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On the pathway of the η^1–η^5 migration of a Cp* ligand

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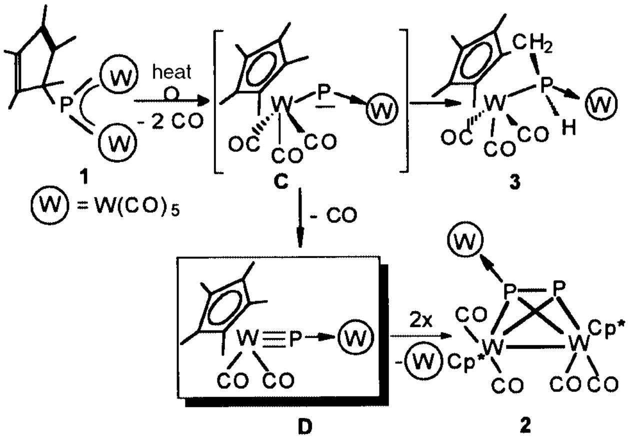
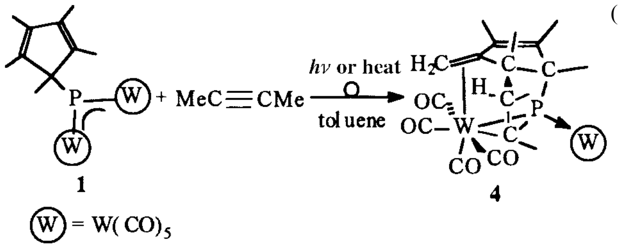
The thermolysis and photolysis, respectively, of the phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ 1 in the presence of MeC≡CMe leads to the three-membered heterocycle $[(\eta^2\text{-}CH_2C_5Me_4)W(CO)_4C\{(CH_3)CH(CH_3)\}PW(CO)_5]$ 4 with an unusual η^2-coordinated $CH_2C_5Me_4$ ligand formed by a 1,4-sigmatropic hydrogen shift; the crystal structure and the spectroscopic data of 4 are discussed.

Complexes with a metal–phosphorus triple bond are a novel class of compounds[1] which exist in two different types; $[L_nM{\equiv}P]$ **A**[2] and $[L_nM{\equiv}P{\rightarrow}M'(CO)_5]$ **B**[3] (M′ = Cr, W). In complexes of type **A** the metal–phosphorus triple bond is kinetically stabilised by sterically demanding substituents at the ML_n fragment. Thus, these complexes react predominantly *end-on* by using the phosphorus lone pair.[4] In complexes of type **B** the lone pair is already used by coordination to Lewis acidic complexes to stabilise the overall complex and thus, revealing a high *side-on* reactivity. If in both types of complex the transition metal is in a high oxidation state, stable compounds can be isolated. In the case of a low oxidation state of the transition metal these complexes exist as highly reactive intermediates.[1] We recently developed a synthetic approach to generate complexes of type **B** directly as highly reactive intermediates revealing a high *side-on* reactivity.[5] The principle of their generation is based on migration of a σ-bound Cp* at the phosphorus atom to give an η^5-coordination mode at the transition metal as shown in Scheme 1. Thus, the thermolysis of $[Cp^*P\{W(CO)_5\}_2]$ **1** leads, *via* CO elimination, to an intermediate of the formula $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ **D** containing a phosphorus tungsten triple bond. The dimerisation of **D** leads to the major product $[Cp^*_2(CO)_4W_2\{\mu,\eta^2\text{-}P_2[W(CO)_5]\}]$ **2**. The CH-activated phosphine **3** can be isolated as a minor product. Its formation can be regarded as a subsequent side-reaction of the first formed intermediate **C**. The chemistry of the highly reactive intermediate **D** offers synthetic routes to a large variety of unprecedented phosphametallocycles. Herein we report on the thermolysis as well as the photolysis of $[Cp^*P\{W(CO)_5\}_2]$ **1** in the presence of but-2-yne, which gives an insight into the Cp* migration process.



Scheme 1 Reaction pathway for the thermolysis of $[Cp^*P\{W(CO)_5\}_2]$ **1**.

The photolysis of $[Cp^*P\{W(CO)_5\}_2]$ **1** in the presence of MeC≡CMe in toluene at ambient temperatures leads to the yellow crystalline complex **4** in 80% yield.[6] However, the thermolysis of **1** with MeC≡CMe leads to a mixture of products. The $^{31}P\{^1H\}$ NMR of the crude reaction mixture shows besides the major product **4** small amounts of **2** and **3** as the thermolysis products of **1** alone and an additional singlet at 19.2 ppm with a $J_{W,P}$ of 226 Hz. Column chromatographic work-up on silica gel leads to a 30% isolated yield of **4**.† Unfortunately the product leading to the above-mentioned singlet decomposes on the column material. Due to our results on the reaction of **1** with other alkynes[7] one can speculate that this compound contains a four-membered WPC_2 ring formed by the reaction of intermediate **D** with MeC≡CMe.



