Thermal Rearrangement of 1,5,8-Triphosphaisolumibullvalenes (1,5,8-Triphosphatetracyclo[4.4.0.0^{2,8}.0^{5,7}]deca-3,9-dienes)[‡]

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Keywords: Alkyne complexes / Heterocycles / Phosphorus-carbon cage compounds / Rearrangements

1,5,8-Triphosphaisolumibullvalenes (1,5,8-triphosphatetracyclo[4.4.0.0^{2,8}.0^{5,7}]deca-3,9-dienes) **3**, when suitably substituted, undergo thermal rearrangement to afford the 1,1b,2a-triphosphahomoquadricyclanes (tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]-pentalenes) **6**. The structure of the rearranged compound **6d** was elucidated by X-ray crystallography. The newly synthesized compound **6a** undergoes addition of oxygen or sulfur with an increase in the coordination at the phosphorus atom P-1 to yield the products **10a/b**; it also undergoes complexation with $Co_2(CO)_8$ at the newly formed P–C≡C– unit to afford product **11**.

Introduction

The family of $(CH)_{10}$ hydrocarbons encompasses 71 different constitutional formulae that can be described by planar graphs[2] and that are linked with each other by valence isomerizations and mutual interactions. These compounds include prominent members such as bullvalene, triquinacene, and basketene.[3] Isolumibullvalene, **3**, a further representative of the $(CH)_{10}$ family[4] (CH in place of P; H in place of *t*Bu; R = R′ = H; Scheme 1), has been prepared by photolysis of bullvalene and readily undergoes thermal isomerization to afford *cis*-9,10-dihydronaphthalene.[5] Persubstituted *cis*-9,10-dihydronaphthalenes, in contrast, furnish the isosemibullvalene skeleton upon isomerization.[6]

Recently, we described the Diels–Alder/homo-Diels–Alder reaction sequence of the 1,3,5-triphosphinine[7] **1a** with various alkynes that proceeds smoothly through the triphosphabarrelenes **2a–d** (not isolated) to yield the 1,5,8-triphosphaisolumibullvalenes (1,5,8-triphosphatetracyclo-[4.4.0.0^{2,8}.0^{5,7}]deca-3,9-dienes) **3a–d**.[8] A similar method for the synthesis of the isolumibullvalene skeleton is known in the all-carbon case: it starts from barrelene and involves a homo-Diels–Alder reaction with electron-poor alkynes.[9]

The reaction of triphosphabenzene **1a** with *tert*-butylacetylene did not afford a triphosphaisolumibullvalene of type **3**. The reaction did not start until the temperature reached 100 °C and resulted in the formation of the phosphorus/carbon cage compound **4**.[8,10]

Here we report on the unexpected thermal behavior of the 1,4,8-triphosphaisolumibullvalenes (1,5,8-triphosphatetracyclo[4.4.0.0^{2,8}.0^{5,7}]deca-3,9-dienes) **3** that involves a previously unknown skeletal rearrangement (**3** → **6**) in which, as in the case of the formation of **4**, an exocyclic triple bond is observed.

Preparation of the Triphosphahomoquadricyclanes 6a–h

As previously reported, the 1,3,5-triphosphinine **1a** reacts selectively at 60 °C with 2 equiv. of phenylacetylene (**5a**) to afford the triphosphaisolumibullvalene **3a**.[8] When a solution of **3a** is heated at 100 °C, however, ^{31}P NMR spectroscopy of the mixture reveals the slow conversion of **3a** into the tetrahydro-1*H*,1,1b,2a-triphosphadicyclopropa-[*cd*,*gh*]pentalene (**6a**) possessing the skeleton of a triphosphahomoquadricyclane (Scheme 2). This skeleton may also be considered as an edge-opened cuneane or, respectively, a dihydrocuneane. After direct reaction of the 1,3,5-triphosphinine **1a** with phenylacetylene (**5a**) for 5 d at 110 °C, compound **6a** is the sole reaction product. The formation of **6a** as single isomer is remarkable and is probably caused by the selective formation of **3a**. This feature has been described before and explained by steric factors.[8]

Similar product patterns were obtained in the reactions of the 1,3,5-triphosphinine **1a** with mesitylacetylene (**5b**), (4-methoxyphenyl)acetylene (**5c**), (4-cyanophenyl)acetylene (**5d**), (4-nitrophenyl)acetylene (**5e**), and 1-hexyne (**5f**) at 110 °C with formation of the tetracyclic products **6b–f** (Scheme 3). The yields vary widely depending on the acetylene employed and only in the cases of (4-methoxyphenyl)acetylene (**5c**) and (4-cyanophenyl)acetylene (**5d**) are

[‡] Organophosphorus Compounds, 170. Part 169: Ref.[1]

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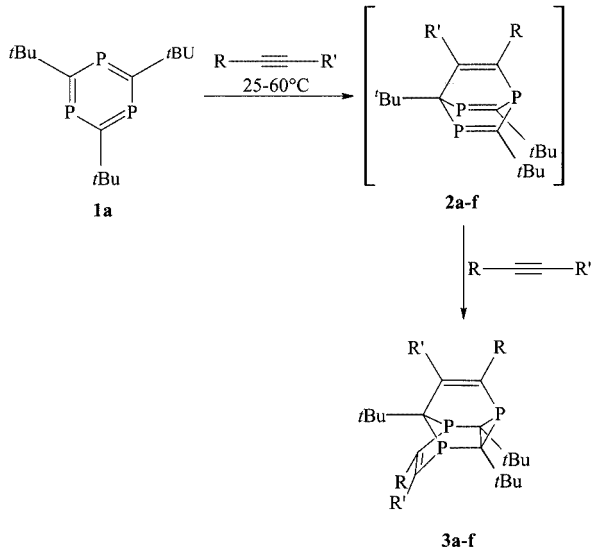
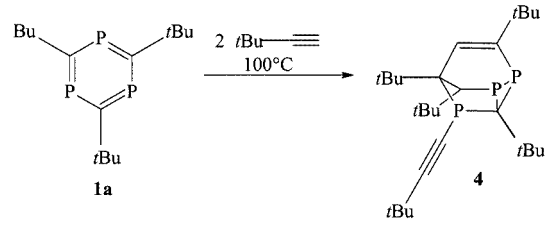
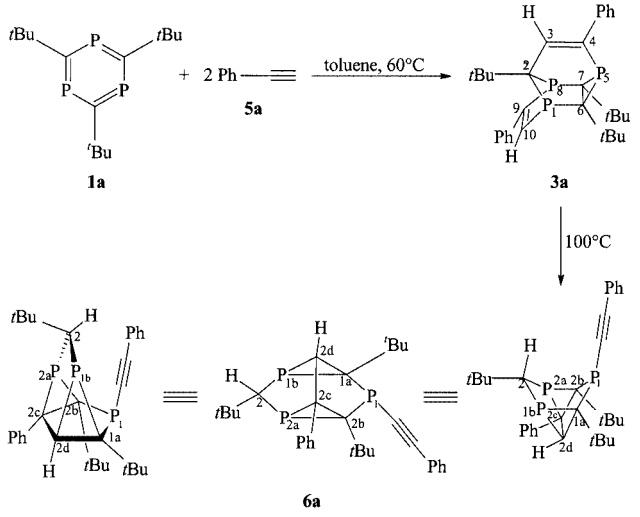
  DOI: 10.1002/ejoc.200300173



2,3	a	b	c	d	e	f
R	Ph	H	CO_2Me	$-(CH_2)_6-$	COMe	Ph
R'	H	H	H		H	D

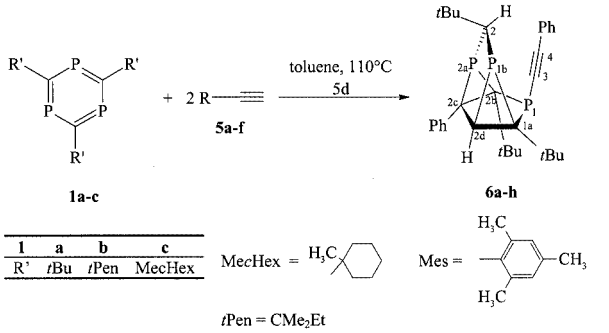


Scheme 1



Scheme 2

they similar to the good yield obtained using phenylacetylene (**5a**). The products are obtained in yields ranging from 19% (**6b**) to 71% (**6a**) after workup by column chromatography over silica gel. In addition, rearrangement reactions to furnish the tetracyclic products **6g**,**h** are observed when the 1,3,5-triphosphinines **1b**,**c** are treated with phenylacetylene



1	a	b	c
R'	tBu	tPen	MecHex

5	a	b	c	d	e	f		
6	a	b	c	d	e	f	g	h
R	Ph	Mes	OMe	CN	NO_2	nBu	Ph	Ph
R'	tBu	tBu	tBu	tBu	tBu	tBu	tPen	MecHex
%	71	19	68	62	41	23	62	61

Scheme 3

(**5a**). The choice of the substituent R′, however, is limited by the use of kinetically stabilized phosphaalkynes in the synthesis of the 1,3,5-triphosphinines **1**.[11]

The cage compounds **3b**−**d**[8] — as well as **3e**, prepared here for the first time by reaction with but-3-yn-2-one — do not undergo the above rearrangement at 110 °C. When they are heated to markedly higher temperatures, unspecific decomposition occurs. Thus, whether the thermal rearrangement reaction occurs or not is strongly dependent on the substituents and must be a consequence of the mechanism.

