

Is it Possible to stabilise Complexes with a Tungsten–Phosphorus Triple Bond?

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$[\text{W}(\text{CO})_2\{\eta^4\text{-(Bu}^t\text{C}_2\text{P}_2)\text{W}(\text{CO})_5\}\{\eta^2\text{-(Bu}^t\text{CP})\text{W}(\text{CO})_5\}]$ **1** is prepared by treatment of $\text{Bu}^t\text{C}\equiv\text{P}$ with $[\text{W}(\text{CO})_5\text{THF}]$; the reaction of $[\text{W}_2(\text{OBu}^t)_6]$ with $\text{Bu}^t\text{C}\equiv\text{P}$ in the presence of $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr, W}$) affords novel compounds of the type $[(\text{Bu}^t\text{O})_3\text{W}\equiv\text{P}\rightarrow\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr, W}$), the first examples of a formal $\text{W}\equiv\text{P}$ containing complex.

Speculation for the existence of intermediates of the type $[\text{L}_n\text{M}\equiv\text{P}]$ ($\text{L}_n\text{M} = (\text{RO})_3\text{W}$, $\text{R} = \text{Bu}^t$, Np (neopentyl))—which are termed herein as metallaphosphaalkynes—are found in the literature.^{1–4†} In 1987, Chisholm and coworkers described the formation of complexes with a W_3P - and a WP_3 -core by the reaction of $[\text{W}_2(\text{ONp})_6(\text{HNMe}_2)_2]$ with P_4 .³ It was postulated that a metallaphosphaalkyne of the type $[(\text{NpO})_3\text{W}\equiv\text{P}]$ is an intermediate of this reaction that reacts with another W^{III} -alkoxide dimer to give the W_3P -cluster. Becker and coworkers carried out the reaction of $[\text{W}_2(\text{OBu}^t)_6]$ with the phosphalkyne $\text{Bu}^t\text{C}\equiv\text{P}$.^{4a} Based on the characterisation of the final product as $[(\text{Bu}^t\text{O})_2\text{W}\{(\text{Bu}^t\text{C})_2\text{P}(\text{OBu}^t)\}]$, which possesses a WC_2P -four-membered ring unit, it was postulated that $[(\text{Bu}^t\text{O})_3\text{W}\equiv\text{CBu}^t]$ and $[(\text{Bu}^t\text{O})_3\text{W}\equiv\text{P}]$ are formed as intermediates.^{4b}

Recently, Scheer and coworkers developed the concept of a three-component reaction to study the transformation pathway of tetrahedral P_4 in the coordination sphere of transition metals.⁵ The addition of a soft Lewis acid scavenger such as $[\text{Cr}(\text{CO})_5\text{THF}]$, which does not itself react rapidly with white phosphorus, P_4 , allows the trapping of activated P_n ligands formed during the reaction between P_4 and a reactive coordination compound. As an extension of this approach we herein report the first results of the three-component reaction of $[\text{W}_2(\text{OBu}^t)_6]$ with $\text{Bu}^t\text{C}\equiv\text{P}$ in the presence of $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr, W}$).

For a successful three-component reaction it is necessary to know the reaction behaviour of the individual two-component systems. Consequently, it was important to determine the outcome of the reaction between $\text{Bu}^t\text{C}\equiv\text{P}$ and $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr, W}$). Therefore, we investigated the 1 : 1 reaction carried out in THF at ambient temperature for 24 h as well as under reflux for 30 min. The 'trimerisation' product $[\text{W}(\text{CO})_2\{\eta^4\text{-(Bu}^t\text{CP})_2\text{W}(\text{CO})_5\}\{\eta^2\text{-(Bu}^t\text{CP})\text{W}(\text{CO})_5\}]$ **1** was obtained in an almost quantitative yield.‡

Compound **1** is a red crystalline compound and is stable in air for short periods. It is readily soluble in all common organic

