New Phosphorus−Carbon Cage Compounds by Diels−Alder and Homo Diels−Alder Reactions of 1,3,5-Triphosphabenzenes with Alkenes[‡]

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Dedicated to Professor Elmar Vilsmaier on the occasion of his 60th birthday

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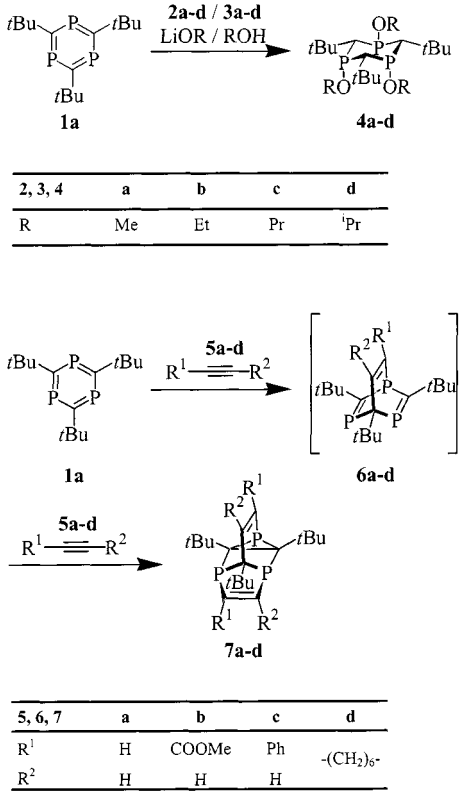
Ethylene, various monosubstituted alkenes (acrylic acid derivatives, styrene), as well as some selected disubstituted alkenes (maleic acid derivatives, fumaric acid derivatives, norbornene, cyclopentadiene) undergo Diels–Alder reactions with the 1,3,5-triphosphabenzenes **1** under mild conditions to furnish the dihydrotriphosphabarrelenes **9**, **11a–c**, **13a–e**, **15a–d**, **17a**,**b**, and **24**. The monoadduct **26** as well as the diadducts **27** and **28** are isolated following the reaction with norbornadiene. Cyclopropene is the only alkene to undergo a Diels–Alder/homo Diels–Alder reaction sequence to afford the hexacyclic system **20**.

Introduction

2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene (**1a**) was first prepared in 1995.[2] Shortly thereafter, a simple one-pot synthesis was developed that also made the isolation of other triphosphabenzene derivatives possible.[3]

Although their physicochemical properties (NMR spectroscopic data,[2,3] crystal structure analysis[4]) as well as theoretical investigations[5] clearly demonstrate the aromatic character of the 1,3,5-triphosphabenzenes **1**, the compounds exhibit a surprisingly high reactivity in, for example, 1,2-additions[6] or [4 + 2] cycloaddition reactions.[7] Thus, alcohols undergo addition to the P−C double bond in alkaline media to furnish the 1,3,5-trialkyloxy-1,3,5-triphosphinanes **4**,[6] while alkynes **5** react to afford the novel triphospha cage compounds **7** through a Diels−Alder/homo Diels−Alder reaction sequence (Scheme 1) with the 1,3,5-triphosphabicyclo[2.2.2]octa-2,5,7-trienes **6** as intermediates.[7] Some of these reactions can even be performed at room temperature.

We now report on the reactions of 1,3,5-triphosphabenzenes **1a−d** with various alkenes that also proceed under mild conditions. In contrast to the corresponding cycloaddition processes with alkynes, we generally observe solely the [4 + 2] cycloaddition reactions in the present cases. A subsequent homo Diels−Alder reaction only occurs with the very reactive cyclopropene.



2, 3, 4	a	b	c	d
R	Me	Et	Pr	^{i}Pr

5, 6, 7	a	b	c	d
R^1	H	COOMe	Ph	-$(CH_2)_6$-
R^2	H	H	H	

Scheme 1

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Results and Discussion

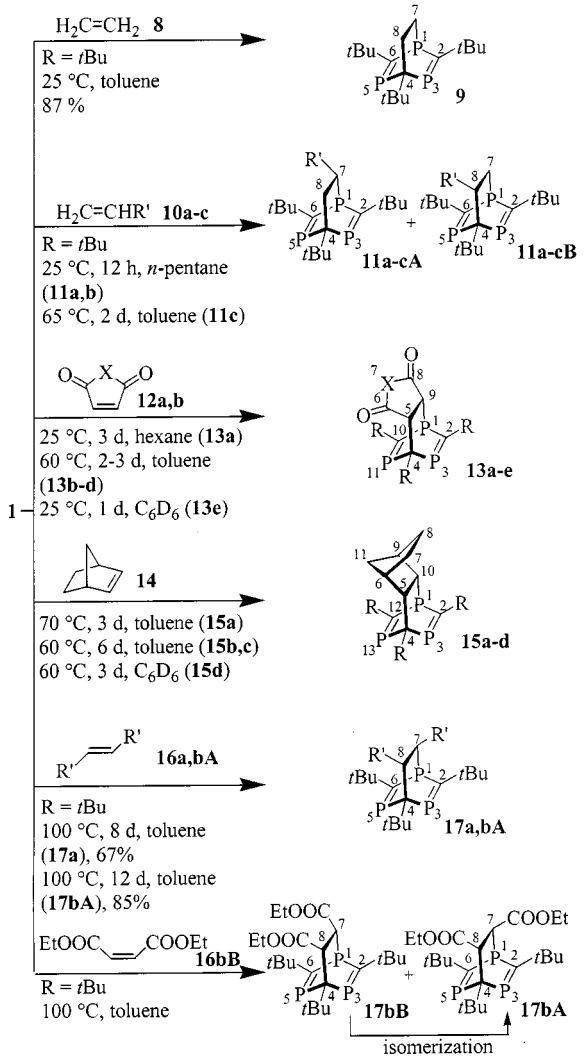
Cycloaddition Reactions of 1,3,5-Triphosphabenzenes 1 with Alkenes

When ethylene (**8**) is bubbled into a toluene solution of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1a**), a [4 + 2] cycloaddition reaction occurs at room temperature to afford the 7,8-dihydro-1,3,5-triphosphabarrelene **9** (Scheme 2). The pale-yellow, moisture-sensitive bicyclic compound **9** is obtained in 87% yield after recrystallization from *n*-pentane.

Acceptor-substituted alkenes such as methyl acrylate (**10a**) and acrylonitrile (**10b**) also react readily at 25 °C with the triphosphabenzene **1a** to give the corresponding dihydrobarrelenes **11a** and **11b**, whereas the reaction with styrene (**10c**) to furnish **11c** requires a large excess of the alkene and a higher reaction temperature. The possible regioisomers **11a−cA** and **11a−cB** that may arise from the reaction with the terminal alkenes **10** are both found, with formation of the regioisomers **11a−cA** apparently being favored for electronic reasons. The lack of complete regioselectivity may stem from a sterically hindered approach in the formation of the favored regioisomer. The major product **11aA** formed from the acrylate **10a** can be isolated by fractional crystallization.

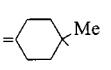
Cyclic disubstituted alkenes such as *N*-phenylmaleimide (**12a**), maleic anhydride (**12b**), and norbornene (**14**) also readily undergo [4 + 2] cycloaddition reactions with the triphosphabenzene **1a** to afford the dihydrobarrelenes **13a**,**b** and **15a** in good yields (64−88%).

In contrast, open-chain, disubstituted electron-poor alkenes such as fumaric dinitrile (**16a**) and diethyl fumarate (**16bA**) require longer reaction times at 100 °C to form the cycloadducts **17a**,**bA** with **1a**. The reaction of 1,3,5-triphosphabenzene **1a** with diethyl maleate (**16bB**) follows an unexpected course: After 8 d at 100 °C in toluene, the reaction mixture contains unchanged substrate and the *trans*-[4 + 2] cycloadduct **17bA** together with an approximately equimolar amount of the *cis*-[4 + 2] cycloadduct **17bB**, characterized by ^{31}P NMR signals at δ = 332.1, 314.2, and −93.2. After a total of 18 d, the bicyclic compound **17bA** is the sole product and can be isolated in 81% yield. Accordingly,



Scheme 2

*t*Pen = $C(CH_3)_2CH_2CH_3$

MecHex =  1-Ad = 

1	a	b	c	d
R	*t*Bu	*t*Pen	MecHex	1-Ad

10, 11	a	b	c
R'	CO_2Me	CN	Ph
% yield (**11A+B**)	75	73	63
ratio **11A**:**11B**	4:1	2:1	2.5:1

12	a	b
X	N-Ph	O

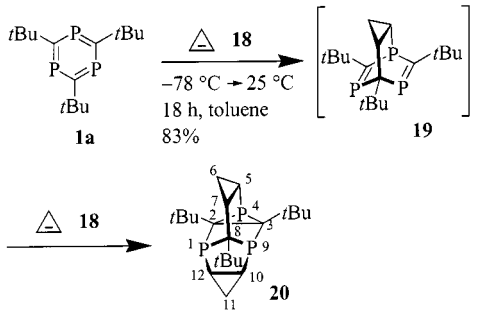
13	a	b	c	d	e
X	N-Ph	O	O	O	O
R	*t*Bu	*t*Bu	*t*Pen	MecHex	1-Ad
% yield	88	64	65	35	4

15	a	b	c	d
R	*t*Bu	*t*Pen	MecHex	1-Ad
% yield	73	40	64	4

16, 17	a	b
R'	CN	COOEt

it can be assumed that the initially formed *cis* cycloadduct **17bB** undergoes complete isomerization to the *trans* cycloadduct **17bA** (Scheme 2). The necessary bond cleavage seems to be feasible on account of the reversibility of Diels–Alder reactions.

The reactivity of cyclopropene (**18**) makes it an exceptional case: It even reacts with **1a** at −78 °C. However, 2 equiv. of **18** are required for complete reaction because the initially formed [4 + 2] cycloadduct **19** reacts spontaneously with further **18** in a homo Diels–Alder reaction to form the novel cage compound **20** (Scheme 3). The Diels–Alder cycloadduct cannot be isolated or even detected by spectroscopy. A similar behavior of alkynes has been described.[7]



Scheme 3

By using the cycloalkenes **12b** and **14**, we addressed the question as to whether other kinetically stabilized triphosphabenzenes such as **1b–d** were amenable to this synthetic protocol. We found that triphosphabenzenes with sterically demanding groups in the 2,4,6-positions, such as the tri-*tert*-pentyl derivative **1b** or the tris(1-methylcyclohexyl) derivative **1c**, reacted with maleic anhydride (**12b**) and norbornene (**14**) at 60 °C to give the corresponding [4 + 2] cycloadducts **13c**,**d** and **15b**,**c** in comparable yields to that of the reaction of **1a**, whereas the 2,4,6-tris(1-adamantyl)-1,3,5-triphosphabenzene (**1d**) furnished the corresponding thermally unstable cycloadducts **13e** and **15d** in merely 4% yield, presumably as a result of steric effects.

The described dihydrobarrelenes were mostly isolated as microcrystalline, air-sensitive powders that were found to be stable up to about 100 °C. However, when the dihydrobarrelenes **13** and **15** were heated at 150–175 °C/10^{-3} mbar, retro Diels–Alder reactions took place that were complete within a few hours, and the respective triphosphabenzenes **1** could be recovered, e.g. by bulb-to-bulb distillation.

The previously unknown dihydrobarrelenes **9**, **11a–c**, **13a–e**, **15a–d**, and **17a**,**b** were unambiguously characterized by elemental-analytical, mass-spectrometric, and NMR-spectroscopic data. This identification is described in detail below in the case of the dihydrobarrelene **9**.

The 1:1 composition of the adduct **9** was unequivocally demonstrated by its elemental analysis and the molecular ion peak at $m/z = 328$ in its mass spectrum. In agreement with the mirror-plane symmetry of the molecule, the $^{31}P\{^1H\}$ NMR spectrum reveals an A_2X spin system with a characteristic $^2J_{P,P}$ coupling constant of 15.5 Hz. The two $\lambda^3\sigma^2$-phosphorus atoms give the expected doublet signal at low field ($\delta = 319.2$), while the bridgehead phosphorus atom gives rise to a triplet signal at $\delta = -95.8$. In the $^{13}C\{^1H\}$ NMR spectrum, the two carbon atoms of the two P–C double bonds constitute the X part of an AA′MX spin system centered at $\delta = 223.2$. The signal due to the bridgehead carbon atom C-4 at $\delta = 73.0$ is split into a double triplet by a characteristic, direct coupling of 56.4 Hz with the phosphorus atoms P-3 and P-5 and a $^3J_{C,P}$ coupling of 1.7 Hz. The signals of the two sp^3-carbon atoms C-7 and C-8 exhibit the expected heteronuclear couplings. The signal due to the carbon atom C-7 adjacent to the bridgehead phosphorus atom is split into a doublet ($\delta = 27.8$, $^1J_{C,P} = 12.7$ Hz), whereas that due to the carbon atom C-8 appears as a double triplet ($\delta = 21.1$, $^2J_{C,P} = 4.2$ and 2.5 Hz). The ^1H NMR spectrum is in complete accord with the proposed constitution of the bicyclic compound **9**.

