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**PAPER**

# *C*,*C*-Diacetylenic phosphaalkenes in palladium-catalyzed cross-coupling reactions†

**Elisabet Öberg, Xue-Li Geng, Marie-Pierre Santoni and Sascha Ott***

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The reactivity of bis-TMS-substituted *C*,*C*-diacetylenic phosphaalkene ($A_2PA$) **1** in Sonogashira–Hagihara cross-coupling reactions has been examined. The selective and successive deprotection of the two silyl groups in **1** is enabled by the steric bulk of the Mes* group which renders the acetylene *trans* to Mes* more reactive and thereby facilitates selective and consecutive couplings with iodoarenes. *In situ* transformation of the TMS-protected acetylenes into Cu(I)acetylides is the key step in the synthetic sequence and enables the preparation of the first dimeric $A_2PA$ linked by a phenylene spacer. *cis–trans* Isomerization across the P═C bond is triggered by a tertiary amine and exclusively observed in the case of nitrophenyl-substituted $A_2PA$s. The introduced aryl groups are integral parts of the entire π-system as evidenced by spectroscopic and electrochemical studies.

## Introduction

The inclusion of heteroatoms into π-conjugated systems for potential applications in organic electronic devices or within single-molecule electronics is an attractive field of research.[1–4] Inclusion of sulfur or nitrogen, as in the case of thiophenes, pyridines and pyrimidines, offers a possibility of modifying the electronic properties of the π-conjugates, as well as allowing post-synthetic manipulations such as oxidations or the coordination of Lewis acids.[1] For example, molecular rectification can be achieved by combining an electron-deficient dipyrimidinyl motif with a diphenyl subunit to introduce a polarization in the molecule which gives rise to the diode-like behavior.[5] Phosphorus-containing π-conjugated oligomers and polymers have recently attracted a large amount of attention[6–9] both through the synthesis of phosphaalkene- and diphosphene-containing oligo- and polyphenylvinylene analogues[10–12] as well as oligo- and poly(phospholes).[13–21] Since the phosphorus heteroatoms can easily be coordinated to different metals and converted to their oxides or sulfides, a facile tuning of the electronic and optical properties can be obtained. These reports highlight the advantages compared to all-carbon based oligomers and polymers, where these options are not feasible.

For the preparation of all-carbon-based π-conjugates, acetylenes are in a prominent position as building blocks for oligomeric and polymeric materials mainly due to their synthetic versatility and their participation in both homo- and heterocoupling reactions.[1,22–25] Compounds such as oligo(arylene vinylenes), oligo- and poly(arylene ethynylenes) as well as oligoenynes are appropriate for applications in various electronic and optic devices.[1,23–25] Combining the advantages of phosphorus inclusion with the beneficial properties of oligoacetylenes, phosphapericyclynes as well as phosphinoalkyne oligo- and polymers have been reported.[26–29] In these systems, however, the $\sigma^3\lambda^3$ phosphorus heteroatoms are not an integral part of the compounds' π-system and constitute an insulator within the acetylene scaffold. To overcome this shortcoming, $\sigma^2\lambda^3$ phosphorus heteroatoms have to be combined with acetylenes to form a new class of acetylenic phosphaalkenes (APAs). Both *P*-APAs and *C*-APAs can be obtained from a *P*-chloro-, and *C*-bromophosphaalkene, respectively, with metalacetylide reagents, in the latter case through a palladium(0) catalyzed coupling.[30–31] In our previous work, a route to *C*,*C*-diacetylenic phosphaalkenes ($A_2PA$s) and butadiyne-substituted phosphaalkenes has been established by adopting a protocol from Yoshifuji and others.[32–35] In particular the bis-TMS (TMS = $Me_3Si$) terminated $A_2PA$ **1** appears to be an appealing building block for the preparation of oligomeric structures like **I** due to the ease with which the TMS groups can presumably be removed and the resulting terminal acetylenes be engaged in Sonogashira cross coupling reactions (Chart 1). In the present work, we study the underlying chemistry that is the basis for the

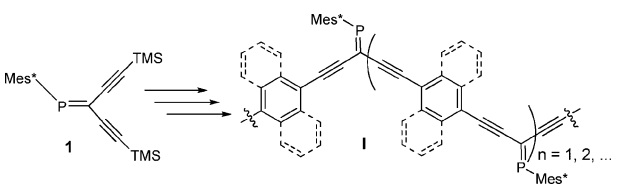



**Chart 1**

*Department of Photochemistry and Molecular Science, Ångström Laboratories, Uppsala University, Box 523, 75120, Uppsala, Sweden. E-mail: sascha.ott@fotomol.uu.se*

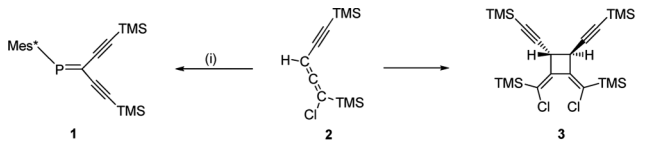
† Electronic supplementary information (ESI) available: $^1$H-, $^{13}$C-, $^{31}$P-{1H}-NMR spectra of all new compounds and cyclic voltammograms. CCDC reference numbers 816322 and 815037. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05705g

future preparation of **I** with a special emphasis on the possibility to sequentially deprotect the two TMS-acetylenes of **1**. The control gained over the subsequent coupling chemistry enables the introduction of aryl groups at specific acetylene termini. We furthermore present the *cis–trans* isomerization of a certain kind of $A_2PA$ and the preparation of the first dimeric $A_2PA$ that is bridged by a 1,4-phenylene linker.

## Results and discussion

### Deprotection studies and Sonogashira–Hagihara cross-coupling reactions of *C*,*C*-diacetylenic phosphaalkenes

The synthesis of $A_2PA$ **1** from chloroallene **2** with Mes*$PCl_2$ at –100 °C in the presence of LDA has been described earlier.[33] It is important to note that **2** cannot be stored for an extended period of time as it engages in a [2 + 2] cycloaddition reaction to form cyclobutene **3** (Scheme 1).[36]




[a]Key: (i) Mes*$PCl_2$, LDA, THF, 2 h, -100 °C to -20 °C, 59 % from neat **2**. Mes* = 2,4,6-($^t$Bu)$_3$Ph

**Scheme 1** Synthesis of *C*,*C*-diacetylenic phosphaalkene **1** and unwanted [2 + 2] cycloaddition of **2**.[a]

With the aim of using Sonogashira cross-coupling reactions to elaborate $A_2PA$ **1** into oligomeric systems, it was natural to first investigate the protodesilylation behavior of the two TMS-groups at the acetylene termini of **1**. Since they are either *cis* or *trans* to the Mes* group, they may possess different reactivity. While addition of $Bu_4NF$ to solutions of **1** in THF leads to immediate decomposition, saturated methanolic $K_2CO_3$ was chosen as the desilylation agent in analogy to previous works on butadiyne-substituted phosphaalkenes.[34,35,37] The progression of protodesilylation was followed by $^{31}P$-{$^1H$}-NMR spectroscopy with benzene-$d_6$ as an external standard (Fig. 1). The $^{31}P$-{$^1H$}-NMR signal of the starting material **1** at $\delta = 346.1$ ppm is found to disappear within 1 h and a major new signal is detected at $\delta = 344.5$ ppm together with a minor signal at 342.8 ppm. After additional reaction time, the former signal also disappears, and **1** completely converts to the compound that is characterized by the signal at $\delta =$ 342.8 ppm.

The final product is a colorless solid which rapidly decomposes in the absence of solvent. $^1H$-NMR analysis disclosed the globally deprotected $A_2PA$ **5** with two signals in the typical acetylene region at $\delta$ = 3.57 and 3.18 ppm with $^4J_{PH}$ coupling constants of 11.9 Hz and 8.6 Hz, respectively (Scheme 2). Based on observations during subsequent coupling reactions (*vide infra*), we assign the larger coupling constant of $^4J_{PH} = 11.9$ Hz to the acetylene proton *trans* to Mes*, while the smaller one belongs to the proton in the *cis* position. The substantial coupling constants over relatively large distances are indicative of a large degree of communication through the entire π-system, a feature that encourages its extension to structures of type **I** by subsequent reactions.

