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C,*C*-Diacetylenic Phosphaalkenes as Heavy Diethynylethene Analogues

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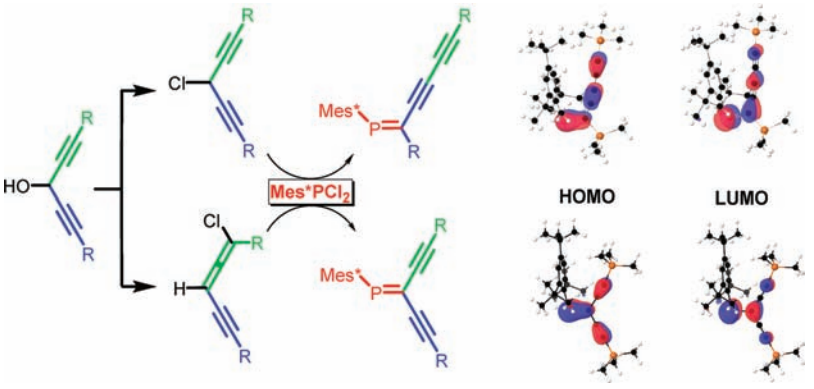

A series of *C*,*C*-diacetylenic phosphaalkenes **1b**−**e** has been prepared from 1-chloropenta-1,2-dien-4-ynes **6b**−**e** in a reaction with Mes*PCl_2 (Mes* = 2,4,6-(^{t}Bu)$_3$Ph) in the presence of LDA. Under identical conditions, isomeric butadiyne-substituted phosphaalkenes **2c**−**f** can be obtained from 3-chloropenta-1,4-diynes **5c**−**f**. The title compounds represent rare examples of diethynylethenes in which a constituting methylene has been replaced by a phosphorus center. The formation of both isomers can be rationalized by a common pathway that involves isomeric allenyllithium species. Spectroscopic, electrochemical, and theoretical investigations show that the phosphorus heteroatoms are an intrinsic part of the compounds' π−systems and lead to decreased HOMO−LUMO gaps compared to those in all-carbon-based reference compounds.

Introduction

The art to prepare monodisperse oligoacetylenes of high complexity has reached a considerable level of sophistication over the last decades.[1−3] The combination of highly unsaturated acetylenes and aromatic units has produced a multitude of carbon-rich, π-conjugated compounds with potential applications in organic electronic devices such as organic light-emitting diodes and field effect transistors[4−6] or as potential unimolecular electronics components such as molecular diodes[7] and wires.[8,9] The inclusion of heteroaromatics such as pyridines, thiophenes, or furans into these π-conjugates alters their electronic properties and, in addition, offers coordination sites for Lewis acids.[10] In contrast to the plethora of acetylenic (hetero)aromatic compounds, oligoacetylenes in which sp- or sp^2-hybridized carbon centers of the one-dimensional backbone are replaced by heavier

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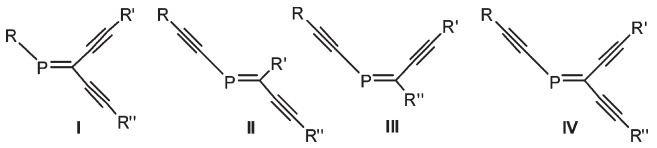
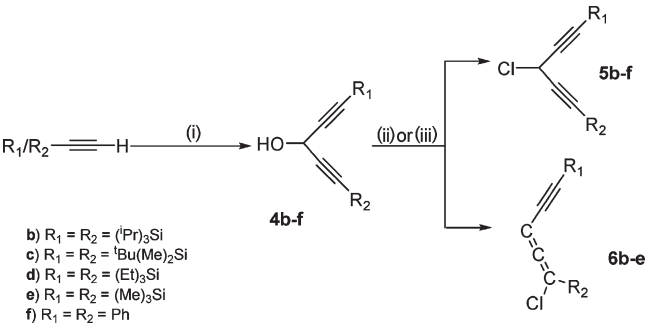


FIGURE 1. Conceivable diacetylenic (**I**−**III**) and peracetylenic (**IV**) phosphaalkenes.

main group elements are essentially unknown. Considering the analogy between carbon and its diagonal neighbor in the periodic table, phosphorus,[11] it seems conceivable to incorporate phosphorus heteroatoms in the form of phosphaalkenes into fully π-conjugated oligoacetylenes.[12] The interest in acetylenic phosphaalkenes (APAs) as alternative organophosphorus π-conjugated materials[13,14] is further fuelled by recent findings that phosphole-containing π-systems exhibit relatively small HOMO−LUMO gaps. This effect arises from the pyrimidalization of the phosphorus centers which are thus only partly involved in the conjugation and can act as n-dopants.[15−21] The chemistry of phosphaalkenes has matured continuously over the last decades and is nowadays well established. In a material science context, it is noteworthy that phosphaalkenes can be employed in a living anionic polymerization to afford phosphorus-containing polymers where the phosphorus centers are saturated.[22,23] Unsaturated, π-conjugated polymers with intact phosphaalkenes were realized in poly(phenylenephosphaalkene)s.[24−26]

Phosphaalkenes can be combined with acetylenes in a number of ways. Three different diacetylenic phosphaalkenes (A_2PA) **I**−**III** and peracetylenic phosphaalkenes (A_3PA) **IV** are challenging synthetic targets (Figure 1). Furthermore, they represent attractive building blocks which should allow for the preparation of more elaborate oligomeric and cyclic architectures once they can be accessed. Apart from our own exploratory study toward **I**,[12] **I**−**IV** are unknown which is presumably a result of the general instability of phosphaalkenes. Stabilization of **I**−**IV** can be expected from the incorporation of P=C into a conjugated framework as is the case in phosphinine,[27] from a complexation of P=C to metal fragments[28] or from a kinetic stabilization by large substituents at the *P*-terminus.[29] In this report, we utilized the latter stabilization to target *C*,*C*-A_2PA **I** and to study its electronic properties by spectroscopic, electrochemical and computational techniques. Particular focus is put on comparisons with known all-carbon-based literature compounds.

