

3-Hexyne Complexes of Molybdenum(II) and Tungsten(II) Containing 2, 2'-Bipyridine. X-Ray Crystal Structure of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$

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3-Hexyne Complexes, Molybdenum(II), Tungsten(II)

Reaction of $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ($\text{M} = \text{Mo}, \text{W}$) with one equivalent of 2,2'-bipyridine (bipy) in CH_2Cl_2 at room temperature gives either the neutral complex, $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ (**1**) or the cationic complex, $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]\text{I}$ (**2**). The neutral molybdenum complex **1**, has been crystallographically characterised, and has a *pseudo*-octahedral geometry with the iodo-ligand *trans* to the 3-hexyne, and with the bipy, carbon monoxide and other iodo-ligand occupying the equatorial face. ¹³C NMR studies show the 3-hexyne is donating four electrons to the molybdenum in **1**.

the cationic tungsten complex, $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]\text{I}$ (**2**).

Experimental

Physical measurements and instruments

Elemental analyses (C,H and N) were determined using a Carlo Erba Elemental Analyser MOD1108 (using helium as a carrier gas). Infrared spectra were obtained using CHCl_3 films between NaCl plates and recorded on a Perkin-Elmer 1430 ratio recording IR spectrophotometer. ¹H and ¹³C {¹H}NMR spectra were recorded in a Bruker AC250 MHz NMR spectrometer and referenced to SiMe₄.

Reagents and materials

All reactions and purifications were carried out under an atmosphere of dry nitrogen using standard Vacuum/Schlenk line techniques. The starting materials, $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by the literature method [16]. All solvents and chemicals used were of reagent grade quality and were purchased from commercial sources. The solvents used were dried and distilled before use.

Preparation of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ (**1**)

To a stirred solution of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ (0.25 g, 0.31 mmol) in 20 ml of CH_2Cl_2 at room temperature was added bipy (0.05 g, 0.32 mmol). The solution was stirred at r.t. for 24 h. Filtration, followed by removal of the solvent *in vacuo* gave a crystalline powder, which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give suitable single crystals for X-ray crystallography of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ (**1**) (yield = 0.11 g, 58%). – IR (CHCl_3 , film): $\nu = 1946(\text{s}) (\text{C}=\text{O}) \text{ cm}^{-1}$; $\nu = 1641(\text{w}) (\text{C}\equiv\text{C}) \text{ cm}^{-1}$; – ¹H NMR (CDCl_3 , 25 °C) $\delta = 9.2\text{--}7.6$ (v.br, 8H, 2,2'-bipyridyl); 3.6 (q, 4H, 2CH₂); 1.3 (t, 6H, 2CH₃). – ¹³C {¹H}NMR (CDCl_3 , 25 °C) $\delta = 16.50, 19.30$ (2s, 2CH₃); 34.37, 35.61 (2s, 2CH₂); 121.46, 125.47, 126.39, 132.04, 135.63, 136.34 (6s, 2,2'-bipyridyl); 211.95 (s, C≡C); 228.45(s, C≡O). – C₁₇H₁₈N₂OI₂Mo (616): calcd. C 45.4, H 3.6, N 3.0; found C 45.4, H 3.8, N 3.2.

Introduction

The halocarbonyl alkyne chemistry of molybdenum(II) and tungsten(II) has been very well developed over the years [1–15]. For similar types of reactions, the two metals generally exhibit similar reaction patterns for molybdenum(II) and tungsten(II).

In 1999 [16], we described the synthesis and reactions with phosphines of the bis(3-hexyne) complexes $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ($\text{M} = \text{Mo}$ and W). Two of the reaction products with phosphine ligands were crystallographically characterised, namely $[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Et})]$ and $[\text{WI}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Et})]$. In this paper, we describe the differing reactivity of the bis(3-hexyne) complexes $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ with bipy (bipy = 2,2'-bipyridine) to give the structurally characterised neutral molybdenum complex, $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ (**1**), and

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Preparation of

 $[WI(CO)(bipy)(\eta^2-EtC_2Et)_2]I.Et_2O$ (**2**)

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.10 g, 0.15 mmol) in 20 ml of CH_2Cl_2 at r.t. was added bipy (0.023 g, 0.15 mmol). The reaction was stirred at room temperature for 24h. Filtration, followed by removal of the solvent *in vacuo* gave a yellow crystalline powder, which was recrystallized from CH_2Cl_2/Et_2O (50:50 ratio) at $-17^\circ C$ to give the pure product, $[WI(CO)(bipy)(\eta^2-EtC_2Et)_2]I.Et_2O$ (**2**) (yield = 0.08 g, 68%).

