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Alternative Synthesis and Structures of *C*-monoacetylenic Phosphaalkenes

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Abstract. An alternative synthesis of *C*-monoacetylenic phosphaalkenes *trans*-Mes*P=C(Me)(C≡CR) (Mes* = 2,4,6-^{t}Bu$_3$Ph, R = Ph, SiMe$_3$) from *C*-bromophosphaalkenes *cis*-Mes*P=C(Me)Br using standard Sonogashira coupling conditions is described. Crystallographic studies confirm *cis-trans* isomerization of the P=C double bond during Pd-catalyzed cross coupling, leading exclusively to *trans*-acetylenic phosphaalkenes. Crystallographic studies of all synthesized compounds reveal the extend of π-conjugation over the acetylene and P=C π-systems.

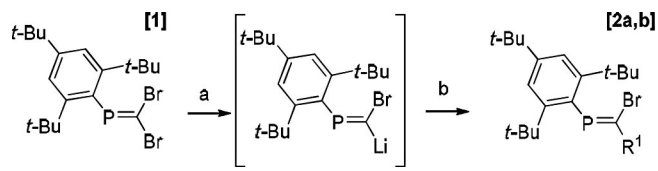
Introduction

Originating from the curiosity of breaking the double bond rule, different synthetic routes have been suggested for the synthesis of low-valent and low-coordinated phosphorus compounds. Furthermore, extensive work has been conducted on synthesis and spectroscopic studies of phosphaalkenes ($\sigma^2\lambda^3$ phosphanes) with pendant π-conjugated systems for potential use in organic electronics,[1] including a range of P=C containing poly- and oligomers.[1e] Moreover, the introduction of electro-active centers, such as metallocenes, has been of great interest.[2] The all carbon ene-yne and ene-diyne motifs display interesting opto-electronic[3] and conductive[4] properties that suggest possible applications in single molecule electronics,[3,5] and the insertion of a heteroatom such as phosphorus offers the possibility of further interesting properties.[6] While the versatility of acetylene bridges in building up large π-conjugated and cross-conjugated molecular structures has been extensively explored in organic chemistry,[7] examples of heavier element analogues thereof are very rare.[8]

Recent work in our laboratory has focused on finding different routes to *C*-mono- and di-acetylenic phosphaethenes.[9] *Van der Sluis* et al. have described coupling reactions of 2-bromo-1-phosphaethenes, which allow the introduction of various groups bonded directly to phosphaalkenes, including an acetylene moiety.[10] In the present work, we describe an alternative synthesis of 2-acetylenic phosphaethenes from methyl-substituted 2-bromo-1-phosphaethenes using standard Sonogashira coupling conditions. This may allow greater functional group tolerance than the original procedure, which employed Grignard reagents. Oxidative acetylene homo-coupling under modified Glaser-type conditions afforded a butadiyne-bridged bis-phosphaethene. All reported phosphaalkenes have been structurally characterized by means of X-ray crystallography.

Results and Discussion

2,2-Dibromophosphaethene (**1**) was prepared by treatment of Mes*PCl$_2$ with CHBr$_3$ in the presence of LDA, according to published procedures.[10,11] Substitution of one bromide functionality by a methyl group can be achieved by stirring a solution of **1** with *n*-BuLi at low temperatures, followed by quenching of the intermediate with MeI (Scheme 1).[11,12] 2,2-Dihalophosphaethenes bearing the Mes* group are usually selective towards *trans* functionalization.[11, 13] In order to achieve highest possible selectivity, it is important to perform the lithiation of 2,2-dibromophosphaethene **1** at –130 °C; which yields the *cis*-phosphacarbenoid species exclusively.[13a] By doing so, (*Z*)-**2a** is obtained as the single isomer in excellent yields without detectable traces of (*E*)-**2a**.



Scheme 1. Selective *trans* metal/halogen exchange of dibromophosphaethene **1**. Isomerization of the lithiated intermediate is suppressed at low temperatures. For **2a** R^1 = CH$_3$, and **2b** R^1 = C(OH)Ph$_2$; (a) *n*-BuLi, –130 °C, Trapp mixture, 30 min; (b) MeI (**2a**) or Ph$_2$C=O (**2b**), –130 °C, 30 min then to r.t., 2 h. 93 % (**2a**), 71 % (**2b**).

