Cyclooligomerization Reactions of Different Phosphaalkynes in the Presence of [W(CO)$_5$thf] − A Route to Tungsten-Stabilised Phosphorus Heterocycles

Peter Kramkowski[a] and Manfred Scheer*[a]

Dedicated to Professor Arndt Simon in occasion of his 60th birthday

Keywords: Phosphaalkynes / Tungsten / Cyclizations / 1,3-Diphosphete ligands / Reaction mechanisms

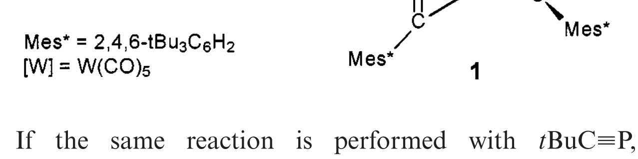
The reactivity of various phosphaalkynes versus [W(CO)$_5$thf] has been studied. The reaction with Mes⋆C≡P (Mes⋆ = 2,4,6-tBu$_3$C$_6$H$_2$) exclusively leads to the low yield formation of [W(CO)$_2${(η^2-PCMes⋆)W(CO)$_5$}$_2$] (**1**). The reaction of the less bulky tBuC≡P with [W(CO)$_5$thf] results in high yields in [W(CO)$_2${η^4-(tBuC)$_2$P$_2$W(CO)$_5$}{η^2-(tBuCP)W(CO)$_5$}] (**2**) which possesses a 1,3-diphosphete ligand as well as a side-on coordinated tBuCP unit. Experiments employing MesC≡P (Mes = 2,4,6-Me$_3$C$_6$H$_2$) give the complexes [W(CO)$_4${η^4-(MesC)$_2$P$_2$}] (**3**), [W(CO)$_2${η^4-(MesC)$_2$P$_2$}{η^2-(MesCP)W(CO)$_5$}] (**4**) and [W(CO)$_2${η^4-(MesC)$_2$P$_2$W(CO)$_5$}⟨η^2-(MesCP)W(CO)$_5${μ-W(CO)$_4$}⟩] (**5**) which have a 1,3-diphosphete ligand in their coordination sphere and are partly substituted with an additional side-on coordinated MesC≡P unit. In **5**, two P atoms of the 1,3-diphosphete and the side-on coordinated MesC≡P are further bridged by a W(CO)$_4$ moiety. Additionally, the unusual product [{W(CO)$_3$}⟨η^6-1,2,4-(RC)$_3$P$_3${RCP→W(CO)$_5$}$_2$⟩] (R = Mes) (**6**) resulting from a pentamerization of MesC≡P initiated by [W(CO)$_5$thf], could be obtained in moderate yield. Comprehensive spectroscopical and structural investigations of all products are presented.

Introduction

Almost twenty years ago the first kinetically stabilised phosphaalkyne tBuC≡P was designed by G. Becker and coworkers.[1] The synthesis of this compound was further improved in the groups of M. Regitz and G. Becker and has therefore become accessible to all chemists.[2] The chemistry of tBuC≡P has undergone a rapid and exciting development. Co-oligomerization and complex-chemical stabilisation of such compounds have been intensively studied and reviewed in detail.[3,4] Investigations involving phosphaalkynes with a residue R different from tBu, however, are scarce. Only a few examples of complexes derived from AdC≡P[5] (Ad = C$_{10}$H$_{15}$) and Mes*C≡P[6,7] (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) are known in the literature. Our interest is focussed on the reactivity of RC≡P towards cluster frameworks such as e.g. *nido*-[Ru$_4$(CO)$_{13}$(μ$_3$-PPh)],[6] and especially on the use of phosphaalkynes in the metathesis reaction with alkoxides of the type [(RO)$_3$W≡W(OR)$_3$].[8,9] The goal of the latter chemistry has been the development of an efficient procedure for the synthesis of phosphido complexes of the type [(RO)$_3$W≡P]. Since these compounds possess a highly reactive metal-phosphorus triple bond, it is necessary to stabilise these complexes with Lewis-acidic M(CO)$_5$-fragments to form [(RO)$_3$W≡P→M(CO)$_5$] (M = Cr, W; R = tBu; 2,6-Me$_2$C$_6$H$_3$).[10] Before one is able to explore the three component system [(RO)$_3$W≡W(OR)$_3$]/RC≡P/[M(CO)$_5$thf], one must be aware of the reaction of phosphaalkynes with [M(CO)$_5$thf] alone. We established that [Cr(CO)$_5$thf] does not react at all with RC≡P, regardless of the reaction conditions employed. However, [W(CO)$_5$thf] reveals a broad reactivity towards Mes*C≡P, tBuC≡P and MesC≡P (Mes = 2,4,6-Me$_3$C$_6$H$_2$), which we have reported herein. Furthermore, for the first time metal complexes derived from MesC≡P have been synthesised. The molecular structures and spectroscopic properties of these novel compounds will be presented.

Results and Discussion

Mes*C≡P (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) reacts with [W(CO)$_5$thf] to give [W(CO)$_2${(η^2-PCMes*)W(CO)$_5$}$_2$] (**1**) in low yield (6%) and most of the phosphaalkyne remains unchanged regardless of the reaction conditions employed [Equation (1)].[7]



If the same reaction is performed with tBuC≡P, [W(CO)$_2${η^4-(tBuC)$_2$P$_2$W(CO)$_5$}{η^2-(tBuCP)W(CO)$_5$}] (**2**) is formed almost quantitatively as the only phosphorus-containing product [Equation (2)]. The same quantities of **2** are obtained independent of whether the reaction mixture is kept at ambient temperature for 48 h or refluxed for a period of 2 h.