–IR($CHCl_3$, film); $\nu = 2053(s)$ ($C\equiv O$) cm^{-1} ; $\nu = 1604(w)$, ($C=C$) cm^{-1} . – 1H NMR ($CDCl_3$, $+25^\circ C$) $\delta = 9.2-7.2$ (v.br, 8H, 2,2-bipyridyl); 3.5 (q, 4H, OCH_2); 3.2 (q, 8H, $\equiv CCH_2$); 1.5 (t, 6H, OCH_2CH_3); 1.2 (t, 12H, $\equiv CCH_2CH_3$). – $C_{27}H_{38}N_2O_2I_2W$ (860); calcd. C 37.7, H 4.4, N 3.3; found C 37.9, H 4.8, N 3.6.

X-ray data and processing for **1**

Crystal data are given in Table 1, together with refinement details. Selected bond lengths (\AA) and angles ($^\circ$) are given in Table 2. Whilst the molecular structure is presented in Fig. 1, a crystal of **1** was mounted in a random orientation on a glass wool fibre glued to a glass capillary. Combined phi and omega scans were performed at 150 K on a Nonius KappaCCD equipped with a Nonius FR591 rotating anode ($\lambda Mo-K_\alpha = 0.71073 \text{\AA}$). The structure was solved by direct methods, SHELXS-97 [17] and refined using SHELXL-97 [18]. Hydrogen atoms were included in the refinement, but were constrained to ride on the atom to which

Table 1. Crystal data and collection parameters for **1**.

1	
Formula	$[MoI_2(CO)(bipy)(\eta^2-EtC_2Et)]$
Empirical formula	$C_{17}H_{18}N_2O_2I_2Mo$
Formula weight	616.07
Crystal system, space group	monoclinic, $P2_1/c$
$a =$	8.012(2) \AA
$b =$	16.760(3) \AA
$c =$	14.216(3) \AA
$\beta =$	95.28(3) $^\circ$
Volume	1900.8(7) \AA^3
Z, Calculated density (Mgm^{-3})	4, 2.153
Absorption coefficient (mm^{-1})	3.943
$F(000)$	1160
Crystal size	$0.2 \times 0.05 \times 0.05$ mm
θ Range ($^\circ$)	2.43–30.49
Index range	$-11 \leq h \leq 11, -23 \leq k \leq 23, -19 \leq l \leq 20$
Reflections collected/unique	30893/5638
R_{int}	0.0781
Data/restraints/parameters	5638/0/210
Final R indices [$I > 2\sigma(I)$] $R1, wR2$	0.0383, 0.1010
R indices (all data) $R1, wR2$	0.0562, 0.1169
ρ_{max}, ρ_{min} ($e.\text{\AA}^{-3}$)	2.006, –1.496

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for **1**.

I(1)–Mo(1)	2.8701(6)	Mo(1)–N(2)	2.244(3)
I(2)–Mo(1)	2.8113(8)	C(11)–C(12)	1.504(6)
Mo(1)–C(17)	1.949(4)	C(12)–C(13)	1.486(5)
Mo(1)–C(14)	2.006(4)	C(13)–C(14)	1.310(5)
Mo(1)–C(13)	2.056(4)	C(14)–C(15)	1.495(5)
Mo(1)–N(1)	2.189(3)	C(15)–C(16)	1.530(6)
C(17)–Mo(1)–C(14)	111.60(16)	C(17)–Mo(1)–C(13)	74.00(15)
C(14)–Mo(1)–C(13)	37.61(15)	C(17)–Mo(1)–N(1)	98.85(14)
C(14)–Mo(1)–N(1)	90.91(13)	C(13)–Mo(1)–N(1)	96.49(13)
C(17)–Mo(1)–N(2)	164.45(14)	C(14)–Mo(1)–N(2)	82.68(13)
C(13)–Mo(1)–N(2)	120.00(13)	N(1)–Mo(1)–N(2)	73.99(11)
C(17)–Mo(1)–I(2)	89.62(12)	C(14)–Mo(1)–I(2)	96.01(10)
C(13)–Mo(1)–I(2)	96.21(10)	N(1)–Mo(1)–I(2)	166.29(8)
N(2)–Mo(1)–I(2)	95.11(8)	C(17)–Mo(1)–I(1)	81.72(12)
C(14)–Mo(1)–I(1)	165.48(11)	C(13)–Mo(1)–I(1)	154.94(10)
N(1)–Mo(1)–I(1)	81.01(8)	N(2)–Mo(1)–I(1)	83.50(8)
I(2)–Mo(1)–I(1)	89.627(19)		

they are bonded. The data were corrected for absorption effects using SORTAV [19,20].

