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A stable phosphanyl phosphaketene and its reactivity†‡

Zhongshu Li,[a,b] Xiaodan Chen,[b] Maike Bergeler,[b] Markus Reiher,[b] Cheng-Yong Su[a] and Hansjörg Grützmacher*[a,b]

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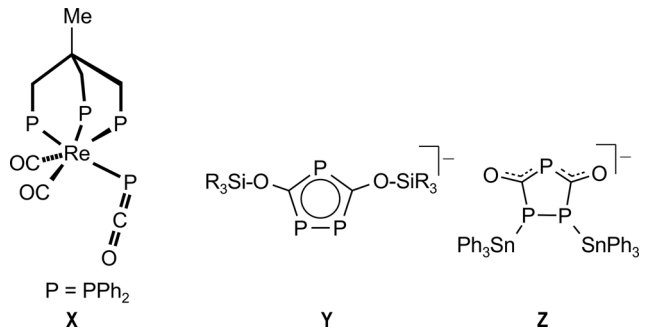
Sodium phosphaethynolate, Na(OCP), reacts with the bulky P-chloro-diazaphosphole yielding a phosphanyl phosphaketene, which is stable for weeks under an inert atmosphere in the solid state. This compound is best described as a tight ion pair with a remarkably long P–P bond distance (2.44 Å). In solution, this phosphaketene dimerizes under loss of CO to give 1,2,3-triphosphabicyclobutane identified by an X-ray diffraction study. As an intermediate, a five-membered heterocyclic diphosphene was trapped in a Diels–Alder reaction with 2,3-dimethylbutadiene. The formation of this intermediate in a hetero-Cope-rearrangement as well as dimerization/CO loss were computed with various DFT methods which allowed us to understand the reaction mechanisms.

Introduction

The search and synthesis of new reactive intermediates is an everlasting active field of research. Often these species allow for the elegant synthesis of new molecules and materials or help to understand reaction mechanisms.[1] Prominent examples are carbenes, CR_2,[2] or isovalent electronic phosphinidenes, RP,[3,4] which have yet to be isolated as stable entities. The development of synthetic strategies for precursor molecules which allows the generation or transfer of such reactive intermediates is therefore an active area of research. Phosphinidene metal complexes, $L_nM{=}PR$, as spectroscopically observable intermediates[5] or even isolated stable compounds are established "RP" transfer reagents for the synthesis of a multitude of organophosphorus compounds.[6] Cummins and coworkers have recently reported a very elegant method which allows the transfer of RP and P_2 units from simple organophosphorus precursor molecules.[7] We developed a simple large scale synthesis of sodium(phosphaethynolate), Na(OCP),[8] and showed that this serves under loss of carbon monoxide as a P-transfer reagent.[9] Experimental and computational results indicate that phosphaketenes, R–P=C=O, are intermediates in these reactions. These are easily obtained in salt metathesis reactions between main group elements or transition metal halides and Na(OCP), however, they are remarkably reactive.[10] So far, only the rhenium(I) phosphaethynolate complex **X** has been fully characterized including a structure analysis by X-ray diffraction methods.[10a] Trisorganyl tetrel substituted phosphaketenes, $R_3E{-}P{=}C{=}O$ (E = Si–Pb),[10b] show a surprising reactivity and may rearrange into two new heterocycles **Y** and **Z** which contain three phosphorus centers (Scheme 1). These reactions proceed under loss of CO and formal transfer of "P^-" units.[10c] Since R_3E groups can be regarded as π-acceptor substituents through negative hyperconjugation we became interested in the synthesis of phosphaketenes with π-donor substituents. It is noteworthy in this context that computations predict that phosphinidenes with π-donor substituents such as amino or phosphanyl groups lead to stabilized RP species with a singlet ground state.[11]



Scheme 1 A stable Re(I) phosphaketene complex **X**. The triphosphaheterocycles **Y** and **Z** are obtained by complex rearrangement reactions of trisorganyl tetrel phosphaketenes, $R_3E{-}P{=}C{=}O$ (E = Si–Pb).

[a]*Lehn Institute of Functional Materials (LIFM), Sun Yat-Sen University, 510275 Guangzhou, China. E-mail: hgruetzmacher@ethz.ch*
[b]*Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland*

† Dedicated to Prof. Dr Koop Lammertsma on occasion of his 65th birthday.

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Results and discussion

The reaction between Na(OCP) (**1**) in the form of its dioxane adduct and simple chlorophosphanes, R_2PCl, gave inseparable mixtures of products. Reactions with haloamines, R_2N–X, led to the oxidation of Na(OCP) to $[Na_2(C_4P_4O_2)]$[12] which is not surprising given the rather negative irreversible oxidation potential of the OCP^- anion[10a] making this a strong reductant. However, the reaction between **1** and P-chloro-diazaphosphole **2** with the very bulky bis(2,6-diisopropyl)phenyl substituent (Dipp, see Scheme 2) at the nitrogen atoms cleanly leads to the desired phosphanyl phosphaketene **3** (Scheme 2). This was isolated as a yellow crystalline solid and characterized by a structure determination by single crystal X-ray diffraction (Fig. 1).

The most notable feature in the structure of **3** is the very long P–P distance of 2.4414(5) Å which is much longer than typical P–P distances in diphosphanes (about 2.2 Å),[13] and even significantly exceeds the distance in the sterically overcrowded diphosphane $[(TMS)_2CH]_2P$–$P[CH(TMS)_2]_2$ (2.3 Å).[14] Only diazaphospholyl-phospholes which are best described as close diazaphospholenium cation–phospholide anion pairs have equally long or even slightly longer P–P bonds.[15] The P2 center deviates only by 0.236 Å from the plane passing through N1–C8–C9–N2 which supports the assumption that **3** retains a large $(diazaphospholenium)^+$, OCP^--anion character. The ^{31}P NMR data show that **3** preserves its structure in solution indicated by the $^1J_{PP}$ coupling constant of 253 Hz and the chemical shifts, δ P1 = −233 ppm and δ P2 = 165 ppm. Computations show that the phosphaketene-type isomer, "P–P=C=O", is about 18 kcal mol^{-1} more stable than the oxy-phosphaalkyne isomer, "P–O–C≡P" (see ESI‡ for details). This result is in accord with our previous findings which show that all R_3E–P=C=O compounds with E = C–Pb are more stable than R_3E–O–C≡P.[10b] Reactions between **3** and Ph_3SnCl or Ph–Mg–Br proceed smoothly and give $Ph_3Sn(OCP)$ (**4**)[10b] or BrMg(OCP) (**6**) apart from diazaphospholes **2** and **5**, respectively.[15] These simple salt metathesis reactions further support the view that **3** can be described as a very tight ion pair. Hydrolysis of **3** gives **7** as the only detectable phosphorus containing product while the fate of the OCP part remains unclear.[16]

