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Phosphaalkene Synthesis

Direct, Sequential, and Stereoselective Alkynylation of *C,C*-Dibromophosphaalkenes

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Abstract: The first direct alkynylation of *C,C*-dibromophosphaalkenes by a reaction with sulfonylacetylenes is reported. Alkynylation proceeds selectively in the *trans* position relative to the P substituent to afford bromoethynylphosphaalkenes. Owing to the absence of transition metals in the procedure, the previously observed conversion of dibromophosphaalkenes into phosphaalkynes through the phosphorus analog of the Fritsch–Buttenberg–Wiechell rearrangement is thus suppressed. The bromoethynylphosphaalkenes can subsequently be converted to *C,C*-diacetylenic, cross-conjugated phosphaalkenes by following a Sonogashira coupling protocol in good overall yields. By using the newly described method, full control over the stereochemistry at the P=C double bond is achieved. The substrate scope of this reaction is demonstrated for different dibromophosphaalkenes as well as different sulfonylacetylenes.

Introduction

Organic electronics as well as single-molecule electronics have become a wide field of interest for theoretical, experimental, and applied science. Over the last decade, different carbon-rich organic scaffolds have been utilized in the fabrication of materials for applications in organic light-emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs), thin film transistors, etc.[1] Recently, it was demonstrated theoretically and experimentally that cross-conjugated systems exhibit intriguing conjugative properties depending on the applied bias.[2] The search for innovative motifs with novel optical and electronic properties has given rise to a completely new area in main-group chemistry. Incorporation of heavier main-group elements has long been known to alter the optical and electronic properties of conjugated frameworks, but only recently have the first examples of silicon-, boron-, and phosphorus-containing molecules for organic electronics applications been presented.[3] Introducing an acetylenic moiety at the C-terminus of a phosphaalkene offers the possibility of building larger conjugated or cross-conjugated frameworks with unsaturated exocyclic P=C units, linked through an acetylene bridge. Having such a phosphaalkene unit in the backbone of a conjugated molecule leads to significant stabilization of the LUMO level, while the HOMO is essentially unaffected.[4]

Recently, *C*-monoacetylenic phosphaalkenes—obtained by a transition-metal-mediated coupling reaction from their monobromo precursors[5]—have been used in the dynamic stabilization of gold nanoparticles,[6] and monohalogenated phosphaalkenes are valuable precursors in the synthesis of complex structures featuring P=C units.[7]

C,C-Diacetylenic phosphaalkenes have hitherto not been accessible directly from halogenated precursors. Unlike dibromoalkenes, which can be used to access diethynylethenes in Pd-mediated Sonogashira couplings,[8] the P counterpart, that is, *C,C*-diacetylenic phosphaalkenes, are not accessible through such a sequence owing to a transition-metal-mediated phosphorus version of the Fritsch–Buttenberg–Wiechell (FBW) rearrangement,[9] which leads to phosphaalkynes (R–C≡P) and polymeric decomposition products thereof instead of the desired acetylenic phosphaalkenes (Figure 1).[5a] As a matter of fact, the FBW rearrangement is a common way to access phosphaalkynes from dibromophosphaalkenes nowadays (Figure 1 a).[5b,10]

Inspiration for how to circumvent this problem came from a study by Smorada and Truce who demonstrated a coupling of in situ generated organolithium species at low temperatures with arylsulfonylacetylenes to afford the anti-Michael acetylenic coupling products with C_{Aryl}–C_{sp} bond formation.[11] Recently, García Ruano et al. have extended this strategy and demonstrated its high stereo- and regioselectivity.[12] The wide scope of this reaction was demonstrated to enable C_{sp2}–C_{sp} and C_{sp3}–C_{sp} bond formations as well as having a large tolerance for the various electronic natures of the employed reactants.[13] Considering the limitations of transition-metal-mediated coupling reactions of *C,C*-dibromophosphaalkenes owing to the FBW rearrangement, we opted to investigate the scope and limita-

