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A Stable Phosphanyl Phosphaketene and Its Reactivity

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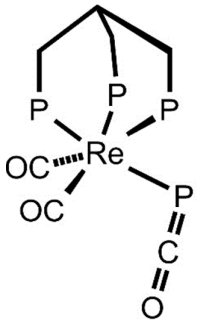
Dedication: *To Prof. Dr. Koop Lammertsma on occasion of his 65th birthday*

Abstract:

Sodium phospaethynolate, Na(OCP), reacts with the bulky P-chloro-diazaphosphole yielding a phosphanyl phosphaketene, which is stable for weeks under inert atmosphere in the solid state. This compound is best described as tight ion pair with a remarkable long P–P bond distance (2.44 Å). In solution, this phosphaketene dimerizes under loss of CO to give a 1,2,3–triphosphabicyclobutane compound 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 the dimerization/CO loss were computed with various DFT methods which allows to suggest reaction mechanisms.

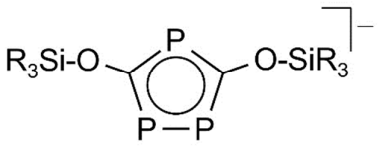
Introduction: The search and synthesis of new reactive intermediates is an everlasting active field of research. Often those species allow for the elegant synthesis of new molecules and materials or help to understand reaction mechanisms.[1] Prominent examples are carbenes, CR_2,[2] or isovalence electronic phosphinidenes, RP,[3,4] which have not been isolated as stable entities, yet. The

development of synthetic strategies for precursor molecules which allows the generation or the 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 co-workers 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 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 element or transition metal halides and Na(OCP), however, they are remarkably reactive.[10] So far, only the rhenium(I) phosphaethynolate complex **X** could be fully characterized including a structure analysis with 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 to new heterocycles **XX**, **XXX** which contain three phosphorus centers. 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. Note 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]

