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Cascade Reactions Forming Highly Substituted, Conjugated Phospholes and 1,2-Oxaphospholes[**]

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Dedicated to Professor Peter J. Garratt on the occasion of his 78th birthday

Highly unsaturated hydrocarbons[1] based on aromatics, alkenes, acetylenes, and combinations thereof are organic semiconductors. As such, they are interesting both from a basic research viewpoint[2] and in terms of their applications in electronics and photonics devices.[3] The replacement of carbon centers of such compounds by heavier low-valent main group elements, phosphorus in particular, has become increasingly popular. Polyheteroaromatic structures based on the phosphole motif (**I**; Figure 1) have achieved a considerable degree of maturity and found application, for example, in organic light-emitting diodes (OLEDs);[4] phosphorus analogues of polyphenylvinylenes (**II**)[5] and oligoacetylenes (**III**)[6] have also been reported. In all examples depicted in Figure 1, phosphorus inclusion greatly alters the electronic properties of the compounds compared to all-carbon-based analogues, and also offers a number of options for post-synthetic manipulations, such as metal complexations or oxidations.[7]

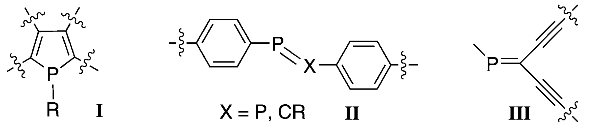
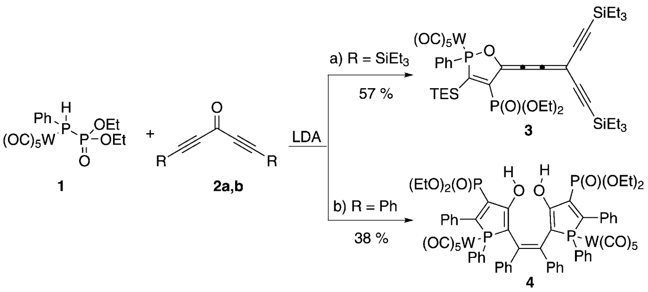


Figure 1. Examples of phosphorus-containing π conjugates.

In contrast to the plethora of synthetic procedures that are available for the preparation of pure hydrocarbons, the synthetic arsenal for the construction of **I–III** is limited. Considering the reliability of the Wittig reactions for the conversion of aldehydes and ketones into alkenes, we were intrigued by the option to use the analogous phospha-Wittig–Horner (pWH) reaction[8–10] to prepare P-containing oligoacetylenes from appropriate acetylenic ketones. Whereas traditional phosphonium ylides react with diacetylenic ketones exclusively in a 1,2-addition, which makes Wittig-type reactions a reliable tool for the preparation of 1,1-diethynylethenes,[11,12] herein we demonstrate that a pWH reagent **1** exhibits a completely different reactivity. The observed 3,4-addition initiates a cascade of reactions that ultimately leads to the formation of either penta-substituted bis-phospholes or 2,5-dihydro-1,2-oxaphospholes, depending on the substituent at the acetylene termini of the diethynylketone (Scheme 1).



Scheme 1. Reaction of phospha-Wittig–Horner reagent **1** with diacetylenic ketones **2a**,**b**.

As with all Wittig-type reactions, the pWH reaction is also initiated under basic conditions, in this case, by the addition of lithium diisopropylamide (LDA). The Li salt of **1**[9] is added to 1,5-bis(TES)-penta-1,4-diyne-3-one (**2a**, TES = $SiEt_3$),[13,14] resulting in a red solution from which a bright red product **3** can be isolated in 57% yield after silica gel chromatography. Mass spectrometric analysis of the product indicates that no simple pWH reaction occurred, as the observed molecular weight ($m/z = 1159.15577$, corresponding to $C_{43}H_{60}O_9P_2Si_3W + Ag$) suggests that both P units of the pWH reagent are still present in the product and that **1** has reacted with two equivalents of ketone **2a**. Consistently, the ^{31}P NMR spectrum features two phosphorus centers ($\delta(^{III}P) = 167.4$ ppm, $\delta(^{V}P) = 6.8$ ppm), which couple to each other with $J_{P\text{-}P} = 63$ Hz. A high degree of unsaturation can be expected from the presence of 11 quaternary carbon atoms in the ^{13}C NMR spectrum. Unambiguous structural confirmation of **3** was obtained by X-ray diffraction analysis of single crystals obtained by slow evaporation of a pentane solution at −30 °C (Figure 2).

