Different Transformation Pathways in the Photolysis of [Cp*P{W(CO)$_5$}$_2$]

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Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday

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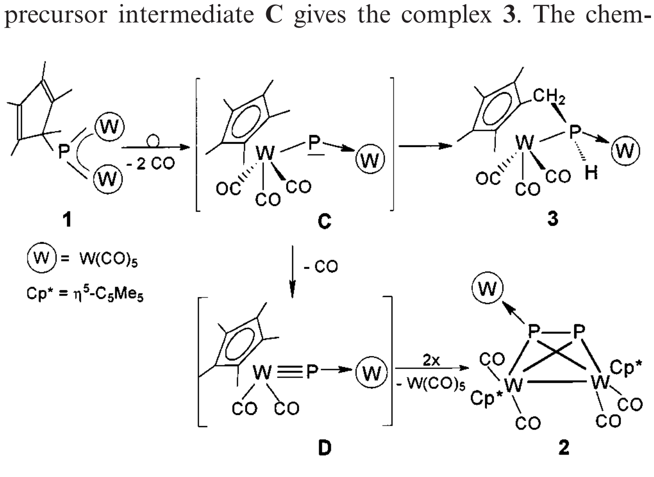
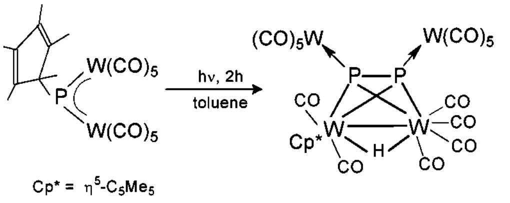
Photolysis of [Cp*P{W(CO)$_5$}$_2$] (**1**) leads to the novel complex [{Cp*(CO)$_6$W$_2$}(μ-H)(μ-η^1:η^1:η^1-P$_2$){W(CO)$_5$}$_2$] (**4**), which was structurally and spectroscopically characterised. The product is formed by a Cp* migration within **1** to give the phosphido complex intermediate [Cp*(CO)$_2$W≡P→W(CO)$_5$], as well as by a Cp* elimination to form an intermediate of the type [P{W(CO)$_5$}$_2$], both of which dimerise to yield product **4**.

The novel class of complexes with a metal−phosphorus triple bond[1] contains two different types of compounds: [L$_n$M≡P] **A**[2] and [L$_n$M≡P→M′(CO)$_5$] **B** (M′ = Cr, W).[3] If in both types of complexes the transition metal is in a high oxidation state, stable compounds are obtained. In the case of a low oxidation state of the transition metal, these complexes exist as highly reactive intermediates.[1] We recently found a synthetic approach to generate complexes **B** directly as highly reactive intermediates.[4] In contrast to the sterically demanding complexes of type **A**, they reveal a high "side-on" reactivity. The principle of their generation is based on the migration of a σ-bound Cp* substituent at the phosphorus atom to an η^5-coordination at the transition metal (Scheme 1). Thus, the thermolysis of [Cp*P{W(CO)$_5$}$_2$] (**1**) leads, via CO elimination, to an intermediate of the formula **D** containing a phosphorus−tungsten triple bond. This intermediate dimerises to form the tetrahedral complex **2** as the major product. As a side-reaction, a C−H activation in a possible precursor intermediate **C** gives the complex **3**. The chemistry of this highly reactive intermediate **D** offers promising synthetic routes to a large variety of unprecedented phosphametallocycles.[5] Herein we report on the photolysis of **1**, which reveals a different transformation pathway in contrast to the transformation involved in the thermolysis reaction of **1**.



Scheme 1. Proposed reaction pathway of the thermolysis of [Cp*P{W(CO)$_5$}$_2$] (**1**)

The photolysis of **1** in toluene at room temperature results in a colour change from blue to brown after two hours indicating the completeness of the transformation of **1** [Equation (1)]. Column chromatographic workup resulted in a yellow fraction of the minor product **3** as well as an orange fraction from which **4** could be obtained as a red crystalline compound in 60% yield. Complex **4** is sparingly soluble in toluene and readily soluble in THF and CH$_2$Cl$_2$. The IR spectrum reveals absorptions for terminal CO ligands. In the mass spectrum of **4**, the highest mass peak found corresponds to the molecular ion peak minus W(CO)$_5$.



