An Approach to Novel Complexes with a Tungsten−Phosphorus Triple Bond†

Manfred Scheer,* Peter Kramkowski, and Kay Schuster

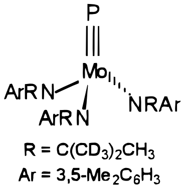
Institut für Anorganische Chemie der Universität Karlsruhe, D-76128 Karlsruhe, Germany

Received January 13, 1999

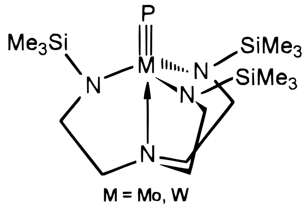
The metathesis reaction of [$W_2(OtBu)_6$] with tBuC≡P leads to the phosphido complex [$(tBuO)_3W≡P$] (**1**), which can be stabilized when the reaction is carried out in the presence of Lewis acidic carbonyl complexes of the type [$M(CO)_5$thf] (M = Cr, W). However, further reaction of the metathesis products [$(tBuO)_3W≡CtBu$] and [$(tBuO)_3W≡P\rightarrow M(CO)_5$] [M = W (**4a**), Cr (**4b**)] with tBuC≡P leads after subsequent 1,3-OtBu shift to the metallaphosphacyclobutadiene derivatives [$(tBuO)_2W\{C(tBu)\}_2P(OtBu)$] (**2a**) and [$(tBuO)_2WC(tBu)P\{M(CO)_5\}P(OtBu)$] [M = W (**5a**), M = Cr (**5b**)]. To prevent the latter, the bulky phosphaalkyne Ar′C≡P (Ar′ = 2,4,6-$tBu_3C_6H_2$) was employed in the three-component reaction instead of tBuC≡P. Surprisingly here, a “head-to-tail” dimerization of Ar′C≡P occurs to give the novel phosphinidene complexes [$M(CO)_4P(R')C(Ar')P\{MCO)_5\}$] [M = Cr (**6a**), M = W (**6b**); R′ = 2,4-tBu_2-7-Me_2-indanyl]. In the case of [$W(CO)_5$thf], additionally, the complex [$W(CO)_2\{(\eta^2\text{-}PCAr')W(CO)_5\}_2$] (**7**) is formed. The function of [$W_2(OtBu)_6$] in this reaction is uncertain, but stoichiometric amounts of [$W_2(OtBu)_6$] are essential to obtain complex **6**. Reduction of the size of the alkoxide ligands by the use of [$W_2(ONp)_6$] (Np = CH_2tBu) in the three-component reaction with Ar′C≡P leads to the trinuclear cluster compounds [$W_3\langle(\mu_3\text{-}P)\{W(CO)_5\}\rangle(\mu\text{-}ONp)_3(ONp)_6$] (**8**) and [$W_3(\mu_3\text{-}P)(\mu\text{-}ONp)_3(ONp)_6$] (**9**). The crucial step of the side-product free synthesis of the phosphido complexes **4** is the introduction of MesC≡P (Mes = 2,4,6-$Me_3C_6H_2$) into the three-component system of [$W_2(OtBu)_6$], RC≡P, and [$W(CO)_5$thf]. Comprehensive structural and spectroscopic data are given for the products. Furthermore, a ^{31}P NMR experiment was conducted following the reaction of [$W_2(OtBu)_6$] with MesC≡P from −70 °C to ambient temperature. In the range of −60 to −40 °C, a singlet at 845 ppm with one pair of tungsten satellites ($^1J_{W,P}$ = 176 Hz) was observed for the complex [$(tBuO)_3W≡P$] (**1**).

Introduction

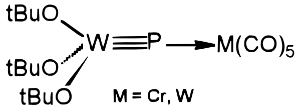
Complexes with terminal phosphido ligands are a new class of compounds.[1] In 1995, in the groups of Cummins[2] and Schrock,[3] the first examples of complexes of type **A** and **B**, respectively, were isolated and structurally characterized. In these compounds the metal−phosphorus triple bond is kinetically stabilized by the very bulky amide ligands. Thus, they reveal exclusively end-on reactivity.[4] Our interest, however, concentrates on the side-on reactivity of W≡P triple bonds. This reactivity pattern is satisfied by the alkoxide-substituted phosphido complexes of type **C**.[5] The flexibility of the alkoxide ligands and the coordination of the lone pair of the terminal P^{3-} ligand to a $W(CO)_5$ group are characteristic for these compounds.



A



B



C

However, due to their high side-on reactivity, the synthesis of type **C** complexes via the metathesis reaction of [$W_2(OtBu)_6$] with phosphaalkyne in the presence of [$M(CO)_5$thf] (M = Cr, W) is problematic. Until recently we had only been able to obtain insepa-

---

* To whom correspondence should be addressed: (fax) +49 (0) 721 662119; (e-mail) mascheer@achibm6.chemie.uni-karlsruhe.de.

† Dedicated to Prof. Dr. E. Niecke on the occasion of his 60th birthday.

(1) Reviews: Scheer, M. *Angew. Chem.* **1995**, *107*, 2151−2153. Scheer, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1997−1999. Scheer, M. *Coord. Chem. Rev.* **1997**, *163*, 271−286.

(2) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem.* **1995**, *107*, 2181−2183; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042−2043.

(3) Zanetti, N.; Schrock, R. R.; Davis, W. M. *Angew. Chem.* **1995**, *107*, 2184−2186; *Angew. Chem., Int Ed. Engl.* **1995**, *34*, 2044−2046.

(4) (a) Johnson-Carr, M. J. A.; Lee, P. M.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *Angew. Chem.* **1997**, *109*, 110−113; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 87−91. (b) Johnson, M. J. A.; Odom, A. L.; Cummins, C. C. *J. Chem. Soc., Chem. Commun.* **1997**, 1523−1524. (c) Johnson-Carr, J. A.; Zanetti, N. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11305. (d) Scheer, M.; Müller, J.; Baum, G.; Häser, M. *J. Chem. Soc., Chem. Commun.* **1998**, 1051−1052.

(5) Scheer, M.; Schuster, K.; Budzichowski, T. A.; Chisholm, M. H.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 1671−1672.

10.1021/om990019e CCC: $18.00

Table 1. ^{31}P NMR Data of the Complexes 1−9 in C_6D_6 at 300 K (δ in ppm, *J* in Hz[a])

	δ	$^1J_{P,P}$	$^1J_{W,P}$
$[(tBuO)_3W{\equiv}P]$ **1**[a]	845 (s)		176
$[(tBuO)_2W\langle\{C(tBu)\}_2P(OtBu)\rangle]$ **2a**	−166.2 (s)		
$[(tBuO)_2W\langle\{C(Ad)\}_2P(OtBu)\rangle]$ **2b**	−170.3 (s)		
$[(tBuO)_2W\langle\{C(Mes)\}_2P(OtBu)\rangle]$ **2c**	−156.2 (s)		
$[(tBuO)_2W\langle C(tBu)PP(OtBu)\rangle]$ **3a**	412.2 (d)	435	213
	−109		
$[(tBuO)_2W\langle C(Mes)PP(OtBu)\rangle]$ **3b**	413.2 (d)	438	213
	−105.9 (d)		
$[(tBuO)_3W{\equiv}P{\rightarrow}W(CO)_5]$ **4a**	546.0 (s)		553 and 163
$[(tBuO)_3W{\equiv}P{\rightarrow}Cr(CO)_5]$ **4b**	595.4 (s)		536
$[(tBuO)_3W{\equiv}P{\rightarrow}Cp''Mn(CO)_2]$ **4c**	614.0 (s)		565.8
$[(tBuO)_2W\langle C(tBu)P\{W(CO)_5\}P(OtBu)\rangle]$ **5a**	291.7 (d)	447	223 and 183
	−127.4 (d)		
$[(tBuO)_2W\langle C(tBu)P\{Cr(CO)_5\}P(OtBu)\rangle]$ **5b**	352.5 (d)	466	235
	−130.6 (d)		
$[(tBuO)_2W\langle C(tBu)P\{Cp''Mn(CO)_2\}P(OtBu)\rangle]$ **5c**	421.4 (d)	445	277
	−131.2 (d)		
$[(tBuO)_2W\langle C(Ad)P\{Cp''Mn(CO)_2\}P(OtBu)\rangle]$ **5d**	418.5 (d)	448	279
	−132.6 (d)		
$[Cr(CO)_4P(R')C(Ar')P\{Cr(CO)_5\}]$ **6a**	983.8 (d)	40.6	
	391.9 (d)		
$[W(CO)_4P(R')C(Ar')P\{W(CO)_5\}]$ **6b**	787.3 (s)		186 and 117
	313.9 (s)		202
$[W(CO)_2\{\eta^2\text{-}PCAr')W(CO)_5\}_2]$ **7**	318.1		250
$[W(\mu\text{-}ONp)_3(ONp)_6\langle(\mu\text{-}P)\{W(CO)_5\rangle]$ **8**	165.4		228
$[W(\mu\text{-}ONp)_3(ONp)_6(\mu\text{-}P)]$ **9**	273.3		45.3
$[\langle(tBuO)_2WP{\rightarrow}W(CO)_5\rangle_2]$ **10**	437.1		220

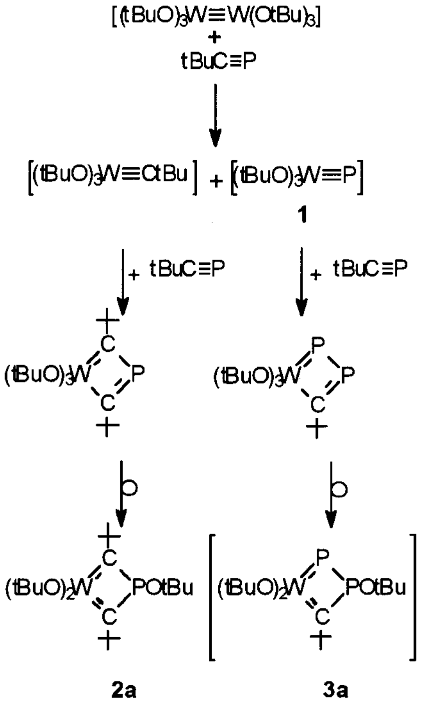
[a] In toluene-d_8 at 243 K.

rable mixtures containing the desired products with a tungsten−phosphorus triple bond, as well as four-membered-ring derivatives which arose from the subsequent cycloaddition of the phosphido and alkylidyne complex with phosphaalkyne followed by a 1,3-OR shift.[5] Herein we report how we overcame these problems and present a new strategy for the synthesis of alkoxide-substituted tungsten phosphido complexes under sufficient exclusion of the side products.

