A Novel Synthetic Approach to Highly Reactive Intermediates Containing a Metal – Phosphorus Triple Bond

Manfred Scheer,* Eva Leiner, Peter Kramkowski, Michael Schiffer, and Gerhard Baum

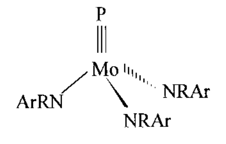
Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday

Abstract: Thermolysis of [Cp*P{W(CO)$_5$}$_2$] (**1a**) induces a Cp* migration from a σ-bound state at the phosphorus atom to η^5 coordination at the transition metal. Thereby the unsaturated P atom undergoes an unusual C–H activation to yield the novel complex [(CO)$_3$W(η^5-C$_5$Me$_4$CH$_2$)P(H) $\rightarrow$ W(CO)$_5$] (**2**). Additionally, a highly reactive intermediate of the type [Cp*(CO)$_2$W≡P $\rightarrow$ W(CO)$_5$], containing a tungsten – phosphorus triple bond, is formed. The dimerisation of this sterically unprotected intermediate leads to [Cp*$_2$(CO)$_4$W$_2$-(μ,η^2-P$_2${W(CO)$_5$}] (**3**). Furthermore, the tetranuclear cluster [{W(CO)$_3$Cp*W}$_2$(μ_3-P)$_2${μ_3-PW(CO)$_5$}$_2$] (**4**) was isolated. The existence of a phosphido-ligand intermediate finds further support by a trapping reaction in the presence of *t*BuC≡P. Here, the thermolysis of **1a** leads to the formation of the novel complex [Cp*(CO)$_2$W{η^3-(PPC(O)C*t*Bu)W(CO)$_5$}] (**5**), containing a diphosphacyclobutenone ligand. Comprehensive structural and spectroscopic data are given for the products.

Keywords: C–H activation • cyclopentadienes • intermediates • P ligands • tungsten

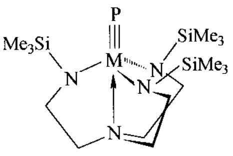
Introduction

Complexes with terminal ligands of the heavier Group 15 elements are a new class of compounds. For more than a decade speculations about the existence of such possible reaction intermediates containing M≡E moieties have been proposed, both with and without spectroscopic evidence.[1] Recently, Cummins[2] and Schrock[3] succeeded in the synthesis of the first isolated and structurally characterised complexes **A** and **B** with a terminal phosphido ligand. In both molecular structures the metal – phosphorus triple bond is protected by bulky amide ligands. Our investigations revealed that as a result of the sterically encumbered triple bond, **B** reacts predominantly to give end-on coordination by use of the lone pair on the phosphido phosphorus.[4] Our interest, however, is mainly focused on the high side-on reactivity of phosphido complexes of the type **C,** first synthesised in our group.[5] These complexes are stable in solution and as solids. However, due to their sensitivity it has not been possible to obtain sufficient amounts of pure compounds so far. Instead of using stable complexes with a metal – phosphorus triple bond as starting materials, we can conceive different strategies to generate phosphido complexes as highly reactive intermediates. From these intermediates, in the presence of reactive molecules, it should be possible to obtain a large number of novel heterocyclic compounds. Recently, we reported a synthetic approach from the reaction of [ClP{M(CO)$_5$}$_2$] with different metallates.[6]



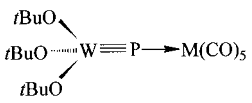
R = C(CD$_3$)$_2$CH$_3$; Ar = 3,5-C$_6$H$_3$Me$_2$

A



M = Mo, W

B



M = Cr, W

C

Another much more effective synthetic concept is shown in Scheme 1. The σ-bound Cp* (Cp* = η^5-C$_5$Me$_5$) phosphinidene complex **1**[7] reacts under Cp* migration from the phosphorus atom to give η^5 coordination at the transition metal centre. A phosphido-complex intermediate **D** is created. Since the triple bond in **D** is not kinetically stabilised by steric protection, the complex dimerises in the absence of an additional reactive species to yield a

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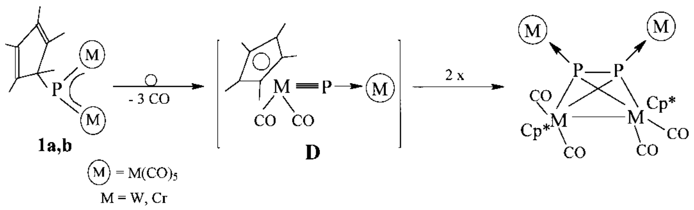
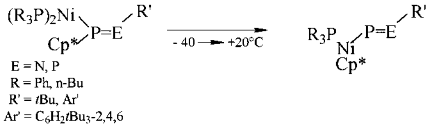


Scheme 1. Concept for the generation of highly reactive intermediates containing a metal–phosphorus triple bond.

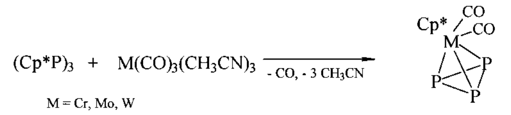
P_2M_2-tetrahedral complex. Migration of a σ-bound Cp* moiety from a main group element to give η^5 coordination at a transition metal centre was first reported by Niecke[8] and Jutzi.[9] The reactions given in Equations (1)–(3) illustrate this, starting either from iminophosphenes, diphosphenes, arsaphosphenes or *cyclo*-triphosphines. In all cases an η^5 bonding mode of the Cp* ligand at the transition metal occurs.