The positions and splittings of all NMR signals of the dihydrotriphosphabarrelenes **11–17** are in good agreement with those of the dihydrotriphosphabarrelene **9**. However, the two P–C double bonds are no longer identical on account of the substituents at the bridgehead carbon atom. Accordingly, the A_2X spin system in the $^{31}P\{^1H\}$ NMR spectrum of **9** is replaced by an ABX spin system. The signals for the A and B parts appear at $\delta = 305.5$ to 340.8, while those of the X part are observed in the region $\delta = -74.8$ to −103.9 (see Table 1).

The assignment of the regiochemistry of the cycloadducts **11a–c** is based principally on the ^1H NMR spectrum recorded for the pure bicyclic compound **11aA**. The position of the 7-H signal at $\delta = 2.53$ and the coupling constants $^3J_{H,H} = 9.8$ and 6.0 Hz as well as $^2J_{H,P} = 9.5$ Hz clearly demonstrate this assignment. A comparison of the chemical shifts of 7-H and 8-H and selective ^{31}P-decoupling experiments on **11bA** and **11cA** confirm the same regiochemistry for these cycloaddition products.

The *endo*/*exo* stereochemistry of the cycloadduct **15** with regard to the norbornanediyl group is not completely clear. However, MM2 force field calculations as well as PM3 geometry optimization point to a slight energetic preference for the *exo* isomer.[8]

An X-ray crystallographic analysis (see Figure 1) of the cobalt complex **22** provided further evidence of the constitution; the complex was prepared from the dihydrotriphosphabarrelene **11aA** and (η^5-cyclopentadienyl)bis(η^2-ethylene)cobalt (**21**) and was obtained as wine-red crystals in 95% yield (Scheme 4).

Complexation of the P–C double bonds results in an extreme high-field shift of the $^{31}P\{^1H\}$ NMR signals of the two $\lambda^3\sigma^2$-phosphorus atoms by approximately 400 ppm to $\delta = -78.7$ and −92.0, respectively. The signals due to the sp^2-carbon atoms are also shifted to very high field, appearing at $\delta = 53.8$. Similar shifts upon coordination have been observed for the Cp–cobalt complex of a tetraphosphabarrelene.[9] In addition to the expected bonding of the ligands to the central atom through the heteroatom double bonds, an interaction with the bridgehead phosphorus atom is apparent because the signal due to P-1 is also shifted

Table 1. $^{31}P\{^1H\}$ NMR spectroscopic data of compounds **9**, **11a−cA**, **11a−cB**, **13a**,**b**, **15a**, **17a**,**bA**, and **17bB** (all derived from 1,3,5-triphosphabenzene **1a**)

Product[a]	$\sigma^3\lambda^3$-P	$\sigma^2\lambda^3$-P		$^2J_{\sigma^2P,\sigma^2P}$ [Hz]	$^2J_{\sigma^2P,\sigma^3P}$ [Hz]
9	−95.8 (t)	319.2 (d)		−	15.5
11aA	−88.1 (pt)	320.2 (dd)	329.2 (dd)	21.3	6.6
11aB	−95.0 (pt)	313.5 (dd)	317.6 (dd)	20.5	12.1
11bA	−103.9 (dd)	305.5 (dd)	311.8 (dd)	19.6	12.2, 10.2
11bB	−99.8 (pt)	313.0 (dd)	324.1 (dd)	23.6	4.7
11cA	−74.8 (dd)	312.9 (dd)	327.6 (dd)	21.6	11.0, 7.2
11cB	−85.0 (dd)	311.8 (dd)	327.6 (dd)	21.0	12.3, 11.2
13a	−90.9 (dd)	317.3 (dd)	324.3 (dd)	20.5	7.1, 6.3
13b	−93.1 (pt)	321.7 (dd)	325.9 (dd)	20.4	5.3
15a	−83.1 (dd)	318.2 (dd)	327.6 (dd)	21.4	12.7, 10.5
17a	−96.3 (pt)	316.7 (dd)	317.7 (dd)	20.3	3.2
17bA	−84.4 (dd)	317.3 (dd)	324.1 (dd)	22.2	5.9, 3.6
17bB	−93.2 (s)	314.2 (d)	332.1 (d)	21.5	−

[a] δ values, solvent C_6D_6, 25 °C.

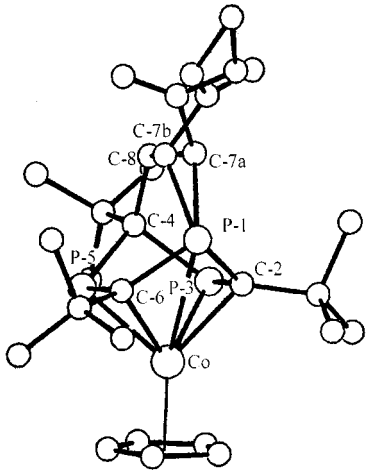
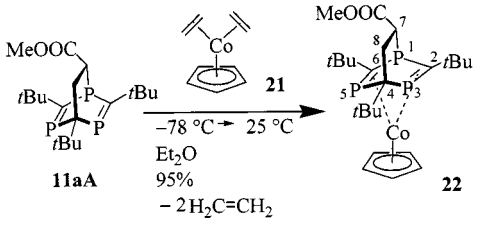


Figure 1. Crystal structure of **22**; selected bond lengths [Å] and angles [°] (the methoxycarbonyl function and C-7 show a disorder): P(5)−C(6) 1.767(7), P(3)−C(2) 1.765 (7), P(1)−C(2) 1.834(7), P(3)−C(4) 1.869(7), P(5)−C(4) 1.858(7), P(1)−C(6) 1.821(7), P(1)−Co 2.909(2), P(5)−Co 2.273(2), C(6)−Co 2.090(7), P(3)−Co 2.270(2), C(2)−Co 2.110(7); P(3)−C(4)−P(5) 95.1(3), C(2)−P(1)−C(6) 90.6(3), P(5)−C(6)−P(1) 120.2(4), C(6)−P(5)−C(4) 104.0(3)



Scheme 4

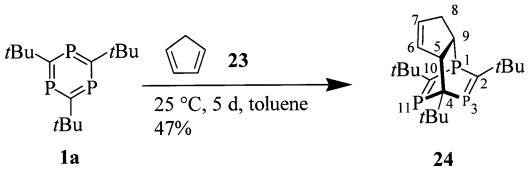
to higher field (δ = −36.4). The crystal structure analysis confirmed the regiochemistry of the cycloaddition deduced from the NMR investigations. Although the methoxycarbonyl function of complex **22** exhibits disorder, the other structural parameters could be unambiguously determined. As expected, the lengths of the two P−C double bonds C-2−P-3 and C-6−P-5 of 1.765(7) Å and 1.767(7) Å, respectively, are stretched by the complexation in comparison with the free P−C double bonds. The Co−P-1 separation of 2.909(2) Å is indicative of a weak interaction between the metal atom and P-1. The other determined bond lengths are all of the expected magnitudes and are in good agreement with the structure of a cobalt complex of 1,3,5,8-tetraphosphabarrelene.[9]

The composition and structure of the cage compound **20** were deduced from a combination of mass-spectrometric and NMR-spectroscopic data. However, it could not be unequivocally determined whether the cyclopropane ring introduced by the homo Diels−Alder reaction is linked to the rest of the molecule in an *endo* or *exo* fashion. In the $^{31}P\{^1H\}$ NMR spectrum, the signal due to the phosphirane phosphorus atom P-4 appears at highest field (δ = −166.7, $^2J_{P,P}$ = 8.5 and 4.5 Hz) as a double doublet, while those due to P-1 and P-9 appear as double doublets at δ = 59.2 ($^2J_{P,P}$ = 24.7 and 4.5 Hz) and δ = 66.4 ($^2J_{P,P}$ = 24.7 and 8.5 Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the two methylene carbon atoms C-6 and C-11 of the cyclopropane unit, identified by recording a DEPT spectrum, give signals at δ = 14.6 and δ = 26.4, respectively. The signal due to C-6 at δ = 14.6 is split into a double doublet of doublets by a $^2J_{C,P}$ coupling of 19.5 Hz together with two $^3J_{C,P}$ couplings of 6.8 Hz and 1.7 Hz. For C-11, we observe a double doublet at δ = 26.4 with $^2J_{C,P}$ couplings of 5.1 Hz and 3.4 Hz. The signals due to the four methine carbon atoms of the two cyclopropane rings can also be assigned on the basis of their coupling patterns. Finally, the quaternary skeletal carbon atom C-8 gives rise to a pseudo triplet signal at δ = 63.7 with two $^1J_{C,P}$ couplings of 15.8 Hz each. The signals due to the two phosphirane carbon atoms C-2, C-3 appear at δ = 59.4 ($^1J_{C,P}$ = 44.1 and 42.4 Hz, $^2J_{C,P}$ = 3.4 Hz) and δ = 60.1 ($^1J_{C,P}$ = 47.1 and 41.1 Hz, $^2J_{C,P}$ = 4.2 Hz), respectively, as double doublets of doublets.

Cycloaddition Reactions of the 1,3,5-Triphosphabenzene 1a with Dienes

[4 + 2] Cycloaddition reactions of the triphosphabenzene **1a** with dienes have hitherto only been examined with cyclic

dienes such as cyclopentadiene (**23**) and norbornadiene (**25**). In such reactions, cyclopentadiene (**23**) reacts exclusively as a dienophile and undergoes regioselective addition to **1a** even at room temperature to furnish **24** (Scheme 5). The dihydrobarrelene **24** is sensitive to hydrolysis and was isolated by crystallization from *n*-pentane.

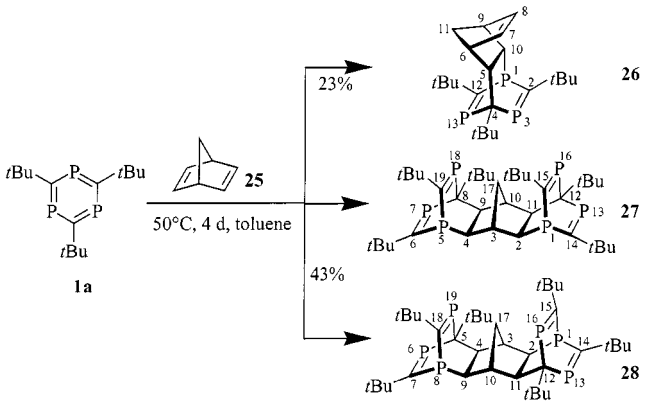


Scheme 5

The 1:1 stoichiometry of the addition was confirmed by mass-spectrometric and elemental-analytical data. Consideration of the carbon−phosphorus coupling constants in the $^{13}C\{^1H\}$ NMR spectrum of **24** and a DEPT experiment provided information concerning the regioselectivity of this cycloaddition process.

In analogy to the dihydrobarrelenes **11a**−**c**, **13a**−**e**, **15a**−**d**, and **17a**,**b**, the $^{31}P\{^1H\}$ NMR spectrum features signals due to the two $\lambda^3\sigma^2$-phosphorus atoms P-3, P-11 at characteristically low field positions of δ = 320.3 and δ = 330.2, each as a double doublet, whereas the bridgehead phosphorus atom P-1 gives rise to a double doublet at δ = −78.2. The $^2J_{P,P}$ coupling constants are in a characteristic range of 7.6 to 21.0 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the chemical shifts of the signals of the skeletal carbon atoms of the dihydrotetraphosphabarrelene unit are comparable with the values for the dihydrotetraphosphabarrelene compounds described in this paper. The signals of the cyclopentene unit yield decisive diagnostic information concerning the regiochemistry of the reaction. With the help of a DEPT spectrum, the signal at δ = 35.7 can be assigned to the methylene group C-8. The signal appears as a doublet with a $^2J_{C,P}$ coupling constant of 18.5 Hz. If the other conceivable isomer had been formed, the methylene group signal would have exhibited merely $^3J_{C,P}$ couplings. These can be expected to be markedly smaller in magnitude since even the signal due to the methine group C-5 at δ = 51.6 exhibits a $^2J_{C,P}$ coupling of just 1.4 Hz. In the regioisomer that is not formed, the methylene group would be adjacent to this methine group. A comparison with the chemical shift values of compound **15a** further facilitates the assignment of the regiochemistry. The carbon atom C-9 in compound **15a** shows a $^2J_{C,P}$ coupling constant of 16.2 Hz, whereas carbon C-6 exhibits a $^3J_{C,P}$ coupling constant of merely 1.0 Hz.

