Exploitation of an unprecedented silica-promoted acetylene–allene rearrangement for the preparation of *C*,*C*-diacetylenic phosphaalkenes†

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***C*,*C*-Diacetylenic phosphaalkenes have been obtained from a 1-chloro-3-ethynyl-1,2-allene which becomes accessible from a silica-promoted rearrangement of a 3-chloropenta-1,4-diyne; oxidative acetylene homo-coupling of the phosphadiethynylethene is described for the first time and affords a dimeric, cross-conjugated product which features a largely decreased HOMO–LUMO gap compared to all-carbon-based reference compounds.**

Well-defined, monodisperse oligoacetylenes have attracted chemists' attention for many decades as their large degree of unsaturation gives rise to a plethora of interesting (opto)-electronic properties with many conceivable applications.[1–5] Improved synthetic protocols for cross-conjugated structures such as dendralenes,[6] expanded radialenes[7] and radiaannulenes[8] have recently refueled the interest in these compounds.[9] Despite the vast literature on oligoacetylenes, it is surprising that heavy analogues of these structures where one or more carbon centers are substituted by a heavy main group element are essentially unknown. Considering the analogy between phosphorus and carbon,[10] we are currently aiming at introducing phosphorus heteroatoms in the form of phosphaalkenes into oligoacetylene frameworks.[11] The inclusion of phosphorus into related aromatic π-conjugated assemblies has brought forward a number of compounds and materials with intriguing properties.[12–14] For example, it has been shown that the pyramidalization of the phosphorus center in phospholes causes a diminished participation of the lone-pair in π-delocalization and ultimately leads to decreased HOMO–LUMO gaps.[15–17] It could furthermore be shown that phosphaalkenes and diphosphenes can be incorporated in poly(phenylphosphaalkene)[18] and diphosphenes,[19] respectively.

We have recently reported that treatment of alcohol **1** with thionyl chloride gives access to diacetylenic chloride **2a**, the ^{1}H-NMR spectrum of which features the chloromethyl proton at δ = 5.50 ppm with the ^{13}C-NMR spectrum showing four signals in the customary acetylene region.[11] We were surprised to find that attempts to remove small amounts of impurities by silica gel column chromatography (hexane) resulted in the disappearance of **2a** and the formation of a new product **2b** which features a singlet in its ^{1}H-NMR spectrum at δ = 5.75 ppm and very different ^{13}C-NMR chemical shifts, most prominently one at δ = 211.7 ppm.[20] In addition, EI-MS of **2a** and **2b** showed identical peaks for the molecular ions, supporting the notion that a rearrangement has occurred. Based on this analysis and in analogy to reported analytical data of a bromoallene,[21] we identified **2b** as the chloroallene shown in Scheme 1.

^{1}H-NMR experiments unambiguously identified silica as the responsible reagent for this transformation as its addition to a solution of **2a** in $CDCl_3$ resulted in complete conversion within 1 day (Fig. 1). Similar experiments were conducted with a range of different acids to probe whether the effect can be attributed to the acidity of silica. Whereas no reaction was observed with toluenesulfonic acid (5–10 mM in CD_3CN, 5 mM of **2a**) or acetic acid (20 v/v in $CDCl_3$) after 36 and 60 hours, respectively, addition of CF_3COOH catalyzed the transformation within 2 hours. The high acidity that is required to drive the transformation and that has been observed to be necessary for a somewhat related acid-catalyzed acetylene–allene rearrangement[22] is however not provided by silica. The observed activity thus has to be attributed mostly to silica itself.

