Tropone as Reaction Partner for Kinetically Stabilized Phosphaalkynes. Synthesis and Cycloaddition Behavior of a Tetracyclic Phosphorus–Carbon Cage Compound†

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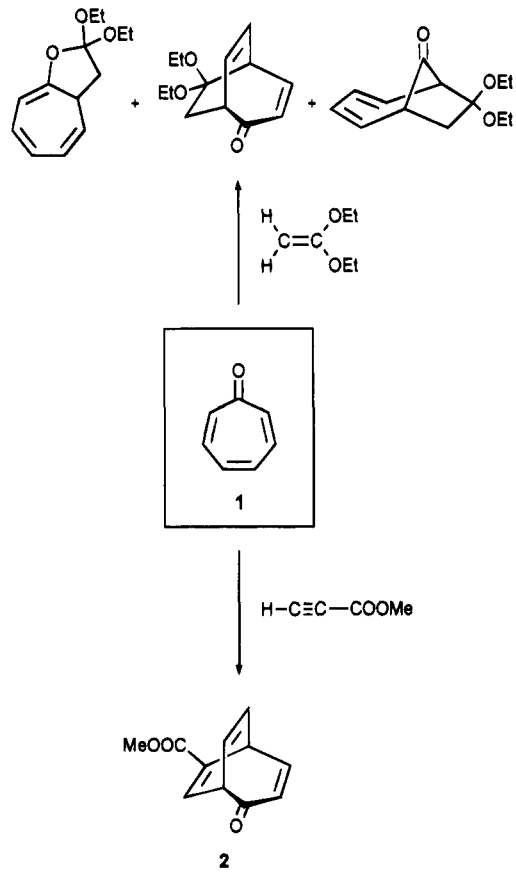
Received April 12, 1995®

Tropone (**1**), with its 8π-electron system, and the kinetically stabilized phosphaalkynes **3a–c** undergo cycloaddition reactions, in dependence on the stoichiometry and reaction conditions, to furnish co-oligomeric phosphorus–carbon cage compounds **5a,b** or **9a–c**, respectively. When tropone (**1**) is subjected to thermolysis conditions in the presence of an excess of the phosphaalkyne **3a** or **b** but in the absence of a solvent, the homo-Diels–Alder adducts **5a** or **b** are isolated in 21% or 23% yield, respectively. The peri- and regioselectivities observed for this two-step reaction sequence can be precisely defined on the basis of semiempirical MO calculations (frontier orbital theory, PM3). On the other hand, when tropone (**1**) is heated with equimolar amounts of the phosphaalkynes **3a–c** in toluene, the pentacyclic compounds **9a–c** are formed in 51–64% yields as subsequent products of the [8 + 2] cycloaddition of tropone with the tetracyclic species **5a–c**. Diels-Alder or, respectively, 1,3-dipolar cycloaddition reactions of the tetracyclic species **5a** with 2,3-dimethylbutadiene or mesitylnitrile oxide give rise to polycyclic products with differing skeletons (**11** or **13** and **15**, respectively). An X-ray crystal structure analysis of the cage compound **9a** has been performed.

Introduction

The pronounced potential for cycloaddition reactions of the 8π-electron system of tropone (**1**) has facilitated the preparations of numerous polycyclic systems with various structures[1–3] and frequently provided an access to important intermediates in natural product synthesis.[4,5] The Hückel aromaticity deduced solely from the planar structure of tropone is only of secondary importance,[6] so that the description of tropone as a polyenone is justified. The *s-cis* conformation of the endocyclic diene unit in **1**, predetermined by the ring system, is favorable for cycloaddition reactions in which, in addition to thermal reaction conditions,[1] photolytic processes have also been successful in individual cases.[3,7] In this context, the Diels–Alder reaction is of major significance. Although tropone (**1**) possesses a relatively electron-poor, carbocyclic triene unit, it reacts with both electron-rich and electron-poor dienophiles to produce bicyclic products (Scheme 1). Alkynes as well as variously-substituted alkenes have been employed successfully as reaction partners. With the exception of the intramolecular cycloaddition reactions of appropriately substituted tropones,[4] only low peri-, regio-, and stereoselectivities are observed in the reactions with alkenes so that the target molecules are often produced in small amounts and require tedious separation processes.[8,9] The situation

Scheme 1



† Contribution to Organophosphorus Compounds. 101. For Part 100 see: Regitz, M.; Bergsträsser, U.; Hoffmann, A. *Chem. Rev.*, in press.

® Abstract published in *Advance ACS Abstracts,* August 1, 1995.

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(6) (a) Redington, R. L.; Latimer, S. A.; Bock, C. W. *J. Phys. Chem.* **1990**, *94*, 163–169. (b) Sanna, N.; Ramondo, F.; Bencivenni, L. *J. Mol. Struct.* **1994**, *318*, 217–235.

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changes, however, with the use of alkynes as 2π components.[10] Thus, for example, the homobarrelenone **2** was obtained selectively.[11]

Pericyclic reactions are also dominant in the chemistry of the phosphaalkynes which thus differ clearly from the homologous nitriles.[12]

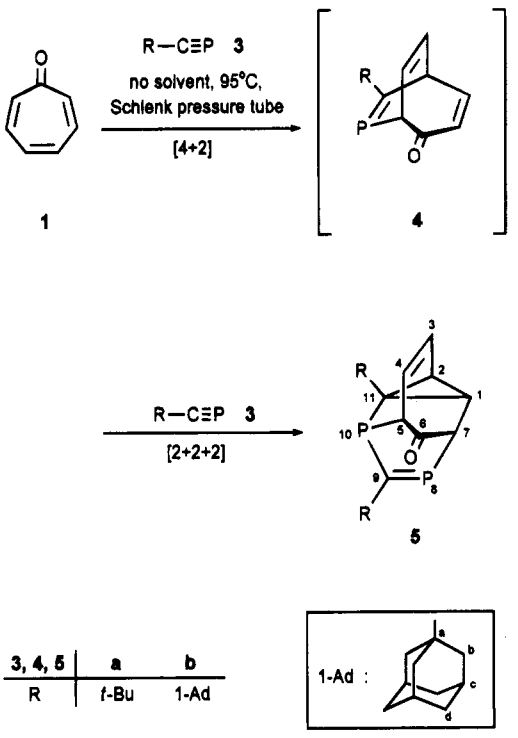
In this context, we became interested in the question of how kinetically stabilized phosphaalkynes **3**, RC≡P, would react with the carbocyclic system of tropone (**1**). Under particular consideration of the complementary cycloaddition behavior of the two species and the directing influence of the bulky phosphaalkyne substituents, we felt that such reactions would provide a selective access to cagelike organophosphorus compounds. In the present paper, we report on the preparation of cooligomeric cage compounds on the basis of tropone (**1**) and phosphaalkynes **3** resulting from unusual rearrangement processes.