SCHEME 1. Synthesis of Alcohols 4b−f, Chloropentadiynes 5b−f, and Allenes 6b−e[a]



[a]Key: (i) (1) BuLi, −30 °C; (2) ethyl formate, −78 to −30 °C, 2 h, **4b** (54%), **4c** (66%), **4d** (76%), **4e** (73%), **4f** (75%); (ii) $SOCl_2$, Et_2O or CH_2Cl_2, rt, 12 h or reflux 2 h, **5b** (82%), **5c** (84%), **5d** (66%), **5e** (71%); (iii) $SOCl_2$, Et_2O, 2 drops of DMF, 2 h, **5e** (31%), **6e** (53%).

Results and Discussion

Synthesis of Diacetylenic Phosphaalkenes. A_2PAs of type **I** can potentially be synthesized by a number of different synthetic approaches. In analogy to the preparation of ethynylethenes, metal-mediated cross-coupling reactions of *C*-bromo-functionalized phosphaalkenes with monosubstituted acetylenes could be considered. It has, however, been shown in the literature that such a strategy will fail due to a rearrangement that follows the insertion of the metal into the carbon−halogen bond that ultimately leads to the formation of phosphaalkynes.[30] We have therefore devised an alternative route that relies on the formation of the P=C bond in the last step of the synthetic sequence by reacting Mes^*PCl_2 with a 3-chloropenta-1,4-diyne **5** in the presence of LDA.[31] The latter was envisaged to become accessible from the corresponding propargylic alcohol **4**.

Alcohols **4b**−**f** were synthesized from the respective acetylenes and ethyl formate following a published procedure.[32] Treatment of **4b**−**f** with thionyl chloride in refluxing CH_2Cl_2 afforded 3-chloropenta-1,4-diynes **5b**−**f** in reasonable to good yields (Scheme 1).[33] The chloromethyl protons of **5b**−**e** feature as singlets between 5.22 and 5.28 ppm in their respective ^1H NMR spectra, whereas that of phenyl-substituted **5f** can be observed at 5.78 ppm. Two signals are visible in the acetylene region of the ^{13}C NMR spectra, confirming the symmetric structures of **5b**−**f**. During chlorination of **4b**−**e**, it was found that a side product is

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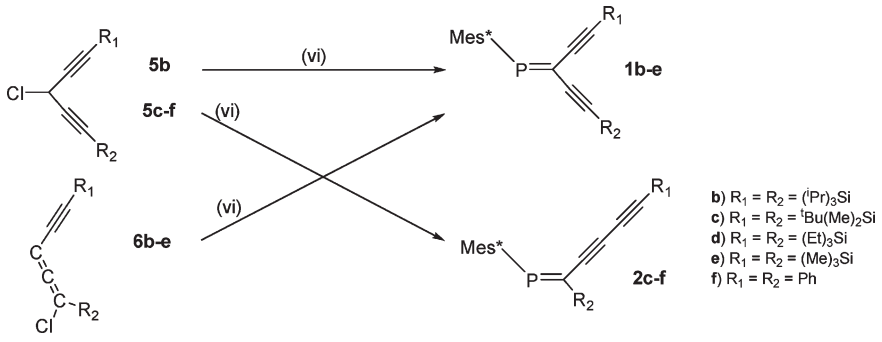
SCHEME 2. Synthesis of the Acetylenic Phosphaalkenes 1 and 2 from 5 and/or 6[a]



[a]Key: (vi) $Mes*PCl_2$, LDA, THF, 2 h, −100 to −20 °C, **1b** (40%) from **5b**, **1c** (11%) and **2c** (32%) from a mixture of **5c** and **6c** (ca. 5:1), **1d** (12%) and **2d** (32%) from a mixture of **5d** and **6d** (ca. 5:1), **1e** (59%) from neat **6e**, **2e** (57%) from neat **5e**, **2f** (48%) over two steps from **4f**.

formed in addition to **5b**−**e** with a maximum yield of 20% depending on reaction time and temperature. ^{1}H NMR spectra of the concomitantly formed products exhibit a singlet that is slightly downfield shifted by ca. $\Delta\delta = 0.2$ ppm compared to that of the chloromethyl proton of the corresponding **5**. ^{13}C NMR spectra show a diagnostic peak around $\delta = 210$ ppm in addition to four peaks in the customary acetylene region between 100 and 80 ppm. Based on this analysis and in analogy with analytical data of a previously reported bromoallene,[34] the side product was identified as chloroallene **6b**−**e**. Whereas TMS-terminated **5e** and **6e** could be separated by column chromatography, purification of **5b**−**d** and **6b**−**d** was unsuccessful. The proportion of allene **6e** could be increased dramatically until it was obtained as the major product by adding two drops of DMF to the reaction. No allene was observed during the chlorination of phenyl-terminated **4f**.

With purified **5e**,**f** in hand, their reaction with supermesityl phosphonous dichloride ($Mes*PCl_2$) in the presence of LDA was investigated.[31] Although these reactions yielded phosphaalkenes, we were surprised to find that an isomerization of the acetylene framework had occurred and that butadiyne-substituted phosphaalkenes **2e**,**f** had formed (Scheme 2). Disappointed by the failure of the initial strategy, we turned our focus to the reactivity of chloroallene side products **6**. Exposing chloroallene **6e** to equivalent reaction conditions ($Mes*PCl_2$, LDA), we were delighted to find that the desired A_2PA **1e** was formed selectively and in acceptable yields. When mixtures of **5c**,**d** and **6c**,**d** are used in the phosphaalkene preparation, product mixtures of **1c**,**d** and **2c**,**d** are obtained in ratios that reflect the relative proportions of the starting materials **5c**,**d** and **6c**,**d**. Conveniently, **1c**,**d** can be separated from **2c**,**d** by careful column chromatography. Noteworthy is that the reaction of **5c**−**f** produces exclusively **2c**−**f**, but none of the isomer where Mes* is *trans* to the butadiyne. The only exception to the observed trend in reactivity is **5b** and **6b** with the bulky TIPS substituents which both result in the formation of diacetylenic phosphaalkene **1b**. Isomers **1** and **2** can be distinguished by the chemical shift of the P=C carbon in their respective ^{13}C NMR spectra. Whereas this signal features as a doublet beyond $\delta = 160$ ppm in isomer **2**, it is shifted upfield to less than $\delta = 140$ ppm in **1**. In addition, the acetylene carbons in **1** resonate at higher chemical shift than those of **2**. Further proof for the structural assignment could be deduced from X-ray crystallography (vide infra).[12]

