Trapping Reactions of an Intermediate Containing a Tungsten – Phosphorus Triple Bond with Alkynes

Michael Schiffer and Manfred Scheer*[a]

Dedicated to Professor Kurt Dehnicke on the occasion of his 70th birthday

Abstract: The thermolysis of the phosphinidene complex $[\mathrm{Cp^*P\{W(CO)_5\}_2}]$ (**1**) in toluene in the presence of $t\mathrm{BuC{\equiv}CMe}$ leads to the four-membered ring complexes $[[\{\eta^2\text{-C(Me)C}(t\mathrm{Bu})\}\mathrm{Cp^*(CO)W}(\mu_3\text{-P})\{\mathrm{W(CO)_3}\}]\{\eta^4{:}\eta^1{:}\eta^1\text{-P}\{\mathrm{W(CO)_5}\}\mathrm{WCp^*(CO)C(Me)C}(t\mathrm{Bu})\}]$ (**4**) as the major product and $[[\mathrm{W\{Cp^*(CO)_2\}W(CO)_2WCp^*(CO)}\{\eta^1{:}\eta^1\text{-C(Me)C}(t\mathrm{Bu})\}](\mu,\eta^3{:}\eta^2{:}\eta^1\text{-}\mathrm{P_2\{W(CO)_5\}})]$ (**5**). The reaction of **1** with $\mathrm{PhC{\equiv}CPh}$ leads to $[[\mathrm{W(CO)_2}\{\eta^2\text{-C(Ph)C(Ph)}\}][(\eta^4{:}\eta^1\text{-P}\{\mathrm{W(CO)_5}\}\mathrm{W\{Cp^*(CO)_2\}C(Ph)C(Ph)}]]$ (**6**). The products **4** and **6** can be regarded as the formal cycloaddition products of the phosphido complex intermediate $[\mathrm{Cp^*(CO)_2W{\equiv}P \rightarrow W(CO)_5}]$ (**B**), formed by Cp* migration within the phosphinidene complex **1**. Furthermore, the reaction of **1** with $\mathrm{PhC{\equiv}CPh}$ gives the minor product $[[\{\eta^2{:}\eta^1\text{-C(Ph)C(Ph)}\}_2\{\mathrm{W(CO)_4}\}_2]\{\mu,\eta^1{:}\eta^1\text{-P}\{\mathrm{C(Me)\{C(Me)\}_3C(Me)}\}\{\mathrm{C(Ph)}\}\{\mathrm{C(Ph)}\}]$ (**7**) as a result of a 1,3-dipolaric cycloaddition of the alkyne into a phosphaallylic subunit of the Cp*P moiety of **1**. Compounds **4** – **7** have been characterized by means of their spectroscopic data as well as by single-crystal X-ray structure analysis.

Keywords: alkynes · cycloaddition · intermediates · P ligands · tungsten

Introduction

In 1995 the first isolable complexes with a metal – phosphorus triple bond were synthesized and structurally characterized.[1, 2] In these complexes, the metal – phosphorus triple bond is kinetically stabilized through the sterically demanding substituents at the amido ligands. Thus, these complexes react predominantly with the lone pair of electrons on the phosphido phosphorus atom to coordinate Lewis-acidic compounds in an *end-on* manner.[3] Our interests have been focussed on the synthesis of phosphido complexes of the type $[\mathrm{(RO)_3W{\equiv}P \rightarrow M(CO)_5}]$ ($\mathrm{R} = t\mathrm{Bu}$, 2,4,6-$\mathrm{Me_2C_6H_3}$; $\mathrm{M} = \mathrm{Cr}$, W). In these stable complexes, the lone pair of electrons on the phosphido phosphorus atom is coordinated by $\mathrm{M(CO)_5}$ ($\mathrm{M} = \mathrm{Cr}$, W), which stabilizes the overall complex. Furthermore, the flexibility of the alkoxide ligands open a high *side-on* reactivity.[4] Additionally, we were interested in obtaining compounds containing metal – phosphorus triple bonds as highly reactive intermediates. Thus, starting from $[\mathrm{Cp^*P\{W(CO)_5\}_2}]$ (**1**; $\mathrm{Cp^*} = \mathrm{C_5Me_5}$) we recently developed a novel synthetic approach to a highly reactive intermediate that possesses a tungsten – phosphorus triple bond.[5] This approach is based on the migration of the σ-bound Cp* ligand at the phosphinidene phosphorus atom in **1** to a η^5-Cp* ligand at a tungsten atom by thermolysis (Scheme 1). In a side reaction, the initially formed intermediate of the type $[\{\mathrm{Cp^*W(CO)_3}\}\mathrm{P\{W(CO)_5\}}]$ (**A**) undergoes C–H activation to give the phosphane complex $[\mathrm{(CO)_3W}(\eta^5\text{-}\mathrm{C_5Me_4CH_2})\mathrm{P(H) \rightarrow W(CO)_5}]$ (**2**; Scheme 1). Further loss of CO leads to the highly reactive phosphido complex intermediate of the type $[\mathrm{Cp^*(CO)_2W{\equiv}P \rightarrow W(CO)_5}]$ (**B**). The dimerization of **B** results in the major product $[\mathrm{Cp^*_2(CO)_4W_2}(\mu,\eta^2{:}\eta^1\text{-}\mathrm{P_2\{W(CO)_5\}})]$ (**3**). This novel synthetic approach to the highly reactive intermediate **B** opens unconventional routes to a large variety of unprecedented metallaphosphaheterocycles. Herein we report for the first time on the use of this in situ generated phosphido complex intermediate in trapping reactions with different alkynes.