Results and Discussion

When tropone (**1**)[13] is heated at 95 °C in the presence of a 7- to 8-fold excess of *tert*-butylphosphaacetylene (**3a**) and the reaction is stopped after 4.5 h, the tetracyclic cage compound **5a** can be isolated in 21% yield after column chromatographic workup (Scheme 2).[14]

The fact that two molecules of *t*-BuC≡P (**3a**) have apparently reacted with one molecule of tropone (**1**) can be deduced unequivocally from the elemental analysis and mass spectral data. Unambiguous confirmation for the presence of the $\lambda^3\sigma^2$-phosphorus atom P-8 is provided by the low field position of the $^{31}P\{^1H\}$ NMR signal at δ = 323.1 ppm. This signal is split into a doublet by a $^2J_{P,P}$ coupling with the $\lambda^3\sigma^3$-phosphorus atom P-10 which gives a signal at δ = −38.9 ppm. The presence of a phosphorus–phosphorus single bond can be discounted on account of the small magnitude (14.8 Hz) of the $J_{P,P}$ coupling constant.[15] Further information and final confirmation for the constitution of **5a** are provided by homo- and heteronuclear correlated 2D NMR and ^{13}C NMR spectroscopy (see supporting information). Thus, five pronounced cross peaks are observed in the ^1H–^1H-COSY NMR spectrum demonstrating the five $^3J_{H,H}$ spin–spin interactions. Furthermore, the chemical shifts of the six skeletal protons are in harmony with the proposed structure for the tetracyclic system of **5a**. The additional

Scheme 2



signal splittings result from ^{31}P,^1H couplings and can be detected in the inverse correlated ^{31}P–^1H 2D NMR spectrum. The expected $^2J_{P,H}$ values for the protons H-5 (19.3 Hz) and H-7 (18.9 Hz) are seen in this spectrum.[15] The functional groups can be identified in the $^{13}C\{^1H\}$ NMR spectrum on the basis of their typical shift and coupling constant values. The carbon atom C-9 experiences a pronounced deshielding (δ = 229.2 ppm) owing to the π-bond with the $\lambda^3\sigma^2$-phosphorus atom P-8. The spin multiplicity (dd) and the $J_{C,P}$ coupling constants (67.6 and 50.2 Hz) reveal the direct neighborhood to the two phosphorus atoms. The $^1J_{C,H}$ coupling constants of the two CH moieties (C-1 and C-2) of the cyclopropane unit (157.4 and 160.0 Hz) are also characteristic, as is the carbonyl ^{13}C signal at δ = 202.0 ppm. Finally, an intense carbonyl band at ν = 1688 cm^{-1} can be seen in the IR spectrum of **5a**.

The adamantyl-substituted tetracyclic compound **5b** was isolated in 23% yield. Apart from the different substituents (1-adamantyl in place of *tert*-butyl), the NMR data of **5b** agree well with those of **5a**.

The compositions of the tetracyclic compounds **5a** and **b** are suggestive of a two-step reaction mechanism. The first step implies a Diels–Alder reaction with reverse electron demand[16] in which the phosphaalkynes **3a** and **b** act as 2π-components and tropone (**1**) acts as a 4π-component. Semiempirical molecular orbital calculations at the PM3 level for the example of the *tert*-butyl-substituted compounds **3a** and **4a** as well as **1** provide further insights.[17] The periselectivity can be derived on the basis of the dominating LUMO(tropone **1**) − HOMO(phosphaalkyne **3a**) interaction (Figure 1). Since the carbonyl function lies in the nodal plane of the LUMO-

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(13) In comparison to the parent compound tropone (**1**), the derivatives 2-butyltropone, 2-phenyltropone, 2-methyltropone, and 4-methyltropone revealed a different reactivity toward *t*-BuC≡P (**3a**); thus, after thermolysis in toluene only weak $^{31}P\{^1H\}$ NMR signals indicating the presence of cooligomers could be observed. In these cases cyclotetramerization of *t*-BuC≡P (**3a**) predominates. α-Tropolone, 2-methoxytropone, 2-chlorotropone, as well as tropothione did not undergo any reaction with *t*-BuC≡P (**3a**), even after heating of the reaction mixtures for several days at elevated temperatures.
(14) When a solvent is used or the procedure is carried out at elevated temperatures a 2:2 adduct is generated (**9a**). The same result was observed when the reaction mixture was heated at 95 °C for more than 5 h in the absence of a solvent.
(15) Berger, S.; Braun, S.; Kalinowski H.-O. *NMR-Spektroskopie von Nichtmetallen*; Thieme: Stuttgart, 1993; Vol. 3.
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(17) The semiempirical MO calculations were carried out using VAMP (Erlangen Vectorized Molecular Orbital Package; Ver. 4.50), implemented on a Siemens-Nixdorf workstation. For PM3 see: (a) Stewart, J. J. P *J. Comput. Chem.* **1989**, *10*, 209–220 and 221–264. (b) Stewart, J. J. P *J. Comput. Chem.* **1991**, *12*, 320–341. (c) Stewart, J. J. P. *J. Comp.-Aided Mol. Design* **1990**, *4*, 1–105.

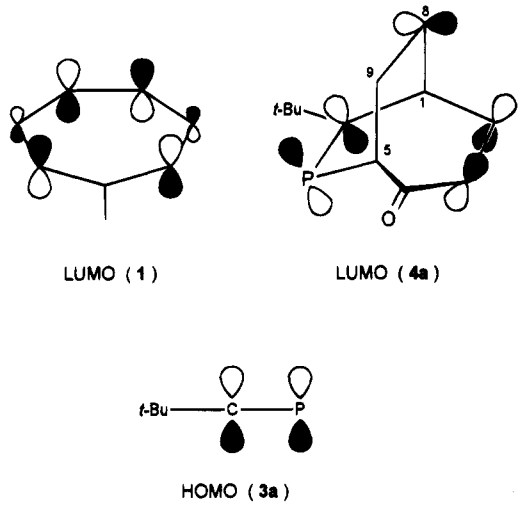


Figure 1. Decisive frontier orbitals of tropone (**1**), *tert*-butylphosphaacetylene (**3a**) and phosphahomobarrelenone **4a** using PM3 calculations.[17]

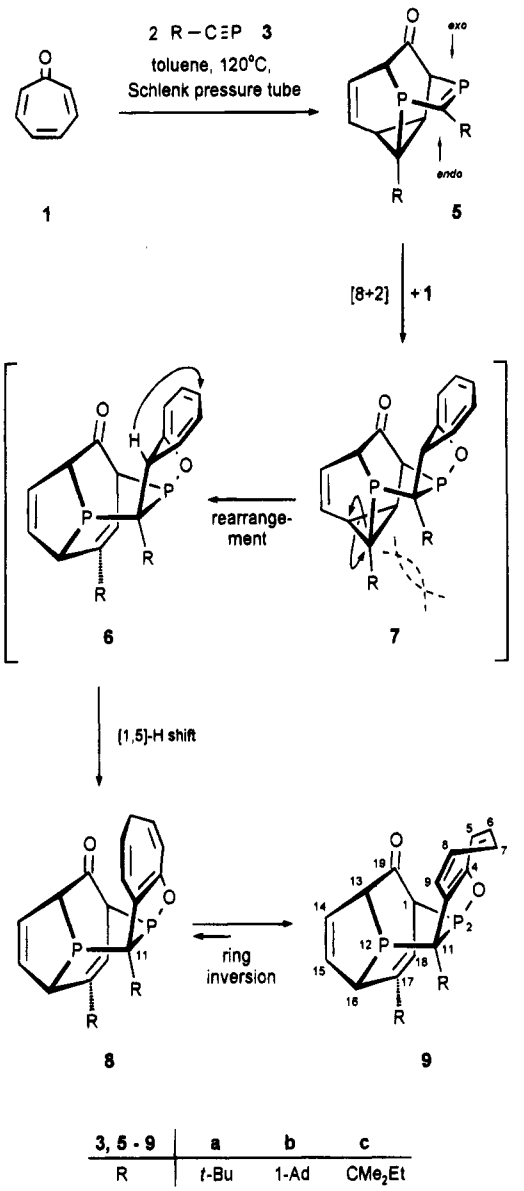
(**1**), it is not available for an [8 + 2] cycloaddition. In addition to charge effects (net atomic charges), steric factors (*tert*-butyl group) are most certainly also responsible for the regiochemistry of the initial [4 + 2] cycloaddition. Although the phosphahomobarrelenone **4a** could not be isolated, evidence for its existence can be found in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution (signal at δ = 238.6 ppm).