(1)

Complex **4** is moderately soluble in pentane and readily soluble in toluene and CH_2Cl_2. **4** was fully characterised on the basis of its spectroscopic data ‡ and by single-crystal X-ray structure analysis.§ In the IR spectra **4** shows CO stretching frequencies in the range of terminal CO ligands. The appropriate molecular ion peak is observed in the mass spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a singlet at 73.3 ppm with $^1J_{W,P}$ coupling constants of 234 Hz for the $P{\rightarrow}W(CO)_5$ bond and 38 Hz for a $P\text{–}W(CO)_4$ single bond, the latter revealing a reduced s-character.

The X-ray crystal structure analysis of **4** (Fig. 1) reveals a tricyclic complex with a dominant three membered [WCP] ring with a distorted tetrahedrally coordinated phosphorus atom. The bond distance W(1)–P [2.5516(19) Å] corresponds to a typical W–P single bond whereas the bond distance P–C(10) at 1.755(7) Å is significantly shorter than a P–C single bond. This distance is comparable to the P–C bond length in the three membered ring complex $[Cp(CO)_2\overline{MoPPh_2C}H_2]$.[8] As a result of the complicated tricyclic arrangement the P–C bond distance to the atom C(14) of the previously Cp* ligand corresponds to a lengthened P–C single bond [1.919(7) Å], which is 0.017 Å longer than the P–C bond in the starting material **1**.[5] Another interesting structural feature of **4** is the η^1- (at the P atom) and η^2- (at the W atom) coordinated previously Cp* ligand. As mentioned before, the thermolysis of **1** leads to a $\eta^1{\rightarrow}\eta^5$ Cp* migration from the phosphorus to the tungsten atom. Thus, compound **4** can be considered as a snapshot of the Cp* migration process trapped by the alkyne. The alkyne binds to

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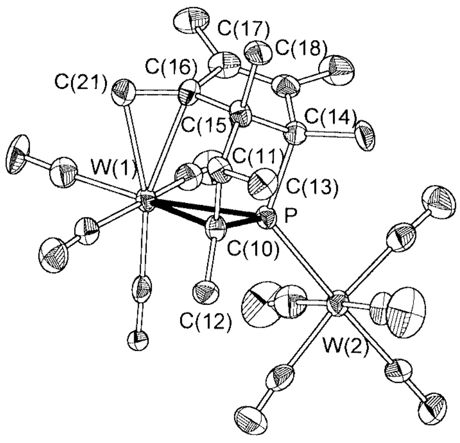
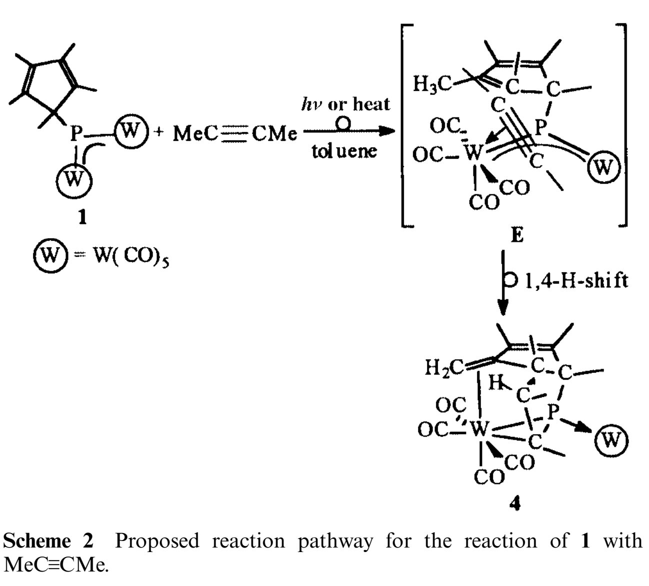


Fig. 1 Molecular structure of **4** (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): W(1)–P 2.5516(19), W(1)–C(10) 2.385(7), W(1)–C(21) 2.523(8), W(1)–C(16) 2.572(8), P–C(10) 1.755(7), P–C(14) 1.919(7), P–W(2) 2.5367(18), C(10)–C(11) 1.545(10), C(11)–C(13) 1.526(9), C(11)–C(15) 1.531(10), C(15)–C(14) 1.560(10), C(15)–C(16) 1.529(10), C(17)–C(18) 1.350(12), C(21)–C(16) 1.368(11), W(1)–C(10)–P 74.4(2), W(1)–P–C(10) 64.2(2), P–W(1)–C(10) 41.47(17), W(1)–P–W(2) 127.52(7), W(1)–P–C(14) 102.4(2), C(14)–P–W(2) 124.2(2), C(14)–P–C(10) 96.7(3).

the W(1) and P atoms but also to the Cp* ligand. The carbon atom C(21) of a previous methyl group of the Cp* ligand loses one hydrogen atom which migrates *via* a 1,4 H-shift to the carbon atom C(11) resulting in a CH_2 moiety at C(21) and giving a C–C double bond [*d*(C21–C16) = 1.368(11) Å], which is now η²-coordinated to the $W(CO)_4$ fragment. The bond distance C(10)–C(11) of the former alkyne corresponds, after incorporation within the tricyclic system, to a C–C single bond [1.545(10) Å]. Complex **4** possesses several chiral centres, most of them included in rigid ring systems but also at the carbon atom C(11). However, no diastereomers can be observed in the NMR spectrum since the hydrogen attack at C(11) from the back of the molecule is the only possible reaction pathway for the H-migration.