Results and Discussion

The starting materials [16] used in this research, namely $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ ($M = Mo, W$) were prepared by reacting the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ with 3-hexyne. Equimolar quantities of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and 2,2'-bipy react in CH_2Cl_2 at room temperature to give either the neutral molybdenum(II) complex $[MoI_2(CO)(bipy)(\eta^2-EtC_2Et)]$ (**1**) *via* displacement of the acetonitrile ligand and a 3-hexyne, or the cationic tungsten(II) complex $[WI(CO)(bipy)(\eta^2-EtC_2Et)_2]I.Et_2O$ (**2**) *via* displacement of the acetonitrile and an iodo ligand. Complexes **1** and **2** have been characterised by elemental analysis, IR and 1H NMR spectroscopy, and **1** by ^{13}C NMR spectroscopy and X-ray crystallography, (see experimental details). Complex **2** was confirmed as a diethyl ether solvate by repeated elemental analyses and 1H NMR spectroscopy. Complexes **1** and **2** are air-sensitive in solution, but can be stored in the solid state for several months at $-17^\circ C$. The complexes are soluble in polar chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but only slightly soluble (**1**) or insoluble (**2**) in diethyl ether and hydrocarbons. Complex **1** is more soluble in $CHCl_3$ than complex **2**, hence it was not possible to obtain a high quality ^{13}C NMR spectrum of **2**.

Suitable single crystals of $[MoI_2(CO)(bipy)(\eta^2-EtC_2Et)]$ (**1**) were grown by cooling a CH_2Cl_2/Et_2O (50:50 ratio) solution of **1** to $-17^\circ C$ for 24 h. The structure of **1** is shown in Fig. 1, together with the atomic numbering scheme. The dimensions in the metal coordination sphere are given in Table 2. If

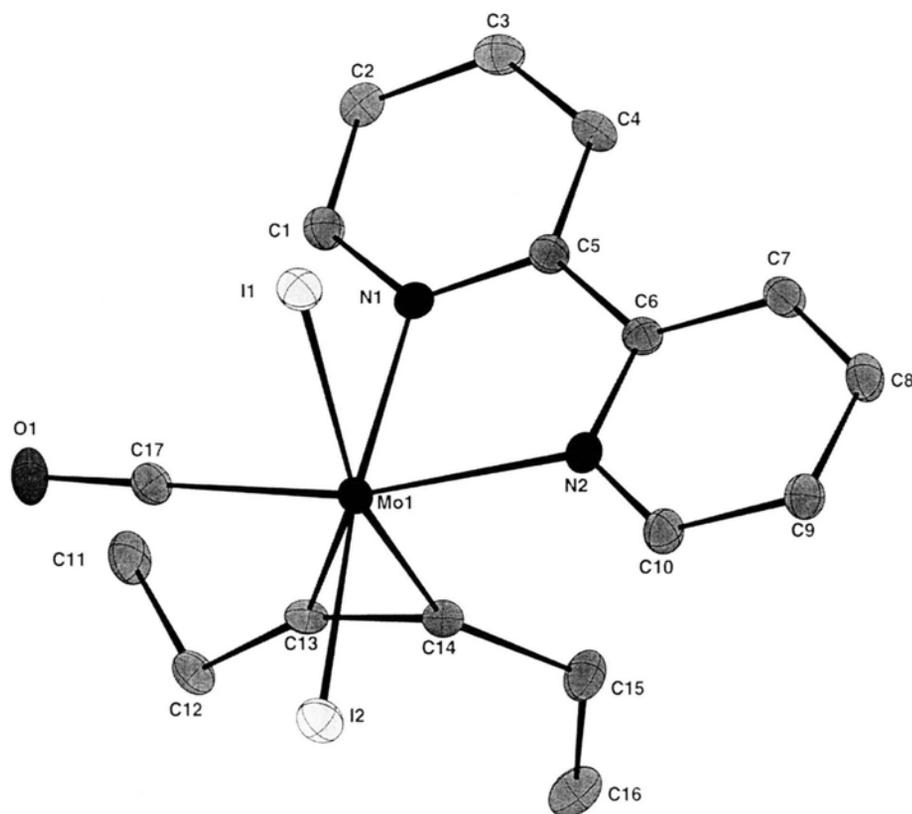


Fig. 1. The structure of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ (**1**), with the atom numbering scheme. Ellipsoids are shown at 30% probability.

