Synthesis and Structural Determination of Allyl-complexes of Molybdenum and Tungsten by Spectroscopic Methods (IR, NMR, MS and X-ray Diffraction Studies)

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Summary: Synthesis and characterization of η^3–allyl complexes of molybdenum and tungsten of the type $[MX(CO)_2L_2(\eta^3\text{-allyl})]$. A numbers of crystal structures have been determined and discussed, NMR, IR and MS spectra were also taken to determine the Structure of the complexes.

Introduction

Complexes of the general formula $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ in which X is either a halide or seudohalide and L_2 can be a wide range of bidentate and monodentate neutral ligands, have been known [1] since 1968. The first reported compounds aere $[MoX(CO)_2(MeCN)_2(\eta^3\text{-allyl})]$ (X= Cl, Br, I, SCN; allyl= C_3H_5, C_4H_7, C_3H_4Cl, cis-hexenyl) obtained by the reaction of either $[Mo(CO)_6]$ in acetonitrile or $[Mo(CO)_3(MeCN)_3]$ with alkyl halide [2]. The labile acetonitrile molecules can be replaced by other ligands to give $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ (L_2= bipy, phen, diphos etc). When the bis-acetonitrile complexes are heated in benzene, the dimmers $[\{Mo(CO)_2(MeCN)(\eta^3\text{--allyl})\}_2(\mu\text{-}X)_2]$ are formed. These in turn reat with pyridine to give $[MoX(CO)_2py_2(\eta^3\text{-allyl})]$ Complexes of formula $[MoA(CO)_2py(\eta^3\text{-}C_3H_5))]$ (A = acac, R_2NCS_2) have been prepared by treating $[MoCl(CO)_2(bipy)(\eta^3\text{-}C_3h_5)]$ with $[A]^-$ in the presence of pyridine [3]. Treatment of $[MoCl(CO)_2\{di(2\text{-pyridyl})amine\}(\eta^3\text{-}C_3H_5)]$ with 2-formylphenolate, $PhNH_2$, and Pyridine gives complex $[Mo(acac)(CO)_2(py)(\eta^3\text{-}C_3H_5)]$, X-ray structural studies reveal that complex adopt the coordination geometry.

$[W_2Cl_3(CO)_6(\eta^3\text{-}C_3H_5)$ is formed when $[W(CO)_6]$ is reacted with allyl chloride under UV radiation, but with the other allyl halides, $[WX(CO)_4(\eta^3\text{-}C_3H_5)]$ (X = Br, I) is formed. The structure of the dimmer is unknown but is thought to contain bridging chloride atoms. . The bromo and iodo complexes both exist as mixture of two isomers and react with bipy (L_2), PPh_3 triphenyl phosphine and py (L) to afford $[WX(CO)_2L_2(\eta^3\text{-}C_3H_5)]$[4].

Recently new complexes derived via substitution of acetonitrile in $[MX(CO)_2(NCMe)_2(\eta^3\text{-allyl})]$ have been prepared. $[MoX(CO)_2(R^1{}_2PCH_2CH_2PR^2{}_2)(\eta^3\text{-}C_3H_5)]$ (X= Br or Cl; R=Ph, R_2=C_6H_4F or $C_6H_4CF_3$, R_1=R_2=C_6H_4Me) and the semicarbazone [5-7] (E=O) and thiosemicarbazone (E=S) complex $[MoX(CO)_2\ \{E=C(NH_2)NHN=CR_2\}(\eta^3\text{-allyl})]$ (X= halide; R=alkyl or aryl)

The carboxylate complexes $[Mo(O_2CR_2)(CO)_2(bipy)(\eta^3\text{-}C_3H_4R^1)(R^1$=H or Me; R^2=CF_3, C_2F_5 etc) may be obtained by sequential treatment of $[MoCl(CO)_2(bipy)\ (\eta^3\text{-}C_3H_4R)]$ with $AgBF_4$ then NaO_2CR_2,. In the case of $[Mo(O_2CCF_3)(CO)_2(bipy)(\eta^3\text{-}C_3H_5)]$, NMR studies reveal two coexistent isomeric forms [8].

X-ray crystallographic studies on $[Mo(NCS)(CO)_2(phen)\{(\eta^3\text{-}(1\text{-syn-Ph})\text{-}C_3H_4\}]$ [9] and $[\{Mo(CO)_2(bipy)(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-Cl})]^+$ [10] show the expected ligand arrangement in which the halide or pseudohalide ligand is located trans to the allyl ligand. An additional feature of interest is the asymmetry in the Mo-allyl(C)distances [Mo-C(1) 2.29(4) A; Mo-C(3) 2.311(5) A]. The confermational preference of allyl ligand in $MX(CO)_2L_2$ $(\eta^3\text{-allyl})]$, in which the open face of the allyl ligand points toward the carbonyl has been rationalized by a molecular orbital analysis [11].

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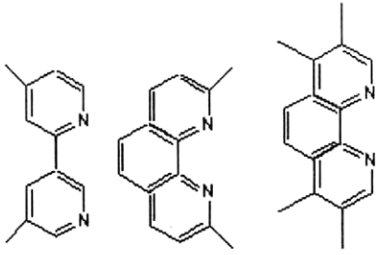
This work concern the synthesis of novel η^3–allyl complexes of general formula $[MX(CO)_2L_2(\eta^3$-allyl)] (M=Mo, W; X=halide; L_2=substituted bipy and phen derivatives and dppe). It then goes to discuss the reactivity of these complexes and attempt to prepare novel oxatrimethylenemethane complexes of molybdenum and tungsten.

Results and Discussion

Spectroscopic and Structural Properties of Ally Complexes.

Treatment of $[MoCl(CO)_4L_2]$ with allyl chloride in refluxing THF afforded η^3–allyl complexes $[MoCl(CO)_2L_2(\eta^3$-$C_3H_5)]$ (complex 1) (L_2= 4,4-dimethyl-2,2-bipyridine (dmb) (complex 2) (L_2= 2,9-dimethyl-1,10-phenanthroline (dmp)) and (complex 3) (L_2= 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp)) in good yield, (Fig1) iodide analogue (complex 4) has also been prepared. From the ^1H NMR spectrum it can be seen that the tmp derivatives exist as a pair of isomers, as these isomers are assumed to be due to the arrangement of the allyl ligand, with the central carbon pointing towards the tmp group in one isomers from it in other.

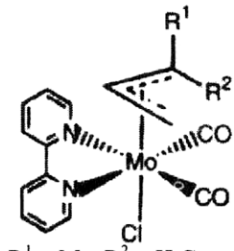
$[Mo(CO)_4(bipy)$ reacts with 1-substituted allyl halides in refluxing THF to afford complexes 5 and 6 in reasonable yields, figure 2 (complex 5) exist as a pair of isomers as the methyl group can be either sym or anti.