With the exception of **5** and **6b**, it emerges that chloroallenes **6** always give rise to A_2PAs **1** whereas butadiynes **2** are formed in the reaction of 3-chloropentadiynes **5**. The reactions are thus regioselective and proceed at the β-carbon relative to the chloride. The reactivity of **5c**−**f** with a concomitant 1,2 shift of the acetylene bears a resemblance to that of chromium(0) alkynylcarbenes.[35] Although it is possible to postulate a related C_5 carbene intermediate that is formed from **5** by α-elimination,[36−38] it is appealing to propose a common and more general mechanism to rationalize the formation of **1** and **2** from **6** and **5**, respectively. Furthermore, reactions of nonstabilized carbenes such as a C_5 carbene are known to exhibit poor regioselectivity.[36] The reaction of allene **6** to form A_2PA **1** suggests that allene intermediates may also be present in the reaction of **5**. Our mechanistic proposal thus starts with the abstraction of the relatively acidic protons in **5** and **6** by LDA (Scheme 3). It has previously been shown that propargyllithium species are in equilibrium with allenyllithium and that this equilibrium lies far toward the latter when silyl substituents are present.[39,40] In analogy to these reports, we postulate a tautomerization of **5-P** to the corresponding **5-A**. Support for this hypothesis was obtained from an experiment where **5e** was first exposed to LDA at −78 °C and then quenched by the addition of an aqueous solution of NH_4Cl. ^{13}C NMR analysis of the reaction products revealed a diagnostic signal at $\delta = 211$ ppm together with four signals between 110 and 90 ppm. These results are consistent with the formation of an acetylenic allene which, as expected, is different from **6e**. It is important to note that **5-A** is a regioisomer of deprotonated **6**

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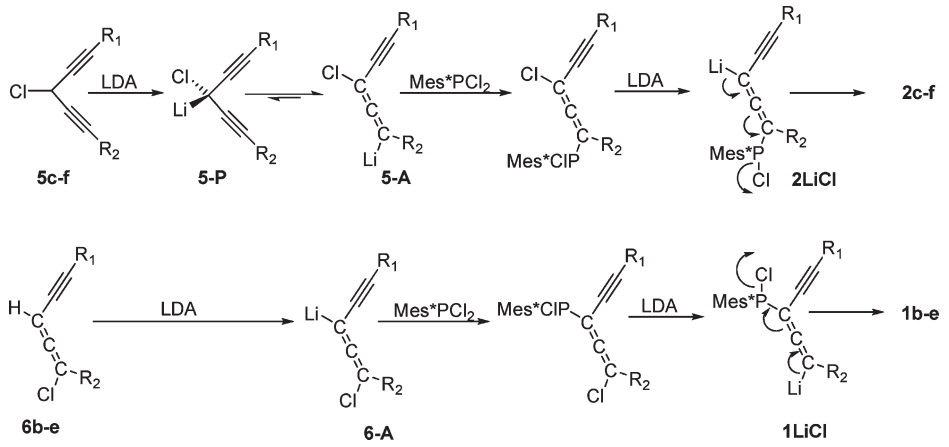
SCHEME 3. Proposed Mechanism[43] for the Preparation of Isomers 2 and 1 from 5 and 6, Respectively



(**6-A**). Compounds **5-A** and **6-A** attack Mes*PCl_2 in a nucleophilic substitution,[41] leading to isomeric 3-chloroallenyl-1-phosphines. Lithium−halogen exchange at the isomeric allene portions[42] establishes new allenyllithium **1LiCl** and 2LiCl which eliminate lithium chloride to afford isomers **1** and **2** (Scheme 3).[43] In the case of **2LiCl**, it is this last elimination step that determines the relative position of the substituents across the P=C double bond in **2c**−**f**. To minimize steric repulsion between Mes* and R_2, the isomer in which the butadiyne is *cis* to Mes* is formed in all instances.

After successful synthesis and purification of **1b**−**e** and **2c**−**f**, the electronic properties of these rather different π-system were studied in more detail. Particular focus was given to the effect of the phosphorus heteroatom. For comparison and a more complete evaluation, we have included the previously reported **2g**,**h** and octatetrayne **7** in this study (Figure 2).[12]

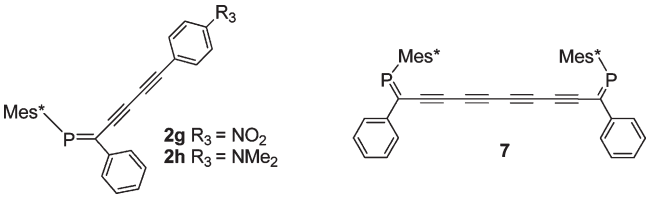


FIGURE 2. Nitrophenyl (**2g**) and *N*,*N*-dimethylaniline (**2h**) substituted 1-phosphahex-1-en-3,5-diyne and bis-phosphaalkene end-capped octatetrayne **7**.[12] Mes* = 2,4,6-(^{t}Bu)$_3$Ph.

As already deducible from the differences in ^{31}P NMR chemical shifts in Table 1, it emerges that the phosphorus heteroatoms in **1**, **2**, and **7** are an intrinsic part of the entire π-conjugated system in all compounds. It is interesting to note that the ^{31}P chemical shifts of the bis-silyl substituted *C*,*C*-A_2PAs **1c**−**e** are lower than those of the 1-phosphahex-1-ene-3,5-diynes **2c**−**e**. Exchanging the silyl substituent at the P=C in **2c**−**e** by a phenyl group in **2f**−**h** results in an upfield shift of the ^{31}P resonance, indicating participation of the phenyl group in the overall π-conjugation. The ^{31}P NMR chemical shifts are even sensitive to perturbation of the remote phenyl groups at the butadiyne terminus. The electron-withdrawing substituent at the phenyl group in **2g** causes a downfield shift compared to **2f**, whereas the electron-donating dimethylamino group in **2h** leads to a shielding of the phosphorus center.

X-ray Crystallography. The crystal structures of **2g** and **2h** are depicted in Figure 3 and 4. Most importantly, both structures feature the butadiyne moieties *cis* to the Mes* group, giving further support to the structural assignments of the synthetically obtained isomers.

The bond lengths in the PC_5 backbone are in the usual region for P=C double, C≡C triple, and C(sp^2)− C(sp) and C(sp)−C(sp) single bonds. The dihedral angle between the plane defined by the phenyl ring at the P=C carbon and the PC_5 scaffold is very small (6° in **2g** and −1° in **2h**), pointing toward a sizable contribution of the phenyl ring in the overall π-conjugation in the solid state.