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[a] Institut für Anorganische Chemie der Universität Karlsruhe,
D-76128 Karlsruhe, Germany
Fax: (internat.) + 49-721/661921
E-mail: mascheer@achibm6.chemie.uni-karlsruhe.de

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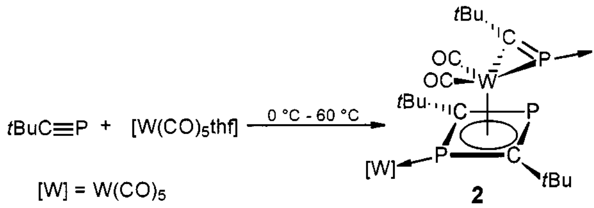
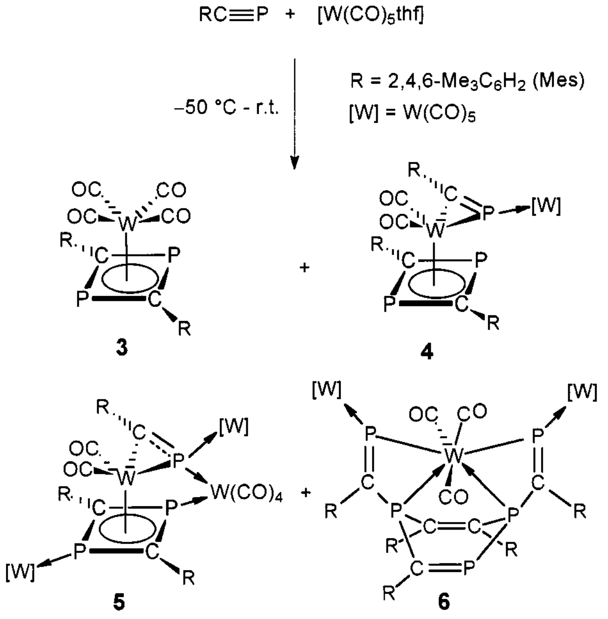


(2)

The use of MesC≡P (Mes = 2,4,6-$Me_3C_6H_2$) in the reaction with [W(CO)$_5$thf], in the temperature range from −50 °C to ambient temperature, however, leads to a variety of different products [Equation (3)].



(3)

All products are purified and separated by column chromatography. The complexes **1**, **2**, **4** are red, **3** is a yellow, **5** is a dark-red, and **6** an orange-red crystalline compound. They are sufficiently stable in the solid state to allow brief handling in air. All compounds are readily soluble in all common organic solvents such as *n*-hexane, toluene, THF, or CH_2Cl_2, apart from **3** which reveals a poor solubility in *n*-hexane.

All products are spectroscopically characterised and their molecular structures are determined by single crystal X-ray structure analysis. The crystal structure and the spectroscopic data of **1**[7] and **6**[11] were published elsewhere. Although compound **2** has been published before,[9] the X-ray structure analysis of **2** reported herein is of much higher quality, and also the spectroscopic data are completed here as well.

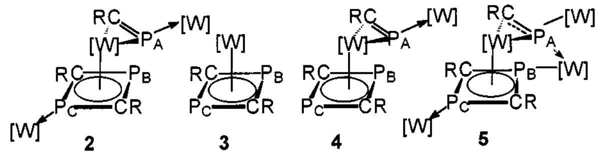
In **1** only side-on coordination of the large Mes*C≡P occurs which is probably due to steric reasons. The dominant feature of all other products is the occurrence of a cyclodimerization and in the case of **6** a pentamerization of RC≡P. Compounds **2−5** possess a 1,3-diphosphete moiety, which in **3** is the only ligand at tungsten besides 4 CO groups. In complexes **2**, **4**, and **5**, two of the CO ligands are replaced by a side-on coordinated phosphaalkyne which further coordinates to a W(CO)$_5$ group (c.f. Figures 1−4). A "head-to-tail" dimerization on 14-valence electron (VE) complexes of cobalt,[12] rhodium,[13] iron,[14] and molybdenum[15] and of 12VE fragments of zirconium and hafnium[16] have been observed in several compounds. However, additional side-on coordination of a phosphaalkyne at the capping metal fragment has not yet been found. While only a few examples exist for a trimerization,[17] and just one for a tetramerization[18] of phosphaalkyne, complex **6** is the first pentamerization product induced by a transition metal complex.[19]

Spectroscopic Properties of Compounds 2−6

The IR spectra of complexes **2−6** reveal bands for CO stretching frequencies in the range of 1900−2100 cm^{-1} as expected for terminal bound CO ligands. The mass spectra of **2−4** show the molecular ion peak and the expected fragmentation patterns.

The ^{31}P NMR data of **2−5** are summarised in Table 1. The signals of the ring phosphorus atoms (P_B and P_C) of the 1,3-diphosphete ligands appear in the region between δ = 13.0 (**2**) and 82.9 (**5**). These chemical shifts are in accordance with those observed for [{η^4−1,3-(tBuC)$_2$P$_2$}Fe(CO)$_3$] (δ = 38.1[14]) and [{η^4−1,3-(tBuC)$_2$P$_2$}CoCp*] (δ = 56.8[12a]) and seem to be fairly independent of whether coordination of the P atom to a W(CO)$_5$ group occurs or not. Zenneck et al. reported a chemical shift of +82.1 ppm for a 1,3-diphosphete complex of iron were both P atoms coordinate to a Cr(CO)$_5$ group.[20]

Table 1. ^{31}P NMR data for the compounds **2−5** in C_6D_6 at 298 K; *J* [Hz]



Compound	δ	*J*(P,P)	*J*(W,P)
2	P_A = 318.9 (d)	P_A,P_B = 38	231.5 & 61.0
	P_B = 13.1 (d)	P_B,P_A = 38	
	P_C = 14.0 (s)		235.0
3	$P_{B,C}$ = 58.1 (s)		62.2
4	P_A = 371.4 (t)	P_A,$P_{B,C}$ = 17	209.4 & 61.6
	$P_{B,C}$ = 64.9 (d)	$P_{B,C}$,P_A = 17	
5	P_A = 264.0 (s)		224.0 & 64.8
	P_B = 82.9 (s)		130.8
	P_C = 44.6 (s)		264.7

Coupling of the ring phosphorus to the tungsten carbonyl cap is only observed in the case of **3**. The signals of P_C in **2** and **5** bear one pair of tungsten satellites with coupling constants typical of an end-on coordination of a W(CO)$_5$ moiety.

