Polyphospha[*m*]cyclo[*n*]carbons ($m+n=15$, 20, 25, 30, 40)

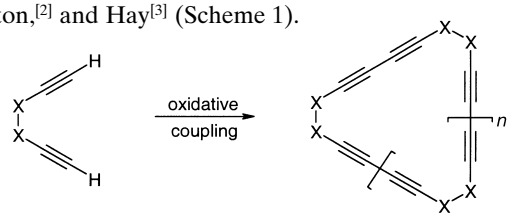
Gottfried Märkl,* Thomas Zollitsch, Peter Kreitmeier, Michael Prinzhorn, Sabine Reithinger, and Ernst Eibler[a]

Abstract: The Eglinton reaction of diethynyl(2,4,6-tri-*tert*-butylphenyl)phosphane (**7a**), that is, the oxidative coupling of 3, 4, 5, or 6 of these phosphane units, affords a mixture of the 15-, 20-, 25-, and 30-membered macrocycles **8**, **9**, **10**, and **11**. Pure triphosphacyclopentadecahexayne **8** and pentaphosphacyclopentacosadecayne **10** were isolated by HPLC, while the mixture of **9** and **11** could not be separated. Multistep syntheses of open-chain polyphosphapolyynes are described, whose intra- or intermolecular coupling yields the phosphamacrocycles **8**, **9**, and **11**. Eglinton coupling of bis(ethynylphosphanyl)butadiyne (**17**) gave a mixture of the 20-membered tetraphosphacycloicosaoctayne **9**, the 30-membered hexaphosphacyclotriacontadodecayne **11**, and the 40-membered octaphosphacyclotetracontahexadecayne **23** as result of a di-, tri-, and tetramerization, respectively. Intramolecular coupling of bis[(ethynylphosphanyl)butadiynyl]phosphane **25a** gave **8**, while intermolecular coupling gave **11**; these two compounds were isolated by chromatography to give yields of 70 and 5%, respectively. The open-chain tetraphosphaeikosaoctayne **28** couples intramolecularly to give **9** and intermolecularly to give the 40-membered octaphosphacyclotetracontahexadecayne **23**, which was isolated in the pure form. Octaphosphatetracontahexadecayne **32** cyclized to give **23**, exclusively. The temperature-dependent ^{1}H and ^{31}P NMR spectra of the open-chain and cyclic ethynylphosphanes indicated a lowering of the inversion barrier of the tertiary phosphanes from the usual 130–140 kJ mol^{-1} to 65–75 kJ mol^{-1}. Ab initio calculations proved that the dramatic reduction of the inversion barriers results from the interaction of the lone pair on phosphorus with the π orbitals of the triple bonds in the planar transition state during inversion. The situation is comparable with the dramatic reduction of the P inversion barrier in phospholes, because of the planar, aromatic transition state. The polyphospha[*m*]cyclo[*n*]carbons may be considered as precursors to cyclic P_mC_n systems.

Keywords: coupling reactions · inversion barriers · macrocycles · NMR spectroscopy · phosphacyclopolyynes · phosphanes

Introduction

The most important synthetic approach to macrocyclic polyynes with diacetylenic links **2** is the oxidative coupling of terminal bisacetylenes **1** by the various methods of Glaser,[1] Eglinton,[2] and Hay[3] (Scheme 1).



1 **2**

Scheme 1. Formation of macrocyclic polyynes **2** with butadiyne-1,3-diyl bridges by oxidative coupling of **1**.

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F. Sondheimer et al.[4, 5] had already achieved the synthesis of [18]annulene by the Eglinton coupling of 1,5-hexadiyne (**1a**; $-X-X- = -CH_2CH_2-$). Dehydrobenzannulenes **2b**[6] are obtained by the oxidative coupling of 1,2-diethynylbenzene (**1b**).

de Meijere et al. described the formation of cyclic polyynes **2c**[7] (*n*-rotanes) with spirocyclopropane-links between 1,3-diyne units by the coupling of 1,1-diethynylcyclopropanes **1c** ($-X-X- =$ 1,1-cyclopropane).

Expanded radialenes **2d** have been synthesized by stepwise oxidative coupling of the diynes **1d** by Diederich et al.[8]

The macrocyclic polyynes became even more fascinating, when Diederich, McElvany et al. observed, by laser-desorption Fourier transform mass spectrometric experiments, that [4*n*+2]- and [4*n*]dehydroannulenes **2e**, $n=1-3$ ($n=3$, $C_{30}(CO)_{10}$)[9] and dehydroannulenes **2f**, $n=1-3$ ($n=3$, $C_{30}(C_{14}H_{10})_5$),[10] the annelation products of cyclobutene-1,2-dione and the anthracene, respectively, form cyclo[*n*]carbon ions C_n^+ ($n=18$, 24, 30) and C_n^- ($n=18$, 24, 30), which coalesce to give fullerenes, through the elimination of CO and anthracene, respectively.[12] Evidently, the size of the full-

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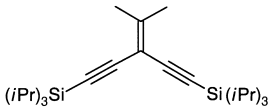
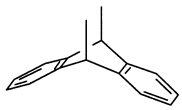
erenes can be determined by the size of the cyclo[*n*]carbon precursors.

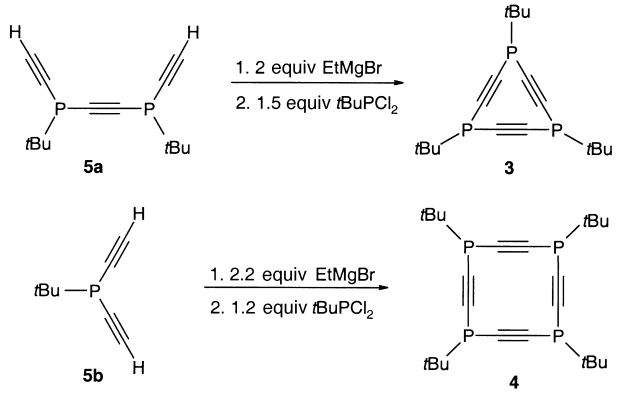
Macrocyclic polyynes with diacetylene units and isopropyl links (**2g**) are also accessible by Cadiot–Chodkiewicz coupling reactions.[11] Table 1 presents the coupling products **2** from various substrates **1**.

In a similar reaction to their synthesis of the [*n*]pericyclines,[13] Scott et al.[14] achieved the first synthesis of the phosphacyclopolyynes tri-*tert*-butyl-1,4,7-triphospha[3]pericycline (**3**) and tetra-*tert*-butyl-1,4,7,10-tetraphospha[4]pericycline (**4**) by coupling of the bis-Grignard derivatives of **5a** and **5b** with *tert*-butyldichlorophosphane (Scheme 2). The expected stereoisomers of **3** and **4** could be isolated because of the configurational stability of the pyramidal phosphines. The structures of the *cis*,*cis*,*trans*-1,4,7-tri-*tert*-butyl-1,4,7-triphospha[3]pericycline and the *cis*,*trans*,*cis*,*trans*-1,4,7,10-tetra-*tert*-butyl-1,4,7,10-tetraphospha[4]pericycline were obtained by X-ray analysis. Scott discussed the tetraphospha[4]pericycline **4** as a possible precursor of phosphacarbons P_mC_n.

Abstract in German: *Die Eglinton-Reaktion von Diethinyl(2,4,6-tri-tert-butylphenyl)phosphan (**7**) liefert durch oxidative Kupplung von 3, 4, 5 und 6 Phosphan-Bausteinen ein Gemisch aus den 15-, 20-, 25- und 30-gliedrigen Makrocyclen **8**, **9**, **10** und **11**. Mittels HPLC gelingt die Abtrennung von Triphosphacyclopentadecahexain **8** und Pentaphosphacyclopentacosadecain **10** in reiner Form; **9** und **11** können nicht getrennt werden. Es werden vielstufige Synthesen offenkettiger Polyphosphapolyine beschrieben, deren inter- bzw. intramolekulare Kupplung gezielt die Phosphamakrocyclen **8**, **9** und **11** liefert. Bei der Eglington-Kupplung von Bis(ethinylphosphanyl)-butadiin **17** wird durch Di-, Tri- und Tetramerisierung ein Gemisch aus dem 20-gliedrigen Tetraphosphacycloeikosaoctain **9**, dem 30-gliedrigen Hexphosphacyclotriacontadodecain **11** und dem 40-gliedrigen Octaphosphacyclotetracontahexadecain **23** gebildet. Bis[(ethinylphosphanyl)butadiinyl]phosphan **25a** liefert durch intramolekulare Kupplung **8** und durch intermolekulare Kupplung **11**, die chromatagraphisch in 70- bzw. 5-proz. Ausb. rein erhalten werden. Das offenkettige Tetraphosphaeikosaoctain **28** wird intramolekular zu **9** und intermolekular zum 40-gliedrigem Octaphosphacyclotetracontahexadecain **23** gekuppelt, die chromatographisch getrennt werden. Das Octaphosphatetracontahexadecain **32** cyclisiert ausschließlich zu **23**. Die temperaturabhängigen ^{1}H-NMR- und ^{31}P-NMR-Spektren der offenkettigen wie der cyclischen Ethinylphosphane zeigen, dass die Inversionsbarrieren der tertiären Phosphane, die im Normalfall bei 130–140 kJ mol^{-1} liegen, auf 65–75 kJ mol^{-1} abgesenkt werden. Ab initio-Rechnungen bestätigen, dass diese dramatische Reduktion der Inversionsbarrieren durch die Wechselwirkung des Phosphinlonepairs mit den π-Orbitalen der Dreifachbindungen im planaren Übergangszustand der Inversion zustandekommt. Diese Situation ist vergleichbar mit der ebenfalls dramatischen Verringerung der P-Inversionsbarriere in Phospholen durch den planaren, aromatischen Übergangszustand. Die Polyphospha[m]cyclo[n]carbone können als Vorstufen cyclischer P_mC_n-Systeme aufgefasst werden.*

Table 1. Macrocyclic polyynes **2** with different X–X bridges.

1, **2**	–X–X–	*n*	Ref.
1a, **2a**	$-CH_2CH_2-$	1, 2, 3, 4	[4, 5]
1b, **2b**		0, 1,2	[6]
1c, **2c**		3, 4, 6	[7]
1d, **2d**		2, 3, 4	[8]
1e, **2e**		1, 2, 3	[9]
1f, **2f**		1	[10]
2g		1, 2, 3, 4	[11]

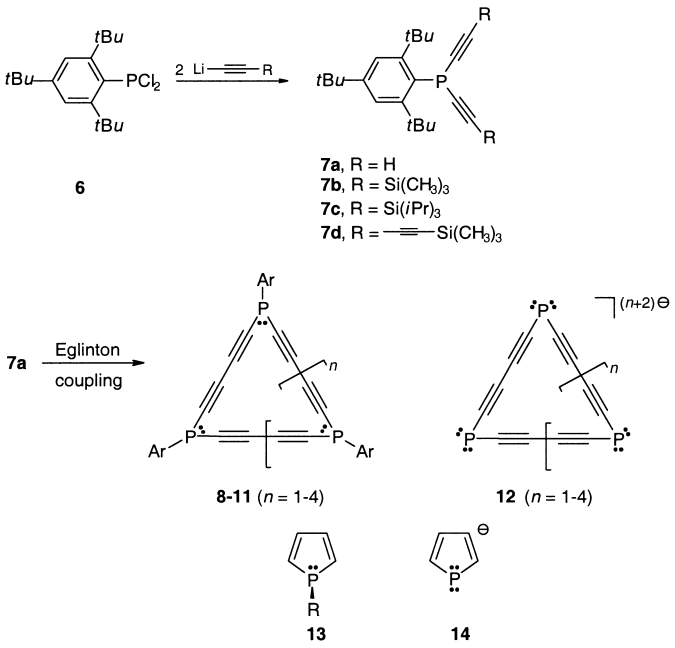


Scheme 2. Synthesis of 1,4,7-triphospha[3]pericycline (**3**) and 1,4,7,10-tetraphospha[4]pericycline (**4**).

In this paper we describe the synthesis of macrocyclic polyphosphapolyynes **8**–**11** with diacetylenic links by a one-pot oxidative coupling reaction of diethynyl(2,4,6-tri-*tert*-butylphenyl)phosphane (**7a**) or by subsequent coupling steps via open-chained polyphosphapolyynes (Scheme 3).

The triphosphacyclopentadecahexayne **8**, $n=1$, and the pentaphosphacyclopentacosadecayne **10**, $n=3$, can be described as formally 18π and 30π systems, respectively.

The question of aromaticity of these systems is similar to that of the phospholes **13**, which are not aromatic because of the pyramidal structure of the tervalent phosphorus.[15] However, Mislow[16] demonstrated a dramatic lowering of the inversion barrier in phospholes ($\approx$16 kcal mol^{-1} vs. $\approx$30 kcal mol^{-1} in *tert*-phosphanes) as result of the aromaticity of the planar transition state. If the inversion of the pyramidal phosphines in the polyphosphacyclopolyynes occurs more or less simultaneously, the transition states of **8** and **10**, which are similar to that of **13**, could be aromatic and the phosphane inversion energy barriers should be reduced.



Scheme 3. Eglinton coupling of **7a** to give polyphosphacyclopolyynes **8**–**11**, polyphosphacyclopolyyne polyanions **12**, and comparison with phospholes **13** and phospholyl anions **14**.

In a similar manner to the phospholyl anions **14**,[17] the phosphides **12** ($n = 1, 3$) could be expected to be aromatic 18π and 30π systems per se.

Since the thermal cleavage of P–aryl bonds has been demonstrated (the P–aryl bond in 1-aryl-1,2(1,4)-dihydrophosphinines can be cleaved thermally to give λ^3-phosphinines),[18] the phosphacyclopolyynes are possible candidates for the access of polyphosphacarbons ($C_{12}P_3$, $C_{16}P_4$, $C_{20}P_5$, $C_{24}P_6$).

Results and Discussion

Eglinton coupling of diethynylphosphane (7a)

*Synthesis of **7a***: The stability of tervalent phosphorus under the reaction conditions is important for the oxidative coupling of ethynylphosphanes. This requirement is fulfilled by the 2,4,6-tri-*tert*-butylphenyl-substituted phosphanes[18] (Scheme 3).

(2,4,6-Tri-*tert*-butylphenyl)-bis[(trimethylsilyl)ethynyl]-phosphane (**7b**) was obtained in 50–60% yield by the reaction of two equivalents of lithium trimethylsilylacetylide ($R = SiMe_3$) with 2,4,6-tri-*tert*-butylphenyldichlorophosphane (**6**) in THF at $-78\,^\circ C$ (Scheme 4). Desilylation of **7b** either with NaOH/MeOH[20] or with TBAF/THF[21] yielded the phosphane **7a** (70%). The synthesis of **7a** is more straightforward by substitution of **6** with the mono-Grignard compound of acetylene itself in THF at room temperature to give colorless crystals of phosphane **7a** in 46–52% yield.

