Organophosphorus Compounds, 138[+]

3,5-Dimesityl-1,2,4-oxadiphosphole – Synthesis and Reactivity of a Novel Heterocycle

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The first synthesis of a 1,2,4-oxadiphosphole **6** has been achieved by vacuum thermolysis of mesitylphosphaalkene **5**. The novel heterocycle **6** exhibits an enormous potential for cycloaddition reactions, which predominantly proceed selectively at low temperatures. Compound **6** undergoes addition with two equivalents of phosphaalkynes **10** by a [4+2] cycloaddition/homo Diels–Alder reaction sequence to form novel oxatetraphosphadeltacyclenes **12** and **13**. Tetrachloro-*o*-benzoquinone (**14**) undergoes a selective [4+1] cycloaddition with **12** and **13** leading to the spirocyclic products **15** and **16** containing λ^5-phosphorus atoms. Treatment of the oxadiphosphole **6** with dimethyl acetylenedicarboxylate (**17**) provides the first access to a 1,2-oxaphosphole **18**, which is formed after an initial [4+2] cycloaddition followed by a retro Diels–Alder reaction. An unexpected reaction of **6** is observed with tri-*tert*-butylazete (**20**) furnishing a new polycyclic system (→ **21**).

Introduction

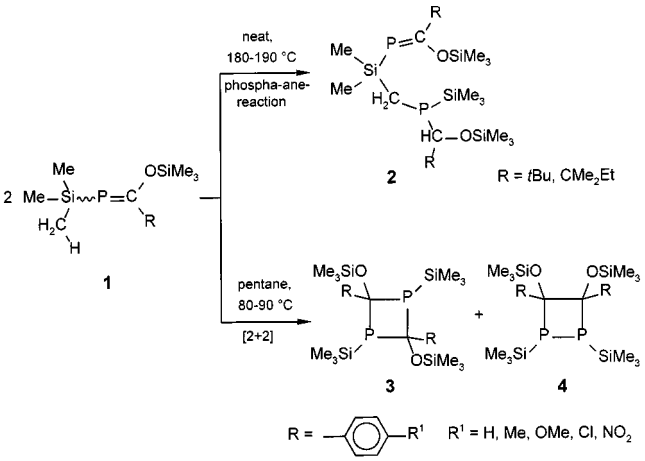
Thermolysis reactions of kinetically stabilized phosphaalkynes have been investigated thoroughly and in most cases lead to cyclotetramers.[2] In contrast, phosphaalkenes, which represent important building blocks in the chemistry of low-coordinated phosphorus compounds,[3][4] mostly undergo dimerization on heating. Kinetically stabilized P−C double bond systems such as **1** bearing tertiary alkyl groups undergo an unusual phospha-ane reaction to afford the dimers **2**.[5] If the phosphaalkenes **1** do not possess sufficient kinetic stabilization, i.e., when they carry merely aryl substituents, they undergo dimerization on heating to furnish 1,3-diphosphetanes **3** and 1,2-diphosphetanes **4**.[6]

We now report on the thermolysis behavior of mesitylphosphaalkene **5** which leads to a novel heterocyclic system with the 1,2,4-oxadiphosphole ring. In addition, the cycloaddition behavior of this new compound towards selected dienophiles is discussed.

Results and Discussion

Synthesis of 3,5-Dimesityl-1,2,4-oxadiphosphole (6)

Unexpectedly, thermolysis of mesitylphosphaalkene **5** at 225°C/10^{-3} mbar results in the formation of the 1,2,4-oxadiphosphole **6**. This procedure was originally performed for the purification of the phosphaalkene **5**. After recovery of unreacted starting material **5** (65%), pure **6** can be isolated by a sequence of bulb-to-bulb distillation and recrystallization processes as colorless crystals in 20% yield.



Scheme 1. Thermal behaviour of phosphaalkenes

The composition of the product **6** was determined by elemental analysis and mass-spectrometric data which clearly indicated that mesitylphosphaalkene **5** had undergone a cyclocondensation with formal elimination of four trimethylsilyl groups and one oxygen atom. The NMR spectra of **6** unambiguously proved its constitution as a 1,2,4-oxadiphosphole and are discussed in detail below.[7]

The ^{31}P-NMR spectrum shows an AB system, both signals being in the region typical for phosphaalkenes.[8] Due to the oxygen substitution, the signal of the $\lambda^3\sigma^2$-phosphorus atom P-2 is significantly shifted downfield (δ = 306.4). The signal of the second phosphorus nucleus P-4 is detected at δ = 145.4. The latter is dramatically shifted upfield when compared with those of the 1,2,4-thia- (δ = 248.1−251.2)[9] or 1,2,4-selenadiphospholes (δ = 260.4).[10]

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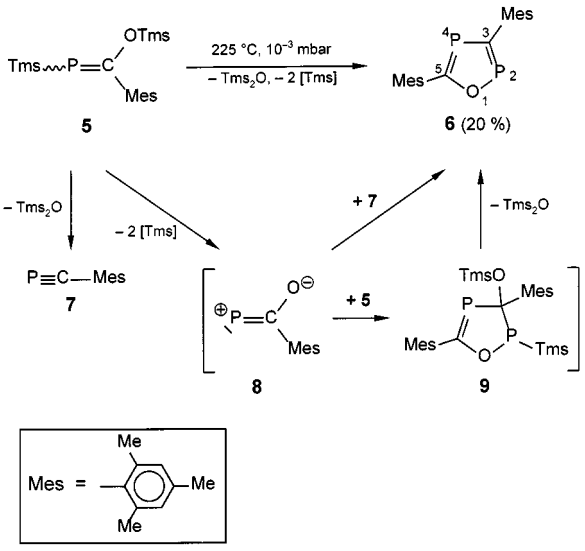


Scheme 2. Thermolysis of phosphaalkene **5**

Furthermore, the $^2J_{P\text{-}2,P\text{-}4}$ coupling constant of 17.5 Hz in the 1,2,4-oxadiphosphole **6** is rather small.[9,10]

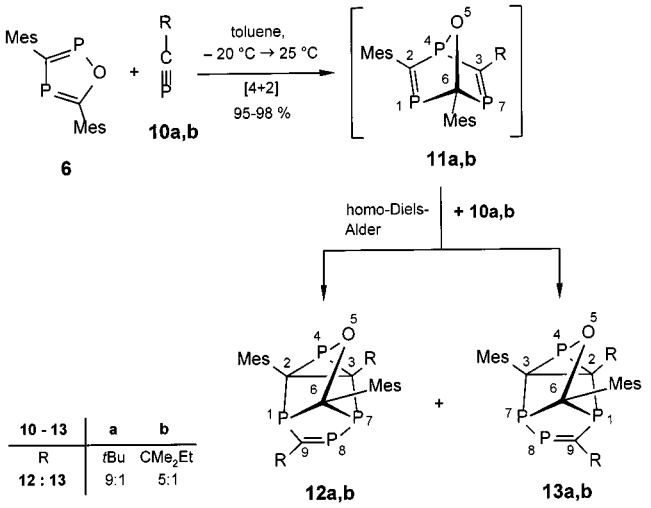
The ^{1}H-NMR spectral data merely demonstrate the presence of two different mesityl substituents in the heterocycle **6**, while the ^{13}C-NMR spectrum provides final proof for the constitution of the product. A total of 14 signals is detected, four of them arise from methyl groups and eight from sp^2-carbon atoms of the aromatic substituents. The remaining two signals are of high diagnostic value: On account of the C,P coupling pattern the double doublet at δ = 208.0 is assigned to the oxygen-substituted C-5, showing a typically large $^1J_{C,P}$ coupling to P-4 (56.0 Hz) and a typically small $^2J_{C,P}$ coupling to P-2 (5.1 Hz).[9–11] The signal of the second ring carbon atom C-3 is observed at δ = 191.9 as a triplet with two identical $^1J_{C,P}$ coupling constants of 64.0 Hz, indicating the direct neighborhood of two phosphorus atoms.[9–11]