The chemical shifts of the P_A atom of the side-on bound phosphaalkyne unit in **2**, **4**, and **5** are observed in the region of $\delta = 264.0$ (**5**) to 371.4 (**4**). The data are in good agreement with those of complex **1** ($\delta = 313$[7]), which only possesses side-on coordinated phosphaalkynes. In **5** an unusual shift towards high field for the signal of P_A is observed which is because of the particular bonding situation in this complex due to the $W(CO)_4$ bridge between P_A and P_B. All P_A atoms in **2**, **4**, and **5** show the appropriate coupling pattern for a coordination to the end-on bound $W(CO)_5$ group and the side-on coordination to the $W(CO)_2$ cap, with coupling constants in the range of 209.0−224.0 Hz and 61.0−64.8 Hz, respectively. In the case of complexes **2** and **4**, a J(P,P) between the phosphorus of the side-on coordinated phosphaalkyne unit and the ring P atoms is observed. The coupling constants are within 38 and 17 Hz, a typical range for a coupling over two bonds.

Molecular Structures of 2−5

Compound **2** crystallises with two independent molecules in the unit cell. Both molecules possess essentially an identical structure. The following refers to molecule A.

The η^4-1,3-diphosphacyclobutadiene ring of **2** (Figure 1) reveals almost equidistant C−P distances and therefore is a square rather than a rectangle [d(P−C) = 1.768(14)−1.806(14) Å]. This is in good agreement with the bond lengths in the complexes $[CpCo\{\eta^4\text{-}(tBuC)_2P_2\}]$ [d(P−C) = 1.79(1)−1.82(1) Å],[12b] $[Cp^*Co\{\eta^4\text{-}(tBuC)_2P_2\}]$ [d(P−C) = 1.797(3)−1.798(3) Å],[13] and $[Mo\{\eta^4\text{-}(tBuC)_2P_2\}_3]$ [d(P−C) = 1.811(4)−1.860(5) Å][21]. In **2**, the ring is folded 169° along the C(13)−C(14) axis and is therefore essentially planar, since all atoms stand out of the idealised plane P(1)−P(2)−C(13)−C(14) by 0.06 Å only, on average. This 1,3-diphosphete unit coordinates to a $W(CO)_2$ cap, which is further coordinated side-on by a phosphaalkyne unit with d[W(1)−P(3)] = 2.369(4) and d[W(1)−C(23)] = 2.13(2) Å. The P−C bond length of this phosphaalkyne is elongated to 1.66(2) Å [c.f. in $tBuC{\equiv}P$: 1.54 Å[22]]. This distance is comparable to the observed bond lengths of the side-on coordinated $tBuC{\equiv}P$ in $[(Ph_3P)_2Pt\{\eta^2\text{-}tBuCP\}]$ [1.672(17) Å][23] or in $[(Cp)_2Ti(PMe_3)\{\eta^2\text{-}tBuCP\}]$ [1.634 Å].[24] This elongation is due to the back donation effects of the tungsten of the $W(CO)_2$ moiety into the π* orbitals of the C−P bond. The high degree of sp^2 hybridisation at C(23) is further reflected in the angle of 0.88° between the planes W(1)−C(23)−P(3) and P(3)−C(23)−C(24) (between the planes W(1)−C(23)−P(3) and W(3)−P(3)−C(23) the angle is 15.50°). The phosphorus atoms P(2) and P(3) further coordinate to $W(CO)_5$ fragments with bond lengths of 2.493(4) and 2.462(4) Å, respectively. This is in the range for coordinative bonds as observed e.g. in $[W(CO)_4\langle(\eta^4\text{-}P_4)\{W(CO)_5\}_4\rangle]$ [average d(WP) = 2.445(7) Å].[25]

Complex **3** (Figure 2) is the first tungsten complex possessing only CO ligands, besides the 1,3-diphosphacyclobutadiene ring. The bond lengths inside the four-membered ring of **3** are slightly longer than those observed in **2** [d(P−C) = 1.818(3)−1.827(3) Å]. The ring system of **3** is almost planar (folding angle: 170.79°, measured along the C(3)−C(3A) axis, maximal deviation of the atoms from the idealised plane is ±0.05 Å, c.f. 0.06 Å in **2**). It is noteworthy that the mesityl ligands of the ring carbon atoms are almost in plane with the 1,3-diphosphete system. They are only twisted by 5.1°. Thus, it appears that a kind of delocalisation of three different π-systems is responsible for this effect.

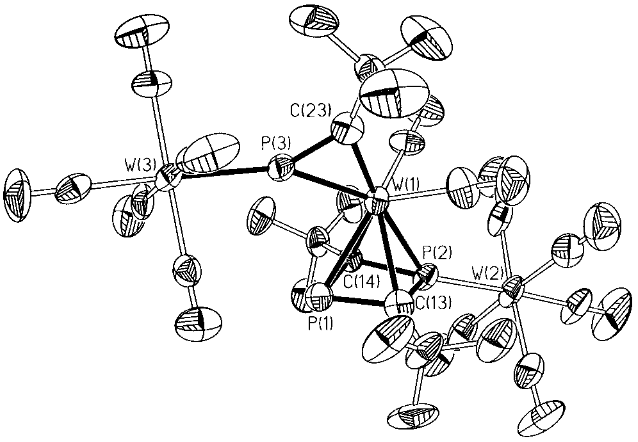


Figure 1. Molecular structure of $[W(CO)_2\{\eta^4\text{-}(tBuC)_2P_2\text{-}W(CO)_5\}\{\eta^2\text{-}(tBuCP)W(CO)_5\}]$ (**1**) (molecule A, ellipsoids drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: P(1)−C(13) 1.806(14), P(1)−C(14) 1.791(14), P(2)−C(13) 1.768(14), P(2)−C(14) 1.778(13), P(1)−W(1) 2.495(4), P(2)−W(1) 2.551(4), C(13)−W(1) 2.33(2), C(14)−W(1) 2.368(2), P(3)−C(23) 1.66(2), P(3)−W(1) 2.369(4), C(23)−W(1) 2.13(2), P(2)−W(2) 2.493(4), P(3)−W(3) 2.462(4), C(14)−P(1)−C(13) 82.8(6), C(13)−P(2)−C(14) 84.5(6), P(1)−C(13)−P(2) 95.9(7), P(2)−C(14)−P(1) 95.7(7)