N-N=dmb Ligand of 1 N-N=dmp Ligand of 2 N-N=tmp Ligand 3

Fig 1

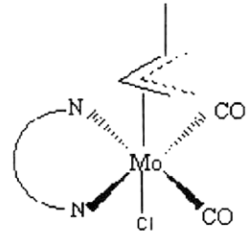
Treatment of $[Mo(CO)_4(dmb)]$ with either crotyl chloride or 2-methylallyl chloride in refluxing THF afford complexes 7 and 8 respectively figure 2 again the presence of the asymmetric ligands cause isomerisation in complex 7.



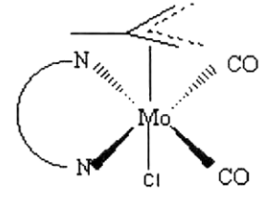
R^1 = Me, R^2 = H Complex 5
$R^1 = R^2$ = Me Complex 6

Fig 2

The 2-methylallyl analogues (complex 9) and (complex 10) (L_2= dmp and tmp respectively) were also prepared by this preparation methods. Also prepare the tungsten analogues of $[WCl(CO)_2(dmb)(\eta^3$-$C_3H_5)]$ (complex 11) which exist as two isomers.

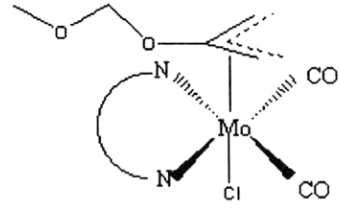


Complex 7



Complex 8 N-N=dmb
Complex 9 N-N=dmp N-N=tmp

Fig 3



Complex 12 M = Mo N-N =bipy
Complex 13 M = Mo N-N = dmb
Complex 14 M = W N-N = bipy
Complex 15 M = W N-N = dmb

Fig 4

Table 1

Complex	N(1)-Mo-N(2)	C(1)-Mo-C(2)
lit complex[12]	73.0(3)	78.3(5)
(1)	72.4(2)	80.9(3)
(3)	73.4(2)	82.0(2)
(4)	74.5(4)	75.3(6)

Table 2

Com-plex	N(1)-Mo-X	N(2)-Mo-X	C(1)-Mo-X	C(2)-Mo-X
lit com-plex[12]	79.3(3)	81.9(3)	88.6(4)	89.9(3)
(1)	82.3(2)	81.5(2)	86.2(3)	89.5(3)
(3)	80.56(8)	80.56(8)	86.79(14)	89.79(14)
(4)	85.0(3)	84.3(3)	86.5(5)	86.2(4)

Table 3

	lit Complex	(compl 1)	(compl 3)	(compl 4)
Mo-C(3)	2.291(11)	2.316(10)	2.212(6)	2.32(2)
Mo-C(4)	2.196(9)	2.219(9)	2.315(4)	2.19(2)
Mo-C(5)	2.351(12)	2.327(8)	2.315(4)	2.32(2)
C(5)-C(4)-C(3)	117.5(11)	116.3(7)	115.7(6)	116.8(13)
mean C-C	1.440(23)	1.394(12)	1.398(6)	1.39(2)
mean Mo-C	1.941(7)	1.949(8)	1.953(4)	1.925(2)
mean C-O	1.178(14)	1.150(10)	1.151(5)	1.18(2)

Four complexes (complexes 12-15,) were prepared with 2-(chloromethyl)-3,5-dioxane-1-ene using this methodology in reasonable yield figure 4.

An alternative to the above method utilises the lability of acetonitrile ligands. Treatment of $[Mo(CO)_6]$ in acetonitrile with 2-(chloromethyl)-3,5-dioxane-1-ene affords the bis-(acetonitrile) complex $[MoCl(CO)_2(MeCN)_2(MeCN)_2(\eta^3\text{-allyl})]$. Further treatment with dppe affords the acetonitrile substituted complex 16.

The values of the complexes compare well with those of the literature complex $[Mo(NCS)(CO)_2(bipy)(C_3H_5)]$ [12]. The angle about the halide ligand, N(1)-Mo-X, N(2)-Mo-X, C(1)-Mo-X and C(2)-Mo-X, approach 90°, being closer for the carbonyl carbons than the nitrogen atoms, (table 1,2)

The central allyl carbon atom is nearer the molybdenum than the two terminal atoms. The allylic inter-carbon angles and the mean C-C bond lengths compare well with those of the structure reported in the literature, as do the mean Mo-C(carbonyl) and C-O(carbonyl) bond length,(table 3)

In complex 3 the molecule is on a mirror plane (Mo, Cl and C(3) are on the plane) and therefore only

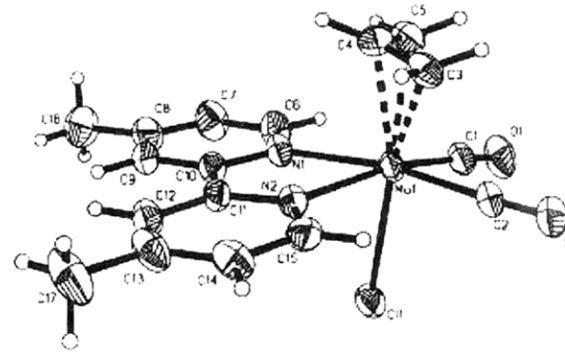


Fig. 5: Molecular Structure of $[MoCl(CO)_2(dmb)(C_3H_5)]$ (complex 1)

Table 4: Selected Bond Lengths and Angles for $[MoCl(CO)_2(dmb)(C_3H_5)]$ (complex 1)

Bond	Length (Å)	Angle	(°)
Mo-Cl	2.484(3)	Cl-Mo-C(1)	86.2(3)
Mo-C(1)	1.955(8)	Cl-Mo-C(2)	89.5(3)
Mo-C(2)	1.943(7)	C(1)-Mo-C(2)	80.9(3)
Mo-C(3)	2.316(10)	Cl-Mo-N(1)	82.3(2)
Mo-C(4)	2.219(9)	C(1)-Mo-N(1)	102.3(3)
Mo-C(5)	2.327(8)	C(2)-Mo-N(1)	170.9(3)
Mo-N(1)	2.252(5)	Cl-Mo-N(2)	81.5(2)
Mo-N(2)	2.245(5)	C(1)-Mo-N(2)	167.2(3)
C(1)-O(1)	1.148(10)	C(2)-Mo-N(2)	102.6(3)
C(2)-O(2)	1.152(9)	N(1)-Mo-N(2)	72.4(2)
C(3)-C(4)	1.370(10)	C(3)-C(4)-C(5)	116.3(7)
C(4)-C(5)	1.418(13)		

half the molecule is crystallographically unique. The chloride atom show weak hydrogen bonds to five almost equidistant hydrogen atom in the unit cell. These are the hydrogen on carbons C(3), C(9), C(9)#1, C(10) and C(10))#1. X-ray crystal structure of complexes 1,3,4 are given in fig 5,6,7 and related bond length and angles are given in table 4,5,6 respectively.