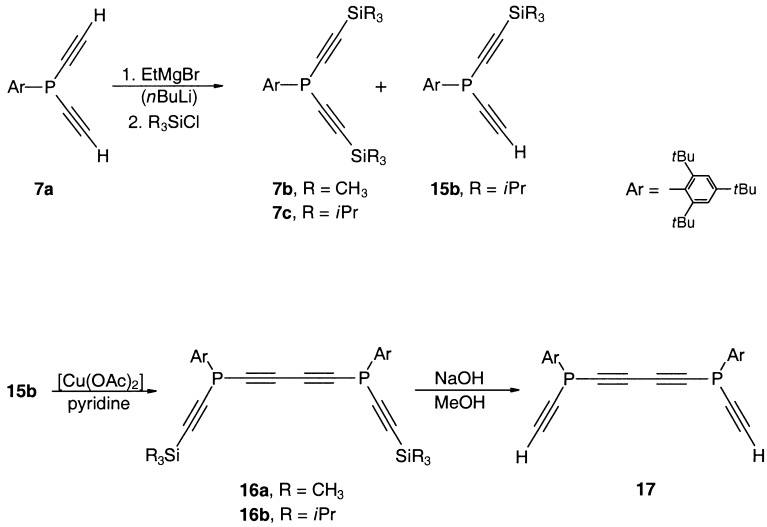
*Eglinton coupling of diethynylphosphane **7a***: A solution of **7a** (10 mmol) in a mixture of pyridine (60 mL) and methanol (30 mL) was added to a solution of [$Cu(OAc)_2$] (60 mmol) in pyridine (250 mL) over a period of 15 min. The stirred solution was heated to $60\,^\circ C$ for 3 h. The solvent was evaporated and the residue extracted with benzene to give a dark yellow product (1.30 g from 3.26 g **7a**), which is soluble in nonpolar solvents (e.g., benzene, toluene, $CHCl_3$, CCl_4), and relatively insoluble in polar solvents (e.g., methanol, CH_3CN, CH_3NO_2). According to the FD-MS (toluene) and the ^{31}P NMR data, a mixture of coupling products had been formed that was partially separated by HPLC (Scheme 3).

It was possible to isolate the 1,6,11-triphosphacyclopentadeca-2,4,7,9,12,14-hexayne (**8**, $n = 1$) and the 1,6,11,16,21-pentaphosphacyclopentacosa-2,4,7,9,12,14,17,19,22,24-decayne (**10**, $n = 3$, "pentamer"), in pure form; however, the mixture of the tetramer **9** ($n = 2$) and hexamer **11** ($n = 4$) could not be separated (Scheme 3).

The HPLC separation of the coupling mixture **8**–**11** is time consuming and only a few milligrams of the pure products were obtained. For this reason, we decided to synthesize the corresponding open-chained polyphosphapolyynes and to study their cyclizing intra- and intermolecular Eglinton coupling reactions. The analytical and spectroscopic data of the phosphacyclopolyynes **8**, **9**, and **11** prepared this way will be presented for this reaction. Only the pentaphosphacyclopentacosaoctayne **10**, not obtained by the stepwise oxidative coupling reactions, is described in the Experimental Section under the Eglinton coupling of **7a**.

Oxidative coupling of bis(ethynylphosphanyl)butadiyne (17)

*Synthesis of **17** by the Eglinton coupling of diethynylphosphane **15b***: One strategy for the synthesis of **17** is the oxidative coupling of the monosilyl-protected diethynylphosphanes **15a** and **15b** to give **16a** and **16b** followed by a twofold desilylation (Scheme 4).



Scheme 4. Synthesis of bis[ethynyl(2,4,6-tri-*tert*-butylphenyl)phosphanyl]butadiyne (**17**) from diethynyl(2,4,6-tri-*tert*-butylphenyl)phosphane (**7a**).

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The monosilylation of diethynylphosphane **7a** was rather difficult. Metallation of **7a** either with one equivalent EtMgBr or *n*BuLi at −78 °C followed by reaction with trimethylchlorosilane yielded a yellow, crystalline reaction product that was a mixture of the bis-trimethylsilyl-substituted derivative **7b**, the desired monosilylated phosphane **15a**, and the starting material **7a** (ratio 0.7:2.0:1.2) according to the EI-MS, and ^{1}H and ^{31}P NMR data. This mixture could not be separated (Scheme 4).

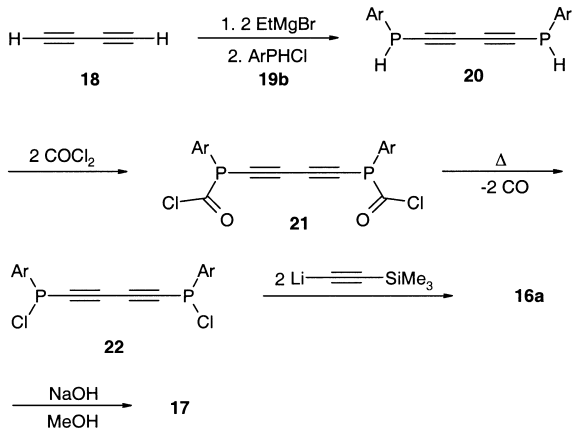
When triisopropylchlorosilane was used in the same procedure, a mixture of **7c**, **15b**, and **7a** was obtained in about the same ratio (1.0:2.0:1.1). We were able to separate this mixture by column chromatography on silica gel.

The Eglinton coupling of **15b** with [Cu(OAc)$_2$] in pyridine at room temperature after hydrolysis and chromatography on silica gel (CH_2Cl_2/hexane, 1:6) produced **16b** in 84% yield.

A modification of the Eglinton coupling by de Meijere[22] with four equivalent [Cu(OAc)$_2$] and three equivalents CuCl in pyridine gave **16b** in ≤95% yield. By desilylation of **16b** with TBAF/THF at −78 °C, **17** was obtained in 90% yield.

*Total synthesis of **17** from 1,3-butadiyne (**18**)*: Since 1,3-butadiyne (**18**) is relatively easy to obtain by dehydrochlorination of 1,4-dichloro-2-butyne,[23] we attempted the synthesis of **17** from **18**.

The bis-Grignard compound of **18** (reaction of **18** with two equivalents of EtMgBr) was treated with two equivalents of (tri-*tert*-butylphenyl)monochlorophosphane **19b**[24] at −78 °C to give bis[(2,4,6-tri-*tert*-butylphenyl)phosphanyl]butadiyne (**20**) as colorless crystals in 33% yield (Scheme 5).

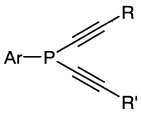
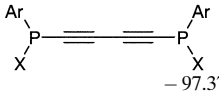
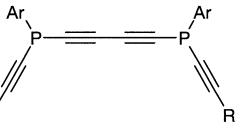


Scheme 5. Synthesis of **17** from 1,3-butadiyne (**18**).

With a twofold excess of phosgene, the secondary phosphine **20** gave the butadiynediylbis[(2,4,6-tri-*tert*-phenylphosphanecarbonylchloride] (**21**, yield 51%), which can be decarbonylated by heating to 160–170 °C to give the butadiynediylbis[(2,4,6-tri-*tert*-butylphenyl)phosphinouschloride] (**22**). The treatment of chlorophosphine **22** with trimethylsilylethynyl-MgBr at 0 °C afforded the bis-trimethylsilyl derivative **16a**. Desilylation with 2 N NaOH/MeOH gave **17** in 55% yield [FD MS(CH_2Cl_2), *m*/*z* 650; ^{31}P{^{1}H} NMR, $\delta = -67.88$].

*^{1}H and ^{31}P NMR spectra of the alkynylphosphanes **7**, **15**, **16**, **17**, and **20***: The ^{31}P NMR data of the bis-alkynylphosphanes **7** and **15** and the 1,6-diphosphanes **20**, **16**, and **17** are given in Table 2.

Table 2. ^{31}P{^{1}H} NMR-data of **7**, **15**, **16**, **17**, and **20** (162 MHz, $CDCl_3$).

	Compound	δ (^{31}P NMR)
		
7a	R = R′ = H	−71.61 (s)
7b	R = R′ = Si(CH$_3$)$_3$	−70.38 (s)
7c	R = R′ = Si(*i*Pr)$_3$	−68.85 (s)
15a	R = Si(CH$_3$)$_3$, R′ = H	−71.11 (s)
15b	R = Si(*i*Pr)$_3$, R′ = H	−70.37 (s)
		
20	X = H	−97.37 (d, ^1J(P,H) = 251.2 Hz)
		
16a	R = Si(CH$_3$)$_3$	−67.33 (s)
16b	R = Si(*i*Pr)$_3$	−66.53; −66.29
17	R = H	−67.88

While the ^{31}P{^{1}H} NMR data of all bis-alkinylphosphanes are singlets in the range of $\delta = -66.29$ to −71.61, the appearance of two signals for **16b** with an integration ratio of 1:1.3 has to be interpreted. The ^{31}P NMR spectrum of **16b** was temperature dependent. Figure 1a and 1b depict the ^{1}H

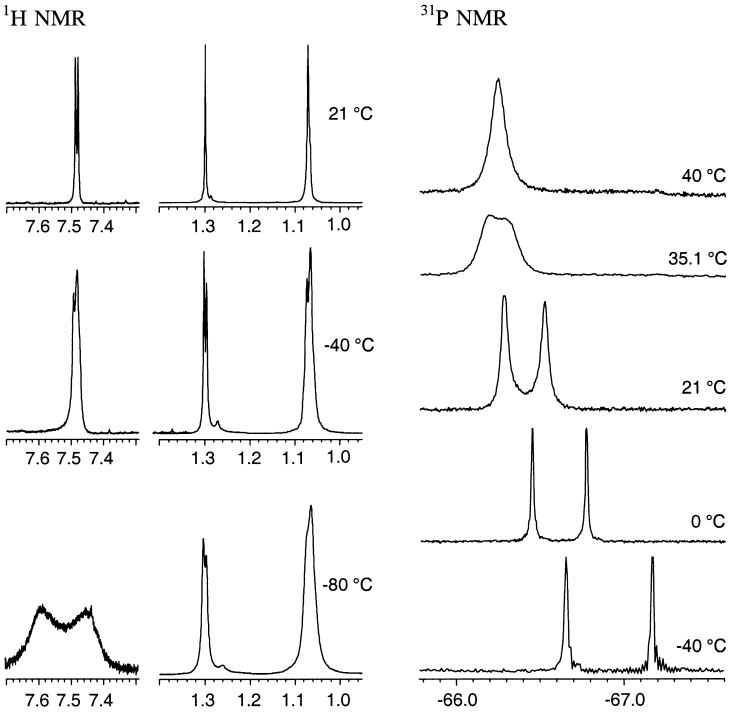


Figure 1. ^{1}H NMR spectra (400 MHz, [D$_8$]THF) (left) and ^{31}P{^{1}H} NMR spectra (162 MHz, THF) (right) of **16b** at various temperatures.

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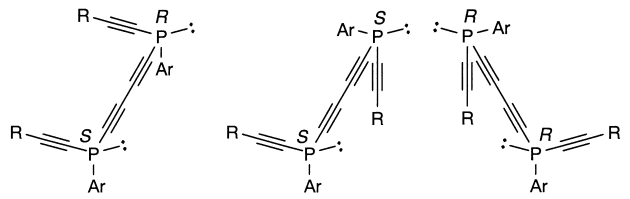
and ^{31}P NMR spectra of **16b** from +21 to −80 °C and from +40 to −40 °C, respectively.

In the ^{1}H NMR spectrum, the signals of *i*Pr–H ($\delta = 1.07$ (s)) and *p*-*t*Bu ($\delta = 1.30$ (s)) split at −40 °C to become doublets. The doublet of the *m*-aryl–H ($\delta = 7.48$, d, ^{4}J(P,H) = 3.2 Hz) at −80 °C changes to two broad signals at $\delta = 7.45$ and 7.60.

The ^{31}P NMR spectra at different temperatures were more informative: the two signals at 21 °C ($\delta = -66.53$ and −66.29) become sharper at 0 °C ($\delta = -67.26$ and −66.73) and are baseline separated at −40 °C ($\delta = -67.26$ and −66.73). These values do not change significantly at −80 °C ($\delta = -67.74$ and −66.75). As the temperature is increased the two signals coalesce at +35.1 °C and appear as a broad singlet at +40 °C.

The explanation of this phenomena is a dramatic reduction of the inversion barrier of the pyramidal phosphine phosphorus in the bis-alkynylphosphine **16b**.

The two ^{31}P NMR signals of **16b** at 21 °C belong to the diastereomeric *meso* and *racemic* forms.



At 35.1 °C the signals coalesce, which means that the phosphane inversion is now so fast that the signals are no longer separated. We observe one broad signal at 40 °C because the high rate of inversion produces only an averaged value. We calculated the inversion barrier according to the method of Friebolin and Mannschreck.[25,26]

With $T_c = 35.1 \pm 2$ °C, the following $\Delta G^{\neq}$ values for the reversible inversions were obtained.

$\Delta G^{\neq}_{A\rightarrow B} = 65.81 \pm 0.4$ kJ mol^{-1}

$\Delta G^{\neq}_{B\rightarrow A} = 65.14 \pm 0.4$ kJ mol^{-1}

Usually the $\Delta G^{\neq}$ values of the inversion barriers of alkylphosphanes, arylphosphanes, and alkylarylphosphanes are ≈130–140 kJ mol^{-1}.[27] Electronegative substituents at the phosphorus atom increase the inversion barriers, while electropositive substituents diminish them (for dimethylfluorophosphane $\Delta G^{\neq} \approx 226$ kJ mol^{-1},[28] and for trimethylsilylisopropylphenylphosphane $\Delta G^{\neq} \approx 80$ kJ mol^{-1}).[29]

To our knowledge, the value of $\Delta G^{\neq} \approx 65$ kJ mol^{-1} for **16b** is one of the lowest known for phosphane inversions.

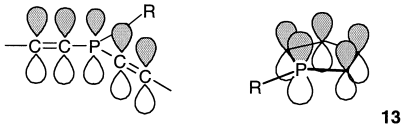
Ab initio calculations possibly give an explanation of this phenomena. According to these results, the pyramidal inversion of ethynylphosphanes is supported by the interaction of the phosphorus lone pair with the π-orbitals of the triple bonds in the planar transition state. The geometries of PH_3, $H_2P(C{\equiv}CH)$, and $HP(C{\equiv}CH)_2$ were calculated for the pyramidal and the planar geometries with DFT. All calculations were carried out with Becke's hybrid functional B3LYP and a 6-31G** basis set.[30]

The energy barriers (in Hartree) for the ground state (GS) and the transition state (TS) of the phosphane inversions are given in Table 3. These values at least qualitatively confirm the decrease of the $\Delta G^{\neq}$ values of the inversion barriers as the number of triple bonds increases.

Table 3. Calculated energy barriers for the inversion of PH_3, $H_2P(C{\equiv}CH)$, and $HP(C{\equiv}CH)_2$.

	PH_3	$H_2P(C{\equiv}CH)$	$HP(C{\equiv}CH)_2$
GS [Hartree]	−343.146208988 (C_{3v})	−419.291730569 (C_s)	−495.436500384 (C_s)
TS [Hartree]	−343.093123849 (D_{3h})	−419.241986342 (C_{2v})	−495.391053894 (C_{2v})
ΔE [Hartree]	0.05308514	0.04974423	0.04544649
ΔE [kJ mol^{-1}]	139.5	130.7	119.4

The stabilization of the planar transition state can be understood by an overlap of the π orbitals of the triple bonds with the P lone pair. The situation is comparable with that of



the phospholes **13**. As already mentioned, Mislow[31] found that the inversion barriers of **13** are lowered considerably by the formation of a planar aromatic transition state.

The overlapping of π orbitals is also the result of the reduction of the inversion barrier by aryl groups ($C_6H_5P(CH_3)C_3H_7$, $\Delta G^{\neq} = 134$ kJ mol^{-1}; *c*-$C_6H_{11}P(CH_3)C_3H_7$, $\Delta G^{\neq} = 149$ kJ mol^{-1})[32] and by carbonyl groups ($H_3CP(CHO)_2$, $\Delta G^{\neq} = 79$ kJ mol^{-1}).[33]

Consequently, the singlet in the ^{31}P NMR spectrum of **17** at room temperature must be interpreted by the configuration of the tervalent pyramidal phosphorus in **16** being even less stable; therefore, the two diastereomers can not be detected at 21 °C. Indeed, the coalescence temperature T_c for the bisterminal acetylene **17** was 2.9 ± 2 °C. Already at −20 °C, the ^{31}P NMR spectrum ([D$_8$]THF) splits into two singlets ($\delta = -68.38$ and −68.41) from the diastereomers of **17**, and at −60 °C the two signals are baseline separated ($\delta = -68.93$ and −69.01).