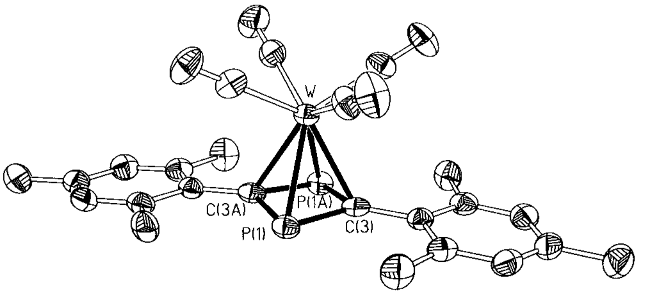


Figure 2. Molecular structure of $[W(CO)_4\{\eta^4\text{-}(MesC)_2P_2\}]$ (**3**) (ellipsoids drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: P(1A)−C(3) 1.818(3), P(1)−C(3) 1.827(3), P(1)−W 2.5265(8), C(3)−W 2.364(3), C(3A)−P(1)−C(3) 83.92(13), P(1A)−C(3)−P(1) 95.67(13)

The molecular structure of **4** (Figure 3) is similar to the tBu derivative **2**. The only difference is that in **4** none of the P atoms of the 1,3-diphosphete ligand bind to a $W(CO)_5$ group. However, the distances within the four-membered ring are slightly longer [d(P−C) = 1.793(4)−1.824(4) Å]. The ring system is folded along the C(18)−C(28) axis by 170.03° and is therefore in accordance with the observations for **2** and **3** (maximal deviation from the average plane in **4** is 0.06 Å). As in **2**, the side-on bound phosphaalkyne unit is coordinated to a further $W(CO)_5$ group. The bond length C(8)−P(1) of this moiety is 1.683(3) Å and is therefore only 0.023 Å longer than the corresponding bond in **2**. The degree of sp^2 hybridisation of C(8) is similar to **2** since the angles between the planes W(1)−C(8)−P(1) and P(1)−C(8)−C(9), and W(1)−C(8)−P(1) and

W(2)−P(1)−C(8) are in good agreement with **2** (**4**: 0.41 and 13.57°, respectively). In contrast to **3**, the mesityl moieties at the ring C atoms of the 1,3-diphosphete ligand are twisted by 10.7° in this complex, which is probably due to the steric influence of the side-on coordinated [MesC≡P→W(CO)$_5$] unit.

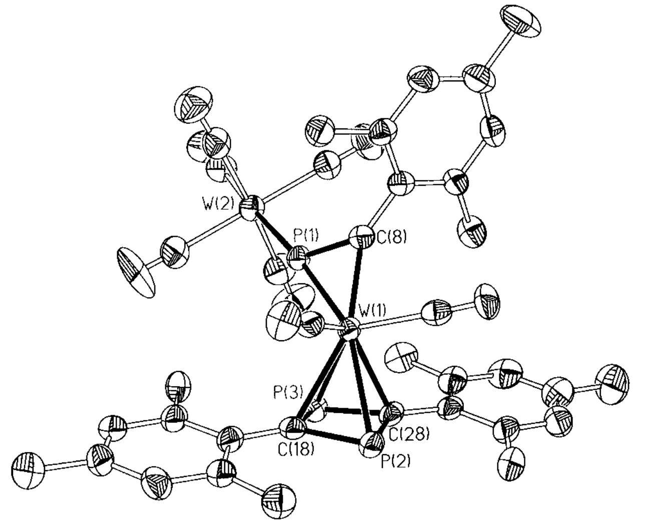


Figure 3. Molecular structure of [W(CO)$_2${η^4-(MesC)$_2$P$_2$}{η^2-(MesCP)W(CO)$_5$}] (**4**) (ellipsoids drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: P(2)−C(18) 1.816(4), P(2)−C(28) 1.798(4), P(3)−C(18) 1.793(4), P(3)−C(28) 1.824(4), P(2)−W(1) 2.5518(12), P(3)−W(1) 2.5218(11), C(18)−W(1) 2.432(4), C(28)−W(1) 2.297(4), P(1)−C(8) 1.683(2), P(1)−W(1) 2.3644(11), C(8)−W(1) 2.072(3), P(1)−W(2) 2.4611(12), C(18)−P(2)−C(28) 83.7(2), C(28)−P(3)−C(18) 83.6(2), P(2)−C(18)−P(3) 96.1(2), P(2)−C(28)−P(3) 95.7(2)