The x-ray crystal structure of complex 5 shown in Figure 8 show that it has different geometry to the other η^3–allyl complexes. The ligands are arranged around the central molybdenum atom in such a way that the bipy group is trans to a carbonyl and the allyl group with the other carbonyl trans to the chloride. This is similar to the arrangement of ligands in phosphine complexes reported in the literature[13]. The carbon-molybdenum-chloride angles are significantly greater than 90° for the carbonyl ligands in complex 5, especially the axial one C(2) which is almost co-linear i.e. nearer 180° than 90° while the other carbonyl-chloride angle is only

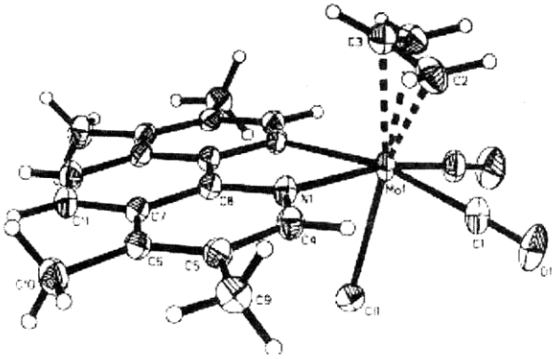


Fig. 6: Molecular Structure of $[MoCl(CO)_2(tmb)(C_3H_5)]$

Table 5:Selected Bond Lengths and Angles in $[MoCl(CO)_2(tmp)(C_3H_5)]$ (complex 3)

Bond	Length (Å)	Angle	(°)
Mo-C(1)	1.953(4)	C(1)-Mo-C(1)#1	82.0(2)
Mo-C(1)#1	1.953(4)	C(1)-Mo-N(1)#1	166.8(2)
Mo-C(3)	2.212(6)	C(1)#1-Mo-N(1)#1	100.9(2)
Mo-N(1)#1	2.247(3)	C(1)-Mo-N(1)	100.9(2)
Mo-N(1)	2.247(3)	C(1)#1-Mo-N(1)	166.8(2)
Mo-C(2)#1	2.315(4)	N(1)#1-Mo-N(1)	73.4(2)
Mo-C(2)	2.315(4)	C(1)-Mo-Cl	86.79(14)
Mo-Cl	2.475(2)	C(1)#1-Mo-Cl	86.79(14)
C(1)-O(1)	1.151(5)	N(1)#1-Mo-Cl	80.56(8)
C(2)-C(3)	1.398(6)	N(1)-Mo-Cl	80.56(8)
C(3)-C(2)#1	1.398(6)	C(2)-C(3)-C(2)#1	115.7(6)

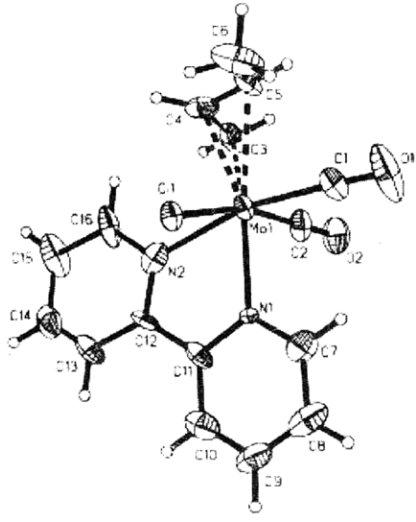


Fig. 8: Molecular Structure of $[MoCl(CO)_2(bipy)(1\text{-Me-allyl})]$

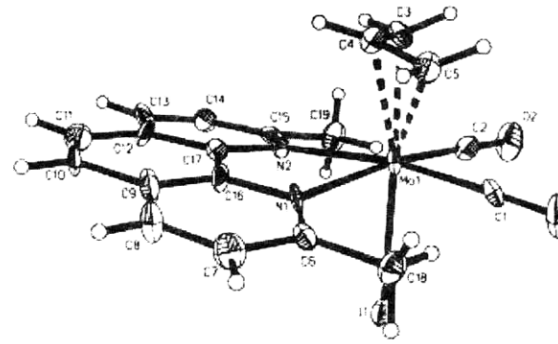


Fig. 7: Molecular Structure of $[MoI(CO)_2(dmp)(C_3H_5)]$

Table 6: Selected Bond Lengths and Angles in $[MoI(CO)_2(dmp)(C_3H_5)]$ (complex 4)

Bond	Length (Å)	Angle	(°)
Mo-C(1)	1.92(2)	C(1)-Mo-C(2)	75.5(6)
Mo-C(2)	1.93(2)	C(1)-Mo-N(1)	104.4(5)
Mo-C(4)	2.19(2)	C(2)-Mo-N(1)	171.2(5)
Mo-N(1)	2.292(10)	C(1)-Mo-N(2)	170.8(5)
Mo-N(2)	2.289(10)	C(2)-Mo-N(2)	104.2(5)
Mo-C(3)	2.32(2)	N(1)-Mo-N(2)	74.5(4)
Mo-C(5)	2.32(2)	C(1)-Mo-I	86.5(5)
Mo-I	2.826(2)	C(2)-Mo-I	86.2(4)
C(1)-O(1)	1.18(2)	N(1)-Mo-I	85.0(3)
C(2)-O(2)	1.18(2)	N(2)-Mo-I	84.3(3)
C(3)-C(4)	1.39(2)	C(3)-C(4)-C(5)	116.8(13)
C(4)-C(5)	1.39(2)		

Table 7: Selected Bond Lengths and Angles in $[MoCl(CO)_2(bipy)(1\text{-Me-allyl})]$ (complex 5)

Bond	Length (Å)	Angle	(°)
Mo-C(2)	1.86(2)	C(2)-Mo-C(1)	76.7(10)
Mo-C(1)	2.02(3)	C(2)-Mo-N(1)	85.0(7)
Mo-N(1)	2.176(13)	C(1)-Mo-N(1)	95.4(8)
Mo-C(4)	2.26(2)	C(2)-Mo-N(2)	99.8(9)
Mo-N(2)	2.27(2)	C(1)-Mo-N(2)	165.9(7)
Mo-C(3)	2.269(14)	N(1)-Mo-N(2)	70.5(6)
Mo-C(5)	2.47(2)	C(2)-Mo-Cl	162.5(7)
Mo-Cl	2.540(4)	C(1)-Mo-Cl	98.5(6)
C(1)-O(1)	1.10(3)	N(1)-Mo-Cl	78.6(4)
C(2)-O(2)	1.16(3)	N(2)-Mo-Cl	80.7(4)
C(3)-C(4)	1.46(3)	C(5)-C(4)-C(3)	113.0(2)
C(4)-C(5)	1.42(3)	C(6)-C(5)-C(4)	129.0(2)
C(5)-C(6)	1.35(3)		

slightly greater than 90^0 [C(1)-Mo-Cl 98.5(6)°, C(2)-Mo-Cl 162.5(7)°]. The nitrogen-chloride angles are similar to those in other allyl complexes [N(1)-Mo-Cl 78.6(4)°, N(2)-Mo-Cl 80.7(4)°].