Although complete NMR spectroscopic data sets are available, the structures of products **6a**−**h** could be elucidated only on the basis of an X-ray crystallographic analysis of **6d** (Figure 1).

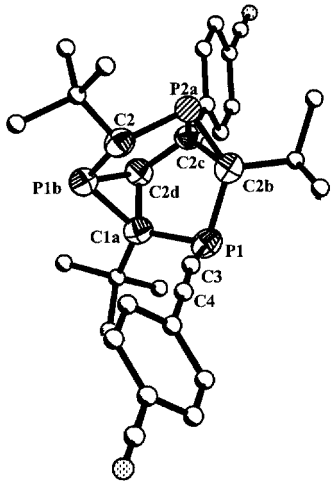


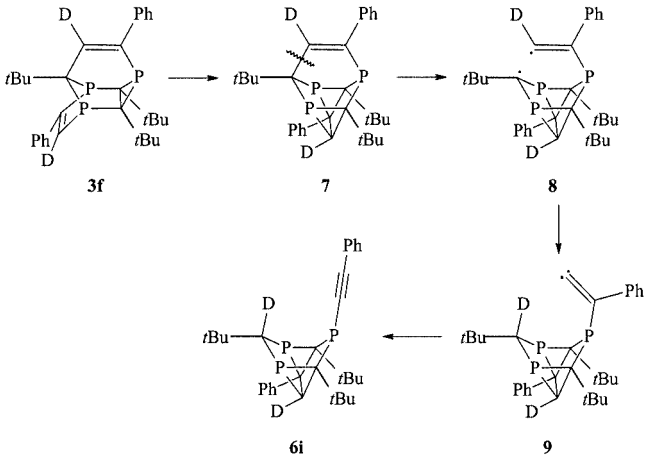
Figure 1. Crystal structure of **6d**; selected bond lengths [Å] and angles (°): P1−C1a 1.838(4), P1−C2b 1.847(4), P1b−C1a 1.876(3), P1b−C2 1.859(4), P1b−C2d 1.846(3), P2a−C2 1.846(3), P2a−C2b 1.864(4), P2a−C2c 1.871(4), C1a−C2d 1.514(4), C2b−C2c 1.543(5), C2c−C2d 1.521(5), C3−C4 1.194(5); P1−C3−C4 166.7(4), C3−C4−C5 178.2(4), C1a−P1b−C2d 48.00(14), C2b−P2a−C2c 48.8(2)

The crystal structure analysis confirmed the P-1/C-2 edge-opened cuneane skeleton. The exocyclic C-3/C-4 triple bond at P-1 points in the direction of the P-1b/C-2/P-2a bridge, while the *tert*-butyl group at C-2 is *trans* to the triple bond. The P−C bond lengths of 1.876(3) Å (P-1b/C-1a), 1.846(3) Å (P-1b/C-2d), 1.864(4) Å (P-2a/C-2b), and 1.871(4) Å (P-2a/C-2c) in the two phosphirane rings are at the upper end of the range of published values (1.78 −1.89 Å).[11] The C−C bond lengths of 1.514(4) Å (C-1a/C-2d) and 1.543(5) Å (C-2b/C-2c) are also compatible with the values published for phosphiranes (1.46−1.59 Å).[12] The endocyclic angles at P-1b and P-2a of 48.00(14) and 48.8(2)°, respectively, differ slightly from each other, but hardly differ from the published average value of 49° for phosphiranes.[12] These values show that the homoquadricyclane skeleton is slightly distorted. The remaining P−C bonds of the skeleton lie between 1.838(4) and 1.859(4) Å, within the normal range for phosphorus/carbon cage compounds. The length of the C-3/C-4 triple bond at P-1 [1.194(5) Å] is practically identical to the average literature value of 1.181 Å.[13] In particular, the angle P-1/C-3/C-4 [166.7(4)°] exhibits a marked deviation from the ideal value of 180°; the deviation of the angle C-3/C-4/C-5 [178.2(4)°] is appreciably smaller.

The spectroscopic data of the novel compounds **6a**−**h** are discussed here using **6a** as an example. First of all, the results of elemental analysis and the presence of a molecular ion peak at m/z = 504 in the mass spectrum of **6a** demonstrate that no fragment has been lost in the formation of **6a** from **3a**. First indications of the structure are found in the IR spectrum, which exhibits a band at 2150 cm^{-1} for a C−C triple bond. In the $^{31}P\{^1H\}$ NMR spectrum, the signals for P-1b and P-2a at δ = −23.5 and −32.1 ppm, respectively, appear at unusually low field for phosphirane phosphorus atoms in phosphorus/carbon cage compounds.[8,14a−14c] The phosphorus atom P-1 carrying the C−C triple bond gives rise to a signal at δ = 7.6 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the carbon atoms C-3 and C-4 of the triple bond give rise to a doublet at δ = 89.6 ppm having $^1J_{C,P}$ = 30.4 Hz and a singlet at δ = 108.1 ppm, respectively, in the region typical for such triple bonds attached to phosphorus atoms.[8] The signals of the five skeletal carbon atoms between δ = 45.7 and 67.9 ppm have little diagnostic value and provide no direct information about the structure of **6a**. They were assigned with the aid of a DEPT spectrum.

Mechanistic Considerations

The thermal isomerization of isolumibullvalene to dihydronaphthalene derivatives[5,9] described in the introduction, which can be considered as a retro-Diels−Alder reaction, does not play a part in the thermolysis of the triphospha analogues **3**. By looking closely at the skeleton of **3**, the structure of a triphosphatricyclo[3.2.1.$0^{2,4}$]oct-6-ene is observed if the bridging atoms C-3 and C-4 are removed. It is known that tricyclo[3.2.1.$0^{2,4}$]oct-6-enes undergo either intramolecular [2π + 2σ] cycloaddition to form homoquadricyclanes (tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]octanes) or react further to give bicyclo[3.2.1]octa-2,6-dienes.[15−18] In the case of the triphosphaisolumibullvalenes **3**, apparently the [2π + 2σ] cycloaddition dominates to afford the triphosphahomoquadricyclane derivative **6**, possibly favored by the substitution of a carbon atom in the cyclopropane ring by a phosphorus atom. In combination with this cycloaddition, we must consider a rearrangement of the alkene bridge formed by C-3 and C-4 to afford the C−C triple bond attached to the phosphorus atom. To obtain more information about the formation of the triple bond, the partially deuterated compound **3f** was subjected to thermolysis. As described above, the tetracyclic species **3f** was formed in situ by the reaction of 1,3,5-triphosphinine **1a** with 2-deuterophenylacetylene and then directly converted into **6i** by heating at 110 °C. The ^1H NMR spectrum of **6i** confirms that both deuterium atoms of **3f** are present in the rearranged product and, thus, that solvent molecules are not involved (Scheme 4).

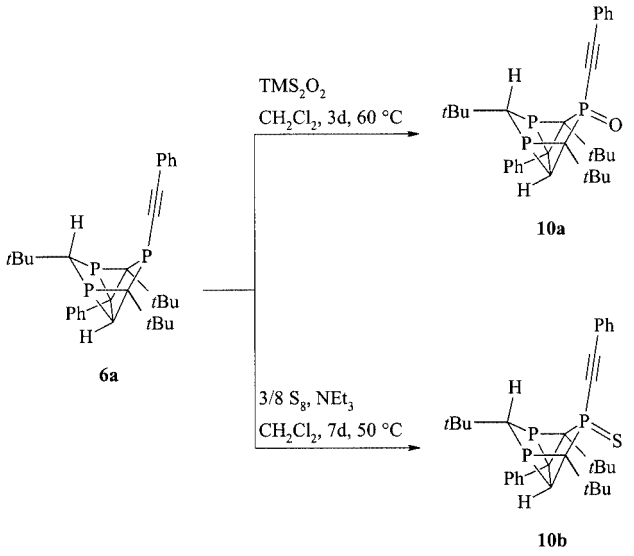


Scheme 4

At the beginning of the proposed mechanism the intramolecular [2π + 2σ] cycloaddition of the phosphirane to the C=C double bond on the opposite side of the molecule **3f** gives rise to the intermediate **7**. This process should induce ring strain in the bridging C=C double bond, which leads to cleavage of the C-2/C-3 bond. The so-formed radical center at C-2 in intermediate **8** abstracts the deuterium atom from C-3 to generate the alkylidenecarbene **9**. In the proposed mechanism the highly reactive intermediate **8** favors an intramolecular deuterium abstraction from the neighboring carbon atom, which should occur immediately after the C−C bond cleavage, over a proton abstraction from the solvent. It is known that alkylidenecarbenes rearrange to alkynes when a substituent amenable to migration is present.[19] This step would explain the observed limitation of the reaction to compounds possessing readily migrating groups.

