# The 1-Phosphaallyl Anion as a Versatile Building Block in Reactions with Alkynes and Fischer-Type Alkynyltungsten Carbene Complexes[†]

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The anionic 1,3-cycloaddition reaction of the (1,2,3-triphenyl-1-phosphaallyl)lithium species $Li(dme)_3[PhP{-}CPh{=}C(Ph)H]$ (**1**) with diphenylacetylene followed by protonation of the anionic intermediate **2** gave diastereoselectively 1,2,3,4,5-pentaphenyl-2,3-dihydrophosphole (**3**). The relative *cis,trans*-stereochemistry of the C4,C5,P-unit has been established by X-ray structure analysis. Addition of **1** to the Fischer-type tungsten amino alkynyl carbene complex $(CO)_5W{=}C[N(CH_2)_4]{-}C{\equiv}CPh$ (**4**) yielded, after protonation, the metal carbene modified dihydrophosphole **8**, which, in contrast, exhibits a *trans,trans*-diphenyl substitution pattern. Thus, a different reaction pathway is suggested, containing an acyclic intermediate, which could be trapped by deuteration to give the (vinylphosphino)vinylcarbene complex $(CO)_5W{=}C\text{-}[N(CH_2)_4]{-}CD{=}C(Ph){-}P(Ph){-}CPh{=}C(Ph)H$ (**10**). Thermal decarbonylation of **10** led to the chelate complex $(CO)_4W{=}C[N(CH_2)_4]{-}CD{=}C(Ph){-}P(Ph){-}CPh{=}C(Ph)H$ (**11**). The reaction of **1** with the tungsten methoxy alkynyl carbene complex $(CO)_5W{=}C{-}(OCH_3){-}C{\equiv}C(p\text{-Tol})$ (**5**) and subsequent protonation afforded the acyclic (vinylphosphino)vinyl carbene complex $(CO)_5W{=}C(OCH_3){-}CH{=}C(p\text{-Tol}){-}P(Ph){-}CPh{=}C(Ph)H$ (**9**), which underwent rearrangement to the allenyl(vinyl)phosphane complex $[(OCH_3)CH{=}C{=}C(p\text{-Tol})][PhC{=}C(H)Ph](Ph)P\text{-}[W(CO)_5]Ph{-}CPh{=}C(Ph)H$ (**12**).

## Introduction

The anionic 1,3-cycloaddition reaction has been widely used for the synthesis of nitrogen containing heterocycles.[1] We recently reported on a reaction of the (1-phosphaallyl)lithium species $Li(dme)_3[PhP{-}CPh{=}C\text{-}(Ph)H]$ (**1**)[2] and diphenylacetylene which generated a lithium dihydrophospholide, providing the first example of a structurally characterized uncoordinated allyl anion **2**. Subsequent protonation by the mild carbon acid phenylacetylene yielded the 2,3-dihydrophosphole **3** (Scheme 1). Since both the cycloaddition and the protonation step are diastereoselective, this reaction sequence offers a stereocontrolled route to densely-substituted dihydrophospholes.[3]

The dihydrophosphole **3** has to date been characterized by means of spectroscopic data, and the stereochemistry with a *cis*-configuration of the vicinal hydrogen atoms at the five-membered ring has been deduced from the $^1$H-NMR spectrum. In this paper, we report the X-ray structure of **3**, which confirms the proposed stereochemistry (Figure 1).

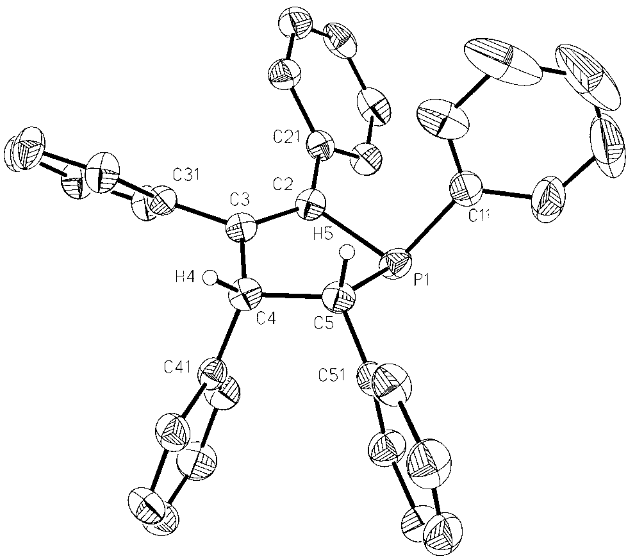
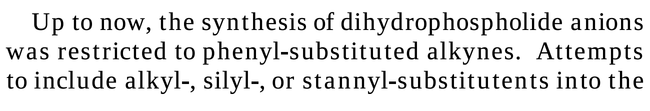


**Figure 1.** Crystal structure of dihydrophosphole **3** (ORTEP, thermal ellipsoids at the 50% probability).

**Scheme 1. Formation of Dihydrophosphole 3**



**1** **2** **3**

Up to now, the synthesis of dihydrophospholide anions was restricted to phenyl-substituted alkynes. Attempts to include alkyl-, silyl-, or stannyl-substitutents into the

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[†] Dedicated to Professor S. D. Peyerimhoff on the occasion of her 60th birthday.

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[§] Institut für Organische Chemie und Biochemie der Universität.

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(1) Kaufmann, T. *Angew. Chem.* **1974**, *86*, 715; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 627.

(2) Niecke, E.; Nieger, M.; Wenderoth, P. *J. Am. Chem. Soc.* **1993**, *115*, 6989.

(3) (a) Niecke, E.; Nieger, M.; Wenderoth, P. *Angew. Chem.* **1994**, *106*, 2045; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1953. (b) Paasch, K.; Wenderoth, P.; Nieger, M.; Niecke, E. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *111*, 54.