*Oxidative Eglinton coupling of bis(ethynylphosphanyl)butadiyne **17** to give tetraphosphacycloicosaoctayne **9** and hexaphosphacyclotriacontadodecayne **11***: The Eglinton coupling of **17** in the de Meijere modification yielded a solid yellow product after column chromatography. According to the MS and the ^{31}P NMR spectroscopic data, the reaction product was a mixture of the 20-membered tetraphosphacycloicosaoctayne **9** (86–87 %), the 30-membered hexaphosphatriacontadodecayne **11** (11.1 %), and the 40-membered octaphosphacyclotetracontahexadecayne **23** (2.4 %) as result of oxidative dimerization, trimerization, and tetramerization, respectively

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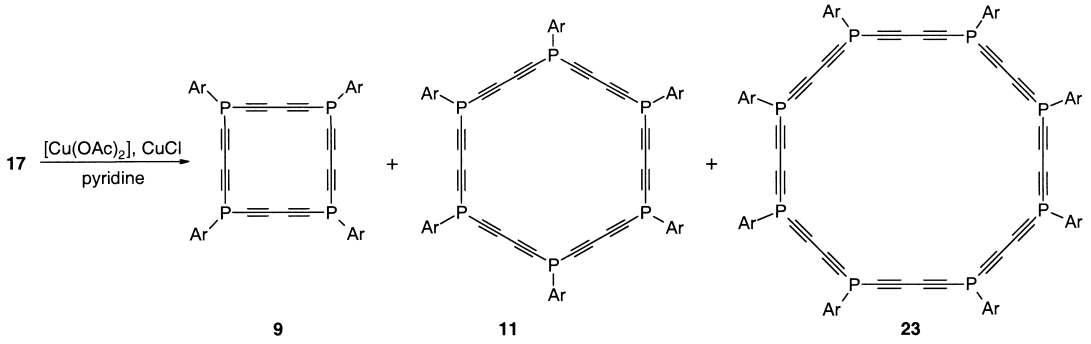


Scheme 6. Formation of the 20-, 30-, and 40-membered polyphosphacyclopolyynes **9**, **11**, and **23** by Eglinton coupling of **17**.

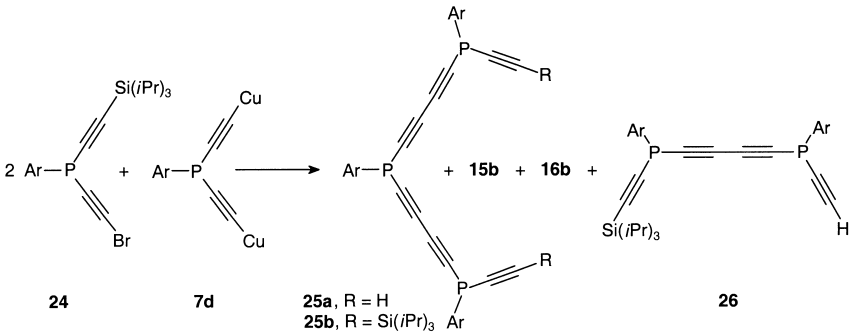
[^{31}P NMR (162 MHz, $C_2D_2Cl_4$) at 120 °C: δ(**9**) = −65.24, δ(**11**) = −63.53, δ(**23**) = −63.03] (Scheme 6).

Since **9**, **11**, and **23** can be obtained in a pure form by different approaches (as described in the following sections), the separation of the reaction mixture was not investigated.

Oxidative coupling of phosphane 25a to give triphosphacyclopentadecahexayne 8 and hexaphosphacyclotriacontadodecayne 11

*Synthesis of **25a***: The strategy for the synthesis of **25a** is the Cadiot–Chodkiewicz coupling of (bromethynyl)(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphane (**24**) with the copper salt **7d** of diethynyl(2,4,6-tri-*tert*-butylphenyl)phosphane (**7a**) followed by desilylation (Scheme 7).

A solution of **15b** in THF was treated with an aqueous solution of NaOBr.[34] Chromatographic purification afforded



Scheme 7. Synthesis of **25a, 25b** by Cadiot–Chodkiewicz coupling.

24 as a colorless viscous oil in 44% yield. The preferred method was the reaction of the lithium acetylide of **15b** (treatment of **15b** with *n*BuLi at −78 °C) with *p*-toluenesulfonylbromide[35] (yield 75%). The spectroscopic data of **24** confirmed the structure (see the Experimental Section).

Several different procedures for the Cadiot–Chodkiewicz coupling have been described in the literature. The reaction of diacetylene **7a** with CuCl and $NH_2OH \cdot HCl$ in THF/isopropylamine (v/v = 1:1) and addition of **24** in THF at room temperature gave the desired hexayne **25b** in only 11% yield. Byproducts were **15b** (6%), the tetrayne **16b** (18%), which is an autocoupling product of **24**, and the hitherto unknown [ethynyl(2,4,6-tri-*tert*-butylphenyl)phosphanyl]{2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphanyl}butadiyne **26** (1%), which is the monocoupling product of **24** with **7a**.

Since the yield of **25b** could not be improved by several variations of this method, we studied the Pd/Cu-catalyzed coupling according to Elbaum et al.[36] However, this method (catalytic amounts of CuI and $[Pd(CH_3CN)_2]$ in isopropylamine) produced a similar composition of reaction products, and the yield of **25b** did not increase.

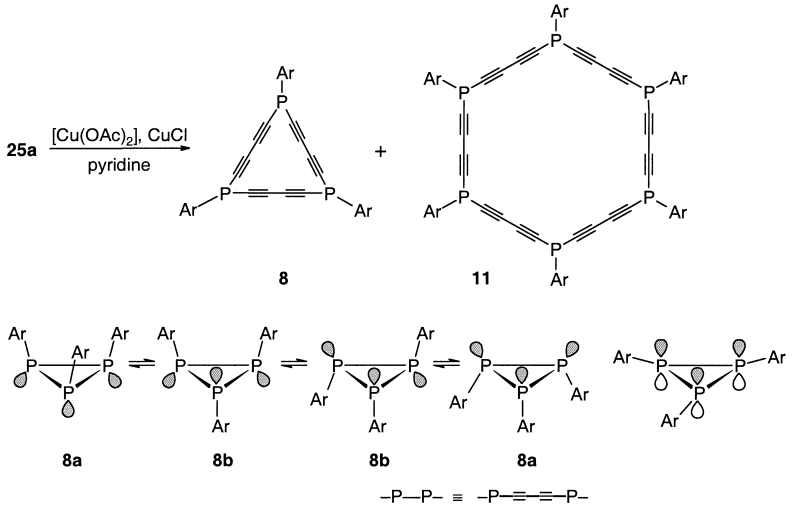
The best approach to **25b** started from the isolated bis-Cu-salt **7d** that can be prepared according to Scott and Cooney[35] by treatment of **7a** with *n*BuLi (2.1 mol) in THF at −78 °C and then with CuCl (2.1 mol) at 0 °C. After replacement of the THF by pyridine, the bromoacetylene **24** was added slowly to the Cu salt **7d**.

The hexayne **25b** was isolated by column chromatography in 27% yield. The byproducts were formed in smaller quantities (**16b** in 10%, **24** in 4% yield, while **15b** could not be detected at all). The phosphane **25a** was obtained by desilylation of **25b** with TBAF/THF at −78 °C in 63% yield as yellow crystals.

*Oxidative Eglinton coupling of **25a***: The oxidative coupling of **25a** according to the modified Eglinton method (as discussed above) can be expected to be either intramolecular to give the 15-membered ring **8** or intermolecular by formation of the 30-membered ring **11** (Scheme 8).

The crude, brown, solid reaction product yielded after chromatography (silica gel, CH_2Cl_2/hexane 1:6) an orange-yellow powder. Repeated chromatography (silica gel, CH_3CN/*n*-hexane 1:200) gave orange-yellow crystals of **8** (m.p. 78–84 °C) and yellow crystals of **11** [m.p. ≈ 175 °C (decomp)].

*Triphosphacyclopentadecahexayne **8***: According to the spectroscopic data, the product with the low melting point was the intramolecular coupling product **8** (70%) and that with the high melting point was the intermolecular coupling product **11** (5%). The latter had been observed already as a byproduct in the oxidative trimerization of **17**.



Scheme 8. Formation of the 15- and 30-membered polyphosphacyclopolyynes **8** and **11** by Eglinton coupling of **25a**.

The $^{31}P\{^1H\}$ NMR spectrum of **8** (Figure 2a) has three signals at $\delta = -68.14$ (s), -68.62 (s), and -69.41 (s) with an integration ratio of 1:2:0.8. This confirms the formation of both possible isomers, the all-*cis*-compound **8a** ($\delta = -69.41$ and the *cis*,*cis*,*trans*-compound **8b** [$\delta = -68.14$ (1P) and -68.62 (2P)]. The $^{31}P\{^1H\}$ NMR spectrum of **8** was temperature dependant. As the temperature was increased, the sharp signals at 21 °C broadened and coalesced at 83.8 °C. At 100 °C an averaged, broad singlet at $\delta = -68.03$ was observed.

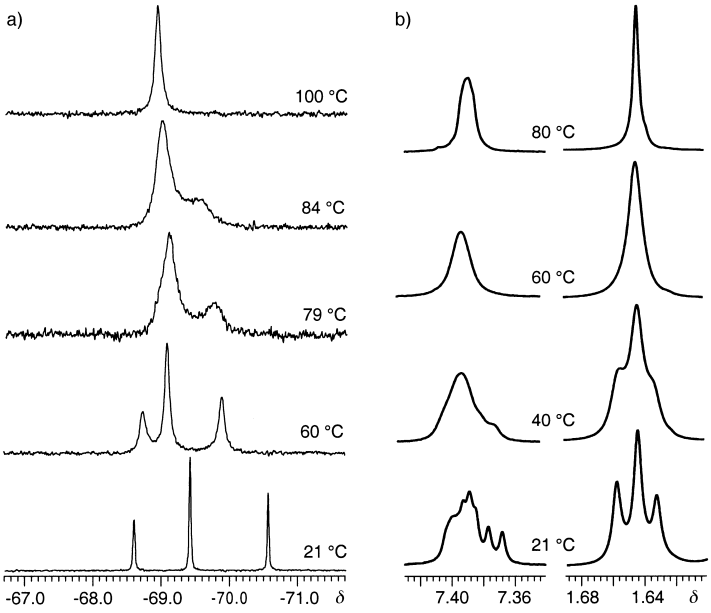


Figure 2. Temperature-dependant NMR spectra of **8**. a) $^{31}P\{^1H\}$ NMR spectra (162 MHz, $C_2D_2Cl_4$) from 21 °C to 100 °C; b) ^1H NMR spectra (400 MHz, $C_2D_2Cl_4$) from 21 °C to 80 °C. (The δ scales are related to the spectra at 21 °C. Because of the temperature drift of the signals at higher temperatures the scales no longer correlate with the values of the signals).

This result can be rationalized—as in the open-chain diphosphanes **16b** and **17**—by a distinct reduction of the inversion barriers of the pyramidal tertiary phosphanes. The Gibbs $\Delta G^{\neq}$ values have been calculated according to the method of Friebolin and Mannschreck[26]:

$\Delta G^{\neq}_{A\rightarrow B} = 74.7 \pm 0.4$ kJ mol^{-1}

$\Delta G^{\neq}_{B\rightarrow A} = 74.0 \pm 0.4$ kJ mol^{-1}

The decrease in the phosphane inversion barrier can be interpreted again by an interaction of the π orbitals of the triple bonds with the orbitals of the P lone pair in the transition state. The singlet at 100 °C can be rationalized in the sense of a more or less synchronous inversion of all three pyramidal phosphine units. In this case we must take an aromatic 18π transition state into account. This assumption is in accordance with the planar aromatic transition state of the phospholes **13** during inversion.[33]

The $^1H\{^{31}P\}$ NMR spectra (400 MHz, $C_2D_2Cl_4$) confirm the conclusion drawn from the ^{31}P NMR data. The three singlets of the *o*-*t*Bu-H at $\delta = 1.632$, 1.647, and 1.660 and the three superimposing doublets of the *m*-aryl-H ($\delta = 7.370 - 7.410$) at 80 °C collapse to two broad singlets (Figure 2b).

*Hexaphosphacyclotriacontadodecayne **11***: The intermolecular oxidative coupling of **29** produced the 30-membered hexamer **11** only as a byproduct in 5% yield. Nevertheless, it was isolated as pure yellow crystals by column chromatography.

The ^{31}P NMR spectrum (400 MHz, $CDCl_3$) of **11** at 21 °C is a broad singlet ($\delta = -63.95$), which sharpens at 50 °C.

In the ^1H NMR spectrum (162 MHz, $CDCl_3$) at room temperature, all *o*-*t*Bu-H appear as one singlet ($\delta = 1.64$, 108H) and the *m*-aryl-H as one doublet ($\delta = -7.45$, $^4J(P,H) = 3.5$ Hz, 12H).

Since in the triphosphacyclopentadecahexayne **8** this phenomena can be observed in both the ^{31}P NMR and the ^1H NMR signals only at elevated temperatures [^{31}P NMR (100 °C), $\delta = -68.03$ (s); ^1H NMR (80 °C), $\delta = 1.647$ (s), *o*-*t*Bu, $\delta = 7.39$ (br s), *m*-aryl-H)], this result can be rationalized by a further reduction of the inversion barrier of the pyramidal phosphorus in **11**.

The discussion, however, also has to take account of the conformational mobility of the whole ring system as a result of the chair–boat–chair conformations. As in hexaphenylcyclohexaphosphane $(P\text{-}C_6H_5)_6$[37] or hexaspirocyclopropylcyclotriacontadodecayne ([6]-rotane),[22] compound **11** should exist in the chair conformation in the solid state.

Oxidative coupling of tetraphosphaicosaoctayne 28 to give 9 and octaphosphacyclotetracontahexadecayne 23 by intra- and intermolecular Eglinton coupling, respectively

*Synthesis of **28** by the Cadiot–Chodkiewicz coupling of **17** with **24***: The strategy for the synthesis of **28** is the Cadiot–Chodkiewicz coupling of the bis-copper salt of **17** with **24**, followed by desilylation of the coupling product **27** (Scheme 9).

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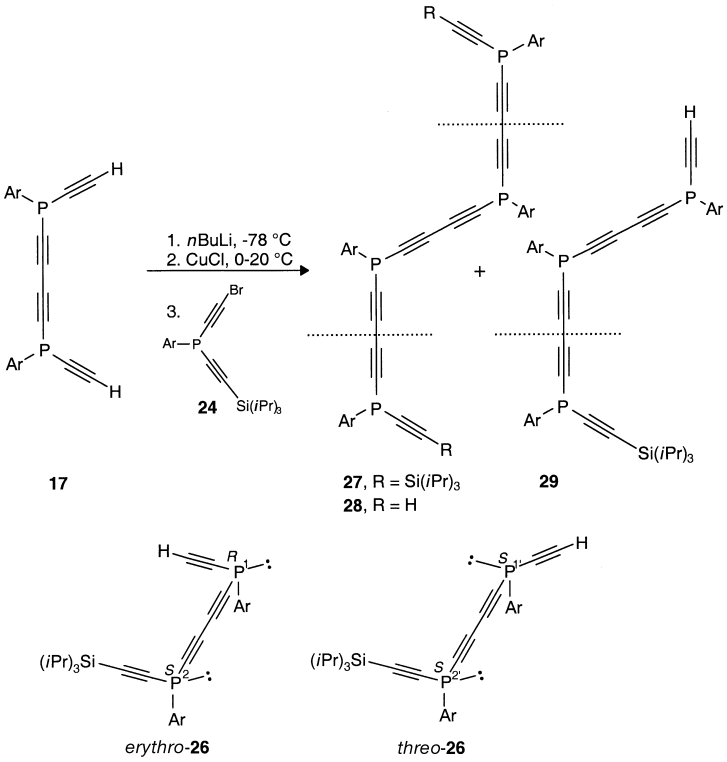


Scheme 9. Formation of 3,8,13,18-tetraphosphaicosaoctaynes **27** and **28** by Cadiot–Chodkiewicz coupling.

