Low-Valent Phosphorus

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Phosphination of Carbon Monoxide: A Simple Synthesis of Sodium Phosphaethynolate (NaOCP)**

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After the discovery of H−C≡P,[1] many derivatives of phosphaalkynes (alkylidynephosphanes) R−C≡P were reported.[2] Relatively bulky groups (for example *t*Bu, 2,6-substituted arenyl) are needed to suppress the oligo/polymerization of these unsaturated compounds.[3] In this respect, some salts of the 2-phosphaethynolate anion $(\text{O}{-}\text{C}{\equiv}\text{P})^-$, the phosphorus analogue of the cyanate ion, are remarkable because they can be isolated despite being small. These materials were prepared by the reaction of lithium or alkali earth metal bis(trimethyl)phosphide and dimethylcarbonate in 1,2-dimethoxyethane (DME) according to Equation (1):

$$[\text{M}\{\text{P}(\text{SiMe}_3)_2\}_x] + \text{MeO}{-}\text{CO}{-}\text{OMe} \rightarrow [\text{M}(\text{O}{-}\text{C}{\equiv}\text{P})_x(\text{dme})_y] + 2\,\text{Me}_3\text{Si}{-}\text{O}{-}\text{Me} \qquad (1)$$
$$(\text{M} = \text{Li}:\ x = 1,\quad y = 2;^{[4]}\ \text{M} = \text{Mg} - \text{Ba}:\ x = 2,\ y = 3^{[5]})$$

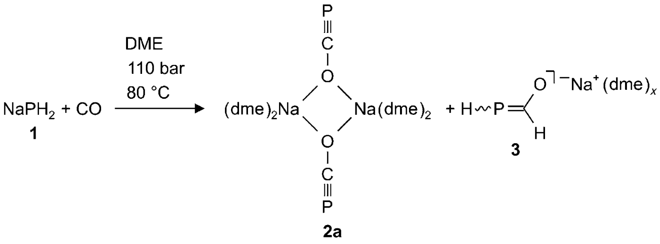
The stability of $[\text{M}(\text{O}{-}\text{C}{\equiv}\text{P})_2]$ (M = Ca–Ba) is strongly dependent on the nature of the cation M^{2+} and the solvent. Only $[\text{Ca}(\text{O}{-}\text{C}{\equiv}\text{P})_2(\text{dme})_3]$ could be isolated as crystalline substance, while with $\text{M} = \text{Sr}^{2+}$ a dianion containing two O−C≡P units was obtained.

The chemistry of 2-phosphaethynolates is relatively unexplored. The reaction between Li(O−C≡P) and carbondisulfide leads to [Li(S−C≡P)].[6] A cycloaddition reaction with an activated acetylene derivative gives a phosphinine derivative.[6] Oxidative tetramerization to give $(\text{P}_4\text{C}_4\text{O}_4)^{2-}$[7] and a transition-metal-promoted dimerization to $(\text{P}_2\text{C}_2\text{O}_2)^{2-}$ have been reported.[8] These reactions do show the high potential of $[\text{M}(\text{O}{-}\text{C}{\equiv}\text{P})_x]$ as reagents.

Herein we present a simple synthesis of the previously unknown and remarkably stable salt, sodium phosphacyanate, Na(O−C≡P),[9] from base chemicals, namely NaPH_2 and CO. A computational study of the reaction points to an unusual α elimination of hydrogen from the phosphorus atom under concomitant transfer of the phosphorus atom to CO as a key step in the mechanism.

