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

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INTRODUCTION

Since fifteen years ago, the halocarbonyl alkyne chemistry of molybdenum (II) and tungsten (II) has been very well developed. In 1999, we described the synthesis and reactions of seven coordinate complexes with 3-hexyne to produce: [Ml₂(CO)(NMe)(η²-EC₂Et₂)] (M = Mo and W) and following by reaction with phosphines ligands. Two of the reaction products with phosphine ligands were crystallographically characterized namely [Ml₂(CO)(PPPh₃)₂(η²-EC₂Et₂)] and [Ml₂(CO)(PPh₂(CH₃)₂PPh₂)(η²-EC₂Et₂)].

In 2000, 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 [Mo₂(CO)₂(bipy)(η²-EC₂Et₂)].

In 2002, P.K.Baker et al. prepared the nitrite exchanged products, [WI(CO)L(P(O)OPr)₂(η²-MeC₂Me)][BPh₄] from reaction of [WI(CO)(NCH₂Me)(P(O)OPr)₂(η²-MeC₂Me)][BPh₄] and L (L= Net, NCPr, NCBu, NCPPh, NCCPh₂, 1,2-C₂H₄(NCH₂)₂, NCH₂(2,4,2-CH₂S-3)); and the complexes for L= NCPr, NCBu, NCCPh₂, 1,2-C₂H₄(NCH₂)₂ have all been crystallographically characterized.

In 2003, Oktay and others reacted pentacarbonyl bis(tri methylsilyl) ethyne) tungsten(0), [W(CO)₅(η²-btmse)] with tricyclohexylphosphine PCY₃ to yield two stable endoprodutcs which could be isolated and fully characterized by using the single crystal x-ray diffractomtr. In this paper we describe the differing reactivity of the bis (2-Pentyne) complexes [Ml₂(CO)(NMe)(η²-EC₂Me₂)] with 2,2-bipyridine to give neutral molybdenum complex [Mo₂(CO)₂(bipy)(η²-EC₂Me₂)] and the cationic tungsten complex [WI(CO)₂(bipy)(η²-EC₂Me₂)](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 CHCl₃ films between NaCl plates and recorded on a perkin-Elmer 1430 ratio recording IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in a Bruker AC 500 MHZ. NMR spectrometer and referenced to SiMe₄.
The $^{13}$C NMR spectrum (CDCl$_3$ + 25 C$^\text{o}$) 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 it’s $^{13}$C NMR alkyne contact carbon chemical shifts suggests that the 2-Pentyne is utilizing both it’s filled $\pi$ -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 [Mo$_2$(CO)(bipy)(\eta^2-Et(\text{C}_3\text{Et})] with the atom numbering scheme. Ellipsoids are shown at 30% probability.

The reaction of equimolar quantities of [WI$_2$(CO)(NMe)(\eta^2-EtC\text{Me})$_2$] and bipy is the cationic complex [WI(CO)(bipy)(\eta^2-EtC\text{Me})$_2$] 1 (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 = Mo the acetonitrile is replaced, whereas for M=W the iodo ligand is displaced in preference to the more strongly bonded 2-Pentyne ligand. The cationic bis (2-Pentyne) complex, [WI(CO) (bipy)(\eta^2-EtC\text{Me})$_2$] 1 (2), is closely related to the previously reported bis (3-hexyne), [WI(CO)(\eta^2-EtC\text{Et})$_2$] 1 [17] and as well bis (2-butyne) complex, [WI(CO)(bipy)(\eta^2-MeC\text{Me})$_2$] [BPh$_4$] [22] which has been crystallographically characterized.

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

Fig. 2: Proposed structure of [WI(CO)(bipy)-(\eta^2-EtC\text{Me})$_2$] 1 (2)
In conclusion, we have shown that two analogous complexes, \([\text{M}_2(\text{CO})(\text{NMe})_3](\eta^5-\text{EtC}_2\text{Me}_5)]\) (M = Mo, W) react in two different ways with bipy to give either the neutral complex, \([\text{M}_2(\text{CO})(\text{bipy})\ (\eta^5-\text{EtC}_2\text{Me}_5)]\) (1) or the cationic complex, \([\text{W}_3(\text{CO})(\text{bipy})(\eta^5-\text{EtC}_2\text{Me}_5)]^+\) (2).