the ethyne moiety of the 3-hexyne ligand is considered as occupying one site in the molybdenum coordination sphere then the geometry about the metal centre may be considered to be octahedral. By locating a dummy atom (D) in the centre of the ethyne bond one obtains a geometry about Mo thus: $\text{I}(1)\text{-Mo}(1)\text{-D} = 171.6(3)$, $\text{I}(2)\text{-Mo}(1)\text{-D} = 96.5(2)$, $\text{C}(17)\text{-Mo}(1)\text{-D} = 92.6(3)$, $\text{N}(1)\text{-Mo}(1)\text{-D} = 93.9(4)$, $\text{N}(2)\text{-Mo}(1)\text{-D} = 101.6(3)^\circ$. This derived geometry is a slightly distorted octahedron, where the distortion is incurred by the rigid coordination demands of the bidentate bipy ligand. The coordination may then be described as $\text{I}(1)$ *trans* to the alkyne ligand in the axial sites, with $\text{I}(2)$, carbon monoxide and the bidentate bipy ligands situated in the equatorial plane. There is a *trans* influence from the alkyne ligand upon the iodide [$\text{I}(1)$] bonding, where a longer bond to the metal centre [$2.8701(6)\text{\AA}$] is formed than from molybdenum to the other iodide ligand in the structure [$2.8113(8)\text{\AA}$] which is *trans* to a bipy coordination site. The coordination geometry is in reasonable agreement with that observed in other

complexes containing one alkyne coordination site and approximating octahedral geometry, $[\text{MoI}_2(\text{CO})(5,6\text{-Me}_2\text{-1,10\text{-phen}})(\eta^2\text{-PhC}_2\text{Ph})]$ [21], $[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ [22], $[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Et})]$ and $[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Et})]$ [16]. It is interesting to note that when comparing the complex most analogous to **1**, $[\text{MoI}_2(\text{CO})(5,6\text{-Me}_2\text{-1,10\text{-phen}})(\eta^2\text{-PhC}_2\text{Ph})]$, coordination geometries are similar, whilst the *trans*- effect is greater in (**1**), which is presumably due to the greater electronic demands of the $\eta^2\text{-PhC}_2\text{Ph}$ ligand in comparison to $\eta^2\text{-EtC}_2\text{Et}$.

The infrared spectrum of **1** has, as expected, a carbonyl band at $\nu(\text{C}=\text{O}) = 1946\text{ cm}^{-1}$, and an alkyne, $\nu(\text{C}\equiv\text{C})$ band at 1641 cm^{-1} . The carbonyl and the alkyne stretching bands are in the expected regions for this type of complex [1,2,22]. The room temperature ^1H NMR (CDCl_3 , $+25^\circ\text{C}$) spectrum for complex **1** conforms with the structure shown in Fig. 1. The ^{13}C NMR spectrum (CDCl_3 , $+25^\circ\text{C}$) shows an alkyne contact carbon

resonance at $\delta = 211.95$ ppm, which from Templeton and Ward's [23], correlation of the number of electrons donated by an alkyne, and its ^{13}C NMR alkyne contact carbon chemical shifts suggests that the 3-hexyne is utilising both its filled $p\pi$ -orbitals and donating four electrons to the molybdenum. This also enables complex **1** to obey the effective atomic number rule.

It is interesting to note that the product from the reaction of equimolar quantities of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ and bipy is the cationic complex, $[\text{Wl}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]\text{I}$ (**2**). This different reactivity is likely to be due to the greater lability of molybdenum complexes compared to their analogous tungsten complexes in the same oxidation state. After the acetonitrile is replaced, the more labile 3-hexyne is displaced for $\text{M} = \text{Mo}$, whereas for $\text{M} = \text{W}$ the iodo ligand is displaced in preference to the more strongly bonded 3-hexyne ligand. The cationic bis(3-hexyne) complex, $[\text{Wl}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]\text{I}$ (**2**), is closely related to the previously reported bis(2-butyne) complex, $[\text{Wl}(\text{CO})(\text{bipy})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ [24], which has been crystallographically characterised. Their IR properties (CHCl_3) are very similar {for **2**, $\nu(\text{CO}) = 2053 \text{ cm}^{-1}$; for $[\text{Wl}(\text{CO})(\text{bipy})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$, $\nu(\text{CO}) = 2052 \text{ cm}^{-1}$ }. Hence, the structure of **2** is likely to be as shown in Fig. 2.

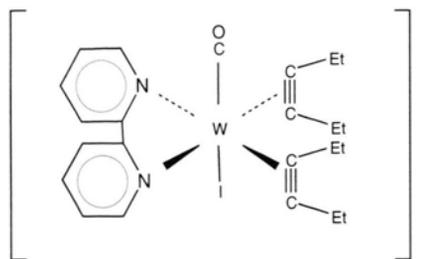


Fig. 2. Proposed structure of $[\text{Wl}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]\text{I}$ (**2**).

In conclusion, we have shown that two analogous complexes, $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ($\text{M} = \text{Mo}, \text{W}$) react in two different ways with bipy to give either the crystallographically characterised neutral complex, $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]$ (**1**) or the cationic complex, $[\text{Wl}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]\text{I}$ (**2**).

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