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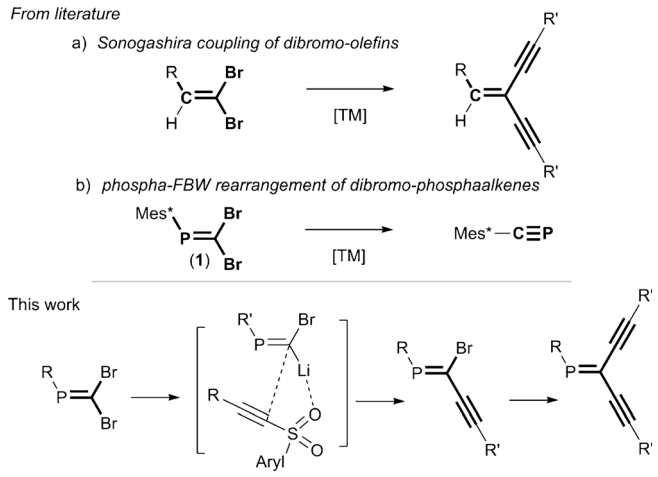


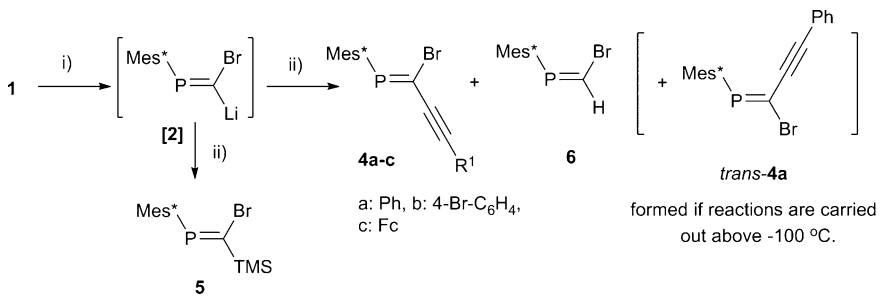
Figure 1. a) Commonly used strategy to convert dibromoolefins to acetylenic alkenes by using transition-metal (TM)-catalyzed reactions. b) TM-mediated phospha-FBW rearrangement of *C,C*-dibromophosphaalkene to phosphaalkynes, which precludes the formation of acetylenic phosphaalkenes. This work: novel approach for the direct alkynylation of a lithium phosphacarbenoid intermediate by using sulfonylacetylenes, followed by a TM-mediated second alkynylation.

tions of an arylsulfonyl-mediated alkynylation of a phosphaalkene through an in situ generated phosphavinylidene carbenoid species (Scheme 1, **2**). It is important to note that prior to 2008, the introduction of two acetylenic units at the C-terminus of a phosphaalkene was inconceivable.[14] However, stereospecific control of the acetylenic substituents is precluded by using the "propargylic" approach and the stereochemistry is predetermined by the acetylenic substituents.[4b,15]

Results and Discussion

The current work demonstrates a sequential coupling of two acetylenes that avoids the transition-metal-mediated coupling of the first acetylenic fragment. With this strategy, we have full control over the stereochemistry at the P=C double bond, which enables a reliable retro-synthetic approach towards complex motifs.