Having identified the structure of **5**, it is clear from the experiment depicted in Fig. 1 that deprotection of **1** is selective

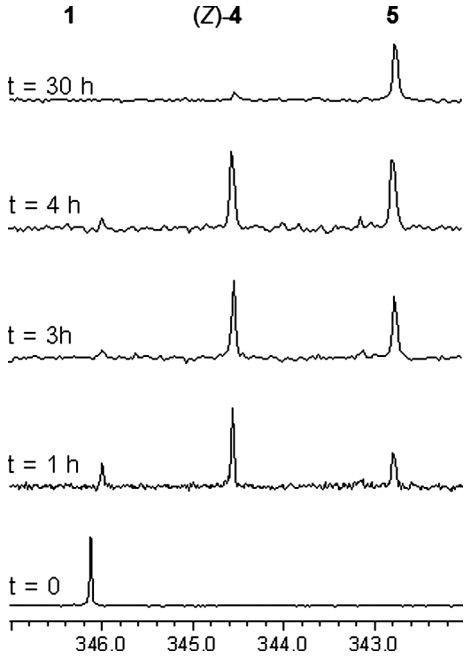
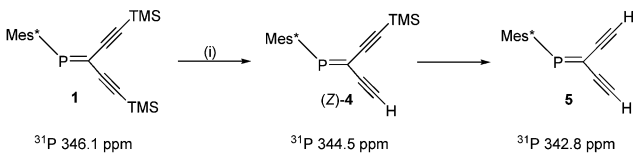



**Fig. 1** Protodesilylation of **1**, followed by $^{31}P$-{$^1H$}-NMR; $A_2PA$ **1** (39 mM), THF : MeOH 5 : 3, saturated with $K_2CO_3$, rt; $C_6D_6$ as external standard.

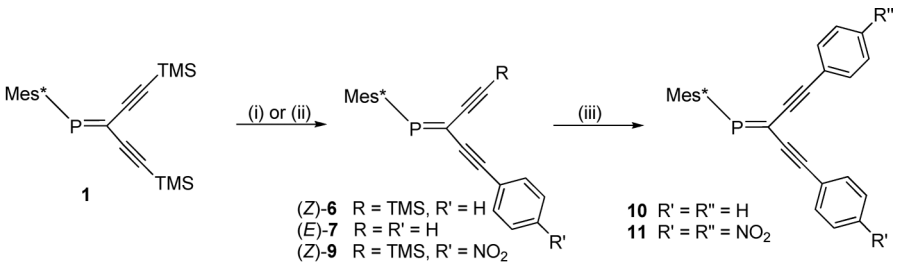



[a]Key: (i) $K_2CO_3$, MeOH, THF.

**Scheme 2** Deprotection study of **1**.[a]

for one of the two TMS acetylenes, since two transient signals would be expected if two isomeric mono-deprotected species had been formed. Subsequent reactions (*vide infra*) clearly show that protodesilylation occurs first at the TMS acetylene *trans* to Mes* and that the exclusively formed mono-deprotected isomer is compound (*Z*)-**4**. It is interesting to note that such a differentiation in reactivity is to our knowledge unprecedented in all-carbon-based 1,1-diethynylethene analogues and usually has to be introduced into the system by utilizing two orthogonal silyl protecting groups.[22,25] In the case of $A_2PA$ **1**, however, the Mes* group, which has the primary function to kinetically stabilize the P═C bond, provides an in-built selectivity.

Considering the steric bulk of the Mes* group, it is intuitive that protodesilylation first occurs at the acetylene in the *trans* position. To prove this hypothesis, **1** was converted to a mixed TMS/Ph terminated $A_2PA$, which we have previously synthesized and characterized in both isomeric forms *via* a different route.[34] When a THF/MeOH solution of **1** was exposed to $K_2CO_3$ in the presence of iodobenzene and catalytic amounts of $Pd(PPh_3)_2Cl_2$ and CuI, mixed Ph/TMS terminated (*Z*)-**6** was obtained as the only phosphaalkene product, although only in modest isolated yield (Scheme 3). The analytical data of (*Z*)-**6** are identical to those of an authentic sample which features the phenyl-group *trans* to the Mes*, thus strengthening the assignment that initial deprotection

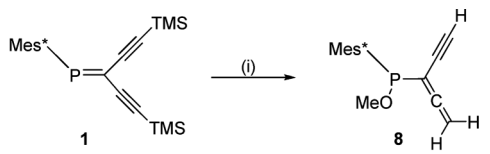



[a]Key: (i) iodobenzene, $K_2CO_3$, CuI, $Pd(PPh_3)_2Cl_2$. For (*Z*)-**6**: THF:MeOH 3:2, 16 h, r.t., 27 %. For (*E*)-**7**: THF:MeOH 1:9, 6 h, 27 %. (ii) iodoarene, CuCl, $Pd(PPh_3)_2Cl_2$, DIPEA, DMF, THF, 35 °C. For (*Z*)-**6**: 1.5 h, 35 %. For (Z)-**9**: 30 min, 41 %. (iii) iodoarene, CuCl, $Pd(PPh_3)_2Cl_2$, DIPEA, DMF, THF, 6 h, 40 °C. For **10**: 29 %. For **11**: 32 %.

**Scheme 3** Sonogashira cross-coupling reactions of **1**.[a]

occurs at the more exposed *trans* acetylene. Increasing the polarity of the medium by increasing the ratio of MeOH : THF from 2 : 3 to 9 : 1 increases the solubility of $K_2CO_3$ and results in an additional desilylation of the second acetylene *cis* to Mes* to form deprotected (*E*)-**7**. The coupling constant for the acetylene proton to the phosphorus in (*E*)-**7** is 8.5 Hz, and thus very similar to that found for the terminal acetylene *cis* to Mes* in **5**.

Synthetically, the use of methanolic $K_2CO_3$ as a deprotecting agent is far from ideal since its solubility, and thus concentration, depends to a large extent on the MeOH/THF solvent composition and can, therefore, be difficult to control. Moreover, during the preparation of (*Z*)-**6** and (*E*)-**7**, as well as the reaction depicted in Scheme 3, partial decomposition of the phosphaalkenes is observed, mostly resulting in the formation of a side product with a $^{31}P\{^1H\}$-NMR chemical shift at $\delta = 110$ ppm. This species can be prepared from **1** in a separate experiment simply by exposing the latter to high $K_2CO_3$ concentrations. The $^1H$-NMR spectrum of the new species shows the absence of any TMS groups and a doublet ($^3J_{PH}$ = 14.6 Hz) at 3.82 ppm that integrates to three protons relative to the two Mes* protons. Together with a signal at 211.5 ppm in the $^{13}C$-NMR spectrum that is characteristic for an allene carbon, the reaction product was identified to be **8**, arising from the base-induced 1,4-addition of MeOH over the 1-phosphabut-1-en-3-yne (Scheme 4).[38]



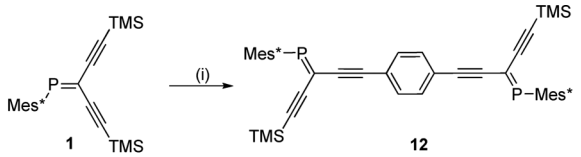

[a]Key: (i) MeOH:THF:$H_2O$ = 2:3:1, saturated with $K_2CO_3$, r.t., 6 h, 27%.

**Scheme 4** 1,4-Addition of MeOH across the acetylenic phosphaalkene.[a]

Hence, alternative reaction conditions for the deprotection of **1** were sought that would avoid nucleophilic reagents. It has recently been shown that treatment of alkynyl silanes with CuCl results in the direct formation of Cu(I)acetylides which can serve as substrates in Pd-mediated coupling reactions.[39] In a slightly modified protocol, a solution of $A_2PA$ **1** in a DMF/THF mixture was exposed to a slight excess of CuCl (2 eq), in the presence of *N*,*N*-diisopropylethylamine (DIPEA) and catalytic amounts of $Pd(PPh_3)_2Cl_2$ (Scheme 3). Keeping the reaction temperatures below 35 °C results in the selective formation of the Cu(I)acetylide *trans* to Mes* which is consumed to produce the phenyl-substituted $A_2PA$ (*Z*)-**6** in 1.5 h. When the more reactive electron-deficient 1-iodo-4-nitrobenzene is employed as the coupling partner, the reaction proceeds faster and (*Z*)-**9** is obtained after 30 to 45 min. This difference in reaction time suggests that the rate limiting step of the transformation is the coupling step, not the deprotection. The transiently formed Cu(I)acetylide exhibits a limited stability which precludes the reaction with less reactive electron-rich arenes such as 4-iodo-*N*,*N*-dimethylaniline or 4-iodoanisole.