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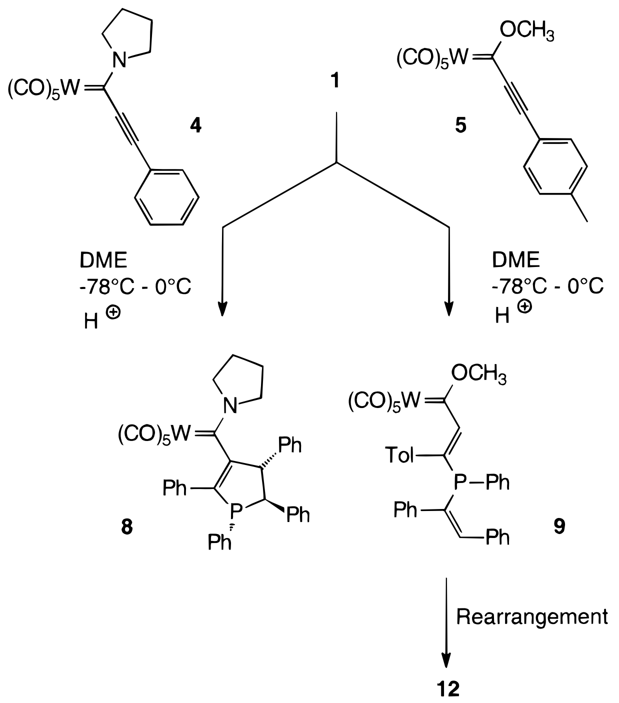
**Scheme 2. Reaction of the 1-Phosphaallyl Anion 1 with the Fischer Carbene Complexes 4 and 5**



five-membered heterocycle have failed so far.[4] Since the 1,3-anionic cycloaddition is generally favored by electron deficient alkynes, we decided to investigate the reactivity of alkynyl-substituted tungsten carbene complexes (CO)$_5$W=C(XR)−C≡CR′ (X = O, NR)[5] as electron-deficient triple-bond systems toward the 1-phosphaallyl anion [PhP−CPh=C(Ph)H]$^-$ (**1**) (Scheme 2). In addition, the pronounced polarization within the metal carbene functionalized alkyne is expected to allow further control over the regiochemistry of the cycloaddition.[6]

In this paper, we report the reactivity of the 1-phosphaallyl anion [PhP−CPh=C(Ph)H]$^-$ (**1**) toward alkynyl-substituted amino- and alkoxytungsten carbene complexes (CO)$_5$W=C[N(CH$_2$)$_4$]−C≡CPh (**4**) and (CO)$_5$W=C(OCH$_3$)−C≡C(*p*-Tol) (**5**). In the case of the amino-substituted carbene complex **4**, the reaction on protonation forms the dihydrophosphole **8**. The reaction with an electronically modified methoxy-substituted derivative **5** yields the corresponding acyclic bis(vinylphosphane) complex (CO)$_5$W=C(OCH$_3$)−CH=C(*p*-Tol)−P(Ph)−CPh=C(Ph)H, **9**. In addition, we propose a new reaction mechanism in which the different structures of the products are considered.

## Results and Discussion

**Structural Investigation of 1,2,3,4,5-Pentaphenyl-2,3-dihydrophosphole (3).** By reaction of the 1-phosphaallyl anion [PhP−CPh=C(Ph)H]$^-$ (**1**) with diphenylacetylene in dimethoxyethane (DME) and subsequent protonation of the cyclic anion **2** with phenylacetylene[7] at room temperature, we obtained the 2,3-dihydrophosphole **3**.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3**

| | | | |
|---|---|---|---|
| P(1)−C(2) | 1.825(2) | P(1)−C(11) | 1.823(3) |
| C(2)−C(3) | 1.349(3) | C(2)−C(21) | 1.480(3) |
| C(3)−C(4) | 1.523(3) | C(3)−C(31) | 1.494(3) |
| C(4)−C(5) | 1.565(3) | C(4)−C(41) | 1.517(3) |
| C(5)−P(1) | 1.871(2) | C(5)−C(51) | 1.514(3) |
| P(1)−C(2)−C(3) | 112.5(2) | C(4)−C(5)−P(1) | 105.9(2) |
| C(2)−C(3)−C(4) | 116.5(2) | C(5)−P(1)−C(2) | 89.3(1) |
| C(3)−C(4)−C(5) | 105.7(2) | C(11)−P(1)−C(2) | 102.9(1) |

Recrystallization of the product from a CH$_2$Cl$_2$/pentane mixture yielded crystals suitable for X-ray structure analysis. The molecular structure confirms the *cis*-configuration of the hydrogen atoms H4 and H5, as indicated previously by $^1$H-NMR data (Figure 1). The ring exhibits an envelope conformation with the phenyl substituent at the phosphorus atom in a flag pole position. Selected bond lengths and angles are given in Table 1.

Thus, the dihydrophospholide anion **2** must have been attacked by the proton from the sterically less hindered side, i.e., *cis* relative to the existing hydrogen atom, to give the *cis*-configuration product **3**. The overall reaction can be understood in terms of a concerted diastereoselective anionic 1,3-cycloaddition with a hydrogen shift followed by stereoselective protonation.

**Reaction of the 1-Phosphaallyl Anion with an Amino-Substituted Alkynyltungsten Carbene Complex.** The 1-phosphaallyl anion [PhP−CPh=C(Ph)H]$^-$ (**1**) was treated with 1 equiv of the tungsten alkynyl amino carbene complex (CO)$_5$W=C[N(CH$_2$)$_4$]−C≡CPh (**4**) in DME at −78 °C. The reaction was monitored by a color change from purple to red. In contrast, the reaction of the 1-phosphaallyl anion **1** with diphenylacetylene does not start at temperatures below room temperature. The reaction mixture was allowed to warm up to 0 °C, and protonation with phenylacetylene gave the dihydrophosphole **8** as a yellow solid in 48% yield after column chromatography.

Recrystallization from a CH$_2$Cl$_2$/hexane mixture gave crystals suitable for X-ray structure analysis. The molecular structure of **8** is depicted in Figure 2, selected bond lengths, angles, and torsion angles are given in Table 2.

Like in **3**, the five-membered ring exhibits an envelope conformation. The tungsten−carbene bond is rather long (W(1)−C(41) = 2.263(7) Å), which indicates a weak back-bonding as a consequence of the strong interaction between the carbene carbon atom and the nitrogen atom. The latter is confirmed by the short C(41)−N(41) distance (1.301(9) Å). The long C(1E)−O(1E) bond (1.192(11) Å) may be associated with the bending of the carbonyl ligand (W(1)−C(1E)−O(1E) = 170.8(8)°). This is due to a hydrogen bond between O(1E) and one of

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(4) Issberner, K.; Niecke, E. unpublished results.

(5) A paper dealing with the electronic and structural features of alkynyl-substituted tungsten carbene complexes is in preparation: Wittchow, E.; Dötz, K. H.; Nieger, M. Manuscript in preparation. See also: (a) Duetsch, M.; Stein, F.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556. (b) Duetsch, M.; Stein, F.; Pohl, E.; Funke, F.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1993**, *126*, 2535. (c) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502. (d) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 2475. (e) Fischer, H.; Meiser, T.; Hofmann, J. *Chem. Ber.* **1990**, *123*, 1799.

(6) (a) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 231. (b) Camps, F.; Llebaria, A.; Moretó, J.; Ricart, S.; Viñas, J. *J. Organomet. Chem.* **1991**, *401*, C17.

(7) This unusual proton source proved to be suitable for our intention because of its moderate acidity.