Increases in Coordination at Phosphorus

Compound **6a** can be selectively oxidized at the phosphorus atom P-1 by treatment at 60 °C with the mild oxidizing agent, Tms_2O_2. After workup by chromatography, the phosphane oxide **10a** was obtained in 76% yield (Scheme 5).



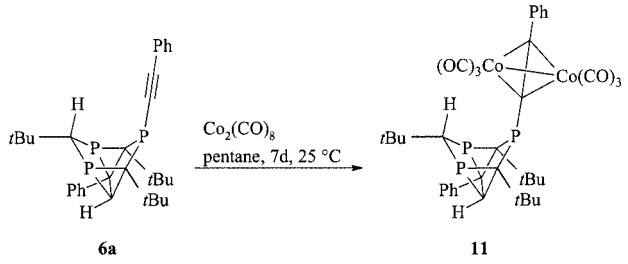
Scheme 5

Attempts to oxidize P-1b and P-2a further by use of two or three equiv. of Tms_2O_2 led to decomposition. After treatment of **6a** with three equiv. of sulfur in the presence of triethylamine, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows only chalcogenization at P-1. Thus, the phosphorus atoms of the phosphirane unit seem to prefer the $\sigma^3\lambda^3$ configuration. The phosphane sulfide **10b** was isolated in 51% yield after column chromatography.

The single chalcogenization is confirmed unequivocally by the presence of molecular ion peaks at m/z = 520 (**10a**) and m/z = 536 (**10b**) in the mass spectra. The selective chalcogenization at P-1 can also be deduced from the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. As a result of the transformation of the $\sigma^3\lambda^3$-phosphorus atom in **6a** to a $\sigma^4\lambda^5$-phosphorus atom in **10a** and **10b**, the $^{31}P\{^1H\}$ NMR signal of P-1 is shifted to lower field by ca. 40 ppm. This signal occurring at δ = 7.6 ppm in the starting material **6a** now appears at δ = 37.5 ppm for the oxygenated compound **10a** and at δ = 46.4 ppm for the sulfurized compound **10b**. In contrast, the chemical shifts of the $\sigma^3\lambda^3$-phosphorus atoms P-1b and P-2a remain practically unchanged. The chalcogenization at P-1 has a drastic effect on the coupling constants in the $^{13}C\{^1H\}$ NMR spectrum while the chemical shifts of the skeletal carbon atoms are changed only slightly. Thus, the $^1J_{C,P}$ coupling constant of C-3 is increased about fivefold (**6a**: δ = 89.6 ppm, $^1J_{C,P}$ = 30.4 Hz; **10a**: δ = 88.0 ppm, $^1J_{C,P}$ = 161.0 Hz; **10b**: δ = 87.5 ppm, $^1J_{C,P}$ = 144.1 Hz). In addition, the second carbon atom of the triple bond, C-4, which gives a singlet in the ^{13}C NMR spectrum of **6a**, now couples with P-1 (**10a**: $^2J_{C,P}$ = 29.1 Hz; **10b**: $^2J_{C,P}$ = 26.3 Hz).

Complexation of the Triple Bond

The reaction of **6a** with octacarbonyldicobalt is complete after stirring at room temperature for 7 d. The metal fragment complexes with the C−C triple bond and the hexacarbonyldicobalt complex **11** was obtained in 73% yield after column chromatography (Scheme 6).



Scheme 6

The IR spectrum of the cobalt complex **11** contains absorption bands at 2084, 2048, and 2022 cm^{-1} for the CO groups attached to the metal atom. Complexation of the C-3/C-4 triple bond does not have a major influence on the chemical shifts of these atoms in the $^{13}C\{^1H\}$ NMR spectrum. A similar observation has been reported for cobalt complexation of the triple bond in phenylacetylene.[20] The coupling of C-3 and C-4 with P-1 is markedly increased after complexation of the triple bond when compared to that in the starting material. For C-3, a doublet with a $^1J_{C,P}$ coupling constant of 121.1 Hz is seen at δ = 91.6 ppm (**6a**: δ = 89.6 ppm, $^1J_{C,P}$ = 30.4 Hz); C-4 now gives rise to a signal at δ = 110.3 ppm (**6a**: δ = 108.1 ppm), but, in contrast to **6a**, it has a $^2J_{C,P}$ coupling constant of 13.4 Hz. The signal for the CO ligands appears as a broad singlet at δ = 200.5 ppm. The CO ligands of the hexacarbonyldicobalt complex of phenylacetylene give rise to a signal at δ = 200.0 ppm.[20] In the $^{31}P\{^1H\}$ NMR spectrum, the signal of the phosphorus atom P-1 attached to the complexed triple bond is clearly shifted to lower field. In comparison to **6a**, the signal is shifted by about 70 ppm to lower field and now appears at δ = 77.9 ppm. The positions and coupling constants of the remaining signals are hardly influenced by the complexation.

Conclusion

In this paper, we present a previously unknown skeletal rearrangement of 1,5,8-triphosphaisolumibullvalenes (1,5,8-triphosphatetracyclo[4.4.0.$0^{2,8}$.$0^{5,7}$]deca-3,9-dienes) **3** into 1,1b,2a-triphosphahomoquadricyclanes (tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa-[*cd*,*gh*]-pentalenes) **6**. Additionally, we have demonstrated that this rearrangement occurs only with suitable substitution of **3**, and have presented a mechanism for this reaction. This study indicates, once more, that phosphorus/carbon cage compounds are capable of remarkable rearrangement reactions that are often different from those of their carbon analogues.

Experimental Section

All reactions were performed under argon (purity > 99.998%) by using Schlenk techniques. When heating of the solvent was necessary, we used special pressure Schlenk tubes (glass tubes, 3 × 10 cm, wall thickness 2 mm) with screw-threaded, Teflon stoppers and Teflon stopcocks. The solvents were dried by standard pro-

cedures, distilled, and stored under argon prior to use. Compounds **1a**,[11] **1b**,[11] **1c**,[11] **5b**,[21] **5d**,[22] **5e**,[22] and Tms_2O_2[23] were prepared by published methods. Column chromatography was performed in water-cooled glass tubes under argon. Silica gel and aluminum oxide were heated for 3 h in vacuo and then deactivated with 4% argon-saturated water (Brockmann activity II). Melting points were determined on a Mettler FP61 apparatus (heating rate: 3 °C/min) and are uncorrected. Microanalyses were performed with a Perkin−Elmer Analyzer 2400. ^1H and ^{13}C NMR spectra were recorded using Bruker AC 200 and AMX 400 spectrometers and are referenced to the solvent as internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (81.1 MHz) spectrometer with 85% H_3PO_4 as an external standard. Mass spectra were recorded on a Finnigan MAT 90 spectrometer at an ionization voltage of 70 eV. IR spectra were measured on a Perkin−Elmer 16 PC FT-IR spectrophotometer.

Tetracyclic Compounds 6a−i. General Procedure: A solution of a 1,3,5-triphosphinine (**1a**, **1b**, or **1c**) and two equiv. of the acetylene **5** in toluene (5 mL) was heated for 5 d at 110 °C in a pressure Schlenk tube at an argon pressure of 3 bar. After evaporation of the solvent (25 °C/10^{-3} mbar) the residue was taken up in Et_2O and, after the addition of a small amount of silica gel, the solvent was evaporated again. The adsorbate was transferred to a glass column (diameter: 1.5 cm, length: 15 cm) filled with silica gel and the eluent. Chromatography was performed using pentane as eluent in the case of **6a**,**b** and **6f**−**i**, pentane/Et_2O (50:1) in the case of **6d**, and pentane/Et_2O (100:1) in the case of **6c**,**e**. After eluting a yellow fraction containing impurities, the compounds **6a**−**i** were obtained.

