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Phosphaalkyne Insertions

Ring Expansion of a Cp* Moiety: Formation of a 1,2-Diphosphacyclooctatetraene Ligand**

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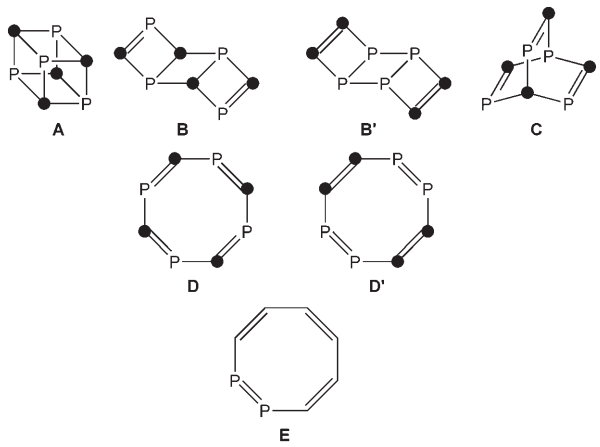
Dedicated to Professor Ulrich Zenneck in the occasion of his 60th birthday.

The chemistry of phosphaalkynes has been intensively investigated over the years in their various aspects of organophosphorus[1] as well as coordination chemistry.[2] The oligomerization of phosphaalkynes is one of the most challenging targets in this field.[3] Whereas only dimerization was found for transformations in the coordination sphere of transition metals,[4] cyclooligomerization to form cage compounds[5] was successfully realized for the cyclotrimer triphosphabenzene,[6] as well as for other oligomers up to a hexameric cage compound.[7] Looking closer at previously reported tetramerization reactions, synthesis of the tetraphosphacubane **A** (●: *t*BuC groups) was achieved,[8] and its isomers **B** and **B′**[9] were obtained as dimerization products of a 1,2-diphosphete after abstraction from a transition-metal complex. Also, the tetraphosphabarrelene **C**[10] was synthesized in a metal-controlled reaction. The synthesis of the cyclic isomers of the tetraphosphacyclooctatetraenes **D** and **D′** are still a challenge in this field since no bond-opening reactions of **B** or **B′** have yet to be achieved. The corresponding dianions are interesting aromatic systems, which would have broad perspectives for their use as ligands in coordination chemistry.



For the diphospha derivatives, which would represent a first step into the area of P-rich cyclooctatetraenes, according to our MP2 calculations the 1,2-isomer **E** with C_s symmetry is the most stable form, followed by its C_2-symmetric isomer (Figure 1, see the Supporting Information). All other isomers of type **E** are less stable.[11]

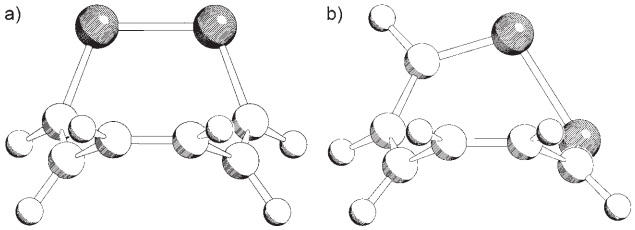


Figure 1. Optimized geometries of 1,2-diphosphacyclooctatetraene a) C_s isomer, b) C_2 isomer (● P, ○ C, ○ H).

Among our various approaches to synthesize reactive compounds with a transition-metal–phosphorus triple bond,[12–14] one strategy is based on the transformation of the phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ (**1**; $Cp^* = C_5Me_5$).[15] By the thermally induced migration of the σ-bound Cp* substituent, the η^5 coordination mode at the transition-metal center is achieved in generation of the intermediate $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ (**2**) with a W–P triple bond. In the absence of any reactive substrate, the intermediate stabilizes itself by dimerization to yield the tetrahedrane complex $[\{Cp^*W(CO)_2\}_2\{\mu,\eta^2\text{-}P_2W(CO)_5\}]$ (**3**). As a side product of the thermolysis the C–H-activated complex $[(CO)_3W(\mu,\eta^5\text{-}C_5Me_4CH_2)P(H)W(CO)_5]$ (**4**) is formed.[15]

The reactivity of the phosphido complex intermediate **2** towards alkynes[16] has been investigated in our group, whereby different cage compounds were formed. With the phosphaalkyne *t*BuC≡P,[15] the formation of a diphosphacyclobutenonyl complex **5** [Eq. (1)] is observed in high yield. In contrast, by using MesC≡P (Mes = 2,4,6-$Me_3C_6H_2$) a novel subsequent product **7** of the intermediate **2** with two molecules of phosphaalkyne is formed. However, as the