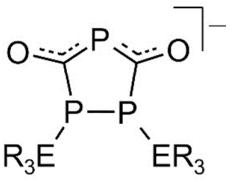


P = PPh_2

X



XX

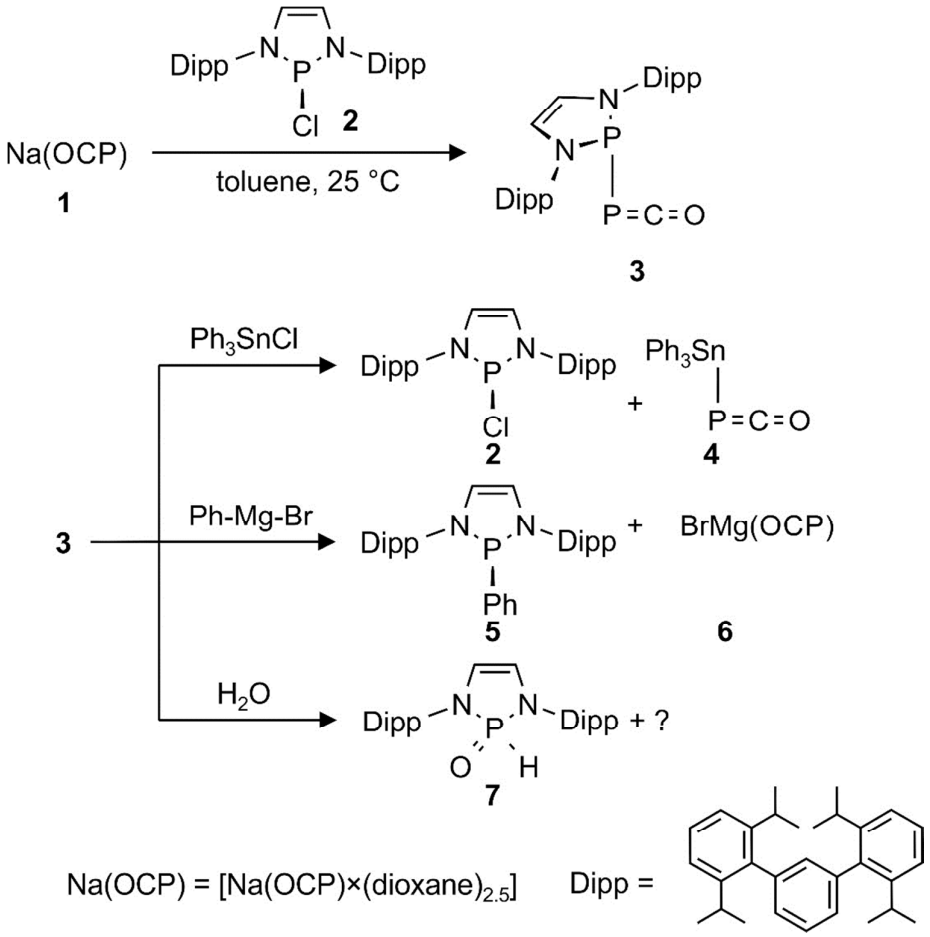


E = Ge - Pb

XXX

Scheme 1. A stable Re(I) phosphaketene complex **X** and triphosphaheterocycles **XX** and **XXX** obtained by complex rearrangement reactions of trisorganyl tetrel phopshaketenes, R_3E-P=C=O (E = Si – Pb).

Results and discussion: The reaction between Na(OCP) (**1**) in form of its dioxane adduct and simple chlorophosphanes, R_2PCl, gave inseparable mixtures of products. Reactions with haloamines, R_2N-X, led to 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. But the reaction between **1** and the P-chloro-diazaphosphole **2** with the very bulky bis(2,6-diisopropyl)phenyl substituent (Dipp, see Scheme 1) 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 X-ray diffraction with single crystals. The result is displayed in Figure 1.



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

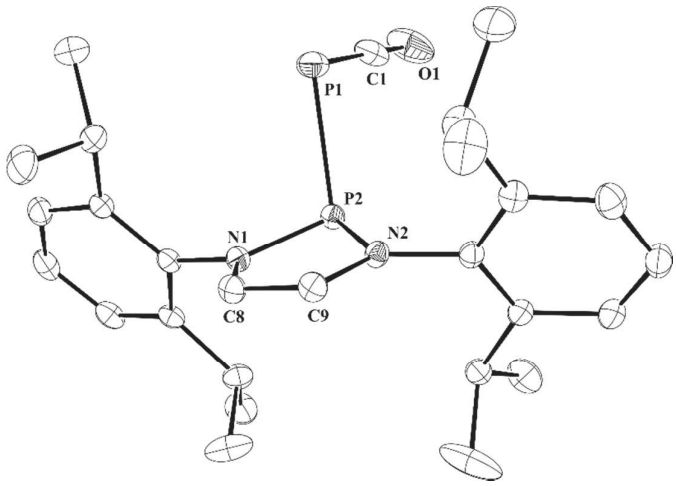
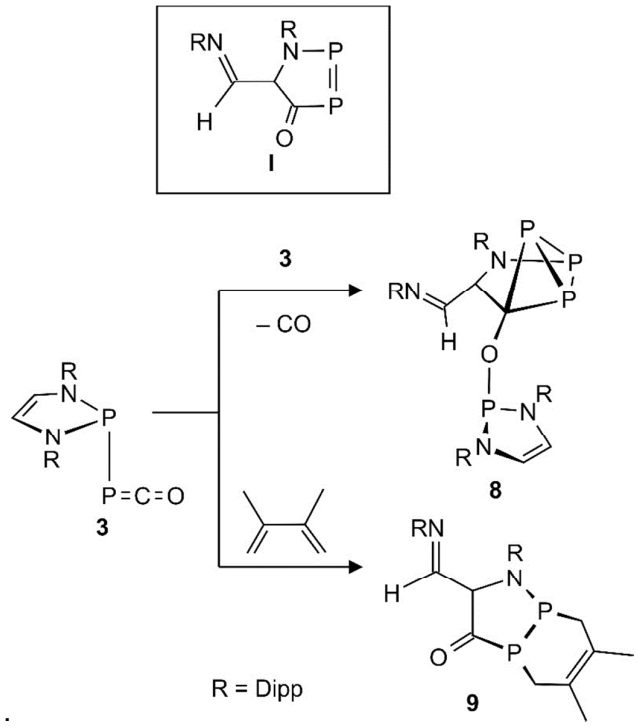


Figure 1. Molecular structure of **3** in the solid state (H atoms omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-P2 2.4414(5),

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).