Exposing the mono-coupled $A_2PA$s (*Z*)-**6** and (*Z*)-**9** to identical reaction conditions at slightly elevated temperatures for an extended period of time results in the conversion of the second TMS-acetylenes to their respective Cu(I)acetylides, which subsequently engage in coupling reactions (Scheme 3). This strategy gives access to bis-aryl-substituted $A_2PA$s **10** and **11** which were not available by previous methods.[33] In general, the reactions described above using the CuCl deprotection strategy are fairly high yielding as judged from crude $^{31}P\{^1H\}$-NMR analysis.[40] However, the isolated yields are lower since the compounds are somewhat unstable when not in solution, rendering purification and quantitative analysis difficult.

Encouraged by these findings, we were intrigued as to whether the synthetic procedure could also be utilized for the preparation of the first segments of type **I**. Hence, $A_2PA$ **1** was reacted with 1,4-diiodobenzene under the reaction conditions established above (Scheme 5). As expected, the reaction proceeds selectively at the acetylene *trans* to Mes* and the dimeric product **12** is afforded as a single isomer in 35% isolated yield.




[a]Key: (i) 1,4-diiodobenzene, $Pd(PPh_3)_2Cl_2$, CuCl, DIPEA, DMF/THF, 35 °C, 2-3 h; 35 %.

**Scheme 5** Sonogashira cross-coupling reactions of **1** for formation of **12**.[a]

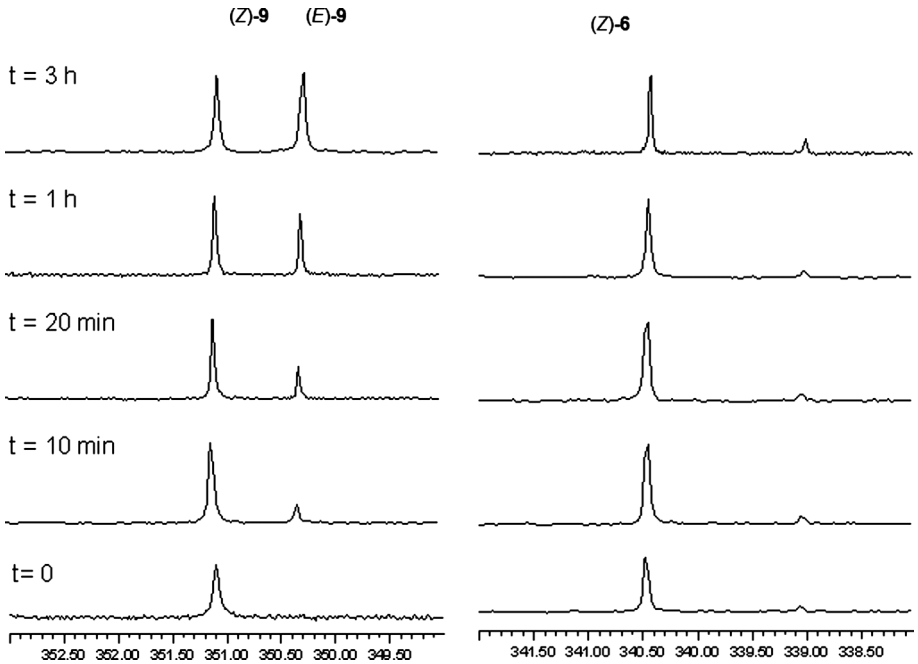



**Fig. 2** Isomerization study of (*Z*)-**9** and (*Z*)-**6**, followed by $^{31}$P-{$^{1}$H}-NMR. (*Z*)-**9** (30 mM) or (*Z*)-**6** (70 mM), DMF : THF 2 : 1, DIPEA (0.5 M). In the experiment of (*Z*)-**6**, a small amount of impurity is present from the start, however it remains constant throughout the experiment.

### *cis–trans* Isomerization and mechanistic implications

In attempts to synthesize unsymmetrically bis-aryl-substituted $A_2PAs$, isomerically pure (*Z*)-**6** was exposed to the customary coupling conditions (DMF : THF = 4 : 1, DIPEA (<0.2 M), $Pd(PPh_3)_2Cl_2$, CuCl, 6 h, 35 °C) in the presence of 1-iodo-4-nitrobenzene. Apart from unreacted starting material, two new signals were observed in the crude $^{31}$P-{$^{1}$H}-NMR at 343.8 and 344.4 ppm in a ratio of *ca.* 1 : 1. The two signals correspond to the two isomers (*E*)- and (*Z*)-**13**, both with one phenyl- and one *para*-nitrophenyl-substituent, a reaction outcome that can only be explained by an isomerization that occurs under the reaction conditions. However, it is not possible to deduce from this experiment whether isomerization occurs for (*Z*)-**6**, the Cu(I)acetylide of (*Z*)-**6**, or the final bis-aryl-substituted product **13**.

The observed isomerization raises a number of mechanistic questions that revolve around the reaction at the TMS-acetylene *cis* to Mes* and the formation of bis-coupled products **10** and **11**. Isomerization already at the stage of (*Z*)-**6** or (*Z*)-**9** would convert the sluggish *cis* acetylene to the more reactive *trans* position, thus enabling a mechanism that would allow for facile deprotection and coupling. On the other hand, the formation of two bis-coupled products can also be explained by isomerization at the product stage.

In attempts to elucidate these mechanistic questions and to identify the agent that triggers isomerization, we studied the behavior of (*Z*)-**9**. Isomerization does not only occur during the reaction of (*Z*)-**6** with *p*-iodonitrobenzene as described above, but is also observed for (*Z*)-**9** in the absence of any CuCl that would promote desilylation. From a mechanistic viewpoint, it is tempting to assume that a temporary coordination of palladium to the P=C double bond enables isomerization,[41,42] thereby reflecting the reactivity of alkenes in the presence of Pd(0) and Pd(II) catalysts.[43,44] However, dissolving isomerically pure (*Z*)-**9** in a 2 : 1 mixture of DMF : THF and adding an excess $Pd(PPh_3)_2Cl_2$ does not promote isomerization, not even at 45 °C over 4 h. In contrast, addition of DIPEA (0.5 M) to (*Z*)-**9** in a 2 : 1 mixture of DMF : THF in the absence of any metal species has a drastic effect and isomerization is observed both at room temperature and at 45 °C (Fig. 2). The isomerization is completed within one hour when both isomers are obtained in a final equilibrium of approximately 1 : 1. In contrast to the reactivity of (*Z*)-**9**, (*Z*)-**6** does not isomerize under identical conditions and timescales (Fig. 2). It is thus clear that isomerization does not only depend on the presence of DIPEA, but also requires the presence of a nitro substituent at the remote acetylene terminus. An electron-withdrawing group at this position may facilitate a reversible nucleophilic attack at the phosphorus center through delocalization of the evolved negative charge. This transiently formed species would feature a decreased phosphaalkene bond order that enables free rotation and thus facilitates *cis–trans* isomerization. The postulated intermediate bears resemblance to the *P*-methoxy-substituted compound **8**, which is however formed irreversibly. A similar mechanism has been proposed for the isomerization of (*Z*)-nitroalkenes which can be converted to (*E*)-nitroalkenes upon exposure of catalytic amounts of nucleophiles such as triethylamine.[45] On the other hand, addition of DIPEA increases the polarity of the solvent mixture, which may just be enough to overcome the inversion barrier of polar (*Z*)-9, thereby inducing isomerization.

In summary, DIPEA can be identified as the agent that promotes isomerization, albeit only of compounds that contain a nitrophenyl-group at the acetylene terminus. From a mechanistic viewpoint, this finding implies that the reaction of (*Z*)-**6** with iodobenzene to form bis-phenyl-substituted **10** proceeds at the

acetylene *cis* to Mes*. In case of the analogous reaction of (*Z*)-**6** with 4-iodo-nitrobenzene, the same initial mechanism holds. At the stage of the mixed Ph/$NO_2$Ph product, however, *cis–trans* isomerization is enabled by the presence of the introduced nitro-substituent. For the coupling of the TMS-acetylene of (*Z*)-**9**, a fundamentally different mechanism is potentially available that involves initial isomerization to (*E*)-**9**, the TMS-acetylene of which ought to be more reactive than that of the former. The rate of isomerization is dependent on the amine concentration, reaction time and temperature. As illustrated in Fig. 2, isomerization is relatively slow, which is consistent with the fact that isomerically pure (*Z*)-**9** can be prepared from **1** as long as the reaction times are kept short (30 min). Longer reaction times for the reaction of **1** with iodonitrobenzene result in isomerization and (*E*)-**9** is observed in addition to (*Z*)-**9**.[46]

The structure of the isomerization product (*E*)-**9** was unambiguously identified by X-ray crystallography (Fig. 3) which shows the TMS acetylene nicely exposed in the position *trans* to Mes* (Fig. 3). The nitrophenyl-group is somewhat twisted out of the plane of the $A_2$PA system with an inter-planar angle of 22.4°, thus exhibiting a non-optimal conformation for π-conjugation in the solid state. One proton *meta* to the nitro group points into the central void of the Mes* group with a distance to the Mes* plane of 3.04 Å that is in good agreement with earlier published results.[34] This interaction also explains the somewhat unusual chemical shift of 6.99 ppm for the *meta* protons in the $^1$H NMR spectrum of (*E*)-**9**.