Considerations on the reaction mechanism lead to the following reasonable proposals: An initial cleavage of hexamethyldisiloxane to furnish mesitylphosphaacetylene (**7**; unequivocally observed by ^{31}P-NMR spectroscopy) is very likely.[12] Alternatively, the loss of two silyl groups leads to an acylphosphinidene intermediate, which can be drawn as the 1,3-dipole structure **8** indicating its potential for [3+2] cycloadditions. This decisive intermediate **8** can now undergo addition with either the phosphaalkene **5** (→ **9**), or the in situ generated mesitylphosphaacetylene (**7**) to furnish directly the 1,2,4-oxadiphosphole **6**. The formation of the final product **6** from the intermediate **9** is also easy to rationalize in terms of a thermally induced elimination of hexamethyldisiloxane. It should be mentioned that thermolysis of **5** in a pressure tube (210°C) proceeds very unselectively and the heterocycle **6** is only obtained in traces. This result clearly demonstrates that the vacuum is essential for the elimination of the volatile cleavage products (hexamethyldisiloxane).

A combination of the X-ray crystallographic data and ab initio calculations[13] clearly indicates that the title compound **6** exhibits a planar aromatic structure. However, if we compare the relative NICS aromaticity[14] of **6** (NICS = −11.01)[13] with the corresponding data for the 1,2,4-thiadiphosphole (NICS = −12.43)[13] and the 1,2,4-selenadiphosphole (NICS = −12.05)[13] we find that the oxygen-containing heterocycle **6** shows a significantly lower aromaticity. Thus, the more localized 1,3-diene system in the 1,2,4-oxadiphosphole should enable us to investigate its cycloaddition behavior towards various dienophiles.

Cycloadditions of 3,5-Dimesityl-1,2,4-oxadiphosphole (6) with Phosphaalkynes 10

Phosphaalkynes are known to have an enormous potential for cycloaddition reactions.[15] For this reason we investigated the reactions of phosphaacetylenes **10** with the 1,2,4-oxadiphosphole **6**. Even at low temperatures, the addition of two equivalents of **10** furnishes the novel oxatetraphosphadeltacyclenes **12** and **13** which can be isolated by column chromatography as a mixture in very good yield.



Scheme 3. Cycloaddition of phosphaalkynes onto the oxadiphosphole **6**

A separation of the two regioisomers **12** and **13** has so far not been possible by chromatographic means. However, isolation of the major products **12a** and **12b** is possible by crystallization from non-polar solvents.

The addition of two equivalents of the phosphaalkynes **10** to the 1,2,4-oxadiphosphole **6** is immediately apparent from the ^{31}P-NMR spectra (showing four signals each) of the reaction products **12** and **13**. Their composition is further demonstrated by elemental analyses and EI- as well as EI-HR-MS data. The NMR spectra of the cage compounds **12** and **13** are in full agreement with the proposed constitutions and are discussed in detail below for the example of product **12a** (R = *t*Bu).

The ^{31}P-NMR spectrum contains four signals, of which the low-field double-doublet resonance at δ = 346.8 (P-8) clearly indicates the presence of a phosphaalkene subunit in **12a**.[8] The signal of P-8 shows the direct bonding to P-7

(δ = 90.4) by a large $^1J_{P,P}$ coupling constant of 309.3 Hz and is further split by a typical $^2J_{P,P}$ coupling[11] of 16.3 Hz to P-1 (δ = 81.8). Both chemical shifts of P-1 and P-7 are in good harmony with those of $\lambda^3\sigma^3$-phosphorus atoms in comparable compounds.[16] The P-1 signal has a 1:2:2:2:1 multiplet structure and therefore can best be explained as two overlapping triplets due to $^2J_{P,P}$ couplings to P-4 and P-8 (16.3 Hz each) as well as to P-7 (32.6 Hz). The signal of P-4 is detected at δ = −2.3, an unusually low-field position for phosphirane rings.[17] However, on comparison with other phosphorus−carbon cage compounds, it is apparent that the incorporation of phosphorus atoms into other, larger rings results in a low-field shift.[18] Moreover, the vicinity of the strongly electronegative oxygen atom to P-4 should also have a similarly directed effect.

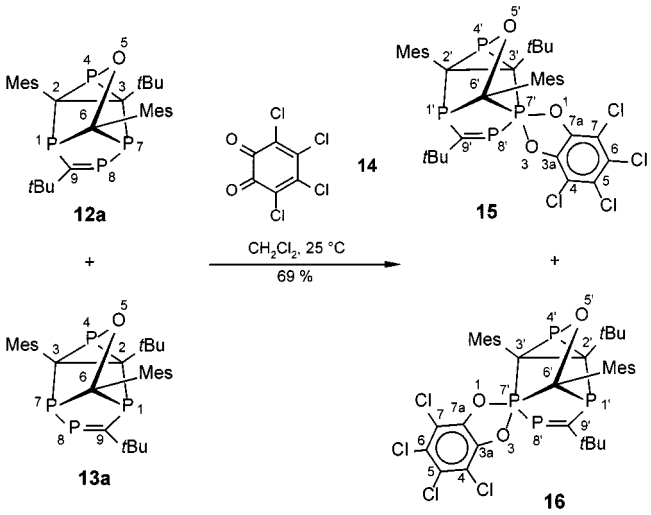
The comparison of the ^{31}P-NMR shifts and coupling patterns of the two regioisomers **12** and **13** with *tert*-butyl (**a**) or 1,1-dimethylpropyl substitution (**b**) show a strong analogy and thus proves the presence of the same cage structure.

The ^{1}H-NMR spectrum of **12a** demonstrates the presence of two chemically different *tert*-butyl and mesityl substituents but does not furnish any further diagnostic information.

An analysis of the ^{13}C-NMR spectral data clearly proves the tetracyclic constitution of **12a**, showing four characteristic signals for the cage carbon atoms: The two carbon atoms C-2 and C-3 of the three-membered ring both give overlapping multiplet signals at δ = 62.3 and can therefore not be assigned accurately. Due to oxygen substitution, the signal of the third sp^3-carbon atom C-6 is detected at low field (δ = 114.2) as a double double doublet. The three $J_{C,P}$ coupling constants have different but relatively small values (32.2, 11.3, 5.0 Hz), two of them being $^1J_{C,P}$ couplings.[19] Relatively large $^1J_{C,P}$ coupling constants[11] (79.7, 57.7 Hz) are recorded for the sp^2-carbon atom C-9 signal at δ = 244.3.

Although no intermediates can be detected by ^{31}P-NMR monitoring, a plausible mechanistic explanation for the formation of the oxatetraphosphadeltacyclenes **12** and **13** involves an initial regiospecific [4+2] cycloaddition of the phosphaalkyne **10** to the oxadiphosphole **6**, furnishing the unsymmetrical oxatriphosphanorbornadiene **11**. The subsequent homo Diels−Alder reaction with a further equivalent of **10** proceeds specifically with P−P attack. However, both possible orientations for the phosphaalkynes **10** are observed and thus two regioisomers (**12** and **13**) are obtained. Interestingly, the cage compounds **12** are formed preferably (i.e., R = *t*Bu: **12a**/**13a** = 9:1) in spite of the only minor differences in the intermediate **11**.

