Chemistry Europe
European Chemical Societies Publishing

WILEY VCH

Excellence in Chemistry Research

Announcing our new flagship journal

- Gold Open Access
- Publishing charges waived
- Preprints welcome
- Edited by active scientists

Meet the Editors of *ChemistryEurope*

Luisa De Cola
Università degli Studi di Milano Statale, Italy

Ive Hermans
University of Wisconsin-Madison, USA

Ken Tanaka
Tokyo Institute of Technology, Japan

Research Article
doi.org/10.1002/cplu.202300054

Chemistry Europe
European Chemical Societies Publishing

www.chempluschem.org

Special Collection

1-Phospha-Butadienes and 1H-Phospholes via Alkynylation of Acetylenic Phosphaalkenes

Muhammad Anwar Shameem,[a] Arvind Kumar Gupta,[a] Mate Erdelyi,[b] and Andreas Orthaber*[a]

This work is dedicated to Prof. Dietrich Gudat on occasion of his retirement.

Carbon-rich motifs are important building blocks for the fabrication of functional and opto-electronic materials. Electronic tuning can be achieved by alteration of bonding topologies but also via incorporation of heteroelements, for example phosphorus. Herein we present the palladium/copper mediated formation of branched 1-phospha-butadiene derivatives through an unusual alkynylation of a phospha-enyne fragment. Structural and NMR studies provide mechanistic insights into this alkynylation. Furthermore, we disclose a complex cyclisation of the thus obtained 3-yne-1-phosphabutadiene motifs to give highly substituted phosphole derivatives identified by 2D NMR and SC-XRD analysis.

Introduction

The exploration of linearly and cross-conjugated motifs in which alkene and alkyne fragments are combined has led to a large variety of carbon-rich compounds with different bonding topologies introducing a large variation of their electronic and optical properties (Figure 1: **A**–**D**).[1] Different applications ranging from single molecule conductors,[2] conductivity switches,[3] and as building blocks for highly conjugated and fused (hetero-)aromatic systems[4] have been explored in the past decades. The combination of different bonding topologies, 2- and 3-dimensionally conjugated frameworks,[5] as well as introduction of electron-withdrawing and -accepting units have been fundamentally successful approaches to tailor the electronic properties towards low "band-gap" materials.[6] Recently, the incorporation of heteroelements into the conjugated backbone has proven a viable alternative to achieve specific HOMO/LUMO tailoring[7] and responsive materials.[8] Examples of this approach are the heavier group 15 hetero-alkenes in which one or multiple carbene fragments are substituted by isolobal pnictene (e.g. R–P:)[9] unit leading to fascinating conjugated main group materials with stabilized LUMO levels, i.e. acceptor materials. Similarly, the use of λ^3-phospholes (**J**–**L**, where Z = lone pair), and their oxides (**J**–**L**, where Z=O) provide a unique opportunity for tailoring acceptor materials[10] that incorporate an sp^3 hybridized, i.e. non-planar, center as integral part of the conjugated framework.[8a,11] Despite the simplicity of this building block, specific substitution and fusion patterns allowed to diversify the opto-electronic properties and expand towards various application as sensors and memory materials.[12]

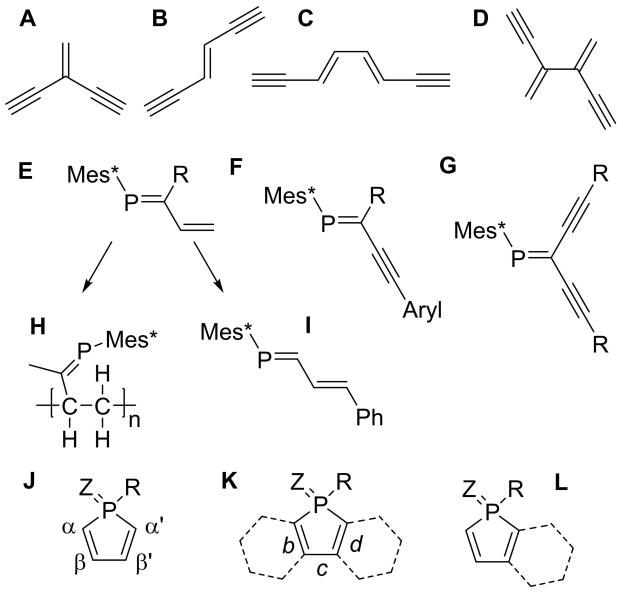


Figure 1. Different bonding topologies of all-carbon ene-diyne and diene-diyne motifs (**A**–**D**). Phosphaalkenes with conjugated vinylic (**E**, **I**) and acetylenic substituents (**F**, **G**). Phosphaalkene containing polymer (**H**) obtained via anionic polymerization of **E**. Substituted and fused phospholes (**J**–**L** for Z = lone pair, O, S, …)

[a] Dr. M. Anwar Shameem, Dr. A. Kumar Gupta, Prof. A. Orthaber
Department of Chemistry – Ångström Laboratories. Synthetic Molecular Chemistry.
Uppsala University.
BOX 523
75120 Uppsala (Sweden)
E-mail: andreas.orthaber@kemi.uu.se
[b] Prof. M. Erdelyi
Department of Chemistry – BMC
Uppsala University,
BOX 576
751 23 Uppsala (Sweden)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cplu.202300054

Special Collection *Part of a Special Collection: "From Light to Heavy: Advancing the Chemistry of Pnictogen Compounds"*

Previous synthetic routes towards phosphoros containing 1,3-butadiene system, i.e. 1-phosphabutadiene, led to low yields of isolated materials due to their intrinsic instability and the tendency towards polymerization.[13] Recently, Gates et al. reported the controlled anionic polymerization of such a 1-phospha-1,3-butadiene (**E**), in which the reaction predominantly takes place through the C=C unit providing a phosphorus analogue of natural rubber with an intact phosphaalkene motif, i.e. a $\lambda^2\sigma^3$-phosphorus center (**H**).[14]