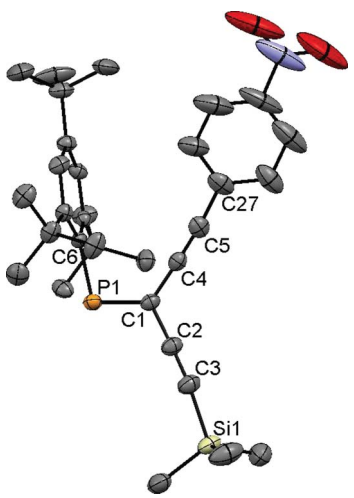



**Fig. 3** ORTEP drawing (at 50% probability level) of (*E*)-**9**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg). P1–C6 1.838(2), P1–C1 1.699(2), C1–C2 1.428(3), C2–C3 1.219(3), C3–Si1 1.841(3), C1–C4 1.426(3), C4–C5 1.185(3), C5–C27 1.436(4). Angles C6–P1–C1 103.5(1), P1–C1–C2 117.3(2), P1–C1–C4 124.6(2). Torsion angle C6–P1–C1–C2 179.0(2).

### $^{31}$P-NMR, UV/Vis spectroscopy and cyclic voltammetry of $A_2$PAs

When comparing the $^{31}$P-{$^1$H}-NMR chemical shifts of the different aryl-substituted $A_2$PAs in Table 1, it becomes apparent that the aryl-groups are an integral part of the compounds' π-systems. Introduction of one phenyl-group in (*Z*)-**6** gives rise to an upfield shift of ~7 ppm compared to the starting material **1**. A second phenyl-group as in **10** results in an additional shift of another ~7 ppm. Attaching electron-withdrawing nitrophenyl-substituents causes a downfield shift of ~6 ppm, respectively 4 ppm for each group. The $^{31}$P-{$^1$H}-NMR signal of the two mixed Ph/$NO_2$Ph-substituted $A_2$PAs **13** described above (data not shown in Table 1) are observed around 344 ppm. The downfield shift of ~2 ppm compared to the chemical shift of **1** is the simple sum of the effects caused by the individual aryl-substitutions in (*Z*)-**6** and (*Z*)-**9**, respectively, suggesting that the electronic effects are additive. The $^{31}$P-{$^1$H}-NMR chemical shifts thus clearly reflect the electronic nature of the arene that is attached to the $A_2$PA system. Even though the arene substituents are four bonds away from the phosphorus heteroatom, the communication is visible through the whole conjugated system both in (*E*)- and (*Z*)-position to the Mes*.

**Table 1** $^{31}$P-{$^1$H}-NMR chemical shifts of the $A_2$PAs ($CDCl_3$)

| | Substituents | | |
|---|---|---|---|
| Entry | $R_1$ | $R_2$ | $^{31}$P-{$^1$H}-NMR |
| **1** | TMS | TMS | 346.3 |
| (*Z*)-**6** | TMS | Ph | 339.8 |
| **10** | Ph | Ph | 332.2 |
| (*Z*)-**9** | TMS | $PhNO_2$ | 351.8 |
| **11** | $PhNO_2$ | $PhNO_2$ | 355.8 |
| **12** | TMS | n.a. | 342.1 |

Conjugation between the aryl-groups and the $A_2$PA systems is further evidenced by an inspection of the UV/Vis data summarized in Table 2. The introduction of the first aryl-group in (*Z*)-**6** and (*Z*)-**9** has a pronounced effect and shifts the lowest energy absorption maxima bathochromically by 20 and 39 nm, respectively, compared to that of **1**. The second aryl-group in **10** and **11** inflicts a comparably small additional shift of 3 and 4 nm compared to the mono-substituted compounds. As expected, the spectrum of dimeric $A_2$PA **12** features the most red-shifted absorption maximum of the series, with a shift of almost 50 nm compared to that of (*Z*)-**6**. It is thus clear that communication between the two $A_2$PA units operates across the *para*-phenylene linker.

A comparison between (*Z*)-**9** ($\lambda_{max}$ = 386 nm) and an all-carbon 1,1-diethynylethene analogue with an identical π-system including the nitrophenyl-substituent ($\lambda_{max}$ = 354 nm)[47] illustrates the effect of phosphorus inclusion in the $A_2$PAs, as their HOMO–LUMO gaps are greatly decreased compared to that of all-carbon-based reference compounds. Comparing the absorption profiles of **10** with that of its constitutional 1-phospha-1-ene-3,5-hexadiyne

**Table 2** Absorption band maxima and molar extinction coefficients from UV/vis spectroscopic measurements in $CH_2Cl_2$ at 25 °C

| | Substituents | | | |
|---|---|---|---|---|
| Entry | $R_1$ | $R_2$ | $\lambda_{max}$ [nm] ($\varepsilon$ [$10^3$ $M^{-1}cm^{-1}$]) | |
| **1**[a] | TMS | TMS | 347 (11.5) | |
| (*Z*)-**6**[b] | TMS | Ph | 367 (15) | |
| **10** | Ph | Ph | 284 (11.0) | 370 (9.5) |
| (*Z*)-**9** | TMS | $PhNO_2$ | 313 (62.7) | 386 (70.7) |
| **11** | $PhNO_2$ | $PhNO_2$ | 353 (51.5) | 390 (46.9)[c] |
| **12** | TMS | n.a. | 283 (16.7), 359 (16.6) | 415 (26.3) |

[a] Ref. 33. [b] Ref. 34. [c] Shoulder.

**Table 3** Electrochemical data for ~1 mM solutions (0.1 M $NBu_4PF_6$), $\nu$ = 100 mV $s^{-1}$ (All potentials are given $Fc^{+/0}$)

| | Substituents | | | |
|---|---|---|---|---|
| Entry | $R_1$ | $R_2$ | $E_{p,a}$ (V) | $E_{p,c}$ (V) |
| **1**[a] | TMS | TMS | 1.16 | −2.07 |
| (*Z*)-**6**[b] | Ph | TMS | 1.02 | −2.04 |
| **10** | Ph | Ph | 0.93 | −1.96[c], −2.18 |
| (*Z*)-**9** | TMS | $PhNO_2$ | 1.12 | −1.43[c], −1.85[c], −2.15 |
| **11** | $PhNO_2$ | $PhNO_2$ | 1.10 | −1.50[c], −1.95[c], −2.35 |
| **12** | TMS | n.a. | 1.17 | −1.83[c], −2.03[c] |

[a] Ref. 33. [b] Ref. 34. [c] Reversible at scan rates >1V $s^{-1}$.

isomer, *i.e.* a butadiyne-substituted phosphaalkene ($\lambda_{max}$ = 379 nm),[33] shows that the HOMO–LUMO gap of cross-conjugated **10** is slightly larger than that of its corresponding through-conjugated isomer. A similar ordering of cross- *vs.* through-conjugated systems has been found in the all-carbon cases.[48–50]

Table 3 summarizes the electrochemical data for the $A_2PA$s. In analogy to unsubstituted $HP{=}CH_2$[51] and 1-phosphahexa-1-ene-3,5-diyne,[33] the HOMOs of the $A_2PA$s are described by molecular orbitals of the π-system. The HOMOs of (*Z*)-**6** and **10** contain additional contributions by the terminal phenyl groups as evident from a shift of the oxidation potentials upon introduction of each phenyl group in (*Z*)-**6** and **10** to lower values by ~100 mV compared to that of **1**. Remarkable is the fact that the corresponding shift in nitrophenyl-substituted (*Z*)-**9** and **11** is considerably smaller. This phenomenon can be explained by a lack of participation of the nitrophenyl-groups in the compounds' HOMOs, thus not affecting the oxidation potentials to the same extent as the phenyl-groups in (*Z*)-**6** and **10**. This effect has precedence in butadiyne-substituted phosphaalkenes that bear nitrophenyl substituents.[33] Also, dimeric $A_2PA$ **12** seems to belong to this group of compounds as its oxidation potential is basically identical to that of **1**, pointing towards two degenerate HOMOs on either halves of the molecule.[37]

From the cathodic scans, it emerges that the phenyl-groups in (*Z*)-**6** and **10** have a rather minor impact on the reduction potentials of the π-conjugate. In contrast, nitrophenyl-containing (*Z*)-**9** and **11** are reduced at a potential of *ca.* −1.45 V that is shifted by more than 500 mV compared to the reduction potential of **1**. The large shift, together with a comparison with other nitrophenyl-substituted compounds of this type,[48] suggest that this process is mainly localized at the nitrophenyl-group, with negligible contributions from the $A_2PA$ framework. The latter is presumably involved in subsequent electron uptakes that are observed for (*Z*)-**9** and **11** at *ca.* −1.9 V and thus at a similar potential to those of (*Z*)-**6** and **10**. It is thus interesting to note that the HOMO can selectively be perturbed by phenyl-substitution, while the LUMO is much more responsive to nitrophenyl-incorporation. In contrast to the HOMO of dimeric **12**, its LUMO is delocalized across the *para*-phenylene bridge and contains contributions from both $A_2PA$ units, as its reduction potential is shifted anodically by *ca.* 200 mV compared to that of **1** and (*Z*)-**6**.