In order to finally prove the cage constitution of the products **12** and **13**, we attempted to synthesize a crystalline derivative for X-ray diffraction analysis. Conjugated systems such as *ortho*-benzoquinones are known to undergo both [4+2] cycloaddition reactions with phosphaalkenes[20] and [4+1] cycloaddition reactions with the lone-electron pairs of phosphanes.[21] The reaction of the isomeric mixture of **12a** and **13a** with one equivalent of tetrachloro-*ortho*-benzoquinone (**14**) leads specifically to the new spirocyclic products **15** and **16** isolated in 69% yield after chromatographic work-up.



Scheme 4. Reaction of the isomers **12a/13a** with the quinone **14**

Surprisingly, no [4+2] cycloaddition reaction at the P-9/C-8 double bond is observed even in the presence of an excess of the *ortho*-benzoquinone **14**. The analytical and spectroscopic data are discussed in the following for the major product **15**, which is isolated by crystallization from appropriate solvents.

The 1:1 composition of the cage compound **15** from **12a** and the *ortho*-benzoquinone **14** is clearly apparent from the combination of elemental analysis, EI-MS, and EI-HR-MS data. In analogy to the starting compound **12a**, the ^{31}P-NMR spectrum shows four different signals which arise from one and the same molecule. When compared to **12a**, all four resonances in **15** are shifted upfield. The signal at δ = 298.4 (P-8′) convincingly demonstrates that the phosphaalkene moiety has remained unchanged after the *ortho*-benzoquinone addition. The remaining signals as well as the coupling patterns are in good agreement with those of the cage compound **12a**. An exact assignment of the phosphorus signals to the respective atoms and the position of the new dioxaphosphole ring is not possible. This information has been obtained by an X-ray crystallographic analysis of **15**.

The structure of the spirocyclic compound **15** (Figure 1) clearly illustrates that attack of the *ortho*-benzoquinone has occurred at P-7. Moreover, a combination of the X-ray results and the unchanged spin system in the ^{31}P-NMR spectrum of **15** (compared to **12a**) unambiguously proves the structure of the tetracyclic skeleton in **12a** and **15**. The X-ray data also reveal that the major isomer in the reaction of the system **6**/**10** resembles the product **12**. Figure 2 illustrates the tetracyclic skeleton and the catechol fragment without substituents. The phosphaalkene moiety exhibits the typical geometry with a P-8′−C-9′ bond length of 1.657(4) [ref.[22]: 1.670 Å] and a planar environment around C-9′ (Σ = 359.7°). The P−P bond length [2.2391(14) Å] is slightly longer than the mean literature value of 2.214 Å.[23]

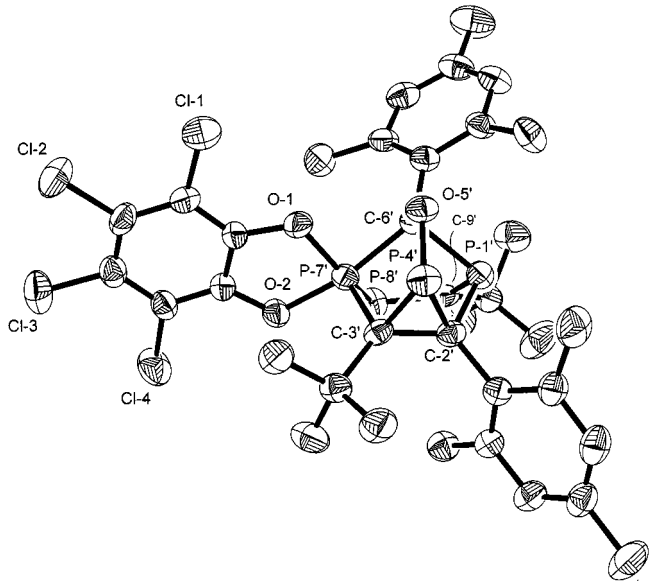


Figure 1. Molecular structure of **15** (back view); selected bond lengths [Å] and angles [°]; H atoms omitted for clarity; displacement ellipsoids at the 50% probability: P-8′−C-9′ 1.657(4), P-7′−P-8′ 2.2391(14), C-2′−C-3′ 1.542(4), P-4′−O-5′ 1.646(3), C-6′−O-5′ 1.453(4), P-1′−C-2′ 1.864(4), P-1′−C-9′ 1.839(4), P-1′−C-6′ 1.898(4), P-7′−C-6′ 1.925(3), P-7′−C-3′ 1.849(4), P-4′−C-2′ 1.888(3), P-4′−C-3′ 1.838(4), P-7′−O-1 1.719(2), P-7′−O-2 1.787(2); P-8′−C-9′−P-1′ 120.5(2), C-9′−P-8′−P-7′ 96.57(13), P-1′−C-6′−P-7′ 99.58(16), C-6′−O-5′−P-4′ 110.7(2), C-3′−P-4′−C-2′ 48.85(14), C-2′−C-3′−P-4′ 67.3(2), C-3′−C-2′−P-4′ 63.88(17), O-1−P-7′−O-2 86.23(11), C-3′−P-7′−C-6′ 90.13(16), C-6′−P-7′−P-8′ 94.14(12), O-1−P-7′−C-6′ 88.60(13), P-8′−P-7′−C-3′ 111.56(11), O-1−P-7′−C-3′ 105.59(14), O-1−P-7′−P-8′ 142.72(10), O-3−P-7′−C-6′ 165.30(15)

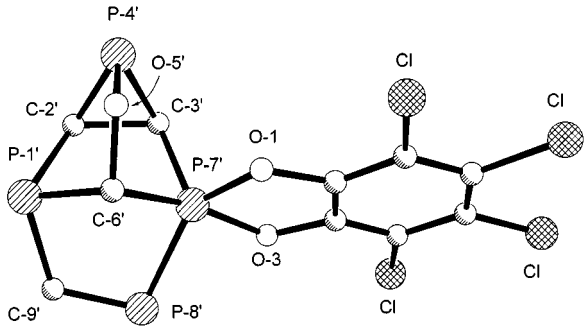
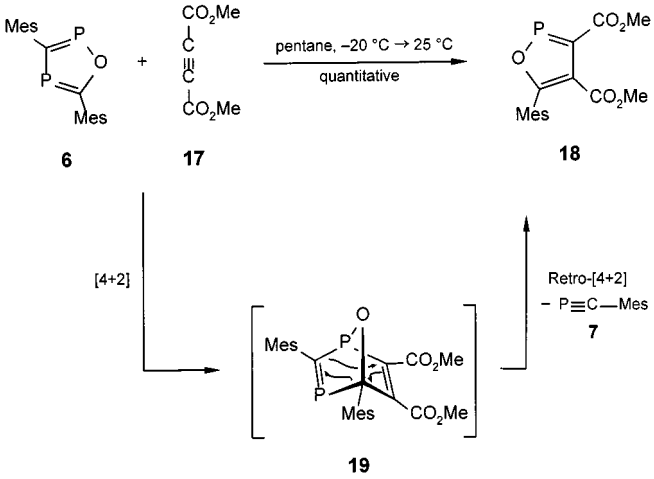


Figure 2. Cage skeleton of **15** without substituents (front view)

The C-2′−C-3′ bond length [1.542(4) Å] is typical for phosphiranes.[17] The broad range of P−C single-bond lengths [1.837(4)−1.917(4) Å] is a common consequence of distortion in strained cage compounds. The environment at P-7′ is that of a distorted trigonal bipyramid with the axial P-7′−O-2 bond [1.787(2) Å] being significantly longer than the equatorial P-7′−O-1 bond [1.719(2) Å].[24]

Cycloaddition of 3,5-Dimesityl-1,2,4-oxadiphosphole (6) with Dimethyl Acetylenedicarboxylate (17)

With the successful reaction of the 1,2,4-oxadiphosphole **6** with kinetically stabilized phosphaalkynes we were encouraged to transfer the reaction principle to alkynes.