Compound **3** is a persubstituted 2,5-dihydro-1,2-oxaphosphole heterocycle in which C14 is part of an exocyclic butatriene system that is terminated by two TES-acetylenes. The ^{V}P group of the pWH reagent is no longer bound to the ^{III}P center, but rather features as a substituent at C13 of the

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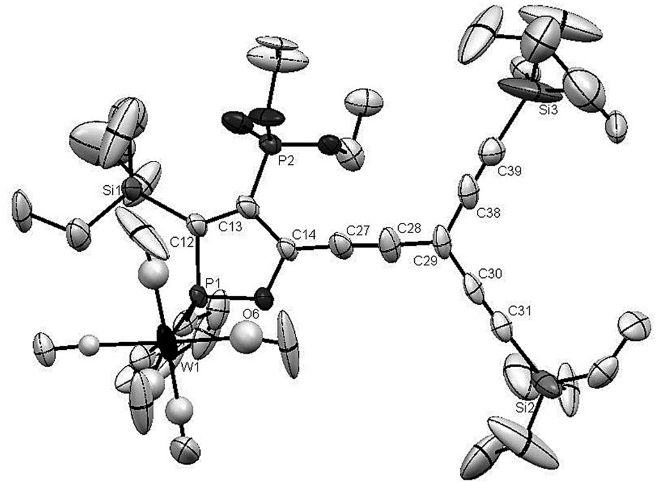


Figure 2. Crystal structure of compound **3** (ellipsoids set at 50% probability). All protons are omitted for clarity.

oxaphosphole. A third TES group at C12 completes the substitution pattern of the heterocyle. The endocyclic double bond of the oxaphosphole is in conjugation with the bis-acetylene-substituted cumulene system, deviating only by 3.5° (dihedral angle C12-C13-C14-C27, Figure 2) from ideal coplanarity.

Reaction of bis(phenylacetylene)-substituted ketone **2b**[13,14] with the same pWH reagent **1** under identical conditions generates an orange crystalline solid **4** in 38% yield of isolated product. Compound **4** is structurally fundamentally different from **3**, with a mass spectrum that shows a highest weight molecular ion ($m/z = 1709.01456$, $C_{64}H_{52}O_{18}P_4W_2 + Ag$) that corresponds exactly to the mass of two molecules of **1** plus two molecules of ketone **2b**. ^{13}C NMR analysis of compound **4** shows no signal in the typical acetylene region, while the ^{31}P NMR spectrum features a simple AX coupling pattern ($\delta(^{III}P) = 38.4$ ppm, $\delta(^{V}P) = 13.6$ ppm) with $J_{P\text{-}P} = 38$ Hz, suggesting the absence of any diastereomers and a symmetric structure for compound **4**.

Final proof of the molecular structure of **4** was obtained by single crystal X-ray diffraction analysis (Figure 3). Compound **4** consists of two per-substituted phospholes that are interconnected by an ethylene bridge at C9 of the respective heterocycle. The *cis* relationship of the phospholes across the double bond brings the two hydroxy groups of the two phosphole-C8 centers into proximity, giving rise to a helical twist between the two phosphole subunits (dihedral angle C8-C9-C26-C26 = 37.5° in Figure 3). Further substituents on the two phospholes are phenyl groups at C6, and ^{V}P fragments that originate from the pWH reagent at C7. The C8−OH protons are within hydrogen-bonding distance of the oxygen atoms of the phosphonate groups (OH···O 1.891 Å) of the respective phosphole ring. Compound **4** has a twofold rotational axis in the solid state and exhibits a C_{2v} point group symmetry. It is noteworthy that **4** is the only phosphole-containing product of the reaction and that no other stereoisomers, which are often encountered in other phosphole preparations, are observed.[7]