## Conclusions

Bis-TMS substituted $A_2PA$ **1** is a valuable starting material for Sonogashira–Hagihara reactions as it allows the preparation of bis-aryl-substituted $A_2PA$s like **10** and **11** that were not available by earlier methods. The steric protection by the Mes* group in **1** offers a control over the reactivity of the two different acetylene moieties, making the acetylene *trans* to Mes* both deprotect and react faster. The key step in the synthetic sequence is the direct *in situ* transformation of the TMS-acetylenes to Cu(I)acetylides by reaction with CuCl, thus circumventing basic conditions that lead to undesirable addition reactions. Owing to this new protocol, the first dimeric $A_2PA$ with a *para*-phenylene bridge could be synthesized. DIPEA has been identified as a reagent that can induce *cis–trans* isomerization in $A_2PA$s that contain electron-withdrawing nitrophenyl substituents. From a functional viewpoint, spectroscopic and electrochemical studies show that π-conjugation is not limited to the $P{=}C(C{\equiv}C)_2$ frameworks, but also extends over the aryl moieties at the acetylene termini. This finding, together with the control over the reactivity of **1**, encourages the preparation of more elaborate oligomeric and polymeric structures of type **I**, an endeavor that is encouraged by the successful preparation of **12**.

## Experimental

### Materials and general methods

Chemicals were purchased from Sigma-Aldrich and used as received. THF and $Et_2O$ were distilled from sodium/benzophenone. $CH_2Cl_2$ was distilled from calcium hydride. All reactions were performed under an inert atmosphere of nitrogen or argon. Flash chromatography was performed on Merck silica gel SI-60 Å (35–70). Compounds **1** and **2** were prepared according to their literature procedures.[33] (*E*)- and (*Z*)-**6** have been reported earlier,[34] but were prepared by a different route in this work.

### X-ray crystallography

Crystal structure data for **3** and (*E*)-**9** have been deposited at the Cambridge Crystallographic Data Centre, and allocated the respective deposition number CCDC 816322, CCDC 815037.†Table 4 summarizes the crystallographic data for (*E*)-**9**.

**Table 4** Crystallographic data for (*E*)-**9**

| Compound | (*E*)-**9** |
|---|---|
| Formula | $C_{32}H_{42}NO_2PSi$ |
| $M_w$ (g $mol^{-1}$); $F(000)$ | 531.73; 2288 |
| $T$/K; $\lambda$/Å | 100; 0.71073 |
| Crystal system | Orthorhombic |
| Space group | *Pbcn* |
| Unit cell: $a$/Å | 46.284(3) |
| $b$/Å | 12.2793(7) |
| $c$/Å | 11.1201(7) |
| $\beta$ (°) | 90 |
| $V$/Å$^3$; $Z$; $d_c$/g $cm^{-3}$ | 6319.9(7); 8; 1.118 |
| $\theta$ range (°); completeness | 0.88 to 31.24 |
| collected reflections; $R_\sigma$ | 122634; 0.0679 |
| unique reflections; $R_{int}$ | 9959; 0.081 |
| $\mu$/$mm^{-1}$; Abs. corr. | 0.152;Semi-empirical from equivalents |
| $R_1(F)$; w$R(F^2)$ [$I > 2\sigma(I)$] | 0.0732; 0.2194 |
| $R_1(F)$; w$R(F^2)$ (all data) | 0.1212; 0.2376 |
| GoF($F^2$) | 1.058 |
| Residual electron density ($e^-$/Å$^{-3}$) | 1.124 and −0.835 |

### NMR spectroscopy

$^1$H-NMR spectra were recorded on a JEOL Eclipse + 400 MHz spectrometer (operating at 399.8 MHz). Chemical shifts are given in ppm and referenced internally to the residual solvent signal ($CHCl_3$, $\delta_H$ = 7.26 ppm). $^{13}$C NMR spectra were recorded on the same instrument (100.5 MHz) and were also referenced internally to the residual solvent signal ($CHCl_3$, $\delta_C$ = 77 ppm, central signal). $^{31}$P-{$^1$H}-NMR spectra were recorded on JEOL Eclipse + 400 MHz spectrometer (operating at 161.8 MHz).

### UV/Vis spectroscopy

UV/Vis was performed using a Varian Cary 50 instrument. The measurements were performed in 1 × 1 cm$^2$ optical quartz cells as solutions in $CH_2Cl_2$.

### Electrochemistry

The electrochemical measurements were conducted in dry $CH_2Cl_2$. An Autolab potentiostat with a GPES electrochemical interface (Eco Chemie) were used for the cyclic voltammetry measurements with a glassy carbon disc (diameter 3 mm, freshly polished) for voltammetry as the working electrode. The counter electrode was a glassy carbon rod and the reference electrode a non-aqueous $Ag^+/Ag$ electrode (a silver wire immersed into 10 mM $AgNO_3$ in acetonitrile) with a potential of –0.08 V *vs.* the ferrocenium/ferrocene ($Fc^+/Fc$) couple in $CH_2Cl_2$ as an external standard. The cyclic voltammograms were conducted at a scan rate of $v$ = 100 mV s$^{-1}$. All solutions were conducted on ~1 mM solutions of the $A_2$PAs in dry $CH_2Cl_2$ with 0.1 M tetrabutylammonium hexafluorophosphate ($NBu_4PF_6$) as the supporting electrolyte. Before all measurements, oxygen was removed by bubbling with argon and during the measurement all samples were kept under argon.

### Mass spectrometry

Mass spectrometry of all compounds was performed on a Finnigan MAT ThermoQuest GCQ mass spectrometer with electron impact (EI) ionization. Mass spectrometry for **13** was performed on a Thermo LCQ Deca XP Max with electrospray ionization (ESI). $A_2$PA **13** ~1 mg was dissolved in a minimum amount of THF and 5 ml of a solution of ~2.5 mM $AgBF_4$ in MeOH.

### (1*Z*,1′*Z*)-(3,4-Bis((trimethylsilyl)ethynyl)cyclobutane-1,2-diylidene)bis(chloromethan-1-yl-1-ylidene)bis(trimethylsilane) (3)

A mixture of allenic chloride **2** and the corresponding propargylic chloride was left in concentrated form in the fridge for 2 months or at room temperature for one week when white crystals precipitated.$^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 3.70 (s, 2H CH), 0.33 ppm (s, 18H, $Si(CH_3)_3$). 0.16 ppm (s, 18H, $Si(CH_3)_3$). $^{13}$C-NMR ($CDCl_3$, 100 MHz): $\delta$ = 143.9, 134.5, 105.7, 89.4, 41.3, –0.2, –0.9. EI MS (70 eV): *m*/*z* [M$^+$] 483.9 (22), [M$^+$ – Cl] 449.0 (12), [M$^+$ – Cl-Si$CH_3$] 376.1 (100). Elemental analysis (%) calcd. for ($C_{22}H_{38}Cl_2Si_4$): C 54.39, H 7.88. Found C 54.40, H 7.83%

### Deprotection study of 1

$A_2$PA **1** (15 mg, 0.031 mmol) in 0.5 ml THF was added to an NMR tube with a $C_6D_6$ external standard. 0.3 ml of a slurry of $K_2CO_3$ in MeOH (~0.1 mmol ml$^{-1}$) was added and the deprotection was followed by $^{31}$P-{$^1$H}-NMR.

