Organophosphorus Compounds, 139[+]

On the Behavior of 5,8-Bis(trimethylsilyl)cycloocta-1,3,6-triene in Cycloaddition Reactions and Subsequent Chemistry

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Dedicated to Professor Otto J. Scherer on the occasion of his 65th birthday

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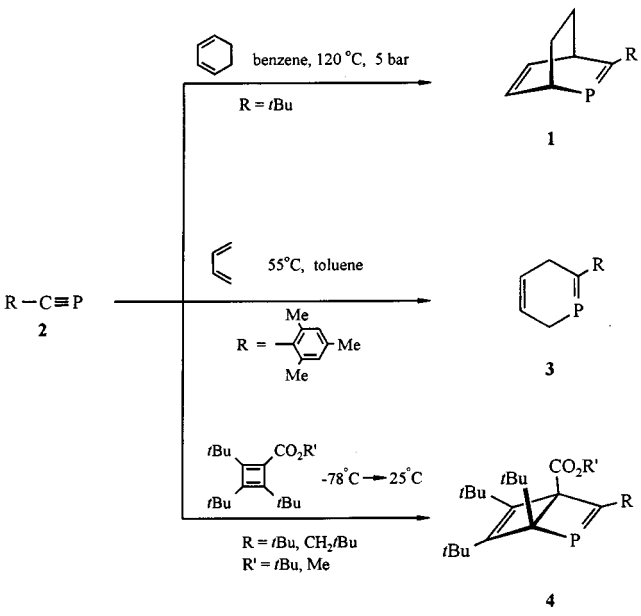
Phosphaalkynes **2** and electron-deficient alkynes **11** readily react in a [4 + 2] cycloaddition process with 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (**8**) in its bicyclic form **10** to furnish regioselectively the tricyclodecadienes **12** and **13**, respectively. The phosphorus-containing compounds **12** exhibit structural features which make them suitable for homo-Diels–Alder reactions with electron-deficient acetylenes. A single crystal structure analysis of the homo-Diels–Alder adduct **14b** confirmed the structure and relative configuration of the phophatricyclodecadienes **12**. In solution the tricyclodecadienes **13** are prone to facile cycloreversion yielding the phthalic esters **15** and the cyclobutene **16**. The latter is rapidly converted into the corresponding 1,3-butadiene **18**, which can be trapped in a Diels–Alder/phospha-ene/Diels–Alder tandem reaction sequence by phosphaalkyne **2a**. The phosphatricyclodecadiene **12** is thermally more stable; loss of cyclobutene **16** only occurs under FVP conditions to afford the λ^3-phosphinine **22**.

Introduction

Cycloaddition reactions play a major role in the chemistry of kinetically stabilized phosphaalkynes. Besides [2 + 1][2] and [3 + 2] cycloaddition reactions[3], Diels–Alder reactions are of particular interest since they provide a simple access to numerous organophosphorus polycyclic systems.

Thus, for example, the thermal reaction of cyclohexa-1,3-diene with *tert*-butylphosphaacetylene **2** furnishes the stable phosphabicyclo[2.2.2]octadiene **1**[4]. Reaction of **2** with 1,3-butadienes also gives rise to a primary [4 + 2] cycloadduct; however, a phosphacyclohexadiene of the type **3** can only be isolated when the substituent R is 2,4,6-trimethylphenyl[5]. In all other cases, a series of subsequent reactions occurs[6]. The phosphaalkyne **2** also readily participates in Diels–Alder reactions with kinetically stabilized, antiaromatic 4π-electron systems with formation of the Dewar 2-phosphabenzenes **4**[7].

We have now turned our attention to the reactions of kinetically stabilized phosphaalkynes with cyclooctatrienes. The latter are known to possess favorable prerequisites for [4 + 2] cycloadditions and, in analogy to the cyclooctatetraenes[8], to react exclusively from their bicyclic forms[9]. Accordingly, the reaction of cycloocta-1,3,6-triene or, cycloocta-1,3,5-triene **5** with dimethyl acetylenedicarboxylate proceeds to furnish the tricyclic product **7** derived from the bicyclic 1,3-diene form **6**[10].



Scheme 1

No concrete conclusions can be drawn about the stereochemistry of the cyclobutane ring (*syn*- or *anti*-attack of the dienophile) although mechanistic and steric considerations would favor an *anti* arrangement. In the present report we describe the reaction behavior of the easily accessible 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (**8**)[11].

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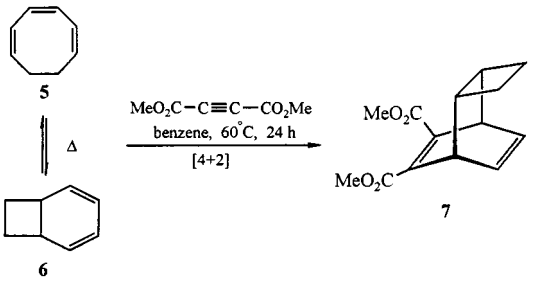


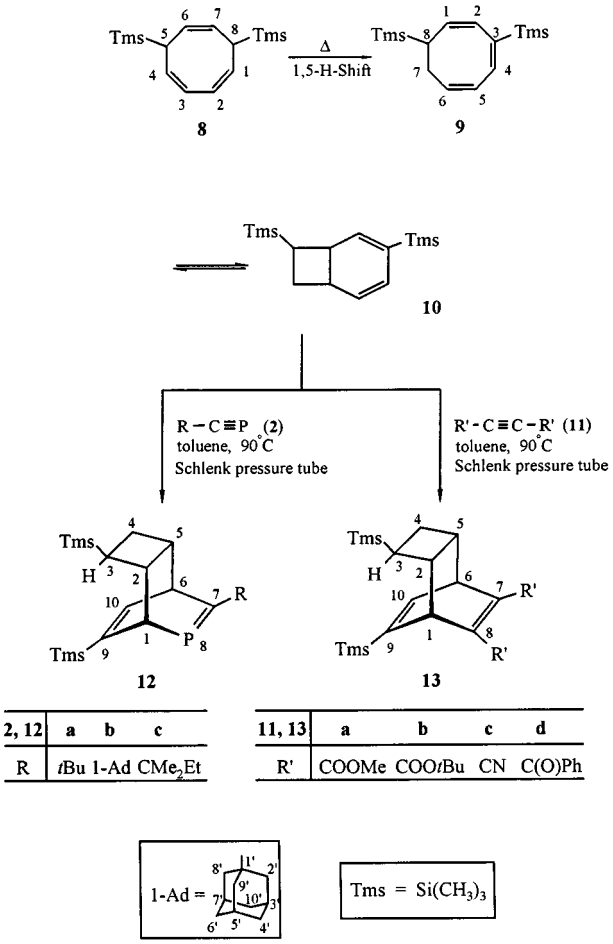
Scheme 2

Results and Discussion

Diels−Alder Reactions of Phosphaalkynes 2 and Acetylenes 11 with 5,8-Bis(trimethylsilyl)cycloocta-1,3,6-triene (8)

Thermolyses of **8** with the phosphaalkynes **2a−c** for 24 hours furnish the phosphatricyclodecadienes **12** almost irrespective of the stoichiometry. The tricyclic products are isolated in the form of colorless needles in good yields (52−64%) after separation by distillation and crystallization from dichloromethane at −78 °C. Elemental analyses and high resolution mass spectra unequivocally demonstrate a 1:1 stoichiometry for the adducts. The constitutions proposed for products **12** are supported by their NMR spectra and are discussed here in detail only for the *tert*-butyl derivative **12a**. The proposed stereochemisty was based on considerations of the mechanism and confirmed by single crystal X-ray crystallography after successful derivatization (see below).

The phosphaalkene unit in **12a** is immediately apparent from the characteristic low-field position of the signal in the $^{31}P\{^1H\}$ NMR spectrum (δ = 219.0); this value corresponds well with those of structurally related compounds[4]. In the $^{13}C\{^1H\}$ NMR spectrum the signal of the phosphaalkene carbon atom is markedly shifted to low field and appears as a doublet at δ = 222.4 ($^1J_{C,P}$ = 45.0 Hz). The other two sp^2-hybridized carbon atoms C-9 and C-10 also give rise to doublet signals at δ = 148.0 ($^2J_{C,P}$ = 6.4 Hz) and δ = 142.4 ($^3J_{C,P}$ = 11.2 Hz) and can be irrevocably assigned with the help of the proton coupled ^{13}C-NMR spectrum. The bridgehead carbon atoms C-1 and C-6 give signals at δ = 49.9 and δ = 49.8, both being split into doublets. The carbon atom adjacent to phosphorus (C-1) exhibits a $^1J_{C,P}$ coupling constant of 38.6 Hz while C-6 shows a $^2J_{C,P}$ coupling of 9.6 Hz. The signal for the methylene carbon atom of the cyclobutane unit (C-4) appears at δ = 21.5 while those for the methine carbon atoms occur at δ = 39.0, δ = 35.5, and δ = 22.9. The ^{1}H-NMR spectrum recorded for the tricyclic product **12a** is in complete harmony with the proposed constitution. Assignments of the skeletal protons, some of which exhibited complex splitting patterns, were possible by means of a 2-D ^{1}H,^{1}H-COSY NMR experiment. The signal δ = 6.65 can be securely assigned to the only present olefinic hydrogen atom 10-H on account of its low-field position. The signal appears as a double pseudo-triplet as a result of three homonuclear couplings.



Scheme 3

The allylic signals of the two bridgehead protons at δ = 4.01 (pseudo-quintet) and δ = 3.95 (doubled double doublet) are also characteristic. The protons of the cyclobutane unit give signals in the expected region between δ = 0.95 and 2.20.