The molecular structure of **5** (Figure 4) also features a capped 1,3-diphosphete ligand. In contrast to the complexes **2−4**, both of the P atoms of the diphosphete ligand in **5** coordinate to tungsten carbonyl fragments. One of the P atoms is coordinated to a W(CO)$_4$ moiety, which further bridges to the side-on coordinated phosphaalkyne. While the bond lengths and the grade of folding along the C(27)−C(37) axis of the ring are still in accordance with the data of **2−4** [d = 1.788(9)−1.817(9) Å; maximal deviation from the average plane is ±0.06 Å], the situation of the side-on coordinated MesC≡P unit has changed considerably due to the coordination of this phosphorus atom to the bridging W(CO)$_4$ group [W(2)] and a terminal W(CO)$_5$ moiety [W(3)]. The P(1)−C(17) bond length is 1.747(9) Å and is considerably elongated in comparison to **2** and **4** and can be considered as an elongated double bond. The low degree of sp^2 hybridisation of the atom C(17) in **5** becomes obvious when the angle between the planes W(1)−C(17)−P(1) and P(1)−C(17)−C(18) is 12.2° [between W(1)−C(17)−P(1) and W(3)−P(1)−C(17) the angle is 37.7°]. The considerable difference in the bonding situation of the side-on coordinated phosphaalkyne group is further reflected in the comparably short W(1)−C(17) distance, of only 2.032(8) Å [c.f. **2**: 2.13(2) Å and **4**: 2.072(3) Å] and the elongated W(1)−P(1) bond with 2.544(2) Å [c.f. **2**: 2.369(4) Å and **4**: 2.3644(11) Å]. The bond lengths of P(1)−W(2) and P(1)−W(3) [2.562(3) Å and 2.512(3) Å, respectively] are longer than the distances observed in **2** and **4**, but are still in the range for coordinative bonds as e.g. found in [Ph$_3$P→W(CO)$_5$] [d(W−P) = 2.544 Å].[26] The special situation of this P atom is also reflected in its ^{31}P NMR resonance signal as discussed above. Due to the coordination of P(2) to the W(CO)$_4$ bridge and P(3) to a W(CO)$_5$ group, the mesityl moieties of the ring carbon atoms are much more twisted as in **3** or **4**. In **5**, the angles between the planes of the mesityl groups at the atoms C(27) and C(37) and the idealised plane C(27), C(37), P(2), and P(3) are 77.1° and 78.9°, respectively.

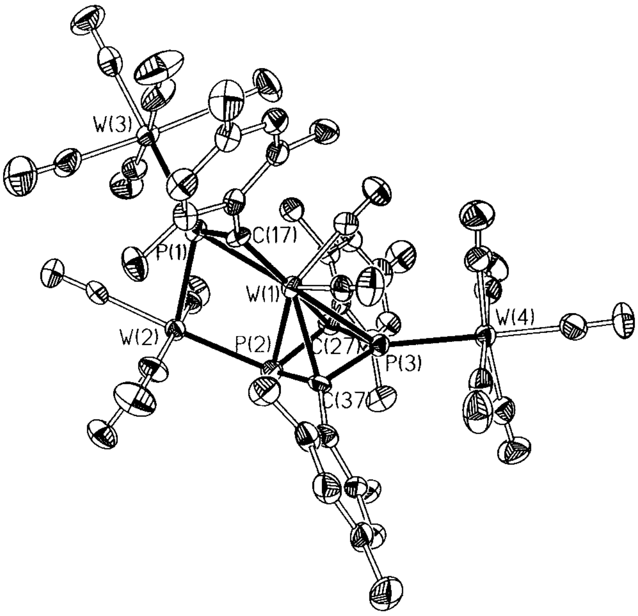
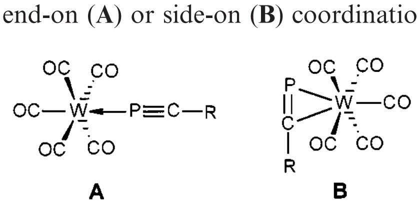


Figure 4. Molecular structure of **5** (ellipsoids drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: P(2)−C(27) 1.817(9), P(2)−C(37) 1.803(9), P(3)−C(27) 1.788(9), P(3)−C(37) 1.800(9), P(2)−W(1) 2.466(3), P(3)−W(1) 2.550(3), C(27)−W(1) 2.424(8), C(37)−W(1) 2.287(9), P(1)−C(17) 1.747(9), P(1)−W(1) 2.544(2), C(17)−W(1) 2.032(8), P(1)−W(2) 2.562(3), P(1)−W(3) 2.512(3), P(2)−W(2) 2.446(3), P(3)−W(4) 2.446(2), C(27)−P(2)−C(37) 85.2(4), C(27)−P(3)−C(37) 86.2(4), P(2)−C(27)−P(3) 93.7(4), P(2)−C(37)−P(3) 93.8(4)

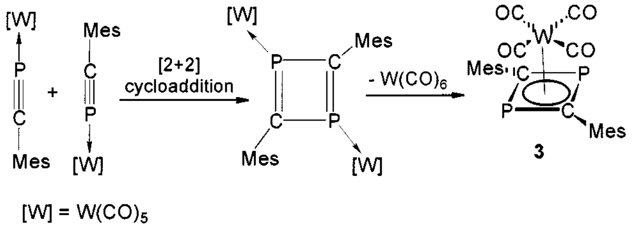
Proposal for a Reaction Pathway for the Formation of the Compounds 1−6

The nature of the products leads us to propose that the first step of these reactions must be the activation of the C≡P triple bond via the coordination of the phosphaalkyne to W(CO)$_5$. Two different coordination modes appear most likely, the end-on (**A**) or side-on (**B**) coordination.



To shed light onto this problem we followed the reaction of MesC≡P with [W(CO)$_5$thf] as a function of temperature by ^{31}P NMR spectroscopy. Indeed a singlet at δ = −74.3 ([D$_8$]toluene, 243 K; MesC≡P: δ = 2.1 (s), [D$_8$]toluene, 243 K) without any tungsten satellites is observed as an intermediate of this reaction. This singlet has a maximum intensity at 273 K and decreases after the signals of the products increase. For an end-on coordination of type **A** a singlet shifted into the highfield region bearing one pair of tungsten satellites is expected, revealing a coupling constant of approximately 150−280 Hz. Examples for complexes revealing an end-on coordinated phosphaalkyne are rare. In the complex $[(CO)_3W(PCy_3)_2(\eta^1\text{-}P{\equiv}CMes^*)]$, synthesised in our group, a highfield shift of 10 ppm is observed [δ = 24.4, J(W,P) = 280 Hz], in comparison to free Mes*C≡P.[27] In the group of Nixon, the compound $[FeH(\eta^1\text{-}P{\equiv}CtBu)(dppe)_2][BPh_4]$ could be isolated revealing a highfield shift of about 85 ppm after coordination of *t*BuC≡P (δ = −154; *t*BuC≡P: δ = −69.2).[28] A side-on coordination mode **B** requires a downfield shift as found for the P_A atoms of the side-on coordinated phosphaalkynes in **2**, **4**, and **5**. In this case only a small coupling between tungsten and phosphorus of less than 60 Hz would be expected due to the low s-character in the W−P bond. Recently Nixon et al. described a complex containing a η^2 coordinated phosphaalkyne in $[WF(C_6H_4CH_2NMeCH_2CH_2NMe_2)(CO)(\eta^2\text{-}P{\equiv}CtBu)]$ with a chemical shift at δ = 452.4 and a ^1J(W,P) of 82 Hz.[29] Although the high-field shift of our intermediate at δ = −74.3 seems to favour **A** as the first formed intermediate, without a resolved J(W,P) no unequivocal evidence for either of these activation modes could be achieved from the NMR spectroscopic experiment.

