Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 5298

www.rsc.org/obc

PAPER

Reactions of 1-alkyl-1,2-diphospholes with 1,3-dipoles: diphenyldiazomethane and nitrones†

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Received 12th March 2012, Accepted 15th May 2012
DOI: 10.1039/c2ob25532d

The reaction of 1-alkyl-1,2-diphosphacyclopenta-2,4-dienes (1-alkyl-1,2-diphospholes) (**1**) with diphenyldiazomethane proceeds at room temperature *via* unstable [3+2] cycloadducts to form bicyclic phosphiranes (**2**). However, 1-alkyl-1,2-diphospholes (**1**) react with *N*,alpha-diphenylnitrone or *N*-*tert*-butyl-alpha-phenylnitrone depending on the temperature to give either dimers of 1-alkyl-1-oxo-1,2-diphospholes (**5**) or 1-alkyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-enes (**7**) – phosphorus analogues of β-lactams.

Introduction

Reactions of dipolarophiles with 1,3-dipoles (Huisgen reaction)[1] are effective synthetic tools for the construction of five-membered heterocycles and have been successfully employed for preparation of natural products,[2] drugs and agricultural chemicals.[3] Novel types of dipolarophiles leading to novel heterocyclic compounds are of interest due to high regio- and stereoselectivity of 1,3-dipolar cycloaddition reactions.[4] Thus, two-coordinate organophosphorus compounds can be regarded as dipolarophiles for construction of novel phosphaheterocycles with useful properties.[5] For example, 1,3-dipolar cycloaddition reactions of heterophospholes which additionally contain O, N, S heteroatoms have been carried out with a variety of 1,3-dipoles.[6] Addition of diazoalkanes to the C=P unit of heterophospholes led to products with either C–N or P–N bonds depending on the substituents of the diazoalkane.[7] The cycloadducts resulting from addition of diazoalkanes and azides are usually stabilized by proton shift or loss of nitrogen.[8] The reactions with nitrile oxides,[9] nitrilimines and nitrile ylides[10] proceed highly regioselective – the carbon atom of the 1,3-dipole is bonded to the phosphorus atom of the heterophosphole.

At the same time, 1,3-dipolar cycloaddition reactions of phosphacyclopenta-2,4-dienes (phospholes) have been poorly studied in contrast to their Diels–Alder reactions.[11] This fact can be related to the different reactivity of the two tautomeric forms of phospholes – 1*H*- and 2*H*-phospholes. 1*H*-Phospholes are typically stable compounds that exhibit, however, poor reactivity in cycloaddition reactions due to aromatic stabilization within the ring. Formed by a *H*[1,5]-sigmatropic shift, 2*H*-phospholes are very reactive but unstable compounds.[11c] To the best of our knowledge, there are only two examples of regiospecific [2 + 3] cycloaddition reactions of 2*H*-phospholes with mesitylnitrile oxide[12] which lead to the bicyclic phosphaisooxazolines.

However, in our opinion, use of 1,3-dipoles containing N–O-bonds in reactions with phosphaalkenes or other P=C compounds could be accompanied by oxidation of the phosphorus atom. Indeed oxygen atom transfer proceeds upon mixing of phosphines with nitrile oxides or nitrones *via* nucleophilic attack of phosphine on the positively charged carbon atom at the NO-fragment, formation of four-membered azaphosphaoxetane ring and following cleavage into phosphine oxide and nitrile or imine.[13]

Therefore, it is interesting to study the reactivity of 1-alkyl-1,2-diphospholes, which demonstrate high thermal stability like 1*H*-phospholes and high reactivity as 2*H*-phospholes,[14] toward different 1,3-dipoles – diphenyldiazomethane and nitrones.

Results and discussion

The reactions of heterophospholes with diazoalkanes proceed with formation of either five-membered bicyclic diazophospholanes[8] or bicyclic phosphiranes.[15] However, we have found that 1-alkyl-1,2-diphospholes (**1**) react with diphenyldiazomethane cleanly at room temperature to form exclusively 2-alkyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo-[3.1.0]-hex-3-enes (**2**) (Scheme 1).

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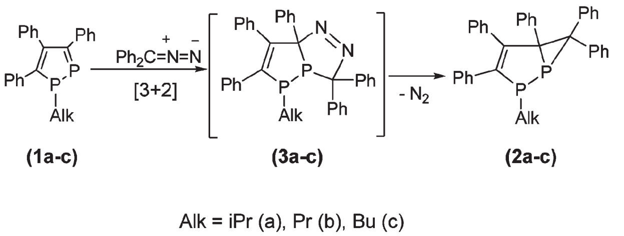
† Electronic supplementary information (ESI) available: Copies of NMR ^{1}H, ^{13}C, ^{31}P spectra of **2a**, **5a**, **7a** and **7d**. CCDC 865460 (**2a**), 865363 (**5a**), 865361 (**7a**) and 865362 (**7d**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25532d



Scheme 1 Reaction of 1-alkyl-1,2-diphospholes with diphenyldiazomethane.

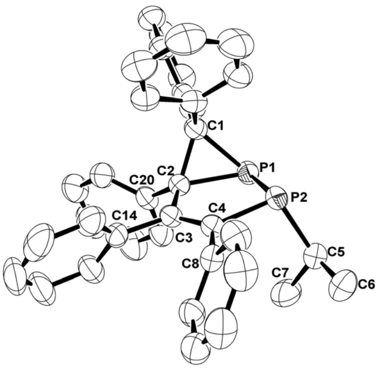


Fig. 1 ORTEP view of 2-isopropyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo-[3.1.0]hex-3-ene (**2a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.884(2); P1–C2 1.890(2); P1–P2 2.183(9); P2–C4 1.827(2); P2–C5 1.869(3); C1–C2 1.561(3); C2–C3 1.516(3); C3–C4 1.351(3); C1–P1–C2 48.9(9); C1–P1–P2 99.9(7); C2–P1–P2 94.5(7); C4–P2–C5 103.9(1); C4–P2–P1 93.9(8); C5–P2–P1 −99.8(9).

Presumably, first an unstable [3 + 2] cycloaddition product **3** as intermediate is formed, which rapidly undergoes further rearrangement with loss of N_2 and formation of **2**. Although we were not able to detect **3** by low temperature NMR experiments, a similar rearrangement is proposed for dipolar cycloaddition reactions of heterophospholes with diazomethane derivatives.[8]

Bicyclic phosphiranes **2** were fully characterized by ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR spectroscopy, and **2a** was additionally structurally characterized by X-ray structure analysis (Fig. 1).

The ^{31}P{^{1}H} NMR spectra of **2a–c** reveal two doublets at 23 and −123 ppm with a large coupling constant $^1J_{PP}$ = 354 Hz shifted upfield in comparison to free 1-alkyl-1,2-diphosphole (**1**) by *ca.* 50 and 300 ppm, respectively. Note that the existence of only one group of signals confirms the formation of one diastereoisomer only instead of the possible eight.

The P–C bond lengths (1.884(2) and 1.890(2) Å) of the three-membered ring in **2a** are in the typical range of other phosphiranes (1.78–1.89 Å).[16] The sum of bond angles around P1 (Σ(∠P1) = 243.28°) in **2a** indicates a pyramidal environment at phosphorus comparable to other bicyclic phosphiranes, *e.g.*, phosphirano[1,2-*c*][1,2,3]diazaphospholes (Σ(∠P) = 234.0°)[17] or spiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex-3-enes] (247.8°).[18]

While 1-alkyl-1,2-diphospholes (**1**) demonstrate similar behavior in reactions with diphenyldiazomethane like other heterosubstituted phospholes,[8] reactions of **1** with nitrones (**4**) are more complicated. At room temperature, only dimers of 1-alkyl-1-oxo-1,2-diphospholes (**5**) are obtained in 70–80% isolated yield (Scheme 2).

The structure of **5a–c** was unambiguously confirmed by ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR spectroscopy and for **5a** additionally by X-ray structure analysis (Fig. 2). The latter revealed partial oxidation (50% occupancy of O2).

Only the *endo* isomer of **5a** is formed. The inner angle P6–P7–C8 (90.28(1)°) is less acute than in similar compounds, *e.g.*, the angle at the bridgehead phosphorus atom of the dimer of 1-dimethylamino-phosphole-1-oxide (82.27°)[19] or the sterically hindered 1-(2,4,6-tri-*tert*-butylphenyl)phosphole-1-oxide (80.2°).[20]

Nitrones (**4**) probably act as mild oxidant, leading to unstable oxides of 1-alkyl-1,2-diphospholes (**6**), which immediately undergo [4 + 2] cycloaddition reactions to yield compounds **5**. Note that [4 + 2] cycloaddition of monophosphole oxides to give the corresponding dimers is a known reaction.[21,22]

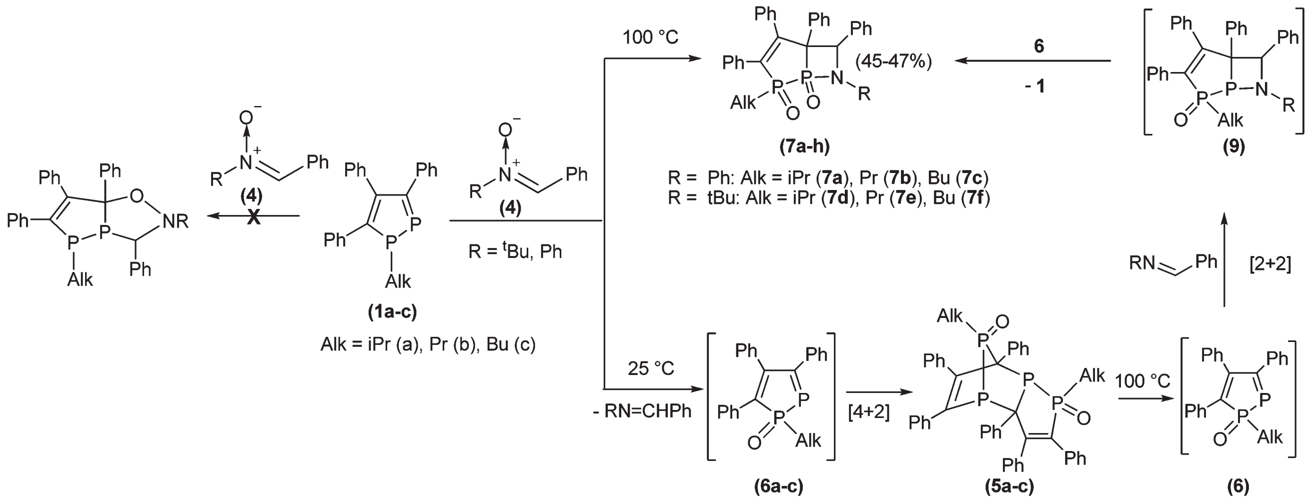
Moreover, the reactivity of 1-alkyl-1,2-diphospholes (**1**) toward nitrones (**4**) clearly depends on the temperature. Thus, heating 1-alkyl-1,2-diphospholes (**1**) and 10% excess of nitrones (**4**) up to 100 °C in toluene leads to formation of 1-alkyl-2,3,4,5-tetraphenyl-6-phenyl(*tert*-butyl)-1,7-dioxo-6-azo-1,7-diphosphabicyclo[3.2.0]hept-2-enes (**7**) (eqn (2)). The ^{31}P{^{1}H} NMR spectrum of the reaction mixtures shows only two doublets in the range of 45 and 35 ppm with $^1J_{PP}$ coupling constants of around 55 Hz, albeit together with decomposition products. Simple recrystallization gives pure products **7a–f** in 40–50% yield.