In contrast to the reaction with cyclopentadiene (**23**), the steric situation in norbornadiene (**25**) apparently permits the formation of bisadducts (Scheme 6). After reaction of equimolar amounts of **25** and **1a** for 4 d at 50 °C, chromatographic workup of the reaction mixture on silica gel furnished the monoadduct **26** in 23% yield together with a mixture of the bisadducts **27** and **28** in 43% yield. When an excess of **1a** was used, the yield of **26** increased. The bisadducts **27** and **28** could also be obtained from the reaction



Scheme 6

of **26** with **1a**. It would seem that the first and second cycloadditions to the double bonds of norbornadiene proceed at comparable rates.

The monoadduct **26** is easily separated from the reaction mixture by column chromatography, whereas it has not yet been possible to separate the two bisadducts. However, their ratio could be estimated as 3:1 based on integration of the ^1H NMR spectrum. We are as yet unable to distinguish which of the two formed regioisomers is the major product on the basis of the NMR-spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum features two sets of signals, each composed of three double doublets; these can be rationalized in terms of the C_S-symmetrical structure of **27** and the C_2-symmetrical structure of **28**, respectively. The signals in the $^{13}C\{^1H\}$ NMR spectrum are also consistent with the proposed constitutions of **27** and **28**; resonances typical of the dihydrotriphosphabarrelene structural unit are seen. The mass spectrum and the elemental analytical data confirm the formation of the adducts from 2 equiv. of triphosphabenzene **1a** and 1 equiv. of norbornadiene (**25**). The spectroscopic data of the monoadducts **26** are also in agreement with the dihydrotriphosphabarrelene structure, although their stereochemistry cannot be deduced from these data. The same holds for the stereochemistry of the bisadducts **27** and **28**. Nevertheless, semiempirical calculations at the PM3 level and MM2 force field calculations clearly show that the *exo* annulation is especially preferred for the bisadducts.[8] Thus, in Scheme 6, the pure *exo* structures are shown for the monoadduct **26**, as well as for the two bisadducts **27** and **28**. The two bisadducts differ in the regiochemistry of the second step of the cycloaddition.

Experimental Section

General: All reactions were carried out under argon using Schlenk techniques. The solvents were anhydrous and were stored under argon. − ^1H and ^{31}P NMR: Bruker AC 200, AM 200, AC 300, and AMX 400. − ^{13}C NMR: Bruker AC 300 and AMX 400; chemical shifts are referenced to the solvent as an internal standard; in the case of ^{31}P NMR, 85% H_3PO_4 was used as an external standard. − IR: Perkin−Elmer FT-1310 and FT-1600. − MS: Finnigan MAT 90 and MAT 311aDF. − Elemental analyses: Perkin−Elmer

EA240 and Mikroanalytisches Labor Dornis & Kolbe, Mülheim an der Ruhr. – Melting points: Mettler FP61 (heating rate 2 °C/min) and SG 2000, HWS Mainz Laboratoriumstechnik (heating rate 3 °C/min); uncorrected values. Compounds **1a**,[3] **1b**,[3] **1c**,[3] **1d**[3] and **21**[10] were prepared by published methods. All other starting materials were obtained from commercial suppliers and used without further purification. Cyclopentadiene (**23**) was freshly prepared from bis(cyclopentadiene) prior to use.

2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene (9): Ethylene (**8**) was bubbled through a solution of triphosphabenzene **1a** (197 mg, 0.66 mmol) in toluene (8 mL) until the reaction was complete (^{31}P NMR monitoring). The solvent was then removed in vacuo (10^{-3} mbar/25 °C) and the residue was redissolved in *n*-pentane. Impurities were removed by filtration through Celite and the dihydrobarrelene **9** was crystallized from *n*-pentane at −78 °C. Yield 178 mg (87%) as a pale-yellow, microcrystalline powder; m.p. 152 °C. – ^{1}H NMR (C_6D_6): δ = 1.13−1.35 (m, 4 H, 7- and 8-H), 1.40 [s, 18 H, $C(CH_3)_3$ at C-2 and C-6], 1.42 [s, 9 H, $C(CH_3)_3$ at C-4]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 21.1 (dt, $^2J_{C,P}$ = 4.2 and 2.5 Hz, C-8), 27.8 (d, $^1J_{C,P}$ = 12.7 Hz, C-7), 29.1 [t, $^3J_{C,P}$ = 10.2 Hz, $C(CH_3)_3$ at C-4], 31.3 [X part of AA′MX spin system, $C(CH_3)_3$ at C-2 and C-6], 36.4 [t, $^2J_{C,P}$ = 17.4 Hz, $C(CH_3)_3$ at C-4], 43.8 [X part of AA′MX spin system, $C(CH_3)_3$ at C-2 and C-6], 73.0 (td, $^1J_{C,P}$ = 56.4 Hz, $^3J_{C,P}$ = 1.7 Hz, C-4), 223.2 (X part of AA′MX spin system, C-2 and C-6). – ^{31}P{^{1}H} NMR (C_6D_6): δ = −95.8 (t, $^2J_{P,P}$ = 15.5 Hz, P-1), 319.2 (d, $^2J_{P,P}$ = 15.5 Hz, P-3 and P-5). – MS (EI, 70 eV): *m*/*z* (%) = 328 (84) [M$^+$], 313 (100) [M$^+$ − Me], 271 (17) [M$^+$ − *t*Bu], 169 (38) [$PC_2tBu_2^+$], 57 (21) [*t*Bu$^+$]. – IR (CCl_4): ṽ = 2960, 2929, 2866, 1472, 1459, 1364, 1118 cm^{-1}. – $C_{17}H_{31}P_3$ (328.35): calcd. C 62.19, H 9.52; found C 61.91, H 9.46.

Methyl 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene-7-carboxylate (11aA) and Methyl 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene-8-carboxylate (11aB): A solution of methyl acrylate (**10a**; 1.7 mL, 1 M in *n*-pentane) was added dropwise to a solution of triphosphabenzene **1a** (500 mg, 1.66 mmol) in *n*-pentane (5 mL). The solution was stirred for 12 h at room temperature, all volatile components were removed in vacuo (10^{-3} mbar/25 °C), and the residue was redissolved in *n*-pentane. The resulting solution was filtered through 2 cm of silica gel. Removal of the solvent left a yellow oil consisting of the regioisomers **11aA** and **11aB** in a ratio of 4:1. The main product could be crystallized from *n*-heptane (0.8 mL) at −78 °C. Yield 385 mg of **11aA** (60%) as a yellow powder; m.p. 115 °C. – ^{1}H NMR (C_6D_6): **11aA**: δ = 1.36 (d, $^4J_{H,P}$ = 2.4 Hz, 9 H) and 1.38 [d, $^4J_{H,P}$ = 2.4 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.43 [s, 9 H, $C(CH_3)_3$ at C-4], 1.57 (m, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 9.8 Hz, 1 H) and 2.07 (m, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 6.0 Hz, 1 H, 8-H), 2.53 [ddd, $^2J_{H,P}$ = 9.5 Hz, $^3J_{H,H}$ = 9.8 (*cis*) and 6.0 (*trans*) Hz, 1 H, 7-H], 3.35 (d, $^4J_{H,P}$ = 0.8 Hz, 3 H, $COOCH_3$); **11aB:** δ = 1.33 (d, $^4J_{H,P}$ = 2.2 Hz, 9 H) and 1.38 [d, $^4J_{H,P}$ = 2.2 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.48 [s, 9 H, $C(CH_3)_3$ at C-4], 1.80 (m, 2 H, 7-H), 2.74 (m, 1 H, 8-H), 3.68 (d, $^5J_{H,P}$ = 0.8 Hz, 3 H, $COOCH_3$). – ^{13}C{^{1}H} NMR (C_6D_6): **11aA:** δ = 25.9 (pt, $^2J_{C,P}$ = 3.1 Hz, C-8), 29.2 [pt, $^3J_{C,P}$ = 9.7 Hz, $C(CH_3)_3$ at C-4], 31.4 (dd, $^3J_{C,P}$ = 14.3 and 10.1 Hz) and 31.4 [dd, $^3J_{C,P}$ = 15.3 and 9.2 Hz, $C(CH_3)_3$ at C-2 and C-6], 36.6 [pt, $^2J_{C,P}$ = 17.3 Hz, $C(CH_3)_3$ at C-4], 43.2 (dd, $^2J_{C,P}$ = 25.9 and 17.8 Hz) and 44.1 [dd, $^2J_{C,P}$ = 27.5 and 18.3 Hz, $C(CH_3)_3$ at C-2 and C-6], 47.2 (d, $^1J_{C,P}$ = 22.4 Hz, C-7), 51.6 (s, $COOCH_3$), 74.5 (ptd, $^1J_{C,P}$ = 57.0 Hz, $^3J_{C,P}$ = 4.1 Hz, C-4), 172.7 (d, $^2J_{C,P}$ = 8.1 Hz, $COOCH_3$), 215.9 (ddd, $^1J_{C,P}$ = 58.0 and 44.7 Hz, $^3J_{C,P}$ = 6.1 Hz) and 223.8 (ddd, $^1J_{C,P}$ = 58.0 and 41.7 Hz, $^3J_{C,P}$ = 7.1 Hz, C-2 and C-6). – ^{31}P{^{1}H} NMR (C_6D_6): **11aA**: δ = −88.1 (pt, $^2J_{P,P}$ = 6.6 Hz, P-1), 320.2 (dd, $^2J_{P,P}$ = 21.3 and 6.6 Hz) and 329.2 (dd, $^2J_{P,P}$ = 21.3 and 6.6 Hz, P-3 and P-5); **11aB:** δ = −95.0 (pt, $^2J_{P,P}$ = 12.1 Hz, P-1), 313.5 (dd, $^2J_{P,P}$ = 20.5 and 12.1 Hz) and 317.6 (dd, $^2J_{P,P}$ = 20.5 and 12.1 Hz, P-3 and P-5). – MS (EI, 70 eV): *m*/*z* (%) = 386 (74) [M$^+$], 371 (78) [M$^+$ − Me], 356 (3) [M$^+$ − 2Me], 329 (5) [M$^+$ − *t*Bu], 185 (100) [M$^+$ − $P_2C_2tBu_2H$], 169 (58) [$PC_2tBu_2^+$]. – **11aA:** $C_{19}H_{33}O_2P_3$ (386.47): calcd. C 59.06, H 8.61; found C 58.92, H 8.56.

2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene-7-carbonitrile (11bA) and 2,4,6-*Tri*-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene-8-carbonitrile (11bB): A solution of acrylonitrile (**10b**; 0.7 mL, 1 M in *n*-pentane) was added dropwise to a solution of triphosphabenzene **1a** (200 mg, 0.66 mmol) in *n*-pentane (3 mL) and the mixture was stirred for 12 h at room temperature. The solvent was then removed in vacuo (10^{-3} mbar/25 °C) and the residue was redissolved in *n*-pentane. Filtration through 2 cm of silica gel and removal of the solvent gave a 2:1 mixture (^{1}H NMR integration) of the regioisomers **11bA** and **11bB**. Yield 170 mg (73%) as a yellow oil. – ^{1}H NMR (C_6D_6): **11bA:** δ = 1.36 (d, $^4J_{H,P}$ = 2.2 Hz, 9 H) and 1.38 [d, $^4J_{H,P}$ = 2.2 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.43 [s, 9 H, $C(CH_3)_3$ at C-4], 1.57 (m, 1 H) and 2.07 (m, 1 H, 8-H), 2.48 (m, 1 H, 7-H); **11bB:** δ = 1.36 (d, $^4J_{H,P}$ = 2.2 Hz, 9 H) and 1.38 [d, $^4J_{H,P}$ = 2.2 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.43 [s, 9 H, $C(CH_3)_3$ at C-4], 1.57 (m, 1 H, 8-H), 1.98 (m, 1 H) and 2.07 (m, 1 H, 7-H). – ^{13}C{^{1}H} NMR (C_6D_6): **11bA:** δ = 25.5 (pt, $^2J_{C,P}$ = 2.5 Hz, C-8), 29.9 [pt, $^3J_{C,P}$ = 11.6 Hz, $C(CH_3)_3$ at C-4], 30.9 [m, $C(CH_3)_3$ at C-2 and C-6], 36.2 (dpt, $^1J_{C,P}$ = 18.6 Hz, $^3J_{C,P}$ = 2.3 Hz, C-7), 37.5 [pt, $^2J_{C,P}$ = 17.4 Hz, $C(CH_3)_3$ at C-4], 43.8 (dd, $^2J_{C,P}$ = 18.3 and 12.7 Hz) and 44.3 [dd, $^2J_{C,P}$ = 18.4 and 12.4 Hz, $C(CH_3)_3$ at C-2 and C-6], 71.9 (ptd, $^1J_{C,P}$ = 61.7 Hz, $^3J_{C,P}$ = 4.1 Hz, C-4), 120.9 (d, $^2J_{C,P}$ = 10.7 Hz, CN), 222.2 (ddd, $^1J_{C,P}$ = 60.7 and 41.5 Hz, $^3J_{C,P}$ = 6.7 Hz) and 227.5 (ddd, $^1J_{C,P}$ = 60.8 and 38.0 Hz, $^3J_{C,P}$ = 6.9 Hz, C-2 and C-6). – ^{31}P{^{1}H} NMR (C_6D_6): **11bA:** δ = −103.9 (dd, $^2J_{P,P}$ = 12.2 and 10.2 Hz, P-1), 305.5 (dd, $^2J_{P,P}$ = 19.6 and 12.2 Hz) and 311.8 (dd, $^2J_{P,P}$ = 19.6 and 10.2 Hz, P-3 and P-5); **11bB:** δ = −99.8 (pt, $^2J_{P,P}$ = 4.7 Hz, P-1), 313.0 (dd, $^2J_{P,P}$ = 23.6 and 4.7 Hz) and 324.1 (dd, $^2J_{P,P}$ = 23.6 and 4.7 Hz, P-3 and P-5). – MS (EI, 70 eV): *m*/*z* (%) = 353 (82) [M$^+$], 338 (100) [M$^+$ − Me], 323 (4) [M$^+$ − 2Me], 296 (23) [M$^+$ − *t*Bu], 169 (99) [$PC_2tBu_2^+$], 131 (92) [P_2CtBu^+], 57 (61) [*t*Bu$^+$].