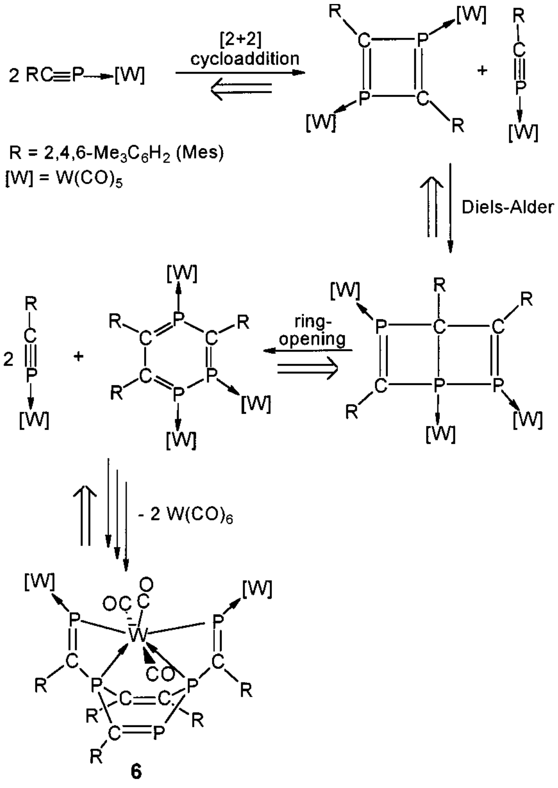
However, the nature of the reaction products also suggests a more end-on coordination as the first step. Firstly, this is supported by the fact that in reaction (1) Mes*C≡P does not form a 1,3-diphosphete ligand, which is likely starting from a complex of type **B**. In the case of the initially formed intermediate **A**, the bulky supermesityl group would interact sterically with the end-on coordinated $W(CO)_5$ group of the second phosphaalkyne and thus a [2+2] cycloaddition is inhibited. By contrast, for the sterically less encumbered MesC≡P the end-on intermediate **A** can undergo a cycloaddition and therefore the formation of **3** is best explained by the reaction shown in Scheme 1. Secondly, in the compounds **2**, **4**, **5**, and **6** all side-on coordinated phosphaalkynes further bear a $W(CO)_5$ group in end-on position.



Scheme 1. Proposed reaction pathway for the formation of **3**

Thus, we propose that in the first step two activated molecules of type **A** approach each other. Since a head-to-tail [2+2] cycloaddition is sterically hindered for the bulky supermesityl groups, the attack on a $W(CO)_5$ unit leads only to the spirocyclic product **1**. For *t*Bu as well as the mesityl substituents, cycloaddition is the predominant reaction pathway (Scheme 1). By elimination of $W(CO)_6$ as the driving force[30] a 1,3-diphosphete ring system capped by a $W(CO)_4$ group is generated to give compound **3**. After further elimination of CO, RC≡P→$W(CO)_5$ is coordinated side-on to give the complexes **2**, **4**, and **5**, respectively. Experiments conducted with complex **3** showed, that the phosphorus atoms of the 1,3-diphosphete ligand are still able to coordinate further $W(CO)_5$ units.

The proposed 1,3-diphosphete unit formed first can also serve as an intermediate for the formation of **6** (Scheme 2). A subsequent Diels−Alder reaction with further end-on activated phosphaalkyne leads then to a Dewar benzene like intermediate which reacts after ring opening with two more activated phosphaalkynes to give compound **6**, after elimination of two equivalents of $W(CO)_6$.



Scheme 2. Proposed reaction pathway for the formation of **6**

Conclusions

The comparison of the reactivity of different phosphaalkynes with $[W(CO)_5thf]$ reveals that MesC≡P possesses the highest potential for yielding novel complexes because its sterical and electronical properties are somewhat between those of the other phosphaalkynes used in former investigations. It is to be expected that further variations of these properties (e.g. in $R_2NC{\equiv}P$[31] and OC≡P,[32] respectively) influence the reaction behaviour dramatically and open up the approach to novel products.

Experimental Section

General Techniques: All reactions were performed under an atmosphere of dry argon using Schlenk and glove box techniques. Solvents were purified and degassed by standard procedures and distilled prior to 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 on a Bruker IFS 28 FT-IR-spectrometer. − MS: Finnigan MAT 711 at 70 eV. − Correct elemental analyses for the isolated products were performed by the analytical laboratory of the institute.