A crystal structure analysis of **7a** and **7d** showed that both 5-membered P_2C_3 and 4-membered PNC_2 cycles are almost planar (Fig. 3 and 4). The oxygen atoms are in an *anti* orientation. Each phosphorus atom has a typical pyramidal environment.

The formation of **7** at elevated temperature can be explained assuming following route (Scheme 2). First, the dimer of 1-alkyl-1,2-diphosphole-1-oxide (**5**) that is formed at room temperature could undergo a retro-Diels–Alder reaction on heating to give 1-alkyl-1,2-diphosphole-1-oxide (**6**). Then a [2 + 2] cycloaddition reaction of 1-alkyl-1,2-diphosphole-1-oxide (**6**) with imine RN = CHPh formed as side product by oxidation of 1-alkyl-1,2-diphospholes (**1**) with nitrones (**4**) could lead to intermediate **9** which could be oxidized with **6** or excess of nitrone to form 1-alkyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-enes (**7**). Indeed, heating of **5a** with *N*-phenylimine in toluene proceeds with formation of **7a** in 44–48% yield. The low yield can be explained by partial decomposition of 1-alkyl-1,2-diphosphole-1-oxide (**6**) during the reaction; some decomposition products were detected by ^{31}P{^{1}H} NMR spectroscopy. Thus, at room temperature, kinetic reaction control prevails and the less stable dimer of 1-alkyl-1,2-diphosphole-1-oxide (**5**) is the main reaction product, while at 110 °C and after long reaction times the thermodynamically more stable 1-alkyl-2,3,4,5-tetraphenyl-6-phenyl(*tert*-butyl)-1,7-dioxo-6-azo-1,7-diphosphabicyclo[3.2.0]hept-2-ene (**7**) is formed.

Conclusions

In summary, we have, for the first time, clearly demonstrated differences in reactivity of 1-alkyl-1,2-diphospholes (**1**) toward



Scheme 2 Reaction of 1-alkyl-1,2-diphospholes (**1**) with nitrones (**4**).

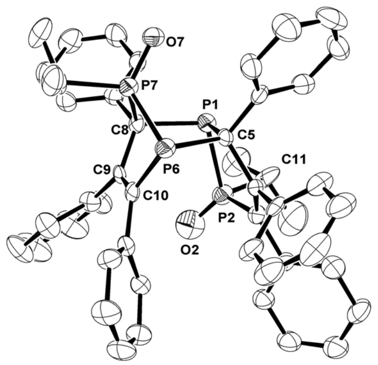


Fig. 2 ORTEP view of 2,3,4,4*a*,5,6-hexaphenyl-1-isopropyl-1-oxo-1,7,7*a*-triphospha-4,7-(isopropylphosphinidene-oxide)-indene (**5a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–P2 2.195(18); P1–C5 1.878(4); P1–C8 1.930(4); P2–O2 1.385(7); P2–C3 1.805(4); P2–C11 1.866(5); C3–C4 1.322(6); C4–C5 1.547(5); C5–P6 1.925(4); P6–C10 1.817(4); P6–P7 2.178(16); P7–O7 1.472(3); P7–C32 1.834(4); P7–C8 1.864(4); C8–C9 1.508(5); C9–C10 1.364(5); O2–P2–C3 118.9(3); O2–P2–P1 124.9(3); C5–P1–C8 99.3(2); C5–P1–P2 93.9(14); C8–P1–P2 103.3(14); C3–P2–P1 94.1(16); C10–P6–C5 99.5(2); C10–P6–P7 87.6(14); C5–P6–P7 89.2(13); C8–P7–P6 90.3(14).

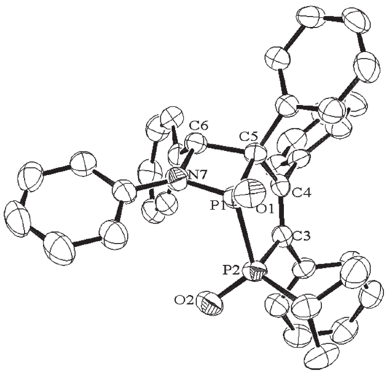


Fig. 3 ORTEP view of 1-isopropyl-2,3,4,5,6-pentaphenyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (**7a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths [A] and angles [°]: P1–O1 1.472(11); P2–O2 1.484(12); P1–P2 2.194(6); P1–N7 1.655(13); P1–C5 1.840(15); P2–C3 1.812(15); P2–C8 1.820(16); C3–C4 1.351 (2); C4–C5 1.543(2); C5–C6 1.609(2); C6–N7 1.484(19); O1–P1–N7 121.3(7); O1–P1–C5 127.6(7); N7–P1–C5 80.4(7); O1–P1–P2 116.2(5); N7–P1–P2 106.9(5); C5–P1–P2 97.4(5); O2–P2–C3 115.7(7); O2–P2–C8 113.7(7); C3–P2–C8 109.6(7); O2–P2–P1 114.7(5); C3–P2–P1 92.46(5); C8–P2–P1 108.7(6).

common 1,3-dipoles: diphenyldiazomethane and nitrones. The bicyclic phosphiranes **2** can be obtained in high yield by reaction of **1** with diphenyldiazomethane. At the same time, mixing of **1** with nitrones **4** at room temperature leads to oxidation of **1** and formation of dimers of 1-alkyl-1,2-diphosphole-1-oxide (**5**) which undergo [2 + 2] cycloaddition reactions with imine at elevated temperatures resulting 1-alkyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-enes (**7**). The novel P-containing heterocycles **7** may be interesting as phosphorus analogues of β-lactam antibiotics,[23] while the dimers of 1-alkyl-1,2-diphosphole-1-oxide (**5**) could be used as novel drugs in cancer therapy.[24]

Experimental section

All reactions and manipulations were carried out under dry pure N_2 in 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. 1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes (**1a–d**)[13a] and diphenyldiazomethane[25] were obtained according to literature procedures. *N-tert*-butyl-α-phenylnitrone and *N*-α-diphenylnitrone were purchased from Aldrich and used without additional purification.

X-ray structure analyses

Data for crystals of **2a** and **7d** were collected on a Bruker Smart Apex II CCD diffractometer and for **5a** and **7a** on a Bruker

Kappa Apex II CCD diffractometer using graphite-monochromated $\mathrm{Mo_{K\alpha}}$ (0.71073 Å) radiation. Programs used: data collection APEX2 (Bruker, 2004),[26] data reduction SAINT (Bruker, 2004),[26] absorption correction SADABS version 2.10 (Sheldrick, Bruker AXS Inc., 2002),[27] structure solution SIR,[27] SHELXS97 (Sheldrick, 1997),[28] structure refinement by full-matrix least-squares against F^2 using SHELXL-97[28] and WinGX.[29] Details concerning data collection and refinement are collected in Table 1. Pictures were generated with ORTEP3 for Windows.[30] CCDC 865460 (**2a**), 865363 (**5a**), 865361 (**7a**) and 865362 (**7d**) contain the supplementary crystallographic data for this paper.

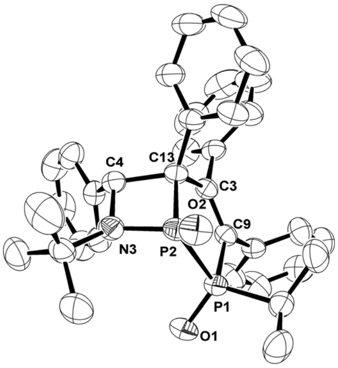
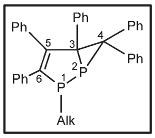


Fig. 4 The ORTEP view of 1-isopropyl-2,3,4,5-tetraphenyl-6-*tert*-butyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (**7d**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–O1 1.481(12); P2–O2 1.467(13); P1–C9 1.811(17); P1–C11 1.813(18); P1–P2 2.224(8); P2–N3 1.651(14); P2–C13 1.836(16); P2–C4 2.365(17); N3–C4 1.487(2); C3–C9 1.344(2); C4–C13 1.612(2); O1–P1–N7 121.3(7); O1–P1–C5 127.6(7); N7–P1–C5 80.4(7); O1–P1–P2 116.2(5); N7–P1–P2 106.9(5); C5–P1–P2 97.4(5); O2–P2–C3 115.7(7); O2–P2–C8 113.7(7); C3–P2–C8 109.6(7); O2–P2–P1 114.6(5); C3–P2–P1 92.5(5); C8–P2–P1 108.7(6).