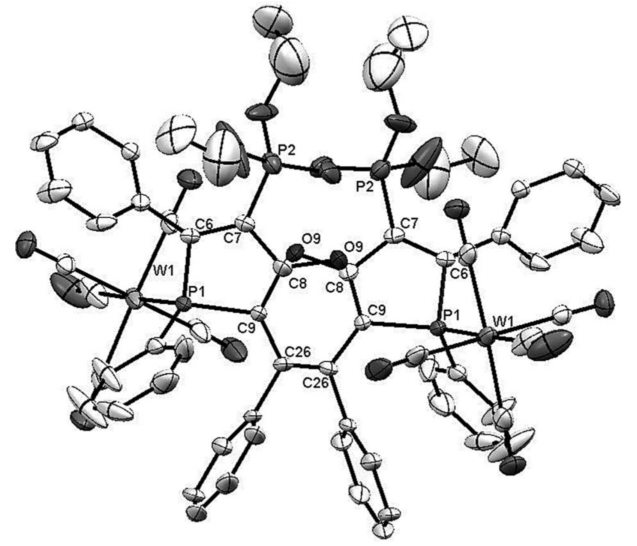
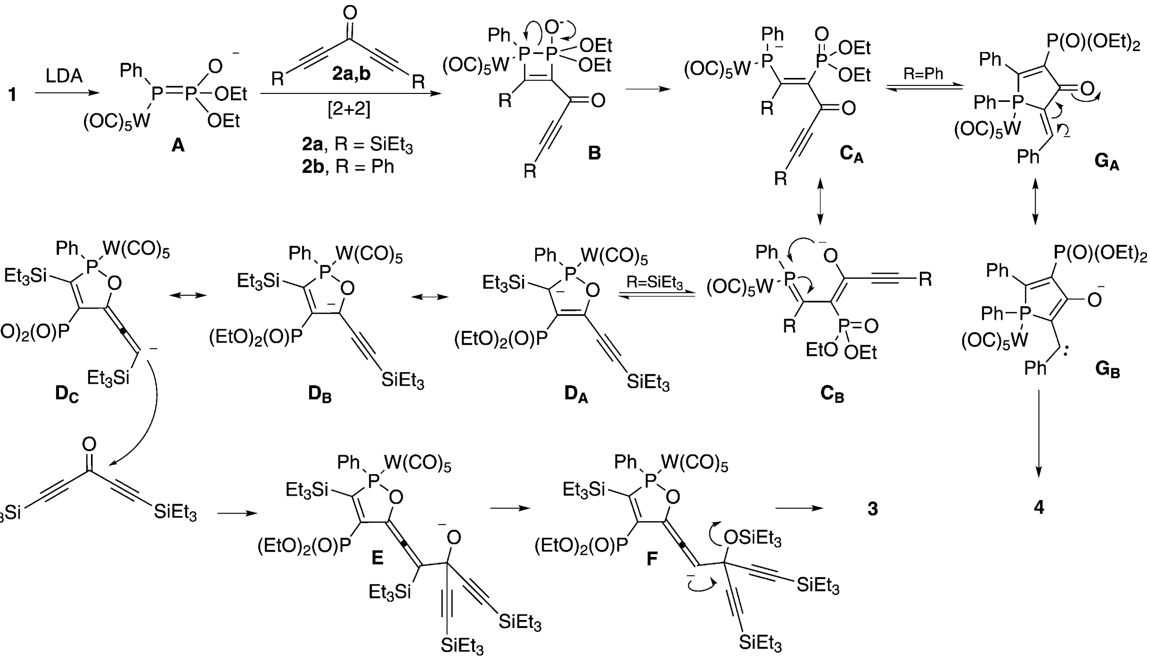


Figure 3. Crystal structure of compound **4** (ellipsoids set at 50% probability). All protons are omitted for clarity.