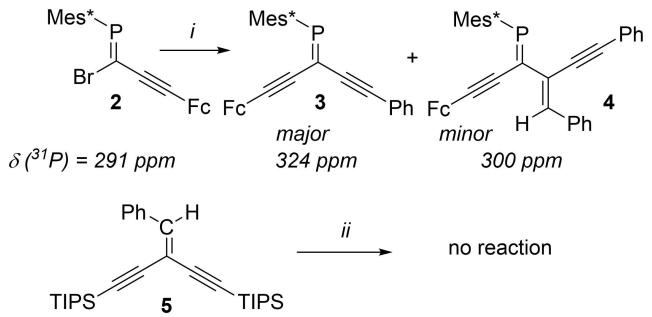
In our previously reported synthesis of (di-)acetylenic phosphaalkenes (**F**, **G**),[15] we observed during prolonged reaction times, excess of catalyst and acetylene reagent the formation of a minor side product characterized by shielded resonances in the ^{31}P NMR, which remained elusive at that time. (Scheme 1) In this work, we elaborate on the formation of this side product, the substrate scope of this unprecedented reactivity, and follow-up chemistry to give highly substituted phosphole (oxides) as valuable molecular building blocks for opto-electronic materials. Furthermore, we provide a mechanistic picture that elucidates the alkynylation leading to 3-yne-1-phosphabutadiene motifs, and the nucleophile induced cyclisation affording substituted and fused phospholes.

Results and Discussion

Alkynylation of (di-)acetylenic phosphaalkenes

In order to elucidate the nature of this previously unidentified side product we systematically investigated the Sonogashira coupling of in situ prepared **2** with excesses of phenyl acetylene and (co-) catalysts (CuI, and $[PdCl_2(PPh_3)_2]$). Optimized conditions indeed directed the synthesis towards the side product **4** with its characteristic ^{31}P NMR chemical shift at 300.0 ppm. Besides the known *C,C*-diacteylenic phosphaalkene **3** – present as the major product (31 % isolated yield) – with a ^{31}P NMR resonance of 324 ppm, chromatographic purification of the reaction mixture yielded analytically pure compound **4** (13 % isolated yield). The upfield shift of 24 ppm suggested a significant alteration of the conjugated framework, and bears similarities with other extended conjugated frameworks containing phosphaalkenes.[16]

Orange crystals of **4** suitable for single crystal X-ray diffraction were obtained by crystallization from a pentane/acetonitrile solvent mixture. The molecular structure reveals the formation of a 1-phospha-1,3-butadiene-2,3-diyne structure with a typical phosphaalkene distance (P1-C19: 1.7018(19) Å) in extended conjugated systems.[16–17] In agreement with previous findings,[15] the ferrocenylacetylene fragment is in *cis*-arranged with respect to the Mes* substituent on the phosphaalkene. The newly formed 1-phospha-1,3-butadiene fragment is almost planar (maximum deviation from the least squares plane spanned by P1, C19, C32, and C41: 0.064(2) Å). The two acetylenic fragments attach at C19 (ferrocenyl acetylene) and C32 (phenylacetylene) in the 1-phospha-butadiene-2,3-diyne motif. The former C_2-fragment is only slightly twisted out of the least squares plane, by 0.167(2) and −0.163(2) Å, while the latter deviates by 0.258(2) and–0.477(2) Å from coplanarity from the *phospha*-butadiene plane. Extension of the conjugation between the central fragment and the external phenyl rings is slightly broken by a twist of 10.20(8)° and 33.73(8)° but totally distorted with respect to the ferrocenyl unit (89.54(9)°). The angles around the phosphaalkene show the larger impact of the heteroatoms lone pair resulting in a C1-P1-C19 angle of close to 100°. The angles at the C-terminus (C19) are 123.20(15) and 119.46(14)°, towards the *cis* and *trans* substituent, respectively, showing the slight deviation from an ideally sp^2 hybridized carbon C19. (Figure 2)



Scheme 1. Conversion of monoacetylenic phosphaalkene **2** into the diacetylenic phosphaalkene **3** (32 % yield) and formation of the 2,3-diyne-1-phospha-1,3-butadiene derivative **4** (14 % yield). Attempted conversion of all carbon ene-diyne **5**. i) THF, NEt_3, 5 mol % $[PdCl_2(PPh_3)_2]$, 10 mol % CuI. Ph-CCH (xs.) ii) THF, NEt_3, 5 mol % $[PdCl_2(PPh_3)_2]$, 10 mol % CuI. Ph-CCH (xs.), 70 °C, 30 h. For further experimental details, see the Supporting Information.

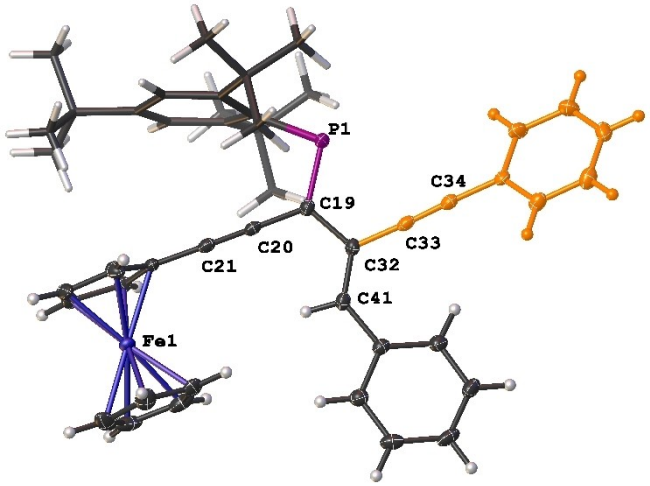


Figure 2. ORTEP[18] representation of the solid state structure of **4** (thermal ellipsoids plotted at a probability level of 50 %). The part of the molecule originating from the phenyl acetylene reagent is highlighted in orange. Selected parameters (distances [Å], angles [°]): P1-C19 1.7018(19), P1-C1 1.847(2), C20-C19 1.423(3), C21-C20 1.203(3), C32-C19 1.481(3), C32-C33 1.436(3), C33-C34 1.195(3), C41-C32 1.349(3), C19-P1-C1 99.35(9).