Results and Discussion

The thermolysis of $[\mathrm{Cp^*P\{W(CO)_5\}_2}]$ (**1**) in the presence of $t\mathrm{BuC{\equiv}CMe}$ leads to **4** as the major, and **5** as the minor product [Eq. (1)]. The thermolysis of **1** with $\mathrm{PhC{\equiv}CPh}$ affords the complexes **6** and **7** [Eq. (2)]. In both reactions, small amounts of **2** (≈5%) were detected by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy of

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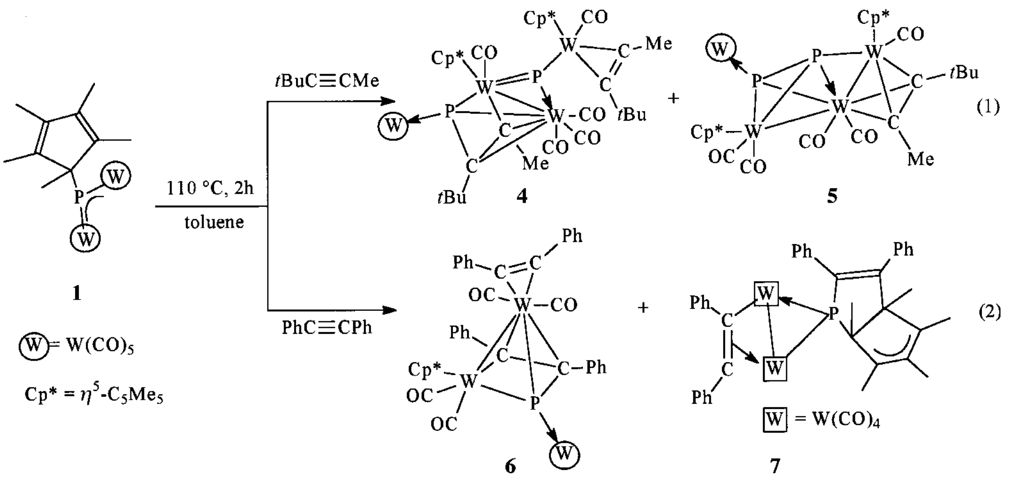
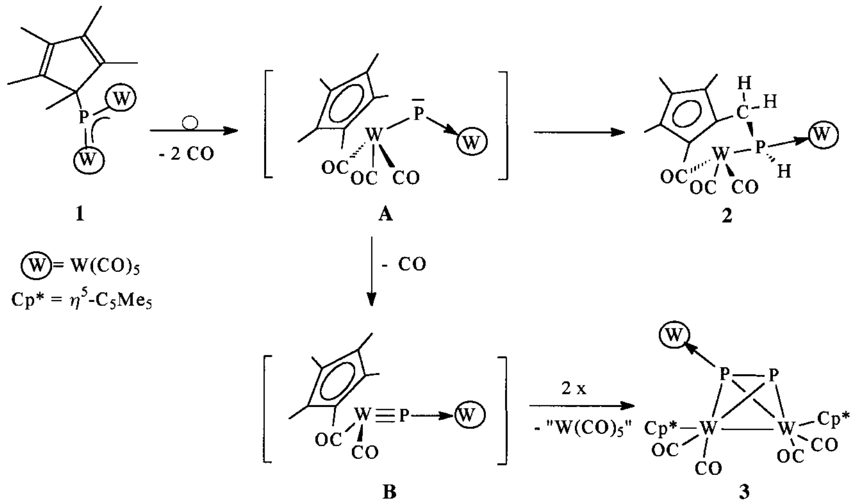
[a] Prof. Dr. M. Scheer, Dr. M. Schiffer
Institut für Anorganische Chemie der Universität Karlsruhe
76128 Karlsruhe (Germany)
Fax: (49) 721-661921
E-mail: mascheer@achibm6.chemie.uni-karlsruhe.de



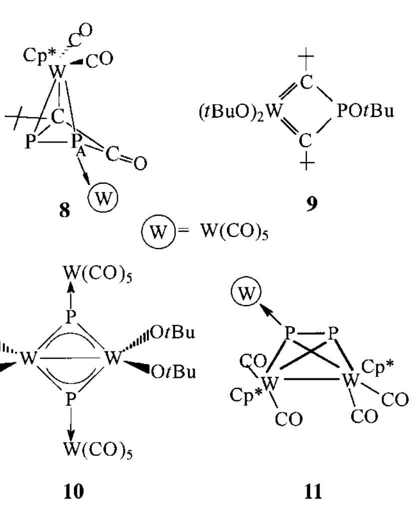


Scheme 1. Proposed reaction pathway of the thermolysis of **1**.

the crude reaction mixture. No signals were observed for **3**, which indicates an almost quantitative reaction of the triple bond intermediate **B** with the alkynes. Furthermore, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of **1** with PhC≡CPh in toluene contains, in addition to the signals for **6**, **7**, and **2**, two further doublets at $\delta = -98.3$ and $\delta = -232.0$ ($^1J_{P,P} = 413$ Hz, $^1J_{W,P} = 208$ Hz). These chemical shifts and coupling constants are in good agreement with a complex similar to **5** ($\delta = -79.6$ and -220.5, $^1J_{P,P} = 407$ Hz) which was obtained by the reaction between **1** and *t*BuC≡CMe. Unfortunately, this compound could not be isolated either by column chromatographic work-up, which was possible for the isolation of **4**, **6**, and **7**, or by fractional crystallization as in the case of **5**.

Spectroscopic properties: The products are black (**4** and **5**), red (**6**), and yellow (**7**) crystalline compounds. All compounds are readily soluble in toluene and dichloromethane. They were fully characterized on the basis of their spectroscopic data and by single-crystal X-ray structural analysis. The IR spectra of the products show CO stretching frequencies of terminal ligands. In the mass spectra of all compounds, no molecular ion peak was observed. In all cases, it is diminished by carbonyl groups as well as by Cp* and by RC≡CR moieties.

