

Preliminary communication

Synthesis, molecular structure and reactions of the novel organometallic phosphine ligand, $[\text{Wl}_2(\text{CO})(\eta^2\text{-triphos})(\eta^2\text{-MeC}_2\text{Me})].0.75\text{CH}_2\text{Cl}_2$ {triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ }

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Received 24 March 1995

Abstract

Reaction of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ with an equimolar quantity of triphos {triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ } in CH_2Cl_2 at room temperature gave the triphos complex $[\text{Wl}_2(\text{CO})(\eta^2\text{-triphos})(\eta^2\text{-MeC}_2\text{Me})]$ (1). The crystal structure of (1) shows that the triphos is attached to the tungsten via two adjacent phosphorus atoms, with the third phosphorus atom uncoordinated. Two crystallographically independent molecules are present, which are diastereoisomers. Preliminary studies of the reactions of (1) are described.

Keywords: Tungsten(II); Phosphine ligand; 2-butyne; X-ray structure; Triphos, $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$

Organophosphine ligands play a central role in the chemistry of coordination and organotransition-metal complexes [1–5]. In recent years uncoordinated organophosphine groups bound to organotransition-metal centres have become important; for example, in phosphinoferrocenes [6]. Until this work very few examples of tungsten(II) alkyne complexes containing an unbound organophosphine group have been used as phosphine ligands to be attached to other transition-metal centres. In this communication we describe the synthesis, molecular structure and preliminary studies of some reactions of the novel monodentate phosphine ligand complex $[\text{Wl}_2(\text{CO})(\eta^2\text{-triphos})(\eta^2\text{-MeC}_2\text{Me})]$.

Equimolar quantities of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ [7], and triphos react in CH_2Cl_2 at room temperature to give the acetonitrile and 2-butyne-displaced product $[\text{Wl}_2(\text{CO})(\eta^2\text{-triphos})(\eta^2\text{-MeC}_2\text{Me})]$ in 95% yield. Complex (1) has been fully characterised by elemental analysis (C, H and N), infrared and ^1H NMR spectroscopy ¹. The crystal structure of (1) contains

$0.75 \text{CH}_2\text{Cl}_2$, in keeping with the elemental analysis and ^1H NMR spectrum of the bulk sample ¹. Complex (1) is soluble in CH_2Cl_2 (single crystals of (1) suitable for X-ray crystallography were grown from a cooled (-15°C) solution of CH_2Cl_2 /diethyl ether 80:20 ratio), less soluble in chloroform, and only sparingly soluble in diethyl ether. The infrared spectrum (CHCl_3) of (1) shows a broad strong carbonyl band at 1957cm^{-1} , and a weak alkyne ($\text{C}\equiv\text{C}$) stretching band at 1656cm^{-1} , i.e. at a frequency considerably lower than observed for the free alkyne.

¹ Selected data for complex 1: (1) Anal.: $(\text{C}_{39}\text{H}_{39}\text{OP}_3\text{Wl}_2)(\text{CH}_2\text{Cl}_2)_{0.75}$, requires C, 44.7%; H, 3.7%; Found, C, 44.4%; H, 3.7%. IR (CHCl_3) $\nu(\text{C}=\text{O}) = 1957(\text{s}) \text{cm}^{-1}$, $\nu(\text{C}\equiv\text{C}) = 1656 \text{cm}^{-1}$. ^1H NMR (25°C , CDCl_3) 7.9–7.3 (brm, 25H, Ph-H); 5.3 (s, 1.5H, CH_2Cl_2); 2.9, 3.1 (2s, C_2Me); 2.95, 3.15 (2s, C_2Me); 2.5 (brm, 4H, Ph_2PCH_2); 2.4 (brm, 4H, PhPCH_2) ppm (referenced to SiMe_4).

² Selected data for complex 2: (2) Anal.: $\text{C}_{44}\text{H}_{42}\text{O}_4\text{NP}_3\text{Wl}_4$ requires C, 32.7%; H, 2.6%; N, 0.8%. Found, C, 32.6%; H, 2.7%; N, 0.6%. IR (CHCl_3) $\nu(\text{N}\equiv\text{C}) 2305(\text{w}) \text{cm}^{-1}$; $\nu(\text{C}=\text{O}) = 2068(\text{s})$, 2002 (br) 1947 (br) cm^{-1} ; $\nu(\text{C}\equiv\text{C}) 1665(\text{w}) \text{cm}^{-1}$. ^1H NMR (25°C , CDCl_3) 8.1–7.1 (brm, 25H, Ph-H); 3.15, 3.05 (2s, C_2Me); 3.25, 2.95 (2s, C_2Me); 2.8 (brm, 4H, Ph_2PCH_2); 2.35 (brm, 4H, PhPCH_2); 2.2 (s, NCMe); 2.02 (s, NCMe).