In order to facilitate the introduction of the acetylenic moieties, we investigated the direct coupling of terminal acetylenes using regular Sonogashira coupling conditions. Phenyl- or trimethylsilylacetylene undergoes C–C bond formation in the presence of 5 mol-% Pd-catalyst (different types), CuI and base (triethylamine or pyridine) in DMF/THF or NEt$_3$ solutions. In order to assess the *E*/*Z* stereochemistry of the product

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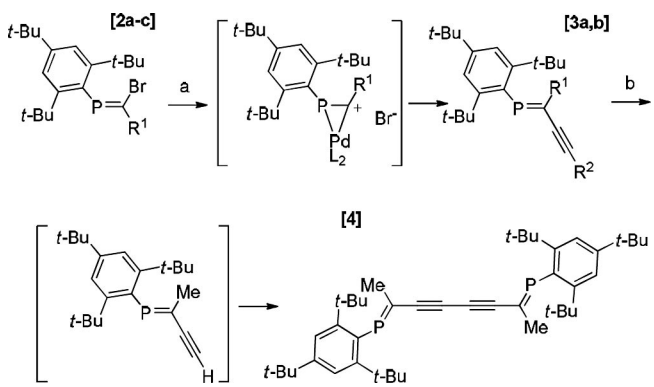
we carried out X-ray crystallographic analysis of both products and starting materials. Our investigations clearly show that isomerization of the P=C double bond occurs during the palladium mediated introduction of the acetylene moiety in the case of both phenyl- and trimethylsilylacetylene. This is in line with the findings from *van der Sluis* et al., who reported similar behavior for the coupling of the related compound *cis*-Mes*P=C(H)Br (**2c**), with Grignard reagents, including phenylethynyl magnesium bromide.[10] . Moreover, the use of a more efficient catalyst, [$PdCl_2$(dppf)], which exhibits superior reactivity to [$PdCl_2(PPh_3)_2$] (complete conversion of **2a** within 5 minutes as monitored by TLC), also does not result in retention of the P=C double bond stereochemistry. The proposed mechanism suggests that the coupling proceeds via a cationic palladacycle intermediate (Scheme 2).[10] Hence, introduction of more sterically demanding substituents at R^1 in **2** or the use of other catalysts may lead to a *cisoid* attack of the acetylene moiety. However, the presence of a more sterically demanding methyl group in **2a** in place of the proton in **2c** does not result in a retention of the stereochemistry at the P=C double bond. Irrespective of the catalyst ([$PdCl_2$(dppf)] or [$PdCl_2(PPh_3)_2$]) or the acetylene (TMS- or phenylacetylene) being used, the coupling leads exclusively to the *trans*-product. Thus, it is evident that the reactivity of the postulated palladium intermediate is mainly governed by steric effects.



Scheme 2. Coupling of 2-bromophosphaethene **2** under inversion of configuration and synthesis of butadiyne bridged bisphosphaalkene **4**. Phosphaethenes **2a–c**: **2a** R^1 = CH_3, **2b** R^1 = $C(OH)Ph_2$, **2c** R^1 = H. (a) **3a** R^2 = Ph: *Alternative 1*: Phenylethynyl magnesium bromide; [$Pd(dba)_2$], PPh_3, THF, 3h, 50 °C, **3a** 42%. *Alternative 2*: Phenylacetylene, [$PdCl_2(PPh_3)_2$], CuI, NEt_3, 14 h, r.t, **3a** 40%. **3b** R^2 = $SiMe_3$. *Alternative 1*: Ethynyltrimethylsilane, [$Pd(PPh_3)_2Cl_2$] or [$PdCl_2$(dppf)], CuI, pyridine, NEt_3, THF/DMF, **3b** 78%. *Alternative 2*: Ethynyltrimethylsilane, [$PdCl_2(PPh_3)_2$], CuI, NEt_3 (solvent), 14 h, r.t, **3b** 63% (b) **4**: Bu_4NF, THF, 30 min, then $Cu(OAc)_2$, TMEDA, 14 h, 52%.

With the aim to increase the steric demand of the substituent and thereby suppress the *cis-trans* isomerization during the Sonogashira coupling step, we introduced a diphenylhydroxymethane moiety through reaction of **1** with benzophenone to afford **2b** (Scheme 1). However, attempts to perform coupling reactions with **2b** were unsuccessful, resulting only in partial decomposition of the starting material and no detectable coupling products. It seems that the diphenylhydroxymethyl substituent introduces more steric bulk than the reaction can tolerate, as the bromide may no longer be accessible to the palladium catalyst or the incoming acetylene.

An extended π-conjugated compound was prepared by homocoupling of TMS-acetylenic phosphaalkene **3b**. In order to prepare the butadiyne bridged bisphosphaalkene **4**, the phosphaalkene **3b** is deprotected in situ and the intermediate subsequently subjected to slightly modified Glaser-Eglinton coupling conditions. After chromatographic workup the phosphaalkene dimer **4** is obtained in moderate yields (Scheme 2).