(8) The O(1E)−H(44C) distance is 2.67 Å. The corresponding molecule can be generated by using the symmetry operator (1 + *x*, *y*, *z*). Further information is available in the Supporting Information. Review: Braga, D.; Grepioni, F.; Biradha, K.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156.

**Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for 8**

| | | | |
|---|---|---|---|
| W(1)−C(1E) | 1.984(11) | C(1E)−O(1E) | 1.192(11) |
| W(1)−C(1D) | 1.993(10) | P(1)−C(5) | 1.819(7) |
| W(1)−C(1A) | 2.032(10) | P(1)−C(2) | 1.844(9) |
| W(1)−C(1B) | 2.044(10) | C(2)−C(3) | 1.507(10) |
| W(1)−C(1C) | 2.050(9) | C(3)−C(4) | 1.566(10) |
| W(1)−C(41) | 2.263(7) | C(4)−C(5) | 1.326(10) |
| C(1B)−O(1B) | 1.138(10) | C(41)−N(41) | 1.301(9) |
| O(1E)−C(1E)−W(1) | 170.8(8) | C(5)−P(1)−C(2) | 89.8(4) |
| N(41)−C(41)−C(4) | 115.7(6) | | |
| C(5)−P(1)−C(2)−C(3) | 28.3(6) | | |
| C(11)−P(1)−C(2)−H(2) | 23(1) | | |
| C(11)−P(1)−C(2)−C(21) | −90.2(6) | | |
| P(1)−C(2)−C(3)−C(4) | −26.8(7) | | |
| H(2)−C(2)−C(3)−H(3) | −168(2) | | |
| C(2)−C(3)−C(4)−C(5) | 11.2(9) | | |
| C(2)−P(1)−C(5)−C(4) | −23.0(6) | | |
| C(3)−C(4)−C(5)−P(1) | 10.6(8) | | |
| C(41)−C(4)−C(5)−P(1) | −161.5(6) | | |
| C(1A)−W(1)−C(41)−C(4) | −144.6(6) | | |
| C(1B)−W(1)−C(41)−N(41) | −53.7(7) | | |
| C(5)−C(4)−C(41)−W(1) | 82.7(8) | | |
| C(5)−C(4)−C(41)−N(41) | −98.7(9) | | |

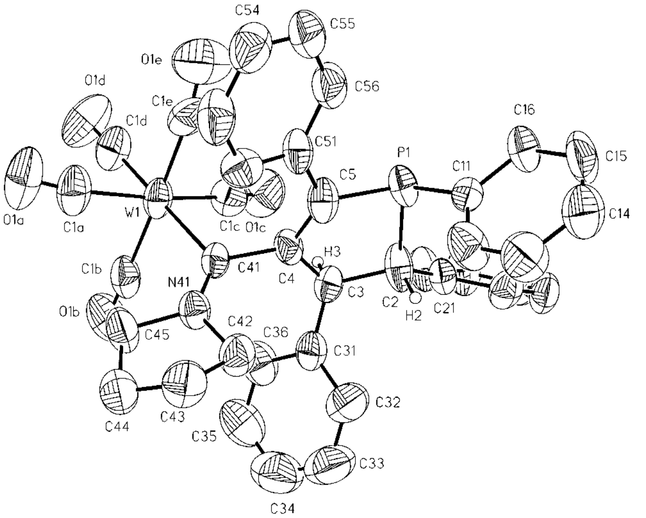
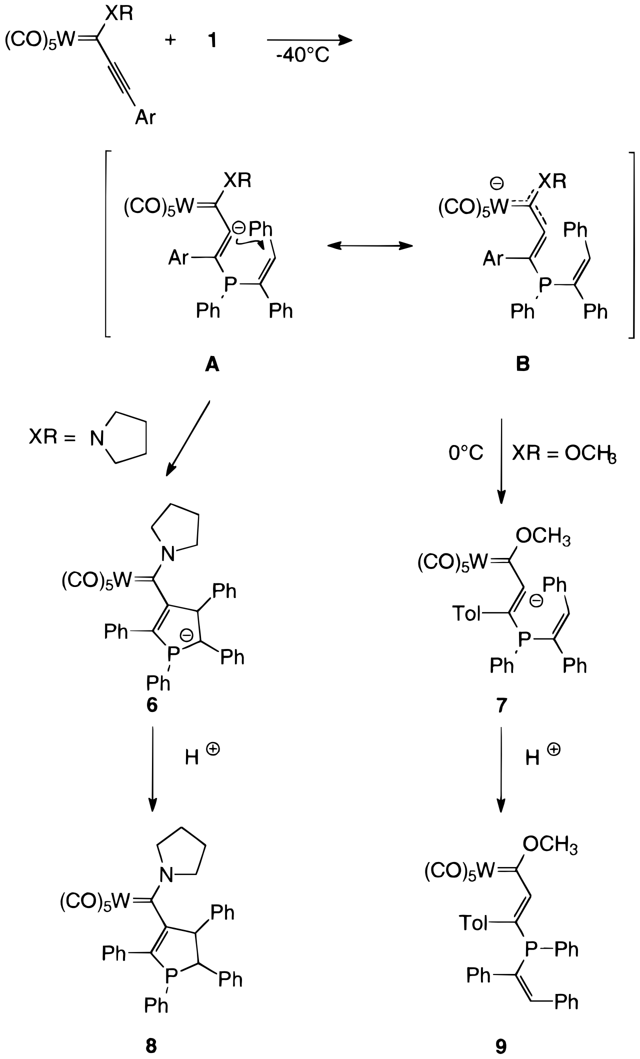


**Figure 2.** Crystal structure of the dihydrophosphole **8** (ORTEP, thermal ellipsoids at the 50% probability).

the pyrrolidine hydrogen atoms in a neighboring molecule.[8] The plane of the C═C bond (C(4)−C(5)) is nearly orthogonal to that of the W═C bond ($\phi$(C(5)−C(4)−C(41)−W(1)) = 82.7(8)°). Thus, there is no interaction possible between the phosphorus lone pair and the carbene fragment. In contrast to the per-phenyl-substituted dihydrophosphole **3**, where the two phenyl groups at the adjacent sp$^3$-carbon atoms are *cis* to each other, the structure of the metal carbene modified analogue **8** exhibits a *trans*-orientation.