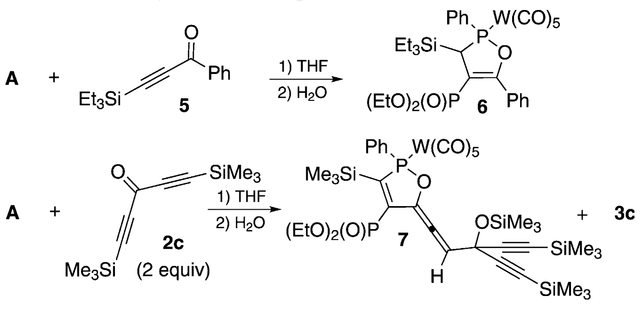
Compounds **3** and **4** are highly complex structures that are obtained from rather simple starting materials. A mechanistic model for their formation must account for multiple bond-breaking and bond-forming steps. Particularly intriguing are the formation of the cumulene system in **3** and the origin of the exocylic C=C bond in **4**. Because of the similarities in the substrates, the initial steps of the reaction cascades are presumably identical.

The first step of the sequence is the reaction of **1** with LDA to produce the enolate form of the pWH reagent with a formal P=P double bond character, as evidenced by a large $^{1}J_{P\text{-}P}$ coupling constant of 381 Hz (**A** in Scheme 2).[9] Lithium salt **A** undergoes a formal [2+2] addition with one of the acetylene bonds of the starting ketones, presumably through nucleophilic attack of the low valent ^{III}P at the acetylenic ketone in a Michael fashion, followed by ring closure. An alternative 1,4-addition that would involve the ketone of **2a**,**b** is unfavorable, as the six-membered ring thereby formed would contain an internal allene. It is important to underline that the direction of the classical Wittig reaction with acetylene-substituted carbonyl compounds has previously been described as being controlled by a fine balance between electronic and steric factors.[15] The formation of intermediates of type **B** has precedence in the classical Wittig reaction, and was described for a reaction between phosphonium ylides and a propargylic aldehyde[16] or an acetylene dicarboxylic acid ester.[17] Rearrangement of intermediate **B** includes ring opening and reestablishment of the phosphonate group to form anion **C**. Intermediate **C** can be described by two resonance structures that carry increased negative charge either at ^{III}P (**C$_A$**) or at the enolate-*O* (**C$_B$**). Intermediate **C** can thus act as a nucleophile in two different fashions, giving rise to the two different products, **3** and **4**. Nucleophilic attack of the enolate-*O* on the ^{III}P center establishes the 1,2-oxoaphosphole ring of **3**. Again, a series of resonance structures can be depicted for intermediate **D**. Experimental support for the mechanistic proposal leading to **D** can be



Scheme 2. Mechanistic proposal for the formation of 1,2-oxaphosphole-terminated butatriene **3** and ethene-bridged bis-phosphole **4**.

obtained from the reaction of **A** with TES-acetylene phenyl ketone **5**, from which oxaphosphole **6**, which is the protonated form of a $\mathbf{D_A}$ analogue, can be isolated after aqueous workup (Scheme 3 and ESI). In the presence of a second acetylene, however, an additional resonance structure $\mathbf{D_C}$ can be postulated that carries a negative charge at the periphery of the molecule and which is conveniently set up to react with a second ketone **2a** by nucleophilic attack on the carbonyl carbon and the formation of intermediate **E**. A 1,3-silyl shift gives rise to intermediate **F**, in which the newly formed oxysilyl group can function as a leaving group to establish the final butatriene framework in **3**. Support for the final elimination step comes from the analogous reaction of **1** with 1,5-bis(TMS)-penta-1,4-diyne-3-one **2c** (TMS = SiMe_3), where premature quenching of the reaction mixture allows the isolation of compound **7**, which is a protonated analogue of **F** (Scheme 3, also see the Supporting Information). Compound **7** already features the allene system, but still contains the OTMS leaving group. However, the reaction of **1** with **2c** is generally characterized by lower yields compared to those with **2a**, presumably because of the instability of **2c** towards the organolithium species.