Electronic and steric effects influence the spectroscopic and crystallographic properties of the described phosphaalkenes as compared to those of the structurally well characterized 2,2-dibromophosphaethene.[14] Table 1 shows the $^{31}P\{^1H\}$ NMR chemical shifts of phosphaethenes **1–4** in $CDCl_3$. The electronic influence of the substituents on the phosphorus chemical shift is clearly observable: in **1**, the two electron-withdrawing bromines connected to the phosphaalkene carbon result in a downfield signal in the $^{31}P\{^1H\}$ NMR spectrum at δ = 270.5 ppm. In comparison, **2a,** which has one bromine and one methyl substituent, has a chemical shift of 242.4 ppm. Diphenylhydroxymethyl substitution in **2b** again leads to a downfield shift (276.5 ppm) and the largest $^1J_{PC}$ coupling in this series (71.6 Hz). Increasing the electron delocalization by introducing acetylene substituents, as in **3a**,**b**, results in even further downfield $^{31}P\{^1H\}$ NMR shifts to 284.0 ppm and 288.5 ppm, respectively. Dimer **4** exhibits the largest delocalization and a $^{31}P\{^1H\}$ NMR signal of 302.9 ppm is thus observed.

Table 1. $^{31}P\{^1H\}$ and ^{13}C NMR chemical shifts and $^1J_{PC}$ of the P=C double bond for phosphaethenes **1–4**.

	$\delta^{31}P^{a)}$	$^1J_{P=C}{}^{b)}$	$\delta^{13}C^{a)}$
1[15]	270.5	57.6	139.3
2a	242.4	65.0	161.2
2b	276.5	71.6	170.9
3a	284.0	33.7	160.5
3b	288.5	34.6	160.8
4	302.9	68.8	166.0

a) ppm b) Hz.

The UV/Vis spectrum of TMS-substituted **3b** shows a longest wavelength absorption maximum of λ_{max} = 309 nm in dichloromethane, while the presence of the phenyl group in **3a** induces an additional red-shift of 17 nm (for **3a** λ_{max} = 326 nm). Dimer **4** exhibits the lowest energy absorption maximum at λ_{max} = 359 nm. Compared to our previously reported C,C-diacetylenic phosphaalkenes with both TMS- and phenyl groups, the monoacetylenic phosphaethenes presented here have higher energy absorption maxima.[9d]

We were able to grow single crystals of compounds **2–4** that were suitable for X-ray diffraction by slow diffusion or slow evaporation of suitable solvent mixtures. The solid state structures confirm that the isomerization of the P=C double bond occurs during the coupling step in all cases (Figure 1, Figure 2).

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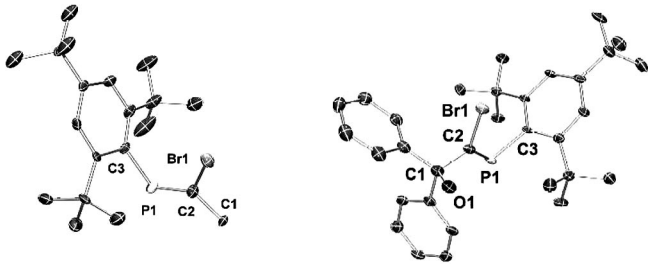

Figure 1. ORTEP plot of phosphaalkenes **2a** (left) and **2b** (right) (ellipsoids are drawn at a probability level of 50 %). Hydrogen atoms and a disordered *tert*-butyl group with occupancy of less than 0.5 in **2a** are omitted for clarity. For **2b** only one of the two independent molecules is displayed.

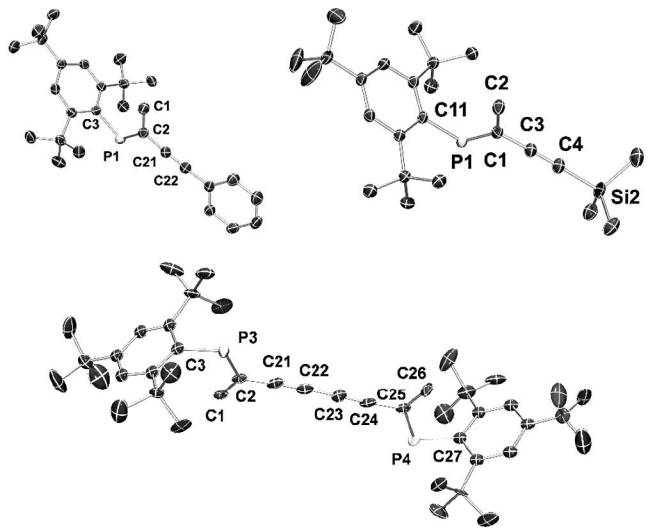

Figure 2. ORTEP plot of phosphaalkenes **3a** (top left), **3b** (top right) and **4** (bottom) (ellipsoids are drawn at a probability level of 50 %). Hydrogen atoms and a disordered *tert*-butyl group (**3b**) with occupancy of less than 0.5 are omitted for clarity. For **3a** and **4** only one of the two independent molecules is displayed.