The methyl substituent lies in the syn position on the terminal carbon of the allyl group, the C(4)-

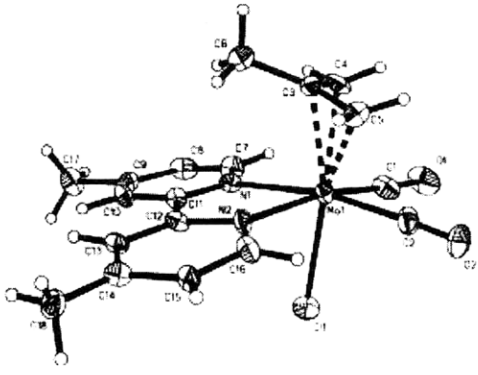


Fig. 9: Molecular Structure of[$MoCl(CO_2)(dmb)(C_4H_7)$]

Table 8: Selected Bond Lengths and Angles in [$MoCl(CO_2)(dmb)(C_4H_7)$] (complex 8)

Bond	Length (Å)	Angle	(°)
Mo-C(1)	1.931(11)	C(1)-Mo-C(2)	77.6(2)
Mo-C(2)	1.960(11)	C(1)-Mo-N(2)	167.9(4)
Mo-N(2)	2.213(10)	C(2)-Mo-N(2)	103.0(5)
Mo-N(1)	2.248(9)	C(1)-Mo-N(1)	104.6(4)
Mo-C(3)	2.237(3)	C(2)-Mo-N(1)	169.8(4)
Mo-C(5)	2.310(9)	N(2)-Mo-N(1)	72.75(13)
Mo-C(4)	2.330(10)	C(1)-Mo-Cl	87.4(3)
Mo-Cl	2.4982(11)	C(2)-Mo-Cl	90.3(3)
C(1)-O(1)	1.21(2)	N(2)-Mo-Cl	80.6(3)
C(2)-O(2)	1.10(2)	N(1)-Mo-Cl	79.8(2)
C(3)-C(4)	1.35(2)	C(4)-C(3)-C(5)	115.0(4)
C(4)-C(5)	1.45(2)	C(4)-C(3)-C(6)	120.7(14)
C(3)-C(6)	1.512(5)	C(5)-C(3)-C(6)	124.3(14)

C(5)-C(6) angle being 129.0(2). The central carbon atom of the allyl group lies closer to the molybdenum atom than the terminal carbon atoms [Mo-C(4) 2.26(2)Å, Mo-C(3) 2.269(4)Å Mo-C(5) 2.47(2)Å]. The mean C-CH_2 bond length in the allyl is 1.44(3)Å while the C-CH_3 bond distance is 1.35(3)Å and the inter-carbon angle C(3)-C-(4)-C(5) is 113.0 (2)°

The molecular structure of complex 8 is shown in figure 9 while table 8 shows selected bond length and angles. The central allyl carbon atom is closer to molybdenum at 2.237(3) Å, than two terminal carbon atoms at 2.330(10) Å and 2.310(9) Å respectively. The allylic CH_2-C-CH_2 angle is 115.0(4)° and the C-CH_3 and mean C-CH_2 bond length are 1.512(5) Å and 1.40(2) Å respectively, while the mean Mo-C (carbonyl) and C-O bond length having 1.946(11) Å and 1.16(2) Å respectively. These compare well with the values for

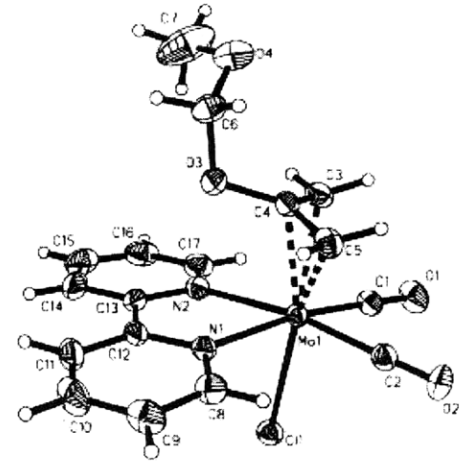


Fig. 10: Molecular Structure of $[MCl(CO)_2(bipy)(C_5H_9O_2)]$

Table 9:Selected Bond Lengths in$[MCl(CO)_2(bipy)(C_5H_9O_2)]$ { M = Mo (12), M = W (14)}

Bond	Length (Å) (12)	(14)
M-C(2)	1.950(3)	1.959(9)
M-C(1)	1.962(3)	1.957(9)
M-N(1)	2.224(3)	2.216(7)
M-C(4)	2.240(3)	2.219(8)
M-N(2)	2.241(3)	2.217(7)
M-C(3)	2.325(3)	2.326(9)
M-C(5)	2.333(3)	2.313(9)
M-Cl	2.4967(9)	2.489(2)
C(1)-O(1)	1.153(4)	1.159(11)
C(2)-O(2)	1.159(4)	1.150(10)
C(3)-C(4)	1.399(4)	1.427(13)
C(4)-O(3)	1.404(4)	1.406(10)
C(4)-C(5)	1.401(5)	1.362(12)

literature structure of [Mo(NCS) $(CO)_2$(phen) (C_4H_7)] [12]. The Mo-CO angle have been found to be nearly linear, the mean value being 173.1(10) similar to the literature value of 177.7(1)°. The molecular structure of complexes 12 and 14 are shown in figure 10 and 11 respectively while table 11 and 12 shown the selected bond length and angles. If the allyl ligand is considered to occupy one coordinate site about the metal atom and the bipy ligands two then the complex may be considered to have a distorted octahedral arrangement of ligands. The main distortion are found at the angles between the metal and the bipy ligand and the metal and the carbonyl atoms. These angles have been found to be significantly different from 90° (table 11).