2,4,6-Tri-*tert*-butyl-7-phenyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene (11cA) and 2,4,6-Tri-*tert*-butyl-8-phenyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene (11cB): Styrene (**10c**; 540 mg, 5.20 mmol) was added to a solution of triphosphabenzene **1a** (312 mg, 1.04 mmol) in toluene (5 mL). After stirring for 2 d at 65 °C, all volatile components were removed in vacuo (10^{-3} mbar/25 °C). Column chromatography on silica gel (glass column, diameter 2 cm, length 15 cm, eluent *n*-pentane) gave a yellow fraction consisting of the regioisomers **11cA** and **11cB** in a ratio of 2.5:1 (^{1}H NMR integration). It was not possible to separate these regioisomers by column chromatography or by fractional crystallization from *n*-pentane. Yield 265 mg (63%) as a yellow powder. – ^{1}H NMR (C_6D_6): **11cA:** δ = 1.17 (d, $^4J_{H,P}$ = 1.9 Hz, 9 H) and 1.45 [d, $^4J_{H,P}$ = 1.9 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.46 [s, 9 H, $C(CH_3)_3$ at C-4], 1.75 (m_c, 1 H) and 1.96 (m_c, 1 H, 8-H), 2.84 (m_c, 1 H, 7-H), 6.96−7.22 (m, 5 H, Ph-H); **11cB:** δ = 1.17−1.60 (m, 2 H, 7-H, signals under those of the *tert*-butyl groups), 1.42 (d, $^4J_{H,P}$ = 1.9 Hz, 9 H) and 1.51 [d, $^4J_{H,P}$ = 1.9 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.46 [s, 9 H, $C(CH_3)_3$ at C-4], 2.85 (m_c, 1 H, 8-H), 6.96−7.22 (m, 5 H, Ph-H, signals under aromatic signals of main compound). – ^{13}C{^{1}H} NMR (C_6D_6): **11cA:** δ = 29.2 [m_c,

C(CH_3)$_3$ at C-4], 30.1 (s, C-8), 31.6 [dd, $^3J_{C,P}$ = 14.5 and 9.6 Hz, C(CH_3)$_3$ at C-2 and C-6], 36.7 [pt, $^2J_{C,P}$ = 17.7 Hz, C(CH_3)$_3$ at C-4], 43.8 (dd, $^2J_{C,P}$ = 24.9 and 17.7 Hz) and 44.1 [dd, $^2J_{C,P}$ = 25.7 and 18.5 Hz, C(CH_3)$_3$ at C-2 and C-6], 48.3 (d, $^1J_{C,P}$ = 15.2 Hz, C-7), 74.7 (ptd, $^1J_{C,P}$ = 56.8 Hz, $^3J_{C,P}$ = 4.3 Hz, C-4), 128.2 (d, $^4J_{C,P}$ = 2.2 Hz, *meta*-C), 128.3 (d, $^3J_{C,P}$ = 5.1 Hz, *ortho*-C), 130.0 (s, *para*-C), 143.0 (d, $^2J_{C,P}$ = 8.0 Hz, *ipso*-C), 218.8 (ddd, $^1J_{C,P}$ = 57.8 and 47.8 Hz, $^3J_{C,P}$ = 6.0 Hz) and 227.3 (ddd, $^1J_{C,P}$ = 57.4 and 44.2 Hz, $^3J_{C,P}$ = 7.6 Hz, C-2 and C-6); **11cB**: 29.2 [m$_c$, C(CH_3)$_3$ at C-4, under signals of main compound], 31.4 [dd, $^3J_{C,P}$ = 14.5 and 9.6 Hz, C(CH_3)$_3$ at C-2 and C-6], 38.1 [pt, $^2J_{C,P}$ = 18.1 Hz, C(CH_3)$_3$ at C-4], 42.4 (d, $^1J_{C,P}$ = 15.2 Hz, C-7), 43.4 (dd, $^2J_{C,P}$ = 25.7 and 18.5 Hz) and 44.3 [dd, $^2J_{C,P}$ = 24.9 and 17.7 Hz, C(CH_3)$_3$ at C-2 and C-6], 45.5 (s, C-8), 77.0 (ptd, $^1J_{C,P}$ = 58.6 Hz, $^3J_{C,P}$ = 4.3 Hz, C-4), 126.4 (d, $^4J_{C,P}$ = 3.2 Hz, *ortho*-C), 126.5 (s, *para*-C), 128.9 (s, *meta*-C), 146.3 (s, *ipso*-C), 220.4 (ddd, $^1J_{C,P}$ = 60.2 and 37.8 Hz, $^3J_{C,P}$ = 6.8 Hz) and 227.3 (m$_c$, under signal of main compound, C-2 and C-6). − $^{31}P\{^1H\}$ NMR (C_6D_6): **11cA:** δ = −74.8 (dd, $^2J_{P,P}$ = 11.0 and 7.2 Hz, P-1), 312.9 (dd, $^2J_{P,P}$ = 21.6 and 11.0 Hz) and 327.6 (dd, $^2J_{P,P}$ = 21.6 and 7.2 Hz, P-3 and P-5); **11cB**: δ = −85.0 (dd, $^2J_{P,P}$ = 12.3 and 11.2 Hz, P-1), 311.8 (dd, $^2J_{P,P}$ = 21.0 and 12.3 Hz) and 327.6 (dd, $^2J_{P,P}$ = 21.0 and 11.2 Hz, P-3 and P-5). − MS (EI, 70 eV): *m*/*z* (%) = 404 (8) [M$^+$], 389 (4) [M$^+$ − Me], 347 (2) [M$^+$ − *t*Bu], 57 (21) [*t*Bu$^+$]. − IR (CCl_4): $\tilde{\nu}$ = 2960, 2897, 2862, 1493, 1471, 1457, 1393, 1362, 1209, 1238, 700 cm^{-1}. − $C_{23}H_{35}P_3$ (404.45): calcd. C 68.30, H 8.72; found C 67.09, H 8.82.

2,4,10-Tri-*tert*-butyl-7-phenyl-7-aza-1,3,11-triphosphatricyclo-[5.2.2.0^{5,9}]undeca-2,10-diene-6,8-dione (13a): To a solution of triphosphabenzene **1a** (71 mg, 0.24 mmol) in *n*-hexane (3 mL) was added *N*-phenylmaleimide (**12a**; 41 mg, 0.24 mmol). After stirring for 3 d at room temperature, all volatile components were removed in vacuo (10^{-3} mbar/25 °C), the yellow residue was redissolved in *n*-pentane/diethyl ether (1:3), and the resulting solution was filtered through Celite. Removal of the solvent gave the tricyclic product **13a**. Yield 100 mg (88%) as a yellow powder; m.p. 129 °C. − ^1H NMR: δ = 1.57 [s, 18 H, C(CH_3)$_3$ at C-2 and C-10], 2.00 [s, 9 H, C(CH_3)$_3$ at C-4], 2.72 (dd, $^3J_{H,H}$ = 8.6 Hz, $^2J_{H,P}$ = 3.7 Hz, 1 H, 9-H), 2.93 (m$_c$, 1 H, 5-H), 7.20 (m$_c$, 1 H, *para*-CH), 7.29−7.36 (m, 2 H, *meta*-CH), 7.54−7.57 (m, 2 H, *ortho*-CH). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 30.8 (pt, $^3J_{C,P}$ = 10.1 Hz), 30.9 (pt, $^3J_{C,P}$ = 9.6 Hz), and 31.5 [dd, $^3J_{C,P}$ = 14.9 and 8.8 Hz, C(CH_3)$_3$ at C-2, C-4, and C-10], 37.4 [pt, $^2J_{C,P}$ = 7.5 Hz, C(CH_3)$_3$ at C-4], 43.5 (dd, $^2J_{C,P}$ = 17.5 and 9.8 Hz) and 43.7 [dd, $^2J_{C,P}$ = 17.9 and 9.0 Hz, C(CH_3)$_3$ at C-2 and C-10], 44.7 (d, $^2J_{C,P}$ = 2.8 Hz, C-5), 51.3 (dpt, $^1J_{C,P}$ = 20.1 Hz, $^3J_{C,P}$ = 1.6 Hz, C-9), 75.6 (ptd, $^1J_{C,P}$ = 62.8 Hz, $^3J_{C,P}$ = 5.1 Hz, C-4), 126.3 (s) and 128.7 (s, *ortho*-C and *meta*-C), 132.5 (s, *ipso*-C), 132.9 (s, *para*-C), 172.2 (d, $^2J_{C,P}$ = 6.2 Hz, C-8), 174.4 (s, C-6), 221.0 (ddd, $^1J_{C,P}$ = 62.8 and 39.8 Hz, $^3J_{C,P}$ = 6.7 Hz) and 221.6 (ddd, $^1J_{C,P}$ = 60.0 and 46.2 Hz, $^3J_{C,P}$ = 6.0 Hz, C-2 and C-10). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −90.9 (dd, $^2J_{P,P}$ = 7.1 and 6.3 Hz, P-1), 317.3 (dd, $^2J_{P,P}$ = 20.5 and 6.3 Hz) and 324.3 (dd, $^2J_{P,P}$ = 20.5 and 7.1 Hz, P-3 and P-11). − MS (EI, 70 eV): *m*/*z* (%) = 473 (26) [M$^+$], 458 (27) [M$^+$ − Me], 373 (2) [M$^+$ − PC*t*Bu], 300 (3) [$P_3C_3tBu_3^+$], 169 (88) [$PC_2tBu_2^+$], 57 (49) [*t*Bu$^+$], 41 (100) [$C_3H_5^+$]. − IR (CCl_4): $\tilde{\nu}$ = 2961, 2861, 1774, 1715 (CO), 1500, 1397, 1376, 1187, 689, 668 cm^{-1}. − $C_{25}H_{34}NO_2P_3$ (473.47): calcd. C 63.42, H 7.24, N 2.96; found C 63.12, H 7.15, N 3.10.

General Procedure for the Preparation of the Triphosphadihydrobarrelenes 13b−e: The appropriate triphosphabenzene **1** and 1 equiv. of maleic anhydride (**12b**) were stirred in toluene (5 mL, or 0.5 mL C_6D_6 in the case of **13e**) at 60 °C for 2 d (in the case of **13b**), for 3 d (**13c**, **13d**), or for 1 d at room temperature (**13e**) in a Schlenk pressure tube. The reaction mixture was allowed to cool to room temperature and, except in the case of **13e**, all volatile components were removed in vacuo (10^{-3} mbar/25 °C). The residue was redissolved in *n*-pentane and purified by column chromatography on silica gel (glass column, diameter 1 cm, length 20 cm, eluent pentane/diethyl ether, 5:1). After a fraction containing impurities, a microcrystalline yellow powder (**13b**, **13d**) or a yellow oil (**13c**), respectively, was obtained from the second fraction after evaporation of the solvent.