The regiochemistry of the cycloaddition can be rationalized in terms of a conjugate addition of the phosphorus terminus of the heteroallyl anion **1** to the alkynyl carbene ligand. The addition of heteroatom nucleophiles to the $\beta$-carbon atom of metal carbene Michael acceptor systems is well-precedented[6] and is usually preferred under thermodynamic control, while kinetic control favors nucleophilic addition to the carbene carbon center. The resulting anionic intermediate (**A**) is supposed to undergo cyclization, and subsequent protonation of the anionic five-membered phosphorus heterocycle **6** is expected to result in the formation of the metal carbene functionalized 2,3-*trans*-diphenyldihydrophosphole **8** (Scheme 3). In contrast, the formation of the 2,3-*cis*-diphenyldihydrophosphole **3**, has been explained by a concerted cycloaddition of the 1,3-dipolar 1-phosphaallyl anion to the diphenylacetylene followed by a formal 1,3-hydrogen shift and subsequent protonation.[3a]

**Scheme 3. Mechanism of the Reaction of 1 with the Carbene Complexes 4 and 5**



In an attempt to support the mechanism outlined above, we tried to trap the presumed acyclic intermediate **A** by a suitable electrophile. We chose 1-deuterophenylacetylene.[9] At −40 °C, deuteration occured at the α-position of the former C≡C bond next to the carbene carbon atom. Under these conditions, cyclization via the anionic intermediate **6** could not successfully compete with the deuteration to give the acyclic bis(vinylphosphane) derivative **10** (Scheme 4).

**Chelation.**[10] When **10** is heated to its melting point of 150 °C, a deepening of the color from yellow to red occurs while loss of carbon monoxide is observed. The fomation of the tungsten carbene chelate complex **11** is accompanied by a characteristic bathochromic shift of the $\nu$(CO) frequencies due to the better donor abilities

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[9] *In situ* preparation from PhC≡CLi and $D_2O$.

[10] Dötz, K. H.; Erben, H.-G.; Staudacher, W.; Harms, K.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *355*, 177.

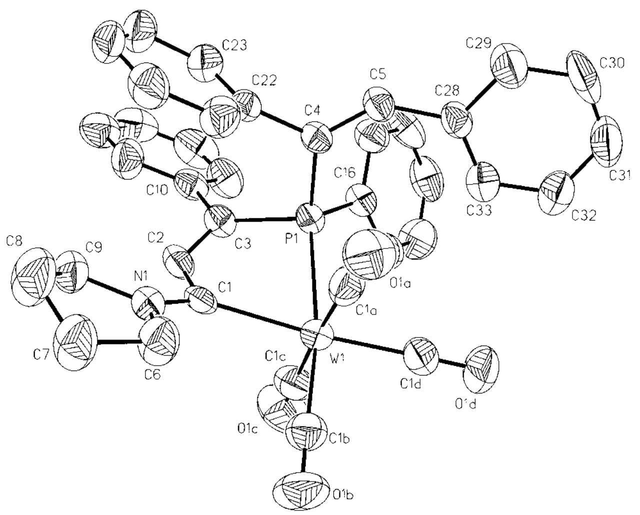
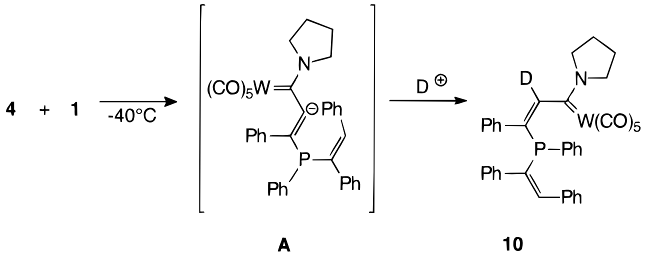
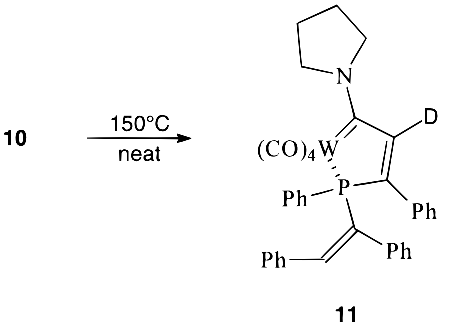


**Figure 3.** Crystal structure of chelate complex **11** (ORTEP, thermal ellipsoids at the 50% probability).

**Scheme 4. Deuteration of the Acyclic Intermediate A**



**Scheme 5. Formation of the Tetracarbonyl Chelate Complex 11**



of the phosphorus atom in comparison to the former carbonyl ligand (Scheme 5).[11]

To our knowledge, the X-ray structure of **11** represents the first structure analysis of a phosphorus containing chelate Fischer carbene complex (Figure 3). It contains a five-membered chelate ring which adopts an envelope conformation. The tungsten atom is bent out of the plane of the metallacycle ($\phi$ (W(1)−C(1)−C(2)−C(3)) = 33.3(9)°), as has been observed for comparable sulfur und nitrogen containing derivatives (Table 3).[11] In contrast, the oxygen containing five-membered chelates form planar systems.[11b] The W(1)−C(1) distance (2.223(7) Å) is shorter than that in **8** (2.263(7) Å); no *trans*-effect is observed. The diphenylvinylphosphino moity exhibits a (*Z*)-configuration, which is well-precedented for these systems.[12]

**Table 3. Selected Bond Lengths (Å) (deg) for 11**

| | | | |
|---|---|---|---|
| W(1)−C(1B) | 1.988(8) | P(1)−C(4) | 1.820(7) |
| W(1)−C(1D) | 1.993(8) | P(1)−C(3) | 1.853(7) |
| W(1)−C(1A) | 2.010(9) | N(1)−C(1) | 1.317(8) |
| W(1)−C(1C) | 2.016(9) | C(1)−C(2) | 1.463(10) |
| W(1)−C(1) | 2.223(7) | C(2)−C(3) | 1.335(9) |
| W(1)−P(1) | 2.507(2) | C(4)−C(5) | 1.358(9) |

**Reaction of the 1-Phosphaallyl Anion 1 with a Methoxy-Substituted Alkynyltungsten Carbene Complex.** To scrutinize the influence of the electronic features of the alkynyl carbene complex on the reaction mechanism, we included the tungsten alkynyl methoxy carbene complex $(CO)_5W{=}C{-}(OCH_3){-}C{\equiv}C(p\text{-Tol})$ (**5**) in our investigations. In these complexes, the carbene moiety is known to be a stronger electron-withdrawing functional group because of the higher electronegativity of the oxygen in comparison with the nitrogen atom.