(1)

The ^{31}P{^{1}H} NMR spectrum of **4** reveals two doublets at δ = −166.2 and −223.7 with a $^1J_{P,P}$ coupling constant of 447 Hz, indicating magnetically nonequivalent P atoms. This magnetic nonequivalency probably results from the different orientations of the P atoms to the Cp* ligand at one of the W atoms of the stereochemically rigid tetrahedral P$_2$W$_2$ framework. While the first doublet shows one $J_{W,P}$ coupling of 233 Hz, the other doublet reveals two $J_{W,P}$ couplings of 69 and 209 Hz, respectively. Since the larger $J_{W,P}$ usually corresponds to the coupling to the terminal W(CO)$_5$ groups, the smaller must reflect the coupling to the W atoms of the W$_2$P$_2$ tetrahedral framework, which is probably not resolved in the signal at δ = −166.2

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($w_{1/2}$ > 50 Hz). For [$\{Cp^*W(CO)_2\}_2(\mu,\eta^2\text{-}P_2)$][6] and [$\{CpW(CO)_2\}_2(\mu,\eta^2\text{-}P_2)$],[7] no $^1J_{W,P}$ couplings are observed in the singlets found at $\delta = -154.6$ and -299.0, respectively. In the ^1H NMR spectra of **4**, a singlet for the methyl protons of the Cp* ligand is found at $\delta = 2.29$. Furthermore, a singlet at $\delta = -16.7$ for the (μ-H) ligand is observed containing two different $^1J_{W,H}$ couplings of 30 and 38 Hz. The magnitude of the coupling is in good agreement with the data obtained for [$W_2(\mu\text{-H})(CO)_xL_y$] (L = NO, RNC, PPh_3; R = Me, *t*Bu, $PhCH_2$, *i*Pr; $x = 6-9$; $y = 1, 2$), where the signal for the μ-hydrido ligand was found between $\delta = -5.21$ and -13.1, with each of them containing two $^1J_{W,H}$ couplings of between 30 and 60 Hz.[8] The origin of the μ-H ligand in **4**, which completes the electronically precise nature of this compound, was confirmed by carrying out the reaction in Equation (1) in [D_8]toluene (99% labeled with D) as solvent. Since the obtained compound **4a** contains only traces of the protonated complex **4**, one can speculate that the solvent acts as the source of the proton.

The molecular structure of **4** (Figure 1) shows a slightly distorted W_2P_2 tetrahedron containing a $Cp^*(CO)_2W$ and a $W(CO)_4$ unit. Both of the phosphorus atoms coordinate to $W(CO)_5$ groups. The bond length P(1)−P(2) of 2.166(6) Å is shorter than a single bond length found, for example, in the structure of β-P_4 at −185 °C [2.190−2.212 Å].[9] Since the P−P bond length in **4** is longer than in the non-substituted tetrahedral P_2W_2 complex [$\{CpW(CO)_2\}_2(\mu,\eta^2\text{-}P_2)$] [2.104(4) Å],[7] and also longer than in the monosubstituted complex [$Cp^*W(CO)_2\}_2(\mu,\eta^2{:}\eta^1\text{-}P_2)\{W(CO)_5\}$] [2.092(4) Å],[4] one can conclude that the coordination of the phosphorus lone pairs in **4** lengthens the P−P bond. Furthermore, each of the P atoms of **4** is more closely bound to a different W atom of the tetrahedral P_2W_2 moiety. Thus, the bond lengths P(1)−W(1) and P(2)−W(2) are 2.492(4) Å and 2.510(4) Å, respectively, in comparison to the other P(1)−W(2) and P(2)−W(1) bond lengths of 2.540(4) Å and 2.554(4) Å, respectively. The W(1)−W(2) bond length [3.1417(9) Å] in **4** is slightly longer than the W−W bond length in other W_2P_2 tetrahedral complexes: [$\{Cp^*(CO)_2W\}_2\{\mu,\eta^2{:}\eta^1\text{-}P_2W(CO)_5\}$] [3.0920(7) Å][4] and [$\{Cp(CO)_2W\}_2(\mu,\eta^2\text{-}P_2)$] [3.0026(11) Å].[7]

