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Cycloaddition Reactions of 1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes

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1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes **1**, obtained by alkylation of sodium 1,2-diphospha-3,4,5-triphenylcyclopentadienide, exhibit dual reactivity in cycloaddition reactions: as dienes (with maleic anhydride and maleimide) or as dienophiles (with 2,3-dimethylbutadiene). Thermolysis of **1** occurs with a [1,5] sigmatropic shift to form a [2+2] cyclodimerization product.

Introduction

Cycloaddition reactions of phosphacyclopentadienes (phospholes) are of significant interest for the preparation of phosphanorbornenes and phosphanorbornadienes, which can be employed as weak, bulky ligands in asymmetric Heck reactions,[1] asymmetric hydrogenation,[2] enantioselective *C*- and *N*-alkylation,[3] and in the rhodium-catalyzed hydroformylation of olefins.[4,5] The thermolysis of phosphanorbornadienes or their transition-metal complexes is a common method for the generation of phosphanylidene species and the synthesis of phosphirenes and phosphiranes.[6–8]

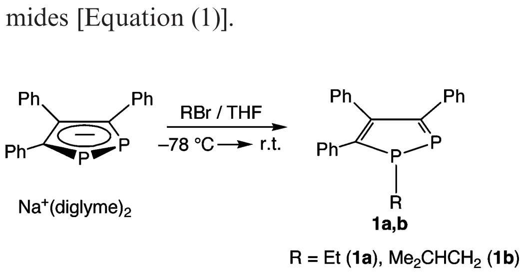
It has been stated that the diene system of trivalent phospholes is only poorly reactive due to delocalization within the ring, which diminishes the availability of the four π electrons.[9,10] Thus, head-to-tail [2+2] cyclodimerization of 1,2,5-triphenylphosphole has been observed under UV irradiation.[11] Moreover, [2+2] and [4+2] cyclodimerization of arylphospholes can be realized in the coordination sphere of transition metals (Cr, Mo, W).[12] The [4+2] cycloaddition reactions of 1*H*-phospholes (e.g., 1,2,5-triphenyl- or 1,2,3,4,5-pentaphenylphosphole) with maleic anhydride proceed at elevated temperatures with low yields (3–11%).[13,14] Improved yields of the cycloaddition products were achieved by using *N*-methyl(aryl)maleimide[15–17] or fumaronitrile[18] as the dienophile or in the coordination sphere of transition-metal complexes.[19]

More reactive are 2*H*-phospholes containing a reactive P=C bond formed as a result of a [1,5] sigmatropic shift.[9,20] For example, 2*H*-phospholes undergo a [4+2] cyclodimerization reaction at low temperatures with the formation of *endo* dimers,[21] which on heating rearrange to *exo* isomers.[22] The 2*H*-phospholes exhibit dual reactivity in cycloaddition reactions: as powerful dienes towards carbon–carbon double or triple bonds or C=O double bonds[23] and as dienophiles towards conjugated dienes.[24] However, 2*H*-phosphole still remains unknown, but can be stabilized by bulky substituents at the carbon atoms,[25] by complexation with transition metals[26] or by inclusion in an aromatic fragment.[27]

We now report on our investigations of the cycloaddition reactions of 1-alkyl-1,2-diphosphacyclopenta-2,4-dienes **1**, which represent both 1*H*- and 2*H*-phospholes in one molecule.

Results and Discussion

1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes **1** are readily available by alkylation of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide with alkyl bromides [Equation (1)].



(1)

R = Et (**1a**), Me$_2$CHCH$_2$ (**1b**)

The structures of diphospholes **1** were unambiguously confirmed by NMR spectroscopy: the ^{31}P NMR spectra of **1** showed two doublets in the range of 70 and 200 ppm,

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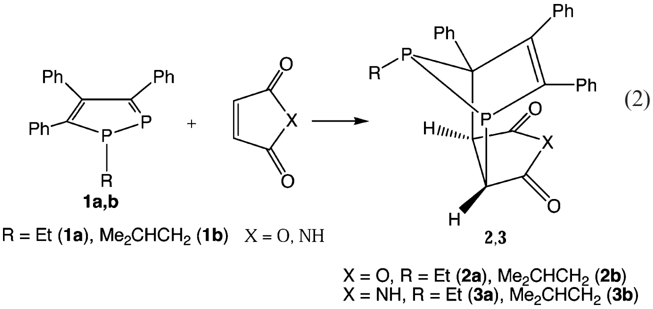
characteristic of sp^3- and sp^2-hybridized phosphorus atoms, with large $^1J_{PP}$ coupling constants of around 400 Hz.

The 1-alkyl-1,2-diphospholes **1** react with maleimide or maleic anhydride on heating in toluene to give the cycloaddition products **2** or **3** with high regio- and stereoselectivity [Equation (2)]. The ^{31}P NMR spectra of the reaction mixtures show only two doublets in the range of 85 and –25 ppm.



(2)

A crystal structure analysis of **2b** showed that only the *endo* isomer was obtained with the alkyl group in an *anti* orientation to the double bond of the ring. Compound **2b** crystallizes with three independent molecules in the asymmetric unit that exhibit similar molecular geometry; therefore, only one molecule is discussed here (Figure 1, see also the Supporting Information). Each phosphorus atom has a typical pyramidal environment. The inner angle at the bridging phosphorus atom (P2) is very acute (C1–P2–P1 84.87°). For the two carbon atoms of the double bond (C2 and C3), little pyramidalization[28] is observed with ψ = 8.21 and 9.41°, respectively.