Synthesis

2-Isopropyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo-[3.1.0]-hex-3-ene (2a). A solution of diphenyldiazomethane (0.15 g, 0.79 mmol) in toluene (1 ml) was added dropwise to solution of 1-isopropyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (**1a**) (0.27 g, 0.72 mmol) in toluene (10 ml) at room temperature. After the addition was complete, the solution was stirred for 5 h at room temperature. Concentration of the reaction mixture to 5 ml and cooling to −20 °C afforded 0.30 g (76%) light yellow crystals of 2-isopropyl-3,4,5,6,6-pentaphenyl-1,2-diphospha-bicyclo-[3.1.0]hex-3-ene (**2a**) with m.p. = 220 °C.



^{1}H NMR ($CDCl_3$, ppm): 1.24 (dd, $^3J_{HP}$ = 15.7 Hz, $^2J_{HH}$ = 7.14 Hz, 3H, Me), 1.31 (dd, $^3J_{HP}$ = 9.7 Hz, $^2J_{HH}$ = 7.1 Hz, 3H, Me), 1.88 (dqq, $^2J_{HP}$ = 13.9 Hz, $^2J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 7.1 Hz, 1H, CH), 6.26 (m, 2H, Ph), 6.38 (dd, J_{HH} = 7.3, J_{HH} = 1.2 Hz, 2H, Ph), 6.80–7.20 (m, 16H, Ph), 7.45 (m, 3H, Ph), 7.63 (dd, J_{HH} = 6.6 Hz, J_{HH} = 1.4 Hz, 2H, Ph).

^{31}P{^{1}H} NMR ($CDCl_3$, ppm): 23.3 (d, $^1J_{PP}$ = 278.5 Hz, P^1), −123.5 (d, $^1J_{PP}$ = 278.5 Hz, P^2).

^{13}C{^{1}H} NMR ($CDCl_3$, ppm): 20.83 (d, $^2J_{CP}$ = 4.0 Hz, Me), 20.94 (d, $^2J_{CP}$ = 3.7 Hz, Me), 25.89 (dd, $^1J_{CP}$ = 21.1 Hz, $^2J_{CP}$ = 6.8 Hz, $CHMe_2$), 54.68 (dd, $^1J_{CP}$ = 36.1 Hz, $^2J_{CP}$ = 2.0 Hz, C^4), 73.48 (dd, $^1J_{CP}$ = 39.4 Hz, $^2J_{CP}$ = 1.1 Hz, C^3), 125.36 (s, *p*-C^{Ph}), 125.60 (s, *p*-C^{Ph}), 125.80 (s, *p*-C^{Ph}), 126.62 (s, *m*-C^{Ph}), 126.84 (s, *m*-C^{Ph}), 127.03 (s, *m*-C^{Ph}), 127.07 (s, *m*-C^{Ph}), 127.28 (br.s., *m*-C^{Ph}), 127.43 (s, *m*-C^{Ph}), 128.76 (d, J_{CP} = 7.7 Hz, *o*-C^{Ph}), 129.50 (dd, J_{CP} = 15.4 Hz, J_{CP} = 1.8 Hz, *o*-C^{Ph}), 131.29 (s, *o*-C^{Ph}), 134.01 (d, J_{CP} = 7.7 Hz, *o*-C^{Ph}), 134.91 (d, J_{CP} = 2.6 Hz, *o*-C^{Ph}), 137.83 (dd, $^3J_{CP}$ = 1.8 Hz, $^3J_{CP}$ = 1.9 Hz, *ipso*-C^{Ph}), 139.07 (d, $^2J_{CP}$ = 3.7 Hz, *ipso*-C^{Ph}), 139.63 (dd, $^2J_{CP}$ = 16.1 Hz,

Table 1 Crystallographic data for **2a**, **5a**, **7a** and **7d**

Compound reference	**2a**	**5a**	**7a**	**7d**
Chemical formula	$C_{37}H_{32}P_2$	$C_{48}H_{44}O_{1.5}P_4$	$2(C_{37}H_{33}NO_2P_2)\cdot 3(C_7H_8)$	$C_{35}H_{37}NO_2P_2$
Formula mass	538.57	768.71	723.79	565.60
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
a (Å)	10.185(2)	10.7260(10)	11.3080(9)	10.231(3)
b (Å)	10.300(2)	19.139(2)	11.3298(9)	14.736(4)
c (Å)	15.865(4)	19.555(2)	15.5036(8)	20.826(5)
α (°)	72.942(2)	90.00	76.884(3)	90.00
β (°)	82.792(2)	96.130(6)	88.093(2)	102.290(4)
γ (°)	67.620(2)	90.00	85.182(2)	90.00
Unit cell volume (Å^3)	1471.1(6)	3991.4(7)	1927.4(2)	3067.9(14)
Temperature (K)	296(2)	198(2)	150(2)	296(2)
Space group	*P*2(1)/*n*	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)/*n*
No. of formula units per unit cell, *Z*	2	4	2	4
No. of reflections measured	14 791	30 279	82 675	27 222
No. of independent reflections	5684	7607	7370	7279
R_{int}	0.0265	0.2130	0.0450	0.0417
Final R_1 values ($I > 2\sigma(I)$)	0.0464	0.0517	0.0376	0.0427
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1397	0.0586	0.1140	0.1060
Final R_1 values (all data)	0.0598	0.2242	0.0495	0.0694
Final $wR(F^2)$ values (all data)	0.1536	0.0836	0.1211	0.1160

$^3J_{CP}$ = 1.8 Hz, *ipso*-C^{Ph}), 139.91 (d, $^2J_{CP}$ = 16.1 Hz, *ipso*-C^{Ph}), 142.60 (d, $^2J_{CP}$ = 10.6 Hz, *ipso*-C^{Ph}), 147.49 (d, $^1J_{CP}$ = 28.2 Hz, C^6), 150.25 (dd, $^2J_{CP}$ = 3.3 Hz, $^2J_{CP}$ = 1.5 Hz, C^5).

IR (KBr, cm^{-1}): 437 (w), 476 (w), 494 (w), 541 (w), 570 (m), 593 (m), 625 (w), 697 (s), 720 (w), 753 (m), 787 (m), 809 (w), 848 (w), 877 (w), 919 (w), 966 (w), 1031 (m), 1073 (m), 1154 (w), 1177 (w), 1236 (m), 1314 (w), 1364 (w), 1384 (w), 1441 (m), 1489 (m), 1552 (w), 1594 (m), 1804 (m), 1881 (w), 1945 (w), 2858 (w), 2921 (w), 2950 (w), 3022 (w), 3058 (w), 3078 (m).

$C_{37}H_{32}P_2$ (538.59): calcd C 82.51, H 5.99, P 11.50; found C 82.73, H 6.18, P 11.48.

2-Propyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0] hex-3-ene (2b). In a similar manner **2b** was obtained from 1-propyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (**1b**) (0.40 g, 1.23 mmol) and diphenyldiazomethane (0.22 g, 1.13 mmol) as light yellow powder (0.45 g, 71%); m.p. = 210 °C.

^{1}H NMR (CDCl$_3$, ppm): 0.89 (t, $^2J_{HH}$ = 5.6 Hz, 3H, Me), 1.51 (m, 2H, C*H*$_2$), 1.58 (m, 2H PC*H*$_2$), 6.15–7.54 (m, 25H, Ph).

^{31}P{^{1}H} NMR (CDCl$_3$, ppm): 1.9 (d, $^1J_{PP}$ = 263.7 Hz, P^1), −115.7 (d, $^1J_{PP}$ = 263.7 Hz, P^2).

^{13}C{^{1}H} NMR (CDCl$_3$, ppm): 15.03 (d, $^3J_{CP}$ = 9.1 Hz, Me), 25.74 (d, $^2J_{CP}$ = 16.9 Hz, CH$_2$), 28.51 (dd, $^1J_{CP}$ = 21.7 Hz, $^2J_{CP}$ = 9.7 Hz, PCH$_2$), 54.84 (dd, $^1J_{CP}$ = 35.5 Hz, $^2J_{CP}$ = 1.2 Hz, C^4), 74.00 (d, $^1J_{CP}$ = 39.3 Hz, C^3), 125.25 (s, *p*-C^{Ph}), 125.54 (s, *p*-C^{Ph}), 125.67 (s, *p*-C^{Ph}), 126.45 (s, *m*-C^{Ph}), 126.74 (s, *m*-C^{Ph}), 126.95 (s, *m*-C^{Ph}), 127.22 (s, *m*-C^{Ph}), 127.33 (s, *m*-C^{Ph}), 127.38 (s, *m*-C^{Ph}), 128.64 (d, J_{CP} = 7.8 Hz, *o*-C^{Ph}), 129.31 (d, J_{CP} = 14.9 Hz, *o*-C^{Ph}), 131.17 (s, *o*-C^{Ph}), 133.98 (d, J_{CP} = 7.9 Hz, *o*-C^{Ph}), 134.78 (d, J_{CP} = 2.48 Hz, *o*-C^{Ph}), 137.76 (d, $^3J_{CP}$ = 2.1 Hz, *ipso*-C^{Ph}), 138.84 (d, $^2J_{CP}$ = 4.1 Hz, *ipso*-C^{Ph}), 139.20 (br.s., *ipso*-C^{Ph}), 139.36 (br.s., *ipso*-C^{Ph}), 142.39 (d, $^2J_{CP}$ = 10.3 Hz, *ipso*-C^{Ph}), 148.58 (d, $^1J_{CP}$ = 26.0 Hz, C^6), 149.25 (d, $^2J_{CP}$ = 2.9 Hz, C^5).

IR (KBr, cm^{-1}): 431 (w), 4648 (w), 499 (w), 537 (w), 571 (m), 595 (m), 622 (w), 697 (s), 721 (w), 755 (m), 786 (m), 803 (w), 851 (w), 872 (w), 920 (m), 971 (w), 1032 (m), 1074 (m), 1155 (w), 1176 (w), 1235 (w), 1314 (w), 1371 (w), 1408 (w), 1430 (m), 1487 (m), 1595 (m), 1804 (w), 1885 (w), 1944 (w), 2863 (w), 2897 (w), 2921 (w), 2951 (w), 3023 (w), 3055 (w), 3078 (w), 3098 (w).

$C_{37}H_{32}P_2$ (538.59): calcd C 82.51, H 5.99, P 11.50; found C 82.65, H 6.13, P 11.46.