1a,2,2b-Tri-*tert*-butyl-2c-phenyl-1-(phenylethynyl)tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene (6a): From **1a** (245 mg, 0.816 mmol) and phenylacetylene **5a** (176 mg, 1.72 mmol); yield: 294 mg (71%); colorless powder; m.p. 55 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.96 (s, 9 H) and 1.13 (s, 9 H) and 1.43 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.84 (dd, $J_{H,P}$ = 20.6, $J_{H,P}$ = 3.5 Hz, 1 H) and 3.09 (br. s, 1 H) (2-H and 2d-H), 7.29−7.39 (m, 6 H) and 7.47−7.49 (m, 2 H) and 7.65−7.67 (m, 2 H) (Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 28.9 (dd, $^3J_{C,P}$ = 10.5, $^3J_{C,P}$ = 8.8 Hz) and 29.8 (pt, $^3J_{C,P}$ = 9.4 Hz) and 31.2 (pt, $^3J_{C,P}$ = 11.1 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 33.9 (pt, $^2J_{C,P}$ = 16.9 Hz) and 35.6 (dd, $^2J_{C,P}$ = 24.9, $^2J_{C,P}$ = 11.6 Hz) and 37.2 (dd, $^2J_{C,P}$ = 24.6, $^2J_{C,P}$ = 13.0 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 45.7 (pt, $^1J_{C,P}$ = 45.3 Hz, C-2), 46.8 (dd, $^1J_{C,P}$ = 49.8, $^1J_{C,P}$ = 15.5 Hz, C-1a or C-2b), 56.2 (br. d, $^1J_{C,P}$ = 38.1 Hz, C-2d), 57.1 (dd, $^1J_{C,P}$ = 45.3, $^1J_{C,P}$ = 21.6 Hz, C-1a or C-2b), 67.9 (ddd, $^1J_{C,P}$ = 34.8, $^2J_{C,P}$ = 5.5, $^2J_{C,P}$ = 3.3 Hz, C-2c), 89.6 (d, $^1J_{C,P}$ = 30.4 Hz, C-3), 108.1 (s, C-4), 123.4 (s) and 127.1 (s) and 128.0 (s) and 128.4 (s) and 128.5 (s) and 131.1 (d, $J_{C,P}$ = 1.1 Hz) and 132.3 (br. s) and 140.4 (d, $J_{C,P}$ = 11.6 Hz) (Ph-C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −32.1 (dd, $^2J_{P,P}$ = 21.0, $^2J_{P,P}$ = 1.8 Hz) and −23.5 (d, $^2J_{P,P}$ = 21.0 Hz) (P-1b and P-2a), 7.6 (d, $^2J_{P,P}$ = 1.8 Hz, P-1) ppm. IR (CCl_4): ṽ = 2957, 2899, 2862, 2150 (C≡C), 1488, 1472, 1461, 1442, 1391, 1364, 1217, 702, 689 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 504 $[M]^+$ (9), 489 $[M - CH_3]^+$ (1), 447 $[M - C_4H_9]^+$ (1), 84 (100), 57 $[C_4H_9]^+$ (32). $C_{31}H_{39}P_3$ (504.57): calcd. C 73.79, H 7.79; found C 73.65, H 7.90.

1a,2,2b-Tri-*tert*-butyl-2c-mesityl-1-(mesitylethynyl)tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene (6b): From **1a** (227 mg, 0.756 mmol) and mesitylacetylene (**5b**; 274 mg, 1.90 mmol); yield: 84 mg (19%); colorless powder; m.p. 206 °C. ^1H NMR (C_6D_6, 25 °C, 400.1 MHz): δ = 1.66 (s, 9 H) and 1.77 (s, 9 H) and 1.97 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.64 (s, 3 H) and 2.71 (s, 3 H) and 3.04 (s, 6 H) and 3.10 (s, 3 H) and 3.46 (s, 3 H) (Mes-CH_3), 3.31 (dd, $J_{H,P}$ = 20.5, $J_{H,P}$ = 4.4 Hz, 1 H) and 4.04 (br. s, 1 H) (2-H and 2d-H), 7.34−7.35 (m, 2 H) and 7.74−7.75 (m, 2 H) (Mes-H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 100.6 MHz): δ = 20.4 (s) and 20.9 (s) and 21.1 (s) and 25.0 (s) and 25.2 (s) and 25.9 (d, $J_{C,P}$ = 8.8 Hz) (Mes-CH_3), 29.8 (pt, $^3J_{C,P}$ = 9.2 Hz) and 29.9 (pt, $^3J_{C,P}$ = 8.4 Hz) and 31.3 (pt, $^3J_{C,P}$ = 10.2 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 33.8 (pt, $^2J_{C,P}$ = 18.3 Hz) and 35.8 (dd, $^2J_{C,P}$ = 24.5, $^2J_{C,P}$ = 12.0 Hz) and 37.5 (dd, $^2J_{C,P}$ = 24.1, $^2J_{C,P}$ = 14.1 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 45.4 (pt, $^1J_{C,P}$ = 47.4 Hz, C-2), 45.5 (dd, $^1J_{C,P}$ = 47.2, $^1J_{C,P}$ = 16.5 Hz) and 53.4 (dd, $^1J_{C,P}$ = 41.4, $^1J_{C,P}$ = 24.5 Hz) (C-1a and C-2b), 56.6 (br. d, $^1J_{C,P}$ = 38.5 Hz, C-2d), 63.4 (br. d, $^1J_{C,P}$ = 40.6 Hz, C-2c), 96.5 (d, $^1J_{C,P}$ = 35.3 Hz, C-3), 109.9 (s, C-4), 120.2 (d, $J_{C,P}$ = 0.8 Hz) and 127.7 (s) and 129.5 (s) and 130.4 (s) and 136.0 (s) and 137.5 (s) and 138.2 (d, $J_{C,P}$ = 1.2 Hz) and 139.8 (d, $J_{C,P}$ = 1.2 Hz) (Aryl-C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −48.3 (dd, $^2J_{C,P}$ = 20.8, $^2J_{C,P}$ = 1.2 Hz) and −17.0 (d, $^2J_{P,P}$ = 20.8 Hz) (P-1b and P-2a), 1.2 (d, $^2J_{P,P}$ = 1.2 Hz, P-1) ppm. IR (CCl_4): ṽ = 2958, 2864, 2133 (C=C), 1611, 1473, 1480, 1392, 1364, 1223, 1033, 852 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 588 $[M]^+$ (100, 573 $[M - CH_3]^+$ (26), 487 (56), 57 $[C_4H_9]^+$ (35). $C_{37}H_{51}P_3$ (588.73); calcd. C 75.49, H 8.73; found C 75.52, H 9.18.

1a,2,2b-Tri-*tert*-butyl-2c-(4-methoxyphenyl)-1-[(4-methoxyphenyl)-ethynyl]tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]-pentalene (6c): From **1a** (173 mg, 0.576 mmol) and (4-methoxyphenyl)acetylene (**5c**; 153 mg, 1.16 mmol); yield: 221 mg (68%); colorless powder; m.p. 65 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.94 (s, 9 H) and 1.09 (s, 9 H) and 1.41 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.77 (dd, $J_{H,P}$ = 20.3, $J_{H,P}$ = 3.1 Hz, 1 H) and 3.09 (br. s, 1 H) (2-H and 2d-H), 3.84 (s, 6 H, OCH_3), 6.88−6.90 (m, 4 H) and 7.38−7.41 (m, 2 H) and 7.50−7.55 (m, 2 H) (Aryl-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 28.9 (pt, $^3J_{C,P}$ = 9.2 Hz) and 29.7 (pt, $^3J_{C,P}$ = 8.4 Hz) and 31.1 (pt, $^3J_{C,P}$ = 10.7 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 33.9 (pt, $^2J_{C,P}$ = 16.9 Hz) and 35.5 (dd, $^2J_{C,P}$ = 24.2, $^2J_{C,P}$ = 11.1 Hz) and 37.1 (dd, $^2J_{C,P}$ = 24.2, $^2J_{C,P}$ = 13.4 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 45.5 (pt, $^1J_{C,P}$ = 45.2 Hz, C-2), 46.7 (dd, $^1J_{C,P}$ = 49.1, $^1J_{C,P}$ = 16.1 Hz, C-1a or C-2b), 55.2 (s) and 55.3 (s) (OCH_3), 56.1 (br. d, $^1J_{C,P}$ = 36.0 Hz, C-2d), 57.0 (dd, $^1J_{C,P}$ = 45.2, $^1J_{C,P}$ = 21.5 Hz, C-1a or C-2b), 67.0 (br. d, $^1J_{C,P}$ = 33.7 Hz, C-2c), 87.9 (d, $^1J_{C,P}$ = 29.1 Hz, C-3), 108.0 (s, C-4), 114.0 (s) and 115.6 (s) and 132.3 (d, $J_{C,P}$ = 11.5 Hz) and 132.7 (s) and 133.0−133.3 (m) and 158.7 (s) and 159.8 (s) (Aryl-C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −31.5 (dd, $^2J_{P,P}$ = 21.1, $^2J_{P,P}$ = 1.8 Hz) and −22.7 (d, $^2J_{P,P}$ = 21.1 Hz) (P-2a and P-1b), 7.2 (d, $^2J_{P,P}$ = 1.8 Hz, P-1) ppm. IR (CCl_4): ṽ = 2958, 2860, 2837, 2148 (C=C), 1606, 1508, 1464, 1363, 1292, 1248, 1172, 1038 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 564 $[M]^+$ (42), 549 $[M - CH_3]^+$ (7), 507 $[M - C_4H_9]^+$ (9), 375 (29), 364 (28), 57 $[C_4H_9]^+$ (100). $C_{33}H_{43}O_2P_3$ (564.60); calcd. C 70.20, H 7.68; found C 70.36, H 7.93.