2,4,10-Tri-*tert*-butyl-7-oxa-1,3,11-triphosphatricyclo[5.2.2.0^{5,9}]-undeca-2,10-diene-6,8-dione (13b): From **1a** (199.5 mg, 0.665 mmol) and **12b** (65.2 mg, 0.665 mmol). Yield 169.5 mg (64%) as a pale-yellow microcrystalline powder; m.p. 50 °C. − ^1H NMR (C_6D_6): δ = 1.34 (d, $^4J_{H,P}$ = 2.0 Hz, 9 H) and 1.36 [d, $^4J_{H,P}$ = 2.0 Hz, 9 H, C(CH_3)$_3$ at C-2 and C-10], 1.72 [s, 9 H, C(CH_3)$_3$ at C-4], 2.46 (dd, $^3J_{H,H}$ = 9.1 Hz, $^2J_{H,P}$ = 2.7 Hz, 1 H, 9-H), 2.73 [m, 1 H, $^3J_{H,H}$ = 9.1 Hz (determined by a selective ^{31}P NMR decoupling experiment), 5-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 30.8 (dd, $^3J_{C,P}$ = 12.9 and 10.4 Hz), 31.0 (dd, $^3J_{C,P}$ = 14.3 and 9.4 Hz), and 31.4 [dd, $^3J_{C,P}$ = 14.9 and 8.8 Hz, C(CH_3)$_3$ at C-2, C-4, and C-10], 37.5 [pt, $^2J_{C,P}$ = 17.3 Hz, C(CH_3)$_3$ at C-4], 43.8 (pt, $^2J_{C,P}$ = 17.7 Hz) and 44.1 [pt, $^2J_{C,P}$ = 18.1 Hz, C(CH_3)$_3$ at C-2 and C-10], 45.7 (d, $^2J_{C,P}$ = 2.4 Hz, C-5), 51.9 (d, $^1J_{C,P}$ = 23.3 Hz, C-9), 75.1 (ptd, $^1J_{C,P}$ = 63.9 Hz, $^3J_{C,P}$ = 6.0 Hz, C-4), 168.4 (d, $^2J_{C,P}$ = 8.4 Hz, C-8), 169.7 (s, C-6), 220.1 (ddd, $^1J_{C,P}$ = 64.2 and 45.6 Hz, $^3J_{C,P}$ = 6.2 Hz) and 222.1 (ddd, $^1J_{C,P}$ = 63.6 and 39.6 Hz, $^3J_{C,P}$ = 7.2 Hz, C-2 and C-10). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −93.1 (pt, $^2J_{P,P}$ = 5.3 Hz, P-1), 321.7 (dd, $^2J_{P,P}$ = 20.4 and 5.3 Hz) and 325.9 (dd, $^2J_{P,P}$ = 20.4 and 5.3 Hz, P-3 and P-11). − MS (EI, 70 eV): *m*/*z* (%) = 398 (32) [M$^+$], 383 (75) [M$^+$ − Me], 370 (22) [M$^+$ − CO], 300 (12) [$P_3C_3tBu_3^+$], 169 (93) [$PC_2tBu_2^+$], 131 (49) [P_2CtBu^+], 69 (37) [C*t*Bu$^+$], 57 (100) [*t*Bu$^+$]. − IR (CCl_4): $\tilde{\nu}$ = 2962, 2862, 1859 and 1784 (cyclic anhydride), 1471, 1458, 1363, 1229, 1193, 1065, 941, 920 cm^{-1}. − $C_{19}H_{29}O_3P_3$ (398.36): calcd. C 57.29, H 7.34; found C 58.09, H 7.36.

2,4,10-Tris(1,1-dimethylpropyl)-7-oxa-1,3,11-triphosphatricyclo-[5.2.2.0^{5,9}]undeca-2,10-diene-6,8-dione (13c): From **1b** (250 mg, 0.73 mmol) and **12b** (72 mg, 0.73 mmol). Yield 208 mg (65%) as yellow crystals; m.p. 54 °C. − ^1H NMR (C_6D_6): δ = 0.75 [ptd, $^3J_{H,H}$ = 7.4 Hz, $^5J_{H,P}$ = 0.7 Hz, 6 H, C(CH_3)$_2$CH_2CH_3 at C-2 and C-10], 1.07 [t, $^3J_{H,H}$ = 7.4, 3 H, C(CH_3)$_2$CH$_2$CH_3 at C-4], 1.31 (d, $^4J_{H,P}$ = 1.2 Hz, 3 H), 1.32 (d, $^4J_{H,P}$ = 1.4 Hz, 3 H), 1.34 (d, $^4J_{H,P}$ = 1.6 Hz, 3 H), and 1.37 [d, $^4J_{H,P}$ = 1.4 Hz, 3 H, C(CH_3)$_2$CH$_2$CH$_3$ at C-2 and C-10], 1.70 (s, 3 H) and 1.74 [s, 3 H, C(CH_3)$_2$CH$_2$CH$_3$ at C-4], 1.74 [m, 4 H, C(CH_3)$_2$CH_2CH$_3$ at C-2 and C-10], 2.20 [m, 2 H, C(CH_3)$_2$CH_2CH$_3$ at C-4], 2.55 (dd, 1 H, $^3J_{H,H}$ = 9.2 Hz, $^2J_{H,P}$ = 2.7 Hz, 9-H), 2.83 (m, 1 H, $^3J_{H,H}$ = 9.2 Hz, 5-H). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.0 (s), 9.1 (s), and 9.3 [s, C(CH_3)$_2$CH$_2$CH_3 at C-2, C-4, and C-10], 26.7 (dd, $^3J_{C,P}$ = 12.4 and 10.4 Hz), 27.2 (pt, $^3J_{C,P}$ = 13.8 Hz), 28.2 (m), 28.4 (m), 28.4 (m), and 29.0 [dd, $^3J_{C,P}$ = 15.9 and 10.2 Hz, C(CH_3)$_2$CH$_2$CH$_3$ at C-2, C-4, and C-10], 34.6 (dd, $^3J_{C,P}$ = 8.0 and 7.2 Hz), 34.8 (dd, $^3J_{C,P}$ = 20.5 and 10.2 Hz), and 34.9 [dd, $^3J_{C,P}$ = 20.1 and 10.0 Hz, C(CH_3)$_2$CH_2CH$_3$ at C-2, C-4, and C-10], 40.5 [pt, $^2J_{C,P}$ = 15.1 Hz, C(CH_3)$_2$CH$_2$CH$_3$ at C-4], 46.9 (dd, $^2J_{C,P}$ = 24.5 and 15.7 Hz) and 47.3 [dd, $^2J_{C,P}$ = 25.7 and 16.1 Hz, C(CH_3)$_2$CH$_2$CH$_3$ at C-2 and C-10], 45.3 (d, $^2J_{C,P}$ = 2.0 Hz, C-5), 51.8 (d, $^1J_{C,P}$ = 24.1 Hz, C-9), 77.2 (ptd, $^1J_{C,P}$ = 65.0 Hz, $^3J_{C,P}$ = 5.9 Hz, C-4), 168.4 (d, $^2J_{C,P}$ = 8.4 Hz, C-8), 169.8 (s, C-6), 217.7 (ddd, $^1J_{C,P}$ = 64.2 and 47.5 Hz, $^3J_{C,P}$ = 4.3 Hz) and 219.6 (ddd, $^1J_{C,P}$ = 64.5 and 39.8 Hz, $^3J_{C,P}$ = 5.4 Hz, C-2 and C-10). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ =

−91.9 (pt, $^2J_{P,P}$ = 4.6 Hz, P-1), 325.9 (dd, $^2J_{P,P}$ = 20.3 and 4.6 Hz) and 330.0 (dd, $^2J_{P,P}$ = 20.3 and 4.6 Hz, P-3 and P-11). − MS (EI, 70 eV): *m/z* (%) = 440 (19) [M$^+$], 425 (12) [M$^+$ − Me], 412 (26) [M$^+$ − CO], 411 (100) [M$^+$ − Et], 342 (4) [M$^+$ − $C_4H_2O_3$], 197 (32) [$PC_2tPen_2^+$], 145 (13) [P_2CtPen^+]. − IR (CCl_4): $\tilde{\nu}$ = 2965, 2879, 1859 and 1784 (cyclic anhydride), 1461, 1228, 1197, 1066, 931 cm^{-1}. − $C_{22}H_{35}O_3P_3$ (440.44): calcd. C 60.00, H 8.01; found C 60.46, H 8.02.

2,4,10-Tris(1-methylcyclohexyl)-7-oxa-1,3,11-triphosphatricyclo-[5.2.2.0^{5,9}]undeca-2,10-diene-6,8-dione (13d): From **1c** (180 mg, 0.43 mmol) and **12b** (42.0 mg, 0.43 mmol). Yield 79 mg (35%) as a yellow microcrystalline powder; m.p. 62 °C. − ^{1}H NMR (C_6D_6): δ = 1.23−2.42 (m, 39 H, Me*c*Hex substituents), 2.61 (dd, $^3J_{H,H}$ = 9.1 Hz, $^2J_{H,P}$ = 2.5 Hz, 1 H, 9-H), 3.00 (d, $^3J_{H,H}$ = 9.1 Hz, 1 H, 5-H). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 22.6 (m), 23.0 (m), 25.9 (s), 26.2 (s), 26.4 (s), 26.8 (m), 36.6 (m), 37.7 (m), and 38.8 (m, Me*c*Hex substituents), 41.0 (pt, $^2J_{C,P}$ = 15.1 Hz, $C_{quat.}$ adjacent to C-4), 45.8 (d, $^2J_{C,P}$ = 1.6 Hz, C-5), 47.0 (dd, $^2J_{C,P}$ = 23.7 and 14.9 Hz) and 47.6 (dd, $^2J_{C,P}$ = 24.5 and 14.5 Hz, $C_{quat.}$ adjacent to C-2 and C-10), 52.5 (d, $^1J_{C,P}$ = 24.9 Hz, C-9), 77.8 (ptd, $^1J_{C,P}$ = 65.8 Hz, $^3J_{C,P}$ = 5.2 Hz, C-4), 168.3 (d, $^2J_{C,P}$ = 8.8 Hz, C-8), 169.8 (s, C-6), 218 (m) and 222 (m, C-2 and C-10). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −93.9 (br. s, P-1), 324.3 (br. s) and 336.3 (br. s, P-3 and P-11). − MS (EI, 70 eV): *m/z* (%) = 518 (8) [M$^+$], 503 (4) [M$^+$ − Me], 490 (5) [M$^+$ − CO], 420 (14) [M$^+$ − $C_4H_2O_3$], 280 (2) [$P_2C_2MecHex_2^+$], 249 (100) [$PC_2MecHex_2^+$], 202 (24) [$P_3CMecHex^+$], 171 (5) [$P_2CMecHex^+$], 140 (7) [$PCMecHex^+$], 109 (36) [$CMecHex^+$], 97 (14) [$MecHex^+$]. − IR (CCl_4): $\tilde{\nu}$ = 2930, 2861, 1859 and 1784 (cyclic anhydride), 1466, 1445, 1229, 1196, 1064, 931, 668 cm^{-1}. − $C_{28}H_{41}O_3P_3$ (518.55): calcd. C 64.86, H 7.97; found C 65.08, H 7.90.

2,4,10-Tris(1-adamantyl)-7-oxa-1,3,11-triphosphatricyclo[5.2.2.0^{5,9}]-undeca-2,10-diene-6,8-dione (13e): From **1d** (99 mg, 0.19 mmol) and **12b** (18 mg, 0.19 mmol); because of instability, workup was not possible. Crude yield 4%. − ^{1}H NMR (C_6D_6): δ = 1.40−2.08 (m, adamantyl substituents), 2.49 (dd, $^3J_{H,H}$ = 10.5 Hz, $^2J_{H,P}$ = 6.6 Hz, 1 H, 9-H), 2.64 (d, $^3J_{H,H}$ = 10.5 Hz, 1 H, 5-H). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −98.5 (br. s, P-1), 321.1 (d, $^2J_{P,P}$ = 17.5 Hz) and 340.8 (d, $^2J_{P,P}$ = 17.5 Hz, P-3 and P-11).