2-Butyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0] hex-3-ene (2c). In a similar manner **2c** was obtained from 1-butyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (**1c**) (0.45 g, 1.16 mmol) and diphenyldiazomethane (0.22 g, 1.13 mmol) as light yellow powder (0.48 g, 75%); m.p. = 221 °C.

^{1}H NMR (CDCl$_3$, ppm): 0.87 (t, $^2J_{HH}$ = 5.6 Hz, 3H, Me), 1.42 (m, 2H, C*H*$_2$), 1.49 (m, 2H, C*H*$_2$), 1.64 (m, 2H PC*H*$_2$), 6.05–7.33 (m, 25H, Ph).

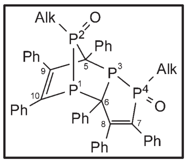
^{31}P{^{1}H} NMR (CDCl$_3$, ppm): 1.2 (d, $^1J_{PP}$ = 254.3 Hz, P^1), −117.2 (d, $^1J_{PP}$ = 254.3 Hz, P^2).

^{13}C{^{1}H} NMR (CDCl$_3$, ppm): 14.92 (d, $^3J_{CP}$ = 3.2 Hz, Me), 21.23 (d, $^2J_{CP}$ = 7.9 Hz, CH$_2$), 24.79 (d, $^2J_{CP}$ = 17.2 Hz, CH$_2$), 28.34 (dd, $^1J_{CP}$ = 20.4 Hz, $^2J_{CP}$ = 9.1 Hz, PCH$_2$), 54.23 (dd, $^1J_{CP}$ = 35.1 Hz, $^2J_{CP}$ = 0.9 Hz, C^4), 74.16 (d, $^1J_{CP}$ = 39.8 Hz, C^3), 125.52 (s, *p*-C^{Ph}), 125.56 (s, *p*-C^{Ph}), 125.62 (s, *p*-C^{Ph}), 126.26 (s, *m*-C^{Ph}), 126.77 (s, *m*-C^{Ph}), 126.98 (s, *m*-C^{Ph}), 127.19 (s, *m*-C^{Ph}), 127.36 (s, *m*-C^{Ph}), 127.42 (s, *m*-C^{Ph}), 128.75 (d, J_{CP} = 6.2 Hz, *o*-C^{Ph}), 129.27 (d, J_{CP} = 14.1 Hz, *o*-C^{Ph}), 131.12 (s, *o*-C^{Ph}), 133.76 (d, J_{CP} = 7.3 Hz, *o*-C^{Ph}), 134.34 (d, J_{CP} = 2.3 Hz, *o*-C^{Ph}), 136.34 (d, $^3J_{CP}$ = 1.9 Hz, *ipso*-C^{Ph}), 137.49 (d, $^2J_{CP}$ = 4.7 Hz, *ipso*-C^{Ph}), 138.94 (br.s., *ipso*-C^{Ph}), 139.22 (br.s., *ipso*-C^{Ph}), 144.25 (d, $^2J_{CP}$ = 11.5 Hz, *ipso*-C^{Ph}), 147.12 (d, $^1J_{CP}$ = 24.2 Hz, C^6), 150.49 (d, $^2J_{CP}$ = 1.7 Hz, C^5).

IR (KBr, cm^{-1}): 434 (w), 462 (w), 488 (w), 531 (w), 560 (m), 581 (m), 614 (w), 684 (s), 729 (w), 740 (m), 799 (m), 814 (w), 847 (w), 866 (w), 946 (m), 984 (w), 1022 (m), 1049 (m), 1179 (w), 1188 (w), 1225 (w), 1317 (w), 1389 (w), 1433 (w), 1429 (m), 1499 (m), 1545 (m), 1822 (w), 1875 (w), 1989 (w), 2829 (w), 2823 (w), 2941 (w), 2950 (w), 3015 (w), 3064 (w), 3079 (w), 3014 (w).

$C_{38}H_{34}P_2$ (552.62): calcd C 82.59, H 6.20, P 11.21; found C 82.55, H 6.10, P 11.35.

2,3,4*a*,4,5,6-Hexaphenyl-1-isopropyl-1-oxo-1,7,7*a*-triphospha-4,7-(isopropylphosphinidene-oxide)-indene (5a). Dry *N-tert*-butyl-alpha-phenylnitrone (**4a**) (0.16 g, 0.90 mmol) or *N*-alpha-diphenylnitrone (**4b**) (0.18 g, 0.90 mmol) in toluene (5 ml) was added to a solution of 1-isopropyl-1,2-diphosphacyclopenta-2,4-diene (**1a**) (0.34 g, 0.91 mmol) in toluene (5 ml) and stirred for 12 h (overnight) at 25 °C. Then the solvent was evaporated under reduced pressure and the residue was washed with *n*-hexane (2 × 5 ml). The residue was dried, dissolved in toluene (2 ml) and 1 ml of *n*-hexane was slowly added dropwise. The solution was kept at 0 °C overnight to give light yellow crystals which were isolated by filtration and dried *in vacuo* to leave 0.26 g (74%) of **5a** as light yellow powder; m.p. 166–167 °C.



^{1}H NMR (CDCl$_3$, ppm): 1.20 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 15.4 Hz, 3H, Me), 1.32 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 15.6 Hz, 3H, Me), 1.43 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 16.9 Hz, 3H, Me), 1.51 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 16.6 Hz, 3H, Me), 2.40 (m, 1H, CH), 2.53 (m, 1H, CH), 6.80 (tr, $^3J_{HH}$ = 7.5 Hz, 3H, Ph), 6.91 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 6.96–7.16 (m, 15H, Ph), 7.22–7.30 (m, 5H, Ph), 7.31–7.39 (m, 3H, Ph), 7.50 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph).

^{31}P{^{1}H} NMR (CDCl$_3$, ppm): 100.5 (ddd, $^1J_{PP}$ = 173.4 Hz, $^2J_{PP}$ = 38.5 Hz, $^3J_{PP}$ = 19.2 Hz, P^2), 75.7 (dd, $^1J_{PP}$ = 278.7 Hz, $^3J_{PP}$ = 19.2 Hz, P^4), −10.6 (dd, $^1J_{PP}$ = 278.7 Hz, $^2J_{PP}$ = 38.5 Hz, P^3), −29.7 (d, $^1J_{PP}$ = 173.4 Hz, P^1).

^{13}C{^{1}H} NMR (CDCl$_3$, ppm): 26.34 (dd, $^2J_{CP}$ = 19.1 Hz, $^3J_{CP}$ = 3.4 Hz, Me), 27.03 (dd, $^2J_{CP}$ = 15.2 Hz, $^3J_{CP}$ = 2.6 Hz, Me), 27.58 (dd, $^2J_{CP}$ = 9.8 Hz, $^3J_{CP}$ = 5.1 Hz, Me), 28.92 (dd, $^2J_{CP}$ = 10.7 Hz, $^3J_{CP}$ = 4.5 Hz, Me), 43.52 (dd, $^1J_{CP}$ = 43.8 Hz, $^2J_{CP}$ = 10.0 Hz, CH), 48.91 (dd, $^1J_{CP}$ = 35.8 Hz, $^2J_{CP}$ = 15.1 Hz, CH), 73.07 (dd, $^1J_{CP}$ = 27.5 Hz, $^2J_{CP}$ = 8.7 Hz, C^5), 74.29 (dd, $^1J_{CP}$ = 19.3 Hz, $^2J_{CP}$ = 10.5 Hz, C^6), 126.61 (s, *p*-C^{Ph}), 126.70

(s, *p*-C^{Ph}), 126.89 (s, *p*-C^{Ph}), 127.19 (s, *p*-C^{Ph}), 127.26 (s, *p*-C^{Ph}), 127.40 (s, *p*-C^{Ph}), 127.58 (s, *p*-C^{Ph}), 127.82 (s, *p*-C^{Ph}), 127.95 (s, *m*-C^{Ph}), 128.00 (s, *m*-C^{Ph}), 128.06 (s, *m*-C^{Ph}), 128.14 (s, *m*-C^{Ph}),128.31 (s, *m*-C^{Ph}), 128.40 (s, *m*-C^{Ph}), 128.52 (s, *m*-C^{Ph}), 128.61 (s, *m*-C^{Ph}), 128.71 (s, *o*-C^{Ph}), 128.86 (s, *o*-C^{Ph}), 128.92 (s, *o*-C^{Ph}), 129.40 (s, *o*-C^{Ph}), 129.61 (s, *o*-C^{Ph}), 129.86 (s, *o*-C^{Ph}), 130.09 (s, *o*-C^{Ph}), 130.26 (dd, $^{3}J_{CP}$ = 4.7 Hz, $^{2}J_{CP}$ = 9.1 Hz, *ipso*-C^{Ph}), 131.26 (dd, $^{2}J_{CP}$ = 7.1 Hz, $^{2}J_{CP}$ = 14.2 Hz, *ipso*-C^{Ph}), 132.78 (d, $^{2}J_{CP}$ = 10.1 Hz, *ipso*-C^{Ph}), 134.29 (d, $^{3}J_{CP}$ = 6.9 Hz, *ipso*-C^{Ph}), 135.96 (dd, $^{2}J_{CP}$ = 15.6 Hz, $^{2}J_{CP}$ = 14.9 Hz, *ipso*-C^{Ph}), 137.36 (d, $^{3}J_{CP}$ = 7.6 Hz, *ipso*-C^{Ph}), 139.43 (dd, $^{1}J_{CP}$ = 12.9 Hz, $^{2}J_{CP}$ = 3.9 Hz, C^{7}), 141.09 (dd, $^{1}J_{CP}$ = 17.93 Hz, $^{2}J_{CP}$ = 3.8 Hz, C^{8}), 155.63 (d, $^{2}J_{CP}$ = 18.1 Hz, C^{9}), 157.28 (dd, $^{2}J_{CP}$ = 16.5 Hz, $^{2}J_{CP}$ = 15.8 Hz, C^{10}).

IR (KBr, cm^{-1}): 457 (m), 463 (m), 482 (w), 496 (w), 517 (m), 531 (w), 567 (m), 610 (w), 647 (w), 692 (s), 793 (s), 854 (m), 921 (w), 932 (m), 1022 (s), 1098 (s), 1179 (m, P═O), 1245 (s, P═O), 1378 (w), 1408 (m), 1438 (m), 1496 (m), 1592 (m), 2870 (w), 2875 (w), 2930 (m), 2962 (m), 3052 (m).