solvents including hexane. The molecular structure of **1** was determined by single-crystal X-ray diffraction study.§ Several problems encountered during data collection and refinement. However, seriously limit our discussion of the results of this study.§ Nevertheless, the core atoms were located with reasonable precision and a few structural features are noteworthy. First, the molecule contains a cyclo- C_2P_2 ring capped by a tungsten dicarbonyl fragment. A phosphalkyne binds to the latter in a η^2 manner. The P atom of this $\text{Bu}^t\text{C}\equiv\text{P}$ unit and one from the essentially planar C_2P_2 ring each coordinate to $[\text{W}(\text{CO})_5]$ groups. No steric hindrance occurs between the carbonyl fragments. Owing to the orientation of the $\eta^2\text{-Bu}^t\text{C}\equiv\text{P}$ unit the C_2P_2 ring is slightly distorted in a 'kite-like' manner. The P–C bonding distances of the P_2C_2 unit are 1.74(4)–1.80(4) Å, longer than those of the phosphalkenes $\text{R}_2\text{C}=\text{PR}'$ (1.69 Å), which is in accordance with a reduction of the P–C bond order. They correspond to the distances found in the 1,3-diphosphacyclobutadiene complexes $[(\text{C}_5\text{H}_5)\text{Co}\{\eta^4\text{-(Bu}^t\text{C}_2\text{P}_2)\}]$ (1.797(3)–1.798(3) Å)⁷ and $[(\text{C}_5\text{Me}_5)\text{Co}\{\eta^4\text{-(Bu}^t\text{C}_2\text{P}_2)\}]$ (1.79(1)–1.82(1) Å).⁸ The P–C distance in the side-on coordinated phosphalkyne in **1** is 1.64(4) Å which is longer than observed for free $\text{Bu}^t\text{C}\equiv\text{P}$ (1.54 Å). The distance is comparable with those of the side-on coordinated phosphalkynes in $[(\text{Ph}_3\text{P})_2\text{Pt}\{\eta^2\text{-(Bu}^t\text{CP})\}]$ [1.672(17) Å]⁹ and $[(\text{C}_5\text{H}_5)_2\text{Ti}(\text{PMe}_3)\{\eta^2\text{-(Bu}^t\text{CP})\}]$ (1.634 Å)^{4c} and is, therefore, consistent with population of the π^* orbitals due to π back donation from the W atom. Consequently a nearly sp^2 hybridised C(41) atom is expected and is evident by the planarity of the $\text{W}(2)\text{P}(5)\text{C}(41)\text{C}(42)$ moiety.

The ¹H NMR spectrum¶ of **1** shows two singlets in the ratio 1 : 2. The ³¹P{¹H} NMR spectrum¶ reveals a low-field shifted signal for a side-on coordinate phosphalkyne (cf. $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{PMe}_3)\{\eta^2\text{-(Bu}^t\text{CP})\}]$: δ 196.9)^{4c} and two different signals at higher field corresponding to the P atoms of the 1,3-diphosphacyclobutadiene [cf. $[(\text{C}_5\text{R}_5)\text{M}\{\eta^4\text{-(Bu}^t\text{CP})_2\}]$ ($\text{R} = \text{H, M} = \text{Co}$: δ 38.17; $\text{R} = \text{Me, M} = \text{Co}$: δ 26; $\text{R} = \text{Me, M} = \text{Rh}$: δ 38.37) and $[(\text{CO})_3\text{Fe}\{\eta^4\text{-(Bu}^t\text{CP})_2\}]$ ¹⁰ (δ 56.8)].

We were thus able to initiate investigations of the reaction between $[\text{W}_2(\text{OBu}^t)_6]$ and $\text{Bu}^t\text{C}\equiv\text{P}$ in the presence of $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr, W}$) in THF at low temperatures. The ³¹P NMR spectra of the crude product mixture indicate the formation of several different products (Scheme 1), which is comparable with the behaviour of the reaction in the absence of $[\text{M}(\text{CO})_5\text{THF}]$.^{4b} Under our conditions the following sequence is proposed. First, the reaction produces the alkylidyne complex **2** and the desired product $[(\text{Bu}^t\text{O})_3\text{W}\equiv\text{P}\rightarrow\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}$ **3a**, W **3b**). Further reaction with $\text{Bu}^t\text{C}\equiv\text{P}$ leads to four-membered ring derivatives **4–7**. Finally, an additional 1,3-OR shift results in the formation of the products **8** and **9**.

Separation of the compounds proved impossible by column chromatography owing to the facile decomposition of the alkoxide ligands on the column. Only *via* sublimation was it possible to isolate $[(\text{Bu}^t\text{O})_3\text{W}\equiv\text{CBu}^t]$ **2** and $[(\text{Bu}^t\text{O})_2\text{W}\{(\text{CBu}^t)_2\text{POBu}^t\}]$ **8**. By comparison of all the NMR data obtained from these reactions and the one in the absence of $[\text{M}(\text{CO})_5\text{THF}]$ we infer the existence of the complexes shown in Scheme 1 without brackets.