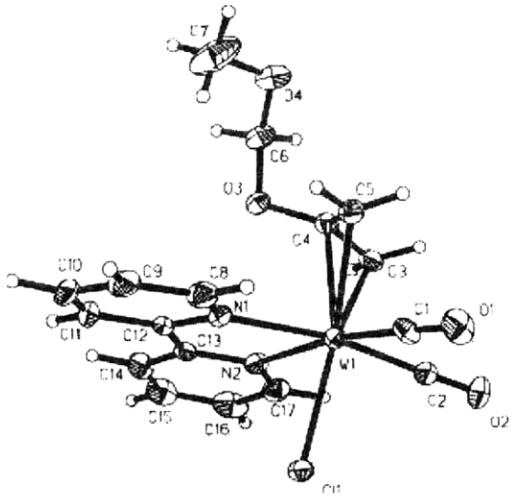


Fig. 11: Molecular Structure of [$MCl(CO_2)$(bipy) $(C_5H_9O_2)$]

Table 10: Selected Bond Angles in [$MCl(CO_2)$(bipy) $(C_5H_9O_2)$] { M = Mo (12), M = W (14) }

Angle	(°) (12)	(14)
C(2)-M-C(1)	76.55(13)	77.2(4)
C(2)-M-N(1)	103.44(11)	103.1(3)
C(1)-M-N(1)	170.66(11)	170.2(3)
C(2)-M-N(2)	170.68(11)	170.3(3)
C(2)-M-N(2)	105.65(12)	105.5(3)
N(1)-M-N(2)	72.88(9)	72.6(3)
C(2)-M-Cl	89.74(9)	90.1(2)
C(1)-M-Cl	89.73(9)	91.2(3)
N(1)-M-Cl	80.93(6)	80.0(2)
N(2)-M-Cl	81.26(7)	80.6(2)
C(3)-C(4)-O(3)	121.3(3)	118.8(8)
C(3)-C(4)-C(5)	117.3(3)	118.2(8)
O(3)-C(4)-C(5)	121.1(3)	122.9(8)
O(3)-C(4)-M	114.1(2)	115.5(5)
C(3)-O(3)-C(6)	111.8(3)	111.9(7)
O(4)-C(6)-O(3)	113.7(3)	114.5(8)
C(6)-O(4)-C(7)	113.0(4)	115.4(11)

Table 11

Complex	N(1)-M-N(2)	C(1)-M-C(2)
(12)	72.88(9)	76.55(13)
(14)	72.6(3)	77.2(4)

Table 12

Complex	N(1)-M-Cl	N(2)-M-Cl	C(1)-M-Cl	C(2)-M-Cl
(12)	80.93(6)	81.26(7)	89.73(9)	89.74(9)
(14)	80.0(2)	80.6(2)	91.2(3)	90.1(2)

The C-Mo-C and N-Mo-Cl angles however, do approach 90, being closer for the carbonyl carbons than the bipy nitrogens, table 12.

The mean M-C and C-O bond length are 1.956(3) Å and 1.156(4) Å, respectively, for the molybdenum complex with 1.958(9) Å and 1.156(11) Å for the tungsten analogue. The central allylic carbon atoms are nearer the metal than the two terminal atoms. The allylic inter-carbon angles are 117.3(3)° and 118.2(8)° for complex 12 and 14 respectively, while the mean C-CH_2 bond lengths are 1.400(5) and 1.395(13). The angle of the CH_3OCH_2O substituent to the allyl group, O(3)-C(4)-M, is 114.1(2) and 115.5(5) for complex 12 and 14 respectively.

Spectroscopic Properties of Allyl Complexes

The ^{1}H NMR spectrum of a simple)(η^3–C_3H_5 allyl complex shows three signals for the allyl grup due to three sets of protons-central (H_A), syn(H_b) and anti (H_C), the central proton couples with both syn and anti protons to give a 1H multiplet, while the syn proton (H_B) appear as a 2H doublet showing cis coupling to the central proton (H_A). The anti proton also occurs as a doublet but this time with trans coupling to H_A. The coupling between the syn and anti proton is not observed in any of the spectra for these complexes. The signal due to the central proton appears further downfield than the syn and anti ones due to the double bond character of the allyl group. The anti protons are usually further upfield than the syn proton due to their closer proximity to the metal.

The ^{1}H NMR spectra of complexes (1) (2) and (4) are as expected for such symmetrical allyl complexes, the anti protons appear as a doublet J=9-10 H_Z in the region δ 1.16 – 1.8 ppm while the doublet J= 6-7 H_Z) due to the syn protons appears between δ 2.54 and 3.53 ppm. The complex multiplet assigned to the central allylic proton occurs in the range δ 2.39 to 3.72 ppm.

However, with complex 3 (L_2=tmp) the ^{1}HNMR spectrum is more complicated. It shows two sets of signals indicating the presence of two isomers, the signals can be assigned as shown in table 13 by looking at cross peak in the spectrum and relative intensities. From these it is observed that one isomer (labeled i) is predominant over the other in the ratio 4:3. The two isomers are due to the allyl group taking

up different orientations which are slow to interconvert on the NMR timescale at room temperature. A lake of solubility prevented a temperature dependent NMR study.

The ^{1}H NMR spectral data for complexes 1-16 are given in table13-16. where the allyl group is the 2-methyl substituted allyl C_4H_7, are less complicated than those for the C_3H_5 complexes. This is due to the central proton being replaced by the methyl group, therefore removing coupling to the terminal protons. The coupling between the syn and anti proton is not observed so the spectyra show three signals, one each for the methyl group, syn protons and anti protons intregrating to 3H, 2H and 2H respectively. The methyl protons appear in the range 0.5 – 1.04 ppm with the anti protons between 1.27 and 1.38 ppm and the syn ones between 2.44 and 2.83 ppm.

The ^{1}H NMR spectra for the complexes containing an allyl group substituted at the terminal carbon are much more complex. This is due to the complexes being unsymmetrical, hence making all the proton inequivalent in the molecules.

Complex 6 has a 1-dimethyl substituted allyl group. The methyl group appears as two singlet (3H), one further downfield at δ 2.27 ppm than the other proton Ha appears as a multiplet, due to coupling with the two terminal protons, at δ 3.82 ppm. The two terminal protons appear as separate doublets, one further downfield the another δ 2.91 and 1.77 ppm respectively, each integrating to 1H. They both show coupling to the central proton HA but not to each other. In complex 5 and 7 the allyl group contains a methyl substituted on one of the terminal carbons. This methyl group can be either syn or anti resulting in two possible isomer for each complex. The X-ray crystal structure obtained for complex 5 shows the methyl group in the syn position which agrees with the geometry of related complex reported in literature [9].

The tungsten complex (11) has the simple C_3H_5 allyl ligand has also been found to exist as two isomers as confirm by NMR spectrum. The two isomers occur because the allyl group can take up two orientations where in one its point toward the dmb group and in the other away from it, these isomers exist in the ratio 4:5.

In complex 12-15 there is an actual group CH_3OCH_2O attached to the central carbon of the allyl fragment. The methyl group appearsas a siglet around δ 2.89 – 3.43 ppm, downfield due to deshielding effect of the oxygen.. The CH_2 also appear as a singlet, further downfield than the methyl atoms either side of it. The terminal allyl protons also appear as singlets with the anti ones (δ 1.56 – 2.71 ppm) further upfield the syn ones (δ 3.02 – 4.14 ppm).