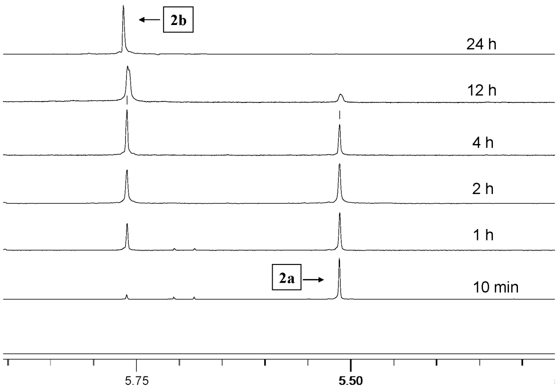

Fig. 1 Transformation of **2a** (5 mM, $CDCl_3$, 20 °C) to **2b** in the presence of silica gel (15 mg). Shown is the characteristic region of the chloromethyl (**2a**) and allenic proton (**2b**) of the ^{1}H-NMR spectra.

Our interest in heavy ethynylethene analogues prompted us to investigate the reaction of **2b** with Mes*PCl$_2$ (Mes* = 2,4,6-(^{t}Bu)$_3$Ph) in the presence of LDA (Scheme 1). In contrast to the reactivity of **2a** which forms 1-phosphahexa-1-ene-3,5-diyne **3a**,[11] allene **2b** gives rise to diacetylenic phosphaalkenes ***E*/*Z*-3b**, in a ratio of 3 : 1, as evidenced by two signals at δ = 338.3 ppm and 339.9 ppm, respectively, in the ^{31}P-NMR spectrum of the crude product mixture. The isomers were successfully separated by preparative HPLC on a C18 chromatographic column using a mixture of THF and methanol as

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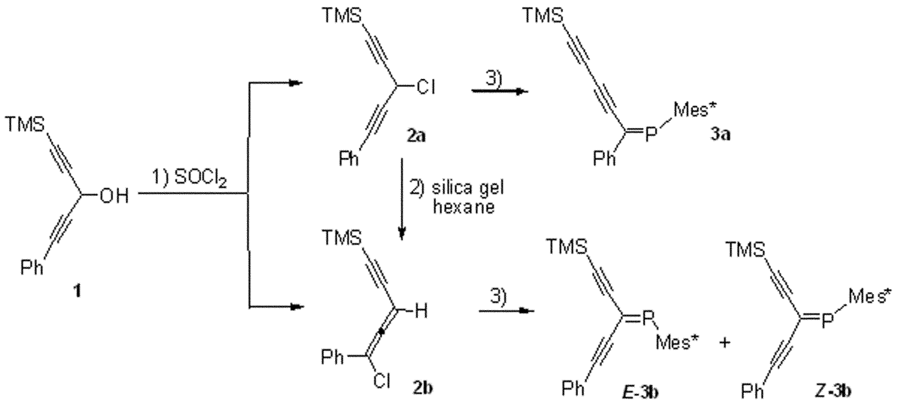


Scheme 1 Synthesis of diacetylenic phosphaalkenes ***E*-3b** and ***Z*-3b** from allene **2b**. (1) $SOCl_2$, DMF (cat.), Et_2O, 3 h, rt (20 °C). (**2a**/**2b** = 10/1, estimated from Fig. 1). (2) Column chromatography on silica gel using hexane as eluent. (**2b**, 72%). (3) Mes*PCl_2, LDA, THF, 1 h, −98 °C to −40 °C. (55%, ***E*-3b**/***Z*-3b** = 3 : 1, identified by ^{31}P-NMR).

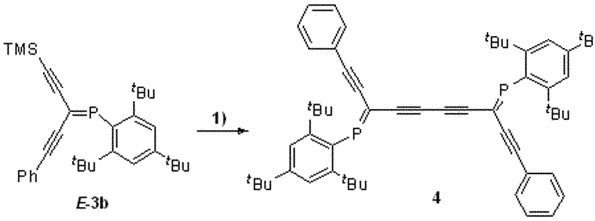
eluent. Attempts to grow single crystals of **3b** for X-ray analysis failed and the structures of the two isomers could only be established by the experiments described below. ^{13}C-NMR spectra of both isomers show the characteristic chemical shift for the P═C carbon of *C*,*C*-diacetylenic phosphaalkenes around δ = 141, which are thus also remarkably shifted upfield compared to that of **3a** (above δ = 160 ppm).[11]

The mechanistic proposal for the formation of diacetylenic phosphaalkene **3b** starts with the abstraction of the acidic proton in **2b** by LDA. Nucleophilic substitution on Mes*PCl_2 establishes a single bond between phosphorus and the central carbon of **2b**. Lithium–chloride exchange at this intermediate, followed by elimination of LiCl, gives rise to ***E*/*Z*-3b**, the ratio of which is determined in the final elimination step.

