# Organophosphorus Compounds, Part 168;[1] 1,3-Dipolar Cycloaddition Reactions of 1,3,5-Triphosphinines with Nitrile Oxides

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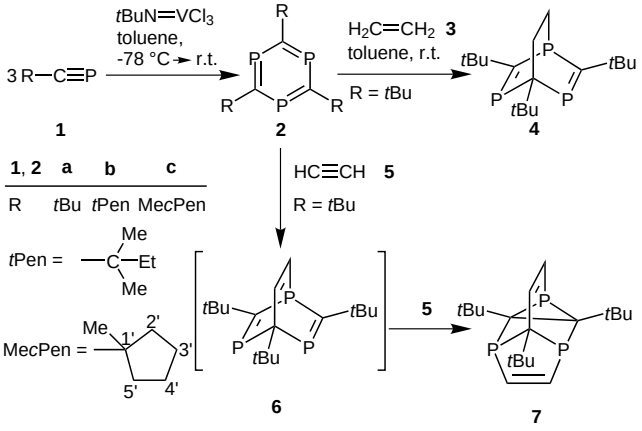
Dedicated to Professor Gerhard Himbert on the ocassion of his 60th birthday.

**Abstract:** Phenylnitrile oxide as well as mesitylnitrile oxide underwent 1,3-dipolar cycloaddition reactions with the 1,3,5-triphosphinines **2** under mild conditions to furnish the condensed heterocyclic compounds **9** and **11**, respectively. Oxadiphospholes **14** were accessible by fragmentation reactions of **11**.

**Key words:** phosphorus, 1,3-dipolar cycloadditions, nitrile oxides, 1,2,4-oxazaphospholes, 1,2,4-oxadiphospholes

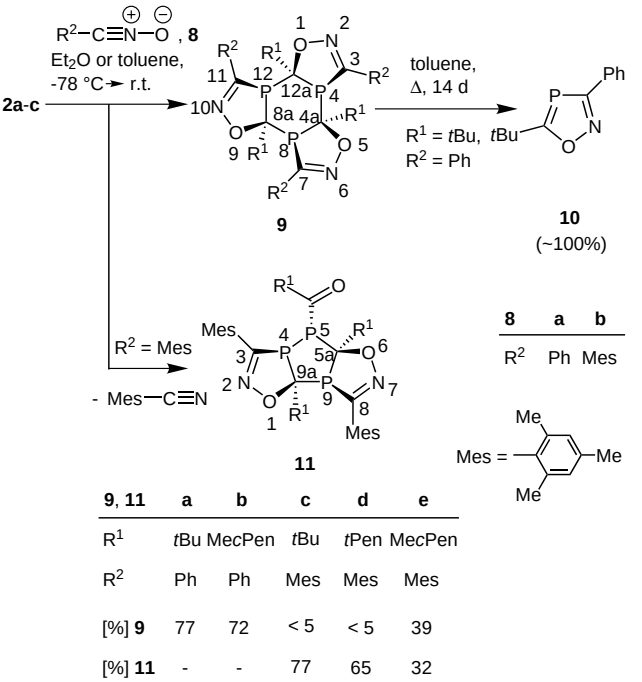
2,4,6-Tri-*tert*-butyl-1,3,5-triphosphinine (**2a**) was first prepared in 1995.[2] Shortly thereafter, a simple one-pot synthesis comprising the cyclotrimerization of the phosphaalkynes **1** in the presence of a vanadium catalyst was developed that also made the isolation of other triphosphinines possible.[3] Although their physicochemical properties (NMR spectroscopic data[2,3], crystal structure analysis[4]) as well as theoretical investigations[5] clearly demonstrated the aromatic character of the 1,3,5-triphosphinines **2**, the compounds have been exhibiting a surprisingly high reactivity in, for example [4+2] cycloaddition reactions.[6] When ethylene **3** was bubbled into a toluene solution of **2a**, a [4+2] cycloaddition reaction occurred at room temperature to afford the 7,8-dihydro-1,3,5-triphosphabarrelene **4**.[7] Various monosubstituted alkenes (acrylic acid derivatives, styrene), as well as some selected disubstituted alkenes (maleic acid derivatives, fumaric acid derivatives, norbornene, cyclopentadiene) also underwent Diels–Alder reactions with **2** to furnish comparable dihydrotriphosphabarrelenes. Alkynes like acetylene **5** itself reacted with **2a** to afford the novel triphospha cage compound **7** through a Diels–Alder/homo-Diels–Alder reaction sequence with the 1,3,5-triphosphabicyclo-[2.2.2]octa-2,5,7-triene **6** as intermediate (Scheme 1).[8]




**Scheme 1**

On account to their relatively weakly pronounced aromaticity, 1,3,5-triphosphinines should, in principle, be able to act as dipolarophiles in [3+2]-cycloaddition reactions. In order to test this assumption 1,3,5-triphosphinines **2a**–**c** were allowed to react with 1,3-dipoles, namely phenyl- and mesitylnitrile oxides (Scheme 2).

Depending on the substituents $R^1$ and $R^2$, reactions of the 1,3,5-triphosphinines **2** with the nitrile oxides **8** in $Et_2O$ or toluene led either to the trisadducts **9** or proceeded with ring contraction from a six- to a five-membered ring to afford the heterocycles **11** with a P-acyl substituent.[9] Benzonitrile oxide **8a** reacted smoothly with **2a**,**c** to give the trisadducts **9a**,**b**. When the steric overcrowding in the nitrile oxide was increased by substituting the phenyl group




**Scheme 2**

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by a mesityl group (**8b**), the formation of trisadducts at all three P–C bonds of the 1,3,5-triphosphinine was no longer favored.

As shown in Figure 1, the reaction path branches presumably at the stage of the monocycloadduct **A**, because attack of the second nitrile oxide can occur from the C-5(*Si*)–P-6(*Re*) or C-5(*Re*)–P-6(*Si*) side of the monoadduct. Addition of **8** to the double bond C-7–P-8 of **A** leads to the same types of intermediates and is therefore not further discussed here.

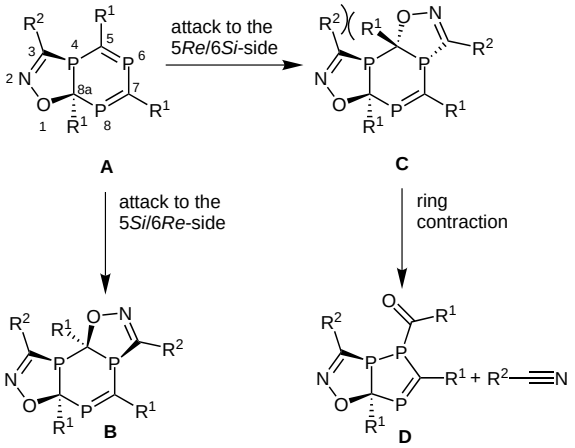



**Figure 1** Plausible intermediates in the 1,3-dipolar cycloaddition reaction of nitrile oxides towards 1,3,5-triphosphinines

When the C-5(*Si*)/P-6(*Re*) side is accessible the reaction sequence leads to the cycloadduct **B** and ends at the tetracyclic species **9**; when this side is shielded attack at the C-5(*Re*)/P-6(*Si*) side leads to the cycloadduct **C** with subsequent ring contraction under cleavage of the nitrile (→ **D**), and finally to the formation of product **11**. With the 1-methylcyclopentyl and mesityl substituents both reaction paths are equally possible as an approximately 1:1 mixture of **9e** and **11e** was obtained.