As described for the synthesis of **25b**, the isolated bis-copper salt of **17** in pyridine was treated with **24** at room temperature. Four fractions were isolated from the reaction mixture by column chromatography: these fractions yielded yellow crystals of **16b** (2%, reductive coupling of **24** with itself; m.p. 111–113 °C), yellow crystals of the desired twofold coupling product **27** (16%, m.p. 80–111 °C), **15b** (2%), and the monocoupling product **29** (6%, as viscous yellow oil).

3,8,13,18-Tetraphosphaicosa-1,4,6,9,11,14,16,19-octayne (**28**) can be isolated in 54% yield by desilylation with TBAF in THF at −78 °C and column chromatography. The doublet at $\delta = 3.25$ (^3J(P,H) = 0.4 Hz) in the ^{1}H NMR spectrum indicates the terminal acetylenic hydrogens. The ^{31}P{^{1}H} NMR spectrum shows two singlets at $\delta = -63.85$ and −67.81. The first one belongs to the two inner P atoms and the second one to the two outer P atoms.

Synthesis of 28 by Eglinton coupling of butadiyne 26:

*Synthesis of **26***: The alternative synthetic approach to **28** is the monodesilylation of **16b** to give **26** followed by an Eglinton coupling to give **27** and formation of **28** by desilylation (Scheme 9). Treatment of **16b** with TBAF (0.13 mol) in THF at −78 °C (1 h) and column chromatography [Al_2O_3, petroleum ether (40–60)] of the reaction mixture gave the starting material **16b** (30%). The desired monodesilylated **26** (39%) was isolated with CH_2Cl_2/petroleum ether (v/v = 1:20). The third fraction, eluted with CH_2Cl_2/hexane (v/v = 1:6), is the bis-desilylated **17** (pale yellow crystals, 15%).

The EI MS (70 eV) and the fragmentation pattern confirm the structure of **26**. In the ^{1}H NMR spectrum, the acetylenic H appears at $\delta = 3.24$ (d, ^3J(P,H) = 0.4 Hz).

The ^{31}P{^{1}H} NMR spectrum ($CDCl_3$) of **26** at 21 °C contains three signals at $\delta = -66.12$, −66.28, and −67.87, which can be interpreted by the presence of two diastereomers (*erythro*-**26**, and *threo*-**26** Scheme 9). By comparison with the ^{31}P NMR spectra of **15b** and **17**, the signals at $\delta = -66.12$ and −66.28 can be assigned to P2 and P2′, and the signal at $\delta = -67.87$ to P1 and P1′. The temperature-dependant ^{31}P NMR spectra (from −20 to +50 °C) allows the rationalization of the stereochemistry of **26** (Figure 3). At −20 °C two signals are

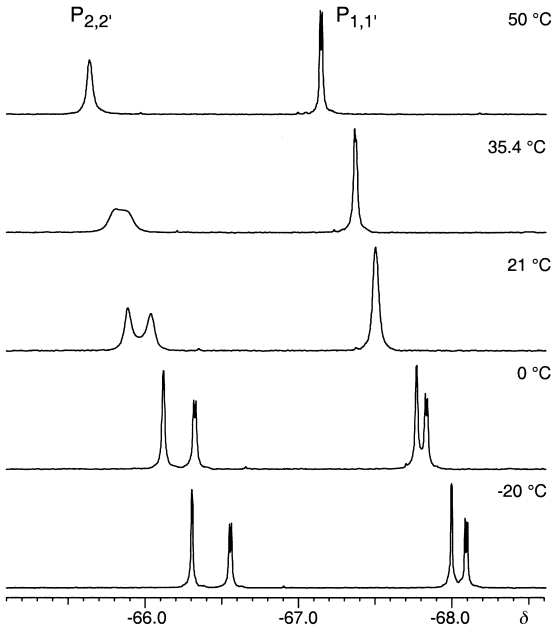


Figure 3. Temperature-dependent ^{31}P{^{1}H} NMR spectrum (162 MHz, [D_8]THF) of **26**.

observed for each diastereomer. One isomer shows a P–P coupling ^6J(P,P) = 2.3 Hz. The coalescence temperature for P2/P2′ is 35.4 ± 2 °C. The free activation energy $\Delta G^{\neq}$ for the inversion energy of P2/P2′ was determined by the method of Friebolin and Mannschreck.[25]

$\Delta G^{\neq}_{A\rightarrow B}$ (P2/P2′) = 66.75 ± 0.4 kJ mol^{-1}

$\Delta G^{\neq}_{B\rightarrow A}$ (P2/P2′) = 66.48 ± 0.4 kJ mol^{-1}

The coalescence temperature of P1/P1′ is between 0 and 21 °C. The lineshape does not allow the determination of an exact value.

The temperature-dependant NMR spectra of **26** confirm that the dramatic reduction of the inversion barriers in tervalent phosphines by adjacent triple bonds is a general phenomenon.

The Eglinton coupling of **26** was carried out by stirring it with [Cu(OAc)$_2$] (4 equiv) and CuCl (3 equiv) in pyridine for 15 h at room temperature. Chromatography of the crude oil at Al_2O_3 gave **27** as yellow crystals in a nearly quantitative yield, m.p. 76–111 °C.

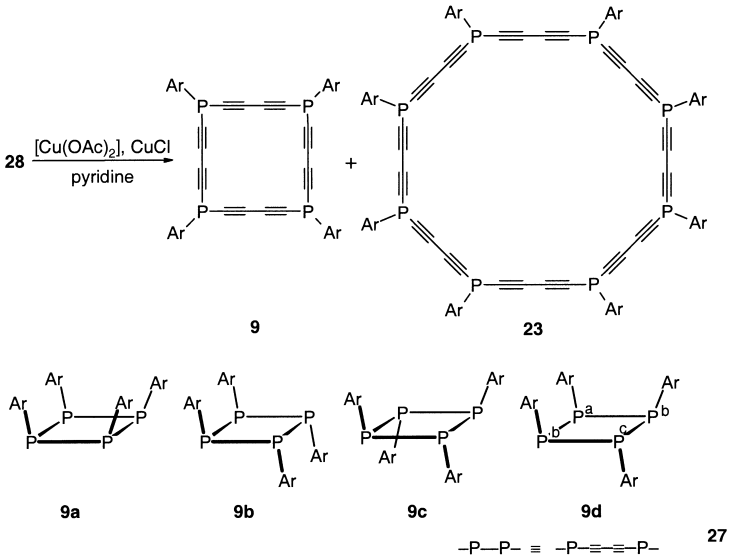
In the ^{31}P{^{1}H} NMR spectrum, two singlets at $\delta = -63.87$ and −66.17 (ratio 1:1) are observed. By comparison with the ^{31}P{^{1}H} signals of **25a**, the signal at $\delta = -63.87$ can be assigned

to the two inner phosphorus atoms, and the signal at $\delta = -66.17$ to the two outer P atoms.

The large melting interval of more than 30 °C for **27** is probably caused by the presence of a mixture of stereoisomers. Theoretically, compound **27** has four chiral phosphorus atoms in the symmetric system and could form ten stereoisomers. Since in **27** the inversion barriers of the pyramidal tervalent phosphanes are expected to be reduced considerably, the stereochemical situation certainly is rather complex.

The desilylation of **27** to give **28** is achieved with TBAF in THF as described above.

Oxidative coupling of 28 to give the polyphosphacyclopolyynes 9 and 23: The modified Eglinton coupling of **28** yields, after column chromatography, two yellow, crystalline compounds. These are the tetraphosphacycloicosaoctayne **9** (65 %) and the octaphosphacyclotetracontahexadecayne **23** (2 %, Scheme 10).



Scheme 10. Formation of the 20- and 40-membered polyphosphacyclopolyynes **9** and **23** by an intra- and intermolecular Eglinton coupling of **28**.

The $^{31}P\{^1H\}$ NMR spectrum (Figure 4) at 21 °C shows several broad signals from $\delta = -64.7$ to -66.2. On heating the sample to 140 °C, only one sharp signal at $\delta = -64.9$ remains. The broad signals of **9** at room temperature sharpen at -20 °C. The temperature dependence of the ^{31}P spectrum of **9** is clearly the result of the temperature dependence of the inversion of the pyramidal phosphorus. At -20 °C the inversion is frozen, and so we observe the signals for all four possible isomers **9a**–**9d**.

Since the all-*cis*-configured **9a** is the less favored one for steric reasons, we believe it to be formed in the lowest yield ($\delta = -68.13$, 5 %). The main isomer **9d** (46.3 %) has the lowest symmetry and therefore gives rise to three signals at $\delta = -65.56$ (t, $^6J(P^c,P^b) = 1.1$ Hz, P^c), -66.18 (t, $^6J(P^a,P^b) = 8.4$ Hz, P^a) and -66.80 (dd, $^6J(P^a,P^b) = 8.4$ Hz, $^6J(P^b,P^c) = 1.1$ Hz, $2P^b$). The signal at $\delta = -65.56$ (27 %) is assigned to **9c** and that at $\delta = -66.26$ (22 %) to **9b**.

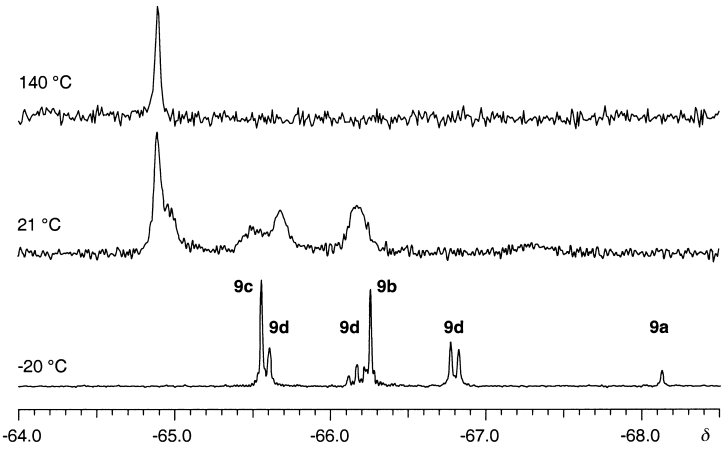


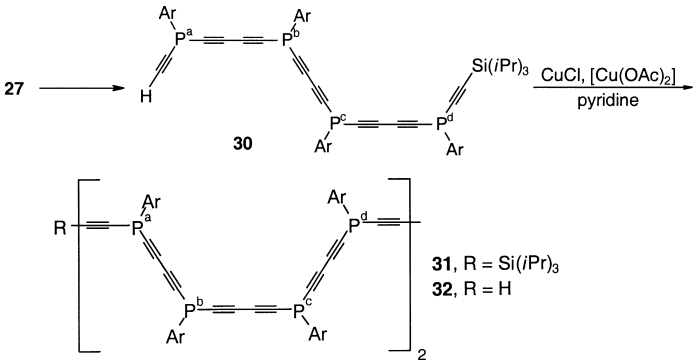
Figure 4. Temperature-dependent ^{31}P NMR spectrum of **9** (162 MHz, $CDCl_3$): 21 °C, -20 °C; ($C_2D_2Cl_4$): 140 °C.

In the ^1H NMR spectrum of **9** at 21 °C, the singlet observed at $\delta = 1.29$ corresponds to the *p*-*t*Bu-H and the signal at $\delta = 1.64$ to the *o*-*t*Bu-H, while the doublet at $\delta = 7.43$ (d, $^4J(P,H) = 3.1$ Hz) corresponds to the *m*-aryl-H. At -20 °C these signals are split because of the slower inversion of the tervalent phosphane phosphorus atoms.

The physical and spectroscopic data of the 40-membered octaphosphacyclotessaracontahexadecayne **23** is discussed in the following section.

Oxidative coupling of hexadecayne 32 to give 23:

*Synthesis of octayne **30***: The synthetic strategy is the monodesilylation of **27** to give **30** followed by a modified Eglinton coupling to give the bis(triisopropylsilyl) derivative **31** (Scheme 11).



Scheme 11. Synthesis of octaphosphatetracontahexadecayne **32**.

The monodesilylation of **27** was carried out by treatment with TBAF (0.3 equiv) in THF at -78 °C for 2 h. One obtains a mixture of the substrate **27** and the mono- and bis-desilylated tetraphosphaicosaoctynes **30** and **28** as a yellow oil; this mixture can be separated by column chromatography on Al_2O_3.

In accordance with the unsymmetrical structure of **30**, in the $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) four different signals with equal intensity are observed. These can be assigned by comparison with the values of **27** and **28**: $\delta =$

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– 67.78 (s, P^a), – 63.82 (s, P^b), – 63.88 (s, P^c) and – 66.16 (s, P^d). The FD MS (CH_2Cl_2), *m*/*z* 1455 also supports the formula of **30**.

*Eglinton coupling of **30** to give hexadecayne **31***: The oxidative coupling of **30** was carried out according to the modified Eglinton method. The disappearance of **30** was monitored by TLC. After column chromatography, **31** was isolated as a pale yellow microcrystalline solid (yield 87 %).

In the ^{1}H NMR (400 MHz, $CDCl_3$) of **31** the signal of the acetylenic hydrogen ($\delta = 3.25$, s) disappeared. The integration proves the presence of two triisopropylsilyl groups ($\delta = 1.04$, s, 42 H). In the IR spectrum the ≡CH signal at $\nu = 3300$ cm^{-1} also disappears.

In agreement with the symmetric structure of **31**, the ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) shows three broad singlets with an integration ratio of 2:1:1. The assignment is possible by comparison with the ^{31}P NMR spectrum of **27** [$\delta = -66.17$ (s, 2 P^a); – 63.87 (s, 2 P^b), – 63.70 (s, 2 P^c, 2 P^d)]. In the FD-MS (CH_2Cl_2) the expected peak of **31** (*m*/*z* 2908) cannot be detected, probably because the molecule is no longer desorbed from the RhC emitter or it decomposes below the desorption temperature.

The desilylation of **31** occurs smoothly by means of the standard method (TBAF in THF at – 78 °C) and **32** is obtained as a pale yellow precipitate. The IR spectrum [ν(≡CH) = 3300 cm^{-1} (w); ν(C≡C) = 2160 (w), 2060 cm^{-1} (m)] confirms the formation of **32**. As a result of the insolubility in all the usual solvents, no satisfactory ^{1}H and ^{13}C NMR and no FD-MS spectra could be obtained.

*Intramolecular Eglinton coupling of **32** to give hexadecayne **23***: The oxidative coupling of **32** was achieved again by means of the modified Eglinton method ([$Cu(OAc)_2$] (4 equiv), $CuCl_2$, (3 equiv), and pyridine). Because of the insolubility of **32**, the coupling was carried out by adding small portions of the solid **32** to the reaction mixture over a period of four hours at 65 °C. Heating was continued for a further two hours and the mixture was then stirred for 24 hours at room temperature. After hydrolysis, column chromatography of the crude brown solid yielded the yellow, microcrystalline compound of the 40-membered octaphospha ring system **23** in 9 % yield.