According to the procedure as described in the case of the amino-substituted derivative $(CO)_5W{=}C{-}[N(CH_2)_4]{-}C{\equiv}CPh$ (**4**), the reaction of the 1-phosphaallyl anion $[PhP{-}CPh{=}C(Ph)H]^-$ (**1**) with the methoxy carbene complex **5** led to an open chain product, the bis(vinylphosphane) complex $(CO)_5W{=}C(OCH_3){-}CH{=}C(p\text{-Tol}){-}P(Ph){-}CPh{=}C(Ph)H$ (**9**). This result is in accordance with the proposed multistep mechanism, in which the ring closure step of the anionic intermediate **B** does not take place. The more effective stabilization of a negative charge in methoxy carbene complexes of the type $(CO)_5W{=}C(OCH_3){-}C(H)R_2$ than in the amino derivatives $(CO)_5W{=}C(NR'_2){-}C(H)R_2$ is also represented by their higher α-acidity.[13] Thus, the nucleophilicity of the negatively charged carbon atom is not high enough for an intramolecular Michael-type addition. The protonation then yields exclusively one isomer of the product **9**, which could be recrystallized from a $CH_2Cl_2$/hexane mixture to give crystals suitable for X-ray structure analysis (Figure 4). The molecular structure reveals an (*E*)-configuration of both double bonds and bond lengths and angles in the expected range (Table 4). There is no significant *trans*-effect of the carbonyl groups observable. The torsion angle W(1)−C(6)−C(8)−C(9) is 137.7(9)°, which indicates that the double bond is arranged nearly orthogonal to the plane which is spread by the $sp^2$-carbene center. Therefore, a stabilizing interaction of the carbene fragment with the phosphorus lone pair can be excluded.

Surprisingly, the bis(vinylphosphane) complex $(CO)_5W{=}C(OCH_3){-}CH{=}C(p\text{-Tol}){-}P(Ph){-}CPh{=}C(Ph)H$ (**9**) rearranges quantitatively to the allenylphosphane complex $(OCH_3)CH{=}C{=}C(p\text{-Tol}){-}P[W(CO)_5]Ph{-}CPh{=}C(Ph)H$ (**12**), already at room temperature with a half-life of 70 h (Scheme 6). By heating **9** in solution or in the solid state, the rearrangement is quantitative after 30 min. In the allenylphosphane **12**, the $W(CO)_5$ group is coordinated to the phosphorus atom, which is confirmed by a $^1J$(PW) coupling of 243 Hz in the $^{31}P$-NMR spectrum. The migration of the $W(CO)_5$ fragment is thought to be intramolecular since neither metal-free

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(11) (a) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267. (b) Dötz, K. H.; Popall, M.; Müller, G. *J. Organomet. Chem.* **1987**, *334*, 57. (c) Dötz, K. H.; Popall, M. *Chem. Ber.* **1988**, *124*, 665.

(12) Issberner, K.; Wenderoth, P.; Niecke, E. Manuscript in preparation.

(13) $(CO)_5Cr{=}C(NMe_2){-}CH_3$, $pK_S$ = 20.4, see: Anderson, B. A.; Wulff, W. D.; Rahm, A. *J. Am. Chem. Soc.* **1993**, *115*, 4602. Alkoxy carbene complexes, $pK_S$ = 8, see: Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

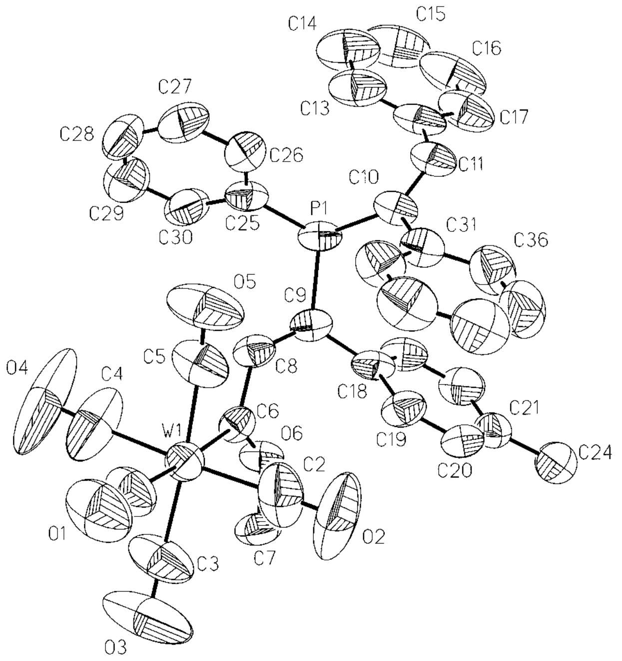
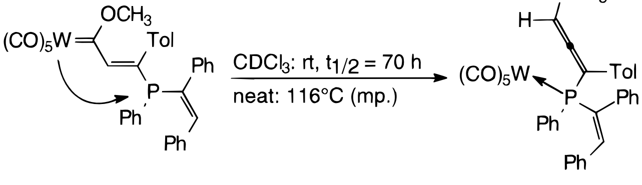


**Figure 4.** Crystal structure of the bis(vinylphosphane) **9** (ORTEP, thermal ellipsoids at the 50% probability).

**Table 4. Selected Bond Lengths (Å), and Angles (deg), and Torsion Angles (deg) for 9**

| | | | |
|---|---|---|---|
| W(1)−C(3) | 1.985(13) | P(1)−C(9) | 1.836(9) |
| W(1)−C(5) | 2.000(12) | P(1)−C(10) | 1.840(11) |
| W(1)−C(1) | 2.008(13) | O(6)−C(6) | 1.142(14) |
| W(1)−C(4) | 2.01(2) | C(6)−C(8) | 1.479(13) |
| W(1)−C(2) | 2.01(2) | C(8)−C(9) | 1.354(13) |
| W(1)−C(6) | 2.151(9) | C(10)−C(11) | 1.324(13) |
| C(9)−C(8)−C(6) | 127.9(9) | C(8)−C(9)−P(1) | 122.4(8) |
| C(5)−W(1)−C(6)−C(8) | −9.9(9) | C(6)−C(8)−C(9)−P(1) | 172.5(8) |
| W(1)−C(6)−C(8)−C(9) | 137.7(9) | C(9)−P(1)−C(10)−C(11) | 152.0(9) |
| O(6)−C(6)−C(8)−C(9) | −38.9(9) | | |

**Scheme 6. Rearrangement of the Bis(vinylphosphane) Carbene Complex 9**



**9** **12**

byproducts nor hexacarbonyltungsten can be detected. The constitution of the product is confirmed by mass spectral and NMR data: The $^1$H-NMR resonance of the methoxy group is significantly shifted upfield by 0.98 ppm, which indicates the absence of an electron-withdrawing group in the neighborhood. The former carbene atom now shows a $^{13}$C resonance at 82.8 ppm, with a $^3J$(PC) coupling constant of 10.5 Hz. The $^{13}$C-NMR shift of the allene carbon atom shows the typical value of 197.8 ppm. In the $^{13}$C-NMR spectrum, four *cis*- and one *trans*-carbonyl ligand with the corresponding couplings to the W and P atom, respectively, are observed whereas the signal for the carbene carbon atom has disappeared.