Results and Discussion

Two-Component Reaction of $[W_2(OtBu)_6]$ with RC≡P (R = tBu, Mes; Mes = 2,4,6-$Me_3C_6H_2$). Investigations concerning the metathesis reaction of dinuclear tungsten alkoxide complexes such as $[W_2(OtBu)_6]$ containing a tungsten−tungsten triple bond were first performed by Schrock and co-workers. They reported the formation of carbyne and nitrido complexes via the conversion of these alkoxides with alkynes and nitriles.[6,7] In 1985, Becker and co-workers investigated the metathesis reaction of $[W_2(OtBu)_6]$ with tBuC≡P. They were able to isolate $[(tBuO)_2W\{C(tBu)\}_2P(OtBu)]$ (**2a**) and had ^{31}P NMR spectroscopic evidence for the formation of $[(tBuO)_2W\{(tBu)CPP(OtBu)\}]$ (**3a**). These results led to the postulation of a phosphido complex $[(tBuO)_3W{\equiv}P]$ (**1**) as a possible intermediate in this reaction (Scheme 1).[8] According to the proposed reaction pathway, the first step of the conversion is the formation of the alkylidyne complex $[(tBuO)_3W{\equiv}CtBu]$ and the phosphido complex **1**, which undergoes a further formal cycloaddition with another equivalent of tBuC≡P followed by a 1,3-OR migration to give the four-membered-ring derivatives **2a** and **3a** as the only reaction products.

Scheme 1. Metathesis Reaction of $[W_2(OtBu)_6]$ with tBuC≡P



For comparison we repeated this reaction in THF at −21 °C. After workup at ambient temperature, the ^{31}P NMR spectrum (Table 1) of the crude reaction mixture revealed a sharp singlet at high field (−166 ppm) which could be assigned to **2a** (50 mol % P), as well as two doublets at 412.2 and −109 ppm ($^1J_{P,P}$ = 435 Hz) indicating the formation of **3a**. The doublet at downfield

---

(6) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(7) Schrock, R. R.; Listemann, M. L. *Organometallics* **1985**, *4*, 74.

(8) (a) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weeber, U.; Westerhausen, M. *Nova Acta Leopoldina* **1985**, *59*, 55−67. (b) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildenbrand, U.; Westerhausen, M. *Phosphorus Sulfur* **1987**, *30*, 349. (c) Binger, P. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; p 100.

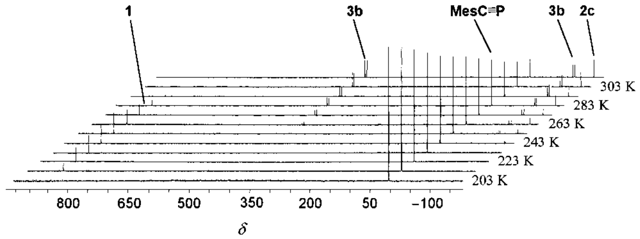


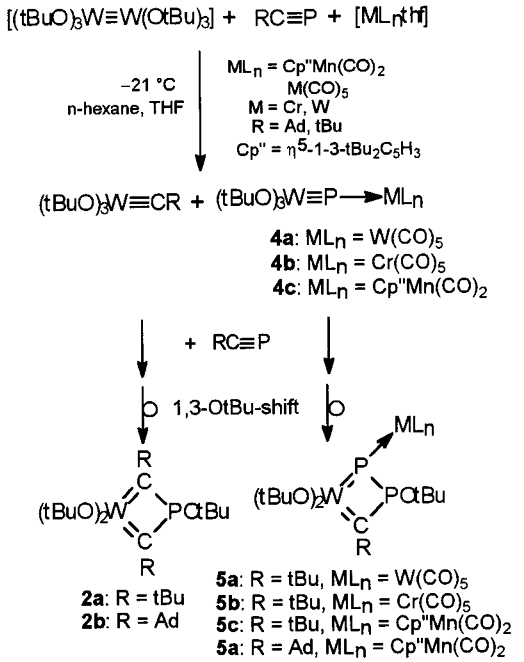
Figure 1. $^{31}P\{^1H\}$ NMR spectra of the reaction between MesC≡P and $[W_2(OtBu)_6]$ at different temperatures in toluene-d_8 (SF = 101.256 MHz). For clarity, the intensity of the starting material MesC≡P at 2.5 ppm (300 K) is reduced by ~30%. **1**, $[(tBuO)_3W{\equiv}P]$; **2c**, $[(tBuO)_2W\langle\{C(Mes)\}_2P(OtBu)\rangle]$; **3b**, $[(tBuO)_2W\langle C(Mes)PP(OtBu)\rangle]$.

bears one pair of tungsten satellites with a coupling constant of $^1J_{W,P}$ = 213 Hz. Those results verified Becker's observations and confirmed the very high reactivity of the alkylidyne and especially of the phosphido complex with additional phosphaalkyne.

To gain more information on whether a phosphido intermediate exists or not, we followed the reaction of $[W_2(OtBu)_6]$ with MesC≡P (Mes = 2,4,6-$Me_3C_6H_2$) by $^{31}P\{^1H\}$ NMR spectroscopy as a function of temperature from −70 to 25 °C.[9] Indeed, a signal at 845 ppm with one pair of tungsten satellites was detected ($^1J_{W,P}$ = 176 Hz), which can be assigned to the complex $[(tBuO)_3W{\equiv}P]$ (**1**) (Figure 1). The $^{31}P\{^1H\}$ NMR chemical shift of **1** appears also in the downfield region as observed for the phosphorus signal of the terminal phosphido complex **B** (M = W)[3] (1080 ppm), and the $^1J_{W,P}$ is in the same range as found for **B** (138 Hz). Additionally, at 243 K the formation of the WC_2P derivative $[(tBuO)_2W\{C(Mes)\}_2P(OtBu)]$ (**2c**) (−156.2 ppm) and at 253 K the WCP_2 ring compound $[(tBuO)_2W\{(Mes)CPP(OtBu)\}]$ (**3b**) (δ = 413.2 and −105.9 ppm; $^1J_{P,P}$ = 438 Hz) was observed. This indicates that the alkylidyne complex $[(tBuO)_3W{\equiv}CMes]$ is more reactive than the phosphido complex **1**. At 293 K, the phosphido complex is transformed completely into the four-membered-ring derivative **3b**.

Three-Component Reaction between $[W_2(OtBu)_6]$ and RC≡P in the Presence of $[ML_n thf]$ [ML_n = $Cr(CO)_5$, $W(CO)_5$, $Cp''Mn(CO)_2$ (Cp'' = η^5-1,3-$tBu_2C_5H_3$)]. (a) Reactions Starting from RC≡P [R = tBu, Ad (adamantyl, $C_{10}H_{15}$)]. We developed the concept of the three-component reaction in our group in order to investigate the transformation pathway of the P_4 tetrahedron in the coordination sphere of transition metals. By addition of Lewis acidic compounds such as $[Cr(CO)_5thf]$ to the reaction mixtures of P_4 and the corresponding coordination compound, the lone pairs of the P_n ligands formed first are able to coordinate to the $Cr(CO)_5$ moieties, and thus, intermediates can be stabilized along the reaction pathway.[10−12] The fundamental success in P_4 chemistry implied that application of this method to the system $[W_2(OtBu)_6]$/RC≡P in order to stabilize type **C** complexes should be possible.

Scheme 2. Three-Component Reaction between $[W_2(OtBu)_6]$ and RC≡P (R = tBu, Ad) in the Presence of Lewis Acidic Carbonyl Complexes



We carried out the reaction of $[W_2(OtBu)_6]$ with tBuC≡P in the presence of $[M(CO)_5thf]$ at −21 °C. Workup was conducted at 0 °C in order to prevent the reaction of tBuC≡P with $[W(CO)_5thf]$ alone.[5] Small quantities of $W(CO)_6$ and almost the whole amount of $[(tBuO)_3W{\equiv}CtBu]$ were removed from the crude product by sublimation under high vacuum. The ^{31}P NMR spectrum of the remaining product mixture reveals signals for the WC_2P four-membered-ring derivative **2a** (40−45 mol % P) as well as for the WP_2C derivatives $[(tBuO)_2WC(tBu)P\{M(CO)_5\}P(OtBu)]$ [M = W (**5a**), M = Cr (**5b**)] (30−35 mol % P). Additionally, a sharp singlet at downfield is observed for the phosphido complexes $[(tBuO)_3W{\equiv}P{\rightarrow}M(CO)_5]$ [M = W (**4a**), Cr (**4b**)] (15 mol % P).

The nature of the products indicates a similar course of the reaction as observed without $[M(CO)_5thf]$ (Scheme 2). First the formation of $[(tBuO)_3W{\equiv}CtBu]$ and the phosphido complex $[(tBuO)_3W{\equiv}P{\rightarrow}M(CO)_5]$ [M = W (**4a**), M = Cr (**4b**)] occurs. The cycloaddition of **4a,b** and the alkylidyne complex with tBuC≡P yields, after subsequent 1,3-OR shift, the metallaphosphabutadiene derivatives **5a,b** and **2a**, respectively.[13] Due to the coordination of phosphorus to a $M(CO)_5$ group in the phosphido complex, a subsequent reaction can be partially prevented.