The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits two singlets at $\delta = 19.9$ and $\delta = -49.2$, corresponding to the two chemically nonequivalent phosphorus atoms, which do not couple over the connecting W(2) atom (see Figure 1). Even though both phosphorus atoms bind to three tungsten atoms, only two pairs of ^{183}W satellites per singlet can be observed. The singlet at $\delta = 19.9$ belongs to the phosphorus atom P(2) and possesses two $^1J_{W,P}$ values of 192 and 84 Hz. The other singlet at $\delta = -49.2$ belongs to the phosphorus atom P(1) and possesses two $^1J_{W,P}$ values of 207 and 52 Hz. The larger coupling constant is consistent with the bonding of the phosphorus atom to the [W(CO)$_5$] moiety. The chemical shift of the P(1) atom is in good agreement with the comparable complex **8**, which shows a doublet at $\delta = -64.6$ ($^1J_{W,P} = 195$ and 63 Hz) for the ring phosphorus atom P_A.[5] The $^{31}P\{^1H\}$ NMR spectrum of **5** reveals two doublets at $\delta = -79.6$ and $\delta = -220.5$ with a $^1J_{P,P}$



coupling constant of 407 Hz, which is in good agreement with P–P multiple-bond character. A coupling of the phosphorus atoms with tungsten cannot be observed in the spectrum, which is a general feature of known P_2W_2 tetrahedral cores. The $^{31}P\{^1H\}$ NMR spectrum of **6** shows a singlet at $\delta = -2.8$ with $J_{W,P}$ coupling constants of 202 and 88 Hz. As in **4** (atom P(1)) and **8** (atom P_A), the larger $J_{W,P}$ value is consistent with coupling constants of the phosphorus center to a $[W(CO)_5]$ unit; the smaller one seems to correspond to the coupling to the ring W atom W(1) and not to the capping W(2) atom, likely due to the higher s character of the first mentioned bond. The $^{31}P\{^1H\}$ NMR spectrum of **7** reveals a singlet at $\delta = 18.4$ with a $^1J_{W,P}$ value of 232 Hz.

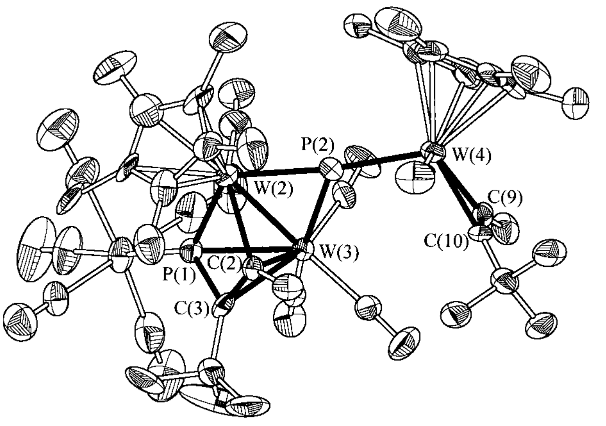


Figure 1. Molecular structure of **4** (showing 50 % probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.594(2), W(2)–P(2) 2.336(3), W(2)–P(1) 2.462(2), W(2)–C(2) 2.219(9), W(2)–W(3) 2.8546(9), W(3)–C(2) 2.303(8), W(3)–C(3) 2.438(9), W(3)–P(1) 2.484(2), W(3)–P(2) 2.508(3), W(4)–P(2) 2.311(3), P(1)–C(3) 1.829(9), C(2)–C(3) 1.366(14), C(9)–C(10) 1.304(13); C(3)-P(1)-W(2) 86.4(3), C(2)-W(2)-P(1) 63.2(3), C(3)-C(2)-W(2) 109.7(7), C(2)-C(3)-P(1) 99.7(7), W(3)-P(2)-W(4) 116.90(11), W(3)-P(2)-W(2) 72.12(7), W(2)-P(2)-W(4) 170.93(13).

Crystal structure analysis: Details of the crystallographic data are given in Table 1. The molecular structure of **4** (Figure 1) reveals a "kitelike" distorted WC_2P ring consisting of the atoms W(2), P(1), C(2), and C(3). This WC_2P ring system results formally from the [2+2] cycloaddition of the intermediate $[Cp^*(CO)_2W{\equiv}P \rightarrow W(CO)_5]$ (**B**) with tBuC≡CMe. This moiety is further capped by a tungsten carbonyl group of a second molecule of **B** (P(1)–W(2) 2.462(2), P(1)–W(3) 2.484(2) Å), and forms a W–W single bond (2.858(9) Å). The P(1)–C(3) bond length (1.829(9) Å) is characteristic of a P–C single bond and is comparable to the P–C single bond lengths in the four-membered ring of **9** (d(P–C) 1.814(5), 1.822(5) Å).[4a] The C(2)–C(3) bond length (1.366(14) Å) corresponds to a slightly elongated C–C double bond. The WPC_2 ring is almost planar with a folding angle of 169.5° along the P(1)···C(2) axis. The phosphorus atom P(1) coordinates to a $W(CO)_5$ group. The P(1)–W(1) bond (2.594(2) Å) is longer than the bonds in comparable compounds such as $[Ph_3P \rightarrow W(CO)_5]$ (d(W–P) 2.544 Å)[6] and $[(tBuO)_3W{\equiv}P \rightarrow W(CO)_5]$ (d(W–P) 2.476(4) Å).[4a] Another important structural feature of **4** is the μ_3-bridging phosphorus atom P(2) which connects

Table 1. Crystallographic data for compounds **4**–**7**.