As unambiguously demonstrated by the discussion of the spectral data, the kinetically stabilized phosphaalkynes **2a−c** do not react with the 1,3-diene unit originally present in the cyclooctatriene **8**. Instead, an initial, thermally induced sigmatropic [1,5]-hydrogen shift to furnish the conjugated triene **9** occurs. Similar thermal isomerizations between cycloocta-1,3,6-trienes and cycloocta-1,3,5-trienes are well known[12]. The subsequent electrocyclic ring closure which, in this case, leads to the bicyclic species **10** has been the subject of intensive investigations[13]. Although eight different regio- and stereoisomers (without consideration of enantiomers) are feasible as reaction products after the final [4 + 2] cycloaddition, the reaction occurs with high selectivity. In the $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture a second signal appearing in the phosphaalkene region (intensity ratio: ca. 9:1) is an indication for the formation of two isomers of which only the one described here can be isolated.

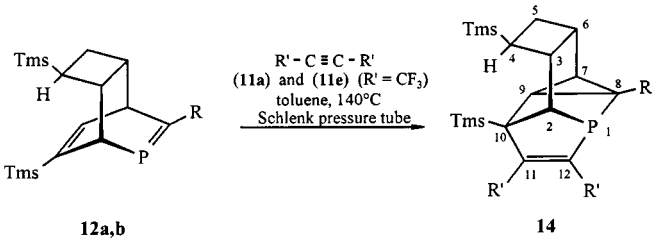
The *exo*-arrangement of the trimethylsilyl groups in **12** is reasonable from steric considerations in the electrocyclic

ring closure as is the *anti*-arrangement of the cyclobutane ring as a result of the more favorable approach geometry in the [4 + 2] cycloaddition.

The reactivity of the phosphaalkynes **2a-c** towards the cyclooctatriene **8** can be compared with that of electron-deficient alkynes. Accordingly, the acceptor-substituted alkynes **11a−d**, but not alkyl- or aryl-substituted alkynes, react with **8** under thermal conditions for several days to afford the tricyclodecadienes **13a−d** which can be isolated as colorless solids or oils by column chromatography. The structures of these products are readily elucidated on the basis of their spectroscopic data in comparison with those of the tricyclic phosphorus compounds **12**. Exact assignments of the ^{1}H-NMR signals are again possible with the help of a ^{1}H,^{1}H-COSY NMR experiment (on **13b** as an example). On account of the very good agreement between the spectroscopic data of compounds **13** with those of **12**, it is reasonable to assume that the all-carbon analogues have the same stereochemistry as the phosphorus compounds.

Homo-Diels−Alder Reactions of the Phosphatricyclodecadienes 12a, b

The 1,4-diene units in the tricyclic phosphorus compounds **12** described above possess the constitutional prerequisities for a homo-Diels−Alder reaction. In contrast to Diels−Alder reactions, this type of reaction has been observed only rarely in organic chemistry[14], although it is not unusual in the chemistry of kinetically stabilized phosphaalkynes. In the latter case, mainly phosphaalkynes[15], but also electron-poor alkynes[15c] have been employed as the dienophile.



12a,b **14**

14	a	b	c
R	*t*Bu	*t*Bu	1-Ad
R'	COOMe	CF_3	COOMe

Scheme 4

When the polycyclic compounds **12a** and **12b** are heated at 140 °C in the presence of excess alkynes **11a**, **e** the pentacyclic products **14a−c** are formed. The reaction time varies between 4 and 72 hours. After workup by distillation or column chromatography and subsequent crystallization from *n*-pentane the homo-Diels−Alder adducts are obtained in satisfactory yields (26−51%) as colorless or light yellow crystals. The molecular composition of the adducts can be deduced directly from their elemental analysis and mass spectral data while their constitutions are evident from the spectroscopic data as illustrated by the following discussion of the NMR data for the *tert*-butyl derivative **14a**. The spectral patterns of **14b** are more complicated as a result of the additional couplings with the fluorine atoms.

Relative to that of the starting material **12a**, the ^{31}P{^{1}H} NMR spectrum of **14a** reveals a significant shift of the signal to higher field by 230.3 ppm which confirms the conversion of the $\sigma^2\lambda^3$-phosphorus atom into a $\sigma^3\lambda^3$ state. The homo-Diels−Alder reaction is regiospecific with formation of a phosphacyclopentene unit. The opposite direction of addition can be excluded on the basis of the shift to even higher field that would be expected for formation of a phosphirane unit[6][16]. The ^{13}C{^{1}H} NMR spectrum also supports the proposed structure for **14a**. Thus, the low-field region contains, in addition to signals for the carbonyl carbon atoms, those for the olefinic carbon atoms C-11 (δ = 165.4, $^2J_{C,P}$ = 19.2 Hz) and C-12 (δ = 144.7, $^1J_{C,P}$ = 29.9 Hz), both as doublets on account of couplings with phosphorus. The skeletal carbon atom C-10 also gives a double doublet signal at δ = 52.9 ($^2J_{C,P}$ = 9.3 Hz), while the signal at δ = 58.1 ($^1J_{C,P}$ = 5.3 Hz) is assigned to the carbon atom C-2. Although the $^1J_{C,P}$ coupling of C-2 is remarkably small the assignment is unequivocally confirmed by the proton-coupled ^{13}C-NMR spectrum. Structurally related systems also show comparably small couplings[15a]. The signal for C-8 experiences a noticeable paramagnetic shift for a cyclopropane carbon atom on account of its proximity to the phosphorus atom and the *tert*-butyl substitution (δ = 47.7, $^1J_{C,P}$ = 33.2 Hz). The remaining carbon atoms of the three-membered ring as well as those of the cyclobutane ring give signals in the expected high-field region (δ = 24.0−34.3)[17]; however, an exact assignment of the individual atoms is not possible. The ^{1}H-NMR spectrum contains signals for the methyl protons of the ester groups, as well as for the *tert*-butyl group and the trimethylsilyl substituents in the characteristic regions. However, the ^{1}H-NMR spectrum is of little value for assignments of the skeletal protons. The signals appear as complicated, in some cases overlapping, multiplets as a result of numerous homonuclear and heteronuclear couplings so that an exact analysis is not possible.

A single crystal of the pentacyclic compound **14b** suitable for X-ray crystallography was obtained by crystallization from *n*-pentane at −28 °C. The results of this structure analysis not only supported the proposed regiochemistry of the homo-Diels−Alder reaction but also confirmed the structures deduced for the tricyclic compounds **12** and **13**. The *anti*-arrangement of the cyclobutane ring as well as the *exo*-orientation of the trimethylsilyl group are clearly visible (Figure 1). A conspicuous feature is the almost perfect equilateral triangle formed by the atoms C7−C8−C9 in spite of the lack of symmetry in the molecule.

Relative to other polycyclic compounds containing $\sigma^3\lambda^3$-phosphorus atoms[6,15c] the bond lengths and angles are all in the expected ranges.

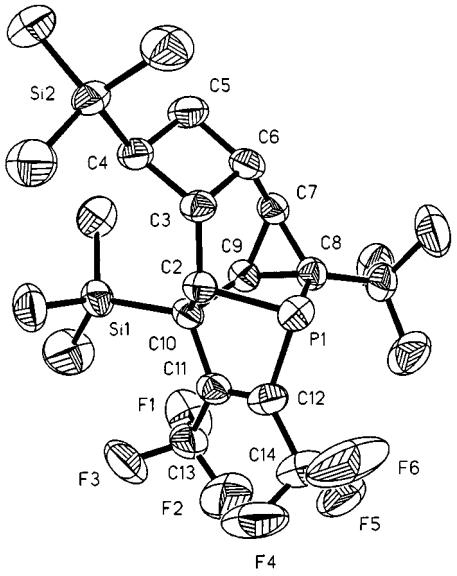
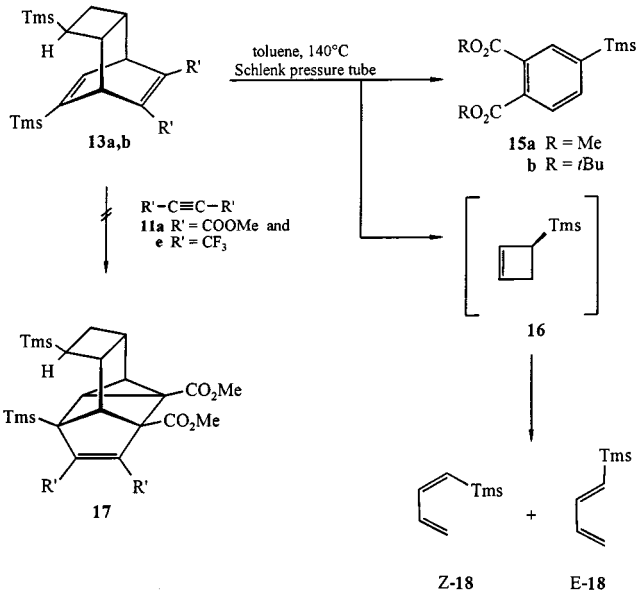


Figure 1. Molecular structure of the phosphapentacyclododecene **14b** as XP plot; thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted of reasons of clarity. Selected bond lengths [Å] and angles [°]: P1−C2 1.865(2), P1−C8 1.888(2), P1−C12 1.846(2), C7−C8 1.511(3), C8−C9 1.511(3), C7−C9 1.519(3), C11−C12 1.347(3); C12−P1−C2 86.57(10), C2−P1−C8 89.70(9), C12−P1−C8 94.54(9), C7−C8−C9 60.35(13), C8−C7−C9 59.82(13), C8−C9−C7 59.83(13).



