DOCTOR OF PHILOSOPHY

New organometallic complexes of molybdenum(II) and tungsten(II) containing 3-hexyne and/or tripodal triphos (MeC(CHPPH)) ligands

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IN THE NAME OF

ALLAH

MOST GRACIOUS MOST MERCIFUL

بسم الله الرحمن الرحيم

THANKING

HIM

WITH A FULL HEART AND DEVOTED TONGUE

وَقُل رَّبِّ زِدْنِي عِلْمًا ○

say, "O My Lord! Advance Me In Knowledge"

NEW ORGANOMETALLIC COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II) CONTAINING 3-HEXYNE AND/OR TRIPODAL TRIPHOS $\{MeC(CH_2PPh_2)_3\}$ LIGANDS.

A thesis submitted to the University of Wales, Bangor

by

Mutlaq Al-jahdali

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To my parents, to my wife Fowzia
and my children Manar and Rakan

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Abstract :-

The first chapter, the introduction contains a general background concerning the chemistry of molybdenum(II) and tungsten(II), their properties, and the synthesis and reactions of their complexes.

The second chapter describes the synthesis, reactions and characterisation of the bis(3-hexyne)(EtC$_2$Et) complexes of molybdenum(II) and tungsten(II), [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$]. The crystal structures of the bis(PPh$_3$) complex [WI$_2$(CO)(PPh$_3$)$_2$(η^2-EtC$_2$Et)](**4**) and the PPh$_2$(CH$_2$)$_3$PPh$_2$ complex, [WI$_2$(CO){Ph$_2$P(CH$_2$)$_3$PPh$_2$}(η^2-EtC$_2$Et)](**8**) are discussed. The reaction of equimolar amounts [MoI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] and bipy to give the crystallographically characterised complex, [MoI$_2$(CO)(bipy)(η^2-EtC$_2$Et)](**12**) is also described.

The third chapter describes the reactions of the complexes [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] with one and two equivalents of phosphite ligands, P(OR)$_3$ (R = Me, Et, ^{i}Pr, ^{n}Bu and Ph) to give [MoI$_2$(CO)(NCMe){P(OR)$_3$}(η^2-EtC$_2$Et)](R = Ph or ^{i}Pr), [WI$_2$(CO){P(OR)$_3$}(η^2-EtC$_2$Et)$_2$](R = Me, Ph or ^{i}Pr) and [MI$_2$(CO){P(OR)$_3$}$_2$(η^2-EtC$_2$Et)](M = Mo, R = Me, Et, ^{i}Pr, and ^{n}Bu; M = W, R = Me, Et, ^{i}Pr, ^{n}Bu and Ph) respectively. The reactions of the crystallographically characterised complex [MoI$_2$(CO)(NCMe){P(OPh)$_3$}(η^2-EtC$_2$Et)](**13**), with a series of neutral and anionic donor ligands is described. The crystal structures of one of the reaction products, [MoI$_2$(CO)(dppe)(η^2-EtC$_2$Et)](**24**) is discussed. The structures of [MI$_2$(CO){P(O^{i}Pr)$_3$}$_2$(η^2-EtC$_2$Et)] {M = Mo(**31**) and W(**32**)}, have also been crystallographically determined.

The fourth chapter is divided into two parts. The first part deals with the synthesis and characterisation of tripodal triphos {MeC(CH$_2$PPh$_2$)$_3$} seven-coordinate didentate phosphine complexes of molybdenum(II) and tungsten(II), namely $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**36** and **37**), which have the tripodal triphos ligand coordinated in a bidentate manner. The intramolecular rearrangement of **36** and **37** to give the dicarbonyl complexes, $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ (**38** and **39**) is also discussed. The reactions of **36** and **37** with $[MI_2(CO)_3(NCMe)_2]$(M = Mo or W), $[MI_2(CO)_3(NCMe)L]\{L = PPh_3, AsPh_3, SbPh_3, P(OMe)_3, P(OEt)_3, P(OPh)_3\}$, $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$(n = 1 or 2), $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$, $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X = Cl or Br; R = H, Me), $[Fe_2(CO)_9]$ and $[FeI(CO)_2(Cp \text{ or } Cp')]$ to give a wide range of multimetallic complexes is also described.

The fifth chapter describes the synthesis and characterisation of the seven-coordinate dichloro complex $[WCl_2(CO)_3(NCMe)_2]$, by reacting the complex $[WI_2(CO)_3(NCMe)_2]$ with excess of NaCl in acetone/CH_2Cl_2 (50:50). The reaction of $[WCl_2(CO)_3(NCMe)_2]$ with 3-hexyne gives $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**80**), which reacts with a wide range of ligands, such as NPh_3, PPh_3, $Ph_2P(CH_2)_nPPh_2$, (n = 1 or 2), $P(OPh)_3$, cis-$Ph_2PCH{=}CHPPh_2$, bipy and NaS_2CNR_2 (R = Me or Et) to give a series of new chloro 3-hexyne complexes of tungsten(II).

Chapter six gives full experimental details for Chapters two to five. In conclusion, ninety seven new organomolybdenum and tungsten complexes containing a wide variety of ligands have been prepared and characterised, which form the main part of this thesis. Finally, an investigation of the catalytic activity of the complex $[WCl_2(CO)_3(NCMe)_2]$ towards the polymerisation of phenylacetylene, PhC_2H is briefly discussed.

Abbreviations

Ar	Aryl
^{t}Bu	Tertiary butyl $C(CH_3)_3$
Cod	Cyclooctadiene C_8H_{12}
Cp	Cyclopentadienyl (η^5-C_5H_5)
Cp'	Methylcyclopentadienyl (η^5-C_5H_5Me)
bipy	2.2'-bipyridyl
1,10-Phen	1,10-Phenanthroline, $C_{12}H_8N_2$
dppm	bis(diphenylphosphino) methane
dppe	bis(diphenylphosphino) ethane
dppp	bis(diphenylphosphino) propane
dppb	bis(diphenylphosphino) butane
dpppe	bis(diphenylphosphino) pentane
dpph	bis(diphenylphosphino) hexane
Et	Ethyl, C_2H_5
Me	Methyl, CH_3
Ph	Phenyl, C_6H_5
^{i}Pr	Isopropyl, $(CH_3)_2CH$-
Py	Pyridine, C_5H_5N
THF	Tetrahydrofuran, C_4H_8O

Linear triphos	$PhP(CH_2CH_2PPh_2)_2$
Tripodal triphos	$MeC(CH_2Ph_2)_3$
X	Halide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
M	Transition Metal

Instruments :-

EA	Elemental Analytical
IR	Infrared
NMR	Nuclear magnetic resonance
uv/vis	ultraviolet/visible

Units :-

Å	Angstroms
°C	Degrees Centigrade
cm^3	Centimetres cubed
g	grams
h	hour
Hz	Hertz
mins	minutes
mls	millilitres
mol	moles

mmol	millimoles
ppm	part per million
s	seconds
V	Volts

CHAPTER ONE

INTRODUCTION

Chapter One

1.1-Chemical and Physical Properties of Molybdenum and Tungsten:-

The chemistry of molybdenum and tungsten display very similar behaviour. They are classed together in terms of their properties and reactions. Molybdenum and tungsten are members of group 6 of the periodic table, and they are d-block transition metals. Molybdenum has the electronic configuration $[Kr]4d^5 5s^1$, and it is an element in the second transition series , whereas tungsten has the electronic configuration $[Xe]5d^4 6s^2$, and is an element of the third transition series. Since tungsten has 5d electrons, the atom size of tungsten is slightly larger than Molybdenum, although the Lanthanide contraction makes tungsten smaller than would be expected from going down a transition series.

Both of them have typically metallic bcc structures, and the most obvious characteristic of molybdenum and tungsten are their refractive nature, and tungsten has the highest melting point of all metals. The metallic nature of Mo and W is fabricated by the techniques of powder metallurgy, and in consequence, many of their bulk physical properties depend critically on the nature of their mechanical history. Both metals can exist in several oxidation states ranging from (-2 to +6) and they have a wide range of coordination numbers. (Some of their properties are given in table 1.1).

Table (1-1) Some properties of Molybdenum and Tungsten.

PROPERTY		MOLYBDENUM	TUNGSTEN
Symbol		Mo	W
Element Configuration		$[Kr]4d^5 5s^1$	$[Xe]5d^4 6s^2$
Atomic Number		42	74
Atomic Mass		95.94	183.85
Number of naturally occurring isotopes		7	5
Metal radius (12-coordinate)/pm		139	139
Ionic radius (6-coordinate)/pm	VI	59	60
	V	61	62
	IV	65	66
	III	69	-
MP/^{0}C		1620	3380
BP/^{0}C		4650	5500
Density (20 ^{0}C)/g.cm^{-3}		10.28	19.3
Electrical resistivity (20 ^{0}C)/μohm.cm		~5	~5
Atomic Radius (A)		1.40	1.41
ΔH Ionization 1st (kJ/Mol^{-1})		685	770

1.2-Preparation and Applications of Molybdenum and Tungsten:

Both molybdenum and tungsten have approximately the same abundance in nature ($\sim10^{-10}$ %). Molybdenum has been found as Molybdenite, but tungsten is found as Tungstates. Molybdenum is found both as a primary product, and as a by product in the production of copper, in the manufacture of stainless steel and high-speed tools, the MoO_3 may be used directly or after conversion to ferromolybdenum by the aluminothermic process. Purification is possible by dissolving ferromolybdenum in aqueous ammonia and the crystallizing of ammonium molybdate as $[NH_4]_6[Mo_7O_{24}].4H_2O$ or $[NH_4]_2[Mo_2O_7]$, depending on conditions. Ammonium molybdate is used in the manufacture as a starting material for molybdenum chemicals. In 1980, the world produced equivalent to 108,000 tonnes of molybdenum ores.

Molybdenum is important in biological systems, (as metalloenzymes), and their complexes have been used as catalysts[1]. Molybdenum is an integral part of the nitrogen fixing enzyme, nitrogenase[2]. Tungstic acid is roasted to WO_3, which is reduced to the metal by heating with hydrogen at 850^0C, and is also found in a few bacterial enzymes (format dehydrogenases [3]). Half of tungsten production is used as the carbide , WC , and for wear resistant alloys. The pure metal is the most important user as a filament in electrical light bulbs, since first used in 1908. In 1980, the world production was 50,000 tonnes of tungsten ores.

1.3-Bonding of an Alkyne to a Transition-Metal :-

The bonding of alkyne ligands in transition-metal complexes can be understood in the light of the bonding of alkene ligands to transition-metals. In 1831, Zeise[4] described the synthesis of the first complex involving preparation of Zeise's salt, K[$PtCl_3(\eta^2$-$C_2H_4)$].H_2O, by reacting ethene with $K_2[PtCl_4]$ for several days in hydrochloric acid. The structure has been characterised by X-ray crystallography[5,6], (see Fig1.1).

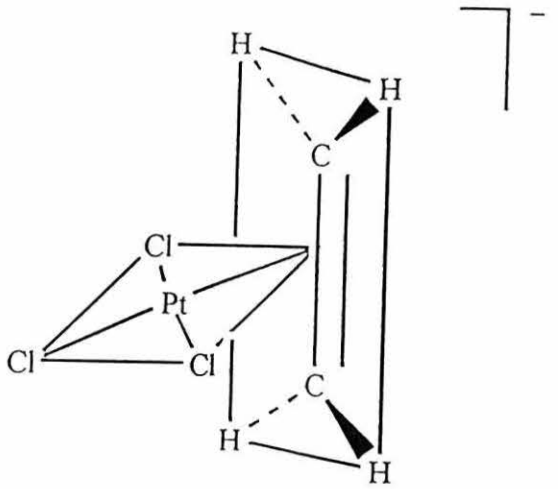
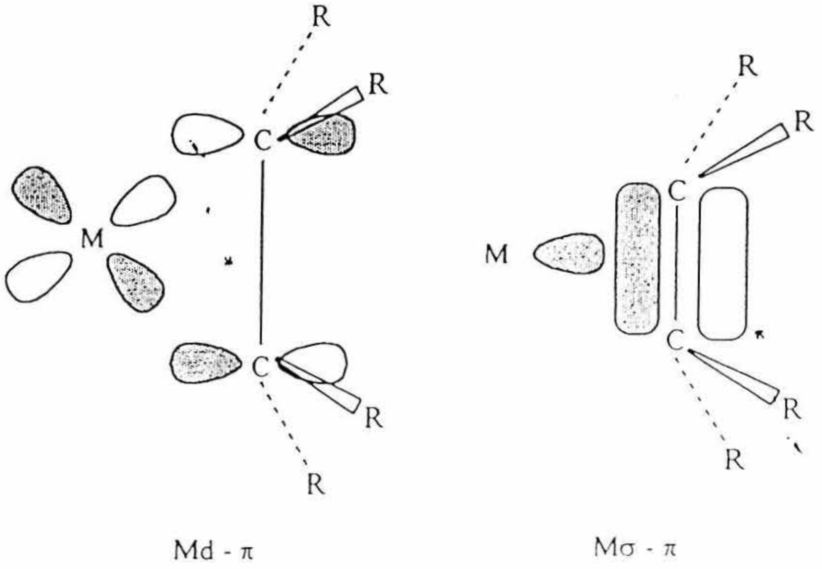


Fig (1-1). The structure of the anion of Zeise's salt. $[PtCl_3(\eta^2$-$C_2H_4)]^-$

Studies have shown that the bonding between metal and alkyne in transition-metal complexes suggests that the alkynes and alkenes are similar for the kind of bond with the metal[7]. The earliest papers concerning the bonding of alkenes to metals were published by Dewar[8], in 1951 and Chatt and Duncanson[9] in 1953. They suggested the bonding to be synergic. The bonding of an alkene with a centre consists of a σ-bonding component and a π-bonding component.

The interaction between a transition-metal with π-electron density can occur providing the similar energy of the alkene and metal electron density is transferred from the alkene filled π-orbitals to empty metal dπ orbitals. The contribution which both the components make to the bonding between an alkene and a metal depends on the relative energies of the s, pz, dz^2 metal orbitals, and the position of the metal in the periodic table.

If the electron density is transferred into π^*-alkene orbitals, then the length of the alkene carbon-carbon distance will change to a single bond. This changes the hybridization of the carbon atoms from sp^2 to sp^3, and that lowers the angle between substituents at the carbon atoms and displaces them away from the metal. The strong π-acceptor properties of the alkene makes a longer distance between carbon-carbon double bonds and leaves these alkene carbon atoms close to sp^3 hybridisation.(see Figure1.2).



(Fig1.2) A diagram to show the displacement of substituents on the alkene upon co-ordination with a transition-metal.

However, alkynes have two π-orbitals at right angles to each other. Interaction between filled π-orbitals of the alkyne to empty metal d-acceptor orbitals with simultaneous back donation of electron density from a suitable filled d-orbital into an empty antibonding π^* orbital on the alkyne can explain the bonding in complexes where alkynes act as two electron donors e.g $[M(\eta^2\text{-}RC_2R)Cp_2]$ (M = Mo or W).

It has been suggested by King,[10] that the $\pi_\perp$ orbitals on the alkyne could allow the alkyne ligand to be three or four-electron donor ligand. It is possible in certain cases for donation from the $\pi_\perp$ alkyne orbitals to contribute considerably to the metal alkyne bond and metal complexes can also be stabilised by steric interactions as in $[Mo(CO)_3\{P(C_6H_{11})_3\}_2]$($C_6H_{11}$ = Cyclohexyl), while a combination of steric and electronic (π-donor) interactions may be responsible for the existence of a range of formally 16-electron Mo(II) and W(II) halogen and sulphur derivatives, such as $[MX_2(CO)_2L_2]$(X = halogen; L = tertiary phosphine or arsine)[11] (see Figure1.3).

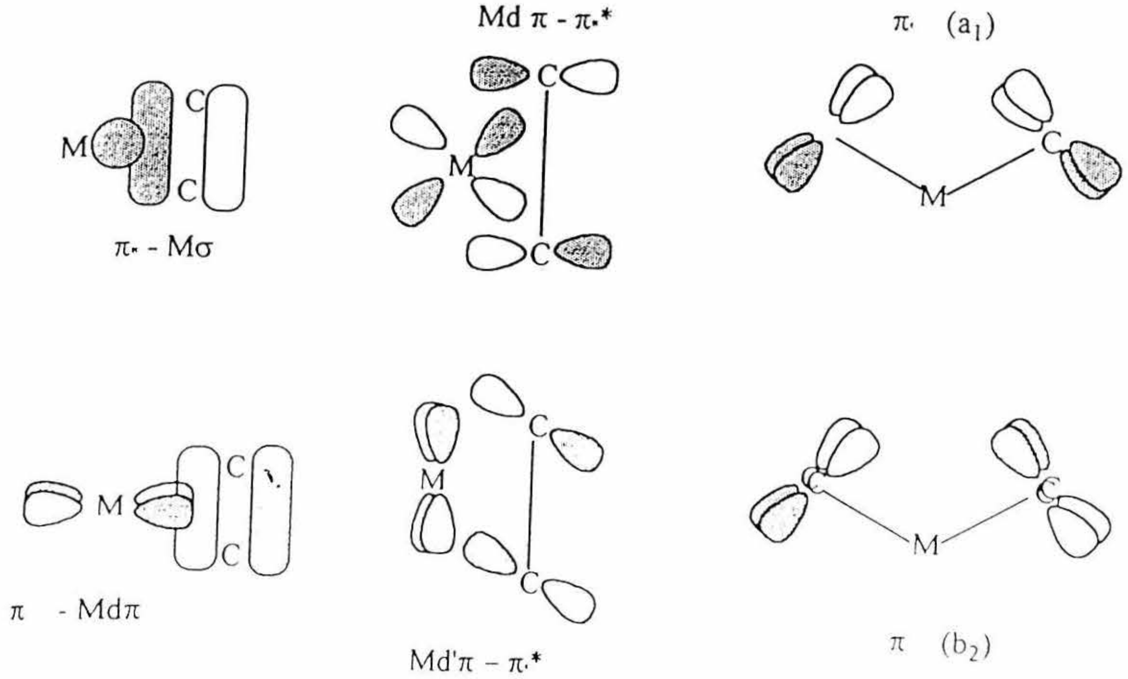


Fig. 1.3- A diagram to show the interaction between $\pi_\perp$ alkyne orbitals and metal d-orbitals.

In 1980, Templeton and Ward[12,13] and Hoffman[14] have confirmed that ethyne can act as a two or four electron-donor to form (η^2-alkyne) tungsten(II) complexes. Two *cis*-alkyne ligands each donate two electrons from $\pi_\perp$ orbitals into vacant σ-metal acceptor orbitals, donation of electron density from $\pi_\perp$ orbitals is restricted . Three-electron donation occurs because *cis*-alkyne ligands have C_{2v} symmetry, giving rise to $\pi_\perp$ orbital combination of a_1 and b_2 symmetry. When an alkyne coordinates with a transition-metal, the substituents on the alkyne are bent backwards, (Fig 1.4).

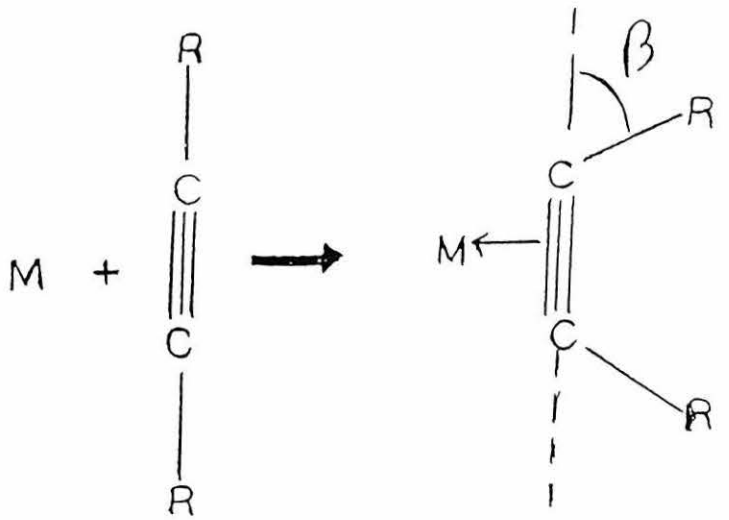


Fig.(1-4) A diagram to show the bend back angle of a co-ordinated alkyne ligand to a transition-metal.

1.4-Synthesis of alkyne complexes of Molybdenum(II) and Tungsten(II):-

1.4a-Mono(alkyne) complexes of molybdenum(II) and tungsten(II) :-

There are many methods to prepare mono(alkyne) complexes of molybdenum(II) and tungsten(II). The simplest method involves the direct reaction of an alkyne with a molybdenum(II) or tungsten(II) complex. For example,[15] reaction of $[MoX_2(CO)_3L_2]$ (L = PEt_3, PPh_3, py) with RC_2R (R = H and Me) to give the carbonyl displaced complexes $[MoX_2(CO)L_2(\eta^2\text{-}RC_2R)]$ (where L = PEt_3, PPh_3, py).

The first molybdenum(II) and tungsten(II) alkyne complexes were synthesised by Otsuka *et al*[16] in 1969 by refluxing $[MoH_2Cp_2]$ with diphenylacetylene in toluene for three hours, to give the thermally stable but air-sensitive complex $[Mo(\eta^2\text{-}PhC_2Ph)Cp_2]$.

In 1973, Thomas[17] prepared the bis(cyclopentadienyl)alkyne complexes $[M(\eta^2\text{-}RC_2R)(\eta^5\text{-}Cp)_2]$ (M = Mo and W; R = Ph, CF_3, Me)(see Equation 1.1), by reduction of the Mo(IV) and W(IV) complexes $[MCl_2(\eta^5\text{-}Cp)_2]$, in the presence of the alkyne in toluene.

$$[MCl_2(\eta^5\text{-}Cp)_2] + RC_2R \xrightarrow{\text{Na/Hg, Toluene, 17h}} [M(\eta^2\text{-}RC_2R)(\eta^5\text{-}Cp)_2] + 2NaCl + [MH_2(\eta^5\text{-}Cp)_2]$$

(Equation 1.1)

Irradiation of the complex $[Mo(CO)(\eta^5\text{-}Cp)_2]$ with UV light[18,19] in the presence of RC_2R forms the molybdenum ethyne and butyne deravatives, $[Mo(\eta^2\text{-}RC_2R)Cp_2]$(R = H, Me). The easiest method to prepare cyclopentadienyl mono(alkyne) complexes is by heating $[MoCl(CO)_3Cp)]$ with internal alkynes in hexane to afford $[MoCl(CO)(\eta^2\text{-}RC_2R)Cp]$, (where R = CF_3, Me, Ph)[20]

The dppe ligand can also be replaced by RC_2R (R = Me, Ph) from $[Mo(dppe)_2Cp][X]$(X = BF_4 or PF_6) with RC_2R (R = Me, Ph) to give $[Mo(dppe)(\eta^2\text{-}RC_2R)Cp][X]$.[21] The molybdenum and tungsten acyl complexes of the type $[M(COR)(CO)(\eta^2\text{-}R_1C_2R_2)(\eta^5\text{-}Cp$, Cp' or Cp*)] have also been prepared by Alt *et al*[22,23], by photolysis of $[WR(CO)_3(\eta^5\text{-}Cp$, Cp' or Cp*)] with alkynes $R_1C_2R_2$ at low temperature to afford the complexes $[W(COR)(CO)(\eta^2\text{-}R_1C_2R_2)(\eta^5\text{-}Cp$, Cp' or Cp*)] (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph; $R_1 = R_2$ = H, Me and Ph; Cp'= C_5H_4Me; Cp* = C_5Me_5). Acyl derivatives of the general complexes $[W(COR)(L)(\eta^2\text{-}R_1C_2R_2)(\eta^5\text{-}Cp)]$[25] are formed by reacting the alkyne complexes $[W(COR)(\eta^2\text{-}R_1C_2R_2)(\eta^5\text{-}Cp)]$ with two-electron donor ligands, (L) {L = PR_3, $P(OR)_3$, CO}.

An excellent route to prepare mono(alkyne) complexes is by displacement of an alkyne ligand from bis(alkyne) cyclopentadienyl derivatives. For example, in 1981 Green and co-workers[25] have prepared the cationic molybdenum complexes $[Mo(CO)(L)(\eta^2\text{-}RC_2R')(\eta^5\text{-}Ar)]^+$ by replacement of an alkyne ligand by phosphine ligands from $[Mo(CO)(\eta^2\text{-}RC_2R_1)_2(\eta^5\text{-}Ar)]^+$ (where R = ^{t}Bu or ^{i}Pr, R_1 = H; R = Ph, R_1 = Me, L = PEt_3, PPh_3 or PCy_3; Ar = Cp or In; R = R_1 = Me or *p*-tol). (see equation 1.2).

$$[Mo(CO)(\eta^2\text{-}RC_2R_1)_2(\eta^5\text{-}Ar)][BF_4] + L \longrightarrow [Mo(CO)L(\eta^2\text{-}RC_2R_1)(\eta^5\text{-}Ar)][BF_4] + RC_2R_1$$

Equation (1.2)

The cationic complexes $[Mo(dppm)(\eta^2\text{-}RC_2R_1)(\eta^5\text{-}Cp)]^+$ [26] were prepared by reaction of $[Mo(NCMe)(\eta^2\text{-}RC_2R_1)_2(\eta^5\text{-}Cp)]^+$ (R, R_1 = H and Ph) with dppm involving displacement of both NCMe and an alkyne ligand in these reactions.

The cationic bis(phosphine) complexes, $[Mo(L_2 \text{ or } L\hat{\ }L)(\eta^2\text{-}RC_2R_1)(\eta^5\text{-}Ar)]^+$ can be synthesised by reaction of $[Mo(NCMe)(\eta^2\text{-}RC_2R_1)_2(\eta^5\text{-}Ar)]^+$ with two equivalents of L (L = PMe_3, PEt_3 or $PMePh_2$) or one equivalent of bidentate phosphine {L^L = dppe, dmpe}. In 1987, Bergman, *et al*[27] prepared the mono(alkyne) products by irradiating in Et_2O with the complex, $[W(\eta^1\text{-}CH_2COEt)(CO)_3Cp]$ with UV light in the presence of

PhC_2H to afford the oxallyl complex, $[W(\eta^1\text{-}CH_2COEt)(CO)_2(\eta^2\text{-}PhC_2H)Cp]$. In 1982, Umland and Vahrenkamp[28] reported the reactions of alkynes, RC_2R with the seven-coordinate complexes $[WI_2(CO)_4L]$ to afford $[WI_2(CO)_2L(\eta^2\text{-}RC_2R_1)]$ (L = PMe_3, $AsMe_3$, CN^tBu; R = R_1 = H; R = Ph, R_1 = H). In 1983, Templeton and co-workers[29] reported the synthesis and characterisation of complexes of the type $[MoBr_2(CO)L_2(\eta^2\text{-}RC_2R_1)]$(R = R'= Me and Ph) by refluxing seven-coordinate complexes $[MoBr_2(CO)_3(PEt_3)_2]$ with excess alkyne (see equation 1.3)

$$[MoBr_2(CO)_3(PEt_3)_2] + RC_2R_1 \longrightarrow [MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}RC_2R_1)].$$

Equation (1.3)

In 1986[30], the reactions of the seven-coordinate complexes, $[MX_2(CO)_3L_2]$ with alkynes were expanded to include a wide variety of ligands (M = M and W, X= Cl and Br, L = PPh_3, PEt_3, py, L_2 = dppe, R = R_1 = Me, Ph, Et, R = H, R_1 = ^tBu, ^nBu, Ph), in refluxing CH_2Cl_2 for a period of many days to give $[MX_2(CO)L_2(\eta^2\text{-}RC_2R_1)]$. The preparation of mono(alkyne) complexes[31] such as $[MX_2(CO)L_2(\eta^2\text{-}RC_2R_1)]$, by reaction of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ with RC_2R_1 (R = R_1= Me, Ph, Et; R = Me, R_1 = Ph) in hexane have been described. These react with four equivalents of nucleophilic ligands L {L = CN^tBu, PPh_3 and $P(OMe)_3$} (as shown in Equation 1.4), to give mono(alkyne) complexes.[31]

$$\begin{tikzcd} {[W(\mu\text{-}Br)Br(CO)_4]_2 + \text{Excess } RC_2R_1} \arrow[r] & {[W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R_1)_2]_2 + 6CO\uparrow} \arrow[d, "L"] \\ & {[WBr_2(CO)L_2(\eta^2\text{-}RC_2R_1)] + RC_2R_1} \end{tikzcd}$$

Equation (1.4)

Reacting the seven-coordinate complex, $[MoBr_2(CO)_3(PEt_3)_2]$ with cyclooctyne was reported by Bennett and Boyd[32] to give $[MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}C_8H_{12})]$.

In.1978,[33] the alkyne complex, $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}HC_2H)]$ has been prepared by reacting the tungsten complex, $[W(CO)_2(PPh_3)(S_2CNEt_2)_2]$ with HC_2H, whereby the ethyne ligand replaces both the CO and PPh_3. The mixed alkene/alkyne cationic complex $[Mo(CO)(\eta^2\text{-}C_2H_4)(\eta^2\text{-}MeC_2Me)Cp][BF_4]$ has been prepared by Green *et al*[34], as shown in Equation(1.5)

$$\begin{tikzcd}
{[\mathrm{Mo(CO)}(\eta^2\text{-}\mathrm{MeC_2Me})_2\mathrm{Cp}]^+} \arrow[r, "\mathrm{EtMgBr}"] & {[\mathrm{MoBr(CO)}(\eta^2\text{-}\mathrm{MeC_2Me})_2\mathrm{Cp}]} \arrow[d, "\mathrm{AgBF_4} + \mathrm{C_2H_4}"] \\
 & {[\mathrm{Mo(CO)}(\eta^2\text{-}\mathrm{H_2C_2H_2})(\eta^2\text{-}\mathrm{MeC_2Me})\mathrm{Cp}][\mathrm{BF_4}].}
\end{tikzcd}$$

Equation (1.5)

The alkyne complex $[WCl(CO)_2(acac)(\eta^2\text{-}HOC_2tol\text{-}p)]$ was prepared in 1979[35] by Fischer and Friedrich by photolysis of $[W(\equiv Ctol\text{-}p)Cl(CO)_4]$ with excess Na[acac] in diethyl ether to give a coordinated hydroxy alkyne by replacement of a carbonyl ligand by $acac^-$.(see Equation1.6).

$$\textit{trans}\text{-}[W(\equiv Ctol\text{-}p)Cl(CO)_4] + Na[acac] \xrightarrow{Et_2O,hv} [WCl(CO)_2(acac)(\eta^2\text{-}HOC_2tol\text{-}p)] + 2CO\uparrow.$$

Equation (1.6)

MacDonald and co-workers,[36] reported the reaction of the molybdenum complex $[Mo(CO)_2(S_2P^iPr_2)_2]$ with ethyne in CH_2Cl_2 at room temperature to give $[Mo(\eta^2\text{-}ethyne)_2(S_2P^iPr_2)_2]$. Complexes containing triphenylphosphine can be prepared by simple substitution of the carbonyl ligand. For example, reaction of the complex $[Mo(SC_6F_5)(CO)(\eta^2\text{-}CF_3C_2CF_3)Cp]$ with PPh_3 at ambient temperature in diethyl ether gave the complex $[Mo(SC_6F_5)(CO)(PPh_3)(\eta^2\text{-}CF_3C_2CF_3)Cp]$.[37] For the related tungsten complexes[38], photolysis was necessary because the activation energy which is needed for carbonyl dissociation is higher.

1.4b-Bis(alkyne) Complexes of Molybdenum(II) and Tungsten(II) :-

Some bis(alkyne) complexes of tungsten have been prepared by cleavage of the iodide-bridges with NCMe in $[\{W(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}PhC_2R)_2\}_2]$ (R = Me or Ph)[39] to give $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2R)_2]$. These complexes react with one equivalent of L (L = py, 3-Cl-Py, or 3,5-Me_2Py) in CH_2Cl_2 at room temperature to give the acetonitrile displaced products $[WI_2(CO)L(\eta^2\text{-}PhC_2R)_2]$. $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ was reacted with two equivalents of pyridine gave firstly, mono(alkyne) complex, $[WI_2(CO)(py)(\eta^2\text{-}PhC_2R)_2]$, which is reacted again with displaced but-2-yne ligand to afford the cationic bis(but-2-yne) complex, $[WI(CO)(py)_2(\eta^2\text{-}MeC_2Me)_2]I$[40].

Six coordinate bis(alkyne) complexes such as $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R)_2\}_2]$ can be prepared by addition of internal alkynes to $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ in hexane at room temperature to yield the dimeric products $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R)_2\}_2]$, see Equation (1.7)[31].

$$[\{W(\mu\text{-}Br)Br(CO)_4\}_2] + 4RC_2R \longrightarrow [\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R)_2\}_2].$$

(Equation 1.7).

The reactions of these dimers with monodentate nucleophilic ligands to afford mono (alkyne) complexes has already been discussed, in section 1.4a the intermediate bis(alkyne) complexes were isolated from reaction of $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}MeC_2Me)_2\}_2]$ and CN^tBu to afford $[WBr_2(CO)(CN^tBu)(\eta^2\text{-}MeC_2Me)_2]$.

In 1982[41], the first molybdenum bis(alkyne) complexes with dithiocarbamate ligands were reported by refluxing $[Mo(CO)_2(S_2CNEt_2)_2]$ with excess alkyne in dichloromethane overnight to produce $[Mo(S_2CNEt_2)_2(\eta^2\text{-}RC_2R)_2]$. When the solvent was changed to toluene or benzene, the reaction takes one hour. Mixed alkyne complexes were synthesised by reaction of $[Mo(CO)(S_2CNR_2)_2(\eta^2\text{-}RC_2R)]$ with an amount equimolar of alkyne, see Equation (1.8).

$$[Mo(CO)(S_2CNR_2)_2(\eta^2\text{-}R^1C_2R^2)] + R^3C_2R^4 \xrightarrow[\text{benzene, refluxing}]{\text{1-3 hours}} [Mo(S_2CNR_2)_2(\eta^2\text{-}R^1C_2R^2)(\eta^2\text{-}R^3C_2R^4)].$$

(Equation 1-8)

R= Et, R^1= H, R^2= Ph, R^3= R^4= Ph;

R= Me, R^1= R^2= Ph, R^3= R^4= CO_2Me;

R= Me, R^1= H, R^2= Ph, R^3= R^4= Et;

R= Me, R^1= R^2= Ph, R^3= H, R^4= ^{n}Bu.

Over the last twenty years the complexes of cyclopentadienyl bis(alkyne) of Mo and W have been extensively studied. In 1974, Stone *et al*[42], have prepared cyclopentadienyl complexes with two alkynes of the type $[MCl(\eta^2\text{-}RC_2R')_2Cp]$ (M = Mo or W; R = R' = CF_3, Ph or Me; R = Me, R' = Ph), by reacting the complexes $[MCl(CO)_3Cp]$ with internal alkynes in refluxing hexane. Mixed bis(alkyne) cyclopentadienyl[43] complexes have been prepared by refluxing the complexes $[MCl(CO)(\eta^2\text{-}PhC_2Ph)Cp]$ (M = Mo or W) with hexafluorobut-2-yne at 40^0C to produce $[MCl(\eta^2\text{-}CF_3C_2CF_3)(\eta^2\text{-}PhC_2Ph)Cp]$.

In 1975, Davidson and Sharp[44] synthesised the complexes $[MCl(\eta^2\text{-}RC_2R)_2Cp]$(M = Mo or W; R = Me, CF_3, CO_2Me) by reacting $[MoCl(CO)_3Cp]$ with $MeC{\equiv}CMe$, $CF_3C{\equiv}CCF_3$ and $MeCH_2C{\equiv}CCH_2Me$ in hexane. The molybdenum bromo and iodo derivatives, $[MoX(CO)_3Cp]$ (X = Br or I) have been reported to react with the alkyne, (MeC_2Me) in THF (THF = Tetrahydrofurane) to give $[MoX(CO)(\eta^2\text{-}MeC_2Me)Cp]$, but the yields were very low[43]. The same group also prepared mixed alkyne complexes, $[MoCl(\eta^2$-

$RC_2R^1)(\eta^2\text{-}R^2C_2R^3)Cp]$ from reaction of $[MoCl(CO)(\eta^2\text{-}RC_2Ph)Cp]$(R = H and Me), and an equivalent amount of alkyne at room temperature, see equation (1.9).

$$[MoCl(CO)(\eta^2\text{-}RC_2R^1)Cp] + R^2C_2R^3 \longrightarrow [MoCl(\eta^2\text{-}RC_2R^1)(\eta^2\text{-}R^2C_2R^3)Cp].$$

$R= Me, R^1= Ph, R^2= R^3= CF_3;$

$R= R^1= Ph, R^2= R^3= CF_3,$

$R= R^1= Ph, R^2= H, R^3= CF_3.$

Equation (1.9)

Davidson and Sharp[44] reported complexes of the type $[MoCl(\eta^2\text{-}ClCH_2C_2CH_2Cl)_2Cp]$ by refluxing $[MoCl(CO)_3Cp]$ with excess of $ClCH_2C_2CH_2Cl$ in hexane, but when using different alkynes containing OH of the type $HOCH_2C_2CH_2OH$, in refluxing CH_2Cl_2, gives the cationic complex $[Mo(CO)(\eta^2\text{-}HOCH_2C_2CH_2OH)_2Cp][Cl]$.

1.5-Reactions of alkyne complexes of Molybdenum(II) and Tungsten(II):

I.5a-Reactions of mono(alkyne) complexes:-

One of the most common reactions of alkyne complexes is substitution. When the complexes $[M(SC_6F_5)(CO)(\eta^2\text{-}CF_3C_2CF_3)Cp]$ (M = Mo and W) were reacted with L in diethyl ether at room temperature a carbonyl ligand was displaced to afford $[M(L)(SC_6F_5)(\eta^2CF_3C_2CF_3)Cp]\{L = PEt_3, PPh_3, PMe_2Ph, P(OMe)_3\}$.

Electrophilic attack by $[OEt_3][BF_4]$ to the acyl oxygen on complexes of the type $[W(\eta^1\text{-}COR)(CO)(\eta^2\text{-}HC_2H)Cp]$ affords the cationic carbene complexes $[W\{(\eta^1\text{-}C(R)OEt)\}(CO)(\eta^2\text{-}HC_2H)(\eta^5\text{-}Cp)][BF_4]$ (R= Me, Et, ^nPr, ^nBu)[45].