1a,2,2b-Tri-*tert*-butyl-2c-(4-cyanophenyl)-1-[(4-cyanophenyl)-ethynyl]tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]-pentalene (6d): From **1a** (170 mg, 0.566 mmol) and (4-cyanophenyl)-acetylene (**5d**; 145 mg, 1.15 mmol); yield: 194 mg (62%); colorless powder; m.p. 214 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.84 (s, 9 H) and 1.02 (s, 9 H) and 1.29 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.67 (dd, $J_{H,P}$ = 20.5, $J_{H,P}$ = 3.7 Hz, 1 H) and 2.80 (br. s, 1 H) (2-H and 2d-H), 7.42−7.45 (m, 2 H) and 7.56−7.67 (m, 6 H) (Aryl-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 50.3 MHz): δ = 28.7 (pt, $^3J_{C,P}$ = 9.1 H z) and 29.6 (pt, $^3J_{C,P}$ =

10.2 H z) and 31.0 (pt, $^3J_{C,P}$ = 11.2 Hz) [C(CH_3)$_3$ groups at C-1a, C-2, and C-2b], 33.8 (pt, $^2J_{C,P}$ = 17.0 Hz) and 35.5 (dd, $^2J_{C,P}$ = 24.4, $^2J_{C,P}$ = 11.7 Hz) and 37.3 (dd, $^2J_{C,P}$ = 24.4, $^2J_{C,P}$ = 13.4 Hz) [C(CH$_3$)$_3$ groups at C-1a, C-2, and C-2b], 46.4 (pt, $^1J_{C,P}$ = 45.5 Hz, C-2), 46.8 (dd, $^1J_{C,P}$ = 50.0, $^1J_{C,P}$ = 15.7 Hz, C-1a or C-2b), 55.5 (br. d, $^1J_{C,P}$ = 38.1 Hz, C-2d), 58.0 (dd, $^1J_{C,P}$ = 46.0, $^1J_{C,P}$ = 21.8 Hz, C-1a or C-2b), 67.2 (ddd, $^1J_{C,P}$ = 35.2, $^2J_{C,P}$ = 6.4, $^2J_{C,P}$ = 3.8 Hz, C-2c), 94.7 (d, $^1J_{C,P}$ = 36.0 Hz, C-3), 106.7 (s, C-4), 110.9 (d, $J_{C,P}$ = 0.8 Hz) and 111.6 (s) and 118.2 (s) and 118.5 (s) and 127.4 (d, $J_{C,P}$ = 0.8 Hz) and 131.2 (d, $J_{C,P}$ = 1.3 Hz) and 131.8 (s) and 132.1 (s) and 132.7 (br. s) and 145.9 (dd, $J_{C,P}$ = 12.7, $J_{C,P}$ = 0.9 Hz) (Aryl-C and CN) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −31.7 (dd, $^2J_{P,P}$ = 21.0, $^2J_{P,P}$ = 1.5 Hz) and −22.0 (d, $^2J_{P,P}$ = 21.0 Hz) (P-1b and P-2a), 7.6 (d, $^2J_{P,P}$ = 1.5 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2960, 2901, 2863, 2231 (C≡N), 2148 (C=C), 1604, 1498, 1472, 1463, 1392, 1364 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 554 [M]$^+$ (50), 539 [M − CH_3]$^+$ (13), 497 [M − C_4H_9]$^+$ (10), 366 (22), 327 (33), 57 [C_4H_9]$^+$ (100). $C_{33}H_{37}N_2P_3$ (554.59): calcd. C 71.47, H 6.72; found C 71.51, H 6.81.

1a,2,2b-Tri-*tert*-butyl-2c-(4-nitrophenyl)-1-[(4-nitrophenyl)-ethynyl]tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]-pentalene (6e): From **1a** (177 mg, 0.589 mmol) and (4-nitrophenyl)acetylene (**5e**; 175 mg, 1.19 mmol); yield: 144 mg (41%); yellow powder; m.p. 141 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.91 (s, 9 H) and 1.09 (s, 9 H) and 1.36 (s, 9 H) [C(CH_3)$_3$ groups at C-1a, C-2, and C-2b], 2.74 (dd, $J_{H,P}$ = 20.6, $J_{H,P}$ = 4.0 Hz, 1 H) and 2.84 (br. s, 1 H) (2-H and 2d-H), 7.53−7.55 (m, 2 H) and 7.75−7.76 (m, 2 H) and 8.18−8.23 (m, 4 H) (Aryl-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 28.9 (pt, $^3J_{C,P}$ = 9.2 Hz) and 29.8 (pt, $^3J_{C,P}$ = 9.6 Hz) and 31.2 (pt, $^3J_{C,P}$ = 10.7 Hz) [C(CH$_3$)$_3$ groups at C-1a, C-2, and C-2b], 34.0 (pt, $^2J_{C,P}$ = 16.9 Hz) and 35.7 (dd, $^2J_{C,P}$ = 24.9, $^2J_{C,P}$ = 11.9 Hz) and 37.5 (dd, $^2J_{C,P}$ = 24.2, $^2J_{C,P}$ = 13.4 Hz) [C(CH$_3$)$_3$ groups at C-1a, C-2, and C-2b], 46.8 (pt, $^1J_{C,P}$ = 46.4 Hz, C-2), 47.0 (dd, $^1J_{C,P}$ = 49.8, $^1J_{C,P}$ = 16.1 Hz, C-1a or C-2b), 55.8 (br. d, $^1J_{C,P}$ = 39.1 Hz, C-2d), 58.4 (dd, $^1J_{C,P}$ = 46.0, $^1J_{C,P}$ = 22.2 Hz, C-1a or C-2b), 67.1 (br. d, $^1J_{C,P}$ = 38.3 Hz, C-2c), 96.0 (d, $^1J_{C,P}$ = 36.0 Hz, C-3), 106.7 (s, C-4), 123.3 (s) and 123.8 (s) and 129.4 (s) and 131.5 (s) and 133.0 (d, $J_{C,P}$ = 9.2 Hz) and 147.0 (s) and 147.1 (s) and 148.3 (d, $J_{C,P}$ = 12.3 Hz) (Aryl-C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −31.7 (dd, $^2J_{P,P}$ = 21.0, $^2J_{P,P}$ = 1.7 Hz) and −20.9 (d, $^2J_{P,P}$ = 21.0 Hz) (P-1b and P-2a), 8.0 (d, $^2J_{P,P}$ = 1.7 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2960, 2178 (C=C), 1594, 1526 (NO_2), 1463, 1365, 1346 (NO_2), 1109, 863 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 594 [M]$^+$ (6), 511 (13), 481 (15), 451 (10), 57 [C_4H_9]$^+$ (100). $C_{31}H_{37}N_2O_4P_3$ (594.56): calcd. C 62.62, H 6.27; found C 62.75, H 6.66.

1a,2,2b-Tri-*tert*-butyl-2c-*n*-butyl-1-(hexyn-1-yl)tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene (6f): From **1a** (250 mg, 0.833 mmol) and hex-1-yne (**5f**; 172 mg, 2.09 mmol); yield: 89 mg (23%); colorless oil. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.90 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H) and 1.06 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H) (*n*Bu-CH$_3$), 1.17 (s, 9 H) and 1.34 (s, 9 H) and 1.51 (s, 9 H) [C(CH_3)$_3$ groups at C-1a, C-2, and C-2b], 1.34−1.55 (m, overlapped by *tert*-butyl signals) and 1.85−2.25 (m, 6 H) (*n*Bu-CH$_2$), 2.64 (dd, $J_{H,P}$ = 21.0, $J_{H,P}$ = 3.5 Hz, 1 H) and 3.30 (s, 1 H) (2-H and 2d-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 13.2 (s) and 14.0 (s) (*n*Bu-CH$_3$), 19.9 (s) and 21.8 (s) and 23.1 (s) (*n*Bu-CH$_2$), 28.6 (dd, $^3J_{C,P}$ = 11.0, $^2J_{C,P}$ = 8.2 Hz) and 30.2 (pt, $^3J_{C,P}$ = 10.0 Hz) and 30.9 (pt, $^3J_{C,P}$ = 11.2 Hz) [C(CH$_3$)$_3$ groups at C-1a, C-2, and C-2b], 30.3 (d, $J_{C,P}$ = 1.2 Hz) and 32.7 (d, $J_{C,P}$ = 14.9 Hz) and 33.4 (d, $J_{C,P}$ = 5.2 Hz) (*n*Bu-CH$_2$), 33.9 (pt, $^2J_{C,P}$ = 17.7 Hz) and 35.0 (dd, $^2J_{C,P}$ = 24.9, $^2J_{C,P}$ = 11.6 Hz) and 36.7 (dd, $^2J_{C,P}$ = 25.1, $^2J_{C,P}$ = 12.6 Hz) [C(CH$_3$)$_3$ groups at C-1a, C-2, and C-2b], 45.2 (dd, $^1J_{C,P}$ = 49.4, $^1J_{C,P}$ = 14.5 Hz, C-1a or C-2b), 45.7 (dd, $^1J_{C,P}$ = 47.0, $^1J_{C,P}$ = 43.4 Hz, C-2), 53.4 (br. d, $^1J_{C,P}$ = 38.1 Hz, C-2d), 54.3 (dd, $^1J_{C,P}$ = 46.2, $^1J_{C,P}$ = 20.5 Hz, C-1a or C-2b), 61.9 (br. d, $^1J_{C,P}$ = 35.3 Hz, C-2c), 79.6 (d, $^1J_{C,P}$ = 26.5 Hz, C-3), 109.9 (s, C-4) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −35.5 (dd, $^2J_{P,P}$ = 20.5, $^2J_{P,P}$ = 2.2 Hz) and −27.9 (d, $^2J_{P,P}$ = 20.5 Hz) (P-1b and P-2a), 9.1 (d, $^2J_{P,P}$ = 2.2 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2959, 2901, 2862, 2168 (C=C), 1747, 1718, 1462, 1391, 1363, 1218, 909, 612 cm^{-1}.