### Penta-1,4-diyn-3-ylidene(2,4,6-tri-*tert*-butylphenyl)phosphine (5)

$A_2$PA **1** (70 mg, 0.15 mmol) was dissolved in 3 ml THF, 2 ml MeOH, 3 drops of water and $K_2CO_3$ (41 mg, 0.34 mmol) was added. The reaction mixture was heated with a heat gun until a clear solution was obtained and the reaction was run at room temperature for 1 h when additional $K_2CO_3$ (41 mg, 0.34 mmol) and 1 ml of water was added to increase the reaction rate. After 2.5 h, when $^{31}$P-{$^1$H}-NMR showed a 1 : 1 ratio between **5** and **8**, the reaction was quenched with a saturated aqueous $NH_4Cl$ and extracted with pentane. The combined organic phases were dried with $Na_2SO_4$. The product was purified by column chromatography (pentane). Yield: **5** (12 mg, 0.036 mmol, 24%) as a white solid that decomposes rapidly to a black oil and **8** (10 mg, 0.031 mmol, 22%). **5** $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.44 (s, 2H, Mes*), 3.57 (d, $^4J_{PH}$ = 11.9 Hz, 1H, alkyne-H), 3.18 (d, $^4J_{PH}$ = 8.6 Hz, 1H, alkyne-H), 1.49(s, 18H, *tert*-Bu), 1.32 (s, 9H, *tert*-Bu). $^{13}$C-NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.3 (Mes*), 151.0 (Mes*), 139.6 (d, $^1J_{PC}$ = 36.1 Hz, P=C), 134.1 (d, $^1J_{PC}$ = 55.8 Hz, P–C), 89.8 (d, $^3J_{PC}$ = 9.7 Hz, acetylene-H), 83.5 (d, $^2J_{PC}$ = 26.0 Hz, acetylene), 83.4 (d, $^3J_{PC}$ = 16.8 Hz, acetylene-H), 81.3 (d, $^2J_{PC}$ = 19.6 Hz, acetylene), 37.9 (*tert*-Bu), 35.0(*tert*-Bu), 33.0 (d, $J_{PC}$ = 6.0 Hz, *tert*-Bu), 31.3 (*tert*-Bu). $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 349.2 ppm. EI MS (70 eV): *m*/*z* [M$^+$] 338.1 (32), [Mes*P$^+$ – H] 275.2 (100), [Mes*P$^+$ – *tert*-Bu] 219.2 (42)

### Methoxy(penta-1,2-dien-4-yn-3-yl)(2,4,6-tri-*tert*-butylphenyl)phosphine (8)

$A_2$PA **1** (50 mg, 0.10 mmol) was dissolved in 3 ml THF and 2 ml of MeOH. The yellow solution was deaerated with argon and $K_2CO_3$ (14 mg, 0.10 mmol) was added. The brown reaction mixture was stirred at room temperature for 6 h. The reaction mixture was filtered through celite, the celite was washed with $CH_2Cl_2$ and the solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1% EtOAc in hexane). Brown oil (due to fast decomposition), yield 10 mg (0.027 mmol, 27%). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.38, 7.39 (2 s, 2H, Mes*), 4.24 (m, 2H), 3.82 (d, $^3J_{PH}$ = 14.6, 3H, OMe), 2.97 ppm (m, 1H, acetylene-H), 1.52 (s, 18H, *tert*-Bu), 1.28 (s, 9H, *tert*-Bu). $^{13}$C-NMR ($CDCl_3$, 100 MHz): 211.5 (d, $^2J_{PC}$ = 15.0 Hz, allene), 156.8 (d, $^2J_{PC}$ = 14.7 Hz, Mes*), 151.1 (Mes*), 135.2 (d, $^1J_{PC}$ = 52.7 Hz, Mes*P–C), 122.1 (Mes*), 93.3 (d, $J_{PC}$ = 35.6 Hz), 80.5, 74.8, 59.2 (d, $^2J_{PC}$ = 33.6 Hz, $CH_3O$), 38.7 (*tert*-Bu), 35.0 (*tert*-Bu), 34.0 (d, $J_{PC}$ = 8.9 Hz, *tert*-Bu), 31.1 (*tert*-Bu). $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 110.0 ppm EI MS (70 eV): *m*/*z* [MesPOMe$^+$] 307.3 (100).

### (*Z*)-(1-Phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-ylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (*Z*)-(6)

$A_2$PA **1** (140 mg, 0.29 mmol) was dissolved in 6 ml THF and 4 ml MeOH. The yellow solution was deaerated with argon and $K_2CO_3$ (40 mg, 0.29 mmol), iodobenzene (0.14 ml, 1.3 mmol),

$Pd(PPh_3)_2Cl_2$ (20 mg, 0.029 mmol) and CuI (5.5 mg, 0.029 mmol) was added. The brown reaction mixture was stirred overnight. Solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1% EtOAc in hexane). Yellow oil, yield 39 mg (0.079 mmol, 27%).

**Alternative procedure.** $A_2PA$ **1** (500 mg, 1.04 mmol) and iodobenzene (1.1 ml, 9.8 mmol) were dissolved in 3 ml THF, 12 ml DMF and 0.5 ml DIPEA. The yellow solution was deaerated with the freeze–pump–thaw technique and bubbled with argon, meanwhile $Pd(PPh_3)_2Cl_2$ (145 mg, 0.21 mmol) and CuCl (205 mg, 2.1 mmol) were added. The reaction mixture changed colour to deep red, then brown and finally to black during stirring for 1.5 h at 35 °C. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with EtOAc. The product was purified by column chromatography (gradient 0 to 5% EtOAc in hexane). Yellow oil, yield 175 mg (0.36 mmol, 35%). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.53–7.55 (m, 2H, Ph), 7.49 (s, 2H, Mes*), 7.31–7.33 (m, 3H, Ph), 1.52 (s, 18H, *tert*-Bu), 1.34 ppm (s, 9H, *tert*-Bu), 0.10 ppm (s, 9H, $SiMe_3$).$^{13}$C-NMR ($CDCl_3$, 100 MHz): 153.7 (Mes*), 150.5 (Mes*), 141.0 (d, $^1J_{PC}$ = 35.5 Hz), 134.6 (d, $^1J_{PC}$ = 57.1 Hz), 131.6 (d, $J_{PC}$ = 5.7 Hz, Ph), 128.3 (d, $J_{PC}$ = 1.9 Hz, Ph), 128.2 (Ph), 123.3 (d, $J_{PC}$ = 7.6 Hz, Ph), 122.5 (Mes*), 108.2 (d, $J_{PC}$ = 9.4 Hz, acetylene), 102.8 (d, $J_{PC}$ = 18.4 Hz, acetylene), 96.3 (d, $J_{PC}$ = 16.5 Hz, acetylene), 89.9 (d, $J_{PC}$ = 26.2 Hz, acetylene), 38.3 (*tert*-Bu), 35.2 (*tert*-Bu), 33.0 (d, $J_{PC}$ = 6.3 Hz, *tert*-Bu), 31.3 (*tert*-Bu), –0.41 ($SiMe_3$).$^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 339.9 ppm. EI MS (70 eV): *m/z* [$M^+$] 486.46 (75), [MH–*t*Bu$^+$] 430.5 (15), [Mes*$P^+$ – H] 275.4 (100), [Mes*–2*t*Bu$^+$] 219.4 (20).