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 exceeds significantly the distance in the sterically over-crowded diphosphane $[(TMS)_2CH]_2P\text{-}P[CH(TMS)_2]_2$ (2.3 Å).[14] Only diazaphospholyl-phospholes which are best described as close diazaphospholenium cation-phospholide anion pairs have equally long or even slighter 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 Supporting information for details). This result is in accord with our previous findings which show that all $R_3E\text{-}P{=}C{=}O$ compounds with E = C – Pb are more stable than $R_3E\text{-}O\text{-}C{\equiv}P$.[10b] Reactions between **3** and Ph_3SnCl or Ph-Mg-Br proceed smoothly and give $Ph_3Sn(OCP)$ (**4**)[10b] or BrMg(OCP) (**6**) aside the 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 only detectable phosphorus containing product while the fate of the OCP part remains unclear.[16]

Under an inert atmosphere, solid **3** can be stored 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.



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

Species **8** was unequivocally identified as a compound with 1,2,3–triphosphabicyclobutane substructure by X-ray diffraction with a single-crystal which was obtained from a 4:1 acetonitrile/ diethylether solution. The structure is shown in Figure 2. The P–P distances within the P_3 unit in this new tricyclic compound are about 2.2 Å which are 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 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 from **I** and a second equivalent of "P-PCO" **3** under loss of one CO molecule.

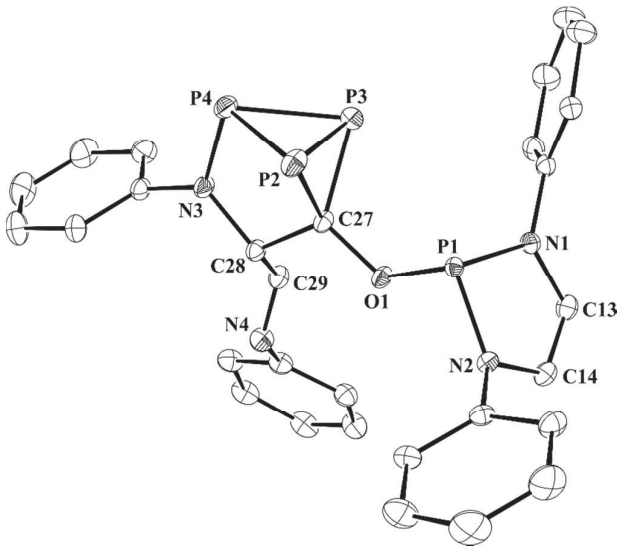


Figure 2. Molecular structure of **8** in the solid state (only the arene groups at the nitrogen atoms are shown while the *i*Pr groups and H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-N1 1.7061(9), N1-C13 1.4030(15), C13-C14 1.3371(16), 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).

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 trapping agent for **I**. Frequently, 2,3-DMB has been successfully used 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 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 Figure 3.[20]

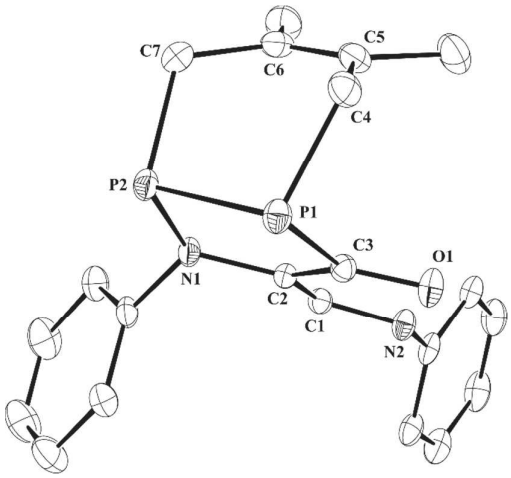
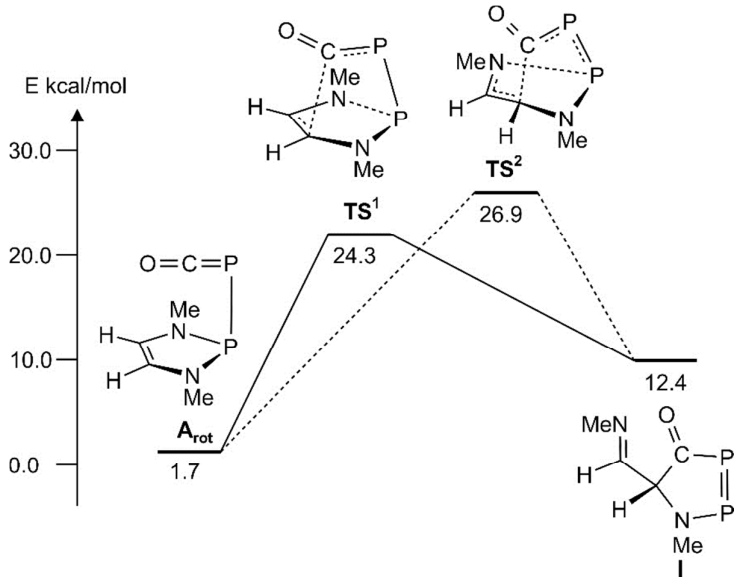