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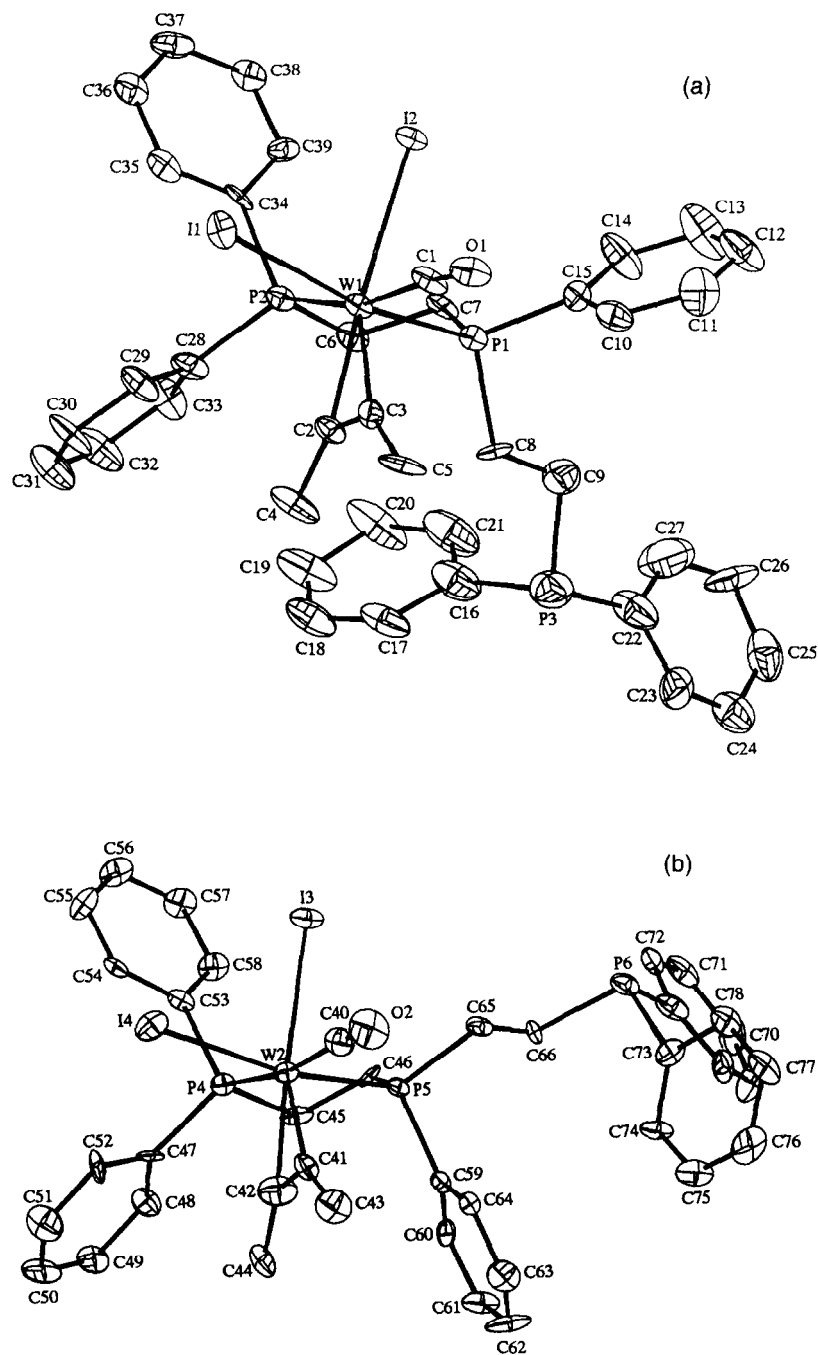
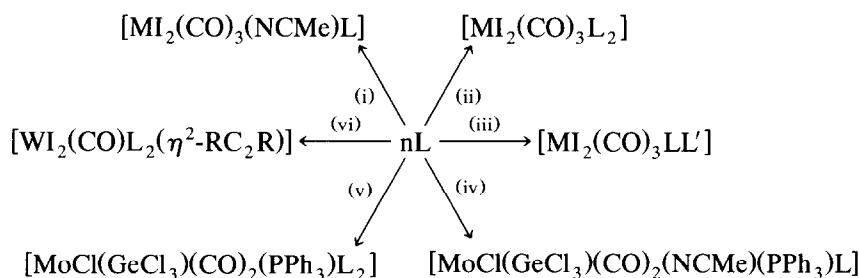


Fig. 1. The X-ray crystal structures of the two diastereoisomers in the asymmetric unit of $[W_{12}(CO)(\eta^2\text{-triphos})(\eta^2\text{-MeC}_2\text{Me})]$ (1), showing the atom numbering scheme. (a) Molecule a; (b) Molecule b (some labelling removed for clarity). Selected bond lengths are: W1–C2 2.025(8), W1–C3 1.997(8), W1–P1 2.470(2), W1–P1 2.556(2), W1–C1 1.970(11), W1–I1 2.815(2), W1–I2 2.851(2) Å for molecule a. Correspondingly, W2–C42 2.086(10), W2–C41 2.005(8), W2–P4 2.569(2), W2–P5 2.492(2), W2–C40 2.014(10), W2–I4 2.808(2), W2–I3 2.849(2) Å for molecule b.