	4	**5**·0.5 C_5H_{12}	**6**	**7**
formula	$C_{44}H_{54}O_{10}P_2W_4$	$C_{39.5}H_{47}O_{10}P_2W_4$	$C_{47}H_{35}O_9PW_3$	$C_{46}H_{35}O_8PW_2$
M_r	1540.21	1444.05	1326.27	1114.41
crystal size [mm]	0.34 × 0.15 × 0.08	0.11 × 0.08 × 0.04	0.20 × 0.10 × 0.10	0.18 × 0.04 × 0.01
T [K]	220(1)	210(1)	293(2)	190(1)
space group	$P2(1)$ (no. 4)	$P\bar{1}$ (no. 2)	$Pbca$ (no. 61)	$P2_1/n$ (no. 14)
crystal system	monoclinic	triclinic	orthorhombic	monoclinic
a [Å]	11.643(2)	11.285(2)	11.173(2)	18.547(4)
b [Å]	14.409(3)	12.185(2)	19.581(4)	9.479(19)
c [Å]	14.460(3)	19.715(4)	42.117(8)	23.964(5)
α [°]	90.00	76.54(3)	90.00	90.00
β [°]	97.49(3)	90.00	90.00	102.81(3)
γ [°]	90.00	64.20(3)	90.00	90.00
V [Å^3]	2405.1(8)	2393.3(8)	9215(3)	4108.2(14)
Z	2	2	8	4
ρ_{calcd} [g cm^{-3}]	2.127	2.053	1.912	1.802
μ [cm^{-1}]	0.9653	0.9696	0.7559	0.5688
radiation [λ, Å]	0.71073	0.71073	0.71073	0.71073
diffractometer	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS
2Θ range [°]	$5.08 \leq 2\Theta \leq 54.86$	$3.80 \leq 2\Theta \leq 54.54$	$3.86 \leq 2\Theta \leq 44.68$	$4.64 \leq 2\Theta \leq 51.94$
index range	$-14 \leq h \leq 14$,	$-13 \leq h \leq 12$,	$-11 \leq h \leq 11$,	$-22 \leq h \leq 14$,
	$-17 \leq k \leq 17$,	$-14 \leq k \leq 14$,	$-19 \leq k \leq 20$,	$-11 \leq k \leq 11$,
	$-17 \leq l \leq 17$	$-24 \leq l \leq 22$	$-44 \leq l \leq 44$	$-28 \leq l \leq 29$
data/restrains/parameters	8243/1/554	8461/0/462	5860/0/526	7139/0/519
independent reflections with $I > 2\sigma(I)$	7932 ($R_{int} = 0.0991$)	4071 ($R_{int} = 0.1220$)	3673 ($R_{int} = 0.1798$)	5308 ($R_{int} = 0.0579$)
goodness-of-fit on F^2	1.085	0.898	1.128	0.901
R_1,[a] ωR_2[b] [$I > 2\sigma(I)$]	0.0296, 0.0764	0.0817, 0.1934	0.0923, 0.2175	0.0332, 0.0702
R_1,[a] ωR_2[b] [all data]	0.0315, 0.0799	0.1546, 0.2206	0.1402, 0.2359	0.0531, 0.0748
largest diff peak and hole [e$^-$/Å^{-3}]	1.722, −1.047	2.378, −3.327	3.010, −2.369	1.199, −1.267

[a] $R = \Sigma|F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma\omega(F_o^2 - F_c^2)^2]/[\Sigma(F_o^2)^2]^{1/2}$.

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three W fragments. The W(4)-P(2)-W(3) unit seems to result from a second [Cp*(CO)$_2$W≡P → W(CO)$_5$] (**B**) molecule coordinating to the WPC$_2$ cycloaddition product by loss of three CO molecules. One molecule of the alkyne coordinates to the Cp*(CO)W fragment of the W(4) atom. The C(9)–C(10) bond length (1.304(13) Å) of the side-on-coordinated alkyne at the Cp*W(CO) unit corresponds to a C–C double bond length, revealing a four-electron donating alkyne. The P(2)–W(2) (2.336(3) Å) and P(2)–W(4) bond lengths (2.311(3) Å) are short in comparison to the P(2)–W(3) bond length (2.508(3) Å) and are therefore in the range of the W–P multiple bond lengths, as found, for example, in **10** (2.272(2) Å and 2.293(3) Å).[4a] Consequently, **4** shows an almost linear arrangement along the W(2)-P(2)-W(4) axis with an angle of 170.93(13)°. The W(2)–W(3) bond length (2.8546(9) Å) is comparable to other W–W single bonds. It is shorter than the W–W bond in **11** (3.0920(7) Å)[5] and in [{CpW(CO)$_2$}$_2$(μ,η^2-P$_2$)] (3.0026(11) Å),[7] but comparable to the W–W bonds in **10** (2.8738(6) Å)[4a] Furthermore, the W(2)-P(1)-W(3)-P(2) moiety adopts an almost planar arrangement; the two three-membered rings reveal a folding angle of 179.08°.