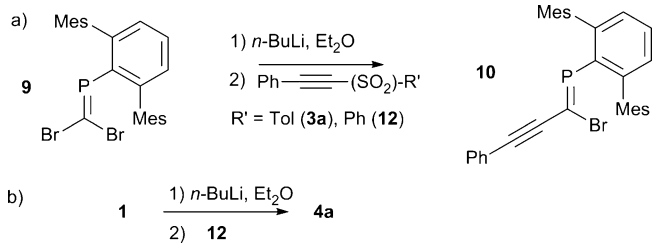
It is known that dihalophosphaalkenes can be selectively lithiated below −90 °C to give the kinetically favored *cis*-lithium phosphacarbenoids, which are stable up to approximately −60 °C,[16] but decompose to phosphaalkynes and other unidentified products above −50 °C.[17] The selectivity of the metal halogen exchange is lost at −78 °C, giving mixtures of the *cis*- and *trans*-lithium phosphacarbenoids (Scheme 1). For our initial experiments, we chose dibromophosphaalkene Mes*-P=CBr_2 (**1**) as the starting material as **1** benefits from the kinetic stabilization provided by the Mes* group (Mes* = 2,4,6-tBu_3Ph). The reaction of intermediate **2** at low temperatures with sulfonylacetylenes **3a–c** (for R^1 = **a**: Ph, **b**: 4-Br-C_6H_4, **c**: Fc) results in the formation of acetylenic phosphaalkenes **4**, which are characterized by their downfield shifted ^{31}P NMR resonances (291.0 ppm (**4a**), 294.2 ppm (**4b**), and 280.3 ppm (**4c**)) relative to that of **1** (271.0 ppm).[18] After chromatographic purification, the targeted acetylenic phosphaalkenes were obtained as colorless solids in moderate to good yields. The ^1H NMR data also underline the *trans* relationship of the introduced acetylene relative to Mes* through retention of the configuration at the Li–carbenoid intermediate. For derivatives **4a** and **4b**, the absence of distinct aromatic protons at higher fields (≈6.9 ppm) preclude positioning of the phenyl substituent in the ring current of the Mes* substituent, as previously observed for other phenylacetylene substituted phosphaalkenes.[14b,15] Unambiguous confirmation of the molecular structure was obtained by X-ray diffraction of single crystals (see below). It is important to note that the Li/Br exchange reaction must be carried out at temperatures below −90 °C; otherwise, the selectivity in the Li/X exchange reaction is lost and a mixture of *cis*- and *trans*-isomers is obtained. Reaction of **1** with *n*BuLi at around −80 °C followed by the addition of sulfonylacetylene **3a** gives *cis*-**4a** as well as the opposite isomer *trans*-**4a**. In contrast, controlled temperatures (below −100 °C) during the Li/halogen exchange step give *cis*-**4a** exclusively. The only exception in this series of sulfonylacetylenes was observed in the attempted coupling of trimethylsilyl (TMS) terminated acetylene **3d** (R^1 = TMS). This reagent does not show a clean alkynylation. Among several phosphorus containing species, we could identify a TMS coupling reaction that resulted from a β-attack to afford the *C*-silylated phosphaalkene **5**, which was identified by X-ray crystallography and on the basis of literature NMR data.[17] On the other hand, the successful introduction of a *para*-bromophenylacetylene substituent as in **4b** shows the functional group tolerance of this method and indicates future possibilities for the preparation of larger oligomeric and cyclic structures. Surprisingly, the ferrocenylacetylene derivative **4c** was unstable towards chromatographic



Scheme 1. Reaction of dibromophosphaalkene Mes*-P=CBr_2 (**1**) with arylsulfonylacetylenes R^1-C≡C-(SO_2)-Tol (**3a**: R^1 = Ph, **3b**: R = 4-Br-C_6H_4, **3c**: R = Fc, **3d**: R = TMS), leading to desired bromoethynylphosphaalkenes **4a–c** and undesired **5**. Conditions: i) *n*BuLi, −100 °C, Et_2O; ii) R-C≡C-(SO_2)-Tol (**3a–d**), −100 °C.

workup and could only be characterized as a crude product by ^{31}P and ^{1}H NMR spectroscopy after extraction with pentane. Interestingly, reacting dibromophosphaalkene **1** with 2.1 equivalents of *n*BuLi (Et_2O, −78 °C) followed by addition of sulfonylacetylene **2a** gives rise to two major products, which are attributed to the *cis*-monoacetylenic phosphaalkene *cis*-**4a** and the symmetrically disubstituted *C,C*-diacetylenic phosphaalkene.[4b] Although formation of a dilithiated intermediate is unlikely, a four-step sequence of a consecutive Li/halogen exchange then an alkynylation step followed by a second Li/halogen exchange and alkynylation can be excluded owing to the immediate reaction of *n*BuLi with tosyl acetylenes. The exact mechanism underlying the disubstituted derivative remains elusive at this stage.

To assess the further scope of this reaction, we have also tested a different dibromophosphaalkene. The Dmp substituent (Dmp = 2,6-bis-(2,4,6-trimethylphenyl)phenyl) is a commonly used *meta*-terphenyl-based moiety for kinetic stabilization of phosphaalkenes[19] and other unsaturated main-group compounds.[20] Thus, our newly developed coupling protocol was also tested on Dmp-P=CBr_2 (**9**; Scheme 2a).[21]