(1)

$$\mathrm{Cp^*E{=}PAr'} + \mathrm{M(CO)_3(CH_3CN)_3} \xrightarrow{-3\,\mathrm{CH_3CN}} \mathrm{Cp^*(CO)_3M{-}E{=}PAr'} \quad (2)$$

E = P, As
M = Cr, Mo, W



(3)

Herein we report our results concerning the thermal reaction of $[\mathrm{Cp^*P\{W(CO)_5\}_2}]$, establishing a simple synthetic approach to generate highly reactive intermediates with a metal–phosphorus triple bond.

Results and Discussion

Synthesis of the starting material: The starting phosphinidene complexes $[\mathrm{Cp^*P\{M(CO)_5\}_2}]$ (**1a**, M = W; **1b** M = Cr) were synthesised by a method described by Jutzi and Kroos[7] from the reaction of $\mathrm{Cp^*PCl_2}$ with $[\mathrm{M_2(CO)_{10}}]^{2-}$. We found that these reactions do not exclusively yield the complexes **1a** and **1 b**; $[\mathrm{Cp^*PCl_2M(CO)_5}]$ (M = Cr, W) was formed as the main product.[10] In contrast to compound **1b**, the tungsten complex **1a** could be isolated in 23 % yield and was thus preferred as the starting material for further investigations. An X-ray structure analysis was performed for **1a** (Figure 1) to confirm the chances of the desired Cp* migration.

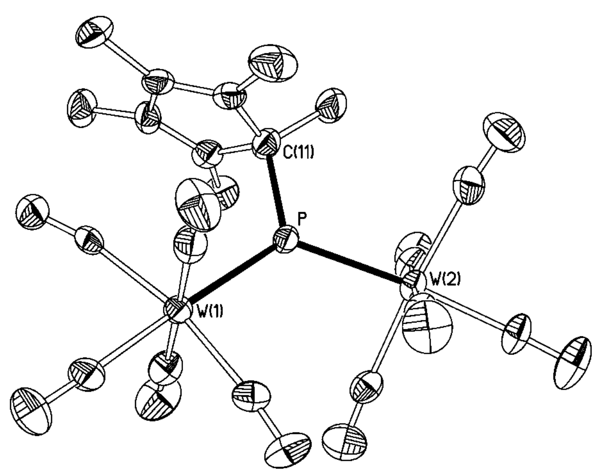
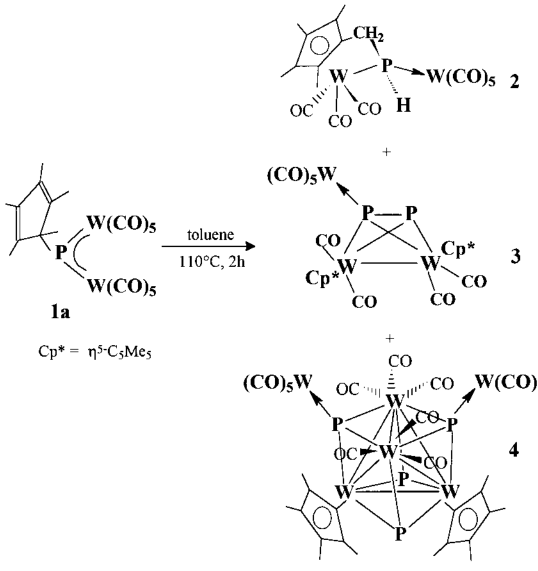


Figure 1. Molecular structure of $[\mathrm{Cp^*P\{W(CO)_5\}_2}]$ (**1a**) (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances [Å] and angles [°]: W(1)–P 2.445(2), W(2)–P 2.428(2), P–C(11) 1.902(7), W(2)-P-W(1) 124.60(7), C(11)-P-W(1) 117.8(2), C(11)-P-W(2) 117.6(2).

Crystal structure of 1a: In **1a** the phosphorus atom is in a trigonal planar environment surrounded by two almost equivalent $[\mathrm{W(CO)_5}]$ moieties and one σ-bound Cp* group (Figure 1). It is important to notice that the Cp* ring is already oriented towards one of the $[\mathrm{W(CO)_5}]$ groups. Therefore we can interpret this situation as a preformed conformation for a possible Cp* migration. The distances P–W(1) and P–W(2) are 2.445(2) Å and 2.428(2) Å, respectively, and are comparable to those found in other phosphinidene complexes.[11] Although there is no significant difference in the P–W bond lengths, this deviation could serve as an explanation for the existence of two different $^1J_{\mathrm{W,P}}$ coupling constants in the ^{31}P NMR spectrum ($^1J_{\mathrm{W,P}} = 187.6$ and 165.7 Hz). We found identical behaviour of the $^1J_{\mathrm{W,P}}$ coupling constants for the chlorophosphinidene complex $[\mathrm{ClP\{W(CO)_5\}_2}]$ (121.1 and 247.9 Hz).[12] The singlet for the methyl groups in the ^{1}H NMR spectra at ambient temperature indicates a fast fluxional process by a series of 1,2-shifts.