In 1984, Green *et al*[46] prepared the neutral complexes $[Mo(SR)\{P(OMe)_3\}(\eta^2\text{-}MeC_2Me)Cp]$ by replacement one of the phosphite ligands in the cationic complex $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)Cp][BF_4]$ with excess of RS^- (where R = Me, $4NH_2C_6H_4$,4-$MeOC_6H_4$, 4-MeC_6H_4, C_6H_5, 4-$NO_2C_6H_4$).

In 1985, Templeton *et al*[47] have synthesised the complexes $[Mo(S_2CNR_2)_2(\eta^2\text{-alkene})(\eta^2\text{-}RC_2R)]$ by treating $[Mo(CO)(S_2CNR_2)_2(\eta^2\text{-}RC_2R)]$ (M = Mo, W) with electron deficient alkenes, MA (methyl acetelene), TCNE (tetracyanoethylene) and *trans*-DCNE (dicyano ethene) in toluene at room temperature. Templeton *et al*[48] have reacted $[M(CO)(S_2CNR_2)_2(\eta^2\text{-}RC_2R)]$ with two equivalents of the two-electron donor ligands (L) {L = $P(OR)_3$, PR_3, RCN) which replaces the alkyne ligand, see Equation (1.10).

$$[M(CO)(S_2CNR_2)_2(\eta^2\text{-}R^1C_2R^2)] + 2L \longrightarrow [M(CO)L_2(S_2CNR_2)_2].$$

Equation (1.10)

Bennett *et al*[49] treated the complexes $[M(CO)(S_2CNR_2)_2(\eta^4\text{-}C_8H_{12})]$ (M = Mo or W, R = Me or Et) in presence of cyclooctyne to produce a mixture of $[M(CO)(S_2CNR_2)_2\{(\eta^4\text{-}C_8H_{12})_2CO\}]$ and $[M(S_2CNR_2)_2(\eta^4\text{-}C_8H_{12})_2(CO)]$ (M = Mo or W, R = Me or Et), and the percentage yield of product depends on the M and R ligands, and both contain the $\{(\eta^4\text{-}C_8H_{12})_2CO\}$ unit, which is formed from condensation of two C_8H_{12} units, and a carbonyl ligand, Figure (1.5). When M = Mo, the cyclooctyne complex is formed in higher yield, but when R = Et, the cyclooctyne complexes are formed in higher yield for both metals.

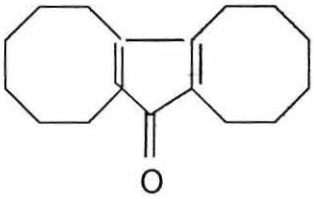


Figure (1-5)

1.5b-Reactions of bis(alkyne) complexes of molybdenum(II) and tungsten(II) :-

One of the main routes to prepare mono(alkyne) complexes is by reaction of bis(alkyne) complexes with nucleophiles. In 1983, Davidson and Vasapollo[31] have described the reaction of the bis(alkyne) dimers, $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R^1)_2\}_2]$, with four equivalents of L $\{L = CN^tBu, P(OMe)_3, PPh_3\}$ in dichloromethane to give monomeric alkyne complexes of the type $[WBr_2(CO)L_2(\eta^2\text{-}RC_2R^1)]$.

In 1983, Templeton *et al*[50], synthesised the sulphur-bridged dimers $[Mo_2(\mu\text{-}S)(\mu\text{-}R^1C_2R^2)(S_2CNR_2)_3(SCNR_2)]$(see Fig.1.6). by reaction of the complexes $[Mo(S_2CNR_2)_2(\eta^2\text{-}R^1C_2R^2)_2]$ with one equivalent of PEt_3 in refluxing toluene for 1.5hr (where R = Me, Et; $R^1 = R^2 =$ Et; $R^1 =$ H, $R^2 =$ Ph, ^{n}Bu; $R^1 =$ Me, $R^2 =$ Ph).

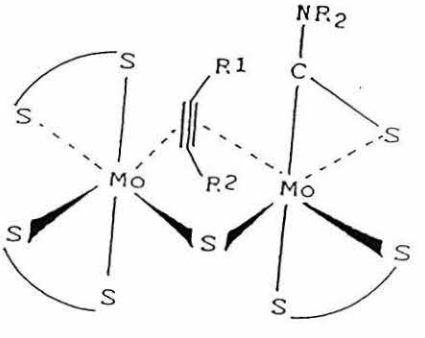
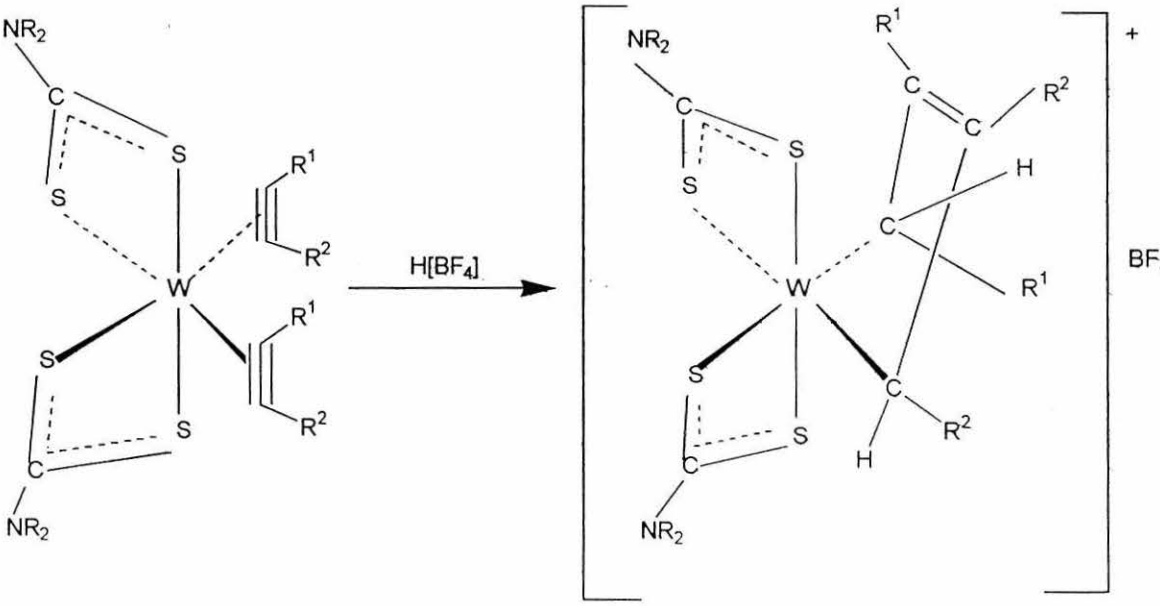


Figure (1-6)

In 1985, Templeton *et al*[51] protonated the complexes, $[W(S_2CNR_2)_2(\eta^2\text{-}R^1C_2R^2)_2]$ (R, R^1, R^2 = H, Me and Ph respectively) with $H[BF_4]$, which led to oxidative-coupling of the alkyne ligands to form a $\eta^4\text{-}C_4R_4H$ ligand, see equation (1.11)



Equation (1-11)

A number of "eighteen-electron" complexes of the type $[M(SC_6F_5)(\eta^2\text{-}RC_2R)_2Cp]$ were prepared by inserting $TlSC_6F_5$ into the bis(alkyne) complexes $[MCl(\eta^2\text{-}RC_2R)_2Cp]$ (M = Mo or W, R = CF_3 or Ph). In 1974, Stone *et al*[42], reacted the same complexes with $KBHpz_3$ ($KBHpz_3$ = tripyrazole hydro borate potassium) to give η^3-allylic complexes, as shown in Figure (1-7).

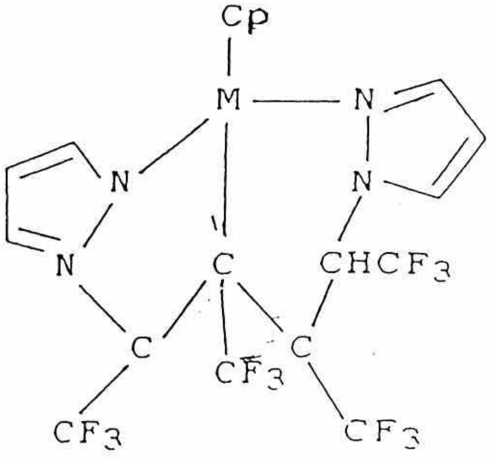
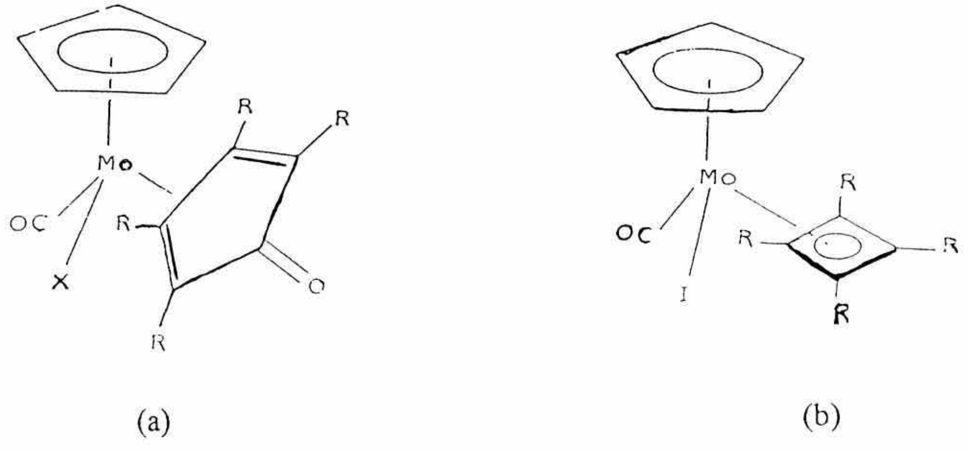


Figure (1-7)

In 1980, Davidson[52] prepared the cyclopentadienone complexes [MoX(CO)(η^4-Cyclopentadienone)Cp] (Fig.1.8a) by reacting [MoX(η^2-HFB)$_2$(η^5-Cp)] (X = I, Br, Cl) in presence of CO in hexane, but when X = I, the Cyclobutadiene complex, shown in Fig.1.8b can be isolated. The ligand NaS_2CNMe_2 reacts with [MoI(CO)(η^4-cbd)Cp] to afford the complex without carbonyl and iodo groups, [Mo(S_2CNMe_2)(η^4-cbd)Cp].



(a)

(b)

R= CF_3, X= Cl, Br, I.

Figure (1-8a,b)

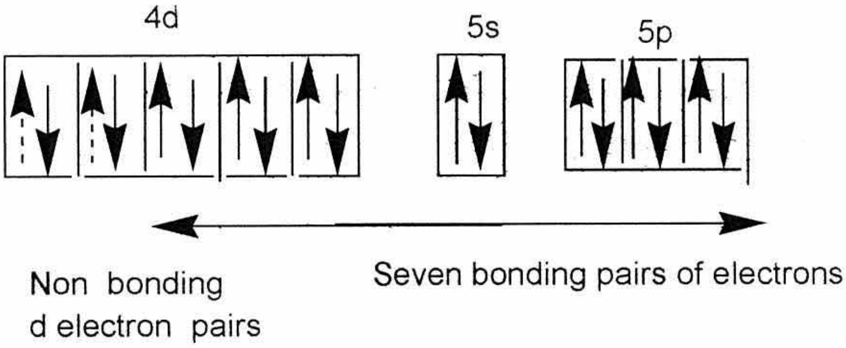
In 1981, Green *et al*[53], have described substitution for both cations, {$[Mo(CO)_2(\eta^2\text{-}RC_2R^1)(\eta^5\text{-}Ar)]^+$} and {$[Mo(NCMe)_2(\eta^2\text{-}RC_2R^1)(\eta^5\text{-}Ar)]^+$}, one of them contains carbonyl with alkyne, and the other contains acetonitrile ligands. The complex, {$[Mo(NCMe)_2(\eta^2\text{-}RC_2R^1)(\eta^5\text{-}Ar)]^+$} which contains acetonitrile, reacts with two equivalents of L (L_1 = monodentate phosphine such as PEt_3, PMe_3 and $PMePh_2$; L_2 = bidentate phosphorus, dppe or dmpe) to afford complexes of the type $[Mo(L)_2(\eta^2\text{-}RC_2R^1)(\eta^5\text{-}Ar)]^+$ or $[Mo(L_2)(\eta^2\text{-}RC_2R^1)(\eta^5\text{-}Ar)]^+$, which have carbonyl and alkyne reacts with one equivalent of L (L = monodentate phosphine) such as PEt_3, PPh_3 and PCy_3 to give the complexes $[Mo(CO)L(\eta^2\text{-}RC_2R^1)(\eta^5\text{-}Ar)]^+$ (where Ar = Cp or In).

Green and co-workers[54] reacted complexes of the type $[Mo(CO)(\eta^2\text{-}RC_2R^1)Cp]^+$ ($R = R^1 = Me$, $R = H$, $R^1 = {}^tBu$) and dpps (o-diphenyl phosphino styrene) in refluxing CH_2Cl_2, where the dpps join through both phosphorus and the alkene ligands to give $[Mo(dpps)(\eta^2\text{-}RC_2R^1)Cp]$. Sodium dithiocarbamate replaces CO and alkyne from cationic complexes of the type $[Mo(CO)(\eta^2\text{-}RC_2R^1)_2Cp]^+$, to afford $[Mo(S_2CNMe_2)(\eta^2\text{-}RC_2R^1)Cp]$ ($R = R^1 = Me$, $R = {}^tBu$ $R^1 = H$), but with $(SC_6H_4SPh\text{-}o)^-$ two products are formed with one alkyne and two alkynes, $[Mo(SC_6H_4SPh\text{-}o)(\eta^2\text{-}RC_2R^1)Cp]$ and $[Mo(SC_6H_4SPh\text{-}o)(\eta^2\text{-}RC_2R^1)_2Cp]$, respectively.

1.6-Seven-coordinate complexes of Molybdenum(II) and Tungsten(II) :-

The first seven-coordinate complexes of molybdenum(II) and tungsten(II), $[MoX_2(CO)_3(diars)]$ (X = Br or I), were described by Nyholm *et al* in 1960[55]. by the controlled oxidation of $[Mo(CO)_4(diars)]$ with iodine or bromine to give $[MoX_2(CO)_3(diars)]$, {diars = $1,2\text{-}Me_2As(C_6H_4)AsMe_2$}.

These complexes are diamagnetic, and molecular weight and molar conductivity in nitrobenzene show that they are seven-coordinate derivatives of bivalent molybdenum. The electron configuration of seven-coordinate complexes of Mo(II) and W(II) is shown in Scheme 1.1 :-



(Scheme 1.1)

Under similar conditions, the controlled oxidation of the tungsten complex $[W(CO)_4(diars)]$ with X_2 gives two kinds of seven-coordinate complex, depending on the oxidising agent used. The product with bromine gave the tungsten(III) complex $[WBr_2(CO)_3(diars)]Br$, but with iodine the complex $[WI(CO)_4(diars)]I_3$ was isolated[55].

In 1971, Colton *et al*[56,57] prepared dimeric complexes of the type $[\{M(\mu\text{-}X)X(CO)_4\}_2]$ (M = Mo, W; X = Cl, Br, I), and the first of this type of complex, $[\{Mo(\mu\text{-}Cl)Cl(CO)_4\}_2]$ was prepared in 1966,[58,59] by the reaction of $[Mo(CO)_6]$ with chlorine at -78°C. The same methodology was used to prepare similar bromo bridged dimers, $[\{M(\mu\text{-}Br)Br(CO)_4\}_2]$ (M = Mo, W). The crystal structure of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ has been determined[60] and shows each tungsten atom to be a *fac*-$[WBr_3(CO)_3]$ octahedron with a capping carbonyl on the tricarbonyl face, see Figure. 1.9.

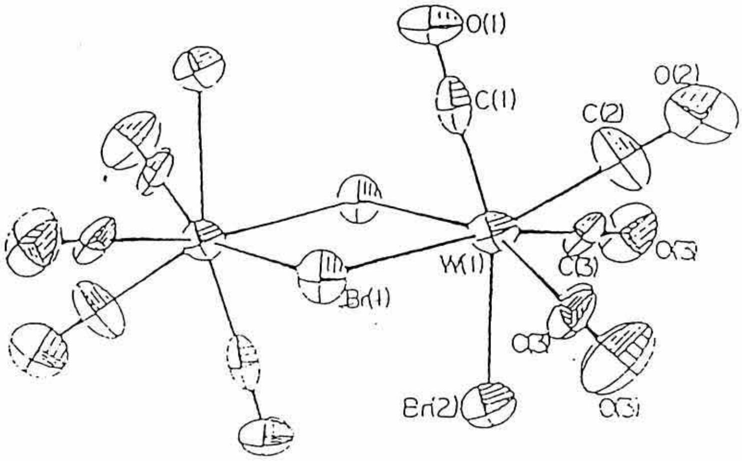


Figure.1.9-Crystal structure of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$

The complexes $[\{M(\mu\text{-}I)I(CO)_4\}_2]$ (M = Mo, W) were prepared by the photochemical reaction of I_2 with $[W(CO)_6]$ at ambient temperatures. There are many examples of reactions of these dihalide-bridged dimers, $[\{M(\mu\text{-}X)X(CO)_4\}_2]$ with a variety of donor ligands[61-70]. Carbon monoxide react with the blue dicarbonyl bis (triphenylphosphine) complex $[MoCl_2(CO)_2(PPh_3)_2]$, to rapidly gave the yellow tricarbonyl complex $[MoCl_2(CO)_3(PPh_3)_2]$[71].

The decomposition of the tricarbonyl dihalide complexes is a reversible reaction when refluxed in dichloromethane, and it is an equilibrium reaction in solution as shown in Equation (1.12) :-

$$[MX_2(CO)_3(PPh_3)_2] \rightleftharpoons [MX_2(CO)_2(PPh_3)_2] + CO\uparrow$$

Equation 1.12

1.7-Structures of Seven-coordinate complexes of Molybdenum(II) and Tungsten(II) :-

There are two reviews describing the structures of seven-coordinate complexes[72,73], they all indicate that there are three main geometries, and involve the seven ligands around the central metal as follows :-

1.7i-Pentagonal Bipyramid (PB) :-

A pentagonal bipyramid contains five equatorial ligands and two axial ligands (Figure 1.10). The equatorial positions are generally suited to tri, tetra, and Pentadentate ligands, as they are able to stay planar while occupying the equatorial girdle. The five equatorial ligands create a very crowded girdle around the metal and are not suited to bulky substituents.

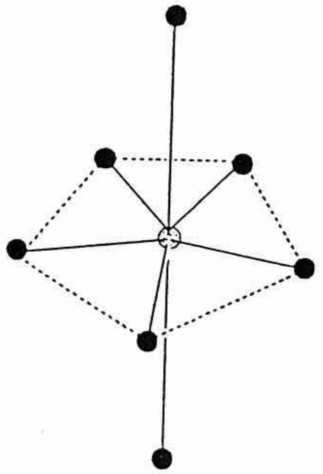


Figure (1-10)

Pentagonal bipyramidal structure.

1.7ii-Capped octahedron (COct) :-

The Capped Octahedron consists of a distorted octahedron made up of six ligands with the seventh ligand "capping" one of the trigonal faces of the octahedron (Figure 1-11). A capped octahedral geometry is exhibited by many seven-coordinate halocarbonyl complexes of Mo(II) and W(II).

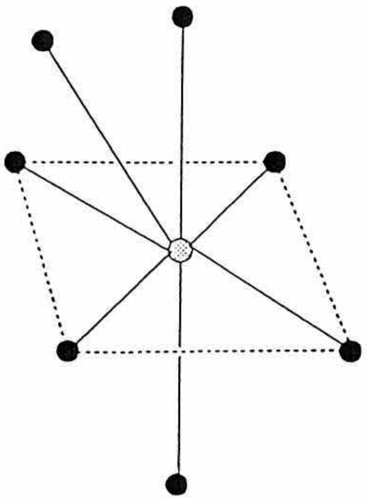


Figure (1-11)

Capped octahedral structure

1.7iii-Capped Trigonal Prism (CTP) :-

The capped trigonal prismatic geometry structure is frequently observed by seven coordinate halocarbonyl complexes. It consists of a trigonal prism with six ligands at each vertex with a seventh ligand "capping" one of the rectangular faces of the prism (Figure 1-12). As the case with COct geometry, the CTP is rarely found with bidentate donor ligands.

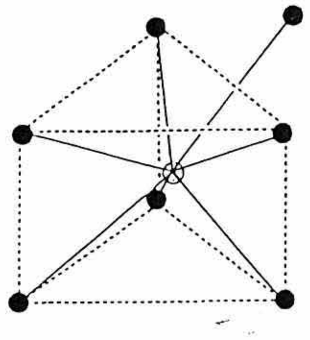


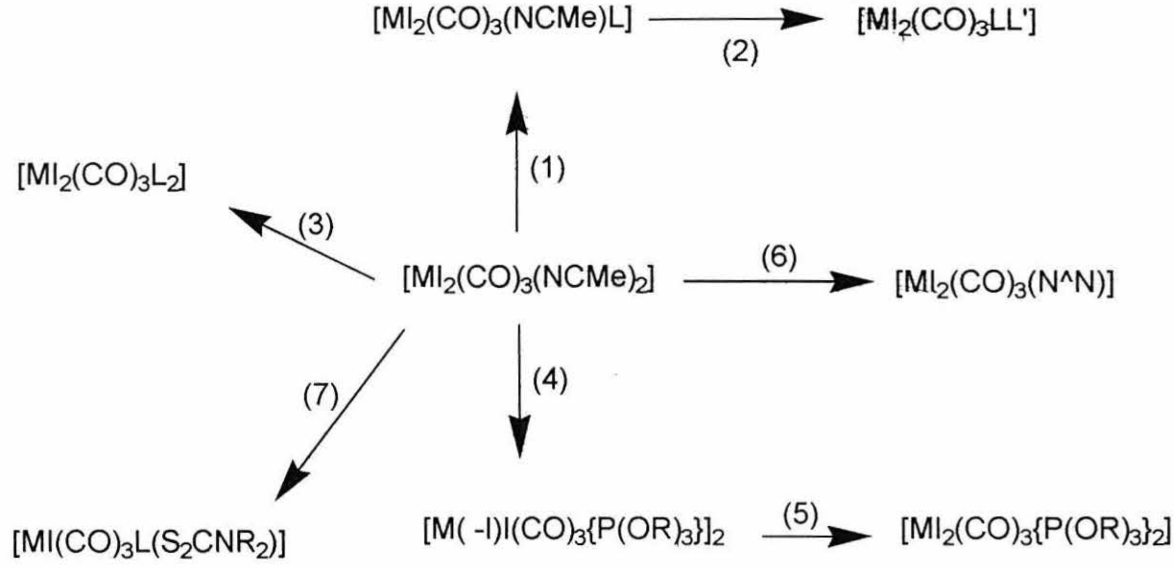
Figure (1-12)

Capped Trigonal prismatic structure.

1.8-Synthesis of the Seven-Coordinate complexes of Molybdenum(II) and Tungsten(II) of the type $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) :-

The seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ were reported in 1986[74] by Baker and co-workers. Refluxing the metal hexacarbonyls, $[M(CO)_6]$ (M = Mo, W), in acetonitrile (for M = Mo, 24hrs; M = W, 72hrs) gave the yellow complexes *fac*-$[M(CO)_3(NCMe)_3]$. Reaction *in situ* with one equivalent of I_2 at 0 °C afforded quantitative yields of the brown crystalline complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W).

Both the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (Mo and W) are very important starting materials for a wide range of reactions in organometallic chemistry. It is easy to replace the acetonitrile group by other ligands, and they have been used to synthesise over two thousand new compounds. The following scheme gives some examples of the reactions of $[MI_2(CO)_3(NCMe)_2]$ with donor ligands. (See Scheme 1.2).



Scheme (1.2)

(1) L = PPh_3, $AsPh_3$, $SbPh_3$, in CH_2Cl_2.

(2) L = PPh_3, $AsPh_3$, $SbPh_3$, py, $P(OR)_3$.

(3) L = PPh_3, $AsPh_3$, $SbPh_3$, $BiPh_3$.   (4) +(5) L = $P(OR)_3$ (R = Me, Ph) in CH_2Cl_2.

(6) L = N-N = 2,2'- bipyridyl; 1,10-Phenanthroline.

(7) L = PPh_3, $AsPh_3$, $SbPh_3$, in CH_2Cl_2 followed by $Na[S_2CNR_2]$. (R = Me, Et).

The seven-coordinate complexes molybdenum(II) and tungsten(II), $[MI_2(CO)_3(NC\ Me)_2]$ are soluble in CH_2Cl_2, $CHCl_3$, NCMe and hydrocarbon solvents, and as expected they obey the effective atomic number rule. The metals, M (Mo, W) are in oxidation state of +2 in $[MI_2(CO)_3(NCMe)_2]$, and contribute four d electrons, together with two electrons contributed from each of the seven-ligands to give a total of eighteen electrons.

The complex $[WI_2(CO)_3(NCMe)_2]$ has been crystallographically characterised,[75] and exhibits a capped octahedral geometry with a carbonyl group in the capping position. (see Figure 1.13). The second and third carbonyls are *cis* to one another, with one iodide making up the capped face of the octahedron. The iodide groups are *trans* one to another. In the same paper they described the ^{13}C NMR spectra for the above complex. At low temperature (-70° C, CD_2Cl_2) the spectrum showed carbonyl resonances at $\delta = 202.36$ and 228.48 ppm with intensity ratio of 2:1. However, at the room temperature the ^{13}C NMR spectrum shows a single resonance at $\delta = 219.65$ ppm, which suggests that the complex is fluxional at room temperature, (see Fig 1-13).

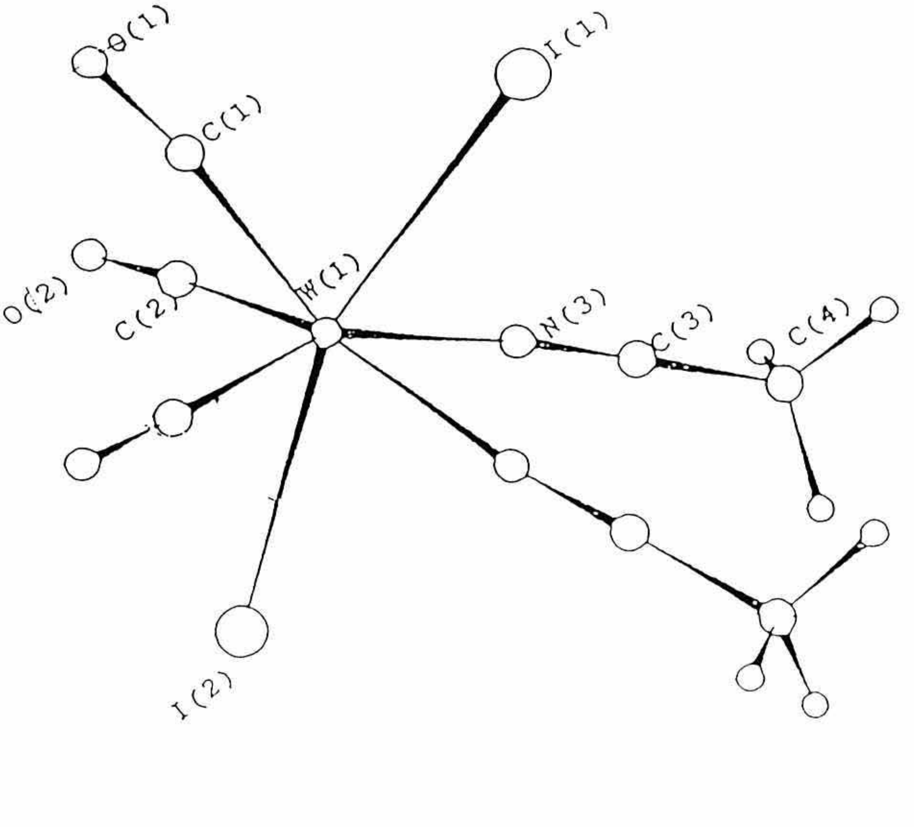


Figure (1-13):- Molecular structure of $[WI_2(CO)_3(NCMe)_2]$.

1.9-Reactions of the Seven Coordinate complexes of the Molybdenum(II) and Tungsten(II), $[MI_2(CO)_3(NCMe)_2]$ with donor ligands :-

In reactions of NCR with $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W), the acetonitrile ligands are exchanged to afford $[MI_2(CO)_3(NCR)_2]$ (for M = Mo, R = Ph; for M = W, R = Et, ^tBu, CH_2Ph, Ph), which react with one equivalent of L (L = PPh_3; $AsPh_3$; $SbPh_3$) to give the mixed ligand complexes of the type $[MI_2(CO)_3(NCR)L]$.[76] The crystal structures for the mixed-ligand seven-coordinate complexes, $[MI_2(CO)_3(NCR)(AsPh_3)]$ (R = Et or Ph) are also described.

In 1987[77], the reactions of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of pyridine (py) has been described to give two kinds of complexes, the monomers $[MI_2(CO)_3(NCMe)(py)]$ or the iodide-bridged dimers $[\{M(\mu\text{-}I)I(CO)_3(py)\}_2]$ by displacement of acetonitrile when (M = Mo and W; py = 2Me-py, 4Me-py, 3,5-Me_2-py, 3Cl-py, 3Br-py, 4Cl-py, 4Br-py). depending on the electronic properties, and the steric effects of the substituted pyridines.

The reaction of $[MI_2(CO)_3(NCMe)_2]$ with L_2 (L_2 = py_2, bipy, phen) gives the neutral acetonitrile exchanged products, $[MI_2(CO)_3L_2]$.[78] Reaction of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of 4-$HO_2CC_5H_4N$ in methanol afforded $[MI_2(CO)_3(NC_5H_4CO_2H\text{-}4)_2]$, which is soluble in water. When equimolar amounts of 3-$NaO_3SC_5H_4N$ are added, the mixed ligand complexes of the type $[MI_2(CO)_3(NC_5H_4CO_2H\text{-}4)(3\text{-}NC_2H_4SO_3Na)]$ are obtained [79].

In 1989, Baker *et al*[80] have synthesised the complexes $[MI_2(CO)_3(RN{=}CHCH{=}NR)]$ (M = Mo, W; R = Bu^i , Cy, Ph, 4-MeOPh) by displacement of acetonitrile ligands from $[MI_2(CO)_3(NCMe)_2]$ with 1,4-diaza-1,3-butadienes, (RN=CHCH=NR).

In 1986, Baker and Fraser[81] have reported the first reactions of $[MI_2(CO)_3(NCMe)_2]$ with phosphites, $P(OR)_3$ (R = Me, Ph) to give $[MI_2(CO)_3\{P(OR)_3\}_2]$. Reactions of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of L (L = PPh_3, $AsPh_3$, $SbPh_3$ gave $[MI_2(CO)_3L_2]$, which are under investigation as catalysts for the ring-opening polymerisation of norbornene.[82] The bidentate phosphine ligand complexes, $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (M = Mo or W; n = 1-6) have been reported in 1987[83], by reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of $\{Ph_2P(CH_2)_nPPh_2\}$ (n = 1-6).

Krishnamurthy *et al*[84] have been described the reactions of $[MI_2(CO)_3(NCMe)_2]$ with the diphosphazene ligands $RN\{P(OPh)_2\}_2$ (R = Me, Ph) to give $[MI_2(CO)_3\{RN\{P(OPh)_2\}_2]$, which was structurally characterised for M = W, R = Ph. (Figure 1-14).

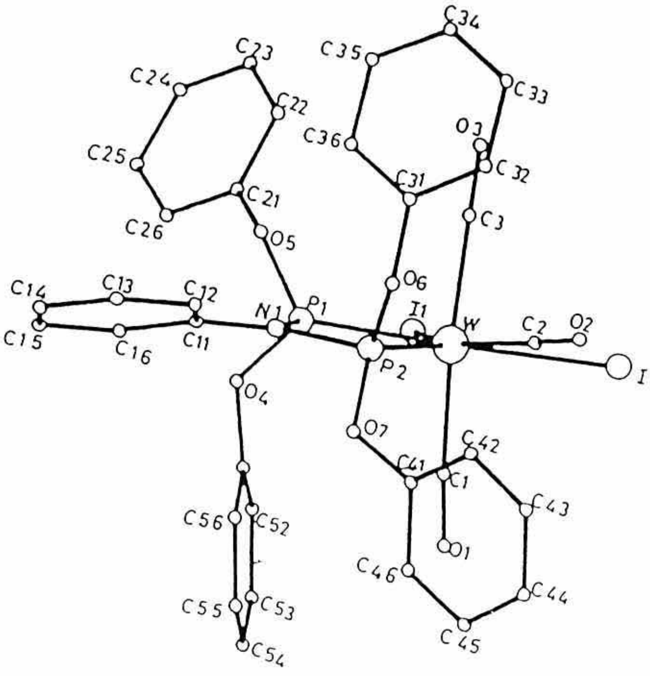


Figure (1-14)

In 1986, Baker *et al*[85] reported the complexes [$MI_2(CO)_3(\eta^2$-dppf)] (M = Mo, W), and [$MoI_2(CO)_2(\eta^2$-dppf$)_2$] {where dppf =1,1-bis(diphenyl phosphino)ferrocene}.

In 1995, Yeh *et al*[86] prepared the complex [$W(CO)_3(NCMe)(\eta^2$-dppf)] by reaction of *fac*-[$W(CO)_3(NCMe)_3$] with dppf then added I_2 to give [$WI_2(CO)_3(\eta^2$-dppf)], which when reacted with H_2O_2 gave the P=O, oxidised complex [$WI_2(CO)_3\{\eta^2$-dppf(=O)}], which was crystallographically characterised. (see Figure 1-15). The structure of this complex can be described as a distorted capped octahedron with a carbonyl ligand in the unique capping position.

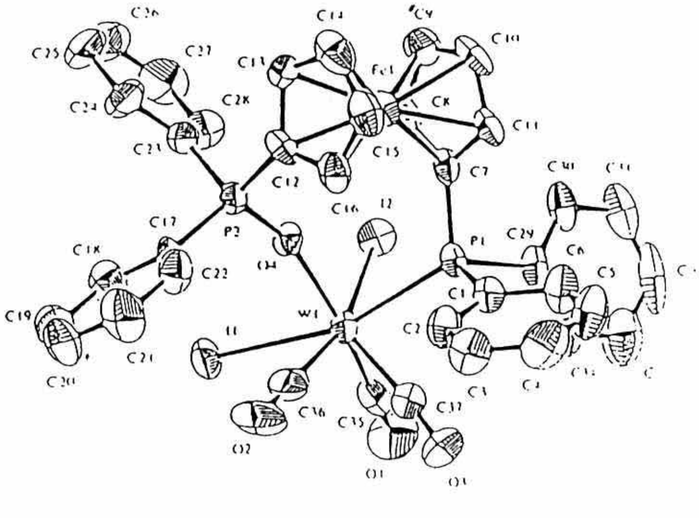


Figure (1-15).

The phosphine-bridged complexes, $[M_2I_4(CO)_6(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ were prepared by reaction of $[MI_2(CO)_3(NCMe)_2]$ and $Ph_2PC{\equiv}CPPh_2$, but when two equivalents of the ligand ($Ph_2PC{\equiv}CPPh_2$) was used the monodentate $Ph_2PC{\equiv}CPPh_2$ bonded complexes $[MI_2(CO)_3(\eta^1\text{-}Ph_2P\,C{\equiv}CPPh_2)_2]$, are observed.[87]

In 1994, Baker and Sherlock[88] synthesised complexes of the type $[MoI_2(CO)_2\{\eta^3\text{-}PhP(CH_2CH_2PPh_2)_2\}]$ and $[WI_2(CO)_3\{\eta^2\text{-}PhP(CH_2CH_2PPh_2)_2\}]$(a tricarbonyl complex which changed to a dicarbonyl complex after refluxing for 15 minutes) by reaction of $[MI_2(CO)_3(NCMe)_2]$ with linear triphos, $PhP(CH_2CH_2PPh_2)_2$.

The reactions of monodentate phosphines and derivatives with the seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ gave either $[MI_2(CO)_3(NCMe)L]$,[89,90] or $[\{M(\mu\text{-}I)I(CO)_3L\}_2]$ $\{L = PPh_3, AsPh_3, SbPh_3, PPh_2Cy, P(OPh)_3\}$, which depends on the electronic and steric effects of the ligands, and the complexes $[MI_2(CO)_3(NCMe)L]$ have a labile acetonitrile ligand which can be used to prepare a variety of new mixed ligand complexes.

Sulphur donor ligands react with the seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ in a variety of ways. In 1994, Baker *et al*[91] reported the reactions of $[MI_2(CO)_3(NCMe)_2]$ with $RS(CH_2)_2SR$ to yield $[MI_2(CO)_3\{RS(CH_2)_2SR\}]$ (M = W, Mo, R= Ph, 4-MeC_6H_4, 4-FC_6H_4), and they have reported the crystal structure for $[WI_2(CO)_3\{(4\text{-}MeC_6H_4)S(CH_2)_2S(4\text{-}MeC_6H_4)\}]$, and the reaction of $MeS(CH_2)_2S(CH_2)_2SMe$ with $[MI_2(CO)_3(NCMe)_2]$ to afford $[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}]$ and $[MI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S'\}]$ (M = W, Mo).

1.10-Reactions of $[MI_2(CO)_3(NCMe)_2]$ with alkynes :-

Reaction of one equivalent of alkyne, (RC_2R), with the seven coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ gave $[MI_2(CO)(NCMe)_2(\eta^2\text{-}RC_2R')]$, which dimerizes to produce the iodo-bridged complexes, $[\{M(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}RC_2R')\}_2]$ (R = R' = Me, Ph, CH_2Cl_2; R = Ph, R' = Me, CH_2OH; R = Me, R' = PhS, *p*-tol)[39]. When an excess of alkyne (RC_2R') is used, the bis(alkyne) complexes, $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$, are obtained.

In 1988, Baker *et al*[92] synthesised the above products by reaction of $[MI_2(CO)_3(NCMe)_2]$ with excess of RC_2R' to yield $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$, (R = R' = Ph; R = Me, R' = Ph; for M = W; R = R' = Me, CH_2Cl_2; *p*tol; R = Ph, R' = CH_2OH), and the dimeric molybdenum complex, $[\{Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2\}_2]$. The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph), were crystallographically characterised, (see Figure 1.16) for R = Me.