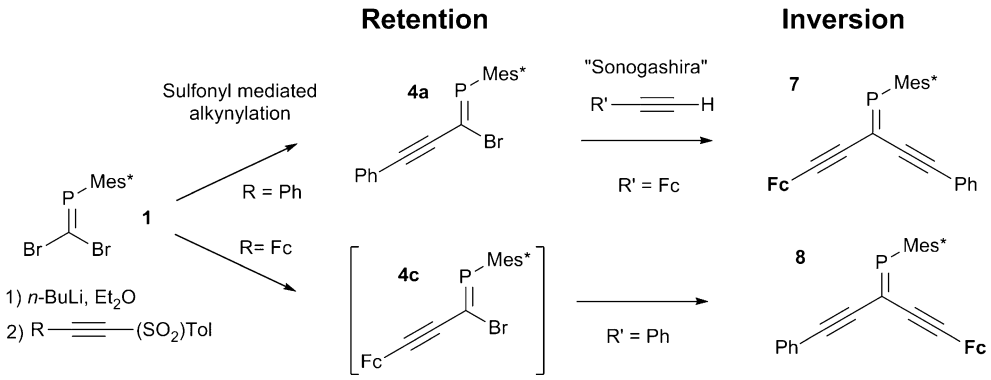
Scheme 2. a) Coupling of 2,6-dimesitylphenyl substituted dibromophosphaalkene **9** with sulfonylacetylene **3a** and **12**. Mes = 2,4,6-trimethylphenyl. b) Coupling of dibromophosphaalkene **1** with phenylsulfonylacetylene **12**.

Utilizing tolyl-sulfonyl acetylene **3a**, we obtained the corresponding acetylenic phosphaalkene **10** only as a minor product of the reaction whereas the major product stems from simple hydrolysis of the lithium phosphacarbenoid. Alternatively, phenyl-sulfonyl acetylene **12** gave almost full conversion of dibromophosphaalkene **9** into the monoacetylenic derivative **10**. Isolated yields (30%) are compromised by the slow decomposition of the product during column chromatography. Similarly, by using this reagent (**12**), we could demonstrate good conversion of **1** into **4a**, slightly improving the NMR yields to 81% compared with the original tosyl alkynylating reagent **3a** (Scheme 2b). Variation of the sulfonyl substituent presumably has an impact on the solubility and consequently the availability of the sulfonyl reagent especially at low temperatures.

Consequently, this transition-metal-free coupling reaction circumvents all problems associated with conventional coupling reactions of dihalophosphaalkenes using transition-metal catalysis. Having a second reactive C–Br moiety available opens new possibilities for the construction of larger and complex frameworks. We and others have demonstrated that Pd-mediated Sonogashira-type couplings of monobromophosphaalkenes gives an inversion of the stereochemistry through formation of a three-membered cationic palladacycle.[5] To confirm this reactivity and selectively synthesize asymmetrically substituted phosphaalkenes, we attempted to convert **4a** into its diacetylenic congener through a C–C cross-coupling with ferrocenylacetylene (Scheme 3). As expected, we obtain the corresponding *trans*-isomer **7**. Characteristic upfield shifted aromatic protons and a unique ^{31}P NMR resonance at 324.4 ppm unambiguously support the formation of this product.[22] Conversely, the other stereoisomer was obtained by inverting the sequence of the coupling steps, that is, by using in situ generated **4c** in the coupling reaction with phenyl acetylene, which afforded the diacetylenic phosphaalkene **8** with a ^{31}P NMR resonance at 322.5 ppm. The two steps, that is, sulfonyl coupling followed by the Sonogashira coupling, give the desired diacetylenic phosphaalkene **8** in 32% combined yield.

Structural and electrochemical characterization

The monobromophosphaalkene *cis*-**4a** crystallizes in the monoclinic space group $P2_1/c$ as colorless blocks, whereas *trans*-**4a** crystallizes in the space group $P2_1/n$ as colorless plates. Crystal structure analysis confirms the NMR assignment of the two isomers. Both structures show very similar parameters for the P=C double bond (1.682(4) and 1.684(4) Å) and the



Scheme 3. Stereoselective synthesis of diacetylenic phosphaalkene **7** and its isomer **8** through the sequential ethynylation with sulfonylacetylene, followed by Sonogashira coupling. Conditions: $[PdCl_2(PPh_3)_2]$, CuI, THF, pyridine, NEt_3.

angle between the Mes* and the P=C unit (101.9(2) and 101.6(2)°; Figure 2). Interestingly, the angle between the acetylene and Br substituents is significantly affected by the relative stereochemistry. Generally, the angle of the substituent *cis* to Mes* is wider (>125°) than for the *trans*-substituent (<123°). In compound **5**, the P=C–Si angle (*trans*-substituent) is the largest in this series as a result of the steric demand of the $SiMe_3$ moiety. The P=C bond in **5** shows similar parameters compared to the acetylenic derivatives *cis*-/*trans*-**4a**, indicating similar delocalization involving the silyl substituent. In contrast, the dibromophosphaalkene **9** exhibits a shorter P=C bond (1.673(2) Å), which is, however, longer than the P=C bond in the closely related Mes*-P=CBr_2 (**1**: 1.65(2) Å),[23] The P=C–Br angles are nevertheless remarkably similar in dibromophosphaalkenes **1** and **9**.

