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Acetylene-Expanded Dendralene Segments with Exotopic Phosphaalkene Units

Xue-Li Geng and Sascha Ott*[a]

Abstract: Bis-TMS protected *C*,*C*-diacetylenic phosphaalkene (A_2PA) **1** (Mes*P=C(C≡CTMS)$_2$; Mes* = 2,4,6-*t*Bu$_3$Ph) has been used as a building block for the construction of butadiyne-expanded dendralene fragments in which phosphaalkenes feature as exotopic double bonds. Treatment of **1** with CuCl gives rise to a Cu^I acetylide that is selectively formed at the acetylene *trans* to the Mes* group. The *cis*-TMS-acetylene engages in similar chemistry, albeit at higher temperatures and longer reaction times. The differentiation between the two acetylene termini of **1** allows for the controlled synthesis of the title compounds by a variety of different Cu- and Pd-catalyzed oxidative acetylene homo- and heterocoupling protocols. Crystallographic characterization of A_2PA **1** and dimeric Mes*P=C(C≡CR^1)C$_4$-(R^{2}C≡C)C=PMes* (**3b**, R^1 = R^2 = Ph; **6**, R^1 = R^2 = TMS), and **10** (R^1 = R^2 = C≡CPh) verifies that the stereochemistry across the P=C bond is conserved during the coupling reactions, whereas spectroscopic evidence reveals *cis*/*trans* isomerization in an iodo-substituted A_2PA intermediate **4** (Mes*P=C-(C≡CTMS)(C≡CI). UV/Vis spectroscopic and electrochemical studies reveal that efficient π conjugation operates through the entire acetylenic phosphaalkene framework, even in the cross-conjugated dimeric structures. The P centers contribute considerably to the frontier molecular orbitals of the compounds, thereby leading to smaller HOMO–LUMO gaps than in all-carbon-based congeners. Phenyl- and/or ethynylphenyl substituents at the A_2PA framework influence the HOMO and LUMO to a varying degree depending on their relationship to the Mes* group, thus enabling a fine-tuning of the frontier molecular orbitals of the compounds.

Keywords: carbon-rich compounds · conjugation · dendralenes · oxidative acetylene coupling · phosphaalkenes

Introduction

Highly unsaturated linear, two- or three-dimensional compounds with acetylene or ethylene subunits are appealing for a myriad of different applications such as organic semiconductors, organic components in (opto)electronic devices, or as sensor materials.[1,2] Despite having been a popular field of research over the last decades,[3–13] the underlying fundamental research on well-defined oligoacetylenes and -vinylenes continues to fascinate chemists to date.[14–16] From a structural viewpoint, one may divide the compounds into those that contain arene moieties like oligo-phenylacetylenes or -vinylenes[14,17,18] or structures in which the π system exclusively consists of acetylene and/or vinylene units, the latter sometimes being referred to as "acetylenic scaffolding."[19,20] Many of these systems have reached an impressive maturity, with elaborate systems approaching the effective conjugation length of polymers, thereby bridging the gap between structurally defined molecular chemistry and polymer science.

The incorporation of main-group elements other than carbon into the π conjugates provides the possibility to alter the electronic properties of the structures and to allow for postsynthetic manipulations such Lewis acid coordination or oxidations.[21,22] In the case of oligo-phenylacetylenes and -vinylenes, the constituting arenes can formally be replaced relatively easily by other heteroaromatic units such as pyridines, thiophenes, and others.[1,2,11,23] The introduction of heteroatoms in the form of higher alkenes as surrogates of traditional alkenes has been explored to a much lesser extent, despite the advantages in terms of lower HOMO–LUMO gaps and polarizability that are offered by this strategy.[24–26] The first oligo-phenylethylene analogues that feature disilenes,[27–29] phosphaalkenes,[30,31] and diphosphenes[32,33] instead of classical C=C bonds have emerged in the literature only recently. The reason for the sporadic presence of such structures is caused by a shortage of synthetic protocols that allow for their preparation as well as the general instability of higher element π bonds. The introduction of heteroatoms into purely acetylenic scaffolds is even more in its infancy. We have recently reported the incorporation of phosphaalkenes into acetylenic frameworks to form acetylenic phosphaalkenes (A_xPA, x = number of acetylene substituents),[34–36] an effort that has now also been extended into group 12 elements with the report of a disi-

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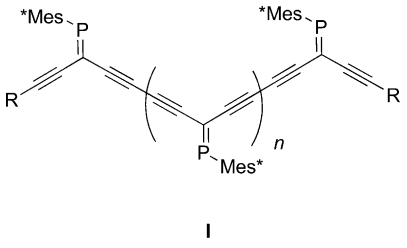
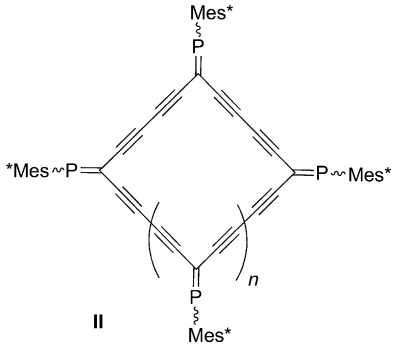
lene analogue of (*E*)-enediyne by Sato et al.[37] The ultimate goal of our program is to establish access to all geminal and *P,C*-A_2PAs and to use them as building blocks for the preparation of larger oligomeric, polymeric, and cyclic structures of, for example, type **I** and **II**, the all-carbon analogues of which are well-established entities with intriguing properties.[38,39]



I



II

n=0, 1, 2...

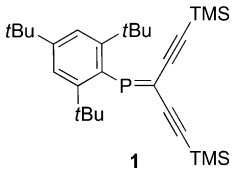
In this paper, we scrutinize the viability of this concept and present an in-depth investigation of *C,C*-A_2PAs that engage in oxidative acetylene homo- and heterocoupling reactions. The synthesis, crystallographic, spectroscopic, and electrochemical characterization of the first acetylene-expanded dendralene fragments in which the exotopic C=C double bonds have been replaced by P=C units is presented.

Results and Discussion

C,C-A_2PA **1** is a promising building block for the construction of elaborate structures such as **I** and **II** due to the presence of the TMS groups that can presumably be removed under mild conditions similar to what has been shown for ene-1,1-diynes.[40] Single-crystal X-ray analysis of compound **1** (Figure 1) shows that the aromatic ring of the Mes* group is almost perpendicular to the plane defined by P1-C1-C2-C3-C4-C5 (hereafter referred to as the PC_5 subunit). The interplanar angle of 87.1° basically prevents all π conjugation between the Mes* and PC_5 subunits. In addition, the Mes* ring resides on top of the TMS-acetylene that is *cis* relative to the P=C double bond, thus leaving the *trans*-TMS-acetylene rather exposed. This feature suggests that the two TMS groups may potentially be removed selectively, thereby enabling a high degree of control in subsequent coupling chemistry of the terminal acetylenes.

Developing mild desilylation strategy for TMS-protected *C,C*-A_2PA and suitable oxidative acetylene coupling protocols: In a previously reported paper, we could demonstrate for the first time that the strategy to assemble larger structures from A_2PA building blocks may indeed by viable.[41] One-pot in situ deprotection of **2a** with K_2CO_3 and oxidative acetylene homocoupling under the classical Eglinton conditions (MeOH, py, $Cu(OAc)_2$; py = pyridine)[42] afforded the dimeric product **3a** in good yield (Scheme 1).[41] When a mixture of **2a** and **2b** was used in the experiment, only **2a** reacted and **2b** remained unchanged. The work thus indicated that desilylation of the two TMS-acetylenes in **2a** and **2b** proceeds at different rates—an encouraging finding as it potentially enables site-selective reactions and the controlled assembly of elaborate structures. The TMS-acetylene *trans* to the Mes* group is more reactive, presumably due to an additional steric protection of the TMS group *cis* to the very bulky, adjacent Mes*.