Scheme 5

Subsequent Reactions of the Tricyclic Products 13a, b

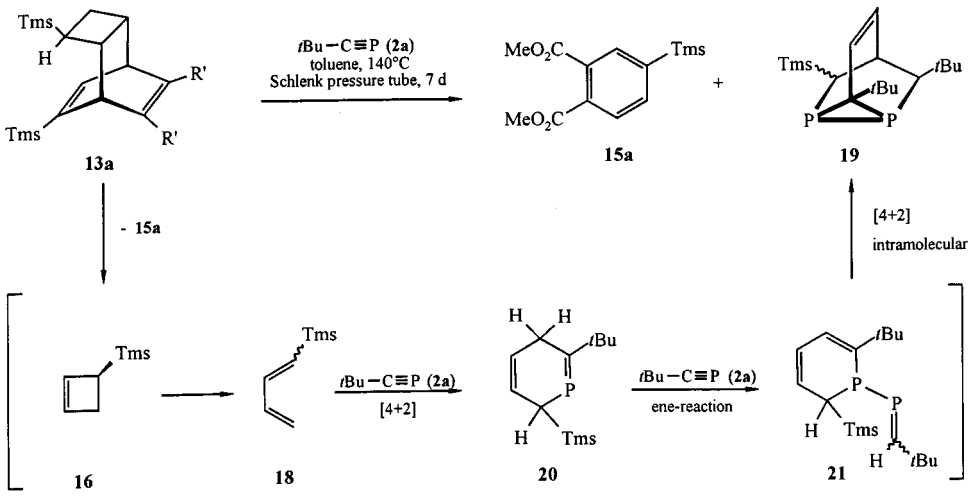
In view of their structural similarities with norbornadienes, barrelenes, and bicyclo[2.2.2]octa-2,5-dienes, which have all been successfully used as dienes in homo-Diels−Alder reactions[14a,14b,14d], we were prompted to attempt [2 + 2 + 2] cycloaddition reactions with the tricyclic compounds **13**. However, after heating of **13a** for 2 days in the presence of an excess of the acetylenes **11a**, **e** merely the phthalic acid ester **15a** was isolated. There was no evidence for the formation of the pentacyclic compound **17** or of the homo-Diels−Alder adduct with the opposite regiochemistry. When the polycyclic compounds **13a**, **b** were heated at 140 °C for 3 days in the absence of the acetylene, column chromatographic workup furnished the phthalic acid esters **15a**, **b** together with the 1,3-butadiene **18** as mixture of (*E*/*Z*) isomers.

The phthalates **15a**, **b** are easily identified on the basis of their spectroscopic and analytical data. After chromatographic separation, the volatile 1,3-butadienes (*E*)- and (*Z*)-**18** can be detected in pentane solution by combined GC/MS analysis. Distillative removal of the solvent made the recording of a ^{1}H-NMR spectrum possible and the data obtained agreed with those in the literature[18]. The intermediate occurrence of the putative primary product, the cyclobutene **16**, of the retro-Diels−Alder reaction cannot be confirmed since no allylic resonances were observed. The ratio of the isomeric butadienes was determined to be 3:2 by integration.

When the tricyclic compound **13a** is subjected to thermolysis at 140 °C for seven days in the presence of the phosphaalkyne **2a** a new, phosphorus-containing product is formed. After workup by distillation and column chromatography eluting with *n*-pentane the diphosphatricyclooctene **19** is isolated in good yield (55% referred to the amount of phosphaalkyne employed). Increasing the polarity of the eluent by adding diethyl ether subsequently furnishes the phthalate **15a**, unequivocally identified by NMR spectroscopy.

Both elemental analysis and mass spectroscopy confirm the 2:1 stoichiometry of the starting materials in the diphosphatricyclooctene **19**. The two doublets in the ^{31}P{^{1}H} NMR spectrum with a coupling constant of 157.6 Hz and chemical shifts of δ = −170.1 and δ = −188.2 indicate the presence of a diphosphirane unit[6]. The ^{13}C{^{1}H} NMR spectrum exhibits a signal pattern in full harmony with the observed chemical shifts and coupling constants of previously described diphosphatricyclooctenes[6]. The signal for C-2 is seen at δ = 42.7 as a pseudo-triplet with two equal $^1J_{C,P}$ coupling constants of 46.6 Hz. The signals of the two carbon atoms C-6 and C-8 appear at δ = 34.0 ($^1J_{C,P}$ = 54.3) and δ = 62.1 ($^1J_{C,P}$ = 48.3), with that of C-8 being additionally split into a double doublet by a $^2J_{C,P}$ coupling of 3.4 Hz. The signal for the carbon atom C-5 at δ = 34.5 exhibits coupling to only one phosphorus atom ($^2J_{C,P}$ = 2.6 Hz). The ^{1}H-NMR spectrum contains two signals in the olefinic region (δ = 6.20 and δ = 5.36), with the signal at higher field being assigned to 4-H on account of the two homonuclear couplings. The identical $^3J_{H,H}$ coupling constants of 9.3 Hz confirm the adjacency of the two protons. The hydrogen atom 5-H produces a multiplet signal at a chemical shift of 2.90 ppm typical for allylic protons.

From the mechanistic point of view the first step of the reaction is most certainly again a retro-Diels−Alder reaction. Similar cycloreversion reactions of other tricyclooctenes under flash vacuum pyrolysis conditions have been reported[9b,9c,10,19]. In the present case the generated cyclo-



Scheme 6

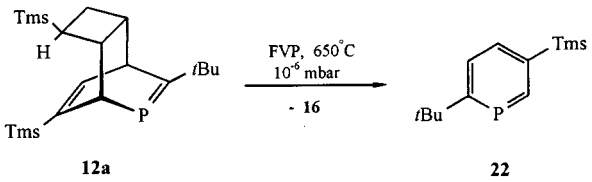
butene **16** undergoes ring opening to the buta-1,3-diene **18**. Analogous electrocyclic reactions have often been described, they are thermal conrotatory processes[20]. 1-Trimethylsilylbuta-1,3-diene **18** then reacts in a [4 + 2] cycloaddition with one equivalent of the phosphaalkyne **2a** to afford the phosphacyclohexa-1,4-diene **20**. Although a second regioisomer is feasible in this step − and has been found with 1-methylbuta-1,3-diene to an extent of 15%[6b] − the highly regioselective course of the reaction between **18** and the phosphaalkyne **2a** can be demonstrated by NMR spectroscopy. The individual reaction steps of the tandem sequence (Diels−Alder reaction, phospha-ene reaction, intramolecular Diels−Alder reaction) leading to the formation of **19** are well known from numerous investigations on butadienes[6].

When the phosphaalkyne **2a** is allowed to react with a sample of the (*E*)-buta-1,3-diene **18** prepared by a reported procedure[21] (140 °C, pressure Schlenk tube, 7 days) the diphosphatricyclooctene **19** is also obtained after workup by column chromatography and can be identified securely by its analytical and spectral data. This lends further support for the reaction pathway suggested here involving the generation of a free 1,3-butadiene.

Preparation of the λ^3-Phosphinine 22

The ease with which the tricyclic compounds **13a**, **b** decompose to the phthalates **15a**, **b** and cyclobutene **16** prompted us to undertake a more detailed study of the thermal behavior of the analogous phosphorus-containing compound **12a** since it could provide a new access to a substituted λ^3-phosphinine. In this context, it must be mentioned that we have previously generated a phosphabenzene in a similar way by cleavage of ethene from the phosphabicyclo-[2.2.2]octa-2,5-diene **1** under flash vacuum pyrolysis conditions[4].

When the phosphatricyclodecadiene **12a** is subjected to flash vacuum pyrolysis at 650 °C/10^{-6} mbar, the previously unknown λ^3-phosphinine **22** is isolated in good yield after column chromatographic workup. Cyclobutene could not be identified as the second pyrolysis product. Judging by the mild conditions for the synthesis of the phthalates **15a**, **b**, the phosphatricyclodecadiene **12a** exhibits a much larger thermal stability than **13a**. This is possibly due to the lower aromatic character of the formed phosphinine[22].

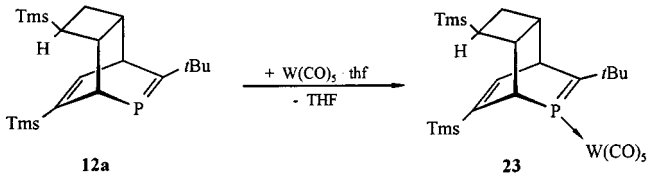


Scheme 7

The $^{31}P\{^1H\}$ NMR spectrum of **22** provides the first indications for the existence of a phosphabenzene: the singlet at δ = 201.6 is in the typical region for a λ^3-phosphinine[4][23]. The chemical shifts and coupling constants observed in the $^{13}C\{^1H\}$ NMR spectrum correlate very well with those of other known phosphinines[4][23]. All aromatic carbon signals occur as doublets with typically large downfield shifts of C-2 (δ = 184.9, $^1J_{C,P}$ = 58.3 Hz) and C-6 (δ = 159.0, $^1J_{C,P}$ = 56.6 Hz). An exact assignment of signals to the atoms C-3 and C-4 is not possible; they appear at δ = 129.7 and δ = 133.7. On account of the trimethylsilyl substitution the signal for C-5 is shifted down field to δ = 144.1. The aromatic character of the phosphinine **22** is clearly illustrated by the chemical shifts of the signals in the ^{1}H-NMR spectrum. The three aromatic protons give signals at very low field between δ = 7.5 and 9.1. The coupling patterns are complicated and not completely resolved.

Complex Behavior of 12a

When the phosphatricyclodecadiene **12a** is treated with an excess of the in situ generated pentacarbonyltungsten · thf complex the η^1-complex **23** is formed after 20 hours at room temperature and can be isolated as a yellow-



Scheme 8

to-orange colored oil in high yield by column chromatography.

The selective *end-on* coordination of the metal fragment to the phosphorus atom is clearly demonstrated by the analytical and spectral data of the complex. In the $^{31}P\{^1H\}$ NMR spectrum the phosphorus signal is shifted by 56.6 ppm to higher field relative to the uncomplexed compound **12a**. Particularly characteristic is the appearance of tungsten satellites with a typical $^1J_{P,W}$ coupling constant of 228.3 Hz. The complexation has only slight influence on the ^{13}C- and ^1H-NMR data of the skeletal atoms. The only conspicuous feature is the disappearance of the $^1J_{C,P}$ coupling in the signal for C-1. A similar trend has previously been observed in homo-Diels−Alder reactions of **12a**. In addition to the signals for the skeleton of **12a** the ^{13}C-NMR spectrum now contains signals for the carbon atoms of the axial and equatorial carbonyl ligands at low field (δ = 196.4 and δ = 199.6). Also typical CO valency vibrations of the terminal carbonyl ligands are seen in the IR spectrum at $\tilde{\nu}$ = 2070 cm^{-1} and 1940 cm^{-1}.

