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- **Title:- 1-10 phenanthroline with 2-pentyne in Seven coordinate complexes of Molybdenum(II) and Tungsten(II)**

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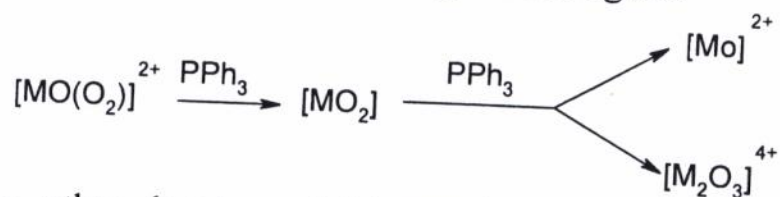
Abstract :

Seven coordinate complexes of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ (M=Mo, W) with equivalent of 1,10-phenanthroline (1,10-phen) in CH_2Cl_2 at room temperature gave two kinds of complexes depends on the type of metal. In Case of Molybdenum a neutral complex $[MoI_2(CO)(1,10-phenanthroline)(\eta^2-EtC_2Me)](1)$ was obtained while in the Case of Tungsten a Cationic complex $[WI(CO)(1,10-phenanthroline)(\eta^2-EtC_2Me)_2] I. (2)$ produced. Electronic absorption spectra of $[M(CO)_4](phen)$ showed a strong band in the visible region Spectrum, due to metal \rightarrow ligand charge transfer (MLCT) $M \rightarrow phen$ and or $M \rightarrow CO_{ax}$ characterized by a highly molar absorptivity.

1-Introduction:-

Triphenylphosphine has played an important role, through transfer of oxygen from dioxo complexes $[MO_2]^{2+}$ (M=Mo, or W), in the development of the chemistry of $[MO]^{2+}$ and $[M_2O_3]^{4+}$ cations¹. Very recently, Maura *etal*² used triphenylphosphine in the conversion of oxoperoxo complexes of Molybdenum(VI) and tungsten (VI) into the corresponding dioxo species² Thus, starting from oxoperoxo

complexes $[\text{MO}(\text{O}_2)]^{2+}$ ($\text{M}=\text{Mo}$ or W), the following species can be stabilized depending upon the design of the ligand³



On the other hand, molybdenum (II) and tungsten (VI) of halocarbonyl alkyne used for the formation of many complexes⁴⁻⁶. We are interested in this area by reaction of bis-(2-pentyne)complexes $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with 2,2-bipyridyl were formed two kinds of products $[\text{MoI}_2(\text{CO})(\text{bipyrid})(\eta^2\text{-EtC}_2\text{Me})]$ and the cationic tungsten complex $[\text{WI}(\text{CO})(\text{bipyrid})(\eta^2\text{-EtC}_2\text{Me})_2]$ ⁵. However, the molybdenum(II) and tungsten(II) of halocarbonyl alkyne chemistry has been prepared and characterized many complexes⁵⁻²⁰.

Also, reaction of amidinato (pyridine) complexes of molybdenum and tungsten with triethyl borane adduct of N-heterocyclic carbene($\text{NHC}\cdot\text{Bet}_3$).²¹

While, reaction of lithiated ferrocene with bipyridine and employed as a bidentate ligand for formation of tetra carbonyl (6-ferrocenyl-2,2'-bipyridine)tungsten(0) was reported.²²

The labile complex penta carbonyl $[\eta^2\text{-bis}(\text{trimethylsilyl})\text{ ethyne}]$ tungsten(0) reacts with fcbpy in CH_2Cl_2 to yield the disubstitution product, $\text{W}(\text{CO})_4(\text{fcbpy})$.²² structure of this Complex as Fig.1.

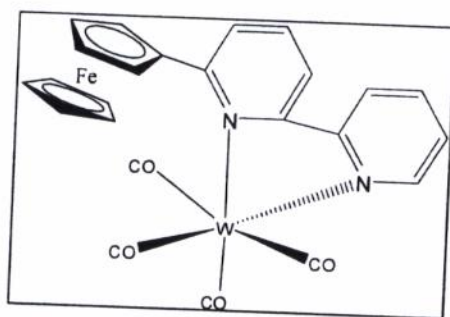


Fig.(1) The proposed structure of $[\text{W}(\text{CO})_4(\text{fcbpy})]$.