Sodium dihydrogen phosphide, NaPH_2 (**1**), is obtained by reacting PH_3 with solutions of sodium in liquid ammonia, or in an especially easy manner as the rather stable adduct $[\text{Na}(\text{PH}_2)\cdot\text{Na}(\text{O}t\text{Bu})_x]$ in the one-pot reaction between sodium metal, elemental phosphorus, and *tert*-butanol in DME.[10]

Originally, we planned to find a simple access to the cyaphide ion, $(\text{C}{\equiv}\text{P})^-$, which we could stabilize as terminal ligand in a ruthenium complex,[11] by reaction of NaPH_2 with CO. However, this reaction does not yield Na(C≡P) and water, but at temperatures between 50–120 °C and CO pressures up to 110 bar gives cleanly $[\text{Na}(\text{O}{-}\text{C}{\equiv}\text{P})(\text{dme})_2]_2$ (**2a**) alongside an insoluble orange-brown precipitate and small amounts of sodium formphosphide *(E/Z)*-$[\text{Na}(\text{O}{-}\text{CH}{=}\text{PH})(\text{dme})_x]$ (**3**, < 5 %, *E*/*Z* = 1.2:1; Scheme 1).



Scheme 1. Synthesis of **2a** in the phosphination of CO in the reaction between NaPH_2 (**1**) and CO.

The brown precipitate was not further characterized and most likely stems from the thermal decomposition of NaPH_2.[12] Na(O−C≡P) can be obtained in pure form as the DME adduct **2a** upon concentration of the reaction solution or more conveniently by adding dioxane, whereby $[\{\text{Na}(\text{O}{-}\text{C}{\equiv}\text{P})(\text{dioxane})_{2.5}\}_\infty]$ (**2b**) precipitates as a colorless microcrystalline powder. In contrast to the lithium and alkaline earth salts, $[\text{Na}(\text{O}{-}\text{C}{\equiv}\text{P})]$ is thermally remarkably stable and does not decompose when heated to 110 °C for 2.5 days in DME or THF in a sealed glass tube. On the contrary, the formphosphide *(E/Z)*-$[\text{Na}(\text{HP}{=}\text{CHO})(\text{dme})_x]$ **3** does slowly decompose to a number of unidentified products.[13] Note that $[\{\text{Na}(\text{O}{-}\text{C}{\equiv}\text{P})(\text{dme})_2\}_2]$ is not obtained, and we have no indication that **3** is an intermediate on the reaction path leading to **2a**. The observed ratios of **2a**:**3** are independent of the CO pressure or the reaction temperature. The yield of isolated **2a** is however highly dependent on the reaction conditions. Because NaPH_2 is thermally unstable, the yields

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drop dramatically at higher reaction temperatures while the reaction times shorten. The best compromise is found at 80 °C, 110 bar CO, and 16 h, giving about 30% of isolated pure $\mathrm{Na(O{-}C{\equiv}P)}$ in the form of its dioxane adduct $[\{\mathrm{Na(O{-}C{\equiv}P)(dioxane)_{2.5}}\}_\infty]$ (**2b**), which is obtained by adding dioxane to the reaction mixture in the work-up process.

Crystals of $[\{\mathrm{Na(O{-}C{\equiv}P)(dme)_2}\}_2]$ (**2a**) and $[\{\mathrm{Na(O{-}C{\equiv}P)(dioxane)_{2.5}}\}_\infty]$ (**2b**) were used for single-crystal X-ray diffraction studies and the results are shown in Figure 1.[14]

In contrast to the previously determined structures of $\mathrm{M(O{-}C{\equiv}P)}$ compounds (M = Li,[4] Ca[5]) which have terminal $(\mathrm{O{-}C{\equiv}P})^-$ anions, the structure of **2a** has a central four-membered $\mathrm{Na_2O_2}$ ring with linear[15] μ_2-bridging $\mathrm{O{-}C{\equiv}P^-}$ anions. The structural parameters of the $(\mathrm{O{-}C{\equiv}P})^-$ anions in **2a** ($\mathrm{O{-}C_{average}}$ 1.208 Å, $\mathrm{C{\equiv}P_{average}}$ 1.575 Å; $\mathrm{C\text{-}P\text{-}O_{average}}$ 179.4°) are in the expected range. The crystal structure of the dioxane adduct **2b** reveals a regular three-dimensional network in which the octahedrally coordinated $\mathrm{Na^+}$ cations are linked by μ_2-(κ^1O, κ^1O)-bridging dioxane molecules. In the cavities of this cationic host lattice, the $(\mathrm{O{-}C{\equiv}P})^-$ anions are embedded in a highly disordered fashion without detectable close Na−O or Na−P distances. In the IR spectrum of **2a**, the C−O stretching mode is observed at $\nu(\mathrm{C{=}O}) = 1262\ \mathrm{cm^{-1}}$ and $\nu(\mathrm{C{\equiv}P}) = 1780\ \mathrm{cm^{-1}}$, while in **2b** with "free" $(\mathrm{O{-}C{\equiv}P})^-$ anions, these absorptions are observed at significantly lower wavenumbers ($\nu(\mathrm{C{=}O}) = 1247\ \mathrm{cm^{-1}}$ and $\nu(\mathrm{C{\equiv}P}) = 1755\ \mathrm{cm^{-1}}$).