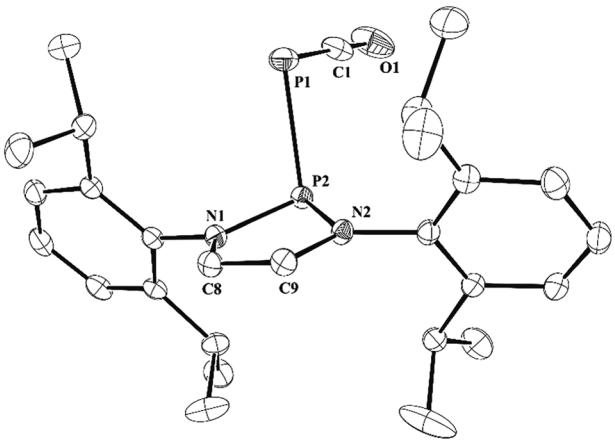
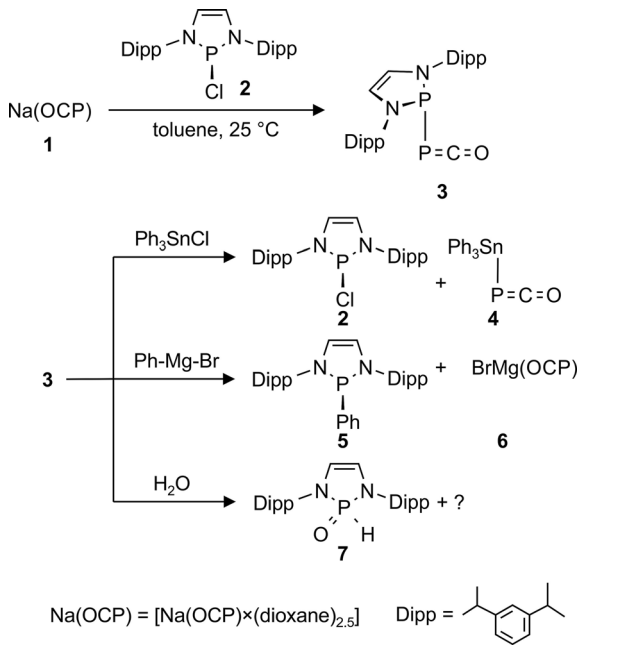


Fig. 1 Molecular structure of **3** in the solid state (H atoms omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1–P2 2.4414(5), P1–C1 1.6418(14), C1–O1 1.1695(17), P2–N1 1.6965(9), P2–N2 1.6942(9), N1–C8 1.4082(13), C8–C9 1.3361(16), C9–N2 1.4009 (13), O1–C1–P1 179.13(11), C1–P1–P2 86.60(4), P1–P2–N1 102.60(3), P1–P2–N2 101.93(3), P2–N1–C8 112.80(7), P2–N2–C9 113.09(7), N1–C8–C9 111.62(9), C8–C9–N2 111.88(9).



Scheme 2 Synthesis of diazaphospholyl phosphaketene **3** and some basic reactions leading to **2**, **4**, **5**, **6**, and **7** as products.

Under an inert atmosphere, solid **3** can be stored for at least a couple of weeks. However, in solution **3** rearranges cleanly under loss of CO at room temperature over 60 h to give **8** as the only product. This process is complete in 2 h in toluene at 60 °C. The decay of **3** follows a first-order rate law with a rate constant $k = 0.025\ h^{-1}$. The concomitant formation of **8** follows the same kinetic profile.

Species **8** was unequivocally identified as a compound with the 1,2,3-triphosphabicyclobutane substructure by X-ray diffraction with a single-crystal which was obtained from a 4 : 1 acetonitrile–diethyl ether solution. The structure is shown in Fig. 2. The P–P distances within the P_3 unit in this new tricyclic compound are about 2.2 Å which is close to values previously found for P_3 units.[17] Clearly **8** is very different from 1,3-diphosphetane-2,4-diones which have been reported as "classical" dimers of other organic phosphaketenes.[18] As a possible intermediate in this remarkable rearrangement reaction the cyclic diphosphene **I** is proposed.[17e] This may form from **3** *via* cleavage of one intra-cyclic P–N bond and displacement of the imino unit, RN=CH, under simultaneous insertion of the CO group. The resulting five-membered P_2NC_2 heterocycle is retained in the final product **8** which may result

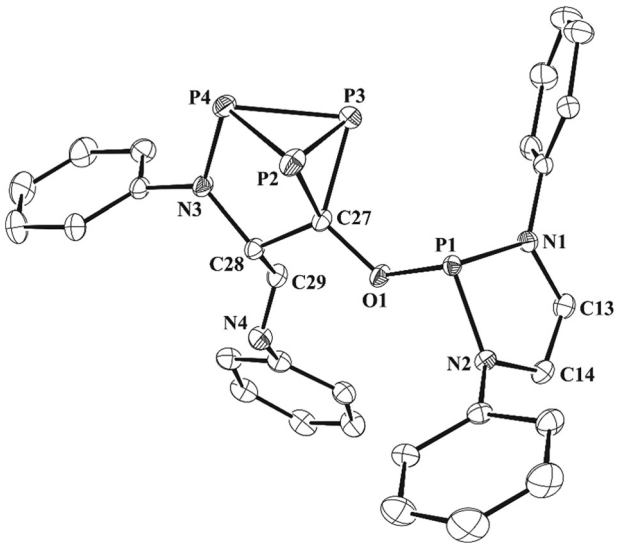


Fig. 2 Molecular structure of **8** in the solid state (only the arene groups at the nitrogen atoms are shown while the iPr groups and H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1–N1 1.7061(9), N1–C13 1.4030(15), C13–C14 1.3371(16), C14–N2 1.4157(14), P1–N2 1.6976(10), P1–O1 1.6864(8), O1–C27 1.4019(13), P3–C27 1.8900(12), P2–C27 1.8974(11), C27–C28 1.5250(15), P2–P3 2.2124(5), P3–P4 2.2104(4), P4–P2 2.1922(4), P4–N3 1.7053(10), N3–C28 1.4546(14), C28–C29 1.5041(16), C29–N4 1.2564(15), P1–N1–C13 111.97(8), P1–N2–C14 111.70(8), P1–O1–C27 116.83(7), O1–P1–N1 101.74(4), O1–P1–N2 99.66(4), O1–C27–P3 118.39(7), O1–C27–P2 120.50(7), O1–C27–C28 110.85(9), C27–P3–P4 78.66(3), C27–P3–P2 54.41(3), C27–P2–P4 78.98(3), C27–C28–N3 105.59(9), C27–C28–C29 113.32(9), C28–C29–N4 119.93(11), P2–P3–P4 59.427(14), P3–P4–P2 60.331(15), P4–P2–P3 60.242(15), P3–P4–N3 96.68(4), P2–P4–N3 97.66(4), P4–N3–C28 115.72(7).