## Conclusion

Alkynyltungsten carbene complexes react as electron deficient alkynes under exceptionally mild conditions with the 1-phosphaallyl anion **1** to give exclusively one isomer of the corresponding product. Starting from the amino carbene complex **4**, the dihydrophosphole **8** is formed after protonation, which exhibits a *trans*-configuration of the ring hydrogen atoms. This is in contrast to previous results. We propose a multistep reaction mechanism which could be supported by trapping the anionic acyclic intermediate. The cyclization step to the dihydrophospholide is dependent on the electronic properties in the anionic acyclic intermediate **A** (respectively **B**), influencing the nucleophilicity, which is responsible for the cyclization tendency. Thus, the methoxy-substituted carbene complex **5** reacts with the 1-phosphaallyl anion **1** to give the open chain product **9** after protonation.

We have been able to introduce with alkynyl-substituted tungsten carbene complexes a new class of substrates for the reaction with 1-phosphaallyl anions, which have a wide range of functionalities. The amino-substituted carbene complexes are of special interest because of the possibility to introduce chiral information, e.g., from the chiral pool, to obtain an enantiomeric excess of the formed heterocycles.

## Experimental Section

All operations were carried out under argon using standard Schlenk techniques. Tetrahydrofuran (THF) and dimethoxyethane (DME) were freshly distilled from potassium sodium alloy before use. Dichloromethane was distilled from $CaH_2$. Petroleum ether (bp 40−60 °C) was dried over molecular sieves. All solvents were saturated with argon. Silica gel (Merck, 0.063−0.200 mm) was degassed in a high vacuum and stored under argon. 1,2,3-Triphenyl-1-phosphaallyllithium,[2] 1,2,3,4,5-pentaphenyl-2,3-dihydrophosphole,[3a] pentacarbonyl[(phenylethynyl)(*N*-pyrrolidino)carbene]tungsten(0)[14] and pentacarbonyl[((p-tolyl)ethynyl)(methoxy)carbene]tungsten(0)[15] were prepared according to procedures described in the literature. All chemical shifts are reported in parts per million.

**Reaction of the (1-Phosphaallyl)lithium Species 1 with the Alkynyltungsten Carbene Complexes 4 and 5.** To a solution of 2.4 mmol of the (1-phosphaallyl)lithium species **1** in 30 mL of DME was slowly added a solution of 2.4 mmol of the alkynyltungsten carbene complex **4** or **5**, respectively, at −78 °C. While the reaction mixture was stirred for 30 min at this temperature, the color changed from purple to red. The solution was allowed to warm up to 0 °C. After 15 min, the temperature was decreased again to −78 °C, and a solution of 0.5 mL (4 mmol) of phenylacetylene in 10 mL of DME was added. After removal of the solvent in vacuo, chromatography of the residue on silica gel (5 °C, petroleum ether/dichloromethane 2/1) yielded 0.92 g (48%) of **8** as a yellow solid, which could be recrystallized from petroleum ether (PE) to get small, yellow crystals. Purification of **9** by column chromatography resulted in 0.65 g (35%) of a red oil, which provided red crystals after recrystallization from PE. The atom numbering is according to the crystal structures.

**Pentacarbonyl[4-(1,2,3,5-tetraphenyl-2,3-dihydrophospholyl)-*N*-(pyrrolidino)carbene]tungsten(0) (8).** Yellow solid; mp 190 °C; $R_f$ 0.42 (2/1); EI-mass spectrum (*m*/*z*) 795 (21, $M^+$). Anal. Calcd for $C_{38}H_{30}NO_5PW$: C, 57.38; H, 3.80; N, 1.76. Found: C, 57.40; H, 4.04; N, 2.04. FT-IR (PE): 2061 (s, $A_1^{(2)}$), 1971 (w, $B_1$), 1923 (vs, E). $^1$H-NMR (300 MHz, $CDCl_3$): 7.51−7.14 (m, 20H, Ar), 5.36 (dd, 1H, $^3J$(HH) = 9.8 Hz, $^3J$(PH) = 1.0 Hz, H3), 4.15 (dd, 1H, $^3J$(HH) = 9.8 Hz,

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[14] Wittchow, E.; Dötz, K. H.; Nieger, M. Manuscript in preparation.

[15] Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47.

**Table 5. Crystallographic Data and Summary of Data Collection and Refinement**

| | **8** | **9** | **3** | **11** |
|---|---|---|---|---|
| mol formula | $C_{38}H_{30}NO_5PW$ | $C_{36}H_{27}O_6PW$ | $C_{34}H_{27}P$ | $C_{37}H_{30}NO_4PW$ |
| dimens, mm | 0.40 × 0.25 × 0.10 | 0.25 × 0.20 × 0.08 | 0.38 × 0.18 × 0.10 | 0.40 × 0.25 × 0.15 |
| cryst syst | monoclinic | triclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ (No. 14) | $P1$ (No. 2) | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) |
| $a$, Å | 9.713(3) | 10.943(3) | 11.609(2) | 14.190(7) |
| $b$, Å | 14.517(4) | 2.047(3) | 6.218(1) | 13.340(7) |
| $c$, Å | 23.933(8) | 13.965(4) | 35.287(7) | 18.534(11) |
| α, deg | | 104.72(2) | | |
| $\beta$, deg | 94.47(3) | 105.24(2) | 91.74(2) | 114.83(4) |
| $\gamma$, deg | | 98.76(2) | | |
| $V$, Å$^3$ | 3364(2) | 1670(1) | 2546(1) | 3184(3) |
| $Z$ | 4 | 2 | 4 | 4 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.57 | 1.53 | 1.22 | 1.60 |
| $\mu$ | 3.53 | 3.55 | 1.09 | 3.72 |
| diffractometer | Nicolet R3m | Nicolet R3m | Enraf-Nonius CAD4 | Nicolet R3m |
| radiation | Mo Kα | Mo Kα | Cu Kα | Mo Kα |
| $\lambda$, Å | 0.710 73 | 0.710 73 | 1.541 78 | 0.710 73 |
| $T$, K | 293 | 293 | 200 | 293 |
| max 2$\theta$, deg | 50 | 50 | 120 | 50 |
| $h$, $k$, $l$ ranges | $-11 \le h \le 11$<br>$-1 \le k \le 17$<br>$0 \le l \le 28$ | $-13 \le h \le 12$<br>$-14 \le k \le 13$<br>$0 \le l \le 16$ | $-5 \le h \le 13$<br>$0 \le k \le 6$<br>$-39 \le l \le 39$ | $-15 \le h \le 16$<br>$0 \le k \le 15$<br>$-22 \le l \le 0$ |
| no. of data | 6644 | 6138 | 4027 | 5836 |
| no. of unique data | 5967 | 5876 | 3749 | 5651 |
| no. of parameters | 415 | 399 | 317 | |
| R for $I > 2\sigma(I)$ | 0.045 | 0.057 | 0.053 | 0.042 |
| wR2($F^2$) for all data | 0.117 | 0.157 | 0.157 | 0.105 |