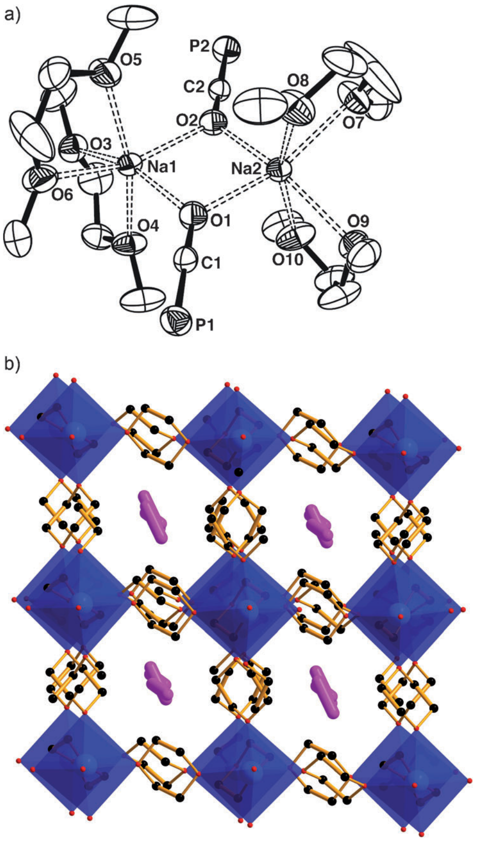


Figure 1. a) ORTEP plot (ellipsoids set at 30% probability) showing the structure of **2a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.589(3), C1–O1 1.203(4), P2–C2 1.575(3), C2–O2 1.213(4), Na1–O 12.349(3), Na1–O2 2.336(3), Na1–O3 2.389(3), Na1–O4 2.354(3), Na1–O5 2.351(3), Na1–O6 2.413(4), Na2–O1 2.344(3), Na2–O2 2.337(3), Na2–O7 2.396(4), Na2–O8 2.345(3), Na2–O9 2.421(3), Na2–O10 2.340(3); P1-C1-O1 179.3(3), P2-C2-O2 179.5(4), C1-O1-Na1 132.6(3), C1-O1-Na2 133.0(3), C2-O2-Na1 132.1(3), C2-O2-Na2 133.6(3), O1-Na1-O2 85.9(1), O1-Na2-O2 86.0(2), O1-Na1-O2 93.8(1), O1-Na2-O2 94.3(1), O3-Na1-O4 69.8(1), O5-Na1-O6 70.1(2), O7-Na2-O8 70.2(2), O9-Na2-O10 69.7(2). b) Crystal structure of **2b**. Hydrogen atoms are omitted for clarity. C black, O red; sodium atoms are represented by their coordination octahedron (blue) with the sodium atom in the center. Highly disordered $\mathrm{O{-}C{\equiv}P^-}$ anions: magenta.