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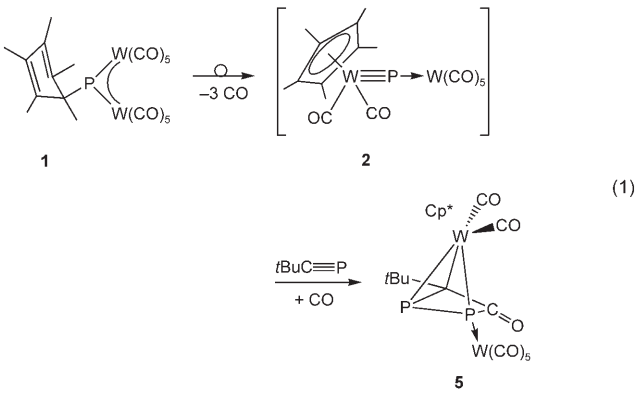
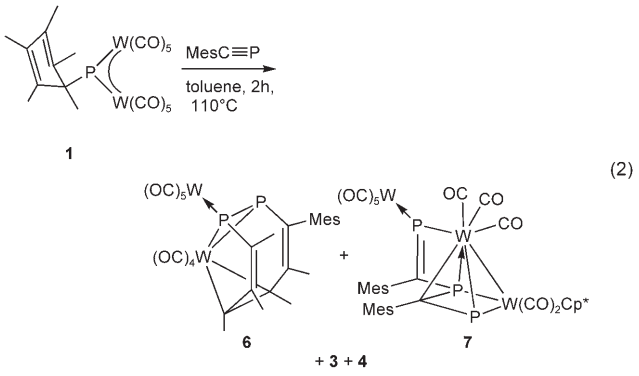
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



(1)

major product among the novel compounds, a complex containing the unprecedented 1,2-diphosphacyclooctatetraene ligand is formed which reveals an unusual insertion reaction of the phosphinidene P atom and the phosphaalkyne P atom into the Cp* ring. Such an expansion of the Cp* ligand gives a novel insight into the "inertness" of this ligand,[17] the results of which we report herein.

After thermolysis of $[Cp^*P\{W(CO)_5\}_2]$ in the presence of MesC≡P the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows a number of peaks, indicating that several reaction pathways occur during the reaction. The strongest signals can be assigned to **3** and **4**, which are also the main products of the thermolysis without a trapping reagent.[15] Chromatographic work up yields, besides **3** and **4**, the new products **6** and **7**. The novel products are yellow and red crystalline compounds, respectively, which are slightly soluble in hexane but readily soluble in solvents like toluene and CH_2Cl_2 [Eq. (2)].



(2)

The $^{31}P\{^1H\}$ NMR spectrum of **6** reveals two doublets at $\delta = 15.6$ ppm and -9.9 ppm with a $^1J(P,P)$ coupling constant of 518 Hz. The first doublet shows two pairs of tungsten satellites with $^1J(P,W)$ coupling constants of 240 Hz und 36 Hz, respectively. The larger coupling is assigned to the coupling with the $\{W(CO)_5\}$ group. In accordance the other doublet reveals tungsten satellites with a coupling constant of 18 Hz.

The molecular structure of **5**[18] (Figure 2) reveals an unprecedented four-membered diphosphacyclobutenonyl ligand (for examples of larger CO-containing P rings, see below), which is η^3-coordinated at a $\{Cp^*(CO)_2W\}$ unit. The

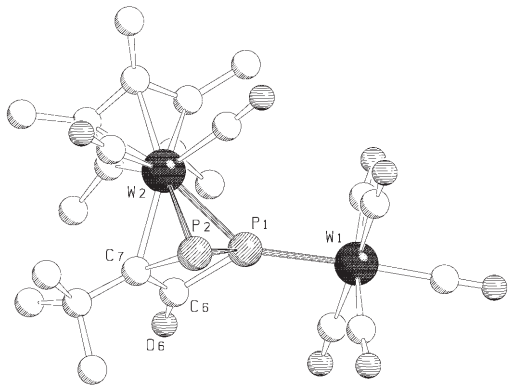


Figure 2. Molecular structure of **5** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.175(2), W1-P1 2.511(16), W2-P1 2.515(16), W2-P2 2.508(18), W2-C7 2.317(6), W2···C6 2.810(9), C6-P1 1.900(6), C7-P2 1.854(6), C6-C7 1.467(9), C6-O6 1.194(8); C6-P1-P2 77.9(2), C7-P2-P1 77.1(2), C7-C6-P1 96.2(4), C6-C7-P2 100.8(4), W2-P1-W1 143.54(7).