The first incentive of the current work was thus to find synthetic protocols to deprotect the less reactive TMS-acetylene *cis* to the Mes* and to engage



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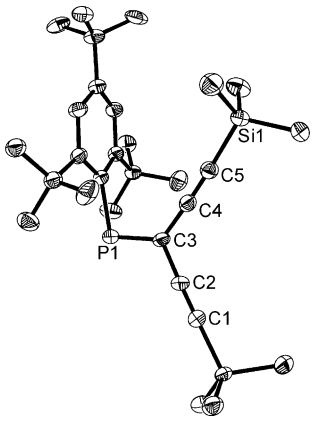
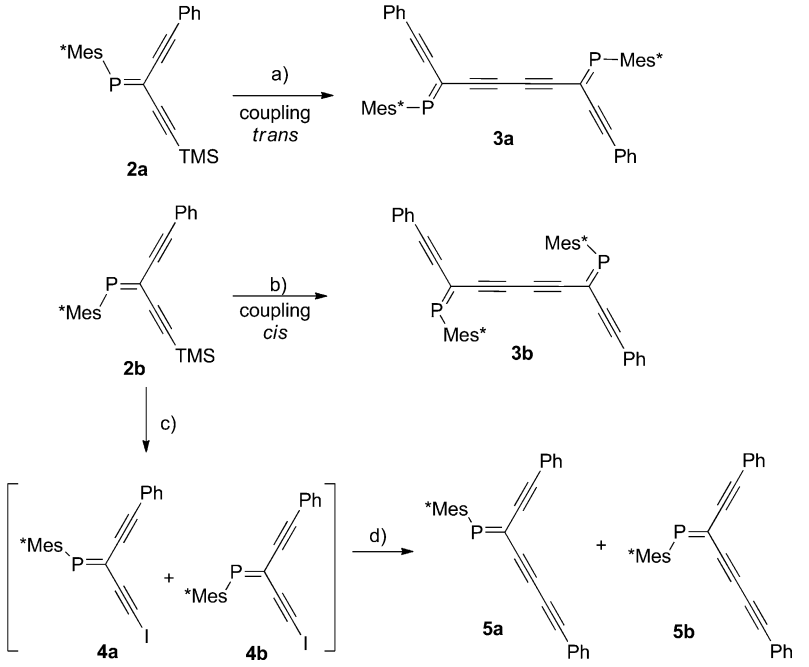


Figure 1. Molecular structure of A_2PA **1** (35% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.187(8), C2–C3 1.454(7), C3–C4 1.413(7), C4–C5 1.214(7), C3–P1 1.717(5); P1–C6 1.859(4); C2-C3-C4 117.5(4), C2-C3-P1 116.9(3), C4-C3-P1 125.6(4), C3-P1-C6 101.7(2), C4-C5-Si1 177.5(4). Dihedral angle [°]: Mes* aromatic ring to P1-C1-C2-C3-C4-C5 87.1(4).

the thus-formed terminal acetylene in coupling reactions. A simple increase in reaction time and temperature using the conditions described for the synthesis of **3a** led to the consumption of **2b**, but did not result in the formation of isolable amounts of desired product. Inspired by a report by Mori and co-workers,[43,44] we attempted the direct transformation of the TMS-protected alkyne to a copper(I) acetylide by treating **2b** with equimolar amounts of CuCl in DMF. This protocol circumvents the use of K_2CO_3 and other nucleophiles that we believe to promote decomposition. Using these conditions, we were delighted to find that the TMS group *cis* to the Mes* was removed at slightly elevated temperatures, thereby forming a red Cu acetylide that is



Scheme 1. Desilylation and coupling reactions on TMS-protected *C,C*-A_2PA **2b**; *cis* and *trans* are relative to the 2,4,6-*t*Bu_3Ph (Mes*) substituent. Conditions: a) K_2CO_3, $Cu(OAc)_2$, MeOH, pyridine, 1 h, 20 °C, **3a** 68 %. b) $[Pd(PPh_3)_2Cl_2]$, CuCl, air, DMF/THF, 38 °C, 2 h, **3b** 87 %. c) i) CuCl, DMF/THF, 40 °C, 1–2 h; ii) I_2, RT, 1 h. d) Phenylacetylene, $[Pd(PPh_3)_2Cl_2]$, CuCl, DIEA, DMF/THF, RT, 3–5 h, **5** 71 % (2 steps, **5a** 27 %, **5b** 73 %).

available for subsequent coupling reactions. Unfortunately, employing the Cu acetylide of **2b** under customary Hay homocoupling conditions (CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), O_2) resulted either in no reaction or decomposition. If CuCl and TMEDA were added in equimolar amounts, the reaction does not occur because Cu–TMEDA will not lead to the formation of the Cu acetylide of **2b**. If CuCl is added in excess amount or before the addition of TMEDA, the Cu acetylide is formed; however, it decomposes rapidly due to the presence of TMEDA and O_2.

Mild and efficient homocoupling conditions were found when $[Pd(PPh_3)_2Cl_2]$ was added to an aerated solution of the Cu acetylide of **2b** in DMF/THF, thereby affording the dimeric phosphaalkene **3b** in 87 % yield (Scheme 1b).[45] It is interesting to note that the formation of the Cu acetylide and its subsequent Pd-mediated coupling proceeds without any isomerization across the P=C double bond, even though the isomer in which the phenyl group is *cis* to Mes* can be assumed to be thermodynamically more favorable.[41]

Single-crystal X-ray analysis of **3b** illustrates the *cis* relationship between the butadiyne (C2′-C1′-C1-C2) and the Mes* rings, thus verifying that the stereochemistry across the P=C bond in compound **2b** is conserved during the homocoupling reaction (Figure 2, bottom). The two bulky Mes* rings of **3b** reside above/under the butadiyne vector and are almost orthogonal (91.1°) to the planes defined by their respective monomeric PC_5 subunits. These two factors lead to a solid-state conformation in which the two PC_5 planes are twisted by an angle of 43.6°, thus preventing efficient π conjugation. Moreover, the phenyl groups at the acetylene termini are rotated out of their respective PC_5 plane by 24.4°, further decreasing the conjugation level. In contrast, the phenyl groups in **3a** (Figure 2, top) are almost coplanar with the plane of two PC_5 systems and deviate by only 6.6°.[41]

Encouraged by the synthesis of **3b**, we explored the Pd/CuCl-catalyzed cross-coupling of **2b** with phenylacetylene. Employing an excess amount of phenylacetylene (5 equiv) in the presence of $[Pd(PPh_3)_2Cl_2]$ and 2 equiv of CuCl in DMF/THF/*N,N*-diisopropylethylamine (DIEA) (10:2:1) gave dissatisfying results as the coupling proceeded very slowly at 35 °C, and decomposition of starting material dominated at higher temperatures. The failure is at least partially caused by a difference in reactivity of the Cu^I acetylide of **2b** relative to that of the phenylacetylene, which, however, ought to be similar for a heterocoupling to occur. To avoid unwanted homocoupling reactions and the depletion of a coupling partner in the reaction mixture, a differentiation of the two reaction partners was desired. The selective heterocoupling between a haloacetylene and a terminal acetylene similar to what is achieved in the Cadiot–Chodkiewicz protocol,[46] and a modified version using Pd catalysis was considered suitable.[47] We therefore turned to synthesize the iodo-substituted A_2PA **4** by quenching the Cu acetylide of **2b** with I_2 (Scheme 1c). The reaction is accompanied by a color change from reddish-brown to reddish-yellow, and the appearance of a new yellow spot on the TLC plates. NMR spectroscopic analysis reveals the formation of two products with ^{31}P chemical shifts at $\delta = 341.6$ (**4a**) and 342.8 ppm (**4b**). Neither of the products contains TMS groups, nor ^{1}H NMR spectroscopic signals in the diagnostic acetylene region that point towards the formation of two isomers of **4**. It thus seems that the activation barrier for *cis*/*trans* isomerization in iodo-acetylene **4** is lower than that in **2b** and its Cu acetylide. The interconversion proceeds at ambient temperature and can be followed by ^{31}P NMR spectroscopy (Figure 3), which shows that the steady-state equilibrium between **4a**/**4b** of 2:1 is reached after about 12 h.

Iodo-substituted **4a**,**b** possess limited stability, which once more suggests a one-pot procedure for the preparation of **5a**,**b**. Thus, when the crude reddish-yellow solution of **4a,b** was transferred directly into a suspension of phenylacetylene in DMF/THF/DIEA (10/1/1) in the presence of catalytic amounts (5 mol %) of $[Pd(PPh_3)_2Cl_2]$ and CuCl, **5a** and