$^2J$(PH) = 7.5 Hz, H2), 3.98 (m, 1H, N−C$H'$H), 3.72 (m, 1H, N−CH′$H$), 3.62 (m, 1H,; N−C′$H'$H), 3.00 (m, 1H, N−C′H′$H$), 1.98 (m, 1H, $CH_2$−C$H'$H), 1.81 (m, 1H, $CH_2$−CH′$H$), 1.69 (m, 1H, $CH_2$−C$H'$H), 1.34 (m, 1H, $CH_2$−CH′$H$). $^{13}$C-NMR (75.47 MHz, $CDCl_3$): 251.9 (d, $^1J$(WC) = 90 Hz, $^3J$(PC) = 4.7 Hz, W═C), 201.3 (s, $^1J$(WC) = 125.4 Hz, $CO_{trans}$), 198.4 (s, 4C, $^1J$(WC) = 127.6 Hz, $CO_{cis}$), 157.2 (d, $^1J$(PC) = 11.2 Hz, C5), 135.9 (d, $^2J$(PC) = 15.5 Hz, C4), 141.2−126.6 (4Ar), 62.6 (d, $^2J$(PC) = 4.3 Hz, C3), 61.1, 56.1 (2C, N−$CH_2$), 53.8 (d, $^1J$(PC) = 9.0 Hz, C2), 24.9, 24.4 ($CH_2$−$CH_2$). $^{31}$P-NMR (121.50 MHz, $CDCl_3$): 30.6.

**(*E*,*E*)-Pentacarbonyl[(3-phospha-3,4,5-triphenyl-2-(*p*-tolyl)-1,4-pentadienyl)(methoxy)carbene]tungsten(0) (9).** Red solid; mp 116 °C; yield 35%; $R_f$ 0.29 (4/1); EI-mass spectrum (*m*/*z*) 769.8 (17, $M^+$). Anal. Calcd for $C_{36}H_{27}O_6PW$: C, 56.10; H, 3.53. Found: C, 55.87; H, 3.51. FT-IR (PE): 2064 (s, $A_1^{(2)}$), 1980 (w, $B_1$), 1949 (vs, $A_1^{(1)}$), 1943 (vs, E). $^1$H-NMR (300 MHz, $CDCl_3$): 7.56−7.02 (m, 15 H, Ar), 7.38 (d, 1H, $^3J$(PH) = 0.2 Hz; H-C8), 6.79 (d, 2H, $^3J$(HH) = 7.8 Hz, Ar), 6.55 (d, 2H, $^3J$(HH) = 7.8 Hz, Ar), 3.96 (s, 3H, $OCH_3$), 2.21 (s, 3H, $CH_3$), H−C(11) in Ar region. $^{13}$C-NMR (75.47 MHz, $CDCl_3$): 301.8 (s, W═C), 204.0 ($CO_{trans}$), 197.4 (s, 4C, $^1J$(WC) = 127.6 Hz, $CO_{cis}$), 147.5 (d, $^1J$(PC) = 10.5 Hz, C9), 146.3 (d, $^2J$(PC) = 28.7 Hz, C8), 142.8 (d, $^2J$(PC) = 3.2 Hz, $Tol_{ipso}$), 136.8 (d, $^2J$(PC) = 5.1 Hz, $C_{ipso}$), 136.6 (d, $^1J$(PC) = 20.8 Hz, C10), 134.0 (d, $^2J$(PC) = 18.0 Hz, C11), 129.7, 129.6, 129.3, 128.8, 128.6, 128.3 (d, $^3J$(PC) = 1.0 Hz, $C_{ipso}$), 128.1, 128.0, 127.7, 126.9 (4Ar), 67.8 ($OCH_3$), 21.2 ($CH_3$), $^{31}$P-NMR (121.50 MHz, $CDCl_3$): 5.6.

**(*E*,*E*)-Pentacarbonyl[(3-phospha-1-deuterio-2,3,4,5-tetraphenyl-1,4-pentadien-1-yl)-*N*-(pyrrolidino)carbene]-tungsten(0) (10).** To a solution of 2.4 mmol of the (1-phosphaallyl)lithium species **1** in 30 mL of DME was added a solution of 2.4 mmol of the alkynyltungsten carbene complex **4** at −78 °C. While the reaction mixture was stirred for 30 min at this temperature, the color changed from purple to red. The solution was allowed to warm up to -40 °C. After 15 min, the solution was titrated with a solution of 0.5 mL (4 mmol) of deuteriophenylacetylene (prepared from lithium phenylacetylide and 1.1 equiv of $D_2O$ at 0 °C) in 10 mL of DME until a change of color from red to yellow was observable. After removal of the solvent under reduced pressure, chromatography of the residue on silica gel (5 °C, petroleum ether/dichloromethane 2/1) yielded 0.81 g (45%) of **10** as a yellow solid, which was recrystallized from PE to give small, yellow crystals.

Yellow solid; mp 147−150 °C; $R_f$ 0.42 (2/1); EI-mass spectrum (*m*/*z*) 795 (19, $M^+$). Anal. Calcd for $C_{38}H_{30}NO_5PW$: C 57.30; H, 3.77; N, 1.76. Found: C, 57.36; H, 4.08; N, 2.00. FT-IR (PE): 2061 (s, $A_1^{(2)}$), 1971 (w $B_1$), 1942 (sh, $A_1^{(1)}$), 1923 (vs, E). $^1$H-NMR (300 MHz, $CDCl_3$): 7.68−6.70 (m, 20H, Ar), 6.08 (d, 1H, $^3J$(PH) = 7.1 Hz, H−C(5)), 3.80−3.70 (m, 2H, N−$CH_2$), 3.56−3.50 (m, 1H, N−C′$H'$H), 3.26−3.18 (m, 1H, N−C′H′$H$), 1.99−1.81 (m, 4H, $CH_2$−$CH_2$). $^{31}$P-NMR (121.50 MHz, DME, external reference $H_3PO_4$): 2.8.

**(*E*,*E*)-Tetracarbonyl[(3-phospha-1-deuterio-2,3,4,5-tetraphenyl-1,4-pentadienyl)-*N*-(pyrrolidino)carbene-*P*]tungsten(0) (11).** Phosphapentadienylcarbene complex **10** (0.30 g, 0.38 mmol) was warmed under vacuum to its melting point of 150 °C. A deepening in color and a loss of CO were observable. Chromatography of the residue on silica gel (0 °C, petroleum ether/dichloromethane 2/1) yielded 0.27 g (95%) of **11** as a red solid, which was recrystallized from pentane to give small, red crystals.