$C_{48}H_{44}O_2P_4$ (776.23): calcd C 74.22, H 5.71, O 4.12, P 15.95; found C 74.27, H 5.79, P 15.85.

2,3,4*a*,4,5,6-Hexaphenyl-1-propyl-1-oxo-1,7,7*a*-tetraphospha-4,7-(propylphosphinidene-oxide)-indene (5b). In a similar manner **5b** was obtained from 1-propyl-1,2-diphosphacyclopenta-2,4-diene (**1b**) (0.24 g, 0.65 mmol) and *N*-*tert*-butyl-alpha-phenylnitrone (**4a**) (0.11 g, 0.63 mmol) as light yellow powder (0.19 g, 79%); m.p. 165 °C.

^{1}H NMR (CDCl$_3$, ppm): 1.01 (tr, $^{3}J_{HH}$ = 6.8 Hz, 3H, Me), 1.07 (tr, $^{3}J_{HH}$ = 6.7 Hz, 3H, Me), 1.78 (m, 2H, CH$_2$), 1.85 (m, 2H, CH$_2$), 1.97 (m, 2H, CH$_2$), 2.01 (m, 2H, CH$_2$), 6.79 (tr, $^{3}J_{HH}$ = 7.2 Hz, 3H, Ph), 6.88 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ph), 6.92–7.10 (m, 15H, Ph), 7.21–7.29 (m, 4H, Ph), 7.31–7.40 (m, 4H, Ph), 7.59 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ph).

^{31}P{^{1}H} NMR (CDCl$_3$, ppm): 93.6 (ddd, $^{1}J_{PP}$ = 167.8 Hz, $^{2}J_{PP}$ = 42.6 Hz, $^{3}J_{PP}$ = 18.9 Hz, P^{2}), 67.3 (dd, $^{1}J_{PP}$ = 270.7 Hz, $^{3}J_{PP}$ = 18.9 Hz, P$_4$), −10.1 (dd, $^{1}J_{PP}$ = 270.7 Hz, $^{2}J_{PP}$ = 42.6 Hz, P$_3$), −31.6 (d, $^{1}J_{PP}$ = 167.8 Hz, P$_1$).

^{13}C{^{1}H} NMR (CDCl$_3$, ppm): 15.64 (d, $^{3}J_{CP}$ = 6.7 Hz, Me), 15.89 (d, $^{3}J_{CP}$ = 6.5 Hz, Me), 17.98 (d, $^{2}J_{CP}$ = 15.7 Hz, CH$_2$), 18.56 (d, $^{2}J_{CP}$ = 18.2 Hz, CH$_2$), 31.63 (dd, $^{1}J_{CP}$ = 46.5 Hz, $^{2}J_{CP}$ = 10.1 Hz, CH$_2$), 37.17 (dd, $^{1}J_{CP}$ = 52.7 Hz, $^{2}J_{CP}$ = 25.8 Hz, CH$_2$), 73.57 (dd, $^{1}J_{CP}$ = 27.6 Hz, $^{2}J_{CP}$ = 7.8 Hz, C^{5}), 75.2 (dd, $^{1}J_{CP}$ = 19.3 Hz, $^{2}J_{CP}$ = 9.5 Hz, C^{6}), 126.61 (s, *p*-C^{Ph}), 126.70 (s, *p*-C^{Ph}), 126.89 (s, *p*-C^{Ph}), 127.24 (s, *p*-C^{Ph}), 127.35 (s, *p*-C^{Ph}), 127.38 (s, *p*-C^{Ph}), 127.57 (s, *p*-C^{Ph}), 127.69 (s, *p*-C^{Ph}), 127.88 (s, *m*-C^{Ph}), 128.00 (s, *m*-C^{Ph}), 128.06 (s, *m*-C^{Ph}), 128.14 (s, *m*-C^{Ph}), 128.36 (s, *m*-C^{Ph}), 128.44 (s, *m*-C^{Ph}), 128.49 (s, *m*-C^{Ph}), 128.62 (s, *m*-C^{Ph}), 128.71 (s, *o*-C^{Ph}), 128.86 (s, *o*-C^{Ph}), 128.92 (s, *o*-C^{Ph}), 128.95 (s, *o*-C^{Ph}), 129.32 (s, *o*-C^{Ph}), 129.36 (s, *o*-C^{Ph}), 129.51 (s, *o*-C^{Ph}), 129.58 (s, *o*-C^{Ph}), 129.67 (s, *o*-C^{Ph}), 130.06 (s, *o*-C^{Ph}), 130.22 (dd, $^{3}J_{CP}$ = 3.4 Hz, $^{2}J_{CP}$ = 9.7 Hz, *ipso*-C^{Ph}), 131.56 (dd, $^{2}J_{CP}$ = 5.9 Hz, $^{2}J_{CP}$ = 18.4 Hz, *ipso*-C^{Ph}), 132.03 (d, $^{2}J_{CP}$ = 9.9 Hz, *ipso*-C^{Ph}), 133.37 (dd, $^{2}J_{CP}$ = 7.2 Hz, $^{2}J_{CP}$ = 14.7 Hz, *ipso*-C^{Ph}), 134.38 (d, $^{3}J_{CP}$ = 7.3 Hz, *ipso*-C^{Ph}), 135.87 (dd, $^{2}J_{CP}$ = 17.5 Hz, $^{2}J_{CP}$ = 3.8 Hz, *ipso*-C^{Ph}), 139.42 (dd, $^{1}J_{CP}$ = 16.0 Hz, $^{2}J_{CP}$ = 4.1 Hz, C^{7}), 140.01 (dd, $^{1}J_{CP}$ = 23.5 Hz, $^{2}J_{CP}$ = 3.4 Hz, C^{8}), 153.92 (d, $^{2}J_{CP}$ = 17.2 Hz, C^{9}), 155.55 (dd, $^{2}J_{CP}$ = 15.3 Hz, $^{2}J_{CP}$ = 13.9 Hz, C^{10}).

IR (KBr, cm^{-1}): 459 (m), 483 (w), 497 (w), 523 (m), 539 (m), 567 (m), 611 (w), 641 (w), 696 (s), 800 (s), 866 (m), 923 (w), 1026 (s), 1094 (s), 1174 (m, P═O), 1262 (s, P═O), 1378 (w), 1405 (m), 1442 (m), 1493 (m), 1596 (m), 2871 (w), 2928 (m), 2963 (m), 3056 (m).

$C_{48}H_{44}O_2P_4$ (776.23): calcd C 74.22, H 5.71, O 4.12, P 15.95; found C 74.11, H 5.80, P 16.01.

2,3,4*a*,4,5,6-Hexaphenyl-1-butyl-1-oxo-1,7,7*a*-tetraphospha-4,7-(butylphosphinidene-oxide)-indene (5c). In a similar manner **5c** was obtained from 1-butyl-1,2-diphosphacyclopenta-2,4-diene (**1c**) (0.28 g, 0.73 mmol) and *N*-*tert*-butyl-alpha-phenylnitrone (**4a**) (0.13 g, 0.73 mmol) as light yellow powder (0.22 g, 76%); m.p. 168 °C.

^{1}H NMR (CDCl$_{3,}$ ppm): 0.71 (tr, $^{3}J_{HH}$ = 7.5 Hz, 3H, Me), 0.78 (tr, $^{3}J_{HH}$ = 7.1 Hz, 3H, Me), 1.16 (m, 2H, CH$_2$), 1.21 (m, 2H, CH$_2$), 1.26 (m, 2H, CH$_2$), 1.30 (m, 2H, CH$_2$), 1.88 (m, 4H, 2CH$_2$), 6.65 (tr, $^{3}J_{HH}$ = 7.3 Hz, 3H, Ph), 6.77–6.96 (m, 10H, Ph), 6.98–7.08 (m, 4H, Ph), 7.09–7.19 (m, 4H, Ph), 7.29 (tr, $^{3}J_{HH}$ = 7.6 Hz, 3H, Me), 7.44 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ph), 7.66 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ph), 7.69 (d, $^{3}J_{HH}$ = 6.3 Hz, 2H, Ph).

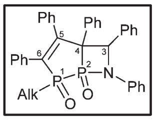
^{31}P{^{1}H} NMR (CDCl$_3$, ppm): 92.5 (ddd, $^{1}J_{PP}$ = 165.3 Hz, $^{2}J_{PP}$ = 41.5 Hz, $^{3}J_{PP}$ = 18.5 Hz, P$_2$), 66.3 (dd, $^{1}J_{PP}$ = 266.7 Hz, $^{3}J_{PP}$ = 18.5 Hz, P$_4$), −9.2 (dd, $^{1}J_{CD}$ = 266.7 Hz, $^{2}J_{CB}$ = 41.5 Hz, P$_3$), −30.5 (d, $^{1}J_{AB}$ = 165.9 Hz, P$_1$).