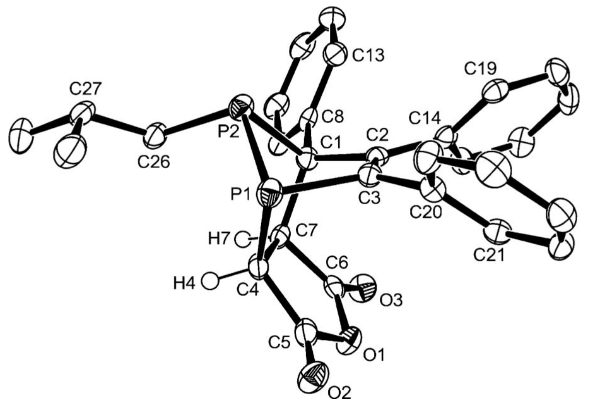


Figure 1. ORTEP view of *anti-endo*-($P_SP_RC_RC_RC_S$)-10-(2-methylpropyl)-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (**2b**). Hydrogen atoms other than H4 and H7 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C3 1.848(3), P1–C4 1.880(3), P1–P2 2.197(1), P2–C26 1.846(2), P2–C1 1.903(3), C3–P1–C4 93.2(1), C3–P1–P2 86.73(8), C4–P1–P2 90.46(9), C26–P2–C1 101.0(1), C26–P2–P1 107.05(9), C1–P2–P1 84.87(8).

The formation of only one diastereomer was clearly observed for maleimide derivative **3b**, which consists of a dimer formed by weak hydrogen bonds between the NH and CO groups of the maleimide fragment of different enantiomers (Figure 2).

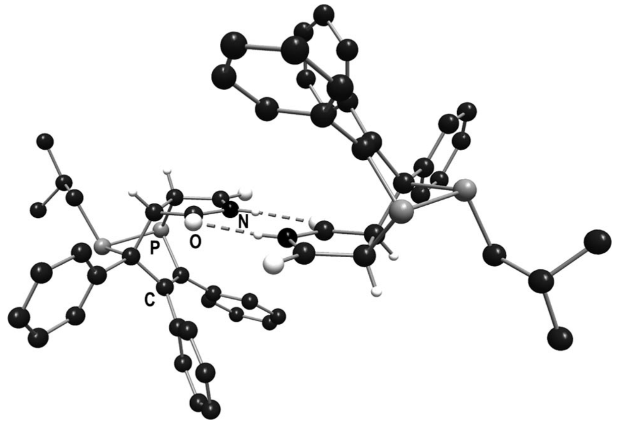
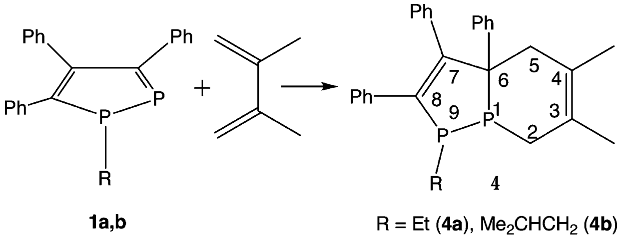


Figure 2. Molecular structure of *anti-endo*-($P_SP_RC_RC_RC_S$/$P_RP_SC_SC_SC_R$)-10-(2-methylpropyl)-7,8,9-triphenyl-4-aza-1,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (**3b**). Hydrogen atoms of the phenyl and alkyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.1862(5), P1–C3 1.847(1), P1–C4 1.881(1), P2–C26 1.846(1), P2–C1 1.903(1), C3–P1–C4 92.93(6), C3–P1–P2 86.27(5), C4–P1–P2 91.94(5), C26–P2–C1 105.38(6), C26–P2–P1 104.35(5), C1–P2–P1 85.16(4).

1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes **1** exhibit dual reactivity and can also act as dienophiles. Thus, diphospholes **1** react with 2,3-dimethylbutadiene at room temperature over 12 h or on heating in toluene over 1 h to give 9-alkyl-3,4-dimethyl-6,7,8-triphenyl-1,9-diphosphabicyclo[4.3.0]nona-3,7-dienes **4** in high yields [Equation (3)].

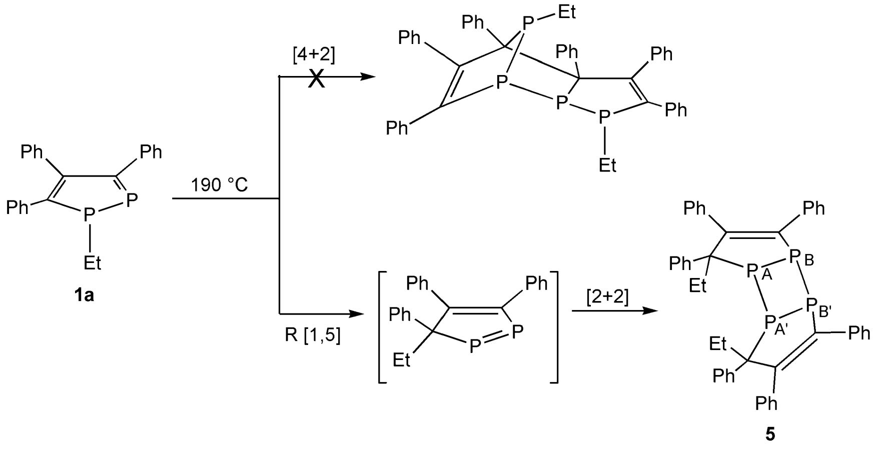


(3)

The structures of compounds **4** were confirmed by NMR spectroscopy. In the ^{31}P NMR spectra two doublets are observed at around +3 and –3 ppm with $^1J_{PP} \approx 210$ Hz. The ^{13}C NMR spectra exhibit a signal corresponding to C6 as a doublet of doublets with $^1J_{CP}$ = 24 and $^2J_{CP}$ = 3.7 Hz at around 67 ppm, characteristic of sp^3-hybridized carbon atoms.