Scheme 1. $L = [Wl_2(CO)(\eta^2\text{-triphos})(\eta^2\text{-MeC}_2\text{Me})]$. All reactions were carried out in CH_2Cl_2 at room temperature. (i) L with an equimolar quantity of $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) for 24 h; (ii) $2L$ with $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) for 24 h; (iii) $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) with an equimolar quantity of L' ($L' = PPh_3$, $AsPh_3$ or $SbPh_3$) for 1 min, 3 min or 5 min respectively followed by an in situ reaction with L for 10 min; (iv) L with an equimolar quantity of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ for 24 h; (v) reaction of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ with $2L$ for 24 h; (vi) reaction of $[Wl_2(CO)(NCMe)(\eta^2\text{-RC}_2\text{R})_2]$ ($R = Me$ or Ph) with $2L$ for 24 h.

The crystal contains two independent molecules in the asymmetric unit. Whilst the coordination connectivity is the same in both, the two molecules differ in the arrangement of the pendant groups ($-\text{Ph}$ and $-\text{PCH}_2\text{CH}_2\text{PPh}_2$) at the bonded central phosphine (see Fig. 1³). The two molecules are diastereoisomers. The basic coordination structure can be described as a distorted octahedron, with two *cis*-iodo-ligands, 2-butyne and the central phosphorus atom of the triphos ligand forming an equatorial plane. The end-bonded phosphorus of the triphos ligand and carbon monoxide occupy the axial sites. As is common in d^4 systems [7], the 2-butyne is parallel to the $W\text{--CO}$ axis (Fig. 1), a configuration which optimises both the π -donor and π -acceptor properties of the alkyne moiety.

The room temperature ^1H NMR spectrum of (**1**) shows four 2-butyne resonances that may correspond to the two approximately equally abundant diastereoisomers in solution. Variable temperature ^1H NMR studies did not show any significant change over the range -60°C to $+50^\circ\text{C}$. This was surprising, since the 2-

butyne resonances might be expected to collapse at higher temperatures due to rapid rotation of the alkyne ligand. However, in one of the diastereoisomers shown in Fig. 1 the 2-butyne ligand is in a very crowded environment which might cause marked hindrance to rotation.

The chemistry of complex **1** is extensive. For example, equimolar amounts of $[Wl_2(CO)_3(NCMe)_2]$ [12] and **1** react in CH_2Cl_2 at room temperature to give the novel bimetallic complex $[Wl_2(CO)_3(NCMe)(\mu^2, \eta^1, \eta^2\text{-triphos})Wl_2(CO)(\eta^2\text{-MeC}_2\text{Me})]$ (**2**), which has been fully characterised². It should be noted that the ^{31}P NMR spectrum ($CDCl_3$, 25°C) of **2** is complex, probably because of the presence of at least two diastereoisomeric products in solution. Scheme 1 illustrates the reactions of **1** as a monodentate phosphine ligand with organomolybdenum(II) and tungsten(II) complexes. We are currently studying the reactions of (**1**) with a range of transition-metal complexes.

Acknowledgements

We thank the European Social Fund for supporting MMM and SDR.

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³ Crystal data for $C_{39}H_{39}OP_3Wl_2(CH_2Cl_2)_{0.75}$: $M_r = 1116.05$; triclinic, $a = 10.056(5)$, $b = 17.884(8)$, $c = 24.915(9)$ Å, $\alpha = 105.77(3)^\circ$, $\beta = 94.83(3)^\circ$, $\gamma = 102.41(2)^\circ$, $V = 4163(3)$ Å³, space group $P1(\text{no. } 2)$, $Z = 4$, $D_c = 1.781$ g cm⁻³, $F(000) = 2146$, $\mu(\text{Mo K}\alpha) = 44.96$ cm⁻¹. Data were collected at 120 K, on a FAST TV Area detector diffractometer following previously described procedures [8]. 10095 data were recorded and merged to give 9906 unique ($R_{\text{int}} = 0.0293$). The structure was solved via heavy atom methods (SHELXS-86) [9], to give two independent molecules in the asymmetric unit and then refined by full matrix least-squares on all F_o^2 data (SHELXL-93) [10]. An absorption correction was applied using DI-FABS [11]. The final R , R_w indices [$I > 2\sigma(I)$] were 0.0408, 0.1055 for 889 parameters (non-hydrogen atoms anisotropic; hydrogen atoms in idealised positions, $C\text{--}H = 0.96$ Å, with U_{iso} tied to U_{eq} of the parent atoms). Full details of the data collection and structure refinement and tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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