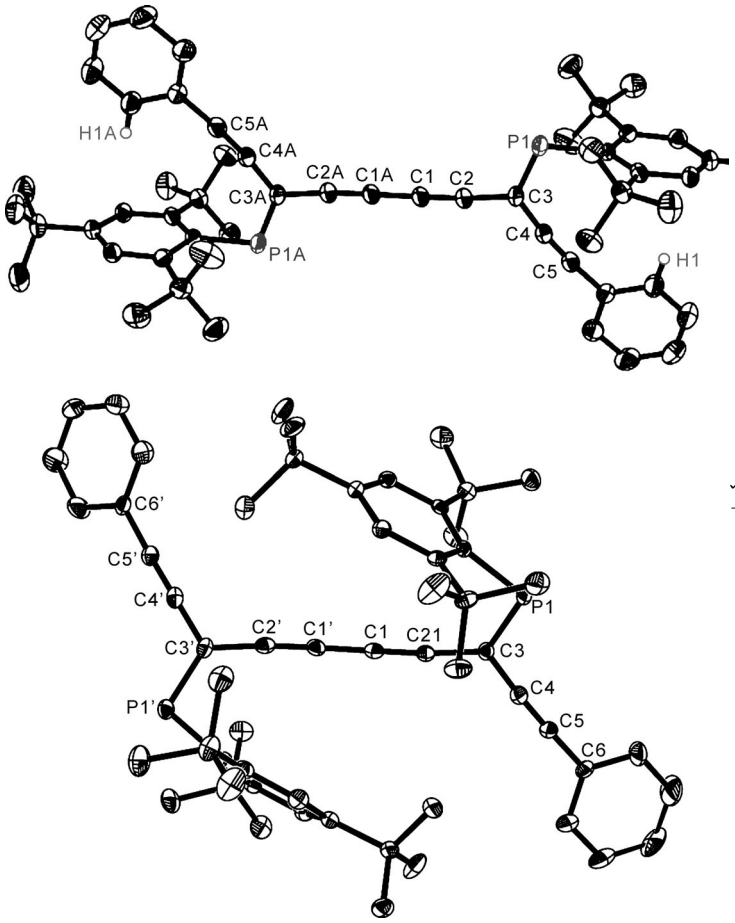


Figure 2. Molecular structure of phosphaalkene **3b** (bottom) (35% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C1′ 1.374(5), C1–C2 1.206(6), C2–C3 1.425(5), C3–C4 1.442(6), C4–C5 1.214(6), C5–C6 1.440(6), C3–P1 1.719(4), P1–C7 1.846(4); C2-C3-P1 122.9(4), C2-C3-C4 120.4(4), C4-C3-P1 116.6(3), C3-P1-C7 101.34(17). Dihedral angle [°]: C7–Mes* aromatic ring to P1-C1-C2-C3-C4-C5 91.1(3), P1-C1-C2-C3-C4-C5 to P1′-C1′-C2′-C3′-C4′-C5' 43.6(2), C6–Phenyl ring to P1-C1-C2-C3-C4-C5 24.4(3). The molecular structure of **3a** is included for comparison (top).[41]

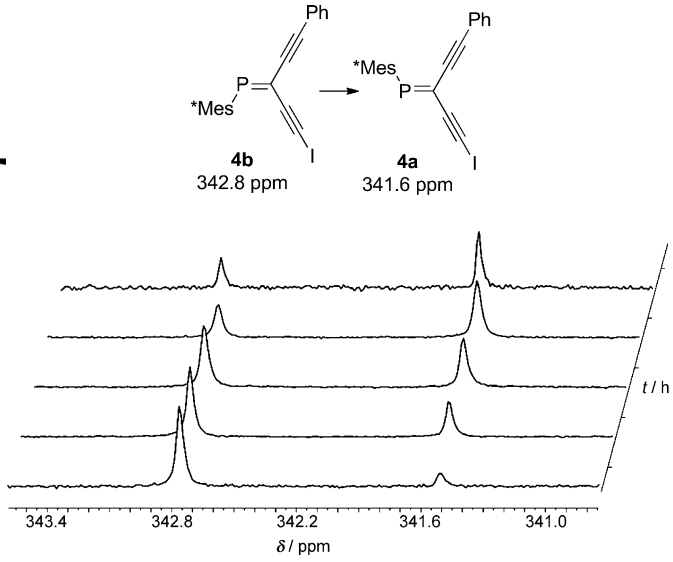


Figure 3. Transformation of **4b** (5 mM, $CDCl_3$, 20 °C) to **4a**. Shown are the ^{31}P NMR spectroscopic signals $\delta = 341.6$ (**4a**) and 342.8 ppm (**4b**).

5b are obtained in an overall yield of 71% from **2b** (Scheme 1d). Compounds **5a,b** are the first examples of APAs that have been realized through an oxidative heterocoupling reaction. It is noteworthy that the ratio of **4a** and **4b** determines the product distribution, thereby indicating that no further *cis*/*trans* isomerization across the P=C bond occurs under the coupling conditions. The two butadiyne-substituted **5a** and **5b** can be separated by careful column chromatography and their stereochemistry identified by ^1H NMR spectroscopy. Whereas the *ortho*-phenyl protons at the acetylene terminus *cis* to Mes* in **5a** resonate at $\delta = 6.86$ ppm on account of the additional shielding above the aromatic Mes* group, the signal of the corresponding proton in **5b** features at $\delta = 7.53$ ppm.

Reactions with bis-TMS A_2PA 1: Having established mild conditions for the in situ desilylation of the less reactive TMS-acetylene and for the subsequent coupling steps, our focus was turned to the bis-TMS-protected A_2PA **1**, that is, the building block for **I** and **II**. Since **1** features a TMS-acetylene *trans* to the Mes* group that resembles the situation in **2a**, synthesis of dimeric **6** was attempted by applying the Eglinton procedure that was used for the formation **3a**. Much to our disappointment, complete decomposition of bis-TMS A_2PA **1** was observed within one hour under these conditions. The phenyl substituent at the second, rather remote and cross-conjugated acetylene in **2a** is thus a crucial factor that stabilizes reaction intermediates and enables the synthesis of **3a** under these conditions. Changing to modified, non-basic Hay coupling conditions (CuCl, air, DMF) to avoid decomposition, A_2PA **1** underwent oxidative homocoupling and up to 81% of desired dimeric **6** was obtained by adding 15 equivalents of CuCl into the reaction within 8 h. The most reliable route for the synthesis of dimer **6** was found when **1** in DMF was treated with CuCl and Pd^{II}, and **6** was obtained in almost quantitative yield within one hour at room temperature (Scheme 2a). The procedure is the same as described above for the preparation of **3b**. Whereas in the latter case, the reaction can only proceed at one acetylene, it is noteworthy that in the case of **1**, selectivity is achieved by the faster deprotection rate of the acetylene *trans* to the Mes* group.

The solid-state structure of **6** (Figure 4) reveals that the acetylene homocoupling of **1** proceeds as expected at the sterically more exposed acetylene *trans* to the Mes* group. The dimerization does not significantly alter the structural features of the monomeric units. The Mes* groups in dimeric **6** are still almost perpendicular to their respective PC_5 planes with an interplanar angle of 87.4° (87.1° for monomer **1**). In addition, the two PC_5 subunits are almost coplanar, being twisted only by 6.8°, thereby allowing good conjugation between the two halves of the molecule. It is interesting to note that the Si atom of the TMS group in compound

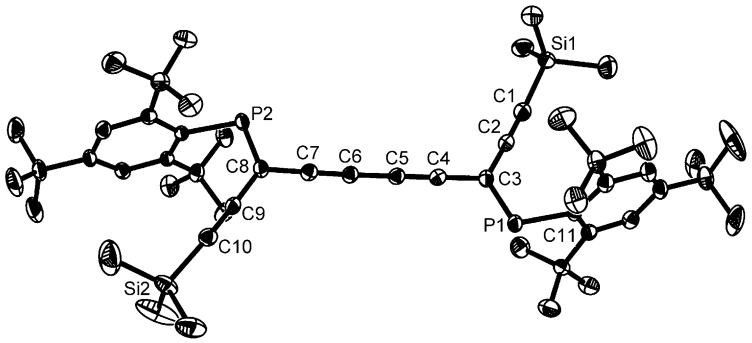


Figure 4. Molecular structure of **6** (35% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1−Si1 1.8437(18), C1−C2 1.209(2), C2−C3 1.429(2), C3−C4 1.422(2), C4−C5 1.209(2), C5−C6 1.362(2), P1−C3 1.7170(17), P1−C11 1.8426(16); C2-C1-Si1 169.27(16), C1-C2-C3 175.83(17), C3-P1-C11 102.10(8), C2-C3-C4 116.82(14), C2-C3-P1 125.94(12), C4-C3-P1 117.22(12). Dihedral angle [°]: C11−Mes*aromatic ring to P1-C1-C2-C3-C4-C5 87.40(2), P1-C1-C2-C3-C4-C5 to P2-C6-C7-C8-C9-C10 6.80(10).

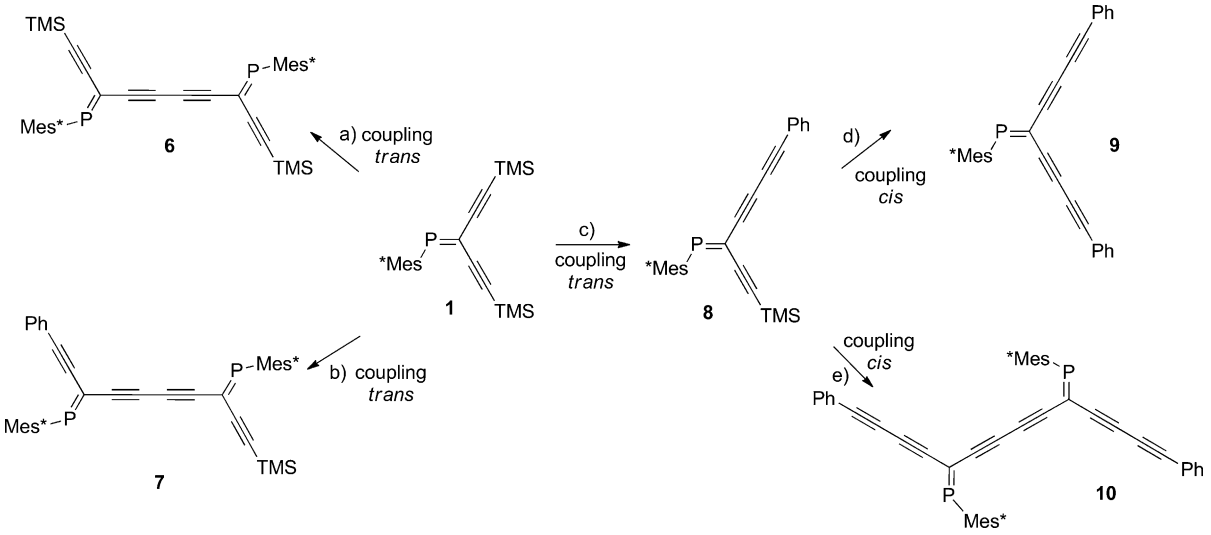
6 was found to bend 11° away from the acetylenic chain of C1-C2-C3 to minimize the steric repulsion between Mes* and TMS group. This bending is significantly bigger than that observed for **1** (2.5°).