Scheme 3. Characterized products with core structures equivalent to those proposed for intermediates in Scheme 2.

In contrast to the above sequence for silyl-terminated (TMS and TES) diacetylenic ketones, the presence of phenyl substituents in **2b** alters the reactivity of intermediate **C** dramatically. Intramolecular nucleophilic attack of the $^{\text{III}}$P at the acetylene in a 5-*exo-dig* fashion gives rise to intermediate **G**, which has an exocyclic carbon center that exhibits a certain carbene character, as formally depicted in resonance structure $\mathbf{G_B}$. The intermediate carbene is stabilized by two adjacent aromatic units: the newly established phosphole, as well as the phenyl substituent that originates from **2b**. As the phenyl group is absent in **2a**,**c**, we propose that this stabilization is what drives the reaction towards **4**. The final steps of the sequence are the dimerization of two carbenes $\mathbf{G_B}$ to establish the exocyclic double bond, followed by protonation to afford **4**.

As evident from the solid-state structure of **3**, the endo- and exocyclic π systems are coplanar, giving rise to the intense color of the compound. The oxaphosphole has a profound effect on the electronic absorption properties of the compound as the longest wavelength absorption maximum of **3** is bathochromically shifted by 46 nm compared to that of a peracetylenic butatriene reference compound ($\lambda_{\max} = 424$ nm, $\varepsilon = 86\,000\,\text{M}^{-1}\text{cm}^{-1}$).[18] It has recently been demonstrated that by altering the torsion angle of biphospholes the communication between the two phosphole rings can be tuned, and thus used to engineer the HOMO–LUMO gap.[19] Owing to the rigidity of the ethylene bridge between the two phosphole units in **4**, π conjugation is well mediated and the lowest energy absorption maximum is observed at 445 nm ($\varepsilon = 7300\,\text{M}^{-1}\text{cm}^{-1}$). The rigidity imposed by the ethylene spacer, as well as its contributions to the overall π system, gives rise to a 50 nm red shift compared to a 5,5′-diphenyl-substituted 2,2′-biphosphole.

In conclusion, we have discovered a remarkable synthetic pathway that converts readily available starting materials into highly functionalized phospholes and 1,2-oxaphospholes that, especially in case of the latter,[20] are difficult to obtain by other methods. Yields for the transformations are high, especially considering the multiple bond-breaking and bond-forming steps that are involved. The outcome of the reaction cascade that leads to the formation of **3** and **4** is determined by the nature of the substituent at the acetylene terminus of **2**. A phenyl substituent stabilizes a carbene intermediate, which leads to the formation of bis-phosphole **4**. Future work will include the elucidation of the generality of this process, post-synthetic chemistry on **3** and **4**, and an investigation of the suitability of the compounds that can be obtained by this method for use in organic electronics devices.