The X-ray structure of **5** (Figure 2) shows a W$_2$P$_2$ as well as a W$_2$C$_2$ tetrahedron sharing one common tungsten atom on an edge and forming an additional P–W bond between P(1) and W(3). This complex can be regarded as the dimerization product of two phosphido ligand intermediates [Cp*-(CO)$_2$W≡P → W(CO)$_5$] (**B**), and an alkyne *t*BuC≡CMe coordinates side-on to the W atoms W(1) and W(3), which form a metal–metal bond. The P–W bond lengths in **5** are between 2.447(8) and 2.557(8) Å and correspond to P–W single bonds. The W(1)–W(2) bond (3.014(2) Å) is slightly longer than other W–W single bonds, whereas the W(1)–W(3) bond (2.641(2) Å) in the W$_2$C$_2$ tetrahedron reveals multiple-bond character and is comparable to the W–W bond length in [W$_2$(OCMe$_2$)$_4$(PhCCPh)$_2$] (2.677(1) Å).[8] The C(12)–C(13) bond (1.400(4) Å) and the P(1)–P(2) bond (2.152(10) Å) are shorter than corresponding single bonds (for a P–P single bond compare β-P$_4$ (2.190–2.212 Å)[9]). The latter one is comparable to the P–P bond lengths in known W$_2$P$_2$ tetrahedral complexes.[5]

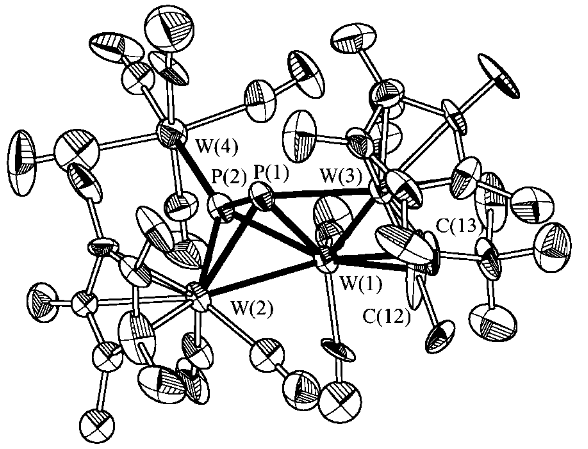


Figure 2. Molecular structure of **5** (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.510(7), W(1)–P(2) 2.447(8), W(1)–W(2) 3.014(2), W(1)–W(3) 2.641(2), W(1)–C(12) 2.39(4), W(1)–C(13) 2.16(2), P(2)–W(4) 2.557(8), P(2)–W(2) 2.472(8), P(2)–P(1) 2.152(10), W(3)–P(1) 2.466(7), W(3)–C(12) 1.99(5), W(3)–C(13) 2.40(3), C(12)–C(13) 1.40(4); W(2)-P(2)-W(4) 145.1(3), W(2)-P(2)-W(1) 75.6(2), W(2)-P(2)-P(1) 65.9(3), W(2)-P(1)-W(3) 125.0(3), W(2)-P(1)-W(1) 73.5(2), W(2)-W(1)-P(1) 53.5(2), W(2)-W(1)-P(2) 52.6(2), W(2)-W(1)-W(3) 102.95(5), W(2)-W(1)-C(12) 113.1(6), W(2)-W(1)-C(13) 148.5(8), W(4)-P(2)-W(1) 135.2(3), W(4)-P(2)-P(1) 134.6(4), P(2)-P(1)-W(3) 118.6(3), P(1)-W(3)-W(1) 58.8(2), P(2)-W(1)-C(12) 145.9(11), P(2)-W(1)-C(13) 150.0(10), P(2)-W(1)-W(2) 52.6(2), P(2)-W(1)-P(1) 51.4(2), P(1)-W(1)-W(3) 57.1(2), P(1)-W(1)-C(12) 94.6(10), P(1)-W(1)-C(13) 116.2(7), W(3)-W(1)-C(12) 46.3(13), W(3)-W(1)-C(13) 59.1(7).

The molecular structure of **6** (Figure 3) reveals a WPC$_2$ ring, which results from the [2+2] cycloaddition of intermediate [Cp*(CO)$_2$W≡P → W(CO)$_5$] (**B**) with PhC≡CPh. This almost planar four-membered ring is further capped by a [W(CO)$_2${η^2-C(Ph)C(Ph)}] unit and slightly bent by 9.53° along the P⋯C(11) axis. Within the ring all bond lengths correspond to slightly shortened single bonds. The W(1)–W(2) bond length (2.9342(17) Å) represents a W–W single bond.

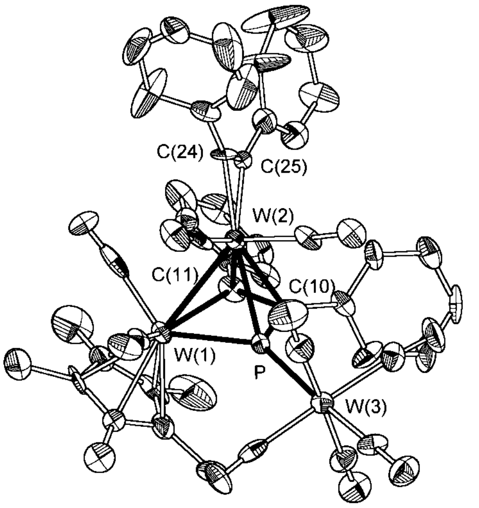


Figure 3. Molecular structure of **6** (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W(1)–P 2.523(8), W(1)–C(11) 2.24(3), W(3)–P 2.531(8), P–C(10) 1.72(3), C(10)–C(11) 1.48(4), W(2)–P 2.531(8), W(1)–W(2) 2.9342(17), W(2)–C(10) 2.38(3), W(2)–C(11) 2.31(3), W(2)–C(24) 2.07(3), W(2)–C(25) 2.08(3), C(24)–C(25) 1.35(4); W(1)-P-C(10) 86.8(9), W(1)-P-W(3) 144.4(3), P-C(10)-C(11) 104.3(18), W(1)-C(11)-C(10) 104.3(18), P-W(1)-C(11) 63.8(8).