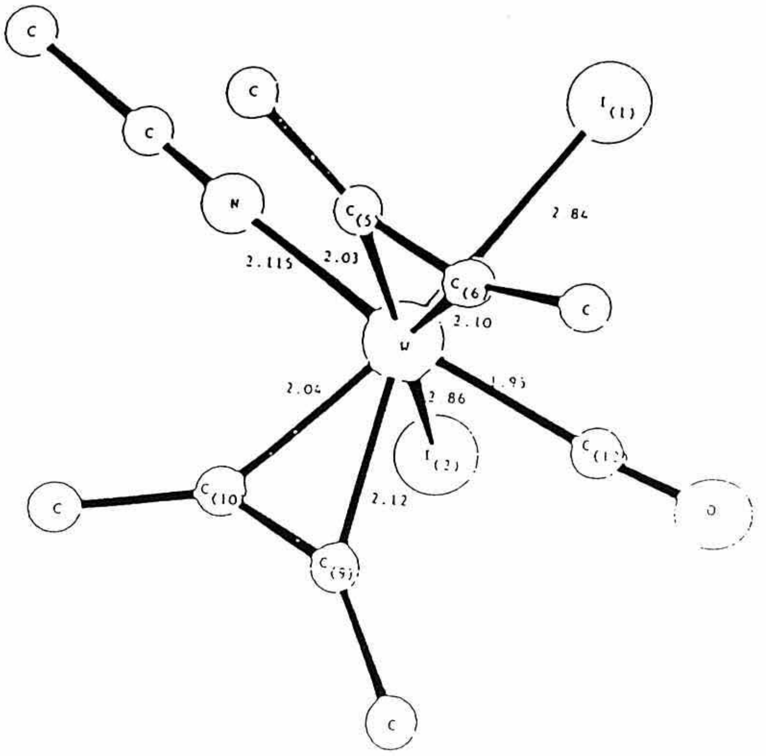


Figure (1-16). The crystal structure of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$

In 1994, Baker *et al*[93] have prepared bis(alkyne) complexes, $[WI_2(CO)(NCR)(\eta^2\text{-}R^1C_2R^1)_2]$ by reaction of the complex, $[WI_2(CO)_3(NCR)_2]$ (R = Et, ^tBu, Ph and CH_2Ph) with excess $R^1C_2R^1$ (R^1 = Me, Ph), and they reported the crystal structure for $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$.

1-11-Reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with donor ligands :-

The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R')_2]$ (R' = Me or Ph) react with one, two, three, four or five equivalents of CN^tBu to give $[WI_2(CO)(CN^tBu)(\eta^2\text{-}R'C_2R')_2]$, $[WI_2(CO)(CN^tBu)_2(\eta^2\text{-}R'C_2R')]$, $[WI_2(CN^tBu)_3(\eta^2\text{-}R'C_2R')]$, $[WI(CN^tBu)_4(\eta^2\text{-}R'C_2R')]I$, and $[W(CN^tBu)_5(\eta^2\text{-}R'C_2R')]2I$ respectively[94]. In 1987, Baker, Drew and Armstrong[95] synthesised the crystallographically characterised complex $[WI_2(CO)_2(\eta^2\text{-}MeC_2Me)_2]$, by reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with carbon monoxide.

In 1992, Baker *et al*[96] refluxed the complex $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ in acetonitrile for 5 hours in the presence of PhC_2Ph to give the bis(acetonitrile) complex $[WI_2(NCMe)_2(\eta^2\text{-}PhC_2Ph)_2]$. The chemistry of this complex with donor ligands was studied. In 1995,[97] imidazole and pyrazole complexes have been reported by replacement the acetonitrile group, in $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ by L (L = imidazole, pyrazole) to afford the complexes $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$ (M = W; R = Me, Ph).

Treatment of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with one equivalent of L {L = bidentate phosphine such as $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3, 4, or 6)} gives the complexes $[MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$, whereas when one or two equivalents of monodentate phosphines such as PMe_3, PEt_3, PPh_3, is used the complexes, $[WI_2(CO)(L)(\eta^2\text{-}RC_2R)_2]$ or

$[WI_2(CO)(L)_2(\eta^2\text{-}RC_2R)]$ are obtained. In 1989, Baker and *et al*[98] prepared the first type of above complexes with tungsten, and they described the molecular structure of $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)]$. The crystal structure of this complex shown in Fig.1.17.

In 1989, Baker *et al*[99] described a series of phosphite complexes of the type $[MI_2(CO)\{P(OR^1)_3\}_2(\eta^2\text{-}RC_2R)]$ (M = W, R = Me, Ph; R' = Me, Et, ^{i}Pr, ^{n}Bu), which were prepared by reaction of the complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with two equivalents of $P(OR^1)_3$. The X-ray crystal structure of the complex $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ has been determined, and has *cis*-phosphite ligands. (see Fig 1.18), which are *trans*-to a carbonyl group, and an iodo-ligand. The ^{13}C NMR chemical shifts of the alkyne contact carbon atoms are above 200 ppm in these complexes, which indicates that the alkyne ligand is acting as a four-electron donor.[13].

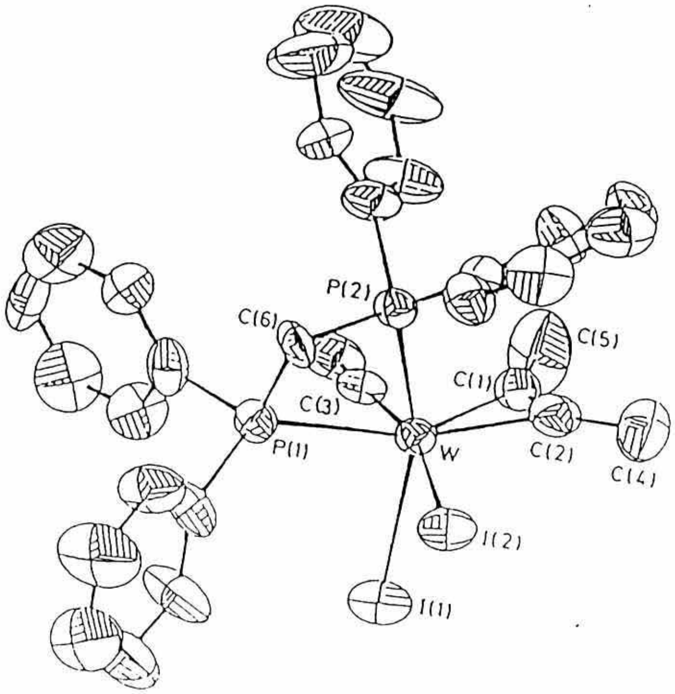


Fig.1.17-Crystal structure of $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)]$

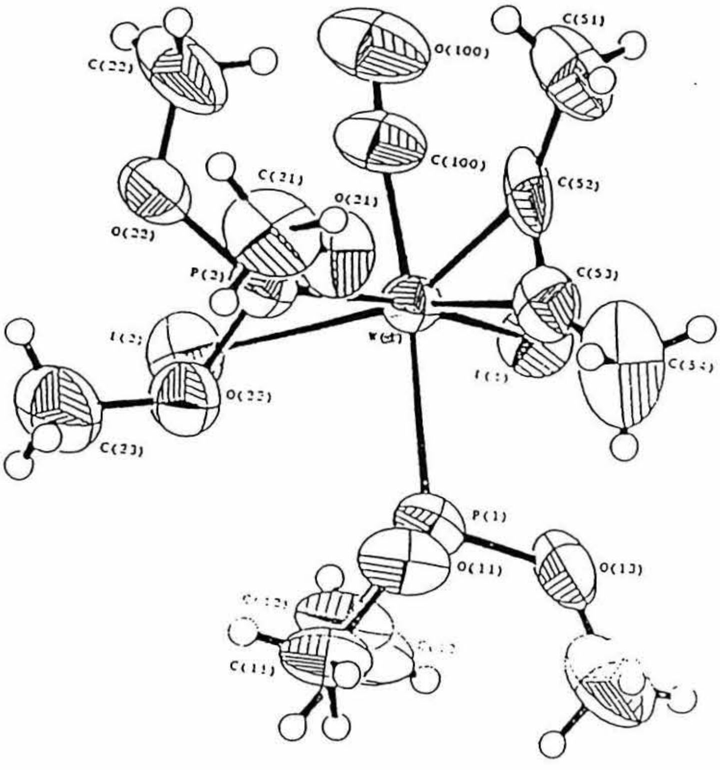


Fig.1.18-Crystal structure of *cis*-$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$

Organophosphine ligands are central to the coordination chemistry of organotransition-metal complexes. Treatment of linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$, with $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ was described by Baker *et al.*[100] in 1995 to yield the new organometallic phosphine ligand, $[WI_2(CO)(\eta^2\text{-triphos})(\eta^2\text{-}MeC_2Me)]$, which has been crystallographically characterised. The linear triphos ligand is attached to the tungsten with two adjacent phosphorus atoms, leaving the third phosphorus atom uncoordinated. (figure 1-19a and b). Two diastereoisomers of the complex were observed as shown in Fig.1.19a and b.

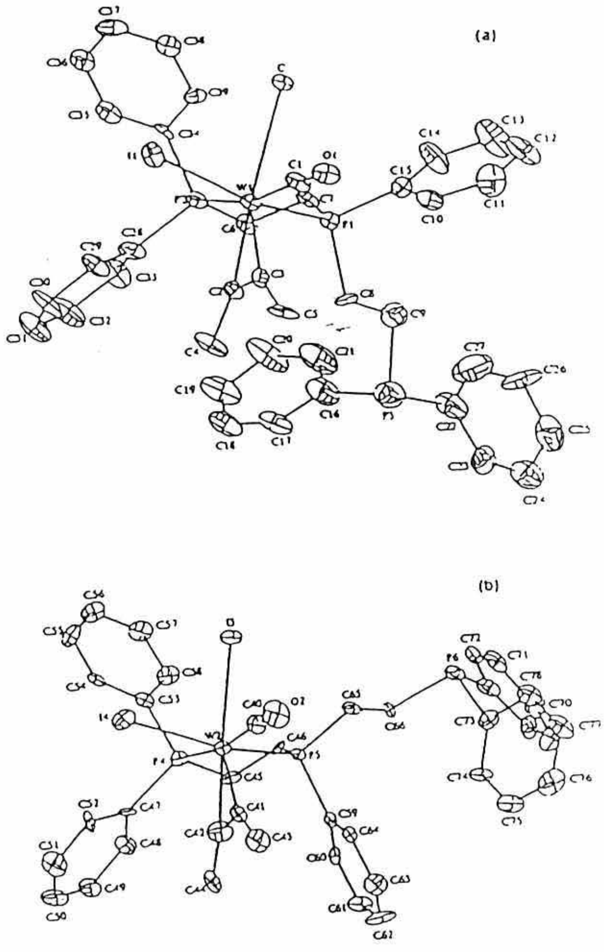


Figure (1-19). The X-ray crystal structure of [$WI_2(CO)(\eta^2$-triphos)(η^2-MeC_2Me)]

In 1988, Armstrong and Baker[101] have reacted anionic donor ligands such as Na[acac], with [$WI_2(CO)(NCMe)(\eta^2$-$MeC_2Me)_2$] to give [WI(CO)(acac)(η^2-$MeC_2Me)_2$], and with two equivalents of Na[acac], the complex [W(CO)$(acac)_2(\eta^2$-$MeC_2Me)$], is obtained. Treatment of [$WI_2(CO)(NCMe)(\eta^2$-$MeC_2Me)_2$] with different salts, such as potassium pyridine-2-thionate affords the bidentate N^S bonded complex [WI(CO)(η^2-$SC_5H_4N)(\eta^2$-$MeC_2Me)_2$].

In 1990, Baker *et al*[102] have described the reactions of a series of dithiocarbamate type ligands, S_2CX^- {X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8, or NC_5H_{10}} with $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ in dichloromethane or diethyl ether to give either the new bis(alkyne) complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$, or the mono(alkyne) complexes, $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$.

The molecular structure of the complex $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ has been described. (see Fig.1.20). The coordination geometry around the tungsten is octahedral, with the two parallel *cis*-but-2-yne ligands *trans* to a sulphur, and an iodide with the other sulphur of the dithiocarbamate, and the carbonyl ligand occupying the axial sites. Variable-temperature ^1H NMR studies show that the complex fluxional in solution. They also reacted the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with two equivalents of S_2CX^- to give the mono(alkyne) complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$, and they reported from ^{13}C NMR spectroscopy, that the alkyne ligands in the bis(alkyne) complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ are donating an average of three electrons each to the metal, whereas the alkyne ligand in the complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ are donating four-electrons to the tungsten[13].

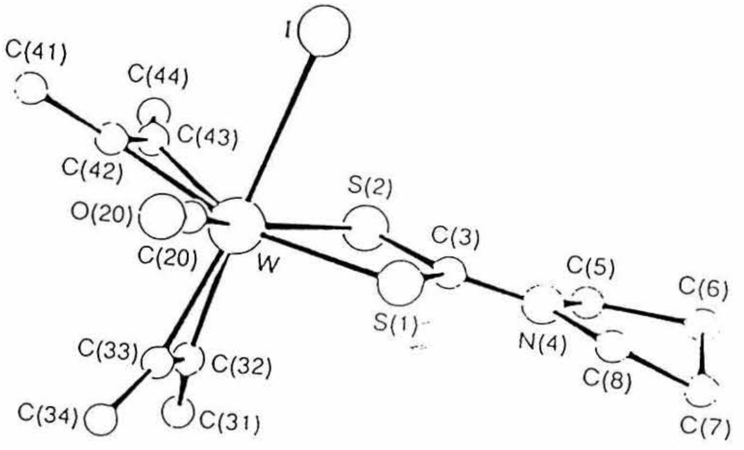


Fig. 1.20-Molecular structure of [WI(CO)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$]

1.12-π-Allyl complexes of Molybdenum(II) and Tungsten(II) :-

1.12a-Reactions of the zero-valent substituted metal carbonyls of molybdenum and tungsten with allyl halides:-

In 1969, Holloway *et al*[103], irradiated [W(CO)$_6$] in the presence of allyl halides to give the π-allyl complexes [W_2Cl_3(CO)$_6$(η^3-allyl)],[WBr(CO)$_4$(η^3-allyl)] and [WI(CO)$_4$(η^3-allyl)] respectively. In 1968, Hayter[104] reported the efficient synthesis of two kinds of π-allyl complexes of molybdenum and tungsten, namely [MX(CO)$_2$(NCMe)$_2$(η^3-allyl)](M = Mo, W; X = Cl, Br; allyl = C_3H_5, C_4H_7, C_3H_4Cl, C_6H_9, C_3H_4Ph), and [M(CO)$_2$(η^3-allyl)Cp]. The versatile complexes, [MX(CO)$_2$(NCMe)$_2$(η^3-allyl)] (M = Mo, W) were prepared by oxidising *fac*-[M(CO)$_3$(NCMe)$_3$] with allyl halides to give [MX(CO)$_2$(NCMe)$_2$(η^3-allyl)] (M = Mo, W; X = Cl, Br; allyl = C_3H_5, 2MeC_3H_4, C_3H_4Cl)[104].

More recently, in 1986, Baker[105] described the reaction of *fac*-[Mo(CO)$_3$(NCMe)$_3$] with CH_2=C(CH_2Cl)$_2$ to give [MoCl(CO)$_2$(NCMe)$_2${η^3-C_3H_4(2-CH_2Cl)}].(the proposed structure is shown in Fig. 1.21).

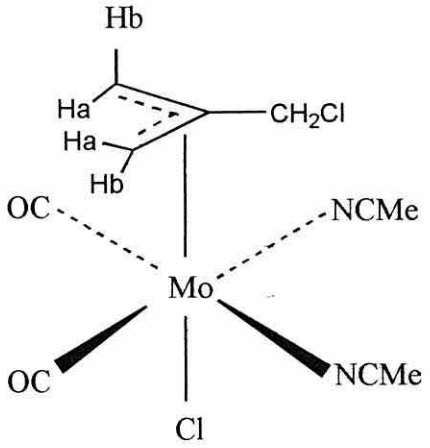


Fig.1.21-Proposed structure of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$.

The reaction of $[Mo(CO)_4L_2]$ (L_2 = bipy, phen ,2,2'-bipyridylamine) with triphenyl cyclopropenyl bromide yield two types of complexes, namely, $[MoBr(CO)_2L_2(\eta^3\text{-}C_3Ph_3)]$ and $[MoBr(CO)_2L_2(\eta^3\text{-}C_3Ph_3O)]$. In 1989, Liu *et al*[106] synthesised by the oxidative-addition of fac-$[Mo(CO)_3(NCMe)_3]$ with 1-halopenta-2-diene to afford $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_5H_7)]$ (X = Cl, Br), and in the second step reacts these complexes with bidentate ligands such as dppe and dmpe to afford $[MoCl(CO)_2(dmpe)(\eta^3\text{-}C_5H_7)]$ and $[MoBr(CO)_2(dppe)(\eta^3\text{-}C_5H_7)]$ respectively. The first successful synthesis of π-allyl complexes of molybdenum(II) and tungsten(II) was described in 1965 by Murdoch[107] by reaction of $[NEt_4][MX(CO)_5]$ with C_3H_5X to give $[NEt_4][M_2(\mu\text{-}X)_3(CO)_4(\eta^3\text{-}C_3H_5)_2]$, (see Figure 1.22).

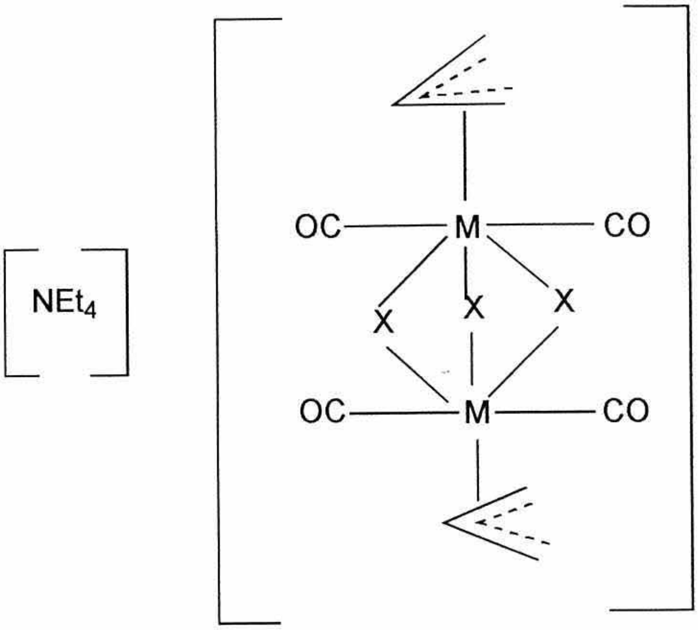


Figure 1.22- Proposed structure of [NEt_4][$M_2(\mu\text{-}X)_3(CO)_4(\eta^3\text{-}C_3H_5)_2$].

Murdoch and Henzi[108] prepared a new complex [$MX(CO)_2(py)_2(\eta^3\text{-}C_3H_4CH_3)$] (where M = Mo; X = Cl)(see Fig.1.23), which is prepared from [NEt_4][$M_2(\mu\text{-}X)_3(CO)_4(\eta^3\text{-}C_3H_4Me)_2$] by splitting the bridge and reacting with nitrogen donor groups such as bipy, pyridine etc.

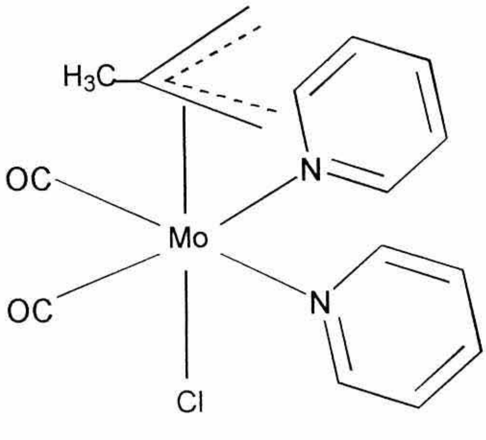


Figure 1.23-Proposed structure of [$MoCl(CO)_2(py)_2(\eta^3\text{-}C_3H_4Me)$]

In 1977, Doyle[109] prepared the anionic π-allyl complexes of the type [MCl(CO)$_2$(diket)(η^3-C_3H_5)]$^-$ by reaction of [M(CO)$_4$(diket)]$^-$ (M = Mo, W; diket = acac; 3Me-acac etc) with allyl chloride. In 1986, Brisdon *et al*[110] described the reaction of [PPh$_4$][MoCl(CO)$_3$(bipy)] with ClCH$_2$C$_2$CH$_2$Cl to give [MoCl(CO)$_2$(bipy)(η^3-CH$_2$-C(CO$_2$Me)=C=CH$_2$)] which has an η^3-bonded *trans*-butadienyl ligand. Under anhydrous conditions the crystallographically characterised complex [MoCl(CO)$_2$(bipy){η^3-CH$_2$-C-(CO$_2$Me)-C(Me)(OMe)}] was isolated.

1.12b-Reactions of [MX(CO)$_2$(NCMe)$_2$(η^3-allyl)] with donor ligands:-

Preparation and reactions of several new mono- and binuclear π-allyl molybdenum complexes were described in 1968 by Tom Dieck and Friedel[111]. The complexes [MX(CO)$_2$(NCMe)$_2$(η^3-C_3H_5)], were prepared by reaction of [M(CO)$_6$] and allyl halides (XC$_3$H$_5$), (see Equation 1.15).

$$[\mathrm{Mo(CO)_6}] + (\eta^3\text{-}\mathrm{C_3H_5X}) \xrightarrow{\mathrm{CH_3CN,\ 80^0C,\ -4CO}} [\mathrm{MoX(CO)_2(CH_3CN)_2}(\eta^3\text{-}\mathrm{C_3H_5})]$$

(where X= Cl, Br, I, NCS)

(Equation 1.15)

In 1974, King and Saran[112] prepared [MoCl(CO)$_2$(CNR)$_2$(η^3-C_3H_5)] from [MoCl(CO)$_2$(NCMe)$_2$(η^3-C_3H_5)], by reaction with two equivalents of CNR (R = Me, Et, ^{i}Pr, ^{t}Bu, Neopentyl, Cy). In 1981, Deaton and Walton[113] have shown zero-valent complexes, [Mo(CO)$_2$(CNR)$_2$L$_2$] can be prepared by reacting the complexes [MoCl(CO)$_2$ (CNR)$_2$(η^3-C_3H_5)] with two equivalents of L(L = PEt$_3$, P^{n}Pr$_3$, PMePh$_2$, PEtPh$_2$ *etc*).

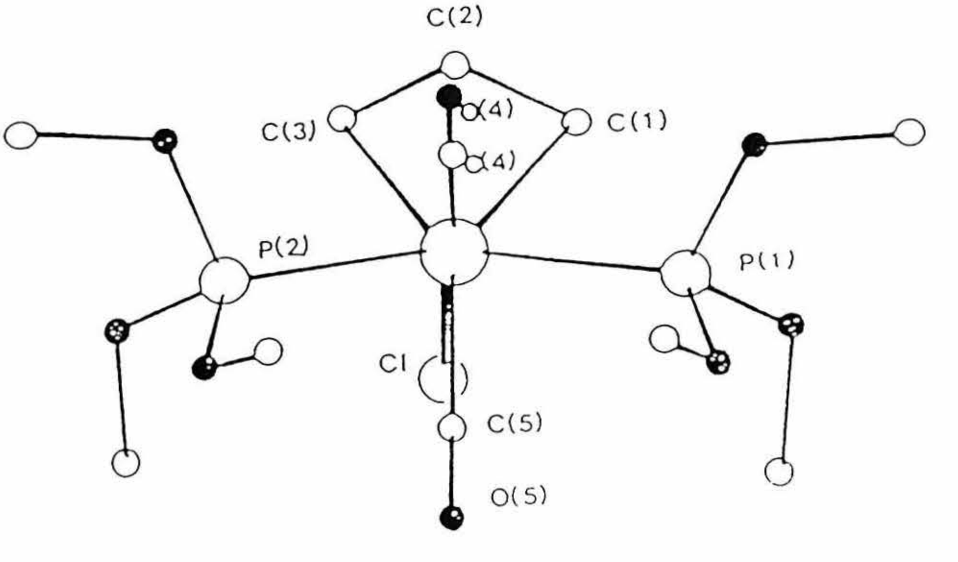
The first reaction between $[MX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ with nitrogen donor ligands was described in 1976 by Hsieh and West[114]. They used R'N=CHCH=NR' to replace two acetonitrile ligands to yield $[MX(CO)_2(R'N{=}CHCH{=}NR')(\eta^3\text{-}C_3H_4R)]$ (M = Mo, W; X = Cl, Br, I, NCS; R = H, Me, Et, ^{i}Pr, ^{t}Bu, Cy, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$), and the reactions of these complexes with a number of reagents including MeLi, C_5H_5Tl, $SnCl_2$, Ag^+ and Lewis bases have been investigated.

Brisdon *et al*[115] reacted bi-and tridentate nitrogen donor ligands with $[MX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ to produce $[MoCl(CO)_2(N\text{^}N)(\eta^3\text{-}C_3H_4R)]$ (N^N = bipy; 2,2'-bipyridyl amine), or the cationic complexes $[Mo(CO)_2(N\text{^}N\text{^}N)(\eta^3\text{-}C_3H_4R)]^+$ {N^N^N = dien, bis (2-pyridylmethyl) amine}. In 1969, Tom, Dieck and Friedel[116] prepared the unstable zero-valent complexes, $[Mo(CO)_2(NCMe)_2(PPh_3)_2]$ by reaction of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-allyl})]$ with PPh_3. Brisdon and Paddick[117] have prepared the complexes $[MoX(CO)_2\{Ph_2As(CH_2)_2AsPh_2\}(\eta^3\text{-}C_3H_5)]$ (X = Cl, Br, I), and the dimeric complexes $[\{MoX(CO)_2(\eta^3\text{-}C_3H_5)\}_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$ by reacting the complexes $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ with $Ph_2As(CH_2)_2AsPh_2$.

Semicarbazones have been used as bidentate ligands in classical coordination chemistry, and no organometallic compounds have been reported containing these as attached ligands until Campbell *et al*,[118,119] have prepared the semicarbazone complexes by reaction of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$, with an equimolar amount of the semicarbazone to give $[MX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3\text{-}C_3H_4R)]$ (X = Cl, Br, I; R = H, 2Me; R',R'' = H or Me and Me, Et, Pr^n, Ph), which are the first organotransition-metal complexes and also the first d^4 compounds containing a semicarbazone as a bidentate ligand coordinated to molybdenum.

In 1986, Campbell *et al*[120] have reacted the complexes $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ with thiosemicarbazide to give $[MoX(CO)_2(H_2NNHCSNH_2)(\eta^3\text{-}C_3H_4R)]$ (X= Cl, Br; R = H, Me), which are the first organometallic complexes containing thiosemicarbazide.

η^3-Allyl-phosphite complexes of the transition-elements from groups VI and VII have been studied and shown to be very effective homogeneous catalysts or exhibit unusual structures. In 1979, Drew *et al*[121] have described an unusual pentagonal bipyramidal geometry for the bis(trimethylphosphite) complex, namely $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$, (see Figure 1.24).



(figure 1.24)

The molecular structure of $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$

(1-13) Introduction to spectroscopic methods :-

The study that deals with the theory and interpretation of such interactions between molecules and radiant energy is called spectroscopy[122]. Radiation of different wavelengths can cause changes in the electronic or molecular structures of both inorganic and organic compounds. There are different characteristics of electromagnetic radiation which deal with different spectroscopic methods. The relationships between energy (E), frequency (ν) and wavelength (λ) is as following :-

$$E = h\nu \qquad (h = 6.63 \times 10^{-27} \text{ erg sec})$$

$$\nu = c/\lambda \qquad (c = 2.998 \times 10^{10} \text{ cm sec}^{-1})$$

$$E = hc/\lambda$$

A spectroscopic analysis of a molecule requires at least one spectrum, which is a record of the changes that occur as you scan over the desired energy range. The most familiar type of spectrum results from plotting the change in the absorption of energy versus the wavelength of the energy being used. In this introduction, the spectroscopic methods, which are briefly discussed are infrared (IR), ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy and X-ray crystallography.

(1-14) Infrared spectroscopy(IR) :-

Infrared (IR)[123] spectra result from absorption of energy that affects the vibrational modes of atoms that are bonded to one another. Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. For the organic and inorganic chemist it is generally limited portion between 4000 and 400 cm^{-1}.

Infrared radiation of frequencies less than about 100 cm^{-1} are absorbed and converted by an organic molecule into energy of molecular rotation, and infrared radiation in the range from about 10,000-100 cm^{-1} is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantized, but vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes, particularly those occurring between 4000 and 400 cm^{-1} which are the concern of this thesis. The frequency or wavelength of the absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

Band positions in IR spectra are presented here as wavenumbers (ν), whose unit is the reciprocal centimeter (cm^{-1}); band intensities can be expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm, to the base 10 of the reciprocal of the transmittance; $A = \log_{10}(1/T)$. Organic and inorganic chemists usually report intensity in semiquantitative terms (s = strong, m = medium, w = weak).

There are two types of molecular vibrations : stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the atoms in the group with respect to one another. The stretching frequencies of the following bonds in the general absorption regions[124] are indicated in Table 1.2 :

Bond Type	**Absorption Region (cm^{-1})**
C — C, C — O, C — N	1300-800
C = C, C = O, C = N, N = O	1900-1500
C ≡ C, C ≡ N	2300-2000
C — H, O — H, N — H	3800-2700

Table 1.2- General absorption regions in IR.

There are generally two groups usually looking to them in IR, which is related to the complexes in the thesis, they are the alkyne and carbonyl groups.

The two stretching vibrations in alkynes (3-hexyne) involve C≡C and C—H stretching. Absorption due to C—H bending is characteristic of 3-hexyne and monosubstituted alkynes. The weak C≡C stretching band of alkyne molecules occurs in the region of 2260-2100 cm^{-1}, and the C—H stretching band of monosubstituted alkynes occurs in the general region of 3333-3267 cm^{-1}. This is a strong band, and is narrower than the OH bonds and NH bonds occurring in the same region.

The C—H bending vibration of alkynes or monosubstituted alkynes leads to strong, broad absorption in the 700-610 cm^{-1} region. The first overtone of the C—H bending vibration appears as a weak, broad band in the 1370-1220 cm^{-1} region.

With reference to complexes described in this thesis, when 3-hexyne coordinates to molybdenum(II) and tungsten(II) centres, the alkyne shifts two C≡C unit to around 1600 cm^{-1}, and the band is very weak. This is due to the back-donation of electron density from filled metal d-type orbitals to the empty π*-orbitals on the alkyne, which results in a rehybridisation of the alkyne.

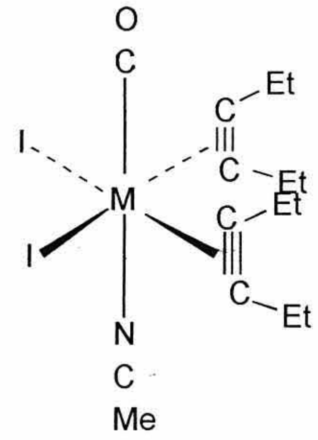
The CO group generally shifts, from 2143 cm^{-1} (stretching frequency for uncoordinated carbon monoxide) to 2095-1940 cm^{-1}, depending on the other groups coordinated to the central metal. This shifts because of back-bonding of electron density from filled metal d-type orbitals to the empty π*-orbitals of the CO group, which changes the order of the bond.

(1-15) Proton Nuclear Magnetic Resonance spectroscopy (^{1}H NMR) :-

The NMR phenomenon (first observed in 1946),[124] is observable because certain nuclei behave like bar magnets. Most important among such nuclei are ^{1}H, ^{13}C, ^{19}F and ^{31}P. All having a nuclear spin (*I*) of $^1/_2$; those with nuclear spin of 1 include deuterium ^{2}H and ^{14}N. Certain other nuclei which are important in organic and inorganic chemistry have a nuclear spin of zero, and therefore give no nuclear resonance signals; these include ^{12}C and ^{16}O. If one of the above nuclei of spin $^1/_2$ is placed in a magnetic field, it may take up either a low-energy orientation in which the nuclear magnet is aligned with the field, or a high-energy orientation in which it is aligned against the field. Nuclear magnetic resonance (NMR) spectroscopy is basically another form of absorption spectroscopy, under appropriate conditions in a magnetic field, a sample can absorb electromagnetic radiation in the radio frequency (rf) region at frequencies governed by the characteristics of the sample. A plot of the frequencies of the absorption peak intensities constitutes an NMR spectrum. Proton nuclear magnetic resonance (^{1}H NMR)[122] spectra result from absorption of energy that affects the spins of the hydrogen nuclei. Chemical shifts[124] are very important in ^{1}H NMR spectroscopy, only a single peak should be obtained from the interaction of radio frequency (rf) energy and a strong magnetic field on a proton. The peak area (measured by an integrator) is proportional to the number of protons it represents.

The most generally useful reference compound is tetramethylsilane $(CH_3)_4Si$ (TMS). This has several advantages; it is chemically inert, symmetrical, volatile (bp. 27^0C), and soluble in most organic solvents; it gives a single sharp absorption peak, and absorbs at higher field (more shielded) than almost all organic and inorganic protons. When the NMR scale was set up, the TMS peak was set at 0 Hz at the right-hand edge. The magnetic field increases toward the right. Thus, a peak at 60 Hz from TMS at an applied frequency of 60 MHz would be at δ 1.00 (δ scale) or at 1.00 ppm.

The ^{1}H NMR spectra of alkyne ligands in molybdenum and tungsten complexes is affected by the type of alkyne and the size of those groups coordinate to the central metal. In this thesis, the alkyne used is 3-hexyne which is contains two groups of CH_2 and CH_3 and those two groups effected by CO, NCMe, and iodide in complexes of molybdenum and tungsten. (see fig.1-25). In phosphite complexes described in chapter three, the groups attached to the oxygen will shift downfield due to being adjacent to an electronegative oxygen atom.



(Fig.1-25)

(1-16) Carbon Nuclear Magnetic Resonance spectroscopy(^{13}C NMR) :-

Carbon nuclear magnetic resonance (^{13}C NMR)[123,124] spectra are analogous to proton NMR spectra, from ^{13}C NMR spectrum you can generally study the features of every carbon in any organic and diamagnetic inorganic compounds.

Direct observation of the carbon skeleton has been available on a practical basis only since the early 1970's. The ^{12}C nucleus is not magnetically "active" (spin number, *I*, is zero), but the ^{13}C nucleus, like the ^{1}H nucleus, has a spin number of $^{1}/_{2}$. However, since the natural abundance of ^{13}C is only about 1.1% that of ^{12}C, and its sensitivity is only about 1.6% that of ^{1}H, the overall sensitivity of ^{13}C compared with ^{1}H is about 1/5700.

The earlier, continuous wave, slow-scan procedure requires a large sample and a prohibitively long time to obtain a ^{13}C NMR spectrum, but the availability of FT instrumentation, which permits simultaneous irradiation of all ^{13}C nuclei, has resulted in an increased activity in ^{13}C NMR spectrometry, beginning in the early 1970s, comparable to the burst of activity in ^{1}H NMR spectrometry that began in the late 1950s.

An important development was the use of broadband decoupling of protons. Because of the large *J* values for ^{13}C—H (~110-320 Hz) and appreciable values for ^{13}C—C—H and ^{13}C—C—C—H, nondecoupled ^{13}C NMR spectra usually show complex overlapping multiplets that are difficult to interpret.

As it is with ^{1}H NMR spectrometry, the common internal reference is tetramethysilane (TMS), and the scale is given in δ units (ppm) downfield (deshielding) from TMS in positive numbers, and upfield (shielding) from TMS in negative numbers. The shifts encountered in routine ^{13}C spectra range about 240 ppm downfield from TMS; this is a range of about 20 times that of routine ^{1}H spectra (~12 ppm). Several cations have been recorded at approximately 335 ppm downfield, and CCl_4 absorbs at approximately 96 ppm (upfield from TMS).

The definition of chemical shift[124] equivalence given for protons also applies to carbon atoms, interchangeable by a symmetry operation or by a rapid mechanism. The presence of equivalent carbon atoms (or coincidence of shift) in a molecule results in a discrepancy between the apparent number of peaks and the actual number of carbon atoms in the molecule. Routine ^{13}C NMR spectra are usually noise decoupled. Thus coupling information is discarded in the interest of obtaining a spectrum in a shorter time, furthermore, free of complex overlapping absorptions. However, as mentioned earlier, information from residual coupling can be regained through off-resonance decoupling.

In general, the *sp* carbon atoms of alkynes substituted only by alkyl groups absorb in the range of approximately 65-90 ppm. The triple bond shifts the sp^3 carbon atoms directly attached about 5-15 ppm upfield relative to the corresponding alkane. The terminal ≡CH absorbs upfield from the internal ≡CR. Off-resonance decoupling gives a doublet for the terminal ≡CH. Alkyne carbon atoms with a polar group directly attached absorb from about 20-95 ppm.

In this thesis using 3-hexyne ($H_3C-CH_2-C{\equiv}C-CH_2-CH_3$) which contains methyl, ethyl and C≡C groups, and when coordinated to molybdenum or tungsten centre they can act as three or four electron donor ligands. The relationship between the number of electrons donated by an alkyne and the ^{13}C NMR chemical shift is shown in Fig.2.4[13].

In general organic groups, when attached to a transition-metal centre are shifted down field from TMS. For high molecular weight organometallic complexes, it is generally more difficult to obtain good spectra as the complexes are often less soluble in solution, less soluble and contain less protons or carbons atom per unit of molecular weight than the uncoordinated organic groups.

The C≡O (carbon monoxide) when coordinated with complexes of molybdenum and tungsten generally resonates at around ~200 ppm, depending on the other groups coordinated to the central atom in the complexes.

(1-17) Phosphorus Nuclear Magnetic Resonance spectroscopy

(^{31}P NMR) :-

The spin of ^{31}P NMR[124] is $^1/_2$ and has also 100% abundance, so that the multiplicities generated with other nuclei are usually easily interpreted in the ^{31}P NMR spectra, first order splittings are normal, because of the wide range of chemical shifts. The most widely used reference for ^{31}P NMR chemical shifts is an external sample of 85% aqueous phosphoric acid H_3PO_4. There is always a problem in correlating shifts to an external sample, but H_3PO_4 does not produce a sharp resonance signal, and with more recent instruments the shifts can be related *via* the deuterium lock signal to TMS.