Scheme 5. Cycloadditions of the alkyne **17** onto the oxadiphosphole **6**

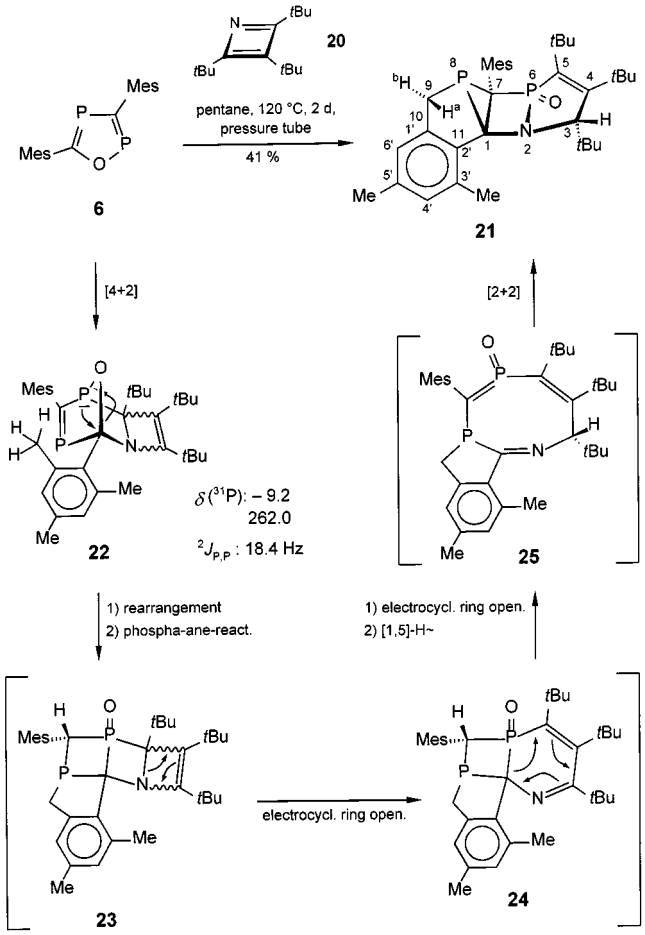
When dimethyl acetylenedicarboxylate (**17**) is allowed to react with the heterocycle **6**, low-temperature ^{31}P-NMR monitoring reveals that a reaction occurs at −20°C. Both the novel 1,2-oxaphosphole **18** and mesitylphosphaacetylene (**7**) are formed concomitantly. Unfortunately, the novel heterocycle **18** is too labile to be isolated by column chromatography or distillation. However, the pure phosphaalkyne **7** is isolated in 90% yield.[12]

The constitution of the 1,2-oxaphosphole **18** is clearly apparent from both the ^{31}P-NMR data and from mechanistic considerations. The singlet resonance at δ = 303.1 of **17** demonstrates the close analogy to **6** and is indicative of an oxygen-substituted $\lambda^3\sigma^2$-phosphorus atom. A 1,3-heteroatom distribution can be excluded by comparison with the data of a 1,3-oxaphosphole (δ = 113.1[25]). From mechanistic points of view, an initial [4+2] cycloaddition to the bicyclic intermediate **19** is most likely to occur. In contrast to the reaction with phosphaalkynes (see above), no subsequent homo Diels−Alder reaction takes place. Instead, a retro Diels−Alder reaction furnishes **7** and the 1,2-oxaphosphole **18**.[26]

Reaction of 3,5-Dimesityl-1,2,4-oxadiphosphole (6) with Tri-*tert*-butylazete (20)

In the previously discussed reactions the used (hetero)alkynes can only act as dienophiles. In contrast to this, cyclobutadienes or azacyclobutadienes are known to function both as dienes[27] and as dienophiles.[28] For this reason we also investigated the reaction of 1,2,4-oxadiphosphole **6** with tri-*tert*-butylazete **20**. Surprisingly, no reaction was observed at room temperature. Use of drastic reaction conditions (120°C, 2 days), however, resulted in the unexpected formation of the polycyclic compound **21**, which was isolated by column chromatography in 40% yield.

If the reaction is stopped after 36 hours reaction time, the not isolable primary product **22** can be detected by ^{31}P-NMR spectroscopy. The signal for the phosphaalkene phosphorus atom in compound **22** is observed at character-



Scheme 6. Reaction of the azete **20** with the oxadiphosphole **6**

istically low field, δ = 262.0[8] with a typical $^2J_{P,P}$ coupling of 18.4 Hz[11] to the oxygen-bonded phosphorus nucleus (δ = −9.2).

The formation of the isolated product **21** from one equivalent each of **6** and **20** is apparent from the EI-MS data [*m*/*z*(M^+): 561]. In the IR spectrum a strong valency vibrational band at $\tilde{\nu}$ = 1229 cm^{-1} demonstrates the existence of a P=O function. The ^{31}P-NMR spectral data is consistent with a phosphane oxide phosphorus atom (P-6) giving a signal at δ = 77.3[29] and a phosphirane phosphorus atom (P-8) giving a typical high-field signal at δ = −118.2.[17] The IR and ^{31}P-NMR spectra are indicative for a complex mechanism during the formation of **21** which includes rearrangement processes. Thus, the spectral data can only be assigned in combination with an X-ray crystallographic analysis (see below).

^{1}H-NMR data show, apart from the characteristic signals of the substituents, three significant signals for hydrogen atoms directly bonded at the polycyclic skeleton. The signal of 9a-H appears as a doublet of doublets at δ = 2.31 and shows a typical $^2J_{H,P}$ coupling of 22.6 Hz to the lone-electron pair of P-8, indicating a *cis* orientation of the respective atoms.[11] The second splitting of the 9a-H signal arises from a geminal coupling (18.1 Hz) to 9b-H, the signal for which is observed at δ = 1.93. The third skeletal proton 3-H gives rise to a doublet at δ = 4.01 with a large $^3J_{H,P}$ coupling constant of 29.6 Hz to P-6.

The ^{13}C-NMR data are in full agreement with the constitution of the polycyclic compound **21**. The three chemically different *tert*-butyl groups, the mesityl substituent at C-7, and the 3′,5′-dimethylbenzo unit give rise to typical signals. The remaining six signals[30] stem from the skeletal carbon atoms and are characteristic: The doublet resonance at lowest field (δ = 169.0) is unequivocally assigned to C-5 and shows a $^1J_{C,P}$ coupling of 26.7 Hz to P-6. The ^{13}C-NMR signal of the nitrogen-substituted sp^3-carbon atoms C-1 (δ = 83.0) and C-3 (δ = 75.3) are both split into double doublets. The assignment to the methine carbon atom C-3 is based on the typical $^1J_{C,H}$ coupling in the proton-coupled spectrum. The signal of phosphirane carbon atom C-7 is detected at higher field (δ = 53.5) and is also split into a doublet of doublets due to large $^1J_{C,P}$ couplings of 83.1 Hz and 49.2 Hz. The newly formed methylene carbon atom C-9 shows a double doublet signal at δ = 26.5 and can be unambiguously recognized by analysis of the DEPT-NMR spectrum.

