

REACTION OF 2,2-BIPYRIDINE COMPOUND WITH 2-PENTYNE COMPLEXES OF MOLYBDENUM (II) AND TUNGSTEN (II)

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تعتبر مركبات المولبدنيوم والتنجستون ذات الأنظمة التناسقية السبعة لديها المقدرة العالية على تكوين مركبات جديدة ومتنوعة، ومن تلك المعقدات $[M_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ ($M = Mo, W$) حيث أنه يتفاعل مع 2,2-Bipyridine ليكون نوعين من المركبات معتمداً على نوعية M حيث يكون مع المولبدنيوم معقد متعادل، (1) $[Mo_2(CO)(bipy)(\eta^2-EtC_2Me)]$ ومع التنجستون معقد كاتيوني وهو (2). $[W(CO)(bipy)(\eta^2-EtC_2Me)_2] I. (2).$

Seven coordinate complexes of $[M_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ ($M = Mo, W$) with one equivalent of 2,2-bipyridine (bipy) in CH_2Cl_2 at room temperature gives two kind of complexes depends on M. If $M = Mo$ gives neutral complex $[Mo_2(CO)(bipy)(\eta^2-EtC_2Me)]$ (1) and If $M = W$, the complex was Cationic: $[W(CO)(bipy)(\eta^2-EtC_2Me)_2] I. (2).$

INTRODUCTION

Since fifteen years ago, the halocarbonyl alkyne chemistry of molybdenum(II) and tungsten (II) has been very well developed. [1-15]. In 1999, [16] we described the synthesis and reactions of seven coordinate complexes with 3-hexyne to produce: $[M_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ ($M = Mo$ and W) and following by reaction with phosphines ligands. Two of the reaction products with phosphine ligands were crystallographically characterized namely $[W_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)]$ and $[W_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2-EtC_2Et)]$.

In 2000 [17], we described the reaction of 3-hexyne complexes of Molybdenum(II) and Tungsten(II) containing 2,2-Bipyridine, and in the same paper we described X-ray crystal structure of $[Mo_2(CO)(bipy)(\eta^2-EtC_2Et)]$.

In 2002, P.K.Baker *et al* [18] prepared the nitrile exchanged products, $[W(CO)L\{P(O^iPr)_3\}_2(\eta^2-MeC_2Me)][BPh_4]$ from reaction of $[W(CO)(NCMe)\{P(O^iPr)_3\}_2(\eta^2-MeC_2Me)][BPh_4]$ and L {L= Net, NC^iPr , NC^iBu , $NCPh$, $NCCH_2Ph$, $1,2-C_6H_4(NCCH_2)_2$, $NCCH_2-(C_4H_3S-3)$ }; and the complexes for L= NC^iPr , NC^iBu , $NCCH_2Ph$, $1,2-C_6H_4(NCCH_2)_2$ have all been crystallographically characterized.

In 2003, Oktay and others[19], reacted pentacarbonyl (η^2 - bis (tri methylsilyl) ethyne) tungsten(0), $[W(CO)_5(\eta^2-btmse)]$ with tricyclohexylphosphine PCy_3 to yield two stable endoproducts which could be isolated and fully characterized by using the single crystal x-ray diffractometry. In this paper we describe the differing reactivity of the bis (2-Pentyne) complexes $[M_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ with 2,2-bipyridine to give neutral molybdenum complex $[Mo_2(CO)(bipy)(\eta^2-EtC_2Me)](1)$ and the cationic tungsten complex $[W(CO)(bipy)(\eta^2-EtC_2Me)_2]I(2).$

EXPERIMENTAL

Physical measurements and instruments:

Elemental analysis (C, H and N) were determined using a carlo Erba Elemental Analysis MoD 1108 (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 ^{13}C NMR spectra were recorded in a Bruker AC 500MH₂. NMR spectrometer and referenced to $SiMe_4$.