For accurate data there is an abundant literature, and for the present survey the chemical shifts in fig 1.26 are illustrative rather than comprehensive. The coupling constants between two phosphorus (J_{pp}) are slightly different from one group to another, depending on the type of group.

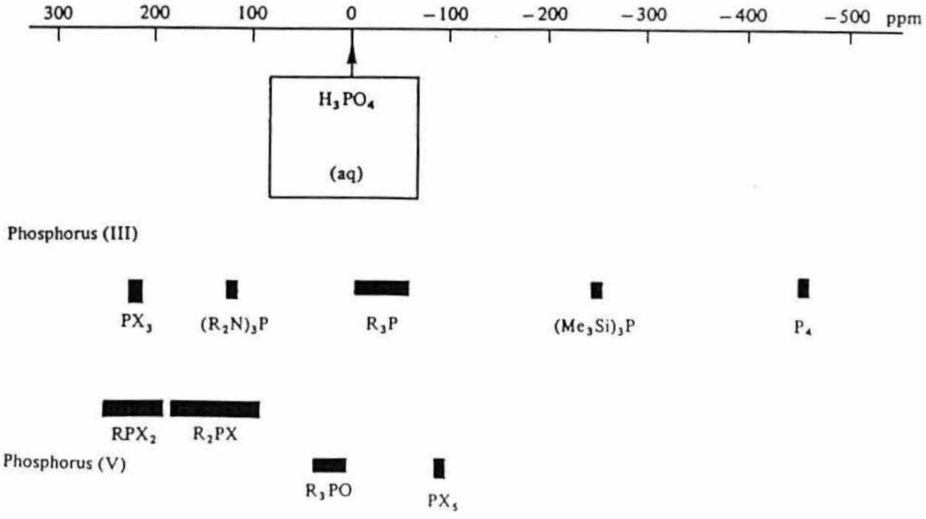


Fig 1.26- ^{31}P NMR Chemical shifts.

The aims from using ^{31}P NMR spectroscopy in this thesis were, firstly to study the cis- and *trans*- isomerism of the bis(phosphite) complexes, $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$, in chapter three, and compare them with the X-ray crystal structures of the complexes where obtained. Another aim was to identify more than one different phosphorus atom in the same complex, especially with reference to the tripodal triphos complexes described in chapter four of this thesis. It was used to establish that there was an uncoordinated phosphorus atom, in the complexes, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$, so that these could be used as phosphine ligands to coordinate to other transition-metal centres. The $^{31}P\{H\}$ NMR spectroscopy was also used to establish the multimetallic nature of the reaction products derived from reaction of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$, with other organometallic complexes.

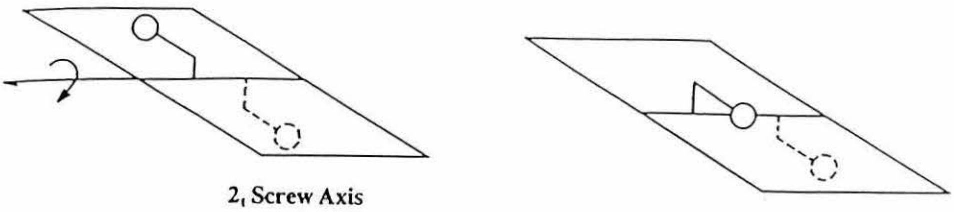
(1-18) *X-Ray* Crystallography :-

The importance of *X-ray*[125] crystallography is clearly highlighted by the unusually large number of scientists who have received Nobel prizes for their pioneering work in this field: von Laue (1914) and the Braggs (1915) for the discovery of X-ray diffraction by single crystals; Perutz, Crowfoot Hodgkin, Kendrew, Sanger and Pauling for later determining the structures of several proteins. Despite all this activity, it was rare, even thirty years ago, to find a synthetic inorganic chemist who contemplated determining the structure of a compound by single-crystal X-ray diffraction.

Today, such structural analyses have become almost routine because of the ready commercial availability of automatic diffractometers and userfriendly, structure-determination software packages. The crystal structure of a molecule containing about

100 atoms can be solved in a matter of days, and the complicated computer programs necessary for structural analysis can even be run on personal computers. An X-ray crystallographic study is simply an attempt to match up the intensities of the diffracted X-rays with those calculated by computer from the known scattering factors of each atom and an assumed spatial arrangement of the atoms in the crystal. The first part of such an X-ray investigation involves determining the space-group symmetry, and the unit-cell dimensions of the crystal lattice. A unit cell is defined as the simplest, three dimensional arrangement of atoms that repeats itself throughout the whole crystal lattice think of it as the repeating pattern of a wallpaper design in three, rather than two dimensions. Six parameters are needed to define a unit cell mathematically : three cell edges (a, b, c) and three angles (α, β, γ). By convention, α is the angle between b and c, β between a and c, and γ between a and b.

There are seven principal types of unit cell possible, each with its own interrelationship of cell edges and angles. These seven unit cells constitute the seven crystal systems, or primitive lattices. Beside these, there are seven other important lattice structures for crystals, giving in all the so-called fourteen *Bravais lattices*. Atoms are located at different but often symmetry-equivalent positions in a unit cell. There are two special types of symmetry element that relate these equivalent positions to one another. Both of these symmetry elements involve translations within the unit cell; they are called *screw axes* and *glide planes*. A n-fold screw axis is designated n_m and involves a $2\pi/n$ rotation followed by a translation of m/n along the rotation axis. A glide plane σ^g combines a reflection and a translation. (see fig 1.27).



2_1 Screw Axis

σ^g Glide Plane

Fig 1.27-Examples of 2_1 screw axis and a glide plane (σ^g).

Many inorganic compounds crystallize in the monoclinic space group, $P2_1/c$. The Hermann-Mauguin labelling in this case indicates that the space group involves a primitive (P) lattice and that there is a two-fold screw axis perpendicular to a glide plane located on the c axis of the unit cell. Once a single crystal suitable for X-ray investigation has been grown, it is glued onto the tip of a very thin glass rod and mounted on the head of a goniometer. All modern X-ray diffractometers are fully automated so that the computer searches for a specified number of strong reflections usually twenty-five to fifty. The computer also uses these strong reflections to determine the unit-cell parameters and eventually the space group.

The next step is to collect a large enough data set to solve the structure. Often, several thousand independent reflections are collected, especially if there are many atoms to be located in the structure. This procedure may take several days, depending on the time interval allowed for measuring the intensity of the scattered X-ray radiation for each reflection.

Complete lists of bond lengths and bond angles are also part of the output from the least-squares refinements. For a good structure involving not too many atoms, the accuracy of the bond lengths is about ±0.5 pm, while the angles can be measured to within 0.5°.

There are three main reasons for wanting an X-ray crystal structure : (1) To identify an unknown compound, although crystallography is becoming a routine analytical technique, it is still time and resource-consuming. (2) To obtain accurate interatomic distances and angles. For normal organic structures with no elements heavier than chlorine, bond lengths and angles will probably have an accuracy of 0.005 Å, 0.5° or slightly better. (3) To determine the absolute configuration of a chiral compound. This is a less common, but still important requirement.

In this thesis, X-ray cystallography has been used for determining the structure of six complexes, and data containing bond lengths and angles, which helps to explain the relationship between the ligands and central metal for all of these complexes.

CHAPTER TWO

3-HEXYNE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II).

Chapter Two

2.1- Introduction :-

Alkyne ligands have orthogonal π-orbitals, and are both good single faced π-acceptors and good single-faced π-donors. The ligand to metal π-donor potential of the filled alkyne perpendicular π-bonding component allows variable electron donor interactions that can range from two to four electrons depending on the complex under consideration.

There has been considerable interest in alkyne complexes of molybdenum(II) and tungsten(II) over the last 30 years, and the ability of alkyne ligands to act as four-electron donor ligands to a transition-metal centre has been well illustrated in the alkyne complexes of molybdenum(II) and tungsten(II). Although a number of 2-butyne, methylpropyne, Phenylacetylene and related alkyne complexes of molybdenum(II) and tungsten(II) have been prepared[126,127,128-130], few 3-hexyne derivatives have been reported ; these include the dimeric tungsten complex, $[\{W(\mu\text{-Br})Br(CO)(\eta^2\text{-EtC}_2\text{Et})_2\}_2]$[11], molybdenum dichloro- and dibromo-phosphine complexes $[MoX_2(CO)L_2(\eta^2\text{-EtC}_2\text{Et})]$ (X = Cl, L = PPh_3; X = Br, L =PEt_3, PPh_3; X = Cl, Br, L_2= dppe)[15] and the bis(dialkyldithiocarbamate) complexes $[Mo(CO)(\eta^2\text{-EtC}_2\text{Et})(S_2CNEt_2)_2]$[131] and $[Mo(\eta^2\text{-PhC}_2\text{H})(\eta^2\text{-EtC}_2\text{Et})(S_2CNEt_2)_2]$[41].

None of the above 3-hexyne complexes have been crystallographically characterised, and until this work no diiodo-3-hexyne complexes of molybdenum(II) and tungsten(II) have been reported.

Baker *et al*, in 1989[92], reported the synthesis and X-ray crystal structures of the tungsten bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph). Very recently, in 1998[132] Baker and co-workers also described the synthesis and crystal structures of the related molybdenum complexes $[MoI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph). The chemistry of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (M = Mo, W; R = Me, Ph) with both neutral and anionic ligands has been studied in detail[127, 133].

The main aim for this chapter were react the seven-coordinate starting materials $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with 3-hexyne to give $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$, which should act as a good starting materials for reactions with a variety neutral and anionic donor ligands. The second aim was to investigate the chemistry of these complexes, in order to compare the chemistry of these bis(3-hexyne) complexes with the closely related bis(alkyne) complexes, $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (M = Mo, W; R = Me or Ph).

2.2-Reactions of $[MI_2(CO)_3(NCMe)_2]$(M = Mo and W) with 3-Hexyne :-

The starting materials used in this research, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) were prepared by treating the zero-valent complexes *fac*-$[M(CO)_3(NCMe)_3]$ (prepared *in situ*) with one equivalent of I_2 at 0°C[74] (see equation 2.1)

$$fac\text{-}[M(CO)_3(NCMe)_3] \xrightarrow{I_2,\ 0\ ^\circ C} [MI_2(CO)_3(NCMe)_2]$$

(Equation 2.1.)

Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) with two equivalents of EtC_2Et in CH_2Cl_2 at room temperature gave good yields of the bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1** and **2**), (see equation 2.2).

$$[MI_2(CO)_3(NCMe)_2] \xrightarrow{EtC_2Et,\ CH_2Cl_2} [MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$$

(Equation 2.2)

Both complexes **1** and **2** were characterised by elemental analysis (C, H, and N) (Table 2.1), IR (Table 2.2), ^1H and ^{13}C NMR spectroscopy (Table 2.3 and 2.4). Both complexes are air-sensitive in solution, but can be stored under nitrogen or argon in the solid state for an indefinite period. The complexes are very soluble in polar organic solvents such as CH_2Cl_2 and $CHCl_3$, but only slightly soluble in diethyl ether. The IR spectra ($CHCl_3$) for **1** and **2** show carbonyl stretching bands at $\upsilon(C\equiv O) = 2055$ and $2056\ cm^{-1}$ respectively. These are in very similar positions to their related 2-butyne derivatives $[MI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ $\{\upsilon(C\equiv O) = 2061\ cm^{-1}\ (M = Mo)^{132},\ 2050\ cm^{-1}\ (M = W)^{92}\}$. The nitrile bands at $\upsilon(N\equiv C)$ at 2305 and $2253\ cm^{-1}$ are typical of complexes where the acetonitrile is acting as a simple σ-donor ligand[134].

The weak alkyne stretching bands at around $1600\ cm^{-1}$ (which are difficult to observe) for **1** and **2** are at considerably lower wavenumber than the uncoordinated alkyne, which is expected since there is back-donation of electron density from filled metal d-type orbitals to empty π^*-orbitals on the 3-hexyne ligands. The IR spectra of **1** and **2** are shown in Fig.2.1(a and b).

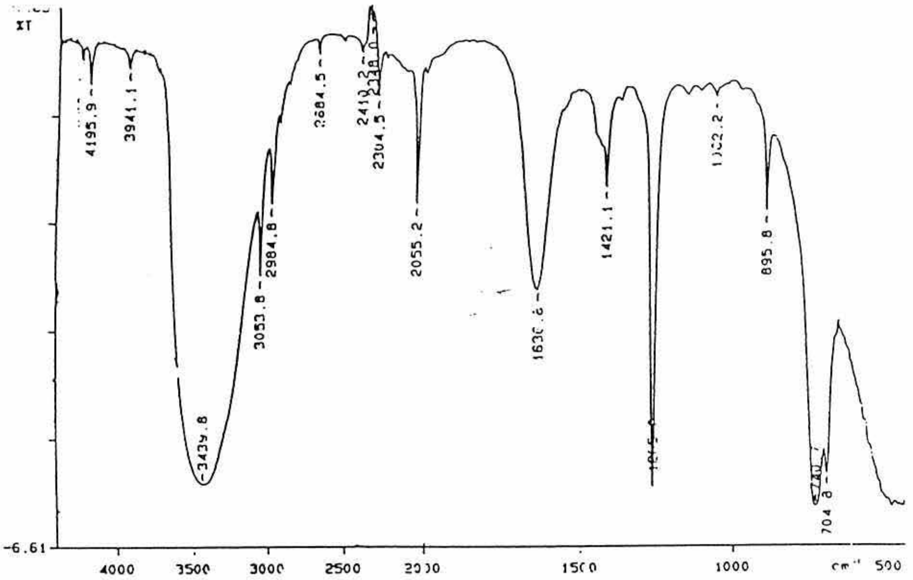


Fig.2.1a-(IR spectrum of **1** in CHCl$_3$).

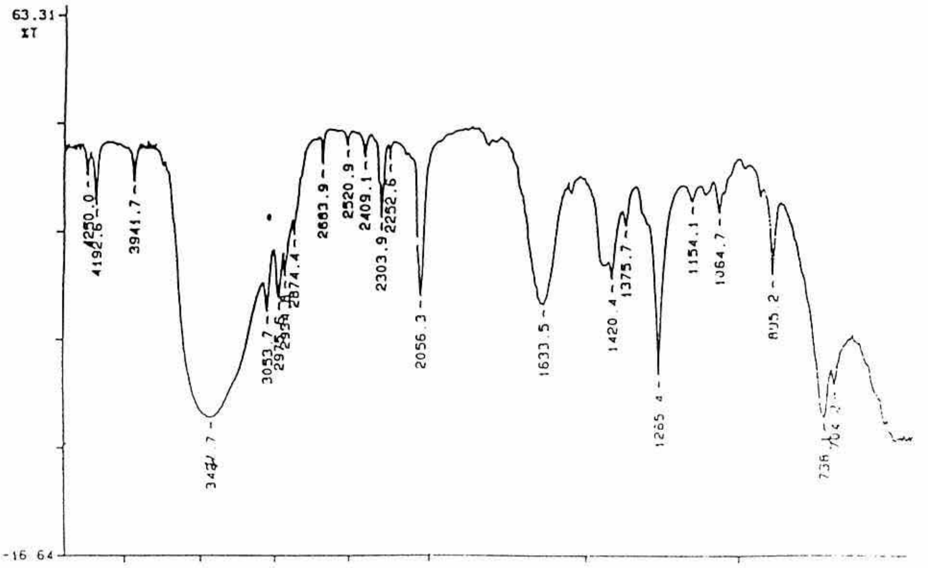


Fig.2.1b-(IR spectrum of **2** in CHCl$_3$).

The X-ray crystal structures of a number of these bis(alkyne) complexes, $[MI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ (M = W, R = Me, R' = Me, Ph[92], M = Mo, R = Me, R' = Me, Ph[132]) have been reported, and all have the structure shown in Figure 2.2, It is most probable the structure of the bis(3-hexyne) complexes **1** and **2** is very similar as shown in Figure-2.2.

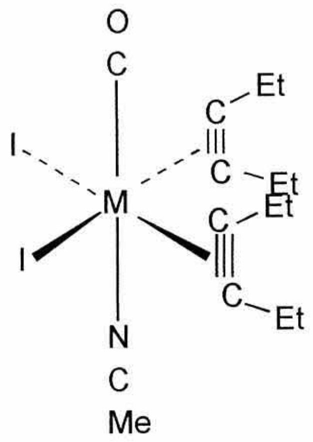


Figure 2.2- Proposed structure of $[MI_2(CO)(NCR)(\eta^2\text{-}EtC_2Et)_2]$(**1** and **2**)

The spectroscopic properties are similar to the previously reported bis(alkyne) complexes of molybdenum(II) and tungsten(II)[126,127]. The ^1H NMR spectra for complex **1** show there are two different sets of CH_2 groups at $\delta = 3.15\text{-}3.4$ ppm as quartet for $2CH_2$ and at $\delta = 2.9\text{-}3.1$ ppm for another $2CH_2$, because they are in different environments and affected by different group which is CO and NCMe, and the spectrum shows triplet for CH_3 at $\delta = 1.2\text{-}1.35$ ppm (see fig 2.3).

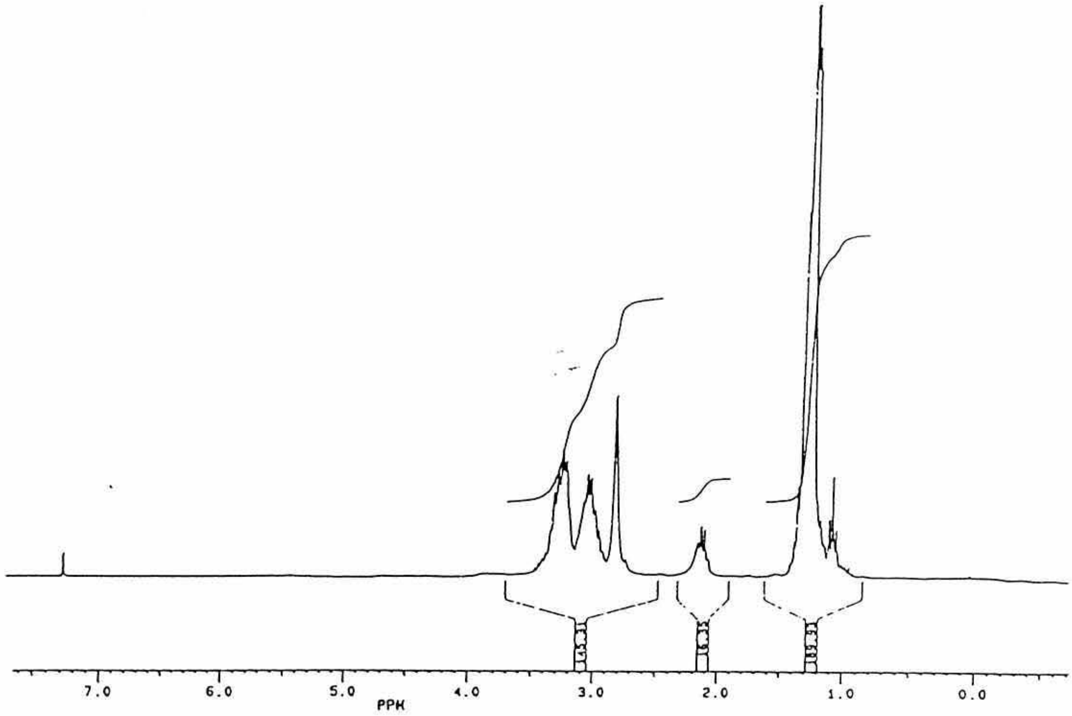


Fig 2.3- ^{1}H NMR spectrum of **1**

The room temperature ^{13}C NMR spectra of **1** and **2** have alkyne carbon contact resonances at δ = 163.48 and 172.18 ppm (for **1**) and 160.82 and 171.44 ppm (for **2**). And the carbonyl group at 217.04 and 206.5 ppm respectively. And the spectrum for complex **1** shows peak at 160.08 ppm which is a noise from NMR machine.

Templeton and Ward[13] have shown how the ^{13}C NMR alkyne contact carbon chemical shifts can be correlated with the number of electrons donated by the alkyne to the metal (see Fig 2.4). The ^{13}C NMR resonances observed for complexes **1** and **2** are in accord with the two alkynes donating a total of six electrons to the metal centre, which also enables the complexes to obey the effective atomic number rule. The ^{13}C NMR spectrum for **1** is shown in Fig.2.5.

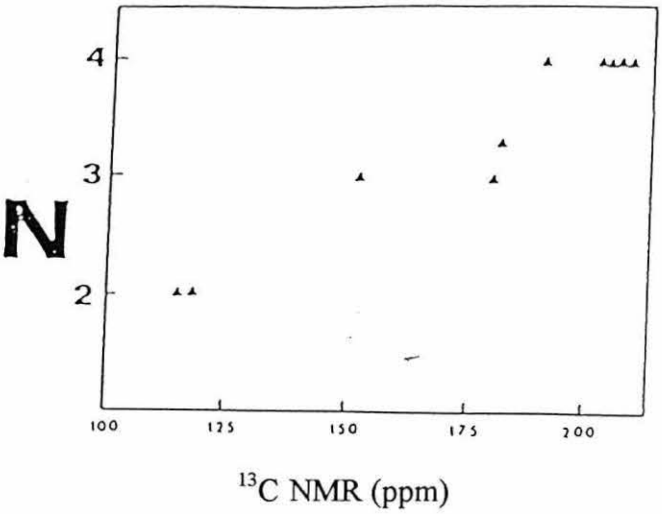


Fig.2.4-A plot of ^{13}C NMR alkyne chemical shift vs. Formal number of electrons donated per alkyne ligand (**N**)[13]

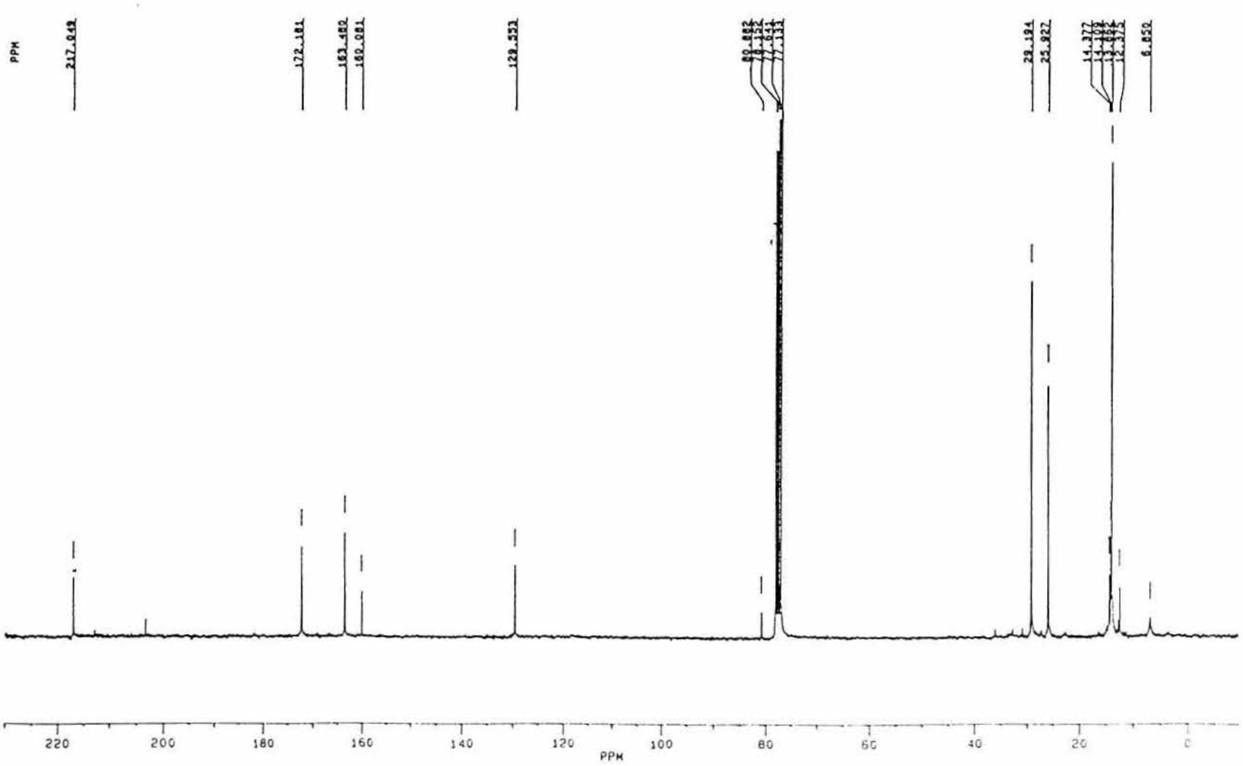


Fig.2.5-^{13}C NMR spectrum of **1**.

2.3-Reactions of [$MI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] with PPh_3. X-ray crystal structure of [$WI_2(CO)(PPh_3)_2(\eta^2$-$EtC_2Et)$](4) :-

Reactions of [$MI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (M = Mo, W) with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gave the bis(PPh_3) complexes [$MI_2(CO)(PPh_3)_2(\eta^2$-$EtC_2Et)$] (**3** and **4**), (see equation 2.3).

$$[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)] \xrightarrow{2PPh_3\text{ , }CH_2Cl_2} [MI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$$

(Equation 2.3)

Complexes **3** and **4** have also been characterised by elemental analysis (Table 2.1), IR (Table 2.2), ^1H NMR (Table 2.3) and ^{31}P NMR spectroscopy (Table 2.5). Complexes **3** and **4** are more stable in solution and very much less soluble than their bis(3-hexyne) precursors **1** and **2**.

They are both reasonably soluble in CH_2Cl_2 and $CHCl_3$, however it was difficult to obtain good ^{13}C NMR spectra of **3** and **4** due to their moderate solubility in polar NMR solvents. The IR and ^1H NMR spectral properties of **3** and **4** are similar to their 2-butyne tungsten analogue, [$WI_2(CO)(PPh_3)_2(\eta^2$-$MeC_2Me)$][98], which has a carbonyl stretching band at 1940 cm^{-1}, which is in a similar position to **4** {$\upsilon(C{\equiv}O) = 1942\ cm^{-1}$} in the same solvent.

The ^1H NMR for complex **4** which has been crystallographically characterised by X-ray crystallography shows that the resonances at δ = 7.2-7.65 ppm are for phenyl group (integration 30H), δ = 3.0-3.2 ppm for CH_2 groups(integration 4H) and at δ = 1.0-1.25 ppm for the CH_3 groups(integration 6H).

The $^{31}P\{H\}$ NMR spectra for **3** and **4** have single resonances at δ = -2.69 and -15.93 ppm respectively, this indicates a *trans*-arrangement of the PPh_3 groups, which is also shown by the X-ray crystal structure of the tungsten complex **4**.

J coupling between tungsten and phosphorus shown in ^{31}P NMR spectrum as a satellites close to the peak for the phosphorus atom. Usually, satellites appear because the spin for tungsten is half, and for phosphorus atom is also half, so there is coupling between them. This does not happen with molybdenum Mo^{96}. To work out the J coupling between W and P by measured the distance between two peaks, which in ppm and then change the value from ppm to Hz, which is the unit for J coupling.

Suitable single crystals of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ **(4)** were grown by cooling a CH_2Cl_2 /Et_2O (80:20) solution of **4** to -20°C for 24h. The structure of **4** is shown in Figure 2.6 together with the atom numbering scheme.

2.4-Reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with $Ph_2P(CH_2)_nPPh_2$ ($M = Mo, n = 1; M = W, n = 1$ to 6) :-

Equimolar quantities of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo, W) and $Ph_2P(CH_2)_n$ PPh_2 (M = Mo, n = 1; M = W, n = 1 to 6) react in CH_2Cl_2 at room temperature to yield the mono(3-hexyne) complexes $[MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Et)]$ **(5-11)**, (see equation 2.4)

$$[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2] \xrightarrow{Ph_2P(CH_2)_nPPh_2,\ CH_2Cl_2} [MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Et)] + EtC_2Et$$

(M = Mo, n = 1; M = W, n = 1 to 6)

(Equation 2.4)

Complexes **5-11** were fully characterised except ^{13}C NMR was difficult to obtain for most of them (see Tables 2.1 to 2.5). Complexes **5-11** are in between the solubility of **1**, **2** and **3**, **4**. They are also of similar air- sensitivity to the bis(PPh_3) complexes **3** and **4**. The colours and spectroscopic properties of **5-11** are analogous to their 2-butyne analogues, $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)]$ as previously reported [98].

For example, the room temperature ^{13}C NMR spectrum ($CDCl_3$) for complex **9** has alkyne contact carbon resonances about 205.02 ppm (see table 2.4) which indicates from Templeton and Ward's[13] correlation (see Fig.2.4), between the alkyne contact carbon resonances and the number of electrons donated by the alkyne to the metal, that the 3-hexyne is donating four electrons to the metal in these complexes. This enables complex **9** to obey the effective atomic number rule. The ^{31}P NMR spectra of $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Et)]$ (n = 3, 4 and 6) have two resonances (Table 2.5), which is required for a single isomer of **8**, **9** and **11**. For example, complex **8** has $\delta = -23.73$ and -36.21 ppm which is indicative for the two different phosphorus atoms. In order to obtain solid state information, suitable crystals of $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$(**8**) for X-ray analysis were grown by cooling a CH_2Cl_2/Et_2O solution of **8** to -20°C for 24h.

The structures of **4** and **8** are shown in Figures 2.6 and 2.7 together with their atomic numbering schemes. The dimensions in the metal coordination sphere are listed in appendix 2.7a and 2.7b). In both structures, if the hexyne is considered as occupying one position in the coordination sphere, then the geometry around the metal is octahedral. The crystal data for **4** and **8** are given in appendix 2.6a).

In **4**, the two monodentate phosphorus atoms are mutually *trans*-with W(1)-P(1) 2.584 (5), W(1)-P(2) 2.599(6)Å. One iodine atom is *trans*-to the alkyne, and the bond to the tungsten is significantly shorter at 2.843(3)Å, than the bond from the iodine which is *trans*-to the carbonyl group at 2.900(3)Å.

This arrangement of donor atoms around the tungsten centre is the same as that found in $[MoBr_2(CO)(PMePh_2)_2(\eta^2\text{-}MeC_2Me)]$[135] and $[WCl_2(CO)(PMe_3)_2(\eta^2\text{-}PhC_2Ph)]$[136].

In complex **8**, the two phosphorus atoms from the dppp ligand are mutually *cis*- to each other with a P(1)-W(1)-P(5) angle of 92.15(11)Å. The two bond lengths are very different, in that the W-P(1) with P(1) *trans*-to iodine is shorter at 2.545(3)Å than W-P(5) with P(5) *trans*- to carbonyl. The alkyne group is *trans*- to iodide with W-C distances 2.006(10), 2.023(9) and W-I(2) at 2.862(3)Å. The remaining distances are at W(1)-C(100) 1.967(10)Å, and W(1)-I(3) 2.824(2)Å. Thus I(2) *trans*- to 3-hexyne forms a longer bond than I(3) *trans*- to phosphorus.

This arrangement of donor atoms around the tungsten is very different from that found in $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)]$[98] and $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Ph)]$[137], where the two *cis*- phosphorus atoms are in fact *trans*- to iodine and ethyne, rather than the iodine and carbonyl group as observed in complex **8**. It is not certain why this difference is found, but the size of the dppp ligand bite angle compared to that of dppm could be a significant factor in explaining this.

2.5-Reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and 2,2'-bipyridyl :-

Complex **12**, $[MoI_2(CO)(2,2'\text{-bipyridyl})(\eta^2\text{-}EtC_2Et)]$ was prepared by reacting $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of 2,2'-bipyridyl in CH_2Cl_2 at room temperature. The IR spectrum shows a single carbonyl band at $\nu(CO)(CHCl_3) = 1946$ cm^1, which is expected as mono(alkyne) carbonyl shifts for this type of complex occurs at less than 2000 cm^{-1}.

The ^1H NMR spectrum shows resonances from 9.2 to 7.6 ppm which confirms the presence of 2,2'-bipy. The ^{13}C NMR spectrum ($CDCl_3$) shows alkyne contact carbon chemical shifts above 200 ppm which suggests the 3-hexyne is utilising both its filled pπ-orbitals and donating 4-electrons to the molybdenum, $\{\delta(C{\equiv}C)(CDCl_3) = 211.95$ ppm$\}$. Complex **12** is soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, not very soluble in diethyl ether, and can be stored under dinitrogen for several days. Complex **12** has been characterised by X-ray crystallography, and the structure of the 2,2'-bipyridyl complex is shown in Fig.2.8. The structure has the 3-hexyne ligand *trans*- to the iodo-group, with the 2,2'-bipyridyl, carbon monoxide and the other iodo-ligand in the equatorial plane. (see appendix 2.6b for crystal data and 2.7c for bond lengths).

2.6-Conclusions for chapter two :-

The reactions of $[MI_2(CO)_3(NCMe)_2]$ with 3-hexyne to give $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$, are analogues to the reaction of $[MI_2(CO)_3(NCMe)_2]$ with other alkynes, such as 2-butyne and diphenyl acetylene which has been previously described[127]. The reaction chemistry of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with neutral and anionic donor ligands is similar to their 2-butyne and diphenyl acetylene analogues.[127]

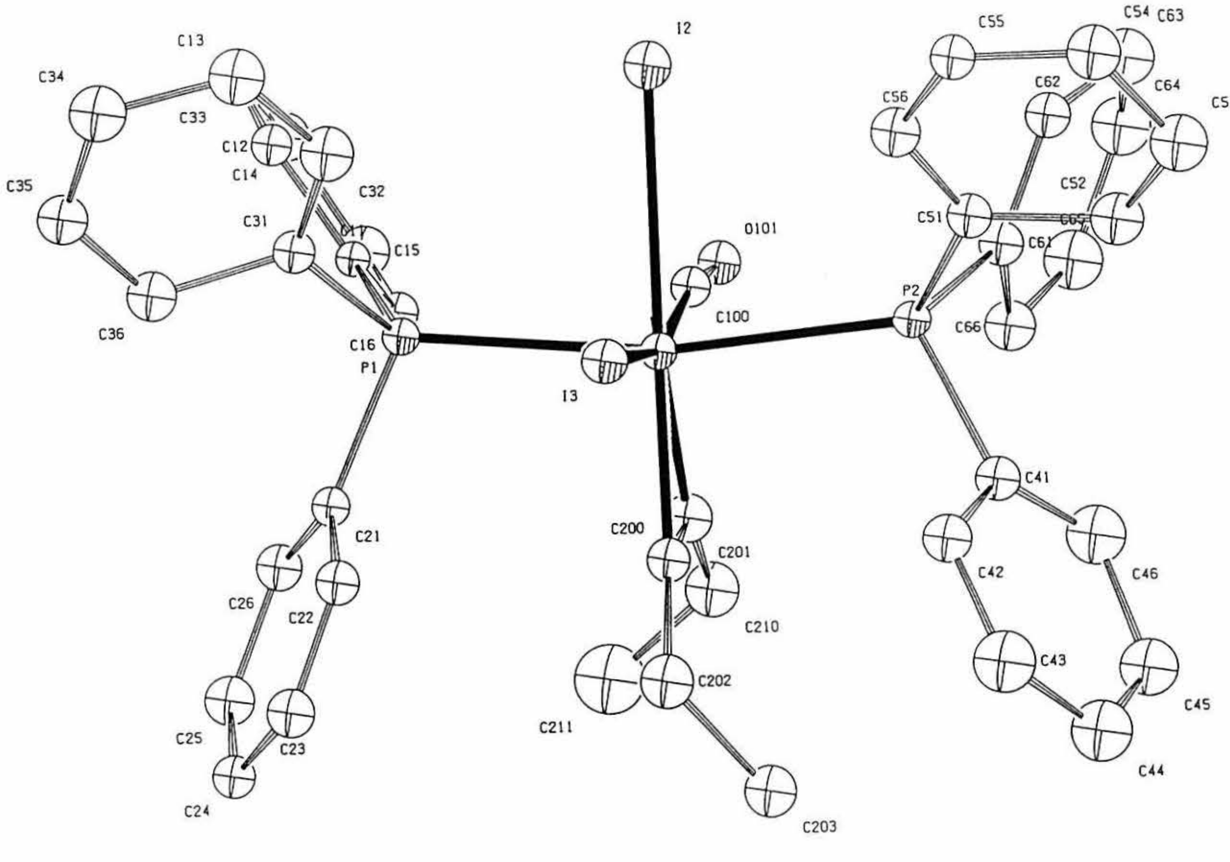


Figure 2.6- The structure of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**4**) with the atom numbering scheme. (Ellipsoids are shown at 30% probability).

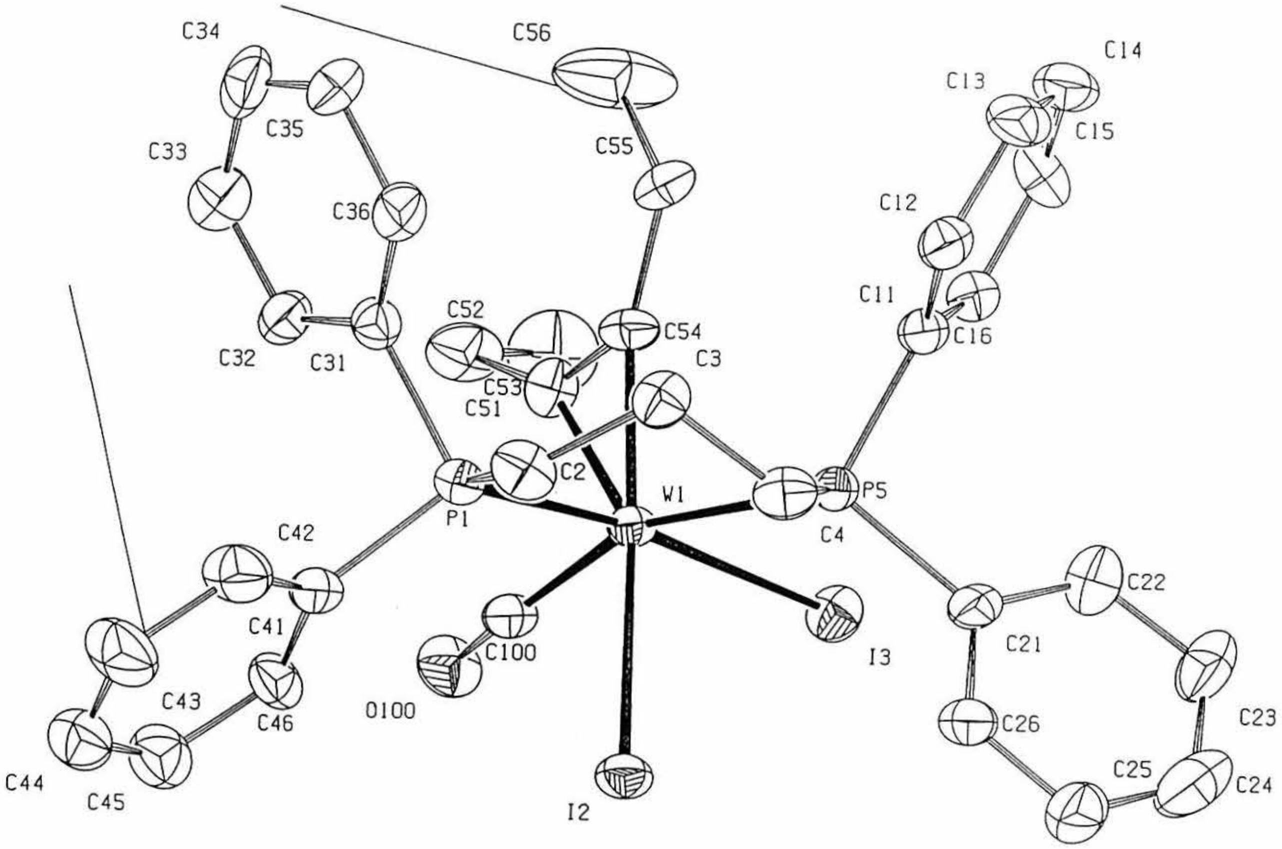


Figure 2.7- The structure of $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**8**) with the atom numbering scheme. Ellipsoids are shown at 30% probability.