As mentioned above, elucidation of the constitution of the polycyclic compound **21** was only possible by an X-ray diffraction analysis. At first sight, **21** cannot be easily divided into the starting compounds **6** and **20**. However, the original oxadiphosphole (O-1−P-6−C-7−P-8−C-1) and the azete (N-2−C-3−C-4−C-5) parts can be identified (Figure 4). The oxygen atom is now found in the phosphane oxide moiety with a P-6−O-1 interatomic separation of 1.471(2) Å,[24] typical for a double bond. All other bond lengths and angles in **21** show typical values.

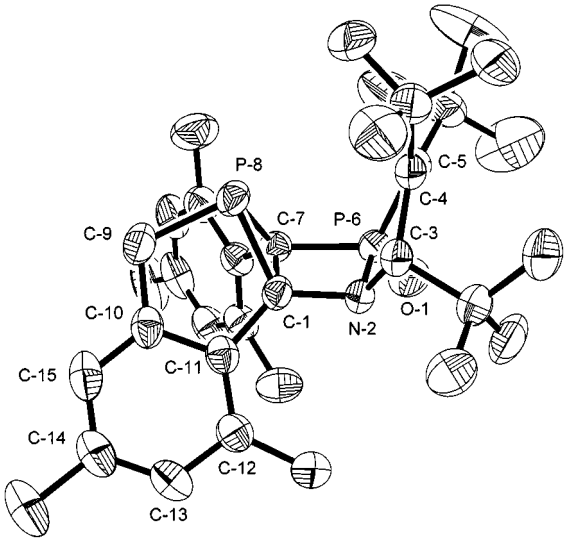


Figure 3. Molecular structure of **21**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity; displacement ellipsoids at the 50% probability: C-5−C-4 1.356(3), C-4−C-3 1.558(3), C-1−C-7 1.569(3), P-8−C-1 1.865(3), P-8−C-7 1.877(2), P-8−C-9 1.850(3), P-6−C-7 1.839(2), P-6−C-5 1.822(2), P-6−O-1 1.471(2), P-6−N-2 1.693(2), N-2−C-1 1.484(3), N-2−C-3 1.483(3); C-1−P-8−C-7 49.57(10), C-7−C-1−P-8 65.60(12), C-1−C-7−P-8 64.83(12), N-2−P-6−C-5 82.50(10), C-1−N-2−P-6 93.01(13), C-1−C-7−P-6 84.92(13), N-2−C-1−C-7 99.6(2), C-5−P-6−C-7 114.76(10), C-3−N-2−P-6 109.51(14), N-2−C-3−C-4 108.0(2), C-5−C-4−C-3 113.3(2), C-4−C-5−P-6 115.6(2)

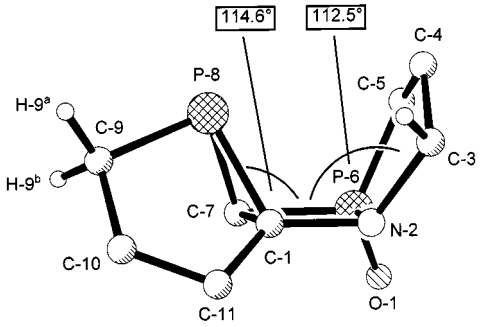


Figure 4. Cage skeleton of **21** without substituents showing interplanar angles

The polycyclic skeleton of the new compound **21** can be formally divided into four parts: (1) a benzo-condensed dihydrophosphole unit (C-1−P-8−C-9−C-10−C-11); (2) a phosphirane unit with typical geometry;[17] (3) the central, planar λ^5-azaphosphetidine fragment; and (4) the five-membered ring N-2−C-3−C-4−C-5−P-6. Figure 4 shows the boat-type arrangement of the rings (2), (3), and (4) and illustrates the interplanar angles of these fragments relative to each other.

A reasonable mechanistic interpretation for the formation of the novel product **21** involves an initial [4+2] cycloaddition of the respective heterocyclic species **6** and **20** to the observed primary product **22** (see above). This reaction does not occur below 120°C indicating that the steric shielding by three *tert*-butyl groups in **20** prevents an easy attack on compound **6**. At this temperature, the tricyclic intermediate **22** undergoes rearrangement to the final product **21**. Even when no intermediates can be observed by NMR monitoring the following rearrangements are well feasible: An intramolecular redox reaction and addition of a C−H single bond to the P−C double bond (phospha-ane reaction[5]) leads to **23** containing a phosphane oxide moiety. A subsequent electrocyclic ring opening furnishes the intermediate **24**, which itself is converted into the eight-membered ring intermediate **25** by a further electrocyclic ring opening and [1,5]-proton shift. From **25** it is obvious that a final [2+2] cycloaddition of the P−C double bond to the imine moiety will give rise to the polycyclic product **21**, which is thermodynamically favored: It does not contain any P−C or C−N multiple bond and bears a stable P=O function.

Conclusion

The novel heterocyclic compound 3,5-dimesityl-1,2,4-oxadiphosphole (**6**) exhibits an enormous potential for various cycloaddition reactions. This is very likely due to a reduced aromaticity when compared to the thia or selena analogues. In all reactions so far examined, we have found that **6** acts as a diene. The results of our investigations provide an access to the field of cycloaddition chemistry of 1,2,4-heterodiphospholes which we are currently investigating further and expect more fascinating results.

Experimental Section

General Remarks: All reactions were carried out under argon (purity > 99.998%) in a previously baked-out and evacuated apparatus (Schlenk techniques). The solvents were dried by standard procedures (*n*-pentane: Na, diethyl ether and THF: Na/K alloy), distilled, and stored under argon prior to use. − Melting points: Mettler FP 61 (heating rate: 2°C/min). − FT-IR spectra: Perkin-Elmer infrared-spectrometer 16PC. − Mass spectra: Finnigan MAT 90 spectrometer. − NMR spectra: Bruker AMX 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz; ^{31}P: 162 MHz) and Bruker AC 200 (^{13}C: 50 MHz; ^{31}P: 81 MHz) spectrometers, solvent as internal standard (^{1}H and ^{13}C); the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. Compounds **5**,[12] **10a**,[31] **10b**,[32] and **20**[33] were prepared according to reported methods.