The constitution of the trisadducts **9** could be deduced unambiguously from their spectroscopic data, which showed, in particular, that all three equivalents of nitrile oxides added to the 1,3,5-triphosphinine from the same side. Thus, all the $^{31}$P NMR spectra contained only one singlet signal confirming the high symmetry of the system **9**. The chemical shifts were between δ = 17.4 and 30.9 ppm thus clearly indicating the loss of three P-C double bonds. Compounds **9c** and **9d** were identified as minor products on the basis of their $^{31}$P NMR singlet resonances of δ = 28.1 and 29.0 ppm, respectively in the crude reaction mixtures. The $^{2}J_{P,P}$ coupling constants of **9** were determined as simulation parameters of the $^{13}$C NMR data and amounted to between 1.8 and 9.4 Hz. The $^{13}$C NMR spectra contained only one signal between δ = 97.6 and 98.3 ppm for the three chemically equivalent atoms C-4a, C-8a, C-12a in agreement with the $C_3$ symmetry. As shown by a simulation of the AA′A″X spin system, all the signals of these skeletal carbon atoms possessed two characteristic $^{1}J_{C,P}$ coupling constants of between 52.0 and 71.0 Hz, confirming the attachment to two phosphorus atoms. In addition, the chemically equivalent imine carbon atoms C-3, C-7, C-11 gave signals at typically low field between δ = 156.4 and 159.3 ppm, each with a characteristic $^{1}J_{C,P}$ coupling constant ranging from 40.6 to 50.3 Hz, again demonstrating the direct attachment to a phosphorus atom and confirming the deduced direction of addition of the 1,3-dipole to the P–C double bond.

The cleavage of mesityl nitrile in the formation of the tricyclic compounds **11** was confirmed by correct elemental analysis results. Moreover, the IR spectrum of **11** revealed strong absorptions between 1671 cm$^{-1}$ and 1674 cm$^{-1}$ that could be assigned to the carbonyl vibrations of the newly formed P-acyl group. The phosphorus atoms P-4, P-5, P-9 of the central 1,2,4-triphospholane appeared as an AMN spin system in the $^{31}$P NMR spectrum at about δ = 50 (P-4, P-5) ppm and δ = 80 (P-9) ppm. Further characteristic parameters were the large $^{1}J_{P,P}$ coupling constants of between 255.8 and 264.1 Hz, demonstrating the direct attachment of P-4 and P-5, as well as typical $^{2}J_{P,P}$ coupling constants of 10.7–23.4 Hz between P-4–P-9 on the one hand and P-5–P-9 on the other hand. Final confirmation of the structure of **11** was provided by an X-ray crystallographic analysis of **11c**.

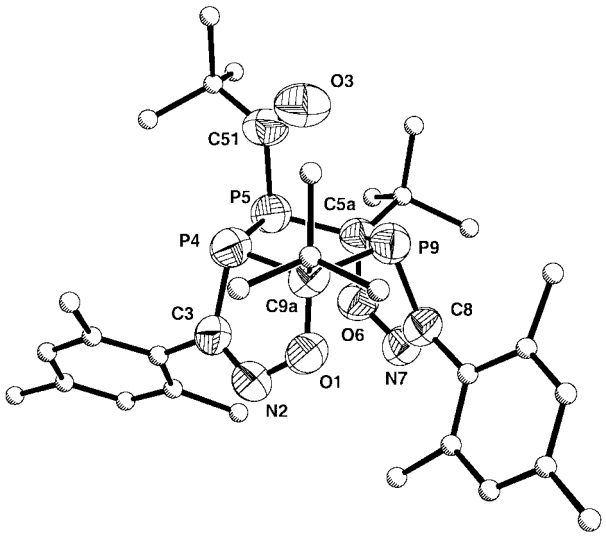


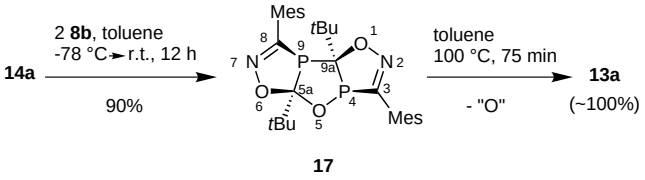

**Figure 2** Molecular structure of **11c**; selected bond lengths [Å] and bond angles [°]: P4–P5 2.196(2), P4–C3 1.812(5), P5–C5a 1.895(5), P5–C51 1.888(6), C5a–P9 1.848(5), P9–C9a 1.918(5), P9–C8 1.846(5), C9a–P 4 1.871(5); C9a–P4–P5 101.81(19), C9a–P4–C3 88.5(2), P4–P5–C5a 99.04(17), P4–P5–C51 86.93(18), C5a–P5–C51 104.1(2), P5–C5a–P9 114.2(3), C5a–P9–C9a 102.0(2), C5a–P9–C8 86.6(2), C9a–P9–C8 96.7(2), P9–C9a–P4 111.7(3)

Figure 2 clearly shows that the central 1,2,4-triphospholane ring possessed a distorted envelope conformation, that the newly formed pivaloyl group on P-5 was located on the opposite side to the plane of the central five-membered ring as did the two condensed 4,5-dihydrooxazaphosphole rings, and that the oxygen of the carbonyl group was located below the five-membered ring.

In order to exclude the subsequent formation of **11** from **9** by cleavage of the nitrile, compound **9a** was heated in toluene at 100 °C for 14 days. NMR spectroscopic control did not reveal any ring contraction, instead a quantitative [2+2+2]-cycloreversion to the previously known 5-*tert*-butyl-3-phenyl-1,2,4-oxazaphosphole (**10**)[10,21] was observed.

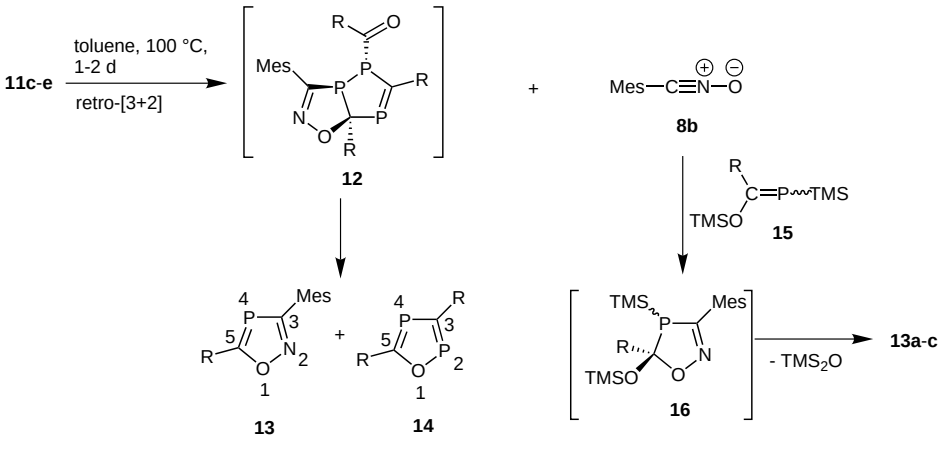
When the tricyclic compounds **11** were subjected to a comparable thermolysis, an initial [3+2]-cycloreversion with liberation of mesitylnitrile oxide (**8b**) and formation of the bicyclic species **12** occurred with subsequent decomposition into the oxazaphospholes **13** and the oxadiphospholes **14** as indicated in Scheme 3.

Whereas the oxazaphospholes **13** are well known, oxadiphospholes **14** have as yet only been poorly investigated[11,12] and this synthetic route has potential for exploitation as a specific access to this novel class of heterodiphospholes. Since control experiments showed that the oxadiphospholes **14** reacted with mesitylnitrile oxide under formation of compound **17** (Scheme 4), which reduced their yields or prevented their isolation, it seemed reasonable to remove the inevitably formed 1,3-dipole by means of a trapping reagent. It is well known that phosphaalkenes of the Becker type react with nitrile oxides via the 4,5-dihydro-1,2,4-oxazaphospholes **16** and cleavage of hexamethyldisiloxane to afford oxazaphospholes of the type **13**.[10,13,20] Thus, when the thermolysis of compounds **11** was performed in the presence of the phosphaalkene corresponding to the employed compound **11**, we could indeed isolate the oxadiphospholes **14** in good yields of 68–71%. It was even possible to carry out the synthesis of **14** as a one-pot process starting with **2**, three equivalents of **8b**, and one equivalent of the respective phosphaalkene. As shown for the example of **14a** it is possible to obtain this heterocyclic species by this procedure in yields between 60–65%.