Compound **2b** in particular is remarkably stable and can be handled in air without decomposition. In deoxygenated water, **2a**,**b** can be dissolved (chemical shift in $\mathrm{D_2O}$: $\delta^{31}\mathrm{P} = -396.4$ ppm) and are only slowly hydrolyzed ($t_{1/2}$ at 298 K of a 0.5 to 0.7 M solution ca. 2 days) to $\mathrm{PH_3}$ ($\delta^{31}\mathrm{P} = -239$ ppm), sodium phosphinate, $\mathrm{Na(H_2PO_2)}$ ($\delta^{31}\mathrm{P} = 8$ ppm), $\mathrm{NaHCO_3}$, CO, and a third not yet identified product, which contains a $\mathrm{PH_2}$ group ($\delta^{31}\mathrm{P} = -134$ ppm, t, $J_{\mathrm{PH}} = 217$ Hz). Note that we have no indication for the formation of $\mathrm{HO{-}C{\equiv}P}$, for which computations predict a chemical shift of the $^{31}\mathrm{P}$ nucleus in the range of $\delta^{31}\mathrm{P} = -281$ to -292 ppm.[16]

The reaction of $\mathrm{PH_2^-}$ with CO was computed at the BHLYP/6311 + G(3df,2p)//BHLYP/6-31 + G(d) level[17] in the gas phase to gain insight in the reaction mechanism. The computed minimum energy reaction pathway (MERP) is depicted in Figure 2. We expected that the highly nucleophilic $\mathrm{PH_2^-}$ anion attacks CO at the electrophilic carbon center. However, only a loose adduct **AD** is formed between both reagents, with a very long P···C distance of 3.176 Å in a weakly exothermic reaction ($-7.1\ \mathrm{kJ\,mol^{-1}}$). The same adduct is obtained when the stable Bertrand-type[18] phosphinocarbene $\mathrm{H_2P{-}C{-}OH}$ (**PC**) is deprotonated at the OH group.

The non-dissociated $[\mathrm{H_2P{\cdots}CO}]^-$ adduct ions may loose $\mathrm{H_2}$ via the transition state **TS** at $216.6\ \mathrm{kJ\,mol^{-1}}$. The products $(\mathrm{O{-}C{\equiv}P})^-$ and $\mathrm{H_2}$ are formed in a rather exothermic reaction ($-65.1\ \mathrm{kJ\,mol^{-1}}$), indicating the stability of $(\mathrm{O{-}C{\equiv}P})^-$. The loss of $\mathrm{H_2}$ as shown in Figure 2b is an interesting process. An inspection of the internal reaction coordinate (IRC) starting from **TS** in both directions shows that at an early stage of the reaction, as the reactants start to approach at a P···C distance of about 2.75 Å, the H−P−H angle closes drastically. The P−H bond lengths (ca. 1.43 Å) do not change significantly. The reaction enthalpy, $\Delta H_{\mathrm{r},298}$, increases steeply, and at **TS**, the H−H distance (H−H 0.869 Å) is close to that in a $\mathrm{H_2}$ molecule, while the P−C distance (P−C 2.329 Å, C−O 1.146 Å) is still long. Therefore one can envision the structure of the activated complex at **TS** as a complex, $[(\mathrm{H_2}){\rightarrow}\mathrm{P}{\leftarrow}\mathrm{CO}]^-$, in which formally a $\mathrm{P^-}$ ion is coordinated by a $\mathrm{H_2}$ and a CO molecule. From **TS**, the $\mathrm{H_2}$ molecule is expelled under further shortening of the P−C bond to give the final products $(\mathrm{O{-}C{\equiv}P})^-$ (C≡P 1.618 Å, C−O, P-C-O 180°) and $\mathrm{H_2}$. The computed data for the free $(\mathrm{O{-}C{\equiv}P})^-$ anion agree well with previously reported values.[16] The $\mathrm{C{\equiv}P_{calc}}$ bond (1.618 Å) is slightly longer than the C≡P bond in the salts **2a** (1.575 Å), while the CO bond is marginally shorter (1.191 versus 1.208 Å).