Mechanistic studies towards the formation of the 2,3-diyl-1-phospha-1,3-butadiene framework

With this addition of an acetylenic fragment to give a 2,3-diyl-1-phospha-1,3-butadiene framework we decided to investigate why this product is formed and whether the synthesis could be directed towards the highly conjugated and unusually branched systems. As this product seems to originate from the addition of a third acetylenic fragment to the diacteylenic phosphaalkene we conducted further experiments with *C,C*-ene-diyne substrates. In order to substantiate the role of the heteroelement, we started from an analogous carbon-based compound **5** and subjected this substrate to reaction conditions similar to those used during the formation of **4**. However, the all-carbon-diacetylenic system **5** showed no additional reactivity and even after heating the reaction mixture at 70 °C for 30 h only unreacted starting material was recovered. However, the alkynylation is reminiscent of an observed alkynyl addition to all carbon ene/yne fragments with donor sites (N, or O) facilitating the process.[19] Despite a lack of a mechanistic proposal, similarities of reaction conditions and the observed stereo- and regio-selectivity suggest an analogous mechanism in the formation of these carbon diene-yne derivatives. Similarly, Pd-mediated C–H activation in ethene fragments using directing groups has been achieved illustrating the necessity of heteroelement donor sites (Figure 3 iii).[20]

In order to corroborate the role of the phosphaalkene unit we studied the stoichiometric reaction of diacetylenic phosphaalkene **3** (dissolved in THF-d^8) with a Pd(0) source, i.e. [Pd(PPh$_3$)$_4$]; immediately after addition, a change to a dark brown colored solution was observed. Formation of a new species **6**, was concluded from the ^{31}P NMR data; a triplet at 306.0 ppm (**A**: $^3J_{PP}$ = 228 Hz), and a doublet at 23.6 ppm (**B**: $^3J_{PP}$ = 228 Hz) indicate coordination of the phosphaalkene to a Pd(PPh$_3$)$_2$ fragment. Additionally, appearance of a singlet at 24.1 ppm confirms the release of triphenylphosphine from the Pd-precursor (Figure 3 ii). Notably, both triphenyl phosphine ligands are chemically equivalent on NMR time-scales, however the significant line broadening indicates hindered exchange within this coordination compound. We hypothesize that a partial coordination/interaction of the triple bond with the metal center establishes a quasi-square planar coordination environment, however no crystallographic proof of this intermediate could be obtained. Full conversion to the Pd-complex was observed after 24 h. Addition of the phenylacetylene reagent caused no reaction. However, when triethylamine and one equiv. of CuI iodide was added and the mixture was stirred for 2 h at r.t., we observed moderate conversion to the previously observed addition product **4**. Hence, these investigations using stoichiometric conditions clearly suggest that Cu and Pd react in concert. We hypothesize that NEt$_3$ deprotonation results in in situ formation of a copper acetylide, which adds to the triple bond of the Pd-coordinated intermediate **6** shown in Figure 3 ultimately giving product **4** upon protonation.

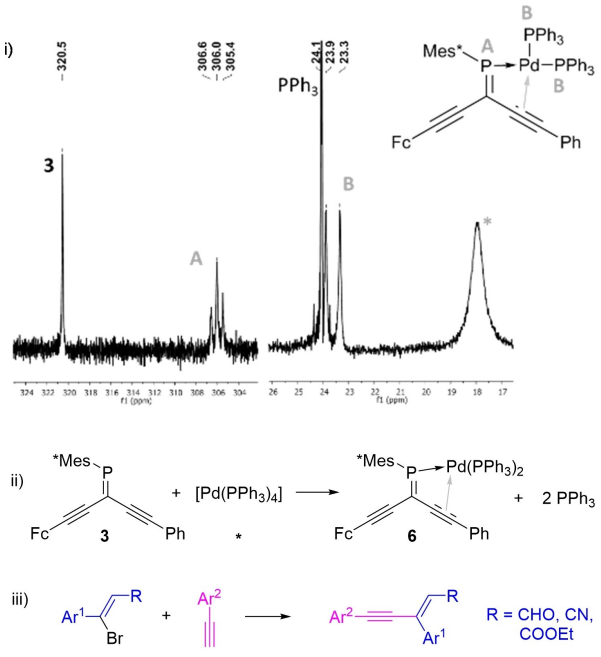


Figure 3. i) ^{31}P NMR coordination studies of **3** towards [Pd(PPh$_3$)$_4$]. The shielded triplet (**A**: 306 ppm) is assigned to the coordination of **3** to a Pd(PPh$_3$)$_2$ fragment. **B**: doublet at 23.6 ppm indicating 2 equivalent diphenylphosphine moieties and liberation of PPh$_3$.* indicates unreacted of [Pd(PPh$_3$)$_4$]. ii) reaction of equimolar amounts of **3** and [Pd(PPh$_3$)$_4$] in THF-d^8. iii) Reported alkynylation of bromo-alkenes having O or N donor donor atoms.[19a]

The alkynylation of monoacetylenic phosphaalkenes

Having established the key reagents for this reaction, we set out to explore the reactivity of monoacetylenic phosphaalkenes Mes*P=C(CH$_3$)CCR (**7**)[16] towards such an alkynylation (Figure 4 top). We wanted to investigate if the scope of this reaction