This result confirms that both the intermolecular coupling of the tetraphosphine **28** and the intramolecular coupling of **32** form the same 40-membered ring system **23**.

In the IR spectrum (KBr) of **23** the ν(≡CH) band at 3300 cm^{-1} disappears; the following signals are observed: ν(C≡C) = 2200 (w), 2165 (w), 2100 cm^{-1} (m).

Amazingly, the ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 21 °C) of **23** is extremely simple. The 72 H of the *p*-*t*Bu groups form a singlet at $\delta = 1.30$, the 144 H of the *o*-*t*Bu groups form a singlet at $\delta = 1.63$, and the 16 *m*-aryl-H groups form a doublet at $\delta = 7.45$, ^4J(H,H) = 3.5 Hz. The ^{31}P{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) shows one broad singlet for all eight phosphine phosphorus atoms in the expected region ($\delta = -63.52$). Neither the FD MS (CH_2Cl_2) nor the ESI MS ($CHCl_3$/MeOH/H_2O 10:10:1) confirm the molecular weight of **23** (*m*/*z* = 2596); however, this does not place doubt on the structure of the ring system.

Comparison of the pyramidal inversion barriers of the 15-, 20-, 25-, 30-, and 40-membered tri-, tetra-, penta-, hexa-, and octaphospha ring systems 8, 9, 10, 11, and 23: In the ^{31}P NMR of the 15-membered triphosphacyclopentadecahexayne **8** the three signals of the two isomers at room temperature are sharp lines. However, the inversion barrier of the pyramidal phosphorus atoms is dramatically lowered (74.8 kJ mol^{-1}). The coalescence temperature is 83 °C and at 100 °C only one sharp signal ($\delta = -68.3$) is observed. In the ^{31}P NMR spectrum of the 20-membered tetraphosphacycloeikosaoctyne **9** at – 20 °C, sharp signals for all four possible isomers are observed. However, at room temperature the signal broadening indicates that there is a high rate of pyramidal inversion of the phosphorus atoms in all isomers. At 140 °C, the inversion is so fast that only one ^{31}P NMR signal ($\delta = -64.91$) is observed. In the 25-membered pentaphosphacyclopentaicosadecayne **10** and the 30-membered hexaphosphacyclotriacontadodecayne **11** the reduction of the barrier of the P inversion is no longer restricted by ring strains and, therefore, at room temperature only broad ^{31}P signals (**10**: $\delta = -65.51$; **11**: $\delta = -63.95$) are observed. In the ^{31}P NMR spectrum of the 40-membered octaphosphacyclotetracontahexadecayne **23** at room temperature these effects already lead to one sharp signal for all eight pyramidal phosphorus atoms ($\delta = -65.52$).

Experimental Section

General methods: ^{1}H NMR spectra were recorded on a Varian T60 (60 MHz), Bruker AW 80 (80 MHz), and Bruker ARX 400 (400.13 MHz) spectrometers. ^{13}C NMR spectra on a Bruker ARX 400 (100.61 MHz), ^{31}P NMR spectra on Bruker ARX 400 (196.98 MHz) instruments. The UV/Vis spectra were recorded on a Hitachi U-2000. The mass spectra are obtained with a Finnigan MAT 311A and 112 S (EI) and a Finnigan MAT 95 (FAB, FD). The ESI-mass spectra were studied with a Finnigan MAT SSQ 7000.

2,4,6-Tri-*tert*-butyldichlorophosphane (6): The dichlorophosphane **6** was synthesized according to the procedure of Yoshifuji et al.,[19] improved by Kreitmeier[38] and Reithinger[39] from 1-bromo-2,4,6-tri-*tert*-butylbenzene.[40] Colorless needles, m.p. 70–71 °C (from acetonitrile), 70 %; ^{1}H NMR (60 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9 H, *p*-*t*Bu), 1.62 (s, 18 H, *o*-*t*Bu), 7.39 (d, ^4J(P,H) = 4.2 Hz, 2 H, *m*-aryl).

Diethynyl(2,4,6-tri-*tert*-butylphenyl)phosphane (7a):[41]. A saturated solution of acetylene in THF was prepared by bubbling acetylene into THF (200 mL) at 0 °C for 30 min. EtMgBr (10.0 mL, 10 M in THF, 100 mmol) was then added dropwise at 0 °C, while the addition of acetylene was continued (30 min). The reaction mixture was allowed to warm to room temperature and a solution of **6** (13.9 g, 40.0 mmol) in THF (200 mL) was added. After stirring for 12 h, the mixture was hydrolyzed with NH_4Cl solution (10 %, 200 mL). The organic layer was separated and the aqueous solution extracted with diethyl ether (3 × 40 mL). After drying and evaporation, the crude solid product was purified by column chromatography (SiO_2; $CHCl_3$/hexane 1:2). Recrystallization from ethanol (99 %, 15 mL) afforded **7a** in 52 % yield as colorless crystals. M.p. 91–92 °C; ^{1}H NMR (60 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9 H, *p*-*t*Bu), 1.72 (s, 18 H, *o*-*t*Bu), 3.23 (s, 2 H, ≡CH), 7.43 (d, ^4J(P,H) = 3.6 Hz, 2 H, *m*-aryl); IR (KBr): $\tilde{\nu} = 3300$, 3260 (s, ≡CH), 2030 cm^{-1} (m, C≡C); elemental analysis calcd (%) for $C_{22}H_{31}P$ (326.46): C 80.94, H 9.57; found C 80.55, H 9.70.

(2,4,6-Tri-*tert*-butylphenyl)bis[(trimethylsilyl)ethynyl]phosphane (7b): A solution of trimethylsilylacetylene (1.96 g, 20 mmol) in diethyl ether (20 mL) was metallated with *n*BuLi (12.5 mL, 20.0 mmol) at – 50 °C over a period of 30 min. This solution was then added slowly to a solution of **6** (3.58 g, 10.0 mmol) in diethyl ether (30 mL) at – 78 °C. The mixture was allowed to warm to room temperature and the LiCl was filtered off in a sintered glass tube. All operations were carried out with the exclusion of

moisture. After removal of the solvent, the yellow, crystalline crude **7b** was purified by column chromatography (SiO_2/hexanes). The byproduct 1,3,5-tri-*tert*-butylbenzene was removed by sublimation at 70 °C/10^{-2} mm Hg. Recrystallization from methanol gave **7b** as colorless crystals (72 %). M.p. 105.5 – 106.5 °C; ^{1}H NMR (60 MHz, $CDCl_3/CD_2Cl_2$): $\delta = 0.25$ (s, 18 H, $Si(CH_3)_3$), 1.36 (s, 9 H, *p*-*t*Bu), 1.71 (s, 18 H, *o*-*t*Bu), 7.51 (d, ^4J(P,H) ≈ 4 Hz, 2 H, *m*-aryl); ^{13}C NMR (22.64 MHz, $CDCl_3$): $\delta = 0.36$ (s, C11), 31.23 (s, C8), 34.20 (d, ^4J(P,C) = 7.30 Hz, C6), 34.98 (s, C7), 39.95 (d, ^3J(P,C) = 4.64 Hz, C5), 104.21 (d, ^1J(P,C) = 12.61 Hz, C9), 116.62 (d, ^2J(P,C) = 3.98 Hz, C10), 123.92 (d, ^3J(P,C) = 9.29 Hz, C3), 125.06 (s, C1), 151.50 (d, ^4J(P,C) = 1.99 Hz, C4), 157.79 (d, ^2J(P,C) = 17.25 Hz, C2); ^{31}P NMR (101.27 MHz, $CDCl_3$): $\delta = -70.20$; IR (KBr): $\tilde{\nu} = 2080$ (m, C≡C), 1240, 840 cm^{-1} (vs, $Si(CH_3)_3$); elemental analysis calcd (%) for $C_{28}H_{47}PSi_2$ (470.83): C 71.42 H 10.06; found C 71.29 H 10.09.

Bis(ethinyl)-2,4,6-tri-*tert*-butylphenylphosphane (7a) by desilylation of 7b: NaOH (2 N, 5 mL) was added to a solution of **7b** (0.47 g, 1.00 mmol) in methanol/diethyl ether (30 mL, 2:1). The mixture was stirred for 1 h and then poured into HCl (2 N, 50 mL) and diethyl ether (50 mL). The aqueous phase was washed with diethyl ether (3 × 10 mL), and the combined diethyl ether solutions were dried with Na_2SO_4 and evaporated. Recrystallization from ethanol afforded colorless crystals of **7a**, (71 %). M.p. 91 – 92 °C.

Eglinton coupling of 7a to give a mixture of the polyphosphacyclopolyynes 8, 9, 10, and 11: A solution of **7a** (500 mg, 1.50 mmol) in pyridine/methanol (15 mL, 2:1) was added dropwise over a period of 15 min at room temperature to a solution of $[Cu(OAc)_2] \cdot H_2O$ (2.00 g, 10.0 mmol) in pyridine (50 mL). The mixture was heated to 60 °C for 3 h. After evaporation in vacuo, the residue was extracted with benzene (2 × 50 mL). The organic solution was washed with water (2 × 20 mL), HCl (2 N, 10 mL), and again with water (3 × 10 mL). Column chromatography (SiO_2/benzene) yielded a dark yellow powder (decomp ≈ 250 °C), 402 mg (82 % related to **7a**). The product was a mixture of the polyphosphacyclopolyynes **8**, **9**, **10**, and **11** and was soluble in nonpolar solvents and insoluble in polar solvents. It was possible to partially separate the mixture by HPLC (Polygosil 60.7 cm, Machery-Nagel, Büren), *n*-hexane/methylpentane (99.6 %)/CH_3CN (0.04 %), 40 bar). The 15-membered ring system **8** and the 25-membered ring **10** were isolated in pure form; compounds **9** and **11** could not be separated. Since **8**, **9**, and **11** are obtainable in better yields by a consecutive, multistep synthesis, only **10**, not available otherwise, is described here.

1,6,11,16,21-Pentakis(2,4,6-tri-*tert*-butylphenyl)-1,6,11,16,21-pentaphosphacyclopentacosa-2,4,7,9,12,14,17,19,22,24-decayne (10): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (s, 45 H, *p*-*t*Bu), 1.64 (s, 90 H, *o*-*t*Bu), 7.44 (d, ^4J(P,H) = 2.7 Hz, 10 H, *m*-aryl); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 121.4$ (d, ^1J(P,H) = 20.5 Hz, Aryl-C1), 92.99 (d, ^1J(P,C) = 16.9 Hz, C9), 81.33 (s, C10); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = -65.51$ (br s); IR (KBr): $\tilde{\nu} =$ 2070 cm^{-1} (C≡C); MS (PI FD, toluene): *m*/*z* (%): 1621 (90) $[M-H]^+$, 1622.1 (100) $[M]^+$, 1623.1 (60) $[M+H]^+$, 1624.2 (30) $[M+2H]^+$, 1625 (10) $[M+3H]^+$; elemental analysis calcd (%) for $C_{110}H_{145}P_5$ (1622.2): C 81.45, H 9.01; found C 81.78 H 9.22.

(2,4,6-Tri-*tert*-butylphenyl)bis[(triisopropylsilyl)ethynyl]phosphane (7c) and ethynyl(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphane (15b) by silylation of 7a: A solution of **7a** (816 mg, 2.50 mmol) in THF (70 mL) was metallated at −78 °C with *n*BuLi (1.56 mL, 2.50 mmol, 1.6 M in hexane). After stirring for another hour at −78 °C, triisopropylchlorosilane (0.60 g, 2.80 mmol) was added. After further 3 h reaction time at room temperature, hydrolytic workup provided a dark oil, which was purified by column chromatography (Al_2O_3/hexane). The first fraction contained **7c** (200 mg, 13 %), which was isolated as colorless oil, followed by **15b** (330 mg, 25 %) as a yellow oil, and finally unreacted starting material **7a** (m.p. 90 – 91 °C) was recovered (110 mg, 14 %).

*Compound **7c***: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.04$ (s, 42 H, *i*Pr), 1.30 (s, 9 H, *p*-*t*Bu), 1.69 (s, 18 H, *o*-*t*Bu), 7.43 (d, ^4J(P,H) = 3.1 Hz, 2 H, *m*-aryl); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.29$ (d, ^4J(P,C) = 1.0 Hz, C11), 18.56 (d, ^5J(P,C) = 0.1 Hz, C12), 31.12 (s, C8), 34.14 (d, ^4J(P,C) = 7.6 Hz, C6), 34.92 (s, C7), 39.72 (d, ^3J(P,C) = 4.7 Hz, C5), 105.87 (d, ^1J(P,C) = 14 Hz, C9), 113.58 (d, ^2J(P,C) = 2.9 Hz, C10), 123.47 (d, ^3J(P,C) = 9.0 Hz, C3), 125.13 (d, ^1J(P,C) = 24 Hz, C1), 151.37 (d, ^4J(P,C) = 2.1 Hz, C4), 157.69 (d, ^2J(P,C) = 17 Hz, C2); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), $\delta = -68.85$; IR (Film): $\tilde{\nu} =$ 2070 cm^{-1} (m, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 286 (3200), 238 (18600), 216 nm (31800); MS (70 eV, EI): *m*/*z* (%): 638 (100) $[M]^+$, 623 (2) $[M-CH_3]^+$, 595 (5) $[M-C_3H_7]^+$, 481 (3) $[M-C_9H_{21}Si]^+$, 231 (9) $[C_{17}H_{27}]^+$, 57 (38) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{40}H_{71}PSi_2$ (639.2): C 75.17, H 11.20; found C 75.10, H 10.92.

*Compound **15b***: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.05$ (s, 21 H, *i*Pr), 1.30 (s, 9 H, *p*-*t*Bu), 1.68 (s, 18 H, *o*-*t*Bu), 3.18 (d, ^3J(P,H) = 1.1 Hz, 1 H, ≡CH), 7.44 (d, ^4J(P,H) = 3.1 Hz, 2 H, *m*-aryl); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.25$ (d, ^4J(P,C) = 0.9 Hz, C11), 18.56 (s, C12), 31.11 (s, C8), 34.10 (d, ^4J(P,C) = 7.6 Hz, C6), 34.92 (s, C7), 39.80 (s, ^3J(P,C) = 4.8 Hz, C5), 82.98 (d, ^3J(P,C) = 8.8 Hz, C13), 96.40 (d, ^2J(P,C) = 13 Hz, C14), 104.63 (d, ^1J(P,C) = 15 Hz, C9), 114.40 (d, ^2J(P,C) = 2.2 Hz, C10), 123.71 (d, ^3J(P,C) = 9.2 Hz, C3), 124.20 (d, ^1J(P,C) = 23 Hz, C1), 151.65 (d, ^4J(P,C) = 2.4 Hz, C4), 157.87 (d, ^2J(P,C) = 18 Hz, C2); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = -70.37$; IR (film): $\tilde{\nu} = 3310$, 3280 (m, ≡CH), 2100, 2040 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 290 (3300), 237 (17600), 210 nm (44400); MS (EI, 70 eV): *m*/*z* (%): 638 (100) $[M]^+$, 623 (2) $[M-CH_3]^+$, 595 (5) $[M-C_3H_7]^+$, 481 (3) $[M-C_9H_{21}Si]^+$, 231 (9) $[C_{17}H_{27}]^+$, 57 (38) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{31}H_{51}PSi$ (482.8): C 77.12, H 10.64; found C 77.57, H 10.94.