four-membered ring formed by the atoms P1, P2, C7, and C6 is folded along the P1···C7 axis by 29.8(5)°. All bonds within this ligand represent single bonds, with the exception of the P1–P2 bond (2.175(2) Å), which is shortened. The C6–O6 bond length (1.194(8) Å) is in the range of bridging carbonyl groups (compare $d(C{-}O) = 1.233(9)$ Å in $[WF\{CH_2N(CH_2Ph)CH_2CH_2NMe_2\}(CO)\{\eta^4\text{-}PC\textit{t}Bu(CO)C\textit{t}BuP\}]$;[19a] $d(C{-}O) = 1.250(3)$ Å in $[Cp^*_2Rh_2CO\{PCRC(O)CRP\}]$ (R = adamantyl);[19b,c] $d(C{-}O) = 1.247(5)$ Å in $[Mo(C\textit{t}Bu)\{\eta^4\text{-}P_2(C\textit{t}Bu)_2(CO)\}\{\eta^5\text{-}P_3(C\textit{t}Bu)_2\}]$[20]).

Compound **6** (Figure 3) exhibits a 1,2-diphosphacyclooctatetraene ligand which is η^4-bound to a $\{W(CO)_4\}$ group and additionally coordinates with one P atom to a $\{W(CO)_5\}$ moiety. This complex is the first example of a transition-metal-stabilized unsaturated eight-membered ring containing two phosphorus atoms. The nonplanar structure of the eight-membered ring exhibits isolated single (C11–C12 1.52(2) Å, C13–C14 1.51(2) Å, P–C 1.84(1) and 1.82(2) Å) and double bonds (C10–C11 1.34(2) Å, C14–C15 1.33(2) Å). Owing to

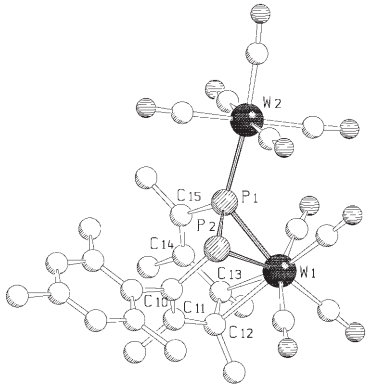


Figure 3. Molecular structure of **6** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.169(5), P1-W2 2.524(4), P2-W1 2.612(4), P1-W1 2.542(4), P1-C15 1.84(1), P2-C10 1.82(2), C10-C11 1.34(2), C11-C12 1.52(2), C12-C13 1.43(2), C13-C14 1.51(2), C14-C15 1.33(2); P1-W1-P2 49.8(1), C12-W1-C13 33.2(4), C15-P1-P2 110.6(5), P1-P2-C10 106.9(4).

the coordination to W1 the C12–C13 double bond (1.43(2) Å) as well as the P1–P2 bond (2.169(5) Å) are clearly elongated (compare uncoordinated P–P double bonds in (*E*)-$(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (2.003(3) Å)[21] and (*E*)-MesP=PN*i*Pr$_2$ (2.049(1) Å),[22] while single-bond distances are about 2.21 Å[23]).

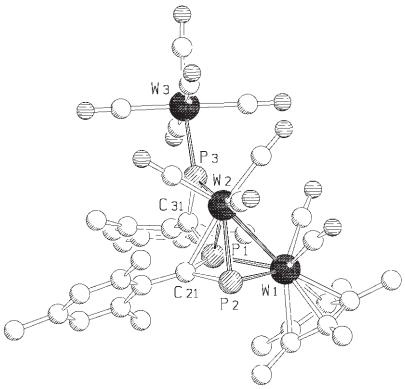
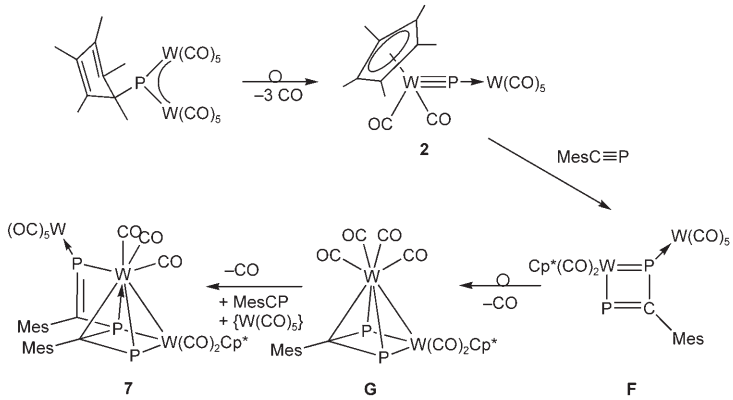