**Scheme 4**

The constitutions of the novel oxadiphospholes **14a–c** were confirmed by correct elemental analysis results, the presence of molecular ion peaks in their EI-mass spectra, and examination of their spectroscopic data. Hence, each $^{31}$P NMR spectra each a signal at low field between $\delta$ = 313.9 and 316.4 ppm for the phosphorus atom P-2 directly attached to the oxygen atom, whereas the signal for P-4 was appreciably shifted to higher field and appeared between $\delta$ = 122.0 and 127.3. ppm The $^2J_{P,P}$ coupling constants were on average 24.0 Hz. These and all other NMR data were in complete accord with those of the previously reported 3,5-dimesityl derivative (**14**, R = Mes)[12] (see also experimental section). Finally, the selective reaction of **14a** with mesitylnitrile oxide should be mentioned. Even under mild conditions two equivalents of mesitylnitrile oxide (**8b**) underwent addition to the two P–C double bonds of **14a** to furnish in high diastereo- and regioselectivity the heterocyclic species **17** which was isolated in the form of colorless needles in 90% yield. The spectroscopic data of **17** were closely compatible with those of the already known analogue in which the oxygen atom in position 5 is replaced by sulfur.[22] The only significant differences were observed for P-4 and C-5a, i.e., the atoms directly adjacent to the oxygen O-5 or sulfur S-5, respectively. The signals for both atoms in the corresponding spectra of **17** were markedly shifted to lower field (P-4: $\delta$ = 156.7 vs. 78.3 ppm; C-5a: $\delta$ = 140.0 vs. 125.8 ppm). The proposed relative stereochemistry in




| 13 -16 | a | b | c |
|---|---|---|---|
| R | *t*Bu | *t*Pen | *Mec*Pen |
| [%] **14** | 71 | 69 | 68 |

**Scheme 3**

which both equivalents of **8b** added from the same side to **14a** is plausible under consideration of the known angle-dependency of the $^2J_{C,P}$ coupling constants.[14] They were 23.5 and 24.8 Hz for the quaternary carbon atoms of the *tert*-butyl groups bonded to C-5a and C-9a, respectively, thus supporting the *cis*-orientation of these groups to the free electron pairs on the phosphorus atoms P-4 and P-9.

When **17** was subjected to thermolysis under the same conditions as employed for compounds **11** above, decomposition was complete within 75 minutes and the known compound **13a**[15] was formed quantitatively. The fate of the thus liberated oxygen was not followed.

All reactions were carried out under an Ar atmosphere in oven-dried glassware. The solvents were anhydrous and stored under Ar. $^1$H NMR spectra were measured on Bruker AMX 400 spectrometer and the chemical shifts are referenced to the solvent as internal standard.$^{13}$C NMR spectra were measured on Bruker AMX 400 spectrometer and the chemical shifts are referenced to the solvent as internal standard. $^{31}$P NMR spectra were recorded on Bruker AC 200 instrument at 80.8 MHz with 85% $H_3PO_4$ as the external standard. IR spectra were taken on a Perkin-Elmer 1000 series FTIR spectrometer. MS (EI) was performed on Finnigan MAT 90 instrument. MS (CI) was carried out on Finnigan MAT SSQ 7000 instrument with isobutene as carrier. MS (FAB) data were collected on Finnigan MAT TSQ 7000 instrument with following settings: Xe: 5–6 keV; 3-nitrobenzyl alcohol matrix, $CHCl_3$. GC–MS was performed on HP 6890 series with MSD and a HP-5MS capillary column (30 m × 250 μm). Elemental analysis was carried out on Perkin-Elmer 2400 CHN. Analytical TLC was done on plastic sheets coated with silica gel (Polygram SIL G/UV$_{254}$, Machery-Nagel). Column chromatography was performed with Merck silica gel (0.063–0.2 mm). Bulb-to-bulb distillation was done with Büchi GKR 50 apparatus; the temperatures stated are oven temperatures. Melting points were determined on Mettler FP61 with a heating rate of 2 °C/min and are uncorrected.

Compounds **2a**,[3] **2b**,[3] **2c**,[3] **8a**,[16] **8b**,[17] **15a**,[18] **15b**,[19] **15c**[20] were prepared by published methods. All other starting materials were obtained from commercial suppliers and were used without further purification.

**4a,8a,12a-Tri-*tert*-butyl-3,7,11-triphenyl-4,4a,8,8a,12,12a-bis-[1,2,4]oxazaphospholo[4′,5′:3,4;4″,5″:5,6][1,3,5]triphosphinino[1,2-*d*][1,2,4]oxazaphosphole (9a); Typical Procedure**

To compound **2a** (150 mg, 0.50 mmol) and $Et_3N$ (152 mg, 1.50 mmol) in $Et_2O$ (10 mL), was added dropwise a solution of *N*-hydroxybenzenecarboximidoyl chloride (233 mg, 1.50 mmol) in $Et_2O$ (10 mL) under magnetic stirring at 0 °C. The solution was allowed to warm to r.t., the reaction mixture was filtered over Celite and the residue rinsed twice with $Et_2O$ (15 mL). After concentration of the solvent under oil pump vacuum ($10^{-3}$ mbar/25 °C), **9a** crystallized at –25 °C. Yield: 253 mg (0.38 mmol, 77%); colorless crystals; mp 184 °C (decomp).

IR (KBr): 3054 (m), 3029 (w), 2960 (vs), 2902 (m), 2867 (m), 1598 (m), 1578 (m), 1538 (m, br), 1490 (m), 1475 (s), 1464 (s), 1443 (s), 1393 (s), 1363 (s), 1267 (m), 1196 (m), 1075 (m), 1028 (w), 1001 (m), 977 (m), 946 (m), 901 (s), 876 (s), 845 (m), 760 (vs), 696 (vs), 659 (m), 626 (m), 603 (s), 487 (m) cm$^{-1}$.

$^1$H NMR ($CD_2Cl_2$): δ = 1.06 [s, 27 H, C(C$H_3$)$_3$], 7.40–7.47 (m, 9 H, H-phenyl), 7.64–7.71 (m, 6 H, H-phenyl).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 27.4 [AA′A″*X* spin system, $^3J_{C,P}$ = 12.0 Hz, 10.8 Hz, $^5J_{C,P}$ = 0.5 Hz, C(*C*H$_3$)$_3$], 43.2 [AA′A″*X* spin system, $^2J_{C,P}$ = 25.9 Hz, 23.6 Hz, $^4J_{C,P}$ = 0.8 Hz, *C*(CH$_3$)$_3$], 98.3 (AA′A″*X* spin system, $^1J_{C,P}$ = 64.0 Hz, 53.0 Hz, $^3J_{C,P}$ = 0.7 Hz, C-4a, C-8a, C-12a), 128.3 (s, *meta*-C-phenyl), 129.1 (s, *ortho*/*para*-C-phenyl), 132.6 (AA′A″*X* spin system, $^2J_{C,P}$ = 19.0 Hz, $^4J_{C,P}$ = 0.0 Hz, 0.0 Hz, *ipso*-C-phenyl), 159.3 (AA′A″*X* spin system, $^1J_{C,P}$ = 40.6 Hz, $^3J_{C,P}$ = 0.7 Hz, 0.7 Hz, C-3, C-7, C-11); simulation parameter of AA′A″X spin systems: $^2J_{P,P}$ = 1.8 Hz.

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 18.5 (s, P-4, P-8, P-12).

MS (FAB): *m*/*z* = 658 [M + H]$^+$.

Anal. Calcd for $C_{36}H_{42}N_3O_3P_3$ (657.67): C, 65.75; H, 6.44; N, 6.39. Found: C, 65.63; H, 6.44; N, 6.33.

**4a,8a,12a-Tris(1-methylcyclopentyl)-3,7,11-triphenyl-bis-[1,2,4]oxazaphospholo[4′,5′:3,4;4″,5″:5,6][1,3,5]triphosphinino[1,2-*d*][1,2,4]oxazaphosphole (9b); Typical Procedure**

To compound **2c** (348 mg, 0.92 mmol) and $Et_3N$ (279 mg, 2.76 mmol) in $Et_2O$ (15 mL), was added dropwise a solution of *N*-hydroxybenzenecarboximidoyl chloride (429 mg, 2.76 mmol) in $Et_2O$ (15 mL) under magnetic stirring at 0 °C. The solution was allowed to warm to r.t., the reaction mixture was filtered over Celite and the residue rinsed twice with toluene (15 mL). After removal of the solvent under oil pump vacuum ($10^{-3}$ mbar/25 °C), the residue was taken up in THF–$Et_2O$ (1:1) and crystallization at –25 °C afforded **9b**. Yield: 482 mg (0.66 mmol, 72%); colorless crystals; mp 173 °C (decomp).