Since the ratio of the product distribution was not satisfactory, we increased the bulk at the phosphaalkyne and at the carbonyl fragment using AdC≡P and $[Cp''Mn(CO)_2thf]$ in order to prevent the side-on reaction of the desired products. However, a combination of both variations led only to an increased yield of the WP_2C ring

---

(9) In the analogous ^{31}P NMR experiment with tBuC≡P, the ^{31}P NMR data of **1** could not be observed due to the fast consecutive reaction of it with tBuC≡P.

(10) Scheer, M.; Troitzsch, C.; Jones, P. G. *Angew. Chem.* **1992**, *104*, 1395; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1377−1379. Scheer, M.; Troitzsch, C.; Hilfert, L.; Dargatz, M.; Kleinpeter, E.; Jones, P. G.; Sieler, J. *Chem. Ber.* **1995**, *128*, 257.

(11) Scheer, M.; Becker, U.; Huffman, J. C.; Chisholm, M. H. *J. Organomet. Chem.* **1993**, *461*, C1.

(12) Scheer, M.; Becker, U.; *Chem. Ber.* **1996**, *129*, 1307−1310. Scheer, M.; Becker, U.; Magull, J. *Polyhedron* **1998**, *17*, 1983−1989.

(13) A 1,3-alkoxide migration is also found after the cycloaddition of phosphaalkynes to metal alkylidenes: Jamison, G. M.; Saunders, R. S.; Wheeler, D. R.; McClain, M. D.; Loy, D. A.; Ziller, J. W. *Organometallics* **1996**, *15*, 16−18.

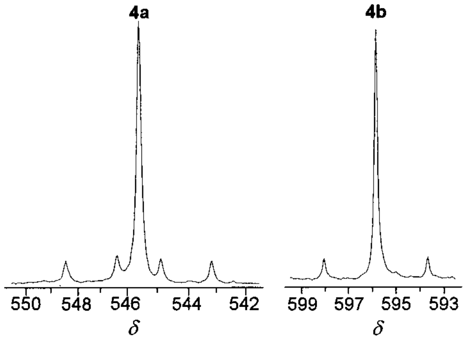
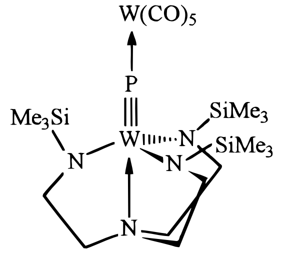


Figure 2. $^{31}P\{^1H\}$ NMR resonances of the phosphido complexes **4a** and **4b** in benzene-d_6 (SF = 101.256 MHz).

derivative **5d**. The best results were achieved for the system $[W_2(OtBu)_6]/tBuC{\equiv}P/[Cp''Mn(CO)_2thf]$. According to the ^{31}P NMR spectrum of the crude reaction mixture, the amount of the formed phosphido complex $[(tBuO)_3W{\equiv}P{\rightarrow}MnCp''(CO)_2]$ (**4c**) could be increased to 25 mol % P. In this system, the steric demand of the Lewis acidic carbonyl fragment is of great importance. The phosphido complex $[(tBuO)_3W{\equiv}P{\rightarrow}ML_n]$ is better stabilized with a $[Cp''Mn(CO)_2]$ group than with $M(CO)_5$ (M = Cr, W). Use of AdC≡P does not seem to have any influence on the product distribution and is not able to inhibit the cycloaddition to any greater extent than tBuC≡P.

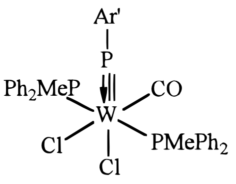
Complexes with alkoxide ligands are very sensitive to moisture and oxygen. Thus, a separation of the reaction mixture by column chromatography resulted in an undefined decomposition of all products independent of the type and method of preparation of the column material employed (activated or deactivated silica gel, Al_2O_3, silanized silica gel, Biobeads[14]). A separation of the reaction mixture can be partially achieved by fractional crystallization in *n*-pentane. In the first fraction, unreacted $[W_2(OtBu)_6]$ is removed. From the second fraction, crystals of pure $[(tBuO)_2W(CR)_2P(OtBu)]$ (**2a,c**) (R = tBu, Ad) can be isolated. It was not possible to obtain crystals of any other product from these mixtures. By fractional crystallization, however, we were able to enrich the concentration of phosphido complex **4a**−**c** in these solutions up to 45 mol % P with respect to the other phosphorus-containing species.

In the ^{31}P NMR spectrum, **4a**−**c** show a singlet at downfield (546−614 ppm) with satellites revealing a large coupling constant for the tungsten−phosphorus triple bond (536−566 Hz). Due to the coordinative bond of the lone pair of the P^{3-} ligand to the $W(CO)_5$ moiety (Figure 2) for **4a**, a further coupling is observed ($^1J_{W,P}$ = 163 Hz). Experimental and theoretical studies in our group confirmed that, due to the linear coordination of the lone pair of the phosphido ligand to Lewis acids, the s-character of the W≡P triple bond is dramatically increased, and in correspondence with the Fermi contact term, a drastic increase of the $^1J_{W,P}$ coupling constant occurs.[15] A shift toward high field for the phosphorus resonance after coordination to a Lewis acidic carbonyl complex is characteristic, too.[16] This is demonstrated by the comparison of coupling constant and chemical shift in the $^{31}P\{^1H\}$ NMR spectrum of the terminal phosphido ligand complex **1** (δ = 845 ppm, $^1J_{W,P}$ = 176 Hz) and the coordinated compounds **4a**−**c**. The same effect is observed for the tungsten complexes **B** (δ = 1080 ppm, $^1J_{WP}$ = 138 Hz)[3] and **D** (δ = 662.6 ppm; $^1J_{W,P}$ = 450 and 135 Hz).[15] For the phophinidene complex **E**, a chemical shift at 193 ppm with a $^1J_{W,P}$ of 649 Hz is found.[17] This complex possesses a linear arrangement along the W−P−R axis, and due to coordination of the free electron pair of the phosphinidene ligand, a formal W≡P triple bond is formed [**E**, d(WP) = 2.169(1) Å; **B**, d(WP) = 2.162(4) Å]. The bent phosphinidene complex **F**, however, reveals the opposite situation: the free electron pair is localized at the P atom. Thus, the W−P−R core is not linear, and the signal of **F** in the ^{31}P NMR spectrum appears downfield at 661.1 ppm with a significantly smaller coupling constant $^1J_{W,P}$ of only 153.5 Hz [**F**, d(WP) = 2.349(5) Å].[18]

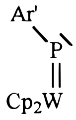


D

Ar' = 2,4,6-tBu$_3$C$_6$H$_2$



E



F

The ^{31}P NMR spectra (Table 1) of the WC_2P ring derivatives **2a**−**c** show high-field-shifted resonances in the range of −156 to −160 ppm, indicating the existence of a OtBu group bound to the P atom in all cases. For the WCP_2 complexes **3a,b** and **5a**−**d**, two doublets at downfield and high field are detected. The large $^1J_{P,P}$ coupling constants of these compounds (435−466 Hz) indicate the multiple-bond character of the P−P bond. It is of interest, that the ring system in the complexes **3a,b**, which do not reveal exocyclic coordination to a metal carbonyl fragment, shows smaller $^1J_{P,P}$ coupling constants. All doublets at high field are within a small range (−109.0 to −132.6 ppm) and can therefore be assigned to the phosphorus bearing the OR group. The doublets at downfield show a considerable difference in their chemical shifts, which is due to the coordination of this P atom to a different exocyclic metal atom of the complex fragments ML_n. Whereas the coordination to Mn complex fragments has no considerable influence on the ^{31}P chemical shifts, coordination to a Cr or W pentacarbonyl fragment causes a high field shift of approximately 70 and 130 ppm, respectively. However, all $^1J_{W,P}$ of the ring tungsten atoms with the phosphorus are quite comparable (213−279 Hz); again, the smaller values correspond to the complexes **3a,b** without the exocyclic ML_n moiety. Additionally, **5a** further reveals a $^1J_{W,P}$ of 183 Hz for its coupling of the ring phosphorus atoms to the exocyclic $W(CO)_5$ group.

---

[14] With Biobeads, no decomposition but also no separation was observed.

[15] Scheer, M.; Müller, J.; Häser, M. *Angew. Chem.* **1996**, *108*, 2637−2641; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2492.

[16] Wagener, T.; Frenking, G. *Inorg. Chem.* **1998**, *37*, 1805−1811.

[17] Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734.

[18] Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

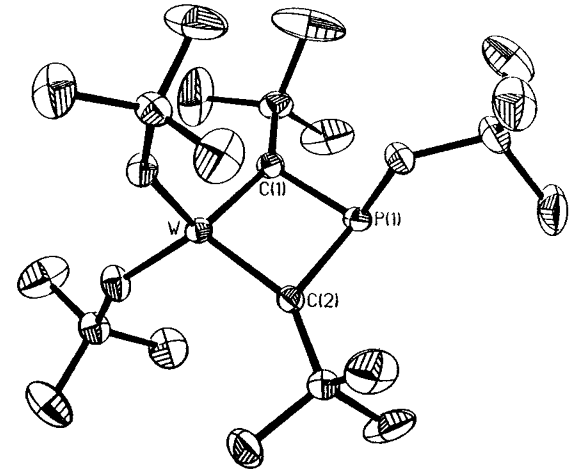


Figure 3. Molecular structure of [$(tBuO)_2W(CtBu)_2P(OtBu)$] (**2a**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W−C(1) 1.871(5), W−C(2) 1.857(5), P(1)−C(1) 1.814(5), P(1)−C(2) 1.822(5), P(1)−O(3) 1.648(4), C(2)−C(7) 1.515(7), C(1)−C(3) 1.526(7), W−O(1) 1.858(4); C(2)−P(1)−C(1) 94.3(2), C(1)−W−C(2) 91.3(2), W−C(2)−P(1) 86.3(2), P(1)−C(1)−W 86.1(2), W−O(2)−C(19) 146.3(3), P(1)−O(3)−C(11) 124.3(3).