Electronic Absorption Spectroscopy and Cyclic Voltammetry. Comparing the longest wavelength absorption maxima of silyl-terminated diacetylenic phosphaalkenes **1c**−**e** with those of **2c**−**e**, it emerges that the end absorptions of the latter are slightly shifted toward lower energies (Table 2). Since the absorption arises from similar $\pi\rightarrow\pi^*$ transitions (vide infra), this finding suggests a lower degree of π-delocalization in cross-conjugated isomer **1** compared to that in linear conjugated **2**. The introduction of a phenyl group at the phosphaalkene carbon in **2f**−**h** and **7** gives rise to larger shifts of the end absorptions which in addition are strongly dependent on the substituent at the peripheral butadiyne terminus. Significant alterations of the participating frontier molecular orbitals are necessary to account for the observed shifts of the longest wavelength absorption maxima that range from 379 nm (**2f**) over 407 (**2g**) and 441 (**2h**) to 484 nm in octatetrayne **7**.

An all-carbon analogue of **1e** with a corresponding 1,1′-diethynylethene skeleton, namely 3-methylene-1,5-bis(trimethylsilyl)penta-1,4-diyne,[44] has a reported end absorption of 247 nm which is at considerably higher energy than that of **1e**. A second carbon-based analogue (4-phenyl-2-phenylethynylbut-1-en-3-ynyl)benzene,

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(43) In principle, lithium−halogen exchange could also occur at the *P*-bound chloride. This species would, however, give rise to the same product after elimination.

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TABLE 1. ^{31}P NMR (ppm) Chemical Shifts of *C*,*C*-Diacetylenic Phosphaalkenes 1 and 1-Phosphahex-1-en-3,5-diynes 2

	substituents		diacetylenic phosphaalkenes (isomer **1**)	1-phosphahex-1-en-3,5-diyne (isomer **2**)
entry	R_1	R_2	^{31}P NMR	^{31}P NMR
b	TIPS	TIPS	331	
c	TBDMS	TBDMS	340	372
d	TES	TES	339	367
e	TMS	TMS	346	364
f	Ph	Ph		311
g	$PhNO_2$	Ph		319
h	$PhNMe_2$	Ph		304
7		Ph		331

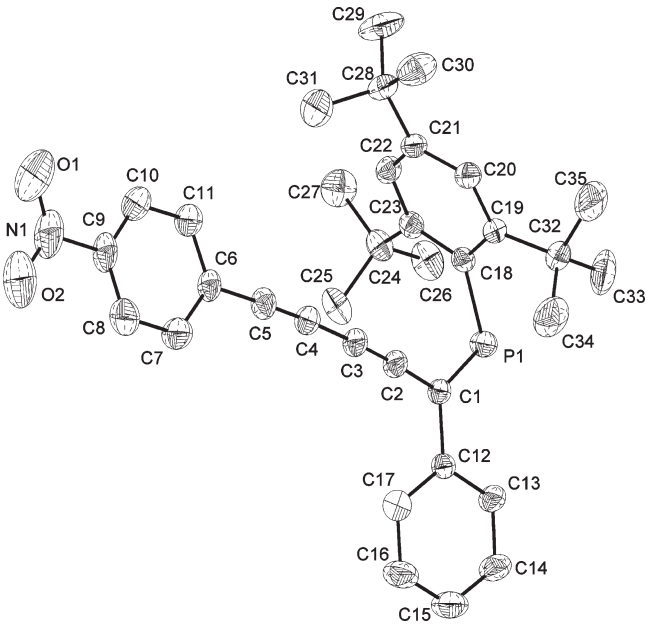

FIGURE 3. ORTEP drawing (at 30% probability level) of **2g**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.686(3), C1−C2 1.420(3), C2−C3 1.195(3), C3−C4 1.364(4), C4−C5 1.194(4). Angles: C1−P1−C18 101.0(1), P1−C1−C2 123.0(2), P1−C1−C12 121.0(2). Dihedral angle: C12−C1−P1-C18 −175.9(2).

λ_{max} = 340 nm)[45] with additional phenyl rings at both acetylene termini that increase the π-system features an end absorption that is still at higher energy compared to that of **1** and **2**. It thus seems that the inclusion of a phosphorus heteroatom in **1** and **2** causes a sizable decrease of their HOMO−LUMO gaps. This effect becomes even more apparent when comparing the longest wavelength absorption maximum of **7** with that of dodeca-1,11-diene-3,5,7,9-tetrayne[46] which is shifted by 80 nm toward higher energy. The reduction of the HOMO−LUMO gap in APAs thus appears to be a general effect that is caused by the λ^3−σ^2 phosphorus heteroatoms. Although different orbitals are involved, the effect of the λ^3−σ^2 phosphorus in phosphaalkenes on the HOMO−LUMO gaps of appended π-systems is thus similar to that of the λ^3−σ^3 phosphorus lone pair in phospholes.[15−21]

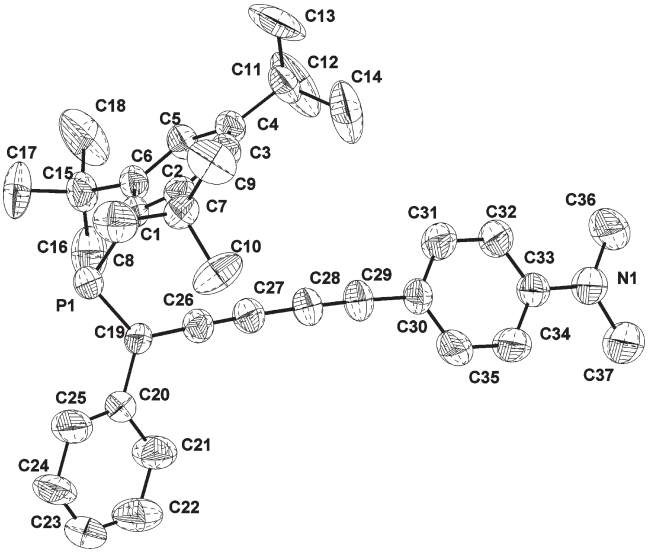

FIGURE 4. ORTEP drawing (at 30% probability level) of **2h**. For clarity, only one of the two crystallographic independent molecules is shown, and hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): P1−C19 1.695(5), C19−C26 1.409(7), C26−C27 1.203(7), C27−C28 1.377(8), C28−C29 1.207(7). Angles: C1−P1−C19 100.8(2), P1−C19−C26 123.9(4), P1−C19−C20 120.3(4). Dihedral angle: C1−P1−C19-C20 178.6(5).