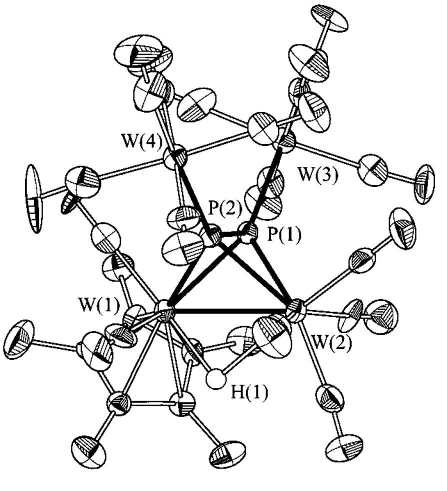
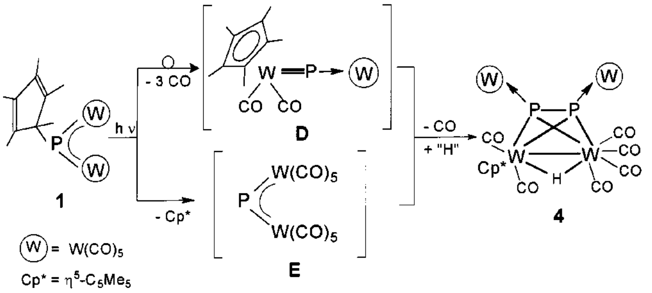


Figure 1. Molecular structure of **4** (showing 50% probability ellipsoids; hydrogen atoms of the Cp* ligand are omitted for clarity); selected bond lengths [Å] and angles [°]: W(1)−P(1) 2.492(4), W(1)−P(2) 2.554(4), W(1)−W(2) 3.1417(9), W(2)−P(2) 2.510(4), W(2)−P(1) 2.540(4), W(3)−P(1) 2.547(4), W(4)−P(2) 2.519(4), P(1)−P(2) 2.116(6); P(1)−W(1)−P)(2) 49.58(13), P(1)−W(1)−W(2) 51.04(8), P(2)−W(1)−W(2) 51.02(9), P(2)−W(2)−P(1) 49.56(13), P(2)−W(2)−W(1) 52.29(8), P(1)−W(2)−W(1) 50.68(6), P(2)−P(1)−W(1) 66.75(15), P(2)−P(1)−W(2) 64.49(14), W(1)−P(1)−W(2) 77.28(10), P(2)−P(1)−W(3) 130.19(18), W(1)−P(1)−W(3) 144.15(15), W(2)−P(1)−W(3) 136.99(15), P(1)−P(2)−W(2) 65.95(15), P(1)−P(2)−W(4) 136.01(19, W(2)−P(2)−W(4) 140.18(16), P(1)−P(2)−W(1) 63.67(14), W(2)−P(2)−W(1) 76.69(11), W(4)−P(2)−W(1) 139.39(17)

The formation of **4** from the photolysis of [$Cp^*P\{W(CO)_5\}_2$] (**1**) can be regarded as a dimerisation of two reactive intermediates (Scheme 2): the triple bond intermediate **D**, formed by Cp* migration as described in Scheme 1, and a second intermediate **E** created by elimination of the Cp* ligand. Since complex **4** is obtained in high isolated yields, both of the pathways can be regarded as equivalent. Each of these intermediates opens up broad perspectives for trapping reactions to obtain novel main-group−transition-metal cage compounds with unusual coordination polyhedrons.



Scheme 2. Proposed reaction pathway of the photolysis of [$Cp^*P\{W(CO)_5\}_2$] (**1**)

Experimental Section

General: All reactions were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were purified and degassed by standard procedures. NMR spectra were recorded on a Bruker AC 250 [^1H: 250.13 MHz; ^{31}P: 101.256 MHz; standard Me_4Si (^1H), 85% H_3PO_4 (^{31}P)]. The IR spectra were recorded in KBr on a Bruker IFS 28 FT-IR spectrometer, the mass spectrum on a Finnigan MAT 711 at 70 eV and the UV spectra on a Perkin−Elmer Lambda 900 UV/Vis/NIR. Photolysis reactions were carried out with a Hanau type TQ150 mercury lamp.