Surprisingly, the 1-alkyl-1,2-diphospholes **1** are extremely stable; no cyclodimerization was observed on heating in toluene or in xylene. Only when decalin was used as the solvent was the cycloaddition product **5** obtained, albeit together with decomposition products [Equation (4)].

The ^{31}P NMR spectrum of **5** (Figure 3) shows the coupling pattern with 20 lines of an AA′BB′ system, characteristic of products from [2+2] cycloaddition reactions of 1,2-



(4)

diphospholes[29] formed by a [1,5] shift of alkyl groups.[22] The chemical shifts and coupling constants were obtained by simulation of the experimental spectrum.[30]

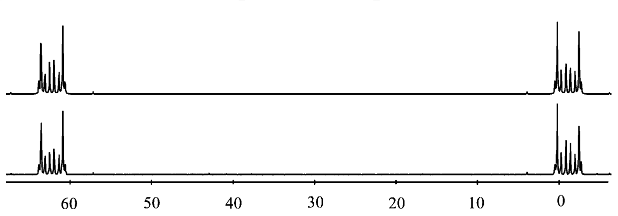


Figure 3. Experimental (bottom) and simulated (top) ^{31}P NMR spectra of **5**.

Conclusions

We have demonstrated that 1-alkyl-3,4,5-triphenyl-1,2-diphosphacylopenta-2,4-dienes **1** can act both as dienes and dienophiles in cycloaddition reactions, similar to 2*H*-phospholes. However, in contrast to 2*H*-phospholes the cyclodimerization reactions of **1** occur only under harsh reaction conditions to give a [2+2] cycloaddition product.

Experimental Section

General: All reactions and manipulations were carried out under dry pure N_2 in a standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone and stored under nitrogen before use. The NMR spectra were recorded with a Bruker MSL-400 spectrometer (^1H: 400 MHz; ^{31}P: 161.7 MHz; ^{13}C: 100.6 MHz). $SiMe_4$ was used as the internal reference for ^1H and ^{13}C NMR chemical shifts, and 85% H_3PO_4 as the external reference for ^{31}P NMR spectroscopy. Sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide was obtained according to the literature procedure.[31,32] Bromoethane, 1-bromo-2-methylpropane, maleic acid anhydride, maleimide, and 2,3-dimethylbutadiene were purchased from Aldrich and used without additional purification.

X-ray Analyses: The X-ray data were collected with an Xcalibur-S diffractometer (Oxford Diffraction) using Mo-K_α radiation (λ = 71.073 pm) with ω and ϕ scans. Data reduction was performed with CrysAlisPro[33] and the program SCALE3 ABSPACK[34] for empirical absorption correction. The structures were solved by direct methods and all non-hydrogen atoms were refined with SHELX97.[35] With the exception of H4 and H7 (first molecule), H33 and H36 (second molecule), and H62 and H65 (third molecule) of **2b** all hydrogen atoms were calculated at idealized positions, whereas for **3b** the hydrogen atoms were only calculated for disordered regions (Table 1). The diagrams of the structures were generated with ORTEP[36] and DIAMOND-3.[37]

CCDC-704769 (for **2b**) and -704770 (for **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-Ethyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (1a): A solution of bromoethane (0.80 g, 7.34 mmol, 20% excess) in THF (10 mL) was added to a solution of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (3.81 g, 6.16 mmol) in THF (40 mL) at –80 °C and then stirred for 12 h at room temp. Then the solvent was evaporated under reduced pressure and the residue was extracted with *n*-hexane (2 × 30 mL). The *n*-hexane extract was evaporated in vacuo to leave 1.30 g (59%) of 1-ethyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (**1a**); m.p. 57 °C. ^1H NMR (C_6D_6): δ = 0.94 (dt, $^3J_{HH}$ = 7.34, $^3J_{HP}$ = 14.5 Hz, 3 H, Me), 2.13 (m, 2 H, CH_2), 6.96 (t, $^3J_{HH}$ = 6.4 Hz, 4 H, Ph), 7.00 (d, $^3J_{HH}$ = 4.9 Hz, 4 H, Ph), 7.03 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, Ph), 7.07 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ph), 7.23 (d, $^3J_{HH}$ = 5.4 Hz, 1 H, Ph), 7.31 (t, $^3J_{HH}$ = 8.3 Hz, 1 H, Ph), 7.34 (d, $^3J_{HH}$ = 7.3 Hz, 1 H, Ph) ppm. ^{31}P NMR (C_6D_6): δ = 209.5 (d, $^1J_{PP}$ = 408.9 Hz), 73.1 (d, $^1J_{PP}$ = 408.9 Hz) ppm. ^{13}C NMR (C_6D_6): δ = 13.98 (d, $^2J_{CP}$ = 2.9 Hz, Me), 17.87 (dd, $^1J_{CP}$ = 16.1, $^2J_{CP}$ = 5.8 Hz, CH_2), 126.37 (s, *p*-Ph), 126.52 (s, *p*-Ph), 126.88 (s, *p*-Ph), 127.52 (s, *m*-Ph), 128.03 (s, *m*-Ph), 128.26 (s, *m*-Ph), 128.65 (dd, $^2J_{CP}$ = 11.17, $^3J_{CP}$ = 2.5 Hz, *o*-Ph), 129.23 (d, $^3J_{CP}$ = 9.3 Hz, *o*-Ph), 131.38 (t, $^2J_{CP}$ = 9.1 Hz, *o*-Ph), 137.34 (d, $^2J_{CP}$ = 5.4 Hz, *ipso*-Ph), 138.33 (dd, $^2J_{CP}$ = 10.3, $^2J_{CP}$ = 4.1 Hz, *ipso*-Ph), 142.89 (d, $^2J_{CP}$ = 19.0 Hz, *ipso*-Ph), 150.28 (pseudo t, $^2J_{CP}$ = 15.1 Hz, C_{ring}), 164.14 (dd, $^1J_{CP}$ = 10.8, $^2J_{CP}$ = 4.6 Hz, C_{ring}), 191.90 (dd, $^1J_{CP}$ = 56.9, $^2J_{CP}$ = 14.3 Hz, C_{ring}) ppm. $C_{23}H_{20}P_2$ (358.36): calcd. C 77.09, H 5.63, P 17.29; found C 76.89, H 5.22, P 17.89.