Thermolysis of 1a: Refluxing a solution of **1a** in toluene for two hours results in the formation of **2** and **3** as the main products, as well as a small quantity of complex **4** [Eq. (4)].[13] Complexes **2–4** were isolated after column chromatographic workup.



(4)

Table 1. NMR, IR and mass spectral data of the complexes **1**–**4**; J in Hz, $\tilde{\nu}$ in cm^{-1}.

	1a	**2**	**3**	**4**
^{1}H[a]	1.75 (s)	2.21[b] (PH: ddd, $^{1}J_{P,H} = 295$, $^{3}J_{H(P),H(B)} = 8.2$, $^{3}J_{H(P),H(B)} = 8.9$) 2.20 (CH_3, s), 2.22 (CH_3, s) 2.28 (CH_3, s), 2.30 (CH_3, s) 3.29 (CH_AH_B, ddd: $^{2}J_{H(A),H(B)} = 14.2$, $^{2}J_{P,H(A)} = 2.4$, $^{3}J_{H(P),H(A)} = 8.2$) 4.16 (CH_AH_B, ddd: $^{2}J_{H(A),H(B)} = 14.2$, $^{2}J_{P,H} = 8.2$, $^{3}J_{H(P),H(B)} = 8.9$)	1.84 (s)	1.82 (s)
^{31}P[a]	1076.5 ($^{1}J_{W,P} = 187.6$ and 165.7)	– 325.2 ($^{1}J_{W,P} = 202.8$ and 74.3, $^{2}J_{P,H} = 2.4$ and 8.2, $^{1}J_{P,H} = 295$)	T = 333 K: – 185[c]	450.4 (d)
	1b: 1331.8		T = 203 K: – 142.6 (d) – 249.9 (d) ($J_{P,P} = 433$, $J_{W,P} = 196$, $J_{W,P} = 106$)	846.7 (d) ($^{2}J_{P,P} = 15$, $^{1}J_{W,P} = 173$)
$\tilde{\nu}$ (CO)[d]	2088(s) 2041(s) 1938(br) 1910(vs)	2069 (m) 2011 (s) 1977 (m) 1953 (s) 1929 (s) 1908 (vs) 1888 (s)	2061(m) 1996(sh) 1993(m) 1924(vs) 1896(s) 1841 (br m)	[e]
EI-MS:[f] m/z (%)	727 (8) [$M^+ - 3CO$] 677 (35) [$M^+ - Cp^*$] 648 (32) [$M^+ - Cp^*(CO)$] 620 (22) [$M^+ - Cp^*(CO)_2$] 135 (90) [Cp^*]	758 (92) [M^+] 729.8 (49)[$M^+ - CO$] 701,9 (8) [$M^+ - 2CO$] 589,9 (100) [$M^+ - 6CO$]	1136 (4) [M^+] 814 (52) [$M^+ - W(CO)_5$] 726 (89) [$M^+ - W(CO)_8$] 28 (70) [CO]	1135.8 (58) [$M^+ - Cp^*W_2(CO)_{11}$] 1107.9 (9) [$M^+ - Cp^*W_2(CO)_{12}$] 1079.9 (8) [$M^+ - Cp^*W_2(CO)_{13}$]

[a] In C_6D_6; [b] In [D_8]THF; [c] In [D_8]toluene; [d] In KBr; [e] Sample contained traces of **3**; the obtained spectrum is similar to that of **3** and therefore no exact $\tilde{\nu}$(CO) can be given; [f] 70 eV, 140 °C.

Spectroscopic properties: Compounds **2**–**4** are crystalline and are yellow, orange and green, respectively. They are sparingly soluble in n-hexane and toluene, but readily soluble in CH_2Cl_2 and THF. The IR spectra of all compounds reveal coupled vibration modes for terminally bound carbonyls in the region of the CO-stretching frequencies (Table 1). In the mass spectra the parent molecular ion peak was observed in all cases, with exception of **4** in which the highest fragment detected corresponds to a loss of a Cp* moiety, two W atoms and 12 CO units.

The ^{31}P{^{1}H} NMR spectrum of **2** (Table 1) reveals a singlet at $\delta = -325.2$ bearing two pairs of tungsten satellites with coupling constants $^{1}J_{W,P} = 203$ Hz and 74 Hz. The first coupling constant is consistent with the bonding of a phosphorus atom to a [$W(CO)_5$] moiety; the latter indicates σ-bonding to the [$Cp^*W(CO)_2$] fragment. Additionally, in the ^{31}P NMR spectrum of **2** (Figure 2) a $^{1}J_{P,H}$ of 295 Hz is observed. The expected doublet is further split into a doublet of doublets with $^{2}J_{P,H} = 8$ and 2.4 Hz; this is due to the coupling with the diastereotopic methylene protons of the σ-bound CH_2 group at the P atom. In the ^{1}H NMR spectrum of **2** the CH_2 protons appear at different chemical shifts as a result of their diastereotopic character. Each signal is split into a doublet of doublets of doublets as required for their coupling with each other, the coupling to the phosphorus and the H atom at the phosphorus. Furthermore, the spectrum reveals four different singlets for the four methyl groups on the Cp ring. Owing to the coupling of the inequivalent CH_2 protons, the doublet of the PH proton undergoes further splitting.