The X-ray structure analysis of **7** (Figure 4) reveals a W$_2$C$_2$ unit in which the W–W bond is bridged by a phosphorus atom of a 1-phosphabicyclo[3.3.0]octane unit. The phosphorus atom possesses a distorted tetrahedral geometry. The molecular structure of **7** can be regarded as the reaction product of two molecules of PhC≡CPh with **1**. The first molecule of PhC≡CPh is added to a phosphaallylic system of the PCp* unit, formed by the atoms P, C(11), and C(12), and the second molecule is coordinated at both W atoms. The resulting W–W bond (3.0045(7) Å) corresponds to a longer single bond. The carbon atom C(34) of this alkyne is bound through a longer bond to the atom W(1) (2.451(6) Å) and through a shorter

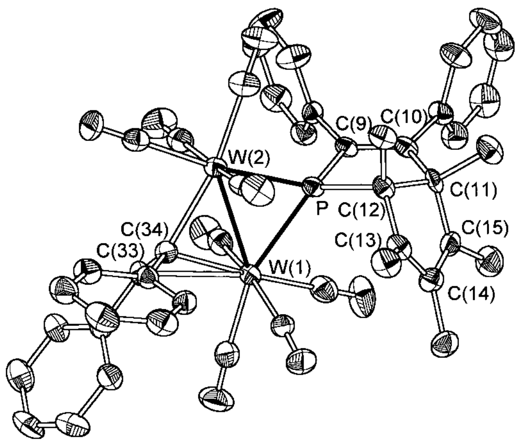
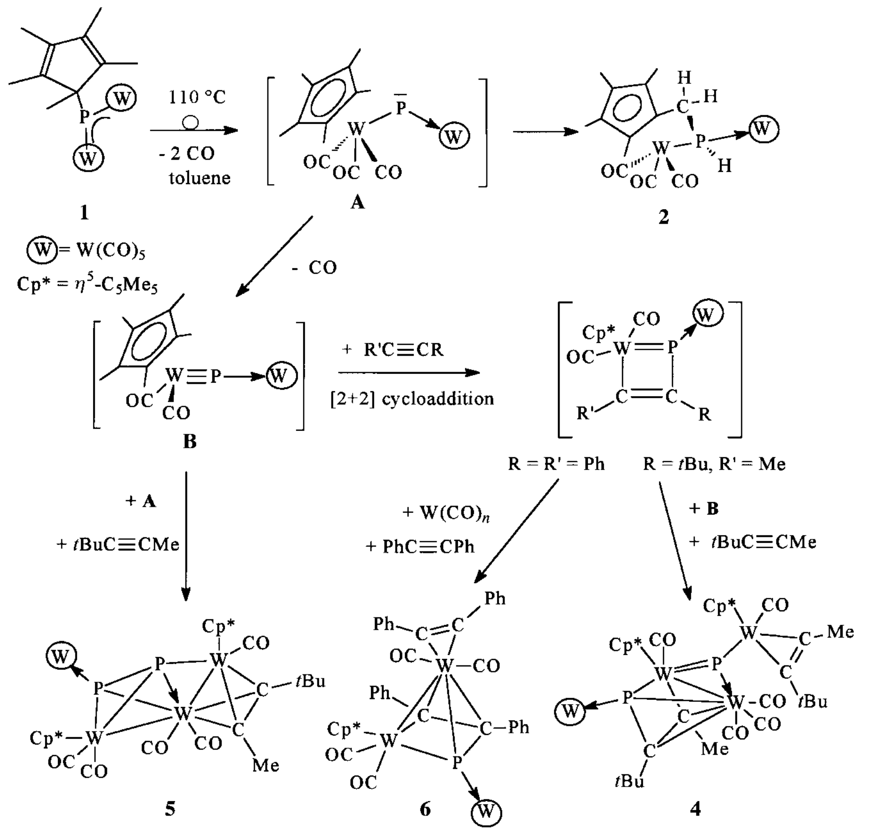


Figure 4. Molecular structure of **7** (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W(1)–W(2) 3.0045(7), W(1)–C(34) 2.451(6), W(1)–C(33) 2.517(7), C(33)–C(34) 1.382(10), W(2)–C(34) 2.249(6), W(2)–P 2.4493(18), W(1)–P 2.5508(17), P–C(12) 1.881(7), P–C(9) 1.809(5), C(9)–C(10) 1.351(10), C(10)–C(11) 1.543(9), C(11)–C(12) 1.509(9); W(2)-P-W(1) 73.84(5), W(2)-P-C(9) 124.8(2), W(2)-P-C(12) 125.9(2), W(1)-P-C(9) 117.3(2), W(1)-P-C(12) 127.40(19), W(2)-C(34)-W(1) 79.34(19).

bond to W(2) (2.2493(18) Å). The resulting asymmetry at the tungsten atoms is balanced by the longer bond of the atom C(33) to the atom W(1) (2.517(7) Å). Thus, the alkyne is coordinated to the tungsten atom in a η^1- and η^2-fashion. Within the bent bicyclic ring of **7**, a delocalization of the π-electron system is found between the atoms C(13), C(14), and C(15) (d(C13–C14) 1.449(10) Å; d(C14–C15) 1.351(8) Å).



Scheme 2. Proposed reaction pathway of the thermolysis reaction of **1** with different alkynes.