Selected structural parameters of phosphaaethenes **1**–**4** are shown in Table 2. Replacement of the first bromine atom by an electron donating methyl group leads to a significant elongation of the P=C double bond. Introducing the bulkier diphenylhydroxymethyl moiety barely effects the P=C bond length, but increases the bond angle to approximately 124°. Interestingly, there is only a slight elongation upon coupling with trimethylsilyl- or phenylacetylene. Concomitant with acetylene coupling and consequent isomerization is a shortening of the C1(methyl)–C2 bond length. Inversion of the relative geometry of the P=C bond also leads to a widening of the P=C2–C1 bond angle from 121.6(5)° to approximately 128°. Interestingly, the C_{ipso}–P=C angle is also influenced by the different substituents, either for steric or electronic reasons. In the case of phosphaalkene **3a**, the solid state structure clearly shows the extended conjugation of the π-system over the P=C double bond and the phenyl unit, which are almost coplanar (the acute angle between the least squares (l.s.) planes is 9.2(2)°). In the phosphaalkene dimer **4**, we observe an s-*trans* arrangement of the P=C units.

Conclusions

In summary, we have demonstrated that isomerization to the thermodynamically favored *trans*-Mes*P=C(Me)(C≡CR) **3a,b** occurs during the Pd-catalyzed cross coupling of *cis*-Mes*P=C(Me)Br **2a**, and cannot be suppressed by the use of more efficient catalysts. Further increase of the steric bulk at the phosphaalkene as in **2b** completely inhibits coupling. Crystallographic investigations reveal an almost planar arrangement over the whole acetylenic phosphaethene portion of the molecule, giving rise to extended conjugation pathways and bathochromically shifted lowest energy absorption maxima.

Experimental Section

General: Syntheses were carried out under a dry nitrogen atmosphere using modified Schlenk techniques. NMR spectra were recorded in $CDCl_3$ using a JEOL Eclipse+ 400 MHz or a Varian Mercury+ spectrometer operating at a proton frequency of 399.8 MHz and 300.02 MHz, respectively. ^{1}H- and ^{13}C NMR spectra were internally referenced to solvent residual peaks (7.16 ppm and 77.1 ppm, respectively); ^{31}P{^{1}H} NMR spectra were externally referenced to 85 % aqueous H_3PO_4. Solvents and starting materials were purchased from Sigma Aldrich, ABCR, or VWR and used as received, except for THF, which was dried with sodium and benzophenone, and freshly distilled prior to use. Column chromatography was performed on Merck silica gel SI-60 Å (35–70). High-resolution mass spectral analyses (HRMS) were performed on a high-resolution and FTMS+pNSI mass spectrometer (orbitrapXL) or on a MicroTOF spectrometer with ESI core. Compound **1** was prepared according to a previously described procedure.[15]

Crystallographic Studies: All measurements were performed using graphite-monochromatized Mo-K_α radiation at 100(1) K with a Bruker

Table 2. Selected structural parameters of phosphaethenes **1**–**4**.

	R^1	R^2	P=C$^{a)}$	C1-Me$^{b)}$	P=C-Me$^{b)}$
1[14a]	Br	Br $^{c)}$	1.65(2)	–	–
2a	Me	Br $^{c)}$	1.680(8)	1.548(11)	121.6(5)
2b	C(OH)PH$_2$	Br $^{c)}$	1.675(9)	1.537(12)	123.5(6)
			1.676(9)	1.542(12)	124.5(6)
3a	Me	Ph	1.693(2)	1.504(3)	128.3(2)
3b	Me	TMS	1.691(1)	1.510(2)	128.5(1)
4	Me	n.a.	1.681(7)	1.498(15)	127.8(7)
			1.720(8)	1.612(19)	131.5(10)

a) distances in Å b) angles in degrees; c) substituent *cis* to Mes*.

Smart APEXII. Data integration and absorption correction was carried out with SAINT and SADABS, respectively.[16] Structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[17] using WinGX.[18] Graphical representations were prepared with ORTEP for Windows[19] and POV-Ray. The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the phenyl rings were put at the external bisector of the C–C–C angle at a C–H distance of 0.95 Å. The hydrogen atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the X–C bond, and C–H distances of 0.98 Å.

Synthesis of Phosphaalkene (2a): Phosphaalkene **2a** was prepared using modifications to the procedures reported by *Appel* et al.[11] and *van der Sluis* et al.[10] Mes*P=C(Br)$_2$ **1** (2.6 g, 5.8 mmol) was dissolved in THF (100 mL), Et_2O (25 mL), and pentane (25 mL). The mixture was cooled to –120 °C with dry ice and liquid nitrogen in a cooling bath containing 4:1:1 THF:Et_2O:pentane or a bath containing only pentane. *n*-BuLi (2.5 M, 2.3 mL, 5.80 mmol) was added drop wise and the yellow to orange reaction mixture was kept at –120 °C for 30 min. MeI (0.72 ml, 11.6 mmol) was added dropwise, during which the color of the reaction mixture became slightly paler. The solution was maintained at –120 °C for 30 min before warming up to r.t. for 2 h. A 1:1 V:V mixture of NH_3 (28 %, in water):EtOH (20 mL) was added and the solution was stirred for 30 min. Afterwards, the organic phase was washed with a saturated aqueous $NaHCO_3$ solution (2 × 50 mL) and a saturated aqueous NH_4Cl solution (2 × 50 mL). The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed in vacuo and the residue purified on a silica column (pentane) to yield a white solid (2.07 g, 5.40 mmol). Yield: 93 %. Recrystallization from dichloromethane/acetonitrile yielded white crystals.