TABLE 2. Absorption Band Maxima and Molar Extinction Coefficients from UV/vis Spectroscopic Measurements in CH_2Cl_2 at 25 °C. Electrochemical Data for 1 mM Solutions (0.1 M NBu_4PF_6), ν = 100 mV/s (All Potentials Are Given vs $Fc^{+/0}$)

compd	λ_{max}[nm] (ε [10^3 M^{-1} cm^{-1}])			$E_{p,c}$ (V)	$E_{p,a}$ (V)
1b	349 (18.5)			−2.07	1.15
1c	347 (17.0)			−2.12[b]	1.12
1d	343 (12.0)	355 (12.5)		−2.12[b]	1.14
1e	347 (11.5)			−2.07	1.16
2c	346 (13.5)	359 (13.0)		−2.21	1.18
2d	346 (12.5)	359 (12.5)		−2.19	1.19
2e	343 (13.0)	358 (13.0)		−2.17	1.18
2f	379 (17.0)			−1.98[c]	1.05
2g	332 (21.5)	407 (15.5)		−1.40[c], −1.84[c]	1.08
2h	328 (46.5)	441 (26.5)		−2.04[c]	0.47, 1.07
7	286 (52.0)	336 (22.0)		−1.62[c], −1.96[c]	1.06
	389 (22.5)	443 (15.0)	484 (10.0)		

[a]Shoulder. [b]Reversible at scan rates higher than 1 V/s. [c]Electrochemically reversible $E_{1/2}$ = ($E_{p,c}$ + $E_{p,a}$)/2.

The cyclic voltammograms (CVs) of **1b**−**e** and **2c**−**e** feature two electrochemically irreversible processes, an oxidation between 1.12 and 1.19 V (all potentials are vs $Fc^{+/0}$) and a reduction between −2.07 and −2.21 V (see Table 2). In analogy to the optical spectroscopy, the situation changes dramatically when phenyl substituents are introduced. First, the oxidations of **2f**−**h** and **7** are shifted to milder potentials by ca. 100 mV, pointing toward a participation of the P=C phenyl ring in the HOMO. The first oxidation that is observed at 0.47 V in the CV of **2h** can be assigned to an isolated process on the *N*,*N*-dimethylaniline.[47] Second, the reductions of **2f**−**h** and **7** become electrochemically

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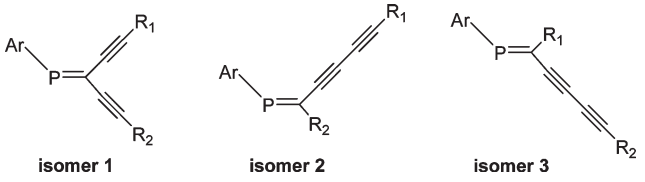

FIGURE 5. Three possible isomers with an unsaturated PC_5 framework: *C*,*C*-A_2PA (isomer **1**), *cis*-1-phosphahex-1-en-3,5-diyne (isomer **2**), and *trans*-1-phosphahex-1-en-3,5-diyne (isomer **3**).

quasi-reversible. The potentials that are associated with the reduction of the π-system are highly dependent on the substituent on the peripheral phenyl ring and become increasingly more negative with increasing donor strength of the phenyl terminus. Owing to the dimeric character of octatetrayne **7**, a second reduction can be observed that is separated from the first by ΔE = 340 mV, indicating a sizable communication between the two phosphaalkenes. The communication is very similar to that observed in related bis(diphosphene) systems where the coupling is mediated through a ferrocene or *p*-phenylene spacer.[48,49] The first reduction of **2g** at −1.40 V is assigned to an isolated process on the nitrophenyl group.[50]

DFT Calculations. In addition to **1** and **2** which were synthesized in this study, the unsaturated PC_5 unit can potentially be arranged in a third isomeric form **3** in which the butadiyne is *trans* to the *P*-substituent (Figure 5). DFT calculations at the B3LYP/6-311++G**//B3LYP/6-31G* level of theory were performed on all three isomers to identify the lowest energy isomer and to gain insight into factors that may explain the synthetic preference for their formation. Conformers of each isomer used in the DFT study were obtained from a conformational search with the OPLS2005 force field.

A comparative study for isomers **1**−**3** using the two functionals BLYP and BH&HLYP was performed in order to validate our method of choice. These calculations showed that the relative energies of the constitutional isomers varied somewhat, but the order was maintained over the different functionals (see the Supporting Information). Furthermore, the results obtained with the two hybrid functionals (B3LYP and BH&HLYP) were very similar. Table 3 summarizes the calculated energies of the lowest energy conformation that was found of each isomer. In every entry, the energies of the isomers are relative to the energy of the lowest energy isomer.

In the absence of any bulky substituents at the acetylene termini and a phenyl as *P*-substituent (entry **a**), steric factors are kept to a minimum and the results of the calculations can be interpreted from a conjugation perspective. Butadiyne-substituted phosphaalkenes **2a** and **3a** are lowest in energy of the **a**-series with the latter being lower by 6 kJ/mol. This difference is easily explained by looking at the dihedral angle between the benzene ring and the plane defined by the remaining molecule in **2a** and **3a** which is 50.4° and 31.7°, respectively. The phenyl ring in **3a** is able to participate in

TABLE 3. Relative Energies (kJ/mol) of the Three Isomers 1−3 of a−g, As Calculated at the B3LYP/6-311++G//B3LYP/6-31G* Level of Theory**[a]

entry		Ar	isomer **1**	isomer **2**	isomer **3**
a	$R_1 = R_2$ = H	Ph	47.4	6.0	0
b	$R_1 = R_2$ = TIPS	Mes*[b]	0	6.8	74.1
c	$R_1 = R_2$ = TBDMS	Mes*[b]	6.0	0	28.9
d	$R_1 = R_2$ = TES	Mes*[b]	1.3	0	23.8
e	$R_1 = R_2$ = TMS	Mes*[b]	4.5	0	25.3
f	$R_1 = R_2$ = Ph	Mes*[b]	13.6	0	22.1

[a]The isomer of lowest energy was set to 0 kJ/mol, and the energies of the other two are relative to this value. [b]Mes* = (^{t}Bu)$_3$Ph.