Experimental Section

General: All reactions were performed under argon using Schlenck techniques. Diethyl ether and THF were freshly distilled from sodium/benzophenone prior to use. ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a 400 MHz spectrometer. Chemical shifts (ppm) are reported and referenced to the internal signal of the residual protic solvent. High resolution mass spectral analyses (HRMS) were performed on a high resolution and FTMS + pNSI mass spectrometer (OrbitrapXL) with an ESI source. CIF files of **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre under CCDC 848671 (**3**) and 848208 (**4**) and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oxaphosphole **3**: LDA (0.35 mL of a 2 M solution in THF/heptanes) was added dropwise to a solution of **1** (0.4 g, 0.7 mmol) in THF at −30 °C. The reaction mixture was stirred for 30 min and then cooled down to −78 °C before ketone **2a** (0.43 g; 1.4 mmol) was added. After stirring for 2.5 h and warming to room temperature, the resulting red solution was filtered through a plug of silica gel and eluted with THF. After all solvents were removed, the residue was purified by column chromatography (50 % CH_2Cl_2 in pentane; $R_f = 0.48$), affording **3** as a bright red amorphous solid. Compound **3** can be recrystallized from pentane at −30 °C. Yield: 0.42 g, 57 %. ^{31}P ($CDCl_3$, 161.83 Hz): $\delta = 167.5$ (d, $^{1}J_{PP} = 63$, $^{1}J_{PW} = 277$ Hz, ^{III}P), 6.8 ppm (d, ^{V}P); ^{1}H ($CDCl_3$, 399.78 Hz): $\delta = 7.62$–7.52 (m, 5 H, Ph), 4.27–4.23 (m, 2 H, OCH_2), 4.15–4.08 (m, 2 H, OCH_2), 1.40 (t, $^{3}J_{HH} = 8$ Hz, 3 H, OCH_2CH_3), 1.35 (t, $^{3}J_{HH} = 8$ Hz, 3 H, OCH_2CH_3), 1.00 (t, $^{3}J_{HH} = 8$ Hz, 9 H, $SiCH_2CH_3$), 0.97 (t, $^{3}J_{HH} = 8$ Hz, 9 H, $SiCH_2CH_3$), 0.79 (t, $^{3}J_{HH} = 8$ Hz, 9 H, $SiCH_2CH_3$), 0.65–0.61 ppm (m, 16 H, $SiCH_2CH_3$); ^{13}C ($CDCl_3$, 100.53 Hz): $\delta = 197.8$ (d, $J = 28$ Hz), 195.3 (d, $J_{CP} = 8$, $J_{CW} = 126$ Hz), 168.9 (dd, $J = 18$, 22 Hz), 157.5 (s), 143.0 (d, $J = 188$ Hz), 142.0 (d, $J = 3$ Hz), 141.7 (d, $J = 3$ Hz), 134.0 (d, $J = 28$ Hz), 133.1 (s), 131.8 (d, $J = 16$ Hz), 129.0 (d, $J = 11$ Hz), 127.9 (d, $J = 8$ Hz), 111.9 (s), 111.8 (s), 100.6 (s), 100.1 (s), 63.2 (d, $J = 5$ Hz), 63.1 (d, $J = 7$ Hz), 16.6 (d, $J = 6$ Hz), 16.3 (d, $J = 6$ Hz), 7.9 (s), 7.4 (s), 5.3 (d, $J = 2$ Hz), 4.4 (s), 4.3 ppm (s). IR (solution in CH_2Cl_2): $\tilde{\nu}$ =2076, 1993, 1946, 1608, 1576, 1213, 1029 cm^{-1}. HRMS (solution in a mixture of $CHCl_3/CH_3OH$ with the addition of $AgCF_3COO$) calculated for $C_{43}H_{60}O_9P_2Si_3WAg$, $[M{+}Ag]^+$: 1159.15772, found: 1159.15577.