As is a common finding in the chemistry of phosphaalkynes,[18] the second step of the sequence can be considered as a [2 + 2 + 2] cycloaddition (homo-Diels–Alder reaction).[19] The semiempirically (PM3) calculated LUMO(**4a**) clearly shows that the orbital-controlled attack of the second molecule of **3a** cannot occur at the secondary bridge (C-1/C-8/C-9/C-5) since the orbital coefficients at C-9 tend toward zero (Figure 1).

When the reaction of tropone (**1**) with *tert*-butylphosphaacetylene (**3a**) is performed in toluene solution in a molar ratio **1**:**3a** = 2:2.6 with the reaction time (5 d) and temperature (120 °C) being increased additionally, the tetracyclic product **5a** is not obtained after column chromatographic workup; instead, the pentacyclic cage compound **9a** is isolated selectively in 52% yield (Scheme 3).

The composition of **9a** from equal proportions of the starting materials **1** and **3a** is apparent from the elemental analysis and mass spectral data. The molecular ion peak is observed at m/z = 412, thus confirming the 2:2 structure of **9a**. The ^{31}P NMR signals for the two phosphorus atoms P-2 and P-12 in **9a** are observed at δ = 141.1 and 35.8 ppm in the region typical for $\lambda^3\sigma^3$-phosphorus atoms,[20] although, surprisingly, no $^2J_{P,P}$ coupling can be detected. The assignment of these two ^{31}P NMR signals was achieved by evaluation of heteronuclear irradiation experiments ($^1H\{^{31}P\}$ NMR). Both

Scheme 3



3, 5 - 9	a	b	c
R	*t*-Bu	1-Ad	CMe_2Et

the ^1H and the ^{13}C NMR data are in accord with the proposed constitution,[21] but do not permit any concrete conclusions about the conformation of the annelated cycloheptatrienone ring to be drawn. A rapid ring inversion at room temperature must be assumed;[22] however, the equilibrium **8a**/**9a** should lie on the side of **9a** since the calculated (PM3[17]) enthalpy of formation of **9a** is about 2.9 kcal/mol lower.[23]

The more favorable conformer **9a**, as calculated by the PM3 method, also represents the result of an X-ray crystal structure analysis (Figure 2).[24] In contrast to the

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(20) *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby J. C., Ed.; CRC Press: Boca Raton, 1991.

(21) A ^1H–^1H-COSY 45 NMR spectra of the pentacyclic compound **9c** was recorded confirming the proposed constitution (supporting information).

(22) Anet, F. A. L.; Anet, R. In *Dynamic NMR Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 543–619.

(23) If the PM3 calculations of **8a** and **9a** are performed using hydrogen atoms instead of the *tert*-butyl groups, the energy gap disappears; this is indicative of repulsive interactions between the *tert*-butyl group at C-11 and the annelated cycloheptatriene ring in **8a**.

(24) The authors have deposited atomic coordinates, bond lengths, and angles for the structure of **9a** with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallograhic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

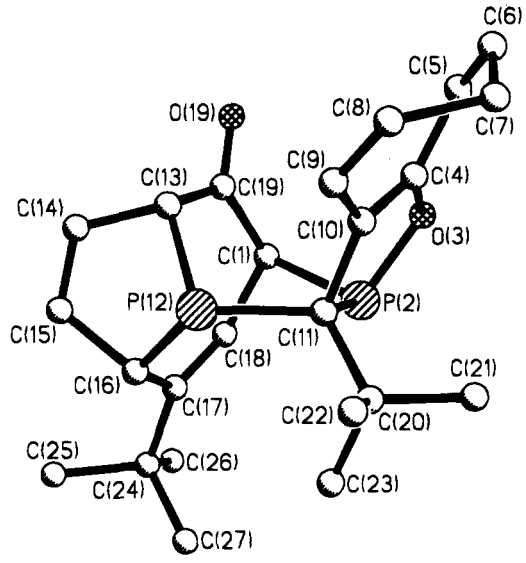


Figure 2. Molecular structure of pentacycle **9a**.[24]

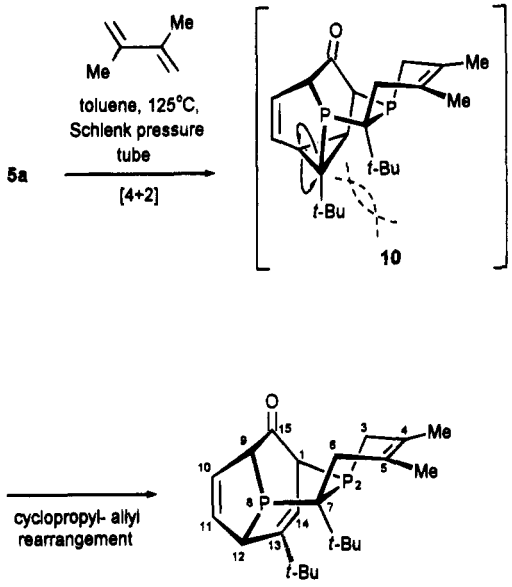
tetracyclic product **5a**, the pentacyclic system **9a** cannot formally be dissected into its starting materials without difficulty. A C_3OP five-membered ring can be recognized easily; this is apparently formed by the [8 + 2] cycloaddition of tropone to the PC double bond in **5a**. The fragment P-2/C-11/*t*-Bu can be assigned to the original phosphaalkyne unit, while the fate of the second phosphaalkyne molecule cannot directly be deduced from the molecular structure. From Figure 2, it can be seen that the second *tert*-butyl group is at carbon C-17 and thus no longer on a carbon atom in an α-position to the phosphorus atom P-12.

^{31}P NMR monitoring of the conversion shown in Scheme 3 reveals that the pentacyclic compound **9a** is a subsequent product of the reaction of the tetracyclic species **5a** with tropone (**1**). The stereoselective [8 + 2] cycloaddition of the second equivalent of tropone (**1**) to the PC double bond in the tetracyclic species **5a** leads to an unstable, hexacyclic intermediate **7a**. Repulsive interactions between the two *tert*-butyl groups in **7a** induce a disrotatory cyclopropyl–allyl rearrangement to furnish the pentacyclic system **6a**. Sigmatropic hydrogen shift and ring inversion steps then complete the reaction sequence (**6a** → **8a** → **9a**).

2-(1-Adamantyl)phosphaacetylene (**3b**) (yield of **9b**, 64%) and 2-(2,2-dimethyl-1-propyl)phosphaacetylene (**3c**) (yield of **9c**, 51%) react analogously with tropone (**1**). Product **9b** differs from **9a** and **c** in its lower solubility in common solvents.