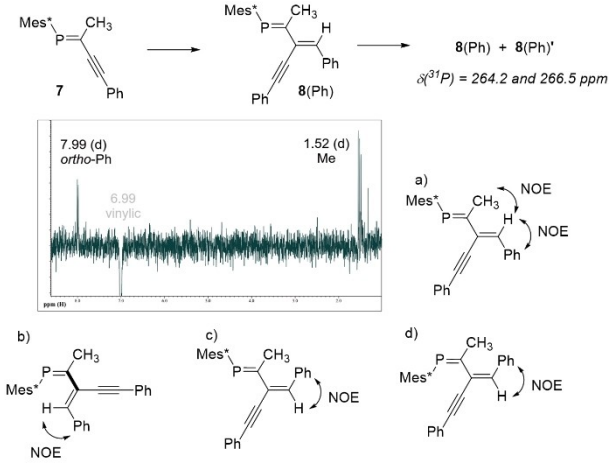


Figure 4. 1D-NOE experiment of compound **8**(Ph) and possible isomers of **8′**(Ph) (b, c, d). Possible stereoisomers originating from P=C (*b*), C=C (*c*) isomerization and simultaneous P=C and C=C isomerization (*d*). The arrows indicate the expected NOE correlations in these different isomers. Restricted rotation about the single bond (bold) in b) could explain the absence of an observable NOE between the vinylic and methyl protons. Formation of **8**(Ph) and **8′**(Ph)

depends on both substituents at the C-terminus of the phosphaalkene and whether it would be possible to use catalytic conditions to form the 1-phosphabutadiene motif starting from acetylenic phosphaalkenes. Thus monoacetylenic phosphaalkene **7** was reacted with 1 equiv. of phenylacetylene in the presence of 5 mol% $[Pd(PPh_3)_2Cl_2]$, 10 mol% CuI, 1 mL of Et_3N in 50 mL THF. The reaction progress was followed by ^{31}P NMR spectroscopy. After 12 h heating in a sealed Schlenk flask at 75 °C the reaction showed almost 40% conversion to the target compound (**8**(Ph)). This reaction mixture was then loaded with additional 5 mol% of the $[Pd(PPh_3)_2Cl_2]$ catalyst and additionally 1 equiv. of phenylacetylene. After 5 h at 75 °C conversion was estimated by ^{31}P NMR measurements to be 60%. In order to achieve quantitative conversion, the reaction mixture was loaded with further $[Pd(PPh_3)_2Cl_2]$ and continued to stir for additional 14 h at the same temperature, totally adding 20 mol% of the palladium catalyst. Conversely, omitting the Pd catalyst precludes any conversion even at elevated temperatures and extended reaction times. From the above experimental results, we postulate that both Cu(I) and Pd(I) are required in catalytic amounts, albeit relatively high Pd-catalysts loadings were needed to achieve high conversions.

Isomerization of the 1-phosphabutadiene fragment

Ultimately, phosphaalkene **8**(Ph) was purified by flash column chromatography on silica using *n*-pentane as eluent. The purified fraction was dissolved in deuterated benzene and NMR data analysis showed a single compound (**8**(Ph)) with a characteristic ^{31}P NMR chemical shift at 264.2 ppm. Surprisingly, the compound slowly isomerized and/or rearranged to a secondary product with ^{31}P NMR resonances in the same region if exposed to light and silica for a longer period (see Supporting Information). This additional species (**8′**(Ph)) with a single ^{31}P NMR resonance at 266.5 ppm could be separated chromatographically. Further spectroscopic data of this isolated species indicate only a minor structural change, such as a double bond isomerization, nonetheless thermal interconversion between compound **8**(Ph) and **8′**(Ph) could be excluded by variable temperature (VT−)NMR studies. Selective 1D-NOE experiments of both isomers have been performed. **8**(Ph) displays a clear NOE between the P=C methyl group with the vinylic protons and the *ortho* protons of the geminal phenyl ring. This observation is consistent with the structure a) drawn in Figure 4, and matches the arrangement of substituents observed of the crystallographically characterized phosphaalkene **4**. In contrast, in a series of 1-D NOE experiments of **8′**(Ph) only through space correlation of the vinylic proton and its geminal phenyl substituent could be detected. Together with the similar ^{31}P NMR shift ($\Delta\delta = 2.5$ ppm) we concluded that isomer **8′**(Ph) could be associated with a P=C isomerization (Figure 4 b) together with a restricted C–C bond rotation owing to efficient delocalisation and/or effects of the sterically demanding substituents. Alternatively isomers associated with a C=C isomerization (Figure 4c), or both P=C and C=C isomerization (Figure 4d) could explain be observed NOE.

Exploring the substrate scope. We tested the reactivity of acetylenic phosphaalkene towards other alkynyls, including alkyl, heteroaryl and silyl substituted derivatives. Based on analysis of crude ^{31}P NMR spectra of crude reaction mixtures of **7** with cyclohexyl (cyc) and 2-thienyl (thie) acetylene under the previously optimized conditions only indicates trace amounts of the target alkynylation products **8**(cyc) and **8**(thie), respectively. Further studies regarding silyl-substituted derivatives **8**(R) (for R=TMS, and TIPS) where not formed based on ^{31}P NMR analysis of the crude reactions.

To further explore the scope of this reaction the extended acetylenic phosphaalkene **9a**, **b** were prepared. Compound **9a** could also be characterized crystallographically showing the expected stereochemistry and unexceptional bond metrics (Figure 5). Its reaction with phenyl acetylene gave the alkynylation product **10a**, **b** as a minor component in a complex mixture of products, which could not be separated. (see below for further reactivity)

Cyclisation of 3-yne-1-phospha-butadiene to substituted phospholes

Depending on the electronic and steric nature of the substituents the 3-yne-1-phosphabutadiene derivative can be isolated or is only observed as an intermediate. In some cases, the presence of this species can only be postulated based on the subsequently identified products. We observe that compound **8**(Ph) (also in a mixture with the isomerized **8′**(Ph)) slowly re-arranges on silica gel and in halogenated solvents to a mixture of species with shielded signals in the ^{31}P NMR (3.0, 2.4, 1.8 ppm). Isolation and careful analysis of 2D NMR data of the reaction product with a ^{31}P NMR resonance at 3.0 ppm indicates that a highly substituted phosphole derivative **11**(Ph) is formed