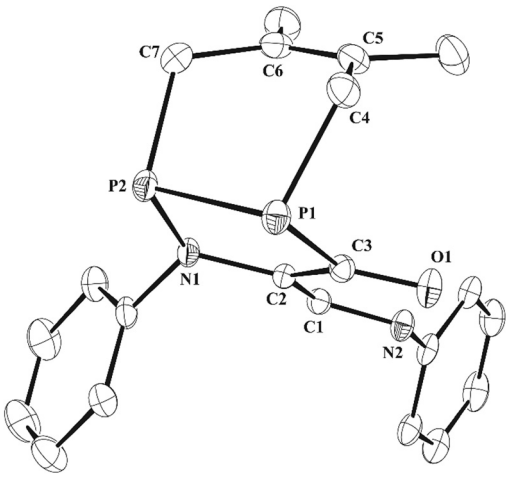


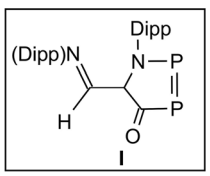
Fig. 3 Molecular structure of **9** in the solid state (only the arene groups at the nitrogen atoms are shown while the iPr groups and H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1–P2 2.2064(6), P1–C3 1.8765(16), C3–O1 1.2383(19), C3–C2 1.436(2), C2–C1 1.364(2), C1–N2 1.343(2), C2–N1 1.433(2), N1–P2 1.7239(14), P2–C7 1.873(2), C7–C6 1.501(2), C6–C5 1.337(3), C5–C4 1.505(3), C4–P1 1.874(2), P2–P1–C3 92.23(5), P1–C3–O1 120.52(12), P1–C3–C2 114.89(11), C3–C2–C1 122.16(14), C2–C1–N2 125.43(15), C3–C2–N1 116.39(13), C2–N1–P2 119.37(10), N1–P2–P1 94.04(5), N1–P2–C7 105.64(8), P2–C7–C6 115.72(14), C7–C6–C5 119.53(17), C6–C5–C4 120.08(15), C5–C4–P1 112.33(12), C4–P1–P2 95.80(8), P1–P2–C7 97.61(6).

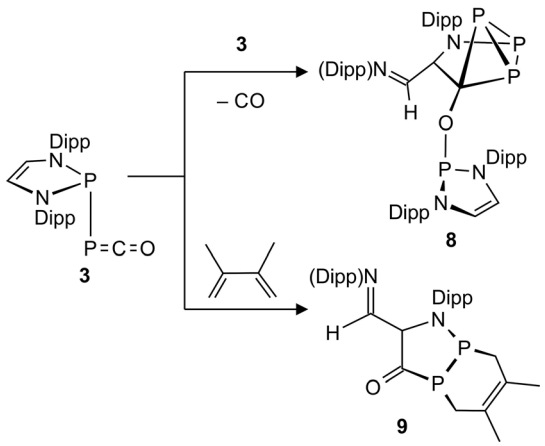
from **I** and a second equivalent of "P–PCO" **3** under loss of one CO molecule.

In order to strengthen this hypothesis, a solution of compound **3** was stirred at room temperature in neat 2,3-dimethylbutadiene (2,3-DMB) as a trapping agent for **I**. 2,3-DMB has been successfully used frequently to capture reactive P≡P triple and P=P double bonds.[19] Indeed, after 72 hours at room temperature, 11% of the bicyclic compound **9** with an aza-1,2-diphosphane moiety was isolated together with compound **8** as the main product. Compound **9** is the product of the [2 + 4] Diels–Alder-cycloaddition between the P–P double bond in **I** and the diene unit 2,3-DMB and was isolated in pure form and characterized by NMR spectroscopy and single-crystal X-ray diffraction. The structure of **9** is shown in Fig. 3.[20]

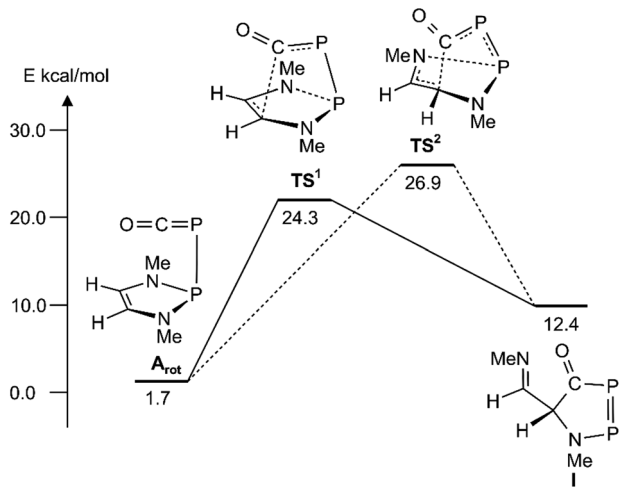
These experiments give strong evidence that the heterocycle **I** with a P=P double bond is indeed the key intermediate in the reactions shown in Scheme 3. Possible Minimum Energy Reaction Pathways (MERPs) were calculated for the formation of **I** from the phosphanyl phosphaketene (Scheme 4).

Furthermore, the further rearrangement of **I** to the tricyclic triphosphane **9** (Scheme 5A), as well as the trapping reaction with 2,3-DMB (Scheme 5B) were computed. Model compounds in which the Dipp substituents were replaced by methyl groups were used in calculations at the BP86/def2-TZVP level.





Scheme 3 Rearrangement of phosphaketene **3** and the formation of **8** and **9** with **I** as the assumed intermediate.