2,4,12-Tri-*tert*-butyl-1,3,13-triphosphatetracyclo[6.2.2.1^{6,9}.0^{5,10}]-trideca-2,12-diene (15a): Norbornene (**14**) (66 mg, 0.70 mmol) was added to a solution of triphosphabenzene **1a** (210 mg, 0.70 mmol) in toluene (5 mL) and the resulting mixture was heated for 3 days at 70 °C in a Schlenk pressure tube. It was then allowed to cool to room temperature and the solvent was removed in vacuo (10^{-3} mbar/25 °C). The residue was redissolved in *n*-pentane, the resulting solution was filtered through Celite, and the tetracyclic product **12a** was subsequently crystallized from *n*-pentane at −78 °C. Yield 201 mg (73%) as a yellow solid; m.p. 97 °C. − ^{1}H NMR (C_6D_6): δ = 0.82−1.72 (m, 6 H, 7-, 8-, and 11-H, signals overlapped by those of the *tert*-butyl groups), 1.39 (d, $^4J_{H,P}$ = 2.0 Hz, 9 H) and 1.44 [d, $^4J_{H,P}$ = 1.8 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-12], 1.62 [s, 9 H, $C(CH_3)_3$ at C-4], 1.91 (m_c, 1 H) and 1.99 (m_c, 1 H, 6- and 9-H), 2.09 (m_c, 1 H) and 2.62 (br. s, 1 H, 5- and 10-H). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 31.2 [dd, $^3J_{C,P}$ = 15.3 and 9.5 Hz, $C(CH_3)_3$ at C-2 and C-12], 31.5 [s, $C(CH_3)_3$ at C-4], 33.1 (s) and 33.6 (s, C-7 and C-8), 35.6 (d, $^3J_{C,P}$ = 4.8 Hz, C-11), 37.7 [ptd, $^2J_{C,P}$ = 18.1 Hz, $^4J_{C,P}$ = 1.0 Hz, $C(CH_3)_3$ at C-4], 41.2 (d, $^3J_{C,P}$ = 1.0 Hz, C-6), 41.5 (d, $^2J_{C,P}$ = 16.2 Hz, C-9), 43.2 (pt, $^2J_{C,P}$ = 19.1 Hz) and 43.4 [pt, $^2J_{C,P}$ = 19.1 Hz, $C(CH_3)_3$ at C-2 and C-12], 48.8 (d, $^2J_{C,P}$ = 3.8 Hz, C-5), 54.1 (d, $^1J_{C,P}$ = 16.2 Hz, C-10), 78.3 (pt, $^1J_{C,P}$ = 58.7 Hz, C-4), 221.5 (ddd, $^1J_{C,P}$ = 55.3 and 44.4 Hz, $^3J_{C,P}$ = 6.7 Hz) and 226.3 (ddd, $^1J_{C,P}$ = 59.4 and 37.4 Hz, $^3J_{C,P}$ = 7.8 Hz, C-2 and C-12). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −83.1 (dd, $^2J_{P,P}$ = 12.7 and 10.5 Hz, P-1), 318.2 (dd, $^2J_{P,P}$ = 21.4 and 12.7 Hz) and 327.6 (dd, $^2J_{P,P}$ = 21.4 and 10.5 Hz, P-3 and P-13). − MS (EI, 70 eV): *m/z* (%) = 394 (29) [M$^+$], 379 (20) [M$^+$ − Me], 337 (11) [M$^+$ − *t*Bu], 169 (67) [$PC_2tBu_2^+$], 131 (20) [P_2CtBu^+], 57 (100) [tBu^+]. − IR (CCl_4): $\tilde{\nu}$ = 2959, 2927, 2870, 1472, 1459, 1396, 1365, 1261, 1221, 1182, 1146, 1118, 1100, 1023 cm^{-1}. − $C_{22}H_{37}P_3$ (394.46): calcd. C 66.99, H 9.45; found C 65.59, H 9.22.

General Procedure for the Preparation of the Triphosphadihydrobarrelenes 15b−d: The appropriate triphosphabenzene **1** and 1 equiv. of norbornene (**14**) were heated in toluene (5 mL, or 0.5 mL C_6D_6 in the case of **15d**) at 60 °C for 6 d (in the case of **15b**, **15c**) or for 3 d (**15d**) in a Schlenk pressure tube under argon at a pressure of 3 bar. The reaction mixture was allowed to cool to room temperature and, except in the case of **15d**, all volatile components were subsequently removed in vacuo (10^{-3} mbar/25 °C). The residue was redissolved in *n*-pentane and purified by column chromatography on silica gel (glass column, diameter 1 cm, length 3 cm, eluent *n*-pentane). A second yellow fraction was collected, evaporation of the solvent from which left a yellow oil (**15b**) or a yellow microcrystalline powder (**15c**).

2,4,12-Tris(1,1-dimethylpropyl)-1,3,13-triphosphatetracyclo-[6.2.2.1^{6,9}.0^{5,10}]trideca-2,12-diene (15b): From **1b** (171 mg, 0.50 mmol) and **14** (57 mg, 0.60 mmol). Yield 88 mg (40%) as a yellow oil. − ^{1}H NMR (C_6D_6): δ = 0.74−1.68 (m, norbornane ring), 0.92 [pt, $^4J_{H,P}$ = 7.3 Hz, 6 H, $C(CH_3)_2CH_2CH_3$ at C-2 and C-12], 1.09 [pt, $^4J_{H,P}$ = 7.3 Hz, 3 H, $C(CH_3)_2CH_2CH_3$ at C-4], 1.50 (s, 3 H), 1.52 (s, 3 H), 1.57 (s, 3 H), and 1.59 [s, 3 H, $C(CH_3)_2CH_2CH_3$ at C-2 and C-12], 1.75 (s, 3 H) and 1.78 [s, 3 H, $C(CH_3)_2CH_2CH_3$ at C-4], 1.83−1.95 (m) and 2.08−2.25 [m, $C(CH_3)_2CH_2CH_3$ at C-2, C-4, and C-12], 2.33 (m, 1 H) and 2.79 (br. s, 1 H, 10- and 5-H). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.1 (s) and 9.4 [s, $C(CH_3)_2CH_2CH_3$ at C-2, C-4, and C-12], 28.2 [dd, $^3J_{C,P}$ = 20.3 and 7.8 Hz] and 28.5−29.1 [m, $C(CH_3)_2CH_2CH_3$ at C-2, C-4, and C-12], 31.6 (s) and 35.2 [m, $C(CH_3)_2CH_2CH_3$ at C-2, C-4, and C-12], 33.6 (s) and 33.7 (s, C-7 and C-8), 36.0 (d, $^3J_{C,P}$ = 4.0 Hz, C-11), 41.0 [pt, $^2J_{C,P}$ = 16.5 Hz, $C(CH_3)_2CH_2CH_3$ at C-4], 41.5 (s, C-6), 41.8 (d, $^2J_{C,P}$ = 16.1 Hz, C-9), 46.4 (dd, $^2J_{C,P}$ = 23.7 and 16.5 Hz) and 46.8 [dd, $^2J_{C,P}$ = 23.3 and 16.5 Hz, $C(CH_3)_2CH_2CH_3$ at C-2 and C-12], 49.2 (ptd, $^3J_{C,P}$ = 2.6 and 0.8 Hz, C-5), 53.5 (dpt, $^1J_{C,P}$ = 16.9 Hz, $^3J_{C,P}$ = 2.0 Hz, C-10), 80.6 (ptd, $^1J_{C,P}$ = 59.2 Hz, $^3J_{C,P}$ = 4.0 Hz, C-4), 219.2 (m) and 223.5 (m, C-2 and C-12). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −84.9 (br. s, P-1), 322.7 (br. s) and 336.3 (br. s, P-3 and P-13). − MS (EI, 70 eV): *m/z* (%) = 436 (21) [M$^+$], 421 (10) [M$^+$ − Me], 407 (66), 361 (85), 259 (28) [$P_3tPen_2C_2^+$], 247 (90), 197 (17) [$PC_2tPen_2^+$], 191 (52), 162 (100). − IR (CCl_4): $\tilde{\nu}$ = 2963, 2877, 1461, 1261, 1099, 1021, 668 cm^{-1}.

2,4,12-Tris(1-methylcyclohexyl)-1,3,13-triphosphatetracyclo-[6.2.2.1^{6,9}.0^{5,10}]trideca-2,12-diene (15c): From **1b** (257 mg, 0.61 mmol) and **14** (69 mg, 0.73 mmol). Yield 202 mg (64%) as a yellow microcrystalline powder. − ^{1}H NMR (C_6D_6): δ = 1.00−2.30 (m, norbornane ring and Me*c*Hex substituents), 2.36 (m, 1 H) and 2.86 (br. s, 1 H, 10- and 5-H). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 22.9−56.7 (m, norbornane ring and Me*c*Hex substituents), 81.2 (dpt, $^1J_{C,P}$ = 59.6 Hz, $^3J_{C,P}$ = 6.1 Hz, C-4), 220.9 (ddd, $^2J_{C,P}$ = 56.9 and 44.4 Hz, $^3J_{C,P}$ = 4.6 Hz) and 225.2 (ddd, $^2J_{C,P}$ = 59.7 and 34.9 Hz, $^3J_{C,P}$ = 9.6 Hz, C-2 and C-12). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −85.6 (br. s, P-1), 321.3 (br. s) and 337.0 (br. s, P-3 and P-13) − MS (EI, 70 eV): *m/z* (%) = 514 (100) [M$^+$], 499 (44) [M$^+$ − Me], 417 (43) [M$^+$ − Me*c*Hex], 411 (96). − IR (CCl_4): $\tilde{\nu}$ =

2928, 1447, 1370, 1346, 1145 cm^{-1}. − $C_{31}H_{49}P_3$ (514.65): calcd. C 72.35, H 9.60; found C 71.21, H 9.38.

2,4,12-Tris(1-adamantyl)-1,3,13-triphosphatetracyclo-[6.2.2.1^{6,9}.0^{5,10}]trideca-2,12-diene (15d): From **1d** (168 mg, 0.31 mmol) and **14** (36 mg, 0.38 mmol); because of instability, workup was not possible. Crude yield 4%. − ^{1}H NMR (C_6D_6): δ = 0.7−2.1 (m, norbornane ring and adamantyl substituents). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −90.0 (br. s, P-1), 318.3 (br. s) and 334.3 (br. s, P-3 and P-13).

(7*S*,8*S*)-2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene-7,8-dicarbonitrile (17a): To a solution of triphosphabenzene **1a** (176 mg, 0.59 mmol) in toluene (3 mL), a solution of fumaric dinitrile (**16a**; 46 mg, 0.59 mmol) in toluene (2 mL) was added at room temperature and the resulting mixture was heated at 100 °C for 8 d. The solvent was then removed in vacuo (10^{-3} mbar/25 °C), the residue was redissolved in *n*-pentane, and the resulting solution was filtered through Celite. Crystallization at −78 °C gave the bicyclic product **17a** as yellow crystals. Yield 150 mg (67%); m.p. 118 °C. − ^{1}H NMR (C_6D_6): δ = 1.19 (d, $^4J_{H,H}$ = 2.2 Hz, 9 H) and 1.29 [d, $^4J_{H,H}$ = 2.5 Hz, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.38 [s, 9 H, $C(CH_3)_3$ at C-4], 2.51 [m, $^3J_{H,H}$ = 4.4 Hz (determined by a selective ^{31}P NMR decoupling experiment), 1 H, 7-H], 2.77 [m, $^3J_{H,H}$ = 4.4 Hz (determined by a selective ^{31}P NMR decoupling experiment), 1 H, 8-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 29.7 [m, $C(CH_3)_3$ at C-4], 31.1 (dd, $^3J_{C,P}$ = 15.8 and 10.0 Hz) and 31.3 [dd, $^3J_{C,P}$ = 14.9 and 9.1 Hz, $C(CH_3)_3$ at C-2 and C-6], 32.3 (s, C-8), 37.5 [pt, $^2J_{C,P}$ = 17.0 Hz, $C(CH_3)_3$ at C-4], 37.9 (d, $^1J_{C,P}$ = 24.9 Hz, C-7), 43.8 (dd, $^2J_{C,P}$ = 26.1 and 17.9 Hz) and 44.6 [dd, $^2J_{C,P}$ = 26.5 and 17.4 Hz, $C(CH_3)_3$ at C-2 and C-6], 72.4 (ptd, $^1J_{C,P}$ = 63.0 Hz, $^3J_{C,P}$ = 6.6 Hz, C-4), 118.7 (d, $^2J_{C,P}$ = 9.1 Hz, CN at C-7), 120.7 (s, CN at C-8), 220.8 (ddd, $^1J_{C,P}$ = 62.2 and 43.1 Hz, $^3J_{C,P}$ = 6.0 Hz) and 221.4 (ddd, $^1J_{C,P}$ = 62.2 and 41.5 Hz, $^3J_{C,P}$ = 6.2 Hz, C-2 and C-6). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −96.3 (pt, $^2J_{P,P}$ = 3.2 Hz, P-1), 316.7 (dd, $^2J_{P,P}$ = 20.3 and 3.2 Hz) and 317.7 (dd, $^2J_{P,P}$ = 20.3 and 3.2 Hz, P-3 and P-5). − MS (EI, 70 eV): *m*/*z* (%) = 378 (27) [M^+], 363 (31) [M^+ − Me], 321 (8) [M^+ − *t*Bu], 169 (37) [$PC_2tBu_2^+$], 131 (53) [P_2CtBu^+], 57 (52) [tBu^+]. − IR (KBr): $\tilde{\nu}$ = 2960, 2236, 1469, 1360, 1236 cm^{-1}. − $C_{19}H_{29}N_2P_3$ (378.37): calcd. C 60.31, H 7.73, N 7.41; found C 59.51, H 8.00, N 6.83.