3,5-Dimesityl-1,2,4-oxadiphosphole (6): Phosphaalkene **5** (10.00 g, 30.81 mmol) was distilled at 225°C/10^{-3} mbar in a Kugelrohr apparatus for 1 h whereupon 6.50 g (20.10 mmol, 65%) of **5** were recovered. The orange-brown residue was then subjected again to bulb-to-bulb distillation (250°C/10^{-3} mbar) which led to the product **6** together with dimesitylacetylene (proven by analytical data[34]). Fractional crystallization from pentane/diethyl ether (5:1) gave pure **6** (1.05 g, 20% yield, colorless needles). − IR (pentane, cm^{-1}): $\tilde{\nu}$ = 1724 (w), 1700 (w), 1652 (w), 1608 (s), 1568 (m), 1438 (s), 1372 (m), 1260 (m), 1144 (s), 992 (s), 868 (vs), 780 (s), 718 (s), 652 (m). − ^{31}P NMR (C_6D_6): δ = 145.4 (d, $^2J_{P,P}$ = 17.5 Hz, P-4), 306.4 (d, $^2J_{P,P}$ = 17.5 Hz, P-2). − ^{1}H NMR (C_6D_6): δ = 2.10 (s, 3 H, CH_3), 2.18-2.21 [br., 15 H, CH_3 (5 ×)], 6.75 (s, 2 H, *meta*-H), 6.85 (s, 2 H, *meta*-H). − ^{13}C NMR (C_6D_6): δ = 20.5, 20.9, 21.1 (each s, CH_3), 22.0 (d, $^4J_{C,P}$ = 1.7 Hz, *ortho*-CH_3), 128.4, 128.6 (each s, *meta*-CH), 132.4 (d, $^2J_{C,P}$ = 15.3 Hz, 5-*ipso*-*C*), 135.3 (dd, $^2J_{C,P}$ = 6.8 Hz and 3.4 Hz, 3-*ipso*-*C*), 136.9, 137.0 (each s, *ortho*-C), 137.1, 139.7 (each s, *para*-C), 191.9 (pseudo-t, $^1J_{C,P}$ = 64.0 Hz, C-3), 208.0 (dd, $^1J_{C,P}$ = 56.0 Hz, $^2J_{C,P}$ = 5.1 Hz, C-5). − MS (EI, 70 eV); *m*/*z* (%): 340 (65) [M$^+$], 162 (4) [MesCP$^+$], 147 (100) [MesCO$^+$], 119 (14) [Mes$^+$]. − HR MS (EI): calcd. 340.1146; found 340.1143. − $C_{20}H_{22}OP_2$ (340.3): calcd. C 70.6, H 6.5; found C 69.8, H 6.5.

General Procedure for the Synthesis of Oxatetraphosphadeltacyclenes 12 and 13: A solution of oxadiphosphole **6** in toluene (3 mL) was cooled to −20°C and two equivalents of the phosphaalkyne **10a,b** in toluene (3 mL) were added during 5 min with magnetic stirring. The previously colorless solution changed its color to yellow. The cooling bath was removed and stirring was continued for 30 min at 25°C. All volatile components were removed at 25°C/10^{-3} mbar and the remaining crude product was purified by column chromatography on silica gel (water-cooled column).

3,9-Di-*tert*-butyl-2,6-dimesityl-5,1,4,7,8-oxatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (12a) and 2,9-Di-*tert*-butyl-3,6-dimesityl-5,1,4,7,8-oxatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (13a): Amounts: 284 mg (0.83 mmol) of **6** and 166 mg (1.66 mmol) of **10a**. Column chromatography with pentane/ether (20:1) gave an isomeric mixture of **12a/13a** (ratio **12a/13a** = 9:1; by ^{1}H-NMR spectroscopy) (440 mg, 98% yield, yellow powder). Pure **12a** was obtained by crystallization from pentane/CH_2Cl_2 (5:1) at 0°C as yellow crystals (m.p. 158°C).

12a: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2960 (s), 2914 (m), 2857 (m), 1609 (w), 1469 (s), 1451 (s), 1393 (m, *t*Bu), 1373 (m), 1360 (s, *t*Bu), 1261 (s), 1218 (w), 1095 (s, br.), 1016 (s, br.), 910 (m), 886 (m), 844 (s), 801 (vs), 711 (m). − ^{31}P NMR (C_6D_6): δ = −2.3 (pseudo-t, $^2J_{P,P}$ = 16.3 Hz, P-4), 81.8 [dt, $^2J_{P,P}$ = 32.6 Hz, $^2J_{P,P}$ = 16.3 Hz (2 ×),

P-1], 90.4 (ddd, $^1J_{P,P}$ = 309.3 Hz, $^2J_{P,P}$ = 32.6 Hz and 16.3 Hz, P-7), 346.8 (dd, $^1J_{P,P}$ = 309.3 Hz, $^2J_{P,P}$ = 16.3 Hz, P-8). − ^{1}H NMR (C_6D_6): δ = 1.05 (d, $^4J_{H,P}$ = 1.7 Hz, 9 H, *t*Bu), 1.29 (s, 9 H, *t*Bu), 1.96 (s, 3 H, *para*-CH_3), 2.04 (s, 3 H, *para*-CH_3), 2.24 (s, 3 H, *ortho*-CH_3), 2.83 (br. s, 6 H, *ortho*-CH_3), 3.06 (s, 3 H, *ortho*-CH_3), 6.63 (br., 3 H, *meta*-H), 6.75 (s, 1 H, *meta*-H). − ^{13}C NMR (CD_2Cl_2): δ = 20.4, 20.6 (each s, CH_3), 24.3 (dd, $J_{C,P}$ = 22.8 Hz, $J_{C,P}$ = 3.3 Hz, CH_3), 25.6 (s, CH_3), 31.4 [dd, $^3J_{C,P}$ = 11.4 Hz and 9.6 Hz, C(*C*H_3)$_3$], 34.5 [pseudo-t, $^3J_{C,P}$ = 6.8 Hz, C(*C*H_3)$_3$], 35.2 [dd, $^2J_{C,P}$ = 16.7 Hz and 11.0 Hz, *C*$(CH_3)_3$], 45.2 [dd, $^2J_{C,P}$ = 22.9 Hz and 11.1 Hz, *C*$(CH_3)_3$], 62.3 (m, C-2 and C-3, overlapping), 114.2 (ddd, $J_{C,P}$ = 32.2 Hz, 11.3 Hz and 5.0 Hz, C-6), 129.5, 130.4, 131.3, 135.2 , 137.1, 137.2, 138.9, 139.2 (each s, aryl-C), 244.3 (dd, $^1J_{C,P}$ = 79.7 Hz and 57.7 Hz, C-9). − MS (EI, 70 eV); *m*/*z* (%): 540 (5) [M^+], 440 (2) [M^+ − PC*t*Bu], 340 (2) [M^+ − 2 PC*t*Bu], 162 (3) [$PCMes^+$], 147 (100) [$MesCO^+$], 119 (7) [Mes^+], 57 (12) [$t Bu^+$]. − HR MS (EI): calcd. 540.2029; found 540.2014. − $C_{30}H_{40}OP_4$ (540.54): calcd. C 66.7, H 7.5; found C 66.5, H 7.3.

13a: ^{31}P NMR (C_6D_6): δ = −7.2 (pseudo-t, $^2J_{P,P}$ = 16.3 Hz, P-4), 67.0 [dt, $^2J_{P,P}$ = 32.6 Hz, $^2J_{P,P}$ = 16.3 Hz (2 ×), P-1], 98.7 (ddd, $^1J_{P,P}$ = 313.3 Hz, $^2J_{P,P}$ = 32.6 Hz and 16.3 Hz, P-7), 356.0 (dd, $^1J_{P,P}$ = 313.3 Hz, $^2J_{P,P}$ = 16.3 Hz, P-8). − ^{1}H NMR (C_6D_6): δ = 1.19, 1.24 (each s, 9 H, *t*Bu), 6.66, 6.79 (each s, 2 H, *meta*-H). Due to overlap with signals of **12a** no assignment of *ortho*-/*para*-methyl groups is possible.