π-delocalization to a greater extent and is thus responsible for the lower energy of **3a**. The corresponding dihedral angle in **1a** is 45.4°, and the participation of its phenyl ring in the overall π-conjugation is thus comparable to that in **2a**. The calculations, however, show that isomer **1a** is greatly disfavored by 41.4 kJ/mol compared to **2a**. This energy differences thus have to be attributed to the isomeric PC_5 units, which are arranged in a cross-conjugated fashion in **1a** compared to the linear geometry in **2a** and **3a**. The PC_5 system thus follows a similar trend as all-carbon based π-conjugates in that structures with linear conjugation are usually lower in energy than isomeric cross-conjugated systems.[51,52]

In the presence of the synthetically important Mes* group and substituents R_1 and R_2 in isomers **1b**−**3f**, the dihedral angle between Mes* and the PC_5 framework is close to 90° and communication between the two units becomes negligible. Most importantly, however, the energetic order of the compounds changes drastically. In all cases **b**−**f**, isomer **3** becomes the most energy-rich one due to steric clashes between Mes* and R_1 that are directly attached to the P=C double bond in a *cis* relationship. The high energy of **3b**−**f** correlates well with the observation that isomer **3** is never found synthetically. It thus seems that the steric arguments that make **3b**−**f** highest in energy also raise the energies of the transition states that would lead to their formation.

A further interesting correlation between the calculated energies and the reactivity of the chlorides can be observed when comparing entry **b** with **c**−**f**. In the latter cases, isomer **2** is always lowest in energy whereas isomer **1** has the lowest energy of the **b** series. Since all silyl groups can be expected to be electronically very similar, the difference in energetic preference has to be caused by steric factors. From a synthetic viewpoint, it thus seems that the vast steric bulk of the TIPS groups that destabilizes **2b** also prevents the allenyllithium species of **5b** to react in the customary fashion and a reaction of the propargyllithium occurs instead.

The calculations strongly indicate that the stability of isomer **2** is a result of a favorable π-delocalization term. A similar stabilization is operating in isomer **3** but is obscured by strongly disfavoring steric clashes between Mes* and R_1 which are in a *cis* relationship across the P=C double bond. The acetylene spacer in isomer **1** and the butadiyne in **2** increase the spatial separation between the two units and thus lead to a reduction of the strain. Although one would anticipate that the longer butadiyne in **2** would lead to less

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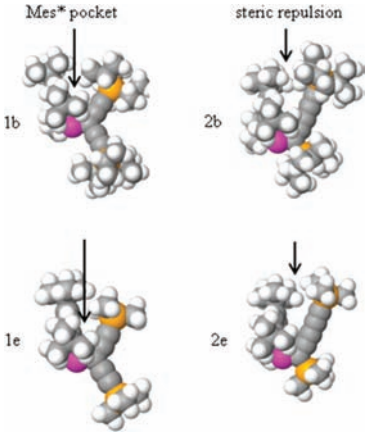

FIGURE 6. Graphic representation of **1b**,**e** and **2b**,**e** at the B3LYP/6-311++G**//B3LYP/6-31G* level of theory. Highlighted is the void in the center of the *P*-Mes* group that can accommodate an acetylene substituent in **1b**,**e** and the steric demands at its periphery that lead to clashes with the butadiyne substituent in **2b**,**e**. Mes* = $(^t\mathrm{Bu})_3\mathrm{Ph}$.

steric constraints compared to those in **1**, it is interesting to note that the opposite is the case and that the energy difference between **1c**−**f** and **2c**−**f** (1.3−13.6 kJ/mol) is relatively small compared to that between **1a** and **2a** (41.4 kJ/mol). In other words, there seems to be a factor that destabilizes isomer **2** more than **1** and leads to a situation where the two isomers are closer in energy than accounted for by the π-conjugation term. We believe to have found the reason for this unexpected effect in the special nature of the Mes* group which is sterically very demanding at the peripheral *ortho* and *para* positions, but is rather uncongested in its center. As visible from the graphical representations of the structure optimizations for **1b**,**e** and **2b**,**e** in Figure 6, the acetylene spacer in isomer **1** places the silyl substituents in a position where they can extend into the void of the Mes* center. In contrast, the butadiyne in **2** forces the silyl substituents into a position where they clash with the *para*-^{t}Bu group of Mes*. As a result, the repulsive Mes*$\cdots$R$_1$ interaction in isomer **2** is greater than that in **1**. In case of the most bulky TIPS substituents, the Mes*$\cdots$R$_1$ repulsion in **2b** dominates even over the stabilization from π-delocalization and renders **1b** the lowest energy isomer of the **b** series.

Calculated Frontier Molecular Orbitals. As representatively shown for structures **1e** and **2e**−**h** in Figure 7, the calculated frontier molecular orbitals (FMOs) are almost exclusively of π-character and for **1b**−**e** and **2c**−**e**, both HOMO and LUMO are localized over the same atoms. The lowest energy absorptions in the UV/vis spectra can therefore be expected to result from $\pi\rightarrow\pi^*$ transitions. Furthermore, the calculations show that the phosphaalkenes are an intrinsic part of the π-delocalized systems and present in all FMOs, except for the LUMO of **2g**. The calculated HOMO−LUMO gaps are in good to excellent agreement with the values obtained for the lowest energy absorption maxima in the UV/vis absorption experiments. For example, for **2e**,**f**,**h**, the calculated HOMO−LUMO separations of 3.45, 3.25, and 2.85 eV correlate very well with the experimentally determined 3.46 (358 nm), 3.27 (379 nm), and 2.81 eV (441 nm), respectively. As already anticipated from

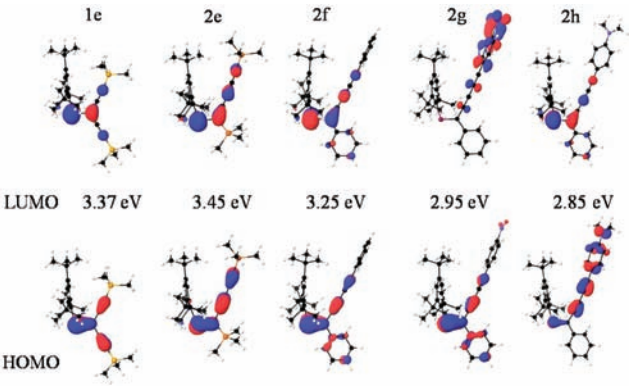

FIGURE 7. Calculated HOMO and LUMO with relative orbital energies for **1e** and **2e**−**h** at the B3LYP/6-311++G**//B3LYP/6-31G* level.