Figure 3. Molecular structure of **9** in the solid state (only the arene groups at the nitrogen atoms are shown while the *i*Pr groups and H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-P2 2.2064(6), P1-C3 1.8765(16), C3-O1 1.2383(19), 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).

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



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

Furthermore, the further rearrangement of **I** to the tricyclic triphoshane **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.

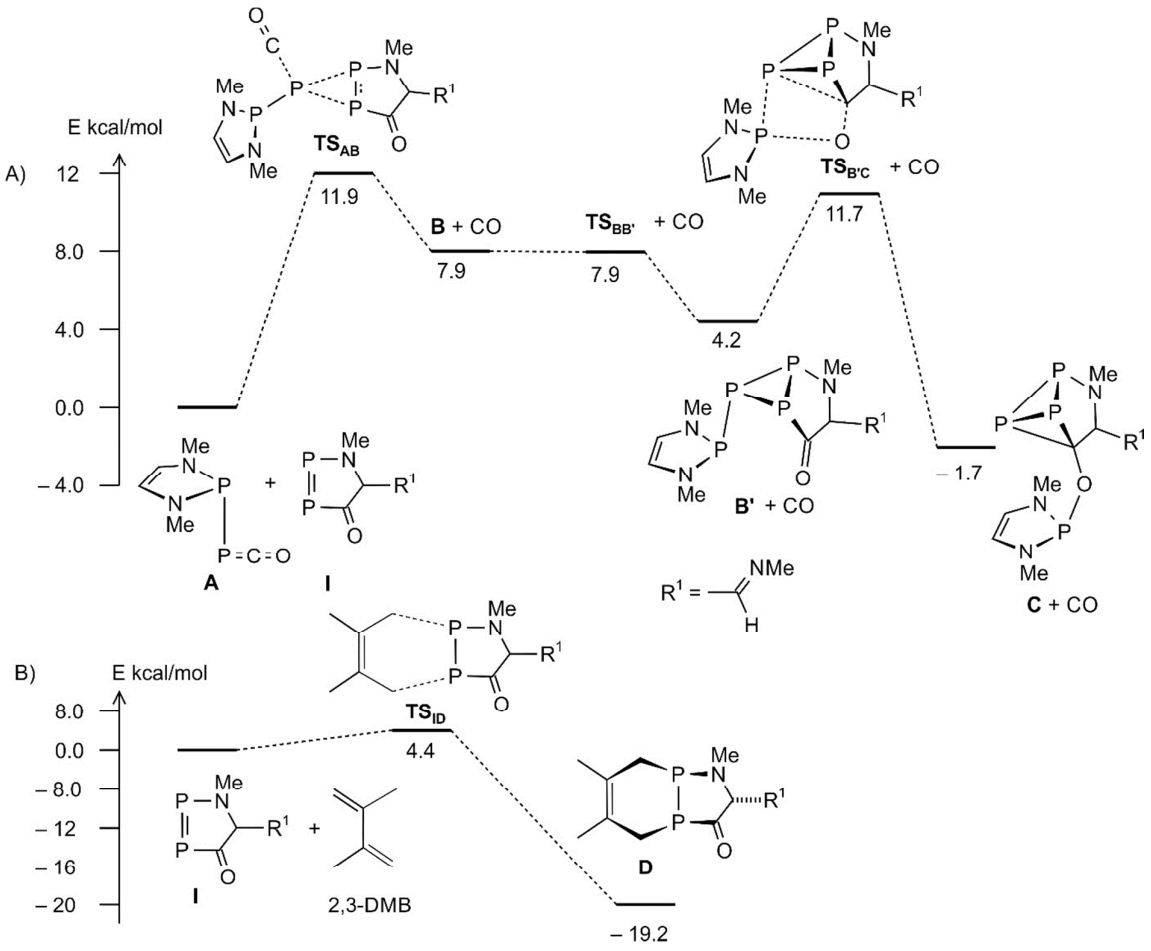
The ground state rotamer **A** with an OCP group turned outwards with respect to the PN_2C_2 heterocycle will not lead to the product **I**. Hence, we inspected its rotamer $\mathbf{A_{rot}}$ which is only 1 – 2 kcal mol^{-1} higher in energy.