The rate of Cu acetylide formation of the acetylene *trans* to Mes* in **1** is similar to that of the *trans* acetylene in **2a**, thus enabling the synthesis of unsymmetrically terminated **7**. Compound **7** is the first report of a dimeric A_2PA that stems from an oxidative acetylene heterocoupling. The ^{31}P NMR spectrum of **7** features a pair of doublets at $\delta = 348.5$ and 356.3 ppm due to the presence of chemically different P=C units. Considering the P···P distance of 8.7 Å (as deduced from **3b** and **6**), the coupling constant of $^{7}J(P,P) = 25.8$ Hz is stunningly large, which indicates that the two P centers in **7** are part of one common π system that provides a large degree of communication. If the P centers were not part of the same π system, a much lower coupling constant would be expected, for example, that between two tertiary $\sigma^3\lambda^3$ phosphanes that are bridged by a butadiyne linker ($^{5}J(P,P) = 2.3$ Hz).[48] The $^{7}J(P,P)$ coupling in **7** is comparable to the $^{2}J(P,P)$ of 32 Hz that has been reported between the two endocyclic P centers of a 1,3,6-triphosphafulvene.[49]

To further develop the chemistry of A_2PAs while maintaining a large degree of reaction control, we started to explore the possibility of A_2PA **1** to engage in heterocoupling reactions of differentially polarized acetylenes. Unfortunately, attempts to convert A_2PA **1** into an iodo-substituted product by treating the former with CuCl and quenching the copper acetylide with iodine at room temperature failed, presumably due to the low stability of the formed iodo-substituted A_2PA. Again, the only difference between **4a**,**b** and the elusive iodo-substituted analogue of **1** is the phenyl group at the cross-conjugated acetylene terminus of the former, which seems to be crucial for the stability of such an intermediate. Having identified this shortcoming, the inverse reaction of a copper acetylide of **1** with 1-haloalkynes was investigated. The widely used Cadiot–Chodkiewicz coupling protocol for unsymmetrically terminated alkynes seemed to be inapplicable to the A_2PAs because of their incompatibility with secondary amine. In seeking neutral and mild conditions, it was found that Scott and coworkers described a modified Cadiot–Chodkiewicz conditions for the synthesis of polydiacetylenes by coupling separately prepared copper(I) acetylides with bromoalkynes in pyridine.[50] With slight modifications to these conditions, A_2PA **1** was converted to its Cu acetylide by the continuous addition of an excess amount of CuCl in degassed DMF at room temperature over 5 min, followed by quenching with a solution of an excess amount of phenylethynyl iodide in degassed pyridine (Scheme 2c), thereby affording **8** in 52% overall yield based on A_2PA **1**. The same protocol can be used a second time on compound **8** to afford the bis- butadiyne-substituted phosphaalkene **9** (Scheme 2d). However, the direct synthesis of **9** from **1** by heating the reaction to 35–40°C results in very low yields of **9**. The homocoupling of **8** proceeds smoothly under the Pd/CuCl-mediated coupling conditions that were developed for the reaction of acetylenes *cis* to Mes*, and dimeric **10** was obtained in 68% isolated yield (Scheme 2e).

X-ray analysis of a single crystal of **10**, grown from a mixture of CH_2Cl_2 and acetonitrile, revealed that the *cis* relationship of two bulky Mes* groups forces dimeric **10** to adopt a somewhat twisted geometry around the central butadiyne vector, similar to what is observed for **3b** (Figure 5). The two PC_5 planes (defined by P1-C1-C2-C3-C4-C5 and P2-C1′-C2′-C3′-C4′-C5′, respectively) describe an interplanar angle of 50.2°, thus limiting the communication between the two P=C units in the solid state. It is interesting to note that the phenyl substituents at the terminal butadiynes are not symmetrical (Figure 5, bottom, side view). The C8−Ph group is twisted out of its PC_5 plane by 67.7°, whereas the other C8′−Ph group almost lies within its PC_5 plane and deviates by only 7.2°, thus allowing the participation of the C8′-phenyl ring in π conjugation.

Electronic absorption spectroscopy: The electronic absorption spectra of A_2PAs **3b** and **5–10** are shown in Figure 6. In contrast to the observations from the solid-state structures of **3a** and **3b** (Figure 2), which indicated different degrees of π conjugation within the two compounds, their UV/Vis spectra are literally identical. The unfavorable conformation caused by steric repulsion between the two Mes* groups in **3b** thus seems to be obsolete in solution. In contrast, **5a** and **5b** show somewhat different longest-wavelength absorption maxima of 383 and 379 nm, respectively. The spectrum of **5a** is more similar to that of **8** and points towards a negligible



Scheme 2. Synthesis of dimeric phosphaalkenes from bis-TMS-protected A_2PA **1**; *cis* and *trans* are relative to the Mes* substituent. Conditions: a) [Pd-$(PPh_3)_2Cl_2$], CuCl, DIEA, DMF/THF, RT, 1–2 h, **6** > 95%. b) **2a**, [$Pd(PPh_3)_2Cl_2$], CuCl, DIEA, DMF/THF, RT, 1–2 h, **7** 76% (based on **2a**). c) i) CuCl, DMF/THF, RT, 5 min. ii) Phenylethynyl iodide, pyridine, RT, 5 h, **8** 52%. d) i) CuCl, DMF/THF, 35 °C, 30 min. ii) Phenylethynyl iodide, pyridine, RT, 6 h, **9** 27%. e) [$Pd(PPh_3)_2Cl_2$], CuCl, DMF/THF, 35 °C, 2–3 h, **10** 68%.

contribution of the second phenyl group at the acetylene *cis* to the Mes* group in the overall π conjugation of **5a**.

Due to the larger π-conjugation system, dimeric **3**, **6**, and **10** exhibit longest-wavelength absorption maxima at 446, 441, and 456 nm, which are considerably redshifted by 79, 94, and 83 nm, respectively, compared to the corresponding monomers.[35,41] The presence of two additional phenyl groups that extend the π system in **3a** relative to that in **6** has only a small effect on the observed absorption maxima with a $\Delta\lambda_{max}$ of 5 nm. By contrast, in comparing the UV/Vis spectra of **10** and **3**, it becomes apparent that the two additional acetylenes in **10** lead to a greater redshift of 9 nm relative to that in **3b**, and a remarkable increase in molar extinction coefficient, both indicative of a more extended π system in **10** than that of **3**.

In comparison with structurally closely related all-carbon-based reference compounds, the longest-wavelength absorption maxima of all A_2PAs are generally redshifted, thus further supporting the notion that the HOMO–LUMO gaps of oligoacetylenes can be lowered dramatically by replacing some of the constituting alkenes by heavier congeners such as phosphaalkenes. For example, bis-phenylbutadiyne-substituted phosphaalkene **9** shows a lowest-energy absorption maximum at 396 mm that is thus considerably redshifted relative to that of its all-carbon endiyne analogue (λ_{max} = 330 nm, shoulder at 350 nm).[51] The effect is even more dramatic in the dimeric systems with phosphaalkene **6**, which features an end absorption that is bathochromically shifted by $\Delta\lambda_{max}$ = 112 nm relative to a suitable reference with a similar all-carbon-based π framework.[52] Similarly, A_2PAs **3** and **10** are also bathochromically shifted by more than 100 nm compared to their all-carbon-based analogues with $-NO_2$ or $-NMe_2$ substituents at the phenyl groups.[51] The effect of the P=C units on the HOMO–LUMO gap in **10** is comparable to that imposed by two additional tetrathiafulvalene units that formally replace the P centers of **10** at an otherwise identical acetylene skeleton (λ_{max} = 354, shoulder at 425 and 460 nm).[53]

Electrochemistry: Electrochemical measurements of A_2PAs **3b** and **5–10** were performed to further investigate their electronic properties and to evaluate the role of the phosphorus centers (Table 1). A_2PAs **3**, **5**, and **7** that contain a phenylacetylene subunit directly at the P=C feature oxidation potentials that are noticeably shifted cathodically compared to those of the TMS-terminated compounds. This observation thus suggests that the HOMOs of these compounds experience additional contributions from the phenyl groups. However, if the phenyl group is separated by a butadiyne like in **8**, its contribution to the HOMO becomes negligible, as the oxidation potential of **8** remains unchanged compared to that of **1** ($E_{p,a}$ = 1.16 V),[35] consistent with a previous finding for another butadiynylphenyl-substituted phosphaalkene.[35] An additional trend that is visible from the anodic scans is that the dimeric A_2PAs **3b**, **6**, and **10** exhibit milder oxidation potentials than their monomeric building blocks **2b**, **1**, and **8** by 80, 90 and 110 mV, respectively. It is thus clear that the HOMO of the dimeric species extends well beyond the monomeric subunits, thereby providing a viable communication path between the two P=C units.