1-(2-Methylpropyl)-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (1b): In a similar manner **1b** was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (4.12 g, 6.66 mmol) and 1-bromo-2-methylpropane (1.09 g, 7.95 mmol, 20% excess) as a

Table 1. Crystallographic data for **2b** and **3b**.

Compound	**2b**	**3b**
Empirical formula	$C_{29}H_{26}O_3P_2{\cdot}CHCl_3$	$C_{29}H_{27}NO_2P_2$
Formula weight	504.33	483.46
Crystal size [mm]	0.1 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Temperature [K]	130(2)	130(2)
Wavelength, λ [pm]	71.073	71.073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [pm]	1788.39(3)	1021.80(2)
b [pm]	2196.73(3)	967.46(2)
c [pm]	1938.03(3)	2550.24(5)
β [°]	93.391(1)	92.044(2)
V [nm^3]	7.6004(2)	2.51944(9)
Z	12	4
$\rho_{\mathrm{calcd.}}$ [Mg m^{-3}]	1.322	1.275
Absorption coefficient [mm^{-1}]	0.254	0.199
F(000)	3164	1016
θ range for data collection [°]	2.51–26.37	2.64–30.51
Index ranges	$-22 \le h \le 22$ $-27 \le k \le 27$ $-24 \le l \le 24$	$-14 \le h \le 14$ $-13 \le k \le 13$ $-36 \le l \le 36$
Reflections collected	127657	49195
Independent reflections	15528 [R(int) = 0.1251]	7679 [R(int) = 0.0525]
Restraints/parameters	6/973	0/396
Goodness of fit on F^2	0.856	0.959
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0501 wR_2 = 0.0705	R_1 = 0.0430 wR_2 = 0.0878
R indices (all data)	R_1 = 0.1263, wR_2 = 0.0830	R_1 = 0.0760, wR_2 = 0.0955
Largest diff. peak and hole [e Å]$^{-3}$	0.492 and –0.520	0.462 and –0.259

light-yellow oil; yield 1.37 g (55%). ^{1}H NMR (C_6D_6): δ = 0.84 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 6 H), 1.48 (m, 1 H, CH), 1.74 (m, 2 H, CH_2), 6.7–7.2 (m, 15 H, Ph) ppm. ^{31}P NMR (C_6D_6): δ = 207.5 (d, $^{1}J_{\mathrm{PP}}$ = 420.7 Hz), 62.8 (d, $^{1}J_{\mathrm{PP}}$ = 420.7 Hz) ppm. ^{13}C NMR (C_6D_6): δ = 23.54 (d, $^{3}J_{\mathrm{CP}}$ = 7.9 Hz, Me), 23.81 (d, $^{3}J_{\mathrm{CP}}$ = 7.0 Hz, Me), 27.24 (d, $^{2}J_{\mathrm{CP}}$ = 5.0 Hz), 33.57 (d, $^{2}J_{\mathrm{CP}}$ = 17.0 Hz), 126.42 (s, *p*-Ph), 126.45 (s, *p*-Ph), 126.78 (s, *p*-Ph), 127.50 (s, *m*-Ph), 128.09 (s, *m*-Ph), 128.24 (s, *m*-Ph), 128.59 (s, *o*-Ph), 129.24 (s, *o*-Ph), 130.38 (d, $^{3}J_{\mathrm{CP}}$ = 1.2 Hz, *o*-Ph), 137.46 (d, $^{3}J_{\mathrm{CP}}$ = 6.2 Hz, *ipso*-Ph), 138.24 (dd, $^{3}J_{\mathrm{CP}}$ = 10.3, $^{3}J_{\mathrm{CP}}$ = 3.7 Hz, *ipso*-Ph), 142.81 (d, $^{3}J_{\mathrm{CP}}$ = 19.4 Hz, *ipso*-Ph), 149.17 (pseudo t, $^{3}J_{\mathrm{CP}}$ = 15.5 Hz, C_{ring}), 164.56 (dd, $^{3}J_{\mathrm{CP}}$ = 7.2, $^{3}J_{\mathrm{CP}}$ = 3.1 Hz, C_{ring}), 188.82 (dd, $^{3}J_{\mathrm{CP}}$ = 57.1, $^{3}J_{\mathrm{CP}}$ = 14.9 Hz, C_{ring}) ppm. $C_{25}H_{24}P_2$ (386.41): calcd. C 77.71, H 6.26, P 16.03; found C 77.82, H 6.04, P 16.14.