In attempts to further develop the chemistry of acetylenic phosphaalkene, it was investigated whether ***E*-3b** was a suitable substrate for Eglinton homo-coupling reactions (Scheme 2). Employing a one-pot deprotection–coupling protocol,[11] the reaction proceeds smoothly to afford dimeric **4** in 68% yield. It is important that the reaction time is kept short due to the limited stability of **4** under the basic Eglinton conditions. ^{31}P-NMR of the crude reaction mixture showed only one signal in the P═C region at δ = 348.9 ppm, and that the stereochemistry across the P═C bond is conserved during the reaction.

Single crystals of **4** were successfully grown from a mixture of CH_2Cl_2 and methanol and their analysis by X-ray diffraction revealed the *trans* relationship between the butadiyne (C2–C1–C1A–C2A) and Mes* (Fig. 2). Since no isomer scrambling was observed during the homo-coupling, it is safe to assume that also the employed **3b** starting material features an *E*-configuration across the P═C bond. Secondly, P1 and C1–C5 all lie within the same plane within 0.02 Å. The π-system extends even over the peripheral phenyl groups which are twisted by only 6.4° out of the PC_5 plane. Thirdly, the phenyl ring on the acetylene terminus and the aromatic portion of the supermesityl group are nearly perpendicular to each other as described by an inter-planar angle of 96°. H1 of the phenyl ring thus points towards the center of the Mes* ring with a vertical distance of 3.02 Å. This distance is within the range of a relatively strong intramolecular hydrogen bond which makes ***E*-3b** thermodynamically more stable and may be the reason for its preferred formation over ***Z*-3b**. This interaction can also be observed in solution by ^{1}H-NMR spectroscopy. Whereas H1 in ***E*-3b** resonates at δ = 6.86 ppm owing to the additional shielding above the aromatic Mes* group, the signal of the corresponding proton in ***Z*-3b** features at δ = 7.53 ppm.

The UV/Vis absorption spectra of compound **3b** and **4** are shown in Fig. 3. As expected, the isomeric ***E*-3b** and ***Z*-3b** possess almost identical absorption profiles with longest wavelength absorption maxima around 367 nm. Due to the larger π-system, dimeric **4** exhibits a longest wavelength absorption maximum at 446 nm that is thus red-shifted by 79 nm. In comparison with similarly substituted all-carbon-based diethynylethenes,[23] the acetylenic phosphaalkenes **3b**



Scheme 2 Homo-coupling reaction of ***E*-3b** to form **4**. (1) K_2CO_3, $Cu(OAc)_2$, MeOH, pyridine, 1 h, 20 °C, 68%. TMS = trimethylsilyl.

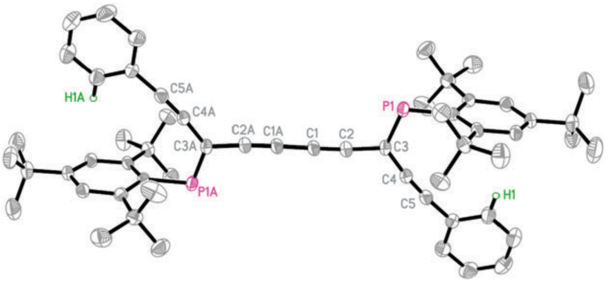


Fig. 2 Molecular structure of dimer **4** (25% probability ellipsoids). All hydrogen atoms except H1 and H1A are omitted for clarity. Selected bond lengths [Å] and angle [°]: C1A–C1 1.373, C1–C2 1.201, C2–C3 1.429, C3–C4 1.426, C4–C5 1.193, C5–C6 1.441, C3–P1 1.705, P1–C3–C2 115.2, P1–C3–C4 124.7, C2–C3–C4 120.1. Dihedral angle between phenyl and Mes* ring planes [°]: 96. Distance from H1 to Mes* ring plane [Å]: 3.02.