Partial desilylation of 7c to 15b: A solution of TBAF in THF (0.50 mL, 0.50 mmol, 1 M in THF) was added to a solution of **7c** (3.20 g, 5.00 mmol) in THF (100 mL) at −78 °C. After 3 h, the mixture was quenched with water and dried with Na_2SO_4, and the solvent evaporated under reduced pressure. The resulting yellow oil was purified by column chromatography (Al_2O_3, hexane). Fraction 1: starting material **7c**, colorless oil (927 mg, 29 %); fraction 2: **15b**, light yellow oil (941 mg, 39 %); fraction 3: **7a**, m.p. 90 – 91 °C (261 mg, 16 %).

General procedure for the Eglinton coupling in the de Meijere modification:[21] A solution of the terminal acetylene (1.00 mmol) in pyridine (10 mL) was added dropwise to a stirred solution of $[Cu(OAc)_2]$ (4 mmol) and CuCl (3 mmol) in pyridine (10 mL) at room temperature. The reaction mixture was stirred for a further 10 h, and after evaporation in vacuo, the residue was dissolved in CH_2Cl_2/water (40 mL, 1:1). The organic phase was washed with HCl (2 N, 10 mL), saturated $NaHCO_3$ solution (7 mL), and water (10 mL). The CH_2Cl_2 solution was dried over Na_2SO_4 and then filtered through silica gel (CH_2Cl_2/hexanes, 1:6).

Eglinton coupling of 15b to give bis{(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphanyl}butadiyne (16b): The 3-phosphapentadiyne **15b** (1.54 g, 3.20 mmol) was coupled according to the general procedure. The coupling product **16b** formed as a yellow oil, which crystallized within a few days (1.47 g, 95 %). M.p. 111 – 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.07$ (s, 42 H, *i*Pr), 1.30 (s, 18 H, *p*-*t*Bu), 1.65 (s, 36 H, *o*-*t*Bu), 7.48 (d, ^4J(P,H) = 3.2 Hz, 4 H, *m*-aryl); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.24$ (s, C13), 18.56 (s, C14), 31.10 (s, C8), 34.10 (d, ^4J(P,C) = 7.5 Hz, C6), 34.95 (s, C7), 39.73 (d, ^3J(P,C) = 4.8 Hz, C5), 82.82 (m, C9, 9′), 93.18 (m, C10, 10′), 103.58 (d, ^1J(P,C) = 12 Hz, C11), 115.19 (d, ^2J(P,C) = 1.6 Hz, C12), 123.52 (m, C1), 123.81 (d, ^3J(P,C) = 9.8 Hz, C3), 151.83 (m, C4), 157.88 (d, ^2J(P,C) = 18 Hz, C2); ^{31}P{^{1}H} NMR (162 MHz, THF): $\delta = -66.53$, −66.29 (ratio 1:1.3); IR (KBr): $\tilde{\nu} = 2090$, 2060 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 329 (6700), 289 (33900), 232 (47100), 211 nm (94200); elemental analysis calcd (%) for $C_{62}H_{100}P_2Si_2$ (963.6): C 77.28, H 10.46; found C 77.62, H 10.65.

2,4,6-Tri-*tert*-butylphosphane (19a): The reduction of **6** with $LiAlH_4$ was described for the first time by Issleib et al.[24] and optimized by Kreitmeier.[38] Yield: 63 %; colorless needles (from acetonitrile); m.p. 159 – 161 °C; ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.23$ (s, 9 H, *p*-*t*Bu), 1.50 (s, 18 H, *o*-*t*Bu), 4.15 (d, ^1J(P,H) = 211 Hz, 2 H, P-H), 7.37 (d, ^4J(P,H) = 2.6 Hz, 2 H, *m*-Aryl); IR (KBr): $\tilde{\nu} = 2410$, 2350, 2280 cm^{-1} (m, P-H).

(2,4,6-Tri-*tert*-butylphenyl)monochlorophosphane (19b): The monochlorophosphane was prepared from **19a** by reaction with CCl_4/azoisobutyronitrile according to Escudie et al.[24b] The procedure was improved by Reithinger.[39] Colorless product, m.p. 105 – 112 °C (further purification of the crude **19b** by recrystallization was not possible); ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9 H, *p*-*t*Bu), 1.60 (s, 18 H, *o*-*t*Bu), 7.24 (d, ^1J(P,H) = 213 Hz, 1 H, P-H), 7.46 (d, ^4J(P,H) = 4.0 Hz, 2 H, *m*-aryl); IR (KBr): $\tilde{\nu} =$ 2405 cm^{-1}, (w, P-H).

1,3-Butadiyne (18):[44] This compound is accessible in good yields by dehydrochlorination of 1,4-dichloro-2-butyne[43] with aqueous KOH (yield about 50 %). Because of its instability the 1,3-butadiyne was prepared just before use. It can be stored only in THF solution at −78 °C.

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Bis[ethynyl(2,4,6-tri-*tert*-butylphenyl)phosphanyl]butadiyne (20):[45] A solution of EtMgBr in THF (13.9 mL, 26.5 mmol, 1.9 M in THF) was added to a solution of 1,3-butadiyne (670 mg, 13.4 mmol) in THF (20 mL) at −78 °C. At 0 °C (2,4,6-tri-*tert*-butylphenyl)monochlorophosphane (8.29 g, 26.5 mmol) in THF (70 mL) was added dropwise to the bis-Grignard compound of 1,3-butadiyne over a period of 35 min. After hydrolysis and extraction with diethyl ether, the obtained crude product (2.16 g) was recrystallized from hexane (43%). Colorless crystals (1.85 g); m.p. 147–148 °C (decomp); ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.26$ (s, 18H, *p*-*t*Bu), 1.56 (s, 36H, *o*-*t*Bu), 5.80 (d, $^1J(P,H) = 252$ Hz, 2H, P-H), 7.42 (d, $^4J(P,H) = 2.4$ Hz, 4H, *m*-aryl); IR (KBr): $\tilde{\nu} = 2410$ cm^{-1} (w, P-H).

Butadiynediylbis[(2,4,6-tri-*tert*-butylphenyl)phosphinecarbonylchloride] (21):[38] A solution of phosgene (3.00 mL, 12.0 mmol, 4.0 M in toluene) was added to a solution of 1,6-diphosphahexadiyne **20** (1.81 g, 3.00 mmol) in toluene (20 mL). The mixture was stirred for 1 h at room temperature. After removal of the excess phosgene and the solvent, the residue was recrystallized from petroleum ether (80–100 °C) to give yellow crystals of **21** (57%). M.p. 165–166 °C (decomp); ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.28$ (s, 18H, *p*-*t*Bu), 1.55 (s, 36H, *o*-*t*Bu), 7.50 (d, $^4J(P,H) = 4.0$ Hz, *m*-aryl); IR (KBr): $\tilde{\nu} = 2080$ cm^{-1} (w, C≡C).

Butadiynediylbis[(2,4,6-tri-*tert*-butylphenyl)phosphinouschloride] (22)[38]: The chloroformyl derivative **21** (1.09 g, 1.50 mmol) was heated to 160–170 °C, until the elimination of CO ceased (15–20 min). Column chromatography (SiO_2, diethyl ether/hexanes 1:2) and recrystallization from benzene/CH_3CN yielded yellow crystals of **22** (35%). M.p. 190–193 °C; ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.27$ (s, 18H, *p*-*t*Bu), 1.67 (s, 36H, *o*-*t*Bu), 7.44 (d, $^4J(P,H) = 3.2$ Hz, *m*-aryl); IR (KBr): $\tilde{\nu} = 2060$ cm^{-1} (w, C≡C).

Bis{(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphanyl}butadiyne (16a): Trimethylsilylacetylene-MgBr (1.82 mL, 0.74 mmol, 0.4 M in THF) was added dropwise to a stirred solution of **22** (190 mg, 0.28 mmol) in THF (5 mL) at 0 °C. After 4 h at room temperature, hydrolytic workup, and extraction with diethyl ether, a yellow-brown product was obtained which was purified by column chromatography (SiO_2, CH_2Cl_2/hexanes 1:5) to give yellow crystals of **16a** (56%). M.p. 44–46 °C; ^{1}H NMR (400 MHz, [D$_8$]THF, TMS): $\delta = 0.15$ (s, 18H, $Si(CH_3)_3$), 7.49 (d, $^4J(P,H) = 3.2$ Hz, 4H, *m*-aryl); ^{13}C NMR (101 MHz, [D$_8$]THF): $\delta = -0.60$ (d, $^4J(P,C) = 0.9$ Hz, C13), 31.32 (s, C8), 34.49 (d, $^4J(P,C) = 7.5$ Hz, C6), 35.62 (s, C7), 40.47 (d, $^3J(P,C) = 4.9$ Hz), 83.46 (m, C9, 9′), 93.28 (m, C10, C10′), 102.50 (d, $^1J(P,C) = 10$ Hz, C11), 119.14 (d, $^2J(P,C) = 4.0$ Hz, C12), 123.73 (d, $^1J(P,C) = 20$ Hz, C1), 124.90 (d, $^3J(P,C) = 9.8$ Hz), C3), 153.05 (d, $^4J(P,C) = 2.4$ Hz, C4), 158.76 (d, $^2J(P,C) = 18$ Hz, C2); IR (KBr): $\tilde{\nu} = 2090$, 2060 cm^{-1}; UV/Vis (*n*-hexane): λ_{max} (ε) = 331 (8600), 286 (40500), 261 (44600), 234 (55000), 209 nm (109600); MS (70 eV, EI): *m*/*z* (%): 794 (79) $[M]^+$, 779 (15) $[M - CH_3]^+$, 737 (16) $[M - C_4H_9]^+$, 721 (3) $[M - C_3H_9Si]^+$, 231 (35) $[C_{17}H_{27}]^+$, 73 (79) $[C_3H_9Si]^+$, 57 (100) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{50}H_{76}P_2Si_2$ (795.3): C 75.51, H 9.63; found C 75.48, H 9.67.

Bis[ethynyl(2,4,6-tri-*tert*-butylphenyl)phosphanyl]butadiyne (17): NaOH (2 N, 0.5 mL) was added to a stirred solution of **16a** (79.5 mg, 0.10 mmol) in MeOH/diethyl ether (3.0 mL, 2:1). After 1 min, HCl (2 N, 5 mL) and diethyl ether (2 mL) were added. The diethyl ether solution was washed with water and dried over Na_2SO_4. Filtration over silica gel (CH_2Cl_2/hexanes, 1:5) afforded **17** as yellow crystals (55%), which could not be purified further. M.p. 164–167 °C (decomp); ^{1}H NMR (400 MHz, [D$_8$]THF, TMS): $\delta = 1.30$ (s, 18H, *p*-*t*Bu), 1.64 (s, 36H, *o*-*t*Bu), 3.86 (s, 2H, ≡CH), 7.44 (d, $^4J(P,H) = 3.2$ Hz, 4H, *m*-aryl); ^{13}C NMR (101 MHz, [D$_8$]THF): $\delta = 31.23$ (s, C8), 34.38 (d, $^4J(P,C) = 7.6$ Hz, C6), 35.54 (s, C7), 40.36 (d, $^3J(P,C) = 4.9$ Hz, C5), 81.00, 83.19 (m, C9, C9′, C10, C10′), 93.27 (m, C10, C10′), 100.11 (m, C12), 123.42 (d, $^1J(P,C) = 201$ Hz, C1), 124.77 (d, $^3J(P,C) = 9.9$ Hz, C3), 153.07 (d, $^4J(P,C) = 2.2$ Hz, C4), 158.85 (d, $^2J(P,C) = 18$ Hz, C2); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): $\delta = -67.88$; IR (KBr): $\tilde{\nu} = 3260$ (m, ≡CH), 2060, 2030 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 326 (7000), 282 (31100), 265 (32700), 226 (39100), 206 nm (74100); elemental analysis calcd (%) for $C_{44}H_{60}P_2$ (650.9): C 81.19, H 9.29; found C 80.73, H 10.09.

Eglinton coupling of 17 to give 9, 11, and 23: The Eglinton coupling of **17** (87.6 mg, 150 mmol) according to the general procedure afforded 40 mg (41% with respect to **17**) of a yellow solid (m.p. ≈175 °C, decomp) as a mixture of **9**, **11**, and **23**, which could not be separated. ^{1}H NMR (400 MHz, $CDCl_3$) of the mixture: $\delta = 1.286$ (s), 1.295 (s), 1.303 (s, 9H, *p*-*t*Bu), 1.64 (s, 18H, *o*-*t*Bu), 7.43 (d, $^4J(P,H) = 3.2$ Hz), 7.45 (d, $^4J(P,H) = 3.5$ Hz), 7.46 (s, *m*-aryl); ^{31}P NMR (162 MHz, $C_2D_2Cl_4$) at 21 °C: several broad signals from $\delta = -64.33$ to -69.03, at 120 °C: three sharp singlets at $\delta = -63.03$, -63.53, and -65.24 with an intensity of 1 (**23**), 4.5 (**11**) and 35 (**9**); IR (KBr): $\tilde{\nu} =$ 2160 (w), 2060 (w, C≡C), the ≡CH signal at ≈3300 cm^{-1} had disappeared.

1-(Bromoethynyl)(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphane (24): A solution of **15b** (770 mg, 1.60 mmol) in THF (50 mL) was metallated at −78 °C with *n*BuLi (1.20 mL, 1.92 mmol, 1.6 M in *n*-hexane). After 20 min, *p*-tosylbromide (450 mg, 1.90 mmol) in THF (4 mL) was added slowly at −78 °C. The reaction mixture was stirred at room temperature 2 h and then hydrolyzed (10 mL). The organic phase was treated with H_2SO_4 (2 N, 5 mL), saturated $NaHCO_3$ solution (5 mL), and water (2 × 20 mL). Evaporation afforded a reddish brown oil, which was purified by column chromatography (Al_2O_3, hexanes). The phosphane **24** was obtained as a pale yellow oil (675 mg, 75%). A small amount (108 mg, 14%) of the starting material **15b** was recovered. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.05$ (s, *i*Pr), 1.31 (s, 9H, *p*-*t*Bu) 1.66 (s, 18H, *o*-*t*Bu), 7.44 (d, $^4J(P,H) = 3.2$ Hz, 2H, *m*-aryl); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.25$ (d, $^4J(P,C) = 0.8$ Hz, C11), 18.56 (s, C12), 31.11 (s, C8), 34.10 (d, $^4J(P,C) = 7.6$ Hz, C6), 34.92 (s, C7), 39.77 (d, $^3J(P,C) = 4.7$ Hz, C5), 66.02/78.38 (d,d, $^1J(P,C) = 14.8$ Hz, $^2J(P,C) = 14.8$ Hz, C13/C14), 104.48 (d, $^1J(P,C) = 16.6$ Hz); 114.52 (d, $^2J(P,C) = 1.5$ Hz, C10), 123.80 (d, $^3J(P,C) = 9.1$ Hz, C3), 124.26 (d, $^1J(P,C) = 23.4$ Hz, C1), 151.63 (d, $^4J(P,C) = 2.4$ Hz, C4), 157.85 (d, $^2J(P,C) = 17.7$ Hz, C2); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = -64.86$ (s); IR (film): $\tilde{\nu} = 2110$, 2080 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 279 (3800), 240 (17400), 210 nm (43400); MS (70 eV, EI): *m*/*z* (%): 561 (18) $[M]^+$, 546 (1) $[M - CH_3]^+$, 517 (3) $[M - C_3H_7]^+$, 482 (9) $[M - Br]^+$, 245 (6) $[C_{18}H_{29}]^+$, 231 (60) $[C_{17}H_{27}]^+$, 57 (100) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{31}H_{50}BrPSi$ (561.7): C 66.29, H 8.97, Br 14.23; found C 66.58, H 9.17, Br 14.15.