Red solid; $R_f$ 0.42 (2/1); EI-mass spectrum (*m*/*z*) 768.1 (14, $M^+$). Anal. Calcd for $C_{37}H_{29}DNO_4PW$: C, 57.83; H, 4.28; N, 1.82. Found: C, 57.66; H, 4.09; N, 1.99. FT-IR ($CH_2Cl_2$): 2004 (m, $A_1^{(2)}$), 1895 (vs, $B_1$), 1852 (s, $B_2$), 1573 (s, C═C, Ar), 1538 (s, C═C). $^1$H-NMR (300 Mz, $CDCl_3$): 7.71−6.90 (m, 20H, Ar), 6.08 (d, 1H, $^3J$(PH) = 7.1 Hz, H−C(5)), 4.28−4.22 (m, 2H, N−C′$H_2$), 3.45−3.40 (m, 1H, N−C$H'$H), 2.91−2.88 (m, 1H, N−CH′$H$), 2.21−2.09 (m, 4H, $CH_2$−$CH_2$). $^{13}$C-NMR (75.47 MHz, $CDCl_3$): 247.9 (s, $^1J$(PC) = 4.3 Hz, W═C), 214.2 (d, $^1J$(WC) = 134.8 Hz, $^2J$(PC) = 6.2 Hz, $CO_{cis-P,\ trans-W}$), 212.1 (d, $^1J$(WC) = 156.2 Hz, $^2J$(PC) = 27.8 Hz, $CO_{trans-P,\ cis-W}$), 206.1 (d, $^1J$(WC) = 129.6 Hz, $^2J$(PC) = 4.3 Hz, $CO_{cis}$), 203.6 (d, $^1J$(WC) =124.8 Hz, $^2J$(PC) = 8.6 Hz, $CO_{cis}$), 160.4 (d, $^1J$(PC) = 20.6 Hz, $^2J$(CH) = 2.9 Hz,; C(4)), 156.3 (d, $^2J$(PC) = 29.3 Hz, C1), 137.3 (d, $^1J$(PC) = 22.6 Hz, C2), 135.5 (d, $^2J$(PC) = 13.5 Hz, C5), 143.3, 142.7, 137.9, 135.4, 130.4, 130.0, 129.2, 128.4, 127.7, 127.65, 127.6, 127.4, 127.1, 127.0 (4Ph), 63.3, 52.5 (N−$CH_2$), 26.3, 24.8 ($CH_2$−$CH_2$). $^{31}$P-NMR (121.50 MHz, DME, external reference $H_3PO_4$): 42.4 (s, $^1J$(PW) = 222 Hz).

**(*E*)-Pentacarbonyl[3-phospha-6-methoxy-1,2,3-triphenyl-4-tolyl-1,4,5-hexatriene-*P*]tungsten(0) (12).** A solution of 0.30 g (0.39 mmol) of **9** in 30 mL of $CH_2Cl_2$ was deoxygenated by the freeze−thaw method (three cycles) and stirred for 7 days at room temperature. Alternatively, 0.30 g (0.39 mmol) of **9** was heated under argon to the melting point of 116 °C. The reaction was quantitative in both cases. Recrystallization from petroleum ether yielded 0.29 g of **12** as a red solid.

Red solid; $R_f$ 0.35 (4/1); EI-mass spectrum ($m/z$) 658 (17 M − 4CO); HRMS ($m/z$) 628.1269 (M − 5CO; calcd for $C_{31}H_{27}OP^{182}W$, 628.1257). FT-IR (PE): 2071 (s, $A_1^{(2)}$), 1982 (w, $B_1$), 1943 (vs, E). $^1$H-NMR (300 MHz, $CDCl_3$): 7.85−7.02 (m, 19H, Ar), 6.39 (d, 2H, $^3J$(HH) = 1.9 Hz, Ar), 6.37 (d, 2H, $^3J$(HH) = 1.9 Hz, Ar), 4.56 (d, $^4J$(PH) = 0.3 Hz, H6), 2.98 (s, 3H, $OCH_3$), 2.22 (s, 3H, $CH_3$), H1 not observed. $^{13}$C-NMR (75.47 MHz, $CDCl_3$): 198.4 (d, $^2J$(PC) = 22 Hz, $CO_{trans}$), 197.8 (s, C5), 197.2 (d, 4C, $^1J$(WC) = 126.2 Hz, $^2J$(PC) = 6.7 Hz, $CO_{cis}$), 146.1 (d, $J$(PC) = 2.4 Hz, $C_{ipso}$), 144.0 (d, $J$(PC) = 7.2 Hz), 143.5 (d, $^1J$(PC) = 14.9 Hz, $C_{ipso}$), 143.1 (d, $J$(PC) = 5.8 Hz), 142.8 (d, $J$(PC) = 7.7 Hz), 140.9 (d, $^1J$(PC) = 33.6 Hz, C4), 138.4 (d, $^2J$(PC) = 10.5 Hz, C1), 136.2, 134.6, 133.3 (d, $^1J$(PC) = 41.3 Hz, C2), 133.2 (d, $J$(PC) = 12 Hz), 133.1, 130.4 (d, $J$(PC) = 1.9 Hz), 130.1, 129.7, 129.0 (d, $J$(PC) = 3.9 Hz), 128.6, 128.5, 128.4, 128.3, 128.0, 127.8 (d, $J$(PC) = 1.9 Hz), 126.8, 124.4, 123.0 (4Ar), 82.8 (d, 1C, $^3J$(PC) = 10.5 Hz, $^1J$(CH) = 140 Hz, C6), 53.3 (s, $OCH_3$), 21.3 (s, $CH_3$). $^{31}$P-NMR (121.50 MHz, $CDCl_3$): 0.0 (s, $^1J$(PW) = 243 Hz).

**X-ray Crystallographic Studies of 3, 8, 9, and 11.** The structures were solved by Patterson methods (**8**, **9**, **11**) and direct methods (**3**) (SHELXTL-Plus).[16] The non-hydrogen atoms were refined anisotropically on $F^2$ (SHELXL-93).[17] Hydrogen atoms were refined isotropically using a riding model. An absorption correction ($\psi$-scans; **8** $T_{max/min}$ = 0.988/0.653; **9**, $T_{max/min}$ = 0.958/0.618; **11** $T_{max/min}$ = 1.000/0.689; and DIFABS, **3**)[18] and an extinction correction (**3**) were applied. Further details are given in Table 5.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft (Grant No. SFB 334) for financial support. K.I. is grateful to the Fonds der Chemischen Industrie for a scholarship.

**Supporting Information Available:** Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **3**, **8**, **9**, and **11** (26 pages). Ordering information is given on any current masthead page.

OM960984U

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