The structure of **4** gives an insight into the Cp* migration process as the first step of the formation of intermediate **C** which leads, *via* the triple bond intermediate **D**, finally to complex **2** (compare Scheme 1). Starting from $[Cp^*P\{W(CO)_5\}_2]$ **1** the loss of one molecule of CO, initiated by the thermal or photochemical activation leads to an approach of but-2-yne and the movement of the Cp* ligand. The alkyne coordinates *side-on* at the $W(CO)_4$ unit to give intermediate **E** (Scheme 2).



Scheme 2 Proposed reaction pathway for the reaction of **1** with MeC≡CMe.

P–C and W–C bond formation leads to migration of the hydrogen atom at C(21) to the carbon atom C(11) of the alkyne under C–C bond formation. Since, hydrogen attack from the back of the alkyne is the only possible pathway for this reaction, just one diastereomer is formed.

Acknowledgements

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Notes and references

† Synthesis of **4**. A solution of Me–C≡C–Me in *n*-hexane (0.042 g, 0.77 mmol) was added to a solution of **1** (0.630 g, 0.77 mmol) in toluene (40 ml) and refluxed/photolysed for 2 hours 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 transferred onto silica gel and separated by column chromatography. Elution with *n*-hexane–toluene (10 : 1) gave a yellow fraction containing **4**, which was recrystallised from *n*-hexane to give yellow crystals (thermolysis: 0.193 g, 0.23 mmol, 30%; photolysis: 0.344 g, 0.42 mmol, 55%). Anal. Calcd. for $C_{24}H_{21}O_8PW_2$: C, 34.48; H, 2.53. Found: C, 34.10; H, 2.28%.

‡ Spectroscopic data for **4**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 73.3 (s, $^1J_{WP}$ 234 and 38 Hz); ^1H NMR (C_6D_6): δ 3.55 (m, 1 H, H21A), 3.26 (d, $^1J_{HH}$ 6.9 Hz, 1 H, H21B), 2.15 (d, J_{HH} 14.1 Hz, 3 H, CH_3), 1.64 (dd, J_{HH} 1.1 Hz, 3 H, CH_3), 1.40 (d, J_{HH} 17.8 Hz, 3 H, CH_3), 1.00 (dd, J_{HH} 1.1 Hz and 5.5 Hz, 3 H, CH_3), 0.88 (s, br, 1 H, H11), 0.73 (d, J_{HH} 7.2 Hz, 3 H, CH_3), 0.37 (s, 3 H, CH_3); IR (KBr) $\tilde{\nu}$ (CO) [cm^{-1}]: 2072 (s), 2045 (s), 1997 (w), 1974 (br), 1921 (br); MS (EI): *m*/*z* (%): 840 (14) [M^+], 644 (61) [$M^+ - 7$ CO], 402 (14) [$M^+ - W(CO)_9$].

§ Crystallographic data for **4**: $C_{24}H_{21}O_8PW_2$, $M = 836.08$, monoclinic, space group $P2_1/n$; $a = 16.077(3)$ Å, $b = 10.499(2)$ Å, $c = 16.773(3)$ Å, $\beta = 114.44(3)°$, $U = 2577.6(9)$ Å³, $Z = 4$, $\lambda(\text{Mo-K}_\alpha) = 0.71073$, $\mu = 9.025$ mm^{-1}. Data were collected at 200(1) K on a STOE IPDS “image-plate” diffractometer for the range $4.58 \le 2\theta \le 51.9°$. The structure was solved by direct methods using SHELXS-86,[9a] a full-matrix least-squares refinement on F^2 in SHELXL-97[9b] with anisotropic displacement for non-H atoms (except of the atom O2, due to the limited quality of the crystal used). Hydrogen atoms were located in idealised positions and refined isotropically according to the riding model. Final residuals for a total of 17327 reflections, of which 4916 were independent [$R_{int} = 0.0772$] was $R_1 = 0.0511$ and $wR_2 = 0.966$ and for the 4039 reflections with $I \ge 2\sigma(I)$, $R_1 = 0.0401$ and $wR_2 = 0.0924$. CCDC reference number 186/2043. See http://www.rsc.org/suppdata/dt/b0/b004941g/ for crystallographic files in .cif format.

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