The ^{13}C . NMR spectrum (CDCl_3 , + 25 $^\circ\text{C}$) shows an alkyne contact carbon resonance at $\delta = 209.86$ ppm, which from Templeton and Ward's [21]. Correlation of the number of electrons donated by an alkyne, and its ^{13}C . NMR alkyne

contact carbon chemical shifts suggests that the 2-Pentyne is utilizing both its filled $\text{P}\pi$ -orbitals and donating four electrons to the molybdenum. This also enables complex 1 to obey the effective atomic number ruler:

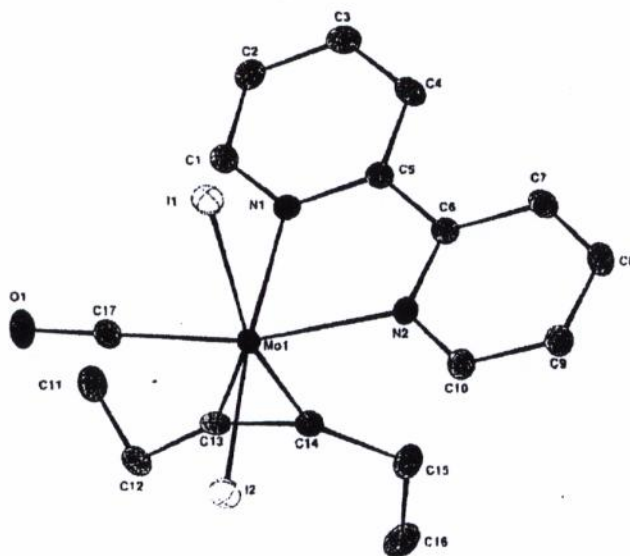


Fig. 1: The structure of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ with the atom numbering scheme. Ellipsoids are shown at 30 % probability.

The reaction of equimolar quantities of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ and bipy is the cationic complex $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})_2]$ 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.

When $M = \text{Mo}$ the acetonitrile is replaced, whereas for $M = \text{W}$ the iodo ligand is displaced in preference to the more strongly bonded 2-Pentyne ligand. The cationic bis (2-Pentyne) complex, $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})_2]$ I (2), is closely related to the previously reported bis (3-hexyne), $[\text{WI}(\text{CO})(\eta^2\text{-EtC}_2\text{Et})_2]$ I [17] and as well bis (2-butyne) complex, $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-MeC}_2\text{Me})_2]$ $[\text{BPh}_4]$ [22] which has been crystallogradically characterized.

IR. properties for complex (2) are very similar where carbonyl at $\nu(\text{CO}) = 2051 \text{ cm}^{-1}$ and for $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})_2]$ I at $\nu(\text{CO}) = 2053 \text{ cm}^{-1}$, and for $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-MeC}_2\text{Me})_2]$ $[\text{BPh}_4]$ at $\nu(\text{CO}) = 2052 \text{ cm}^{-1}$. Hence, the structure of (2) is likely to be as shown in Fig. 2.

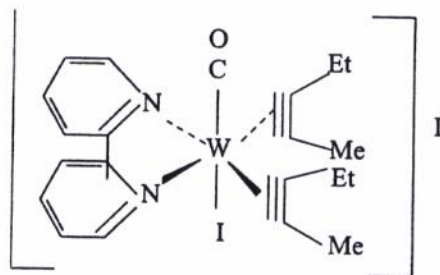


Fig. 2: Proposed structure of $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})_2]$ I (2)

In conclusion, we have shown that two analogous complexes, $[M_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ ($M = Mo, W$) react in two different ways with bipy to give either the neutral complex, $[M_2(CO)(bipy)(\eta^2-EtC_2Me)](1)$ or the cationic complex, $[W(CO)(bipy)(\eta^2-EtC_2Me)_2]I(2)$.

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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 $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by the literature of preparation of 3-hexyne complexes [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 $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})]$ (1):