^{1}H NMR (399.8 MHz, $CDCl_3$): δ = 1.36 (s, 9H, *para-tert*-butyl), 1.50 (s, 18H, *ortho-tert*-butyl), 2.68 (d, $J_{P,H}$ = 24.4 Hz, 3H, CH_3) 7.43 (s, 2H, Ar). **^{31}P{^{1}H} NMR** (161.8 MHz, $CDCl_3$): δ = 242.4. **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ = 31.3 (d, $J_{P,C}$=35.2 Hz, CH_3), 31.4 (s, *para*-C(CH_3)$_3$), 32.6 (s, *ortho*-C(CH_3)$_3$), 32.7 (s, *ortho*-C(CH_3)$_3$), 35.0 (s, *para-C*(CH_3)$_3$), 37.8 (s, *ortho*-C(CH_3)$_3$), 122.0 (s, *meta*-Ar), 138.7 (d, P–C, $J_{P,C}$ =52.2 Hz), 150.7 (s, *para*-Ar), 152.9 (s, *ortho*-Ar), 161.2 (d, P=C, $J_{P,C}$ = 57.0 Hz). ESI MS: *m/z* [2M+Ag] $^+$ 872.95 (100), [MH+Ag] $^+$ 490.96 (50).

Crystal Structure Analysis of (2a): Single crystals of **2a** suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane/acetonitrile solution. Compound **2a** crystallized in the monoclinic space group $P2_1/n$ (No. 14), $C_{20}H_{32}BrP$, M = 383.33, crystal dimensions = 0.15 × 0.30 × 0.30 mm, a = 6.1700(5) Å, b = 25.056(2) Å, c = 13.0356(10) Å, β = 90.041(1)°, V = 2015.3(3) Å^3, Z = 4, $2\theta_{max}$ = 52.74°, ρ = 1.263 g·cm^{-1}, μ(Mo-K_α) = 2.116 mm^{-1}, F(000) = 808, 29543 reflections measured, 4123 unique (R_{int} = 0.0453), $R1$ = 0.0892(I>2.0σ(I)), Rw = 0.2333, GooF = 1.406), 210 parameters, 0 restraints.

Synthesis of Phosphaalkene (2b): To a cold (–100 °C) solution of **1** (155 mg, 0.35 mmol) in THF (15 mL) was added one equivalent of *n*-BuLi (140 µL, 2.5 M) and the solution stirred for approximately 30 min. After addition of benzophenone (75 mg, 0.41 mmol) the temperature was maintained for another 30 min and then gradually allowed to reach r.t. The slurry was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate. After drying ($MgSO_4$) and removal of the solvent, the crude product was purified on a silica gel column (ethyl acetate/dichloromethane 3:1) Recrystallization from methanol/ethyl acetate gave phosphaalkene **2b** as a white solid (137 mg, 0.25 mmol). Yield: 71 %.

^{1}H NMR (300.0 MHz, $CDCl_3$, 25 °C): δ= 1.32 (s, 9H, *para-tert*-butyl), 1.48 (s, 18H, *meta-tert*-butyl), 3.33 (br. s., 1H, OH), 7.33 (m, 6 H, Ph), 7.40 (d, $^5J_{PH}$ = 1.6 Hz, 2H, Mes*), 7.53 (dd, 1.9 Hz, 8.0 Hz, Ph). **^{13}C NMR** (75.5 MHz, $CDCl_3$, 25 °C): δ=31.40 (s, *para*-C(CH_3)$_3$), 33.13 (d, $^4J_{PC}$ = 7.3 Hz, *meta*-C(CH_3)$_3$), 35.05 (s, *para-C*(CH_3)$_3$), 37.98 (br. s., *meta-C*(CH_3)$_3$), 85.61 (d, $^3J_{PC}$ = 22.9 Hz, COH), 122.48 (s, Mes*), 127.81 (s, Ph), 128.26 (d, 2.6 Hz, Mes*), 130.12 (s, Ph), 132,47 (s, Ph), 137.67 (s, Ph), 144.17 (d, 7.9 Hz, Mes*), 150.90 (s, Mes*) 153.23 (d, 3.0 Hz Mes*), 170.87 (d, $^1J_{PC}$ = 71.6 Hz, P=C). **^{31}P{^{1}H} NMR** (125.5 MHz, $CDCl_3$, 25 °C): δ = 276.5 (s). λ_{max} (CH_2Cl_2): 327 nm.