When 2,3-dimethylbutadiene is employed in place of tropone as the cycloaddition partner, a comparable reaction sequence is observed (Scheme 4). When the tetracyclic compound **5a** is allowed to react with 2,3-dimethylbutadiene at 125 °C, cycloaddition occurs regio- and stereoselectively at the PC double bond. The intermediate **10** cannot be detected experimentally but is assumed to undergo stabilization by ring opening to form the tetracyclic final product **11** which is isolated in 70% yield. In this case also, the cyclopropyl–allyl rearrangement is a consequence of the steric interactions between the two *tert*-butyl groups in the putative primary adduct **10**. The increase in coordination at the originally $\lambda^3\sigma^2$-phosphorus atom in **5a** is apparent from the dramatic high field shift of the corresponding ^{31}P NMR signal (P-2) in **11** (δ = 323.1 ppm in **5a**, 1.4 ppm in **11**). Both ^1H and ^{13}C NMR data clearly demonstrate the disappearance of the three-membered ring unit in favor of a CC double bond.

Scheme 4



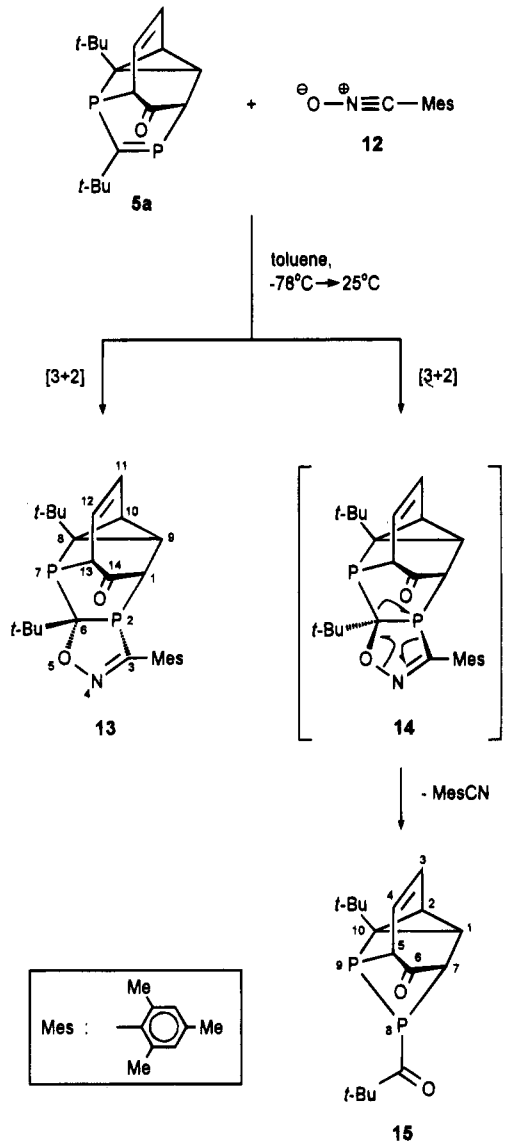
The 1,3-dienes tested to date, namely tropone (**1**) and 2,3-dimethylbutadiene, undergo ready cycloaddition to the PC double bond in **5a** upon heating (but not at room temperature); however, the attack is *exo*-selective, apparently for steric reasons (Scheme 3).

When the tetracyclic compound **5a** is allowed to react with mesitylnitrile oxide (**12**) at low temperature (−78 °C) (Scheme 5), the formation of two major products, **13** and **15**, can be demonstrated by ^{31}P NMR spectroscopy, and the compounds can be separated by column chromatography. Product **13** is obtained in the form of colorless needles (24% yield) upon concentration of the second petroleum ether/ether fraction. Elemental analysis and mass spectral data are indicative of an addition of the 1,3-dipole **12** to a double bond in **5a**. The participation of the PC double bond in this [3 + 2] cycloaddition is obvious from the significant high field shift of the ^{31}P NMR signal of the originally $\lambda^3\sigma^2$-phosphorus atom (δ = 38.7 ppm in **13** as compared to 323.1 ppm in **5a**). The presence of the cyclopropane element is irrevocably confirmed by the ^1H and ^{13}C NMR data. Thus, a cyclopropyl–allyl rearrangement can be excluded.[25] The postulated stereochemistry for compound **13** is supported by the consideration that only in the given configuration can repulsive interactions between the two *tert*-butyl groups be discounted.

The cage compound **15** can be eluted as the second major product (third petroleum ether/ether fraction). The elemental analysis and mass spectral data indicate an unexpected result: among others, the molecular ion peak (m/z = 322) excludes the formation of a [3 + 2] cycloadduct with a constitution isomeric to that of **13**. Instead, the results rather suggest the transfer of oxygen from **12** to the tetracyclic compound **5a**. The missing MesCN fragment can be detected as mesityl cyanide in the first eluted petroleum ether/ether fraction. The formation of the PP bond is clearly proven by the $^{31}P\{^1H\}$ NMR

(25) Compound **13** decomposes unselectively upon being heated in toluene for several hours.

Scheme 5



spectrum. Thus, an AB spin system with a characteristic $^1J_{P,P}$ coupling constant of 208.0 Hz is observed for the two phosphorus atoms. The number of signals recorded in the ^{1}H NMR spectrum together with their coupling patterns is in agreement with the proposed structure. The $^{13}C\{^1H\}$ NMR spectrum provides further evidence for the constitution of **15**. Accordingly, both carbon atoms of the carbonyl groups give signals at low field (δ = 227.2 and 195.3 ppm), and the signal at 227.2 ppm [C(O)*t*-Bu] is additionally split into a doublet by a $^1J_{C,P}$ coupling constant of 73.8 Hz. Published ^{13}C NMR data for compounds containing similar phosphino-substituted carbonyl groups are in good agreement with the values recorded for **15**.[26] As can be expected, two carbonyl bands are seen in the IR spectrum at ν = 1709 and 1648 cm^{-1}.

The mechanism apparently responsible for the formation of the tetracyclic product **15** (Scheme 5) comprises an *exo* attack of the 1,3-dipole **12** at the PC double bond in **5a**, similar to that observed in [8 + 2] cycloaddition of tropone (**1**) (cf. Scheme 3). In contrast to the latter, however, for the reaction of mesitylnitrile oxide (**12**) the primary addition gives rise to an energetically disfavored intermediate **14** (steric interactions between the two *tert*-butyl groups) which is followed by a 1,3-cycloreversion with extrusion of mesityl cyanide instead of a cyclopropyl–allyl rearrangement. The assumption of a synchronously occurring [1,2] rearrangement[27] in the basic skeleton then gives credence to the formation of the PP bond.

It can finally be concluded that kinetically stabilized phosphaalkynes, as alternative to alkenes and alkynes, represent suitable cycloaddition partners for the carbocyclic 8π-electron system of tropone (**1**). In contrast to the CC multiple bond systems, however, competition between differing cycloaddition reactions is not observed in the case of the phosphaalkynes **3**. Instead, the sequential and selective construction of organophosphorus compounds mediated by pericyclic reactions takes place.

Experimental Section

General. The reactions were carried out under argon (purity > 99.998%) in a previously baked-out and evacuated apparatus (standard Schlenk techniques). The solvents used were dried by standard procedures (toluene, Na; ether and petroleum ether 30–75 °C, Na/K alloy; dichloromethane, P_4O_{10}) and then distilled and stored under argon. Compounds **1**,[28] **3a**,[29] **3b**,[30] **3c**,[31] and **12**[32] were prepared by the published methods. **CAUTION:** if reactions are performed in Schlenk pressure tubes at elevated temperatures, additional safety shields should be used. Column chromatography was performed in water-cooled glass tubes with a positive pressure of argon on the column. The eluate was monitored with a UV absorbance detector (λ = 254 nm). Silica gel and alumina were heated for 3 h in vacuo and then deactivated with 4% water (Brockmann activity II). Melting points are uncorrected (heating rate: 3 °C/min). All NMR spectra were taken on a Bruker AMX 400 instrument. Coupling constants (J) are reported in Hertz.