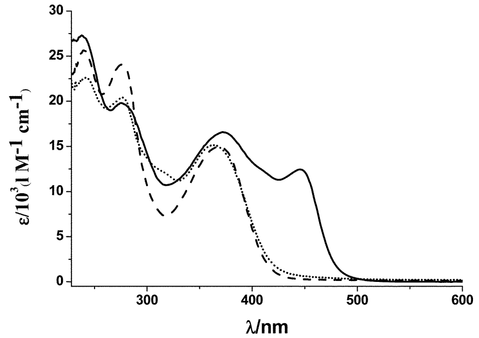


Fig. 3 UV/Vis absorption spectra of compounds ***E*-3b** (---), ***Z*-3b** (· · ·) and **4** (—) in CH_2Cl_2 at 25 °C.

Table 1 Electrochemical data for **3b** and **4**[a]

Compound	Reduction $E_{p,c}$/V P=C–C	Oxidation $E_{p,a}$/V P=C–C
***E*-3b**	−2.04	1.03
***Z*-3b**	−2.04	1.02
4	−1.67[b], −2.2[c]	0.95

[a] 1 mM solutions in CH_2Cl_2 (0.1 M NBu_4PF_6), ν = 100 mV s^{-1}. Potentials are given *vs.* Fc$^{+/0}$. [b] $E_{1/2} = (E_{p,c} + E_{p,a})/2$. [c] Reversible at ν > 1 V s^{-1}.

generally feature end absorptions at lower energy by around 45 nm. This effect is even more pronounced in the case of **4**, the absorption of which is red-shifted by more than 100 nm compared to a suitable reference with a similar all-carbon-based π-system with $–NO_2$ or $–NMe_2$ substituted phenylacetylene termini.[24] This comparison strengthens our previous finding that introduction of phosphorus heteroatoms in the form of phosphaalkenes into oligoacetylenes results in a dramatic red-shift of the longest wavelength absorption maxima and thus to decreased HOMO–LUMO gaps. The presence of the λ^3-σ^2 phosphorus in phosphaalkenes thus seems to have a similar effect on the HOMO–LUMO gaps of appended π-systems as the λ^3-σ^3 phosphorus lone-pair in phospholes.[15–17]

In comparison to a linear bis-phosphaalkene end-capped octatetrayne[11] that is a regioisomer of **4**, the lowest energy absorption maximum of the latter is however blue-shifted by *ca.* 40 nm. This order thus resembles that of all-carbon-based oligoacetylenes where linear conjugation is generally more effective than that in a cross-conjugated system.

The cyclic voltammogram of **4** shows an irreversible oxidation at 0.95 V *vs.* Fc$^{+/0}$ that is cathodically shifted by *ca.* 70 mV compared to those of monomers **3b** (Table 1). The effect of the extended π-system in **4** is however more pronounced in the reductive scan where the first electron uptake is shifted by 370 mV to milder potential compared to those of **3b**. The second reduction of **4** proceeds at a potential more than 500 mV more negative than that of the first process, indicating a large degree of communication through the entire π-system.

The discovery of an unprecedented silica-promoted acetylene–allene rearrangement has paved the way to *C*,*C*-diacetylenic phosphaalkenes. Dimeric oligoacetylene **4** can be regarded as an expanded dendralene where the peripheral methylene groups are exchanged by phosphorus centers. This modification leads to greatly decreased HOMO−LUMO gaps which make our phosphorus-containing oligoacetylenes appealing compounds for future molecular electronics applications.[25] The general applicability of the rearrangement reaction, efforts to further extend the unsaturated framework in **4** and to prepare expanded phospharadialenes are subjects of ongoing work.

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