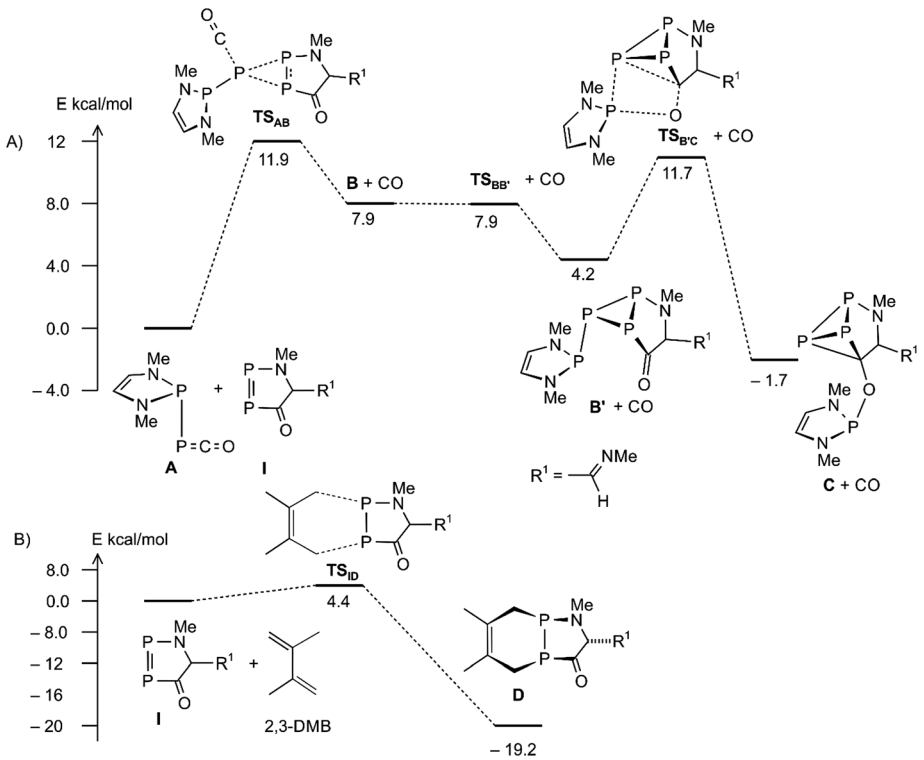


Scheme 4 BP86/def2-TZVP transition path from structure A_{rot} to **I**. The energies are reported relative to **A**.

The ground state rotamer **A** with an OCP group turned outwards with respect to the PN_2C_2 heterocycle will not lead to product **I**. Hence, we inspected its rotamer $\mathbf{A_{rot}}$ which is only 1–2 kcal mol^{-1} higher in energy.

We found two possible, slightly different reaction pathways for the rearrangement of $\mathbf{A_{rot}}$ to **I** (as shown in Scheme 4). Educt and product are directly connected *via* only one activated complex (*i.e.* transition state, TS), either $\mathbf{TS^1}$ or $\mathbf{TS^2}$. Since $\mathbf{TS^1}$ has a slightly lower energy (24.3 kcal mol^{-1}) than $\mathbf{TS^2}$ (26.9 kcal mol^{-1}), the preferred transformation from $\mathbf{A_{rot}}$ to **I** occurs through $\mathbf{TS^1}$. However, note that the energy difference between both transition states is method-dependent. In particular, they turn out to be of equal height in B3LYP optimizations. We only discuss the BP86 results in the main paper, because in general the results turned out to be only slightly method-dependent (details can be found in the ESI‡).

In $\mathbf{TS^1}$, the carbon center in the PN_2C_2 heterocycle can be viewed as part of an electron rich *cis*-diamino olefin which attacks the electrophilic carbon center of the phosphaketene under concomitant opening of the P–N bond on the opposite side. The newly formed C···C interaction (1.9 Å) is rather long while the breaking P–N bond remains rather short (1.9 Å). The contrary is seen in the energetically slightly higher $\mathbf{TS^2}$ which resembles more closely the final product (late TS) with a shorter new C–C (1.6 Å) and longer cleaving P···N (2.6 Å) interaction. On both pathways, **I** is formed as the product of an endothermic heteroatom-Cope-rearrangement (ΔH_r = 12.4 kcal mol^{-1}). The heterocycle **I** reacts further with non-reacted starting material **A** to give a cyclo-triphosphane **B** which in a practically barrier-less reaction rearranges to **B′**. Both, **B** and **B′** have very similar structures and are merely rotamers with respect to the orientation of the diazaphosphole unit, $(CH)_2(NMe)_2P$. The reaction **A** → **B** proceeds *via* the activated complex $\mathbf{TS_{AB}}$ in a transition state at 11.9 kcal mol^{-1} which is the highest barrier



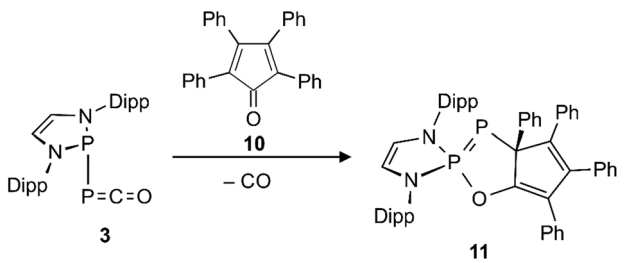
Scheme 5 (A) BP86/def2-TZVP transition path from **A** and **I** to **C** and CO. (B) BP86/def2-TZVP transition path for the Diels–Alder reaction between **I** and 2,3-DMB to **D**. The structure of **B** is very similar to **B′** and not shown here (for details see Fig. S28 in the ESI‡).

along the MERP from **A** to **C**. Note that the activated complex $\mathbf{TS_{AB}}$ can be viewed as a complex of phosphanyl phosphinidene, $(HC)_2(NMe)_2P$–P coordinated by a CO molecule and the P═P bond in **I**.[21] A similar observation was made for the activated complex computed for the reaction of PH_2^- and CO which is best described as a P^- anion coordinated by H_2 and CO molecules.[8b] In the final step the diazaphosphol moiety migrates from the *exo*-cyclic phosphorus atom to the C═O group under the simultaneous formation of a C–P bond which closes the P_3C cage in **C**. This reaction is associated with a barrier of 7.5 kcal mol^{-1} at $\mathbf{TS_{B'C}}$.

The MERP of the trapping reaction of the heterocyclic intermediate **I** with 2,3-DMB was also computed. An activated complex $\mathbf{TS_{ID}}$ at a remarkably low energy (4.4 kcal mol^{-1}) was found for this Diels–Alder type [2 + 4] reaction which proceeds with a normal electron demand (the HOMO of the P═P interacts favorably with the LUMO of 2,3-DMB). The product **D** is found to be 19.2 kcal mol^{-1} more stable than the educt state. At first glance the computations are not in accord with the experimental results which show that triphosphabicyclobutane **8** is obtained as the major product even when the reaction is performed with 2,3-DMB in large excess as the solvent. However, the [2 + 4] cyclo reversion of **D** which leads back to **I** and 2,3-DMB has an activation barrier of 23.6 kcal mol^{-1} which is in the same range as the Cope-rearrangement **A** → **I** and is accessible under the experimental conditions. Indeed, a kinetic modelling of the reaction starting from the phosphaketene **A** and with the energies shown in Schemes 4 and 5 shows that the reaction evolves slowly to product **E** which is formed irreversibly because of the loss of CO. It is well possible that the bulky substituents Dipp instead of methyl and the inclusion of solvent effects would further favor the formation of triphosphabicyclobutane **8**.

To a certain extent the reaction between phosphanyl phosphaketene **3** and the cyclic diphosphene intermediate **I** can be regarded as a Michael-addition of the stabilized OCP^- anion in **3** to the activated P═P–C═O unit of **I**. Therefore the reaction between **3** and pentaphenylcyclopentadienone (tetracyclone) **10** was investigated (Scheme 6).