We also investigated the possibility that $\mathrm{PH_2^-}$ anions may decompose to give $\mathrm{P^-}$, which indeed combines with CO. Although the reaction of $\mathrm{P^-}$ in its singlet state with CO is a barrierless reaction, loss of $\mathrm{H_2}$ from $\mathrm{PH_2^-}$ is a high-energy

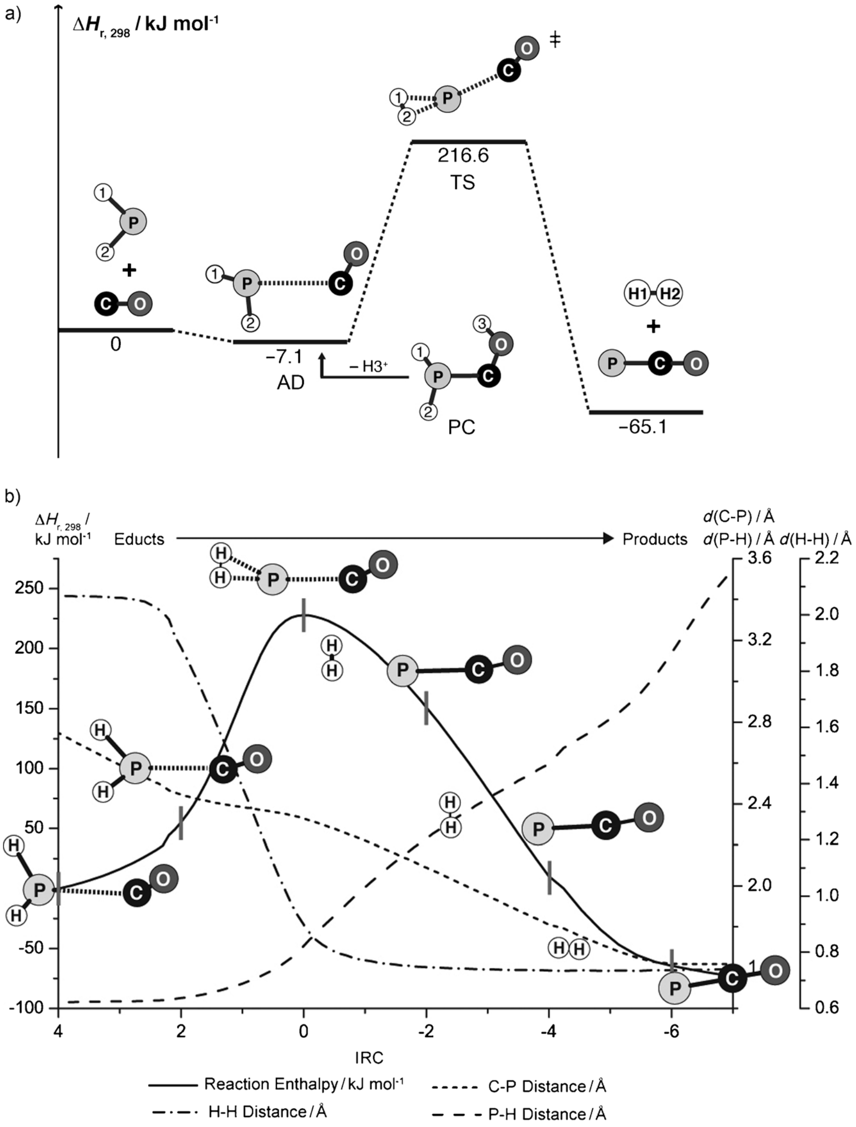


Figure 2. a) Computed structures along the minimum-energy reaction path (MERP) for the reaction of sodium dihydrogen phosphide with CO leading to OCP$^-$ in the gas phase. Selected bond lengths [Å] and angles [°]: CO: C–O 1.124; PH_2^-: P–H 1.430, H-P-H 92.54; AD: P–C 3.177, C–O, P–H1 1.427, P–H2 1.429, H-P-H 93.13, P-C-O 116.71; TS: P–C 2.329, C–O 1.146, H1–P 1.706, H2–P 1.704, H1–H2 0.869, H1-P-H2 29.5, P-C-O 142.1; H_2: H1–H2 0.735; (O-C≡P)$^-$: P–C 1.618, C–O 1.191, P-C-O 180.0; PC: P–C 1.828; C–O 1.299, P–H1 1.421, P–H2 1.400, H-P-H 97.75, P-C-O 115.36. See the Supporting Information for more computational details. b) Intrinsic reaction coordinate (IRC) showing the changes of relevant bond lengths (C–P, P–H, H–H). Snapshots of structures are given along the IRC at the selected points (4, 2, 0, −2, −4, −6).