Experimental Section

All reactions were carried out under an argon atmosphere in oven-dried glassware. The solvents were anhydrous and stored under argon. − ^1H NMR and ^{13}C NMR: Bruker AC 200 and AMX 400; chemical shifts are referenced to the solvent as internal standard. − ^{31}P NMR: Bruker AC 200 (80.8 Hz); 85% H_3PO_4 as external standard. − IR: Perkin−Elmer 1310 series FTIR spectrometer. − MS: Finnigan MAT 90. − GC/MS: HP 6890 series with MSD; column: HP-5MS capillary column 30 m × 250 μm. − Elemental analyses: Perkin−Elmer EA240. − Melting points: Mettler FP61 (heating rate 2 °C/min), uncorrected. − Analytical TLC: Plastic sheets, silica gel, Polygram SIL G/UV_{254}, Machery−Nagel. − CC: Merck silica gel (0.063−0.2 mm). − Bulb-to-bulb distillation: Büchi GKR 50 apparatus; the temperatures stated are oven temperatures.

Compounds **2a**[24], **2b**[25], **2c**[26], **8**[11], **11c**[27], **11d**[28], and (*E*)-**18**[21] were prepared by published methods. All other starting materials were obtained from commercial suppliers and used without further purification.

General Procedure for the Preparation of the Phosphatricyclodecadienes 12a−c: The appropriate phosphaalkyne **1** and the cycloocta-1,3,6-triene **8** were heated in 5 mL toluene to 90 °C for 24 hours. in a Schlenk pressure tube. The reaction mixture was allowed to cool to room temperature and subsequently all volatile components were removed in vacuo. The residue was purified by bulb-to-bulb distillation. Crystallization from CH_2Cl_2 at −78 °C yielded **12a−c** as colorless crystals.

7-*tert*-Butyl-3,9-bis(trimethylsilyl)-8-phosphatricyclo[4.2.2.0^{2,5}]deca-7,9-diene (12a): From 0.5 g (2.0 mmol) of **8** and 0.32 g (3.2 mmol) of **2a**. Yield: 0.45 g (1.28 mmol, 64%), b.p. 90 °C/10^{-2} mbar, m.p. 72 °C. − ^1H NMR (C_6D_6): 0.01 [s, 9 H, Si(CH_3)$_3$], 0.11 [s, 9 H, Si(CH_3)$_3$], 0.95 [ddd, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,H}$ = 6.3 Hz, 1 H, 3-H], 1.19 [d, $^4J_{H,P}$ = 1.3 Hz, 9 H, C(CH_3)$_3$], 1.38 [dpt, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 5.3 Hz, 1 H, 4-H], 1.68 [ddd, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-H], 2.08 [m$_c$, $^3J_{H,H}$ = 12.1 Hz, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 5.3 Hz, $^3J_{H,H}$ = 3.1 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, 5-H], 2.20 [ddd, $^3J_{H,H}$ = 12.1 Hz, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,H}$ = 3.0 Hz, 1 H, 2-H], 3.95 [ddd, $^2J_{H,P}$ = 19.9 Hz, $^3J_{H,H}$ = 3.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, 1-H], 4.01 [pquin, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 3.1 Hz, $^3J_{H,P}$ = 3.1 Hz, 1 H, 6-H], 6.65 [dpt, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 1.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, 10-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.3 [s, Si(*C*H_3)$_3$], −2.3 [s, Si(*C*H_3)$_3$], 21.5 [s, C-4], 22.9 [s, C-2, C-3, or C-5], 29.7 [d, $^3J_{C,P}$ = 12.9 Hz, C(*C*H_3)$_3$], 35.5 [d, $J_{C,P}$ = 1.6 Hz, C-2, C-3, or C-5], 39.0 [d, $J_{C,P}$ = 8.0 Hz, C-2, C-3, or C-5], 40.5 [d, $^2J_{C,P}$ = 15.3 Hz, *C*(CH$_3$)$_3$], 49.8 [d, $^2J_{C,P}$ = 9.6 Hz, C-6], 49.9 [d, $^1J_{C,P}$ = 38.6 Hz, C-1], 142.4 [d, $^3J_{C,P}$ = 11.2 Hz, C-10], 148.0 [d, $^2J_{C,P}$ = 6.4 Hz, C-9], 222.4 [d, $^1J_{C,P}$ = 45.0 Hz, C-7]. − $^{31}P\{^1H\}$ NMR (C_6D_6): 219.0 (s). − MS (EI, 70 eV); *m/z* (%): 350 (97) $[M]^+$, 335 (40) $[M - CH_3]^+$, 293 (40) $[M - C_4H_9]^+$, 277 (58) $[M - Si(CH_3)_3]^+$, 250 (10) $[M - C_5H_9P]^+$, 235 (9) $[M - C_5H_9P - CH_3]^+$, 73 (100) $[Si(CH_3)_3]^+$, 57 (8) $[C_4H_9]^+$. − HRMS (EI, 70 eV): $C_{19}H_{35}PSi_2$ calcd. 350.2015, found 350.2015.

7-(1-Adamantyl)-3,9-bis(trimethylsilyl)-8-phosphatricyclo-[4.2.2.0^{2,5}]deca-7,9-diene (12b): From 0.58 g (2.32 mmol) of **8** and 0.57 g (3.2 mmol) of **2b**. Yield: 0.59 g (1.38 mmol, 60%), b.p. 150 °C/10^{-2} mbar, m.p. 140 °C. − ^1H NMR (C_6D_6): −0.03 [s, 9 H, Si(CH_3)$_3$], 0.14 [s, 9 H, Si(CH_3)$_3$], 0.98 [m$_c$, 1 H, 3-H], 1.43 [dpt, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 5.4 Hz, 1 H, 4-H], 1.6−1.9 [m, 16 H, adamantyl-H and 4-H], 2.07 [m$_c$, 1 H, 5-H], 2.23 [ddd, $^3J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 3.0 Hz, 1 H, 2-H], 4.00 [m$_c$, $^2J_{H,P}$ = 19.5 Hz, 1 H, 1-H], 4.08 [pquin, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 3.1 Hz, $^3J_{H,P}$ = 3.1 Hz, 1 H, 6-H], 6.64 [d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 10-H]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): −3.6 [s, Si(*C*H_3)$_3$], −2.4 [s, Si(*C*H_3)$_3$], 21.0 [s, C-4], 22.3 [s, C-2, C-3, or C-5], 28.6 [s, C-3′, C-5′, C-7′], 34.7 [s, C-2, C-3, or C-5], 36.9 [s, C-4′, C-6′, C-10′], 38.5 [d, $J_{C,P}$ = 8.6 Hz, C-2, C-3 or C-5], 41.9 [d, $^3J_{C,P}$ = 13.4 Hz, C-2′, C-8′ or C-9′], 42.4 [d, $^2J_{C,P}$ = 13.4 Hz, C-1′], 47.9 [d, $^2J_{C,P}$ = 10.5 Hz, C-6], 49.1 [d, $^1J_{C,P}$ = 38.2 Hz, C-1], 141.9 [d, $^3J_{C,P}$ = 11.4 Hz, C-10], 147.5 [d, $^2J_{C,P}$ = 6.7 Hz, C-9], 223.4 [d, $^1J_{C,P}$ = 43.9 Hz, C-7]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): 218.6 (s). − MS (EI, 70 eV); *m/z* (%): 428 (97) $[M]^+$, 413 (8) $[M - CH_3]^+$, 355 (47) $[M - Si(CH_3)_3]^+$, 293 (16) $[M - C_{10}H_{15}]^+$, 135 (62) $[C_{10}H_{15}]^+$, 73 (100) $[Si(CH_3)_3]^+$. − HRMS (EI, 70 eV): $C_{25}H_{41}PSi_2$ calcd. 428.2484, found 428.2484.

7-(1,1-Dimethylpropyl)-3,9-bis(trimethylsilyl)-8-phosphatricyclo-[4.2.2.0^{2,5}]deca-7,9-diene (12c): From 1.00 g (3.99 mmol) of **8** and 0.56 g (4.91 mmol) of **2c**. Yield: 0.75 g (2.06 mmol, 52%), b.p. 90 °C/10^{-2} mbar, m.p. 57 °C. − ^1H NMR (C_6D_6): −0.01 [s, 9 H, Si(CH_3)$_3$], 0.10 [s, 9 H, Si(CH_3)$_3$], 0.72 [t, $^3J_{H,H}$ = 7.6 Hz, 3 H, C(CH$_3$)$_2$(CH$_2$CH_3)], 0.92 [m$_c$, 1 H, 3-H], 1.13 [d, *J* = 1.5 Hz, 3 H, C(CH_3)$_2$(CH$_2$CH$_3$)], 1.21 [d, *J* = 1.7 Hz, 3 H, C(CH_3)$_2$(CH$_2$CH$_3$)], 1.3−1.75 [m, 4 H, 4-H, 4-H- and C(CH$_3$)$_2$(CH_2CH$_3$)], 2.0−2.2 [m, 2 H, 2-H and 5-H], 3.85−4.0 [m, 2 H, 1-H and 6-H], 6.60 [dpt, $^3J_{H,H}$ = 6.3 Hz, *J* = 1 Hz, *J* = 1 Hz, 1 H, 10-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.3 [s, Si(*C*H_3)$_3$], −2.3 [s, Si(*C*H_3)$_3$], 9.2 [s, C(CH$_3$)$_2$(CH$_2$*C*H$_3$)], 21.6 [s, C-4], 23.0 [s, C-2, C-3, or C-5], 27.1 [d, $^3J_{C,P}$ = 17.8 Hz, C(*C*H$_3$)$_2$(CH$_2$CH$_3$)], 28.0 [d, $^3J_{C,P}$ = 12.7 Hz, C(*C*H$_3$)$_2$(CH$_2$CH$_3$)], 33.5 [d, $^3J_{C,P}$ = 8.5 Hz, C(CH$_3$)$_2$(*C*H$_2$CH$_3$)], 35.4 [s, C-2, C-3, or C-5], 38.9 [d, $J_{C,P}$ = 8.5 Hz, C-2, C-3, or C-5], 43.6 [d, $^2J_{C,P}$ = 13.6 Hz, *C*(CH$_3$)$_2$(CH$_2$CH$_3$)], 49.5 [d, $^2J_{C,P}$ = 10.2 Hz, C-6], 49.9 [d, $^1J_{C,P}$ = 39.0 Hz, C-1], 142.6 [d, $^3J_{C,P}$ = 11.0