The N-N ligands all have multiplets in the aromatic region of the spectra between δ 7.24 and 9.78 ppm. In the dmb complexes the methyl groups are equivalent and appear as singlets between δ 2.41 and 2.54 ppm. In the dmp complexes the two methyl groups are also equivalent and occur as a singlet between δ 3.18 and 3.31ppm, downfield due to being on the carbons adjacent to the nitrogen. The two sets of methyl group in the tmp complexes occur as singlets in the region The CH_2 also appear as a singlet, further downfield than the methyl atoms either side of it δ 2.58 – 2.76 ppm, one being slightly downfield of the other due to deshielding from the nitrogen.

For complex 16 the spectrum shows two multiplets at The CH_2 also appear as a singlet, further downfield than the methyl atoms either side of it δ 2.57 and 3.00 ppm, each integrating to 2H due to the CH_2 group of the dppe ligands. The phenyl protons appears as a multiplet between δ 7.31 and 7.81 ppm.

The ^{31}P-{^{1}H} NMR spectrum of 16 shows a singlets at δ 63.82 ppm indicating that both phosphorus atoms are equivalent and this points to the complex having the structure as reported in the literature[13] for similar complexes.

Infrared and Mass Spectra.

The IR spectral data (table 17) shows two absorption bands in the carbonyl region 1940 to 1805 cm^{-1}, both of equal intensity indicating a cis geometry of carbonyl groups around the metal.

The mass spectra (table 17) show parent ions and fragmentation due to loss of the chloride and successive carbonyl ligands.

Table 13: ^{1}H NMR Data for C_3H_5 Allyl Complexes

COMPLEX	δ/ppm	
	L_2	Allyl
(compl 1) (M = Mo, L_2 = dmb)	2.41 (6H, s), 7.18 (2H, d, J = 5 Hz), 7.79 (2H, s), 8.60 (2H, d, J = 5.7 Hz)	1.38 (2H, d, J = 9 Hz, anti-CH), 3.53 (2H, d, J = 6 Hz, syn-CH), 3.72 (1H, m, central CH)
(comp 2) (M = Mo, L_2 = dmp)	3.24 (6H, s, CH_3), 7.60 (2H, d, J = 8 Hz), 7.73 (2H, s), 8.20 (2H, d, J = 8 Hz)	1.16(2H, d, J = 10 Hz, anti-CH), 2.39 (1H, m, central CH), 2.54 (2H, d, J = 6.6 Hz, syn-CH)
(compl 3) i (M = Mo, L_2 = tmb)	2.66 (s), 2.76 (s), 8.11 (s), 9.12 (bs)	1.54 (d, J = 9 Hz, anti-CH), 3.73 (d, J = 6 Hz, syn-CH), 3.99 (m, central CH)
ii	2.58 (s), 2.71 (s), 8.07 (s), 8.91 (s)	1.39 (d, J = 9 Hz, anti-CH), 3.08 (d, J = 6 Hz, syn-CH)
(compl 4) (M = Mo, L_2 = dmp)	3.18 (6H, s), 7.62 (2H, d, J = 8.5 Hz), 7.76 (2H, s), 8.17 (2H, d, J = 8.5 Hz)	1.29 (2H, d, J = 9.1 Hz, anti-CH), 2.40 (1H, m, central CH), 2.58 (2H, d, J = 6.6 Hz, syn-CH)
(compl 11) i (M = W, L_2 = dmb)	2.54 (s), 7.39 (d, J = 5 Hz), 7.95 (s), 8.91 (bs)	1.64 (m, anti-CH), 2.99 (m, central CH), 3.38 (d, J = 5.7 Hz, syn-CH)
ii	2.51 (s), 7.27 (d, J = 5 Hz), 7.91 (s), 8.72 (d, J = 5.7 Hz)	1.64 (m, anti-CH), 2.09 (m, central CH), 2.77 (d, J = 6 Hz, syn-CH)

Table 14: ^{1}H NMR Data for Complexes (5)-(7)

COMPLEX	δ/ppm L_2	allyl
(compl 5) (L_2 = bipy, allyl = C_4H_7)	7.30-9.75 (m)	1.14 (d, J = 6.6 Hz, CH_3),1.19 (d, J = 6.3 Hz, CH_3), 1.59 (d, J = 5.7 Hz), 1.91 (m), 2.22 (m), 2.93 (m), 3.70 (m, central CH)
(compl 6) (L_2 = bipy, allyl = C_5H_9)	7.54 (2H, m), 7.88 (2H, m), 8.06 (2H,m), 8.43 (1H, d, J = 5Hz), 9.74 (1H, d, J = 5Hz)	1.21 (3H, s, anti-CH_3),1.77 (1H, d, J = 9 Hz, anti-CH), 2.27 (3H, s, syn- CH_3), 2.91 (1H, d, J = 6 Hz, syn-CH), 3.82 (1H, m, central CH)
(compl 7) (L_2 = dmp, allyl = C_4H_7)	7.11-9.60 (m)	1.12 (d, J = 6.6 Hz, CH_3),1.18 (d, J = 6.6 Hz, CH_3), 1.65 (m), 1.85 (m), 2.25 (d, J = 5.7 Hz), 3.03 (d, J = 6.6 Hz), 3.69 (m, central CH)

Table 15: ^{1}H NMR Data for 2-Me-Allyl Complexes

COMPLEX	δ/ppm L_2	allyl
(compl 8) (M = Mo, L_2 = dmb)	2.49 (6H, s, CH3), 7.27 (2H, d, J = 4 Hz), 7.90 (2H, s), 8.67 (2H, d, J = 6 Hz)	1.04 (3H, s, CH_3), 1.32 (2H, s, anti-CH), 2.75 (2H, s syn-CH)
(compl 9) (M = Mo, L_2 = dmb)	3.31 (6H, s), 7.68 (2H, d, J = 8.2 Hz), 7.79 (2H, s), 8.24 (2H, d, J = 8.2 Hz)	0.50 (3H, s, CH_3), 1.27 (2H, s, anti-CH), 2.44 (2H, s syn-CH)
(compl 10) (M = Mo, L_2 = tmp)	2.59 (6H, s, CH3), 2.71 (6H, s, CH_3), 8.06 (2H, s), 8.89 (2H,s)	0.76 (3H, s, CH_3), 1.38 (2H, s, anti-CH), 2.83 (2H, s, syn-CH)