3,9-Bis(1,1-dimethylpropyl)-2,6-dimesityl-5,1,4,7,8-oxatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (12b) and 2,9-Bis(1,1-dimethylpropyl)-3,6-dimesityl-5,1,4,7,8-oxatetraphosphatetracyclo-[4.3.0.0^{2,4}.0^{3,7}]non-8-en (13b): Amounts: 105 mg (0.31 mmol) **6** and 71 mg (0.62 mmol) **10b** (32 mol-% solution in hexamethyldisiloxane). Column chromatography with pentane/diethyl ether (10:1) gave an isomeric mixture of **12b/13b** (ratio **12b/13b** = 5:1; by ^{1}H-NMR spectroscopy) (167 mg, 95% yield, yellow powder). Pure **12b** was obtained by crystallization from pentane at −78°C as yellow crystals (m.p. 101°C).

12b: ^{31}P NMR (CD_2Cl_2): δ = −1.1 (pseudo-t, $^2J_{P,P}$ = 11.4 Hz, P-4), 82.6 (ddd, $^2J_{P,P}$ = 30.6 Hz, 15.2 Hz and 11.4 Hz, P-1), 96.6 (ddd, $^1J_{P,P}$ = 310.8 Hz, $^2J_{P,P}$ = 30.6 Hz and 11.4 Hz, P-7), 354.6 (dd, $^1J_{P,P}$ = 310.8 Hz, $^2J_{P,P}$ = 15.2 Hz, P-8). − ^{1}H NMR (CD_2Cl_2): δ = 0.25, 0.81 [each t, $^3J_{H,H}$ = 7.5, 3 H, $C(CH_3)_2CH_2CH_3$], 0.91 [m, br., 3 H, $C(CH_3)_2CH_2CH_3$], 1.08 [m, br., 3 H, $C(CH_3)_2CH_2CH_3$], 1.20 [m, br., 3 H, $C(CH_3)_2CH_2CH_3$], 1.27 [m, br., 3 H, $C(CH_3)_2CH_2CH_3$], 1.57−1.90 [m, br., 4 H, $C(CH_3)_2CH_2CH_3$], 2.16, 2.21, 2.22, 2.59, 2.71, 2.90 (each s, 3 H, *ortho*- and *para*-CH_3), 6.66-6.90 (br., 4 H, *meta*-H). − MS (EI, 70 eV); *m*/*z* (%): 568 (11) [M^+], 307 (7) [M^+ − C_7H_{11}POMes], 292 (4) [M^+ − C_7H_{11}POMes − CH_3], 245 (11) [M^+ − $C_7H_{11}P_3$OMes], 214 (7) [M^+ − $C_7H_{11}P_4$OMes], 193 (8) [$MesCP_2^+$], 162 (4) [$MesCP^+$], 147 (100) [$MesCO^+$], 119 (9) [Mes^+], 72 (7) [$C_5H_{12}^+$]. − $C_{32}H_{44}OP_4$ (568.66): calcd. C 67.6, H 7.8; found C 66.9, H 7.7.

13b: ^{31}P NMR (CD_2Cl_2): δ = −5.9 (pseudo-t, $^2J_{P,P}$ = 11.5 Hz, P-4), 68.5 (ddd, $^2J_{P,P}$ = 34.4 Hz, 15.2 Hz and 11.5 Hz, P-1), 97.8 (ddd, $^1J_{P,P}$ = 312.8 Hz, $^2J_{P,P}$ = 34.4 Hz and 11.5 Hz, P-7), 361.2 (dd, $^1J_{P,P}$ = 312.8 Hz, $^2J_{P,P}$ = 15.2 Hz, P-8).

Compounds 15 and 16: To a magnetically stirred solution of an isomeric mixture of **12a/13a** (70 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was added dropwise a solution of 3,4,5,6-tetrachloro-1,2-benzoquinone (**14**) (32 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) at 25°C during 2 h. After the reaction mixture had been stirred for additional 12 h, all volatile components were removed at 25°C/10^{-3} mbar. The remaining crude product was purified by column chromatography on silica gel (water-cooled column). Elution with pentane/ether (25:1) gave an isomeric mixture of **15/16** (ratio **15/16** = 9:1; by ^{1}H-NMR spectroscopy) (71 mg, 69% yield, yellow powder). Pure **15** was obtained by crystallization from pentane/ether/CH_2Cl_2 (3:1:1) at 0°C as yellow rhombi (m.p. 141°C, dec.).

15: ^{31}P NMR (C_6D_6): δ = −55.5 (dd, $^2J_{P,P}$ = 54.3 Hz and 15.2 Hz, P-1′ or P-4′), −26.4 (dd, $^2J_{P,P}$ = 15.2 Hz and 2.8 Hz, P-4′ or P-1′), 42.5 (ddd, $^1J_{P,P}$ = 383.1 Hz, $^2J_{P,P}$ = 54.3 Hz and 2.8 Hz, P-7′), 298.4 (d, $^1J_{P,P}$ = 383.1 Hz, P-8′). − ^{1}H NMR (C_6D_6): δ = 0.83, 1.28 (each s, 9 H, *t*Bu), 1.91, 2.00, 2.24, 2.35, 2.82, 2.86 (each s, 3 H, *ortho*- and *para*-CH_3), 6.47, 6.57 (each s, 1 H, *meta*-H), 6.66 (s, 2 H, *meta*-H). − MS (EI, 70 eV); *m*/*z* (%): 786 (1) [M^+], 739 (26) [M^+ − PO], 638 (6) [M^+ − Cl − PC$_2$*t*Bu], 540 (2) [M^+ − $C_6Cl_4O_2$], 525 (3) [M^+ − $C_6Cl_4O_2$ − CH_3], 231 (100) [$P(PCtBu)_2^+$], 147 (83) [$MesCO^+$], 119 (20) [Mes^+], 57 (11) [$t Bu^+$]. − HR MS (EI): calcd. 784.0682; found 784.0677. − $C_{36}H_{40}Cl_4O_3P_4$ (786.42): calcd. C 54.9, H 5.1; found C 53.7, H 5.4.

16: ^{31}P NMR (C_6D_6): δ = −59.6 (dd, $^2J_{P,P}$ = 52.9 Hz and 15.3 Hz, P-1′ or P-4′), −30.9 (dd, $^2J_{P,P}$ = 15.3 Hz and 2.9 Hz, P-4′ or P-1′), 35.4 (ddd, $^1J_{P,P}$ = 388.9 Hz, $^2J_{P,P}$ = 52.9 Hz and 2.9 Hz, P-7′), 296.5 (d, $^1J_{P,P}$ = 388.9 Hz, P-8′).

Dimethyl 5-Mesityl-1,2-oxaphosphole-3,4-dicarboxylate (18): A solution of oxadiphosphole **6** (340 mg, 1.00 mmol) in pentane (5 mL) was cooled to −20°C and freshly distilled dimethyl acetylenedicarboxylate (**17**, 142 mg, 1.00 mmol) in pentane (3 mL) was added under magnetic stirring. After warming up to 0°C and further stirring for another 1 h at this temperature, all volatile components were removed at 25°C/10^{-3} mbar. ^{31}P-NMR analysis of the pale yellow crude product revealed the formation of mesitylphosphaacetylene (**7**) and 1,2-oxaphosphole **18**, which could not be isolated. Either bulb-to-bulb distillation (50°C/10^{-3} mbar) or column chromatography (silica gel, pentane) gave pure **7** exclusively (146 mg, 90% yield, analytical and spectroscopic data identical with that of ref.[12]). Higher distillation temperatures (50−250 C/10^{-3} mbar) or more polar eluting agents (pentane/ether, ether, CH_2Cl_2) only led to unselective decomposition. − ^{31}P NMR (C_6D_6): δ = 303.1 (s).