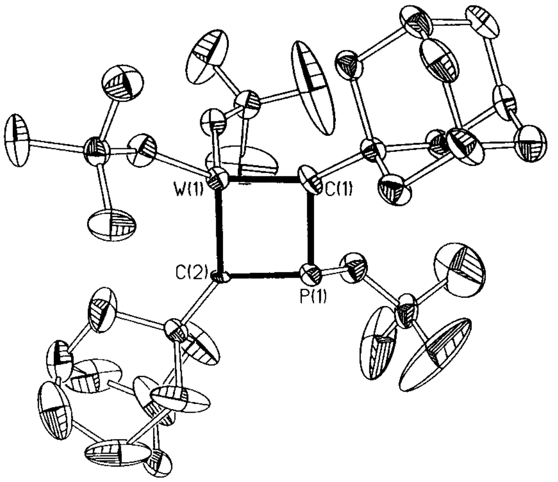


Figure 4. Molecular structure of [$(tBuO)_2W(CAd)_2P(OtBu)$] (**2b**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W−C(1) 1.871(8), W−C(2) 1.931(5), P(1)−C(1) 1.913(10), P(1)−C(2) 1.785(6), P(1)−O(3) 1.680(8), C(2)−C(21) 1.472(9), C(1)−C(11) 1.488(10), W−O(1) 1.883(7); C(2)−P(1)−C(1) 96.3(3), W−C(2)−P(1) 85.8(2), P(1)−C(1)−W 84.0(3), C(1)−W−C(2) 92.9(3), W−O(2)−C(7) 154.0(7), P(1)−O(3)−C(31) 127.5(8).

The X-ray analysis of **2a** (Figure 3) reveals a distorted quadratic WC_2P framework which is folded by 14.3° along the W⋯P axis. The angles deviate only slightly from 90°. The bond lengths between the four vertexes do not differ considerably either. The tungsten atom is surrounded in a distorted tetrahedral manner by two carbon and two oxygen atoms. The tungsten carbon distances are with 1.871(5) and 1.856(5) Å, typical for carbon−tungsten double bonds as found for [$W(=CHtBu)Cl_2(CO)(PMe_3)_2$] [*d*(WC) = 1.859(4) Å][19] and [$W(C_3Et_3)\{OCH_3(CF_3)_2\}_3$] [*d*(WC) = 1.862(17) Å].[20] The P−C distances come to 1.822(5) and 1.871(5) Å, from which the latter corresponds to a slightly shortened P−C single-bond distance as found in 1,3-diphosphacyclobutadiene complexes (e.g., [$CpCo\{\eta^4-(tBu_2C_2P_2)\}$], *d*(PC) = 1.797(3)−1.798(3) Å[21] and [$Cp^*Co\{\eta^4-(tBu_2C_2P_2)\}$], *d*(PC) = 1.79(1)−1.82(1) Å[22]). The P−O distance of 1.648(4) Å is typical for P−O single bonds. The carbon atoms C1 and C2 are coordinated in an approximately trigonal-planar fashion. But due to the steric hindrance induced through the tBuO ligands at the tungsten center and the tBu substituents at C1 and C2, the ideal geometry is distorted.

The structure of **2b** (Figure 4) is similar to that of **2a**, but here the WC_2P ring is folded by only 9.8° along the W⋯P axis (**2a**, 14.3°). While **2a** forms an almost regular square, the WC_2P core in **2b** possesses an irregular trapezoidal shape, and the angles as well as the distances between the vertexes of the four-membered ring have larger deviations than observed for **2a** [**2b**, angle range of 84.0(3)−96.3(3)°; bond lengths, 1.785(6)−1.931(5) Å]. Especially the bond distance W−C2 [1.931(9) Å] is 0.06 Å longer than the average W−C bond length in **2a** (1.8635 Å). This distance is nevertheless still in the range of W=C double bonds as, for example, found in [W(CtBuCCtBu)Cp(Cl)] [*d*(WC) = 1.924(8) Å][23] and [$W(CHCHCPhN)W(OtBu)_6$] [*d*(WC) = 1.943(5) Å].[24] Also the P−C bonds in **2b** differ considerably from each other. Whereas the bond P−C2 is with 1.785(6) Å only 0.03 Å shorter than in **2a**, the bond length of P−C1 is with 1.913(10) Å strongly elongated. Therefore, it is rather comparable to P−C single-bond distances as observed for the diphosphene complex [$Fe_2(CO)_6(PtBu)_2$] [*d*(PC) = 1.875(7) Å].[25] The described bonding situation at the P atom induces an asymmetry in the molecule. Therefore, **2b** crystallizes in enantiomerically pure form in the chiral space group $P2_12_12_1$.

(b) Reactions Starting from Ar′C≡P (Ar′ = 2,4,6-$tBu_3C_6H_2$). The key challenge in the synthesis of phosphido complexes of type **C** is a complete inhibition of the subsequent cycloaddition of further phosphaalkyne. Therefore, we employed supermesitylphosphaalkyne Ar′C≡P to prevent the latter. The conversion of [$W_2(OtBu)_6$] with Ar′C≡P in the presence of [$M(CO)_5(thf)$] (M = W, Cr) was carried out at −21 °C. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture indicated the formation of the complex [$M(CO)_4P(R')C(Ar')P\{M(CO)_5\}$] (**6a**, M = Cr; **6b**, M = W; R′ = 2,4-tBu_2-7-Me_2-indanyl) in addition to relatively large quantities of unreacted Ar′C≡P. The yield of **6** could be increased when the reaction was performed at ambient temperature. For the reaction starting from [$W(CO)_5(thf)$] aside from **6b**, the spirocyclic compound **7** is also obtained in approximately equal amounts (eq 1).

---

[19] Schrock, R. R.; Wengrovius, J. H.; Churchill, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 1739.

[20] Schrock, R. R.; Freudenberger, J. H.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563.

[21] Binger, P.; Milczarek, R.; Mynott, R.; Krüger, C.; Tsay, Y.-H.; Raabe, E.; Regitz, M. *Chem. Ber.* **1988**, *121*, 637.

[22] Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 737.

[23] Schrock, R. R.; Listemann, M. L.; McCullough, L. G.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

[24] Schrock, R. R.; Pedersen, S. F.; McCullough, L. G.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1983**, **2**, 1046.

[25] Vahrenkamp, H.; Wolters, D.; Lal De, R. *Z. Naturforsch.* **1986**, *41*, 283.

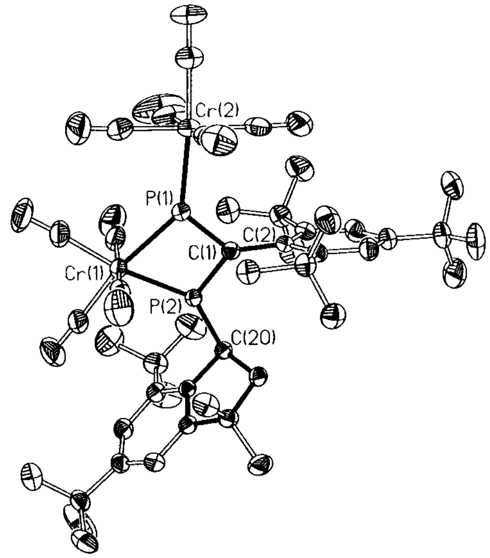
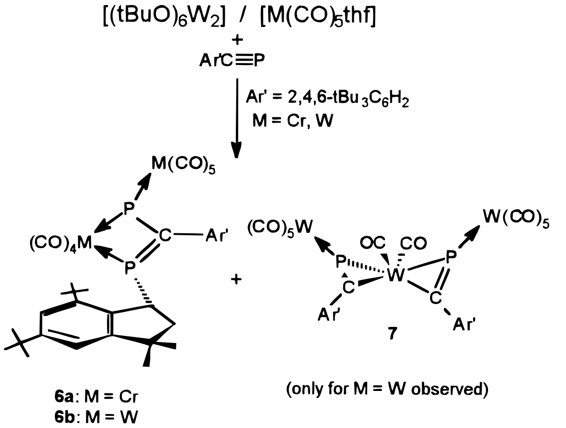


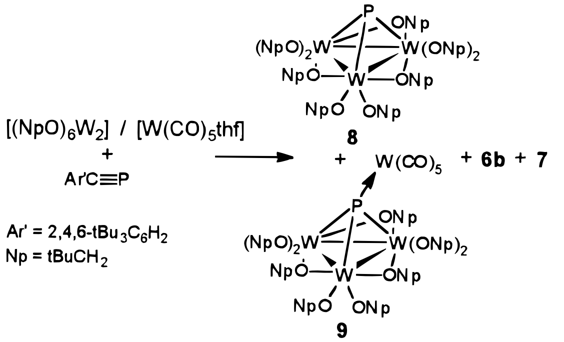
Figure 5. Molecular structure of $[\mathrm{Cr(CO)_4P(R')C(Ar')P\{Cr(CO)_5\}}]$ (**6a**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Cr(1)−P(1) 2.3410(7), Cr(1)−P(2) 2.2675(7), Cr(2)−P(1) 2.3167(7), P(1)−C(1) 1.797(2), P(2)−C(1) 1.712(2), P(2)−C(20) 1.864(2); Cr(1)−P(1)−C(1) 96.63(7), P(1)−C(1)−P(2) 93.81(11), C(1)−P(2)−Cr(1) 101.97(8), P(2)−Cr(1)−P(1) 67.56(2).