Synthesis of 4: A solution of **1** (0.39 g, 0.48 mmol)[10] in 50 mL of toluene was photolysed for 2 h until the colour of the solution changed from deep blue to brown. The solvent was completely removed in vacuo, and the resulting brown residue was coated onto 6 g of silica gel and separated by column chromatography (1.5 × 45 cm). Elution with *n*-hexane/toluene (5:1) gave a yellow fraction of **3** (20 mg, 5.6%) followed by an orange fraction (*n*-hexane/toluene 1:1) containing **4**, which was recrystallised to give 0.2 g (60%) of red platelets at −30 °C. − $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -166.2$ (d, $^1J_{PP} = 447$ Hz, $^1J_{WP} = 233$); -223.7 (d, $^1J_{PP} = 447$ Hz, $^1J_{WP} = 69$ Hz, 209 Hz). − ^1H NMR ([D_8]THF): $\delta = 2.29$ (s, 15 H, Cp*), -16.7 (s, 1 H, $J_{W,H} = 30$ and 38 Hz). − IR (KBr): $\nu(CO) = 2074$ (m), 2063 (w), 1970 (sh), 1930 (s, br) cm^{-1}. − MS (EI): *m*/*z* (%) =

1058 (2) [M − W(CO)$_5$]$^+$, 1002 (1) [M − W(CO)$_7$]$^+$, 890 (3) [M − W(CO)$_{11}$]$^+$. − $C_{26}H_{16}O_{16}P_2W_4$ (1381.75): calcd. C 22.60, H 1.17; found C 22.32, H 1.53

1: UV/Vis (toluene): λ_{max} [nm] (ε) [M^{-1} cm^{-1}] = 572 (13400), 350 (sh, 10300).

4: UV/Vis (toluene): λ_{max} [nm] (ε) [M^{-1} cm^{-1}] = 320 (sh, 6900).

Crystal Structure Determination of 4:[11] A red crystal, obtained from toluene, with the dimensions 0.20 × 0.12 × 0.02 mm was used for data collection at 210(2) K on a STOE IPDS diffractometer with Mo-K_α radiation (λ = 0.71073 Å) with numerical absorption corrections. The structure was solved by direct methods using SHELXS-86,[12a] with full-matrix least-squares refinement on F^2 using SHELXL-97[12b] and anisotropic displacement for non-H atoms (except those of the atoms O6 and C21, due to the insufficient crystal quality). Hydrogen atoms were located in idealised positions and refined isotropically according to a riding model. The bridging H(1) atom was found as residual electron density and was freely refined [U(eq) = 0.06 Å^2]. The flack parameter of the acentric structure of **4** came to a value of −0.07(2). The relatively high residual electron density in the structure of **4** is located close to the atom W(2). Further data of the X-ray structure analysis are given in Table 1.

Table 1. Crystallographic data for **4**

Empirical formula	$C_{26}H_{16}O_{16}P_2W_4$
Molecular weight	1381.73
Space group	Orthorhombic, *Pna*2(1)
a [Å]	21.142(3)
B [Å]	11.706(2)
c [Å]	14.320(2)
V [Å]^3	3544.1(12)
Z	4
ρ(calcd.) [g/cm^3]	2.590
μ [mm^{-1}]	13.098
F(000)	2504
2Θ range [°]	3.86−51.92
Index ranges	$-25 \le h \le 25$ $-14 \le k \le 13$ $-17 \le l \le 17$
Reflections collected	23642
Independent reflections	6834 (R_{int} = 0.2167)
Independent reflections [$F_0 > 4\sigma(F_0)$]	6571
Data/restrains/parameters	6834/1/430
Goodness-of-fit on F^2	1.083
$R1^{[a]}$ [$I > 2\sigma(I)$]/$wR2^{[b]}$	0.0618, 0.1529
Larg. diff peak/hole [e/Å^3]	4.096, −4.794

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

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[11] 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-153619. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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