Crystal Structure Analysis of (2b): Single crystals of **2b** suitable for X-ray diffraction were obtained by solidification of the oily product as colorless blocks. Compound **2b** crystallized in the triclinic space group $P\bar{1}$ (No.2), $C_{32}H_{40}BrOP$, M = 551.52, crystal dimensions = 0.4 × 0.30 × 0.27 mm, a = 13.0800(9) Å, b = 13.6238(10) Å, c = 16.5066(12) Å, α = 86.519(4)°, β = 81.829(4)°, γ = 88.712(4)°, 2905.9(4) Å^3, Z = 4, $2\theta_{max}$ = 53.1°, ρ = 1.261 g·cm^{-1}, μ(Mo-K_α) = 1.491 mm^{-1}, F(000) = 1160, 40726 reflections measured, 11753 unique (R_{int} = 0.0595), $R1$ = 0.1081(I>2.0σ(I)), Rw = 0.3542, GooF = 1.066), 650 parameters, 0 restraints.

Synthesis of Phosphaalkene (3a): Bromoethane (EtBr) (0.5 mL, 6.7 mmol) was added to a suspension of magnesium turnings (700 mg, 28.8 mmol) in THF (2 mL) in a 50 mL 3-necked round bottom flask at 60 °C, resulting in vigorous bubbling. The remaining EtBr (1.5 mL, 20.1 mmol) was added dropwise as a THF solution (15 mL) over 30 min. The mixture was then heated at reflux for 20 min. After cooling to room temperature, the solution was transferred with a cannula into a dropping funnel connected to a 100 mL 3-necked flask containing phenylacetylene (2.94 mL, 26.8 mmol) in THF (10 mL), leaving unreacted magnesium in the original flask. EtMgBr was added dropwise at 0 °C. The reaction was stirred for 20 min, and then warmed to room temperature. It was then stirred at 60 °C for 2 h, which yielded a milky white mixture of phenylethynylmagnesium bromide with a concentration of approx. 0.8 M. Phosphaalkene **2a** (200 mg, 0.57 mmol) was dissolved in THF (20 mL) and [Pd(dba)$_2$] (31 mg, 0.054 mmol), PPh_3 (14 mg, 0.054 mmol) were added. The previously prepared phenylethynylmagnesium bromide (0.8 M in THF, 1.4 mL, 1.1 mmol) was then added. The reaction was stirred for 1.5 h at room temperature, and then for 1.5 h at 50 °C. The reaction mixture was filtered through a plug of silica, which was then rinsed with dichloromethane. The filtrate was concentrated, and then purified on a silica column (pentane). Phosphaalkene **3a** was isolated as a white solid (100 mg, 0.25 mmol). Yield: 43 %.

Alternative Synthesis of (3a): To phosphaalkene **2a** (150 mg, 0.39 mmol), [$PdCl_2(PPh_3)_2$] (14 mg, 0.020 mmol), CuI (4 mg, 0.021 mmol) and deaerated NEt_3 (5 mL) were added. Phenylacetylene (0.086 mL, 0.78 mmol) was added to the yellow suspension which after stirring overnight changed to a brown color. The solvent was removed and the solid dissolved in diethyl ether. The reaction mixture was evaporated on silica and purified on a silica column (pentane). Phosphaalkene **3a** was isolated as a white solid (63 mg, 0.16 mmol). Yield 40 %.

^{1}H NMR (399.8 MHz, $CDCl_3$): δ = 1.36 (s, 9H, *para-tert*-butyl), 1.42 (d, $^4J_{PH}$ = 13.5 Hz, 3H, P=CCH$_3$), 1.53 (s, 18H, *meta-tert*-butyl), 7.29–7.36 (m, 3H, arom., Ph) 7.41 (br. s, 2H, arom.; Mes*), 7.49–7.53 (m, 2H, arom., Ph). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ= 25.0 (d, $^3J_{PC}$ =