At ambient temperature **3** reveals only one broad signal in the ^{31}P{^{1}H} NMR spectrum. At low temperatures the signal splits into two signals indicating a dynamic behaviour (Figure 3). At 203 K **3** has an AX spin system at $\delta = -142.6$ and $\delta = -249.9$ ($J_{PP} = 433$ Hz) with two different J_{WP} of 196 and 106 Hz. At the coalescence temperature of 283 K a $\Delta G^{\neq}_{Tc}$ of about 50 kJ mol^{-1} was determined indicating a transfer process of the $W(CO)_5$ group between two phosphorus atoms.

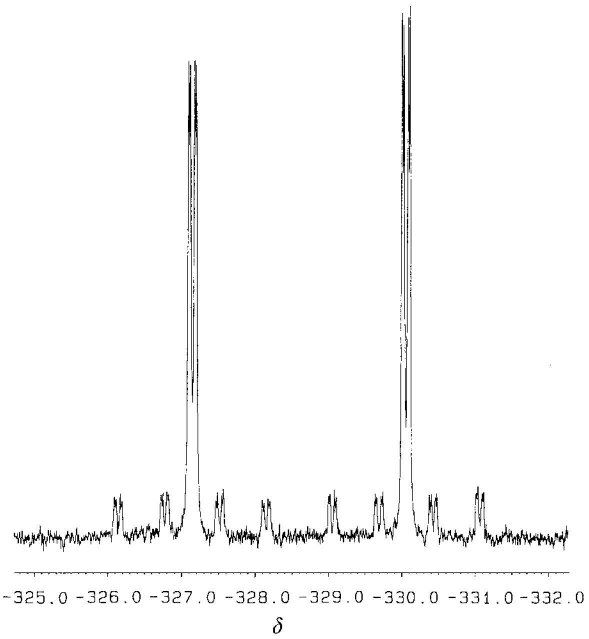


Figure 2. ^{31}P NMR spectrum of **2** at 300 K in [D_8]THF (SF = 101.256 MHz).

For **4** an A_2X_2 spin system at low field is observed in the ^{31}P{^{1}H} NMR spectrum ($\delta = 450.4$ and 846.7). The coupling

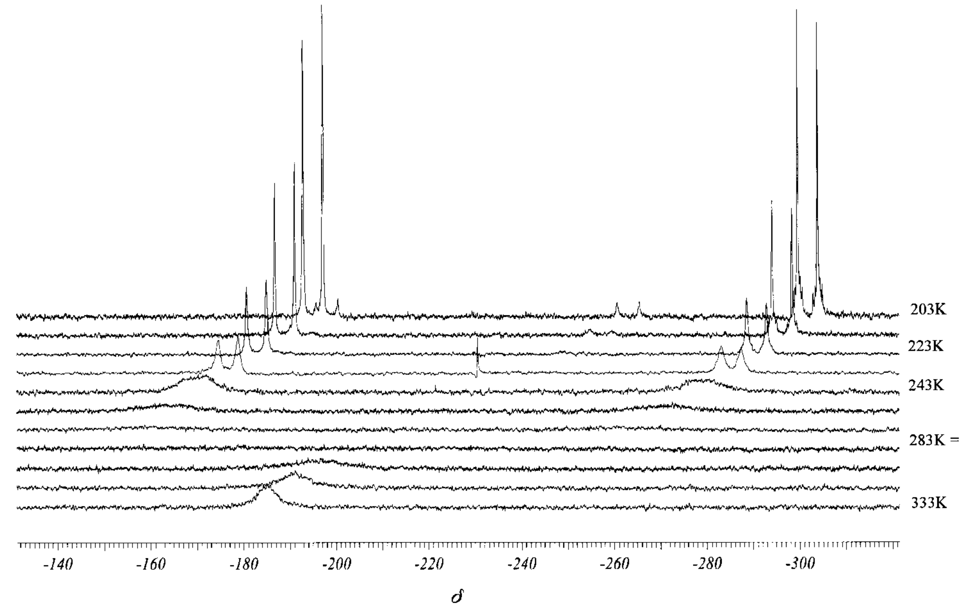


Figure 3. $^{31}P\{^1H\}$ NMR spectra of **3** at different temperatures in [D$_8$]toluene (SF = 101.256 MHz) indicating the intramolecular transfer process of the [W(CO)$_5$] group.

constant $J_{P,P}$ is 15 Hz, which is consistent with a coupling over two bonds.

Crystal structure analysis: Details of the crystallographic data are given in Table 2. The central framework of **2** is a fourfold-coordinated P atom in a slightly distorted tetrahedral arrangement. The phosphorus is surrounded by a W(CO)$_5$ moiety, an H atom and a twofold-bound [(η^5-C$_5$Me$_4$CH$_2$)W(CO)$_3$] group (Figure 4). The H atom at the phosphorus could be freely refined. Compound **2** is one of the very rare examples for C–H activation by a main group element of one methyl group of a η^5-bound Cp* ligand at a transition metal. Such C–H activations caused by a phosphorus atom, leading to a pseudo-five-membered ring, were first described by Weber et al.[14] By contrast, in **2** a pseudo-four-membered ring is formed. As a result of this strained bonding mode the P–C(9) bond in **2** (1.873(7) Å) is slightly elongated in comparison with a single-bond distance. This situation is further reflected in the P–W(2) bond length, which at 2.599(2) Å is also unusually longer than that of the corresponding distance to the W(1) atom of the W(CO)$_5$ group (2.543(13) Å). The relatively small bond angle W(2)-P-C(9) of 87.1(2)° further reflects the strained bonding situation.