Bis-phosphole **4**: LDA (0.25 mL of a 2 M solution in THF/heptanes) was added dropwise at −30 °C to a solution of **1** (0.28 g; 0.50 mmol) in THF. The reaction mixture was stirred for 30 min and then cooled down to −78 °C, before ketone **2b** (0.12 g; 0.53 mmol) was added. The resulting dark red-brown solution was stirred for 2 h at −20 °C. The solvents were removed in vacuo and the residue washed with pentane (3 × 10 mL). Chromatographic purification of the obtained orange solid on silica (2 % acetone in CH_2Cl_2; $R_f = 0.6$) affords **4** as an orange solid. Yield: 0.15 g, 38 %. ^{31}P ($CDCl_3$, 161.83 Hz): $\delta = 38.4$ (d, $^{1}J_{PP} = 38$, $^{1}J_{PW} = 239$ Hz, ^{III}P), 13.6 ppm (d, ^{V}P); ^{1}H ($CDCl_3$, 399.78 Hz): $\delta = 11.17$ (dd, $^{4}J_{HP} = {}^{4}J_{HP} = 1.5$ Hz, 1 H, OH), 7.30–7.27 (m, 1 H, Ph), 7.18–7.16 (m, 5 H, Ph), 7.06 (t, $^{3}J_{HH} = 8$ Hz, 2 H, Ph), 6.79 (d, $^{3}J_{HH} = 8$ Hz, 1 H, Ph), 6.59–6.57 (m, 3 H, Ph), 6.51 (d, $^{3}J_{HH} = 8$ Hz, 1 H, Ph), 6.45 (t, $^{3}J_{HH} = 8$ Hz, 1 H, Ph), 6.16 (t, $^{3}J_{HH} = 8$ Hz, 1 H, Ph), 4.22–4.08 (m, 2 H, OCH_2), 4.01–3.91 (m, 1 H, OCH_2), 3.90–3.80 (m, 1 H, OCH_2), 1.33 (t, $^{3}J_{HH} = 7$ Hz, 3 H, OCH_2CH_3), 1.00 ppm (t, $^{3}J_{HH} = 7$ Hz, 3 H, OCH_2CH_3); ^{13}C ($CDCl_3$, 100.53 Hz): $\delta = 197.9$ (d, $J = 23$ Hz), 196.5 (d, $J_{CP} = 7$, $J_{CW} = 125$ Hz), 167.5 (dd, $J = 26$, 2 Hz), 155.3 (dd, $J = 24$, 19 Hz), 138.8 (d, $J = 3$ Hz), 134.6 (dd, $J = 14$, 9 Hz), 134.0 (dd, $J = 10$, 6 Hz), 132.8 (s), 130.8 (d, $J = 7$ Hz), 130.7 (s), 128.8 (bs), 128.5 (bs), 128.2 (d, $J = 11$ Hz), 128.0 (dd, $J = 175$, 7 Hz), 127.6 (s), 127.4 (d, $J = 35$ Hz), 126.7 (s), 125.9 (s), 125.5 (s), 116.7 (dd, $J = 51$, 12 Hz), 63.5 (d, $J = 5$ Hz), 63.4 (d, $J = 5$ Hz), 16.1 (d, $J = 8$ Hz), 15.9 ppm (d, $J = 8$ Hz). IR (solution in CH_2Cl_2): $\tilde{\nu}$ =2071, 1936, 1609, 1597, 1489, 1320, 1198 cm^{-1}. HRMS (solution in a mixture of $CHCl_3/CH_3OH$ with the addition of $AgCF_3COO$) calculated for $C_{64}H_{52}O_{18}P_4W_2Ag$, $[M{+}Ag]^+$:1709.02080, found: 1709.01456.

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[1] a) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**; b) F. Diederich, P. J. Stang, R. R. Tykwinski, *Acetylene Chemistry*, Wiley-VCH, Weinheim, **2005**; c) M. M. Haley, R. R. Tykwinski, *Carbon-Rich Compounds*, Wiley-VCH, Weinheim, **2006**.

[2] a) W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski, *Angew. Chem.* **2009**, *121*, 8056–8060; *Angew. Chem. Int. Ed.* **2009**, *48*, 7915–7919; b) W. A. Chalifoux, R. R. Tykwinski, *Nat. Chem.* **2010**, *2*, 967–971; c) P. Rivera-Fuentes, J. L. Alonso-Gómez, A. G. Petrovic, F. Santoro, N. Harada, N. Berova, F. Diederich, *Angew. Chem.* **2010**, *122*, 2296–2300; *Angew. Chem. Int. Ed.* **2010**, *49*, 2247–2250; d) A. D. Payne, G. Bojase, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem.* **2009**, *121*, 4930–4933; *Angew. Chem. Int. Ed.* **2009**, *48*, 4836–4839.

[3] a) U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605–1644; b) A. J. Zucchero, P. L. McGrier, U. H. F. Bunz, *Acc. Chem. Res.* **2010**, *43*, 397–408; c) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248.

[4] a) C. Fave, T.-Y. Cho, M. Hissler, C.-W. Chen, T.-Y. Luh, C.-C. Wu, R. Réau, *J. Am. Chem. Soc.* **2003**, *125*, 9254–9255; b) T. Baumgartner, T. Neumann, B. Wirges, *Angew. Chem.* **2004**, *116*, 6323–6328; *Angew. Chem. Int. Ed.* **2004**, *43*, 6197–6201; c) M. Hissler, P. W. Dyer, R. Reau, *Top. Curr. Chem.* **2005**, *250*, 127–163; d) T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681–4727.