### (*E*)-(1-Phenylpenta-1,4-diyn-3-ylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (*E*)-(7)

$A_2PA$ **1** (400 mg, 0.83 mmol) was dissolved in 4 ml THF and 35 ml MeOH. The yellow solution was deaerated with argon and $K_2CO_3$ (114 mg, 0.82 mmol), iodobenzene (0.37 ml, 3.3 mmol), $Pd(PPh_3)_2Cl_2$ (58 mg, 0.083 mmol) and CuI (16 mg, 0.084 mmol) were added. The brown reaction mixture was stirred at room temperature for 6 h. Solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1% EtOAc in hexane). Yellow oil that turns black rapidly, yield 94 mg (0.23 mmol, 27%). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.50–7.55 (m, 2H, Ph), 7.46 (s, 2H, Mes*), 7.32–7.35 (m, 3H), 3.20 (d, $^4J_{PH}$ = 8.5 Hz, 1H), 1.53 (s, 18H, *tert*-Bu), 1.35 ppm (s, 9H, *tert*-Bu).$^{13}$C-NMR ($CDCl_3$, 100 MHz): 153.5 (Mes*), 150.9 (Mes*), 141.7 (Ph), 141.1 (d, $^1J_{PC}$ = 35.9 Hz, P═C), 134.7 (d, $^1J_{PC}$ = 56.4 Hz, P–C), 131.6 (Ph), 128.5 (Ph), 128.3 (Ph), 122.4 (Mes*), 96.4 (d, $J_{PC}$ = 16.9 Hz, acetylene), 90.1 (d, $J_{PC}$ = 24.7 Hz, acetylene), 89.4 (d, $J_{PC}$ = 9.5 Hz, acetylene-H), 81.4 (d, $J_{PC}$ = 19.1 Hz, acetylene), 38.0 (*tert*-Bu), 35.0(*tert*-Bu), 33.1 (d, $J_{PC}$ = 5.6 Hz, *tert*-Bu), 31.3 (*tert*-Bu).$^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 340.2 ppm

### (1,5-Diphenylpenta-1,4-diyn-3-ylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (10)

(*Z*)-**6** (40 mg, 0.082 mmol) was dissolved in 3 ml THF and 2 ml MeOH. The yellow solution was deaerated with argon and $K_2CO_3$ (11.4 mg, 0.082 mmol), iodobenzene (0.08 ml, 0.7 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.010 mmol) and CuI (1.9 mg, 0.010 mmol) was added. The brown reaction mixture was stirred overnight. Solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1% EtOAc in hexane). Orange oil, yield 15 mg (0.030 mmol, 37%).

**Alternative procedure.** $A_2PA$ **1** (175 mg, 0.36 mmol) and iodobenzene (0.8 ml, 7.6 mmol) were dissolved in 1 ml THF, 7 ml DMF and 0.2 ml DIPEA. The yellow solution was deaerated with freeze–pump–thaw technique and bubbled with argon, meanwhile $Pd(PPh_3)_2Cl_2$ (60 mg, 0.085 mmol) and CuCl (80 mg, 0.81 mmol) was added. The reaction mixture changed colour to deep red, then brown and finally black during stirring for 6 h at 35 °C. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with EtOAc. The product was purified by column chromatography (gradient 0 to 5% EtOAc in hexane). Orange oil, yield 52 mg (0.11 mmol, 29%). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.60–7.57 (m, 2H, Ph), 7.51 (s, 2H, Mes*), 7.37–7.33 (m, 3H), 7.14–7.22 (m, 3H),6.88–6.92 (m, 2H), 1.56 (s, 18H, *tert*-Bu), 1.34 ppm (s, 9H, *tert*-Bu).$^{13}$C-NMR ($CDCl_3$, 100 MHz): 154.3 (Mes*), 150.6 (Mes*), 141.5 (d, $^1J_{PC}$ = 35.4 Hz, P═C), 135.4 (d, $^1J_{PC}$ = 57.1 Hz, P–C), 131.6 (2 signals overlapping, Ph), 131.3 (Ph), 128.4 (Ph), 128.3 (Ph), 128.0 (Ph), 123.3 (Ph), 122.3 (Mes*), 103.1 (d, $J_{PC}$ = 9.5 Hz, acetylene), 96.1 (d, $J_{PC}$ = 16.9 Hz, acetylene), 90.2 (d, $J_{PC}$ = 26.1 Hz, acetylene), 89.3.4 (d, $J_{PC}$ = 20.2 Hz, acetylene), 38.2 (*tert*-Bu), 35.1(*tert*-Bu), 33.2 (d, $J_{PC}$ = 5.0 Hz, *tert*-Bu), 31.3 (*tert*-Bu). $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 332.2 ppm. EI MS (70 eV): *m/z* [$M^+$] 490.2 (42), [$M^+$ – *tert*-Bu–H] 434.2 (36), [Mes*$P^+$ – H] 275.2 (100)

### (*Z*)-(1-(4-Nitrophenyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (*Z*)-(9)

$A_2PA$ **1** (600 mg, 1.24 mmol) and 1-iodo-4-nitrobenzene (800 mg, 3.21 mmol) were dissolved in 10 ml THF, 20 ml DMF and 0.5 ml DIPEA. The yellow solution was deaerated with freeze–pump–thaw technique and bubbled with argon, meanwhile $Pd(PPh_3)_2Cl_2$ (180 mg, 0.26 mmol) and CuCl (320 mg, 3.23 mmol) were added. The reaction mixture changed colour to deep red, then brown and finally black during stirring at 35 °C for 0.5 h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with EtOAc. The product was purified by column chromatography (first pentane to elute 1-iodo-4-nitrobenzene and then 1% EtOAc in pentane). Orange solid, yield 273 mg (0.51 mmol, 41%). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.21 (m, 2H, Ar), 7.68 (m, 2H, Ar) 7.50 (s, 2H, Mes*), 1.53 (s, 18H, *tert*-Bu), 1.35 ppm (s, 9H, *tert*-Bu), –0.07 ppm (s, 9H, $Si(CH_3)_3$). $^{13}$C-NMR ($CDCl_3$, 100 MHz): 153.7 (Mes*), 150.9 (Mes*), 146.9 (Ar), 139.7 (d, $^1J_{PC}$ = 36.7 Hz, P═C), 134.3 (d, $^1J_{PC}$ = 57.2 Hz, P–C), 132.2 (d, $J_{PC}$ = 3.6 Hz, Ar), 130.3 (d, $J_{PC}$ = 6.1 Hz, Ar), 123.6 (Ar), 122.6 (Mes*), 109.0 (d, $J_{PC}$ = 7.7 Hz, acetylene), 102.2 (d, $J_{PC}$ = 9.1 Hz, acetylene), 95.2 (d, $J_{PC}$ = 26.5 Hz, acetylene), 93.9 (d, $J_{PC}$ = 16.5 Hz, acetylene), 38.2 (*tert*-Bu), 35.1 (*tert*-Bu), 33.0 (d, $J_{PC}$ = 4.6 Hz, *tert*-Bu), 31.4 (*tert*-Bu), –0.4 ($Si(CH_3)_3$). $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 351.8 ppm. EI MS (70 eV): *m/z* [$M^+$] 531.2 (44), [$M^+$ – *tert*-Bu–H] 475.1 (15) ([$M^+$ – $SiMe_3$] 458.2 (12), [Mes*$P^+$ – H] 275.2 (100). Elemental analysis (%) calcd. for $C_{32}H_{42}NO_2PSi$ 72.28; H 7.96; N 2.63; Found. C 72.45; H 7.94; N 2.67%

**Isomerization studies**

A standard solution of (*Z*)-**9** was prepared by dissolving (*Z*)-**9** (113 mg; 0.21 mmol) in 2 ml THF and 4 ml DMF.

1. To an NMR tube with benzene-$d_6$ as external standard, 0.5 ml of the (*Z*)-**9** standard solution and 0.04 ml of DIPEA was added. The sample was kept at room temperature and isomerization occurred. Within 90 min a ~1 : 1 ratio of (*Z*)-**9** and (*E*)-**9** was established.

2. To an NMR tube with benzene-$d_6$ as external standard, 0.5 ml of the (*Z*)-**9** standard solution and 0.04 ml of DIPEA was added. The sample was heated in the NMR to 45 °C and isomerization occurred. Within 90 min a 1 : 1 ratio of (*Z*)-**9** and (*E*)-**9** was established.

3. To an NMR tube with benzene-$d_6$ as external standard, 0.5 ml of the (*Z*)-**9** standard solution and an excess of $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol) was added. The sample was kept at room temperature for 2 h. No major isomerization of (*Z*)-**9** to (*E*)-**9** could be detected.

4. To an NMR tube with benzene-$d_6$ as external standard, 0.5 ml of the (*Z*)-**9** standard solution and an excess of $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol) was added. The sample was heated in the NMR to 45 °C and kept at this temperature for 3.5 h. No major isomerization of (*Z*)-**9** to (*E*)-**9** could be detected.

5. To an NMR tube with benzene-$d_6$ as external standard, 0.5 ml of the (*Z*)-**9** standard solution was added. The sample was heated in the NMR to 45 °C and kept at this temperature for 2 h. No major isomerization of (*Z*)-**9** to (*E*)-**9** could be detected.

6. (*Z*)-**6** (20 mg, 0.041 mmol) was dissolved in 0.18 ml THF and 0.33 ml DMF in an NMR tube. 0.04 ml DIPEA was added and benzene-$d_6$ was used as external standard. No major isomerization could be detected.

**(*E*)-(2,4-Di-*tert*-butylphenyl)(1-(4-nitrophenyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ylidene)phosphine (*E*)-(9)**

The data are taken from a spectrum with a mixture of (*E*)-(**9**) and (*Z*)-(**9**).