The cell constants of [Cp*$_2$(CO)$_4$W$_2$(μ,η^2-P$_2$){W(CO)$_5$}] (**3**) (Table 2) are identical to those obtained for the complex

Table 2. Crystallographic data for compounds **1a–4**.

	1a	**2**·C$_7$H$_8$	**3**	**4**
formula	C$_{20}$H$_{15}$O$_{10}$PW$_2$	C$_{18}$H$_{15}$O$_8$PW$_2$ · C$_7$H$_8$	C$_{29}$H$_{30}$O$_9$P$_2$W$_3$	C$_{36}$H$_{30}$O$_{16}$P$_4$W$_6$
M_r	813.99	850.10	1136.02	1945.58
crystal size [mm]	0.42 × 0.22 × 0.19	0.42 × 0.15 × 0.08	0.08 × 0.08 × 0.04	0.08 × 0.08 × 0.01
T [K]	203(2)	203(2)	200(2)	200(2)
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic
a [Å]	9.015(3)	7.1560(14)	8.990(2)	9.302(2)
b [Å]	25.423(11)	20.641(4)	18.501(4)	11.524(2)
c [Å]	10.537(4)	18.506(4)	20.297(4)	24.342(5)
α [°]	90	90	90	77.93(3)
β [°]	97.82(3)	97.09(3)	102.48(3)	79.85(3)
γ [°]	90	90	90	72.36(3)
V [Å^3]	2392(2)	2712.6(9)	3296.1(11)	2413.8(8)
Z	4	4	4	2
ρ_{calcd} [g cm^{-3}]	2.260	2.082	2.289	2.677
μ [mm^{-1}]	9.726	8.578	10.590	14.433
radiation [λ, Å]	Mo$_{K\alpha}$ (0.71073)			
diffractometer	STOE STADI IV	STOE IPDS	STOE IPDS	STOE IPDS
2Θ range [°]	$3.2 \leq 2\Theta \leq 62$	$4.86 \leq 2\Theta \leq 52$	$4.86 \leq 2\Theta \leq 52$	$4.4 \leq 2\Theta \leq 52$
index range	$-11 \leq h \leq 11$	$-8 \leq h \leq 8$	$-11 \leq h \leq 7$	$-10 \leq h \leq 11$
	$0 \leq k \leq 31$	$-7 \leq k \leq 23$	$-18 \leq k \leq 22$	$-14 \leq k \leq 14$
	$0 \leq l \leq 13$	$-22 \leq l \leq 22$	$-24 \leq l \leq 24$	$-29 \leq l \leq 28$
data/restrains/parameters	5370/0/314	3691/0/334	5969/0/398	7263/0/309
independent reflections with $I > 2\sigma(I)$	4674 ($R_{int} = 0.0288$)	3042 ($R_{int} = 0.0241$)	4908 ($R_{int} = 0.0706$)	3617 ($R_{int} = 0.0921$)
goodness-of-fit on F^2	1.107	1.063	0.990	1.251
R_1,[a] wR_2[b][$I > 2\sigma(I)$]	0.0340, 0.0829	0.0225, 0.0537	0.0417, 0.1087	0.0906, 0.1432
R_1,[a] wR_2[b] [all data]	0.0448, 0.0937	0.0330, 0.0571	0.0530, 0.1153	0.2091, 0.1775
largest diff. peak and hole [e Å^{-3}]	1.559, −1.323	0.548, −0.470	1.629, −2.017	2.129, −2.177

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

0947-6539/98/0410-1920 $ 17.50+.50/0

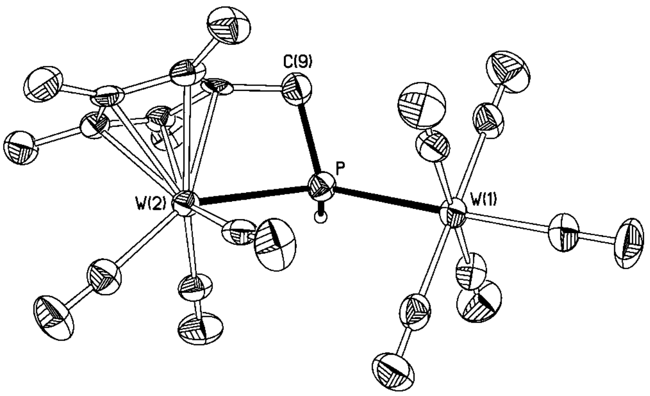


Figure 4. Molecular structure of **2** (showing 50% probability ellipsoids; hydrogen atoms and the toluene molecule is omitted for clarity). Selected bond distances [Å] and angles [°]: P–W(2) 2.599(2), P–W(1) 2.5431(13), P–C(9) 1.873(7), C(9)–C(10) 1.497(10), W(1)-P-W(2) 131.02(6), C(9)-P-W(1) 117.6(2), C(9)-P-W(2) 87.1(2), C(10)-C(9)-P 101.0(4), C(9)-C(10)-W(2) 108.0(4).