Reagents: Unless otherwise stated, commercial-grade chemicals were used without further purification. The silica gel was activated by removing all volatile substances at 180 °C in vacuo (10^{-3}Torr) for 48 h. [$W(CO)_5$thf] was prepared by irradiating a THF solution of $W(CO)_6$ in a UV apparatus for 2 h. *t*BuC≡P was synthesised as described in reference [2]. MesC≡P was obtained as published in ref.[33]

Crystal Structure Analysis of 2−5: Crystal structure analyses of **3** were performed on a STOE IPDS and of **2**, **4**, and **5** on a STOE STADI IV (ω-scan mode) diffractometer with Mo-K_α radiation (λ = 0.71073 Å) with empirical absorption corrections for **2**, **4**, and **5** (Psi-scans). Machine parameters, crystal data and data collection parameters are summarised in Table 2. The structures were solved by direct methods using SHELXS-86,[34a] full-matrix-least-squares refinement on F^2 in SHELXL-93[34b] with anisotropic displacement for non-H atoms. Hydrogen atoms were located in idealised 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 Centre as supplementary publication no. CCDC-139093 to no. CCDC-139096. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

[W(CO)$_2${η^4-(*t*BuC)$_2$P$_2$-W(CO)$_5$}{η^2-(*t*BuCP)W(CO)$_5$}] (2): *t*BuC≡P (100 mg, 1 mmol) dissolved in *n*-hexane (10 mL) was added to [$W(CO)_5$thf] (25 mL of a 0.04 M THF solution, 1 mmol) at ambient temperature. Subsequently the solvent was reduced to 15 mL and the mixture allowed to stir for 48 h. All volatile substances were then removed in vacuo (10^{-3} Torr). The crude product was purified by column chromatography (silica gel, 30 × 2.5 cm, Merck 60) using a *n*-hexane/toluene mixture of 1:1. After reduction of the solvent to dryness the solid was recrystallised by toluene to afford 235 mg (60%) of red crystals of **2**. Crystals suitable for X-ray analysis were grown from concentrated toluene solutions. − $C_{27}H_{27}O_{12}P_3W_3$ (1187.98): calcd. C 27.30, H 2.29; found C 27.99, H 2.84. − IR [Nujol, ṽ (CO), cm^{-1}]: 2072(m), 2018(w), 1975(sh), 1954(vs). ^{1}H NMR (25 °C, C_6D_6): δ 1.66 (s, 9 H, CH_3), 0.87 (s, 18 H, CH_3). − ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ = 318.9 (P3, d), *J*(P,P) = 38 Hz, *J*(W,P) = 231.5 & 61 Hz, 14 (P2, s), *J*(W,P) = 235 Hz, 13.1 (P1, d) *J*(P,P) = 38 Hz. − EI MS: *m*/*z* (%) = 1187.8 (38) [M$^+$], 1103.9 (14) [M$^+$ − 3 CO], 1076.8 (2) [M$^+$ − 4 CO], 1019.9 (6) [M$^+$ − 6 CO], 991.9 (45) [M$^+$ − 7 CO].

Compounds 3−6: MesC≡P (162 mg, 1 mmol) was dissolved in *n*-hexane (10 mL) and cooled to −50 °C. At this temperature the solution was added to 10 mL of a THF solution of [$W(CO)_5$thf] (1 mmol). The mixture was allowed to warm up to room temperature and stirred for further 48 h. The reaction was monitored by ^{31}P NMR spectroscopy indicating a small grade of conversion. Then all volatile substances were removed in vacuo. This reaction was repeated twice, and the combined product mixtures were worked up by column chromatography (silica gel, 30 × 2.5 cm, Merck 60). The first fraction was eluted with a mixture of *n*-hexane/toluene (5:1) giving 100 mg of **3** (10.6%). The second fraction with *n*-hexane/toluene (2:1) yielding 200 mg of red **4** (19%). The third fraction was obtained from *n*-hexane/toluene (1:1) to give orange-

Table 2. Crystal data for the compounds **2−5**

	2	**3**	**4**	**5** · 1.5 C_7H_8
Empirical formula	$C_{27}H_{27}O_{12}P_3W_3$	$C_{24}H_{22}O_4P_2W$	$C_{37}H_{33}O_7P_3W_2$	$C_{56.5}H_{45}O_{16}P_3W_4$
Formula mass	1167.945	620.21	1050.24	1808.23
Crystal size [mm]	0.23 × 0.19 × 0.08	0.42 × 0.11 × 0.04	0.57 × 0.30 × 0.15	0.30 × 0.23 × 0.08
T [K]	200(2)	200(1)	200(2)	200(2)
Space group	$P\bar{1}$ (No. 2)	*Ccca* (No. 68)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Crystal system	triclinic	orthorhombic	triclinic	triclinic
a [Å]	15.103(3)	13.236(3)	10.908(2)	12.816(3)
b [Å]	15.829(3)	22.086(4)	10.927(2)	13.635(3)
c [Å]	17.441(4)	15.743(3)	16.455(3)	19.661(4)
α [°]	73.04(3)	90	86.53(3)	81.48(3)
β [°]	65.91(3)	90	76.52(3)	73.09(3)
γ [°]	83.77(3)	90	77.71(3)	63.27(3)
V [Å^3]	3640.7(13)	4602(2)	1863.4(6)	2935.3(10)
Z	4	8	2	2
d_c [g cm^{-3}]	2.167	1.790	1.872	2.046
μ_c [cm^{-1}]	96.41	51.87	63.44	79.60
Radiation [λ, Å]	Mo-*K*α (0.71073)			
Diffractometer	STOE STADI IV	STOE IPDS	STOE STADI IV	STOE STADI IV
2*Θ* range [°]	$3.10 \leq 2\Theta \leq 52.00$	$4.42 \leq 2\Theta \leq 51.66$	$2.54 \leq 2\Theta \leq 54.92$	$3.34 \leq 2\Theta \leq 52$
hkl range	$-16 \leq h \leq 18$, $-18 \leq k \leq 19$, $0 \leq l \leq 21$	$-15 \leq h \leq 14$, $-26 \leq k \leq 25$, $-19 \leq l \leq 18$	$-13 \leq h \leq 14$, $-14 \leq k \leq 14$, $0 \leq l \leq 21$	$-14 \leq h \leq 15$, $-16 \leq k \leq 16$, $0 \leq l \leq 24$
Data / restraints / parameters	14186 / 0 / 829	2172 / 0 / 144	8273 / 0 / 460	11483 / 0 / 869
Independent reflections with $I > 2\sigma(I)$	8978 (R_{int} = 0.000)	1726 (R_{int} = 0.0431)	7571 (R_{int} = 0.0000)	9138 (R_{int} = 0.0000)
Goodness-of-fit on F^2	1.217	0.950	1.069	1.138
R_1[a] wR_2 [b] [$I > 2\sigma(I)$]	0.0517, 0.0936	0.0219, 0.0542	0.0246, 0.0633	0.0397, 0.0932
R_1 [a] wR_2 [b] (all data)	0.1164, 0.1377	0.0281, 0.0566	0.0289, 0.0683	0.0639, 0.1166
Largest diff peak, hole, [e Å^{-3}]	1.822, −1.278	0.829, −0.593	0.961, −1.826	2.819, −1.291

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

red **6** (100 mg, 10%). Dark red **5** could be eluted with pure toluene (130 mg, 7.6%). Crystals suitable for X-ray diffraction methods of all compounds were obtained by recrystallisation from toluene.