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 **TS²** (26.9 kcal mol^{-1}), the preferred transformation from $\mathbf{A_{rot}}$ to **I** occurs through **TS¹**. However, note that the energy difference between both transition states is method-dependent. In particular, they turn out to be of equal height in the 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 Supporting Information).

In **TS¹**, 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 **TS²** 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 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 along the MERP from **A** to **C**. Note that the activated complex $\mathbf{TS_{AB}}$ can be viewed as a complex of a 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 an H_2 and CO molecule.[8b] In the final

step the diazaphosphol moiety migrates from the *exo*-cyclic phosphorus atom to the C=O group under 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 $\mathbf{TS_{B'C}}$.

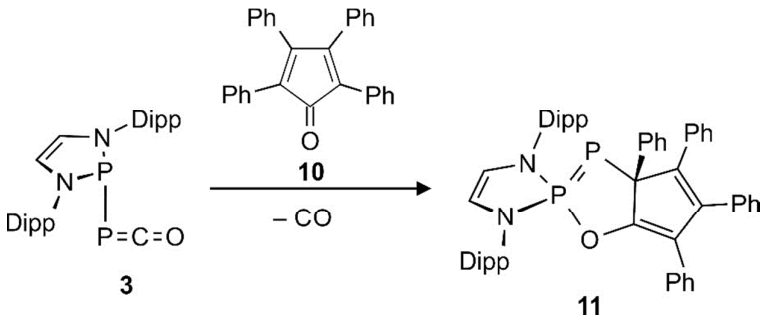


Scheme 5. A) BP86/ def2-TZVP transition path from **A** and **I** to **C** and CO. B) BP86/ def2-TZVP transition path for the Diels-Alder reaction between **I** and 2,3-DMB to **D**. The structure of **B** is very similar to **B'** and not shown here (for details see Figure S28 in the ESI).

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 remarkable low energy (4.4 kcal mol^{-1}) was found for this Diels-Alder type [2+4] reaction which proceeds with 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 the triphosphabicyclobutane **8** is obtained as major product even when the reaction is performed with 2,3-DMB in large excess as 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** $\rightarrow$ **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 Scheme 4 and 5 shows that the reaction evolves slowly to the product **E** which is formed irreversibly because of the loss of the 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 the triphosphabicyclobutane **8**.

To a certain extent the reaction between the 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 the pentaphenylcyclopentadienone (tetracyclone) **10** was investigated (Scheme 6).



Scheme 6

After 2 d at room temperature, a new compound **11** was isolated as yellow powder in about 28 % isolated yield. Again the triphosphabicyclobutane **8** is obtained as further 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 δ = 115 and δ = –143 ppm do not allow to conclude on a structure. This was elucidated by X-ray diffraction studies with single crystals and the result is shown in Figure 4. Compound **11** is a cyclic derivative of a 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.