process (+341.1 kJ mol^{-1}) making this reaction pathway less likely. We also computed the 1,2-hydrogen shift in adduct ($H_2P\cdots CO$)$^-$ (**AD**) to give the formphosphide (HP=CHO)$^-$, but this process, although more exothermic (−81.4 kJ mol^{-1}), proceeds via a higher transition state at 249.6 kJ mol^{-1} (see Supporting Information for more details).

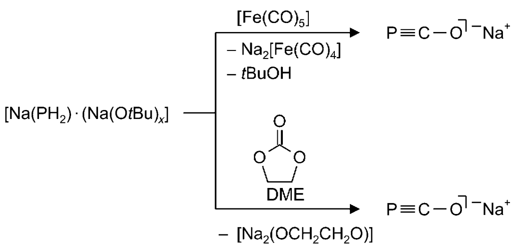
Clearly, a more realistic computation would demand to include a counter cation and solvation energies.[19] Nevertheless, the simple gas-phase model agrees with the experimental results. The computations also imply that binding of CO to a transition metal complex to enhance its electrophilicity should significantly improve the efficiency of the reaction. Indeed, when [$Na(PH_2)\cdot Na(OtBu)_x$], which as a PH_2^- source delivers more formphosphide [Na(HP=CHO)] (**3**) in the reaction with CO than $NaPH_2$, is reacted with [$Fe(CO)_5$] in THF at room temperature, the only phosphorus-containing species detected by ^{31}P NMR spectroscopy in the solution is [$Na(O{-}C{\equiv}P)(thf)_x$]$_y$ (**2**) (Scheme 2). Finally, [$Na(O{-}C{\equiv}P)(dioxane)_{2.5}$]$_\infty$ (**2b**) is obtained in high yield and purity when [$Na(PH_2)\cdot Na(OtBu)_x$] is reacted with ethylene carbonate and the crude product is recrystallized from dioxane.

The serendipitously discovered synthesis of highly unstable H−C≡P from PH_3 required very special reaction conditions, that is, a rotating arc struck between graphite electrodes, and gave very low yields of product. Similarly detected by chance almost exactly 50 years later, a related sterically unprotected species with a P≡C triple bond was synthesized based on very simple chemicals. Na(O−C≡P) is a remarkably stable substance, possibly making it a valuable building block for the synthesis of organophosphorus compounds. For this, the efficiency of its formation from $NaPH_2$ and CO must be further improved. First experiments indicate that this goal may be achieved by transition metal carbonyl compounds, which ideally act as intermediates in a catalytic reaction to make the formation of (O−C≡P)$^-$ truly atom-economic.

Experimental Section

$NaPH_2$ was prepared according to a slightly modified literature procedure.[20]

2a,b: In a glove box filled with rigorously dried and oxygen-free argon, $NaPH_2$ (100 mg, 1.79 mmol) was dispersed in DME (15 mL) in a 15 mL vial and transferred into a 100 mL Parr autoclave equipped with a glass inlay. The reactor was sealed and the argon removed



Scheme 2. Alternative syntheses of Na(OCP) **2a,b**.

under reduced pressure, while applying the reduced pressure for only a short time (1–2 seconds) to avoid evaporation of higher quantities of the DME solvent. The autoclave was then pressurized with 105 bar of carbon monoxide at 25 °C and then warmed to the reaction temperature (80 °C) such that the final pressure attained 110 bar. If needed, minimum pressure adjustments were made by releasing pressure through the sealing valve. After 16 h, the autoclave was cooled to 25 °C and vented under an argon counterstream. The reaction mixture was transferred (by syringe) into a glass Schlenk flask, and the brown precipitate was filtered off (frit covered with Celite) and the solvent removed to dryness to give $[\{Na(O{-}C{\equiv}P)(dme)_2\}_2]$ (**2a**). Alternatively, the filtrate volume was reduced to 1 mL. After addition of dioxane (13 mL), a white microcrystalline powder of $[\{Na(O{-}C{\equiv}P)(dioxane)_{2.5}\}_\infty]$ (**2b**) is obtained. Yield based on $NaPH_2$: 28 %.