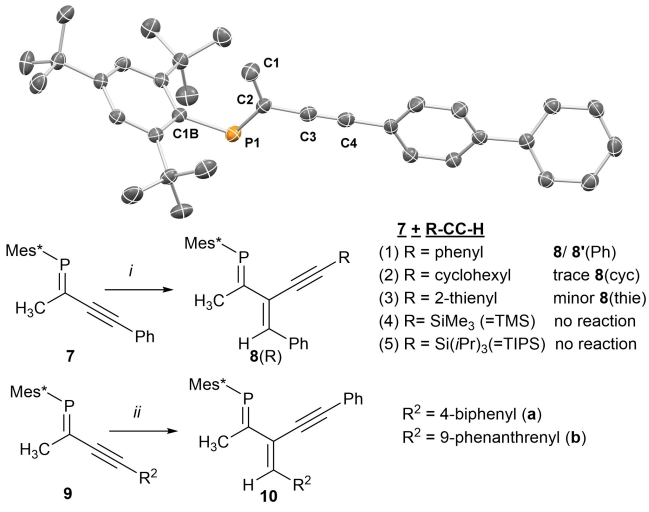
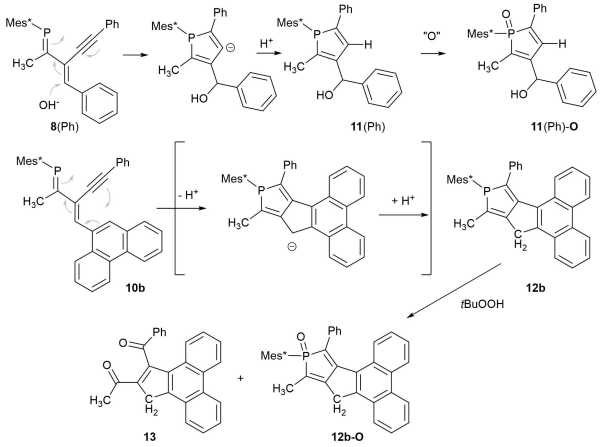


Figure 5. Top: ORTEP representation of **9a** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: P1-C2 1.683(3), C2-C3 1.425(3), C3-C4 1.203(3), P1-C2-C1 128.58(19), C2-C3-C4 176.9(3). Bottom: attempted reactions of monoacetylenic phosphaalkenes with terminal alkynyls. *Conditions:* i) $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, THF, 75 °C, 2 days. ii) THF, NEt_3, pyridine, $[PdCl_2(PPh_3)_2]$, CuI.

possibly via a nucleophile-induced cyclisation (Scheme 2). Interestingly, a recent report discloses two competing pathways of 1,4- and 1,3- nucleophilic ring closure reactions to give phosphole and phosphete products, respectively.[21] Although we were unable to confirm formation phosphetes it is highly likely that a similar mechanism governs cyclisation of **8**(Ph).

Alternate structures such as an 1,2-oxaphosphole motif have been ruled out based on spectroscopic data. The observed reactivity corresponds to the favorable 1,5-endo-dig cyclisation. Alternate routes to phospholes have recently been reported through Lewis acid mediated rearrangements of acetylenes,[22] intramolecular Friedel–Crafts reactions,[23] intramolecular C–H insertion of a phosphinidene,[24] illustrating the interest in new synthetic methods towards phosphole motifs. Further experimental evidence for the phosphole formation is obtained by X-ray diffraction analysis of the corresponding phosphole oxide (**11**(Ph)-O, Figure 6). Single crystals were obtained by slow evaporation from a benzene-d_6 solution under ambient conditions. The compound crystalizes as a benzene solvate in the triclinic space group *P-1* (No. 2) with one molecule in the asymmetric unit. As expected from the 2D NMR analysis the benzylic position (C12) carries a hydroxy substituent. The phosphole ring is essentially planar, but displays longer (1.868(4) Å) and shorter 1.813(3) Å) bonds for P1–C1 and P1–C5, respectively. The PO bond length of 1.493(2) Å is slightly longer compared to other phosphole oxides (typically ranging from 1.470 to 1.486 Å).[25] A notable feature of this structure is the extreme distortion of the Mes*C_{ipso}-P bond single bond being twisted out of the aromatic plane by 51.3°. Similar distortions have been previously observed for a variety of phospholes and phosphole oxide with sterically demanding aryl substituents.[26] The steric crowding and rigid geometry are consistent with the two distinct sharp signals in the ^{1}H NMR spectra assigned to the 2- and 6-ortho-*tert*-butyl groups.

When **9b** was reacted with phenyl acetylene no ^{31}P NMR resonance associated with the formation of the alkynylation product could be observed in the crude reaction mixture, but only one species with a resonance of ca. 23 ppm was detected. Upon oxidation with *t*BuOOH and chromatographic workup two new species with ^{31}P NMR resonances of ca. 43 and 65 ppm are formed. Small amounts of a phosphole oxide **12b**-O crystallized from one of the isolated fractions. Despite only moderate crystal quality the solid state-structure of **12b**-O could be elucidated (Figure 7). Crystallographic analysis revealed that instead of the hydroxy-attack the pendant phenanthrene (C6) might capture a reactive nucleophile or trigger the cyclisation giving a phosphole annulated to a 2H-cyclopenta[l] phenanthrene core. Notably, the phosphole oxide part is partially disordered and the Mes*-substituent is



Scheme 2. Proposed rearrangement of **8**(Ph) and **10b** into phosphole derivatives **11** and **12b**, respectively. Further oxidation to **11**-O and **12b**-O indicates the isolated products of this sequence.

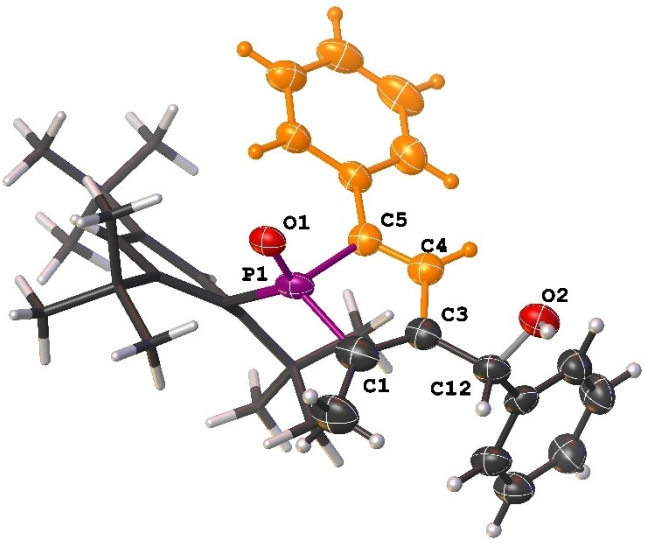


Figure 6. ORTEP[18] representation of **11**(Ph)-O with thermal ellipsoids at a probability level of 50%. The Mes* group is represented as a stick model for clarity. The part of the molecule originating from phenyl acetylene is highlighted in orange. The benzene solvent molecule is omitted. Selected parameters (distances [Å], angles [°]): P1-O1 1.493(2), P1-C5 1.813(3), P1-C19 1.848(4), P1-C1-1.868(4), C1-C3 1.344(5), C1-C2 1.481(5), C3-C4 1.483(5), C4-C5 1.328(5), C5-P1-C1 91.73(16).