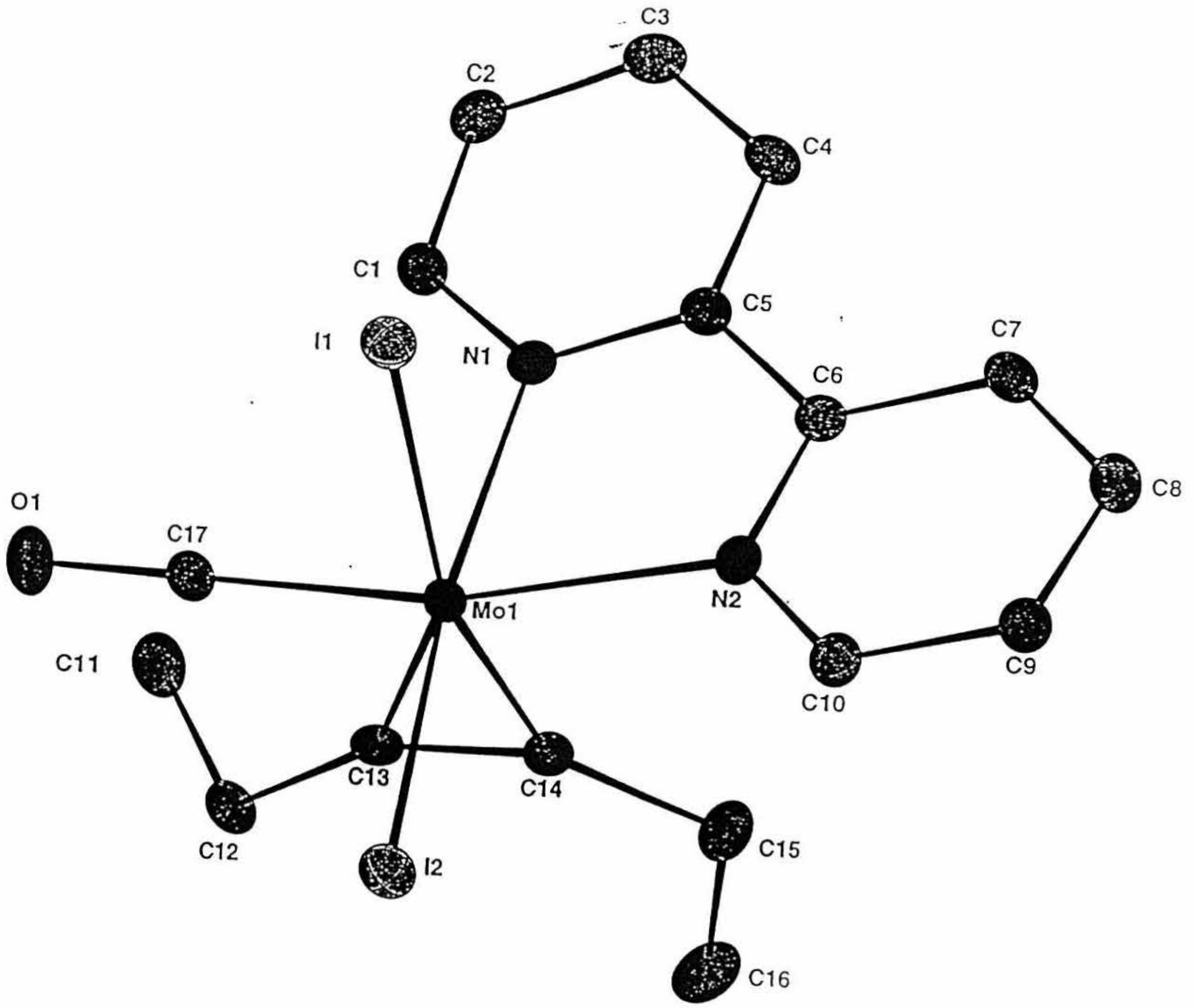


Figure 2.8- The crystal structure of $[MoI_2(CO)(2,2'\text{-bipyridyl})(\eta^2\text{-}EtC_2Et)]$ (**12**) with the atom numbering scheme. Ellipsoids are shown at 30% probability

Table 2.1-Physical and analytical data[a] for the 3-hexyne complexes 1-12

Complex	Colour	Yield%	Analytical data		
			C	H	N
(1) [$MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$]	Brown	56	30.6 (30.9)	3.9 (4.0)	2.5 (2.4)
(2) [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$]	Yellow	79	27.0 (26.9)	3.5 (3.4)	2.0 (2.1)
(3) [$MoI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$]	Brown	48	52.3 (52.3)	4.1 (4.1)	_
(4) [$WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$]	Green	95	48.2 (48.2)	3.7 (3.8)	_
(5) [$MoI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}EtC_2Et)$]	Brown	81	45.2 (45.4)	3.8 (3.8)	_
(6) [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}EtC_2Et)$]	Green	88	41.3 (41.2)	3.7 (3.5)	_
(7) [$WI_2(CO)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Et)$].	Green	40	41.70 (41.9)	3.6 (3.6)	_
(8) [$WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)$]	Green	89	42.5 (42.5)	3.9 (3.8)	_
(9) [$WI_2(CO)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}EtC_2Et)$]	Green	61	43.1 (43.2)	4.0 (3.9)	_
(10) [$WI_2(CO)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}EtC_2Et)$]	Green	31	43.5 (43.8)	4.3 (4.1)	_
(11) [$WI_2(CO)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}EtC_2Et)$]	Green	88	44.7 (44.3)	4.4 (4.2)	_
(12) [$MoI_2(CO)(2,2'\text{-}bipy)(\eta^2\text{-}EtC_2Et)$]	Brown	58	45.4 (45.4)	3.8 (3.6)	3.2 (3.0)

---

[a] **Calculated values in Parenthesis**.

Table 2.2- Infrared data[a] for the 3-hexyne complexes 1-12

Complex No.	$\upsilon(C\equiv O)cm^{-1}$	$\upsilon(N\equiv C)cm^{-1}$	$\upsilon(C\equiv C)cm^{-1}$
(1)	2055(s)	2305(w)	around 1600(vw)
(2)	2056(s)	2253(w)	around 1600(vw)
(3)	1952(s)	_	1664(w)
(4)	1942(s)	_	1654(w)
(5)	1943(s)	_	1658(w)
(6)	1931(s)	_	1603(w)
(7)	1954(s)	_	1603(w)
(8)	1942(s)	_	1656(w)
(9)	1936(s)	_	1639(w)
(10)	1934(s)	_	1635(w)
(11)	1935(s)	_	1658(w)
(12)	1946(s)	_	1641(w)

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates.

s = strong, w = weak.

Table 2.3- ^{1}H NMR data^a for 3-hexyne complexes 1-12.

Complex No.	^{1}H NMR (δ) ppm
(1)	3.15-3.4(br, m, 4H, $C\underline{H}_2$), 2.9-3.1(br, m, 4H, $C\underline{H}_2$), 2.75(s, 3H, $NCC\underline{H}_3$), 1.2-1.35(t, 12H, $C\underline{H}_3$).
(2)	3.2-3.4(m, 4H, $C\underline{H}_2$) , 2.9-3.1(m, 4H, $C\underline{H}_2$), 2.85(s, 3H, $NCC\underline{H}_3$), 1.2(dt, 12H, $C\underline{H}_3$).
(3)	7.1-7.65(br, m, 30H, <u>Ph</u>), 2.6-3.4(br, m, 4H, $C\underline{H}_2$), 0.95-1.3(dt, 6H, $C\underline{H}_3$).
(4)	7.2-7.65(br, m, 30H, <u>Ph</u>), 3.1(dq, 4H, $C{\equiv}CC\underline{H}_2$), 1.0-1.25 (t, 6H, $C\underline{H}_3$).
(5)	6.8-7.35(br, m, 20H, <u>Ph</u>), 4.6(q, 2H, $C{\equiv}CC\underline{H}_2$, $J_{H\text{-}H}$ = 10Hz), 3.45 (q, 2H,$C\underline{H}_2$), 2.9-3.15(br, 2H, $C{\equiv}CC\underline{H}_2$), 0.9-1.25(t, 6H, $C\underline{H}_3$, $J_{H\text{-}H}$ = 7.5Hz).
(6)	7.0-7.8(brm, 20H, <u>Ph</u>), 4.7(dt, 2H, $J_{H\text{-}H}$ = 8Hz, $PC\underline{H}_2$), 3.6(q, 2H, $C{\equiv}CC\underline{H}_2$, $J_{H\text{-}H}$ = 7.5Hz), 3.2(q, 2H, $C{\equiv}CC\underline{H}_2$, $J_{H\text{-}H}$ = 7.3Hz), 1.05-1.25(t, 6H, $C\underline{H}_3$, $J_{H\text{-}H}$ = 7.5Hz).
(7)	7.5-8.1 (m, 20H, <u>Ph</u>), 3.7(brm, 4H, $Ph_2PC\underline{H}_2$), 3.4(q, 4H, $C{\equiv}CC\underline{H}_2$), 1.4 (t, 6H, $C\underline{H}_3$).
(8)	7.4-8.0 (m, 20H, <u>Ph</u>), 3.5 (q, 4H, $C{\equiv}CC\underline{H}_2$), 3.3 (brm, 4H, $Ph_2PC\underline{H}_2$), 1.2 (t, 6H, $C\underline{H}_3$), 0.8 (brm, 2H, $Ph_2PCH_2C\underline{H}_2$).
(9)	6.8-7.7(br, m, 20H, <u>Ph</u>), 3.4(q, 4H, $PC\underline{H}_2CH_2$), 2.6-3.15(br, 4H, $PCH_2C\underline{H}_2$), 1.1(t, 6H, $C\underline{H}_3$).

(10)	6.9-7.6(brm, 20H, $\underline{Ph}$), 3.2-3.4(brm, 4H, $PCH_2C\underline{H}_2$), 2.95-3.2(br, m, 6H, CCH_2, $PCH_2C\underline{H}_2$), 0.8-1.35(t, 6H, $C\underline{H}_3$), 0.8-1.35(brm, 2H, $C\underline{H}_2$).
(11)	7.2-7.7 (m, 20H, $\underline{Ph}$), 3.4(q, 4H, $C{\equiv}CC\underline{H}_2$), 3.0 (brm, 4H, $Ph_2PCH_2CH_2C\underline{H}_2$), 2.4 (brm, 4H, $Ph_2PCH_2C\underline{H}_2$), 0.8 (t, 6H, $C\underline{H}_3$), 0.5 (brm, 4H, $Ph_2PCH_2CH_2C\underline{H}_2$).
(12)	9.2-7.6(v.br, 8H, 2pyridyl), 3.8-3.4(q, 4H, $2C\underline{H}_2$), 1.4-1.1(t, 6H, $2C\underline{H}_3$).

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[a]Spectra recorded in $CDCl_3$ (+25^{0}C) and referenced to $SiMe_4$.

s = singlet, br = broad, d = doublet, m = multiplet, t = triplet, q = quartet.

Table 2.4- ^{13}C NMR data (δ) for selected 3-hexyne complexes[a]

Complex No.	^{13}C (δ) ppm
(1)	6.85(s, $\underline{C}H_3$-CN), 12.37, 13.86, 14.109, 14.37(s, 4$\underline{C}H_3$), 25.92, 29.19(s, 4CH_2), 129.55(s, C≡N), 163.48, 172.18(C≡C); 217.04 (s, C≡O).
(2)	5.03(s, $\underline{C}H_3$-CN), 13.63, 13.75(s, 4$\underline{C}H_3$), 25.73, 28.94, 29.35(s, 4$\underline{C}H_2$), 128.63(C≡N), 160.82, 171.44(C≡C); 206.53(C≡O).
(3)	12.53, 13.73, 14.53 (s, 2$\underline{C}H_3$), 32.66, 33.18, 55.25 (s, 2$\underline{C}H_2$), 128.04,128.63, 128.79, 128.95, 129.72, 130.15, 130.96, 131.87, 132.79, 133.29, 133.41, 133.57, 134.15 (s, Ph).
(4)	11.94, 13.15 (s, 2$\underline{C}H_3$), 31.92 (s, 2$\underline{C}H_2$), 127.48, 127.55, 127.62, 128.20, 128.36, 128.68, 129.35, 130.08, 130.86, 132.21, 133.20, 133.51, 133.66, 133.81, 34.05, 134.40, 134.47, 134.55 (s, Ph).
(5)	12.49, 13.41, 13.77, 14.50 (s, 2$\underline{C}H_3$), 28.13, 29.64, 31.68 (s, 2$\underline{C}H_2$ 131.63, 131.85, 132.04, 132.29, 133.32, 133.67, 133.82 (s, 4Ph), 228.90(C≡O).
(6)	13.40(s, 4$\underline{C}H_3$), 30.72, 31.32, 31.77(s, 4$\underline{C}H_2$), 53.53(s, $\underline{C}H_2$-P), 127.65, 127.82, 128.31, 128.46, 128.62, 128.78, 130.32, 130.80, 130.89, 131.25, 131.42, 131.68, 131.83, 132.40, 133.06, 133.196, 134.13 (s, Ph).
(9)	12.27, 13.48, 14.35, 15.28 (s, $CH_2\underline{C}H_3$), 22.66, 24.91, 25.39 (s, $PCH_2\underline{C}H_2$, $\underline{C}H_2CH_3$), 28.87, 29.67, 30.97, 31.75, 34.21, 53.51, 65.84(s, $P\underline{C}H_2$), 127.55, 127.87, 128.61, 129.51, 130.27,130.55, 130.94, 132.16, 133.69 (s, Ph); 205.02 (s, C≡C); 222.75 (C≡O).

(12)	16.50, 19.30(s, 2CH_3); 34.37, 35.61(s, 2CH_2); 121.46, 125.47, 126.39, 132.04, 135.63, 136.34, (s, 2,2'-bipyridyl); 211.95 (s, C≡C); 228.45(s, C≡O).

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[a] Spectra recorded in $CDCl_3$ (+25 ^{0}C) and referenced to $SiMe_4$, s = singlet, br = broad, d = doublet, m = multiplet.

Table 2.5- ^{31}P NMR Data (δ) for selected 3-hexyne complexes.[a]

Complex No.	**^{31}P (δ) ppm**
(3)	δ(P) = -2.69 ppm
(4)	δ(P) = -15.93 ppm, $J_{W\text{-}P}$ = 272.54 Hz.
(6)	δ(P_A) = -30.05 ppm, -29.64 ppm, $J_{W\text{-}PA}$ = 289.25 Hz (d), δ(P_B) = -54.53 ppm, -54.15 ppm (d)
(8)	δ(P_A) = -23.733 ppm, δ(P_B) = -36.21 ppm
(9)	δ(P_A) = 3.66 ppm, δ(P_B) = -9.50 ppm, $J_{W\text{-}PB}$ = 270.78 Hz
(11)	δ(P_A) = -9.47 ppm, δ(P_B) = -15.79 ppm

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[a] Spectra recorded in $CDCl_3$ (+25 ^{0}C) and referenced to H_3PO_4.

CHAPTER THREE

3-HEXYNE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II) CONTAINING PHOSPHITE DONOR LIGANDS.

X-ray crystal structures of [$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)$], [$MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)$] and [$MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)$] (M = Mo and W).

Chapter Three

3-Hexyne complexes of Molybdenum(II) and Tungsten(II) containing Phosphite donor ligands : X-ray crystal structures of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ and $[MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (M = Mo and W).

3.1-Introduction :-

Halocarbonyl alkyne complexes of molybdenum(II) and tungsten(II) have received considerable attention over the years, and two extensive reviews have been published on this area[126,127]. Although many halocarbonyl alkyne complexes containing phosphine or phosphite ligands of the type $[MXY(CO)L_2(\eta^2\text{-}RC_2R^1)]$ (M = Mo, W; X, Y = Cl, Br, I; R, R^1 = alkyl, aryl etc) have been described[11,28,138-155], few examples containing one phosphine or phosphite ligand have been reported. Some examples are the mono(ligand) complexes, $[WI_2(CO)_2L(\eta^2\text{-}HC_2Bu^t)]$ (L = CN^tBu, PMe_3, $AsMe_3$) described by Umland and Vahrenkamp in 1982[28].

In 1998[155], the preparation of the bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo or W)(see chapter two) was reported, and their reactions with phosphine donor ligands to give a series of bis(phosphine) complexes, including the crystallographically characterised complexes, $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$(see chapter two). In 1989[99], the preparation of the bis(phosphite) complexes $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R')]$ (R = Me, Et, ^iPr and ^nBu; R' = Me or Ph), were described, and structurally characterised for R = R'= Me.

Very recently,[156] the synthesis and crystallographic characterisation of the first mono (phosphite) complexes of the type $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}R'C_2R'')]$ (R' = R'' = Me or Ph; R' = Me, R'' = Ph) have been described, and also extended the series of bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]$ including six, which were crystallographically characterised.

The main aim for this chapter was to study the reactions of phosphite ligands, $P(OR)_3$ (R = Me, Et, ${}^tBu$, ${}^iPr$ and Ph) with the 3-hexyne complexes of molybdenum(II) and tungsten(II), $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$. The second aim was to study the chemistry of the structurally characterised complex $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$, with a variety of ligands to give a range of products. The third aim was to study the *cis*- and *trans*-isomer ratio of the bis(phosphite) complexes, $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ by NMR spectroscopy.

3.2-The Synthesis and X-ray crystal structure (R = Ph) of $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)]$(R = Ph or ^{i}Pr):-

The starting materials used in this research, $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo or W) were prepared by reacting the seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ with 3-hexyne as described in chapter two (see equation 2.2)[155]. Reaction of equimolar quantities of the molybdenum complex $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ (R = Ph or ${}^iPr$) in diethyl ether at room temperature gave the new mixed ligand complexes, $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)]$ (**13** and **14**) in high yield, *via* displacement of one of the 3-hexyne ligands.

The complexes **13** and **14** have been fully characterised by elemental analysis (C, H and N)(Table 3.1), IR (Table 3.2), ^{1}H, ^{13}C NMR spectroscopy (Table 3.3-3.4) and ^{31}P NMR for complex **13** only, and X-ray crystallographyfor for R = Ph (complex **13**). Both complexes **13** and **14** are very soluble in polar chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, and also soluble in diethyl ether, in which the reactions were carried out. The complexes are very air-sensitive in solution, but can be stored under dinitrogen for several months (-17^{0}C) without any significant decomposition.

The IR spectra ($CHCl_3$) (Table 3.2) for both complexes have, as expected single carbonyl bands at 1983 and 1986 cm^{-1} respectively. These are similar to the three closely related crystallographically characterised complexes, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}R'C_2R'')]$ (R'= R''= Me ν(CO) = 1995 cm^{-1}, Ph ν(CO) = 2013 cm^{-1}; R'= Me, R''= Ph ν(CO) = 2000 cm^{-1})[156].

The IR spectra of **13** and **14** also show weak nitrile bands at 2286 cm^{-1} and alkyne stretching bands at 1646 and 1616 cm^{-1} respectively. These alkyne stretching bands are at lower wavenumber compared to the uncoordinated 3-hexyne ligand, due to the back-donation of electron density from the filled d-orbitals to empty π^*-antibonding orbitals on the 3-hexyne ligand, which lowers the bond order and hence the alkyne stretching frequency.

A suitable single crystal of the triphenylphosphite complex, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**13**) was grown by cooling (-17°C) a concentrated diethyl ether solution of **13** for 24h. The structure of **13** is shown in Fig .3.1.

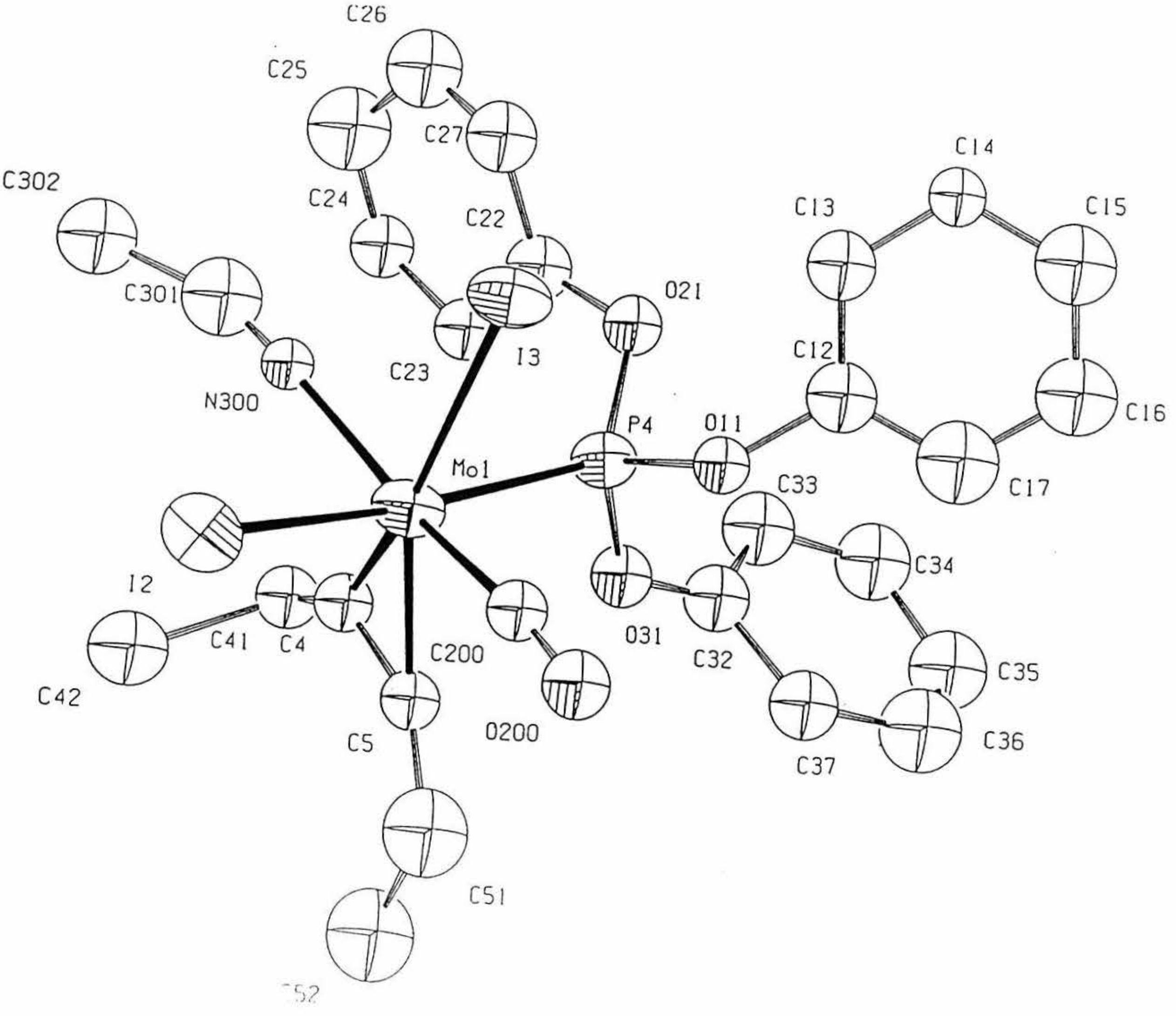


Fig.3.1 The structure of (**13**) with ellipsoids shown at 30% probability.

The crystal data and structure refinement for **13** are given in Table 3.6 (see appendix), and bond lengths and angles are given in Table 3.7(see appendix). The metal environment is best considered as a distorted octahedron with the hexyne moiety occupying one site. The molybdenum atom is bonded to a carbonyl group {Mo(1)-C(200), 1.948(14)A^{0}}, *trans*-to an acetonitrile {Mo(1)-N(300)2.212(13) A^{0}}, and a phosphite ligand {Mo(1)-P(4) 2.485 (4) A^{0}} *trans* to an iodide {Mo-I(2) 2.799 (3)A^{0}}. The coordination sphere is completed by the hexyne Mo(1)-C(5) 2.007(12), Mo(1)-C(4) 2.040 (13) A^{0}), *trans*-to iodide {I(3) at 2.862(3) A^{0}}. The bond from the iodide *trans* to phosphite is significantly shorter than the bond from the iodide *trans* to the hexyne, presumably because the latter bond is weakened by the *trans* effect.

It is probable that the reaction of the complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(M = Mo or W) with $P(OR)_3$ proceed *via* an associative mechanism, as the 3-hexyne ligand can change its bonding from being a 4-electron to a 2-electron donor, upon addition of $P(OR)_3$. This type of associative mechanism has been previously described for these type of substitution reaction in molybdenum(II) and tungsten(II) alkyne complexes[25,48]. The $^{31}P\{^1H\}$ NMR ($CDCl_3$ +25^{0}C) spectrum of **13** has a single resonance at δ = 114.44 ppm (Table 3.5). The ^1H NMR ($CDCl_3$, +25^{0}C) spectrum shows the expected resonances for **13** and **14**, which is confirmed the crystal structure that there is NCMe in the complexes at δ = 2.20 and 2.05 ppm respectively. The ^{13}C NMR spectrum for the structurally characterised complex **13** and **14** show an alkyne contact carbon resonance at δ = 193 and 196.85 ppm which from Templeton and Ward's[13] correlation of the alkyne contact carbon resonances to the number of electron donated by the 3-hexyne is acting as a 4-electron donor to the molybdenum centre. This also conforms with complexes **13** and **14** obeying the effective atomic number rule.

3.3-The synthesis and characterisation of the bis(3-hexyne) tungsten complexes $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (R = Me, ^{i}Pr and Ph) :-

It is interesting to consider the studies reported in 1989[99], that when equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ and $P(OPh)_3$ are reacted in $CHCl_3$ for 48hr a mixture of the mono(triphenylphosphite) complex $[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}PhC_2Ph)_2]$, {ν(CO) = 2030 cm^{-1}}, the bis(triphenylphosphite) complex, $[WI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}PhC_2Ph)]$, {ν(CO) = 1990 cm^{-1}} and the starting material, $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ {ν(CO) = 2090 cm^{-1}} was obtained.

In this section, the successful synthesis and characterisation of the mono(phosphite) complexes, $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$, (R = Me, ^{i}Pr, Ph) (**15-17**), is described by changing the reaction solvent, and the alkyne in these reactions. Treatment of equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ (R = Me, ^{i}Pr or Ph) in diethyl ether at room temperature gave the acetonitrile replaced bis(3-hexyne) complexes, $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (**15-17**) in high yield. Complexes **15-17** have been fully characterised by elemental analysis (Table 3.1), IR (Table 3.2), ^1H, and $^{31}P\{^1H\}$ NMR spectroscopy (Table 3.3 and 3.5). complex **16** characterised by ^{13}C NMR as well, whereas the rest was difficult to obtain ^{13}C NMR for them.

The solubilities and air-stabilities of **15-17** are similar to complexes **13** and **14**. They are slightly more soluble and stable than **13** and **14**. This differing reactivity of the molybdenum and tungsten complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $P(OR)_3$ is not unexpected, as we have previously observed similar differences. For example, reaction of equimolar amounts of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and 2,2'-bipy(bipy) gave the neutral molybdenum mono(2-butyne) complex,

$[MoI_2(CO)(bipy)(\eta^2\text{-}EtC_2Et)]$(see complex **12**), whereas, the reaction of equimolar amounts of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and bipy gave the cationic complex, $[WI(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$, which was crystallographically characterised as its $[BPh_4]^-$ salt.[40]

It is perhaps the change in solvent from CH_2Cl_2 to Et_2O, and using the more electron-rich and more strongly bonded alkyne, 3-hexyne that has enabled isolation of the bis(3-hexyne) complexes, **15-17** described herein. The IR spectra (Table 3.2), all have carbonyl bands above 2000 wavenumbers, which would be expected for complexes of the type, $[WI_2(CO)L(\eta^2\text{-}R'C_2R'')_2]$. They also have, as expected alkyne stretching bands at lower wavenumber compared to the free 3-hexyne.

Several unsuccessful attempts were made to grow single crystals for X-ray crystallography of **15-17**, however, since the reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$(R = Me or Ph) with a range of monodentate neutral donor ligands always go with retention of configuration, it is very likely the reactions of equimolar amounts of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ will also proceed with retention of configuration. The most likely structure for **15-17** is shown in Fig.3.2.

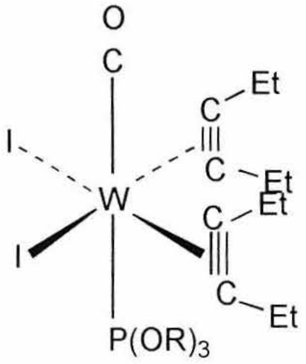


Fig.3.2. Proposed structure of $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$(**15-17**)

The ^1H NMR spectrum for complex **16** does not show full integration for the protons in the complex, but still has the resonances for the isopropyl phosphite and 3-hexyne groups as shown in (table 3-3). The ^{13}C NMR spectrum for complex **16** shows alkyne contact carbon resonances at $\delta = 166.8$ and 169.50 ppm, which suggests[13], that the two 3-hexyne ligands are donating an average of 3-electrons each to the tungsten centre, which also enables this complex to obey the effective atomic number rule. This is very typical for other bis(alkyne) complexes of this type previously described[11,92,126,127,132,155].

3.4-Reactions of [$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)$](13) :-

In a previous very recent study[156] of the reactions of [$MoI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2$] with one equivalent of $P(OPh)_3$ to give the three crystallographically characterised complexes, [$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}R'C_2R'')$] (R' = R'' = Me or Ph; R' = Me, R'' = Ph) no reactions were attempted with these new mono(phosphite) complexes.

In this section, the chemistry of the crystallographically characterised complex, [$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)$](**13**) is discussed. The first simple reaction was carried out by bubbling carbon monoxide through an Et_2O solution of **13**, which gives the acetonitrile replaced product, [$MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)$](**18**), which has been characterised in the normal manner (see tables 3.1-3.5). However, after a number of attempts it was not possible to obtain a satisfactory elemental analysis of this complex, due to its instability. The IR spectrum ($CHCl_3$) for [$MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)$] has a single carbonyl band at 2040cm^{-1}, which is as expected much higher than for **13** which has $\nu(CO) = 1983$ cm^{-1}. The molybdenum(II) complex will likely have two *trans*-strong π-accepting CO groups, an electron deficient phosphite, $P(OPh)_3$ and 3-hexyne ligand, which leaves little excess electron density on the metal to back-donate into the empty π^*-orbitals of the carbon monoxide ligands.

The ^{13}C NMR spectrum of **18** has a single alkyne, ($C\equiv C$) resonance at $\delta = 198.74$ ppm, which suggests that the alkyne is rotating rapidly at room temperature, faster than the NMR timescale. The alkyne contact carbon resonance at $\delta = 198.74$ ppm also indicates[13], that the 3-hexyne is utilizing both of its filled pπ-orbitals and donating 4-electrons to the molybdenum in this complex.

Equimolar quantities of **13** and L $\{L = PPh_3, P(O^iPr)_3, [MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}](M = Mo, W)\}$ in CH_2Cl_2 at room temperature gave the acetonitrile replaced products, $[MoI_2(CO)\,L\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ **(19-22)**. Complexes **19-22** have been fully characterised (see Tables 3.1-3.3 and 3.5 except complex **22**), and as expected are generally less soluble (L = PPh_3, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ than **13-18**, but more stable than these complexes. It should be noted that the organometallic phosphines, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo or W) have been prepared by reacting equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and $MeC(CH_2PPh_2)_3$ in CH_2Cl_2 at room temperature[157], as described in chapter four of this thesis.

The complexes (L = PPh_3)(**19**) and {L = $P(O^iPr)_3$}(**20**) were confirmed as CH_2Cl_2 and Et_2O solvates respectively, by repeated elemental analysis and ^1H NMR spectroscopy.

The reaction of **13** with CO described above, it is very likely the structure of **19-22** will be with the acetonitrile replaced by L in **13**, which is likely to undergo a trigonal twist to give the geometry with the two phosphorus donor ligands *trans*- to each other as shown in Fig.3.3. This was observed for the bis(PPh_3) complex, $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$(**4**) (see chapter two), and other related bis(phosphite) complexes (see scheme 3.1).

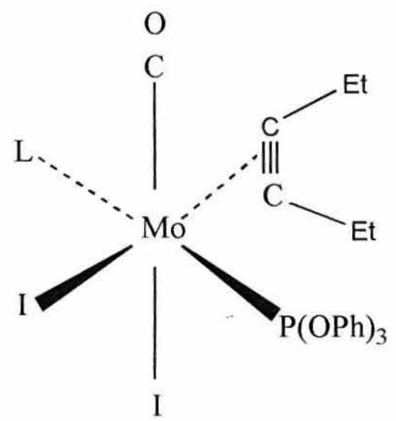
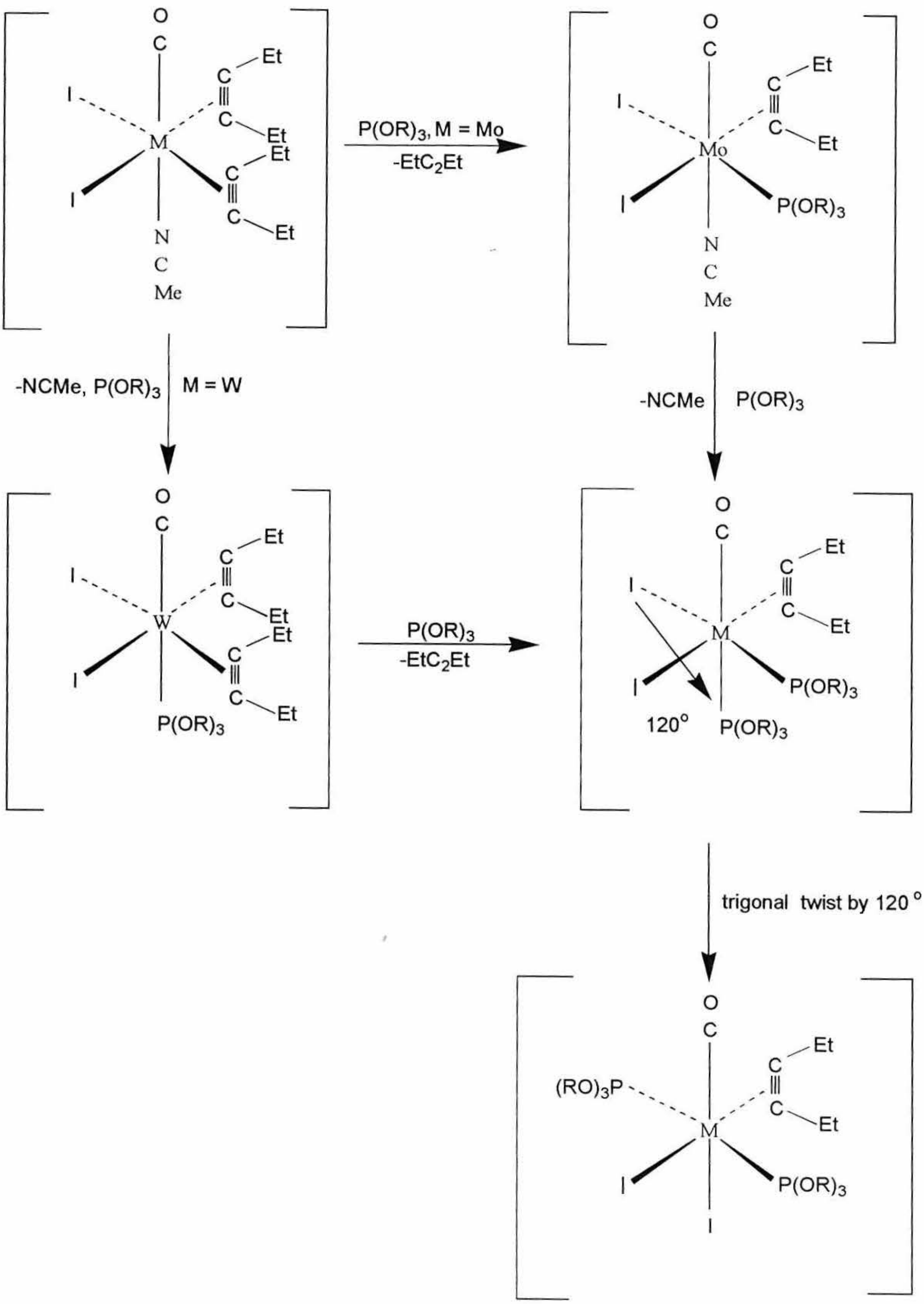


Fig.3.3. Proposed structure of [MoI$_2$(CO)L{P(OPh)$_3$}(η^2-EtC$_2$Et)](**19-22**)

{L = PPh$_3$(**19**); P(O^{i}Pr)$_3$(**20**); L^{Mo}(**21**); L^{W}(**22**)}.