After 2 d at room temperature, a new compound **11** was isolated as a yellow powder in 28% isolated yield. Again triphosphabicyclobutane **8** is further obtained as the major product. A large $^{31}P^{31}P$ coupling constant of J_{PP} = 651 Hz in **11** indicates a species with a P–P bond but the chemical shifts at



Scheme 6

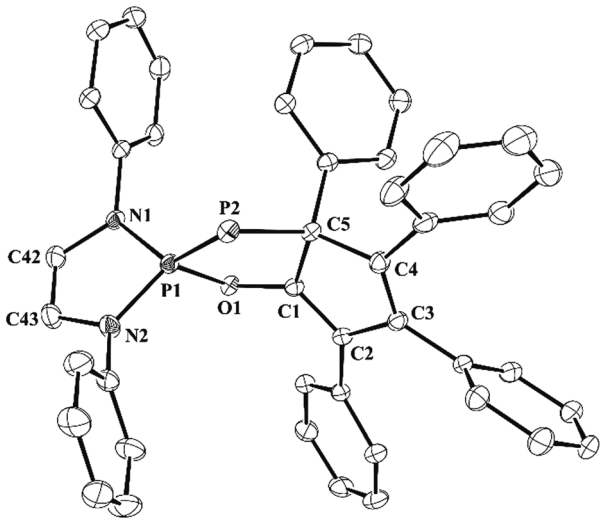


Fig. 4 Molecular structure of **11** in the solid state (only the arene groups at the nitrogen atoms are shown while the iPr groups and H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1–P2 2.0688(8), P1–O1 1.6569(16), O1–C1 1.389(3), C1–C2 1.351(3), C1–C5 1.494(3), C2–C3 1.490(3), C3–C4 1.359(3), C4–C5 1.521(3), C5–P2 1.916(2) P1–N1 1.6785(19), P1–N2 1.664(2), N1–C42 1.411(3), C42–C43 1.328(3), C43–N2 1.415(3), O1–P1–P2 102.92(6), O1–P1–N1 101.64(9), O1–P1–N2 113.11(10), N1–P1–P2 130.48(7), N2–P1–P2 116.70(8), N2–P1–N1 91.33(10), C5–P2–P1 89.40(7), C1–O1–P1 109.40(13), C42–N1–P1 111.62(15), C43–N2–P1 112.19(16), C3–C4–C5 109.41(19), C1–C2–C3 105.24(19), C4–C5–P2 114.85(15), C1–C5–P2 103.48(15), C1–C5–C4 100.57(17), O1–C1–C5 117.57(18), O1–C1–C2 127.8(2), C2–C1–C5 114.01(19), C2–C3–C4 110.44(19), C42–C43–N2 111.9(2), C43–C42–N1 112.3(2).

δ = 115 and δ = −143 ppm do not allow to assign a structure. This was elucidated by single crystal X-ray diffraction studies (Fig. 4). Compound **11** is a cyclic derivative of phosphanylidene-σ^4-phosphorane characterized by a short P–P bond of 2.0688(8) Å which lies in the range of typical P═P double bonds. However, in **11** this bond is best described as an ylidic $P^{\delta+}$–$P^{\delta-}$ bond as found in phospha-Wittig reagents.[22] In contrast to these, **11** is remarkably stable in the solid state and solution even when heated to 60 °C for several hours.

Although **11** is formally the addition product of a phosphanyl phosphinidene and tetracyclone **10**, it is again highly doubtful that this did form an intermediate. Likely alternative pathways at much lower energies which involve the addition of the OCP unit to **10** followed by CO loss are responsible for the formation of **11**. Preliminary results from calculations show that various reaction pathways of this kind may lead to **11** but an explicit and detailed computation of all possible MERPs is beyond the scope of this study.

Concluding remarks

The reaction between Na(OCP) (**1**) and the unsaturated P-chlorophosphane **2** yields **3** as a stable compound in high yield.

This compound was isolated and characterized as a phosphanyl phosphaketene with an unusually long P–P bond. This ketene undergoes a variety of unexpected reactions such as a hetero-Cope-rearrangement to a five-membered heterocycle **I** with a P=P double bond. This heterocycle contains a highly reactive P=P bond and could be successfully trapped with a diene in [2 + 4] Diels–Alder reaction. A phosphanyl phosphinidene as an intermediate in the reaction reported here is highly unlikely[21] and it remains elusive.

Experimental section

General

All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk techniques. Dry, oxygen-free solvents were employed unless otherwise mentioned. Sodium phosphaethynolate (**1**)[8a] and 2-chloro-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholene (**2**)[23] were prepared following literature procedures while all other starting materials were purchased from commercial sources. 2,3-Dimethylbutadiene was distilled from $NaBH_4$ and stored at −20 °C over molecular sieves prior to use. NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers. All spectra were obtained in the solvent indicated at T = 25 °C. Chemical shifts (δ) were measured according to IUPAC and expressed in ppm relative to $SiMe_4$ (^1H, ^{13}C), and 85% H_3PO_4 (^{31}P). Coupling constants J are reported in hertz [Hz] as absolute values. IR spectra were recorded on a Perkin-Elmer-Spectrum ATR 2000 FT-IR-Raman spectrometer with a KBr beam splitter (range 500–4000 cm^{-1}). The ATR technique was used for the analysis of solid compounds. Melting points (M.P.) were measured on a Büchi M-560 apparatus. More details about the synthetic details, the kinetic study for the dimerization of **3**, X-ray diffraction studies, and theoretical details are given in the ESI.‡ Satisfying elemental analyses have not been performed since the compounds reported in this study are very sensitive to oxygen and moisture. But the homogeneity of the materials prepared was ensured by NMR data.

Preparation of 2-phosphaketene-1,3-bis(2,6-diisopropylphenyl)-1,3-diazaphospholene 3. 3.02 g (10 mmol) of sodium phosphaethynolate [Na(OCP)·(dioxane)$_{2.5}$] was added to a stirred solution of **2** (4.43 g, 10 mmol) in toluene (10 mL). After 1 h stirring, the precipitate of sodium chloride was removed by filtration. The filtrate was dried under reduced pressure and the remaining solid was washed with hexane. Drying the residue *in vacuo* afforded **3** as a yellow powder (3.2 g, 6.8 mmol, 68% yield). M.P. = 121.6 °C. ^1H NMR (C_6D_6, 500 MHz): δ = 6.86 (m, 2 H, $C_{ar}H$), 6.77 (m, 4 H, $C_{ar}H$), 5.76 (s, 2 H, NCH), 3.25 (m, 4 H, CHMe$_2$), 1.06 (d, 12 H, CH_3), 0.83 (d, 12 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz): δ = 198.4 (dd, J_{PC} = 95.6 Hz, *P*C*O*, J_{PC} = 22.6 Hz, *PP*C*O*), 146.3 (*ipso*-C), 132.7 (d, J_{PC} = 8.8 Hz, *o*-C), 127.8 (*p*-CH), 123.6 (*m*-CH), 121.0 (d, J_{PC} = 8.8 Hz, NCH), 28.0 (CHMe$_2$), 24.0 (CH$_3$), 23.3 (CHMe$_2$); $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): δ = 165.1 (d, J_{PP} = 252.5 Hz, *P*PCO), δ = −232.6 (d, J_{PP} = 252.5 Hz, *P*CO). IR (solid): 1881 cm^{-1} (s, PCO).