By fractional crystallisation we were able to enrich a solution with the desired products **3a, b**. The ³¹P NMR chemical shifts (C_6D_6) at δ 595.4 (**3a**) and 544.6 (**3b**), the large $^1J_{183\text{W},31\text{P}}$ 535.8

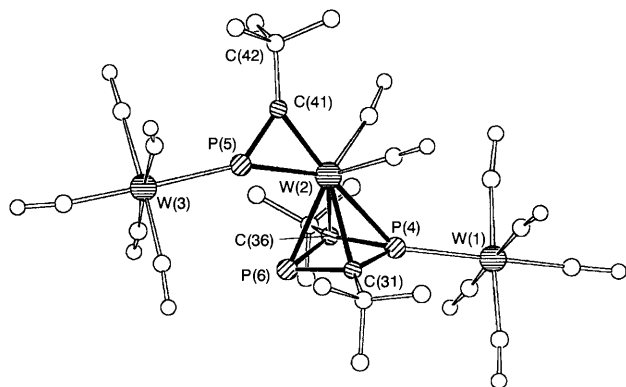
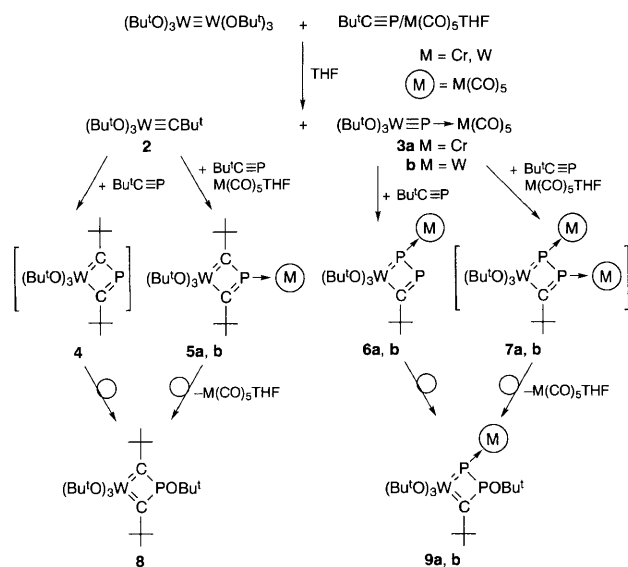


Fig. 1 Molecular structure of **1** with H atoms omitted (two independent molecules, data are given for molecule (A)). Selected bond distances (Å) and angles (°): P(4)–C(31) 1.74(4), P(4)–C(36) 1.76(4), P(6)–C(31) 1.78(4), P(6)–C(36) 1.80(4), P(5)–C(41) 1.64(4), P(5)–W(3) 2.458(12), P(4)–W(1) 2.464(11), W(3)–P(5)–C(41) 138.2(15), P(5)–C(41)–C(42) 138.0(3), W(2)–C(41)–C(42) 144.0(3), P(5)–W(2)–C(41) 42.8(11), C(31)–P(4)–C(36) 81.6(19), C(31)–P(4)–C(36) 79.8(19), P(4)–C(31)–P(6) 99.3(20), P(4)–C(36)–P(6) 97.9(22), W(1)–P(4)–C(36) 137.3(16), W(1)–P(4)–C(31) 137.9(14).



Scheme 1

3a and 554 Hz **3b** and the second coupling in the case of the $[\text{W}(\text{CO})_5]$ substituted product **3b** together with the intensity ratio of the signals $[\text{P}:\text{W}:\text{W} = 1:1:1; ^{31}\text{P}, I = 1/2 (100\%); ^{183}\text{W}, I = 1/2 (14.5\%)]$ indicate the existence of compounds of the formula $[(\text{Bu}^t\text{O})_3\text{W}\equiv\text{P}\rightarrow\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{W}$). The monomeric nature of these products (in contrast to a possible structure with a four-membered W_2P_2 -ring) is supported by two experiments. First, the reaction of a solution of **3b** with $\text{Bu}^t\text{C}\equiv\text{P}$ leads quantitatively to the four-membered ring product $[(\text{Bu}^t\text{O})_3\text{W}\{(\text{Bu}^t\text{C}\equiv\text{P}\{\text{M}(\text{CO})_5\})\}(\text{POBu}^t)]$ **9b**. Secondly, a reaction of $[\text{W}_2(\text{OBu}^t)_6]$ with $\text{Bu}^t\text{C}\equiv\text{P}$ in the presence of an equimolar mixture of $[\text{Cr}(\text{CO})_5\text{THF}]$ and $[\text{W}(\text{CO})_5\text{THF}]$ shows in the ^{31}P NMR spectra no additional signals in comparison with those spectra observed for the individual reactions. In the case of a dimeric structure mixed dimers with additional P–P couplings would be expected. There is no evidence of such compounds.

