidation of cyclohexyl-derivatized anion with elemental iodine causes an intramolecular rearrangement which affords a bicyclic 1,3,2-diazaphospholenium cation which was structurally authenticated and exhibits a singlet resonance in its ^{31}P NMR spectrum at 196.3 ppm. This Umpolung of electronic properties from non-aromatic to highly aromatic is reversible, and the cation can be reduced with elemental magnesium to reform the 1,3,5-diazaphosphinanide anion. Such a notable structural change on oxidation and reduction is remarkable, and the fact the interchange between the anionic 1,3,5-diazaphosphinane and cationic bicyclic 1,3,2-diazaphospholenium ions is reversible may be exploited in the design of mechanically responsive electronic materials.



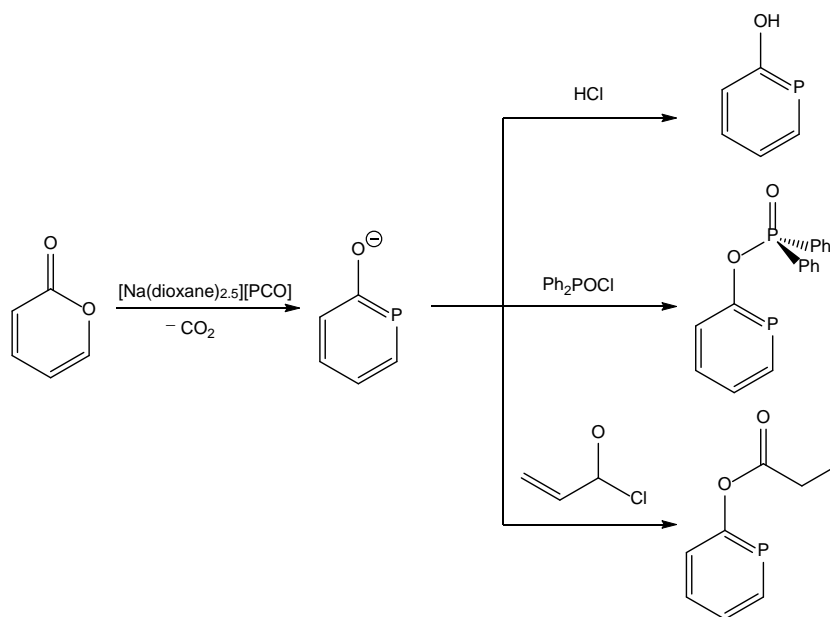
Scheme 24. Reaction of PCO^- with sterically unencumbered carbodiimides and the redox chemistry of resulting species.

Six-membered heterocycles related to those obtained by reaction of PCO^- with non-bulky carbodiimides are also available by reaction of sodium salts of the ion with electronically activated alkynes such as phenylethynylcarboxylic ethylester ($\text{Ph}-\text{C}\equiv\text{C}=\text{CO}_2\text{Et}$) or diethyl but-2-ynedioate ($\text{EtO}_2\text{C}-\text{C}\equiv\text{C}=\text{CO}_2\text{Et}$) as pictured in Scheme 25).⁷¹ Such reactions afford phosphinin-4-olates which are also postulated to react via four-membered ring intermediates which are formally the result of a [2+2] cycloaddition reaction between the $\text{P}\equiv\text{C}$ and $\text{C}\equiv\text{C}$ bonds of the reagents.⁷² An additional equivalent of the alkyne can react with the intermediate inserting into the $\text{P}-\text{C}(\text{O})$ bond in a subsequent [2+2] cycloaddition reaction to give the aromatic products. The ^{31}P NMR spectra of the products were found to be strongly solvent dependent. For the reactions involving the more electron-deficient diethyl but-2-ynedioate a five-membered heterocycle was also observed (*vide infra*) resulting from a ring-opening pathway involving the four-membered cyclic intermediate, and a decarbonylative [3+2] cycloaddition.



Scheme 25. Reaction of PCO^- with electron-deficient alkynes.

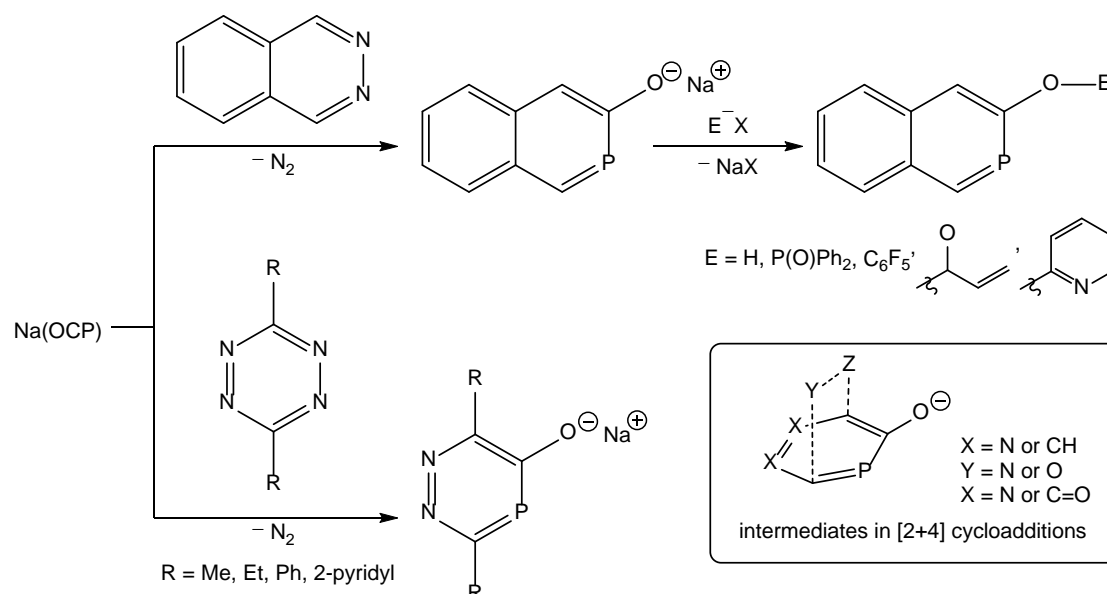
In the same report Benkő, Grützmacher and co-workers reported on the reactivity of PCO^- towards α -pyrone which generates sodium phosphinin-2-olate (Scheme 26).⁷¹ This species can be protonated affording of phosphinin-2-ol ($\delta^{31}\text{P}\{^1\text{H}\} = 149$ ppm; $\text{p}K_s = 8.16$) which is about 17 kcal mol⁻¹ more stable than its tautomer phosphinin-2(1*H*)-one with a PH and exo-cyclic C=O group. Sodium phosphinin-2-olate can also be functionalized at the exocyclic oxygen atom with a number of electrophiles including chlorodiphenylphosphane oxide or acryloyl chloride. Given the reactivity reported for PCO^- thus far, it seems reasonable to suggest that the phosphinin-2-olate product forms by an initial [2+2] cycloaddition reaction involving the $\text{P}\equiv\text{C}$ bond of PCO^- and the $\text{O}-\text{C}(\text{O})$ bond of α -pyrone, followed by a reverse cycloaddition reaction which generates the product and CO_2 .⁷²