Cadiot–Chodkiewicz coupling of 7a with 24 to give (2,4,6-tri-*tert*-butylphenyl)bis-({(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphanyl}butadiynyl)phosphane (25b): A solution of **7a** (196 mg, 0.6 mmol) in THF (8 mL) was metallated at −78 °C with *n*BuLi (0.80 mL, 1.26 mmol, 1.6 M in *n*-hexane). After 30 min the temperature was increased to 0 °C and CuCl (125 mg, 1.26 mmol) was added. The mixture was stirred for a further 20 min at 0 °C and then 30 min at room temperature. The solvent was removed under reduced pressure (not to dryness!), and the residue was dissolved in oxygen-free, dry pyridine (20 mL). A solution of the bromo compound **24** in THF (5 mL) was added dropwise to the copper salt of **7a**. The reaction mixture was stirred for 12 h, the dark solution was poured into HCl (40 mL, 10%), and the mixture was extracted with hexanes (3 × 40 mL). The combined organic phases were washed with HCl (2 N, 20 mL) and saturated $NaHCO_3$ solution (20 mL), and dried over Na_2SO_4. Evaporation and column chromatography (Al_2O_3, hexane) yielded a yellow oil of **16b** (60.0 mg, 10%), the desired coupling product **25b** (210 mg, 27%) as a yellow resin, and **26** (10 mg, 2%). The coupling reaction with $CuCl/NH_2OH \cdot HCl$/isopropylamine/THF produced **25b** in 11% yield, with $CuI/PdCl_2(CH_3CN)$/isopropylamine/benzene (Elbaum et al.[36]) in 15% yield. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.04$ (s, 42H, *i*Pr), 1.30 (s, 9H, *p*-*t*Bu), 1.30 (s, 18H, *p*-*t*Bu), 1.61 (s, 18H, *o*-*t*Bu), 7.43 (d, $^4J(P,H) = 3.4$ Hz, 4H, *m*-aryl), 7.45 (d, $^4J(P,H) = 4.00$ Hz, 2H, *m*-aryl), ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.25$ (d, $^4J(P,C) = 0.9$ Hz, C15), 18.56 (s, C16), 31.07 (s, C8^b), 31.10 (s, C8^a), 34.06 (d, $^4J(P,C) = 6.8$ Hz, C6^b), 34.11 (d, $^4J(P,C) = 7.2$ Hz, C6^a), 34.98 (d, $^5J(P,C) = 0.9$ Hz, C7^a), 35.01 (d, $^5J(P,C) = 0.9$ Hz, C7^b), 39.71 (d, $^3J(P,C) = 5.1$ Hz, C5^b), 39.73 (d, $^3J(P,C) = 4.7$ Hz, C5^a), 80.84 (ddd, $^1J(P^a,C) = 7.3$ Hz, $^4J(P,C) = 4.8$ Hz, $^6J(P,C) = 2.5$ Hz, C9), 83.72 (dd, $^1J(P,C) = 8.8$ Hz, $^4J(P,C) = 3.8$ Hz, C12), 92.96 (dd, $^2J(P,C) = 17.4$ Hz, $^3J(P,C) = 3.8$ Hz, C10, C11), 93.96 (dd, $^2J(P,C) = 17.4$ Hz, $^3J(P,C) = 4.7$ Hz, C10, C11), 103.29 (dd, $^1J(P,C) = 13.0$ Hz, $^6J(P,C) = 1.7$ Hz, C13), 115.50 (d, $^2J(P,C) = 2.0$ Hz, C14), 121.85 (m, C1^b), 123.35, (dd, $^1J(P,C) = 21.4$ Hz, $^6J(P,C) = 1.7$ Hz (C1^a), 123.81 (d, $^3J(P,C) = 9.5$ Hz, C3^a), 124.10 (d, $^3J(P,C) = 10.0$ Hz, C3^b), 151.91 (d, $^4J(P,C) = 2.5$ Hz, C4^a), 152.38 (d, $^4J(P,C) = 2.5$ Hz, C4^b), 157.91 (d, $^2J(P,C) = 17.4$ Hz, C2^a), 157.98 (d, $^2J(P,C) = 17.8$ Hz, C2^b); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = -63.99$ (1P), -66.16 (2P); IR (film): $\tilde{\nu} = 2140$ (w), 2090, 2065 cm^{-1} (m, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 305 (59200), 273 (57500), 233 (73300), 211 nm (131400); MS (FD, CH_2Cl_2): *m*/*z*: 1287; elemental analysis calcd (%) for $C_{84}H_{129}P_3Si_2$ (1288.0): C 78.33, H 10.10; found C 78.71, H 10.48.

Desilylation of 25b to (2,4,6-tri-*tert*-butylphenyl)bis{[ethynyl(2,4,6-tri-*tert*-butyl-phenyl)phosphanyl]butadiynyl}phosphane (25a): A THF solution of TBAF (0.25 mL, 1 M in THF) was added to a solution of **25b** (645 mg,

0.5 mmol) in THF (100 mL) at −78 °C. The mixture was stirred for 2.5 h and then quenched with water. The organic layer was evaporated, and the crude product purified by column chromatography (Al_2O_3, CH_2Cl_2/hexane 1:10) to give yellow crystals of **25a** (307 mg, 63 %). M.p. 170–175 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9H, *p*-*t*Bu), 1.31 (s, 18H, *p*-*t*Bu), 1.61 (s, 18H, *o*-*t*Bu), 1.64 (s, 36H, *o*-*t*Bu), 3.25 (s, 2H, ≡CH), 7.45 (d, ^4J(P,H) = 3.5 Hz, 2H, *m*-aryl), 7.45 (d, ^4J(P,H) = 3.4 Hz, 4H, *m*-aryl); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.07 (s, C8^b), 31.08 (s, C8^a), 34.08 (d, ^4J(P,C) = 7.2 Hz, C6^a, C6^b), 34.99 (d, ^5J(P,C) = 0.9 Hz, C7^a), 35.03 (d, ^5J(P,C) = 0.9 Hz, C7^b), 39.70 (d, ^3J(P,C) = 4.9 Hz, C5^b), 39.77 (d, ^3J(P,C) = 4.9 Hz, C5^a), 81.02 (ddd, ^1J(P^a,C) = 8.1 Hz, ^4J(P,C) = 4.2 Hz, ^6J(P,C) = 2.2 Hz, C9), 81.15 (dd, ^1J(P,C) = 9.1 Hz, ^6J(P,C) = 2.0 Hz, C12, C13), 82.76 (dd, ^1J(P,C) = 10.2 Hz, ^4J(P,C) = 3.7 Hz, C12, C13), 93.11 (dd, ^2J(P,C) = 17.5 Hz, ^3J(P,C) = 3.8 Hz, C10, C11), 93.76 (dd, ^2J(P,C) = 17.4 Hz, ^3J(P,C) = 4.4 Hz, C10, C11), 97.32 (d, ^2J(P,C) = 11.9 Hz, C14), 121.53 (ddd, ^1J(P,C) = 19.8 Hz, ^6J(P^{a,b},C) = 1.5 Hz, C1^b), 122.11 (dd, ^1J(P,C) = 20.9 Hz, ^6J(P,C) = 1.6 Hz, C1^a), 124.04 (d, ^3J(P,C) = 9.7 Hz, C3^a), 124.11 (d, ^3J(P,C) = 9.9 Hz, C3^b), 152.28 (d, ^4J(P,C) = 2.6 Hz, C4^a), 152.51 (d, ^4J(P,C) = 2.6 Hz, C4^b), 158.01 (d, ^2J(P,C) = 17.8 Hz, C2^b), 158.08 (d, ^2J(P,C) = 17.8 Hz, C2^a); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −63.86 (1P), −67.77 (2P); IR (KBr): $\tilde{\nu}$ = 3300 (m, ≡CH), 2140, 2065, 2035 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 296 (30200), 275 (33000), 234 (34700), 207 nm (67900); elemental analysis calcd (%) for $C_{66}H_{89}P_3$ (975.4): C 81.27, H 9.20; found C 81.44, H 9.61.

Eglinton coupling of 25b to give triphosphacyclopentadecahexayne 8 and hexaphosphacyclotriacontadodecayne 11: The Eglinton coupling of **25b** (88.0 mg, 90 μmol) according to the general procedure afforded a yellow-orange solid which was purified by column chromatography (SiO_2, CH_3CN/*n*-hexane 1:200).

Compound ***8***: Yield: 61.4 mg (70 %); yellow-orange crystals; m.p. 78–84 °C (decomp). ^{1}H{^{31}P} NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 27H, *p*-*t*Bu), 1.64 (s), 1.65 (s), 1.67 (s, 54H, *o*-*t*Bu), 7.41 (s), 7.42 (s), 7.43 (s, 6H, *m*-aryl); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ = −68.14, −68.62, −69.41 (integration ratio 1:2:0.8); −69.41 (s, isomer **8a**), −68.14 (s), −68.62 (s, integration ratio 1:2, isomer **8b**); ratio **8a**/**8b** = 21:79; IR (KBr): $\tilde{\nu}$ = 2145 (w), 2060 cm^{-1} (m, C≡C); UV/Vis (*n*-hexane); λ_{max} (ε) = 300 (32800), 254 (95000), 206 nm (114200); MS (FD, CH_2Cl_2): *m*/*z*: 972; elemental analysis calcd (%) for $C_{66}H_{87}P_3$ (973.3): C 81.44, H 9.01; found C81.11, H 9.14.

Compound ***11***: Yield: 4.62 mg (5 %); yellow crystals; m.p. 175 °C (decomp); ^{1}H{^{31}P} NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 54H, *p*-*t*Bu), 1.64 (s, 108H, *o*-*t*Bu), 7.45 (d, ^4J(P,H) = 3.5 Hz, 12H, *m*-aryl); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ = −63.95 (br s); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 50 °C): δ = −63.95 (s, sharp); IR (KBr): $\tilde{\nu}$ = 2145 (w), 2100 (w), 2060 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 290 (72400), 266 (128600), 205 nm (188100); MS (FD, CH_2Cl_2): *m*/*z*: 1946 (in agreement with the calculated spectrum); elemental analysis calcd (%) for $C_{132}H_{174}P_6$ (1946.9): calcd C 81.44, H 9.01; found C 81.17 H 9.11.

[Ethynyl(2,4,6-tri-*tert*-butylphenyl)phosphanyl]{(2,4,6-tri-*tert*-butylphenyl)[(triisopropylsilyl)ethynyl]phosphanyl}butadiyne (26) by monodesilylation of 16b: A solution of **16b** (1.21 g, 1.25 mmol) in THF (50 mL) at −78 °C was treated with TBAF (0.2 mL, 0.2 mmol, 1M in THF) for 1 h. Water (5 mL) was added, and the organic layer dried over Na_2SO_4. Evaporation yielded a yellow oil, which was purified by column chromatography (Al_2O_3, hexane). The first fraction was the starting material **16b**, yellow crystals, m.p. 111–113 °C (390 mg, 30 %). With CH_2Cl_2/hexanes (1:20) **26** was eluted, yellow oil (390 mg, 39 %), and finally with CH_2Cl_2/hexanes (1:6) the bis-desilylation product **17** was obtained, yellow crystals, m.p. 164–168 °C (125 mg, 15 %). Compound **26**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 24H, *i*Pr), 1.30 (s, 18H, *p*-*t*Bu), 1.63 (s, 18H, *o*-*t*Bu), 1.64 (s, 18H, *o*-*t*Bu), 3.24 (d, ^3J(P,H) = 0.4 Hz, 1H, ≡CH), 7.43 (d, ^4J(P,H) = 3.3 Hz, 2H, *m*-aryl^b), 7.44 (d, ^4J(P,H) = 3.4 Hz, 2H, *m*-aryl^a); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 11.24 (d, ^4J(P,C) = 0.7 Hz, C17), 18.56 (s, C18), 31.09/31.10 (s/s, C8^a, C8^b), 34.07/34.11 (d/d, ^4J(P,C) = 7.3 Hz, ^4J(P,C) = 7.2 Hz, C6^a, C6^b), 34.96/34.98 (d/d, ^5J(P,C) = 0.9 Hz, ^5J(P,C) = 1.3 Hz, C7^a, C7^b), 39.73/39.77 (d/d, ^3J(P,C) = 4.7 Hz, ^3J(P,C) = 4.7 Hz, C5^a, C5^b), 81.40 (dd, *J*(P,C) = 2.2, 9.6 Hz, C9, C11, C14), 81.78 (dd, *J*(P,C) = 4.4, 8.8 Hz, C9, C11, C14), 83.19 (dd, *J*(P,C) = 8.5, 4.0 Hz, C9, C11, C14), 92.96/93.48 (m/m, C12, C13), 97.12 (d, ^2J(P,C) = 12.0 Hz, C10), 103.36 (dd, ^6J(P,C) = 1.9 Hz, ^1J(P,C) = 12.7 Hz, C15), 115.35 (d, ^2J(P,C) = 2.1 Hz, C16), 122.34/123.38 (d/d, ^1J(P,C) = 21.0 Hz, ^1J(P,C) = 21.6 Hz, C1^a, C1^b), 123.79/124.03 (d/d, ^3J(P,C) = 9.5 Hz, ^3J(P,C) = 9.6 Hz, C3^a, C3^b), 151.91/152.21 (d/d, ^4J(P,C) = 2.5 Hz, ^4J(P,C) = 2.5 Hz, C4^a, C4^b), 157.88/158.96 (d/d, ^2J(P,C) = 15.4 Hz, ^2J(P,C) = 15.7 Hz, C2^a, C2^b); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ = −66.12, −66.28, −67.87; IR (film): $\tilde{\nu}$ = 3280 cm^{-1} (m, ≡CH), 2050, 2070 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 330 (3800), 284 (28300), 273 (28500), 231 (36300), 210 nm (73200); MS (70 eV, EI): *m*/*z* (%): 807 (2) [*M*]$^+$, 750 (2) [*M* − C_4H_9]$^+$, 562 (2) [*M* − $C_{18}H_{29}$]$^+$, 457 (4) [$C_{23}H_{50}PSi$]$^+$, 231 (100) [$C_{17}H_{27}$]$^+$, 73 (8) [C_3H_9Si]$^+$, 57 (76) [C_4H_9]$^+$; elemental analysis calcd (%) for $C_{53}H_{80}P_2Si$ (807.3): C 78.85, H 9.99; found C 79.08, H 10.17.