IR (KBr): 3054 (w), 3026 (w), 2960 (vs), 2871 (s), 1598 (w), 1578 (w), 1539 (m), 1490 (m), 1461 (m), 1442 (s), 1380 (s), 1323 (m), 1284 (w), 1268 (m), 1232 (m), 1202 (w), 1178 (w), 1118 (w), 1073 (m), 1049 (w), 1020 (m), 1001 (w), 977 (m), 934 (w), 908 (m), 884 (s), 859 (s), 760 (vs), 695 (vs), 674 (m), 655 (m), 629 (m), 602 (s), 498 (m) cm$^{-1}$.

$^1$H NMR ($CD_2Cl_2$): δ = 1.28 (s, 9 H, cyclopentyl-$CH_3$), 1.30–1.60 (m, 24 H, H-cyclopentyl), 7.42–7.48 (m, 9 H, H-phenyl), 7.67–7.73 (m, 6 H, H-phenyl).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 22.7, 23.4 (each s, C-3′-cyclopentyl, C-4′-cyclopentyl), 23.4 (AA′A″*X* spin system, $^3J_{C,P}$ = 15.7 Hz, 15.7 Hz, $^5J_{C,P}$ = 0.9 Hz, 1′-*C*H$_3$-cyclopentyl), 36.0 (AA′A″*X* spin system, $^3J_{C,P}$ = 9.5 Hz, 7.3 Hz, $^5J_{P,C}$ = 0.3 Hz, C-2′- or C-5′-cyclopentyl), 36.4 (AA′A″*X* spin system, $^3J_{C,P}$ = 9.8 Hz, 7.4 Hz, $^5J_{C,P}$ = 0.2 Hz, C-2′- or C-5′-cyclopentyl), 54.4 (AA′A″*X* spin system, $^2J_{C,P}$ = 24.2 Hz, 21.8 Hz, $^4J_{C,P}$ = 1.0 Hz, C-1′-cyclopentyl), 98.1 (AA′A″*X* spin system, $^1J_{C,P}$ = 62.9 Hz, 52.0 Hz, $^3J_{C,P}$ = 0.5 Hz, C-4a, C-8a, C-12a), 128.4 (s, *meta*-C-phenyl), 129.2, 129.3 (each s, *ortho*/*para*-C-phenyl), 132.9 (AA′A″*X* spin system, $^2J_{C,P}$ = 18.8 Hz, $^4J_{C,P}$ = 0.0 Hz, 0.0 Hz, *ipso*-C-phenyl), 159.3 (AA′A″*X* spin system, $^1J_{C,P}$ = 41.1 Hz, $^3J_{C,P}$ = 0.9 Hz, 0.9 Hz, C-3, C-7, C-11); simulation parameter of AA′A″X spin systems: $^2J_{P,P}$ = 1.9 Hz.

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 17.4 (s, P-4, P-8, P-12).

MS (FAB): *m*/*z* = 736 [M + H]$^+$.

Anal. Calcd for $C_{42}H_{48}N_3O_3P_3$ (735.78): C, 68.56; H, 6.58; N, 5.71. Found: C, 68.14; H, 7.02; N, 5.30.

**Reaction of 2a–c with Mesitylnitrile Oxide (8b); General Procedure**

To a solution of the 1,3,5-triphosphinines **2** in toluene was added drop by drop a solution of a three-fold amount of mesitylnitrile oxide (**8b**) in toluene at –78 °C. After warming to r.t., all volatile materials were removed under oil pump vacuum ($10^{-3}$ mbar/25 °C) and the residue was worked up as described for the individual case.

**5a,9a-Di-*tert*-butyl-3,8-dimesityl-5-(2,2-dimethylpropanoyl)-5,5a-dihydro[1,2,4]oxazaphospholo[4′,5′:1,5][1,2,4]triphospholo[4,3-*d*][1,2,4]oxazaphosphole (11c); Typical Procedure**

The above-mentioned compound was prepared from 1,3,5-triphosphinine **2a** (1.55 g, 5.17 mmol) in toluene (10 mL) and **8b** (2.50 g,

15.5 mmol) in toluene (10 mL). After bulb-to-bulb distillation was performed (50–70 °C/10$^{-3}$ mbar) to remove the formed mesitylnitrile, the oily crude product was worked up by column chromatography (silica gel, toluene) and crystallized from toluene–*n*-pentane (1:4) at –25 °C. Yield: 2.55 g (3.99 mmol, 77%); colorless to yellowish crystal powder; mp 154 °C (decomp).

IR (KBr): 2957 (s), 2928 (s), 2863 (m), 1671 (s, C=O), 1610 (m), 1474 (s), 1459 (s), 1393 (m), 1364 (s), 1219 (w), 1032 (w), 978 (w), 941 (w), 918 (m), 911 (m), 849 (s), 796 (w), 776 (w), 733 (w) cm$^{-1}$.

$^1$H NMR ($CD_2Cl_2$): δ = 1.02, 1.12, 1.20 [each s, 9 H, C(C*H*$_3$)$_3$], 2.28, 2.29 (each s, 3 H, *ortho*-C*H*$_3$-mesityl), 2.39 (s, 6 H, *ortho*-C*H*$_3$-mesityl), 2.66, 2.68 (each s, 3 H, *para*-C*H*$_3$-mesityl), 6.88, 7.00 (each s, 1 H, H-mesityl), 6.91 (s, 2 H, H-mesityl).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 20.7 (dd, $J_{C,P}$ = 5.8 Hz, $J_{C,P}$ = 1.9 Hz, *ortho*- or *para*-*C*H$_3$-mesityl), 20.8 (s, *ortho*-*C*H$_3$-mesityl), 20.9 (s, *ortho*- or *para*-*C*H$_3$-mesityl), 22.3 (s, *ortho*- or *para*-*C*H$_3$-mesityl), 22.9 (d, $J_{C,P}$ = 22.2 Hz, *ortho*- or *para*-*C*H$_3$-mesityl), 26.4 [dd, $^3J_{C,P}$ = 4.8 Hz, 2.9 Hz, C(*C*H$_3$)$_3$], 27.0 [*pseudo t*, $^3J_{C,P}$ = 8.1 Hz, C(*C*H$_3$)$_3$], 30.8 [*pseudo* t, $^3J_{C,P}$ = 5.6 Hz, C(*C*H$_3$)$_3$], 40.2 [ddd, $^2J_{C,P}$ = 26.6 Hz, 23.2 Hz, $^3J_{C,P}$ = 2.1 Hz, 9a-*C*(CH$_3$)$_3$], 42.8 [dd, $^2J_{C,P}$ = 22.6 Hz, 13.4 Hz, 5a-*C*(CH$_3$)$_3$], 51.0 [d, $^2J_{C,P}$ = 30.3 Hz, 5-C(O)*C*(CH$_3$)$_3$], 116.1 (ddd, $^1J_{C,P}$ = 53.0 Hz, 40.9 Hz, $^2J_{C,P}$ = 1.2 Hz, C-5a or C-9a), 123.2 (ddd, $^1J_{C,P}$ = 59.5 Hz, 49.4 Hz, $^2J_{C,P}$ = 4.9 Hz, C-5a or C-9a), 125.6 (d, $^2J_{C,P}$ = 15.3 Hz, *ipso*-C-mesityl), 126.7 (d, $^2J_{C,P}$ = 14.2 Hz, *ipso*-C-mesityl), 129.0, 129.7, 130.6, 137.4 (each s, C-mesityl), 137.5 (d, $J_{C,P}$ = 1.5 Hz, C-mesityl), 138.6, 138.9 (each s, C-mesityl), 140.0 (d, $J_{C,P}$ = 2.3 Hz, C-mesityl), 155.7 (dd, $^1J_{C,P}$ = 42.0 Hz, $J_{C,P}$ = 4.0 Hz, C-3 or C-8), 162.1 (d, $^1J_{C,P}$ = 45.2 Hz, C-3 or C-8), 223.6 (dd, $^1J_{C,P}$ = 57.3 Hz, $J_{C,P}$ = 4.8 Hz, *C* = O).