The IR spectra (Table 3.2) for **19** and **20** show as expected single carbonyl bands at 1963 and 1967 cm^{-1} respectively, whereas the IR spectra for the complexes **21** and **22** have bands at 1971 and 1962 cm^{-1} due to the carbonyl group on the molybdenum 3-hexyne centre, and three other bands due to the [MI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}] units. The IR spectrum for the complex [MI$_2$(CO)$_3$ {MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}] has bands at ν(CO) = 2042, 1938 and 1859 (for M = Mo) and at 2037, 1904 and 1852cm^{-1} (for M = W). The bimetallic nature of these complexes was confirmed by molecular weight measurements using Rast's method[158].

The ^{31}P{H} NMR spectra have two resonances due to every phosphorus in the complexes. For example, the triphenylphosphine complex **19** has two singlets at δ = 114.57 ppm {P(OPh)$_3$}(J_{P-P} = 227.94 Hz) and δ = 102.74 ppm due to PPh$_3$.



Scheme. 3.1. Proposed mechanism for the stepwise reaction of two equivalents of phosphite ligands with $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$.

Reaction of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$(**13**) with an equimolar amount of L^L (L^L = bipy or dppe) afforded the new complexes $[MoI_2(CO)(L\hat{}L)(\eta^2\text{-}EtC_2Et)]$(**23** or **24**) in high yield, *via* displacement of the acetonitrile and triphenylphosphite ligands. Complexes **23** and **24** were characterised by elemental analysis (Table 3.1), IR (Table 3.2), ^1H NMR spectroscopy (Table 3.3) and by ^{13}C, $^{31}P\{^1H\}$ NMR spectroscopy for complex **24** (tables 3.4 and 3.5) and X-ray crystallography for the bis(diphenylphosphino) ethane complex, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$(**24**), and the 2,2'-bipyridyl complex (see complex **12**) discussed in chapter two.

Complexes **23** and **24** are considerably less soluble than **13-22** as they do not contain a solubilising phosphite ligand. They are both more air-stable in both the solid state and solution compared to complexes **13-22**. There are many complexes known of the general formula $[MI_2(CO)(L\hat{}L)(\eta^2\text{-}RC_2R')]$, including the following complexes $[MoI_2(CO)$ (5,6-Me_2-1,10-Phen)$(\eta^2\text{-}PhC_2Ph)]^{132}$, $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2R)]$(R = Me^{98}, R = Ph^{137}) and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]^{155}$, which have been structurally characterised. Suitable single crystals for X-ray crystallography of $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$(**24**) were grown by cooling (-17°C) a CH_2Cl_2/Et_2O (80:20) solution of **24**. The structure of **24** is shown in Fig.3.4, together with the atom numbering scheme.

The crystal data and structural refinement are given in Table 3.6. Selected bond lengths (A^0) and angles (^{0}) are given in Table 3.7(see appendix). The structure consists of discrete molecules of $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$(**24**). Although the structure is disordered over a crystallographic mirror plane, the structure of an individual molecule has been unequivically established. Each metal atom occupies an octahedral environment with the hexyne ligand occupying one site.

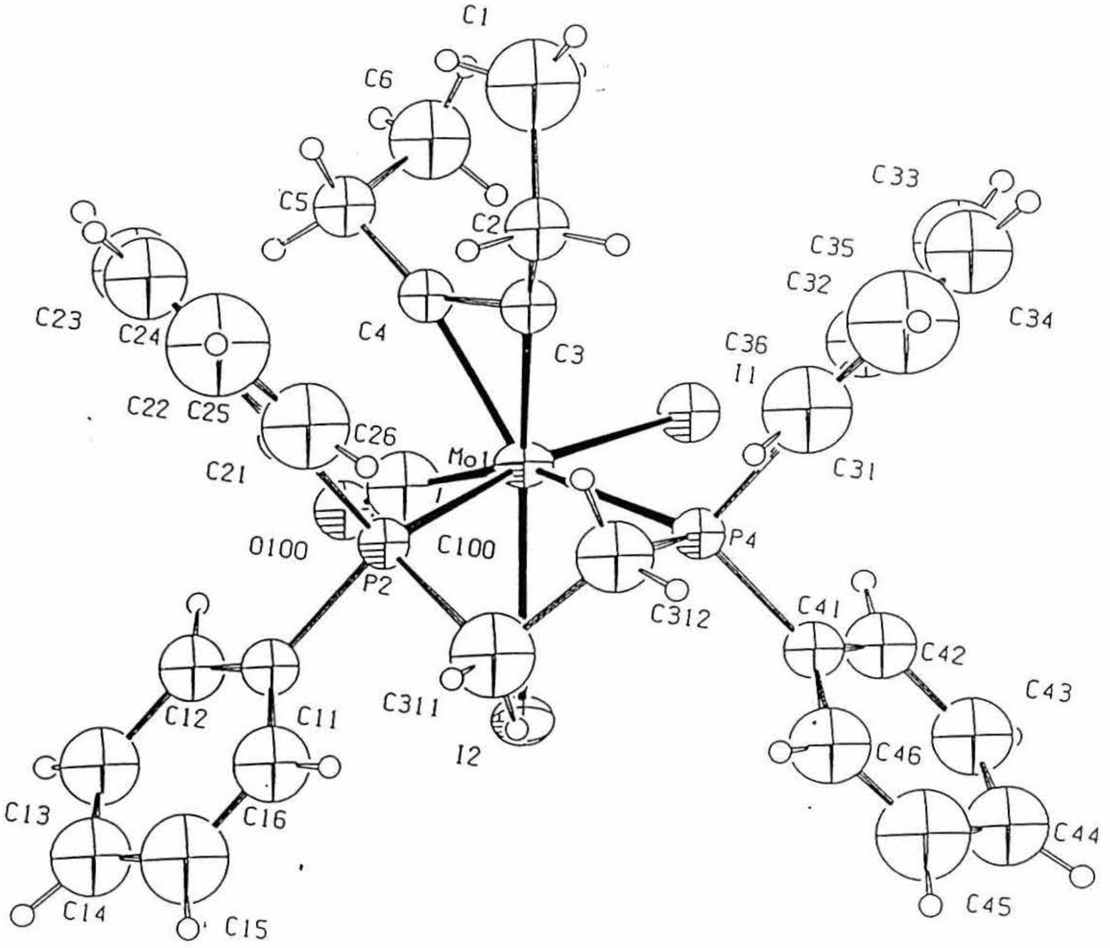


Fig.3.4. The structure of [MoI_2(CO)(dppe)(η^2-EtC_2Et)](**24**) with ellipsoids at 30% probability. The structure is disordered over a crystallographic mirror plane through atoms Mo(1), I(2), C(3), C(2) and C(1). Only one discrete molecule is shown.

The dppe ligand {Mo-P(2) 2.545 (4) A^0} together with an iodide {Mo(1)-I(1) 2.759 (3) A^0}, and a carbonyl group {Mo(1)-C(100) 2.00(4) A^0} occupying an equatorial plane, and the hexyne {Mo(1)-C(3) 2.01(2) and Mo(1)-C(4) 2.08(3) A^0} together with the second iodide {Mo(1)-I(2) 2.853(4) A^0} occuping the axial site. In this coordination sphere C(100), I(1) and (2) are disordered over two sites related by the mirror plane, and are given 50% occupancy in the refinement. As in **13**, the Mo-I bond *trans* to the hexyne is significantly longer than the bond *trans* to phosphorus.

This arrangement in the coordination sphere contrasts with that observed in $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Ph)]$[137] and $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)]$,[98] where the two phosphorus atoms are *trans* to an iodide and the 3-hexyne, with the second iodide *trans* to the carbonyl. The difference in the structure of **24** may be due to the increased bite of dppe compared to dppm, but may also be due to stabilising packing effects in the disordered structure. It is interesting to note that the bidentate ligands, bipy and dppe in these reactions displace both a nitrile and a $P(OPh)_3$ ligand. Triphenylphosphite is the most weakly bonding of the series $P(OR)_3$ (R = Me, Et, ^{i}Pr, Ph), and might be expected to be displaced in this type of reaction rather than an iodo or a carbonyl ligand.

Complexes **23** and **24** have single carbonyl bands at 1949 and 1941 cm^{-1} respectively, in the expected position for this type of complex. The ^1H NMR spectra for **24** conform with the $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ formulation. The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, $+25^0C$) for **24** has a single resonance at $\delta = 31.35$ ppm.

Equimolar quantities of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$(**13**) and NaS_2CNR_2 (R = Me or Et) react in CH_2Cl_2 at room temperature to give the dithiocarbamate complexes, $[MoI(CO)\{P(OPh)_3\}(S_2CNR_2\text{-}S,S')(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$ (**25** and **26**) in good yield, *via* displacement of the acetonitrile and an iodo ligand. The new complexes have been characterised in the normal manner, (see Tables 3.1-3.3 and 3.5), and are confirmed as CH_2Cl_2 solvates by repeated elemental analysis and ^1H NMR spectroscopy.

They are both very soluble in chlorinated solvents, CH_2Cl_2 and $CHCl_3$, but much less soluble in diethyl ether. The complexes are air-sensitive in both the solid state and solution. A number of dithiocarbamate alkyne complexes of molybdenum(II) and tungsten(II) have been previously characterised[41,51,126,127], including the crystallographically characterised complex $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$[102].

It is likely **25** and **26** will have a similar structure, except the 2-butyne ligand is replaced by a $P(OPh)_3$ ligand, and is shown in Fig.3.5. The IR spectra of **25** and **26** have single carbonyl bands at 2039s and 2034s cm^{-1} respectively. The $^{31}P\{^1H\}$ NMR spectra of **25** and **26** have single resonances at 128.01 and 127.26 ppm respectively, due to the triphenylphosphite ligand.

It should be noted that a number of other reactions of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$(**13**) with a variety of neutral and anionic ligands, such as 1,10-phenanthroline, $AsPh_3$, $SbPh_3$ were carried out, and although reactions occurred no pure products could be isolated from these reactions.

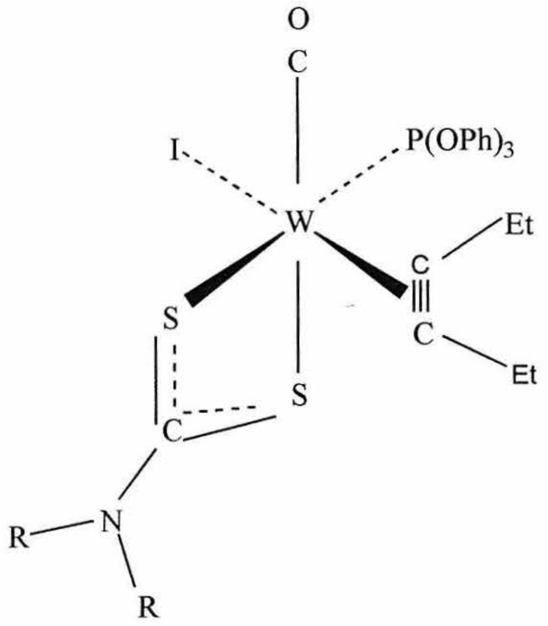


Fig.3.5 Proposed structure of [MoI(CO){P(OPh)$_3$}(S$_2$CNR$_2$)(η^2-EtC$_2$Et)].CH$_2$Cl$_2$.

(**25** and **26**).

3.5-Synthesis and characterisation of the bis(phosphite) complexes

[MI$_2$(CO){P(OR)$_3$}$_2$(η^2-EtC$_2$Et)] :-

When the complexes [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] were reacted with two equivalents of P(OR)$_3$ in diethyl ether at room temperature, the bis(phosphite) complexes [MI$_2$(CO){P(OR)$_3$}$_2$(η^2-EtC$_2$Et)]{M = Mo or W; R= Me, Et, ^{i}Pr, ^{n}Bu, Ph (for M = W only)}(**27-35**) were obtained in high yield, *via* displacement of an acetonitrile and a 3-hexyne ligand.

Complexes **27-35** were characterised by elemental analysis (Table 3.1), IR (Table 3.2),^{1}H (Table 3.3), ^{31}P (Table 3.5 except complex **29**), and in selected cases ^{13}C NMR spectroscopy (Table 3.4 except complex **34**), and for the complexes where M = Mo and W, R = ^{i}Pr(**31**) and (**32**) by X-ray crystallography.

All the bis(phosphite) complexes were extremely soluble in polar solvents, such as CH_2Cl_2 and $CHCl_3$ and also in diethyl ether. They are very air-sensitive in solution, but can be stored under nitrogen in the solid state at -17^0C for several days.

The tungsten complexes $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-EtC}_2\text{Et})]\{R = Et(\mathbf{30})$ and $^n\text{Bu}(\mathbf{34})\}$ were confirmed as Et_2O solvates by repeated elemental analysis and ^1H NMR spectroscopy. These bis(phosphite) 3-hexyne complexes are closely related to the complexes, $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-R'C}_2\text{R'})](R = Me, Et, {}^i\text{Pr}, {}^n\text{Bu}; R'= Me$ or Ph)(structurally characterised for R = R' = Me)[99] and the large series of complexes, $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-R'C}_2\text{R''})]$\{R = Ph, R' = Me, R''= Ph (M = Mo only); M = Mo or W, R = Me, R' = R'' = Me, Ph (M = Mo only); R' = Me, R'' = Ph (M = W only); R = Et, R' = R'' = Me, Ph (M = Mo only); R' = Me, R'' = Ph (M = W only); R = ^{i}Pr, R = R'' = Me, Ph (M = Mo only); R = ^{n}Bu, R' = R'' = Me, Ph (M = Mo only for both complexes)\}\{structurally characterised for M = Mo, R = Me, ^{i}Pr; R' = R'' = Me; M = Mo, R = Ph, R' = Me, R'' = Ph; M = W, R = Et or ^{i}Pr; R' = R'' = Me; R' = Me, R'' = Ph (R = ^{i}Pr only)\}very recently reported[156].

Suitable single crystals for X-ray analysis of $[MI_2(CO)\{P(O^i\text{Pr})_3\}_2(\eta^2\text{-EtC}_2\text{Et})]$(**31**) and (**32**) were grown by cooling (-17^0C) concentrated diethyl ether solutions of **31** and **32** for 24hr. The structure of **32**(M = W) is shown in Fig.3.6 together with the atomic numbering scheme.

Crystal data and structure refinement for **31** and **32** are given in Table 3.6(see appendix), and selected bond lengths (A^0) and angles (^{0}) are given in Table 3.7(see appendix). The structure consists of discrete molecules of $[WI_2(CO)\{P(O^i\text{Pr})_3\}_2(\eta^2\text{-EtC}_2\text{Et})]$(**32**).

The structure of **31** with M = Mo is isostructural with **32** M = W. In both structures the metal atom has a distorted octahedral environment, with the hexyne ligand occupying one site. The two phosphite ligands are mutually *trans-* to each other {W(1)-P(4) 2.541(8)A^0, Mo(1)-P(4) 2.566(5) A^0}. The carbonyl and hexyne groups are mutually *cis*, and each is *trans* to an iodide. The W-I(2) and Mo-I(2) distances are 2.853(3), 2.872(2) A^0 respectively.

This *trans* configuration around the metal has been observed previously[156] with other alkynes phosphite complexes, for example, [MI_2(CO){P(O^iPr)$_3$}$_2$(η^2-MeC_2Me)] (M = W, Mo) which are isostructural and [MoI_2(CO){P(OPh)$_3$}$_2$(η^2-MeC_2Me)], [WI_2(CO){P (OEt)$_3$}$_2$(η^2-MeC_2 Me)], [WI_2(CO){P(O^iPr)$_3$}$_2$(η^2-MeC_2Ph)] which are not. Only two *cis* complexes have been prepared and structurally characterised *viz* [MI_2(CO){P(O Me)$_3$}$_2$(η^2-MeC_2Me)] (M = Mo[156], M = W[99]).

The IR spectra of complexes **27-30**, {P(OMe)$_3$} and {P(OEt)$_3$}, and **33** and **34** {P(O^nBu)$_3$} complexes, have two carbonyl stretching bands in both their solution ($CHCl_3$) and solid state (KBr disc) spectra, and it is very likely the carbonyl bands at higher wavenumber will be due to the *cis*-isomer. For example, for the complex of [MoI_2(CO){P(OEt)$_3$}$_2$(η^2-EtC_2Et)] **(29)** has carbonyl bands ν(C≡O) at 1956 and 1986 cm^{-1} in liquid state and 1967 and 1995 cm^{-1} in the solid state. For the *cis-* phosphite isomers, the carbonyl group with the higher stretching frequencies will be *trans-* to the strong π-accepting phosphite group[99, 156], whereas in the *trans-* isomer the carbonyl is *trans-* to an iodo group (see Fig.3.6), which could conform with being due to the lower carbonyl stretching bands in both the solid and solution state. Phosphites are stronger *trans*- ligands than iodo ligands, which decrease the electron density for back-bonding to the π^*-orbitals of the carbonyl group, and hence increase the C≡O bond order compared to where the carbon monoxide ligand is *trans*- to iodide.

The cone angles[159] for $P(OR)_3$ are {R = Me(107^0), Et ≈ ^{n}Bu(109^0), ^{i}Pr(128^0)}, and hence for the larger triisopropyl phosphite, it would be expected that a greater proportion of *trans*-phosphite complexes for the larger cone angle phosphite ligands.

The ^{31}P NMR data has been used to obtain the *cis* : *trans* isomer ratio of the series of phosphite ligands $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (R = Me, Et, ^{n}Bu or ^{i}Pr) and were found not in similar ratios to those previously observed for the closely related 2-butyne and 1-phenylpropyne complexes of the type, $[MI_2(CO)\ \{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]$ (R' = R'' = Me; R' = Me, R'' = Ph)[156], which was for R = Me: Et: ^{n}Bu: ^{i}Pr 80:20, 40:60, 40:60 and 0:100 respectively. For example, the spectrum for the complex **30** is shows that the ratio between the *cis*- and *trans*- isomers was ≈ 10:90 (Fig 3.7), and the spectrum for complex **32** shows the ratio between *cis*:*trans* was as expected 0:100 (Fig 3.8).

The ^{13}C NMR spectra of complexes, **28** to **33** and **35** all show alkyne contact carbon resonances at 207.50, 203.40 and 204.69 ppm respectively, which conform with the 3-hexyne ligand donating 4-electrons to the molybdenum or tungsten in these complxes[13], which also enables the complexes to obey the effective atomic number rule.

In conclusion, the synthesis and characterisation of a number of new 3-hexyne phosphite complexes of molybdenum(II) and tungsten(II), including the crystallographic characterisation of mono(phosphite) complex $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**13**) has been described. The chemistry of **13** has been extensively studied, and one of the reaction products, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$, has been crystallographically characterised.

The synthesis and structure (M = Mo and W; R = ^{i}Pr) of a series of bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ are also described. Finally, by considering the results of two previous papers describing the reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]$ with phosphites[99,156] and in particular the work described in this chapter, a detailed mechanism of the reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]$ with phosphites can be described, and is shown in Scheme 3.1. This shows the different pathways that when one equivalent of phosphite is added, together with the *cis-trans*-isomerism which occurs due to the steric factors of the phosphite ligands.

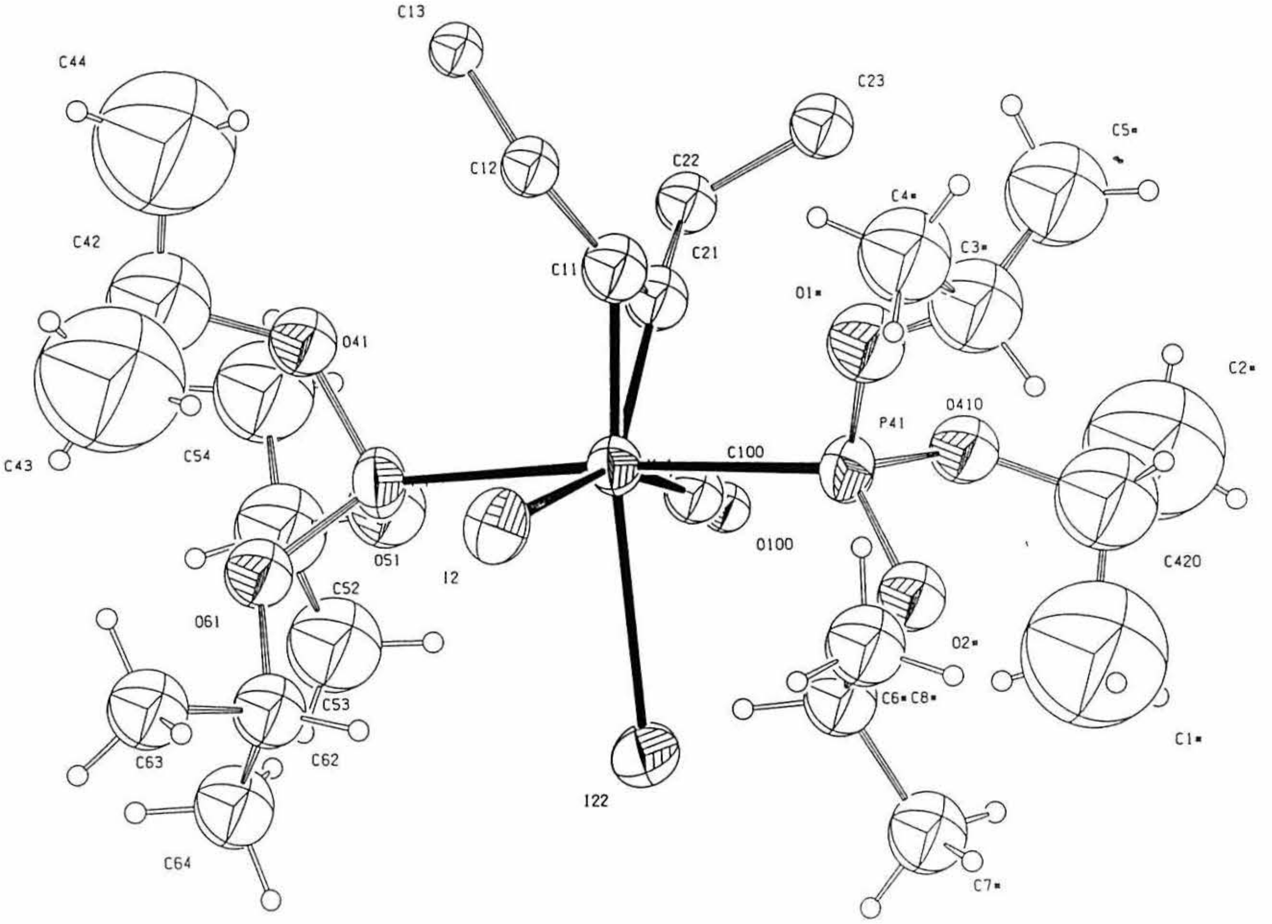


Fig.3.6-The structure of $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$((**32**) with ellipsoids at 30% probability. The structure is disordered over a crystallographic two-fold axis through the metal atom Only one discrete molecule is shown. The structure of (**31**) is isostructural.

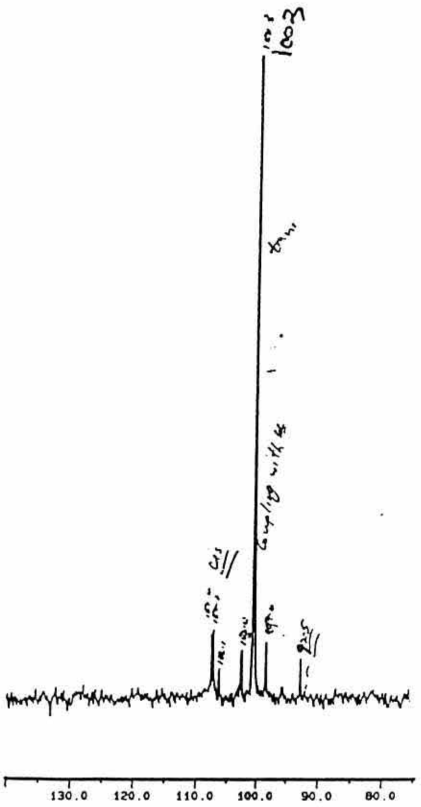


Fig.3.7-The room temperature $^{31}P\{^1H\}$ NMR spectrum for the complex

$[WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**30**).

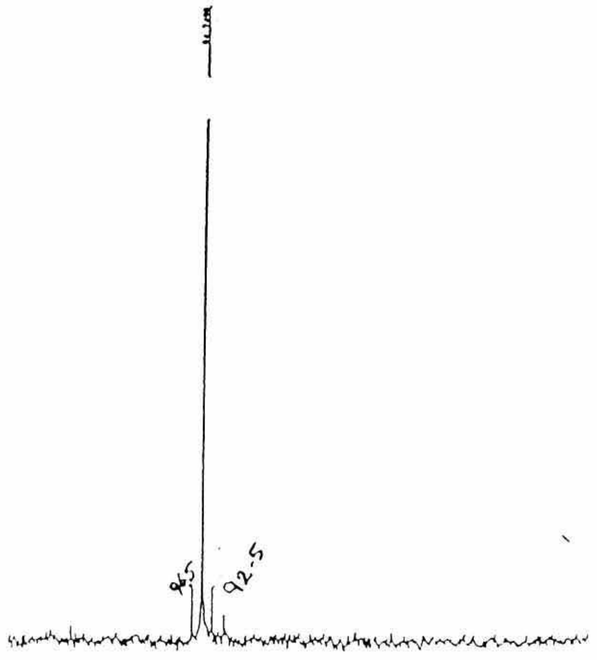


Fig.3.8-The room temperature $^{31}P\{^1H\}$ NMR spectrum for

the complex $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**32**).

Table 3-1 Physical and Analytical data[a] for the phosphite complexes (**13-35**)

Complexes	Colour	Yield%	C%	H%	N%
(13) $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	84	40.0	3.5	1.7
			(39.9)	(3.5)	(1.7)
(14) $[MoI_2(CO)(NCMe)\{P(O^iPr)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	76	30.1	4.7	2.0
			(30.5)	(4.8)	(2.0)
(15) $[WI_2(CO)\{P(OMe)_3\}(\eta^2\text{-}EtC_2Et)_2]$	Green	79	24.1	4.2	_
			(24.3)	(3.9)	
(16) $[WI_2(CO)\{P(O^iPr)_3\}(\eta^2\text{-}EtC_2Et)_2]$	Green	85	31.2	5.4	_
			(31.5)	(4.9)	
(17) $[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$	Green	80	38.2	3.5	_
			(38.8)	(3.8)	
(18) $[MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	42	50.3	4.9	_
			(39.1)	(3.2)	
(19) $[MoI_2(CO)(PPh_3)\{P(OPh)_3\}$	Brown	57	46.8	3.9	_
$(\eta^2\text{-}EtC_2Et)].\ CH_2Cl_2$			(47.3)	(3.8)	
(20) $[MoI_2(CO)\{P(O^iPr)_3\}\{P(OPh)_3\}$	Brown	43	42.9	5.5	_
$(\eta^2\text{-}EtC_2Et)].Et_2O$			(43.3)	(5.4)	
(21) $[MoI_2(CO)(L)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	62	44.5	3.6	_
$\{L = [MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]\}$			(45.3)	(3.5)	

(22) $[MoI_2(CO)(L)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	36	42.5	3.4	–
$\{L= [WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]\}$			(43.2)	(3.4)	
(23) $[MoI_2(CO)(2,2'\text{-bipy})(\eta^2\text{-}EtC_2Et)]$	Brown	–	45.4	3.7	3.2
			(45.4)	(3.6)	(3.0)
(24) $[MoI_2(CO)\{PPh_2(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Et)]$	Green	92	46.2	4.0	–
			(46.2)	(4.0)	
(25) $[MoI(CO)\{(CH_3)_2NCS_2\}\{P(OPh)_3\}$	Brown	36	40.3	4.1	1.9
$(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$			(40.2)	(4.0)	(1.7)
(26) $[MoI(CO)\{(C_2H_5)_2NCS_2\}\{P(OPh)_3\}$	Brown	53	42.5	4.5	1.7
$(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$			(42.5)	(4.3)	(1.6)
(27) $[MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	78	22.1	4.0	–
			(22.1)	(4.0)	
(28) $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Green	57	19.2	3.5	–
			(19.6)	(3.5)	
(29) $[MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	41	28.6	5.2	–
			(28.8)	(5.1)	
(30) $[WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)].Et_2O$	Green	49	27.8	5.0	–
			(28.9)	(5.2)	
(31) $[MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	77	33.9	5.9	–
			(34.3)	(6.0)	
(32) $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Green	91	31.4	5.6	–
			(31.1)	(5.4)	

(33) $[MoI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	56	38.5	6.7	_
			(38.8)	(6.7)	
(34) $[WI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}EtC_2Et)].\ Et_2O$	Green	54	38.0	6.6	_
			(37.5)	(6.6)	
(35) $[WI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Green	80	43.5	3.9	_
			(44.2)	(3.5)	

[a] **Calculated values in Parentheses.**

Table 3.2- Infrared Data for the phosphite complexes **13-35**[a]

Complex	$\upsilon(C\equiv O)$	$\upsilon(C\equiv C)$	$\upsilon(C\equiv N)$
(13)	1983 s cm^{-1}	1646 w cm^{-1}	2286 vw cm^{-1}
(14)	1986 s cm^{-1}	1616 w cm^{-1}	2286 vw cm^{-1}
(15)	2044 s cm^{-1}	1653 w cm^{-1}	–
(16)	2046 s cm^{-1}	1636 w cm^{-1}	–
(17)	2064 s cm^{-1}	1636 w cm^{-1}	–
(18)	2040 s cm^{-1}	1641 w cm^{-1}	–
(19)	1963 s cm^{-1}	1590 w cm^{-1}	–
(20)	1967 s cm^{-1}	1594 w cm^{-1}	–
(21)	(2042 s ,1971 s, 1938 s and 1859 s) cm^{-1}	1648 wcm^{-1}	–
(22)	(2037 s, 1962 s, 1904 s,1852 s) cm^{-1}	1636 w cm^{-1}	–
(23)	1949 s cm^{-1}	1638 w cm^{-1}	–
(24)	1941 s cm^{-1}	1656 w cm^{-1}	–
(25)	2039 s cm^{-1}	1590 w cm^{-1}	–
(26)	2034 s cm^{-1}	1736 w cm^{-1}	–
(27)	2004 s, 1989 sh cm^{-1}	1636 w cm^{-1}	–
(28)	1988 s, 1953 sh cm^{-1}	1654 w cm^{-1}	–

(29)	1986^{a} s, 1956^{a} sh cm^{-1}	1630 w cm^{-1}	–
	1995^{b} s, 1967^{b}sh cm^{-1}	1626 w cm^{-1}	–
(30)	1981^{a} s, 1956^{a} sh cm^{-1}	1636 w cm^{-1}	–
	1938^{b} s, 1987^{b} sh cm^{-1}	1625 w cm^{-1}	–
(31)	1966 s cm^{-1}	1602 w cm^{-1}	–
(32)	1950 s cm^{-1}	1727 w cm^{-1}	–
(33)	1968 s, 1996 sh cm^{-1}	1636 w cm^{-1}	–
(34)	1951 s, 2002 sh cm^{-1}	1602 w cm^{-1}	–
(35)	1976 s cm^{-1}	1631 w cm^{-1}	–

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[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates. s = strong, sh = shoulder, w = weak, vw = very weak.

[b] Spectra recorded in the solid state as KBr discs.

Table(3-3) ^{1}H NMR Data (δ) for the complexes 13-35[a]

complex	^{1}H NMR (δ) ppm
(13)	7.25-7.5(m, 15H, 3Ph), 3.4-3.6(q, 4H, $2CH_2$), 2.20(s, 3H, NCMe), 1.25(t, 6H, $2CH_3$).
(14)	4.2-4.8(m, 3H, O-CH), 3.4(q, 4H, $2CH_2$), 2.05(s, 3H, $NC\underline{Me}$), 1.9(d, 9H, $J_{H\text{-}H}$ = 6.76Hz, $3O\text{-}CH(\underline{CH}_3)_2$), 1.3(d, 9H, $J_{H\text{-}H}$ = 6.1Hz, $3O\text{-}CH(\underline{CH}_3)_2$), 1.2(s, 6H, $2CH_3$).
(15)	3.7(d, 3H, CH_3, $J_{H\text{-}H}$= 7.35); 3.5(d, 6H, $2CH_3$ $J_{H\text{-}H}$= 5.34); 3.6 (q, 4H, $2CH_2$ Hexyne); 1.1(t, 6H, $2CH_3$ Hexyne).
(16)	4.6-4.4(m, 3H Phosphite, 3CH); 3.6-3.4(q, 8H Hexyne, $4CH_2$); 1.35(t, 12H Hexyne, $4CH_3$); 1.15(t, 18H, $6CH_3$ Phosphite).
(17)	7.5-7.1(v.br, 15H, 3Ph); 3.6-3.1(q, 8H, $4CH_2$); 1.4-1.0(t, 12H, $4CH_3$).
(18)	7.5-6.8(m, 15H, 3Ph), 3.4(m, 4H, $2CH_2$ hexyne), 1.4(t, 6H, $2CH_3$ hexyne).
(19)	7.6-7.0(v.br, 30H, 6Ph); 5.2(s, 2H, $\underline{CH_2}Cl_2$) 3.3-2.8(q, 4H, $2CH_2$); 1.0-0.8(t, 6H, $2CH_3$).
(20)	7.6-6.9(m, 15H, 3Ph); 4.7(m, 3H, 3CH ^iPr); 4.8(q, 4H, $2CH_2$ hexyne); 3.4(q, 4H, $2CH_2$ ether); 1.4(d, 18H, $6CH_3$ of ^iPr, $J_{H\text{-}H}$ = 5.60); 1.1(t, 6H, $2CH_3$); 0.9(t, 6H, $2CH_3$ ether).

(21)	7.8-7.0(v.br, 30H, 6Ph); 3.5-3.2(q, 4H, $2CH_2$); 2.4-2.1(m, 6H, $2CH_2$); 1.3(s, 3H, $1CH_3$); 1.2(t, 6H, $2CH_3$).
(22)	7.7-6.7(v.br, 30H, 6Ph); 3.6-3.1(q, 4H, $2CH_2$); 2.4-2.1(m, 6H, $2CH_2$); 1.4-1.15(t, 6H, $2CH_3$); 0.8(s, 3H, $1CH_3$).
(24)	7.3-7.1(v.br, 24H, 4Ph); 4.0(s, 4H, $2CH_2$); 3.5(q, 4H, $2CH_2$); 0.85(t, 6H, $2CH_3$).
(25)	7.4-7.1(m, 15H, 3Ph); 5.3(s, 2H, $\underline{CH_2}Cl_2$); 3.8(q, 4H, $2CH_2$ hexyne); 3.5(q, 6H, $2CH_3$ of $(\underline{CH_3})_2NCS_2$); 1.4(t, 6H, $2CH_3$ hexyne).
(26)	7.5-7.1(m, 15H, 3Ph); 5.3(s, 2H, $\underline{CH_2}Cl_2$); 4.1-3.8(m, 4H, $2CH_2$ $(CH_3\underline{CH_2})_2NCS_2$); 3.8-3.6(q, 4H, $2CH_2$ of hexyne); 1.5(t, 6H, $2CH_3$ of $(\underline{CH_3}CH_2)_2NCS_2$); 1.1(t, 6H, $2CH_3$ hexyne).
(27)	3.95(d, 9H, J_{H-H} =9.91 Hz, OMe), 3.65(q, 4H, $2CH_2$), 3.6(d, 9H, J_{H-H} =10.82, OMe), 1.35(t, 6H, $2CH_3$).
(28)	3.95(d, 2H, J_{H-H} =9.92Hz OMe), 3.75(d, 3H, J_{H-H} =11.9 Hz OMe), 3.6(q, 4H, $2CH_2$), 3.3(d, 9H, J_{H-H} =10.7 Hz OMe), 1.2(t, 6H, $2CH_3$).
(29)	3.9-4.2(m, 12H, O-$\underline{CH_2}CH_3$), 3.1(q, 4H, $2CH_2$), 1.0-1.25(m, 18H, J_{H-H} = 6.97, O-$CH_2\underline{CH_3}$), 0.9(t, 6H, CH_3).
(30)	4.75(m, 12H, $6CH_2$),3.1(q, 4H, $2CH_2$),1.4(t, 18H, O-$CH_2\underline{CH_3}$), 1.1(t, 6H, $2CH_3$ of hexyne).
(31)	4.75(m, 6H, O -$\underline{CH}$), 3.65(q, 4H, $2CH_2$), 1.3(t, 6H, $2CH_3$ of hexyne). 1.2(d, 36H, J_{H-H} =1.21 Hz, 6O-$CH(\underline{CH_3})_2$).

(32)	4.5-4.8(m, 6H, $O\text{-}\underline{CH}$), 3.5(q, 4H, $2CH_2$ of hexyne), 1.36(d, 18H, $J_{H\text{-}H}$ =6.08 Hz, $3O\text{-}CH(\underline{CH_3})_2$), 1.2(d, 18H, $J_{H\text{-}H}$ = 6.15 Hz, $3O\text{-}CH(\underline{CH_3})_2$), 0.85(t, CH_3 of hexyne).
(33)	3.85(t, 12H, $2O\text{-}CH_2$),1.15-1.70(m, 36H, $O\text{-}\underline{CH_2CH_2CH_2}CH_3$), 0.7-0.9(t, 18H, $O\text{-}CH_2CH_2CH_2\underline{CH_3}$), 0.7-0.9(t, 6H, $2CH_3$ of hexyne).
(34)	3.9(md, 12H, $6O\text{-}CH_2$, $O\text{-}CH_2CH_3$), 3.65(q, 4H, 2 $CH_2CH_2\underline{CH_2}CH_3$),1.80-1.20(m, 24H, $O\text{-}..\underline{CH_2CH_2}CH_3$), 0.85(t, 18H, $6CH_3$). 0.85(t, 6H, $2CH_3$).
(35)	7.3-6.65(v.br, 30H, 6Ph); 3.5-3.1(mq, 4H, $2CH_2$); 1.3-1.1 (t, 6H, $2CH_3$).

[a]Spectra recorded in CDCl3 (+25) and referenced to $SiMe_4$, s = singlet, br = broad, d = doublet, m = multiplet, q = quartet, t = triplet.