Preparation of 5 and 6. 0.5 mL (0.5 mmol) of phenylmagnesium bromide (1 M in thf) was added dropwise to a stirred solution of **3** (233 mg, 0.5 mmol) in thf (3 mL) at 0 °C. The mixture was allowed to warm to room temperature under stirring. After 2 hours, the solvent was removed under reduced pressure. The residue was extracted with *n*-hexane (2 × 2 mL) followed by filtration over a glass frit. The filtrate was dried under reduced pressure and washed with acetonitrile (2 × 2 mL) affording **5** as a yellow powder (210 mg, 0.43 mmol, 87% yield). M.P. = 189.2 °C. ^1H NMR (C_6D_6, 300 MHz): δ = 7.54 (m, 2 H, $C_{ar}H$), 6.88 (m, 4 H, $C_{ar}H$), 6.73 (m, 5 H, $C_{ar}H$), 5.60 (d, J_{PH} = 2.3 Hz, 2 H, NCH), 3.59 (m, 2 H, CHMe$_2$), 3.22 (m, 2 H, CHMe$_2$), 1.23 (d, 6 H, CH_3), 1.07 (M, 12 H, CH_3), 0.91 (d, 6 H, CH_3), 0.20 (d, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ = 147.6 (*ipso*-C), 146.9 (d, *ipso*-C′), 143.5, 142.7, 137.1, 136.9, 130.2, 129.8, 129.5, 126.1, 123.4, 123.0, 119.7 (d, J_{PC} = 5.7 Hz, NCH), 27.5 (CHMe$_2$), 27.2 (CH$_3$), 24.5 (CH$_3$), 23.4 (CH$_3$), 23.0 (CHMe$_2$), 22.9 (CH$_3$); $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz): δ = 102.7. The residue from the filtration above was dried *in vacuo* affording **6** as a grey powder (185 mg, 0.487 mmol, 97% yield). According to the NMR spectra and a ^1H NMR titration experiment (14 mg product and 6.2 mg benzene were mixed in [D$_6$]DMSO, see ESI‡), this solid has the composition [**6**·(thf)$_3$] M.P. = 125.6 °C (decomp.). ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 3.59 (m, 4 H, OCH_2), 1.75 (m, 4 H, OCH$_2$CH_2); $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 75 MHz): δ = 169.2 (d, J_{PC} = 60 Hz), 67.0 (OCH$_2$), 25.1 (OCH$_2$CH$_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO, 121 MHz): δ = −381.1. IR (solid): 1736 cm^{-1} (s, OCP).

Preparation of 7. Water (5.4 mg, 0.3 mmol) was added dropwise to a stirred solution of **3** (117 mg, 0.25 mmol) in toluene (2 mL). After stirring for 3 minutes, the reaction mixture was dried under reduced pressure to yield an orange-red solid **7** (97.7 mg, 0.23 mmol, 92% yield). M.P. = 69.3 °C (decomp.). ^1H NMR (C_6D_6, 300 MHz): δ = 8.48 (d, J_{PH} = 642 Hz, 1 H, PH), 6.91 (m, 4 H, $C_{ar}H$), 6.75 (m, 2 H, $C_{ar}H$), 5.44 (d, J_{PH} = 15 Hz, 2 H, NCH), 5.39 (S, 1 H, NCH), 3.77 (m, 2 H, CHMe$_2$), 2.91 (m, 2 H, CHMe$_2$), 1.20 (d, 6 H, CH_3), 0.86 (m, 12 H, CH_3), 0.77 (d, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ = 149.1 (d, J_{PC} = 1.6 Hz, *ipso*-C), 146.9 (d, J_{PC} = 3.2 Hz, *ipso*-C′), 131.6 (d, J_{PC} = 3.7 Hz, *o*-C), 128.0 (*p*-CH), 123.6 (*m*-CH), 122.8 (*m*-C′H), 115.8 (d, J_{PC} = 11.6 Hz, NCH), 27.4 (CH$_3$), 23.9 (CHMe$_2$), 23.6 (C′HMe$_2$), 23.1 (C″HMe$_2$), 22.7 (C‴HMe$_2$); $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz): δ = 2.9 (td, J_{HP} = 15 Hz, *H*CNP, J_{HP} = 639 Hz, *H*P).

Preparation of 8. A solution of **3** (117 mg, 0.25 mmol) in THF (2 mL) was stirred for 60 hours at room temperature or in toluene (3 mL) at 60 °C for 2 hours. The solvent was removed under reduced pressure, and the remaining solid was dissolved in acetonitrile (2 mL) and diethyl ether (0.5 mL). After 24 hours yellow crystals of **8** precipitated from the solution were filtered off, washed with acetonitrile, and dried *in vacuo* (81 mg, 0.09 mmol, 71% yield). M.P. = 189.2 °C. ^1H NMR (C_6D_6, 300 MHz): δ = 7.14 (d, 1 H, $C_{ar}H$), 6.79 (br, 9 H, $C_{ar}H$), 6.61 (m, 2 H, $C_{ar}H$), 5.63 (d, 2 H, J_{PH} = 51 Hz, NCH), 4.45 (s, 1 H, NCH), 3.72 (m, 1 H, CHMe$_2$), 3.14 (m, 3 H, CHMe$_2$), 2.76

(m, 2 H, C*H*Me$_2$), 1.30 (d, 3 H, C*H*$_3$), 0.92 (br, 42 H, C*H*$_3$), 0.64 (d, 3 H, C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 162.6, 148.1, 147.6, 146.4, 145.6, 135.8, 135.6, 134.5, 135.2, 135.1, 134.9, 127.3, 123.5, 123.3, 123.2, 123.1, 121.2, 117.6, 117.1, 69.1, 28.0, 27.8, 27.5, 26.8, 26.4, 25.7, 24.9, 24.2, 24.1, 23.5, 23.3, 22.6, 22.3, 21.6; ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ = 118.0 (dt, J_{PP} = 145.4 Hz, J_{PP} = 34.3 Hz), 0.1 (td, J_{PP} = 207.4 Hz, J_{PP} = 32.4 Hz), −263.4 (ddd, J_{PP} = 33.9 Hz, J_{PP} = 145.2 Hz, J_{PP} = 208.8 Hz), −272.1 (dt, J_{PP} = 206.1 Hz, J_{PP} = 36.4 Hz).