10-Ethyl-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-8-ene-3,5-dione (2a): Maleic anhydride (0.13 g, 1.33 mmol) was added to a solution of 1-ethyl-1,2-diphosphacyclopenta-2,4-diene **1a** (0.40 g, 1.22 mmol) in toluene (30 mL) and stirred for 3 h at 100 °C. After cooling to room temp., the solution was filtered and the filtrate was evaporated under reduced pressure to give 0.46 g (82%) of **2a**; m.p. 127–132 °C. ^{1}H NMR ($CDCl_3$): δ = 0.8 (dt, $^{3}J_{\mathrm{HH}}$ = 8.0, $^{3}J_{\mathrm{HP}}$ = 16.0 Hz, 3 H, Me), 1.29 (ddq, $^{3}J_{\mathrm{HH}}$ = 8.0, $^{2}J_{\mathrm{HP}}$ = 55.0, $^{3}J_{\mathrm{HP}}$ = 1.3 Hz, 2 H, CH_2), 4.36 (dd, $^{3}J_{\mathrm{HH}}$ = 8.8, $^{2}J_{\mathrm{HP}}$ = 9.3 Hz, 1 H, CH), 4.65 (d, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz, 1 H, CH), 6.68 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 2 H, Ph), 6.82 (t, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 2 H, Ph), 6.87 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 1 H, Ph), 6.99 (m, 3 H, Ph), 7.08 (m, 5 H, Ph), 7.16 (d, $^{3}J_{\mathrm{HH}}$ = 5.9 Hz, 1 H, Ph), 7.35 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 1 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 84.1 (d, $^{1}J_{\mathrm{PP}}$ = 198.5 Hz), –22.6 (d, $^{1}J_{\mathrm{PP}}$ = 198.5 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.00 (dd, $^{2}J_{\mathrm{CP}}$ = 16.8, $^{3}J_{\mathrm{CP}}$ = 3.1 Hz, Me), 18.40 (d, $^{1}J_{\mathrm{CP}}$ = 34.7 Hz, CH_2), 48.96 (s, CH), 49.53 (d, $^{1}J_{\mathrm{CP}}$ = 39.7 Hz, CH), 76.86 (dd, $^{1}J_{\mathrm{CP}}$ = 26.5, $^{1}J_{\mathrm{CP}}$ = 4.1 Hz), 126.81 (s, *p*-Ph), 127.44 (s, *p*-Ph), 127.58 (s, *p*-Ph), 127.69 (s, *m*-Ph), 128.21 (s, *m*-Ph), 129.53 (s, *m*-Ph), 129.62 (s, *o*-Ph), 129.73 (s, *o*-Ph), 130.39 (s, *o*-Ph), 136.83 (d, $^{1}J_{\mathrm{CP}}$ = 5.8 Hz, *ipso*-Ph), 137.78 (s, *ipso*-Ph), 138.13 (d, $^{2}J_{\mathrm{CP}}$ = 21.1 Hz, *ipso*-Ph), 140.91 (dd, $^{1}J_{\mathrm{CP}}$ = 27.5, $^{2}J_{\mathrm{CP}}$ = 18.4 Hz, C=C), 158.13 (dd, $^{2}J_{\mathrm{CP}}$ = 18.0, $^{2}J_{\mathrm{CP}}$ = 3.9 Hz, C=C), 169.19 (s, CO), 171.55 (s, CO) ppm. IR (KBr): $\tilde{\nu}$ = 442 (m), 494 (m), 507 (m), 544 (m), 579 (m), 621 (m), 648 (m), 697 (s), 726 (m), 740 (sh), 754 (m), 777 (m), 790 (m), 926 (s), 1029 (m), 1054 (sh), 1070 (m), 1108 (w), 1157 (w), 1210 (s), 1237 (m), 1380 (w), 1412 (w), 1443 (m), 1493 (m), 1576 (w), 1598 (m), 1772 (s, CO), 1850 (s, CO), 1949 (w), 2872 (m), 2928 (m), 2962 (m), 3024 (m), 3057 (m), 3431 (m, sh) cm^{-1}. $C_{27}H_{22}O_3P_2$ (456.42): calcd. C 71.05, H 4.86, O 10.52, P 13.57; found C 71.67, H 4.77, P 13.49.

10-(2-Methylpropyl)-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo-[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (2b): In a similar manner **2b** was obtained from **1b** (0.37 g, 0.96 mmol) and maleic anhydride (0.1 g, 1.02 mmol); yield 0.37 g (80%). ^{1}H NMR ($CDCl_3$): δ = 0.71 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3 H, Me), 0.78 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3 H, Me), 1.8 (m, 1 H, CH), 0.95 (m, 2 H, CH_2), 4.40 (dd, $^{3}J_{\mathrm{HH}}$ = 8.8, $^{2}J_{\mathrm{HP}}$ = 10.3 Hz, CH), 4.65 (d, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz, CH), 6.68 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 2 H, Ph), 6.82 (t, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 3 H, Ph), 6.87 (d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 2 H, Ph), 6.93–7.09 (m, 5 H, Ph), 7.15 (d, $^{3}J_{\mathrm{HH}}$ = 9.3 Hz, 2 H, Ph), 7.34 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 1 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 78.3 (d, $^{1}J_{\mathrm{PP}}$ = 198.5 Hz), –19.8 (d, $^{1}J_{\mathrm{PP}}$ = 198.5 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.58 (d, $^{3}J_{\mathrm{CP}}$ = 7.0 Hz, Me), 23.79 (d, $^{3}J_{\mathrm{CP}}$ = 9.1 Hz, Me), 26.72 (dd, $^{2}J_{\mathrm{CP}}$ = 15.3, $^{3}J_{\mathrm{CP}}$ = 1.7 Hz, CH_2), 34.67 (d, $^{1}J_{\mathrm{CP}}$ = 37.6 Hz, CH), 49.13 (s, CH), 49.62 (d, $^{1}J_{\mathrm{CP}}$ = 39.7 Hz, CH), 77.01 (dd, $^{1}J_{\mathrm{CP}}$ = 26.3, $^{2}J_{\mathrm{CP}}$ = 4.1 Hz, C-Ph), 126.81 (s, *p*-Ph), 127.42 (s, *p*-Ph), 127.59 (s, *p*-Ph), 127.69 (s, *m*-Ph), 128.22 (s, *m*-Ph), 129.53 (s, *m*-Ph), 129.61 (s, *o*-Ph), 129.77 (s, *o*-Ph), 130.41 (s, *o*-Ph), 136.64 (d, $^{3}J_{\mathrm{CP}}$ = 5.8 Hz, *ipso*-Ph), 137.79 (d, $^{3}J_{\mathrm{CP}}$ = 2.1 Hz, *ipso*-Ph), 138.13 (d, $^{3}J_{\mathrm{CP}}$ = 21.1 Hz, *ipso*-Ph), 141.48 (dd, $^{1}J_{\mathrm{CP}}$ = 27.9, $^{2}J_{\mathrm{CP}}$ = 18.4 Hz, C=C), 157.99 (dd, $^{2}J_{\mathrm{CP}}$ = 18.2, $^{2}J_{\mathrm{CP}}$ = 4.1 Hz, C=C), 169.23 (s, CO), 171.53 (s, CO) ppm. IR (KBr): $\tilde{\nu}$ = 507 (w), 580 (w), 649 (w), 697 (s), 726 (w), 740 (m), 755 (m), 801 (s), 864 (w), 926 (s), 1025 (s), 1070 (s), 1210 (m), 1262 (s), 1367 (w), 1383 (w), 1403 (w), 1443 (m), 1462 (w), 1492 (m), 1597 (m), 1772 (s, CO), 1851 (s, CO), 1951 (w), 2869 (m), 2960 (s), 3024 (w), 3057 (w), 3437 (br. m) cm^{-1}. $C_{29}H_{26}O_3P_2$ (484.47): calcd. C 71.90, H 5.41, O 9.91, P 12.79; found C 71.07, H 5.77, P 12.12.