Table (3-4). ^{13}C NMR Data (δ) for selected complexes 13-35[a]

Comp.No.	**^{13}C (δ) ppm**
(13)	5.40 (s, NCMe), 14.36, 15.26 (s, 2CH$_3$), 32.80 (s, 2CH$_2$), 115.45, 120.41, 121.04, 121.11, 130.16 (s, O-Ph), 149.62, 149.77 (s, C≡N), 193.0 (s, C≡C), 208.40 (s, C≡O).
(14)	5.7 (s, NCMe), 14.40, 15.02, 15.34 (s, 2CH$_3$), 31.30 (s, 2CH$_2$), 65.93, 66.3 1(s, O-CH(CH$_3$)$_2$), 135.0 (s, C≡N), 166.85 (s, C≡C), 233.90 (s, C≡O).
(16)	12.70, 13.03, 15.25 (s, 4CH$_3$ of Hexyne); 23.81, 23.87 (s, 6CH$_3$ Phosphite); 31.18, 31.41 (s, 4CH$_2$ Hexyne); 65.81 (s, 3CH Phosphite); 166.8, 169.50(s, C≡C); 202.27, 204.39 (s, C≡O)
(18)	24.95 (s, 2CH$_3$ of Hexyne); 32.84, 34.27 (s, 2CH$_2$ hexyne); 115.44, 120.179, 121.18, 125.80, 126.62, 129.55, 129.97, 130.20 (s, 3Phenyl); 204.0 (s, C≡C) and 204.18 (s, 2 C≡O).
(27)	14.36 (s, 2CH$_3$), 32.55 (s, 2CH$_2$), 53.95 2(s, O-CH$_3$), 235.0 (s, C≡C).
(28)	12.62, 20.28 (s, 2CH$_3$), 31.45 (s, 2CH$_2$), 52.12, 54.27 2(s, O-CH$_3$), 207.5 (s, C≡C); 222.5 (s, C≡O).
(29)	18.68, 23.60 (s, 2CH$_3$), 32.32, 32.41, 35.47 (s, 2CH$_2$),, 65.44, 65.52, 67.38(s, O-CH$_2$CH$_3$), 195.0 (s, C≡C), 200.99 (s, C≡O).

(30)	15,78, 15.89, 16.60 (s, $2CH_3$), 31.41, 33.61 (s, $2CH_2$), 61.74, 61.82, 62.62, 63.29, 63.40, 63.50 (s, O-CH_2CH_3), 203.0, 205.0 (s, C≡C), 227.7(s, C≡O).
(31)	21.93, 22.85, 24.02 (s, $2CH_3$), 30.51, 30.98, 31.34, 32.20, 34.59 (s, $2CH_2$), 65.79, 67.39, 69.57, 70.59, 70.72, 71.77 2(s, O-$CH(CH_3)_2$), 207.82, 208.01 (s, C≡C), 236.21 (s, C≡O).
(32)	23.58, 23.65, 23.94 (s, $2CH_3$),31.15, 31.38 (s, $2CH_2$), 65.78, 67.35, 68.50 2(s, O-$CH(CH_3)_2$), 205.30 (s, C≡C), 236.12 (s, C≡O).
(33)	13.51, 13.68, 13.82 (s, $2CH_3$), 32.33, 32.58, 32.67 (s, $2CH_2$), 65.42, 65.51, 66.12, 66.39, 66.73, 66.86 2(s, O-$CH_2CH_2CH_2CH_3$), 203.40 (s, C≡C), 236.29 (s, C≡O).
(35)	12.56, 13.31, 14.22, 14.45 (s, $2CH_3$); 29.13, 29.31, 29.76, 31.97 (s, $2CH_2$); 115.50, 117.38, 121.04, 121.12, 128.69, 129.50 (s, 6Ph); 204.69 (s, C≡C), 219.81 (s, C≡O).

[a]Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$. s = singlet, br = broad, d = doublet, m = multiplet, q = quartet, t = triplet.

Table (3-5). ^{31}P NMR Data (δ) for complexes 13-35[a]

Complex	^{31}P (δ) ppm
(13)	δ(P) =114.44, (s).
(15)	δ(P) =104.98, (s, $J_{w\text{-}p}$ =205.53 Hz).
(16)	δ(P) = 94.76, (s, $J_{w\text{-}p}$ = 211.6 Hz
(17)	δ(P) = 92.26(s).
(18)	δ(P) = 111.216(s).
(19)	δ(P_1){PPh_3}= 102.74, (s) δ(P_2){$P(OPh)_3$}= 114.57 (s, $J_{P\text{-}P}$ = 227.94 Hz).
(20)	δ(P) = 127.33, {s, $P(OPh)_3$} and 110.88, {s, $P(O^iPr)_3$}.
(21)	δ(P) = (17.58, 2P of L^{Mo} and 32.17, 1P of L^{Mo}); and 114.50, {s, $P(OPh)_3$}.
(24)	δ(P) = 31.35, (s, dppe).
(25)	δ(P) = 128.01, ($J_{w\text{-}p}$ = 72.70 Hz).
(26)	δ(P) = 127.26, {$P(OPh)_3$}(s).
(27)	δ(P) =115.35, (*trans*)(s). δ(P) =126.37, (d, J_{pp} = 53.66 Hz) and 125.30, (d, J_{pp} = 52.60 Hz)(*cis*).
(28)	δ(P) =105.06, (*trans*), ($J_{p\text{-}w}$ =259.14 Hz). δ(P) = 98.0, (d, J_{pp} = 61.97 Hz) and 109.25, (d, J_{pp} = 61.97 Hz) (*cis*).

(30)	δ(P) =100.3, (*trans*), (s, $J_{w\text{-}p}$ =273.36 Hz).
	δ(P) = 107.40, (d, J_{pp} = 20.24 Hz)(*cis*).
	and 92.50, (d, J_{pp} = 20.24 Hz) (*cis*).
(31)	δ(P) =107.48, (*trans*), (s, $J_{w\text{-}p}$ =200.90 Hz).
(32)	δ(P) =94.74, (*trans*), (s, $J_{w\text{-}p}$ =227.73 Hz).
(33)	δ(P) =109.86, (*trans*), (s, $J_{w\text{-}p}$ = 48.59 Hz).
	δ(P) =127.28, (d, J_{pp} = 35.44 Hz)(*cis*).
	and 117.75, (d, J_{pp} = 35.44 Hz) (*cis*).
(34)	δ(P) =99.38, (*trans*), (s, $J_{w\text{-}p}$ =211.21 Hz).
	δ(P) =107.08, (d, J_{pp} = 29.97 Hz)
	and 100.74, (*cis*), (d, $J_{p\text{-}p}$ = 29.97 Hz) (*cis*).
(35)	δ(P) = 92.45, (*trans*), (s, $J_{w\text{-}p}$ =207.58 Hz).

[a]Spectra recorded in $CDCl_3$ (+25 °C) and referenced to H_3PO_4

CHAPTER FOUR

PART I :- TRIPODAL TRIPHOS {$MeC(CH_2PPh_2)_3$} SEVEN COORDINATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

PART II :- REACTIONS OF [$MI_2(CO)_3${$MeC(CH_2PPh_2)_3$-*P,P'*}] with [$MoI(CO)_2(NCMe)_2(\eta^2$-$C_3H_4R)$], [$Fe_2(CO)_9$] and [$FeI(CO)_2$(Cp or Cp')].

Chapter Four

Tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ seven-coordinate complexes of Molybdenum(II) and Tungsten(II).

4.1.1-Introduction :-

A wide range of bimetallic complexes containing bridging-phosphine ligands such as bis(diphenylphosphino)methane have been prepared and described[160-176], very few containing bridging-tridentate phosphines such as linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$ and tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ have been reported. For example, in 1981 Hunt and Balch[177] described the synthesis, characterisation and reactions of $[Pt_2(\mu\text{-dppm})_3]$ with different kinds of halogens and organic halides.

In 1986[74], the synthesis and characterisation of the highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were reported. These complexes have been shown to have a wide range of chemistry[127,133]. In 1994[88], the reactions of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$, to initially give the monodentate phosphines, $[MI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}]$, has been reported. These complexes eventually react intramolecularly to give $[MI_2(CO)_2\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P',P''\}]$. Preliminary studies of the reactions of $[WI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}]$ as a monodentate phosphine ligand have been reported[88]. Recently[100,152,178], the synthesis and crystallographic characterisation of the monodentate phosphine alkyne complexes, $[WX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$ (X = I, R = R' = Me, Ph, R = Me, R' = Ph[152]; X = Br, R = R' = Ph[178]) have been reported.

The reactions of these diiodo complexes as monodentate phosphines with molybdenum(II) and tungsten(II) complexes, molybdenum(II) π-allyl complexes and iron carbonyl complexes have been studied[178].

The main aims of chapter four, part I, was to try and prepare the new organometallic phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$. Another aim was to study the reactions of these formula $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ with a series of molybdenum(II) and tungsten(II) complexes to give a range of new multimetallic complexes.

Part I :-

4.1.1-Reactions of the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ with tripodal triphos $\{MeC(CH_2PPh_2)_3\}$:-

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and tripodal triphos, $\{MeC(CH_2PPh_2)_3\}$ react in CH_2Cl_2 at room temperature for 5 minutes, to give the new complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**36** and **37**), which have the tripodal triphos ligand attached in a bidentate coordination mode. Complexes **36** and **37** have been fully characterised by elemental analysis (C, H and N) (Table 4.1.1), IR (Table 4.1.2), ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Tables 4.1.3 and 4.1.4). The complexes are air-sensitive in solution, but can be stored for several months in the solid state under nitrogen in absence of light. They are soluble in polar chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but only slightly soluble in hydrocarbon solvents and diethyl ether.

The bidentate coordination mode of the tripodal triphos ligand in complexes **36** and **37** is confirmed by both the IR (Table 4.1.2) and $^{31}P\{^{1}H\}$ NMR spectral data (Table 4.1.4). The IR spectra of **36** and **37** show three carbonyl bands in their spectra (Table 4.1.2), with the apparent absence of any isomers in solution. The IR spectrum in the carbonyl region for **37** is shown in Fig.4.1.1. This is by conrast to the analogous linear triphos tungsten complex, $[WI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}]$, which has three carbonyl bands in its IR spectrum[88].

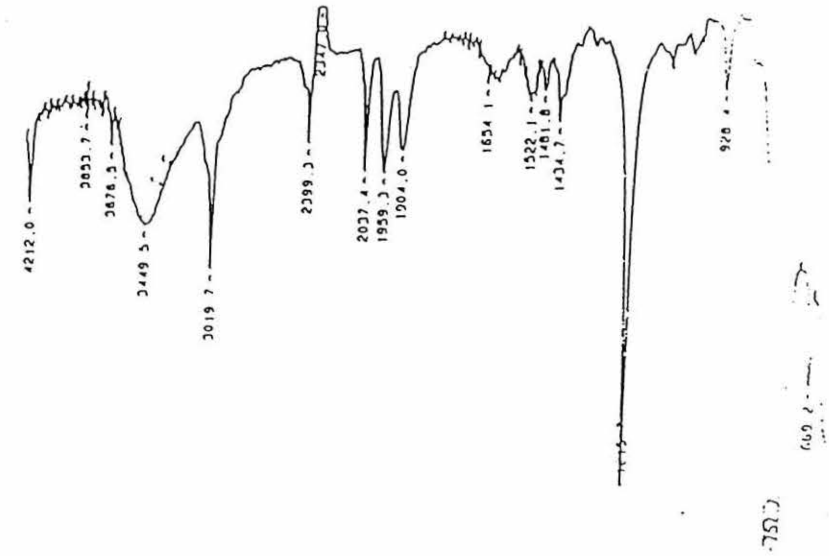


Fig.4.1.1-The IR spectrum for complex **(37)** in $CHCl_3$.

The $^{31}P\{^{1}H\}$ NMR($CDCl_3$) spectra for the molybdenum complex **36**, at -50 °C, 25 °C and +50 °C are shown in Fig.4.1.2. At -50 °C, the spectrum shows a resonance at -29.51 ppm due to the uncoordinated phosphorus atom, a single resonance at 16.67 ppm due to the fluxional seven-coordinate unit, $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$. At +25 °C, the $^{31}P\{^{1}H\}$NMR ($CDCl_3$) spectrum is similar, but the resonance for the coordinated phosphorus atoms appears at $\delta = 12.63$ ppm. At +50 °C, only a resonance at 17.82 ppm is observed, which is due to the dicarbonyl complex, **38**. Since the molybdenum complex **36**, is more labile to carbonyl displacement by the third phosphorus atom compared to its tungsten analogue, **37**, at +50 °C several spectra were obtained, but only a single resonance due to complex **38** was observed. It should be noted that the free ligand, $MeC(CH_2PPh_2)_3$ has a single resonance at δ = -26.32 ppm in $CDCl_3$ at +25 °C, and the resonance at δ = -29.08 ppm for the free phosphorus on **36** is, as expected, close to this value.

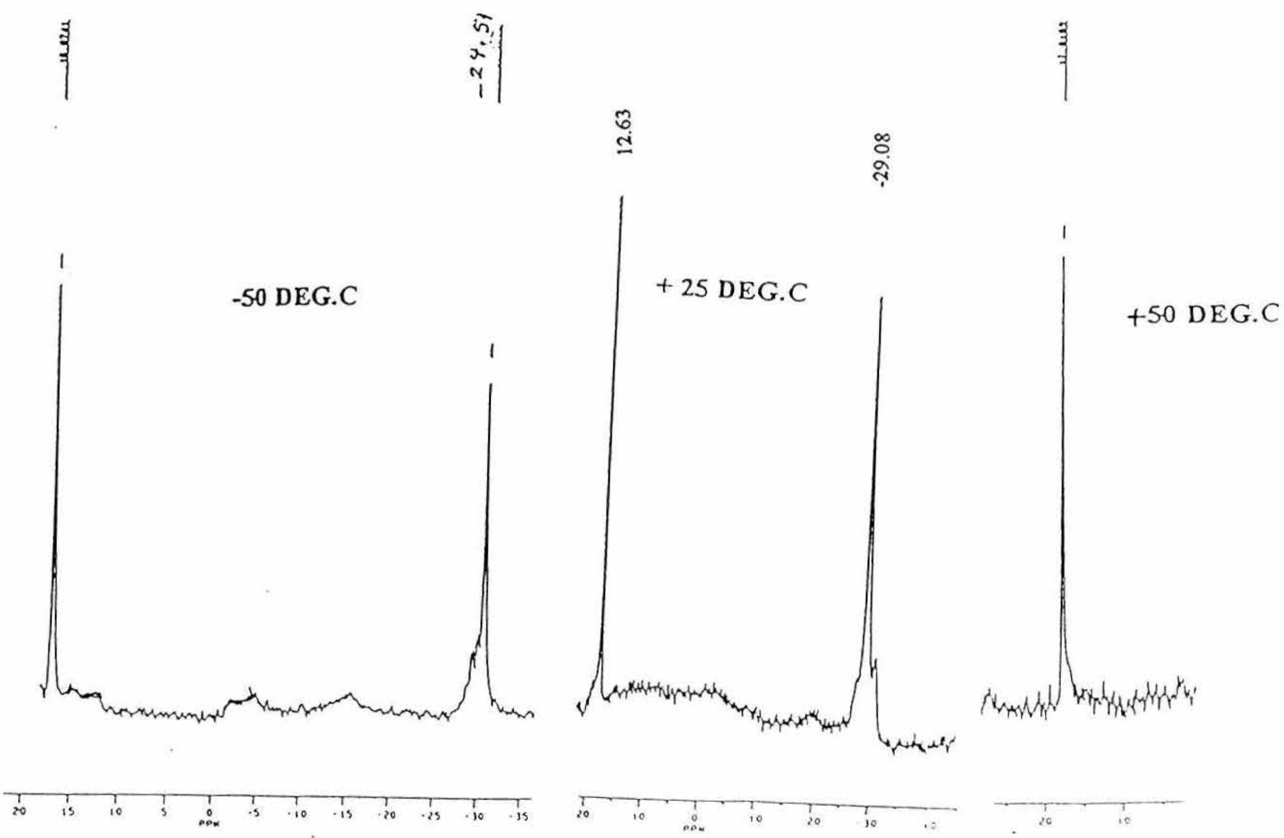


Fig.4.1.2. Variable temperature $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) for $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(36) at -50 °C, 25 °C and +50 °C.

Variable temperature $^{31}P\{^1H\}$NMR spectra in $CDCl_3$ for complex **37**, shows that the a mixture of peaks which indicates to decomposition of the complex and was difficult to explain, but at -50 °C give two doublets at δ = -14.55 ppm and δ = -25.21 ppm, ($J_{P\text{-}P}$ = 38.42 Hz), which can be assigned to the two coordinated phosphorus atoms in different environments, with perhaps one phosphorus atom *trans*-to a carbonyl ligand, and one *trans* to an iodide atom. The coupling $J_{P\text{-}P}$ = 38.42 Hz, can be assigned to the coordinated *cis*- phosphorus atoms, and $J_{W\text{-}P}$ coupling for the resonance at δ = -14.33 ppm is 219.7 Hz. Whilst the resonance at δ = -31.25 ppm at -50 °C. (see Fig.4.1.3), and is due to the uncoordinated phosphorus atom.

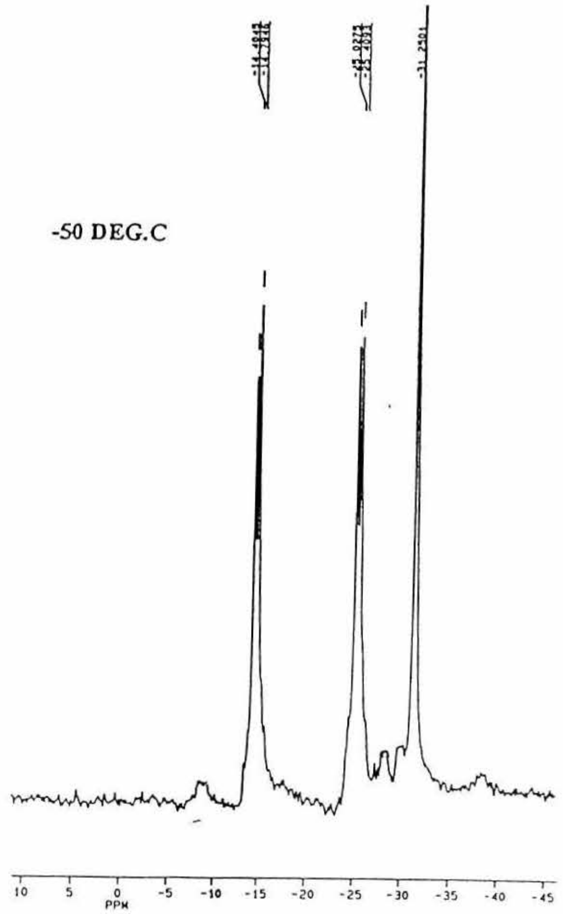


Fig.4.1.3 $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) for $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(37) at -50°C.

Since the structure of a wide range of seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$ have a capped octahedral geometry,[72,73,127,133] it may be that the structure of **36** and **37** have the structure as shown in Fig 4.1.4, in view of the different environment of the phosphorus atoms observed in the -50 °C $^{31}P\{^1H\}$NMR spectrum of **37** as shown in Fig.4.1.3. Many unsuccessful attempts were made to grow suitable single crystals for X-ray analysis of **36** and **37**.

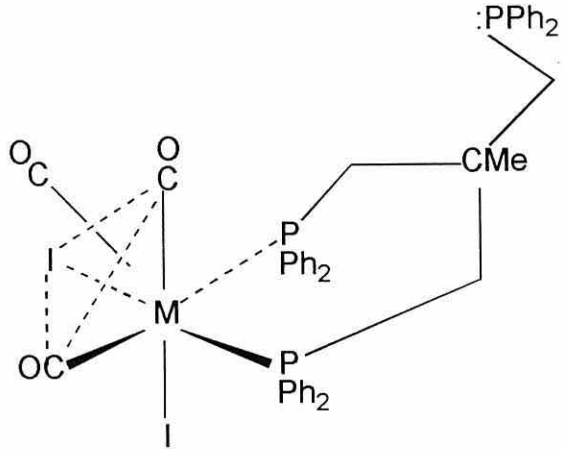


Fig.4.1.4-The proposed structure of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$.

(**36** and **37**)

The intramolecular reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**36** and **37**) in $CHCl_3$ to give $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ (**38** and **39**) were followed by IR spectroscopy. The reactions of **36** and **37** in refluxing $CHCl_3$ at 60 °C takes 15 hours for **36** (M = Mo), and refluxing for 72 hours for **37** (M = W) gives the dicarbonyl complexes, for **38** and mixed of dicarbonyl and tricarbonyl for **39**. The greater lability of molybdenum complexes compared to their analogous tungsten complexes has been previously observed. Complexes **38** and **39** both have, as expected, two carbonyl bands in their IR spectra, which suggests that the carbonyl groups are *cis*- to each other (see Table 4.1.2). The spectrum for the molybdenum complex **38** is shown in Fig.4.1.5. Larger scale reactions of **36** and **37** in $CHCl_3$ at 60 °C to give the dicarbonyl complexes **38** and **39** (see experimental), *via* displacement of a carbonyl ligand by the third phosphorus on the tripodal triphos ligand have been carried out. It is interesting to note the reaction of linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$[88], with $[MI_2(CO)_3(NCMe)_2]$ is much faster than with tripodal triphos to eventually give the dicarbonyl complexes, $[MI_2(CO)_2\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P',P''\}]$ and $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ respectively. This may be due to the ease of coordination of the third phosphorus atom in linear triphos compared to the more restricted tripodal triphos ligand.

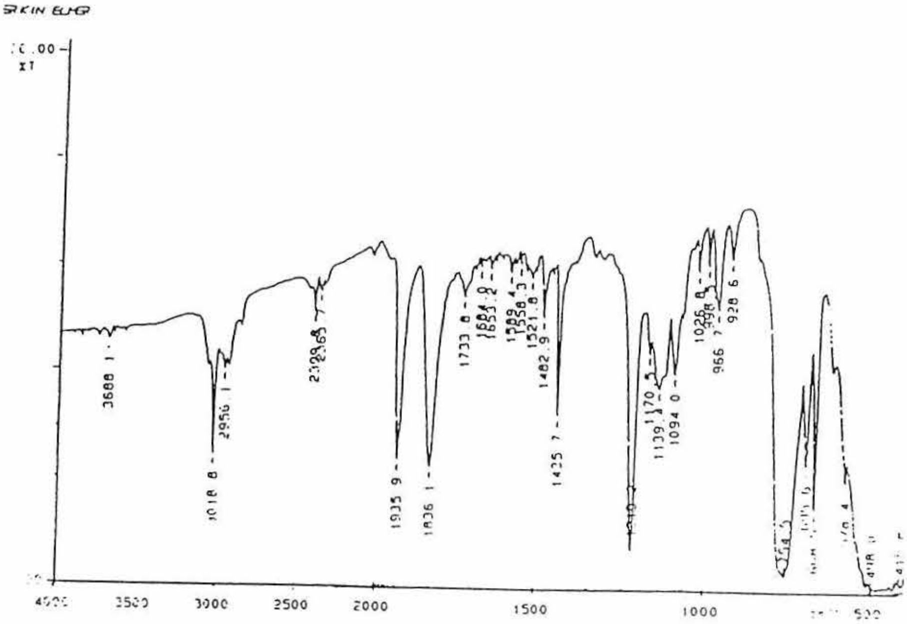


Fig.4.1.5-The IR spectrum of complex **(38)** in $CHCl_3$

For complex **38**, the reaction was totally completed in refluxing in $CHCl_3$ for 15hr. Whereas, complex **39** gave the dicarbonyl complex as a green powder, and very little of the tricarbonyl complex after 72hr reflux. The dicarbonyl complexes **38** and **39** are considerably less soluble in CH_2Cl_2 and $CHCl_3$ than the tricarbonyl complexes **36** and **37**.

This may be due to the symmetrical nature of **38** and **39,** which may pack well in the crystal lattice, whereas the uncoordinated CH_2PPh_2 groups in **36** and **37** may inhibit symmetrical packing of the molecules in the crystal lattice. The structure shows that all three phosphorus atoms of tripodal triphos in **38** and **39** are bonded to the tungsten centre to give them greater stability compared to **36** and **37**. A proposed capped octahedral structure of **38** and **39** is shown in Fig.4.1.6, which conforms with the IR data (Table 4.1.2) and $^{31}P\{^1H\}$ NMR data (Table 4.1.4).

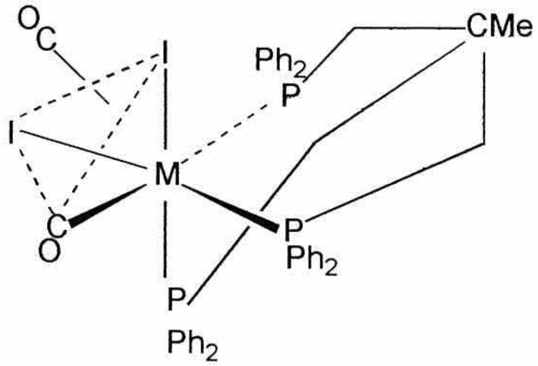
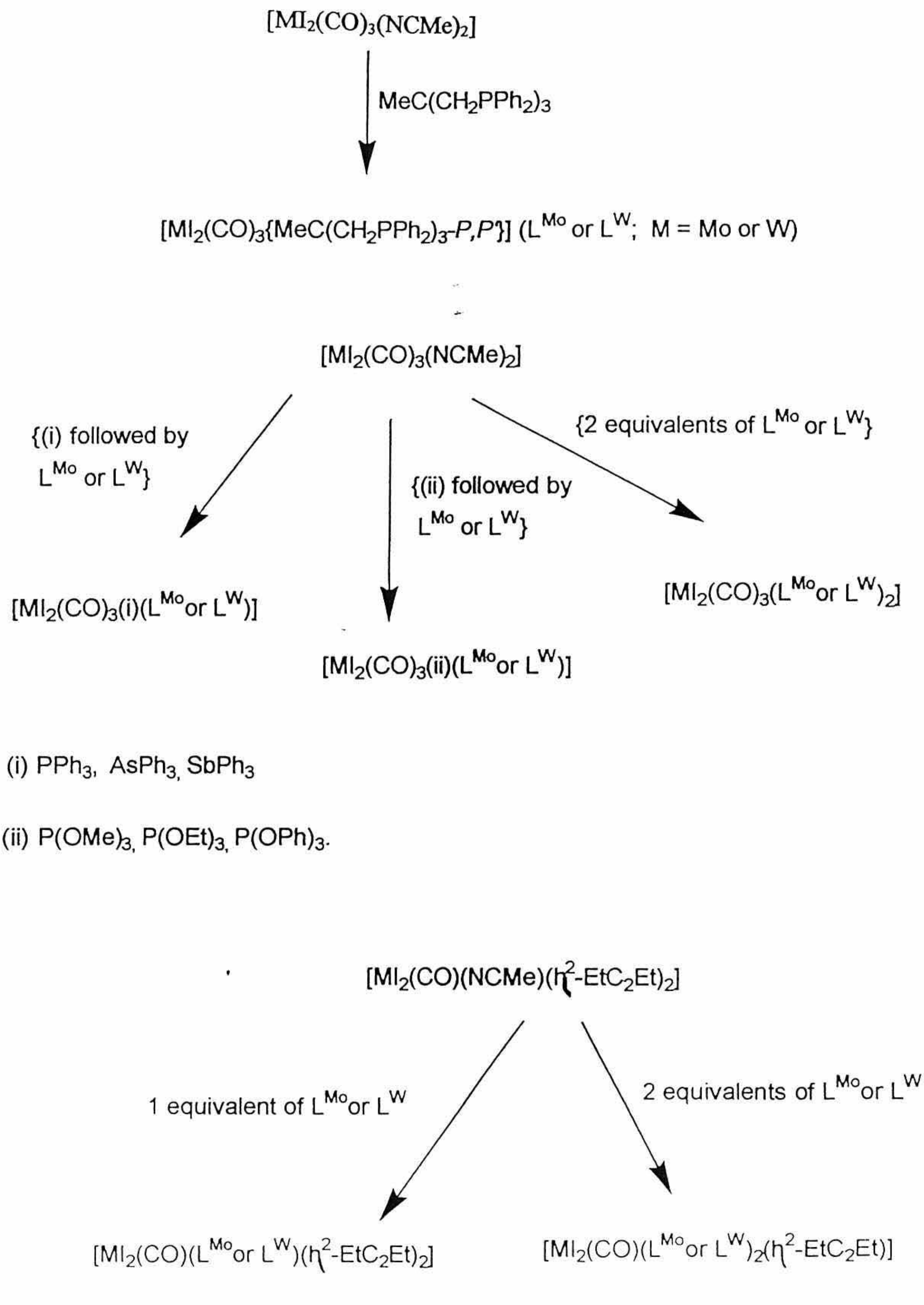


Fig.4.1.6-The proposed structure of $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ (38 and 39)

The IR spectra show two sharp bands, which suggests that there is only one isomer in solution for both **38** and **39**. This is in contrast to many other seven-coordinate complexes of the type $[MI_2(CO)_3L_2]$, which have been studied in the past[127,133], where several isomers are often observed in solution from both the IR and NMR spectral properties of these complexes.

The room temperature $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) of **38** and **39** show one resonance for the phosphorus atoms at δ = 17.82 and 15.72 ppm, respectively. This suggests either that the complexes are fluxional in solution or have equivalent phosphorus atoms. It is much more likely they are fluxional, but also to poor solubility it was not possible to obtain good low temperature NMR spectra, as the complexes crystallised out of solution very rapidly in NMR solvents such as $CDCl_3$ and CD_2Cl_2 at low temperature. The rest of this chapter describes the reactions of the complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**36** and **37**) as monodentate phosphine ligands, from now on designated as L^{Mo}(complex **36**) and L^{W}(complex **37**). A summary of the reactions described in this part is shown in Scheme 4.1.1.



Scheme. 4.1.1-A summary of the reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$, M = Mo or W ($L^{Mo}$ or L^{W}) (**38** and **39**) as discussed in Chapter 4, part I.

4.1.2-Reactions of the seven-coordinate complexes, [$MI_2(CO)_3(NCMe)_2$] with $2L^{Mo}$ or $2L^{W}$ to give [$MI_2(CO)_3(L^{Mo}$ or $L^{W})_2$] (40-43) :-

Reaction of [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) with two equivalents of L^{Mo} or L^{W} in CH_2Cl_2 at room temperature yields the acetonitrile displaced trimetallic complexes [$MI_2(CO)_3(L^{Mo}$ or $L^{W})_2$] (**40-43**) in high yield. Complexes **40-43** have been fully characterised as for **36-39** (see Tables 4.1.1-4.1.4). Complex **40** (M = Mo, L^{Mo}) was confirmed as a bis(diethyl ether) solvate by repeated elemental analysis and ^1H NMR spectroscopy.

Attempts to obtain suitable FAB mass spectra for **40-43** were unsuccessful, as no parent ions were obtained, however, molecular weight measurements by Rast's method[158] (see Table 4.1.5) give an indication that the complexes are trimetallic in nature. The solubility of complexes **40-43** is less than **36** and **37**, and the complexes are only moderately soluble in CH_2Cl_2. They are of similar stability to **36** and **37**, and can be stored under nitrogen in the solid state for several weeks without decomposition.

The IR spectral properties of **40** to **43** all show a number of carbonyl bands, which have overlapping carbonyl bands due to both the tricarbonyl centres, [$MI_2(CO)_3(L)_2$], and the tricarbonyl complexes, **36** and **37** attached to the central molybdenum or tungsten centres. For example, complex **41** has five carbonyl bands at {$\nu(CO)$ = 2074, 2044, 2005, 1939 and 1844 cm^{-1}}. A number of unsuccessful attempts were made to grow suitable single crystals of **40** to **43**, however, since the structure of [$WI_2(CO)_3(NCMe)_2$] has been crystallographically determined, and a structure of the units of [$MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}$] have been proposed (see Fig. 4.1.4), possible structure for **40** to **43** is shown in Fig.4.1.7.

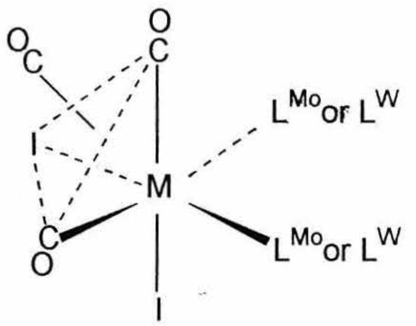


Fig.4.1.7 Proposed structure of [MI$_2$(CO)$_3$(L^{Mo} or L^W)$_2$] (40 to 43)

The ^{1}H NMR (+25 °C, CDCl$_3$) spectra for complexes **40-43** are broad, which might be due to the protons in two L$_{Mo}$ and L$_W$ groups are in slightly different environments as shown in Fig.4.1.7.

The ^{31}P{^{1}H} NMR (+25°C, CDCl$_3$) spectra for **40** to **43** show two resonances; one of them for the two phosphorus atoms on one metal, and the other resonance for the third phosphorus atom on the other metal. For example, complex **40** has two resonances, one at δ = 19.36 ppm, which is due to the same sets of two phosphorus atoms on the fluxional Mo unit of [MoI$_2$(CO)$_3${MeC(CH$_2$P Ph$_2$)$_3$-*P,P'*}] {see complex **36**, δ = 16.67 ppm}, and at δ = 24.99 ppm, which is due for the phosphorus atoms bonded to the [MoI$_2$ (CO)$_3$(L^{Mo})$_2$] centre. The resonance intensities for **40** at 19.36 and 24.99 ppm are in an approximately 2:1 ratio, which is in accord with the structure of the complexes shown in Fig.4.1.7.

4.1.3-Synthesis of the mixed ligand seven-coordinate complexes $[MI_2(CO)_3(L)(L^{Mo}$ or $L^{W})]$ {L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OR)_3$ (R = Me, Et or Ph)}(44-52) :-

Treatment of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L {L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OR)_3$ (R = Me, Et or Ph)} in CH_2Cl_2 at room temperature gives the mono(acetonitrile) complexes $[MI_2(CO)_3(NCMe)L]$, which react in *situ* with equimolar amounts of L^{Mo} or L^{W} to afford the new mixed-ligand bimetallic complexes $[MI_2(CO)_3L(L^{Mo}$ or $L^{W})]$(**44-52**) (M = Mo or W) in high yield. Complexes **44-52** have been characterised by elemental analysis (C, H and N) (Table 4.1.1), IR (Table 4.1.2), ^1H NMR (Table 4.1.3) and in certain cases by $^{31}P\{^1H\}$ NMR spectroscopy (Table 4.1.4). Complex **44** (M = Mo, L = PPh_3, L^{Mo}) was confirmed as a diethyl ether solvate by repeated elemental analysis and ^1H NMR spectroscopy. Molecular weight measurements by Rast's method[158] (Table 4.1.5) of selected complexes suggest the bimetallic nature of these complexes. The stability and solubility of complexes **44** to **52** are similar to the trimetallic complexes **40-43**, with the exception of the phosphite complexes **50-52**, which are considerably more soluble than **44-49**, and slightly less stable. The mechanism of these ligand displacement reactions are likely to be dissociative, since both $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ complexes obey the effective atomic number rule.

The IR spectra of **44-52** show a number of overlapping bands, as with complexes **40-43** described above. For example, complex **47** has bands at ν(CO) = 2036, 1961 and 1910 cm^{-1}, which are likely to be due to the L^{W}, and bands at ν(CO) = 2072, 2019 and 1844 cm^{-1}, which may be due to the $[WI_2(CO)_3(PPh_3)...]$ unit. The $^{31}P\{^1H\}$ NMR spectra of the $AsPh_3$ and $SbPh_3$ complexes show two different resonances due to tripodal triphos ligand. For example, complex **48** has two resonances; one at δ = -14.32 ppm, which is due to the two phosphorus atoms on the fluxional $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ unit, and one at δ = 34.20 ppm for the third phosphorus atom, which is attached to the $[WI_2(CO)_3(AsPh_3)]$ unit. The resonances at δ = -14.32 and 34.20 ppm are in an approximately 2:1 intensity ratio. A possible structure for **44** to **52** is shown in Fig.4.1.8.

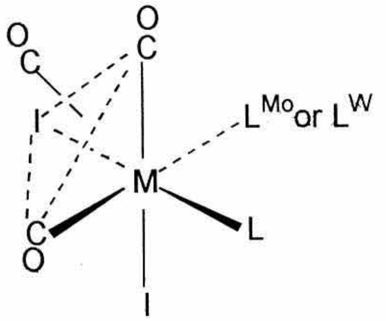


Fig. 4.1.8. Proposed structure of $[MI_2(CO)_3(L)(L^{Mo}$ or $L^W)]$

$\{L = PPh_3, AsPh_3, SbPh_3, P(OR)_3$ (R= Me, Et or Ph)$\}$(**44-52**)

4.1.4-Reactions of the seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ with bidentate phosphines $\{Ph_2P(CH_2)_nPPh_2\}$(n = 1 or 2) followed by L^{Mo} or L^W to give $[MI(CO)_3(L^{Mo}$ or $L^W)\{Ph_2P(CH_2)_nPPh_2\}]I$ (53-56) :-

Reaction of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) in CH_2Cl_2 at room temperature afford the previously described[83] complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$, which react *in situ* with one equivalent of L^{Mo} or L^W to produce the cationic complexes $[MI(CO)_3(L^{Mo}$ or $L^W)\{Ph_2P(CH_2)_nPPh_2\}]I$ (**53-56**) in high yield, which were characterised(see Tables 4.1.1-4.1.4) in the normal manner. Molecular weight studies by Rast's method,[158] suggest the bimetallic nature of these complexes. The IR spectrum of, for example, complex **53**, has bands at 2044, 1972, 1940 and 1866 cm^{-1}. It may be that the bands at 1972, 1940 and 1866 cm^{-1} are due to the

[MoI(CO)$_3$...] unit, and bands at 1972 and 1940 including another band at 2044 cm^{-1}, are due to L^{Mo}. The ^{31}P{^{1}H} NMR spectra have, as expected, four different resonances (see Table 4.1.4). For example, complex **54** has a resonance at δ = -14.41 ppm, which is due to the two phosphorus atoms on fluxional L^W, and at δ = 24.97 ppm due to the third phosphorus atom attached to the [WI(CO)$_3$(L^W){Ph$_2$P(CH$_2$)PPh$_2$}]I centre. Also complex **54** has two doublets at δ = -29.61 and -36.19 ppm, due to the coordinated dppm ligand.