Diethyl (7*S*,8*S*)-2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]-octa-2,5-diene-7,8-dicarboxylate (17bA): To a solution of triphosphabenzene **1a** (154 mg, 0.51 mmol) in toluene (5 mL), diethyl fumarate (**16bA**; 0.5 mL, 3.05 mmol) was added at room temperature and the reaction mixture was heated to 100 °C for 12 d. All volatile components were removed in vacuo (10^{-3} mbar/25 °C), the excess diethyl fumarate at 10^{-3} mbar/60 °C. The residue was redissolved in *n*-pentane, the resulting solution was filtered through Celite, and the solvent was evaporated to leave the bicyclic product **17bA** as a yellow oil, which solidified after a few days at room temperature. Yield 205 mg (85%) as a yellow oil. − ^{1}H NMR (C_6D_6): δ = 0.84 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H) and 0.92 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $COOCH_2CH_3$ at C-7 and C-8), 1.33 (s, 9 H) and 1.45 [s, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.57 [s, 9 H, $C(CH_3)_3$ at C-4], 2.92 (dd, $^3J_{H,H}$ = 6.1 Hz, $^2J_{H,P}$ = 2.3 Hz, 1 H, 7-H), 3.59 [m, $^3J_{H,H}$ = 6.1 Hz (determined by a selective ^{31}P NMR decoupling experiment), 1 H, 8-H], 3.75 (qd, $^3J_{H,H}$ = 7.1 Hz, $^5J_{H,P}$ = 2.0 Hz, 2 H, $COOCH_2CH_3$ at C-7), 3.90 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, $COOCH_2CH_3$ at C-8). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 14.3 (s) and 14.4 (s, $COOCH_2CH_3$ at C-7 and C-8), 30.0 [m, $C(CH_3)_3$ at C-4], 31.4 (dd, $^3J_{C,P}$ = 15.6 and 10.0 Hz) and 31.6 [dd, $^3J_{C,P}$ = 15.6 and 10.1 Hz, $C(CH_3)_3$ at C-2 and C-6], 37.9 [pt, $^2J_{C,P}$ = 18.0 Hz, $C(CH_3)_3$ at C-4], 43.3 (dd, $^2J_{C,P}$ = 26.2 and 18.0 Hz) and 44.2 [dd, $^2J_{C,P}$ = 27.6 and 18.4 Hz, $C(CH_3)_3$ at C-2 and C-6], 46.7 (s, C-8), 55.3 (d, $^1J_{C,P}$ = 26.7 Hz, C-7), 61.4 (s) and 61.5 (s, $COOCH_2CH_3$ at C-7 and C-8), 75.7 (ptd, $^1J_{C,P}$ = 63.4 Hz, $^3J_{C,P}$ = 6.4 Hz, C-4), 171.1 (d, $^2J_{C,P}$ = 8.3 Hz, $COOCH_2CH_3$ at C-8), 175.6 (s $COOCH_2CH_3$ at C-7), 217.3 (ddd, $^1J_{C,P}$ = 57.0 and 41.4 Hz, $^3J_{C,P}$ = 6.6 Hz) and 218.3 (ddd, $^1J_{C,P}$ = 59.8 and 41.4 Hz, $^3J_{C,P}$ = 6.4 Hz, C-2 and C-6). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −84.4 (dd, $^2J_{P,P}$ = 5.9 and 3.6 Hz, P-1), 317.3 (dd, $^2J_{P,P}$ = 22.2 and 5.9 Hz) and 324.1 (dd, $^2J_{P,P}$ = 22.2 and 3.6 Hz, P-3 and P-5). − MS (EI, 70 eV): *m*/*z* (%) = 472 (97) [M^+], 457 (26) [M^+ − Me], 169 (100) [$PC_2tBu_2^+$], 57 (98) [tBu^+]. − IR (KBr): $\tilde{\nu}$ = 2960, 1734, 1369, 1261, 1205, 1096, 1024, 800 cm^{-1}.

Diethyl (7*S*,8*R*)-2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo-[2.2.2]octa-2,5-diene-7,8-dicarboxylate (17bB): To a solution of triphosphabenzene **1a** (154 mg, 0.51 mmol) in toluene (5 mL), diethyl maleate (**16bB**; 0.5 mL, 3.09 mmol) was added at room temperature and the reaction mixture was heated at 100 °C for 18 d. The bicyclic product **17bB** could be detected by ^{31}P NMR spectroscopy, but completely isomerized during this period to the bicyclic compound **17bA**. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −93.2 (s, P-1), 314.2 (d, $^2J_{P,P}$ = 21.5 Hz) and 332.1 (d, $^2J_{P,P}$ = 21.5 Hz, P-3 and P-5).

2,3,8-Tri-*tert*-butyl-1,4,9-triphosphahexacyclo-[6.4.0.0^{2,4}.0^{3,9}.0^{5,7}.0^{10,12}]dodecane (20): To a solution of 1,3,5-triphosphabenzene **1a** (173 mg, 0.58 mmol) in toluene (4 mL), cyclopropene (**18**; 46 mg, 1.15 mmol) was added at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 18 h. After evaporation of all volatile components in vacuo (25 °C/10^{-3} mbar), the residue was redissolved in *n*-pentane. The resulting solution was filtered through Celite and the solvent was evaporated to leave the hexacyclic product **20** as a pale-yellow oil. Yield 182 mg (83%). − ^{1}H NMR (C_6D_6): δ = 1.02−1.70 (m, 8 H, cyclopropane-H, partially overlapped by *tert*-butyl signals), 1.28 (s, 9 H), 1.35 (s, 9 H), and 1.46 [s, 9 H, $C(CH_3)_3$ at C-2, C-3, and C-8]. − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 14.6 (ddd, $^2J_{C,P}$ = 19.5 Hz, $^3J_{C,P}$ = 6.8 and 1.7 Hz, C-6), 18.8 (dd, $^2J_{C,P}$ = 10.5 and 6.4 Hz, C-7), 22.1 (d, $^1J_{C,P}$ = 33.9 Hz, C-5), 23.7 (dd, $^1J_{C,P}$ = 32.2 Hz, $^2J_{C,P}$ = 1.7 Hz) and 24.8 (dd, $^1J_{C,P}$ = 32.2 Hz, $^2J_{C,P}$ = 1.7 Hz, C-10 and C-12), 26.4 (dd, $^2J_{C,P}$ = 5.1 and 3.4 Hz, C-11), 31.3 [dd, $^3J_{C,P}$ = 6.8 and 5.1 Hz, $C(CH_3)_3$ at C-8], 34.4 (dd, $^3J_{C,P}$ = 11.0 and 10.2 Hz) and 34.9 [dd, $^3J_{C,P}$ = 11.0 and 9.3 Hz, $C(CH_3)_3$ at C-2 and C-3], 38.6 [ptd, $^2J_{C,P}$ = 10.1 Hz, $^4J_{C,P}$ = 1.7 Hz, $C(CH_3)_3$ at C-8], 39.5 [dd, $^2J_{C,P}$ = 16.1 and 2.6 Hz, $C(CH_3)_3$ at C-2 and C-3], 59.4 (ddd, $^1J_{C,P}$ = 44.1 and 42.4 Hz, $^2J_{C,P}$ = 3.4 Hz) and 60.1 (ddd, $^1J_{C,P}$ = 47.1 and 41.1 Hz, $^2J_{C,P}$ = 4.2 Hz, C-2 and C-3), 63.7 (pt, $^1J_{C,P}$ = 15.8 Hz, C-8). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −166.7 (dd, $^2J_{P,P}$ = 8.5 and 4.5 Hz, P-4), 59.2 (dd, $^2J_{P,P}$ = 24.7 and 4.5 Hz) and 66.4 (dd, $^2J_{P,P}$ = 24.7 and 8.5 Hz, P-1 and P-9). − MS (EI, 70 eV): *m*/*z* (%) = 380 (6) [M^+], 365 (27) [M^+ − CH_3], 333 (5) [M^+ − *t*Bu], 233 (4) [M^+ − PC*t*Bu − *t*Bu], 169 (13) [$PC_2tBu_2^+$], 131 (59) [P_2CtBu^+], 57 (49) [tBu^+]. − IR (CCl_4): $\tilde{\nu}$ = 3079, 3001, 2995, 2902, 1470, 1462, 1453, 1395, 1365, 1359, 1261, 1181, 1088, 1026, 908 cm^{-1}.

(η^5-Cyclopentadienyl)(methyl 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabicyclo[2.2.2]octa-2,5-diene-7-carboxylate)cobalt (22): To a solution of (η^5-cyclopentadienyl)bis(η^2-ethene)cobalt (**21**; 50 mg, 0.28 mmol) in diethyl ether (3 mL), a solution of dihydrotriphosphabarrelene **11aA** (80 mg, 0.21 mmol) in diethyl ether (2 mL) was added at −78 °C. The resulting mixture was allowed to warm to room temperature overnight and a color change from violet to wine-red was observed. The volatile components were then removed in vacuo (10^{-3} mbar/25 °C) and the residue was redissolved in *n*-heptane. At −78 °C, wine-red crystals of complex **33** were obtained, which

were suitable for a crystal structure analysis. Yield 102 mg (95%); decomp. temp. 90 °C. – ^{1}H NMR (C_6D_6): δ = 1.17 (s, 9 H) and 1.25 [s, 9 H, $C(CH_3)_3$ at C-2 and C-6], 1.32 [br. s, 9 H, $C(CH_3)_3$ at C-4], 1.36 (1 H) and 1.42 (1 H, 8-H, under signal of *tert*-butyl group, chemical shifts obtained by ^{1}H,^{1}H-COSY), 1.76 (br. pt, $^3J_{H,H}$ = 10.5 Hz, 1 H, 7-H), 3.37 (s, 3 H, $COOCH_3$), 4.73 (br. s, 5 H, C_5H_5). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.9 (br. s, C-8), 26.8 [br. pt, $^3J_{C,P}$ = 9.5 Hz, $C(CH_3)_3$ at C-4], 32.0 [dd, $^3J_{C,P}$ = 10.9 and 9.3 Hz, $C(CH_3)_3$ at C-2 and C-6], 34.8 (ddd, $^1J_{C,P}$ = 48.9 and 40.1 Hz, $^3J_{C,P}$ = 2.8 Hz, C-4), 36.4 [pt, $^2J_{C,P}$ = 17.1 Hz, $C(CH_3)_3$ at C-4], 36.9 (dd, $^2J_{C,P}$ = 23.2 and 17.0 Hz) and 38.7 [dd, $^2J_{C,P}$ = 24.4 and 18.1 Hz, $C(CH_3)_3$ at C-2 and C-6], 49.2 (br. d, $^1J_{C,P}$ = 38.3 Hz, C-7), 51.2 (s, $COOCH_3$), 53.8 (m, C-2 and C-6), 84.8 (pt, $^2J_{C,P}$ = 1.4 Hz, C_5H_5), 172.8 (d, $^2J_{C,P}$ = 10.2 Hz, $COOCH_3$). – ^{31}P{^{1}H} NMR (C_6D_6): δ = −92.0 (br. s) and −78.7 (br. s, P-3 and P-5), −36.4 (dd, $^2J_{P,P}$ = 8.2 Hz and 4.0 Hz, P-1). – MS (EI, 70 eV): *m*/*z* (%) = 510 (100) [M^+], 495 (4) [M^+ – Me], 355 (14) [$CpCoP_3C_2tBu_2^+$], 286 (7) [M^+ – CpCoPC*t*Bu], 255 (29) [M^+ – $CpCoP_2CtBu$] or [$CpCoP_2CtBu^+$], 228 (14) [$CoPC_2tBu_2^+$], 124 (9) [$CpCo^+$], 57 (10) [tBu^+]. – IR (KBr): ṽ = 3107 (Cp), 2862 (*t*Bu-H), 1722 (COO), 1361, 1246, 810 cm^{-1}.

2,4,10-Tri-*tert*-butyl-1,3,11-triphosphatricyclo[5.2.2.0^{5,9}]undeca-2,6,10-triene (24): A solution of 1,3,5-triphosphabenzene **1a** (179 mg, 0.60 mmol) and cyclopentadiene **23** (396 mg, 6.0 mmol) in toluene (5 mL) was stirred for 5 d at room temperature. All volatile components were then evaporated in vacuo (25 °C/10^{-3} mbar) and the residue was taken up in *n*-pentane. Crystallization at −78 °C gave the tricyclic compound **24** as a yellow waxy solid. Yield 104 mg (47%); m.p. 52 °C. – ^{1}H NMR (C_6D_6): δ = 1.52 (d, $^4J_{H,P}$ = 2.1 Hz, 9 H), 1.55 (d, $^4J_{H,P}$ = 1.8 Hz, 9 H), and 1.70 [s, 9 H, $C(CH_3)_3$ at C-2, C-4, and C-10], 2.11−2.23 (m, 1 H) and 3.31−3.37 (m, 1 H, 5- and 9-H), 2.31−2.47 (m, 2 H, 8-H), 5.52−5.55 (m, 1 H) and 5.73−5.76 (m, 1 H, 6- and 7-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 30.6 (m_c), 31.1 (dd, $^3J_{C,P}$ = 14.5 and 9.2 Hz), and 31.5 [dd, $^3J_{C,P}$ = 15.3 and 8.8 Hz, $C(CH_3)_3$ at C-2, C-4, and C-10], 35.7 (d, $^2J_{C,P}$ = 18.5 Hz, C-8), 37.3 [pt, $^2J_{C,P}$ = 18.5 Hz, $C(CH_3)_3$ at C-4], 42.8 (dd, $^2J_{C,P}$ = 24.9 and 18.5 Hz) and 43.3 [dd, $^2J_{C,P}$ = 24.9 and 18.5 Hz, $C(CH_3)_3$ at C-2 and C-10], 45.7 (d, $^1J_{C,P}$ = 10.8 Hz, C-9), 51.6 (pt, $^2J_{C,P}$ = 1.4 Hz, C-5), 76.4 (pt, $^1J_{C,P}$ = 57.4 Hz, C-4), 132.1 (d, $^3J_{C,P}$ = 4.0 Hz, C-6), 133.7 (d, $^3J_{C,P}$ = 2.0 Hz, C-7), 221.2 (ddd, $^1J_{C,P}$ = 57.4 and 44.2 Hz, $^3J_{C,P}$ = 6.8 Hz) and 224.9 (ddd, $^1J_{C,P}$ = 59.0 and 37.2 Hz, $^3J_{C,P}$ = 7.2 Hz, C-2 and C-10). – ^{31}P{^{1}H} NMR (C_6D_6): δ = −78.2 (dd, $^2J_{P,P}$ = 11.4 and 7.6 Hz, P-1), 320.3 (dd, $^2J_{P,P}$ = 21.0 and 11.4 Hz) and 330.2 (dd, $^2J_{P,P}$ = 21.0 and 7.6 Hz, P-3 and P-11). – MS (EI, 70 eV): *m*/*z* (%) = 366 (15) [M^+], 351 (6) [M^+ – CH_3], 300 (3) [$P_3C_3tBu_3^+$], 169 (18) [$PC_2tBu_2^+$], 138 (40), 123 (24), 73 (94), 57 (100) [tBu^+], 41 (43) [$C_3H_5^+$]. – IR (CH_2Cl_2): ṽ = 2957, 2898, 2862, 1474, 1396, 1365, 1202 cm^{-1}.