Table 16: ^{1}H NMR Data for $C_5H_9O_2$ Complexes

COMPLEX	δ/ppm L_2	allyl
(compl 12) M = Mo, L_2 = bipy	7.44 (2H, m), 7.99 (4H, m), 8.95 (2H, d, J = 4 Hz)	1.61(2H, s, anti-CH), 2.89 (3H, s, OCH_3), 3.21 (2H, s, syn-CH), 4.31 (2H, s, OCH_2O)
(compl 13) M = Mo, L_2 = dmb	2.46 (6H, s, CH_3), 7.24 (2H, d, J = 5 Hz), 7.85 (2H, s), 8.78 (2H, d,, J = 5 Hz)	1.56 (2H, s, anti-CH), 2.94 (3H, s, OCH_3), 3.17 (2H, s, syn-CH), 4.30 (2H, s, OCH_2O)
(ccompl 14) M = W, L_2 = bipy	7.48 (2H, t), 7.98 (2H, t), 8.11 (2H, d), 8.97 (2H, d)	2.09(2H, s, anti-CH), 2.85 (3H, s, CH_3), 3.04 (2H, s, syn-CH), 4.34 (2H, s, OCH_2O)
(compl 15) M = W, L_2 = dmb	2.50 (6H, s, CH_3), 7.24 (2H, s), 7.90 (2H, s), 8.74 (2H, s)	2.08(2H, s, anti-CH), 2.89 (3H, s, CH_3), 3.02 (2H, s, syn-CH), 4.38 (2H, s, OCH_2O)
(compl 16) M = Mo, L_2 = dppe	2.53 (2H, m, CH_2), 2.94 (2H, m, CH_2), 7.51 (20H, m)	2.63 (2H, s, anti-CH), 3.36 (3H, s, CH_3), 4.09 (2H, s, syn-CH), 4.60 (2H, s, OCH_2O)

Table 17: IR and MS Data for Complexes (complex 1-l 6)

Complex	IR Data ν(CO)/cm^{-1}		Ms Data M^+ / $[MH]^+$	Fragmentation
(1)	1925	1840	414*	$[MH-Cl]^+$ 379; $[MH-2CO]^+$ 358
(2)	1925	1845	422*	$[MH-Cl]^+$ 387; $[MH-2CO]^+$ 366
(3)	1920	1825	466*	$[MH-Cl]^+$ 431; $[MH-2CO]^+$ 410
(4)	1930	1860	530*	$[MH-CO]^+$ 502; $[MH-2CO]^+$ 474
(5)	1910	1820	400*	$[MH-Cl]^+$ 365; $[MH-2CO]^+$ 344
(6)	1915	1810	414*	$[MH-Cl]^+$ 379; $[MH-2CO]^+$ 358
(7)	1920	1820	428*	$[MH-Cl]^+$ 393; $[MH-2CO]^+$ 372
(8)	1925	1840	428	$[M-Cl]^+$ 393; $[M-2CO]^+$ 372
(9)	1920	1830	432	$[M-Cl]^+$ 396
(10)	1920	1835	480*	$[MH-Cl]^+$ 445; $[MH-2CO]^+$ 424
(11)	1920	1825	500	$[M-2CO]^+$ 444
(12)	1920	1840	446	$[M-Cl]^+$ 411; $[M-2CO]^+$ 390
(13)	1940	1850	474*	$[MH-Cl]^+$ 439; $[MH-2CO]^+$ 418
(14)	1910	1870	532	$[M-Cl]^+$ 497
(15)	1925	1835	560	$[M-2CO]^+$ 504
(16)	1940	1805	687	$[M-2CO]^+$ 631

* = MH^+

Conclusions

The preparations of η^3–allyl complexes of general type $[MX(CO)_2L_2(\eta^3\text{-ally})]$, where M=Mo or W, X= Cl or I, L_2= bipy, dmb, dmp or tmp and η^3–allyl = C_3H_5, 2Me-C_3H_4, I-Me-C_3H_4, I-Me2-C_3H_3 or $C_5H_9O_2$, is achieved in reasonable yield with the treatment of either $[Mo(CO)_4L_2$ or $[W(CO)_3L_2(py)]$ with an excess of the allyl halide in refluxing THF. These complexes have been characterized by various technique including ^{1}H NMR, IR, and MS spectroscopies and structure of these complexes has been confirmed by single crystal X-ray diffraction studies.

Preparation of η^3–Allyl Complexes

1. Preparation of $[MoCl(CO)_2(dmb)(\pi\text{-}C_3H_5)]$

A mixture of $[Mo(CO)_4(dmb)]$ (0.300 g, 1.280 m mol) and allyl chloride (0.961 g, 0.012 mol) was refluxed in THF (50 ml) for four hours. The resulting dark red solution was cooled to room temperature, adding light petroleum give the red solid which was filtered, washed with light petroleum, dried in vacuum gives the yield (0 . 50 gm 85 %). (Found: C, 50.33; H, 4.53; N, 6.12. $C_{17}H_{17}ClN_2O_2Mo$ requires; C, 49.45; H, 4.12; N, 6.79 %). Complex was characterized by ^{1}H NMR, IR, MS spectroscopy and X-ray crystal structure.

2. Preparation of $[MoCl(CO)_2(dmp)(\pi\text{-}C_3H_5)]$

A mixture of $[Mo(CO)_4(dmp)]$ (0.290 g, 0.729 m mol) and allyl chloride (0.960 g, 0.012 mol) was refluxed in 50 ml THF for three hours red solid was filtered, wash and dried under vacuum (0.200 g, 68 %). Found C, 51.30; H, 3.85; N, 6.40, requires; C, 50.5; H, 3.88; N, 6.06. Complex was characterized by ^{1}H NMR IR, MS spectrometry.

3. Preparation of $[MoCl(CO)_2(tmp)(\pi\text{-}C_3H_5)]$

A mixture of $Mo(CO)_4(tmp)]$ (0.200 g, 0.450 m mol) and allyl chloride (o.275 g, 0.360 m mol) was refluxed in 50 ml THF for three hours add light petroleum ether obtained red solid, filtered washed and dried under vacuum. (yield 1.35 g, 60 %).Complex was characterized by IR, ^{1}H NMR and mass spectrometry an x-rya crystal structure.

4. Preparation of $Mol(CO)_2(dmp)(\pi\text{-}C_3H_5)$

A mixture of $[Mo(CO)_4(dmp)]$ (0.290 g, 0.730 m mol) and allyl iodide (0.275 g, 0.365 m mol was refluxed in 50 ml THF for three hours. After adding light petroleum ether, obtained red solid, filter washed and dried in vacuum (yield 0.208 g, 65 %). (Found C, 42.41; H, 2.85; N, 5.35, requires C, 43.16; H, 3.20; N 5.30 %). Complex was characterized by ^{1}H-NMR, IR and MS spectrometry.

5. Preparation of $[MoCl(CO)_2(bipy)(\pi\text{-}C_4H_7)]$

A mixture of $[Mo(CO)_4(bipy)]$ (0.265 g, 0.730 m mol) and excess crotyl chloride (0.950 g, 0.010 mol) was refluxed in 5o ml THF for three hours. At room temperature add light petroleum ether obtained dark red solid filtered washed and dried in vacuum (yield 0.215 g, 75 % $C_{16}H_{15}ClMoN_2O_2$), which was identified by H NMR, IR, MS spectrometry and x-ray crystal structure.