Scheme 26. Reactivity of PCO^- with α -pyrone and subsequent functionalization.

The iron-catalysed reactivity of diynes towards siloxyphosphaethynes (generated *in situ* by reaction of sodium salts of the 2-phosphaethynolate ion with silyl triflates) has also recently been explored by Nishibayashi and co-workers.⁷³ Such reactions afforded 2-phosphaphenol derivatives via [2+2+2] cycloaddition reactions. Interestingly, no products were observed when the reactions were carried out in the absence of the silyl triflates, indicating that charge neutral siloxyphosphaethynes are needed in order for the reactions to proceed. This synthetic protocol allows for the synthesis of a broad library of bicyclic 2-phosphaphenol compounds.

When a mixture of phthalazine and Na(OCP) is heated at 80 °C in DME for two weeks, N₂ is extruded and the sodium 2-phosphanaphthalene-3-olate can be isolated in good yield as yellow crystalline material (Scheme 27).⁷⁴ This compound can be easily further derivatized using a range of electrophiles such as ClP(O)Ph₂ or 2-chloropyridine. The resulting neutral compounds can be used as new chelating ligands. In a closely related reaction, Caulton and co-workers have shown that tetrazines react readily with Na(OCP) under elimination of N₂ whereby various 1,2,4-diazaphosphinin-5-olates are obtained as products.⁷⁵ These are again versatile starting materials for further phosphorus heterocycles.



Scheme 27. Reactivity of Na(OCP) towards phthalazine and tetrazines.

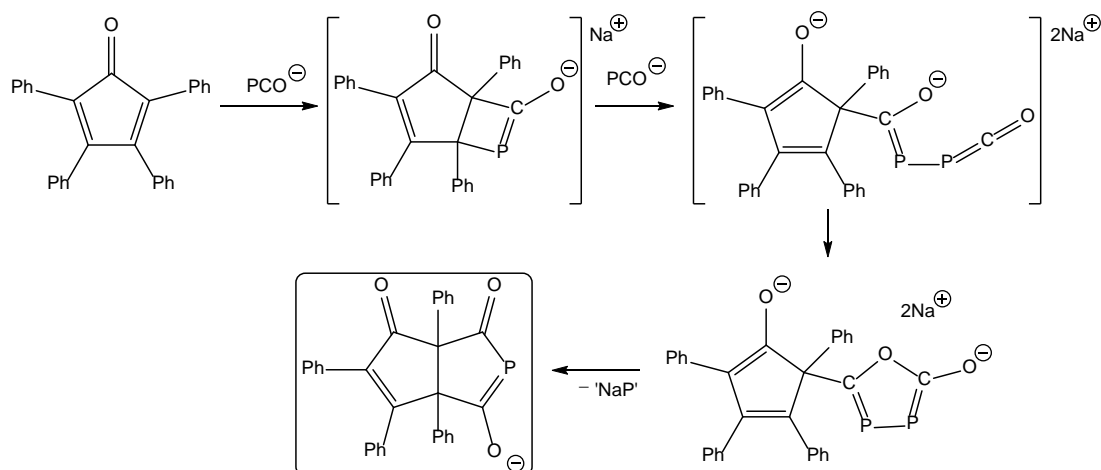
DFT calculations of possible reaction mechanisms show that the reaction between Na(OCP) and α -pyrones, phthalazine, or tetrazines correspond formally to [2+4] cycloadditions, however, these reactions do not proceed like classical Diels-Alder reactions under synchronous bond formations via one activated complex. Instead, bicyclic intermediates are formed which lie in a shallow energy

minimum between educts and products and are best described as loose adducts between CO₂ or N₂, respectively, and the product heterocycles.

6.2. Five-membered heterocycles.

The synthesis of a variety of four- and six-membered heterocycles derived from PCO[−] can be readily envisioned by invoking a series of [2+2] cycloaddition reactions involving the P≡C bond of the anion, as illustrated in numerous examples above. However, there are also a wide range of chemical transformations involving the 2-phosphaethynolate anion that give rise to five-membered heterocycles. Such species are typically formed via decarbonylation pathways such as those described previously for phosphaketanyl compounds of the main-group, transition-metal and actinide elements (*vide supra*). Thus, in purely organic transformations, it is also possible to invoke the use of the PCO[−] ion as a source of a monoanionic phosphorus ion (P[−]).