Hz, C-10], 147.9 [d, $^2J_{C,P}$ = 7.6 Hz, C-9], 220.8 [d, $^1J_{C,P}$ = 45.8 Hz, C-7]. − $^{31}P\{^1H\}$ NMR (C_6D_6): 225.1 (s). − MS (EI, 70 eV); *m/z* (%): 364 (18) $[M]^+$, 349 (10) $[M - CH_3]^+$, 335 (11) $[M - C_2H_5]^+$, 293 (13) $[M - C_5H_{11}]^+$, 291 (15) $[M - Si(CH_3)_3]^+$, 250 (1) $[M - C_6H_{11}P]^+$, 73 (100) $[Si(CH_3)_3]^+$, 71 (7) $[C_5H_{11}]^+$. − CHN: $C_{20}H_{37}PSi_2$ (364.66), calcd. C 65.88, H 10.23; found C 65.37, H 10.11.

General Procedure for the Preparation of the Tricyclodecadienes 13a−d: A toluene solution of the cycloocta-1,3,6-triene **8** and the appropriate acetylene **11a−d** was heated under magnetic stirring to 90 °C in a Schlenk pressure tube. After cooling to room temperature the solvent was removed under reduced pressure. The residue was purified by column chromatography (with the exception of **13c**, which was filtered over Celite to remove insoluble materials prior to chromatography).

Dimethyl 3,9-Bis(trimethylsilyl)tricyclo[4.2.2.0^{2,5}]deca-7,9-diene-7,8-dicarboxylate (13a): From 1.03 g (4.11 mmol) of **8** and 0.75 mL (0.65 g, 4.57 mmol) of **11a** in 7 mL of toluene. Stirring for 48 hours. Chromatography on silica gel (40 × 2 cm) with petroleum ether/diethyl ether, 15:1. Yield: 1.18 g (3.01 mmol, 73%), colorless oil, which was crystallized from *n*-pentane, b.p. 120 °C/10^{-2} mbar, m.p. 98 °C. − ^1H NMR (C_6D_6): −0.02 [s, 9 H, Si(CH_3)$_3$], 0.16 [s, 9 H, Si(CH_3)$_3$], 0.85−0.95 [m, 1 H, 3-H], 1.25−1.35 [m, 1 H, 4-H], 1.60−1.70 (m, 1 H, 4-H], 2.25−2.35 [m, 2 H, 2-H and 5-H], 3.47 [s, 3 H, CO_2CH_3], 3.49 [s, 3 H, CO_2CH_3], 4.10−4.20 [m, 1 H, 1-H], 4.30−4.35 [m, 1 H, 6-H], 6.62 [dd, $^3J_{H,H}$ = 5.7 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, 10-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.5 [s, Si(CH_3)$_3$], −2.0 [s, Si(CH_3)$_3$], 20.4 [s, C-2, C-3, or C-5], 21.5 [s, C-4], 36.8 [s, C-2, C-3, or C-5], 38.4 [s, C-2, C-3, or C-5], 44.7 [s, C-1 or C-6], 47.3 [s, C-1 or C-6], 51.5 [s, CO_2CH_3], 51.6 [s, CO_2CH_3], 140.2 [s, C-7 or C-8], 142.2 [s, C-10], 143.5 [s, C-7 or C-8], 147.3 [s, C-9], 165.9 [s, CO_2CH_3], 166.8 [s, CO_2CH_3]. − MS (EI, 70 eV); *m/z* (%): 392 (7) $[M]^+$, 339 (33), 251 (13), 235 (100), 73 (39) $[Si(CH_3)_3]^+$. − IR (film): $\tilde{\nu}$ = 3030, 2951, 2851, 1716, 1633, 1583, 1435, 1346, 1305, 1260, 1218, 1128, 1075, 1042, 834, 749 cm^{-1}. − CHN: $C_{20}H_{32}O_4Si_2$ (392.64), calcd. C 61.18, H 8.21; found C 60.00, H 8.19.

Di-*tert*-butyl 3,9-Bis(trimethylsilyl)tricyclo[4.2.2.0^{2,5}]deca-7,9-diene-7,8-dicarboxylate (13b): From 0.5 g (2.0 mmol) of **8** and 0.68 g (3.0 mmol) of **11b** in 5 mL of toluene. Stirring for 48 hours. Chromatography on silica gel (120 × 7 cm) with petroleum ether/diethyl ether, 10:1 (R_F = 0.33 with *n*-pentane/diethyl ether, 15:1). Yield: 0.78 g (1.64 mmol, 82%), colorless oil, which was crystallized from *n*-pentane, b.p. 130 °C/10^{-2} mbar, m.p. 74 °C. − ^1H NMR (C_6D_6): −0.11 [s, 9 H, Si(CH_3)$_3$], 0.07 [s, 9 H, Si(CH_3)$_3$], 0.75−0.85 [m, 1 H, 3-H], 1.15−1.35 [m, 1 H, 4-H], 1.41 [s, 9 H, $CO_2C(CH_3)_3$], 1.45 [s, 9 H, $CO_2C(CH_3)_3$], 1.50−1.65 [m, 1 H, 4-H], 2.20−2.35 [m, 2 H, 2-H and 5-H], 4.10−4.15 [m, 2 H, 1-H and 6-H], 6.59 [dd, $^3J_{H,H}$ = 5.9 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, 10-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.9 [s, Si(CH_3)$_3$], −2.3 [s, Si(CH_3)$_3$], 20.1 [s, C-2, C-3, or C-5], 21.3 [s, C-4], 27.8 [s, $CO_2C(CH_3)_3$], 27.9 [s, $CO_2C(CH_3)_3$], 36.6 [s, C-2, C-3, or C-5], 38.2 [s, C-2, C-3, or C-5], 44.5 [s, C-1 or C-6], 47.6 [s, C-1 or C-6], 80.4 [s, $CO_2C(CH_3)_3$], 80.4 [s, $CO_2C(CH_3)_3$], 139.5 [s, C-7 or C-8], 142.3 [s, C-10], 144.0 [s, C-7 or C-8], 146.7 [s, C-9], 164.4 [s, $CO_2C(CH_3)_3$], 165.6 [s, $CO_2C(CH_3)_3$]. − MS (CI, isobutane): *m/z*: 477 $[M + H]^+$. − IR (KBr): $\tilde{\nu}$ = 2977, 2942, 2851, 1734, 1706, 1640, 1584, 1479, 1456, 1368, 1250, 1171, 1072, 1034, 984, 834, 752 cm^{-1}. − CHN: $C_{26}H_{44}O_4Si_2$ (476.80), calcd. C 65.50, H 9.30; found C 64.91, H 9.00.

7,8-Dicyano-3,9-bis(trimethylsilyl)tricyclo[4.2.2.0^{2,5}]deca-7,9-diene (13c): From 0.5 g (2.0 mmol) of **8** and 0.24 g (3.2 mmol) of **11c** in 5 mL of toluene. Stirring for 48 hours. Chromatography on silica gel (40 × 2 cm) with dichloromethane/*n*-pentane, 3:1. Yield: 0.17 g (0.52 mmol, 26%), colorless oil, which was crystallized from *n*-pentane at −78°C, b.p. 160 °C/10^{-2} mbar, m.p. 63 °C. − ^1H NMR (C_6D_6): −0.12 [s, 9 H, Si(CH_3)$_3$], −0.10 [s, 9 H, Si(CH_3)$_3$], 0.85−0.90 [m, 2 H, 3-H and 4-H], 1.30−1.45 [m, 1 H, 4-H], 1.50−1.60 [m, 1 H, 5-H], 1.70−1.80 [m, 1 H, 2-H], 3.20−3.30 [m, 1 H, 1-H], 3.70−3.80 [m, 1 H, 6-H], 6.01 [ddd, $^3J_{H,H}$ = 5.8 Hz, $^4J_{H,H}$ = 1.6 Hz, $^4J_{H,H}$ = 0.9 Hz, 1 H, 10-H]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.6 [s, Si(CH_3)$_3$], −2.4 [s, Si(CH_3)$_3$], 19.8 [s, C-2, C-3, or C-5], 20.8 [s, C-4], 35.9 [s, C-2, C-3, or C-5], 37.6 [s, C-2, C-3, or C-5], 46.5 [s, C-1 or C-6], 48.8 [s, C-1 or C-6], 114.7 [s, CN], 114.8 [s, CN], 130.6 [s, C-7 or C-8], 131.5 [s, C-7 or C-8], 139.8 [s, C-10], 146.4 [s, C-9]. − MS (EI, 70 eV); *m/z* (%): 326 (1) $[M]^+$, 311 (5) $[M - CH_3]^+$, 273 (49), 253 (6) $[M - Si(CH_3)_3]^+$, 185 (8), 126 (9), 73 (100) $[Si(CH_3)_3]^+$. − IR (KBr): $\tilde{\nu}$ = 2961, 1637, 1404, 1262, 1096, 1021, 801, 701 cm^{-1}.