$^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.02 (m, 2H, Ar), 7.52 (s, 2H, Mes*) 6.99 (m, 2H, Ar), 1.54 (s, 18H, *tert*-Bu), 1.37 ppm (s, 9H, *tert*-Bu), –0.30 ppm (s, 9H, $Si(CH_3)_3$). $^{13}$C-NMR ($CDCl_3$, 100 MHz): 154.5 (Mes*), 151.1 (Mes*), 147.0 (Ar), 140.2 (d, $^1J_{PC}$ = 36.7 Hz, P═C), 135.1 (d, $^1J_{PC}$ = 58.4 Hz, P–C), 131.9 (d, $J_{PC}$ = 2.6 Hz, Ar), 130.1 (d, $J_{PC}$ = 4.7 Hz, Ar), 123.4 (Ar), 122.4 (Mes*), 103.4 (d, $J_{PC}$ = 25.3 Hz, acetylene), 102.5 (d, $J_{PC}$ = 14.2 Hz, acetylene), 100.2 (d, $J_{PC}$ = 9.1 Hz, acetylene), 93.8 (d, $J_{PC}$ = 27.4 Hz, acetylene), 38.3 (*tert*-Bu), 35.2(*tert*-Bu), 33.4 (d, $J_{PC}$ = 5.9 Hz, *tert*-Bu), 31.5 (*tert*-Bu), 0.09 ($Si(CH_3)_3$). $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 350.9 ppm.

**(1,5-Bis(4-nitrophenyl)penta-1,4-diyn-3-ylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (11)**

A mixture of (*E*)-(**9**) and (*Z*)-(**9**) (70 mg, 0.13 mmol) and 1-iodo-4-nitrobenzene (108 mg, 0.43 mmol) was dissolved in 2 ml THF, 7 ml DMF and 1 drop of DIPEA. The yellow solution was deaerated with the freeze–pump–thaw technique and bubbled with argon, meanwhile $Pd(PPh_3)_2Cl_2$ (20 mg, 0.029 mmol) and CuCl (27 mg, 0.28 mmol) were added. The reaction mixture changed colour to deep red, then brown and finally black during stirring at 40 °C for 6h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$, extracted with EtOAc. The combined organics where dried with $Na_2SO_4$. The product was purified by column chromatography (1% EtOAc in pentane). Orange solid, yield 25 mg (0.043 mmol, 32%). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.24 (m, 2H, Ar), 8.04 (m, 2H, Ar), 7.71 (m, 2H, Ar) 7.52 (s, 2H, Mes*), 7.02 (m, 2H, Ar), 1.54 (s, 18H, *tert*-Bu), 1.34 ppm (s, 9H, *tert*-Bu). $^{13}$C-NMR ($CDCl_3$, 100 MHz): 154.5 (Mes*), 151.4 (Mes*), 147.0 (Ar) 146.9 (Ar), 138.4 (d, $^1J_{PC}$ = 38.8 Hz, P═C), 134.5 (d, $^1J_{PC}$ = 57.8 Hz, P–C), 132.2 (d, $J_{PC}$ = 2.9 Hz, Ar), 131.9 (Ar), 129.8 (2 d overlapping, Ar), 123.7 (Ar), 123.6 (Ar), 122.5 (Mes*), 100.4 (d, $J_{PC}$ = 8.7 Hz, acetylene), 94.3 (2 d,overlapping, acetylene), 92.8 (d, $J_{PC}$ = 19.1 Hz, acetylene), 38.3 (*tert*-Bu), 35.2 (*tert*-Bu), 33.3 (d, $J_{PC}$ = 4.4 Hz, *tert*-Bu), 31.4 (*tert*-Bu).$^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 355.8 ppm. EI MS (70 eV): *m*/*z* [$M^+$] 580.6 (46), [Mes*$P^+$ – H] 275.3 (100). Elemental analysis (%) calcd for ($C_{35}H_{37}N_2O_4P{\cdot}1\frac{1}{2}$ $CH_3OH$): C 69.73, H 6.89, N 4.46; Found; C 69.59, H 6.48, N 4.90%

**1,4-Bis((*Z*)-3-((2,4,6-tri-*tert*-butylphenyl)phosphinylidene)-5-(trimethylsilyl)penta-1,4-diynyl)benzene (12)**

To a degassed solution of **1** (97 mg, 0.2 mmol) in THF/DMF(1 : 5, v/v) was added 1,4 diiodobenzene (33 mg, 0.1 mmol, 0.5 equiv) and DIPEA(0.5 mL). $Pd(PPh_3)_2Cl_2$ (30 mg, 0.04 mmol, 20 mol%) was added and the mixture was stirred at room temperature for 5 min, then CuCl (59 mg, 0.6 mmol, 3 equiv) was added in one portion. The reaction flask was immersed in an oil bath with a temperature of 30–35 °C. The reaction was monitored by TLC (hexane, 2–3 h) and quenched by the addition of aqueous $NH_4Cl$. The reaction mixture was extracted with hexane (3 × 50 mL), the combined organic phases were dried over $Na_2SO_4$ and concentrated *in vacuo*. The product was purified by column chromatography (silica, hexane/DCM) and afforded as a yellow foam (35%, 31 mg). Further purification was achieved by recrystallization from DCM/$CH_3CN$. mp 144–147 °C (dec.). $R_f$ 0.2 (1% EtOAc in hexane). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.09 (s, 18H), 1.34 (s, 18H), 1.52 (s, 36H), 7.48 (s, 4H), 7.50 (s, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = –0.3, 31.5, 33.1, 35.2, 38.3, 91.2 (d, $J_{(P,C)}$ = 26.8 Hz), 96.3 (d, $J_{(P,C)}$ = 16.1 Hz), 102.7 (d, $J_{(P,C)}$ = 19.1 Hz), 108.4 (d, $J_{(P,C)}$ = 6.1 Hz), 122.6, 123.3, 131.6, 134.7 (d, $^1J_{(P,C)}$ = 58.1 Hz), 140.8 (d, $J_{(P,C)}$ = 35.9 Hz), 150.6, 153.8; $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): $\delta$ = 342.1 ppm; UV/Vis $\lambda$ nm ($\varepsilon$ [$M^{-1}cm^{-1}$]) 283(16 744), 359(16 616), 415 (26 283). Anal. Calcd for 2 $C_{64}H_{72}P_2{\cdot}CH_3CN$ : C 77.37, H 8.97; Found: C 77.30, H 8.81%

**(*E*)- and (*Z*) -(1-(4-nitrophenyl)-5-phenylpenta-1,4-diyn-3-ylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (13)**

(*Z*)-(**6**) (140 mg, 0.29 mmol) and 1-iodo-4-nitrobenzene (144 mg, 0.58 mmol) were dissolved in 2 ml THF, 8 ml DMF and 0.5 ml DIPEA. The yellow solution was deaerated with the freeze–pump–thaw technique and bubbled with argon while $Pd(PPh_3)_2Cl_2$ (40 mg, 0.057 mmol) and CuCl (54 mg, 0.55 mmol) were added. The reaction mixture changed colour to deep red, then brown and finally black during stirring at 40 °C for 6 h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$, extracted with EtOAc. The combined organics where dried with $Na_2SO_4$. The product was purified by column chromatography (1% EtOAc

in pentane). Orange solid, yield 8 mg (0.016 mmol, 6%). In the $^1$H-NMR, the signals of the isomeric mixture were assigned to (*E*)-**13** and (*Z*)-**13** on the basis of the chemical shifts of the nitrophenyl protons, which are shifted upfield in (*Z*)-**13** as a result of the additional shielding provided by the Mes*.[34] (*E*)-**13**: $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta = 8.22$ (m, 2H, Ar), 7.71 (m, 2H, Ar) 7.51 (s, 2H, Mes*), 7.14–7.24 (m, 3H, Ar), 6.90 (m, 2H, Ar), 1.54(s, 18H, *tert*-Bu), 1.33 ppm (s, 9H, *tert*-Bu). (*Z*)-**13**: $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.02 (m, 2H, Ar), 7.51–7.59 (m, 2H, Ar) 7.51 (s, 2H, Mes*), 7.35–7.37 (m, 3H, Ar), 7.00 (m, 2H, Ar), 1.54 (s, 18H, *tert*-Bu), 1.34 ppm (s, 9H, *tert*-Bu). $^{31}$P-{$^1$H}-NMR ($CDCl_3$, 162 MHz): 344.4 ppm, 343.8 ppm. ESI MS: *m*/*z* [$M^+$+Ag] 642.18 (100).

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