Discussion of the possible reaction pathway: Although, at first glance, the structures of the isolated products **4**–**7** seem to be complicated, the central $[WPC_2]$ moiety of the major products **4** and **6** of reactions (1) and (2), respectively, provides evidence for the formation of an intermediate **B** of the formula $[Cp^*(CO)_2W{\equiv}P \rightarrow W(CO)_5]$ with a tungsten–phosphorus triple bond (Scheme 2), which undergoes [2+2] cycloaddition reactions with the alkynes. Thus, one can propose that the thermolysis of the phosphinidene complex **1** leads to Cp* migration to initially form the intermediate **A**, which acts as a precursor to the CH-activated phosphine **2** as a side product of these reactions, as well as after subsequent CO elimination to the triply bound intermediate **B**. From here, the main pathway involves [2+2] cycloadditions of **B** with the corresponding alkyne to form four-membered $[WP_2C]$ ring moieties. These heterocycles need additional stabilization. Consequently, for the reaction of **1** with PhC≡CPh [Eq. (2)], the four-membered heterocycle reacts with a tungsten carbonyl unit, which caps this ring. The tungsten carbonyl unit probably resulting from a molecule **1**, which was cleaved by the reaction with an alkyne. In the case of the reaction of **1** with *t*BuC≡CMe [Eq. (1)], the formed heterocycle reacts with a second molecule of **B** by use of its $[W(CO)_5]$ unit which caps the four-membered moiety. The phosphido phosphorus atom of this second molecule is thereby incorporated into the final coordination core of **4**. In both cases alkynes additionally coordinate to W carbonyl units to give the final products **4** and **6**, respectively. The formation of the bistetrahedral cluster **5**, traces of which were also observed in reaction (2) with the PhC≡CPh analogue, can be exaplained by the reaction of the intermediates **A** and **B** with a subsequent coordination of a molecule of the alkyne. Due to the absence of the dimerization product **3** in the reactions (1) and (2), one can speculate that the cyclization reactions of the intermediate **B** with the alkynes are faster than the dimerization of **B** to form complex **3** (Scheme 1), which was found in the thermolysis reaction of **1** without any additional reagent.

In summary, the major reaction pathway occurs by the formation of the reactive intermediates **A** and **B**, the latter one containing a tungsten–phosphorus triple bond. Furthermore, the isolated bicyclic product **7** of the reaction of **1** with PhC≡CPh indicates the existence of other reaction channels as shown in Scheme 2. Here, the Cp*P unit of **1** acts as a source of a 1,3-dipolaric reagent to add the alkyne in a formal [2+3] cycloaddition.

Conclusion

The results show that $[Cp^*P\{W(CO)_5\}_2]$ (**1**) is an efficient source for generating highly reactive phosphido complex intermediates; the triple bond intermediate $[Cp^*(CO)_2W{\equiv}P\rightarrow W(CO)_5]$ (**B**) seems to play a key role. Thus, predominantly [2+2] cycloaddition products are formed in its trapping reactions with asymmetrically as well as symmetrically substituted alkynes. In continuation of our research in this field, we are currently investigating the reactivity of **1** in the presence of phosphaalkynes, nitriles, and isonitriles. Our interest has also focused on obtaining formally [4+2] cycloaddition products as well as introducing these intermediates into a rich coordination chemistry. In addition, we are currently extending these investigations to the corresponding arsenic and antimony compounds $[Cp^*E\{M(CO)_5\}_2]$ (M = Cr, W; E = As,[10] Sb[11]). Moreover, the occurrence of **7** as the result of a possible 1,3-dipolaric cycloaddition of the Cp*P subunit of **1** gives rise to a variety of different reaction pathways of **1**.

Experimental Section

All reactions were performed under an atmosphere of dry argon with standard vacuum, Schlenk, and glove box techniques. Solvents were purified and degassed by standard procedures. NMR spectra were recorded at 25 °C on a Bruker AC 250 (^{1}H: 250.133 MHz, ^{31}P: 101.256 MHz; standard Me_4Si (^{1}H), 85 % H_3PO_4 (^{31}P)). IR spectra were recorded in KBr on a Bruker IFS28 FT-IR spectrometer. Mass spectra were recorded on a Finnigan MAT 711 spectrometer at 70 eV. Elemental analysis were performed by the analytical laboratory of the Institute.

Reagents: Unless otherwise stated, commercial grade chemicals were used without further purification. The alkynes were distilled before use in the trapping reactions. $[Cp^*P\{W(CO)_5\}_2]$ (**1**) was prepared by literature methods.[12, 5] Column chromatography was carried out under argon on a column ($l = 40$ cm, $\varnothing = 1.5$ cm), packed with silica gel (Merck 60), which was deactivated beforehand by heating under high vacuum (10^{-3} Torr) at 200 °C for two days.

Crystal structure analysis: Crystal structure analyses of **4**–**7** were performed on a STOE IPDS diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Machine parameters, crystal data, and data collection parameters are summarized in Table 1. The structures were solved by direct methods with the program SHELXS-93,[13] and full-matrix least-squares refinement on F^2 in SHELXL-97[14] was performed with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to a riding model. Complex **4** crystallizes in the acentric space group $P2(1)$ in an enantiomeric pure compound [flack parameter = −0.016(12)]. The relatively long c axis of **6** proved to be problematic and may account for the rather limited number of observed reflections in a comparably small 2θ range as well as the relatively poor quality of the data set due to the overlap of some reflections. From several reactions of the synthesis of **5**, only poor quality crystals were obtained leading only to a moderately wR_2 value. For these reasons, the atoms C(3) and C(8) for **5** and C(26) for **4** could not be refined anisotropically.