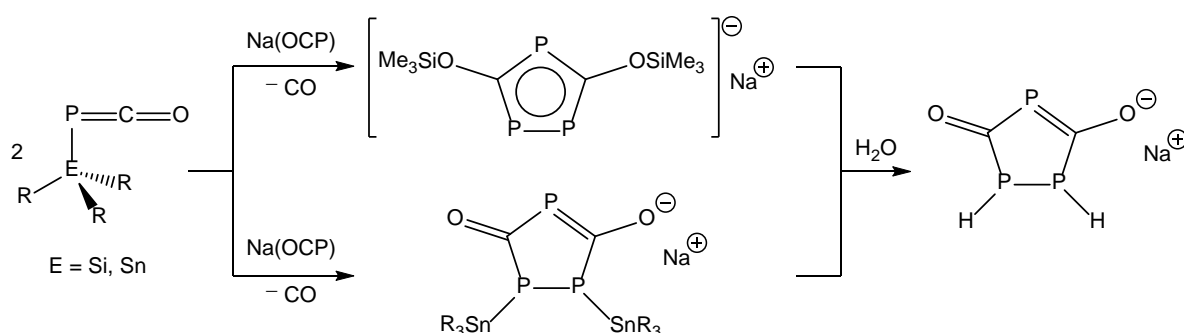
The first evidence for this reactivity mode was observed on reacting PCO[−] with diethyl but-2-ynedioate (EtO₂C–C≡C–CO₂Et) as discussed previously.⁷¹ The reaction is a formal [3+2] cyclization which is accompanied by the loss of one molar equivalent of carbon monoxide. While in the case of EtO₂C–C≡C–CO₂Et a mixture of products is obtained (the six-membered 2-phosphinin-4-olate and the phospholide), selective formation of phospholides is possible using alternative reagents. Reaction of PCO[−] with tetraphenyl-tetracyclone afford an oxadiphospholonide ($\delta^{31}\text{P}\{^1\text{H}\} = 159.2$ ppm) which on thermal treatment formally loses “NaP” to afford a 2-phosphapentalene-1,3-dione ($\delta^{31}\text{P}\{^1\text{H}\} = 66.5$ ppm) as illustrated in Scheme 28.



Scheme 28. Reaction of PCO[−] towards tetraphenyl-tetracyclone.

Related five-membered heterocycles are also available on reacting PCO[−] with main group element halides. The resulting heteroatom-substituted phosphaketenes, R₃E–P=C=O (where E = Si, R = Me; E = Sn; R = Ph, Cy) are relatively stable in non-donor solvents, however on dissolution in Lewis-basic

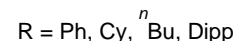
solvents such as dimethyl sulfoxide (DMSO), pyridine, or hexamethylphosphortriamide (HMPTA; $(\text{Me}_2\text{N})_3\text{PO}$), there is immediate evolution of gas (carbon monoxide) and the quantitative formation of five-membered anionic heterocycles (Scheme 29).⁷⁶ Interestingly, the nature of the resulting five-membered heterocycle varies depending on the substituents employed to stabilise the intermediate phosphaketenes, thus the silyl analogue $[\text{P}_3\text{C}_2(\text{OSiMe}_3)_2]^-$ is an aromatic 1,2,4-triphospholide ($\delta^{31}\text{P}\{^1\text{H}\} = 186.1$ (t) and 173.4 (d) ppm; $^2J_{\text{P-P}} = 55.2$ Hz), the stannyl compound $[\text{P}(\text{CO})_2(\text{PSnR}_3)_2]^-$ is a 1,2,4-triphosphacyclopenta-3,5-dionate ($\delta^{31}\text{P}\{^1\text{H}\} = 124.5$ (t) and -68.3 (d) ppm; $^2J_{\text{P-P}} = 20.9$ Hz for $\text{R} = \text{Ph}$).



Scheme 29. Reactions of heteroatom-substituted phosphaketenes, $\text{R}_3\text{E-P=C=O}$ (where $\text{E} = \text{Si}$, $\text{R} = \text{Me}$; $\text{E} = \text{Sn}$; $\text{R} = \text{Ph}$, Cy), with $\text{Na}(\text{OCP})$ and subsequent hydrolysis of products.

Hydrolysis of the silylated or stannylated triphospholide gives in both cases the 2,4-dihydro-1,2,4-triphosphacyclopenta-3,5-dionate ($\delta^{31}\text{P}\{^1\text{H}\} = 116.0$ (t) and -66.23 (d) ppm; $^2J_{\text{P-P}} = 16.3$ Hz) which can be considered as the heavier analogue of the urazolide anion. This anion is stable in aqueous THF solutions for several days but could not be isolated in substance.