In the present investigation, we describe the isolation and characterization of two types of complexes by treatment of some coordinate complexes-mainly based on presence of Mo and or W-

with one equivalent of 1,10-phenanthroline and 2-penyne in CH_2Cl_2 medium at room temperature.

2-Distribution

The reaction between 1,10-phenanthroline and or 2-bipyridyl with $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ and or $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})]$ in CH_2Cl_2 at room temperature for 24h after isolation produced a type of coordinated complexes $[\text{MoI}_2(\text{CO})(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})]$ (1) and or $[\text{WI}(\text{CO})(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})_2]$ I (2) [Fig.2&3] respectively.

3-Experimental:-

Preparation of $[\text{MoI}_2(\text{CO})(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})]$ (1). To a stirred solution of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.3g, 0.54mmol) in 20ml of CH_2Cl_2 at room temperature was added 1,10-phenanthroline (0.11g, 0.55mmol). The solution was stirred at room temperature for 24hr. Filtration, followed by removal of the solvent in vacum gave a crystalline powder $[\text{MoI}_2(\text{CO})(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})]$ (1). (yield=0.2g, 66 %). IR (CHCl_3 film): $\nu = 1940(\text{s}) (\text{C}\equiv\text{O}) \text{ cm}^{-1}$; $\nu = 1632 (\text{w}) (\text{C}\equiv\text{C}) \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 25°C) ($\delta = 9.2 \rightarrow 7.0$) (v. br, 8H, 1,10-phenanthroline); 1.6(s, 3H, CH_3). 3.2(q, 2H, 2, CH_2); 1.1(t, 3H, 1 CH_3). $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (CDCl_3 , 25°C) $\delta = 16.35, 19.00$ (2s, 2 CH_3); 34.0 (1s, 1 CH_2); 122.98, 126.40, 129.0, 146.05, 150.17, (ms, 1,10-phenanthroline); 212.95 (s, $\text{C}\equiv\text{C}$); 230.26 (s, $\text{C}\equiv\text{O}$). C17 H16 N2 OI2 Mo (614): calcd C: 33.2 %, H: 2.6, N: 4.5; found C: 32.9, H: 2.33, N: 4.1 .

Preparation of $[\text{WI}(\text{CO})(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})_2]$ I.(2) To a stirred solution of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})]$ (0.3g, 0.45mmol) in 25ml of CH_2Cl_2 at room temperature was added 1,10-phenanthroline (0.09g, 0.45mmol). The reaction was stirred at room temperature for 24hr. Filtration, followed by removal of the solvent in vacum gave a yellow crystalline powder, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (50.50, ratio) at -15°C to give the pure product $[\text{WI}(\text{CO})(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})_2]$ I.(2) (yield=0.25g, 73%). I.R (CHCl_3 film); $\nu = 2046 (\text{s}) (\text{C}\equiv\text{O}) \text{ cm}^{-1}$; $\nu = 1618 (\text{w}) (\text{C}\equiv\text{C}) \text{ cm}^{-1}$. $^1\text{H. NMR}$ (CDCl_3 , $+25^\circ\text{C}$) $\delta = 8.9-6.5$ (v br, 8H, 1,10-

phenanthroline); 3.4 (q, 4H, \equiv CCH₃); 1.3 (t, 6H, \equiv CCH₂CH₃); 2.7 (s, 6H, \equiv CCH₂).

C₂₂H₂₄N₂OI₂W (770): calcd. C: 34.3; H: 3.1; N :3.6; found C: 34.1, H: 2.9, N :3.2 .

4-Results and Discussion:-

Due to unstability of complexes **1** and **2** formed in solution by air-sensitive, thus can be by keptd stord in a solid state at-17C^o for long months. On the other hand , these complexes was obtained are highly soluble in polar solvents especially chlorinated solvents such as CH₂Cl₂, and CHCl₃ . In addition, the formed new complexes are slightly soluble and or in soluble in diethyl ether and hydro carbons. Especcially complexes **1** is more so luble than other the complex **2** in CHCl₃. Thus, it was not possible to obtain in highly qualidy ¹³C-NMR spectrum of complex **2**.