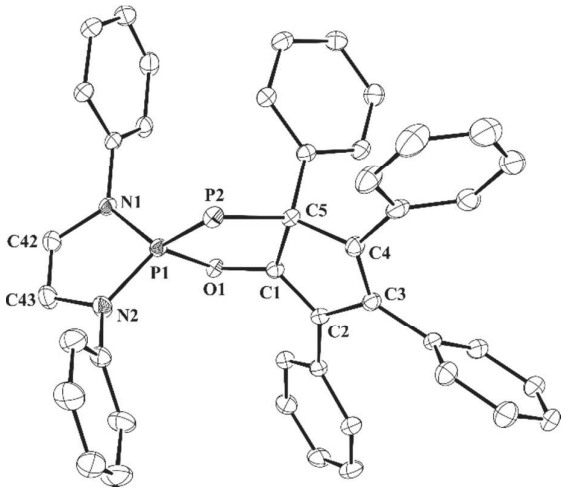


Figure 4. Molecular structure of **11** in the solid state (only the arene groups at the nitrogen atoms are shown while the *i*Pr groups and H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-P2 2.0688(8), P1-O1 1.6569(16), O1-C1 1.389(3), 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).

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

Concluding remarks: The reaction between Na(OCP) (**1**) and the unsaturated P-chlorophosphane **2** yields **3** as stable compound in high yield. This compound was isolated and characterized as a phosphanyl phosphaketene with an unusual 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 intermediate in the reaction reported here is highly unlikely[21] and these remain 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. The 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 were 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. The 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 obtained on a Perkin-Elmer-Spectrum ATR 2000 FT-IR-Raman spectrometer with 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 supporting information. Satisfying elemental analyses have not be obtained 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, NC*H*), 3.25 (m, 4 H, C*H*Me_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,

*PC*O, J_{PC} = 22.6 Hz, *P*P*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 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, NC*H*), 3.59 (m, 2 H, C*H*Me_2), 3.22 (m, 2 H, C*H*Me_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 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 supporting information), 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_2CH_2); $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO, 75MHz): δ = 169.2 (d, J_{PC} = 60 Hz), 67.0 (OCH_2), 25.1 (OCH_2CH_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.). ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.48 (d, J_{PH}= 642 Hz, 1 H, P*H*), 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, NC*H*), 5.39 (S, 1 H, NC*H*), 3.77 (m, 2 H, C*H*Me_2), 2.91 (m, 2 H, C*H*Me_2), 1.20 (d, 6 H, CH_3), 0.86 (m, 12 H, CH_3), 0.77 (d, 6 H, CH_3); ^{13}C{^{1}H} 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{^{1}H} 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 which were filtered off, washed with acetonitrile, and dried *in vacuo*. (81 mg, 0.09 mmol, 71 % yield). M. P. = 189.2 °C. ^{1}H 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, NC*H*), 4.45 (s, 1 H, NC*H*), 3.72 (m, 1 H, C*H*Me_2), 3.14 (m, 3 H, C*H*Me_2), 2.76 (m, 2 H, C*H*Me_2), 1.30 (d, 3 H, CH_3), 0.92 (br, 42 H, CH_3) , 0.64 (d, 3 H, CH_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}PNMR of the reaction mixture, the 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 × 1cm 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* isomer 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 PCH_2), 2.40 (m, 1 H, C*H*Me_2), 1.76 (m, 1 H, PCH_2), 1.59 (m, 9 H, CH_2CH_3), 1.48 (m, 2 H, PCH'_2), 1.24 (d, *J* = 6 Hz, 3 H, CH_3), 1.25 (d, *J* = 6 Hz, 1.5 H, CH'_3), 1.11 (d, *J* = 6 Hz, 1.5 H, CH'_3), 1.07 (d, *J* = 6 Hz, 3 H, CH_3), 0.96 (d, *J* = 6 Hz, 3 H, CH_3), 0.78 (m, 24 H, CH_3 and CH'_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 the products contains **8** and **11** in a ratio around 3:2 according to the ^{31}PNMR 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 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, CH_3), 1.04 (d, 3 H, CH_3), 0.89 (m, 6 H, CH_3), 0.78 (d, 3 H, CH_3), 0.70 (d, 3 H, CH_3), 0.37 (d, 3 H, CH_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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Keywords: phosphaketene • sodium phosphaethynolate • phosphorus heterocycles • cycloaddition • phosphinidene

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20. The isolated 2+4 Diels-Alder adduct is actually the mixture of 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 supporting information).

21. A free phosphanyl phospinidene as intermediate is very unlikely. The computed dissociation energy **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).

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A phosphanyl phosphaketene undergoes a hetero-Cope-rearrangement to a highly reactive heterocyclic diphosphene which can be trapped.