14.1 Hz, P=C-CH_3), 31.3 (s, *para*-C(CH_3)$_3$), 32.6 (d, $^4J_{PC}$ = 6.2 Hz, *meta*-C(CH_3)$_3$), 35.0 (s, *para*-*C*(CH_3)$_3$), 38.0 (s, *meta*-*C*(CH_3)$_3$), 94.7 (d, $^2J_{PC}$ = 28.2 Hz, acetylenic-C), 96.9 (d, $^3J_{PC}$ = 18.9 Hz, acetylenic-C), 121.7 (s, arom. *meta*-C, Mes*), 123.8 (d, $^4J_{PC}$ = 6.9 Hz, arom. *ipso*-C, Ph), 128.0 (s, *para*-C, Ph), 128.2 (s, *meta*-C, Ph), 131.5 (d, $^5J_{PC}$ = 5.3 Hz, arom. *ortho*-C, Ph), 135.90 (d, $^1J_{PC}$ = 60.4 Hz, arom. *ipso* C), 150.5 (s, arom. *para*-C, Mes*) 153.8 (s, arom. *ortho*-C, Mes*), 160.5 (d, $^1J_{PC}$ = 33.7 Hz, P=C). **^{31}P{^{1}H} NMR** (161.8 MHz, $CDCl_3$, 23 °C): δ = 284.0 (s). **HR-MS** (ESI): m/z 427.25261 [M+Na]$^+$; calcd for $C_{28}H_{37}PNa$ 427.2521. Anal. Calcd. for [$C_{28}H_{37}P$•2H_2O]; C, 76.33; H, 9.38. Found C, 76.39; H, 9.84. λ_{max} (CH_2Cl_2): 335 nm

Crystal Structure Analysis of (3a): Single crystals of **3a** suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane/acetonitrile solution. Compound **3a** crystallized in the monoclinic space group *C*2/*c* (No. 15), $C_{28}H_{37}P$, M = 404.55, crystal dimensions = 0.20 × 0.20 × 0.30 mm, *a* = 53.882(3) Å, *b* = 6.1348(3) Å, *c* = 36.151(2) Å, β = 122.653(2)°, *V* = 10061.3(10) Å^3, *Z* = 16, $2\theta_{max}$ = 55.42°, ρ = 1.068 g•cm^{-1}, μ(Mo-K_α) = 0.120 mm^{-1}, *F*(000) = 3520.0, 60462 reflections measured, 11706 unique (R_{int} = 0.0670), *R*1 = 0.0505 (*I*>2.0σ(*I*)), *Rw* = 0.1517, GooF = 1.033), 557 parameters, 0 restraints.

Synthesis of Phosphaalkene (3b): Phosphaalkene **2a** (40 mg, 0.10 mmol) was dissolved in deaerated THF:DMF (5:5 mL). After addition of the catalyst, either [$PdCl_2(PPh_3)$] (3.5 mg, 0.005 mmol) or [$PdCl_2$(dppf)]·CH_2Cl_2 ((4 mg, 0.005 mmol) and CuI (2 mg, 0.01 mmol), NEt_3/pyridine (1 mL of a 3:1 mixture) and ethynyltrimethylsilane were added (35 mg 0.36 mmol). The reaction was monitored by TLC until the starting material had disappeared (approximately 5 min for [$PdCl_2$(dppf)]·CH_2Cl_2). The organic phase was washed with saturated aqueous NH_4Cl solution and brine. The organic phases were dried ($MgSO_4$). The residue was purified on a silica column (pentane) Phosphaalkene **3b** was isolated in good yield as a colorless solid (32 mg 0.078 mmol) Yield: 78 %.

Alternative Synthesis of (3b): To phosphaalkene **2a** (390 mg, 1 mmol), [$PdCl_2(PPh_3)_2$] (35 mg, 0.050 mmol) and CuI (19 mg, 0.10 mmol) deaerated NEt_3 (15 mL) was added. Ethynyltrimethylsilane (0.71 mL, 5 mmol) was added to the yellow suspension which upon stirring overnight changed to a brown color. The solvent was removed and the solid was redissolved in pentane and purified on a silica column (pentane). **3b** was isolated as a white solid (251 mg, 0.63 mmol). Yield 63 %.

^{1}H NMR (399.8 MHz, $CDCl_3$, 23 °C): δ = 0.23 (s, 9H, $SiMe_3$), 1.29 (d, $^4J_{PH}$ = 13.5 Hz, 3H, P=CCH_3), 1.33 (s, 9H, *para*-*tert*-butyl), 1.48 (s, 18H, *meta*-*tert*-butyl), 7.41 (br. s., 2H, arom. Mes*).**^{13}C NMR** (100.5 MHz, $CDCl_3$): δ = 0.27 ($SiMe_3$), 25.1 (d, $^3J_{PC}$ = 13.8 Hz, P=C-*C*H_3), 31.44 (s, *para*-C(*C*H_3)$_3$), 32.70 (d, $^4J_{PC}$ = 6.9 Hz, *meta*-C(*C*H_3)$_3$), 35.10 (s, *para*-*C*(CH_3)$_3$), 38.03 (br. s., *meta*-*C*(CH_3)$_3$), 101.46 (d, $^4J_{PC}$ = 16.1 Hz, acetylenic C_2), 109.57 (d, $^3J_{PC}$ = 27.7 Hz, acetylenic C_1), 121.76 (s, arom. *meta* C), 135.90 (d, $^1J_{PC}$ = 60.7 Hz, arom. *ipso*-C), 150.53 (s, arom. *para*-C) 153.76 (s, arom. *ortho*-C), 160.78 (d, $^1J_{PC}$ = 34.6 Hz, P=C). **^{31}P{^{1}H} NMR** (161.8 MHz, $CDCl_3$, 23 °C): δ = 288.5 (s). λ_{max} (CH_2Cl_2): 309 nm