Compound 21: A solution of oxadiphosphole **6** (160 mg, 0.46 mmol) and tri-*tert*-butylazete (**20**) (104 mg, 0.46 mmol) in pentane (15 mL) was heated to 120°C for 2 d in a Schlenk pressure tube. After all volatile components were removed at 25°C/10^{-3} mbar, the red-brown residue was subjected to column chromatography on silica gel. Pure **21** was obtained with pentane/ether (2:1) (106 mg, 41% yield, colorless powder). Crystallization from pentane/$CHCl_3$ (5:1) at 0°C furnished colorless crystals (m.p. 145°C, dec.). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2955 (s), 2916 (s), 1610 (w), 1478 (m), 1457 (m), 1392 (m, *t*Bu), 1363 (m, *t*Bu), 1229 (vs, P=O), 1105 (m), 1075 (m). − ^{31}P NMR ($CDCl_3$): δ = −118.2 (dd, $^2J_{P,P}$ = 52.0 Hz, $^2J_{P,H}$ = 22.6 Hz, P-8), 77.3 (dd, $^2J_{P,P}$ = 52.0 Hz, $^3J_{P,H}$ = 29.6 Hz, P-6). − ^{1}H NMR ($CDCl_3$): δ = 1.14 (s, 9 H, 3-*t*Bu), 1.52, 1.61 (each s, 9 H, 4- and 5-*t*Bu), 1.93 (d, 1 H, $^2J_{H,H}$ = 18.1 Hz, 9b-H), 2.14 (s, 6 H, *ortho*-CH_3), 2.31 (dd, $^2J_{H,P}$ = 22.6 Hz, $^2J_{H,H}$ = 18.1 Hz, 9a-H), 2.40, 2.55, 2.92 (each s, 3 H, CH_3), 4.01 (d, $^3J_{H,P}$ = 29.6 Hz, 1 H, 3-H), 6.37, 6.65 (each s, 1 H, 4′-H and 6′-H), 6.76 (s, 2 H, *meta*-H). − ^{13}C NMR ($CDCl_3$): δ = 19.9 (s, *para*-CH_3), 20.7 (d, $^4J_{C,P}$ = 3.4 Hz, *ortho*-CH_3), 21.8 (s, 5′-CH_3), 22.4 (d, $^4J_{C,P}$ = 11.9 Hz, 3′-CH_3), 26.5 (dd, $^1J_{C,P}$ = 33.0 Hz, $^3J_{C,P}$ = 6.0 Hz, C-9), 30.0 [s, C(*C*H_3)$_3$], 33.1 [d, $J_{C,P}$ = 5.1 Hz, C(*C*H_3)$_3$], 35.9 [d, $J_{C,P}$ = 6.8 Hz, C(*C*H_3)$_3$], 36.6 [d, $J_{C,P}$ = 13.6 Hz, *C*$(CH_3)_3$], 37.4 [s, *C*$(CH_3)_3$], 38.3 [d, $J_{C,P}$ = 18.7 Hz, *C*$(CH_3)_3$], 53.4 (dd, $^1J_{C,P}$ = 83.1 Hz and 49.2 Hz, C-7), 75.3 (dd, $J_{C,P}$ = 11.7 Hz, $J_{C,P}$ = 9.9 Hz, C-3), 83.0 (dd, $^1J_{C,P}$ = 30.6 Hz, $^2J_{C,P}$ = 13.6 Hz, C-1), 129.6 (d, $J_{C,P}$ = 3.4 Hz, C=C), 123.7 (d, $J_{C,P}$ = 3.4 Hz, C=C), 125.4 (s, C=C), 130.4 (d,

$J_{C,P}$ = 3.4 Hz, C=C), 130.6 (s, C=C), 135.8 (s, C=C), 136.1 (s, C=C), 136.6 (d, $J_{C,P}$ = 3.9 Hz, C=C), 138.0 (d, $J_{C,P}$ = 3.4 Hz, C=C), 140.6 (d, $J_{C,P}$ = 3.4 Hz, C=C), 142.4 (d, $J_{C,P}$ = 5.1 Hz, C=C), 169.0 (d, $^1J_{C,P}$ = 26.7 Hz, C-5). – MS (EI, 70 eV); *m*/*z* (%): 561 (24) [M^+], 546 (3) [$M^+ - CH_3$], 504 (100) [$M^+ - t$Bu], 448 (4) [$M^+ - t$Bu – C_4H_8], 291 (16) [$PC_{20}H_{20}^+$], 119 (7) [Mes^+], 84 (26) [$N(HCtBu)^+$], 57 (66) [tBu$^+$]. – $C_{35}H_{49}NOP_2$ (561.69).

Crystal Structure Analysis of 15:[35] STOE Imaging Plate Diffraction System, graphite monochromator, Mo-K_α radiation (λ = 0.71073), cell determination and refinement by STOE programs Ver. 2.75, structure solution by direct methods (SHELXS-97[36]) and structure refinement by SHELXL-97.[37] $C_{36}H_{40}Cl_4O_3P_4$; M = 786.36 g·mol^{-1}; monoclinic, space group $P2_1/c$; lattice constants a = 13.9230(10), b = 16.7620(10), c = 17.6550(10) Å, β = 111.045(6)°, V = 3845.4(4) Å^3, Z = 4, $D_{calcd.}$ = 1.358 Mg · m^{-3}, μ(Mo-K_α) = 0.508 mm^{-1}, crystal size 0.30 × 0.20 × 0.20 mm; ω scan: 1.98° ≤ Θ ≤ 25.00°. 22012 reflections collected, 6737 independent reflections ($R_{int.}$ = 0.0516); 496 parameters (C, O, Cl, and P anisotropic, H atoms were included in the refinement using riding models; methyl H atoms were allowed to rotate about the C–C bond); S = GOF = 1.051; wR^2 = 0.0852; R^1 = 0.0469 [for 3627 reflections with $F^2 > 2\sigma(F^2)$] $w = 1/[\sigma^2(F_o^2) + (0.01 \cdot P)^2 + 1.5 \cdot P]$; shift/esd$_{max.}$ = 0.08; residual electronic density 0.318 and −0.261 e·Å^{-3}.

Crystal Structure Analysis of 21:[35] STOE Imaging Plate Diffraction System, graphite monochromator, Mo-K_α radiation (λ = 0.71073), cell determination and refinement by STOE programs Ver. 2.75, structure solution by direct methods (SHELXS-86[38]) and structure refinement by SHELXL-93.[39] $C_{35}H_{49}NOP_2$; M = 561.69 g·mol^{-1}; triclinic, space group $P\bar{1}$; lattice constants a = 8.1009(10), b = 11.898(2), c = 17.395(2) Å, α = 78.42(12), β = 80.383(12), γ = 83.032(11)°, V = 1612.7(4) Å^3, Z = 2, $D_{calcd.}$ = 1.157 Mg · m^{-3}, μ(Mo-K_α) = 0.162 mm^{-1}, crystal size 0.35 × 0.25 × 0.15 mm; ω scan: 1.94° ≤ Θ ≤ 24.09°. 9563 reflections collected, 4778 independent reflections ($R_{int.}$ = 0.0325); 352 parameters (C, N, O, and P anisotropic, H atoms were included in the refinement using riding models); S = GOF = 1.019; wR^2 = 0.1079; R^1 = 0.0468 [for 4778 reflections with $F^2 > 2\sigma(F^2)$] $w = 1/[\sigma^2(F_o^2) + (0.0327 \cdot P)^2 + 1.2873 \cdot P]$; shift/esd$_{max.}$ = 0.005; residual electronic density 0.299 and −0.210 e·Å^{-3}.

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