(1)

Complex **7** is the only product of the reaction between $[\mathrm{W(CO)_5thf}]$ and Ar′C≡P alone.[26] Obviously, the influence of $[\mathrm{W_2(OtBu)_6}]$ is responsible for a "head-to-tail" dimerization of Ar′C≡P, yielding the novel phosphinidene complexes **6**. The function of $[\mathrm{W_2(OtBu)_6}]$, however, is uncertain. Experiments show that stoichiometric amounts of $[\mathrm{W_2(OtBu)_6}]$, $[\mathrm{MCO)_5thf}]$, and Ar′C≡P are essential for the formation of **6**. After the "head-to-tail-dimerization", the C20 atom becomes unsaturated (cf. Figure 5). Subsequently, a C−H activation involving a 1,2-H shift from the methyl group of one of the ortho tBu groups to C20 occurs and leads to a five-membered ring. C−H activations are common for systems containing supermesityl groups and a heteroatom at position one of the aromatic ring.[27−29] To the best of our knowledge, **6a,b** are the first examples for the creation of a five-membered indanyl ring system with ring closure to a carbon atom. Usually, five-membered rings containing a heteroatom (e.g., P[28] or Ge[29]) are generated. Recently, Jones et al. showed the formation of a six-membered ring in a complex containing arsenic.[30]

Since no metathesis reaction between Ar′C≡P and $[\mathrm{W_2(OtBu)_6}]$ is observed in the three-component reaction 1, the steric hindrance of the alkoxide ligands at the tungsten atom was reduced by using $[\mathrm{W_2(ONp)_6}]$ (Np = $\mathrm{CH_2tBu}$). Under conditions identical to those described before (−21 °C, workup at 0 °C), the reaction of $[\mathrm{W_2(ONp)_6}]$ with Ar′C≡P in the presence of $[\mathrm{W(CO)_5thf}]$ was carried out (eq 2).



(2)

The grade of conversion is relatively small, but higher than observed for reaction 1. Complex $[\mathrm{W_3\langle(\mu_3\text{-}P)\{W(CO)_5\}\rangle(\mu\text{-}ONp)_3(ONp)_6}]$ (**8**) is obtained as the main product followed by **7**, **6b**, and **9**. The amount of **6b** formed is higher than in the case of the reaction starting from $[\mathrm{W_2(OtBu)_6}]$. The yield of the spirocyclic compound **7** is similar to that of reaction 1 and **7** appears to be a common side product of these reactions resulting from the two-component reaction of Ar′C≡P with $[\mathrm{W(CO)_5thf}]$. If $[\mathrm{Cr(CO)_5thf}]$ is used in reaction 2, the grade of conversion of Ar′C≡P is increased to ∼80%, and complex **6a** is formed as almost the only product. Here, the head-to tail dimerization (eq 1) becomes the favored reaction.

Crystals of **6** and **9** are obtained by fractional crystallization from *n*-pentane solutions of reaction 2. **9** crystallizes in the trigonal space group $R3$ with the lattice constants $a = b = 23.55(8)$ Å, $c = 17.97(6)$ Å. Thus, **9** is identical to the complex $[\mathrm{W_3(\mu_3\text{-}P)(\mu\text{-}ONp)_3(ONp)_6}]$ characterized by Chisholm et al. and obtained from the reaction of $[\mathrm{W_2L_2(ONp)_6}]$ (L = $\mathrm{Me_2NH}$, Py) with white phosphorus.[31] **9** is soluble in all common organic solvents and decomposes within minutes when exposed to oxygen or moisture. The main product of reaction 2 is the complex $[\mathrm{W_3\langle(\mu_3\text{-}P)\{W(CO)_5\}\rangle(\mu\text{-}ONp)_3(ONp)_6}]$ (**8**). However, no suitable crystals for an X-ray structure analysis could be isolated. Nevertheless, **8** could be synthesized independently by the reaction of $[\mathrm{W_3(\mu_3\text{-}P)(\mu\text{-}ONp)_3(ONp)_6}]$ with $[\mathrm{W(CO)_5thf}]$. The ^{31}P NMR spectroscopic properties of both compounds obtained by different routes are identical.

The complexes **6a,b**[32] crystallize in the form of dark green plates and are soluble in all common organic

---

(26) Kramkowski, P.; Scheer, M.; Baum, G. *J. Organomet. Chem.* **1998**, *553*, 511−116.

(27) Yoshifuji, M.; Sato, T.; Inamoto, N. *Chem. Lett.* **1988**, 1735.

(28) Champion, D. H.; Cowley, A. H. *Polyhedron* **1985**, *4*, 1791.

(29) Lange, L.; Meyer, B.; du Mont, W.-W. *J. Organomet. Chem.* **1987**, *329*, C17−C20.

(30) Francis, M. D.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Malik, K. M. A. *J. Chem. Soc., Chem. Commun.* **1996**, 631.

(31) Chisholm, M. H.; Folting, K.; Pasterczyk, J. W. *Inorg. Chem.* **1988**, *27*, 3057.

(32) Properties, spectroscopic data, and X-ray structural analysis of **6b** and **7** are published in ref 26.

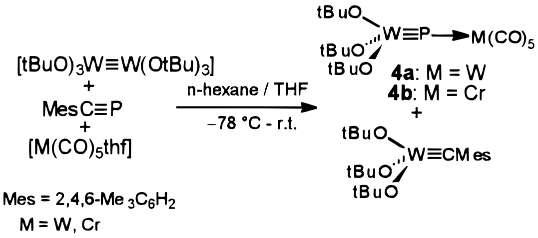
solvents including *n*-pentane. In the solid state **6a,b** are air stable; in solution they appear to be more sensitive. The IR spectra reveal coupled vibrational modes for terminal bound carbonyl groups in the region of CO stretching frequencies. The appropriate molecular ion peaks are observed in the mass spectra. The $^{31}P\{^1H\}$ NMR spectrum of **6a,b** (Table 1) indicates the existence of two chemically different phosphorus atoms. One signal appears downfield at 983.8 and 787.3 ppm, respectively, indicating the existence of phosphinidene P atoms. Additionally, for **6b** the satellite pattern at this signal implies the coordination to two tungsten carbonyl fragments with $^1J_{WP} = 186$ and 117 Hz. This is in good agreement with data found for other tungsten phosphinidene complexes (e.g., $[Cp^*P\{W(CO)_5\}_2]$, $\delta = 1076.2$ ppm, $^1J_{WP} = 187.6$ and 165.7 Hz;[33] $[2\text{-}^iPr\text{-}5\text{-}MeC_6H_9P\text{-}\{W(CO)_5\}_2]$, $\delta = 1041$ ppm, $^1J_{WP} = 168$ Hz[34]). The second signal is observed at 391.9 (**6a**) and 313.9 ppm (**6b**), revealing for **6b** only one pair of satellites ($^1J_{WP} = 202$ Hz).

The $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits one singlet at 165.4 ppm. Only one pair of satellites is observed with a coupling constant $^1J_{WP}$ of 228.6 Hz, which is consistent with a coupling of the phosphorus atom to a $W(CO)_5$ moiety. The spectroscopic data of $[W_3(\mu_3\text{-}P)(\mu\text{-}ONp)_3(ONp)_6]$ (**9**) are in very good agreement with those determined by Chisholm.[31] The $^{31}P\{^1H\}$ NMR spectrum of **9** reveals a singlet at 273.7 ppm with one pair of tungsten satellites. The coupling constant comes to 45.3 Hz. The mass spectrum of complex **9** shows the molecular ion peak.

The molecular structure of **6a** (Figure 5) reveals a "head-to-tail dimer" of two phosphaalkyne molecules forming a phosphinidene ligand and is isostructural to that of **6b**.[26] The phosphinidene phosphorus P(1) is bonded to the C(1) atom via a slightly shortened single bond [1.797(2) Å]. Both phosphorus atoms P(1) and P(2) further coordinate to a $Cr(CO)_4$ moiety creating a planar and slightly distorted four-membered ring. The bonding distance between P(2) and C(1) [1.717(2) Å] corresponds to a double bond.[35] The phosphinidene phosphorus atom P(1) additionally binds to a $Cr(CO)_5$ fragment. Due to the shorter metal−phosphorus bond in **6a** [2.3410(7) and 2.3167(7) Å] the angle P(2)−C(1)−P(1) is smaller than in the W analogue **6b** [96.1(3)°] by 2.3°.

(c) Reactions Starting from Mesitylphosphaalkyne MesC≡P. The discussed results show that the bulky supermesityl group at the phosphaalkyne does not undergo metathesis reactions with $[W_2(OtBu)_6]$. On the other hand, in the reaction with $[W_2(ONp)_6]$, the metathesis reaction seems to occur to a low extent. However, here the tungsten alkoxide reacts further with a phosphido complex intermediate to form the trinuclear tungsten cluster compounds **8** and **9**. Therefore, a phosphaalkyne possessing a moderately steric bulkiness, which lies between those of tBuC≡P and Ar′C≡P, is needed for the metathesis reaction with $[W_2(OtBu)_6]$. We found that MesC≡P meets all these steric requirements.

The metathesis reaction of $[W_2(OtBu)_6]$ with MesC≡P in the presence of $[M(CO)_5thf]$ (M = W, Cr) yields almost exclusively the alkylidyne complex $[(tBuO)_3W{\equiv}CMes]$ and the desired phosphido species $[(tBuO)_3W{\equiv}P{\rightarrow}W(CO)_5]$ (**4a,b**) (eq 3). The steric demand of the mesityl group obviously matches the requirements to undergo metathesis and also to inhibit sufficiently the subsequent cycloaddition with the phosphido complex. According to the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixtures, only the phosphido complexes **4a,b** (80−90 mol % P) and small amounts of the WC_2P ring derivative $[(tBuO)_2W(CMes)_2P(OtBu)]$ (**2c**) (10−20 mol % P) are formed. The subsequent reaction between the phosphido complex and additional phosphaalkyne is not observed anymore. By following reaction 3 (M = W) by $^{31}P\{^1H\}$ NMR spectroscopy from −78 °C to room temperature, it was observed that the formation of the phosphido complex **4a** is favored over the subsequent reaction with additional phosphaalkyne at low temperatures. Only small amounts of the alkylidyne complex $[(tBuO)_3W{\equiv}CMes]$ react in this temperature range to give **2c**. Therefore it is essential to perform the reaction at low temperatures until all starting material is converted before allowing the solution to warm to room temperature.