An evaluation of the cathodic scans reveals that the observed reduction potentials are considerably more sensitive measures for the extent of π conjugation in the A_2PAs than the oxidation potentials. In comparisons with A_2PAs **1** and **2b**, extending the π system by one additional acetylene group as in **5** and **8** results in sizeable anodic shifts of the observed reduction potentials of 200–300 mV. The second

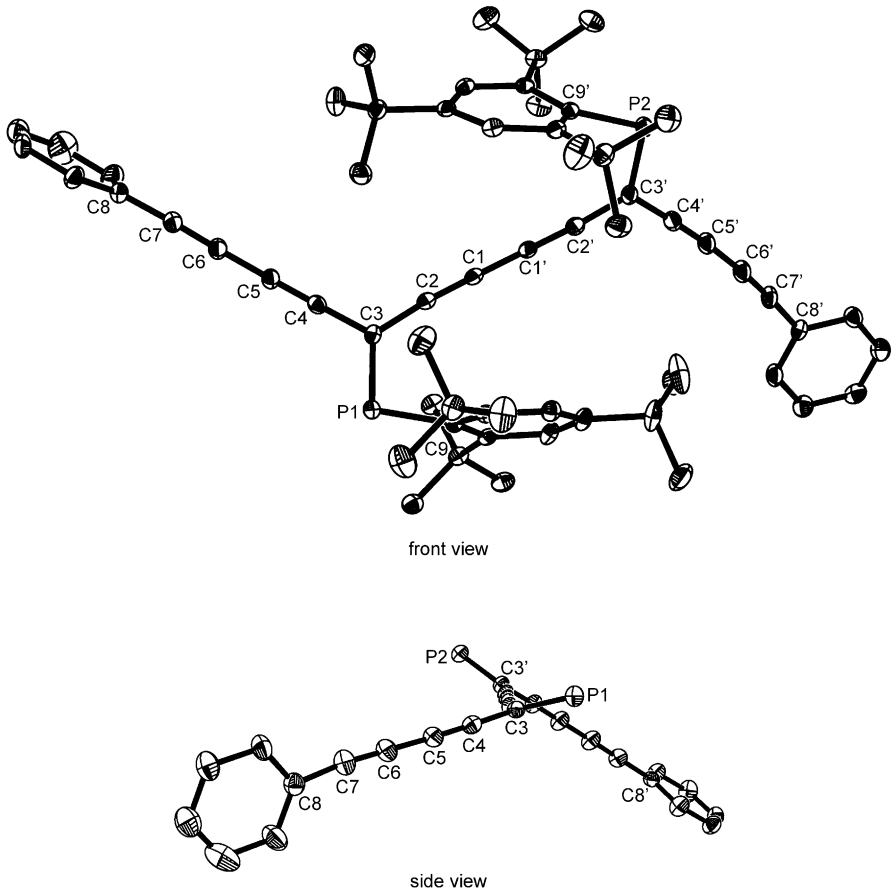


Figure 5. Molecular structure of phosphaalkene **10** (30% probability ellipsoids). All hydrogen atoms are omitted for clarity in front view and Mes* groups are further omitted for clarity in side view. Selected bond lengths [Å] and angles [°]: C1−C1′ 1.373(4), C1−C2 1.210(4), C2−C3 1.416(4), C3−C4 1.429(4), C4−C5 1.198(4), C5−C6 1.379(4), C6−C7 1.190(4), C7−C8 1.443(7), C3−P1 1.715(3), P1−C9 1.848(3), C3′−P2 1.705(3), P2−C9′ 1.844(3); C2-C3-C4 118.0(2), C2-C3-P1 123.5(2), C4-C3-P1 118.5(2), C3-P1-C9 99.80(12). Dihedral angles [°]: the plane of P1-C1-C2-C3-C4-C5 to P2-C1′-C2′-C3′-C4′-C5′ 129.8(2), the aromatic ring of C9−Mes* to the plane of P1-C1-C2-C3-C4-C5 90.1(2), the aromatic ring of C9′−Mes* to the plane of P1′-C1′-C2′-C3′-C4′-C5′ 93.1(2), C8−phenyl ring to the plane of P1-C1-C2-C3-C4-C5 112.30(11), C8′−phenyl ring to the plane of P1′-C1′-C2′-C3′-C4′-C5′ 7.2(2).

acetylene in **9** leads to an additional shift of roughly the same magnitude. Homo-dimeric **3b**, **6**, and **10** feature anodically shifted reduction potentials greater than 400 mV relative to their monomeric building blocks. These often reversible reductions are typically followed by a second, irreversible electron uptake at roughly 500 mV more negative potential. The large separation of these two-electron uptake events is consistent with a delocalization of the primarily obtained radical anion across the entire π system, because localization on one side of the molecules would presumably give rise to a smaller separation of the two cathodic waves.

The expanded dendralene fragment **10** with the largest π system also features the least negative reduction potential as expected. However, comparing the data of **10** with that of **3b**, which possesses the same stereochemistry and only differs in two acetylenes, a stunning possibility to tune the absolute energies of the frontier molecular orbitals (FMOs) emerges. Whereas the HOMO is only sensitive to phenyl groups that are separated from the P=C by not more than one acetylene, the LUMO contains contribu-

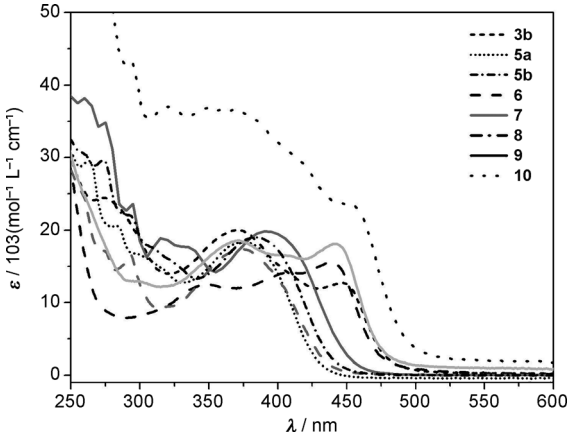


Figure 6. UV/Vis absorption spectra of compounds **3a** and **5–10** in CH_2Cl_2 at 25 °C.

Table 1. Electrochemical data for 1 mM solutions in CH_2Cl_2 (0.1 M NBu_4PF_6).[a]

Compound	Reduction $E_{1/2}$ [V]		Oxidation $E_{p,a}$ [V]
1[35]	−2.07[b]		1.16
2b[41]	−2.04[b]		1.02
3a[41]	−1.67	−2.2[b,c]	0.95
3b	−1.59	−2.00[b,c]	0.94
5a	−1.89[b]		1.00
5b	−1.77		0.96
6	−1.59	−2.17[b]	1.07[d]
7	−1.63	−2.23[b]	1.00
8	−2.02[b]		1.17
9	−1.61		1.05
10	−1.47	−1.91	1.06

[a] Glassy carbon electrode, scan rate (ν) = 100 mV s^{-1}. All potentials are given versus $Fc^{+/0}$. $E_{1/2} = (E_{pa} + E_{pc})/2$. [b] Irreversible peak potentials $E_{p,c}$. [c] Reversible at $\nu > 1$ V s^{-1}. [d] A second oxidation potential was observed at +1.33 V.

tions from the entire π system. The extra acetylenes in **10** thus prevent contributions of the phenyl group in the HOMO and **10** is more difficult to oxidize than **3b**. In contrast, the extra acetylene in **10** renders its reduction more facile than that of **3b**. As a result, HOMO and LUMO of **10** are both anodically shifted relative to the respective FMOs of **3b**, thereby opening an option to tune the energy levels of the FMOs while keeping the HOMO–LUMO gaps more or less constant.