9,11-Di-*tert*-butyl-8,10-diphosphatetracyclo-[5.4.0.0^{2,11}.0^{5,10}]undeca-3,8-dien-6-one (5a). A well-stirred emulsion of **1** (0.40 g, 0.37 mL, 3.77 mmol) and **3a** (2.80 g, 27.97 mmol) was heated in a Schlenk pressure tube at 95 °C and 8 bar argon pressure over a period of 4.5 h and then allowed to cool. The excess of **3a** was removed under vacuum (10^{-3} Torr) at room temperature and frozen out in a cold trap at liquid N_2 temperature. The resultant brown residue was purified by column chromatography on silica gel. Small amounts of a yellow cyclotetramer of **3a** were eluted with petroleum ether. Further elution with petroleum ether/ether (10:1) provided a yellow oil which did not contain any phosphorus ($^{31}P\{^1H\}$ NMR spectroscopy). Using petroleum ether/ether (7:1) as eluent, **5a** was obtained as a highly viscous, yellow oil. Crystallization from petroleum ether at −78 °C gave pure **5a** as a lemon yellow powder (0.24 g, 21%): mp 92–93 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −38.9 (d, $J_{P,P}$ = 14.8), 323.1 (d, $J_{P,P}$ = 14.8); ^{1}H NMR (CD_2Cl_2) δ = 0.96 (s, 9H), 1.39 (d, $J_{H,P}$ = 2.3, 9H), 1.99 (dd, $J_{H,H}$ = 7.8, 5.8, 1H), 2.20 (ddd, $J_{H,P}$ = 5.9, $J_{H,H}$ = 8.0, 7.8, 1H), 2.73 (dd, $J_{H,P}$ = 19.3, $J_{H,H}$ = 9.1, 1H), 4.25 (dd, $J_{H,P}$ = 18.9, $J_{H,H}$ = 5.8, 1H), 5.92 (ddd, $J_{H,P}$ =

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7.2, $J_{H,H}$ = 9.1, 9.0, 1H), 6.42 (ddd, $J_{H,P}$ = 3.4, $J_{H,H}$ = 9.0, 8.0, 1H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 28.9 (s), 29.9 (d, $J_{C,P}$ = 6.7), 31.5 (dd, $J_{C,P}$ = 14.5, 8.2), 33.0 (dd, $J_{C,P}$ = 4.7, 4.7), 33.2 (d, $J_{C,P}$ = 19.3), 42.9 (dd, $J_{C,P}$ = 32.4, 4.6), 44.4 (dd, $J_{C,P}$ = 19.7, 6.8), 44.9 (dd, $J_{C,P}$ = 23.3, 15.9), 58.5 (d, $J_{C,P}$ = 43.9), 122.0 (s), 132.5 (d, $J_{C,P}$ = 4.7), 202.0 (d, $J_{C,P}$ = 6.5), 229.2 (dd, $J_{C,P}$ = 67.6, 50.2); IR (Nujol) 3040, 2856, 1688 (C=O), 1390, 1234, 1108 cm^{-1}; MS (EI, 35 eV) *m/z* (rel int) 306 (100, M^+), 291 (24), 249 (74), 206 (48), 149 (55), 57 (16). Anal. Calcd for $C_{17}H_{24}OP_2$: C, 66.66; H, 7.90. Found: C, 66.75; H, 7.91.

9,11-Di-1-adamantyl-8,10-diphosphatetracyclo-[5.4.0.0^{2,11}.0^{5,10}]undeca-3,8-dien-6-one (5b). A mixture of **1** (0.14 g, 0.13 mL, 1.32 mmol) and **3b** (1.39 g, 7.80 mmol) was slowly heated to 95 °C in a Schlenk pressure tube (8 bar argon pressure) with melting of the phosphaalkyne. Under vigorous stirring the reaction mixture was kept at this temperature for 4.5 h during which time its color darkened to red-brown. After being cooled to room temperature the resulting solid was chromatographed over silica gel. From the first fraction unchanged **3b** was isolated (petroleum ether) as a colorless solid. Using petroleum ether/ether (10:1) as eluent, a yellow cyclotetramer of **3b** was obtained as a byproduct. The second yellow band (petroleum ether/ether, 5:1) was collected and evaporated to dryness to yield **5b** as a yellow solid. The crude product was taken up in toluene/petroleum ether and purified several times by recrystallization at −78 °C (0.14 g, 23%): mp 280–285 °C dec; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −41.0 (d, $J_{P,P}$ = 12.6), 324.0 (d, $J_{P,P}$ = 12.6); ^1H NMR (CD_2Cl_2) δ = 1.43–2.12 (m, 30H), 2.02 (dd, $J_{H,H}$ = 7.3, 5.8, 1H), 2.25 (ddd, $J_{H,P}$ = 6.3, $J_{H,H}$ = 7.3, 7.3, 1H), 2.70 (dd, $J_{H,P}$ = 19.3, $J_{H,H}$ = 9.2, 1H), 4.25 (dd, $J_{H,P}$ = 19.0, $J_{H,H}$ = 5.8, 1H), 5.91 (ddd, $J_{H,P}$ = 7.3, $J_{H,H}$ = 9.2, 8.9, 1H), 6.40 (ddd, $J_{H,P}$ = 3.3, $J_{H,H}$ = 8.9, 7.3, 1H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 26.8 (s), 29.2 (s), 29.2 (s), 31.6 (dd, $J_{C,P}$ = 4.7, 4.7), 34.4 (d, $J_{C,P}$ = 18.2), 36.8 (s), 37.0 (s), 42.2 (d, $J_{C,P}$ = 7.2), 43.7 (dd, $J_{C,P}$ = 32.3, 4.7), 44.0 (dd, $J_{C,P}$ = 15.6, 8.4), 44.4 (dd, $J_{C,P}$ = 20.0, 6.9), 47.2 (dd, $J_{C,P}$ = 21.8, 13.8), 58.2 (d, $J_{C,P}$ = 43.6), 122.2 (s), 132.4 (d, $J_{C,P}$ = 5.1), 202.3 (d, $J_{C,P}$ = 6.5), 229.4 (dd, $J_{C,P}$ = 67.6, 50.1); IR (KBr) 3022, 2902, 2846, 1686 (C=O), 1448 cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 462 (40, M^+), 135 (100). Repeated microanalysis did not give satisfactory results for carbon.