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the National Science Foundation for financial support. We are grateful to the Alexander von Humboldt Foundation for a Feodor-Lynen-Fellowship (M. S.).

Received, 21st February 1995; Com. 5101064K

Footnotes

† Ziegler *et al.* have investigated the reaction behaviour of $[(\text{L}_n\text{Mo})_3(\mu_3\text{-As})]$ clusters. Based on the nature of the products species of the type $[\text{L}_n\text{Mo}\equiv\text{As}]$ and $[\text{L}_n\text{Mo}\equiv\text{MoL}_n]$ [$\text{L}_n\text{Mo} = (\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2$] are proposed intermediates.¹ Recently Rheingold *et al.* reported the detection of species of the type $[(\text{CO})_n\text{M}\equiv\text{Sb}]^-$ ($n = 3, \text{M} = \text{Fe}; n = 4, \text{M} = \text{Cr}, \text{Mo}, \text{W}$) by ion-cyclotron resonance studies.²

‡ A corresponding reaction starting with $[\text{Cr}(\text{CO})_5\text{THF}]$ is not complete and no product could be isolated. **1** is comparable with the cyclo- P_4 ligand complex formed by the reaction of $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr}, \text{W}$) with P_4 .⁶

§ Crystals of **1** were grown from hexane solution. For **1** at 120 K (two independent molecules); $\text{C}_{27}\text{H}_{27}\text{O}_{12}\text{P}_3\text{W}_3$, $M = 1187.97$, monoclinic, space group $P2_1/c$, $a = 32.527(5)$, $b = 9.654(1)$, $c = 24.130(4)$ Å, $\beta = 111.31(1)$, $Z = 8$, $V = 7059.26$ Å³, $D_c = 2.24$ g cm⁻³, $F(000) = 4416$. A total of 9258 reflections with $6 \leq 2\theta \leq 45$ were collected on a Picker four-cycle goniometer with use of graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) and were corrected for Lorentz and polarisation effects. An absorption correction was also applied (AGNOST) with $\mu = 101.5$ cm⁻¹ or $\frac{1}{4}\mu = 0.0246$ mm. The structure was solved by direct methods (MULTAN 78) and standard Fourier techniques. Full-matrix least squares refinement of thermal parameters (anisotropic for W and P, isotropic for all others) led to convergence with final residuals of $R(F) = 0.0788$ and $R_w(F) = 0.0754$ and $\text{GOF} = 1.979$ for 430 variables refined against those 5260 data with $I \geq 2.33 \sigma(I)$.

During the course of structural refinement it was discovered that one Bu^t group was rotationally disordered on each of the two independent molecules observed in the asymmetric unit of the unit cell. The severe nature of this disorder and the rather weak and limited data did not permit a sophisticated modelling scheme. Instead, a simple model wherein four carbon atoms (each with an occupancy of 0.75) were used to account for the electron density associated with these moieties. The rather long a axis proved problematic and may account for the rather limited number of observed intensities as well as the poor quality of the data set due to overlap of the reflections.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Spectroscopic data for the isolated compound **1**: $^{31}\text{P}\{^1\text{H}\}$ NMR (146.185 MHz, CD_2Cl_2 , 301 K, 85% H_3PO_4): δ 322.1 ($J_{\text{PP}} 35$, $J_{\text{WP}} 234.9$ Hz), 13.4 ($J_{\text{WP}} 217.7$ Hz), 12.5 ($J_{\text{PP}} 35$ Hz); ^1H NMR (500.136 MHz, C_6D_6 , 298 K, ref. SiMe_4): δ 0.86 (18H), 1.65 (9H); IR (CH_2Cl_2): $\nu(\text{CO})$ cm⁻¹: 2076m, 2020w, 1997vw, 1975sh, 1954vs, br; EI-MS (50 eV, 100 °C): m/z 1188 (M^+ , 90), 1104 ($\text{M}^+ - 3\text{CO}$, 15), 992 ($\text{M}^+ - 7\text{CO}$, 72), 724 [$\text{M}^+ - \text{W}(\text{CO})_{10}$, 95%].

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