Conclusion

By taking advantage of different rates for the deprotection of the two TMS-acetylene termini in **1**, a series of butadiyne-expanded dendralene fragments with exotopic phosphaalkene units have been successfully prepared. The bulky Mes* that kinetically stabilizes the P=C bond in **1** also decreases the reactivity of the TMS acetylene in the *cis* position, thereby enabling selective deprotection and coupling reactions. Crucial synthetic steps include the mild in situ formation of Cu^I acetylides from the TMS-acetylenes by treatment with CuCl in DMF, followed by immediate Pd-/Cu-catalyzed coupling protocols. Although the stereochemistry across the P=C double bond is conserved during the oxidative acetylene couplings, *cis*/*trans* isomerization occurs in iodoacetylene-containing A_2PA **4** at room temperature.

All spectroscopic, electrochemical, and crystallographic studies show that the $\sigma^2\lambda^3$ phosphorous centers are integral parts of the π systems of the compounds. Mixing the phosphaalkene-based fragment orbitals with those of the appended acetylene framework leads to smaller HOMO–LUMO gaps in the entire π conjugates than in the all-carbon-based reference compounds. Furthermore, communication between the two P=C units is effectively mediated by the central butadiyne as evidenced by the unexpectedly large coupling constant of $^7J(P,P) = 25.8$ Hz in the ^{31}P NMR spectrum of **7**.

Depending on their separation from the P=C units either by an ethyne (as in **3b**) or a butadiyne (as in **10**), terminal phenyl groups affect the energy levels of the frontier molecular orbitals of the A_2PAs to a varying degree, thus offering the possibility to fine-tune their energy levels. Synthetically, phenyl groups at the cross-conjugated acetylene terminus have been found to stabilize the reaction intermediates and are crucial for the oxidative acetylene coupling of the Cu^I acetylides in some instances. This finding suggests synthetic strategies for future oligomeric structures of type **I** and **II** in which extra phenyl groups are introduced into every second butadiyne to increase the stabilities of the structures.

Experimental Section

General: All reactions were performed under argon using Schlenk techniques. Diethyl ether and THF were freshly distilled from sodium/benzophenone prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts (ppm) were reported and referenced to the internal signal of residual protic solvent. UV/Vis spectra were recorded in a 1×1 cm^2 optical quartz cell as solutions in CH_2Cl_2. Cyclic voltammetry (CV) was carried out using a computer-controlled potentiostat (Autolab) and a standard three-electrode arrangement. All electrochemical measurements were carried out in Ar-purged dry dichloromethane with 100 mM Bu_4NPF_4 as the supporting electrolyte. The working electrode was a glassy carbon disc (diameter 3 mm). Potentials were measured against an Ag/Ag^+ reference electrode (10 mM $AgNO_3$ in CH_3CN) with ferrocenium/ferrocene ($Fc^{+/0}$) as internal standard. High-resolution mass spectral analyses (HRMS) were performed using a high-resolution ESI-FTICR mass spectrometer (Varian 7.0 T) and an FTMS+pNSI mass spectrometer (OrbitrapXL).

Compound (1*E*,1′*E*)-3b: CuCl (29 mg, 0.3 mmol, 3 equiv) and [Pd-$(PPh_3)_2Cl_2$] (15 mg, 0.02 mmol, 20 mol%) were added successively to a degassed solution of **2b** (49 mg, 0.1 mmol) in THF/DMF (1:5 v/v) at room temperature under Ar. The resultant solution was allowed to react at 35 °C for 1 h and quenched by the addition of aqueous NH_4Cl. The reaction mixture was extracted with hexane (3×50 mL), the combined organic phases was dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica, 2% EtOAc in hexane) to afford **6** as a yellow solid (72 mg, 87%). M.p. 171–173 °C (decomp); $R_f = 0.1$ (hexane); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.28$ (s, 18H), 1.48 (s, 36H), 7.35–7.37 (m, 6H), 7.38 (s, 4H), 7.51–7.53 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 31.4$, 33.2, 35.0, 37.9, 85.9 (d, $J = 14.0$ Hz), 87.9, 88.7 (d, $J = 27.6$ Hz), 96.7 (d, $J = 16.1$ Hz), 122.4, 123.2, 128.3, 128.5, 131.6, 133.8 (d, $J = 57.4$ Hz), 140.9 (d, $J = 37.4$ Hz), 151.3, 153.5 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 351.1$ ppm; UV/Vis: λ (ε, $10^3\,M^{-1}cm^{-1}$): 273 (25), 372 (20), 446 nm (13); HRMS (ESI): *m*/*z*: calcd for $C_{58}H_{68}P_2$ $[M+Na]^+$: 849.4688; found: 849.4699.

Synthesis of 5: CuCl (29 mg, 0.3 mmol, 3 equiv) was added to a degassed solution of **2b** (54 mg, 0.1 mmol) in THF/DMF (1:5 v/v). The reaction mixture was heated to 40 °C for 1–2 h. I_2 (39 mg, 0.3 mmol, 3 equiv) was added to the reaction mixture. CuCl (2 mg, 0.02 mmol, 20%) and [Pd-$(PPh_3)_2Cl_2$] (15 mg, 0.02 mmol, 20 mol%) were added to another degassed solution of phenylacetylene (31 mg, 0.3 mmol, 3 equiv) in DIEA (0.5 mL)/THF (5 mL) in a second flask. The solution from step 1 was then added dropwise into the second. The reaction was allowed to stir at room temperature for 2–4 h and quenched by the addition of aqueous NH_4Cl. The reaction mixture was extracted with hexane (3×50 mL), and then the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica, hexane) to afford **5a** (19%, 10 mg) and **5b** (52%, 27 mg) as light yellow foam.

Compound 5a (*Z* isomer): $R_f = 0.3$ (hexane); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.32$ (s, 9H), 1.52 (s, 18H), 6.86 (d, $J = 8$ Hz, 2H), 7.13–7.21 (m, 3H), 7.32–7.36 (m, 3H), 7.48 (s, 2H), 7.52 ppm (d, $J = 7.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 29.7$, 31.3, 33.2 (d, $J(P,C) = 6.0$ Hz), 38.2, 74.4 (d, $J(P,C) = 12.7$ Hz), 80.4 (d, $J(P,C) = 17.0$ Hz), 81.7 (d, $J(P,C) = 24.4$ Hz), 86.1 (d, $J(P,C) = 6.4$ Hz), 88.2 (d, $J(P,C) = 17.4$ Hz), 103.5 (d, $J(P,C) = 7.6$ Hz), 122.4, 122.5, 128.0, 128.3, 128.5, 129.3, 131.3, 132.4, 134.5 (d, $^1J(P,C) = 56.6$ Hz), 139.6 (d, $J(P,C) = 37.9$ Hz), 150.9, 154.3 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 349.1$ ppm; UV/Vis: λ (ε, $10^3\,M^{-1}cm^{-1}$) = 262 (29), 283 (21), 308 (shoulder, 16), 379 nm (18); EIMS (70 eV): *m*/*z* (%): 514 (42) $[M]^+$, 515 (14) $[M+H]^+$, 458 (34) $[M+H-t\mathrm{Bu}]^+$, 275 (100) $[\mathrm{Mes^*P}-2H]^+$; HRMS (FTMS+pNSI): *m*/*z*: calcd for $C_{37}H_{39}PAg$: 623.18369; found: 623.18230 (in $CHCl_3$/MeOH with CF_3COOAg).

Compound 5b (*E* isomer): $R_f = 0.28$ (hexane); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.36$ (s, 9H), 1.53 (s, 18H), 7.30–7.35 (m, 8H), 7.49 (s, 2H), 7.52 ppm (d, $J = 7.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 29.7$, 31.4, 33.4 (d, $J(P,C) = 6.2$ Hz), 38.1, 74.4 (d, $J(P,C) = 13.4$ Hz), 79.4 (d, $J(P,C) = 21.4$ Hz), 81.2 (d, $J(P,C) = 14.2$ Hz), 87.6 (d, $J(P,C) = 6.0$ Hz), 89.1 (d, $J(P,C) = 16.6$ Hz), 96.6 (d, $J(P,C) = 16.6$ Hz), 122.2, 122.5, 128.1, 128.4, 129.2, 131.5, 131.7, 132.6, 134.1 (d, $^1J(P,C) = 56.1$ Hz), 140.1 (d, $J(P,C) = 37.0$ Hz), 151.4, 154.2 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 349.6$ ppm; UV/Vis: λ (ε, $10^3\,M^{-1}cm^{-1}$) = 274 (30), 292 (22), 308 (shoulder, 18), 383 nm (19); EIMS (70 eV): *m*/*z* (%): 514 (54) $[M]^+$, 515 (18) $[M+H]^+$,

458 (40) $[M+H-tBu]^+$, 275 (100) $[Mes*P-2H]^+$; HRMS (FTMS+pNSI): *m/z*: calcd for $C_{37}H_{39}PAg$: 621.18403, 623.18369; found: 621.18348, 623.18371 (in $CHCl_3$/MeOH with CF_3COOAg).