$^{31}$P{$^1$H}-NMR ($CD_2Cl_2$): δ = 51.2, 55.3 (A*MN* spin system, $^1J_{P,P}$ = 260.5 Hz, $^2J_{P,P}$ = 23.4 Hz, $^2J_{P,P}$ = 13.0 Hz, P-4, P-5), 83.2 (*A*MN spin system, $^2J_{P,P}$ = 23.4 Hz, $^2J_{P,P}$ = 13.0 Hz, P-9).

MS (CI): *m*/*z* = 639 [M + H]$^+$.

Anal. Calcd for $C_{35}H_{49}N_2O_3P_3$ (638.70): C, 65.82; H, 7.73; N, 4.39. Found: C, 65.56; H, 7.86; N, 4.13.

**3,8-Dimesityl-5-(2,2-dimethylbutanoyl)-5a,9a-bis(1,1-dimethylpropyl)-5,5a-dihydro[1,2,4]oxazaphospholo[4′,5′:1,5][1,2,4]triphospholo[4,3-*d*][1,2,4]oxazaphosphole (11d); Typical Procedure**

The above-mentioned compound was prepared from 1,3,5-triphosphinine **2b** (284 mg, 0.83 mmol) in toluene (5 mL) and **8b** (401 mg, 2.49 mmol) in toluene (5 mL). After bulb-to-bulb distillation was done (50–70 °C/10$^{-3}$ mbar) to remove the formed mesitylnitrile, the oily crude product was worked up by column chromatography (silica gel, *n*-pentane–$Et_2O$, 20:1) and crystallized from *n*-pentane at –25 °C. Yield: 369 mg (0.54 mmol, 65%); colorless to yellowish crystal powder; mp 126 °C (decomp).

IR (KBr): 2966 (vs), 2918 (s), 2879 (m), 1674 (s, C=O), 1610 (m), 1460 (s), 1443 (s), 1422 (m), 1389 (m), 1362 (m), 1294 (w), 1248 (w), 1168 (m), 1036 (w), 1016 (w), 978 (w), 935 (m), 918 (m), 890 (m), 863 (m), 851 (s), 840 (s), 803 (m), 791 (m), 733 (m), 623 (w), 614 (m), 607 (m), 549 (m) cm$^{-1}$.

$^1$H NMR ($CD_2Cl_2$): δ = 0.84 [*pseudo* t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C(CH$_3$)$_2$CH$_2$C*H*$_3$], 0.88 [*pseudo* t, $^3J_{H,H}$ = 7.1 Hz, 3 H, C(CH$_3$)$_2$CH$_2$C*H*$_3$], 0.95 [*pseudo* t, $^3J_{H,H}$ = 7.7 Hz, 3 H, C(CH$_3$)$_2$CH$_2$C*H*$_3$], 1.01, 1.07 (each s, 6 H, C(C*H*$_3$)$_2$CH$_2$CH$_3$], 1.20, 1.23 (each s, 3 H, C(C*H*$_3$)$_2$CH$_2$CH$_3$], 1.30–1.90 [m, 6 H, C(CH$_3$)$_2$C*H*$_2$CH$_3$], 2.33, 2.46 (each s, 6 H, *ortho*-C*H*$_3$-mesityl), 2.71, 2.74 (each s, 3 H, *para*-C*H*$_3$-mesityl), 6.93, 7.04 (each s, 1 H, H-mesityl), 6.95 (s, 2 H, H-mesityl).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 8.5, 8.7, 9.2 [each s, C(CH$_3$)$_2$CH$_2$*C*H$_3$], 20.8 (d, $J_{C,P}$ = 7.7 Hz, *ortho*- or *para*-*C*H$_3$-mesityl), 20.9 (s, *ortho*-*C*H$_3$-mesityl), 21.0 (s, *ortho*- or *para*-*C*H$_3$-mesityl), 22.4 (s, *ortho*- or *para*-*C*H$_3$-mesityl), 22.5 (*broad* s, C(*C*H$_3$)$_2$CH$_2$CH$_3$], 22.9 (d, $J_{C,P}$ = 22.2 Hz, *ortho*- or *para*-*C*H$_3$-mesityl), 23.8 [m, C(*C*H$_3$)$_2$CH$_2$CH$_3$], 26.3 [d, $^3J_{C,P}$ = 5.4 Hz, C(*C*H$_3$)$_2$CH$_2$CH$_3$], 26.7 [s, C(*C*H$_3$)$_2$CH$_2$CH$_3$], 31.2 [br m, C(CH$_3$)$_2$*C*H$_2$CH$_3$], 31.4 [br s, C(CH$_3$)$_2$CH$_2$CH$_3$], 34.8 [br m, C(CH$_3$)$_2$*C*H$_2$CH$_3$], 43.3, 45.9 [each m, *C*(CH$_3$)$_2$CH$_2$CH$_3$], 54.5 [m, C(O)*C*(CH$_3$)$_2$CH$_2$CH$_3$], 117.5 (br m, C-5a or C-9a), 124.3 (br m, C-5a or C-9a), 125.7 (m, *ipso*-C-mesityl), 126.8 (d, $^2J_{C,P}$ = 13.8 Hz, *ipso*-C-mesityl), 129.1, 129.7, 130.7, 137.5, 138.6, 138.9 (each s, C-mesityl), 140.0 (d, $J_{C,P}$ = 2.3 Hz, C-mesityl), 155.9 (d, $^1J_{C,P}$ = 34.5 Hz, C-3 or C-8), 162.1 (d, $^1J_{C,P}$ = 46.0 Hz, C-3 or C-8), 223.4 (d, $^1J_{C,P}$ = 52.9 Hz, *C*=O).

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 51.8, 53.8 (A*MN* spin system, $^1J_{P,P}$ = 264.1 Hz, $^2J_{P,P}$ = 21.2 Hz, $^2J_{P,P}$ = 12.8 Hz, P-4, P-5), 84.8 (*A*MN spin system, $^2J_{P,P}$ = 21.2 Hz, $^2J_{P,P}$ = 12.8 Hz, P-9).

MS (FAB): *m*/*z* = 681 [M + H]$^+$.

Anal. Calcd for $C_{38}H_{55}N_2O_3P_3$ (680.79): C, 67.04; H, 8.14; N, 4.11. Found: C, 66.95; H, 8.25; N, 3.96.

**3,7,11-Trimesityl-4a,8a,12a-tris(1-methylcyclopentyl)-bis-[1,2,4]oxazaphospholo[4′,5′:3,4;4″,5″:5,6][1,3,5]triphosphinino[1,2-*d*][1,2,4]oxazaphosphole (9e) and 3,8-Dimesityl-5a,9a-bis(1-methylcyclopentyl)-5-[(1-methylcyclopentyl)carbonyl]-5,5a-dihydro[1,2,4]oxazaphospholo[4′,5′:1,5][1,2,4]triphospholo[4,3-*d*][1,2,4]oxazaphosphole (11e); Typical Procedure**

The above-mentioned compound was prepared from 1,3,5-triphosphinine **2c** (361 mg, 0.95 mmol) in toluene (5 mL) and **8b** (462 mg, 2.86 mmol) in toluene (5 mL). The oily crude product was worked up by column chromatography (silica gel, toluene). After removal of toluene under oil pump vacuum the residue was several times subjected to fractional crystallization from toluene–*n*-pentane (1:2) at –25 °C yielding 322 mg (0.37 mmol, 39%) **9e** as colorless crystal powder; mp 170 °C (decomp). After further recrystallization from THF–*n*-pentane (1:3) 219 mg (0.31 mmol, 32%) **11e** was obtained as a colorless to yellowish crystal powder; mp 159 °C (decomp).

**9e**

IR (KBr): 2953 (vs, br), 2869 (s), 1610 (m), 1540 (w), 1457 (m), 1445 (m), 1371 (m), 1324 (w), 1296 (w), 1238 (w), 1162 (w), 1067 (w), 1033 (m), 977 (m), 947 (w), 927 (w), 913 (w), 870 (s), 851 (s), 734 (m), 631 (m), 600 (m), 547 (m) cm$^{-1}$.