(3)

After workup, small yellow crystals of **4a,b** could be isolated from *n*-hexane solutions. They are readily soluble in *n*-hexane, toluene, and THF. The compounds are very sensitive to oxygen and moisture and decompose within minutes when exposed to air. Although the $^{31}P\{^1H\}$ NMR spectra indicated a quantitative grade of conversion and a good yield of the desired product, only small amounts of **4a,b** could be obtained in crystalline form due to the excellent solubility even in *n*-pentane. The IR spectra in the region of the CO stretching frequencies shows vibration modes for a distorted C_{4v} symmetry (2 A^1 + E) of the $LW(CO)_5$ moiety. For an estimation of the π-acceptor ability of the phosphido ligand, the location of the A_1^1 band (CO ligand trans to P^{3-}) is important. With 1980 and 1985 cm^{-1}, respectively, they are found to be with their π-acceptor properties between PX_3 (X = halogen) and $P(OR)_3$.[36]

The molecular structure of **4a** reveals an almost linear molecule with an angle W2−P−W1 of 174° (Figure 6). The tungsten atom W2 in **4a** is surrounded in an almost perfect tetrahedral arrangement by its three alkoxide ligands and one phosphido ligand with an average angle O−W2−P of 108.1(3)°. The average angle W2−O−$C(Me_3)$ is ~142° and reveals that the W≡P triple bond is surrounded by the tBuO groups. This situation is also

---

(33) Jutzi, P.; Kroos, R. *J. Organomet. Chem.* **1990**, *390*, 317−322.

(34) Hinke, A. M.; Hinke, M.; Kuchen, W. *Z. Naturforsch.* **1986**, *B 41*, 629

(35) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; pp 160ff.

(36) Huheey, J. E.; Keiter, E.; Keiter, R. *Anorganische Chemie, Prinzipien von Struktur und Reaktivität*, 2nd ed.; de Gruyter: Berlin, 1995; pp 500ff.

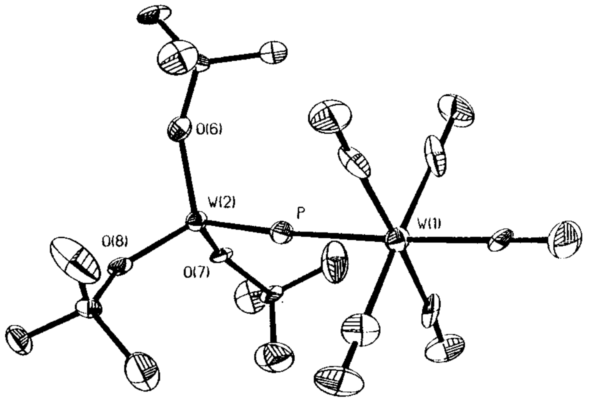


Figure 6. Molecular structure $[(tBuO)_3W{\equiv}P{\rightarrow}W(CO)_5]$ (**4a**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W(2)−P 2.132(4), W(1)−P 2.476(4), W(1)−C(5) 1.99(2), C(5)−O(5) 1.15(2), W(2)−O(6) 1.874(13), W(2)−O(7) 1.837(9), W(2)−O(8) 1.844(8); W(2)−P−W(1) 174.0(2), P−W(1)−C(5) 176.5(2), W(2)−O(6)−C(6) 141.0(10), W(2)−O(7)−C(10) 140.7(9), W(2)−O(8)−C(14) 144.3(8), P−W(2)−O(6) 107.5(3), P−W(2)−O(7) 108.3(3), P−W(2)−O(8) 108.5(3).

found for the alkylidyne complexes $[(tBuO)_3W{\equiv}CR]$ (R = tBu, Ph) obtained from the metathesis of $[W_2(OtBu)_6]$ with the corresponding alkynes.[37]

The most significant feature of the phosphido complex **4a** is the very short bond length W2−P of 2.132(4) Å as the shortest distance of a W−P bond reported so far.[38] The coordinative P−W1 bond in **4a** [2.476(4) Å] is slightly shorter than is usually found for those P−W bond lengths.[39] Only in the phosphido complex $[thf\text{-}(ArO)_3W{\equiv}P{\rightarrow}W(CO)_5]$ (Ar = 2,6-$Me_2C_6H_3$) the W−P bond length comes to 2.127(2) Å.[40] Due to the low basicity of the ArO ligands, an additional coordination of THF to the central tungsten atom, to stabilize the entire complex, becomes necessary, which also leads to a slight shortening of the W−P triple bond.

Due to the high flexibility of the tBuO ligands, however, the triple bond in **4** remains accessible, and therefore, these compounds are highly reactive. Thus, toluene solutions of **4a** react at ambient temperature over time under formal reductive dimerization combined with the loss of two tBuO ligands to give dark-purple crystals of **10** (after 4 days, 30% yield). This process is not observed in hexane solutions of **4a**. **10** is sparingly soluble in *n*-hexane, CH_2Cl_2, Et_2O, or toluene. In THF or DMSO, decomposition is observed at ambient temperature. For the formation of $[W_2(O^tBu)_4(\mu\text{-}CPh)_2]$, thermolytic reaction conditions for the reaction of $[W_2(O^tBu)_6]$ with $PhC{\equiv}CR$ are necessary, whereas at room temperature the metathesis reaction occurs to form the alkylidyne complexes.[41] The mass spectrum of **10** reveals the appropriate molecular ion peak. In the region of the CO stretching frequencies of the IR spectrum of **10**, a typical pattern for a $W(CO)_5$ group with a local C_{4v} symmetry is found. In the ^{31}P NMR spectrum of **10**, in comparison to **4a**, an upfield-shifted singlet at 437.1 ppm is observed, revealing only one pair of tungsten satellites due to the coupling to the exocyclic W atom.

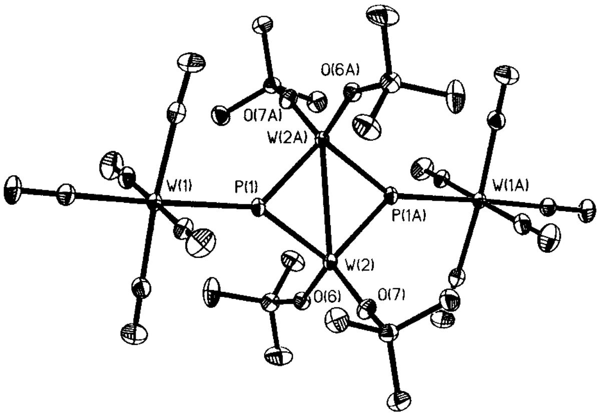


Figure 7. Molecular structure $[W_2(OtBu)_4\langle\mu_3\text{-}P\{W(CO)_5\}\rangle]$ (**10**) (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W(2)−W(2)′ 2.8738(6), W(1)−P 2.500(2), W(2)−P 2.272(2), W(2)−O(6) 1.824(4), W(2)−O(7) 1.823(4); W(2)−P−W(2)′ 77.94(5), P−W(2)−P′ 102.06(5), W(2)−P−W(1) 147.82(8), W(2)−O(6)−C(6) 150.8(4).

The molecular structure of **10** (Figure 7) reveals a planar W_4P_2 framework with a central W_2P_2 ring. The short W−P distances in the ring system with 2.272(2) and 2.298(2) Å indicate a multiple-bond character, whereas the bond length of the ring phosphorus atoms to the exocyclic W1 atom is with 2.500(2) Å in the range of a coordinative bond.[39] The six-membered planar framework of **10** is to a certain extent comparable to the $Re_2P_2W_2$ complex $[Cp^*Re(CO)_2\langle(\mu_3\text{-}P)W(CO)_4\rangle]_2$ (**11**) synthesized by Scherer et al.[42] Although this molecule also possesses a planar W_2P_2 ring system, the W−P and W−W bond lengths are considerably longer as in **10** [**11**, d(W−W) = 3.0523(7) Å; d(W−P) = 2.439(2) and 2.440(2) Å]. The reason lies in the double-bond character of the exocyclic Re−P bonds in **11** where the ring bonds are elongated. In **10**, the exocyclic bond is more a coordinative bond. In **10**, the W−W distance comes to 2.8738(6) Å and is consistent with a W−W single bond. In $[W_2(OtBu)_4(\mu\text{-}CPh)_2]$, this distance is 2.665(1) Å.[41a] The latter compound is a side product of the cothermolysis between $[(tBuO)_6W_2]$ and $PhC{\equiv}CPh$. Pnicogenidene complexes of phosphorus and arsenic with E_2M_2 framework were first synthesized and characterized by Huttner and co-workers.[43]

---

(37) Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. Z. Xue, X. X. *Organometallics* **1992**, *11*, 321−326. Cotton, F. A.; Schmotzer, W.; Shamshoum, E. S. *Organometallics* **1984**, *3*, 1770−1771.

(38) Compare to d(MP) = 2.162(4) Å in $[(N_3N)W{\equiv}P]^3$ and d(MP) = 2.169(1) Å in $[(Ph_2MeP)_2Cl_2(CO)W{=}PAr']$.[16]

(39) Despite neglecting the hybridization at the P atom cf.: d(WP) = 2.544 Å in $[Ph_3P{\rightarrow}W(CO)_5]$ (Aroney, M. J.; Buys, I. E.; Davies, M. S.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1994**, 2827); $\bar{d}$(WP) = 2.445(7) Å in $[W(CO)_4\langle(\eta^4\text{-}P_4)\{W(CO)_5\}_4\rangle]$ (Scheer, M.; Hermann, E.; Sieler, J.; Oehme, M. *Angew. Chem.* **1991**, *103*, 1023−1025; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 969).

(40) Kramkowski, P.; Radius, U.; Baum, G.; Kaupp, M.; Scheer, M. *Chem. Eur. J.*, in press.

(41) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1167. Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *J. Organomet. Chem.* **1985**, *296*, 55. $[W_2(OtBu)_4(\mu\text{-}CPh)_2]$, d(WW) = 2.665(1) Å.