Low-valent organophosphorus conjugated backbones are known to have a great impact on the electrochemistry of ferrocene substituents, giving rise to interesting opto-electronic materials.[24] Having the isomeric compounds **7** and **8** in hand, we investigated potential effects that the opposite substitution patterns may have on the redox chemistry of these cross-conjugated *C,C*-diacteylenic phosphaalkenes by cyclic voltammetry (Figure 3). Both isomers show reversible oxidation, which is ascribed to the $Fe^{3+/2+}$ redox couple. The oxidation of derivative **7** is observed at 0.01 V versus Fc/Fc^+, whereas isomeric compound **8** is oxidized at 110 mV higher potentials. Interestingly, only phosphaalkene **7** shows a quasi-reversible reduction around −2.02 V, whereas compound **8** shows no reduction up to −2.3 V (vs. Fc/Fc^+). These findings clearly demonstrate that the electronic properties of the compounds can be tuned by a conscious choice of substituents and their positions relative to the P substituent. We have previously reported that phosphaalkene-based reductions are highly sensitive to minuscule changes in the extended π-system.[4b–d] We hypothesized that steric interactions of the ferrocenyl substituent might be responsible for substantial geometric changes and alterations in the extended conjugation, thus influencing the phosphaalkene-based reduction. To tap the full potential of this strategy, it is, however, crucial to have full control over the stereochemistry at the P=C double bond through methodologies such as the one reported herein.

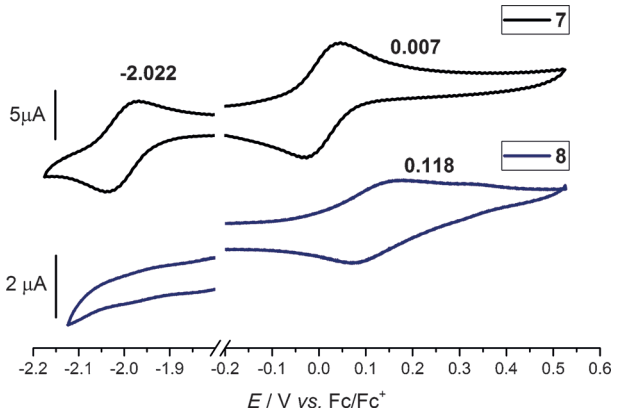


Figure 3. Cyclic voltammograms of diacetylenic phosphaalkenes **7** (5 mM) and **8** (2 mM). Scan-rate 100 mV, supporting electrolyte NBu_4PF_6, $Ag/AgNO_3$, CH_2Cl_2, calibrated versus Fc/Fc^+.