[5] a) V. A. Wright, D. P. Gates, *Angew. Chem.* **2002**, *114*, 2495–2498; *Angew. Chem. Int. Ed.* **2002**, *41*, 2389–2392; b) V. A. Wright, B. O. Patrick, C. Schneider, D. P. Gates, *J. Am. Chem. Soc.* **2006**, *128*, 8836–8844; c) R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2004**, *126*, 2268–2269.

[6] a) B. Schäfer, E. Öberg, M. Kritikos, S. Ott, *Angew. Chem.* **2008**, *120*, 8352–8355; *Angew. Chem. Int. Ed.* **2008**, *47*, 8228–8231; b) E. Öberg, X.-L. Geng, M.-P. Santoni, S. Ott, *Org. Biomol. Chem.* **2011**, *9*, 6246–6255; c) X.-L. Geng, Q. Hu, B. Schäfer, S. Ott, *Org. Lett.* **2010**, *12*, 692–695; d) X.-L. Geng, S. Ott, *Chem. Commun.* **2009**, 7206–7208; e) X.-L. Geng, S. Ott, *Chem. Eur. J.* **2011**, *17*, 12153–12162.

[7] a) F. Mathey, *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*, Elsevier Science Ltd, Oxford, **2001**; b) J. Crassous, R. Réau, *Dalton Trans.* **2008**, 6865–6876; c) M. Sebastian, M. Hissler, C. Fave, J. Rault-Berthelot, C. Odin, R. Réau, *Angew. Chem.* **2006**, *118*, 6298–6301; *Angew. Chem. Int. Ed.* **2006**, *45*, 6152–6155.

[8] A. Marinetti, F. Mathey, *Angew. Chem.* **1988**, *100*, 1435–1437; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1382–1384.

[9] A. I. Arkhypchuk, M.-P. Santoni, S. Ott, *Organometallics* **2012**, *31*, 1118–1126.

[10] A. Marinetti, S. Bauer, L. Ricard, F. Mathey, *Organometallics* **1990**, *9*, 793–798.

[11] K. S. Feldman, C. K. Weinreb, W. J. Youngs, J. D. Bradshaw, *J. Am. Chem. Soc.* **1994**, *116*, 9019–9026.

[12] G. C. L. Dawe, L. Wang, Y. Zhao, *Org. Lett.* **2009**, *11*, 2736–2739.

[13] N. P. Bowling, N. J. Burrmann, R. J. Halter, J. A. Hodges, R. J. McMahon, *J. Org. Chem.* **2010**, *75*, 6382–6390.

[14] E. Öberg, B. Schäfer, X.-L. Geng, J. Pettersson, Q. Hu, M. Kritikos, T. Rasmussen, S. Ott, *J. Org. Chem.* **2009**, *74*, 9265–9273.

[15] G. B. Brown, *J. Chem. Soc. C* **1967**, 2018–2021.

[16] M. F. Braña, M. Moran, M. J. P. d. Vega, I. Pita-Romero, N. Walker, *Tetrahedron* **1995**, *51*, 9127–9138.

[17] J. Barluenga, F. Lopez, F. Palacios, *Tetrahedron Lett.* **1988**, *29*, 381–384.

[18] J.-D. van Loon, P. Seiler, F. Diederich, *Angew. Chem.* **1993**, *105*, 1235–1238; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1187–1189.

[19] H. Chen, W. Delaunay, L. Yu, D. Joly, Z. Wang, J. Li, Z. Wang, C. Lescop, D. Tondelier, B. Geffroy, Z. Duan, M. Hissler, F. Mathey, R. Réau, *Angew. Chem.* **2012**, *124*, 218–221; *Angew. Chem. Int. Ed.* **2012**, *51*, 214–217.

[20] A. Marinetti, F. Mathey, *Organometallics* **1988**, *7*, 633–637.