3,8,13,18-Tetrakis(2,4,6-tri-*tert*-butylphenyl)-1,20-bis(triisopropylsilyl)-3,8,13,18-tetraphosphaicosa-1,4,6,9,11,14,16,19-octayne (27): The modified Eglinton coupling of **26** (1.13 g, 1.40 mmol) according to the general procedure afforded **27** as yellow crystals (1.09 g, 97 %). M.p. 76–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 42H, *i*Pr), 1.302 (s, 18H, *p*-*t*Bu^a), 1.299 (s, 18H, *p*-*t*Bu^b), 1.60 (s, 36H, *o*-*t*Bu^b), 1.64 (s, 36H, *o*-*t*Bu^a), 7.43 (d, ^4J(P,H) = 3.3 Hz, 4H, *m*-aryl^a), 7.44 (d, ^4J(P,H) = 3.6 Hz, *m*-aryl^b); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 11.29 (d, ^4J(P,C) = 0.6 Hz, C17), 18.56 (s, C18), 31.07 (s, C8^b), 31.10 (s, C8^a), 34.06 (d, ^4J(P,C) = 7.0 Hz, C6^b), 34.11 (d, ^4J(P,C) = 7.1 Hz, C6^a), 34.96 (d, ^5J(P,C) = 0.7 Hz, C7^a), 35.02 (d, ^5J(P,C) = 0.8 Hz, C7^b), 39.71 (d, ^3J(P,C) = 4.9 Hz, C5^b), 39.73 (d, ^3J(P,C) = 4.7 Hz, C5^a), 80.50–80.65 (m, C11, C14, C15, C15′), 81.65–81.83 (m, C11, C14, C15, C15′), 83.75–83.89 (m, C11, C14, C15, C15′), 92.77–93.06 (m, C12, C13, C16, C16′), 93.53–93.76 (m, C12, C13, C16, C16′), 94.14 (dd, *J*(P,C) = 17.9, 4.5 Hz, C12, C13, C16, C16′), 103.29 (dd, ^1J(P^a,C) = 12.7 Hz, ^6J(P^b,C) = 1.7 Hz, C9), 115.51 (d, ^2J(P,C) = 2.1 Hz, C10), 121.64 (ddd, ^1J(P^b,C) = 19.5 Hz, ^6J(P^{b,a},C) = 1.6 Hz, C1^b), 123.32 (dd, ^1J(P^a,C) = 21.3 Hz, ^6J(P^b,C) = 1.7 Hz, C1^a), 123.81 (d, ^3J(P,C) = 9.5 Hz, C3^a), 124.11 (d, ^3J(P,C) = 9.9 Hz, C3^b), 151.91 (d, ^4J(P,C) = 2.5 Hz, C4^b); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −63.87 (2P^b), −66.17 (2P^a); IR (KBr): $\tilde{\nu}$ = 2065 cm^{-1} (w); UV/Vis (*n*-hexane): λ_{max}, (ε) = 308 (72500), 278 (82900), 238 (98000), 211 nm (173400); elemental analysis calcd (%) for $C_{106}H_{158}P_4Si_2$ (1612.5): C 78.96, H 9.88; found C 78.84, H 10.24.

Synthesis of 27 by Cadiot–Chodkiewicz coupling of 17 with 24: A solution of **17** (98.0 mg, 0.15 mmol) in THF (4 mL) was metallated at −78 °C with *n*BuLi (0.20 mL, 0.31 mmol, 1.6M in *n*-hexane). After 30 min the temperature was increased to 0 °C, and CuCl (30.9 mg, 0.31 mmol) was added. The mixture was stirred for 20 min at 0 °C and finally for 20 min at room temperature. The solvent was removed under reduced pressure (not to dryness!) and replaced with dry, oxygen-free pyridine (5 mL). A solution of **24** (175 mg, 0.31 mmol) in THF (2.0 mL) was added within 30 min. After 12 h the dark reaction mixture was poured into HCl (2N, 10 mL). The coupling product was extracted with hexane (3 × 20 mL). The combined extracts were washed with HCl (2N, 10 mL), saturated $NaHCO_3$ solution (10 mL), and water. Evaporation and column chromatography (Al_2O_3, CH_2Cl_2/hexanes) afforded yellow crystals of **25** (41 mg, 2 %), m.p. 111–113 °C, and the coupling product **27** as yellow crystals (40.0 mg, 16 %), m.p. 78–111 °C, **15b** as a yellow oil (10 mg, 6 %) and **29** (10 mg, 6 %).

3,8,13,18-Tetrakis(2,4,6-tri-*tert*-butylphenyl)-3,8,13,18-tetraphosphaicosa-1,4,6,9,11,14,16,19-octayne (28) by desilylation of 27: A solution of TBAF (0.20 mmol, 0.20 mL, 1M in THF) was added to the solution of **27** (161 mg, 0.1 mmol) in THF (10 mL) at −78 °C and stirred for 2 h. After quenching of the mixture with water, evaporation of the organic solution and column chromatography (Al_2O_3, CH_2Cl_2/hexanes 1:6) afforded **28** as pale yellow crystals (53 %). M.p. 124–150 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 18H, *p*-*t*Bu^b), 1.31 (s, 18H, *p*-*t*Bu^a), 1.61 (s, 36H, *o*-*t*Bu^b), 1.64 (s, 36H, *o*-*t*Bu^a), 3.25 (d, ^3J(P,H) = 0.4 Hz, 2H, ≡CH), 7.45 (d, ^4J(P,H) = 3.5 Hz, 4H, *m*-aryl^b), 7.46 (d, ^4J(P,H) = 3.4 Hz, 4H, *m*-aryl^a); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.06 (s, C8^b), 31.08 (s, C8^a), 34.06 (d, ^4J(P,C) = 7.2 Hz, C6^b), 34.08 (d, ^4J(P,C) = 7.2 Hz, C6^a), 34.99 (d, ^5J(P,C) = 0.8 Hz, C7^a), 35.03 (d, ^5J(P,C) = 0.9 Hz, C7^b), 39.70 (d, ^3J(P,C) = 4.8 Hz, C5^b), 39.77 (d, ^3J(P,C) = 4.8 Hz, C5^a), [80.82–81.03 (m), 81.15 (dd, *J*(P,C) = 9.3, 1.7 Hz), 83.50–81.75 (m), 82.77 (dd, *J*(P,C) = 10.1, 3.6 Hz)]: C9, C11, C14, C15, C15′; [92.99–93.24 (m), 93.30–94.01 (m), 97.32 (d, ^2J(P,C) = 11.9 Hz)]: C12, C13, C16, C16′; 121.45 (m, C1^b), 122.11 (dd, ^1J(P^a,C) = 21.2 Hz, ^6J(P^b,C) = 1.7 Hz, C1^a), 124.04 (d, ^3J(P,C) = 9.3 Hz, C3^a), 124.12 (d, ^3J(P,C) = 9.8 Hz, C3^b), 152.28 (d, ^4J(P,C) = 2.4 Hz, C4^b), 152.52 (d, ^4J(P,C) = 2.5 Hz, C4^a), 158.02 (d, ^2J(P,C) = 17.9 Hz, C2^b, 158.07 (d, ^2J(P,C) = 18.0 Hz, C2^a); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −63.85 (P^b), −67.81 (P^a); IR (KBr): $\tilde{\nu}$ = 3300 (w, ≡CH), 2060 cm^{-1} (w, C≡C); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 308 (60500), 280 nm (75100); MS (FD, CH_2Cl_2): *m*/*z*: 1299; elemental analysis calcd (%) for $C_{88}H_{118}P_4$ (1299.8): C 81.32, H 9.15; found C 80.80, H 9.35.

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Oxidative coupling of 28 to 9 and 23: The modified Eglinton coupling of **28** (104 mg, 80 mmol) according to the general procedure afforded a yellow-orange solid that was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 1:3), followed by (SiO_2, CH_3CN/*n*-hexane 1:200). Two fractions of yellow solids were obtained: **9** (68 mg, 65 %) and **23** (5.5 mg, 5 %).

Compound ***9***: M.p. ≈250 °C (decomp); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (s, 36H, *p*-*t*Bu, 1.64 (s, 72H, *o*-*t*Bu), 7.43 (d, $^4J(P,H) = 3.1$ Hz, 8H, *m*-aryl); at −20 °C the inversion rate was reduced, the signal at 1.29 split to give a doublet, the other signals gave broad multiplets; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 21 °C): several broad signals from $\delta = -64.7$ to −67.2; $^{31}P\{^1H\}$ NMR (162 MHz, $C_2D_2Cl_4$, 140 °C): $\delta = -64.91$ (s, sharp), fast inversion of all pyramidal phosphine phosphorus atoms; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, −20 °C): $\delta = -68.13$ (s, **9a**), −66.26 (s, **9b**), −65.56 (s, **9c**), −65.56 (t, 1P, $J(P,P) = 1$ Hz, **9d**), −66.17 (t, 1P, $J(P,P) = 8.4$ Hz, **9d**), −66.80 (dd, 2P, $J(P,P) = 8.4$, 1.1 Hz, **9d**); the ratio of **9a**:**9b**:**9c**:**9d** = 1:5.1:6.2:10.6; IR (KBr): $\tilde{\nu} = 2165$ (w), 2065 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 300 (47800), 282 (72400), 256 (130200), 234 (133200), 208 nm (153300); MS (FD, CH_2Cl_2): *m*/*z*: 1296; elemental analysis calcd (%) for $C_{88}H_{116}P_4$ (1297.8): C 81.44, H 9.01; found C 80.22 H 9.12.

Compound ***23***: M.p. ≈280 °C (decomp); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (s, 72H, *p*-*t*Bu), 1.63 (s, 144H, *o*-*t*Bu), 7.45 (d, $^4J(P,H) = 3.5$ Hz, 16H, *m*-aryl); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = -63.52$ (br s); IR (KBr): $\tilde{\nu} = 2200$ (w), 2165 (w), 2100 cm^{-1} (m, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 290 (72500), 267 (130100), 205 nm (208200); elemental analysis calcd (%) for $C_{167}H_{232}P_8$ (2595.6): C 81.44, H 9.01; found C 80.47 H 9.10.

3,8,3,18-Tetrakis(2,4,6-tri-*tert*-butylphenyl)-1-(triisopropylsilyl)-3,8,13,18-tetraphosphaicosa-1,4,6,9,11,14,16,19-octayne (30) by partial desilylation of 27: TBAF (0.20 mmol, 0.20 mL, 1M in THF) was added to a solution of **27** (1.08 g, 0.67 mmol) in THF (100 mL) at −78 °C. After stirring for 2 h, the reaction mixture was quenched with water. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting yellow oil was purified by column chromatography (Al_2O_3, hexane) to give the starting material **27** as yellow crystals (254 mg, 24 %), m.p. 76–111 °C, followed by eluting with CH_2Cl_2/hexanes (1:20) to afford **30** as yellow crystals (323 mg, 33 %), m.p. 90–115 °C, and finally with CH_2Cl_2/hexanes (1:6) to give the bis-desilylated octayne **28** as yellow crystals (181 mg, 21 %), m.p. 124–150 °C (decomp). Compound **30**: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.04$ (s, 21H, Si(*i*Pr)), 1.30 (s, 9H, *p*-*t*Bu, (P^d), 1.30 (s, 18H, *p*-*t*Bu, ($P^{b,c}$), 1.31 (s, 9H, *p*-*t*Bu (P^a), 1.61 (s, 36H, *o*-*t*Bu, $P^{b,c}$), 1.63 (s, 18H, *o*-*t*Bu, P^a), 1.64 (s, 18H, *o*-*t*Bu, P^d), 3.25 (s, 1H, ≡CH), 7.43 (d, $^4J(P,H) = 3.2$ Hz, 2H, *m*-aryl, P^d), 7.44 (d, $^4J(P,H) = 3.4$ Hz, 2H, *m*-aryl, P^c), 7.45 (d, $^4J(P,H) = 3.5$ Hz, 2H, *m*-aryl, P^b), 7.45 (d, $^4J(P,H) = 3.2$ Hz, 2H, *m*-aryl, P^a); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.24$ (d, $^4J(P,C) = 1.35$ Hz, Si-*C*H(CH_3)$_2$), 18.56 (s, Si-CH(*C*H_3)$_2$), 103.27 (dd, $^1J(P,C) = 13.0$ Hz, $^6J(P,C) = 1.8$ Hz, P^d*C*≡C–Si), 115.53 (d, $^2J(P,C) = 2.2$ Hz, P^d–C≡*C*–Si); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = -63.82$ (P^b), −63.88 (P^c), −66.16 (P^d), −67.78 (P^a); IR (KBr): $\tilde{\nu} = 3300$ (w, ≡CH), 2065 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane): λ_{max} (ε) = 308 (70400), 278 (83800), 256 (86900), 238 (94000), 210 nm (167800); MS (FD, CH_2Cl_2): *m*/*z*: 1455; elemental analysis calcd (%) for $C_{97}H_{138}P_4Si$ (1456.2): C 80.01, H 9.55; found: C 80.18, H 9.70.

1,40-Bis(triisopropylsilyl)-3,8,13,18,23,28,33,38-octakis(2,4,6-tri-*tert*-butylphenyl)-3,8,13,18,23,28,33,38-octaphosphatetraconta-1,4,6,9,11,14,16,19,21,24,26,29,31,34,36,39-hexadecayne (31) by Eglinton coupling of 30: The modified Eglinton coupling of **30** (291 mg, 0.20 mmol) according to the general procedure afforded **31** as yellow powder (255 mg, 87 %). M.p. 180–190 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.04$ (s, 42H, Si-*i*Pr, 1.30 (s, 72H, *p*-*t*Bu), 1.60 (s, 108H, *o*-*t*Bu, $P^{b,c,d}$), 1.64 (s, 36H, *o*-*t*Bu, P^a), 7.43 (d, $^4J(P,H) = 3.3$ Hz, 4H, *m*-aryl, P^a), 7.44 (d, $^4J(P,H) = 3.5$ Hz, 4H, *m*-aryl, P^b), 7.45 (d, $^4J(P,H) = 3.5$ Hz, 8H, *m*-aryl, $P^{c,d}$); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 11.24$ (d, $^4J(P,C) = 0.9$ Hz, Si-*C*H(CH_3)$_2$), 18.57 (s, Si-CH(*C*H_3)$_2$), 103.29 (dd, $^1J(P,C) = 12.6$ Hz, $^6J(P,C) = 1.8$ Hz), P-*C*≡C–Si), 115.53 (d, $^2J(P,C) = 2.2$ Hz, P-C≡*C*–Si); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = -63.70$, (P^c, P^d), −63.87 (P^b), −66.17 (P^a); IR (KBr): $\tilde{\nu} = 2065$ (w), 2120 cm^{-1} (w, C≡C); UV/Vis (*n*-hexane); λ_{max} (ε) = 248 (376000), 217 nm (617000); elemental analysis calcd (%) for $C_{194}H_{274}P_8Si_2$ (2908.4): C 80.12, H 9.50; found C 80.33, H 9.54.

3,8,13,18,23,28,33,38-Octakis(2,4,6-tri-*tert*-butylphenyl)-3,8,13,18,23,28,33,38-octaphosphatetraconta-1,4,6,9,11,14,16,19,21,24,26,29,31,34,36,39-hexadecayne (32) by desilylation of 31. A solution of TBAF (1M, 35 mL) was added to a solution of **31** (102 mg, 35.0 μmol) in THF (50 mL) at −78 °C. After 2.5 h, the mixture was quenched with water. The resulting yellow precipitate was separated by centrifugation, washed with THF (2 × 5 mL), and dried in vacuo to give **32** as yellow powder (76.1 mg, 83 %). M.p. ≈190 °C (decomp), insoluble in all usual organic solvents; IR (KBr): $\tilde{\nu} =$ 3300 (w, ≡CH), 2160 (w), 2060 cm^{-1} (w, C≡C); the Si–C band $\tilde{\nu} = 795$ cm^{-1} (m) had disappeared.

Synthesis of octaphosphacyclotetracontahexadecayne (23) by an intramolecular Eglinton coupling of 32: Compound **32** (20.8 mg, 8.00 μmol) was added to a solution of $[Cu(OAc)_2]\cdot H_2O$ (25.6 mg, 128 μmol) and CuCl (9.50 mg, 96 μmol) in small portions over a period of 4 h at 65 °C. The mixture was stirred for a further 2 h at 65 °C and 12 h at room temperature. The solvent was removed and the residue treated with CH_2Cl_2/H_2O (30 mL, 1:1); the organic phase was washed successively with water (5 mL), HCl (5 mL, 10 %), $NaHCO_3$ solution (5 mL), and water (5 mL). Purification by column chromatography (Al_2O_3, CH_2Cl_2/*n*-hexane 1:10) afforded **23** as yellow crystals (5.80 mg, 27 %). M.p. ≈280 °C (decomp).

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