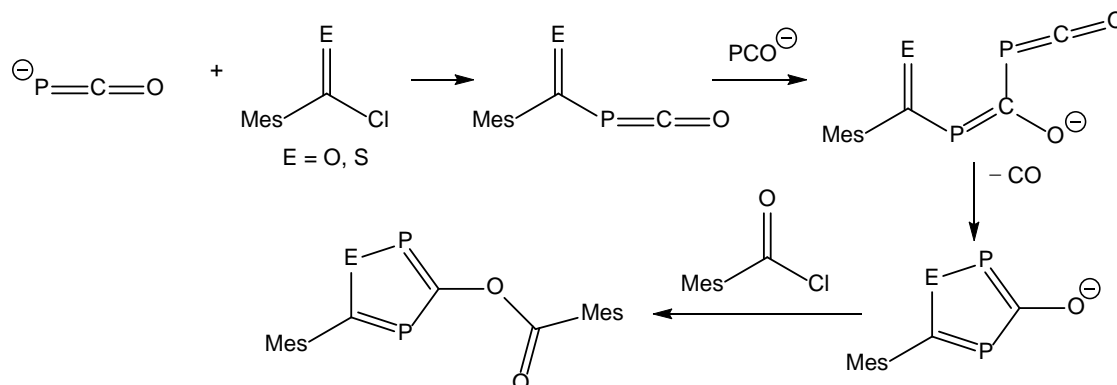
Interestingly, and in contrast to the reactivity of PCO^- with other heteroallenes such as carbodiimides and ketenes, isocyanates (O=C=NR) react in a different manner which also involves the evolution of CO (Scheme 30). While *a priori* one might expect comparable reactivity to that observed with ketenes and carbodiimides, reaction mixtures containing PCO^- and one of a number of several different isocyanates proved to be much more complex and, ultimately, it was demonstrated that the 2-phosphaethynolate anion is an active catalyst for the cyclotrimerization of isocyanates to isocyanurates.⁷⁷ This was established by the identification of two key five-membered heterocyclic intermediates from the reaction mixtures, namely 1,4,2-diazaphospholidine-3,5-dionide anions ($\delta^{31}\text{P}\{^1\text{H}\} = 117.0$ ppm for $\text{R} = \text{Dipp}$) and spiro-phosphoranides ($\delta^{31}\text{P}\{^1\text{H}\} = -42.7$ ppm for $\text{R} = \text{Dipp}$). These species can be considered as the products of the decarbonylative cyclization of PCO^- with two and four equivalents of isocyanate, respectively.



In addition to the two intermediates which were structurally authenticated an additional six-membered heterocycle resulting from the reaction of PCO^- with two equivalents of isocyanate was also spectroscopically observed, albeit at low concentrations in the crude reaction mixtures. In this case, cyclization is not accompanied by loss of carbon monoxide. It is interesting to note that all of the detected intermediates, and PCO^- itself, can be used as catalysts for the cyclotrimerization of isocyanates. The spiro-phosphoranides readily react with a further equivalent of isocyanate to afford cyclic isocyanurates, generating 1,4,2-diazaphospholidine-3,5-dionide anions. This mechanism implies that it should be possible to transfer P^- from one spiro-phosphoranide to another. This was studied stoichiometrically by reaction of the spiro-phosphoranide bearing cyclohexyl functionalities with excess phenylisocyanate. Indeed, it was found that this reaction takes place and generates the phenyl-functionalized spiro-phosphoranide ion and a mixture of isocyanurates, $(\text{NCy})_2(\text{NPh})(\text{CO})_3$ and $(\text{NPh})_3(\text{CO})_3$ as further products.

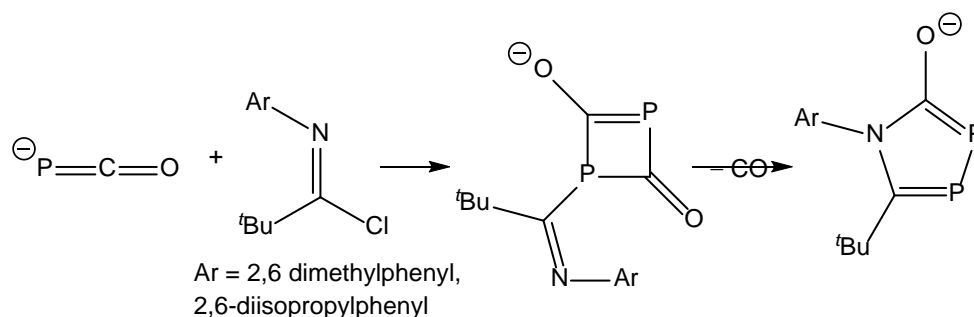
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afford the ester functionalized 1,2,4-oxadiphosphole ($\delta^{31}\text{P}\{^1\text{H}\} = 253.2$ (d), 111.5 (d) ppm; $^2J_{\text{P-P}} = 45.6$ Hz). When using its sulfur-containing analogue (trimethylbenzothioyl chloride), however, the anionic intermediate could be isolated ($\delta^{31}\text{P}\{^1\text{H}\} = 210.0$ (d), 164.1 (d) ppm; $^2J_{\text{P-P}} = 38.5$ Hz); and structurally characterized by single-crystal X-ray diffraction. Interestingly, this species does not react further with trimethylbenzothioyl chloride, but will react with mesitoyl chloride to afford the neutral ester functionalized heterocycle ($\delta^{31}\text{P}\{^1\text{H}\} = 229.1$ (d), 232.6 (d) ppm; $^2J_{\text{P-P}} = 67.0$ Hz).



Scheme 31. Reaction of PCO^- towards acyl halides.

Related transformations are also possible by reaction of PCO^- with *N*-(2,6-dimethylphenyl)pivalimidoyl chloride which affords an imidoxy- functionalized 1,2,4-azadiphosphole ($\delta^{31}\text{P}\{^1\text{H}\} = 110.8$ (d), 184.3 (d) ppm; $^2J_{\text{P-P}} = 50.8$ Hz) as pictured in Scheme 32.⁷⁹ This transformation is similar to that observed with acyl chlorides and requires a 1:1 stoichiometric loading of reagents. By contrast, if the same reaction is carried out in 2:1 $\text{PCO}^-/\text{ArN}=\text{CCl}^t\text{Bu}$ ratio (where Ar = 2,6-dimethylphenyl or 2,6-diisopropylphenyl), anionic four-membered heterocycles are formed resulting from the dimerization of an *N*-(aryl)pivalimidoyl-functionalized phosphaketene with a further equivalent of PCO^- ($\delta^{31}\text{P}\{^1\text{H}\} = 270.1$ (d) and 122.2 (d) ppm; $^2J_{\text{P-P}} = 8.8$ Hz for Ar = 2,6-dimethylphenyl). These species were found to readily rearrange to a 1,3,4-azadiphospholide accompanied by loss of carbon monoxide ($\delta^{31}\text{P}\{^1\text{H}\} = 131.8$ (d) and 13.5 (d) ppm; $^1J_{\text{P-P}} = 394.5$ Hz for Ar = 2,6-dimethylphenyl). Subsequent functionalization at the exocyclic oxygen atom of these anionic heterocycles was possible by reaction with a further equivalent of imidoyl chlorides or chlorosilanes.