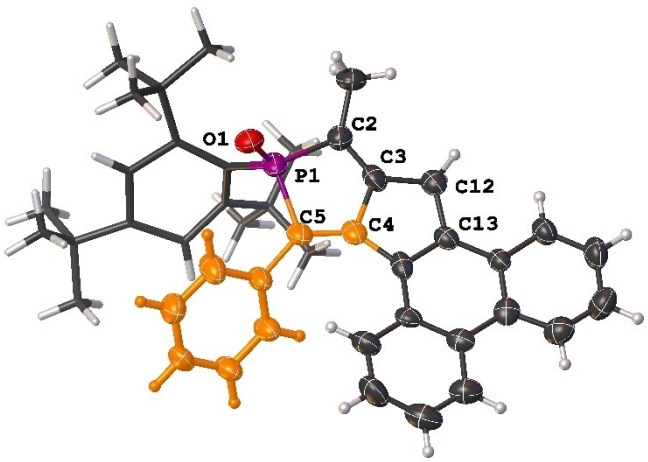


Figure 7. ORTEP[18] representation **12b**-O The part of the molecule originating from phenyl acetylene is highlighted in orange. The benzene solvate is omitted for clarity. Selected parameters (distances [Å]): P1-O1 1.493(2), P1-C(Mes*) 1.849(4), P1-C5 1.813(3), P1-C2 1.868(4), C4-C51.344(5), C2-C3 1.328(5).

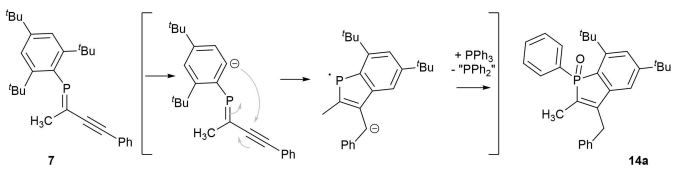
highly distorted, putting substantial strain on the phosphole moiety. In line with that we have also crystallographically identified an oxidative decomposition product of this phosphole, in which the Mes*P=O moiety was eliminated and the P–C bonds were oxidized to ketones (see Supporting Information for structural information). Notably Naka and co-workers recently reported a systematic study on that oxidative cleavage in arsoles, indicating that ring strain plays a significant role in the stability of these five-membered heterocycles.[27] Although the phosphaalkene alkynylation product **10b** could not be identified during this reaction, these crystallographically identified products clearly support the idea that similar alkynylation must precede the cyclisation steps.

Cyclisation of acetylenic phosphaalkenes under the loss of a ^{t}Bu moiety

A different reactivity was seen, when **7**(Ph) was reacted in the presence of 1-ethynyl naphthalene. Formation of **8**(naphthyl) was initially postulated based on the appearance of a new ^{31}P NMR resonance at 265.9 ppm and gradually disappearance of the starting material. At this point the initial observed formation of **8**(naphtyl) remains speculative as insufficient amounts of this product could be made precluding isolation of the product. Extended reaction times and additional catalyst loadings however led to the appearance of a new species with a ^{31}P-resonance of ca. 4 ppm, which upon oxidation with *t*-BuOOH shifted to 42.7 ppm. Chromatographic work-up allowed us to isolate **14a** (besides triphenyl phosphine oxide). Mass spectrometry indicates that the ethynyl-naphthalene moiety was not incorporated and the loss of a tert-Bu group. Detailed 2D NMR analysis of the data clearly supports these findings and suggest the loss of a meta-*tert*-Bu group concomitant with cyclisation to a benzannulated phosphole (phosphindole) ring. A related *tert*-Bu loss of Mes*PHLi in the presence of tolane and formation of a phosphindolyl anion has been observed previously.[28] Despite several efforts we were unable to obtain single crystal to unambiguously support this assignment (Scheme 3).

Conclusion

We report the Cu/Pd mediated alkynylation of *C*-acetylenic phosphaalkenes to give alkynylated 1-phospha-butadiene motifs. Mechanistic studies reveal that a phosphaalkene-coordinated Pd-fragment could activate the *C*-alkynyl substituent facilitating its alkynylationto a 3-alkynyl 1-phospha-butadiene. Exposure of these hetero-butadienes to light and silica gel can trigger double bond isomerisation and further cyclisation to give highly substituted phosphole derivatives. These different paths, albeit highly substrate specific, are new entries towards complex motifs incorporating phosphorus units in unusual bonding environments and extended conjugated systems. Further efforts to exploit this unusual reactivity for the preparation and study of phosphorus doped carbon-rich opto-electronic materials is underway.



Scheme 3. Proposed cyclisation of **7** giving **14a**.