Crystallographic data (excluding structure factors for the structures) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151392 (**4**), CCDC-151393 (**5**), CCDC-151394 (**6**), and CCDC-151395 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Thermolysis of $[Cp^*P\{W(CO)_5\}_2]$ (1) in the presence of $tBuC{\equiv}CMe$, synthesis of 4 and 5: A solution of $tBuC{\equiv}CMe$ in n-pentane (0.047 g, 0.48 mmol) was added to a solution of **1** (0.394 g, 0.48 mmol) in toluene (30 mL) and refluxed for 2 h until the color of the solution changed from deep blue to brown. The volume of the toluene solution was reduced to 3 mL. Compound **5** crystallized at −25 °C as black platelets (0.052 g, 0.036 mmol, 15 %). The remaining solution was evaporated to dryness in vacuo, and the resulting brown residue was transferred onto silica gel and separated by column chromatography. Elution with n-hexane/toluene (10:1) gave a yellow fraction containing **4**, which was recrystallized from toluene to give black rods (0.221 g, 0.15 mmol, 60 %). **4**: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 19.9$ (s, $^1J_{W,P}$ 192 Hz, 84 Hz), −49.2 (s, $^1J_{W,P}$ 207 Hz, 52 Hz); ^{1}H NMR (C_6D_6): $\delta = 1.88$ (s, 15 H, $CH_3(Cp^*)$), 1.69 (s, 15 H, $CH_3(Cp^*)$), 1.64 (s, 9 H, CH_3C), 1.51 (s, 3 H, CH_3), 1.40 (s, 9 H, CH_3C), 1.19 (s, 3 H, CH_3); IR (KBr) $\tilde{\nu} = 2070$ (w), 2063 (w), 1992 (sh), 1939 (br) cm^{-1}; MS (EI): m/z (%): 1388 (1) $[M^+ - (CO)_2MeCC\mathit{t}Bu]$, 1244 (1) $[M^+ - WCp^*]$, 1036 (8) $[Cp^*(CO)WP\{W(CO)_5\}MeCC\mathit{t}Bu(CO)_2W^+]$, 854 (11) $[Cp^*(CO)WP\{W(CO)_5\}MeCC\mathit{t}Bu(CO)_2{}^+]$, 742 (4) $[W_2(CO)_4PC_2(C_4H_9)(CH_3)Cp^{*+}]$, 714 (31) $[Cp^*(CO)WCP\{W(CO)_5\}^+]$; elemental analysis (%) calcd for $C_{44}H_{54}O_{10}P_2W_4$: C 34.30, H 3.50; found: C 35.06, H 4.43. **5**: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -79.6$ (d, $^1J_{P,P}$ 407 Hz), −220.5 (d, $^1J_{P,P}$ 407 Hz); ^{1}H NMR (C_6D_6): $\delta = 1.88$ (s, 15 H, $CH_3(Cp^*)$), 1.82 (s, 3 H, CH_3), 1.68 (s, 15 H, $CH_3(Cp^*)$), 1.40 (s, 9 H, CH_3C); IR (KBr): $\tilde{\nu} = 2061$ (s), 1977 (s), 1934 (sh) cm^{-1}; MS (EI): m/z (%): 1120 (8) $[M^+ - W(CO)_5]$, 1092 (3) $[M^+ - W(CO)_6]$, 1064 (1) $[M^+ - W(CO)_7]$, 1036 (15) $[M^+ - W(CO)_8]$, 1008 (7) $[M^+ - W(CO)_9]$; elemental analysis (%) calcd for $C_{37}H_{42}O_{10}P_2W_4$: C 30.76, H 2.90; found: C 31.22, H 3.31.

Thermolysis of $[Cp^*P\{W(CO)_5\}_2]$ (1) in the presence of $PhC{\equiv}CPh$, synthesis of 6 and 7: $PhC{\equiv}CPh$ (0.082 g, 0.46 mmol) was added to a solution of **1** (0.375 g, 0.46 mmol) in toluene (20 mL) and refluxed for 2 h until the color of the solution changed from deep blue to brown. The solvent was completely removed in vacuo, and the resulting brown residue was transferred onto silica gel and separated by column chromatography. Elution with n-hexane/dichloromethane (4:1) gave a yellow fraction containing **7**, which was recrystallized from n-hexane to give yellow rods at room temperature (0.154 g, 0.14 mmol, 30 %). Elution with n-hexane/dichloromethane (1:1) resulted in a dark red fraction containing complex **6** (0.122 g, 0.09 mmol, 20 %). **6**: $^{31}P\{^1H\}$ NMR ($[D_8]$THF): $\delta = -2.8$ (s, $^1J_{W,P}$ 202; 88 Hz); ^{1}H NMR ($[D_8]$THF): $\delta = 7.65$–6.50 (m, br, 20 H, Ar-H), 1.92 (s, 15 H, $CH_3(Cp^*)$); IR (KBr): $\tilde{\nu} = 2050$ (s), 1992 (s), 1910 (s), 1850 (sh) cm^{-1}; MS (EI): m/z (%): 1136 (12) $[M^+ - 2CO - C_{10}H_{14}]$, 968 (26) $[M^+ - 8CO - C_{10}H_{14}]$, 756 (49) $[M^+ - W(CO)_9 - C_{10}H_{14}]$; elemental analysis (%) calcd for $C_{47}H_{35}O_9PW_3$: C 42.53, H 2.66; found: C 41.95, H 2.30. **7**: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 18.4$ (s, $^1J_{W,P}$ 232 Hz); ^{1}H NMR (C_6D_6): $\delta = 6.97$–6.88 (m, br, 20 H, Ar-H), 1.82 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3); IR (KBr): $\tilde{\nu} = 2075$ (m), 2046 (m), 1973 (sh), 1942 (s), 1903 (s) cm^{-1}; MS (EI): m/z (%): 980 (2) $[M^+ - 2CO(C_6H_5)]$, 758 (10) $[M^+ - 2(PhCCPh)]$; elemental analysis (%) calcd for $C_{46}H_{35}O_8PW_2$: C 49.58, H 3.17; found: C 49.95, H 2.85.

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