$^1$H NMR ($CD_2Cl_2$): δ = 1.29 (s, 9 H, cyclopentyl-C*H*$_3$), 1.30–1.80 (m, 24 H, H-cyclopentyl), 2.29, 2.47, 2.50 (each s, 9 H, *ortho/para*-C*H*$_3$-mesityl), 6.85, 6.99 (each s, 3 H, H-mesityl).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 20.8, 21.6 (each s, *ortho*- or *para*-*C*H$_3$-mesityl), 21.8 (AA′A″*X* spin system, $J_{C,P}$ = 13.8 Hz, $J_{C,P}$ = 0.0 Hz, 0.0 Hz, *ortho*- or *para*-*C*H$_3$-mesityl), 23.6, 24.3 (each s, C-3′- and C-4′-cyclopentyl), 24.4 (m, 1′-*C*H$_3$-cyclopentyl), 35.0, 35.7 (each m, C-2′- and C-5′-cyclopentyl), 55.8 (AA′A″*X* spin system, $^2J_{C,P}$ = 32.0 Hz, 25.9 Hz, $^4J_{C,P}$ = 0.1 Hz, C-1′-cyclopentyl), 97.6 (AA′A″*X* spin system, $^1J_{C,P}$ = 71.0 Hz, 60.4 Hz, $^3J_{C,P}$ = 0.2 Hz, C-4a, C-8a, C-12a), 127.9 (AA′A″*X* spin system, $^2J_{C,P}$ = 13.7 Hz, $^4J_{C,P}$ = 0.0 Hz, 0.0 Hz, *ipso*-C-mesityl), 128.7, 129.9 (each s, *meta*-C-mesityl), 137.2, 138.4, 140.2 (each s, *ortho*/*para*-C-mesityl), 156.4 (AA′A″*X* spin system, $^1J_{C,P}$ = 50.3 Hz, $^3J_{C,P}$ = 0.4 Hz, 0.4 Hz, C-3, C-7, C-11); Simulation parameter of AA′A″X spin systems: $^2J_{P,P}$ = 9.4 Hz.

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 30.9 (s, P-4, P-8, P-12).

MS (FAB): *m*/*z* = 862 [M + H]$^+$.

Anal. Calcd for $C_{51}H_{66}N_3O_3P_3$ (862.02): C, 71.06; H, 7.72; N, 4.87. Found: C, 71.21; H, 7.83; N, 4.52.

**11e**

IR (KBr): 2958 (vs, br), 2866 (s), 2866 (m), 1673 (s, C=O), 1609 (m), 1442 (m, br), 1420 (w), 1376 (m), 1249 (w), 1036 (w), 977 (m), 952 (m), 909 (w), 858 (w), 849 (m), 733 (m), 624 (w), 550 (w) $cm^{-1}$.

$^1H$ NMR ($CD_2Cl_2$): δ = 1.17, 1.23, 1.26 (each s, 3 H, cyclopentyl-C$H_3$), 1.27–2.27 (m, 24 H, H-cyclopentyl), 2.30, 2.31 (each s, 3 H, *ortho*-C$H_3$-mesityl), 2.42 (s, 6 H, *ortho*-C$H_3$-mesityl), 2.63, 2.69 (each s, 3 H, *para*-C$H_3$-mesityl), 6.91 (s, 1 H, H-mesityl), 6.92 (s, 2 H, H-mesityl), 7.01 (s, 1 H, H-mesityl).

$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): δ = 20.7 (d, $J_{C,P}$ = 7.5 Hz, *ortho*- or *para*-C$H_3$-mesityl), 20.8 (s, *ortho*-C$H_3$-mesityl), 20.9, 22.2 (each s, *ortho*- or *para*-C$H_3$-mesityl), 22.9, 24.0, 24.7, 25.1, 25.3 (each s, C-3′- and C-4′-cyclopentyl), 23.0 (d, $J_{C,P}$ = 22.4 Hz, *ortho*- or *para*-C$H_3$-mesityl), 24.1 (m, 1′-C$H_3$-cylopentyl), 25.0 (dd, $J_{C,P}$ = 10.8 Hz, $J_{C,P}$ = 6.6 Hz, 1′-C$H_3$-cyclopentyl), 25.7 (*pseudo* t, $J_{C,P}$ = 10.4 Hz, 1′-C$H_3$-cyclopentyl), 36.7, 36.9 (each *pseudo* t, $^3J_{C,P}$ = 3.7 Hz, $^3J_{C,P}$ = 4.1 Hz, respectively, C-2′- or C-5′-cyclopentyl), 37.0 (br m, C-2′- or C-5′-cyclopentyl), 37.3 (br s, C-2′- or C-5′-cyclopentyl), 38.5 (d, $^3J_{C,P}$ = 5.0 Hz, C-2′- or C-5′-cyclopentyl), 40.7 (br s, C-2′- or C-5′-cyclopentyl), 51.6 (dd, $^2J_{C,P}$ = 26.1 Hz, 24.5 Hz, C-1′-cyclopentyl), 53.5 (m, C-1′-cyclopentyl), 62.3 (d, $^2J_{C,P}$ = 29.0 Hz, C-1′-cyclopentyl), 116.1 (br m, C-5a or C-9a), 122.2 (br m, C-5a or C-9a), 125.7 (d, $^2J_{C,P}$ = 15.8 Hz, *ipso*-C-mesityl), 126.7 (d, $^2J_{C,P}$ = 14.1 Hz, *ipso*-C-mesityl), 129.0, 129.7, 130.6, 137.5, 138.7, 138.9 (each s, C-mesityl), 139.9 (d, $J_{C,P}$ = 2.5 Hz, C-mesityl), 156.2 (d, $^1J_{C,P}$ = 39.8 Hz, C-3 or C-8), 162.1 (d, $^1J_{C,P}$ = 44.8 Hz, C-3 or C-8), 222.7 (d, $^1J_{C,P}$ = 57.2 Hz, *C*=O).

$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): δ = 53.5, 57.9 (A*MN* spin system, $^1J_{P,P}$ = 255.8 Hz, $^2J_{P,P}$ = 20.8 Hz, $^2J_{P,P}$ = 10.7 Hz, P-4, P-5), 84.4 (*A*MN spin system, $^2J_{P,P}$ = 20.8 Hz, $^2J_{P,P}$ = 10.7 Hz, P-9).

MS (FAB): *m*/*z* = 717 $[M + H]^+$.

Anal. Calcd for $C_{41}H_{55}N_2O_3P_3$ (716.82): C, 68.70; H, 7.73; N, 3.91. Found: C, 69.01; H, 7.60; N, 3.88.

### 3,5-Di-*tert*-butyl-1,2,4-oxadiphosphole (14a); Typical Procedure

**Variation A** (thermolysis of **11c)**: A pressure-Schlenk tube was charged with a solution of **11c** (430 mg, 0.67 mmol) in toluene (5 mL) and heated for 35 h at 100 °C. After cooling to r.t., all volatile materials were removed under oil pump vacuum (25 °C/5 × $10^{-1}$ mbar) and the residue was worked up by column chromatography (silica gel, *n*-pentane). Yield: 45.8 mg (0.21 mmol, 32%); colorless oil; bp 50 °C/5 × $10^{-1}$ mbar.

The previously known 1,2,4-oxazaphosphole[21,22] **13a** was identified on the basis of its $^1H$ and $^{31}P$ NMR data as obtained from the crude reaction mixture. Although its isolation by chromatography over silica gel eluting with a polar eluent (*n*-pentane–$Et_2O$ 40:1) is possible,[22] it was not attempted here.

**Variation B** (co-thermolysis of **11c** with the phosphaalkene **15a)**: A pressure-Schlenk tube was charged with a solution of **11c** (433 mg, 0.68 mmol) and phosphaalkene **15a** (178 mg, 0.68 mmol) in toluene (5 mL) and heated for 35 h at 100 °C. The work up was performed as described under variation A. Yield: 104 mg (0.48 mmol, 71%), colorless oil.

**Variation C** (one-pot synthesis starting from **2a**): In a pressure-Schlenk tube a solution of **8b** (2.04 g, 12.7 mmol) in toluene (7 mL) was added to a solution of **2a** (1.27 g, 4.22 mmol) in toluene (8 mL) at –78 °C. The mixture was allowed to warm up to r.t. and was then stirred at this temperature for 1 h. To this mixture the phosphaalkene **15a** (1.11 g, 4.22 mmol) was added and the mixture was heated for 35 h at 100 °C. The work up was performed as described under **Variation A**. Yield: 566 mg (2.62 mmol, 62% related to **2a**), colorless oil.