Experimental Section

Compound **7** (0.781 mmol, 0.316 g) and dichlorido bis-(triphenylphenylphosphine) palladium(II) (0.1 mmol, 54.8 mg) was charged into a Schlenk flask followed by addition of 25 mL of pre degas THF. To this yellow suspension was then added CuI (0.5 mmol, 74 mg) and 1 mL of Et_3N followed by addition of phenylacetylene (0.82 mmol, 84 mg, 0.091 mL) degas the resultant mixture immediately. The Schlenk was sealed and stirred at 75 °C overnight and reaction progress was monitor by ^{31}P NMR showed a new peak at 264.9 ppm chemical shift with approx. 40% conversion. To this reaction mixture was then added additional $Pd[PPh_3]_2Cl_2$ (5 mol%) catalyst, 1 equiv. of phenylacetylene and let it stirred at 75 °C for 5 h. This time ^{31}P NMR analysis revealed 60% of conversion to the target compound. Finally another 10 mol% addition of $Pd[PPh_3]_2Cl_2$ as the catalyst and stirred at 75 °C for next 14 h giving full conversion. The solvent was evaporated from the reaction mixture and the resultant crude was purified using silica gel and *n*-pentane as eluent giving **8**(Ph) in modest isolated yields (30%).

Deposition Numbers 1826843 (for **4**), 2237084 (for **9a**), 2237086 (for 11(**Ph**)-O), 2237087 (for **12b**-O), 2237085 (for **13**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

The authors would like to thank the Swedish research council (Vetenskapsrådet) the Olle-Engkvist foundation and the Carl-Trygger foundation for their financial support. This study made use of the NMR Uppsala infrastructure, which is funded by the Department of Chemistry – BMC and the Disciplinary Domain of Medicine and Pharmacy.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: acetylenic phosphaalkenes · alkynylation · phosphole · π-conjugation · Sonogashira coupling

[1] a) W. A. Chalifoux, R. R. Tykwinski, *Nat. Chem.* **2010**, *2*, 967–971; b) M. Gholami, M. N. Chaur, M. Wilde, M. J. Ferguson, R. McDonald, L. Echegoyen, R. R. Tykwinski, *Chem. Commun.* **2009**, 3038–3040; c) Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1999**, *121*, 458–459; d) M. D. Kilde, A. H. Murray, C. L. Andersen, F. E. Storm, K. Schmidt, A. Kadziola, K. V. Mikkelsen, F. Hampel, O. Hammerich, R. R. Tykwinski, M. B. Nielsen, *Nat. Commun.* **2019**, *10*, 3714; e) M. M. Haley, R. R. Tykwinski, *Carbon-rich compounds: from molecules to materials*, Wiley-VCH Verlag, Weinheim, **2006**, 663 pages, ISBN: 978-3-527-60724-2; f) J. Gu, W. Wu, T. Stuyver, D. Danovich, R. Hoffmann, Y. Tsuji, S. Shaik, *J. Am. Chem. Soc.* **2019**, *141*, 6030–6047.

[2] a) J. Lykkebo, A. Gagliardi, A. Pecchia, G. C. Solomon, *ACS Nano* **2013**, *7*, 9183–9194; b) G. C. Solomon, D. Q. Andrews, R. H. Goldsmith, T. Hansen, M. R. Wasielewski, R. P. Van Duyne, M. A. Ratner, *J. Am. Chem. Soc.* **2008**, *130*, 17301–17308; c) X. Li, Z. Tan, X. Huang, J. Bai, J. Liu, W. Hong, *J. Mater. Chem. C* **2019**, *7*, 12790–12808.

[3] a) H. Löfas, A. Orthaber, B. O. Jahn, A. M. Rouf, A. Grigoriev, S. Ott, R. Ahuja, H. Ottosson, *J. Phys. Chem. C* **2013**, *117*, 10909–10918; b) D. Q. Andrews, G. C. Solomon, R. P. Van Duyne, M. A. Ratner, *J. Am. Chem. Soc.* **2008**, *130*, 17309–17319.

[4] a) A. J. Boydston, M. M. Haley, R. V. Williams, J. R. Armantrout, *J. Org. Chem.* **2002**, *67*, 8812–8819; b) M. Gholami, S. Ramsaywack, M. N. Chaur, A. H. Murray, R. McDonald, M. J. Ferguson, L. Echegoyen, R. R. Tykwinski, *Chem. Eur. J.* **2013**, *19*, 15120–15132.

[5] a) S. Jinnai, Y. Ie, Y. Kashimoto, H. Yoshida, M. Karakawa, Y. Aso, *J. Mater. Chem. A* **2017**, *5*, 3932–3938; b) F. Schlütter, F. Rossel, M. Kivala, V. Enkelmann, J.-P. Gisselbrecht, P. Ruffieux, R. Fasel, K. Müllen, *J. Am. Chem. Soc.* **2013**, *135*, 4550–4557.

[6] M. Kivala, F. Diederich, *Acc. Chem. Res.* **2008**, *42*, 235–248.

[7] a) A. M. Priegert, B. W. Rawe, S. C. Serin, D. P. Gates, *Chem. Soc. Rev.* **2016**, *45*, 922–953; b) M. A. Shameem, A. Orthaber, *Chem. Eur. J.* **2016**, *22*, 10718–10735; c) M. Stolar, T. Baumgartner, *Chem. Asian J.* **2014**, *9*, 1212–1225; d) J. P. Green, J. A. L. Wells, A. Orthaber, *Dalton Trans.* **2019**, *48*, 4460–4466; e) S. M. Parke, M. P. Boone, E. Rivard, *Chem. Commun.* **2016**, *52*, 9485–9505.

[8] a) C. Reus, T. Baumgartner, *Dalton Trans.* **2016**, *45*, 1850–1855; b) F. Vidal, F. Jäkle, *Angew. Chem. Int. Ed.* **2019**, *58*, 5846–5870; *Angew. Chem.* **2019**, *131*, 5904–5929; c) M. Stolar, T. Baumgartner, *Chem. Commun.* **2018**, *54*, 3311–3322.

[9] a) D. Morales Salazar, E. Mijangos, S. Pullen, M. Gao, A. Orthaber, *Chem. Commun.* **2017**, *53*, 1120–1123; b) A. El Nahhas, M. A. Shameem, P. Chabera, J. Uhlig, A. Orthaber, *Chem. Eur. J.* **2017**, *23*, 5673–5677; c) D. Miesel, M. Korb, A. Hildebrandt, H. Lang, *Inorg. Chim. Acta* **2018**, *471*, 741–745; d) H. Miyake, T. Sasamori, N. Tokitoh, *Angew. Chem. Int. Ed.* **2012**, *51*, 3458–3461; *Angew. Chem.* **2012**, *124*, 3514–3517; e) Y. Fang, L. Zhang, C. Cheng, Y. Zhao, M. Abe, G. Tan, X. Wang, *Chem. Eur. J.* **2018**, *24*, 3156–3160; f) G. Tan, S. Li, S. Chen, Y. Sui, Y. Zhao, X. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 6735–6738.