^{13}C{^{1}H} NMR (CDCl$_3$, ppm): 14.56 (s, Me), 14.89 (s, Me), 15.23 (d, $^{3}J_{CP}$ = 6.5 Hz, CH$_2$), 15.91 (d, $^{3}J_{CP}$ = 8.5 Hz, CH$_2$), 17.68 (d, $^{2}J_{CP}$ = 14.7 Hz, CH$_2$), 19.63 (d, $^{2}J_{CP}$ = 19.2 Hz, CH$_2$), 33.64 (dd, $^{1}J_{CP}$ = 36.5 Hz, $^{2}J_{CP}$ = 15.7 Hz, CH$_2$), 36.3 (dd, $^{1}J_{CP}$ = 46.9 Hz, $^{2}J_{CP}$ = 21.3 Hz, CH$_2$), 73.57 (dd, $^{1}J_{CP}$ = 27.5 Hz, $^{2}J_{CP}$ = 8.7 Hz, C^{5}), 74.25 (dd, $^{1}J_{CP}$ = 19.3 Hz, $^{2}J_{CP}$ = 10.5 Hz, C^{6}), 126.63 (s, *p*-C^{Ph}), 126.69 (s, *p*-C^{Ph}), 126.92 (s, *p*-C^{Ph}), 127.20 (s, *p*-C^{Ph}), 127.35 (s, *p*-C^{Ph}), 127.47 (s, *p*-C^{Ph}), 127.57 (s, *p*-C^{Ph}), 127.69 (s, *p*-C^{Ph}), 127.84 (s, *m*-C^{Ph}), 128.00 (s, *m*-C^{Ph}), 128.05 (s, *m*-C^{Ph}), 128.19 (s, *m*-C^{Ph}), 128.36 (s, *m*-C^{Ph}), 128.45 (s, *m*-C^{Ph}), 128.52 (s, *m*-C^{Ph}), 128.64 (s, *m*-C^{Ph}), 128.76 (s, *o*-C^{Ph}), 128.86 (s, *o*-C^{Ph}), 128.91 (s, *o*-C^{Ph}), 129.07 (s, *o*-C^{Ph}), 129.32 (s, *o*-C^{Ph}), 129.36 (s, *o*-C^{Ph}), 129.53 (s, *o*-C^{Ph}), 129.59 (s, *o*-C^{Ph}), 129.68 (s, *o*-C^{Ph}), 130.06 (s, *o*-C^{Ph}), 130.26 (dd, $^{3}J_{CP}$ = 4.2 Hz, $^{2}J_{CP}$ = 9.5 Hz, *ipso*-C^{Ph}), 131.26 (dd, $^{2}J_{CP}$ = 5.9 Hz, $^{2}J_{CP}$ = 15.6 Hz, *ipso*-C^{Ph}), 132.05 (d, $^{2}J_{CP}$ = 10.1 Hz, *ipso*-C^{Ph}), 133.45 (dd, $^{2}J_{CP}$ = 8.8 Hz, $^{2}J_{CP}$ = 14.2 Hz, *ipso*-C^{Ph}), 134.38 (d, $^{3}J_{CP}$ = 7.3 Hz, *ipso*-C^{Ph}), 135.87 (dd, $^{2}J_{CP}$ = 17.5 Hz, $^{2}J_{CP}$ = 3.8 Hz, *ipso*-C^{Ph}), 138.43 (dd, $^{1}J_{CP}$ = 15.8 Hz, $^{2}J_{CP}$ = 6.8 Hz, C^{7}), 141.05 (dd, $^{1}J_{CP}$ = 22.6 Hz, $^{2}J_{CP}$ = 4.8 Hz, C^{8}), 154.52 (d, $^{2}J_{CP}$ = 18.2 Hz, C^{9}), 158.73 (dd, $^{2}J_{CP}$ = 14.4 Hz, $^{2}J_{CP}$ = 13.1 Hz, C^{10}).

IR (KBr, cm^{-1}): 457 (m), 462 (m), 483 (w), 495 (w), 515 (m), 536 (m), 563 (m), 617 (w), 654 (w), 693 (s), 794 (s), 855 (w), 920 (w), 938 (m), 1024 (s), 1097 (s), 1182 (s, P═O), 1257 (s, P═O), 1378 (w), 1412 (m), 1443 (m), 1496 (m), 1594 (m), 2871 (w), 2879 (w), 2933 (m), 2962 (m), 3051 (m).

$C_{50}H_{48}O_2P_4$ (804.26): calcd C 74.62, H 6.01, O 3.98, P 15.39; found C 74.53, H 5.89, P 15.42.

1-Isopropyl-2,3,4,5,6-pentaphenyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (7a). Dry N-α-diphenylnitrone (0.13 g, 0.66 mmol, 10% excess) in toluene (5 ml) was added to a solution of 1-isopropyl-1,2-diphosphacyclopenta-2,4-diene (**1a**) (0.22 g, 0.60 mmol) in toluene (5 ml) and stirred for 10 h at 100 °C. Then the solvent was evaporated under reduced pressure and the residue was washed with *n*-hexane (2 × 10 ml). The residue was dried, dissolved in toluene (2 ml) and 1 ml of *n*-hexane was slowly added dropwise. The solution was kept at 0 °C overnight to give light yellow crystals which were isolated by filtration and dried *in vacuo* to leave 0.17 g (49%) of **7a** as white powder; m.p. 251 °C.



^{1}H NMR (C_6D_6, ppm): 1.36 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 19.9 Hz, 3H, Me), 1.58 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.5 Hz, 3H, Me), 2.47 (m, 1H, CH), 5.11 (d, $^3J_{PH}$ = 8.3 Hz, 1H, C(Ph)H), 6.51 (tr, $^3J_{HH}$ = 8.0 Hz, 3H, Ph), 6.96 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 7.10–7.29 (m, 10H, Ph), 7.37–7.56 (m, 5H, Ph), 7.87–7.96 (m, 5H, Ph).

^{31}P{^{1}H} NMR (C_6D_6, ppm): 43.2 (d, $^1J_{PP}$ = 50.6 Hz, P^1), 32.3 (d, $^1J_{PP}$ = 50.6 Hz, P^2).

^{13}C{^{1}H} NMR (C_6D_6, ppm): 13.24 (dd, $^2J_{CP}$ = 12.3 Hz, $^3J_{CP}$ = 5.2 Hz, Me), 14.12 (dd, $^2J_{CP}$ = 12.6 Hz, $^3J_{CP}$ = 4.8 Hz, Me), 30.18 (dd, $^1J_{CP}$ = 37.6 Hz, $^2J_{CP}$ = 10.0 Hz, CH), 65.41 (d, $^2J_{CP}$ = 13.9 Hz, C^3), 68.80 (dd, $^1J_{CP}$ = 26.8 Hz, $^2J_{CP}$ = 10.1 Hz, C^4), 126.27 (s, *p*-C^{Ph}), 126.56 (s, *p*-C^{Ph}), 126.83 (s, *p*-C^{Ph}), 127.35 (s, *p*-C^{Ph}), 127.68 (s, *p*-C^{Ph}), 127.91 (s, *m*-C^{Ph}), 128.34 (s, *m*-C^{Ph}), 128.40 (s, *m*-C^{Ph}), 128.52 (s, *m*-C^{Ph}), 128.72 (s, *m*-C^{Ph}),128.86 (s, *o*-C^{Ph}), 128.96 (s, *o*-C^{Ph}), 129.39 (s, *o*-C^{Ph}), 131.46 (dd, $^3J_{CP}$ = 7.6 Hz, $^3J_{CP}$ = 3.5 Hz, *ipso*-C^{Ph}), 136.13 (dd, $^3J_{CP}$ = 5.9 Hz, $^2J_{CP}$ = 7.8 Hz, *ipso*-C^{Ph}), 136.95 (dd, $^3J_{CP}$ = 6.8 Hz, $^2J_{CP}$ = 9.1 Hz, *ipso*-C^{Ph}), 137.35 (d, $^3J_{CP}$ = 6.5 Hz, *ipso*-C^{Ph}), 137.91 (dd, $^3J_{CP}$ = 6.3 Hz, $^2J_{CP}$ = 6.1 Hz, *ipso*-C^{Ph}), 139.37 (dd, $^2J_{CP}$ = 9.5 Hz, $^2J_{CP}$ = 9.1 Hz, C^5), 155.13 (dd, $^1J_{CP}$ = 26.9 Hz, $^2J_{CP}$ = 11.1 Hz, C^6).

IR (KBr, cm^{-1}): 485 (w), 517 (m), 523 (m), 538 (m), 546 (m), 585 (w), 680 (m), 712 (s), 745 (m), 787 (m), 811 (w), 879 (w), 1015 (m), 1032 (m), 1052 (m), 1060 (m), 1075 (w), 1184 (s, P═O), 1238 (s, P═O), 1365 (w), 1371 (m), 1393 (m), 1433 (w), 1467 (m), 1490 (m), 1595 (m), 1641 (w), 2896 (w), 2972 (s), 2995 (w), 3037 (w), 3061 (m).

$C_{37}H_{33}NO_2P_2$ (585.61): calcd C 75.89, H 5.68, N 2.39, O 5.46, P 10.58; found C 75.63, H 5.90, N 2.26, P 10.76.

1-Propyl-2,3,4,5,6-pentaphenyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (7b). In a similar manner **7b** was obtained from N-α-diphenylnitrone (**4b**) (0.12 g, 0.59 mmol, 10% excess) and 1-propyl-1,2-diphosphacyclopenta-2,4-diene (**1b**) (0.20 g, 0.54 mmol) as a white powder (0.14 g, 45%); m.p. 249 °C.

^{1}H NMR (C_6D_6, ppm): 1.15 (tr, $^3J_{HH}$ = 6.9 Hz, 3H, Me), 1.73 (m, 2H, CH$_2$), 1.95 (m, 2H, CH$_2$), 5.12 (d, $^3J_{PH}$ = 6.8 Hz, 1H, C(Ph)H), 6.57 (tr, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 6.95 (tr, $^3J_{HH}$ = 8.5 Hz, 1H, Ph), 7.11–7.30 (m, 10H, Ph), 7.36–7.54 (m, 5H, Ph), 7.63 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ph) 7.87–7.96 (m, 5H, Ph).

^{31}P{^{1}H} NMR (C_6D_6, ppm): 35.3 (d, $^1J_{PP}$ = 67.8 Hz, P^1), 31.4 (d, $^1J_{PP}$ = 67.8 Hz, P^2).