Compound (1*E*,1′*E*)-6: CuCl (79 mg, 0.8 mmol, 4 equiv) and $[Pd(PPh_3)_2Cl_2]$ (30 mg, 0.04 mmol, 20 mol%) were added to a degassed solution of **1** (97 mg, 0.2 mmol) in THF/DMF (1:5 v/v) successively at room temperature. The reaction was monitored by TLC (1% EtOAc in hexane, 1 h) and quenched by the addition of aqueous NH_4Cl. The reaction mixture was extracted with hexane (3×50 mL). Then the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica, 1% EtOAc in hexane) to afford **6** as a yellow foam. Yield: 95%; m.p. 166–168°C (decomp); R_f=0.18 (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=−0.11 (s, 18H), 1.33 (s, 18H), 1.48 (s, 36H), 7.46 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=0.5, 31.4, 33.0, 35.0, 38.2, 81.4, 86.7 (m), 101.6 (m), 108.6, 122.6, 134.6 (m), 139.6 (m), 150.7, 153.6 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): δ=355.9 ppm; UV/Vis: λ (ε, 10^3 M^{-1}cm^{-1})=345 (13), 405 (14), 441 nm (16); HRMS (ESI): *m/z*: calcd for $C_{52}H_{76}P_2Si_2$ $[M+Na]^+$: 841.4853; found: 841.4852.

Compound (1*E*,1′*E*)-7: CuCl (79 mg, 0.8 mmol) and $[Pd(PPh_3)_2Cl_2]$ (30 mg, 0.04 mmol, 20 mol%) were added to a degassed solution of **1** (170 mg, 0.4 mmol) and **2a** (54 mg, 0.1 mmol) in THF/DMF (1:5 v/v) successively at room temperature. The reaction was monitored by TLC (1% EtOAc in hexane, 20–30 min) and quenched by the addition of aqueous NH_4Cl. The reaction mixture was extracted with hexane (3×50 mL). Then the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica, 1% EtOAc in hexane) to afford **7** as a yellow solid (62 mg, 76%, based on **2a**). M.p. 106–109°C (decomp); R_f=0.1 (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.12 (s, 9H), 1.32 (s, 9H), 1.33 (s, 9H), 1.48 (s, 18H), 1.50 (s, 18H), 6.85 (d, *J*=8.0 Hz, 2H), 7.13–7.21 (m, 3H), 7.47 (s, 2H), 7.48 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=0.36, 31.3, 31.4, 33.0 (d, ^4J(P,C)=5.4 Hz), 33.2 (d, ^4J(P,C)=5.5 Hz), 35.06, 35.08, 38.19, 38.20, 81.2–81.4 (m, 2C), 86.7–86.6 (m, 2C), 88.1 (d, *J*(P,C)=13.7 Hz), 101.6 (d, *J*(P,C)=20.6 Hz), 103.5 (d, *J*(P,C)=13.5 Hz), 108.8 (d, *J*(P,C)=10.7 Hz), 119.5, 122.4 (2C), 127.9, 128.3, 131.4, 134.1 (d, ^1J(P,C)=64.6 Hz), 134.6 (d, ^1J(P,C)=54.8 Hz), 139.5 (d, ^1J(P,C)=34.0 Hz), 139.8 (d, ^1J(P,C)=35.6 Hz) 150.8, 150.9, 153.7 (2C), 154.3 ppm (2C); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=348.5 (d, *J*(P,P)=25.8 Hz), 356.3 ppm (d, *J*(P,P)=25.8 Hz); UV/Vis: λ (ε, 10^3 M^{-1}cm^{-1}): 300 (13), 367 (18), 404 (17), 443 ppm (18); HRMS (FTMS+pNSI): *m/z*: calcd for $C_{55}H_{72}P_2SiAg$: 929.39294; found: 929.39240; *m/z*: calcd for $C_{55}H_{72}P_2SiAg_2CF_3COO$: 1151.28274; found: 1151.28219 (in $CHCl_3$/MeOH with CF_3COOAg); elemental analysis calcd (%) for $C_{55}H_{72}P_2Si{\cdot}2\,CH_3OH{\cdot}2\,H_2O$: C 74.15, H 9.17; found: C 73.84, H 9.54.

Compound (*Z*)-8: CuCl (150 mg, 1.6 mmol, 8 equiv) was added to a degassed solution of **1** (98 mg, 0.2 mmol) in THF/DMF (1:5 v/v). The reaction was allowed to stir at room temperature for 3 min, then a degassed solution of iodophenylacetylene (364 mg, 1.6 mmol, 8 equiv) in pyridine was added dropwise. The resulting solution was stirred for 3–5 h and quenched with aqueous NH_4Cl. The reaction mixture was extracted with hexane (3×50 mL), then the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica, hexane) to afford **8** (52%, 53 mg) as a yellow foam. R_f=0.35 (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=−0.1 (s, 9H), 1.33 (s, 9H), 1.49 (s, 18H), 7.33–7.36 (m, 3H), 7.48 (s, 2H), 7.49 (d, *J*=1.8 Hz, 1H), 7.51 ppm (d, *J*=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=−0.36, 31.5, 33.1 (d, ^4J(P,C)=6.1 Hz), 35.1, 38.3, 74.5 (d, *J*(P,C)=13.8 Hz), 80.7 (d, *J*(P,C)=17.6 Hz), 81.8 (d, *J*(P,C)=25.2 Hz), 86.2 (d, *J*-(P,C)=6.9 Hz), 101.8 (d, *J*(P,C)=17.6 Hz), 108.8 (d, *J*(P,C)=6.1 Hz), 122.1, 122.6, 128.5, 129.3, 132.5, 134.1 (d, ^1J(P,C)=58.1 Hz), 139.4 (d, *J*-(P,C)=36.7 Hz), 150.8, 153.7 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): δ=356.7 ppm; UV/Vis: λ (ε, 10^3 M^{-1}cm^{-1})=293 (12), 373 nm (13); MS (EI; 70 eV): *m/z* (%): 510 (100) $[M]^+$, 511 (32) $[M+H]^+$, 454 (84) $[M+H-tBu]^+$, 275 (62) $[Mes*P-2H]^+$; HRMS (FTMS+pNSI): *m/z*: calcd for $C_{34}H_{43}PSiAg$: 619.19192; found: 619.19014 (sample in $CHCl_3$/MeOH with CF_3COOAg).

Compound 9: CuCl (60 mg, 0.6 mmol, 3 equiv) was added to a degassed solution of **8** (104 mg, 0.2 mmol) in THF/DMF (1:5 v/v). The reaction was allowed to stir at 35°C for 30 min, after which a degassed solution of iodophenylacetylene (228 mg, 1 mmol, 5 equiv) in pyridine was added dropwise. The resulting solution was stirred at room temperature overnight and quenched with aqueous NH_4Cl. The reaction mixture was extracted with hexane (3×50 mL), then the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica, 4% CH_2Cl_2 in hexane) to afford **9** (27%, 29 mg) as a yellow foam. R_f=0.1 (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.35 (s, 9H), 1.50 (s, 18H), 7.30–7.35 (m, 8H), 7.48 (s, 2H), 7.49 (d, *J*=2.2 Hz, 2H), 7.50 ppm (d, *J*=1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=29.8, 31.4, 33.3 (d, ^1J=5.4 Hz), 38.1, 74.1 (d, *J*=9.2 Hz), 74.2 (d, *J*=15.3 Hz), 78.4 (d, *J*=19.9 Hz), 80.7 (d, *J*=23.7 Hz), 80.9 (d, *J*=19.4 Hz), 86.4 (d, *J*=7.7 Hz), 86.9 (d, *J*=9.9 Hz), 87.9 (d, *J*=4.8 Hz), 121.9, 122.0, 122.6, 128.4, 128.5, 129.2, 129.4, 132.2, 132.5, 133.5 (d, ^1J=54.3 Hz), 138.7 (d, *J*=37.5 Hz), 151.6, 153.9 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): δ=366.3 ppm; MS (EI; 70 eV): *m/z* (%): 538 (100) $[M]^+$, 539 (40) $[M+H]^+$, 482 (54) $[M+H-tBu]^+$, 275 (90) $[Mes*P-2H]^+$, 262 (90) $[Mes*P-CH_3]^+$; UV/Vis: λ (ε, 10^3 M^{-1}cm^{-1}): 274 (35), 295 (23), 316 (19), 336 (18), 396 nm (broad, 20); HRMS (FTMS+pNSI): *m/z*: calcd for $C_{39}H_{39}PSiAg$: 645.18403, 647.18369; found: 645.18339, 647.18321 (in $CHCl_3$/MeOH with CF_3COOAg).