10-Ethyl-7,8,9-triphenyl-4-aza-1,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-8-ene-3,5-dione (3a): Maleimide (0.1 g, 1.03 mmol) was added to a solution of **1a** (0.36 g, 1.01 mmol) in toluene (30 mL) and stirred for 3 h at 100 °C. The solution was filtered and the solvent was evaporated under reduced pressure to give 0.34 g (75%) of **3a**. ^{1}H NMR (CDCl$_3$): δ = 0.72 (dt, $^3J_{HH}$ = 7.8, $^3J_{HP}$ = 16.4 Hz, 3 H, Me), 1.32 (ddq, $^3J_{HH}$ = 7.8, $^2J_{HP}$ = 49.2, $^3J_{HP}$ = 1.5 Hz, 2 H, CH$_2$), 4.24 (dd, $^3J_{HH}$ = 7.4, $^2J_{HP}$ = 11.0 Hz, 1 H, CH), 4.57 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, CH), 6.16 (d, $^3J_{HH}$ = 9.1 Hz, 4 H, Ph), 7.15 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph), 7.07 (d, $^3J_{HH}$ = 6.8 Hz, 4 H, Ph), 7.14 (d, $^3J_{HH}$ = 6.2 Hz, 2 H, Ph), 7.36 (d, $^3J_{HH}$ = 6.8 Hz, 1 H, Ph), 9.02 (s, 1 H, NH) ppm. ^{31}P NMR (CDCl$_3$): δ = 74.2 (d, $^1J_{PP}$ = 192.2 Hz), –26.1 (d, $^1J_{PP}$ = 192.2 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ = 11.12 (dd, $^2J_{CP}$ = 15.9, $^3J_{CP}$ = 3.0 Hz, Me), 18.32 (d, $^1J_{CP}$ = 35.8 Hz, CH$_2$), 48.71 (s, CH), 51.13 (s, CH), 74.85 (dd, $^1J_{CP}$ = 24.3, $^2J_{CP}$ = 2.8 Hz, C-Ph), 125.89 (s, *p*-Ph), 126.69 (s, *p*-Ph), 126.79 (s, *p*-Ph), 127.09 (s, *m*-Ph), 127.19 (s, *m*-Ph), 127.66 (s, *m*-Ph), 127.76 (s, *o*-Ph), 129.35 (s, *o*-Ph), 130.54 (s, *o*-Ph), 130.78 (s, *ipso*-Ph), 138.99 (d, $^2J_{CP}$ = 5.3 Hz, *ipso*-Ph), 139.66 (d, $^1J_{CP}$ = 20.0 Hz, *ipso*-Ph), 140.98 (dd, $^1J_{CP}$ = 27.7, $^2J_{CP}$ = 19.2 Hz, C=C), 157.97 (dd, $^2J_{CP}$ = 18.3, $^2J_{CP}$ = 4.1 Hz, C=C), 174.89 (s, CO), 177.99 (s, CO) ppm. IR (KBr): ṽ = 509 (w), 539 (w), 582 (w), 633 (w), 647 (w), 674 (w), 694 (s), 738 (w), 762 (m), 787 (m), 867 (w), 937 (w), 1029 (w), 1080 (w), 1195 (m), 1265 (w), 1348 (m), 1388 (w), 1461 (m), 1467 (w), 1496 (w), 1579 (w), 1591 (w), 1719 (s, CO), 1777 (m, CO), 2349 (w), 2767 (m, NH), 2877 (m), 2929 (m), 2967 (m), 3045 (m), 3065 (m), 3146 (m), 3443 (m) cm^{-1}. $C_{27}H_{23}NO_2P_2$ (455.43): calcd. C 71.21, H 5.09, N 3.08, O 7.03, P 13.60; found C 71.67, H 5.22, N 3.13, P 13.44.