1a,2,2b-Tris(1,1-dimethylpropyl)-2c-phenyl-1-(phenylethynyl)-tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]-pentalene (6g): From **1b** (109 mg, 0.318 mmol) and phenylacetylene (**5a**; 68.1 mg, 0.666 mmol); yield: 107 mg (62%); colorless resin. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.58 (s, 3 H) and 0.81 (s, 3 H) and 0.97 (s, 3 H) and 1.12 (s, 3 H) and 1.35 (s, 6 H) [C(CH_3)$_2$CH$_2$CH$_3$ at C-1a, C-2, and C-2b], 0.91 (pt, $^3J_{H,H}$ = 7.2 Hz, 6 H) and 1.05 (pt, $^3J_{H,H}$ = 7.4 Hz, 3 H) [C(CH$_3$)$_2$CH$_2$CH_3 at C-1a, C-2, and C-2b], 1.45 (dq, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 7.2 Hz, 1 H) and 1.65 (dq, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 7.2 Hz, 1 H) and 1.79 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H) and 1.86−1.96 (m, 2 H) [C(CH$_3$)$_2$CH_2CH$_3$ at C-1a, C-2, and C-2b], 2.81 (dd, $J_{H,P}$ = 20.7, $J_{H,P}$ = 3.8 Hz, 1 H) and 3.20 (br. s, 1 H) (2-H and 2d-H), 7.27−7.36 (m, 6 H) and 7.44−7.45 (m, 2 H) and 7.65−7.67 (m, 2 H) (Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 8.7 (s) and 8.9 (s) [C(CH$_3$)$_2$CH$_2$$CH_3$ at C-1a, C-2, and C-2b], 24.3−24.6 (m) and 25.8−26.2 (m) and 27.9−28.2 (m) [C(CH$_3$)$_2$CH$_2$CH$_3$ at C-1a, C-2, and C-2b], 35.2 (d, $^3J_{C,P}$ = 13.8 Hz) and 36.0 (pt, $^3J_{C,P}$ = 10.7 Hz) and 36.8 (d, $^3J_{C,P}$ = 13.0 Hz) [C(CH$_3$)$_2$$CH_2CH_3$ at C-1a, C-2, and C-2b], 36.3 (pt, $^2J_{C,P}$ = 16.1 Hz) and 38.4 (dd, $^2J_{C,P}$ = 23.4, $^2J_{C,P}$ = 10.3 Hz) and 39.8 (dd, $^2J_{C,P}$ = 22.6, $^2J_{C,P}$ = 11.1 Hz) [C(CH$_3$)$_2$CH$_2$CH$_3$ at C-1a, C-2, and C-2b], 42.4 (pt, $^1J_{C,P}$ = 45.2 Hz, C-2), 46.1 (dd, $^1J_{C,P}$ = 49.5, $^1J_{C,P}$ = 16.5 Hz, C-1a or C-2b), 55.3 (br. d, $^1J_{C,P}$ = 38.3 Hz, C-2d), 56.8 (dd, $^1J_{C,P}$ = 45.6, $^1J_{C,P}$ = 21.9 Hz, C-1a or C-2b), 65.9 (br. d, $^1J_{C,P}$ = 34.5 Hz, C-2c), 89.3 (d, $^1J_{C,P}$ = 30.7 Hz, C-3), 108.9 (s, C-4), 123.4 (s) and 127.0 (s) and 128.0 (s) and 128.2 (s) and 128.3 (s) and 130.9 (s) and 132.3 (br. s) and 140.7 (d, $J_{C,P}$ = 12.3 Hz) (Ph-C) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = −34.5 (dd, $^2J_{P,P}$ = 20.8, $^2J_{P,P}$ = 1.5 Hz) and −23.6 (d, $^2J_{P,P}$ = 20.8 Hz) (P-1b and P-2a), 5.1 (d, $^2J_{P,P}$ = 1.5 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2963, 2878, 2144 (C=C), 1488, 1460, 1444, 1385, 1363, 702, 689 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 546 (100) [M]$^+$, 531 [M − CH_3]$^+$ (7), 517 [M − C_2H_5]$^+$ (45), 475 [M − C_5H_{11}]$^+$ (10), 71 [C_5H_{11}]$^+$ (30). $C_{34}H_{45}P_3$ (546.6): calcd. C 74.70, H 8.30; found C 74.72, H 8.40.

1a,2,2b-Tris(1-methylcyclohexyl)-2c-phenyl-1-(phenylethynyl)-tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]-pentalene (6h): From **1c** (112 mg, 0.266 mmol) and phenylacetylene (**5a**; 57 mg, 0.558 mmol); yield: 101 mg (61%); colorless powder; m.p. 81 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.90−2.20 (m, 39 H, 1-methylcyclohexyl substituent at C-1a, C-2, and C-2b), 2.89 (dd, $J_{H,P}$ = 20.9, $J_{H,P}$ = 3.7 Hz, 1 H) and 3.39 (br. s, 1 H) (2-H and 2d-H), 7.29−7.39 (m, 6 H) and 7.45−7.47 (m, 2 H) and 7.63−7.68 (m, 2 H) (Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 21.3 (m_c) and 21.7 (s) and 22.0−22.3 (m) and 25.7 (s) and 25.9 (s) and 26.1 (s) and 26.4 (m_c) and 35.7−36.5 (m) and 39.2 (br. pseudo-t, $J_{C,P}$ = 19.9 Hz) (1-methylcyclohexyl substituent at C-1a, C-2, and C-2b), 37.4 (br. d, $^2J_{C,P}$ = 9.2 Hz) and 38.3 (dd, $^2J_{C,P}$ = 22.2, $^2J_{C,P}$ = 9.2 Hz) and 40.3 (dd, $^2J_{C,P}$ = 22.2, $^2J_{C,P}$ = 10.7 Hz) [C(CH$_3$)(CH$_2$)$_2$ at C-1a, C-2, and C-2b], 49.0

(dd, $^1J_{C,P}$ = 49.5, $^1J_{C,P}$ = 15.7 Hz, C-1a or C-2b), 55.3 (br. d, $^1J_{C,P}$ = 37.6 Hz, C-2d), 59.4 (dd, $^1J_{C,P}$ = 45.2, $^1J_{C,P}$ = 22.2 Hz, C-1a or C-2b), 67.5 (br. d, $^1J_{C,P}$ = 36.0 Hz, C-2c), 90.9 (d, $^1J_{C,P}$ = 30.7 Hz, C-3), 108.2 (s, C-4), 123.4 (s) and 126.9 (s) and 127.9 (s) and 128.1 (s) and 128.2 (s) and 130.8 (s) and 132.4 (br. s) and 140.9 (d, $J_{C,P}$ = 11.5 Hz) (Ph-C) ppm; a signal for C-2 was not detected. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = −38.0 (dd, $^2J_{P,P}$ = 20.6, $^2J_{P,P}$ = 0.8 Hz) and −28.2 (d, $^2J_{P,P}$ = 20.6 Hz) (P-1b and P-2a), 3.9 (d, $^2J_{P,P}$ = 0.8 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2974, 2927, 2861, 1488, 1453, 1444, 1376, 702, 689 cm^{-1}. $C_{40}H_{51}P_3$ (624.77): calcd. C 76.90, H 8.23; found C 77.27, H 8.52.

1a,2,2b-Tri-*tert*-butyl-2,2d-dideutero-2c-phenyl-1-(phenylethynyl)-tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene (6i): From **1a** (89 mg, 0.296 mmol) and 2-deutero-1-phenylacetylene (67 mg, 0.65 mmol); yield: 95 mg (63%); colorless powder; m.p. 45 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 0.94 (s, 9 H) and 1.11 (s, 9 H) and 1.41 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 7.27−7.40 (m, 6 H) and 7.44−7.47 (m, 2 H) and 7.63−7.64 (m, 2 H) (Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 28.9 (pt, $^3J_{C,P}$ = 9.6 Hz) and 29.8 (pt, $^3J_{C,P}$ = 9.6 Hz) and 31.3 (pt, $^3J_{C,P}$ = 10.7 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 33.9 (pt, $^2J_{C,P}$ = 16.9 Hz) and 35.6 (dd, $^2J_{C,P}$ = 24.5, $^2J_{C,P}$ = 11.5 Hz) and 37.2 (dd, $^2J_{C,P}$ = 24.5, $^2J_{C,P}$ = 13.0 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 45.7 (m_c, C-2), 46.8 (dd, $^1J_{C,P}$ = 49.5, $^1J_{C,P}$ = 15.7 Hz, C-1a or C-2b), 56.3 (m_c, C-2d), 57.2 (dd, $^1J_{C,P}$ = 45.6, $^1J_{C,P}$ = 21.9 Hz, C-1a or C-2b), 67.8 (br. d, $^1J_{C,P}$ = 33.7 Hz, C-2c), 89.6 (d, $^1J_{C,P}$ = 30.7 Hz, C-3), 108.0 (s, C-4), 123.4 (s) and 127.1 (s) and 128.0 (s) and 128.4 (s) and 128.5 (s) and 131.1 (s) and 132.3 (br. s) and 140.4 (d, $J_{C,P}$ = 11.5 Hz) (Ph-C) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = −33.3 (dd, $^2J_{P,P}$ = 20.8, $^2J_{P,P}$ = 1.0 Hz) and −23.9 (d, $^2J_{P,P}$ = 20.8 Hz) (P-1b and P-2a), 7.5 (d, $^2J_{P,P}$ = 1.0 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2958, 2904, 2863, 2148 (C≡C), 1488, 1463, 1391, 1363, 1219, 702, 689 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 506 (100) $[M]^+$, 491 $[M - CH_3]^+$ (20), 449 $[M - C_4H_9]^+$ (20), 316 (36), 169 (53), 57 $[C_4H_9]^+$ (36). $C_{31}H_{37}D_2P_3$ (506.59): calcd. C 73.50, H/D 8.15; found C 73.51, H/D 7.88.