Crystal Structure Analysis of (3b): Single crystals suitable for X-ray diffraction were obtained by slow evaporation of pentane/chloroform at 4 °C. Phosphaalkene **3b** crystallized in the monoclinic space group $P2_1/c$ (No. 14), $C_{25}H_{41}PSi$, M = 400.64, crystal dimensions 0.18 × 0.2 × 0.2 mm, *a* = 9.2485(6) Å, *b* = 21.6460(15) Å, *c* = 12.7440(9) Å, β = 98.688(1)°, *V* = 2522.0(3) Å^3, *Z* = 4, $2\theta_{max}$= 62.5°, ρ = 1.055 g•cm^{-1}, μ(Mo-K_α) = 0.164 mm^{-1}, *F*(000) = 880, 47957 reflections measured, 7784 unique (R_{int} = 0.0838) *R*1 = 0.0434 (*I*>2.0σ(*I*)), *Rw* = 0.1267 (all data), GooF = 1.008, 257 parameters, 0 restraints.

Synthesis of Phosphaalkene Dimer (4): Bu_4NF (1.0 M in THF, 0.17 mL, 0.17 mmol) was added to a THF solution (10 mL) of phosphaalkene **3b** (69 mg, 0.17 mmol). After stirring at room temperature for 30 min, the reaction mixture was filtered through a plug of silica (ethyl acetate, 1 % H_2O). $Cu(OAc)_2$·H_2O (7 mg, 0.034 mmol) and TMEDA (500μL) were added and the suspension was vigorously stirred. The reaction was monitored by TLC and was complete after 12 h. The organic phase was washed with saturated aqueous NH_4Cl solution and brine. The collected organic phases were dried ($MgSO_4$) and purified on a short silica column (pentane/ethyl acetate 95:5), yielding pure bisphosphaalkene **4** as a slightly yellow solid in moderate yields (29 mg, 0.044 mmol). Yield: 52 %.

^{1}H NMR (399.8 MHz, $CDCl_3$, 23 °C): δ = 1.32 (s, 18H, *para*-*tert*-butyl), 1.34 (d, $^4J_{PH}$ = 15.8 Hz, 6H, P=CCH_3), 1.45 (s, 36H, *meta*-*tert*-butyl), 7.40 (s, 4H, arom. Mes*).**^{13}C NMR** (100.5 MHz, $CDCl_3$): δ = 0.27 ($SiMe_3$), 25.9 (d, $^3J_{PC}$ = 14.2 Hz, P=C-*C*H_3), 30.64 (s, *para*-C(*C*H_3)$_3$), 32.82 (br.s., *meta*-C(*C*H_3)$_3$), 35.23 (br.s., *para*-*C*(CH_3)$_3$), 38.16 (br. s., *meta*-*C*(CH_3)$_3$), 92.80 (br.s, acetylenic), 96.13 (d, $^3J_{PC}$ = 12.3 Hz, acetylenic), 119.70 (s, Mes*), 135.16 (br.s., Mes*) 153.40 (s, Mes*) 154.02 (s, Mes*), 166.01 (d, $^1J_{PC}$ = 68.8 Hz, P=C). **^{31}P{^{1}H} NMR** (161.8 MHz, $CDCl_3$, 23 °C): δ = 302.9 ppm. **HR-MS** (ESI): m/z 677.43762 [M+Na]$^+$; calcd for $C_{44}H_{64}P_2Na$ 677.43755. λ_{max} (CH_2Cl_2): 359 nm.

Crystal Structure Analysis of (4): Single crystals of **4** suitable for X-ray diffraction were obtained by slow evaporation of a chloroform solution at 4 °C. Compound **4** crystallized in the monoclinic space group $P2_1$ (No. 4) as slightly yellow prisms, $C_{44}H_{64}P_2$, M = 654.89, crystal dimensions 0.13 × 0.1 × 0.07 mm, *a* = 18.683(4) Å, *b* = 12.223(3) Å, *c* = 18.775(4) Å, β = 106.539(3)°, *V* = 4110.0(16) Å^3, *Z* = 4, $2\theta_{max}$= 53.1°, ρ = 1.058 g•cm^{-1}, μ(Mo-K_α) = 0.133 mm^{-1}, *F*(000) = 1432, 60200 reflections measured, 16886 unique (R_{int} = 0.1021) *R*1 = 0.1497 (*I*>2.0σ(*I*)), *Rw* = 0.4337 (all data), GooF = 1.519, 742 parameters, 73 restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-890282 (**2a**), CCDC-890280 (**2b**), CCDC-890129 (**3a**), CCDC-890283 (**3b**) and CCDC-890281 (**4**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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