2b through reaction with ethylene carbonate: $[Na(PH_2){\cdot}Na(OtBu)_x]$ ($x = 2.5$–2.7; 7 g, 19.6 mmol) was dissolved in DME (75 mL) and cooled to 0 °C. Ethylene carbonate (2.1 g, 23.5 mmol) dissolved in DME (25 mL) was added dropwise over a period of 60 min. The formation of a precipitate ($[Na_2(OCH_2CH_2O)]$) from the yellow reaction mixture was observed. The suspension was stirred for 12 h at room temperature and then the solvent was removed under reduced pressure. The remaining yellow oil was dissolved in THF (150 mL) and filtered over Celite to remove the disodium glycolate. The filtrate was concentrated to about 15 mL and layered with 100 mL of dioxane, whereby **2b** started to crystallize. After complete mixing of the two solvents, the white precipitate was collected by filtration to give $[\{Na(O{-}C{\equiv}P)(dioxane)_x\}_\infty]$ (**2b**; 4.454 g, 14.7 mmol, 75 %). x can vary between 2.0–2.6 depending on the drying conditions; crystals used for X-ray diffraction contained $x = 2.5$. M.p. (decomp.) = (212 ± 2) °C. $^{31}P\{^1H\}$ NMR (121.3 MHz, $[D_8]$THF, 23 °C): $\delta = -392.0$ ppm (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, $[D_8]$THF, 23 °C): $\delta = 166.3$ ppm (d, $J_{PC} = 46.5$ Hz).

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[13] $[Na(HP{=}CHO)]$ (**3**) can be synthesized independently according to the method of Becker et al.[4] from $NaPH_2$ and ethylformate, HCO(OEt). This species does not rearrange to Na(OCP) even at elevated temperatures, but decomposes to a number of products.

[14] Structure data: $[\{Na(O{-}C{\equiv}P)(dme)_2\}_2]$ (**2a**): Colorless, air-sensitive single crystals of **2a** were obtained by slow evaporation of a concentrated DME solution. $C_{18}H_{40}Na_2O_{10}P_2$, orthorombic, space group $Pna2_1$; $a = 20.084(1)$, $b = 13.6500(6)$, $c = 11.0287(5)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$; $V = 3023.5(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.152\ g\,cm^{-3}$; crystal dimensions $0.48 \times 0.46 \times 0.21\ mm^3$; Bruker SMART Apex diffractometer with CCD area detector; $Mo_{K\alpha}$ radiation (0.71073 Å), 200 K, $2\Theta_{max} = 56.52°$; 28347 reflections, 7491 independent ($R_{int} = 0.0251$); direct methods; empirical absorption correction SADABS (ver. 2.03); refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97; 297 parameters, $R1 = 0.0630$ and $wR2$ (all data) = 0.1937, max./min. residual electron density 0.609/-0.287 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms in their calculated positions was included in the refinement using a riding model. CCDC 774848 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[19] Preliminary calculations at the same level of theory of the reactions $LiPH_2 + CO$ and $NaPH_2 + CO$ were performed to examine the effect of an alkali counterion on the MERP (in the gas phase without solvent). As expected, the addition of a counterion alters the values of $\Delta H_{r,298}$, but the characteristics of the MERPs are not changed. Specifically, no stable adduct with a P–C bond between $LiPH_2$ or $NaPH_2$ and CO is found. Instead, a complex with a bridging alkali ion between H_2P^- and CO is obtained which is, however, not disposed for the further reaction and requires a considerable reorientation of the reactants.

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