prepared by Schwalb, who carried out the reaction of $[\{Cp^*W(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ with an excess of $[W(CO)_5(thf)]$.[15] However, the X-ray data of **3** are of better quality. The ^{31}P NMR and the other spectroscopic data are in good agreement with those determined by Schwalb. The molecular structure of **3** (Figure 5) is best described as a slightly distorted W_2P_2 tetrahedron. The W–W bond is 3.0920(7) Å and is longer than that found in $[\{CpW(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (3.00263(11) Å)[16]. The P–P bond in **3** (2.092(4) Å) is short in comparison with the average single-bond distance in β-P_4 at −185 °C (2.190 to 2.212 Å).[17] In M_2P_2 tetrahedral complexes the P–P bond is usually significantly shorter.[1] Remarkably, the semibridging C(3) atom of one of the CO groups reveals a tendency to coordinate to the W(1) atom. In solution a bridging mode of this carbonyl group is clearly recorded by the IR stretching frequency at 1841 cm^{-1} (Table 1). Although in the solid-state structure the $W(CO)_5$ group coordinates exclusively to one P atom, ^{31}P NMR studies in solution at ambient temperatures revealed that a fast exchange process of this moiety between both P atoms occurs.

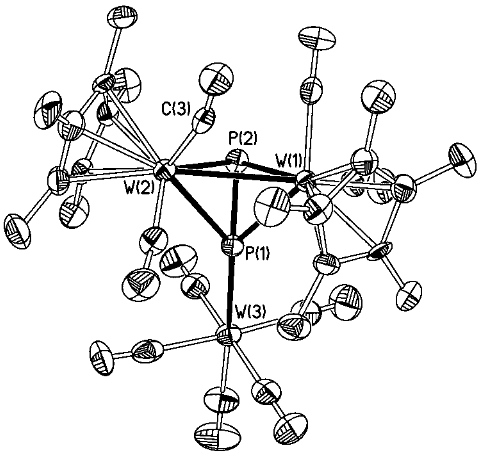


Figure 5. Molecular structure **3** (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances [Å] and angles [°]: W(1)–W(2) 3.0920(7), W(1)–P(1) 2.470(2), W(1)–P(2) 2.541(2), W(2)–P(1) 2.499(2), W(2)–P(2) 2.476(2), P(1)–P(2) 2.092(4), W(3)–P(1) 2.559(2), W(2)–C(3) 1.936(10), W(1)···C(3) 2.857(9), W(1)-P(1)-W(2) 76.96(7), W(1)-P(2)-W(2) 76.08(6), P(1)-W(1)-W(2) 51.94(5), P(2)-W(1)-W(2) 51.01(6), P(1)-W(2)-W(1) 51.09(5), P(2)-W(2)-W(1) 52.91(5), P(2)-P(1)-W(3) 124.75(12).

$[\{Cp^*W(CO)_3\}_2(\mu_3\text{-}P)_2\{\mu_3\text{-}PW(CO)_5\}_2]$ (**4**; Figure 6) crystallises as very thin, small, green plates. However, the collected data on an imaging plate detector system (IPDS) are of good quality. The cluster compound **4** can be described as a distorted heterocubane, the vertices of which are alternately occupied by P or W atoms. However, a description as a W_4 tetrahedron of $W(CO)_3$ and Cp*W units capped by P atoms appears to be more realistic. The two (μ_3-P) ligands connected to the $W_2(CO)_6$ edge coordinate to $W(CO)_5$ moieties. The tetrahedral W_4 cluster description corresponds with the Wade–Mingos Rules to give $n+1$ skeletal electron pairs ($n = 4$). The W–W bond distances are between 2.824(2) Å and 3.094(3) Å and thus lie in the range of W–W single bonds.[16, 18] Due to the bulky Cp* ligands, the longest distance is found between W(2) and W(4).