The infrared spectrum of complex **1** showed the absorption band at ν 1940 cm⁻¹ due to presence of C=O group, and at ν 1636 cm⁻¹ attribute to alkyne (C \equiv C) group. In addition, the carbonyl and alkyne stretching bands which agree the expected regions of this type of complex [45.20]. On the other hand, temperature ¹H. NMR(CDCl₃, + 25 Co) spectrum for complex **1** gave aresonated singls confirmed the postulated structure (Fig.2) . Final structure of complex **1** can be deduced by comparied a Similar single-crystal structure of [MoI₂(CO)(bipy)(η^2 -EtC₂Et)]¹⁷ [Fig-4].

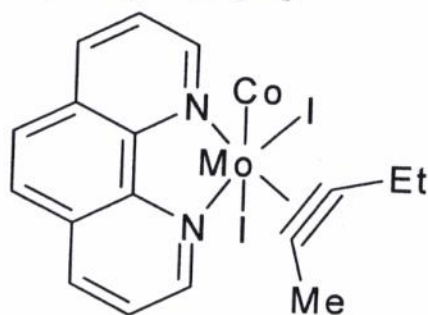


Fig2-The proposed structure of [MoI₂(CO)(1,10-phenanthroline)(η^2 -EtC₂Me)](1)

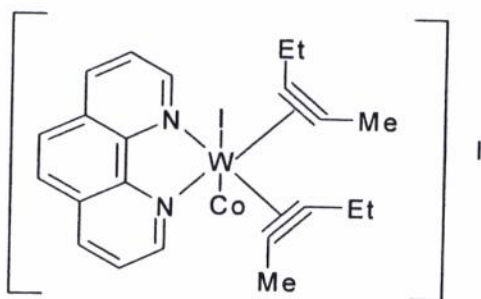


Fig3- The structure of $[W(CO)(1,10\text{-phenanthroline})(\eta^2\text{-EtC}_2\text{Me})_2]I$

With the atom numbering Scheme. Ellipsoids are showed at 3% probability. ^{13}C -NMR spectrum (CDCl_3 , $+ 25^\circ\text{C}$) of complex **1** showed an alkyne contact carbon resonance at $\delta = 230.26$ ppm, agreement of observations Templeton and ward's [21]. Correlation of 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 $P\pi$ -orbitals and ^{13}C . NMR spectrum (CDCl_3 , $+ 25^\circ\text{C}$) shows an alkyne contact carbon resonance at $\delta = 230.26$ 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 $P\pi$ -orbitals and donating four electrons to the molybdenum. This also enables complex **1** to obey the effective atomic number ruler

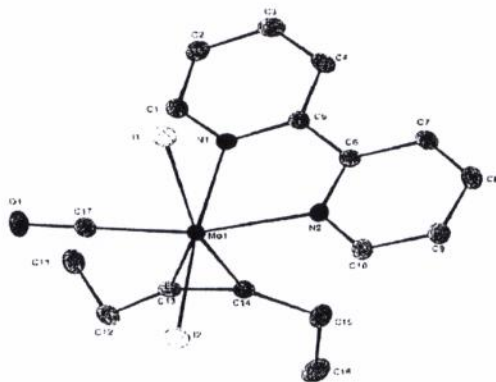


Fig (4). The structure of $[MoI_2(CO)(bipy)(\eta^2\text{-EtC}_2\text{Et})]$ with the atom numbering scheme. Ellipsoids are shown at 30 % probability.

During the Course of our studies we reported that reaction of equimolar quantities of $[Wl_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ and 1,10-phenan is the cationic complex $[Wl(CO)(1,10-phenan)(\eta^2-EtC_2Me)_2] I.(2)$. 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.

Donating four electrons to the molybdenum This, enables of complexe **1** to obey the effective atomic number ruler.

During the Course of our studies we reported that, reaction of equimolar quantity of $[Wl_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ and 1,10-phenan is the cationic complexe $[Wl(CO)(1,10-phenan)(\eta^2-EtC_2Me)_2] I (2)$.

The diller reactivities of both Mo than W may be due to greater ability of molybdenum complexes compared to the analogous tungsten complexes in the same oxidation state.

From above study, we can be concluded that when two analogous complexes : $[Ml_2(CO)(NCMe)(\eta^2-EtC_2Me)_2]$ (M=Mo, W) react in two different methods with bipy to give either the neutral complex in case of Molybdenum (**1**) and the cationic complexe in case Tungsten. (**2**).

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