[10] a) N. Yoshikai, M. Santra, B. Wu, *Organometallics* **2017**, *36*, 2637–2645; b) P.-A. Bouit, A. Escande, R. Szűcs, D. Szieberth, C. Lescop, L. Nyulászi, M. Hissler, R. Réau, *J. Am. Chem. Soc.* **2012**, *134*, 6524–6527.

[11] a) Z. Wang, N. Asok, J. Gaffen, Y. Gottlieb, W. Bi, C. Gendy, R. Dobrovetsky, T. Baumgartner, *Chem* **2018**, *4*, 2628–2643; b) S. Y.-L. Leung, S. Evariste, C. Lescop, M. Hissler, V. W.-W. Yam, *Chem. Sci.* **2017**, *8*, 4264–4273.

[12] a) E. Y.-H. Hong, C.-T. Poon, V. W.-W. Yam, *J. Am. Chem. Soc.* **2016**, *138*, 6368–6371; b) E. Yamaguchi, C. Wang, A. Fukazawa, M. Taki, Y. Sato, T. Sasaki, M. Ueda, N. Sasaki, T. Higashiyama, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2015**, *54*, 4539–4543; *Angew. Chem.* **2015**, *127*, 4622–4626.

[13] M. van der Sluis, A. Klootwijk, J. B. M. Wit, F. Bickelhaupt, N. Veldman, A. L. Spek, P. W. Jolly, *J. Organomet. Chem.* **1997**, *529*, 107–119.

[14] K. Dück, B. W. Rawe, M. R. Scott, D. P. Gates, *Angew. Chem. Int. Ed.* **2017**, *56*, 9507–9511; *Angew. Chem.* **2017**, *129*, 9635–9639.

[15] M. A. Shameem, K. Esfandiarfard, E. Öberg, S. Ott, A. Orthaber, *Chem. Eur. J.* **2016**, *22*, 10614–10619.

[16] E. Öberg, A. Orthaber, C. Lescop, R. Réau, M. Hissler, S. Ott, *Chem. Eur. J.* **2014**, *20*, 8421–8432.

[17] a) E. Öberg, A. Orthaber, F. Howard, M.-P. Santoni, S. Ott, *Phosphorus Sulfur Silicon Relat. Elem.* **2013**, *188*, 152–158; b) B. Schäfer, E. Öberg, M. Kritikos, S. Ott, *Angew. Chem. Int. Ed.* **2008**, *47*, 8228–8231; *Angew. Chem.* **2008**, *120*, 8352–8355.

[18] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[19] a) V. Bandi, V. Kavala, C.-H. Hsu, A. Konala, B. K. Villuri, T. Kotipalli, C.-W. Kuo, C.-F. Yao, *RSC Adv.* **2017**, *7*, 46704–46712; b) Y. Lv, Y. Wang, W. Pu, X. Zhu, N. Wu, Y. Zhao, *Org. Chem. Front.* **2020**, *7*, 2752–2756.

[20] B. S. Schreib, M. Fadel, E. M. Carreira, *Angew. Chem. Int. Ed.* **2020**, *59*, 7818–7822; *Angew. Chem.* **2020**, *132*, 7892–7896.

[21] F. Roesler, M. Kovács, C. Bruhn, Z. Kelemen, R. Pietschnig, *Chem. Eur. J.* **2021**, *27*, 9782–9790.

[22] a) A. Klose, G. Kehr, C. G. Daniliuc, G. Erker, *Dalton Trans.* **2016**, *45*, 2023–2030; b) J. Möbus, A. Galstyan, A. Feldmann, C. G. Daniliuc, R. Frohlich, C. A. Strassert, G. Kehr, G. Erker, *Chem. Eur. J.* **2014**, *20*, 11883–11893; c) J. Möbus, Q. Bonnin, K. Ueda, R. Fröhlich, K. Itami, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2012**, *51*, 1954–1957; *Angew. Chem.* **2012**, *124*, 1990–1993.

[23] B. Wu, R. Chopra, N. Yoshikai, *Org. Lett.* **2015**, *17*, 5666–5669.

[24] X. Wei, Z. Lu, X. Zhao, Z. Duan, F. Mathey, *Angew. Chem. Int. Ed.* **2015**, *54*, 1583–1586; *Angew. Chem.* **2015**, *127*, 1603–1606.

[25] a) X. He, J.-B. Lin, W. H. Kan, S. Trudel, T. Baumgartner, *Org. Lett.* **2014**, *16*, 1366–1369; b) Y. Ren, F. Biegger, T. Baumgartner, *J. Phys. Chem. C* **2013**, *117*, 4748–4758.

[26] a) D. Miesel, A. Hildebrandt, M. Korb, D. A. Wild, P. J. Low, H. Lang, *Chem. Eur. J.* **2015**, *21*, 11545–11559; b) G. Märkl, R. Hennig, H. Ncfth, *Tetrahedron Lett.* **1995**, *36*, 6655–6658; c) G. Keglevich, Z. Böcskei, G. M. Keserü, K. Újszászy, L. D. Quin, *J. Am. Chem. Soc.* **1997**, *119*, 5095–5099.

[27] S. Iwasaki, Y. Miyake, H. Imoto, K. Naka, *Chem. Eur. J.* **2022**, *28*, e202202084.

[28] E. Niecke, M. Nieger, P. Wenderoth, *Angew. Chem. Int. Ed.* **1994**, *33*, 353–354; *Angew. Chem.* **1994**, *106*, 362–363.

Manuscript received: January 25, 2023
Revised manuscript received: March 2, 2023
Accepted manuscript online: March 6, 2023