IR ($CCl_4$ solution): 2962 (s), 2926 (m), 2898 (m), 2863 (m), 1478 (m), 1473 (m), 1457 (m), 1392 (w), 1363 (m), 1252 (w), 1236 (w), 1199 (w), 1145 (m), 1105 (m), 1083 (m), 940 (w), 835 (w), 655 (m), 557 (w), 536 (w) $cm^{-1}$.

$^1H$ NMR ($C_6D_6$): δ = 1.33 [d, $^4J_{H,P}$ = 1.3 Hz, 9 H, 5-C(C$H_3$)], 1.38 [dd, $^4J_{H,P}$ = 2.0 Hz, $^4J_{H,P}$ = 0.4 Hz, 9 H, 3-C(C$H_3$)].

$^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 29.9 [d, $^3J_{C,P}$ = 9.3 Hz, 5-C(*C*$H_3$)$_3$], 34.5 [dd, $^3J_{C,P}$ = 11.9 Hz, $^3J_{C,P}$ = 6.8 Hz, 3-C(*C*$H_3$)$_3$], 37.0 [dd, $^2J_{C,P}$ = 16.5 Hz, $^2J_{C,P}$ = 14.0 Hz, 3-*C*(CH$_3$)$_3$], 40.4 [dd, $^2J_{C,P}$ = 14.4 Hz, $^3J_{C,P}$ = 1.7 Hz, 5-*C*(CH$_3$)$_3$], 211.2 (dd, $^1J_{C,P}$ = 69.5 Hz, $^1J_{C,P}$ = 64.4 Hz, C-3), 223.1 (dd, $^1J_{C,P}$ = 65.3 Hz, $^2J_{C,P}$ = 5.9 Hz, C-5).

$^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 122.0 (d, $^2J_{P,P}$ = 24.4 Hz, P-4), 313.9 (d, $^2J_{P,P}$ = 24.4 Hz, P-2).

MS (EI, 70 eV): *m*/*z* (%) = 216 (33) $[M]^+$, 201 (22) $[M – Me]^+$, 169 (9), 159 (14), 131 (37), 116 (10), 85 (7), 69 (12), 57 (100) $[C_4H_9]^+$, 55 (8), 43 (5), 41 (86).

Anal. Calcd for $C_{10}H_{18}OP_2$ (216.20): C, 55.56; H, 8.39. Found: C, 55.49; H, 8.58.

### 3,5-Bis(1,1-dimethylpropyl)-1,2,4-oxadiphosphole (14b); Typical Procedure

Prepared according to **Variation B** (co-thermolysis of **11d** with the phosphaalkene **15b)**: A pressure-Schlenk tube was charged with a solution of **11d** (302 mg, 0.44 mmol) and phosphaalkene **15b** (123 mg, 0.44 mmol) in toluene (5 mL) and heated for 25 h at 100 °C. The work up was performed as described under **Variation A** for **14a**. Yield: 74.5 mg (0.31 mmol, 69%); colorless oil.

IR ($CCl_4$ solution): 2965 (s), 2921 (m), 2877 (m), 1466 (m), 1461 (m), 1385 (m), 1379 (m), 1362 (m), 1300 (w), 1217 (w), 1172 (w), 1141 (w), 1107 (w), 1051 (w), 1009 (w), 949 (w), 653 (w) $cm^{-1}$.

$^1H$ NMR ($C_6D_6$): δ = 0.70 [td, $^3J_{H,H}$ = 7.4 Hz, $^5J_{H,P}$ = 0.4 Hz, 3 H, C(CH$_3$)$_2$CH$_2$C*H*$_3$], 0.77 [t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C(CH$_3$)$_2$CH$_2$C*H*$_3$], 1.32 [d, $^4J_{H,P}$ = 1.4 Hz, 6 H, 5-C(C*H*$_3$)$_2$CH$_2$CH$_3$], 1.34 [dd, $^4J_{H,P}$ = 2.3 Hz, $^4J_{H,P}$ = 0.7 Hz, 6 H, 3-C(C*H*$_3$)$_2$CH$_2$CH$_3$], 1.66 [qd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,P}$ = 1.1 Hz, 2 H, C(CH$_3$)$_2$C*H*$_2$CH$_3$], 1.68 [qd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,P}$ = 0.7 Hz, 2 H, C(CH$_3$)$_2$C*H*$_2$CH$_3$].

$^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 9.2 [d, $^4J_{C,P}$ = 1.7 Hz, 5-C(CH$_3$)$_2$CH$_2$*C*H$_3$], 9.3 [dd, $^4J_{C,P}$ = 1.7 Hz, $^4J_{C,P}$ = 1.3 Hz, 3-C(CH$_3$)$_2$CH$_2$*C*H$_3$], 27.5 [d, $^3J_{C,P}$ = 10.6 Hz, 5-C(*C*H$_3$)$_2$CH$_2$CH$_3$], 31.7 [dd, $^3J_{C,P}$ = 13.6 Hz,, $^3J_{C,P}$ = 6.8 Hz, 3-C(*C*H$_3$)$_2$CH$_2$CH$_3$], 35.1 [dd, $^3J_{C,P}$ = 5.7 Hz, $^4J_{C,P}$ = 1.1 Hz, 5-C(CH$_3$)$_2$*C*H$_2$CH$_3$], 39.2 [*pseudo* t, $^3J_{C,P}$ = 7.0 Hz, 3-C(CH$_3$)$_2$*C*H$_2$CH$_3$], 40.2 [dd, $^2J_{C,P}$ = 15.3 Hz, $^2J_{C,P}$ = 12.3 Hz, 3-*C*(CH$_3$)$_2$CH$_2$CH$_3$], 43.8 [dd, $^2J_{C,P}$ = 13.1 Hz, $^3J_{C,P}$ = 1.7 Hz, 5-*C*(CH$_3$)$_2$CH$_2$CH$_3$], 209.3 (dd, $^1J_{C,P}$ = 69.9 Hz, $^1J_{C,P}$ = 64.8 Hz, C-3), 222.2 (dd, $^1J_{C,P}$ = 65.3 Hz, $^2J_{C,P}$ = 6.4 Hz, C-5).

$^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 127.3 (d, $^2J_{P,P}$ = 23.9 Hz, P-4), 316.4 (d, $^2J_{P,P}$ = 23.9 Hz, P-2).

MS (EI, 70 eV): *m*/*z* (%) = 244 (48) $[M]^+$, 215 (100) $[M – Et]^+$, 145 (17), 71 (75), 57 (5), 55 (26), 43 (73), 41 (38).

Anal. Calcd for $C_{12}H_{22}OP_2$ (244.25): C, 59.01; H, 9.08. Found: C, 59.01; H, 9.23.

### 3,5-Bis(1-methylcyclopentyl)-1,2,4-oxadiphosphole (14c)

Prepared according to **Variation B** (co-thermolysis of **11e** with the phosphaalkene **15c)**: A pressure-Schlenk tube was charged with a solution of **11e** (192 mg, 0.27 mmol) and phosphaalkene **15c** (77.1 mg, 0.27 mmol) in toluene (5 mL) and heated for 23 h at 100 °C. The work-up was performed as described under **Variation A** for **14a**. Yield: 48.4 mg (0.18 mmol, 68%); colorless oil.

IR ($CCl_4$ solution): 2959 (vs), 2869 (s), 1460 (m), 1448 (s), 1377 (sh), 1372 (m), 1133 (w), 1082 (w), 630 (w) $cm^{-1}$.

$^1$H NMR ($C_6D_6$): δ = 1.39 (d, $^4J_{H,P}$ = 1.2 Hz, 3 H, 5-C*H*$_3$-cyclopentyl), 1.40 (dd, $^4J_{H,P}$ = 1.7 Hz, $^4J_{H,P}$ = 0.4 Hz, 3 H, 3-C*H*$_3$-cyclopentyl), 1.49–1.81 (m, 12 H, C*H*$_2$-cyclopentyl), 1.89–2.08 (m, 2 H, C*H*$_2$-cyclopentyl), 2.09–2.32 (m, 2 H, C*H*$_2$-cyclopentyl).