^{13}C{^{1}H} NMR (C_6D_6, ppm): 10.34 (d, $^3J_{CP}$ = 5.3 Hz, Me), 13.25 (d, $^2J_{CP}$ = 14.5 Hz, CH$_2$), 30.48 (dd, $^1J_{CP}$ = 35.9 Hz, $^2J_{CP}$ = 11.8 Hz, CH$_2$), 65.54 (d, $^2J_{CP}$ = 13.8 Hz, C^3), 67.23 (dd, $^1J_{CP}$ = 25.3 Hz, $^2J_{CP}$ = 9.5 Hz, C^4), 126.16 (s, *p*-C^{Ph}), 126.43 (s, *p*-C^{Ph}), 126.64 (s, *p*-C^{Ph}), 127.29 (s, *m*-C^{Ph}), 127.56 (s, *m*-C^{Ph}), 127.80 (s, *m*-C^{Ph}), 128.24 (s, *m*-C^{Ph}), 128.37 (s, *m*-C^{Ph}), 128.53 (s, *o*-C^{Ph}), 128.72 (s, *o*-C^{Ph}),128.86 (s, *o*-C^{Ph}), 128.96 (s, *o*-C^{Ph}), 129.40 (s, *o*-C^{Ph}), 131.54 (dd, $^3J_{CP}$ = 7.4 Hz, $^3J_{CP}$ = 3.6 Hz, *ipso*-C^{Ph}), 136.45 (dd, $^3J_{CP}$ = 4.9 Hz, $^2J_{CP}$ = 8.8 Hz, *ipso*-C^{Ph}), 136.95 (dd, $^3J_{CP}$ = 6.2 Hz, $^2J_{CP}$ = 8.9 Hz, *ipso*-C^{Ph}), 137.38 (d, $^3J_{CP}$ = 6.6 Hz, *ipso*-C^{Ph}), 137.92 (dd, $^3J_{CP}$ = 5.9 Hz, $^2J_{CP}$ = 6.4 Hz, *ipso*-C^{Ph}), 140.12 (dd, $^2J_{CP}$ = 10.0 Hz, $^2J_{CP}$ = 8.9 Hz, C^5), 156.47 (dd, $^1J_{CP}$ = 30.33 Hz, $^2J_{CP}$ = 12.4 Hz, C^6).

IR (KBr, cm^{-1}): 486 (m), 513 (m), 525 (m), 536 (w), 546 (m), 585 (w), 681 (w), 713 (s), 741 (m), 787 (m), 810 (w), 875 (w), 1012 (m), 1038 (w), 1053 (m), 1068 (m), 1076 (m), 1185 (s, P═O), 1236 (s, P═O), 1365 (w), 1371 (w), 1393 (m), 1435 (m), 1461 (m), 1492 (m), 1587 (m), 1643 (w), 2901 (w), 2976 (s), 2989 (w), 3026 (m), 3051 (m).

$C_{37}H_{33}NO_2P_2$ (585.61): calcd C 75.89, H 5.68, N 2.39, O 5.46, P 10.58; found C 75.78, H 5.72, N 2.46, P 10.56.

1-Butyl-2,3,4,5,6-pentaphenyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (7c). In a similar manner **7c** was obtained from N-α-diphenylnitrone (**4b**) (0.13 g, 0.68 mmol, 10% excess) and 1-butyl-1,2-diphosphacyclopenta-2,4-diene (**1c**) (0.24 g, 0.62 mmol) as a white powder (0.15 g, 41%); m. p. 252 °C.

^{1}H NMR (C_6D_6, ppm): 0.78 (tr, $^3J_{HH}$ = 7.4 Hz, 3H, Me), 1.21 (m, 2H, CH$_2$),1.58 (m, 2H, CH$_2$), 1.88 (m, 2H, CH$_2$), 5.21 (d, $^3J_{PH}$ = 7.1 Hz, 1H, C(Ph)H), 6.50 (tr, $^3J_{HH}$ = 8.5 Hz, 3H, Ph), 6.96 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 7.09–7.24 (m, 10H, Ph), 7.32–7.53 (m, 5H, Ph), 7.82–7.91 (m, 5H, Ph).

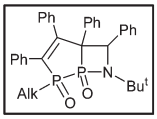
^{31}P{^{1}H} NMR (C_6D_6, ppm): 35.8 (d, $^1J_{PP}$ = 68.1 Hz, P^1), 31.5 (d, $^1J_{PP}$ = 68.1 Hz, P^2).

^{13}C{^{1}H} NMR (C_6D_6, ppm): 11.23 (s, Me), 14.45 (d, $^3J_{CP}$ = 7.4 Hz, CH$_2$), 18.12 (d, $^2J_{CP}$ = 15.6 Hz, CH$_2$), 30.64 (dd, $^1J_{CP}$ = 33.2 Hz, $^2J_{CP}$ = 14.2 Hz, CH$_2$), 64.44 (d, $^2J_{CP}$ = 13.7 Hz, C^3), 68.13 (dd, $^1J_{CP}$ = 26.3 Hz, $^2J_{CP}$ = 10.4 Hz, C^4), 126.25 (s, *p*-C^{Ph}), 126.56 (s, *p*-C^{Ph}), 126.87 (s, *p*-C^{Ph}), 127.38 (s, *m*-C^{Ph}), 127.68 (s, *m*-C^{Ph}), 127.92 (s, *m*-C^{Ph}), 128.35 (s, *m*-C^{Ph}), 128.40 (s, *m*-C^{Ph}), 128.54 (s, *o*-C^{Ph}), 128.72 (s, *o*-C^{Ph}),128.85 (s, *o*-C^{Ph}), 128.96 (s, *o*-C^{Ph}), 129.28 (s, *o*-C^{Ph}), 131.66 (dd, $^3J_{CP}$ = 7.1 Hz, $^3J_{CP}$ = 5.7 Hz, *ipso*-C^{Ph}), 135.36 (dd, $^3J_{CP}$ = 5.2 Hz, $^2J_{CP}$ = 9.8 Hz, *ipso*-C^{Ph}), 136.87 (dd, $^3J_{CP}$ = 5.8 Hz, $^2J_{CP}$ = 9.1 Hz, *ipso*-C^{Ph}), 137.49 (d, $^3J_{CP}$ = 6.9 Hz, *ipso*-C^{Ph}), 138.91 (dd, $^3J_{CP}$ = 6.1 Hz, $^2J_{CP}$ = 6.3 Hz, *ipso*-C^{Ph}), 140.37 (dd, $^2J_{CP}$ = 10.0 Hz, $^2J_{CP}$ = 9.2 Hz, C^5), 154.92 (dd, $^1J_{CP}$ = 29.2 Hz, $^2J_{CP}$ = 11.2 Hz, C^6).

IR (KBr, cm^{-1}): 485 (m), 511 (m), 521 (w), 536 (m), 542 (m), 580 (w), 683 (w), 714 (s), 746 (m), 787 (m), 810 (w), 873 (w), 1015 (m), 1036 (w), 1054 (m), 1063 (m), 1075 (m), 1179 (s, P═O), 1231 (s, P═O), 1365 (w), 1392 (m), 1434 (m), 1457 (m), 1493 (w), 1588 (m), 1641 (w), 2897 (m), 2970 (s), 2992 (w), 3052 (m).

$C_{37}H_{33}NO_2P_2$ (599.64): calcd C 76.11, H 5.88, N 2.34, O 5.34, P 10.33; found C 76.28, H 5.72, N 2.41, P 10.45.

1-Isopropyl-2,3,4,5-tetraphenyl-6-*tert*-butyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (7d). Dry *N-tert*-butyl-α-phenylnitrone (**4a**) (0.17 g, 0.95 mmol, 10% excess) in toluene (5 ml) was added to a solution of 1-isopropyl-1,2-diphosphacyclopenta-2,4-diene (**1a**) (0.32 g, 0.86 mmol) in toluene (5 ml) and stirred for 10 h at 100 °C. Then the solvent was evaporated under reduced pressure and the residue was washed with *n*-hexane (2 × 5 ml). The residue was dried, dissolved in toluene (2 ml) and 2 ml of *n*-hexane were slowly added dropwise. The solution was kept at 0 °C overnight to give light yellow crystals which were isolated by filtration and dried *in vacuo* to leave 0.24 g (49%) of **7d** as white powder; m.p. 245 °C.



^{1}H NMR (C_6D_6, ppm): 1.42 (s, 9H, ^{t}Bu), 1.43 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 19.6 Hz, 3H, Me), 1.66 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 17.4 Hz, 3H, Me), 2.35 (m, 1H, CH), 5.39 (d, $^3J_{PH}$ = 7.2 Hz, 1H, C(Ph)H), 6.50 (tr, $^3J_{HH}$ = 7.9 Hz, 2H, Ph), 6.66 (tr, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 6.87–7.04 (m, 5H, Ph), 7.12–7.36 (m, 7H, Ph), 7.47 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 7.55 (tr, $^3J_{HH}$ = 7.6 Hz, 1H, Ph), 7.73 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ph).

^{31}P{^{1}H} NMR (C_6D_6, ppm): 41.3 (d, $^1J_{PP}$ = 66.9 Hz, P^1), 38.3 (d, $^1J_{PP}$ = 66.9 Hz, P^2).

^{13}C{^{1}H} NMR (C_6D_6, ppm): 1.14 (s, Me), 15.07 (dd, $^2J_{CP}$ = 14.8 Hz, $^3J_{CP}$ = 3.6 Hz, Me), 15.74 (dd, $^2J_{CP}$ = 12.6 Hz, $^3J_{CP}$ = 5.7 Hz, Me), 29.82 (dd, $^1J_{CP}$ = 35.2 Hz, $^2J_{CP}$ = 10.8 Hz, CH), 54.84 (d, $^2J_{CP}$ = 15.1 Hz, C^3), 61.28 (dd, $^2J_{CP}$ = 9.8 Hz, $^3J_{CP}$ = 3.9 Hz, C^{tBu}), 69.28 (dd, $^1J_{CP}$ = 29.8 Hz, $^2J_{CP}$ = 10.5 Hz, C^4), 126.25 (s, *p*-C^{Ph}), 126.81 (s, *p*-C^{Ph}), 127.29 (s, *p*-C^{Ph}), 127.32 (s, *p*-C^{Ph}), 127.67 (s, *m*-C^{Ph}), 127.90 (s, *m*-C^{Ph}), 128.40 (s, *m*-C^{Ph}), 128.49 (s, *m*-C^{Ph}), 128.70 (s, *o*-C^{Ph}), 128.88 (s, *o*-C^{Ph}), 128.97 (s, *o*-C^{Ph}), 129.39 (s, *o*-C^{Ph}), 130.84 (dd, $^3J_{CP}$ = 6.6 Hz, $^3J_{CP}$ = 3.7 Hz, *ipso*-C^{Ph}), 135.68 (dd, $^3J_{CP}$ = 6.2 Hz, $^2J_{CP}$ = 9.7 Hz, *ipso*-C^{Ph}), 136.05 (dd, $^3J_{CP}$ = 6.8 Hz, $^2J_{CP}$ = 10.1 Hz, *ipso*-C^{Ph}), 137.35 (d, $^3J_{CP}$ = 5.9 Hz, *ipso*-C^{Ph}), 138.46 (dd, $^2J_{CP}$ = 10.8 Hz, $^2J_{CP}$ = 9.2 Hz, C^5), 154.50 (dd, $^1J_{CP}$ = 27.3 Hz, $^2J_{CP}$ = 12.8 Hz, C^6).