Scheme 32. Reaction of PCO^- towards N-functionalized pivalimidoyl chlorides.

Recently, a highly versatile one-pot synthesis of annulated 1,3,4-azadiphospholides has been reported by Benkő, Grützmacher and co-workers by reaction of sodium salts of the 2-phosphaethynolate anion with 2-chloropyridines.⁹ As with previous reactions affording five-membered ring systems, these reactions involve the formation of a pyridyl-functionalized phosphaketene, which reacts with a further equivalent of PCO^- prior to a decarbonylative cyclization. The resulting five-membered anionic heterocycles can be readily silylated with $^t\text{BuMe}_2\text{SiCl}$ to afford neutral ring compounds functionalized at the exocyclic oxygen atom. A library of up to ten ring systems (Figure 3) was reported which exhibit notable differences in their electronic properties with absorption wavelengths (λ_{abs}) varying between 381 and 570 nm and emission wavelengths (λ_{em}) varying between 480.3 and 567.8 nm.

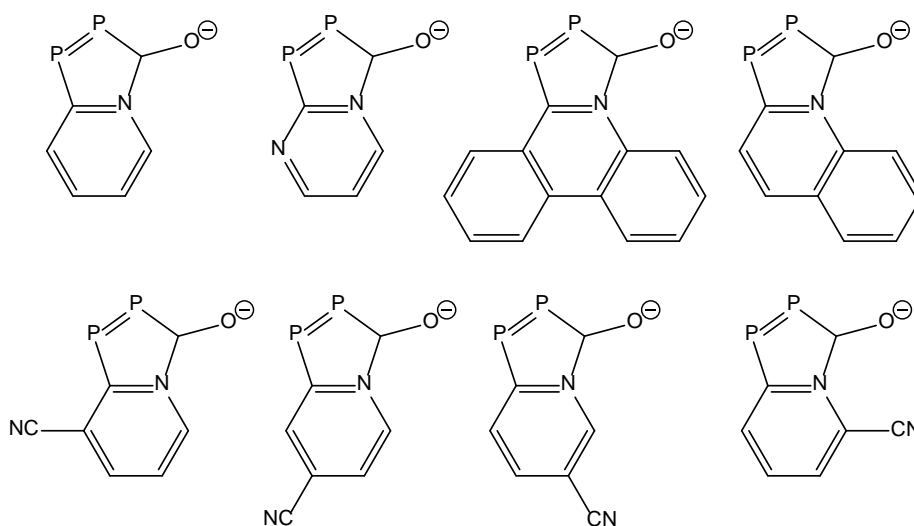
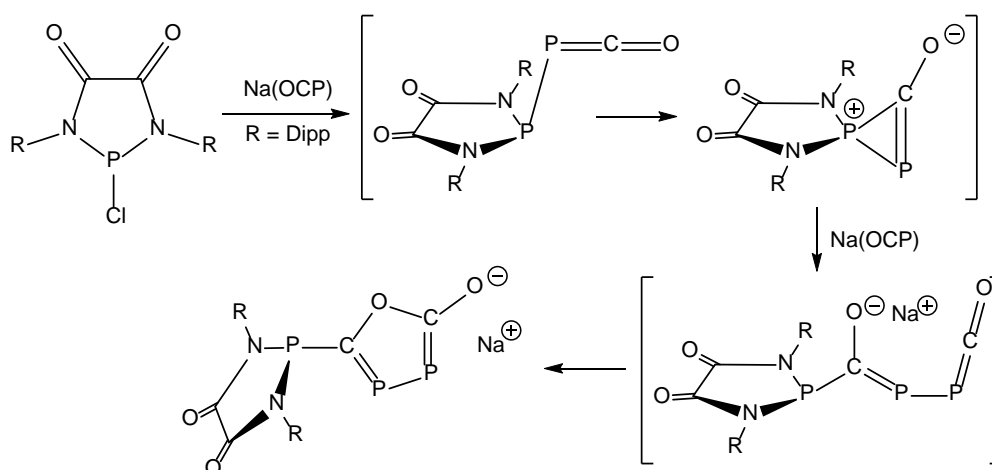


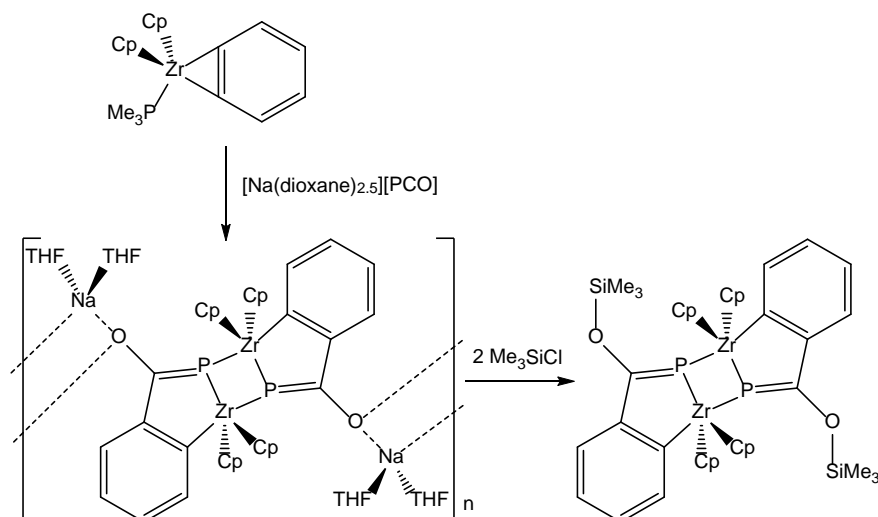
Figure 3. Annulated 1,3,4-azadiphospholides available from reaction of PCO^- with 2-chloropyridines.