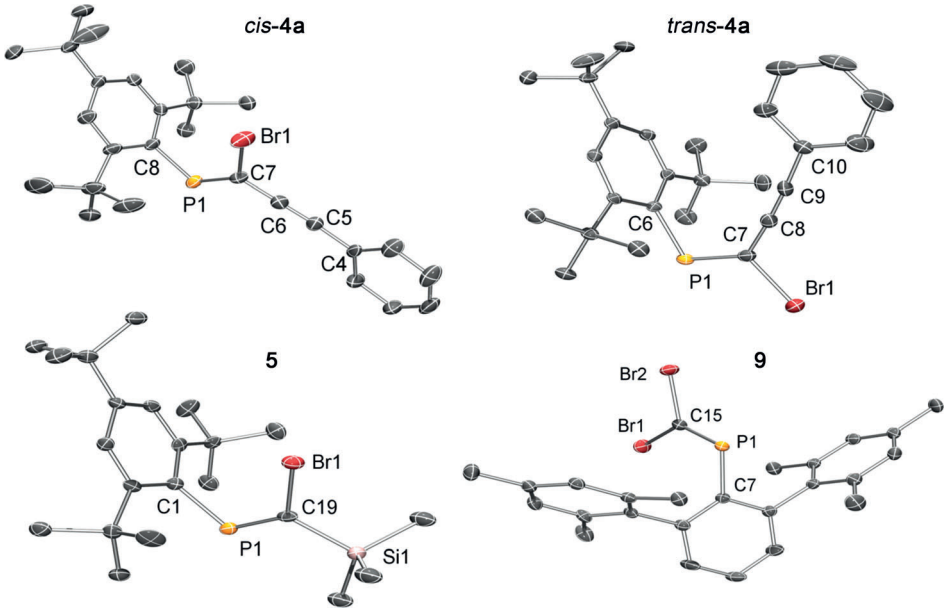


Figure 2. ORTEP representation of monobromophosphaalkenes *cis*-**4a** and *trans*-**4a** and silyl derivative **5** as well as dibromophosphaalkene **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: *cis*-**4a**: C8–P1 1.836(4), P1–C7 1.682(4), C7–C6 1.409(6), C6–C5 1.206(6); C7-P1-C8 101.92(18), C6-C7-Br1 113.2(3), P1-C7-Br1 126.0(2), P1-C7-C6 120.8(3). *trans*-**4a**: P1–C6 1.851(3), P1–C7 1.684(4), C8–C9 1.203(5); C7-P1-C6 101.57(16), P1-C7-Br1 115.1(2), P1-C7-C8 129.0(3). **5**: P1–C1 1.834(4), P1–C19 1.686(5), Br1–C19 1.924(4); C19-P1-C1 103.9(2), P1-C19-Br1 125.1(3), P1-C19-Si1 122.8(3). **9**: P1–C15 1.673(2), P1–C7 1.826(2), Br1–C15 1.878(2); Br2-C15-1.892(2), C15-P1-C7 106.36(10), P1-C15-Br1 129.76(12), P1-C15-Br2 116.36(11).

Conclusions

We have demonstrated for the first time that full stereochemical control of acetylene substituents introduced at phosphaalkenes can be obtained by choosing the correct methodology. We have developed a straightforward approach towards diacetylenic phosphaalkenes, which are interesting cross-conjugated building blocks for opto-electronic applications. The stereospecific synthesis is achieved by a sequential reaction with sulfonylacetylenes, followed by conventional Sonogashira-type reactions. By applying this novel methodology, the transition-metal-mediated Fritsch–Buttenberg–Wiechell rearrangement of dibromophosphaalkenes to phosphaalkynes can be avoided. The procedure opens new tools to synthesize and study complex heteroatomic cross-conjugated systems with a full control over their stereochemistry in the future. Electrochemical analysis of the isomeric compounds **7** and **8** clearly highlights the electronic impact of the stereochemistry at the P=C double bond that underlies the high demand for controlled synthetic methodologies.

Experimental Section

Unless otherwise stated, all reactions were carried out under an inert atmosphere of Ar or N_2 by using modified Schlenk techniques. All solvents were freshly distilled over benzophenone and metallic sodium unless otherwise specified. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride and acetonitrile from phosphorus pentoxide prior to use. The ^{1}H NMR spectra were measured in $CDCl_3$ as solvent by using a JEOL Eclipse + 400 MHz spectrometer. ^{13}C-{^{1}H} and ^{31}P-{^{1}H}-NMR spectra were measured on the same instrument operating at 100 MHz and 162 MHz, respectively. Electrochemical analysis was performed with a Pgstat Metrohm autolab in a three-electrode setup using a glassy carbon working electrode and a $Ag/AgNO_3$ reference electrode. Reported potentials are referenced externally to Fc/Fc^+.