the spectroscopic and voltammetric experiments, the HOMO of **2f** has a contribution from the phenyl substituent at the P=C carbon. On the other hand, the phenyl group at the butadiyne terminus is not participating in the FMOs. This situation changes as electron-withdrawing and -donating substituents are introduced in **2g** and **2h**, respectively. A molecular orbital with large contributions from the peripheral nitrophenyl group becomes the new LUMO of **2g**. It is interesting to note that the calculated LUMO+1 is almost identical to the LUMO of **2f** (see the Supporting Information). The calculations are thus consistent with the electrochemically obtained results that the first reduction is a localized process on the extended nitrophenyl group in **2g**. Similarly, a new orbital with large coefficients on the extended aniline portion features as the HOMO in **2h** and the HOMO-1 is analogous to the HOMO of **2f**,**g**. The calculations are thus again in agreement with the electrochemical experiments where an additional oxidation is observed at milder potential than that associated with the oxidation of the PC$_5$-based π-conjugated system. Due to the partial spatial separation of HOMO and LUMO in **2g**,**h**, the lowest energy optical transitions can be expected to exhibit some charge-transfer character.

Conclusions

We have identified an unexpected isomerization during the chlorination of alcohols **4b**−**e** which leads to the formation of 3-chloropenta-1,4-diyne **5b**−**f** and 1-chloropenta-1,2-dien-4-yne **6b**−**e**. Different regioisomeric acetylenic phosphaalkenes are formed in the LDA-promoted reaction with Mes*PCl$_2$ from both starting chlorides. The reactions proceed selectively at the β-carbon relative to the chloride and lead to *C*,*C*-A$_2$PAs **1b**−**e** from **6b**−**e** and to butadiyne-substituted phosphaalkenes **2c**−**f** from **5c**−**f**. Both products are proposed to be formed in a similar fashion from isomeric allenyllithium species. DFT calculations on the three potentially attainable isomers **1**−**3** reveal that a delicate interplay between electronic and steric factors determines the energetic order of the different isomers. The calculations suggest that steric constraints influence the reaction outcome and the preference for the formation of a certain isomer. The phosphaalkenes are an intrinsic part of the π-conjugated system in all compounds and are responsible for a lowering of their HOMO−LUMO gaps compared to those in all-carbon

based reference compounds. The reliable access to *C*,*C*-A_2PAs, in particular bis-TMS protected **1e**, offers great potential for the preparation of elaborate oligomeric and cyclic structures, since the in situ removal of the silyl protecting group and preceding coupling protocols can both be conducted under mild basic conditions.[53] Efforts in these directions are the subject of ongoing investigations.[54]

Experimental Section

Computational Methods. Conformational searches were performed for all three isomers of the investigated compounds using the OPLS2005 force field in the MacroModel program.[55] Geometry optimizations were in turn performed on typically two to six representative low energy conformers using gas-phase density functional theory (DFT) calculations with the B3LYP hybrid functional[56] and employing the 6-31G* basis set. Single-point calculations were performed with the larger 6-311++G** basis set on the geometries obtained at the B3LYP/6-31G* level. Molecular orbitals were computed using the B3LYP functional and the 6-311++G** basis set. All calculations were performed using the Jaguar 07 program package. For details, see the Supporting Information.

Materials and General Methods. Chemicals were 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 N_2 or Ar. Column chromatography was performed on silica gel SI-60 Å (35−70).

For characterization of **1b**, **2g**,**h**, and **7** see ref 12. For characterization of **1d**,**e**, **2d**−**f**, **4c**−**f**, and **5c**−**f**, see the Supporting Information.

General Procedure for the Preparation of Phosphaalkenes 1b−e and 2c−f. To a solution of 2,4,6-tri-*tert*-butylbromobenzene in THF (20 mL) was added dropwise *n*-butyllithium (2.5 M solution in hexanes) at −78 °C. After 0.5 h of stirring, PCl_3 (3 equiv) was added quickly in one portion at −78 °C. The solution was warmed to room temperature and refluxed for 2−3 h. The volatiles were removed in vacuo. The white solid was dissolved in THF, and 3-chloropenta-1,4-diyne **5** and/or 1-chloro-1,2-pentadien-4-yne **6** were added. LDA (2.2 equiv) was added at −98 °C, and after 15 min, the red solution was allowed to warm to −30 °C over 2 h under stirring. The reaction mixture was quenched by aqueous saturated NH_4Cl, diluted with hexane, washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification and isolation of **1** and **2** was achieved by column chromatography (silica, 1% EtOAc in pentane). Recrystallizations were made from MeOH or MeOH/CH_2Cl_2.

(1,5-Bis(*tert*-butyldimethylsilyl)penta-1,4-diyn-3-ylidene)-(2,4,6-tri-*tert*-butylphenyl)phosphine (1c) and (*E*)-(1,5-Bis(*tert*-butyldimethylsilyl)penta-2,4-diynylidene)(2,4,6-tri-*tert*-butylphenyl)phosphine (2c). From 1,5-bis(*tert*-butyldimethylsilyl)-3-chloropenta-1,4-diyne **5c** and 1-chloro-1,5-bis(*tert*-butyldimethylsilyl)-1,2-pentadien-4-yne **6c** (5:1 mixture: 0.715 g, 1.90 mmol), Mes*Br (0.700 g, 2.15 mmol), *n*-butyllithium (0.87 mL of a 2.5 M solution in hexanes), PCl_3 (0.56 mL 6.45 mmol), and LDA (4.30 mmol). **1c**. Yellow solid. Yield: 0.121 g (0.21 mmol, 11%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44 (s, 2H, CH-Mes*), 1.49 (s, 18H, *t*-Bu-Mes*), 1.32 (s, 9H, *t*-Bu-Mes*), 0.98 (s, 9H, *t*-Bu-Si), 0.73 (s, 9H, *t*-Bu-Si), 0.17 (s, 6H, $SiCH_3$), −0.18 (s, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.5, 150.4, 141.5 (d, $^1J_{PC}$ = 35 Hz), 134.7 (d, $^1J_{PC}$ = 58 Hz), 122.4, 105.7 (d, J_{PC} = 10 Hz), 105.4 (d, J_{PC} = 26 Hz), 103.8 (d, J_{PC} = 19 Hz), 99.6 (d, J_{PC} = 15 Hz), 38.2, 35.0, 33.0 (d, $^4J_{PC}$ = 6 Hz), 31.4, 26.2, 26.1, 17.0, 16.5, −4.7, −4.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 339.6. EI MS (70 eV): *m*/*z* 566.2 (55) [M^+], 509.3 (12) [M^+ − *tert*-butyl], 275.2 (100) [Mes*P^+ − H]. Anal. Calcd for ($C_{35}H_{59}PSi_2$): C, 74.14; H, 10.49. Found: C, 74.35; H, 10.39.