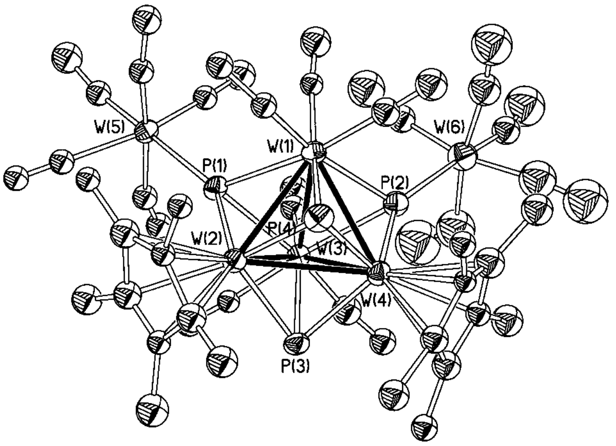
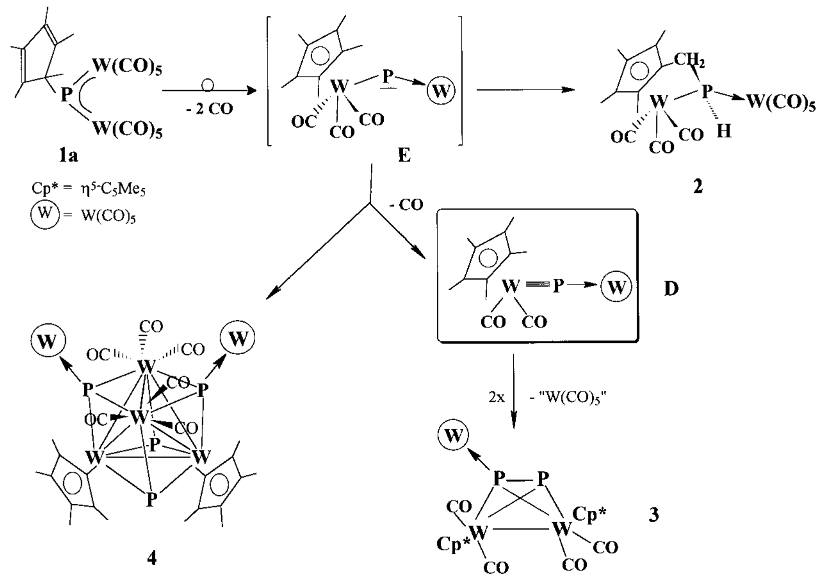


Figure 6. Molecular structure of **4** (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances [Å] and angles [°]:W(1)–W(2) 2.965(2), W(1)–W(3) 2.894(2), W(1)–W(4) 2.984(2), W(2)–W(3) 2.843(2), W(2)–W(4) 3.094(3), W(3)–W(4) 2.824(2), P(1)–W(1) 2.507(11), P(1)–W(2) 2.406(8), P(1)–W(3) 2.513(11), P(2)–W(1) 2.525(12), P(2)–W(3) 2.520(12), P(2)–W(4) 2.379(9), P(3)–W(2) 2.387(11), P(3)–W(3) 2.525(9), P(3)–W(4) 2.396(12), P(4)–W(1) 2.522(9), P(4)–W(2) 2.394(12), P(4)–W(4) 2.383(12), P(1)–W(5) 2.590(9), P(2)–W(6) 2.612(10), W(3)-W(1)-W(2) 58.04(6), W(3)-W(1)-W(4) 57.39(6), W(2)-W(1)-W(4) 62.67(6), W(3)-W(2)-W(1) 59.72(6), W(3)-W(2)-W(4) 56.60(6), W(1)-W(2)-W(4) 58.96(6), W(4)-W(3)-W(2) 66.19(6), W(4)-W(3)-W(1) 62.91(6), W(2)-W(3)-W(1) 62.24(6), W(3)-W(4)-W(2) 57.21(6), W(1)-W(4)-W(2) 58.36(6), W(2)-P(1)-W(1) 74.2(3), W(2)-P(1)-W(3) 70.6(3), W(1)-P(1)-W(3) 70.4(3), W(2)-P(3)-W(3) 70.7(3), W(4)-P(4)-W(2) 80.7(4).

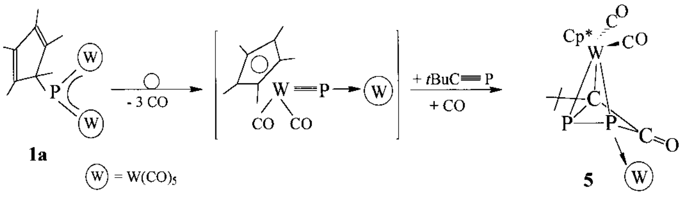
Discussion of the reaction pathway: The proposed pathway of the reaction depicted in Equation (4) is shown in Scheme 2 and is based on the isolated products. Starting from $[Cp^*P\{W(CO)_5\}_2]$ (**1a**), the first step is a Cp* migration from the σ-bound state at the P atom to a π coordination at the W atom to give an intermediate $[\{Cp^*W(CO)_3\}P\{W(CO)_5\}]$ (**E**). Hereafter, the unsaturated P atom causes a C–H activation to form the organophosphorus derivative **2**. Alternatively, fur-



Scheme 2. Proposed reaction pathway of the thermal decomposition of **1a**.

ther CO elimination of **E** occurs to yield the desired intermediate [Cp*(CO)$_2$W≡P→W(CO)$_5$] (**D**) with a tungsten–phosphorous triple bond. Owing to the kinetic instability of this compound, the dimerisation of **D** produces the W$_2$P$_2$ tetrahedral complex **3**. Although one W(CO)$_5$ group is missing, it is known from the work by Schwalb[15] that [Cp*$_2$(CO)$_4$W$_2$(μ,η^2-P$_2$)] reacts with a large excess of [W(CO)$_5$(thf)] to give **3** only. Evidently, under the specific steric conditions of the bulky Cp* ligands, only one W(CO)$_5$ moiety is able to coordinate at the W$_2$P$_2$ tetrahedron. It is shared in solution by both of the P atoms.