11,17-Di-*tert*-butyl-3,2,12-oxadiphosphapentacyclo-[11.5.1.0^{2,11}.0^{4,10}.0^{12,16}]nonadeca-4(10),5,8,14,17-pentaen-19-one (9a). A pale yellow solution of **1** (3.21 g, 2.93 mL, 30.25 mmol) and **3a** (3.93 g, 39.26 mmol) in 15 mL of toluene was heated in a Schlenk pressure tube at 120 °C and 8 bar argon pressure for 5 d. The solvent and excess of **3a** were then removed under vacuum to furnish a brown oily residue which was subjected to flash chromatography (alumina, ether). The resultant light brown solid was purified by chromatography over silica gel. Using petroleum ether as eluent, a small amount of an oligomeric byproduct was separated. Finally, **9a** was eluted with ether to provide an analytically pure white powder. Recrystallization from ether at −3 °C gave **9a** as colorless prisms (4.20 g, 52%): mp 201–203 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 35.8 (s), 141.1 (s); ^1H NMR ($CDCl_3$) δ = 1.07 (s, 9H), 1.08 (s, 9H), 1.83 (ddd, $J_{H,H}$ = 13.0, 6.3, 6.3, 1H), 2.64 (ddd, $J_{H,H}$ = 13.0, 7.3, 7.1, 1H), 3.11 (dd, $J_{H,P}$ = 18.0, $J_{H,H}$ = 5.4, 1H), 3.79 (dd, $J_{H,P}$ = 16.0, $J_{H,H}$ = 3.9, 1H), 3.83 (dd, $J_{H,P}$ = 2.8, $J_{H,H}$ = 8.8, 1H), 5.16 (ddd, $J_{H,H}$ = 9.5, 7.3, 6.3, 1H), 5.24 (dd, $J_{H,P}$ = 4.9, $J_{H,H}$ = 8.8, 1H), 5.42 (ddd, $J_{H,H}$ = 9.7, 7.1, 6.3, 1H), 5.47 (ddd, $J_{H,P}$ = 10.9, $J_{H,H}$ = 5.4, 5.4, 1H), 6.05 (d, $J_{H,H}$ = 9.7, 1H), 6.24 (ddd, $J_{H,P}$ = 10.5, $J_{H,H}$ = 5.4, 3.9, 1H), 6.46 (dd, $J_{H,P}$ = 1.8, $J_{H,H}$ = 9.5, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 27.3 (dd, $J_{C,P}$ = 9.8, 8.0), 27.6 (s), 29.6 (s), 36.8 (dd, $J_{C,P}$ = 24.3, 16.7), 37.7 (d, $J_{C,P}$ = 3.9), 42.6 (dd, $J_{C,P}$ = 29.7, 3.3), 49.7 (d, $J_{C,P}$ = 9.7), 57.5 (dd, $J_{C,P}$ = 47.1, 42.6), 59.3 (d, $J_{C,P}$ = 39.4), 113.8 (d, $J_{C,P}$ = 10.2), 115.6 (s), 120.9 (s), 121.8 (d, $J_{C,P}$ = 7.1), 123.6 (d, $J_{C,P}$ = 17.6), 123.8 (s), 124.7 (d, $J_{C,P}$ = 20.4), 141.0 (dd, $J_{C,P}$ = 15.4, 4.2), 156.7 (dd, $J_{C,P}$ = 17.0, 6.2), 157.8 (dd, $J_{C,P}$ = 10.7, 2.7), 203.9 (d, $J_{C,P}$ = 4.4); IR (KBr) 3020, 2940, 2850, 1660 (C=O), 1605, 1580, 1470, 1455, 1380, 1350, 1190, 1130, 1100, 1070, 1010, 820, 800, 780, 700 cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 412 (6, M^+), 355 (13), 206 (100), 191 (60), 149 (18), 57 (18). Anal. Calcd for $C_{24}H_{30}O_2P_2$: C, 69.89; H, 7.33. Found: C, 69.54; H, 7.30.

Crystal data and summary of data collection parameters for **9a**:[24] diffractometer Siemens P4; radiation Mo Kα; M = 412.4 g/mol; monoclinic $P2_1/n$; a = 972.9(2) pm, α = 90°, b = 2292.0(5) pm, β = 104.88(3)°, c = 1006.3(2) pm, γ = 90°; V = 2.1687(8) nm^3; Z = 4; D_c = 1.263 Mg/m^3; 2Θ range 2.0–50.0°; no. of reflns collcd 4772; no. of obsd reflns 2286; R = 0.0531, wR = 0.0512.

11,17-Di-1-adamantyl-3,2,12-oxadiphosphapentacyclo-[11.5.1.0^{2,11}.0^{4,10}.0^{12,16}]nonadeca-4(10),5,8,14,17-pentaen-19-one (9b). A pale yellow solution of **1** (1.20 g, 1.10 mL, 11.31 mmol) and **3b** (2.22 g, 12.44 mmol) in 10 mL of toluene was heated in a Schlenk pressure tube at 120 °C for 4 d. During this time the color of the reaction mixture changed from yellow to brown. Upon cooling to room temperature **9b** precipitated as a white solid. After the suspension has been concentrated in vacuo, crude **9b** was filtered through a D3 sinter and washed with toluene (5 mL), ether (3 × 5 mL), and petroleum ether (3 × 10 mL). Recrystallization from CH_2Cl_2 at 4 °C gave **9b** as a colorless powder (2.06 g, 64%): mp > 280 °C dec; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 31.5 (s), 139.4 (s); ^1H NMR ($CDCl_3$) δ = 1.55–1.75 (m, 18H), 1.95–2.05 (m, 12H), 1.92 (ddd, $J_{H,H}$ = 12.9, 6.7, 6.2, 1H), 2.78 (ddd, $J_{H,H}$ = 12.9, 7.5, 7.3, 1H), 3.20 (dd, $J_{H,P}$ = 17.8, $J_{H,H}$ = 5.1, 1H), 3.93 (dd, $J_{H,P}$ = 21.2, $J_{H,H}$ = 4.1, 1H), 3.96 (dd, $J_{H,P}$ = 3.0, $J_{H,H}$ = 9.1, 1H), 5.21–5.30 (m, 2H), 5.53 (ddd, $J_{H,H}$ = 9.6, 7.3, 6.7, 1H), 5.55 (ddd, $J_{H,P}$ = 8.2, $J_{H,H}$ = 5.1, 4.0, 1H), 6.16 (d, $J_{H,H}$ = 9.6, 1H), 6.26 (ddd, $J_{H,P}$ = 10.6, $J_{H,H}$ = 4.1, 4.0, 1H), 6.55 (dd, $J_{H,P}$ = 2.6, $J_{H,H}$ = 9.5, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 28.1 (s), 28.6 (s), 28.7 (s), 36.7 (s), 36.8 (s), 38.7 (dd, $J_{C,P}$ = 22.1, 15.2), 38.9 (dd, $J_{C,P}$ = 12.0, 7.8), 39.5 (d, $J_{C,P}$ = 3.9), 41.5 (d, $J_{C,P}$ = 2.9), 42.4 (dd, $J_{C,P}$ = 29.7, 3.3), 49.9 (d, $J_{C,P}$ = 10.6), 58.9 (dd, $J_{C,P}$ = 47.2, 41.8), 59.9 (d, $J_{C,P}$ = 39.5), 114.6 (d, $J_{C,P}$ = 10.0), 115.4 (s), 120.5 (d, $J_{C,P}$ = 5.9), 121.3 (s), 123.6 (d, $J_{C,P}$ = 17.8), 124.2 (s), 125.7 (d, $J_{C,P}$ = 20.8), 141.5 (dd, $J_{C,P}$ = 15.7, 4.4), 157.9 (dd, $J_{C,P}$ = 16.9, 6.1), 158.1 (dd, $J_{C,P}$ = 11.1, 3.3), 204.1 (d, $J_{C,P}$ = 4.1); IR (KBr) 3030, 2880, 2830, 1661 (C=O), 1610, 1440, 1410, 1370, 1330, 1200, 1130, 1110, 820, 700 cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 568 (3, M^+), 284 (100), 135 (37). Repeated microanalysis did not give satisfactory results for carbon.