2c. Yellow solid. Yield: 0.341 g (0.60 mmol, 32%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (s, 2H, CH-Mes*), 1.47 (s, 18H, *t*-Bu-Mes*), 1.34 (s, 9H, *t*-Bu-Mes*), 0.97 (s, 9H, *t*-Bu-Si), 0.87 (s, 9H, *t*-Bu-Si), 0.27 (s, 6H, $SiCH_3$), 0.04 (s, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.1 (d, $^1J_{PC}$ = 78 Hz), 152.6, 150.2, 138.9 (d, $^1J_{PC}$ = 68 Hz), 122.1, 96.4 (d), 95.2 (d, J_{PC} = 11 Hz), 89.2 (d, J_{PC} = 9 Hz), 77.3 (d), 37.8, 34.9, 33.2 (d, ^4J(P,C) = 6 Hz), 31.4, 26.8, 26.1, 18.4, 16.8, −4.7, −4.9 (d, $^3J_{PC}$ = 10 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 371.5. EI MS (70 eV): *m*/*z* 567.26 (10) [M^+ + H], 398.1 (90) [M^+ − (3 *tert*-butyl) + $3H^+$], 397.1 (100) [M^+ − (3-*tert*-butyl) + $2H^+$], 275.2 (66) [Mes*P^+− H]. Anal. Calcd for ($C_{35}H_{59}PSi_2$): C, 74.14; H, 10.49. Found: C, 74.03; H, 10.31.

General Procedure for the Preparation of the Carbinols 4b−f. *n*-Butyllithium (12 mL of a 2.5 M solution in hexanes) was added to a solution of the acetylene (30 mmol) in THF (40 mL) at −30 °C. The colorless solution was stirred for 15 min and cooled to −78 °C before ethyl formate (1.2 mL, 15 mmol) was added via syringe. The reaction was stirred for 2 h, during which time it was allowed to warm to −30 °C. After the yellow solution was quenched at this temperature with a mixture of aqueous saturated NH_4Cl (50 mL) and 1 M HCl (10 mL), the phases were separated and the organic phase extracted with EtOAc (3 × 40 mL). The combined organics were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (5% EtOAc in pentane).

1,5-Bis(triisopropylsilyl)penta-1,4-diyn-3-ol (4b). From *n*-butyllithium (10.5 mL of a 2.5 M solution in hexanes), (triisopropylsilyl)acetylene (5.2 g, 28.5 mmol), and ethyl formate (0.93 g, 12.5 mmol). Colorless oil. Yield: 1.67 g (6.77 mmol, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.11 (d, ^3J = 7.8 Hz, 1H, CH), 2.16 (d, ^3J = 7.8 Hz, 1H, OH), 1.09−1.02 (m, 42H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.3, 85.6, 53.0, 18.5, 11.1.

General Procedures for the Preparation of Chloropentadiynes 5b−f. In Et_2O. Alcohol **4** was dissolved in Et_2O and deaerated with N_2 for 15 min. The solution was cooled to −20 °C, and $SOCl_2$ was added dropwise. The yellow solution was warmed to rt and stirred for 12 h. The solution was diluted with Et_2O, poured on ice, and neutralized with saturated aqueous $KHCO_3$. The phases were separated, the aqueous phase extracted with Et_2O (3 × 40 mL), and the combined organics washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (pentane).

In CH_2Cl_2. Alcohol **4** was dissolved in CH_2Cl_2 (20 mL) and deaerated with N_2 for 15 min. The solution was cooled to 0 °C, and $SOCl_2$ was added dropwise. The yellow solution was warmed to rt and refluxed for 2 h. The solution was diluted with CH_2Cl_2, poured on ice, and neutralized with saturated aqueous $NaHCO_3$. The phases were separated, extracted with Et_2O (3 × 40 mL), and the combined organics washed with brine (40 mL), dried over Na_2SO_4 ,and concentrated in vacuo. Purification by column chromatography (pentane).

1. 5-Bis(triisopropylsilyl)-3-chloropenta-1,4-diyne (5b). From 1,5-bis(triisopropylsilyl)penta-1,4-diyn-3-ol (2.17 g, 5.5 mmol), $SOCl_2$ (5.5 mL, 75 mmol), and Et_2O (8 mL). Colorless oil. Yield: 1.85 g (4.50 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.27 (s, 1H, CH), 1.08 (m, 42H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.0, 88.1, 35.6, 18.5, 11.1.

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1-Chloro-1,5-bis(trimethylsilyl)-1,2-pentadien-4-yne (6e). 1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ol (900 mg, 4 mmol) was dissolved in Et_2O (20 mL), $SOCl_2$ (2.2 mL, 30 mmol) was added dropwise at rt, and two drops of DMF were added. The reaction was allowed to stir for 2−3 h before it was poured into a mixture of ice−water (30 mL) and hexane (80 mL). The organic layer was separated and washed with saturated aqueous $KHCO_3$, water, and brine and then dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography (hexane). 1-Chloro-1,5-bis(trimethylsilyl)-1,2-pentadien-4-yne (**6e**) was obtained as a colorless oil. Yield: 540 mg (2.1 mmol, 53%) accompanied by 1,5-bis(trimethylsilyl)-3-chloropenta-1,4-diyne (**5e**, 0.30 g (1.2 mmol, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.55 (s, 1H, CH), 0.23 (s, 9H, $SiCH_3$), 0.20 (s, 9H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.0, 100.5, 99.6, 96.0, 79.9, −0.2, −2.3.

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Supporting Information Available: Analytical and crystallographic details; comparative computational study with different functionals; calculated FMO energies and Cartesian coordinates of the lowest energy conformations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.