Figure 4. Molecular structure of **7** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: W1-P1 2.439(1), W1-P2 2.515(1), W1-2 3.068(1), W2-P1 2.477(1), W2-P2 2.544(1), W2-P3 2.515(1), W2-C21 2.494(4), W3-P3 2.479(1), P1-C21 1.763(4), P1-C31 1.813(4), P2-C21 1.801(4), P3-C31 1.685(4); P1-W1-P2 65.08(4), W1-P1-C21 100.7(1), P1-C21-P2 96.8(2), W1-P2-C21 96.9(1), W1-P1-C31 135.5(1).

The molecular structure of **7** (Figure 4) shows a distorted tetragonal pyramid with P1, W1, P2, and C21 as basal atoms and W2 as the apical atom. The basal plane is slightly folded along the P1···P2 axis with a dihedral angle of 6.84(3)°. At the atoms W2 and P1, a {MesCP} moiety is side-on attached to the pyramid, additionally coordinating to a $\{W(CO)_5\}$ moiety with the electron lone pair of the P3 atom. The atoms P1, C21, and P2 form an allylic-like four-electron three-center π system and act as a four-electron donor to W2. The presence of a delocalized π system is also indicated by similar bond lengths between atoms C21 and P1 (1.763(4) Å) as well as C21 and P2 (1.801(4) Å). The distances of the phosphorus atoms P1 and P2 to W2 are 2.477(1) and 2.544(1) Å, respectively, which are comparable to the W–P bond lengths in the diphosphete complex $[W(CO)_4\{\eta^4\text{-}(PCMes)_2\}]$ (d(P–W) = 2.527(1) Å).[24] The atom C31 is connected to P1 through a single bond and to P3 through a double bond, as shown by the P–C bond lengths of 1.813(4) Å and 1.685(4) Å, respectively.

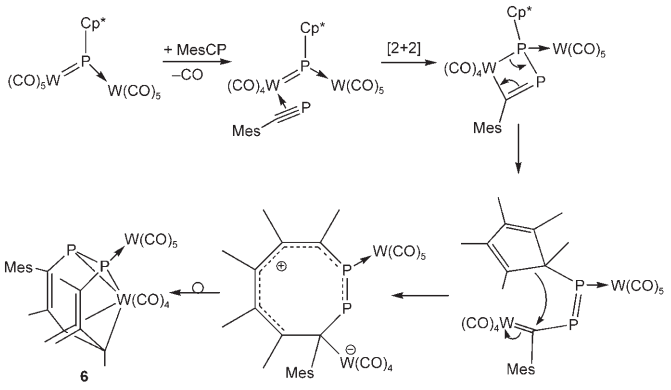
In view of the products **5** and **7**, the reactions in Equations (1) and (2) reveal the formation of the intermediate **2** with a W–P triple bond, which undergoes a formal [2+2] cycloaddition with the corresponding phosphaalkyne. For Equation (1) this reaction occurs in the presence of CO to form the diphosphacyclobutenonyl complex **5**. However, for Equation (2) the resulting four-membered ring containing compound **F** (Scheme 1) has rearranged and is stabilized by η^4 coordination to a tungsten carbonyl fragment (**G**). Elimination of CO in the presence of a further equivalent of MesC≡P and a $\{W(CO)_5\}$ moiety leads to the formation of **7**.

From the formation of **6**, which contains the novel 1,2-diphosphacyclooctatetraene ligand and is formed exclusively in the reaction shown in Equation (2), the principle difference in the reactivity pattern between the two phosphaalkynes is apparent. According to our ab initio calculations on the MP2/TZVPP level, no significant differences in the triple-bond character and the charge distribution are found (see the Supporting Information).[25] However, in MesC≡P, by conjugation with the aromatic π system, the HOMO is increased in energy by 1.8 eV and the LUMO is decreased by about 1 eV, which indicates better donor as well as acceptor properties of MesC≡P in comparison with *t*BuC≡P. Thus, for the formation of **6**, although an initial end-on coordination of the phosphaalkyne at the phosphinidene P atom in **1** can not be excluded (examples of end-on coordination of a phosphaalkyne[26] and of a nitrile[27] to the central P atom in **1** have been reported; for an alternative mechanism that starts with this type of coordination to form **6**, see the Supporting Information), we would propose a side-on coordination of MesC≡P at the tungsten carbonyl moiety after CO elimination. In an initial Dötz-like reaction with the phosphindene, metathesis occurs.[28] After a subsequent opening of the Cp* ring the eight-membered ring and finally the novel diphosphacyclooctatetraene ligand of **6** is formed (Scheme 2).