11,17-Bis(1,1-dimethyl-1-propyl)-3,2,12-oxadiphosphapentacyclo[11.5.1.0^{2,11}.0^{4,10}.0^{12,16}]nonadeca-4(10),5,8,14,17-pentaen-19-one (9c). A pale yellow solution of **1** (0.84 g, 0.77 mL, 7.91 mmol) and **3c** (1.25 g, 10.95 mmol; diluted in approximately 3.4 g of hexamethyldisiloxane[31]) in 4 mL of toluene was heated for 5 d at 120 °C in a Schlenk pressure tube (8 bar argon pressure). The brown mixture was evaporated under vacuum to remove the solvent and excess **3c**. The resulting brown-colored oil consisting mainly of **9c** and unchanged **1** was separated by column chromatography on alumina (petroleum ether/ether, 1:1–2:3) to give **9c** as a beige solid. Repeated crystallizations from petroleum ether/ether (2:1) at −3 °C afforded pale yellow crystals of pure **9c** (0.89 g, 51%): mp 137–138 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 36.1 (s), 141.5 (s); ^1H NMR ($CDCl_3$) δ = 0.71 (dd, $J_{H,H}$ = 7.4, 7.4, 3H), 0.78 (dd, $J_{H,H}$ = 7.4, 7.4, 3H), 0.95 (s, 3H), 1.01 (s, 3H), 1.04 (s, 3H), 1.06 (s, 3H), 1.32 (dq, $J_{H,H}$ = 14.7, 7.4, 1H), 1.41 (m, 1H), 1.49 (dq, $J_{H,H}$ = 14.7, 7.4, 1H), 1.76 (m, 1H), 1.83 (ddd, $J_{H,H}$ = 13.0, 6.6, 6.5, 1H), 2.67 (ddd, $J_{H,H}$ = 13.0, 7.5, 7.5, 1H), 3.11 (dd, $J_{H,P}$ = 17.8, $J_{H,H}$ = 5.3, 1H), 3.78 (dd, $J_{H,P}$ = 19.1, $J_{H,H}$ = 3.0, 1H), 3.85 (dd, $J_{H,P}$ = 3.2, $J_{H,H}$ = 9.3, 1H), 5.16 (ddd, $J_{H,H}$ = 9.5, 7.5, 6.5, 1H), 5.18 (dd, $J_{H,P}$ = 4.3, $J_{H,H}$ = 9.3, 1H), 5.43 (ddd, $J_{H,H}$ = 9.6, 7.5, 6.6, 1H), 5.50 (ddd, $J_{H,P}$ = 10.8, $J_{H,H}$ = 6.3, 5.3, 1H), 6.07 (d, $J_{H,H}$ = 9.6, 1H), 6.20 (ddd, $J_{H,P}$ = 10.7, $J_{H,H}$ = 6.3, 3.0, 1H), 6.47 (dd, $J_{H,P}$ = 2.5, $J_{H,H}$ = 9.5, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 8.1 (s), 8.8 (s), 21.5 (dd, $J_{C,P}$ = 13.0, 7.1), 22.4 (dd, $J_{C,P}$ = 8.8, 8.8), 26.1 (s), 27.4 (d, $J_{C,P}$ = 2.8), 27.7 (s), 31.3 (dd, $J_{C,P}$ = 12.9, 6.7), 33.0 (d, $J_{C,P}$ = 3.9), 39.8 (dd, $J_{C,P}$ = 22.0, 15.4), 40.8 (d, $J_{C,P}$ = 3.8), 42.7 (dd, $J_{C,P}$ = 30.5, 3.9), 49.8 (d, $J_{C,P}$ = 10.1), 59.2 (dd, $J_{C,P}$ = 47.6, 42.9), 59.7 (d, $J_{C,P}$ = 39.1), 115.1 (d, $J_{C,P}$ = 10.1), 115.4 (s), 120.9 (s), 121.5 (d, $J_{C,P}$ = 6.9), 123.7 (d, $J_{C,P}$ = 18.1), 123.9 (s), 125.1 (d, $J_{C,P}$ = 20.5), 140.9 (dd, $J_{C,P}$ = 15.8, 4.2), 155.0 (dd, $J_{C,P}$ = 17.1, 6.4), 158.1 (dd, $J_{C,P}$ = 11.1, 3.3), 204.1 (d, $J_{C,P}$ = 4.7); IR (KBr) 3044, 2964, 2932, 2876, 1668 (C=O), 1618, 1534, 1462, 1390, 1364, 1198, 1134, 798 cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 440 (12,

M⁺), 369 (21), 220 (100), 191 (43), 149 (13), 71 (12). Anal. Calcd for $C_{26}H_{34}O_2P_2$: C, 70.89; H, 7.78. Found: C, 70.90; H, 7.75.

7,13-Di-*tert*-butyl-4,5-dimethyl-2,8-diphosphatetracyclo-[7.5.1.0^{2,7}.0^{8,12}]pentadeca-4,10,13-trien-15-one (11). A lemon yellow solution of **5a** (210 mg, 0.69 mmol) and 2,3-dimethylbutadiene (73 mg, 0.89 mmol) in 3 mL of toluene was heated in a Schlenk pressure tube (8 bar argon pressure) at 125 °C for 9 h to provide a dark mixture. After removal of the solvent under vacuum a green-brown solid remained which was purified by chromatography on silica gel using petroleum ether/ether (10:1) as eluent. The resultant greenish solid was recrystallized twice from a small amount of petroleum ether at −20 °C to furnish **11** as colorless crystals (186 mg, 70%): mp 123−124 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ = 1.4 (s), 29.2 (s); ^1H NMR (C_6D_6) δ = 0.90 (s, 9H), 1.12 (s, 9H), 1.66 (s, 3H), 1.68 (s, 3H), 1.91 (br dd, $J_{H,P}$ = 16.0, $J_{H,H}$ = 16.2, 1H), 1.97 (dd, $J_{H,P}$ = 5.7, $J_{H,H}$ = 16.2, 1H), 2.16 (br dd, $J_{H,P}$ = 27.2, $J_{H,H}$ = 15.6, 1H), 2.31 (ddd, $J_{H,P}$ = 13.8, 6.0, $J_{H,H}$ = 15.6, 1H), 3.08 (dd, $J_{H,P}$ = 20.0, 5.6, 1H), 3.15 (dd, $J_{H,P}$ = 2.2, $J_{H,H}$ = 9.8, 1H), 3.53 (dd, $J_{H,P}$ = 17.5, $J_{H,H}$ = 4.4, 1H), 5.42 (dd, $J_{H,P}$ = 3.5, $J_{H,H}$ = 9.8, 1H), 5.63 (ddd, $J_{H,P}$ = 10.2, $J_{H,H}$ = 6.2, 5.6, 1H), 5.97 (ddd, $J_{H,P}$ = 10.1, $J_{H,H}$ = 6.2, 4.4, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ = 21.5 (s), 21.9 (s), 27.9 (br), 30.2 (d, $J_{C,P}$ = 2.5), 30.9 (d, $J_{C,P}$ = 26.8), 37.1 (d, $J_{C,P}$ = 3.1), 37.6 (dd, $J_{C,P}$ = 25.6, 12.2), 39.8 (dd, $J_{C,P}$ = 26.4, 2.1), 42.0 (dd, $J_{C,P}$ = 44.1, 39.0), 46.1 (d, $J_{C,P}$ = 30.8), 47.5 (d, $J_{C,P}$ = 14.2), 53.6 (d, $J_{C,P}$ = 24.0), 119.6 (d, $J_{C,P}$ = 7.4), 126.5 (d, $J_{C,P}$ = 16.7), 126.9 (s), 129.7 (s), 139.7 (dd, $J_{C,P}$ = 16.1, 3.1), 148.7 (dd, $J_{C,P}$ = 14.4, 6.2), 201.7 (d, $J_{C,P}$ = 4.5); IR (KBr) 3050, 2964, 2906, 2866, 1680 (C=O), 1392, 1362, 1262, 1092, 1022, 804 cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 388 (100, M⁺), 373 (32), 359 (10), 345 (12), 331 (62), 57 (43). Anal. Calcd for $C_{23}H_{34}OP_2$: C, 71.11; H, 8.82. Found: C, 71.26; H, 8.88.