(42) Scherer, O. J.; Ehses, M.; Wolmershäuser, G. *Angew. Chem.* **1998**, *110*, 530−533; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 507−510.

(43) Huttner, G.; Everts, K. *Acc. Chem. Res.* **1986**, *19*, 406−413 and literature therein, especially: Lang, H.; Zsolnai, L.; Huttner, G. *Angew. Chem.* **1983**, *95*, 1016−1017; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 976−977. Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O.; Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 331−348.

Table 2. Crystallographic Data for 2a,b, 4a, 6a, and 10

	2a	**2b**	**4a**	**6a**	**10**
formula	$C_{22}H_{45}O_3PW$	$C_{34}H_{57}O_3PW$	$C_{17}H_{27}O_8PW_2$	$C_{47}H_{58}O_9P_2Cr_2$	$C_{28}H_{36}O_{12}P_2W_4$
M_r	572.40	728.62	758.06	932.87	1361.91
crystal size (mm)	0.50 × 0.30 × 0.15	0.15 × 0.10 × 0.08	0.08 × 0.08 × 0.04	0.65 × 0.41 × 0.11	0.46 × 0.23 × 0.08
T (K)	200(1)	200(1)	200(2)	200(1)	200(2)
space group	*Pbca* (No. 61)	$P2_12_12_1$ (No. 19)	$P2(1)/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2(1)/c$ (No. 14)
crystal system	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic
a (Å)	9.623(2)	10.141(1)	12.201(2)	10.6961(8)	10.878(2)
b (Å)	18.272(3)	10.960(1)	10.034(2)	12.5573(8)	16.796(3)
c (Å)	30.565(8)	31.183(4)	20.883(4)	19.3285(10)	11.577(2)
α (deg)	90	90	90	105.931(5)	90
β (deg)	90	90	94.85(3)	98.744(5)	114.83(3)
γ (deg)	90	90	90	91.686(7)	90
V (Å^3)	5374(8)	3465.8(6)	2547.4(9)	2460.4(3)	1919.6(7)
Z	8	4	4	2	2
ρ_{calc} (g cm^{-3})	1.356	1.396	1.977	1.259	2.370
μ (mm^{-1})	4.375	3.409	9.120	0.557	12.085
radiation (λ, Å)			Mo Kα (0.71073)		
diffractometer	STOE STADI IV	STOE IPDS	STOE IPDS	STOE STADI IV	STOE STADI IV
2Θ range (deg)	$4.46 \leq 2\Theta \leq 50.06$	$9.9 \leq 2\Theta \leq 56.12$	$3.92 \leq 2\Theta \leq 52.02$	$3.38 \leq 2\Theta \leq 54$	$4.12 \leq 2\Theta \leq 55.02$
index range	$-9 \leq h \leq 0$ $-21 \leq k \leq 0$ $0 \leq l \leq 36$	$-13 \leq h \leq 13$ $-14 \leq k \leq 12$ $-40 \leq l \leq 41$	$-12 \leq h \leq 14$ $-5 \leq k \leq 12$ $-25 \leq l \leq 25$	$-13 \leq h \leq 13$ $-16 \leq k \leq 15$ $0 \leq l \leq 24$	$-14 \leq h \leq 12$ $0 \leq k \leq 21$ $0 \leq l \leq 15$
data/restrains/parameters	4458/0/259	8295/0/361	4107/0/262	10701/0/558	4394/0/214
independent reflections with $I > 2\sigma(I)$	3212 (R_{int} = 0.0000)	7506(R_{int} = 0.0569)	2528 (R_{int} = 0.0976)	7343(R_{int} = 0.000)	3943 (R_{int} = 0.0000)
goodness of fit on F^2	1.020	1.107	1.108	1.017	1.107
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0301, 0.0700	0.0504, 0.1167	0.0482, 0.0853	0.0406, 0.1036	0.0264, 0.0642
R_1,[a] wR_2[b] (all data)	0.0561, 0.0798	0.0595, 0.1259	0.0976, 0.0988	0.0807, 0.1197	0.0330, 0.0683
largest diff peak and hole (e Å^{-3})	0.692, −1.074	2.225, −1.658	0.854, −1.182	0.403, −0.416	1.192, −1.283

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = [\sum\omega(F_o^2 - F_c^2)^2]/[\sum(F_o^2)^2]^{1/2}$.

Conclusion

The results show the entire progression from the postulation of the existence of the reactive intermediate $[(tBuO)_3W{\equiv}P]$ by Becker to the realization in a three-component reaction as an effective method for the synthesis of $[(tBuO)_3W{\equiv}P{\rightarrow}M(CO)_5]$ (**4a**, M = W; **4b**, M = Cr) in our group. The way of understanding these metathesis reactions demonstrates the decisive influence of the sterics of the different phosphaalkynes. Only the use of mesitylphosphaalkyne opened the route to a synthesis of complexes containing a tungsten−phosphorus triple bond with hardly any side products. Furthermore, the correct reaction procedure is of crucial importance. For a maximum yield of the phosphido complexes **4**, the reaction between $[W_2(OtBu)_6]$ and MesC≡P in the presence of $[M(CO)_5thf]$ (M = W, Cr) must be performed at low temperature until all phosphaalkyne has reacted in the metathesis reaction. The total amount of the side products formed is thus reduced to 5−10%. The successful synthesis of **4** now opens the perspective to a comprehensive study of the reactivity of these compounds. Due to their very high side-on reactivity, **4a,b** can be used as a source for novel W/P-containing heterocycles. On the other hand, these complexes can also be applied as ligands in coordination complexes creating novel cluster compounds. Investigation of the reaction potential of these type **C** complexes has now become the exciting challenge in this field.

Experimental Section

All reactions were performed under an atmosphere of dry argon using Schlenk and glovebox techniques. Solvents were purified and degassed by standard procedures and distilled prior use. NMR spectra were recorded on a Bruker AC 250 [^{1}H, 250.13 MHz; ^{31}P, 101.256 MHz; standard Me_4Si (^{1}H), 85% H_3PO_4 (^{31}P)]. IR spectra were recorded in Nujol or KBr on a Bruker IFS 28 FT-IR spectrometer. MS was measured on a Finnigan MAT 711 at 70 eV. Elemental analyses were performed by the analytical laboratory of the institute.

Materials. Unless otherwise stated, commercial-grade chemicals were used without further purification. tBuC≡P was synthesized in accordance with 44. AdC≡P was prepared as described in ref 45. Ar′C≡P was obtained according to ref 46. MesC≡P was synthesized as published in ref 47. $[W_2(OtBu)_6]$ and $[W_2(ONp)_6]$ were synthesized by literature procedures.[48]

Crystal Structure Analysis. Crystal structure analyses were performed on a STOE IPDS (**2b** and **4**) and a STOE STADI IV (**2a**, **6a**, and **10**: ω-scan mode) diffractometer with Mo Kα radiation (λ = 0.710 73 Å) with empirical absorption corrections for **2a**, **6**, and **10** (ψ-scans). Machine parameters, crystal data, and data collection parameters are summarized in Table 2. The structures were solved by direct methods using SHELXS-86,[49a] full-matrix least-squares refinement on F^2 in SHELXL-93[49b] with anisotropic displacement for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. According to the absolute structure parameter (−0.03) complex **2b** crystallizes enantiomerically pure in the acentric space group $P2_12_12_1$.

Reaction of $[W_2(OtBu)_6]$ with tBuC≡P. $[W_2(OtBu)_6]$ (0.65 g, 0.8 mmol) was dissolved in THF (20 mL) and cooled to −21 °C. A solution of tBuC≡P (0.08 g, 0.8 mmol) in *n*-hexane (20 mL) was added dropwise over a period of 4 h. The reaction mixture turns from red to dark brown. When the addition of the phosphaalkyne was completed, the solution was allowed

---

(44) Allspach, T.; Regitz, M.; Becker, G.; Becker, W. *Synthesis* **1986**, 31−36.

(45) Rösch, W.; Alspach, T.; Bergsträsser, U.; Regitz, M. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; G. Thieme Verlag: Stuttgart, 1996; Vol. 3, pp 11−16.

(46) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1986**, *27*, 171.

(47) Mack, A.; Pierron, E.; Allspach, T.; Bergsträsser, U.; Regitz, M. *Synthesis* **1998**, 1305−1313.

(48) (a) Chisholm, M. H.; Haitko, D. A.; Murillo, C. A. In *Inorganic Synthesis* Fackler, J. R., Ed.; John Wiley and Sons: New York 1982, Vol. XXI, pp 51−57 and references therein.

(49) (a) Sheldrick, G. M. SHELXS-86, University of Göttingen, 1986. (b) Sheldrick, G. M. SHELXL-93, University of Göttingen, 1993.

to warm to 0 °C. At this temperature, the solvent was reduced to dryness in vacuo (10^{-3} Torr). Subsequently, $[(tBuO)_3W\equiv CtBu]$ was removed by sublimation (50 °C, 10^{-3} Torr). The latter compound and the residue were analyzed by NMR spectroscopy. ^{31}P NMR data for **2a** and **3a** are summarized in Table 1. For $[(tBuO)_3W\equiv CtBu]$: ^{1}H NMR (C_6D_6, 303 K) $\delta = 3.56$ (s, 3 H, $^1J_{H,W} = 7.1$ Hz), 1.43 (s, 27 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 303 K) $\delta = 254.3$ (s, *C*tBu), 80.12 (s, O*C*Me$_3$), 32.76 (q, $^1J_{CH} = 124$ Hz, OC*Me$_3$*), 31.95 (q, $^1J_{CH} = 128$ Hz, C*Me*). For **2a**: ^{1}H NMR (C_6D_6, 303 K) $\delta = 1.57$ (s, 18H), 1.34 (d, 9H, $^1J_{P,H} = 8.6$ Hz), 1.07 (s, 18 H); MS (70 eV, EI) *m/z* (%) 572 (18) [M$^+$], 515 (10) [M$^+$ − tBu], 385 (100) $[\{(tBuO)_2WC_2P\}^+]$. Anal. Calcd for $C_{22}H_{45}O_3PW$ (572.42): C, 46.16; H, 7.92. Found: C, 45.83; H, 7.50.