Preparation of 9. A solution of **3** (233 mg, 0.5 mmol) in 2,3-dimethylbutadiene (3 mL) was stirred for 72 hours at room temperature (according to the ^{31}P NMR of the reaction mixture, products **8** and **9** were obtained in a ratio around 4 : 1). The solvent was removed under reduced pressure, and the remaining solid was dissolved in acetonitrile (1 mL) and diethyl ether (1 mL). After 48 hours, the precipitate of **8** was removed by filtration from the solution. The filtrate was dried under reduced pressure to give a yellow-red residue. This residue was dissolved in 1 mL *n*-hexane and filtered over a 6 × 1 cm column of alumina which was washed with 3 mL hexane. The solvent was removed under reduced pressure to give product **9** as a yellow solid (31 mg, 0.056 mmol, 11% yield). According to NMR data, this solid contains both the *trans* and *cis* isomers in a ratio of about 2 : 1. M.P. = 163.7 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 10.29 (d, J = 12 Hz, 1 H, N*H*), 6.95 (s, 2 H, C$_{ar}$*H*), 6.87 (m, 1 H, C$_{ar}$*H*), 6.77 (m, 3 H, C$_{ar}$*H*), 6.72 (m, 3 H, C$_{ar}$*H*), 6.49 (d, J = 12 Hz, 0.5 H, N*H*′), 5.62 (d, J = 12 Hz, 1 H, NC*H*), 4.97 (d, J = 12 Hz, 0.5 H, NC*H*′), 3.80 (m, 0.5 H, C*H*′Me$_2$), 3.27 (m, 2.5 H, C*H*Me$_2$), 2.80 (m, 5 H, C*H*′Me$_2$ and PC*H*$_2$), 2.40 (m, 1 H, C*H*Me$_2$), 1.76 (m, 1 H, PC*H*$_2$), 1.59 (m, 9 H, CH$_2$C*H*$_3$), 1.48 (m, 2 H, PC*H*′$_2$), 1.24 (d, J = 6 Hz, 3 H, C*H*$_3$), 1.25 (d, J = 6 Hz, 1.5 H, C*H*′$_3$), 1.11 (d, J = 6 Hz, 1.5 H, C*H*′$_3$), 1.07 (d, J = 6 Hz, 3 H, C*H*$_3$), 0.96 (d, J = 6 Hz, 3 H, C*H*$_3$), 0.78 (m, 24 H, C*H*$_3$ and C*H*′$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 215.2 (dd, J_{PC} = 37.5 Hz, *PC*O, J_{PC} = 7.5 Hz, *PPC*O), 148.8, 148.8, 148.2, 147.4, 143.9, 143.5, 142.6, 142.1, 136.9, 136.3, 135.0, 128.7, 126.8, 126.7, 125.7, 125.4, 124.4, 124.3, 123.9, 123.7, 123.0, 123.1, 122.4, 38.1, 37.7, 37.4, 37.1, 31.8, 29.1, 29.0, 28.4, 28.3, 28.1, 27.6, 27.5, 27.1, 26.1, 25.9, 25.3, 25.1, 24.0, 23.6, 23.5, 23.4, 22.9, 22.8, 22.2, 21.8, 21.7, 21.0, 20.6; ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ = 39.4 (d, J_{PP} = 290.4 Hz, *trans*), 36.2 (d, $J_{P'P'}$ = 290.4 Hz, *cis*), −45.8 (d, J_{PP} = 290.4 Hz, *trans*), −51.2 (d, J_{PP} = 290.4 Hz, *cis*).

Preparation of 11. Tetraphenylcyclopentadienone (288 mg, 0.75 mmol) was added to a stirred solution of **3** (117 mg, 0.25 mmol) in THF (3 mL). After stirring for 48 hours, the reaction mixture contains products **8** and **11** in a ratio around 3 : 2 according to the ^{31}P NMR spectrum. For the separation of the products, the solvent of the reaction mixture was removed under reduced pressure, followed by extraction with *n*-hexane (2 × 5 mL) and filtration. Because **8** is hardly soluble in *n*-hexane, the filtrate was dried under reduced pressure and washed with acetonitrile to yield **11** as a yellow powder (57 mg, 0.07 mmol, 28% yield). M.P. = 157.5 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.31 (m, 2 H, C$_{ar}$*H*), 7.15 (m, 2 H, C$_{ar}$*H*), 6.92 (m, 2 H, C$_{ar}$*H*), 6.76 (m, 5 H, C$_{ar}$*H*), 6.67 (m, 5 H, C$_{ar}$*H*), 6.60 (m, 3 H, C$_{ar}$*H*), 6.48 (m, 1 H, C$_{ar}$*H*), 6.33 (m, 6 H, C$_{ar}$*H*), 5.61 (m, 1 H, NC*H*), 5.44 (m, 1 H, NC*H*), 3.66 (m, 1 H, C*H*Me$_2$), 3.37 (m, 1 H, C*H*Me$_2$), 3.03 (m, 1 H, C*H*Me$_2$), 2.67 (m, 1 H, C*H*Me$_2$), 1.36 (m, 6 H, C*H*$_3$), 1.04 (d, 3 H, C*H*$_3$), 0.89 (m, 6 H, C*H*$_3$), 0.78 (d, 3 H, C*H*$_3$), 0.70 (d, 3 H, C*H*$_3$), 0.37 (d, 3 H, C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 158.5 (d, J_{PC} = 1.6 Hz), 148.6, 147.9, 147.1, 146.1, 145.9, 145.8, 145.7, 141.4, 139.4, 136.8, 136.2, 135.0, 133.5, 133.4, 130.3, 129.6, 129.1, 126.9, 126.7, 126.5, 125.3, 125.6, 124.3, 124.8, 121.4, 121.0, 117.2, 66.6 (dd, J_{PC} = 52.2 Hz, *P*C, J_{PC} = 7.5 Hz, *P*PC), 65.7, 31.8, 29.6, 29.0, 28.2, 26.6, 26.2, 26.0, 25.0, 24.2, 23.7, 22.6, 22.2, 15.4, 14.2; ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ = 118.2, 112.8 (d, J_{PP} = 651 Hz), δ = −140.5, −145.9 (d, J_{PP} = 651 Hz).