Compound (1*Z*,1′*Z*)-10: CuCl (30 mg, 0.3 mmol, 3 equiv) and $[Pd(PPh_3)_2Cl_2]$ (15 mg, 0.02 mmol, 20 mol%) were added to a degassed solution of **8** (51 mg, 0.1 mmol) in THF/DMF (1:5 v/v) successively. The resulting solution was allowed to react at 35°C for 4 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, 1% EtOAc, 5% CH_2Cl_2 in hexane) to afford **10** (68%, 29 mg) as a yellow powder. R_f=0.3 (1% EtOAc in hexane); m.p. 171–175°C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.33 (s, 18H), 1.43 (s, 36H), 7.36–7.38 (m, 6H), 7.38 (s, 4H), 7.52 (d, *J*=1.6 Hz, 2H), 7.54 ppm (d, *J*=1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=31.4, 33.2, 35.1, 37.9, 75.4, 80.4–80.6 (m), 81.4–81.5 (m), 85.2–85.4 (m), 86.3, 87.8, 122.0, 122.7, 129.4, 132.5, 133.1 (d, ^1J(P,C)=60.0 Hz), 138.9 (d, *J*(P,C)=29.1 Hz), 151.9, 153.6 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): δ=368.2 ppm; UV/Vis: λ (ε, 10^3 M^{-1}cm^{-1})=294 (43), 320 (37), 347 (37), 371 (37), 416 (30), 456 nm (23); elemental analysis calcd (%) for $2\,C_{62}H_{68}P_2{\cdot}CH_3CN$: C 84.22, H 7.87; found: C 84.43, H 7.92.

X-ray crystallography CCDC-823771 (**1**), 823772 (**10**), 823773 (**3b**) and 823774 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] M. M. Haley, R. R. Tykwinski, *Carbon-Rich Compounds: From Molecules to Materials*, Wiley-VCH, Weinheim, **2006**.

[2] *Acetylene Chemistry: Chemistry, Biology and Material Science* (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**.

[3] J. M. Tour, *Chem. Rev.* **1996**, *96*, 537–553.

[4] P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863–1933.

[5] U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605–1644.

[6] H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.* **2003**, *115*, 518–546; *Angew. Chem. Int. Ed.* **2003**, *42*, 502–528.
[7] M. B. Nielsen, F. Diederich, *Chem. Rev.* **2005**, *105*, 1837–1868.
[8] M. Gholami, R. R. Tykwinski, *Chem. Rev.* **2006**, *106*, 4997–5027.
[9] V. W.-W. Yam, K. M.-C. Wong, *Top. Curr. Chem.* **2005**, *257*, 1–32.
[10] M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248.
[11] A. J. Zucchero, P. L. McGrier, U. H. F. Bunz, *Acc. Chem. Res.* **2010**, *43*, 397–408.
[12] D. K. James, J. M. Tour, *Top. Curr. Chem.* **2005**, *257*, 33–62.
[13] M. J. Frampton, H. L. Anderson, *Angew. Chem.* **2007**, *119*, 1046–1083; *Angew. Chem. Int. Ed.* **2007**, *46*, 1028–1064.
[14] E. L. Spitler, C. A. Johnson, M. M. Haley, *Chem. Rev.* **2006**, *106*, 5344–5386.
[15] W. A. Chalifoux, R. R. Tykwinski, *Nat. Chem.* **2010**, *2*, 967–971.
[16] A. D. Payne, G. Bojase, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem.* **2009**, *121*, 4930–4933; *Angew. Chem. Int. Ed.* **2009**, *48*, 4836–4839.
[17] J. J. Pak, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 8182–8192.
[18] T. Takeda, A. G. Fix, M. M. Haley, *Org. Lett.* **2010**, *12*, 3824–3827.
[19] M. B. Nielsen, F. Diederich, *Chem. Rec.* **2002**, *2*, 189–198.
[20] F. Diederich, *Chem. Commun.* **2001**, 219–227.
[21] T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681–4727.
[22] M. Hissler, P. W. Dyer, R. Réau, *Top. Curr. Chem.* **2005**, *250*, 127–163.
[23] M. Williams-Harry, A. Bhaskar, G. Ramakrishna, T. Goodson, M. Imamura, A. Mawatari, K. Nakao, H. Enozawa, T. Nishinaga, M. Iyoda, *J. Am. Chem. Soc.* **2008**, *130*, 3252–3253.
[24] L. Weber, *Eur. J. Inorg. Chem.* **2000**, 2425–2441.
[25] H. Ottosson, A. Eklöf, *Coord. Chem. Rev.* **2008**, *252*, 1287–1314.
[26] D. Scheschkewitz, *Chem. Lett.* **2011**, *40*, 2–11.
[27] I. Bejan, D. Scheschkewitz, *Angew. Chem.* **2007**, *119*, 5885–5888; *Angew. Chem. Int. Ed.* **2007**, *46*, 5783–5786.
[28] T. Iwamoto, M. Kobayashi, K. Uchiyama, S. Sasaki, S. Nagendran, H. Isobe, M. Kira, *J. Am. Chem. Soc.* **2009**, *131*, 3156–3157.
[29] J. Jeck, I. Bejan, A. J. P. White, D. Nied, F. Breher, D. Scheschkewitz, *J. Am. Chem. Soc.* **2010**, *132*, 17306–17315.
[30] V. A. Wright, D. P. Gates, *Angew. Chem.* **2002**, *114*, 2495–2498; *Angew. Chem. Int. Ed.* **2002**, *41*, 2389–2392.
[31] V. A. Wright, B. O. Patrick, C. Schneider, D. P. Gates, *J. Am. Chem. Soc.* **2006**, *128*, 8836–8844.
[32] R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2004**, *126*, 2268–2269.
[33] R. C. Smith, J. D. Protasiewicz, *Eur. J. Inorg. Chem.* **2004**, 998–1006.
[34] B. Schäfer, E. Öberg, M. Kritikos, S. Ott, *Angew. Chem.* **2008**, *120*, 8352–8355; *Angew. Chem. Int. Ed.* **2008**, *47*, 8228–8231.
[35] E. Öberg, B. Schäfer, X.-L. Geng, J. Pettersson, Q. Hu, M. Kritikos, T. Rasmussen, S. Ott, *J. Org. Chem.* **2009**, *74*, 9265–9273.
[36] X.-L. Geng, Q. Hu, B. Schäfer, S. Ott, *Org. Lett.* **2010**, *12*, 692–695.
[37] T. Sato, Y. Mizuhata, N. Tokitoh, *Chem. Commun.* **2010**, *46*, 4402–4404.
[38] M. B. Nielsen, M. Schreiber, Y. G. Baek, P. Seiler, S. Lecomte, C. Boudon, R. R. Tykwinski, J.-P. Gisselbrecht, V. Gramlich, P. J. Skinner, C. Bosshard, P. Günter, M. Gross, F. Diederich, *Chem. Eur. J.* **2001**, *7*, 3263–3280.
[39] M. Gholami, M. N. Chaur, M. Wilde, M. J. Ferguson, R. McDonald, L. Echegoyen, R. R. Tykwinski, *Chem. Commun.* **2009**, 3038–3040.
[40] Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1999**, *121*, 458–459.
[41] X. L. Geng, S. Ott, *Chem. Commun.* **2009**, *45*, 7206–7208.
[42] G. Eglinton, A. R. Galbraith, *J. Chem. Soc.* **1959**, 889–896.
[43] Y. Nishihara, K. Ikegashira, K. Hirabayashi, J. Ando, A. Mori, T. Hiyama, *J. Org. Chem.* **2000**, *65*, 1780–1787.
[44] Y. Nishihara, M. Takemura, A. Mori, K. Osakada, *J. Organomet. Chem.* **2001**, *620*, 282–286.
[45] A. S. Batsanov, J. C. Collings, I. J. S. Fairlamb, J. P. Holland, J. A. K. Howard, Z. Lin, T. B. Marder, A. C. Parsons, R. M. Ward, J. Zhu, *J. Org. Chem.* **2005**, *70*, 703–706.
[46] W. Chodkiewicz, *Ann. Chim. Paris* **1957**, *2*, 819–869.
[47] J. Wityak, J. B. Chan, *Synth. Commun.* **1991**, *21*, 977–979.
[48] G. Märkl, T. Zollitsch, P. Kreitmeier, M. Prinzhorn, S. Reithinger, E. Eibler, *Chem. Eur. J.* **2000**, *6*, 3806–3820.
[49] S. Ito, H. Sugiyama, M. Yoshifuji, *Angew. Chem.* **2000**, *112*, 2892–2894; *Angew. Chem. Int. Ed.* **2000**, *39*, 2781–2783.
[50] L. T. Scott, M. J. Cooney, D. Johnels, *J. Am. Chem. Soc.* **1990**, *112*, 4054–4055.
[51] Y. Zhao, S. C. Ciulei, R. R. Tykwinski, *Tetrahedron Lett.* **2001**, *42*, 7721–7723.
[52] S. Eisler, R. R. Tykwinski, *Angew. Chem.* **1999**, *111*, 2138–2141; *Angew. Chem. Int. Ed.* **1999**, *38*, 1940–1943.
[53] M. B. Nielsen, N. N. P. Moonen, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2001**, 1848–1849.

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