Properties of [W(CO)$_4${η^4-(MesC)$_2$P$_2$}] (3): $C_{24}H_{22}O_4P_2W$ (620.23): calcd. C 46.48, H 3.58; found C 46.32, H 3.21. − IR [Nujol, $\tilde{\nu}$ (CO), cm^{-1}]: 2052(s), 1977(vs). − ^{1}H NMR (25 °C, C_6D_6): δ 6.52 (s, 2 H, CH), 2.18 (s, 6H, CH_3), 1.99 (s, 3 H, CH_3). − ^{31}P{^{1}H} NMR (25 °C, [D$_8$]THF): δ = 58.1, *J*(W,P) = 62.2 Hz. − EI MS: *m/z* (%) = 620.1 (24) [M$^+$], 592.2 (7) [M$^+$ − CO], 564.1 (15) [M$^+$ − 2 CO], 536.1 (18) [M$^+$ − 3 CO], 506.1 (100) [M$^+$ − 4 CO].

Properties of [W(CO)$_2${η^4-(MesC)$_2$P$_2$}{η^2-(MesCP)W(CO)$_5$}] (4): $C_{37}H_{33}O_7P_3W_2$ (1050.3): calcd. C 42.31, H 3.17; found C 42.48, H 3.35. − IR [Nujol, $\tilde{\nu}$ (CO), cm^{-1}]: 2074(vs), 2027(vs), 1975(s), 1965(s), 1953(vs), 1932 (vs). − ^{1}H NMR (25 °C, C_6D_6): δ = 6.78 (s, 2 H, CH), 6.54 (s, 4 H, CH) 2.36 (s, 3 H, CH_3), 2.34 (s, 12 H, CH_3), 2.03 (s, 6 H, CH_3), 1.59 (s, 6 H, CH_3). − ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ = 371.4 (P1, t), *J*(P,P) = 17 Hz, *J*(W,P) = 209.4 & 61.6 Hz, 64.9 (P2,3, d), *J*(P,P) = 16 Hz. EI MS: m/*z* (%) = 1050.0 (48) [M$^+$], 938.0 (11) [M$^+$ − 4 CO], 910.0 (28) [M$^+$ − 5 CO], 881.9 (30) [M$^+$ − 6 CO], 852.0 (100) [M$^+$ − 7 CO]. − Properties of **5**: IR [Nujol, $\tilde{\nu}$ (CO), cm^{-1}]: 2084(w), 2072(s), 2046(m), 2038(m), 2004(m), 1995(s), 1970(vs), 1960(vs), 1950(vs), 1939(s). ^{1}H NMR (25 °C, C_6D_6): δ 7.1−6.49 aromatic protons, 2.889 (s, 6 H, CH_3), 2.806 (s, 3 H, CH_3), 2.199 (s, 6 H, CH_3), 2.1736 (s, 6 H, CH_3), 1.981 (s, 3 H, CH_3), 1.894 (s, 3 H, CH_3). − ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ = 264.0 (P1, s), *J*(W,P) = 224 & 64.8 Hz, 82.9 (P2, s), *J*(W,P) = 130.8 Hz, 44.6 (P3, s), *J*(W,P) = 264.7 Hz. Properties of **6**: $C_{63}H_{55}O_{13}P_5W_3$ (1726.54): calcd. C 43.83, H 3.21; found C 43.50, H 3.35 . − IR (Nujol, $\tilde{\nu}$ (CO), cm^{-1}): 2075(s), 2065(s), 2041(m), 1987(w), 1962(sh), 1950(vs), 1938(vs), 1931(vs), 1925(vs). − ^{1}H NMR (250.133 MHz, C_6D_6, 298 K, TMS): δ = 1.400, 1.422, 1.720, 1.819, 1.838, 1.900, 1.937, 1.979, 2.002, 2.061, 2.113, 2.163, 2.780, 2.864, 3.229 (CH_3, each s, 3 H, CH_3), 6.82−5.71 (10 singlets, each 1 H, aromatic protons). − ^{31}P{^{1}H} NMR [101.256 MHz, C_6D_6, 298 K, 85proz. H_3PO_4 ext., P_A = P(2), P_B = P(1), P_C = P(3), P_D = P(4), P_E = P(5)]: δ = 497.6 [P_A: d; $^2J(P_A,P_C)$ = 45 Hz, $J(W,P_A)$ = 190 Hz], 456.1 [P_B: d; $^2J(P_B,P_D)$ = 42 Hz, $J(W,P_B)$ = 190 Hz], 370.7 [P_E: dd; $^1J(P_E,P_D)$ = 280 Hz, $^2J(P_E,P_C)$ = 35 Hz], 50.8 [P_C: ddd; $^2J(P_C,P_A)$ = 45 Hz, $^2J(P_C,P_E)$ = 35 Hz, $^2J(P_C,P_D)$ = 15 Hz], 10.4 [P_D: ddd; $J(P_D,P_E)$ = 280 Hz, $^2J(P_D,P_B)$ = 42 Hz, $^2J(P_D,P_C)$ = 14 Hz, $J(W,P_D)$ = 108 Hz].

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