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Notes and references

1 R. A. P. Moss and M. S. Jones Jr., *Reactive Intermediate Chemistry*, Wiley-Interscience, Hoboken, NJ, 2004.
2 M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810–8849.
3 (*a*) K. Lammertsma, in *New Aspects in Phosphorus Chemistry III*, ed. J.-P. Majoral, Springer, Berlin Heidelberg, 2003, vol. 229, ch. 4, pp. 95–119; (*b*) K. L. J. C. Slootweg, *Sci. Synth.*, 2009, **42**, 15–36.
4 (*a*) T. Wong, J. K. Terlouw, H. Keck, W. Kuchen and P. Tommes, *J. Am. Chem. Soc.*, 1992, **114**, 8208–8210; (*b*) G. Bucher, M. L. G. Borst, A. W. Ehlers, K. Lammertsma, S. Ceola, M. Huber, D. Grote and W. Sander, *Angew. Chem., Int. Ed.*, 2005, **44**, 3289–3293.
5 H. Jansen, M. C. Samuels, E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, P. Chen and K. Lammertsma, *Chem. – Eur. J.*, 2010, **16**, 1454–1458.
6 F. Mathey, *Angew. Chem., Int. Ed.*, 2003, **42**, 1578–1604.
7 (*a*) A. Velian and C. C. Cummins, *J. Am. Chem. Soc.*, 2012, **134**, 13978–13981; (*b*) A. Velian, M. Nava, M. Temprado, Y. Zhou, R. W. Field and C. C. Cummins, *J. Am. Chem. Soc.*, 2014, **136**, 13586–15589.
8 (*a*) D. Heift, Z. Benkő and H. Grützmacher, *Dalton Trans.*, 2014, **43**, 831–840; (*b*) F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H. F. Grützmacher and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2011, **50**, 8420–8423. For the synthesis of Na(OCP) from a terminal niobium phosphido complex and CO_2 see (*c*) I. Krummenacher and C. C. Cummins, *Polyhedron*, 2012, **32**, 10–13. For the synthesis of K(OCP) see (*d*) A. R. Jupp and J. M. Goicoechea, *Angew. Chem., Int. Ed.*, 2013, **52**, 10064–10067; and for the first synthesis of Li(OCP) see

(*e*) G. Becker, W. Schwarz, N. Seidler and M. Westerhausen, *Z. Anorg. Allg. Chem.*, 1992, **612**, 72.

9 A. M. Tondreau, Z. Benkő, J. R. Harmer and H. Grützmacher, *Chem. Sci.*, 2014, **5**, 1545–1554.

10 (*a*) S. Alidori, D. Heift, G. Santiso-Quinones, Z. Benkő, H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. – Eur. J.*, 2012, **18**, 14805–14811; (*b*) D. Heift, Z. Benkő and H. Grützmacher, *Dalton Trans.*, 2014, **43**, 5920–5928; (*c*) D. Heift, Z. Benkő and H. Grützmacher, *Chem. – Eur. J.*, 2014, **20**, 11326–11330.

11 Z. Benkő, R. Streubel and L. Nyulaszi, *Dalton Trans.*, 2006, 4321–4327.

12 G. Becker, G. Heckmann, K. Hubler and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1995, **621**, 34–46.

13 (*a*) T. Mizuta, T. Nakazono and K. Miyoshi, *Angew. Chem., Int. Ed.*, 2002, **41**, 3897–3898; (*b*) D. Tofan and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2010, **49**, 7516–7518; (*c*) C. Fave, M. Hissler, T. Karpati, J. Rault-Berthelot, V. Deborde, L. Toupet, L. Nyulaszi and R. Reau, *J. Am. Chem. Soc.*, 2004, **126**, 6058–6063; (*d*) Y. Carpenter, C. A. Dyker, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2008, **130**, 15732–15741.

14 S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. Voigt, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne and P. P. Power, *J. Am. Chem. Soc.*, 2001, **123**, 9045–9053.

15 (*a*) S. Burck, D. Gudat and M. Nieger, *Angew. Chem., Int. Ed.*, 2004, **43**, 4801–4804; (*b*) S. Burck, K. Gotz, M. Kaupp, M. Nieger, J. Weber, J. S. auf der Gunne and D. Gudat, *J. Am. Chem. Soc.*, 2009, **131**, 10763–10774.

16 The expected product would be H–P═C═O which could, however, not be detected; see (*a*) M. T. Nguyen, A. F. Hegarty, M. A. Mcginn and P. Ruelle, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1991–1997; (*b*) C. Dimur, F. Pauzat, Y. Ellinger and G. Berthier, *Spectrochim. Acta, Part A*, 2001, **57**, 859–873.

17 (*a*) R. Appel, B. Niemann and M. Nieger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 957–958; (*b*) H. Zimmermann, M. Gomm, E. Kock and J. Ellermann, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1986, **42**, 1757–1759; (*c*) O. Back, G. Kuchenbeiser, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2009, **48**, 5530–5533; (*d*) E. Niecke, O. Altmeyer and M. Nieger, *J. Chem. Soc., Chem. Commun.*, 1988, 945–946. A comparable rearrangement of the PN_2C_2 ring into a P_2NC_2 ring has been observed in the reaction between a bis(diazaphospholenyl) and acetylene dimethylcarboxylate: (*e*) D. Förster, H. Dilger, F. Ehret, M. Nieger and D. Gudat, *Eur. J. Inorg. Chem.*, 2012, 3989–3994.

18 (*a*) R. Appel and W. Paulen, *Tetrahedron Lett.*, 1983, **24**, 2639–2642; (*b*) V. Plack, J. R. Goerlich, A. Fischer and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1979–1984.

19 (*a*) N. A. Piro, J. S. Figueroa, J. T. McKellar and C. C. Cummins, *Science*, 2006, **313**, 1276–1279; (*b*) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2007, **129**, 14180–14181; (*c*) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052–7055.

20 The isolated 2 + 4 Diels–Alder adduct is actually a mixture of the *cis*/*trans* isomers which are obtained in a 2 : 1 ratio as confirmed by NMR spectroscopy and single-crystal X-ray crystallography (for details see the ESI‡).

21 A free phosphanyl phosphinidene as an intermediate is very unlikely. The computed dissociation energy $\mathbf{A} \rightarrow (HC)_2(NMe)_2P - P + CO$ is endothermic by 29.0 kcal mol^{-1} and is associated with a high activation barrier of 48.7 kcal mol^{-1} (at the BP86/def2-TZVP level).

22 (*a*) S. Shah and J. D. Protasiewicz, *Coord. Chem. Rev.*, 2000, **210**, 181–201; (*b*) S. Shah and J. D. Protasiewicz, *Chem. Commun.*, 1998, 1585–1586; (*c*) S. Shah, M. C. Simpson, R. C. Smith and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 2001, **123**, 6925–6926.

23 S. Burck, D. Gudat, M. Nieger and W. W. Du Mont, *J. Am. Chem. Soc.*, 2006, **128**, 3946–3955.