6. Preparation of [MoCl(CO)$_2$(bipy)(π-C$_5$H$_9$)]

A mixture of [Mo(CO)$_4$(bipy)] (0.500 g, 1.370 m mol) and 1-chloro-3-methyl-2-butane (0.800 g, 7.610 m mol) was refluxed in 50 ml THF for three hours. At room temperature add light petroleum ether filtered washed and dried in vacuum obtained title complex (0.205 g, 35 %) (Found C, 48.90; H, 3.85; N, 6.02. required, C, 50.0; H, 4.10; N, 6.80 %) identified by ^{1}H NMR, IR and Mass spectrometry.

7. Preparation of [MoCl(CO)$_2$(dmb)(π-C$_4$H$_7$).

A mixture of [Mo(CO)$_5$(dmb)] (0.100 g, 0.255 m mol) and crotyl chloride (0.500 g, 0.516 m mol was refluxed in 50 ml THF for five hours, add light petroleum ether after filtered, washed and dried in vacuum obtained dark red solid (0.060 g, 55%), which was characterized by ^{1}H NMR, IR, and MS spectrometry.

8. Preparation of [MoCl(CO)$_2$(dmb)(π-C$_4$H$_7$)]

A mixture of [MO(CO)$_4$(dmb)] (0.50 g, 1.285 m mol) and 3-chloro-2-methyl-propene (0.60 g, 5.08 m mol) was refluxed in 50 ml THF for three hours, add light petroleum ether, filtered dried in vacuum obtained title complex as red solid (0.38 g, 70%) (Found C, 48.75; H, 4.35; N, 6.45. required, C, 48.90; H, 4.35; N, 6.25 %) Complex was characterized by ^{1}H NMR, IR, MS spectroscopy and x-ray structure.

9. Preparation of [MoCl(CO)$_2$(dmp(-C$_4$H$_7$)]

A mixture of [Mo(CO)$_4$(dmp)] (0.200 g, 0.500 m mol) and 3-chloro-2-methyl-propene (0.600 g, 0.665 m mol) was refluxed in 50 ml THF for three hours. Add light petroleum ether filtered washed and dried in vacuum obtained title complex (0.170 g, 75 %) (Found C, 55.40; H, 4.45; N, 6.50, requires, C, 55.50; H, 4.40; N, 6.46), Complex was characterized by ^{1}H NMR, IR, and mass spectrometry.

10. Preparation of [MoCl(CO)$_2$(tmp)(C$_4$H$_7$)]

A mixture of [Mo(CO)$_4$(tmp)](0.100 g, 0.225) and 3-chloro-2-methyl-propene (0.036 g, 0.400) was refluxed in 50 ml THF for three hours. Add petroleum ether in dark red solution obtained precipitate filtered dried in vacuum (0.085 g, 80 %) Found C, 55.15; H, 4.85; N5.85, requires C, 55.15; 4.80, N, 5.85 %). Complex characterized by ^{1}H ^{1}R, IR, and MS spectrometry.

11. Preparation of [WCl(CO)$_2$(dmb)(π-C$_3$H$_5$)]

A mixture of [W(CO)$_3$(dmb)(py)] (0.100 g, 0.188 m mol) and allyl Chloride (1.00 g, 0.012 mol) was refluxed in 50 ml THF for five hours. Add light petroleum in brown solution obtained red brown solid after filtered and dried in vacuum (0.045 g, 50 %) which was characterized by ^{1}H NMR, IR, and MS spectrometry.

12. Preparation of [MoCl(CO)$_2$(bipy)(π-C$_5$H$_9$O$_2$)]

A mixture of [Mo(CO)$_4$(bipy)] (0.500 g, 1.37 m mol) and 2-(chloro)-3,5-dipxane-1-ne((0.273 g, 2.00) was refluxed in 50 ml THF for three hours. Add petroleum ether in brown solution obtained brown solid as title complex, (C$_{17}$H$_{17}$ClMoN$_2$O$_2$) dried in vacuum (yield, 0.425 g 70 %) (Found C, 46.05, H, 3.90; N, 6.45, requires, C, 45.90; H, 3.80; N, 6.30), Complex was characterized by IR, ^{1}H NMR, MS spectrometry and x-Ray Crystal structure.

13. Preparation of [Mo(CO)$_2$(dmb)(-C$_5$H$_9$O$_2$)]

A mixture of [Mo(CO)$_4$(dmb)] (0.100 g, 0.255 m mol and 2-(chloromethyl)-3,5-dioxane-1-en (o.054 g, 0.400 m mol was refluxed in 50 ml THF for three hours. Add light petroleum ether in dark red solution, filtered obtained title complex as dark red solid (0.60 g, 53 %) (Found C, 47.88; H, 4.50; N, 5.30; Requires, C, 48.25; 4.45;, N, 5.90). Complex was characterized by H NMR, IR, and MS spectrometry.

14. Preparation of [WCl(CO)$_2$(bipy)(-C$_5$H$_9$O$_2$)]

A mixture of [w(CO)3 (bipy)(py)] (0.100 g, 0.198 m mol) and 2-(chloromethyl)-3,5-dioxane-1-ene (0.100 g, 0.735 m mol) was refluxed in 50 ml of THF for three hours. Adding light petroleum ether in brown solution obtained title complex (C$_{17}$H$_{17}$ClN$_2$O$_2$) dried in vacuum (0.080 g, 75 %) (Found, C, 38.65; H, 3.24; N, 5.30; requires, C,38.35; H, 3.20; N,5.25), Complex was characterized by H NMR, IR, MS spectrometry and x-Ray crystal structure.

15. Preparation of [WCl(CO)$_2$(dmb)(π-C$_5$H$_9$O$_2$)]

A mixture of [W(CO)$_3$(dmb)(py) (0.15g, 0.280 m mol) and 2-(chloromethyl)-3,5-dioxane-1-ene(0.100 g, 0.735 m mol) was refluxed in 50 ml of THF for three hours. The resulting brown solution cool to room temperature and the addition of light petroleum precipitated a brown solid, washed and dried in vacuum to yield title complex as a brown

solid (0.035 g, 25 %) (Found C, 41.0; H, 3.26; N, 4.90; requires, C, 40.65; H, 3.25;, N, 5.00). Complex was characterized by ^{1}H NMR, IR, and MS spectroscopy.

16. Preparation of [MoCl(CO)$_2$(bppe)(π-C$_5$H$_9$O$_2$)]

$Mo(CO)_6$ (1.00 g, 3. 790 m mol) was refluxed with 2-(chloromethyl)-3,5-dioxahex-1-ene (0.614 g, 4 m mol) in an acetonitrile-benzene mixture for six hours. The resulting solution was filtered under inert atmosphere to give yellow solid (0.58 g) and refluxed with dppe in ethanol for two hours. The resulting mixture was cool to room temperature and filtered to give title complex as yellow solid (o.90 g, 80 %) (Found, C, 57.85; H, 4.85; N, 8.75; requires, C, 57.67; 4.80, N, 9.00 %) which was characterized by ^{1}H NMR, ^{31}P-{^{1}H} NMR, IR, and MS spectro-metry.

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