10-(2-Methylpropyl)-7,8,9-triphenyl-4-aza-1,10-diphosphatricyclo-[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (3b): In a similar manner **3b** was prepared from **1b** (0.42 g, 1.09 mmol) and maleimide (0.11 g, 1.13 mmol); yield 0.42 g (80%) of **3b**. ^{1}H NMR (CDCl$_3$): δ = 0.68 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, Me), 0.76 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, Me), 1.03 (m, 2 H, CH$_2$), 1.48 (m, 1 H, CH), 4.15 (dd, $^3J_{HH}$ = 8.3, $^2J_{HP}$ = 10.3 Hz, 1 H, CH), 4.36 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, CH), 6.75 (d, $^3J_{HH}$ = 9.3 Hz, 4 H, Ph), 6.99 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph), 7.07 (d, $^3J_{HH}$ = 6.9 Hz, 4 H, Ph), 7.14 (d, $^3J_{HH}$ = 6.4 Hz, 2 H, Ph), 7.36 (d, $^3J_{HH}$ = 6.9 Hz, 1 H, Ph), 9.05 (s, 1 H, NH) ppm. ^{31}P NMR (CDCl$_3$): δ = 74.8 (d, $^1J_{PP}$ = 195.6 Hz), –27.3 (d, $^1J_{PP}$ = 195.6 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ = 23.04 (d, $^3J_{CP}$ = 8.7 Hz, Me), 23.26 (d, $^3J_{CP}$ = 8.3 Hz, Me), 25.76 (dd, $^2J_{CP}$ = 15.9, $^3J_{CP}$ = 1.9 Hz, CH), 33.55 (d, $^1J_{CP}$ = 37.6 Hz, CH$_2$), 48.69 (s, CH), 51.06 (s, CH), 74.80 (dd, $^1J_{CP}$ = 24.4, $^2J_{CP}$ = 2.9 Hz, C-Ph), 125.73 (s, *p*-Ph), 126.51 (s, *p*-Ph), 126.77 (s, *p*-Ph), 126.98 (s, *m*-Ph), 127.10 (s, *m*-Ph), 127.53 (s, *m*-Ph), 127.67 (s, *o*-Ph), 129.42 (s, *o*-Ph), 130.30 (s, *o*-Ph), 130.64 (s, *ipso*-Ph), 138.29 (d, $^2J_{CP}$ = 5.4 Hz, *ipso*-Ph), 139.32 (d, $^1J_{CP}$ = 20.7 Hz, *ipso*-Ph), 140.86 (dd, $^1J_{CP}$ = 27.7, $^2J_{CP}$ = 19.0 Hz, C=C), 157.91 (dd, $^2J_{CP}$ = 18.4, $^2J_{CP}$ = 4.3 Hz, C=C), 174.78 (s, CO), 177.76 (s, CO) ppm. IR (KBr): ṽ = 507 (w), 543 (w), 580 (w), 631 (w), 645 (w), 675 (w), 697 (s), 740 (w), 763 (m), 790 (m), 865 (w), 940 (w), 1028 (w), 1078 (w), 1185 (m), 1261 (w), 1343 (m), 1383 (w), 1443 (m), 1462 (w), 1492 (w), 1576 (w), 1598 (w), 1713 (s, CO), 1773 (m, CO), 1947 (w), 2346 (w), 2758 (m, NH), 2869 (m), 2928 (m), 2956 (m), 3028 (m), 3057 (m), 3155 (m), 3412 (m) cm^{-1}. $C_{29}H_{27}NO_2P_2$ (483.49): calcd. C 72.04, H 5.63, N 2.90, O 6.62, P 12.81; found C 72.44, H 5.31, N 2.99, P 12.61.

9-Ethyl-3,4-dimethyl-6,7,8-triphenyl-1,9-diphosphabicyclo[4.3.0]-nona-3,7-diene (4a): 2,3-Dimethylbutadiene (0.12 g, 1.46 mmol) was added to a solution of **1a** (0.52 g, 1.45 mmol) in toluene (30 mL) and stirred for 12 h at room temp. or heated for 1 h at 100 °C. The solvent was evaporated under reduced pressure and the residue was extracted with *n*-hexane (2 × 20 mL). The *n*-hexane extract was evacuated in vacuo to give 0.46 g (72%) of **4a** as a white powder; m.p. 79 °C. ^{1}H NMR (CDCl$_3$): δ = 1.05 (dt, $^3J_{HH}$ = 15.5, $^3J_{HP}$ = 7.7 Hz, 3 H, Me), 1.28 (m, 2 H, CH$_2$), 1.61 (s, 3 H, Me), 1.71 (m, 1 H, CH$_2$), 1.93 (s, 3 H, Me), 2.23 (dq, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 15.5 Hz, 1 H), 2.44 (q, $^3J_{HH}$ = 15.5 Hz, 1 H), 2.58 (m, 1 H, CH$_2$), 6.39 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ph), 6.76–7.41 (m, 11 H, Ph), 7.49 (d, $^3J_{HH}$ = 6.4 Hz, 2 H, Ph) ppm. ^{31}P NMR (CDCl$_3$): δ = 5.9 (d, $^1J_{PP}$ = 210.4 Hz), –2.3 (d, $^1J_{PP}$ = 210.4 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ = 11.98 (dd, $^2J_{CP}$ = 14.5, $^3J_{CP}$ = 7.4 Hz, C-1), 19.46 (pseudo t, J_{CP} = 18.2 Hz), 20.62 (s, C-6), 21.44 (d, J_{CP} = 3.7 Hz), 29.17 (t, J_{CP} = 21.3 Hz), 38.32 (s, CH$_2$), 67.92 (dd, J_{CP} = 24.0, J_{CP} = 3.3 Hz), 126.16, 126.27, 126.44, 126.91, 127.79, 128.09, 128.3, 128.51, 129.83 (d, J_{CP} = 6.6 Hz), 131.16, 138.51 (s), 139.96 (d, J_{CP} = 16.5 Hz), 142.18 (d, J_{CP} = 26.9 Hz), 145.5 (d, J_{CP} = 21.9 Hz), 148.54 (d, J_{CP} = 17.4 Hz), 149.80 (d, J_{CP} = 6.2 Hz) ppm. $C_{29}H_{30}P_2$ (440.50): calcd. C 79.07, H 6.86, P 14.06; found C 79.27, H 681, P 13.92.