Synthesis of aryl sulfonylacetylene 3a

Cerium ammonium nitrate (CAN, 40.25 g, 73.43 mmol, 2.5 equiv) was added to a stirred suspension of ethynylbenzene (3.00 g, 29.4 mmol), sodium-*p*-toluene sulfinate (6.28 g, 35.2 mmol, 1.2 equiv), and sodium iodide (5.26 g, 35.3 mmol, 1.2 equiv) in anhydrous acetonitrile (150 mL) at room temperature under an argon atmosphere. The reaction was monitored by TLC. After completion, the solvent was evaporated and the solid residue was re-dissolved in dichloromethane/diethyl ether, then washed with water (150 mL). The organic phases were combined and washed with $Na_2S_2O_{3(aq.)}$ (3×50 mL) followed by brine. The solvent was removed and the crude product was purified by chromatography to afforded iodophenylvinyl sulfone (6.69 g, 59% yield).[25] The iodophenylvinyl sulfone (0.34 g, 0.89 mmol) was dissolved in THF and *t*BuOK (0.93 g, 0.11 mmol, 1.05 equiv dissolved in THF) was added. The reaction was stirred for 30 min at 50 °C. The solvent was evaporated from the crude mixture and the residue was extract with dichloromethane (3×20 mL). The solution was passed through a plug of silica and re-crystallization from *n*-hexane afforded phenylsulfonylacetylene **3a** (0.18 g, 80% yield).

Synthesis of monoacetylenic phosphaalkene 4a

Dibromophosphaalkene **1** was dissolved in THF and cooled to −100 °C and treated with *n*BuLi (1.1 equiv) while maintaining the temperature between −90 °C and −110 °C for 30–45 min. A solution of sulfonylacetylene **3a** was added and the mixture was allowed to slowly reach room temperature. The solvent was evaporated and the crude mixture was extracted with dichloromethane and purified by column chromatography using hexane as the eluent. The fractions containing *cis*-**4a** were combined to give 78 mg (37%) of the analytically pure product. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50–7.52 (m, 2H, Ar), 7.43 (broad s, 2H Ar), 7.32–7.34 (m, 3H, Ar), 1.52 (s, 18H, *t*Bu), 1.34 ppm (s, 9H, *t*Bu); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.4, 151.6, 137.1 (d, $^1J_{PC}$ = 55 Hz, P=C), 133.0 (d, $^1J_{PC}$ = 45 Hz, P–C), 131.8, 129.0, 128.4, 122.4, 97.6 (d, $^3J_{PC}$ = 22 Hz, C≡C), 92.5 (d, $^2J_{PC}$ = 20 Hz, C≡C), 38.0 (*t*Bu), 35.2 (*t*Bu), 33.0 (*t*Bu), 31.4 ppm (*t*Bu); ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): δ = 291.0 ppm.

Synthesis of diacetylenic phosphaalkene 7

Phosphaalkene *cis*-**4a** (114 mg, 0.213 mmol) was dissolved in deaerated THF (10 mL). $[PdCl_2(PPh_3)_2]$ (8.6 mg, 0.012 mmol), CuI (5.6 mg, 0.024 mmol), Et_3N (5 mL), and ethynylferrocene (56.4 mg, 0.268 mmol) were added to this solution. The reaction mixture was deaerated again for 5 min. The reaction progress was followed by TLC and continued until the starting material was fully consumed. The organic phase was washed with sat. $NH_4Cl_{(aq.)}$ followed by brine. The crude product was purified by column chromatography using toluene/hexane to give **7** (50 mg, 34% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (broad s, 2H, Ar), 7.16 (m, 3H, Ar), 6.89 (d, J = 8 Hz, 2H, Ar), 4.55 (m, 2H, Fc), 4.28 (m, 2H, Fc), 4.27 (s, 5H, Fc), 1.55 (s, 18H, *t*Bu), 1.32 ppm (s, 9H, *t*Bu); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3, 150.6, 142.6 (d, $^1J_{PC}$ = 36 Hz, P–C), 135.8 (d, $^1J_{PC}$ = 57 Hz, P=C), 131.5, 129.2, 128.0, 122.3, 102.8 (d, $^3J_{PC}$ = 9 Hz, C≡C), 96.5 (d, $^3J_{PC}$ = 17 Hz, C≡C), 89.5 (d, $^2J_{PC}$ = 21 Hz, C≡C), 86.8 (d, $^2J_{PC}$ = 26 Hz, C≡C), 71.7 (Fc), 70.2 (Fc), 69.3 (Fc), 65.4 (*ipso*-Fc), 38.3 (*t*Bu), 35.2 (*t*Bu), 33.2 (*t*Bu), 31.4 ppm (*t*Bu); ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): δ = 324.4 ppm.