7,8-Dibenzoyl-3,9-bis(trimethylsilyl)tricyclo[4.2.2.0^{2,5}]deca-7,9-diene (13d): From 0.57 g (2.3 mmol) of **8** and 0.61 g (2.6 mmol) of **11d** in 5 mL of toluene. Stirring for 72 hours. Chromatography on silica gel (40 × 2 cm) with dichloromethane/*n*-pentane, 2:1, and subsequently on silica gel (75 × 3 cm) with *n*-pentane/diethyl ether, 4:1. Yield: 0.19 g (0.39 mmol, 17%), colorless oil, b.p. 160 °C/10^{-2} mbar. − ^1H NMR ($CDCl_3$): 0.01 [s, 9 H, Si(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$], 0.80−0.90 [m, 1 H, 3-H], 1.35−1.50 [m, 1 H, 2-H], 1.75−1.85 [m, 1 H, 5-H], 2.35−2.55 [m, 2 H, 4-H (2×)], 4.20−4.30 [m, 2 H, 1-H and 6-H], 6.97 [m, 1 H, 10-H], 7.05−7.20 [m, 6 H, *m*- and *p*-C_6H_5], 7.30−7.35 [m, 4 H, *o*-C_6H_5]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): −3.5 [s, Si(CH_3)$_3$], −1.8 [s, Si(CH_3)$_3$], 20.7 [s, C-2, C-3, or C-5], 21.6 [s, C-4], 36.6 [s, C-2, C-3, or C-5], 38.3 [s, C-2, C-3, or C-5], 45.9 [s, C-1 or C-6], 48.6 [s, C-1 or C-6], 128.1−138.4 [8s, C_6H_5], 142.2 [s, C-10], 146.7 [s, C-7, C-8 or C-9], 148.1 [s, C-7, C-8 or C-9], 149.9 [s, C-7, C-8 or C-9], 195.1 [s, C_6H_5C=O], 196.2 [s, C_6H_5C=O]. − MS (EI, 70 eV); *m/z* (%): 484 (2) $[M]^+$, 431 (100) $[M - Si(CH_3)_3]^+$, 359 (27), 281 (7), 105 (9), 73 (39) $[Si(CH_3)_3]^+$. − IR (CCl_4): $\tilde{\nu}$ = 2954, 2899, 1783, 1726, 1649, 1551, 1448, 1249, 712 cm^{-1}.

General Procedure for the Preparation of the Phosphapentacyclododecenes 14a−c: The appropriate phosphatricyclodecadiene **12** and alkyne **11** were dissolved in toluene in a Schlenk pressure tube and heated to 140 °C. After completion of the reaction the volatile components were removed in vacuo. The residue was purified by bulb-to-bulb distillation (**14a**, **b**) or column chromatography (**14c**) and subsequent crystallization from *n*-pentane.

Dimethyl 8-*tert*-Butyl-4,10-bis(trimethylsilyl)-1-phosphapentacyclo-[6.4.0.0^{2,10}.0^{3,6}.0^{7,9}]dodec-11-ene-11,12-dicarboxylate (14a): From 0.27 g (0.77 mmol) of **12a** and 0.14 g (0.99 mmol) of **11a** in 3 mL of toluene. Stirring for 4 hours. Bulb-to-bulb distillation at 160 °C/10^{-2} mbar and crystallization from *n*-pentane at −78 °C afforded 0.19 g (0.39 mmol, 51%) of **14a** as a pale yellow solid (m.p. 128 °C). − ^1H NMR (C_6D_6): −0.08 [s, 9 H, Si(CH_3)$_3$], 0.43 [s, 9 H, Si(CH_3)$_3$], 0.97 [s, 9 H, C(CH_3)$_3$], 1.46 [ddd, *J* = 7.4 Hz, *J* = 4.3 Hz, *J* = 2.6 Hz, 1 H], 1.69 [d, *J* = 7.3 Hz, 1 H], 1.8−2.0 [m, 4 H], 2.39 [m_c, 1 H], 2.65 [m_c, 1 H], 3.39 [s, 3 H, CO_2CH_3], 3.61 [s, 3 H, CO_2CH_3]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.8 [s, Si(CH_3)$_3$], 1.1 [s, Si(CH_3)$_3$], 24.0 [d, $J_{C,P}$ = 13.3 Hz, C-3, C-4, C-6, C-7, or C-9], 25.3 [s, C-5], 28.2 [d, $J_{C,P}$ = 7.3 Hz, C-3, C-4, C-6, C-7, or C-9], 29.7 [d, $^3J_{C,P}$ = 4.6 Hz, C(CH_3)$_3$], 31.5 [d, $J_{C,P}$ = 3.3 Hz, C-3, C-4, C-6, C-7, or C-9], 32.3 [d, $^2J_{C,P}$ = 10.0 Hz, C(CH$_3$)$_3$], 32.4 [d, $J_{C,P}$ = 3.3 Hz, C-3, C-4, C-6, C-7, or C-9], 34.3 [d, $J_{C,P}$ = 15.9 Hz, C-3, C-4, C-6, C-7, or C-9], 47.7 [d, $^1J_{C,P}$ = 33.2 Hz, C-8], 51.5 [s, CO_2CH_3], 51.8 [s, CO_2CH_3], 52.9 [d, $^2J_{C,P}$ = 9.3 Hz, C-10], 58.1 [d, $^1J_{C,P}$ = 5.3 Hz, C-2], 144.7 [d, $^1J_{C,P}$ = 29.9 Hz, C-12], 165.4 [d, $^2J_{C,P}$ = 19.2 Hz, C-11], 169.4 [s, CO_2CH_3], 170.6 [s, CO_2CH_3]. −

$^{31}P\{^1H\}$ NMR (C_6D_6): −11.3 (s). − MS (EI, 70 eV); *m/z* (%): 492 (15) $[M]^+$, 477 (33) $[M - CH_3]^+$, 435 (9) $[M - C_4H_9]^+$, 419 (6) $[M - Si(CH_3)_3]^+$, 392 (11) $[M - C_5H_9P]^+$, 73 (100) $[Si(CH_3)_3]^+$, 57 (14) $[C_4H_9]^+$. − HRMS: $C_{25}H_{41}O_4PSi_2$ calcd. 492.2281, found 492.2282. − IR (*n*-pentane): $\tilde{\nu}$ = 1739, 1722 cm^{-1}. − CHN: $C_{25}H_{41}O_4PSi_2$ (492.74), calcd. C 60.94, H 8.39; found C 60.85, H 8.28.

8-*tert*-Butyl-11,12-bis(trifluoromethyl)-4,10-bis(trimethylsilyl)-1-phosphapentacyclo[6.4.0.0^{2,10}.0^{3,6}. 0^{7,9}]dodec-11-ene (14b): From 0.28 g (0.8 mmol) of **12a** and 0.24 g (1.48 mmol) of **11e** in 2.5 mL of toluene. Stirring for 3 days. Chromatography on silica gel (35 × 2 cm) with *n*-pentane afforded 0.13 g (0.25 mmol, 32%) of **14b** as a colorless oil (R_F = 0.5), from which colorless crystals were obtained (*n*-pentane, −25 °C); b.p. 110 °C/10^{-2} mbar, m.p. 94 °C. − ^1H NMR (C_6D_6): −0.08 [s, 9 H, $Si(CH_3)_3$], 0.42 [d, *J* = 1.5 Hz, 9 H, $Si(CH_3)_3$], 0.86 [s, 9 H, $C(CH_3)_3$], 1.25−1.40 [m, 1 H], 1.55−1.65 [m, 1 H], 1.8−2.0 [m, 4 H], 2.25−2.35 [m, 1 H,], 2.55−2.65 [m, 1 H]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): −3.8 [s, $Si(CH_3)_3$], 2.7 [q, $J_{C,F}$ = 3.4 Hz, $Si(CH_3)_3$], 24.4 [d, $J_{C,P}$ = 14.4 Hz, C-3, C-4, C-6, C-7, or C-9], 24.9 [s, C-5], 28.1 [d, $J_{C,P}$ = 10.2 Hz, C-3, C-4, C-6, C-7, or C-9], 29.6 [d, $^3J_{C,P}$ = 5.1 Hz, $C(CH_3)_3$], 31.2 [d, $J_{C,P}$ = 3.4 Hz, C-3, C-4, C-6, C-7, or C-9], 31.7 [d, $^3J_{C,P}$ = 9.3 Hz, $C(CH_3)_3$], 32.6 [s, C-3, C-4, C-6, C-7, or C-9], 34.5 [d, $J_{C,P}$ = 17.0 Hz, C-3, C-4, C-6, C-7, or C-9], 47.4 [d, $^1J_{C,P}$ = 31.4 Hz, C-8], 53.6 [d, $^2J_{C,P}$ = 10.2 Hz, C-10], 59.6 [d, $^1J_{C,P}$ = 3.4 Hz, C-2], 120−129 [m, 2 CF_3], 152.0 [m_c, C-12], 158.5 [m_c, C-11]. − $^{31}P\{^1H\}$ NMR (C_6D_6): 2.0 (q, $^3J_{P,F}$ = 22.9 Hz). − MS (EI, 70 eV); *m/z* (%): 512 (12) $[M]^+$, 497 (5) $[M - CH_3]^+$, 439 (7) $[M - Si(CH_3)_3]^+$, 251 (16), 77 (12), 73 (100) $[Si(CH_3)_3]^+$, 57 (27) $[C_4H_9]^+$. − IR (toluene): $\tilde{\nu}$ = 2954, 2910, 1600, 1448, 1288, 1256, 1176, 1145, 834, 737 cm^{-1}. − CHN: $C_{25}H_{35}F_6PSi_2$ (512.66), calcd. C 53.89, H 6.88; found C 53.65, H 6.88.