REFERENCES

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 [M(η₄-CO)(NCMe)(η²-EtC₂Me₃)]₂ (M = Mo, 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 [MoI₂(CO)(bipy)(η¹-EtC₂Me)]

(1):

To a stirred solution of [MoI₂(CO)(NCMe)- (η¹-EtC₂Me₂)] (0.2 g, 0.36 mmol) in 20 ml of CH₂Cl₂ 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 vacuo gave a crystalline powder [MoI₂(CO)(bipy)(η¹-EtC₂Me₂)] (1). Which we still try to recrystallized from different solvents. (yield = 0.14 g, 63%). IR (CHCl₃ film): ν = 1943(s) (C=O) cm⁻¹; ν = 1637 (w) (C=C) cm⁻¹; ¹H NMR (CDCl₃, 25C) δ = 9.3 → 7.3 (ν br, 8H, 2, 2-bipyridyl); 1.6(s, 3H, CH₃); 3.6(q, 2H, 2, CH₂); 1.3(t, 3H, 1CH₃); ¹³C(¹H)NMR (CDCl₃, 25 C) δ = 16.30, 18.90 (2.5, 2CH₂); 34.22 (1s, 1CH₂); 121.52, 123.56, 127.2, 131.03, 135.67, 137.06 (6s, 2,2-bipyridyl); 210.97 (s, C=O); 227.36 (s, C=O). C₁₆ H₁₆ N₂ O₁ Mo (602): calculated C:31.8 %, H:2.65, N:4.65; found: C:31.3, H:2.57, N:4.48.

Preparation of [WI₂(CO)(bipy)(η¹-EtC₂Me₂)]

(2)

To a stirred solution of [WI₂(CO)(NCMe)- (η¹-EtC₂Me₂)] (0.2 g, 0.30 mmol) in 20 ml of CH₂Cl₂ at room temperature was added bipy (0.05 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 CH₂Cl₂/CH₃OH (50:50, ratio) at -17 °C to give the pure product [WI₂(CO)(bipy)(η¹-EtC₂Me₂)] (2) (yield 0.12 g, 52%). IR (CHCl₃ film): ν = 2058 (s) (C=O) cm⁻¹; ν = 1612 (w), (C=C) cm⁻¹. ¹H NMR (CDCl₃, +25°C) δ = 9.3 → 7.1 (ν br, 8H, 2,2-

bipyridyl); 3.2(q, 4H, =CCH₃); 1.2(t, 6H, =CCH₂CH₃); 2.6(s, 6H, =CCH₃).

C₁₁H₃₂N₂O₂W (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 [MoI₂(CO)(NCMe)(η²-EtC₂Me₂)] (M = Mo, W) were prepared by reacting the seven-coordinate complexes [MoIV(CO)₃(NCMe)₂] with 2-Pentyne.

Equimolar quantities of [MoI₂(CO)(NCMe)(η²- EtC₂Me₂)] and 2,2'-bipy react in CH₂Cl₂ at room temperature to give either the neutral molybdenum(II) complex [MoI₂(CO)(bipy)(η²- EtC₂Me₂)](1) Via displacement of the a cetonitrile ligand and a 2-Pentyne, or the cationic tungsten (II) complex [WI₂(CO)(bipy)(η²-EtC₂Me₂)] (2) via displacement of the acetonitrile an an iodo ligand.

Complexes 1 and 2 have been characterized by elemental analysis, IR and ¹H NMR spectroscopy, and complex (1) by ¹³C 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 CH₂Cl₂ and CHCl₃, but only slightly soluble (1) or insoluble (2) in diethyl ether and hydrocarbons. Complex 1 is more soluble in CH₂Cl₂ than complex 2, hence it was not possible to obtain a high quality ¹³C NMR spectrum of complex 2.

We still trying to obtain suitable single crystal of [MoI₂(CO)(bipy)(η²-EtC₂Me₂)] (1) according to paper [17] about single crystal [MoI₂(CO)(bipy)(η²-EtC₂Et)] which were grown by cooling a CH₂Cl₂/CH₃OH (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 v(C=O) =1948 cm⁻¹ and an alkyne v(C≡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 ¹H NMR (CDCl₃, +25 °C) spectrum for complex 1 confirms when compared by single crystal structure of [MoI₂(CO)(bipy)(η²-EtC₂Et)] [17].