A related 1,3,4-oxadiphospholide was obtained when the P-chloro-diazaphospholidine-4,5-dione was reacted with $\text{Na}(\text{OCP})$. This reaction requires the addition of two equivalents of $\text{Na}(\text{OCP})$. The first equivalent likely gives the expected phosphaketene for which a fast rearrangement to a diphosphirene is proposed in analogy to the isolated compound shown in Scheme 33. This is subsequently attacked by the second equivalent of $\text{Na}(\text{OCP})$ under ring-opening to give a new phosphaketene followed by intra-molecular nucleophilic attack of the oxy-center on the carbon atom of the $\text{P}=\text{C}=\text{O}$ unit whereby ring closure occurs to give the final product.⁶⁶



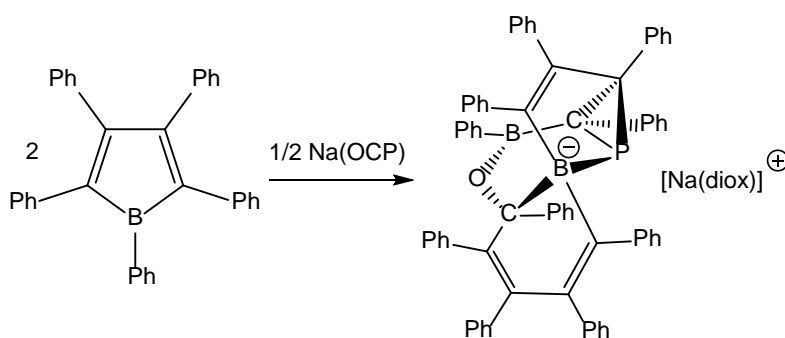
Scheme 33. Reaction of a P-chloro-diazaphospholidine-4,5-dione with Na(OCP).

All of the reactions surveyed thus far which give rise to five-membered heterocycles involve the formation of a functionalized phosphaketene which goes on to further react with an additional equivalent of the 2-phosphaethynolate anion. While this mode of reactivity is the predominant route observed thus far, recently additional examples of reactions giving rise to five-membered ring systems have been reported which differ in their mode of reactivity. In 2017 Grützmaier and Protasiewicz reported on the reaction of a zirconium-benzyne complex $[\text{Cp}_2\text{Zr}(\text{PMe}_3)(\text{C}_6\text{H}_4)]$ with PCO^- .⁸⁰ While the authors originally postulated that such reactions might give rise to 1,3-benzoxaphospholes via a formal [2+3] cycloaddition reaction of the benzyne $\text{C}\equiv\text{C}$ bond with PCO^- , they instead observed the formation of an unusual solid state coordination polymer consisting of $[\text{Cp}_2\text{Zr}\{\kappa\text{-C}, \kappa^2\text{-P-C}_6\text{H}_4\text{C}(\text{O})\text{P}\}]^{2-}$ dimers bridged by $[\text{Na}(\text{THF})_2]^+$ cations which results from the formal insertion of the $\text{P}\equiv\text{C}$ bond of PCO^- inserting into one of the Zr-C bonds of the precursor (Scheme 34). This species can be silylated using trimethylsilyl chloride to afford a bimetallic compound exhibiting a single resonance in its ^{31}P NMR spectrum at 194.0 ppm. Both the coordination polymer and the bimetallic product were structurally authenticated by single crystal X-ray diffraction.



Scheme 34. Reaction of PCO^- towards a zirconium-benzene complex $[\text{Cp}_2\text{Zr}(\text{PMe}_3)(\text{C}_6\text{H}_4)]$.

Another recent example of a heteroatomic five-membered ring system synthesized using $\text{Na}(\text{OCP})$ was recently reported by Koley, So and co-workers (Scheme 35).⁸¹ In their report the authors react two equivalents of pentaphenylborole, $[(\text{PhC})_4\text{BPh}]$, with $[\text{Na}(\text{dioxane})_{1.7}](\text{OCP})$, a reaction which affords a highly unusual fused phosphaboraheterocycle in good yields. A rather complex mechanism for the formation of this species is proposed, which first involves the nucleophilic attack of PCO^- at the boron center of the borole, followed by cleavage of one of the B–C bonds of the ring. This species was characterized by single crystal X-ray diffraction and multi-element NMR spectroscopy. In solution the heterocycle reveals a singlet in its ^{31}P NMR spectrum at -70.5 ppm and two resonances in the ^{11}B NMR spectrum at $\delta = 24.1$ ppm and -2.94 ppm, indicating the presence of two boron centers with different coordinative environments.

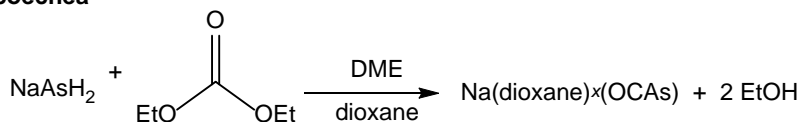
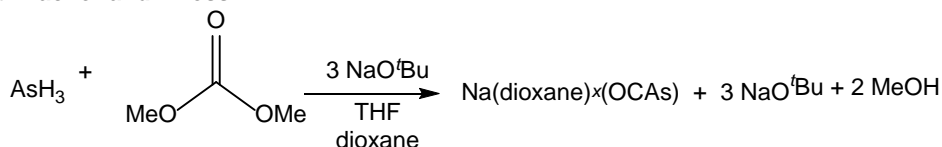


Scheme 35. Reactivity of $\text{Na}(\text{OCP})$ towards pentaphenylborole.