Although compound **4** was obtained in low yield, the formation of this tetrahedral cluster could be caused by a reaction of the intermediate **E** with **D** by the loss of [Cp*W(CO)$_3$]$_2$ and W(CO)$_6$. To confirm the proposed reaction pathway, the thermolysis of **1a** was carried out in the presence of *t*BuC≡P. Now, besides some small amounts of **2** and **3**, the major product of this reaction [Eq. (5)] is



(5)

the diphosphacyclobutenon complex **5**. These results indicate the existence of either intermediate **D** or **E**. Intermediate **D** can undergo an cycloaddition with the phosphaalkyne combined with an insertion of one CO molecule resulting in the unusual diphosphacyclobutenone ligand complex. Alternatively, a nucleophilic attack of **E** towards the phosphaalkyne to give **5** can be discussed.

The yellow crystalline compound **5** is readily soluble in hexane, toluene and CH$_2$Cl$_2$. The ^{31}P NMR spectrum shows two doublets at $\delta = -163.1$ and -64.6, with $^1J_{P,P} = 237$ Hz. The latter signal reveals two different $J_{W,P}$ indicating the additional coordination to a W(CO)$_5$ group. In the IR spetrum of **5** the CO group of the diphosphacyclobutenone ligand is observed at 1641 cm^{-1}.

Conclusions

The results show that [Cp*P{W(CO)$_5$}$_2$] (**1a**) is an efficient source for the production of a triple bond intermediate of the type [Cp*(CO)$_2$W≡P→W(CO)$_5$] (**D**). This opens a perspective for the use of this complex as a synthon in the presence of reactive molecules such as phosphaalkynes, acetylenes or 2,4-dimethylbutadiaene to generate novel W/P containing heterocycles. Furthermore it might be possible to extend these investigations to the heavier congeners of phosphorus to produce other pnicogenido triple-bond compounds, which is still a challenge in this field.

Experimental Section

General techniques: All reactions were performed under an atmosphere of dry nitrogen with Schlenk techniques. Solvents were purified and degassed by standard procedures. NMR spectra were recorded on a Bruker AC250 (^{1}H: 250.13 MHz; ^{31}P: 101.256 MHz; standard ^{1}H: Me$_4$Si; ^{31}P: 85% H$_3$PO$_4$). 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. Correct elemental analysis was performed by the analytical laboratory of the institute.

Reagents: Unless otherwise stated, commercial grade chemicals were used without further purification. Cp*PCl$_2$ was obtained as published in ref. [19]. [Cp*P{M(CO)$_5$}$_2$] **1a,b** (M = W, Cr) was prepared according to a modified procedure as described in ref. [7]. *t*BuC≡P was synthesised in accordance to ref. [20].

Thermolysis of [Cp*P{W(CO)$_5$}$_2$], synthesis of 2, 3 and 4: A solution of **1a** (0.5 g, 0.72 mmol) in toluene (50 mL) was refluxed for 2 hours. Subsequently, the solvent is completely removed. The dark brown residue was transferred onto silicagel and separated by column chromatography (30 × 2.5, Merck 60). Elution with hexane/toluene (5:1) gave a yellow fraction containing **2**, which was recrystallised from toluene to give 191 mg (35%). This was followed by a red fraction of **3** (hexane/toluene 3:1) to yield 288 mg (40%) after recrystallisation. A greenish-red fraction was obtained from toluene and 43 mg (3%) of green platelets of **4** were isolated.

Thermolysis of [Cp*P{W(CO)$_5$}$_2$] in the presence of *t*BuC≡P, synthesis of 5: A solution of **1a** (0.52 g, 0.64 mmol) and *t*BuC≡P (0.064 g, 0.64 mmol) in toluene (50 mL) was refluxed for 2 hours. The solvent was removed to dryness. Subsequently, the residue was extracted with *n*-hexane at ambient temperature to give a red-brown solution. After filtration and removing the solvent in vacuo the residue was recrystallised from toluene to give 318 mg (60%) of **5** as yellow platelets at −30 °C. ^{31}P{^{1}H} NMR (101.256 MHz, [D$_8$]THF, H$_3$PO$_4$): $\delta = -163.1$ (d), -64.6 (d, $^1J_{P,P} = 237$ Hz, $J_{W,P} = 195$, 63 Hz); ^{1}H NMR (250.13 MHz, C$_6$D$_6$, TMS): $\delta = 1.11$ (s, 9H, CH$_3$C), 1.60 (s, 15H, CH$_3$(Cp*)); IR (KBr): $\tilde{\nu}$(CO) = 2072 (m), 2015 (m), 1993 (m), 1968 (m), 1922 (br), 1900 (sh), 1641 cm^{-1} (m); MS (70 eV, EI): *m/z* (%): 858 (31) [M^+], 830 (20) [$M^+ -$ CO], 802 (23) [$M^+ - 2$CO], 717 (87) [$M^+ - 5$CO].

Crystal Structure Analysis: Crystal structure analyses of **1a–4** were performed on a STOE IPDS (**2–4**) and a STOE STADI IV (**1a**: ω-scan mode) diffractometer with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and with empirical absorption corrections for **1a** (6 Psi-scans). Machine parameters, crystal data and data collection parameters are summarized in Table 2. The structures were solved by direct methods with the program SHELXS-86,[21a] and full-matrix least-squares refinement on F^2 in SHELXL-93[20b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-101485. 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).

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