Crystal Data and Summary of Data Collection Parameters for 14b:[29] Diffractometer STOE Imaging Plate Diffraction System; radiation: Mo-K_α; $C_{23}H_{35}F_6PSi_2$; *M* = 512.66 g·mol^{-1}; *T* = 20 °C; Crystal size 0.35 × 0.25 × 0.20 mm; triclinic $P\bar{1}$; *a* = 9.893(2), *b* = 10.380(2), *c* = 13.523(3) Å, α = 88.16(3), β = 87.13(3), γ = 75.16(3)°; *V* = 1340.4(5) $Å^3$; *Z* = 2; $d_{calcd.}$ = 1.270 Mg·m^{-3}; μ = 0.243 mm^{-1}; *F*(000) = 540; Θ range 2.54−26.00°; index ranges: $-12 \le h \le 12$, $-12 \le k \le 12$, $-16 \le l \le 16$; no. of reflections collected: 16659; no. of independent reflections: 4818; structure solution by direct methods (SHELXS-86[30]); structure refinement by full-matrix least-sqaures (SHELXL-93[31]); *R* indices (all data): *R*1 = 0.0538, *wR*2 = 0.1459; final *R* indices [$I > 2\sigma(I)$]: *R*1 = 0.0469, *wR*2 = 0.1302; GoF on F^2: 1.022.

Dimethyl 8-(1-Adamantyl)-4,10-bis(trimethylsilyl)-1-phosphapentacyclo[6.4.0.0^{2,10}.0^{3,6}.0^{7,9}]dodec-11-ene-11,12-dicarboxylate (14c): From 0.30 g (0.7 mmol) of **12b** and 0.14 g (0.99 mmol) of **11a** in 5 mL of toluene. Stirring for 18 hours. Bulb-to-bulb distillation at 200 °C/10^{-2} mbar and crystallization from *n*-pentane at −78 °C afforded 0.10 g (0.18 mmol, 26%) of **14c** as a pale yellow solid. − ^1H NMR (C_6D_6): −0.49 [s, 9 H, $Si(CH_3)_3$], 0.49 [s, 9 H, $Si(CH_3)_3$], 1.5−2.1 [m, 21 H, adamantyl and 6 H], 2.44 [m_c, 1 H], 2.68 [m_c, 1 H], 3.42 [s, 3 H, CO_2CH_3], 3.62 [s, 3 H, CO_2CH_3]. − $^{13}C\{^1H\}$ NMR (C_6D_6): −3.8 [s, $Si(CH_3)_3$], 1.2 [s, $Si(CH_3)_3$], 24.0 [d, $J_{C,P}$ = 13.6 Hz, C-3, C-4, C-6, C-7, or C-9], 25.4 [s, C-5], 28.3 [d, $J_{C,P}$ = 7.6 Hz, C-3, C-4, C-6, C-7, or C-9], 29.2 [s, C-3′, C-5′, C-7′], 30.5 [d, $J_{C,P}$ = 3.4 Hz, C-3, C-4, C-6, C-7, or C-9], 30.7 [d, $J_{C,P}$ = 3.4 Hz, C-3, C-4, C-6, C-7, or C-9], 33.6 [d, $J_{C,P}$ = 9.3 Hz, C-1′], 34.4 [d, $J_{C,P}$ = 15.3 Hz, C-3, C-4, C-6, C-7, or C-9], 37.1 [s, C-4′, C-6′, C-10′], 42.2 [d, $^3J_{C,P}$ = 5.1 Hz, C-2′, C-8′, C-9′], 48.7 [d, $^1J_{C,P}$ = 33.1 Hz, C-8], 51.5 [s, CO_2CH_3], 51.9 [s, CO_2CH_3], 52.5 [d, $^2J_{C,P}$ = 9.3 Hz, C-10], 57.3 [d, $^1J_{C,P}$ = 5.9 Hz, C-2], 144.5 [d, $^1J_{C,P}$ = 29.7 Hz, C-12], 165.5 [d, $^2J_{C,P}$ = 19.5 Hz, C-11], 169.5 [s, CO_2CH_3], 170.5 [s, CO_2CH_3]. − $^{31}P\{^1H\}$ NMR (C_6D_6): −13.2 (s). − MS (EI, 70 eV); *m/z* (%): 570 (2) $[M]^+$, 555 (8) $[M - CH_3]^+$, 497 (2) $[M - Si(CH_3)_3]^+$, 435 (2) $[M - C_5H_{10}]^+$, 135 (79) $[C_{10}H_{15}]^+$, 73 (100) $[Si(CH_3)_3]^+$. − HRMS: $C_{31}H_{47}O_4PSi_2$ calcd. 570.2751, found 570.2750. − IR (*n*-pentane): $\tilde{\nu}$ = 1739, 1722 cm^{-1}.

Thermolysis of the Tricyclodecadienes 13a, b − General Procedure: A toluene solution of the respective tricyclodecadiene **13** was heated to 140 °C in a Schlenk pressure tube under a positive pressure of 5 bar. After 3 days the reaction mixture was subjected to column chromatography without previous evaporation of the volatile components. Upon elution with *n*-pentane a mixture of (*E*)- and (*Z*)-**18** was obtained. After elution of the reaction solvent (toluene) the polarity of the eluent was increased and the phthalic esters **15** were obtained as colorless liquids.

Dimethyl 4-(Trimethylsilyl)phthalate (15a): From 133.4 mg (0.34 mmol) of **13a** in 0.5 mL of toluene. Column chromatography on silica gel (25 × 1.5 cm) yielded 74.5 mg (0.28 mmol, 82%) of **15a** as a colorless liquid (R_F = 0.46 with *n*-pentane/diethyl ether, 1:1); b.p. 80 °C/10^{-2} mbar. − ^1H NMR (C_6D_6): 0.08 [s, 9 H, $Si(CH_3)_3$], 3.59 [s, 3 H, CO_2CH_3], 3.59 [s, 3 H, CO_2CH_3], 7.38 [dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, 5-H], 7.63 [dd, $^3J_{H,H}$ = 7.6 Hz, $^5J_{H,H}$ = 0.5 Hz, 1 H, 6-H], 7.96 [dd, $^4J_{H,H}$ = 1.2 Hz, $^5J_{H,H}$ = 0.5 Hz, 1 H, 3-H]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): −1.6 [s, $Si(CH_3)_3$], 52.3 [s, CO_2CH_3], 52.4 [s, CO_2CH_3], 127.8 [s, C-3, C-5, or C-6], 131.0 [s, C-1 or C-2], 131.6 [s, C-1 or C-2], 133.1 [s, C-3, C-5, or C-6], 135.7 [s, C-3, C-5, or C-6], 145.1 [s, C-4], 167.8 [s, CO_2CH_3], 168.4 [s, CO_2CH_3]. − MS (EI, 70 eV); *m/z* (%): 266 (8) $[M]^+$, 251 (100) $[M - CH_3]^+$, 235 (12) $[M - 2\,CH_3 - H]^+$, 219 (11), 191 (10), 73 (5) $[Si(CH_3)_3]^+$. − IR (film): $\tilde{\nu}$ = 2999, 2954, 2845, 1732, 1435, 1290, 1131, 1114, 1069, 873, 839, 754 cm^{-1}. − CHN: $C_{13}H_{18}O_4Si$ (266.37), calcd. C 58.62, H 6.81; found C 58.42, H 6.78.

Di-*tert*-butyl 4-(Trimethylsilyl)phthalate (15b): From 249.2 mg (0.49 mmol) of **13b** in 0.5 mL of toluene. Column chromatography on silica gel (20 × 2.5 cm) yielded 131.7 mg (0.38 mmol, 78%) of **15b** as a colorless liquid (R_F = 0.6 with *n*-pentane/diethyl ether, 4:1). − ^1H NMR ($CDCl_3$): 0.19 [s, 9 H, $Si(CH_3)_3$], 1.64 [s, 9 H, $CO_2C(CH_3)_3$], 1.65 [s, 9 H, $CO_2C(CH_3)_3$], 7.42 [dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, 5-H], 7.75 [d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 6-H], 7.96 [s, 1 H, 3-H]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): −1.4 [s, $Si(CH_3)_3$], 28.0 [s, $CO_2C(CH_3)_3$], 28.0 [s, $CO_2C(CH_3)_3$], 81.6 [s, $CO_2C(CH_3)_3$], 81.7 [s, $CO_2C(CH_3)_3$], 127.8 [s, C-3, C-5, or C-6], 130.1 [s, C-1 or C-2], 133.0 [s, C-1 or C-2], 133.6 [s, C-3, C-5, or C-6], 135.1 [s, C-3, C-5, or C-6], 144.1 [s, C-4], 166.7 [s, $CO_2C(CH_3)_3$], 167.4 [s, $CO_2C(CH_3)_3$]. − MS (CI, isobutane); *m/z*: 351 $[M + H]^+$. − IR (film): $\tilde{\nu}$ = 2976, 2904, 1853, 1782, 1723, 1456, 1368, 1302, 1252, 1135, 1068, 905, 843, 752 cm^{-1}.

(E)- and (Z)-1-Trimethylsilylbuta-1,3-diene (18): Thermolysis of 133.4 mg (0.34 mmol) of **15a** yielded after column chromatography on silica gel (25 × 1.5 cm; R_F = 0.73 with *n*-pentane), removal of *n*-pentane, and bulb-to-bulb distillation (60°C/45 mbar) 19 mg (0.15 mmol, 44%) of **18** (ratio of stereoisomers ca. 3:2 as determined by integration of the ^1H NMR spectrum). GC/MS analysis of the *n*-pentane solution of **18** afforded two signals with *RT* = 5.53 min and *RT* = 5.70 min, each with *m/z* = 126 $[M]^+$.