Temperature-Dependent $^{31}P\{^1H\}$ NMR Spectroscopic Measurements of the Reaction between $[W_2(OtBu)_6]$ and MesC≡P. $[W_2(OtBu)_6]$ (240 mg, 0.3 mmol) was dissolved in toluene-d_8 (2 mL) and cooled to −196 °C. A solution of MesC≡P (49 mg, 0.3 mmol) in toluene-d_8 (1 mL) was cooled to −70 °C and added. The combined solutions were allowed to warm to −70 °C and subsequently transferred into an NMR tube. $^{31}P\{^1H\}$ NMR spectra were recorded in steps of 10 °C from −70 °C to room temperature. The resulting data for **1**, **2c**, and **3b** are summarized in Table 1.

Reaction of $[W_2(OtBu)_6]$ with RC≡P in the Presence of [ML$_n$thf]. $[W_2(OtBu)_6]$ (0.65 g, 0.8 mmol) was dissolved in a THF solution of $[M(CO)_5thf]$ or $[Cp''Mn(CO)_2thf]$ (20 mL of a 0.04 M solution) and cooled to −21 °C. A solution of RC≡P (R = tBu, 0.08 g, 0.8 mmol; R = Ad, 0.14 g, 0.8 mmol) in *n*-hexane (20 mL) was added dropwise over a period of 4 h. The reaction mixture turns from red to dark brown. When the addition of the phosphaalkyne was completed, the solution was allowed to warm to 0 °C. At this temperature, all of the solvent was removed in vacuo (10^{-3} Torr). Subsequently, $[(tBuO)_3W\equiv CtBu]$ and $[M(CO)_6]$ or $[Cp''Mn(CO)_3]$ was removed by sublimation (50 °C, 10^{-3} Torr). The residue was dissolved in *n*-pentane (30 mL) and filtered. The solution was reduced in vacuo to 10 mL. At 5 °C, small amounts of yellow crystals of **2a,b** were obtained. According to the ^{31}P NMR spectra, these solutions contained mostly **4a**−**c** and some **5a**−**d**. ^{31}P NMR data are summarized in Table 1. For **2b**, Anal. Calcd for $C_{34}H_{57}O_3PW$ (728.65): C, 56.02; H, 6.59. Found: C, 55.67; H, 6.35.

Reaction of $[W_2(OtBu)_6]$ with Ar′C≡P in the Presence of $[M(CO)_5thf]$ (M = Cr, W). To a mixture of $[W_2(OtBu)_6]$ (569 mg, 0.72 mmol) and 24 mL of a 0.04 M solution of $[M(CO)_5thf]$ (M = Cr, W) in THF, a solution of Ar′C≡P (200 mg, 0.72 mmol) in *n*-hexane (40 mL) was added dropwise over a period of 1 h at room temperature. The solution was stirred for an additional hour. The solvent was reduced to dryness, and $M(CO)_6$ was removed by sublimation (25 °C, 10^{-3} Torr). The residue was dissolved in *n*-pentane (30 mL) and subsequently filtered. **6a,b** were recrystallized from *n*-pentane at 0 °C. Isolated yield: **6a**: 120 mg (35%); **6b**: 90 mg (20%). For **6a**: ^{1}H NMR (C_6D_6, 303 K) $\delta = 7.34$ (d, 2H, $J = 1.81$ Hz), 6.99 (d, 2H, $J = 1.77$ Hz), 1.89 (s, 9H, tBu), 1.82 (s, 9H, tBu), 1.54 (s, 6H), 1.41 (s, 9H, tBu), 1.29 (s, 9H, tBu), 1.24 (s, 9H, tBu); IR (KBr) $\tilde{\nu}$(CO) 2069 (w), 2062 (w), 1994 (sh), 1981 (vs), 1958 (w), 1952 cm^{-1} (w); MS (70 eV, EI) *m/z* (%) 932.9 (0.2) [M$^+$], 905.3 (1) [M$^+$ − CO], 288 (17.3) [Ar′C≡P$^+$], 219.7 (100) $[Cr(CO)_6{}^+]$. For **6b**: ^{1}H NMR (C_6D_6, 303 K) $\delta = 7.715$ (d, 2H, $J = 1.81$ Hz), 7.39 (d, 2H, $J = 1.77$ Hz), 1.84 (s, 9H, tBu), 1.79 (s, 9H, tBu), 1.49 (s, 6H), 1.41 (s, 9H, tBu), 1.29 (s, 9H, tBu), 1.26 (s, 9H, tBu); IR (KBr) $\tilde{\nu}$(CO) 2078 (s), 2064 (w), 2017 (s), 2003 (w), 1965 (vs, br), 1941 (vs, sh), 1915 cm^{-1} (s); MS (70 eV, EI) *m/z* (%) 1197.2 (1) [M$^+$], 882.5 (8) $[M^+ - W(CO)_5]$, 351.7 (24) $[W(CO)_6{}^+]$, 288 (58) [Ar′C≡P$^+$]. ^{31}P NMR data are summarized in Table 1. Anal. Calcd for $C_{47}H_{58}O_9PW_2$ (932.91): C, 60.51; H, 6.22. Found: C, 59.93; H, 6.13.

Reaction of $[W_2(ONp)_6]$ with Ar′C≡P in the Presence of $[M(CO)_5thf]$. The procedure was identical to that previously described. Instead of $[W_2(OtBu)_6]$, $[W_2(ONp)_6]$ (641 mg, 0.72 mmol) was used. Isolated yield: **6a**, M = Cr 150 mg (45%); **6b**, M = W 130 mg (30%). ^{31}P NMR data are summarized in Table 1. **9**: 50 mg (5%); ^{1}H NMR (toluene-d_8, 303 K) $\delta = 1.03$ (18H), 1.08 (9H), 4.14 (2H), 4.2 (2H), 4.4 (2H), $J_{H,H} = 10.8$ Hz; MS (70 eV, EI) *m/z* (%) 1365.1 (7) [M$^+$], 1294.1 (1.1) $[M^+ - C_5H_{11}]$, 840.0 (10) $[W_2C_{30}H_{66}O_6{}^+]$.

Reaction of $[W_3(\mu_3\text{-}P)(\mu\text{-}ONp)_3(ONp)_6]$ with $[W(CO)_5thf]$. $[W_3(\mu_3\text{-}P)(\mu\text{-}ONp)_3(ONp)_6]$[31] (100 mg, 0.07 mmol) was dissolved in toluene (5 mL). An excess of $[W(CO)_5thf]$ (10 mL of a 0.04 M solution) was added at room temperature. After 3 h the solvent was removed in vacuo, and the residue was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. **9**: $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K) $\delta = 165.4$ (s, $^1J_{W,P} = 228.6$ Hz).

Reaction of $[W_2(OtBu)_6]$ with MesC≡P in the Presence of $[M(CO)_5thf]$ (M = W, Cr). A THF solution containing $[W_2(OtBu)_6]$ (800 mg, 1 mmol) and $[M(CO)_5thf]$ (M = W, Cr) (25 mL of a 0.04 M solution) was cooled to −196 °C. MesC≡P (162 mg, 1 mmol) dissolved in *n*-hexane (20 mL) was cooled to −70 °C and added to the solid mixture. The solution was allowed to warm to room temperature over 15 h. The solvent was removed in vacuo and the residue was extracted with *n*-hexane (30 mL). After filtration, the solvent was reduced in vacuo until the onset of crystallization. Isolated yields: 190 mg (25%) of **4a** and 125 mg (20%) of **4b**. ^{31}P NMR data are summarized in Table 1. For **4a**: ^{1}H NMR (C_6D_6, 303 K) $\delta = 1.43$ (s); IR (Nujol): $\tilde{\nu}$(CO) 2071 (vs), 1980 (s), 1951 cm^{-1} (vs); MS (70 eV, EI) *m/z* (%) 758.1 (7) [M$^+$], 702.0 (1) [M$^+$ − 2CO], 645.9 (3) [M$^+$ − 4CO], 589.9 (11) [M$^+$ − 4CO − tBu]. Anal. Calcd for $C_{17}H_{27}O_8PW_2$ (758.07): C, 26.94; H, 3.59. Found: C, 26.56; H, 3.85. For **4b**: ^{1}H NMR (C_6D_6, 303 K) $\delta = 1.42$ (s); IR (Nujol) $\tilde{\nu}$(CO) = 2064 (vs), 1985 (s), 1953 cm^{-1} (vs); MS (70 eV, EI) *m/z* (%) 626.2 (12) [M$^+$], 514.1 (3) [M$^+$ − 4CO].

Reductive Dimerization of $[(tBuO)_3W\equiv P\rightarrow W(CO)_5]$. **4a** (380 mg, 0.5 mmol) was dissolved in toluene (10 mL). After 2 days, dark purple crystals of **10** could be isolated. Isolated yield, 60 mg (15%). ^{31}P NMR data are summarized in Table 1. For **10**: ^{1}H NMR (C_6D_6, 303 K) $\delta = 1.04$ (s, 9 H); IR (Nujol) $\tilde{\nu}$(CO) 2060 (vs), 1979 (s), 1915 cm^{-1} (vs); MS (70 eV, EI) *m/z* (%) 1370.0 (11) [M$^+$], 1258.0 (4) [M$^+$ − 4CO], 1202.0 (2) [M$^+$ − 6CO] 1129.0 (4) [M$^+$ − 6CO − tBuO]. Anal. Calcd for $C_{28}H_{36}O_{12}P_2W_4$ (1361.93): C, 24.69; H, 2.64. Found: C, 24.06; H, 2.85.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for comprehensive financial support.

Supporting Information Available: Complete tables of crystal data, atomic coordinates, H-atom parameters, bond distances, and anisotropic displacement parameters and fully labeled figures for **2a,b**, **4a**, **6a**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990019E