Scheme 1. Proposed reaction pathway of the formation of **7**.

The results have shown that *t*BuC≡P is an efficient trapping reagent which undergoes cycloaddition reactions with the thermally generated phosphido complex intermediate **2**. As the minor product **7** shows, with MesC≡P the intermediate **2** is also chemically trapped, but this trapping represents the minor pathway. In the same reaction, an unusual Cp* ring opening occurs to form **6** under insertion of a MesC≡P molecule and the P atom of the phosphinidene complex, a transformation which has not been observed before.[17] With the isolation of **6**, for the first time the synthesis and chemical stabilization of a diphosphacyclooctatetraene moiety as a ligand has been achieved. As the calculated structures of the free diphosphacyclooctatetraene predicted that the 1,2-isomer is energetically favored, the



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

existence of this moiety as a ligand is experimentally proven in the isolation of **6**.

Experimental Section

A solution of MesC≡P (54 mg, 0.33 mmol) in toluene (10 mL) was added to a solution of [Cp*P{W(CO)$_5$}$_2$] (**1**) (163 mg, 0.2 mmol) in toluene (20 mL). The mixture was stirred at reflux for 1.5 h, and the color changed from deep blue to brown. After removal of all volatile compounds in vacuo, the residue was extracted with dichloromethane and filtered over silica gel. The solvent was removed and the residue was separated by thin layer chromatography (hexane/dichloromethane 3:1) in a glove box. The compounds **3** (yellow fraction, 40 %), **4** (orange fraction, 25 %), **6** (yellow fraction, 10 %), and **7** (red fraction, 6 %) were isolated. Crystals suitable for X-ray analysis were obtained at −20 °C from *n*-hexane/toluene (2:1).

6: IR (KBr): $\tilde{\nu}$(CO) = 2073 (m), 2049 (m), 2017 (m), 1992 (s), 1954 (s), 1942 (vs), 1933 (vs), 1918 cm^{-1} (m); ^{1}H NMR (250.13 MHz, CD_2Cl_2): δ = 6.92 (1 H, arom. H), 6.82 (1 H, arom. H), 2.26 (3 H, Me), 2.24 (3 H, Me), 2.23 (3 H, Me), 2.21 (3 H, Me), 2.14 (3 H, Me), 2,13 (3 H, Me), 1.79 (3 H, Me), 1.75 ppm (3 H, Me); ^{31}P{^{1}H} NMR (101.3 MHz, CD_2Cl_2): δ = 15.6 (d, ^1J(P,P) = 518 Hz, ^1J(P,W) = 36 Hz and 240 Hz), −9.9 ppm (d, ^1J(P,P) = 518 Hz, ^1J(P,W) = 18 Hz); MS (EI, 180 °C): *m*/*z* (%): 948 (2.4) [*M*$^+$], 920 (1.8), 892 (1.3) [*M*−CO]$^+$, 864 (4.2) [*M*−2 CO]$^+$, 836 (1.9) [*M*−4 CO]$^+$, 808 (2.5) [*M*−5 CO]$^+$, 780 (2.4) [*M*−6 CO]$^+$.

7: ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, P1 = P_M, P2 = P_X, P3 = P_A): $\delta(P_A)$ = 210.3 (d, $^2J(P_A,P_M)$ = 45.0 Hz), $\delta(P_M)$ = 201.2 (dd, $^1J(P_A,P_M)$ = 45.0 Hz, $^2J(P_M,P_X)$ = 56.5 Hz), $\delta(P_X)$ = 147.0 ppm (d, $^2J(P_M,P_X)$ = 56.5 Hz); Raman (solid state): $\tilde{\nu}$(CO) = 2077 (m), 2062 (m), 1994 (w), 1951 (w), 1929 (w), 1907 cm^{-1} (w); MS (EI, 180 °C): *m*/*z* (%): 262 (100) [Mes_2C_2]$^+$, 247 (55) [Mes_2C_2−Me]$^+$, 232 (46) [Mes_2C_2−2 Me]$^+$.

For the synthesis and spectroscopic characterization of **5**, see reference [15].

The quantum chemical calculations were performed at the (RI-)MP2[29]/TZVPP[30] level using the TURBOMOLE program package.[31] The energies were corrected by zero-point vibrational energies calculated with DFT methods at the (RI-)BP86[32,33]/SV(P)[34] level.

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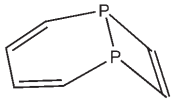

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