2,8-Di-*tert*-butyl-6-trimethylsilyl-1,7-diphosphatricyclo[3.2.1.0^{2,7}]-oct-3-ene (19): To a solution of 470 mg (1.2 mmol) of **13a** in 5 mL of toluene 280 μl (2 mmol) of **2a** were added. The reaction mixture was heated to 140 °C in a Schlenk pressure tube under a positive pressure of 5 bar. The reaction was complete after 7 days (monitoring by ^{31}P NMR). Removal of the volatile components and bulb-

to-bulb distillation of the residue (100 °C/10^{-2} mbar) yielded 390 mg crude product. Pure **19** was isolated by column chromatography (silica gel, 40 × 2 cm, *n*-pentane, R_F = 0.47). Further elution with *n*-pentane/diethyl ether yielded 190 mg (0.85 mmol, 71%) dimethyl phthalate of **15a**. Yield of diphsophatricyclooctene **19**: 180 mg (0.55 mmol, 55%) as a colorless solid; m.p. 126 °C

Alternative Route: A mixture of phosphaalkyne **2a** (178 µL, 1.26 mmol) and 80 mg (0.63 mmol) of (*E*)-**18**, which was prepared by a literature procedure[21], in 1.5 mL of toluene was stirred at 140 °C for 7 days. After evaporation of excess phosphaalkyne and solvent, column chromatography (silica gel, 16 × 2.5 cm, *n*-pentane) yielded 32.8 mg (0.1 mmol, 16%) of **19** as a colorless solid. – ^{1}H NMR (C_6D_6): 0.06 [d, $^4J_{H,P}$ = 0.7 Hz, 9 H, Si(CH_3)$_3$], 0.54 [m$_c$, 1 H, 6-H or 8-H], 1.00 [s, 9 H, C(CH_3)$_3$], 1.10 [s, 9 H, C(CH_3)$_3$], 1.20 [m$_c$, 1 H, 6-H or 8-H], 2.90 [m$_c$, 1 H, 5-H], 5.36 [dd, $^3J_{H,H}$ = 9.3 Hz, , $^3J_{H,H}$ = 8.0 Hz, 1 H, 4-H], 6.20 [d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 3-H]. – ^{13}C{^{1}H} NMR (C_6D_6): 0.1 [d, $^3J_{C,P}$ = 3.4 Hz, Si(CH_3)$_3$], 29.2 [pt, $^3J_{C,P}$ = $^3J_{C,P}$ = 6.4 Hz, 2-C(CH_3)$_3$], 31.7 [d, $^3J_{C,P}$ = 6.8 Hz, 8-C(CH_3)$_3$], 33.2 [d, $^2J_{C,P}$ = 8.5 Hz, 8-*C*(CH$_3$)$_3$], 34.0 [d, $^1J_{C,P}$ = 54.3 Hz, C-6], 34.5 [d, $^2J_{C,P}$ = 2.6 Hz, C-5], 34.9 [pt, $^2J_{C,P}$ = $^2J_{C,P}$ = 10.2 Hz, 2-*C*(CH$_3$)$_3$], 42.7 [pt, $^1J_{C,P}$ = $^1J_{C,P}$ = 46.6 Hz, C-2], 62.1 [dd, $^1J_{C,P}$ = 48.3 Hz, $^2J_{C,P}$ = 3.4 Hz, C-8], 121.3 [s, C-4], 129.4 [s, C-3]. – ^{31}P{^{1}H} NMR ($CDCl_3$): −170.1 [d, $^1J_{P,P}$ = 157.6 Hz, P-1 or P-7], −188.2 [d, $^1J_{P,P}$ = 157.6 Hz, P-1 or P-7]. – MS (EI, 70 eV); *m*/*z* (%): 326 (43) [M]$^+$, 311 (6) [M − CH$_3$]$^+$, 269 (10) [M − C$_4$H$_9$]$^+$, 225 (85) [M − C$_5$H$_{10}$P]$^+$, 73 (63) [Si(CH$_3$)$_3$]$^+$, 57 (7) [C$_4$H$_9$]$^+$, 44 (46), 32 (100). – IR (toluene): $\tilde{\nu}$ = 3019, 1614, 1604, 1494, 1460, 738, 734, 722, 698, 693 cm^{-1}. – CHN: $C_{17}H_{32}P_2Si$ (326.47), calcd. C 62.54, H 9.88; found C 62.01, H 9.80.

2-*tert*-Butyl-5-trimethylsilyl-λ^3-phosphinine (22): A sample of **12a** (260 mg, 0.74 mmol) was slowly evaporated in a flash vacuum pyrolysis apparatus (oven temperature: 650 °C, 5·10^{-6} mbar; Pyrex glass tube: 23 × 1 cm). The yellow-orange reaction products were condensed into a cold trap which was cooled with liquid nitrogen. Chromatography (silica gel, 25 × 2 cm, *n*-pentane, R_F = 0.59) yielded 80 mg (0.36 mmol, 49%) of **22** as a colorless solid (m.p. 49 °C). – ^{1}H NMR (C_6D_6): 0.18 [s, 9 H, Si(CH_3)$_3$], 1.42 [d, $^4J_{H,P}$ = 1.2 Hz, 9 H, C(CH_3)$_3$], 7.50–7.75 [m, 2 H], 8.90–9.05 [m, 1 H]. – ^{13}C{^{1}H} NMR ($CDCl_3$): −1.2 [s, Si(*C*H$_3$)$_3$], 32.7 [d, $^3J_{C,P}$ = 11.7 Hz, C(*C*H$_3$)$_3$], 38.7 [d, $^2J_{C,P}$ = 18.9 Hz, *C*(CH$_3$)$_3$], 129.7 [d, $^3J_{C,P}$ = 11.7 Hz, C-4], 133.7 [d, $^2J_{C,P}$ = 19.8 Hz, C-3], 144.1 [d, $^2J_{C,P}$ = 12.6 Hz, C-5], 159.0 [d, $^1J_{C,P}$ = 56.6 Hz, C-6], 184.9 [d, $^1J_{C,P}$ = 58.3 Hz, C-2]. – ^{31}P{^{1}H} NMR (C_6D_6): 201.6 [s]. – MS (EI, 70 eV); *m*/*z* (%): 224 (15) [M]$^+$, 209 (51) [M − CH$_3$]$^+$, 73 (100) [Si(CH$_3$)$_3$]$^+$, 57 (4) [C$_4$H$_9$]$^+$. – IR (KBr): $\tilde{\nu}$ = 2955, 1456, 1372, 1305, 1247, 1089, 1035, 899, 839, 752 cm^{-1}.

{7-*tert*-Butyl-3,9-bis(trimethylsilyl)-8-phosphatricyclo[4.2.2.0^{2,5}]-deca-7,9-diene}pentacarbonyl-tungsten (23): A solution of pentacarbonyltungsten · thf was prepared by irradiation (HPK, 125 W, Phillips) of a solution of 0.28 g (0.8 mmol) of hexacarbonyltungsten in 60 mL of THF for 45 min. To this solution 0.23 g (0.66 mmol) of **12a** in 5 mL of THF were added and the mixture was stirred at room temperature for 20 hours. The solvent was then removed under reduced pressure and the yellow residue was chromatographed with *n*-pentane (silica gel, 27 × 2.5 cm, R_F = 0.47) after filtration over Celite. After elution of 30 mg of excess hexacarbonyltungsten, complex **23** was isolated as a yellow oil (360 mg, 0.53 mmol, 80%). – ^{1}H NMR (C_6D_6): 0.01 [s, 9 H, Si(CH_3)$_3$], 0.12 [s, 9 H, Si(CH_3)$_3$], 0.80–0.95 [m, 1 H, 3-H], 1.15 [s, 9 H, C(CH_3)$_3$], 1.20–1.30 [m, 1 H, 4-H], 1.60–1.70 [m, 1 H, 4-H], 2.00–2.15 [m, 1 H, 5-H], 2.45–2.55 [m, 1 H, 2-H], 3.92 [ddd, $^3J_{H,P}$ = 11.0 Hz, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 3.8 Hz, 1 H, 6-H], 4.02 [ddd, $^2J_{H,P}$ = 8.9 Hz, $^3J_{H,H}$ = 3.1 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H, 1-H], 6.52 [d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 10-H]. – ^{13}C{^{1}H} NMR (C_6D_6): −3.6 [s, Si(*C*H$_3$)$_3$], −2.1 [s, Si(CH_3)$_3$], 21.3 [s, C-4], 21.9 [s, C-2, C-3, or C-5], 30.1 [d, $^3J_{C,P}$ = 12.1 Hz, C(CH_3)$_3$], 36.3 [d, $J_{C,P}$ = 8.0 Hz, C-2, C-3, or C-5], 39.5 [d, $J_{C,P}$ = 20.1 Hz, C-2, C-3, or C-5], 40.8 [d, $^2J_{C,P}$ = 4.0 Hz, *C*(CH$_3$)$_3$], 51.6 [d, $^2J_{C,P}$ = 9.6 Hz, C-6], 59.5 [s, C-1], 142.6 [d, $^3J_{C,P}$ = 20.9 Hz, C-10], 146.9 [d, $^2J_{C,P}$ = 10.4 Hz, C-9], 196.4 [d, $^2J_{C,P}$ = 8.8 Hz, $^1J_{C,W}$ = 126.1 Hz, CO$_{eq}$], 199.6 [d, $^2J_{C,P}$ = 28.9 Hz, CO$_{ax}$], 211.6 [d, $^1J_{C,P}$ = 41.0 Hz, C-7]. – ^{31}P{^{1}H} NMR (C_6D_6): 162.4 [s, $^1J_{P,W}$ = 228.3 Hz]. – MS (EI, 70 eV); *m*/*z* (%): 674 (54) [M]$^+$, 618 (5) [M − 2 CO]$^+$, 590 (4) [M − 3 CO]$^+$, 562 (4) [M − 4 CO]$^+$, 534 (9) [M − 5 CO]$^+$, 492 (18), 463 (17) [M − 5 CO − Si(CH$_3$)$_3$]$^+$, 462 (74) [M − 4 CO − C$_5$H$_9$P]$^+$, 432 (15), 73 (100) [Si(CH$_3$)$_3$]$^+$, 57 (10) [C$_4$H$_9$]$^+$. – HRMS (EI, 70 eV): $C_{24}H_{35}O_5PSi_2W$ calcd. 674.1276, found 674.1271. – IR (film): $\tilde{\nu}$ = 2956, 2868, 2368, 2070, 1940, 1587, 1475, 1361, 1246, 1154, 1079, 879, 832, cm^{-1}.

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