To a stirred solution of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.2 g, 0.36 mmol) in 20 ml of CH_2Cl_2 at room temperature was added bipy (0.06 g, 0.38 mmol). The solution was stirred at room temperature for 24 hr. Filtration, followed by removal of the solvent in vacuum gave a crystalline powder $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})]$ (1). Which we still try to recrystallized from different solvents. (yield = 0.14 g, 63 %). IR (CHCl_3 film): $\nu = 1943(\text{s}) (\text{C}=\text{O}) \text{ cm}^{-1}$; $\nu = 1637(\text{w}) (\text{C}\equiv\text{C}) \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 25 $^\circ\text{C}$) ($\delta = 9.3 \rightarrow 7.3$) (v. br, 8H, 2, 2-bipyridyl); 1.6(s, 3H, CH_3); 3.6(q, 2H, 2, CH_2); 1.3(t, 3H, 1 CH_3). $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (CDCl_3 , 25 $^\circ\text{C}$) $\delta = 16.30, 18.90$ (2.5, 2 CH_3); 34.22 (1s, 1 CH_2); 121.52, 123.56, 127.2, 131.03, 135.67, 137.06 (6s, 2,2=bipyridyl); 210.97 (s, $\text{C}\equiv\text{C}$); 227.36 (s, $\text{C}=\text{O}$). $\text{C}_{16}\text{H}_{16}\text{N}_2\text{OI}_2\text{Mo}$ (602): calcd C:31.8 %, H:2.65, N:4.65; found C:31.3, H:2.57, N:4.48.

Preparation of $[\text{WI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})_2]$ I. (2)

To a stirred solution of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.2 g, 0.30 mmol) in 20 ml of CH_2Cl_2 at room temperature was added bipy (0.050 g, 0.32 mmol). The reaction was stirred at room temperature for 24 hr. Filtration, followed by removal of the solvent in vacuo gave a yellow crystalline powder, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (50:50, ratio) at -17°C to give the pure product $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})_2]$ I. (2) (yield = 0.12 g, 52%). IR (CHCl_3 film); $\nu = 2058(\text{s}) (\text{C}=\text{O}) \text{ cm}^{-1}$; $\nu = 1612(\text{w}) (\text{C}\equiv\text{C}) \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3 , +25 $^\circ\text{C}$) $\delta = 9.3\text{-}7.1$ (v br, 8H, 2,2-

bipyridyl); 3.2 (q, 4H, $\equiv\text{CCH}_3$); 1.2 (t, 6H, $\equiv\text{CCH}_2\text{CH}_3$); 2.6 (s, 6H, $\equiv\text{CCH}_2$). $\text{C}_{21}\text{H}_{24}\text{N}_2\text{OI}_2\text{W}$ (758): calcd. C:33.0; H:3.1; N:3.7; found C:33.2, H:3.3, N:3.8.

RESULTS AND DISCUSSION

The starting materials used in this research, namely $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by reacting the seven-coordinate complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ with 2-Pentyne.

Equimolar quantities of $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ and 2,2-bipy react in CH_2Cl_2 at room temperature to give either the neutral molybdenum(II) complex $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})]$ (1) via displacement of the acetonitrile ligand and a 2-Pentyne, or the cationic tungsten (II) complex $[\text{WI}(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})_2]$ I. (2) via displacement of the acetonitrile and an iodo ligand.

Complexes 1 and 2 have been characterized by elemental analysis, IR and $^1\text{H NMR}$ spectroscopy, and complex (1) by $^{13}\text{C NMR}$ spectroscopy. (See experimental details).

Complexes 1 and 2 are air-sensitive in solution, but can be stored in the solid state for several months at -17°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 hydrocarbones. Complex 1 is more soluble in CHCl_3 than complex 2, hence it was not possible to obtain a high quality $^{13}\text{C NMR}$ spectrum of complex 2.

We still trying to obtain suitable single crystal of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Me})]$ (1) according to paper [17] about single crystal $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ which were grown by cooling a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (50:50 ratio) solution of complex to -17°C . (The structure is shown in Fig. 1).

The infrared spectrum of 1 has as expected a carbonyl band at $\nu(\text{C}=\text{O}) = 1948 \text{ cm}^{-1}$ and an alkyne $\nu(\text{C}\equiv\text{C})$ band at 1639 cm^{-1} . The carbonyl and the alkyne stretching bands are in the expected regions for this type of complex [1,2,20].

The room temperature $^1\text{H NMR}$ (CDCl_3 , +25 $^\circ\text{C}$) spectrum for complex 1 confirms when we compared by single crystal structure of $[\text{MoI}_2(\text{CO})(\text{bipy})(\eta^2\text{-EtC}_2\text{Et})]$ [17].