3,4-Dimethyl-9-(2-methylpropyl)-6,7,8-triphenyl-1,9-diphosphabicyclo[4.3.0]nona-3,7-diene (4b): In a similar manner **4b** was obtained from **1b** (0.48 g. 1.24 mmol) and 2,3-dimethylbutadiene (0.07 g, 1.3 mmol); yield 0.46 g (79%) of **4b** as a white powder; m.p. 63 °C. ^{1}H NMR (CDCl$_3$): δ = 0.77 (dd, $^3J_{HH}$ = 13.9, $^4J_{PH}$ = 6.6 Hz, 6 H, Me), 1.43 (m, 1 H, CH$_2$), 1.69 (s, 3 H, Me), 1.81 (dt, $^3J_{HH}$ = 13.9, $^3J_{HH}$ = 5.7 Hz, 1 H, CH), 1.97 (m, 1 H, CH$_2$), 2.05 (s, 3 H, Me), 2.41 (m, 1 H, CH$_2$), 2.5 (m, 2 H, CH$_2$), 2.73 (m, 1 H, CH$_2$), 6.55 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ph), 6.92–7.52 (m, 11 H, Ph), 7.62 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ph) ppm. ^{31}P NMR (CDCl$_3$): δ = 1.2 (d, $^1J_{PP}$ = 211.9 Hz), –3.8 (d, $^1J_{PP}$ = 211.9 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.64 (s), 21.36 (d, J_{CP} = 2.9 Hz), 23.67 (dd, J_{CP} = 37.0, J_{CP} = 9.3 Hz), 27.69 (dd, J_{CP} = 16.5, J_{CP} = 4.1 Hz), 29.46 (t, J_{CP} = 21.3 Hz), 36.32 (dd, J_{CP} = 19.2, J_{CP} = 16.8 Hz), 38.32 (s), 67.74 (dd, J_{CP} = 24.0, J_{CP} = 3.7 Hz), 126.15 (s), 126.30 (s), 126.43 (s), 126.94 (s), 127.77 (s), 128.05 (s), 128.32 (s), 128.57 (s), 130.05 (d, J_{CP} = 6.6 Hz), 131.09 (s), 138.66 (s), 139.93 (d, J_{CP} = 17.0 Hz), 142.19 (d, J_{CP} = 27.7 Hz), 145.77 (d, J_{CP} = 21.9 Hz), 148.59 (d, J_{CP} = 16.5 Hz), 149.67 (d, J_{CP} = 7.0 Hz) ppm. $C_{31}H_{34}P_2$ (468.56): calcd. C 79.46, H 7.31, P 13.22; found C 79.12, H 7.01, P 13.87.

Thermolysis of 1-Ethyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (1a): A solution of **1a** in decalin (30 mL) was stirred for 3 h at 187 °C. After cooling to room temp., the solvent was evaporated and the residue was washed with cold *n*-hexane to give *rac-trans*-3,10-diethyl-3,4,5,8,9,10-hexaphenyl-1,2,6,7-tetraphosphatricyclo-[5.3.0.0^{2,6}]deca-3,9-diene (**5a**) as a light-yellow solid; m.p.144–149 °C. ^{1}H NMR (CDCl$_3$): δ = 1.07 (dt, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 12.0 Hz, 6 H, Me), 2.13 (m, 4 H, CH$_2$), 7.05–7.33 (m, 30 H, Ph) ppm. ^{31}P NMR (CDCl$_3$): AA′BB′ spin pattern, δ_A = 65.08 ppm, δ_B = –3.08 ppm, $^1J_{AB}$ = 180.76 Hz, $^1J_{BB'}$ = 43.75 Hz, $^2J_{AB'}$ = 32.41 Hz, $^1J_{AA'}$ = 79.65 Hz. ^{13}C NMR (CDCl$_3$): δ = 10.12 (d, $^2J_{CP}$ = 1.9 Hz, Me), 13.44 (dd, $^1J_{CP}$ = 13.0, $^2J_{CP}$ = 3.7 Hz, CH$_2$), 63.84 (m, 1 C), 125.34 (s, *p*-Ph), 127.23 (s, *p*-Ph), 127.88 (s, *p*-Ph), 128.55 (s, *m*-Ph), 129.0 (s, *m*-Ph), 129.25 (s, *m*-Ph), 129.37 (s, *o*-Ph), 131.75 (s, *o*-Ph), 138.14 (d, $^2J_{PC}$ = 7.0 Hz, *o*-Ph), 139.45 (s, *ipso*-Ph), 140.66 (s, *ipso*-Ph), 141.34 (pseudo t, $^2J_{PC}$ = 8.9 Hz, *ipso*-Ph), 145.89 (pseudo t, $^2J_{PC}$ = 20.1 Hz, C=C), 152.34 (dd, $^1J_{PC}$ = 4.2, $^1J_{PC}$ = 1.2 Hz, C=C) ppm. $C_{46}H_{40}P_4$ (716.7): calcd. C 77.09, H 5.63, P 17.28; found C 77.67, H 5.37, P 16.96.

Supporting Information (see also the footnote on the first page of this article): Molecular structures of two of the three independent molecules of **2b**.

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