6,8-Di-*tert*-butyl-3-mesityl-5,4,2,7-oxazadiphosphapentacyclo[7.5.0.0^{2,6}.0^{7,13}.0^{8,10}]tetradeca-3,11-dien-14-one (13) and 10-*tert*-Butyl-8-(*tert*-butylcarbonyl)-8,9-diphosphatetracyclo[5.3.0.0^{2,10}.0^{5,9}]dec-3-en-6-one (15). A stirred solution of **5a** (90 mg, 0.29 mmol) in toluene (4 mL) was treated dropwise at −78 °C with a solution of **12** (47 mg, 0.29 mmol) in toluene (2 mL) and allowed to warm to ambient temperature overnight. During this time the color of the mixture changed from deep yellow to pale yellow. After the mixture was stirred for 1 d at room temperature $^{31}P\{^1H\}$ NMR spectroscopy showed the absence of **5a**. The reaction mixture was evaporated to dryness to afford the products as colorless solids which were separated by column chromatography on silica gel. Mesityl cyanide was eluted with petroleum ether (10:1). The fraction resulting from elution with petroleum ether/ether (5:1) gave **13** as colorless needles upon cooling and concentrating under vacuum (33 mg, 24%): mp 190−192 °C dec; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −14.2 (s), 38.7 (s); ^1H NMR (CD_2Cl_2) δ = 1.19 (s, 9H), 1.22 (s, 9H), 1.85 (ddd, $J_{H,P}$ = 6.2, $J_{H,H}$ = 8.1, 8.1, 1H), 2.08 (dd, $J_{H,H}$ = 8.1, 5.6, 1H), 2.28 (s, 3H), 2.40 (s, 6H), 3.24 (dd, $J_{H,P}$ = 19.5, $J_{H,H}$ = 9.8, 1H), 3.74 (ddd, $J_{H,P}$ = 5.6, 1.5, $J_{H,H}$ = 5.6, 1H), 5.67 (ddd, $J_{H,P}$ = 6.5, $J_{H,H}$ = 9.8, 9.5, 1H), 6.28 (ddd, $J_{H,P}$ = 3.2, $J_{H,H}$ = 9.5, 8.1, 1H), 6.91 (s, 2H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 21.0 (s), 22.1 (d, $J_{C,P}$ = 7.9), 23.4 (d, $J_{C,P}$ = 1.5), 26.7 (dd, $J_{C,P}$ = 8.0, 8.0), 30.4 (d, $J_{C,P}$ = 5.5), 31.1 (s), 32.4 (d, $J_{C,P}$ = 36.9), 34.4 (d, $J_{C,P}$ = 21.2), 40.5 (dd, $J_{C,P}$ = 25.2, 23.7), 48.2 (dd, $J_{C,P}$ = 27.9, 2.5), 53.1 (d, $J_{C,P}$ = 36.3), 100.6 (dd, $J_{C,P}$ = 45.3, 45.3), 119.8 (s), 126.3 (d, $J_{C,P}$ = 16.4), 129.8 (s), 132.6 (d, $J_{C,P}$ = 4.1), 137.6 (s), 139.3 (s), 156.0 (d, $J_{C,P}$ = 53.3), 204.3 (s); IR (KBr) 3020, 2958, 2920, 2870, 1686 (C=O), 1390, 1362, 1225, 870 cm^{-1}; MS (CI, isobutane, 200 eV) *m/z* (rel int) 467 (100, M⁺). Anal. Calcd for $C_{27}H_{35}NO_2P_2$: C, 69.36; H, 7.55; N 3.00. Found: C, 69.46; H, 7.58; N, 3.06.

A second fraction from petroleum ether/ether (5:1) furnished **15** as colorless prisms after recrystallization from a small volume of ether at −3 °C (49 mg, 52%): mp 143−144 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −49.6 (d, $J_{P,P}$ = 208.0), 50.6 (d, $J_{P,P}$ = 208.0); ^1H NMR (C_6D_6) δ = 0.88 (s, 9H), 1.04 (s, 9H), 1.48 (dddd, $J_{H,P}$ = 4.2, 3.0, $J_{H,H}$ = 7.8, 5.8, 1H), 1.55 (dd, $J_{H,H}$ = 7.8, 6.8, 1H), 3.17 (dd, $J_{H,P}$ = 25.4, $J_{H,H}$ = 9.5, 1H), 3.75 (dd, $J_{H,P}$ = 18.4, $J_{H,H}$ = 5.8, 1H), 5.51 (ddd, $J_{H,P}$ = 5.6, $J_{H,H}$ = 9.5, 9.3, 1H), 5.90 (dddd, $J_{H,P}$ = 0.5, 0.5, $J_{H,H}$ = 9.3, 6.8, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ = 26.3 (s), 28.9 (dd, $J_{C,P}$ = 6.7, 2.3), 30.0 (dd, $J_{C,P}$ = 15.3, 1.3), 31.9 (d, $J_{C,P}$ = 17.5), 33.4 (dd, $J_{C,P}$ = 25.6, 4.0), 41.7 (dd, $J_{C,P}$ = 38.4, 16.8), 42.4 (d, $J_{C,P}$ = 35.8), 48.2 (d, $J_{C,P}$ = 21.7), 58.2 (d, $J_{C,P}$ = 28.0), 120.2 (s), 130.7 (d, $J_{C,P}$ = 3.4), 195.3 (s), 227.2 (d, $J_{C,P}$ = 73.8); IR (KBr) 3063, 3045, 3023, 2993, 2964, 2952, 1709 (C=O), 1648 (C=O), 1472, 1390, 1361, 1089, 928 cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 322 (22, M⁺), 265 (4), 237 (12), 57 (100). Anal. Calcd for $C_{17}H_{24}O_2P_2$: C, 63.35; H, 7.50. Found: C, 63.34; H, 7.52.

Acknowledgment. The authors are grateful to the Fonds der Chemischen Industrie, Frankfurt/Main for generous financial support and a fellowship (M.J.).

Supporting Information Available: NMR peak assignments (**5a,b**, **9a−c**, **11**, **13**, **15**), ^1H NMR (**5a**, **9a**, **11**, **15**), $^1H\{^{31}P\}$ NMR (**9a**, **11**), ^{13}C NMR (**5a**, **9a**, **11**, **13**, **15**), and COSY spectra (**5a**, **9c**) (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO950696S