7. Heavier analogues

The chemistry of the arsenic-containing analogue of the cyanate ion, AsCO^- , has been alluded to in section 5, when discussing the ability of pnictaketene-type compounds to undergo decarbonylative processes, thus acting as sources of a monoanionic pnictogen ions (P^- or As^- , respectively). The

AsCO⁻ ion was first isolated in 2016 by Hinz and Goicoechea using a modified procedure related to Grützmacher's synthesis of PCO⁻ from PH₂⁻ and a carbonate source (scheme 36).⁸² A related synthesis using arsine gas as a precursor was reported shortly afterwards by Grützmacher, Driess and co-workers.⁸³ The isolation of this anion corroborated earlier matrix isolation infrared spectroscopy studies by Zhang, Dong, and Zhou which claimed to have observed the ion spectroscopically.⁸⁴ All of the heavier pnictogen-containing analogues of NCO⁻ have been studied computationally by Lu and Schaefer and are postulated to be chemically accessible, although it is worth noting that the decomposition of such ions to Pn⁻ and CO is progressively easier as one descends the group 15 elements, and computed bond dissociation energies decrease monotonically from NCO⁻ (157.98 kcal mol) to BiCO⁻ (19.32 kcal mol).¹³ The computed values for PCO⁻ (71.95 kcal mol) and AsCO⁻ (52.61 kcal mol) indicate that decarbonylation is much more likely to occur for the arsenic-containing species, and this is in fact what has been observed experimentally. While the chemistry of AsCO⁻ is still at a nascent stage, decarbonylation has been a recurring feature (as discussed in section 5), and often, the isolation of putative arsaketene intermediates has not been possible as such species decompose either thermally or with ambient light. In addition to the known decarbonylation studies, the ion has also been shown to undergo [2+2] cycloaddition reactions with DippN=C=NDipp and O=C=CPh₂ affording four membered anionic heterocycles, as discussed previously for PCO⁻.⁸² Perhaps more interestingly, on reaction with isocyanates (specifically O=C=NDipp) the AsCO ion reacts to afford the expected 1,4,2-diazaarsolidine-3,5-dionide ion, by analogy with the chemistry of PCO⁻ with the same reagent. However, when a stoichiometric deficiency of the isocyanate was employed, three novel Zintl-like ions were observed As₁₀²⁻ and both C_{2h} and D_{4h}-symmetric isomers of As₁₂⁴⁻.⁸² It is worth noting that such clusters are otherwise unobtainable using traditional high-temperature synthetic routes, and that they are formally snapshots of the oxidative decarbonylation of AsCO⁻ which ultimately affords elemental arsenic. These results hint at the possibility that PCO⁻ and AsCO⁻ may be used as precursors for meta-stable clusters and materials in the near future, although careful optimization of reaction conditions is required in order to circumvent the decomposition of such compounds to elemental forms of the pnictogen elements.

Goicoechea**Grützmacher and Driess****Scheme 36.** Known syntheses of the AsCO^- ion.

Computational studies suggest that the antimony- and bismuth-containing analogues of NCO^- will be much harder to access experimentally due to their inherent propensity to lose carbon monoxide. All attempts made by our research groups thus far have been unsuccessful in this regard. While such species are clearly a challenging target, given their propensity to lose CO, they have the potential to be interesting chemical reagents for n-doping of semiconductors.

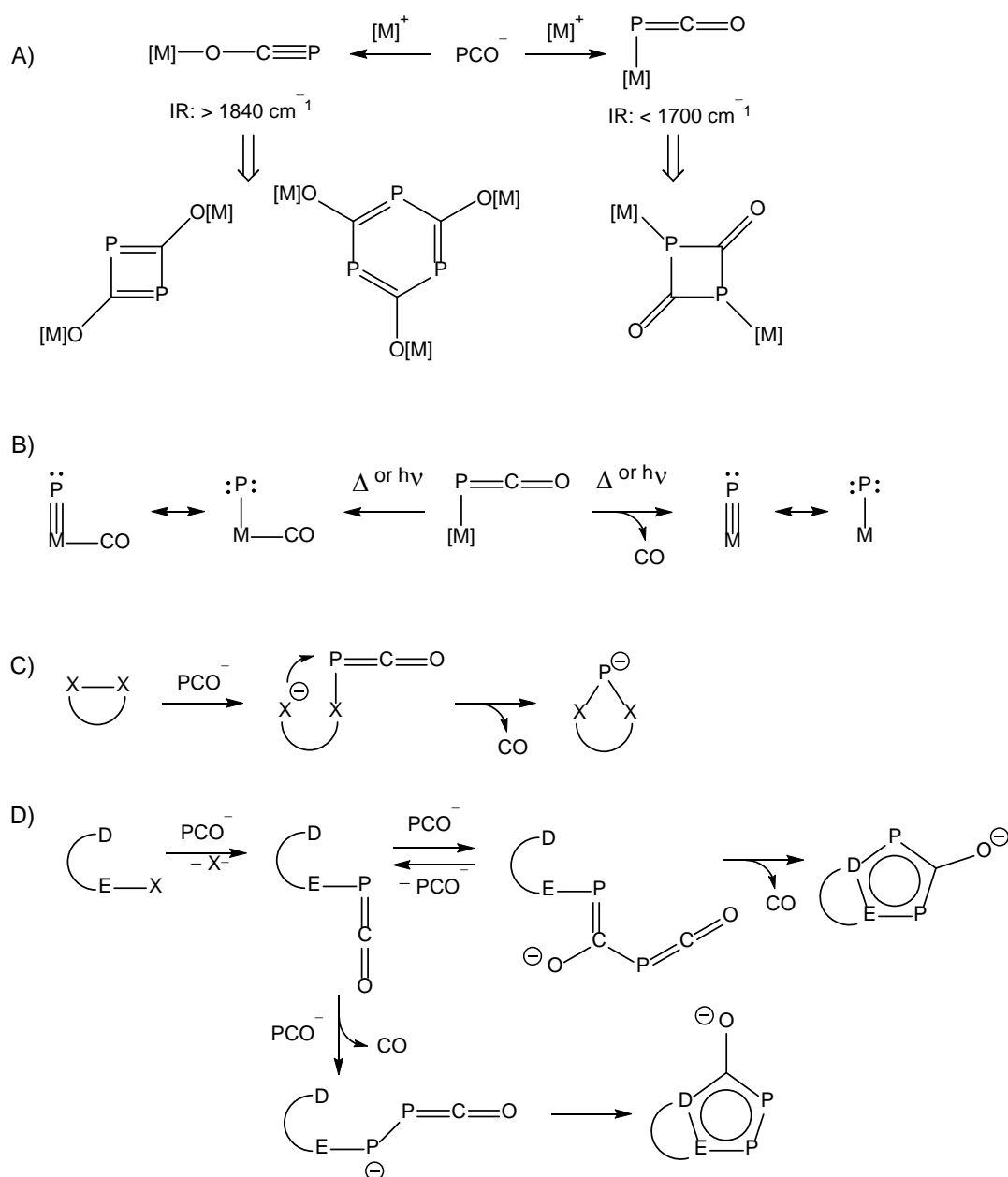
8. Future chemistry and concluding remarks