Reaction of the 1,3,5-Triphosphabenzene 1a with Norbornadiene (25): A solution of 1,3,5-triphosphabenzene **1a** (450 mg, 1.5 mmol) and norbornadiene **25** (138 mg, 1.5 mmol) in toluene (10 mL) was stirred for 4 d at 50 °C in a glass pressure tube. After evaporation of all volatile components in vacuo (25 °C/10^{-3} mbar), the residue was subjected to column chromatography on silica gel (glass column, diameter 2.5 cm, length 15 cm). Firstly, with *n*-pentane as the eluent, 135 mg (23%) of the monoadduct **26** was isolated as a yellow solid. Subsequent elution with *n*-pentane/diethyl ether (10:1) furnished 223 mg (43%) of the bisadducts **27** and **28**, which were obtained as yellow crystals after crystallization from *n*-hexane at −28 °C. They could not be separated. The ratio of the major and minor products was 3:1 according to integration of the ^{1}H NMR spectrum, but no correlation to the structures **27** and **28** could be made.

2,4,12-Tri-*tert*-butyl-1,3,13-triphosphatetracyclo[6.2.2.1^{6,9}.0^{5,10}]-trideca-2,7,12-triene (26): M.p. 88 °C. – ^{1}H NMR (C_6D_6): δ = 1.05−2.15 (m, 2 H, 11-H, partially overlapped by *tert*-butyl signals), 1.44 (s, 9 H) and 1.52 [s, 9 H, $C(CH_3)_3$ at C-2 and C-12], 1.66 [s, 9 H, $C(CH_3)_3$ at C-4], 2.30 (m_c, 1 H), 2.50 (m_c, 1 H), 2.62 (m_c, 1 H), and 3.12 (s, 1 H, 5-, 6-, 9-, and 10-H), 5.94−6.04 (m, 2 H, 7- and 8-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 31.2 [pt, $^3J_{C,P}$ = 7.6 Hz, $C(CH_3)_3$ at C-4], 31.3 (dd, $^3J_{C,P}$ = 15.3 and 9.3 Hz) and 31.5 [dd, $^3J_{C,P}$ = 9.3 and 6.8 Hz, $C(CH_3)_3$ at C-2 and C-12], 35.9 (dd, $^2J_{C,P}$ = 28.0 and 17.5 Hz) and 43.6 [dd, $^2J_{C,P}$ = 24.6 and 17.8 Hz, $C(CH_3)_3$ at C-2 and C-12], 37.8 [dd, $^2J_{C,P}$ = 19.5 and 17.8 Hz, $C(CH_3)_3$ at C-4], 42.9 (d, $^3J_{C,P}$ = 5.1 Hz, C-11), 46.1 (d, $^2J_{C,P}$ = 15.8 Hz, C-9), 46.4 (s, C-6), 48.5 (m_c, C-5), 52.4 (ddd, $^1J_{C,P}$ = 19.5 Hz, $^3J_{C,P}$ = 3.4 and 1.7 Hz, C-10), 76.2 (ddd, $^1J_{C,P}$ = 59.3 and 56.8 Hz, $^3J_{C,P}$ = 1.7 Hz, C-4), 139.5 (s, C-7), 141.3 (d, $^3J_{C,P}$ = 11.9 Hz, C-8), 222.5 (ddd, $^1J_{C,P}$ = 55.7 and 43.7 Hz, $^3J_{C,P}$ = 7.0 Hz) and 227.2 (ddd, $^1J_{C,P}$ = 59.3 and 37.3 Hz, $^3J_{C,P}$ = 8.5 Hz, C-2 and C-12). – ^{31}P{^{1}H} NMR (C_6D_6): δ = −81.8 (dd, $^2J_{P,P}$ = 12.4 and 9.1 Hz, P-1), 324.7 (dd, $^2J_{P,P}$ = 21.8 and 12.4 Hz) and 327.6 (dd, $^2J_{P,P}$ = 21.8 and 9.1 Hz, P-3 and P-13). – MS (EI, 70 eV): *m*/*z* (%) = 392 (18) [M^+], 377 (18) [M^+ – CH_3], 335 (8) [M^+ – *t*Bu], 169 (17) [$PC_2tBu_2^+$], 57 (100) [tBu^+]. – IR (CCl_4): ṽ = 2961, 2897, 2862, 1472, 1457, 1393, 1360, 1099 cm^{-1}. – $C_{22}H_{35}P_3$ (392.44): calcd. C 67.33, H 8.99; found C 67.57, H 8.98.

6,8,12,14,15,19-Hexa-*tert*-butyl-1,5,7,13,16,18-hexaphosphahexacyclo[10.2.2.2^{5,8}.1^{3,10}.0^{2,11}.0^{4,9}]nonadeca-6,13,15,18-tetraene (27) and 5,7,12,14,16,18-Hexa-*tert*-butyl-1,6,8,13,16,19-hexaphosphahexacyclo[10.2.2.2^{5,8}.1^{3,10}.0^{2,11}0^{4,9}]nonadeca-6,13,15,18-tetraene (28): M.p. 205 °C. – ^{1}H NMR (C_6D_6): **Main Product:** δ = 0.89−2.08 (m, 6 H, norbornane-H, partially overlapped by *tert*-butyl signals), 1.40 (s, 18 H), 1.52 (s, 18 H), and 1.66 [s, 18 H, $C(CH_3)_3$], 2.30 (t, *J* = 8.4 Hz, 1 H, norbornane-H), 3.40 (s, 1 H, norbornane-H); **Minor Product:** δ = 0.89−2.08 (m, 6 H, norbornane-H, partially overlapped by *tert*-butyl signals), 1.42 (s, 18 H), 1.44 (s, 18 H), and 1.70 [s, 18 H, $C(CH_3)_3$], 2.94 (d, *J* = 8.9 Hz, 2 H, norbornane-H). – ^{13}C{^{1}H} NMR (C_6D_6) (abbreviation for **27**: a, for **28**: b): **Main and Minor Product:** δ = 31.1−31.6 [m, $C(CH_3)_3$], 33.5−34.3 [m, $C(CH_3)_3$], 34.0 (s) and 34.4 (s, C-15$_a$ and C-15$_b$), 37.8 [pt, $^2J_{C,P}$ = 16.8 Hz, $C(CH_3)_3$], 37.9 [pt, $^2J_{C,P}$ = 16.8 Hz, $C(CH_3)_3$], 38.0 [pt, $^2J_{C,P}$ = 18.3 Hz, $C(CH_3)_3$], 43.4 [pt, $^2J_{C,P}$ = 18.3 Hz, $C(CH_3)_3$], 43.5 [pt, $^2J_{C,P}$ = 17.9 Hz, $C(CH_3)_3$], 43.7 [pt, $^2J_{C,P}$ = 17.5 Hz, $C(CH_3)_3$], 45.8 (s, C-8$_a$ or C-7$_a$ and C-9$_a$), 46.5 (d, $J_{C,P}$ = 16.5 Hz, C-2$_b$ and C-9$_b$ or C-1$_b$ and C-8$_b$), 46.6 (t, $^2J_{C,P}$ = 17.3 Hz, C-1$_a$), 51.3 (s, C-8$_a$ or C-7$_a$ and C-9$_a$), 54.0 (dd, $^2J_{C,P}$ = 8.4 Hz, $^3J_{C,P}$ = 2.8 Hz, C-7$_b$ and C-14$_b$), 55.3 (d, $J_{C,P}$ = 16.5 Hz, C-2$_b$ and C-9$_b$ or C-1$_b$ and C-8$_b$), 58.3 (dd, $^1J_{C,P}$ = 17.9 Hz, $^3J_{C,P}$ = 11.3 Hz, C-2$_a$ and C-14$_a$), 78.1 (dd, $^1J_{C,P}$ = 60.2 and 55.7 Hz, C-6$_b$ and C-13$_b$ or C-6$_a$ and C-10$_a$), 78.3 (pt, $^1J_{C,P}$ = 59.5 Hz, C-6$_b$ and C-13$_b$ or C-6$_a$ and C-10$_a$), 221.6−223.2 (m) and 226.0−228.0 (m, C-4$_b$, C-11$_b$, C-4$_a$, C-12$_a$, C-16$_b$, C-18$_b$, C-16$_a$, and C-19$_a$). – ^{31}P{^{1}H} NMR (C_6D_6) (abbreviation for **27**: a, for **28**: b): **Main Product:** δ = −84.5 (dd, $^2J_{P,P}$ = 11.8 and 9.1 Hz, P-1$_b$ and P-8$_b$ or P-1$_a$ and P-5$_a$), 318.0 (dd, $^2J_{P,P}$ = 21.3 and 11.8 Hz) and 333.1 (dd, $^2J_{P,P}$ = 21.3 and 9.3 Hz, P-6$_b$, P-13$_b$, P-16$_b$, and P-19$_b$ or P-7$_a$, P-13$_a$, P-16$_a$, and P-18$_a$); **Minor Product:** δ = −82.3 (dd, $^2J_{P,P}$ = 12.2 and 10.0 Hz, P-1$_b$ and P-8$_b$ or P-1$_a$ and P-5$_a$), 318.2 (dd, $^2J_{P,P}$ = 21.1 and 12.2 Hz) and 332.6 (dd, $^2J_{P,P}$ = 21.1 and 10.0 Hz, P-6$_b$, P-13$_b$, P-16$_b$, and P-19$_b$ or P-7$_a$, P-13$_a$, P-16$_a$, and P-18$_a$). – MS (EI, 70 eV): *m*/*z* (%) = 692 (15) [M^+], 677 (9) [M^+ – CH_3], 592 (2) [M^+ – PC*t*Bu], 392 (4) [M^+ – $P_3C_3tBu_3$], 169

(53) [$PC_2tBu_2^+$], 57 (100) [tBu^+]. − IR (CCl_4): $\tilde{\nu}$ = 2961, 2947, 2862, 1472, 1458, 1394, 1360, 1238 cm^{-1}. − $C_{37}H_{62}P_6$ (692.74); calcd. C 64.15, H 9.02; found C 64.89, H 9.01.

Crystal Structure Analysis of 22:[11] Crystal Data: $C_{24}H_{38}CoO_2P_3$, M_r = 510.38 g·mol^{-1}, monoclinic, space group $P2_1/n$ (no. 14), a = 16.0420(14), b = 9.5295(8), c = 18.0244(16) Å, β = 112.2720(10)°, V = 2549.9(4) Å^3, Z = 4, $d_{calcd.}$ = 1.330 Mg·m^{-3}. Data Collection: Data were collected with a CCD-SMART-diffractometer (Siemens SMART) at 100 K. Crystal size 0.06 × 0.19 × 0.38 mm, range for data collection 2.15° < θ < 23.32°, λ = 0.71069 Å, Mo-K_α (graphite monochromator), $-17 \le h \le 17$, $-10 \le k \le 9$, $-10 \le l \le 19$; 3668 independent reflections, 9827 reflections measured, of which 2428 were considered observed with $I > 2\sigma(I)$. Structure Solution and Refinement: The structure was solved using direct methods (SHELXS-97)[13] and refined with the full-matrix least-squares procedure against F^2 (SHELXL-97).[12] The anisotropic refinement converged at R_1 = 0.0700 and R_w = 0.1792. Residual electronic density: 0.886 and −0.487 e·Å^{-3}.

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[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158193. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].
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