$^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 24.4 (dd, $^4J_{C,P}$ = 1.7 Hz, $^4J_{C,P}$ = 0.8 Hz, 5-C-3′- or 5-C-4′-cyclopentyl), 25.2 (d, $^4J_{C,P}$ = 1.3 Hz, 3-C-3′- or 3-C-4′-cyclopentyl), 27.8 (d, $^3J_{C,P}$ = 9.3 Hz, 5-*C*H$_3$-cyclopentyl), 32.1 (dd, $^3J_{C,P}$ = 10.6 Hz, $^3J_{C,P}$ = 7.2 Hz, 3-*C*H$_3$-cyclopentyl), 40.5 (d, $^3J_{C,P}$ = 8.5 Hz, 5-C-2′- or 5-C-5′-cyclopentyl), 44.2 (dd, $^3J_{C,P}$ = 11.2 Hz, $^3J_{C,P}$ = 6.1 Hz, 3-C-2′- or 3-C-5′-cyclopentyl), 47.6 (dd, $^2J_{C,P}$ = 15.7 Hz, $^2J_{C,P}$ = 13.1 Hz, 3-C-1′-cylopentyl), 51.8 (dd, $^2J_{C,P}$ = 13.6 Hz, $^3J_{C,P}$ = 2.1 Hz, 5-C-1′-cylopentyl), 210.1 (dd, $^1J_{C,P}$ = 69.1 Hz, $^1J_{C,P}$ = 64.0 Hz, C-3), 222.9 (dd, $^1J_{C,P}$ = 63.8 Hz, $^2J_{C,P}$ = 6.1 Hz, C-5).

$^{31}$P{$^1$H} NMR ($C_6D_6$): δ = 124.0 (d, $^2J_{P,P}$ = 23.7 Hz, P-4), 315.1 (d, $^2J_{P,P}$ = 23.7 Hz, P-2).

MS (EI, 70 eV): *m*/*z* (%) = 268 (79) $[M]^+$, 253 (11) $[M - Me]^+$, 221 (24), 185 (18), 157 (61), 142 (43), 119 (10), 117 (10), 11 (6), 95 (28), 93 (21), 91 (11), 83 (79), 81 (11), 79 (12), 77 (8), 69 (8), 67 (29), 55 (94), 53 (22), 47 (11), 41 (100).

Anal. Calcd for $C_{14}H_{22}OP_2$ (268.27): C, 62.68; H, 8.27. Found: C, 62.57; H, 8.28.

**5a,9a-Di-*tert*-butyl-3,8-dimesityl-[1,2,4]oxazaphospholo-[4′,5′:2,3][1,2,4]oxadiphospholo[4,5-*d*][1,2,4]oxazaphosphole (17)**

To a solution of the oxadiphosphole **14a** (119 mg, 0.55 mmol) in toluene (5 mL) was added dropwise a solution of **8b** (177 mg, 1.10 mmol) in toluene (5 mL) under magnetic stirring at –78 °C. After warming to r.t. the solvent was removed under oil-pump vacuum (25 °C/$10^{-3}$ mbar), the residue was taken up in $Et_2O$ (20 mL) and filtered over Celite. The filtrate was concentrated under oil-pump vacuum (25 °C/$10^{-3}$ mbar) and cooled to –25 °C to induce crystallization. Yield: 267 mg (0.50 mmol, 90%); colorless needles; mp 132 °C (decomp).

IR (KBr): 2953 (vs), 2915 (s), 2864 (s), 1609 (s), 1569 (w), 1545 (m), 1475 (s), 1458 (s), 1421 (m), 1392 (s), 1377 (m), 1363 (s), 1297 (w), 1238 (m), 1224 (m), 1165 (w), 1067 (s), 1039 (m), 1033 (m), 1000 (s), 982 (m), 954 (m), 921 (s), 862 (s), 850 (s), 812 (m), 783 (s), 734 (m), 643 (m), 624 (w), 604 (m), 593 (m), 565 (w), 553 (m), 534 (w), 522 (w) $cm^{-1}$.

$^1$H NMR ($CD_2Cl_2$): δ = 1.13, 1.14, [each s, 9 H, C(C*H*$_3$)$_3$], 2.30, 2.32, (each s, 3 H, *ortho*-C*H*$_3$-mesityl), 2.34 (s, 6 H, *ortho*-C*H*$_3$-mesityl), 2.55, 2.56 (each s, 3 H, *para*-C*H*$_3$-mesityl), 6.94, 6.95 (each s, 2 H, H-mesityl).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 20.7 (d, $^4J_{C,P}$ = 5.1 Hz, *ortho*-*C*H$_3$-mesityl), 20.9 (s, *ortho*-*C*H$_3$-mesityl), 21.0 (s, *ortho*-*C*H$_3$-mesityl), 22.0 (s, *para*-*C*H$_3$-mesityl), 22.2 (s, *para*-*C*H$_3$-mesityl), 25.4 [d, $^3J_{C,P}$ = 6.4 Hz, 5a-C(*C*H$_3$)$_3$], 28.0 [*pseudo* t, $^3J_{C,P}$ = 9.5 Hz, 9a-C(*C*H$_3$)$_3$], 38.5 [*pseudo* t, $^2J_{C,P}$ = 23.5 Hz, 9a-*C*(CH$_3$)$_3$], 40.9 [dd, $^2J_{C,P}$ = 24.8 Hz, $^3J_{C,P}$ = 4.5 Hz, 5a-*C*(CH$_3$)$_3$], 122.7 (*pseudo* t, $^1J_{C,P}$ = 54.0 Hz, C-9a), 126.4 (d, $^2J_{C,P}$ = 16.1 Hz, *ipso*-C-mesityl), 126.8 (d, $^2J_{C,P}$ = 14.8 Hz, *ipso*-C-mesityl), 128.9, 129.9, 137.6, 138.0, 138.9, 139.0 (each s, C-mesityl), 140.0 (dd, $^1J_{C,P}$ = 34.5 Hz, $^2J_{C,P}$ = 19.3 Hz, C-5a), 157.6 (d, $^1J_{C,P}$ = 43.2 Hz, C-3 or C-8), 160.6 (d, $^1J_{C,P}$ = 61.9 Hz, C-3 or C-8).

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 31.3 (d, $^2J_{P,P}$ = 1.5 Hz, P-9), 156.7 (d, $^2J_{P,P}$ = 1.5 Hz, P-4).

MS (FAB): *m*/*z* = 539 $[M + H]^+$.

Anal. Calcd for $C_{30}H_{40}N_2O_3P_2$ (538.60): C, 66.90; H, 7.49; N, 5.20. Found: C, 66.68; H, 7.81; N, 5.32.

**Crystal Structure Analysis of 11c**:[23] Crystal Data: $C_{35}H_{49}N_2O_3P_3$, STOE Imaging Plate Diffraction System, graphite monochromator, MoK$_\alpha$ radiation (λ = 0.71073 Å), cell determination and refinement by STOE programs Version 2.75, structure solution by direct methods (SHELXS-97[24]) and structure refinement by SHELXL-97,[25] hydrogen atoms were included in the refinement using riding models. $C_{35}H_{49}N_2O_3P_3$; $M$ = 638.67 $gmol^{-1}$; orthorhombic; space group Pbca (No. 61); lattice constants $a$ = 9.5560(19), $b$ = 21.160(4), $c$ = 36.096(7) Å, $V$ = 7299(3) Å$^3$; $Z$ = 8; $D_{cal.}$ = 1.162 Mg/m$^3$; $\mu$ = 1.97 $cm^{-1}$; $T$ = 293(2) K; crystal size 0.30 × 0.20 × 0.15 mm$^3$; 2.01 ≤ Θ ≤ 25.20°. 39865 reflections collected, 6358 independent reflections ($R_{int.}$ = 0.2159); 388 parameters; $w^{-1}$ = [σ$^2$($F_o^2$) + (0.0085P)$^2$ + 0.56P] and $P$ = [($F_o^2$) + 2$F_c^2$]/3; $R^1$ = 0.0706, $wR^2$ = 0.1155 for 2080 reflections with $I$ > 2σ(I) and $R^2$ = 0.1848, $wR^2$ = 0.1321 for all data; residual electron density 226 $enm^{-3}$ and –196 $enm^{-3}$, $S$ = *GOF* (on $F^2$) = 0.851.

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