In this article we have attempted to survey the known chemistry of the 2-phosphaethynolate anion (PCO^-) and of its heavier analogues, PCS^- and AsCO^- . As the research described above shows, Na(OCP) has rapidly become an incredibly versatile chemical reagent, which can now be accessed in high yields on a multi-gram scale. Over the past seven years this species has undergone a remarkable transformation, from a chemical curiosity to a viable reagent for the synthesis of novel phosphorus-containing molecules and compounds, and is now used by numerous research groups world-wide.

Some general reaction patterns emerge and these are sketched in simplified form in Scheme 37.

As expected, PCO^- is an ambidentate nucleophile and with highly oxophilic reagents gives access to heteroatom substituted oxy-phosphalkynes (see A) in Scheme 37). These are characterised by asymmetric stretching frequencies ν_{asym} of larger than 1840 cm^{-1} and may dimerise or trimerise to give 1,3-diphospha-2,4-oxy-cyclobutadienes or 1,3,5-triphosphinines, respectively. The majority of electrophiles which were reacted with PCO^- gives a wide range of phosphaketenes which are characterised by asymmetric stretching frequencies ν_{asym} below 1700 cm^{-1} . Phosphaketenes were a scarcely investigated class of unsaturated organophosphorus compounds and the now given simplicity of their synthesis makes PCO^- salts especially valuable reagents. Upon dimersiation phosphaketenes yield 1,3-diphosphetane-2,4-diones as constitutional isomers to 1,3-diphospha-2,4-oxy-cyclobutadienes. Under thermal or photolytic conditions, these phosphaketenes may lose CO either in a dissociation or intramolecular rearrangement reaction which opens the possibility to

generate highly reactive phosphandiyl species which in some cases could be even isolated (see B) in Scheme 37).



Scheme 37. General reaction patterns of PCO^- and phosphaketenes.

A yet little explored but highly attractive way to “dope” molecules with pnictogenyl centers is shown in C) in Scheme 37. As strongly nucleophile, PCO^- , may react with element bonds under ring opening and generation of a new nucleophilic center X^- . This may subsequently displace CO whereby the P^- anion is inserted in the X-X bond (see the insertion in Si-Si or Ga-Ga bonds shown above in Schemes 7 and 10, respectively). Indeed, this displacement of CO by inter- or intramolecular nucleophilic attack is a unique property of phosphaketenes. These are in contrast to related cumulenes like $\text{X}=\text{C}=\text{X}$ ($\text{X} = \text{NR}, \text{O}, \text{S}$) or isocyanates, $\text{R}-\text{N}=\text{C}=\text{O}$, *amphiphilic* electrophiles which can either react at the

carbon center ("classic") or at the phosphorus center ("non-classic"). Another remarkable feature in reactions with PCO^- is that especially neutral phosphaketenes, E-P=C=O , which are formed as primary products in salt metathesis reactions between E-X and PCO^- , are rapidly attacked by a second equivalent of PCO^- and that this reaction is reversible. Depending on the steric bulk and the position of a remote nucleophilic center D, these reactions may lead to a range of five-membered heterocycles with conjugated π -electron systems and two or even three phosphorus centers.

While the results described to date are unquestionably varied in scope, we are of the opinion that they represent a small fraction of a much larger body of chemistry to come. For example, most of the chemistry explored thus far is molecular in nature, and the use of PCO^- for the synthesis of materials such as metal phosphides (both known and unknown) has yet to be experimentally exploited. This is highly attractive option considering the ease with which Na(OCP) can be prepared and manipulated. Moreover, the mild conditions required to induce decarbonylation may permit the synthesis of metastable compounds that are otherwise unattainable using conventional synthetic methods (which typically require high temperature conditions).

Deoxygenative processes, such as those that have been briefly glimpsed to date, are also enormously interesting, and may ultimately be employed to access the cyaphide ion, CP^- , on a preparative scale. This species has enormous potential for the synthesis of coordination polymers and metal-organic frameworks with fascinating optical and electronic properties. After all, its lighter congener, the cyanide ion, is a ubiquitous, and historic, ligand in inorganic chemistry.

Finally, the synthetic methods described for the synthesis of PCO^- may also be used to access heavier analogues such as the unknown ions SbCO^- and BiCO^- , both of which have been studied computationally and predicted to be isolable. Similarly, other related valence isoelectronic anions may also be accessed using related methods.

We eagerly await further developments in the field and are excited to be a part of such a fascinating field of study, which commenced with Gerd Becker's seminal contribution twenty six years ago.

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