X-ray crystallography

CCDC 145800, 1458001, 1458002, 1458003, 1458004, 1458005, and 1458006 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

All the measurements were performed by using graphite-monochromatized $Mo_{K\alpha}$ radiation using a Bruker D8 APEX-II equipped with a CCD camera. The structures were solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/7).[26] The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries.

cis-**4a**: colorless block, 0.42×0.4×0.38 mm, monoclinic, $P2_1/c$, a = 10.5969(7) Å, b = 20.5714(15) Å, c = 11.9720(12) Å, β = 111.607(4)°, V = 2426.4(3) Å^3, ρ_{calc} = 1.285 Mg m^{-3}, $2\theta_{max}$ = 53.0°, $Mo_{K\alpha}$, 0.71073 Å, ω scans, 100(2) K, no. of reflections: 15063 (collected), 4960 (unique), 3559 ($>2\sigma$), no. of parameters/restraints: 278/0, multi-scan absorption correction (min/max transmission: 0.5690/0.7454), R_{int} = 0.0582, R = 0.0585 ($>2\sigma$), $wR2$ = 0.1655 (all).

trans-**4a**: colorless plates, 0.33×0.20×0.12 mm, monoclinic, $P2_1/n$, a = 9.1058(5) Å, b = 29.6319(18) Å, c = 9.2001(6) Å, β = 100.303(2)°, V = 2442.4(3) Å^3, ρ_{calc} = 1.277 Mg m^{-3}, $2\theta_{max}$ = 52.92°, $Mo_{K\alpha}$,

0.71073 Å, ω scans, 100(2) K, no. of reflections: 19329 (collected), 5037 (unique), 4115 ($>2\sigma$), no. of parameters/restraints: 272/0, multi-scan absorption correction (min/max transmission: 0.5558/0.7454), $R_{int}=0.0532$, $R=0.0515$ ($>2\sigma$), $wR2=0.1265$ (all).

5: colorless blocks, $0.28\times0.28\times0.25$ mm, monoclinic, $P2_1/c$, $a=9.5941(6)$ Å, $b=12.3167(8)$ Å, $c=20.3341(12)$ Å, $\beta=94.818(4)^\circ$, $V=2394.3(3)$ Å^3, $\rho_{calc}=1.277$ Mg m^{-3}, $2\theta_{max}=56.82^\circ$, $Mo_{K\alpha}$, 0.71073 Å, ω scans, 100(2) K, no. of reflections: 23232 (collected), 5989 (unique), 3630 ($>2\sigma$), no. of parameters/restraints: 226/0, multi-scan absorption correction (min/max transmission: 0.6497/0.7457), $R_{int}=0.1182$, $R=0.0625$ ($>2\sigma$), $wR2=0.1502$ (all).

9: colorless blocks, $0.33\times0.26\times0.24$ mm, monoclinic, $P2_1/c$, $a=16.1024(4)$ Å, $b=8.0504(2)$ Å, $c=17.3598(4)$ Å, $\beta=92.5520(10)^\circ$, $V=2248.13(9)$ Å^3, $\rho_{calc}=1.525$ Mg m^{-3}, $2\theta_{max}=61.48^\circ$, $Mo_{K\alpha}$, 0.71073 Å, ω scans, 100(2) K, no. of reflections: 48584 (collected), 5037 (unique), 4115 ($>2\sigma$), no. of parameters/restraints: 272/0, multi-scan absorption correction (min/max transmission: 0.5558/0.7454), $R_{int}=0.0515$, $R=0.0515$ ($>2\sigma$), $wR2=0.1265$ (all).

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Keywords: alkynylation · cross-conjugation · phosphaalkenes · Sonogashira coupling · sulfonyl coupling

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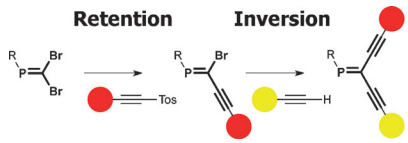

Phosphaalkene C_{sp2}-C_{sp} coupling

* Full stereocontrol
* Good yield

Step by step: Diacetylenic phosphaalkenes were obtained from dibromophosphaalkenes in a sequential stepwise manner; the first step is a direct reaction with sulfonylacetylenes with retention of stereochemistry, this is followed by a transition-metal-catalyzed second step that proceeds with stereochemical inversion (see scheme).

Phosphaalkene Synthesis

M. A. Shameem, K. Esfandiarfard, E. Öberg, S. Ott, A. Orthaber**

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Direct, Sequential, and Stereoselective Alkynylation of *C,C*-Dibromophosphaalkenes