2,6,7-Tri-*tert*-butyl-4,9-bis(1-oxoethyl)-1,5,8-triphosphatetracyclo-[4.4.0.0^{2,8}.0^{5,7}]deca-3,9-diene (3e): The 1,3,5-triphosphinine **1a** (120 mg, 0.400 mmol) and 3-butyn-2-one (68 mg, 1.00 mmol) were dissolved in toluene (5 mL) and heated at 60 °C in a pressure Schlenk tube at an argon pressure of 3 bar for 7 d. After evaporation of the solvent (25 °C/10^{-3} mbar), the residue was taken up in Et_2O and, after the addition of a small amount of silica gel, the solvent was evaporated again. The adsorbate was transferred to a glass column (diameter: 1 cm, length: 20 cm) filled with silica gel and pentane/Et_2O (50:1), which was used as eluent. After eluting a yellow fraction containing impurities, compound **3e** was obtained as a yellow powder; yield: 51 mg (29%); m.p. 165 °C. ^1H NMR (C_6D_6, 25 °C, 400.1 MHz): δ = 1.07 (s, 9 H) and 1.23 (s, 9 H) and 1.28 (s, 9 H) [$C(CH_3)_3$ groups at C-2, C-6, and C-7], 2.44 (s, 3 H) and 2.47 (d, $^4J_{H,P}$ = 2.0 Hz, 3 H) ($COCH_3$ at C-4 and C-9), 7.76 (dd, $^3J_{H,P}$ = 9.6, $^3J_{H,P}$ = 4.6 Hz, 1 H, 3-H), 8.35 (dd, $^2J_{H,P}$ = 47.4, $^3J_{H,P}$ = 3.5 Hz, 1 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 100.6 MHz): δ = 26.4 (d, $^3J_{C,P}$ = 3.8 Hz) and 27.1 (s) ($CO\mathit{C}H_3$ at C-4 and C-9), 32.4 (pt, $^3J_{C,P}$ = 4.6 Hz) and 35.6 (dd, $^3J_{C,P}$ = 13.0, $^3J_{C,P}$ = 10.0 Hz) and 35.8 (dd, $^3J_{C,P}$ = 11.5, $^3J_{C,P}$ = 8.4 Hz) [$C(\mathit{C}H_3)_3$ at C-2, C-6, and C-7], 36.9 (ddd, $^2J_{C,P}$ = 16.1, $^2J_{C,P}$ = 13.4, $^4J_{C,P}$ = 2.3 Hz) and 37.3 (pt, $^2J_{C,P}$ = 9.6 Hz) and 37.4 (signal partially overlapped by previous signal) [$\mathit{C}(CH_3)_3$ groups at C-2, C-6, and C-7], 61.3 (ddd, $^1J_{C,P}$ = 26.8, $^1J_{C,P}$ = 23.8, $^3J_{C,P}$ = 2.3 Hz, C-2), 76.6 (ddd, $^1J_{C,P}$ = 53.7, $^1J_{C,P}$ = 42.9, $^2J_{C,P}$ = 5.4 Hz) and 77.2 (ddd, $^1J_{C,P}$ = 53.7, $^1J_{C,P}$ = 42.9, $^2J_{C,P}$ = 6.1 Hz) (C-6 and C-7), 142.2 (dpt, $^1J_{C,P}$ = 48.6, $^3J_{C,P}$ = 3.6 Hz, C-4), 154.4 (dd, $^2J_{C,P}$ = 13.4, $^2J_{C,P}$ = 6.5 Hz, C-3), 166.7 (dd, $^1J_{C,P}$ = 36.8, $^2J_{C,P}$ = 3.8 Hz, C-10), 172.2 (dd, $^1J_{C,P}$ = 34.9, $^2J_{C,P}$ = 4.2 Hz, C-9), 195.0 (d, $^2J_{C,P}$ = 20.7 Hz) and 197.4 (d, $^2J_{C,P}$ = 29.9 Hz) ($\mathit{C}OCH_3$ at C-4 and C-9) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −117.9 (pt, $^2J_{P,P}$ = 3.5 Hz, P-5), 55.7 (dd, $^2J_{P,P}$ = 19.4, $^2J_{P,P}$ = 3.5 Hz) and 65.1 (dd, $^2J_{P,P}$ = 19.4, $^2J_{P,P}$ = 3.5 Hz) (P-1 and P-8) ppm. IR (CCl_4): $\tilde{\nu}$ = 2964, 2911, 1671 (C=O), 1594, 1571, 1469, 1362, 1237, 1191 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 436 $[M]^+$ (83), 421 $[M - CH_3]^+$ (31), 393 $[M - C_2H_3O]^+$ (7), 379 $[M - C_4H_9]^+$ (100), 57 $[C_4H_9]^+$ (21), 43 $[C_2H_3O]^+$ (16). $C_{23}H_{35}O_2P_3$ (436.45): calcd. C 63.30, H 8.08; found C 63.62, H 7.96.

1a,2,2b-Tri-*tert*-butyl-2c-phenyl-1-(phenylethynyl)tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene 1-Oxide (10a): A solution of **6a** (71.6 mg, 0.142 mmol) and Tms_2O_2 (27.8 mg, 0.156 mmol) in CH_2Cl_2 (5 mL) was heated to 60 °C in a pressure Schlenk tube at an argon pressure of 3 bar for 3 d. After the addition of a small amount of aluminum oxide, the solvent was evaporated in vacuo (25 °C/10^{-3} mbar). The residue was transferred to a glass column (diameter: 1.5 cm, length: 20 cm) filled with aluminum oxide and the eluent. After eluting with pentane/Et_2O (5:1), compound **10a** was obtained as a colorless powder; yield: 57 mg (77%); m.p. 200 °C. ^1H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 1.08 (s, 9 H) and 1.24 (s, 9 H) and 1.45 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.34 (s, 1 H) and 3.13 (dd, $J_{H,P}$ = 20.6, $J_{H,P}$ = 10.6 Hz, 1 H) (2-H and 2d-H), 7.35−7.49 (m, 6 H) and 7.57−7.59 (m, 2 H) and 7.65−7.83 (m, 2 H) (Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 29.5 (dd, $^3J_{C,P}$ = 9.2, $^3J_{C,P}$ = 3.8 Hz) and 30.2 (dd, $^3J_{C,P}$ = 9.2, $^3J_{C,P}$ = 4.6 Hz) and 30.9 (pt, $^3J_{C,P}$ = 11.1 Hz) [$C(\mathit{C}H_3)_3$ groups at C-1a, C-2, and C-2b], 34.8 (pt, $^2J_{C,P}$ = 17.6 Hz) and 36.4 (dd, $^2J_{C,P}$ = 10.0, $^2J_{C,P}$ = 3.1 Hz) and 38.1 (dd, $^2J_{C,P}$ = 11.5, $^2J_{C,P}$ = 3.1 Hz) [$\mathit{C}(CH_3)_3$ groups at C-1a, C-2, and C-2b], 42.4 (ptd, $^1J_{C,P}$ = 47.0, $^3J_{C,P}$ = 12.7 Hz, C-2), 45.3 (dd, $^1J_{C,P}$ = 99.7, $^1J_{C,P}$ = 48.3 Hz, C-1a or C-2b), 53.9 (ddd, $^1J_{C,P}$ = 37.6, $^2J_{C,P}$ = 10.4, $^2J_{C,P}$ = 3.5 Hz, C-2d), 54.9 (d, $^1J_{C,P}$ = 44.5 Hz, C-1a or C-2b), 66.5 (ddd, $^1J_{C,P}$ = 37.2, $^2J_{C,P}$ = 13.4, $^2J_{C,P}$ = 3.1 Hz, C-2c), 88.0 (d, $^1J_{C,P}$ = 161.0 Hz, C-3), 100.7 (d, $^2J_{C,P}$ = 29.1 Hz, C-4), 121.2 (d, $J_{C,P}$ = 3.8 Hz) and 128.2 (s) and 128.6 (s) and 129.0 (s) and 130.6 (s) and 132.4 (s) and 132.5 (s) and 139.3 (dd, $J_{C,P}$ = 11.5, $J_{C,P}$ = 2.3 Hz) (Ph-C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −37.1 (dd, $^2J_{P,P}$ = 19.6, $^2J_{P,P}$ = 8.0 Hz) and −28.3 (dd, $^2J_{P,P}$ = 19.6, $^2J_{P,P}$ = 8.0 Hz) (P-1b and P-2a), 37.5 (pt, $^2J_{P,P}$ = 8.0 Hz) ppm. IR (CCl_4): $\tilde{\nu}$ = 2959, 2904, 2881, 2177 (C≡C), 1490, 1394, 1262, 1228, 1209, 1189, 1031, 844, 702, 688, 658 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 520 (100) $[M]^+$, 505 $[M - CH_3]^+$ (18), 463 $[M - C_4H_9]^+$ (60), 57 $[C_4H_9]^+$ (42). $C_{31}H_{39}OP_3$ (520.57): calcd. C 71.53, H 7.55; found C 71.05, H 7.59.