IR (KBr, cm^{-1}): 481 (m), 507 (m), 515 (m), 530 (m), 546 (m), 578 (w), 663 (m), 700 (s), 735 (m), 775 (m), 799 (w), 879 (w), 1012 (m), 1029 (m), 1075 (m), 1081 (m), 1075 (w), 1172 (s, P═O), 1219 (s, P═O), 1365 (m), 1433 (w), 1454 (m), 1491 (m), 1598 (m), 1637 (w), 2890 (w), 2968 (s), 2982 (w), 3027 (w), 3053 (m).

$C_{35}H_{37}NO_2P_2$ (565.62): calcd C 74.32, H 6.59, N 2.48, O 5.66, P 10.95; found C 74.21, H 6.69, N 2.44, P 10.73.

1-Propyl-2,3,4,5-tetraphenyl-6-*tert*-butyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (7e). In a similar manner **7e** was obtained from *N*-*tert*-butyl-α-phenylnitrone (**4a**) (0.12 g, 0.65 mmol, 10% excess) and 1-propyl-1,2-diphosphacyclopenta-2,4-diene (**1b**) (0.22 g, 0.59 mmol) as a white powder (0.15 g, 46%); m.p. 243 °C.

^{1}H NMR (C_6D_6, ppm): 1.26 (tr, $^3J_{HH}$ = 6.7 Hz, 3H, Me), 1.41 (s, 9H, ^{t}Bu), 1.85 (m, 2H, CH$_2$), 2.01 (m, 2H, CH$_2$), 5.40 (d, $^3J_{PH}$ = 7.2 Hz, 1H, C(Ph)H), 6.53 (tr, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 6.66 (tr, $^3J_{HH}$ = 8.5 Hz, 1H, Ph), 6.90–7.08 (m, 5H, Ph), 7.16–7.32 (m, 8H, Ph), 7.47 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ph), 7.63 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ph).

^{31}P{^{1}H} NMR (C_6D_6, ppm): 40.4 (d, $^1J_{PP}$ = 75.8 Hz, P^1), 35.8 (d, $^1J_{PP}$ = 75.8 Hz, P^2).

^{13}C{^{1}H} NMR (C_6D_6, ppm): 3.13 (s, Me), 15.78 (d, $^3J_{CP}$ = 6.8 Hz, Me), 12.25 (d, $^2J_{CP}$ = 16.2 Hz, CH$_2$), 34.56 (dd, $^1J_{CP}$ = 43.8 Hz, $^2J_{CP}$ = 12.4 Hz, CH$_2$), 56.93 (d, $^2J_{CP}$ = 17.2 Hz, C^3), 62.82 (dd, $^2J_{CP}$ = 10.2 Hz, $^3J_{CP}$ = 4.1 Hz, C^{tBu}), 71.57 (dd, $^1J_{CP}$ = 29.6 Hz, $^2J_{CP}$ = 10.5 Hz, C^4), 126.52 (s, *p*-C^{Ph}), 126.87 (s, *p*-C^{Ph}), 127.23 (s, *p*-C^{Ph}), 127.55 (s, *p*-C^{Ph}), 128.13 (s, *m*-C^{Ph}), 128.43 (s, *m*-C^{Ph}), 128.60 (s, *m*-C^{Ph}),128.84 (s, *m*-C^{Ph}), 128.96 (s, *o*-C^{Ph}), 129.43 (s, *o*-C^{Ph}), 129.51 (s, *o*-C^{Ph}), 129.58 (s, *o*-C^{Ph}), 131.34 (dd, $^3J_{CP}$ = 7.4 Hz, $^3J_{CP}$ = 3.7 Hz, *ipso*-C^{Ph}), 135.68 (dd, $^3J_{CP}$ = 5.4 Hz, $^2J_{CP}$ = 12.7 Hz, *ipso*-C^{Ph}), 136.71 (dd, $^3J_{CP}$ = 8.1 Hz, $^2J_{CP}$ = 9.8 Hz, *ipso*-C^{Ph}), 137.35 (d, $^3J_{CP}$ = 5.9 Hz, *ipso*-C^{Ph}), 139.93 (dd, $^2J_{CP}$ = 11.7 Hz, $^2J_{CP}$ = 9.5 Hz, C^5), 153.93 (dd, $^1J_{CP}$ = 28.4 Hz, $^2J_{CP}$ = 13.8 Hz, C^6).

IR (KBr, cm^{-1}): 474 (m), 506 (w), 512 (m), 532 (m), 549 (m), 576 (w), 664 (m), 701 (s), 741 (m), 775 (m), 883 (w), 1013 (m), 1035 (m), 1067 (m), 1084 (m), 1079 (w), 1175 (s, P═O), 1215 (m, P═O), 1365 (w), 1428 (w), 1450 (m), 1492 (m), 1600 (w), 1637 (m), 2891 (w), 2967 (s), 2984 (w), 3032 (w), 3057 (m), 3061 (m).

$C_{35}H_{37}NO_2P_2$ (565.62): calcd C 74.32, H 6.59, N 2.48, O 5.66, P 10.95; found C 74.43, H 6.70, N 2.47, P 11.06.

1-Butyl-2,3,4,5-tetraphenyl-6-*tert*-butyl-1,7-dioxo-6-azo-1,7-diphospha-bicyclo[3.2.0]hept-2-ene (7f). In a similar manner **7f** was obtained from *N*-*tert*-butyl-α-phenylnitrone (**4a**) (0.13 g, 0.74 mmol, 10% excess) and 1-butyl-1,2-diphosphacyclopenta-2,4-diene (**1c**) (0.26 g, 0.67 mmol) as a white powder (0.17 g, 44%); m.p. 247 °C.

^{1}H NMR (C_6D_6, ppm): 0.85 (tr, $^3J_{HH}$ = 7.2 Hz, 3H, Me), 1.31 (m, 2H, CH$_2$), 1.42 (s, 9H, ^{t}Bu), 1.67 (m, 2H, CH$_2$), 1.94 (m, 2H, CH$_2$), 5.38 (d, $^3J_{PH}$ = 7.4 Hz, 1H, C(Ph)H), 6.61 (tr, $^3J_{HH}$ = 6.9 Hz, 2H, Ph), 6.76 (tr, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 6.97–7.12 (m, 5H, Ph), 7.20–7.31 (m, 5H, Ph), 7.44 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.66 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 7.69 (d, $^3J_{HH}$ = 6.3 Hz, 2H, Ph).

^{31}P{^{1}H} NMR (C_6D_6, ppm): 37.5 (d, $^1J_{PP}$ = 82.3 Hz, P^1), 33.4 (d, $^1J_{PP}$ = 82.3 Hz, P^2).

^{13}C{^{1}H} NMR (C_6D_6, ppm): 2.65 (s, Me), 14.67 (s, Me), 15.59 (d, $^3J_{CP}$ = 7.5 Hz, CH$_2$), 18.43 (d, $^2J_{CP}$ = 17.9 Hz, CH$_2$), 29.45 (dd, $^1J_{CP}$ = 33.5 Hz, $^2J_{CP}$ = 14.8 Hz, CH$_2$), 53.71 (d, $^2J_{CP}$ = 16.4 Hz, C^3), 61.34 (dd, $^2J_{CP}$ = 9.7 Hz, $^3J_{CP}$ = 2.7 Hz, C^{tBu}), 67.95 (dd, $^1J_{CP}$ = 25.8 Hz, $^2J_{CP}$ = 11.5 Hz, C^4), 126.32 (s, *p*-C^{Ph}), 126.94 (s, *p*-C^{Ph}), 127.33 (s, *p*-C^{Ph}), 127.67 (s, *p*-C^{Ph}), 127.84 (s, *m*-C^{Ph}), 127.92 (s, *m*-C^{Ph}), 128.35 (s, *m*-C^{Ph}), 128.49 (s, *m*-C^{Ph}), 128.73 (s, *o*-C^{Ph}),128.90 (s, *o*-C^{Ph}), 128.98 (s, *o*-C^{Ph}), 129.42 (s, *o*-C^{Ph}), 130.88 (dd, $^3J_{CP}$ = 7.6 Hz, $^3J_{CP}$ = 4.9 Hz, *ipso*-C^{Ph}), 135.86 (dd, $^3J_{CP}$ = 6.2 Hz, $^2J_{CP}$ = 15.2 Hz, *ipso*-C^{Ph}), 136.16 (dd, $^3J_{CP}$ = 6.8 Hz, $^2J_{CP}$ = 9.2 Hz, *ipso*-C^{Ph}), 137.35 (d, $^3J_{CP}$ = 6.0 Hz, *ipso*-C^{Ph}), 138.44 (dd, $^2J_{CP}$ = 12.4 Hz, $^2J_{CP}$ = 10.4 Hz, C^5), 155.71 (dd, $^1J_{CP}$ = 22.6 Hz, $^2J_{CP}$ = 13.1 Hz, C^6).

IR (KBr, cm^{-1}): 490 (m), 513 (m), 515 (m), 529 (m), 537 (w), 546 (m), 578 (w), 655 (m), 702 (s), 736 (m), 780 (m), 801 (m), 879 (m), 1015 (m), 1036 (m), 1048 (m), 1059 (m), 1075 (w), 1175 (s, P═O), 1229 (s, P═O), 1365 (m), 1421 (w), 1444 (m), 1463 (m), 1492 (w), 1600 (m), 1643 (w), 2891 (w), 2966 (s), 2979 (m), 2995 (m), 3030 (w), 3058 (m).

$C_{36}H_{39}NO_2P_2$ (579.65): calcd C 74.59, H 6.78, N 2.42, O 5.52, P 10.69; found C 74.71, H 6.83, N 2.50, P 10.94.

Notes and references

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