1a,2,2b-Tri-*tert*-butyl-2c-phenyl-1-(phenylethynyl)tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene 1-Sulfide (10b): Compound **6a** (83.8 mg, 0.166 mmol), S_8 (15.9 mg, 0.498 mmol), and triethylamine (50.4 mg, 0.498 mmol) in CH_2Cl_2 (5 mL) were heated to 50 °C in a pressure Schlenk tube at an argon pressure of 3 bar for 7 d. After the addition of a small amount of aluminum oxide, the solvent was evaporated in vacuo (25 °C/10^{-3} mbar). The residue was transferred to a glass column (diameter: 1.5 cm, length: 20 cm) filled with aluminum oxide and pentane/Et_2O (200:1), which was used as the eluent. After eluting a first fraction containing

impurities, compound **10b** was obtained as a colorless powder; yield: 45 mg (51%); m.p. 183 °C. ^{1}H NMR ($CDCl_3$, 25 °C, 400.1 MHz): δ = 1.17 (br. s, 9 H) and 1.31 (s, 9 H) and 1.40 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.47 (s, 1 H) and 3.15 (dd, $J_{H,P}$ = 20.6, $J_{H,P}$ = 9.5 Hz, 1 H) (2-H and 2d-H), 7.30−7.45 (m, 6 H) and 7.51−7.54 (m, 2 H) and 7.59−7.81 (m, 2 H) (Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 50.3 MHz): δ = 29.3 (dd, $^3J_{C,P}$ = 11.4, $^3J_{C,P}$ = 3.8 Hz) and 30.1 (m_c) and 30.6 (pt, $^3J_{C,P}$ = 11.4 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 34.6 (pt, $^2J_{C,P}$ = 17.4 Hz) and 37.2 (dd, $^2J_{C,P}$ = 11.0, $^2J_{C,P}$ = 5.1 Hz) and 38.9 (dd, $^2J_{C,P}$ = 12.3, $^2J_{C,P}$ = 5.5 Hz) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 42.4 (ptd, $^1J_{C,P}$ = 47.9, $^3J_{C,P}$ = 11.4 Hz, C-2), 47.0 (dd, $^1J_{C,P}$ = 75.9, $^1J_{C,P}$ = 50.4 Hz, C-1a or C-2b), 56.3 (ddd, $^1J_{C,P}$ = 39.8, $^2J_{C,P}$ = 11.9, $^2J_{C,P}$ = 4.2 Hz, C-2d), 56.8 (d, $^1J_{C,P}$ = 46.1 Hz, C-1a or C-2b), 67.8 (ddd, $^1J_{C,P}$ = 39.2, $^2J_{C,P}$ = 12.5, $^2J_{C,P}$ = 4.2 Hz, C-2c), 87.5 (d, $^1J_{C,P}$ = 144.1 Hz, C-3), 101.5 (d, $^2J_{C,P}$ = 26.3 Hz, C-4), 121.0 (d, $J_{C,P}$ = 4.2 Hz) and 127.8 (s) and 128.2 (s) and 128.6 (s) and 130.1 (s) and 131.8 (s) and 131.9 (s) and 138.8 (dd, $J_{C,P}$ = 11.4, $J_{C,P}$ = 2.1 Hz) (Ph-C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −26.1 (dd, $^2J_{P,P}$ = 19.4, $^2J_{P,P}$ = 7.5 Hz) and −15.4 (dd, $^2J_{P,P}$ = 19.4, $^2J_{P,P}$ = 7.5 Hz) (P-1b and P-2a), 46.4 (pt, $^2J_{P,P}$ = 7.5 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2958, 2903, 2865, 2173 (C≡C), 1599, 1489, 1463, 1444, 1392, 1364, 1212, 1030, 847, 703, 688, 658 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 536 $[M]^+$ (28), 521 $[M - CH_3]^+$ (5), 479 $[M - C_4H_9]^+$ (11), 315 (25), 258 (46), 57 $[C_4H_9]^+$ (100).

[1a,2,2b-Tri-*tert*-butyl-2c-phenyl-1-(phenylethynyl)tetrahydro-1*H*-1,1b,2a-triphosphadicyclopropa[*cd*,*gh*]pentalene]hexacarbonyldicobalt (11): A solution of **6a** (95.7 mg, 0.190 mmol) and octacarbonyldicobalt (71.4 mg, 0.209 mmol) in pentane (5 mL) was stirred at room temp. for 7 d. After the solvent was evaporated in vacuo (25 °C/10^{-3} mbar), the residue was subjected to column chromatography (diameter: 1.5 cm, length: 20 cm) on aluminum oxide, eluting with pentane, to furnish compound **11** as a brown oil; yield: 117 mg (78%). ^{1}H NMR (C_6D_6, 25 °C, 400.1 MHz): δ = 0.65 (s, 9 H) and 0.96 (s, 9 H) and 1.27 (s, 9 H) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 2.24 (br. s, 1 H) and 2.78 (br. s, 1 H) (2-H and 2d-H), 7.24−7.63 (m, 10 H, Ph-H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 100.6 MHz): δ = 30.4−30.6 (m) and 31.2 (m_c) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 35.4 (m_c) and 36.4 (m_c) and 37.5 (m_c) [$C(CH_3)_3$ groups at C-1a, C-2, and C-2b], 47.4 (pt, $^1J_{C,P}$ = 47.2 Hz, C-2), 48.8 (dd, $^1J_{C,P}$ = 53.4, $^1J_{C,P}$ = 34.3 Hz, C-1a or C-2b), 57.2 (d, $^1J_{C,P}$ = 38.2 Hz, C-2d), 62.4 (pt, $^1J_{C,P}$ = 44.8 Hz, C-1a or C-2b), 67.1 (d, $^1J_{C,P}$ = 32.4 Hz, C-2c), 91.6 (br. d, $^1J_{C,P}$ = 121.1 Hz, C-3), 110.3 (br. d, $^2J_{C,P}$ = 13.4 Hz, C-4), 127.5 (s) and 128.0 (s) and 128.3 (s) and 128.8 (s) and 130.1 (s) and 132.9 (s) and 139.7 (s) and 141.5 (br. d, $J_{C,P}$ = 8.6 Hz) (Ph-C), 200.5 (br. s, CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = −22.7 (dd, $^2J_{P,P}$ = 19.4, $^2J_{P,P}$ = 1.2 Hz) and −17.9 (d, $^2J_{P,P}$ = 19.4 Hz) (P-1b and P-2a), 77.9 (d, $^2J_{P,P}$ = 1.2 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2961, 2901, 2866, 2084 (C≡O), 2048 (C≡O), 2022 (C≡O), 1596, 1490, 1472, 1467, 1443, 1392, 1364, 1212, 908, 703, 692 cm^{-1}.

Crystal Structure Analysis of 6d: *Crystal Data:* $C_{33}H_{37}N_2P_3$, M_r = 554.59, orthorhombic, space group $Pca2_1$, *a* = 29.585(6), *b* = 9.059(2), *c* = 11.632(2) Å, α = β = γ = 90°, *V* = 3117.6(11) Å^3, *Z* = 4, D_c = 1.181 Mg/m^3. *Data Collection*: The data collection was performed using an STOE Imaging Plate Diffraction System at room temp. Crystal dimensions: 0.6 × 0.3 × 0.2 mm. The measurements were made in the range of 2.23° < θ < 25.01°, λ = 0.71073 Å (graphite monochromator), −35 ≤ *h* ≤ 34, −7 ≤ *k* ≤ 10, −13 ≤ *l* ≤ 13, a total of 10142 reflections, of which 4991 were independent reflections. *Structure Solution and Refinement:* The structure was solved by direct methods (SHELXS-86)[16] and refined with full-matrix least-squares procedure against F^2 (SHELXL-93).[17] The anisotropic refinement converged at *R*1 = 0.0439, *wR*2 = 0.0841 [$I > 2\sigma(I)$] and *R*1 = 0.0711, *wR*2 = 0.0897 [all data]. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 0.177 e/Å^3 and a minimum of −0.169 e/Å^3.[18]

Acknowledgments

We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Phosphor als Bindeglied verschiedener chemischer Disziplinen") for generous financial support. H. D. is grateful to the Fonds der Chemischen Industrie for a postgraduate grant.

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[26] Crystallographic data (excluding structure factors) for the structure **6d** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-220258. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033, E-mail: deposit@ccdc.cam.ac.uk].

Received March 26, 2003