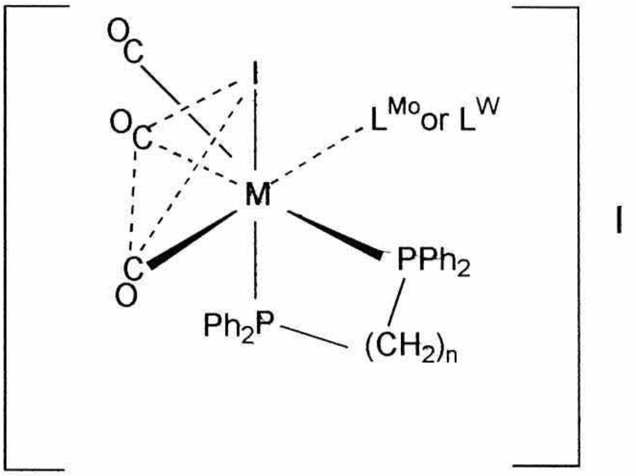


Fig.4.1.9. Proposed structure of [MI(CO)$_3$(L^{Mo} or L^W){Ph$_2$P(CH$_2$)$_n$PPh$_2$}]I **(53-56)**

4.1.5-Reactions of [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$](M = Mo or W) with L^{Mo} or L^W to give bis or mono(3-hexyne) complexes (57-60) :-

The bis(3-hexyne) complexes [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$](M = Mo or W) were prepared by reacting the seven-coordinate complexes [MI$_2$(CO)$_3$(NCMe)$_2$] with two equivalents of 3-hexyne (see Chapter Two). One equivalent of L^{Mo} or L^W react in CH$_2$Cl$_2$ at room temperature with one molar equivalent of [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] to give the bis(3-hexyne) complexes, [MI$_2$(CO)(L^{Mo} or L^W)(η^2-EtC$_2$Et)$_2$](**57** and **58**). Whereas, two equivalents of L^{Mo} or L^{W} react in CH_2Cl_2 at room temperature with one molar equivalent of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ to give the mono(3-hexyne) complexes, $[MI_2(CO)(L^{Mo}$ or $L^{W})_2(\eta^2\text{-}EtC_2Et)]$(**59** and **60**) in high yield. Complexes **57-60** have been fully characterised in the normal manner (see Tables 4.1.1 to 4.1.4).

The IR spectrum of, for example, complex **57** shows four carbonyl bands; three of them at $\nu(CO)(CHCl_3)$ = 2034, 1980, and 1938 cm^{-1}, for the L^{Mo} unit, and one band at $\nu(CO)(CHCl_3)$ = 2046 cm^{-1} for the $[MoI_2(CO)(L^{Mo})(\eta^2\text{-}EtC_2Et)_2]$ part of the molecule. Since the structure of the acetonitrile bis(alkyne) complexes, $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) have *cis*- and parallel alkyne molecules, then it is likely that the structure of **57** and **58** will have the acetonitrile replaced by L^{Mo} (**57**) or L^{W} (**58**), with retention of configuration as shown in Fig.4.1.10.

The spectroscopic data for **57** and **58** confirm with this structure. The $^{31}P\{^1H\}$NMR spectrum of **57** has resonances at δ = 17.56 and 38.95 ppm due to the $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ unit and $[MoI_2(CO)L^{Mo}(\eta^2\text{-}EtC_2Et)_2]$ unit respectively in an approximetly 2:1 intensity ratio. Complexes **59** and **60** have carbonyl bands due to L^{Mo} or L^{W}, and bands due to the $[MI_2(CO)(\eta^2\text{-}EtC_2Et)]$ unit.

For example, The IR spectrum of complex **59** has bands at $\nu(CO)$ = 2029, 1977 and 1937 cm^{-1}, all of them are likely due to the L^{Mo} unit, and the broad band at 1937 cm^{-1} is due to the $[MoI_2(CO)(L^{Mo})_2(\eta^2\text{-}EtC_2Et)]$ unit.

The room temperature $^{31}P\{^1H\}$ NMR spectra for complexes **57-60** show two resonances for tripodal phosphorus coordinated to L^{Mo} or L^W. For example, complex **59** has a resonance at $\delta = 19.78$ ppm due to the two phosphorus atoms on the fluxional L^{Mo} centre, and at $\delta = 25.34$ ppm for the third phosphorus atom in an approximately 2:1 intensity ratio. It is very likely that the structures of **59** and **60** have *trans*- L^{Mo} and L^W ligands in their respective complexes as shown in Fig.4.1.11. This conforms with the spectroscopic properties of these complexes. The 3-hexyne ligand makes these complexes more soluble than their starting materials, **36** and **37**.

In conclusion, tripodal triphos $\{MeC(CH_2PPh_2)_3\}$, reacts with the seven-coordinate complexes of molybdenum(II) and tungsten(II), $[MI_2(CO)_3(NCMe)_2]$ to give $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$. The tricarbonyl complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**36**) and (**37**) eventually react intramolecularly to give the dicarbonyl complexes, $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ (**38**) and (**39**) respectively. The monodentate phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ react with a wide range of complexes including a series of seven-coordinate complexes of molybdenum(II) and tungsten(II) as shown in Scheme 4.1.1.

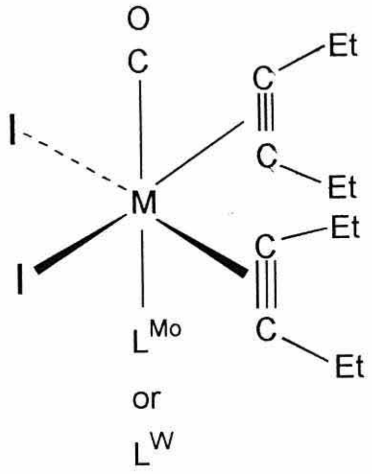


Fig.4.1.10. Proposed structure of [$MI_2(CO)(L^{Mo}$ or $L^W)(\eta^2\text{-}EtC_2Et)_2$](**57** and **58**).

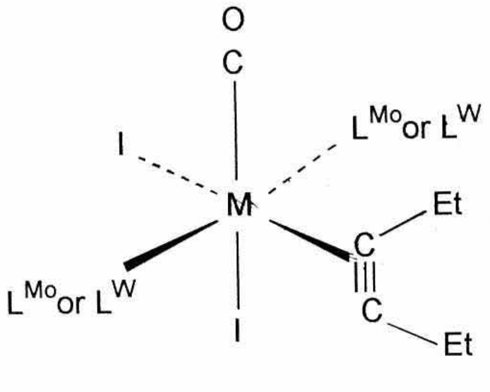


Fig.4.1.11. Proposed structure of [$MI_2(CO)(L^{Mo}$ or $L^W)_2(\eta^2\text{-}EtC_2Et)$](**59** and **60**).

Table 4.1.1-Physical and Analytical data[a] for the tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ complexes of molybdenum(II) and tungsten(II) 36-60 :-

	Complex	Colour	Yield%	C%	H%
(36)	$[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$.	Brown	80	49.7	3.6
				(49.9)	(3.7)
(37)	$[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$.	Orange	91	46.4	3.5
				(46.1)	(3.4)
(38)	$[MoI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$	Brown	66	50.1	3.8
				(50.0)	(3.8)
(39)	$[WI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$	Orange	86	46.5	3.4
				(46.2)	(3.5)
(40)	$[MoI_2(CO)_3[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3$	Brown	87	44.7	3.6
	$\text{-}P,P'\}]_2].2Et_2O$			(44.1)	(3.7)
(41)	$[WI_2(CO)_3[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3$	Brown	78	41.1	3.0
	$\text{-}P,P'\}]_2]$			(41.4)	(3.0)
(42)	$[MoI_2(CO)_3[WI_2(CO)_3\{MeC(CH_2PPh_2)_3$	Yellow	20	40.2	3.2
	$\text{-}P,P'\}]_2]$			(40.0)	(2.9)
(43)	$[WI_2(CO)_3[WI_2(CO)_3\{MeC(CH_2PPh_2)_3$	Orange	85	38.6	3.1
	$\text{-}P,P'\}]_2]$			(38.8)	(2.8)
(44)	$[MoI_2(CO)_3(PPh_3)[MoI_2(CO)_3\{MeC$	Brown	90	46.2	3.5
	$(CH_2PPh_2)_3\text{-}P,P'\}]].Et_2O$			(46.0)	(3.9)

(45)	$[MoI_2(CO)_3(AsPh_3)][MoI_2(CO)_3\{MeC$	Brown	81	43.0	3.2
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(43.4)	(3.0)
(46)	$[MoI_2(CO)_3(SbPh_3)][MoI_2(CO)_3\{MeC$	Brown	70	42.0	3.2
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(42.2)	(3.0)
(47)	$[WI_2(CO)_3(PPh_3)][WI_2(CO)_3\{MeC(CH_2$	Orange	85	40.1	3.0
	$PPh_2)_3$-*P*,*P*′$\}]]$			(40.4)	(2.8)
(48)	$[WI_2(CO)_3(AsPh_3)][WI_2(CO)_3\{MeC$	Yellow	27	40.1	3.0
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(39.5)	(2.8)
(49)	$[WI_2(CO)_3(SbPh_3)][WI_2(CO)_3\{MeC$	Orange	89	38.9	2.8
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(38.6)	(2.7)
(50)	$[WI_2(CO)_3\{P(OMe)_3\}[WI_2(CO)_3\{MeC$	Yellow	58	34.0	2.9
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(33.5)	(2.7)
(51)	$[WI_2(CO)_3\{P(OEt)_3\}[WI_2(CO)_3\{MeC$	Orange	62	35.4	3.0
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(34.7)	(3.0)
(52)	$[WI_2(CO)_3\{P(OPh)_3\}[WI_2(CO)_3\{MeC$	Yellow	59	39.5	2.8
	$(CH_2PPh_2)_3$-*P*,*P*′$\}]]$			(39.5)	(2.8)
(53)	$[MoI(CO)_3\{Ph_2P(CH_2)PPh_2\}[MoI_2(CO)_3$	Brown	64	45.6	3.4
	$\{MeC(CH_2PPh_2)_3$-*P*,*P*′$\}]I$			(45.9)	(3.3)
(54)	$[WI(CO)_3\{Ph_2P(CH_2)PPh_2\}[WI_2(CO)_3$	Orange	71	42.4	2.9
	$\{MeC(CH_2PPh_2)_3$-*P*,*P*′$\}]I$			(42.1)	(3.0)
(55)	$[MoI(CO)_3\{Ph_2P(CH_2)_2PPh_2\}[MoI_2(CO)_3$	Brown	74	45.8	3.3
	$\{MeC(CH_2PPh_2)_3$-*P*,*P*′$\}]I$			(46.2)	(3.3)

(56)	$[WI(CO)_3\{Ph_2P(CH_2)_2PPh_2\}[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]I$	Yellow	66	42.4 (42.4)	3.1 (2.9)
(57)	$[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}](\eta^2\text{-}EtC_2Et)_2]$	Brown	65	42.3 (42.7)	3.6 (3.7)
(58)	$[WI_2(CO)[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}](\eta^2\text{-}EtC_2Et)_2]$	Yellow	56	38.5 (38.5)	3.4 (3.4)
(59)	$[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]_2(\eta^2\text{-}EtC_2Et)]$	Brown	73	44.5 (44.2)	3.9 (3.4)
(60)	$[WI_2(CO)[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]_2(\eta^2\text{-}EtC_2Et)]$	Orange	73	40.3 (40.1)	3.5 (3.1)

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[a] **Calculated values in Parenthesis.**

Table 4.1.2-Infrared Data for Complexes 36-60[a]

Complex	$\nu(C\equiv O)$ cm^{-1}
(36)	2041s, 1938s, 1917s.
(37)	2036s, 1958s, 1904s.
(38)	1936s, 1836s.
(39)	1971s, 1857s.
(40)	2042s, 1971br, 1938s, 1845br.
(41)	2074w, 2044w, 2005br, 1939s, 1844br.
(42)	2074s, 2037s, 1963s, 1935s, 1908s, 1842br.
(43)	2072s, 2035s, 2009s, 1959s, 1908s, 1838br.
(44)	2074w, 2044w, 2023w, 1939s, 1848br.
(45)	2044w, 2027s, 1966s, 1937br, 1848br.
(46)	2028s, 1967s, 1940s, 1899w, 1860w.
(47)	2072w, 2036s, 2019br, 1961br, 1910br, 1844w.
(48)	2072s, 2037w, 2017w, 1933br, 1910w, 1839br.
(49)	2012s, 1934s, 1833br.
(50)	2072s, 2037s, 1935s, 1839br.
(51)	2072s, 2037s, 2007s, 1935s, 1840br.
(52)	2035s, 1965s, 1929s, 1915s, 1840s.
(53)	2044s, 1972m, 1940s, 1866br.
(54)	2036s, 1960s, 1907s, 1855w.

Complex	ν(C≡O) cm^{-1}	ν(C≡C) cm^{-1}
(55)	2041s, 1973s, 1937s, 1861br.	_
(56)	2037s, 1962s, 1907s.	_
(57)	2046s, 2034s, 1980s, 1938s.	1619w.
(58)	2037s, 1960s, 1905s.	1619w.
(59)	2029s, 1977s, 1937 br, s.	1654w.
(60)	2038s, 1961s, 1907 br, s.	1618w.

[a]Spectra recorded in $CHCl_3$ as thin films between NaCl plates,

br = broad, s = strong, m = medium, w = weak

Table 4.1.3-^{1}H NMR spectral data[a] for the tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ complexes of molybdenum(II) and tungsten(II), 36-60 :-

Complex	^{1}H NMR data (δ) ppm
(36)	7.65-7.15(v.br, 30H, 6Ph); 2.55-2.1(v.br, 6H, $3CH_2$, including 3 Peaks); 1.35(br, 3H, free CH_3).
(37)	7.8-7.1(v.br, 30H, 6Ph); 2.5-2.1(v.br 6H, $3CH_2$, including 3 Peaks); 1.4(br, 3H, free CH_3).
(38)	7.65-7.05(v.br, 30H, 6Ph); 2.3-1.9(br, 6H, $3CH_2$ including. 3 peaks); 1.4-0.8(br, 3H, CH_3, including, 3 Peaks).
(39)	7.7-7.3(br, 30H, 6Ph); 2.5-2.2(br.m, 6H, $3CH_2$, including 3 peaks); 1.4-1.0(br, 3H, free CH_3).
(40)	7.9-7.0(v.br, 60H, 12Ph); 3.5(q, 8H, $2CH_2$ ether); 2.5(t, 12H, $2CH_3$ ether; 2.4-2.0(br, 6H, $3CH_2$, including single peak at 2.3 and small peak at 2.1); 1.5-0.9(br, 3H, CH_3, including 3 peaks).
(41)	7.5-7.1(br, 60H, 12Ph); 2.2(br, 12H, $6CH_2$); 1.4-1.15(br, 6H, free $2CH_3$).
(42)	7.65-7.2(v.br, 60H, 12Ph); 2.25(br, 12H, $6CH_2$); 1.4-1.2(br, 6H, free $2CH_3$).
(43)	7.7-7.1(v.br, 60H, 12Ph); 2.45-2.1(br, 12H, $6CH_2$, including peaks at 2.35); 1.4-1.15(br, 6H, free $2CH_3$).

(44) 7.9-7.1(v.br, 45H, 9Ph); 3.5(q, 4H, $2CH_2$ ether); 2.5(t, 6H, $2CH_3$ ether); 2.3-1.9(br, 6H, $3CH_2$, including. sharp peak at 2.2, and br peak at 2.0); 1.4-0.7(br 3H, free CH_3, including 3 peaks).

(45) 7.7-7.25(45H, v.br, 9Ph); 2.15(6H, br, $3CH_2$); 1.2(3H, br, free CH_3)

(46) 7.8-7.0(v.br, 45H, 9Ph); 2.4-1.9(br, 6H, $3CH_2$, including 2 sharp peaks); 1.4-0.9(br, 3H, CH_3).

(47) 7.25(v.br, 45H, 9Ph); 2.6(br, 6H, $3CH_2$, including 3 peaks); 1.5-1.25(br, 3H, free CH_3).

(48) 7.7-7.1(v.br, 45H, 9Ph); 2.65-2.2(br, 6H, $3CH_2$); 1.9-1.4(br, 3H, free CH_3).

(49) 7.7-7.1(v.br, 45H, 9Ph); 2.5-1.9(br, 6H, $3CH_2$, including 3 peaks); 1.4-1.1(br, 3H, free CH_3).

(50) 8.0-6.9(v.br, 30H, 6Ph); 3.8-3.5(d, 6H, 3 CH_2); 1.1(s, 3H, CH_3). 1.3-1.0(ms, 9H, $3CH_3$, phosphite).

(51) 7.7-7.0(v.br, 30H, 6Ph); 4.2-4.0(br, 6H, 3 CH_2, phosphite); 2.4-2.0(v.br, 6H, 3 CH_2); 1.4-1.1(t, 9H, 3 CH_3, phosphite); 1.2(s, 3H, CH_3).

(52) 7.8-6.7(v.br, 45H, 9Ph); 2.4-1.9(br, 6H, 3 CH_2); 1.1(s, 3H, CH_3).

(53) 7.6-6.8(v.br, 50H, 10Ph); 2.6(br, 2H, CH_2); 2.3-1.9(br, 6H, 3 CH_2); 1.4-1.1(br, 3H, CH_3).

(54)	7.6-7.1(v.br, 50H, 10Ph); 2.6(br, 2H, CH$_2$); 2.3-2.1(br, 6H, 3 CH$_2$);
(55)	7-6.9(br, 50H, 10Ph); 2.9-2.6(br, 4H, 2CH$_2$, phosphine); 2.3-1.9(br, 6H, 3 CH$_2$ including 3 peaks); 1.4-1.1(br, 3H, CH$_3$).
(56)	7.7-7.1(br, 50H, 10Ph); 2.9-2.1(br, 4H, 2CH$_2$, phosphine); 1.6- 0.9(br, 6H, 3 CH$_2$, including 3 peaks); 0.8(s, 3H, CH$_3$).
(57)	7.7-7.0(v.br, 30H, 6Ph); 3.5-3.0(q, 8H, 4CH$_2$); 2.4-2.0(v.br, 6H, 3CH$_2$); 1.4-1.0(t, 6H, 2CH$_3$); 1.1(s, 3H, CH$_3$).
(58)	7.9-7.1(v.br, 30H, 6Ph); 3.5-3.2(q, 8H, 4CH$_2$); 3.1-2.5(v.br, 6H, 3CH$_2$); 1.3-0.9(t, 6H, 2CH$_3$); 1.1(s, 3H, CH$_3$).
(59)	7.8-7.2(v.br, 60H, 12Ph); 3.4(q, 4H, 2CH$_2$ hexyne); 2.4-2.1(m, 12H, 6CH$_2$ tripodal triphos); 1.2(t, 6H, 2CH$_3$); 1.1(s, 6H, 2CH$_3$, tripodal triphos);
(60)	7.8-7.1(v.br, 60H, 12Ph); 3.5-3.1(dq, 4H, 2CH$_2$, hexyne); 2.5-2.1(m, 12H, 6CH$_2$, tripodal triphos); 1.4-1.1(t, 6H, 2CH$_3$, hexyne).

[a]Spectra recorded in CDCl$_3$ (+25) and referenced to SiMe$_4$; s = singlet, br = broad, d = doublet, m = multiplet, t = triplet, q = quartet.

Table 4.1.4- ^{31}P NMR Data (δ)^{a} for selected tripodal triphos {$MeC(CH_2PPh_2)_3$} complexes of molybdenum(II) and tungsten(II) complexes (36-60) :-

Complex	^{31}P NMR data (δ) ppm
(36)	at -50 °C (tricarbonyl) complex :- δ(P) = 16.67 due to 2 coordinated P, $MeC(CH_2PPh_2)_3$ atom δ(P) = -29.51 due to free P, $MeC(CH_2PPh_2)_3$ atom. at 25 °C (tricarbonyl) complex :- δ(P) = 12.63 due to 2 coordinated P, $MeC(CH_2PPh_2)_3$ atom and δ(P) = -29.51 due to free P $MeC(CH_2PPh_2)_3$ atom at +50 °C (dicarbonyl) complex:- δ(P) = 17.82 due to the P atom {$MeC(CH_2PPh_2$} of dicarbonyl complex (**38**).
(37)	at -50 °C (tricarbonyl) complex :- δ(P) = -14.55 and -25.21 (d, 38.42 Hz) *cis*, due to the coordinated P, $MeC(CH_2PPh_2)_3$ atoms and δ(P) = -31.25 due to free uncoordinated P, $MeC(CH_2PPh_2)_3$ atom.

(38) δ(P) = 17.80 {Three P, $MeC(CH_2PPh_2)_3$ coordinated}.

(39) δ(P) = 15.72, {Three P, $MeC(CH_2PPh_2)_3$ ($J_{P\text{-}W}$ = 222.46 Hz}.

(40) δ(P) = 19.36 {s, 2P, $MeC(CH_2PPh_2)_3$}; and 24.99 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(41) δ(P) = 17.45 {s, 2P, $MeC(CH_2PPh_2)_3$}; and 35.19 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(42) δ(P) = -12.38 {s, 2P, $MeC(CH_2PPh_2)_3$}, and 32.61 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(43) δ(P) = -15.83 {s, 2P, $MeC(CH_2PPh_2)_3$}, and 28.77 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(44) δ(P) = 17.51 {s, 2P, $MeC(CH_2PPh_2)_3$}, and 29.85 {s, 1P, $MeC(CH_2PPh_2)_3$}.

δ(P) = 71.45 (PPh_3).

(45) δ(P) = 17.51 {s, 2P, $MeC(CH_2PPh_2)_3$}, and 41.14 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(46) δ(P) = 17.55 {s, 2P, $MeC(CH_2PPh_2)_3$} ($J_{p\text{-}p}$= 180.13 Hz); and 25.94 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(47) δ(P) = -13.76 {s, 2P, $MeC(CH_2PPh_2)_3$}, and 25.16 {s, 1P, $MeC(CH_2PPh_2)_3$}.

δ(P) =35.47 (s, PPh_3).

(48) δ(P) = -14.32 {s, 2P, $MeC(CH_2PPh_2)_3$}

and 34.20 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(53) δ(P) = 17.45 {s, 2P, $MeC(CH_2PPh_2)_3$},

($J_{P\text{-}P}$ = 206.86 Hz)

and 39.45 {s, 1P, $MeC(CH_2PPh_2)_3$}.

δ(P) = -22.50 and -29.75 (s, dppm).

(54) δ(P) = -14.41 {s, 2P, $MeC(CH_2PPh_2)_3$} and

24.97 {s, 1P, $MeC(CH_2PPh_2)_3$}.

δ(P) = -29.62 and -36.19 {d, ($J_{P\text{-}P}$ = 53.56 Hz)

dppm}.

(55) δ(P) = 17.52 {s, 2P, $MeC(CH_2PPh_2)_3$},

($J_{P\text{-}P}$ = 229.329 Hz);

and 25.63 {s, 1P, $MeC(CH_2PPh_2)_3$}.

δ(P) = -15.93 and -30.64 {d, ($J_{P\text{-}P}$ = 51.87 Hz)

dppe}.

(56) δ(P) = -13.16 {s, 2P, $MeC(CH_2PPh_2)_3$},

and 25.17 {s, 1P, $MeC(CH_2PPh_2)_3$},

($J_{P\text{-}W}$ = 201.11 Hz);

δ(P) = -13.16 and -29.50 (s, dppe).

(57) δ(P) =17.56 {s, 2P, $MeC(CH_2PPh_2)_3$},

and 38.95 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(58) δ(P) = -12.63 {s, 2P, $MeC(CH_2PPh_2)_3$},

and 49.80 {s, 1P, $MeC(CH_2PPh_2)_3$}.

(59)	$\delta(P) = 19.78$ {s, 2P, $MeC(CH_2PPh_2)_3$}, and 25.34 {s, 1P, $MeC(CH_2PPh_2)_3$}, ($J_{P-P} = 207.49$ Hz.).
(60)	$\delta(P) = -12.76$ {s, 2P, $MeC(CH_2PPh_2)_3$}, and 46.68 {s, 1P, $MeC(CH_2PPh_2)_3$}.

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[a] Spectra recorded in $CDCl_3$ (+25 °C) and refer to H_3PO_4.

Table.4.1.5-Molecular weights of selected complexes[a]

Complex	Molecular weights
(36)	1142(1058)
(37)	1330(1146)
(38)	1143(1029)
(40)	2667(2548)
(41)	2220(2677)
(42)	2667(2765)
(45)	1330(1796)
(46)	1429(1843)
(47)	2000(1969)
(51)	2000(1834)
(56)	2000(2062)
(57)	1600(1600)
(60)	2667(2840)

[a] **Calculated values in parentheses.**

Chapter Four-Part II

Reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ with $[MoX(CO)_2(NCMe)_2(\eta^3\text{-allyl})]$, $[Fe_2(CO)_9]$ or $[FeI(CO)_2(Cp\ or\ Cp')]$

4.2.1-Introduction :-

Bimetallic and multimetallic phosphine-bridged transition-metal complexes have received considerable attention over the years. Although a wide range of bimetallic phosphine-bridged complexes containing bidentate phosphines such as bis(diphenylphosphino) methane as the bridging ligand[171-173,175-177,179-197] have been described, far fewer complexes containing tridentate phosphines as bridging ligands have been reported[198-208]. In 1986[74], the synthesis and characterisation of the highly versatile seven-coordinate complexes, $[MX_2(CO)_3(NCMe)_2]$ (M = Mo or W; X = Br or I) have been described. These complexes react with a wide range of ligands, to give a wide range of new organometallic complexes[127,133]. The characterisation of a range of new organometallic phosphine ligands, such as $[WI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2-P,P'\}]$[88], $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2-P,P'\}(\eta^2\text{-}RC_2R')]$ (R = R' = Me or Ph; R = Me, R' = Ph)[152] and $[MXY(CO)\{PhP(CH_2CH_2PPh_2)_2-P,P'\}(\eta^2\text{-}RC_2R)]$ (M = Mo or W; X, Y = Cl, Br, I; R = Me or Ph)[209] has been described.

The aim for second part of this chapter was to investigate the reactions of starting materials described in first part of this chapter, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (L^{Mo} or L^W) with the π-allyl molybdenum complexes, $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X =

Cl, R = H or Me; X = Br, R = H), the iron(0) carbonyl complex, $[Fe_2(CO)_9]$, and the iron(II) complexes $[FeI(CO)_2$(Cp or Cp')](Cp = C_5H_5; Cp' = C_5H_4Me) to give a variety of new multimetallic complexes.

4.2.2-Preparation and characterisation of the tetrametallic complexes $[\{Mo(\mu\text{-}X)(CO)_2(L^{Mo}$ or $L^{W})(\eta^3\text{-}C_3H_4R)\}_2]$(61-66) :-

The starting materials used in this research, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(M = Mo or W) were prepared by reacting the bis(acetonitrile) complexes $[MI_2(CO)_3(NCMe)_2]$[74], with one equivalent of tripodal triphos, $MeC(CH_2PPh_2)_3$, in CH_2Cl_2 for 5-15 min. at room temperature[210], as described earlier in this Chapter. Equimolar amounts of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X = Cl, R = H or Me; X = Br, R = H) and $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo, L^{Mo}; M = W, L^{W}) react in CH_2Cl_2 at room temperature to eventually give the halo-bridged and tripodal triphos-bridged tetrametallic complexes $[\{Mo(\mu\text{-}X)(CO)_2(L^{Mo}$ or $L^{W})(\eta^3\text{-}C_3H_4R)\}_2]$**(61-66)** in good yield, *via* displacement of both of the acetonitrile ligands. All the complexes **61-66** were characterised by elemental analysis (C, H and N) (Table 4.2.1), IR (Table 4.2.2), ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Table 4.2.3 and 4.2.4).

Molecular weight measurements were determined using Rast's method[158], and the values are given in Table 4.2.5. These measurements confirmed the tetrametallic nature of these complexes. Complex **61** (X = Cl, R = H, L^{Mo}) was confirmed as a CH_2Cl_2 solvate by repeated elemental analyses and ^1H NMR spectroscopy. The new complexes **61-66** are moderately stable in the solid state when stored under dinitrogen, but they all readily decompose in solution when exposed to air. Complexes **61-66** are soluble in $CHCl_3$ and CH_2Cl_2, but only slightly soluble in diethyl ether. The IR spectra of complexes **61-66** (Table 4.2.2) as expected all show a number of carbonyl bands due to both the $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ unit, and the π-allyl molybdenum fragment.

For example, complex **61** showed bands at 2015, 1941, 1933 and 1842 cm^{-1}. It is highly likely that the bands at 1933 and 1842 cm^{-1} are due to the *cis*-carbonyl groups on the π-allyl molybdenum part of the molecule. {The complex, $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ has carbonyl bands at $\nu(CO)(CHCl_3) = 1955$ and 1848 cm^{-1}}[104]. The broad band at 1933 cm^{-1}, together with the bands at 2015 and 1941 cm^{-1} are very likely to be due to the $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ part of the molecule. The complex $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(**36**)[210], has $\nu(CO)(CHCl_3) = 2041$, 1938 and 1917 cm^{-1}.

The molecular structures of several π-allyl complexes of the type $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ (L_2 = nitrogen donor ligands) have been crystallographically determined[211-220], and all show a *cis*-carbonyl geometry in an equivalent plane with the nitrogen donor ligands. The axial sites have the halide and π-allyl groups. However, the only monodentate bis(phosphorus) donor ligand π-allyl complex of this type to be crystallographically characterised is $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$[221].

This complex has a distorted pentagonal bipyramidal geometry, with a carbonyl ligand and a chloride group in axial positions, and the π-allyl group occupying two adjacent sites. In view of the IR carbonyl pattern for the complexes **61-66**, it is likely the *pseudo*-octahedral geometry will be described for the mono(phosphine) complexes **61-66**, rather than the pentagonal bipyramidal geometry shown for $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3$-$C_3H_5)]$[221]. The two halides of the halo-bridged dimers are identical, as only two *cis*-carbonyl groups were observed.

The $^{31}P\{^1H\}$ NMR spectra (Table 4.2.4) show resonances for the two equivalent phosphorus atoms attached to the molybdenum and tungsten centre in the units, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3$-$P,P'\}]$, which are fluxional at room temperature (see part I of this Chapter), and the phosphorus atom attached to the π-allyl fragment. Tungsten satellites were not observed, due to the poor solubility in a range of NMR solvents. For example, the $^{31}P\{^1H\}$ NMR spectrum of **62** has a resonance at $\delta = -17.65$ ppm (due to the fluxional seven-coordinate L^W fragment), and $\delta = 27.30$ ppm due to the phosphorus atoms attached to the π-allyl fragment in an approximately 2:1 intensity ratio.

The assignment of resonances in the $^{31}P\{^1H\}$ NMR spectra were due to the expected resonances of the phosphine ligands $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3$-$P,P'\}]$(**36**) and (**37**), and the generally lower field and less intense resonance due to the phosphorus atom attached to the π-allyl molybdenum moeity.

The geometry of one isomer of complexes **61-66** is shown in Fig.4.2.1, which shows that the L^{Mo} or L^W are coordinated in a *trans* configuration to each other, with a bulky phosphine group and π-allyl group *trans* to other one. A number of unsuccessful attempts to grow suitable single crystals for X-ray crystallography were made, probably due to the large size of these molecules and their poor solubility.

Complexes **61-66** are most likely to be obtained from the bimetallic complexes, $[MoX(CO)_2(NCMe)(L^{Mo}$ or $L^W)(\eta^3\text{-}C_3H_4R)]$, which could not be isolated even with short reaction times, and the tetrametallic nature of the products was confirmed by the lack of nitrogen in the elemental analysis results and no acetonitrile resonances observed in the ^1H NMR spectra. Also molecular weight studies using Rast's method[158] confirmed the tetrametallic nature of **61-66**. Several unsuccessful attempts were made to obtain FAB mass spectra of the complexes, although fragment peaks were obtained the parent ions could not be observed for these complexes.

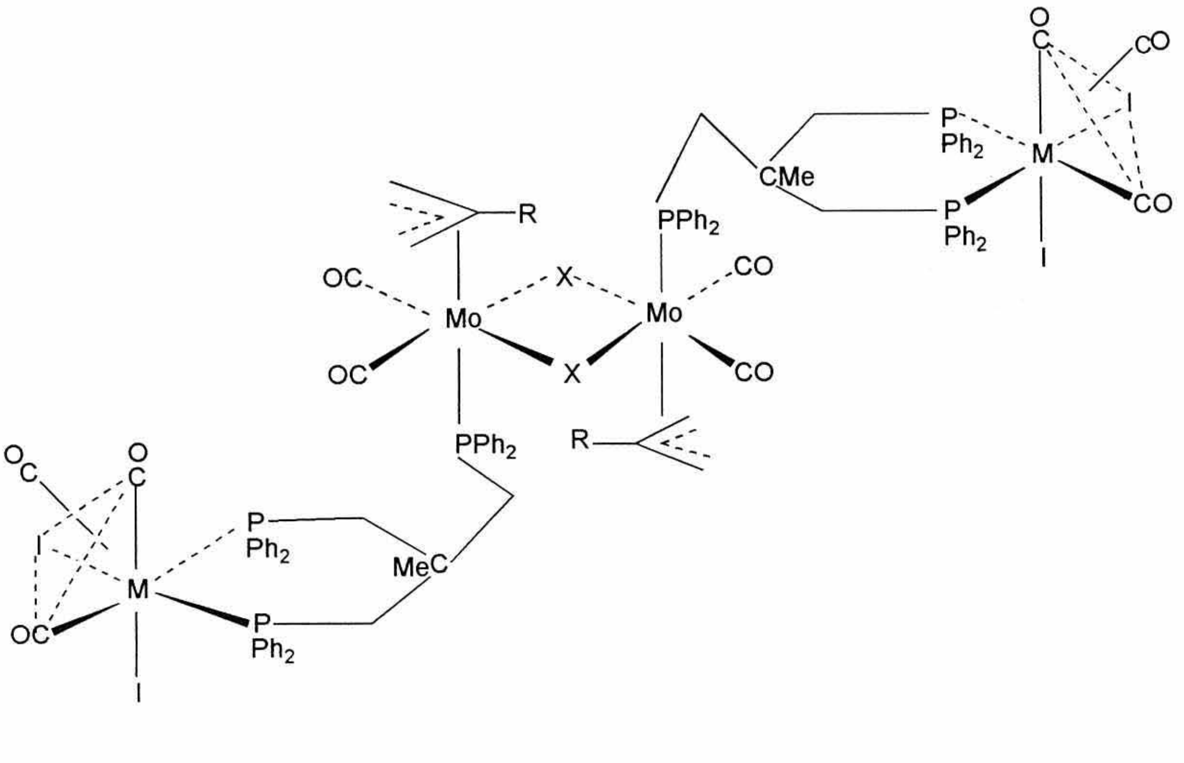


Fig.4.2.1. Proposed structure of $[\{Mo(\mu\text{-}X)(CO)_2(L^{Mo}$ or $L^W)(\eta^3\text{-}C_3H_4R)\}_2]$(**61-66**).

4.2.3-Synthesis and characterisation of the trimetallic complexes, $[MoX(CO)_2(L^{Mo}$ or $L^W)_2(\eta^3\text{-}C_3H_4R)]$(67-72) :-

Reaction of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X = Cl, R = H or Me; X = Br, R = H) with two equivalents of L^{Mo} or L^W in CH_2Cl_2 at room temperature affords the trimetallic, tripodal triphos-bridged complexes, $[MoX(CO)_2(L^{Mo}$ or $L^W)_2(\eta^3\text{-}C_3H_4R)]$ **(67-72)** in good yield, by displacement of both of the acetonitrile ligands. The complexes **67-72** have been fully characterised by elemental analysis (C, H and N), (Table 4.2.1), IR (Table 4.2.2), ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Tables 4.2.3 and 4.2.4), and molecular weight studies using Rast's method[158] (Table 4.2.5).

The complex $[MoBr(CO)_2(L^{Mo})_2(\eta^3\text{-}C_3H_5)].Et_2O$ **(71)** was confirmed as a diethyl ether solvate by repeated elemental analyses and ^1H NMR spectroscopy. FAB mass spectra were attempted without success, as no parent ions were observed. However, molecular weight studies by Rast's method[158] suggest the trimetallic nature of these complexes (see Table 4.2.5). Generally, complexes **67-72** are more stable and less soluble than the tetrametallic complexes **61-66** described earlier. Complexes **67-72** have to be stored under dinitrogen in the solid state.

The IR spectra of the trimetallic complexes, **67-72** are all relatively simple and show the expected bands for the π-allyl molybdenum *cis*-dicarbonyl unit, and the diiodo tricarbonyl molybdenum and tungsten moieties. For example, complex **67** has bands at ν(CO) = 2041, 1959, 1939 and 1846 cm^{-1}, It is very likely the bands at 1939 and 1846 cm^{-1} are due to the *cis*-dicarbonyl π-allyl unit, and the bands at 2041, 1959 and 1939 cm^{-1} (and probably a masked band due to $MI_2(CO)_3$ unit), are due to the L^{Mo} part of the molecule.

The room temperature ^{1}H NMR spectrum for complex 67, may be due to the different CH_2Cl_2 groups attached to both a seven-coordinate Mo centre and a π-allyl Mo centre as shown in Fig.4.2.2. The room temperature $^{31}P\{^{1}H\}$ NMR spectrum for complex **67** shows a resonance due to the equivalent phosphine atoms attached to the fluxional $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ units at $\delta = 17.57$ ppm.

The resonance at $\delta = 32.83$ ppm is due to the two equivalent phosphorus atoms attached to the molybdenum π-allyl unit. The intensity ratio of the resonances at $\delta = 17.57$ and 32.83 ppm is approximately 2:1, which was expected. A number of unsuccessful attempts were made to grow suitable single crystals for X-ray analysis of **67-72** by several different methods of involving mixed solvents. Although, the only crystal structure of a bis(monodentate) phosphorus donor complex $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$[221], has a distorted pentagonal bipyramidal structure with carbonyl and a chloro group in the axial position, the two phosphite ligands are in different environments in the equatorial plane.

In view of the IR and $^{31}P\{^{1}H\}$ NMR spectral data (Tables 4.2.2 and 4.2.4), it is more likely the structure of **67-72** has distorted pentagonal bipyramidal arrangement with the two organometallic phosphine unit *trans*-to each other, with the carbonyl groups, chloro group and π-allyl unit occupying the five equatorial sites, (the π-allyl group occupying two sites).

The proposed structure for **67-72** is shown in Fig.4.2.2. The structure of the seven-coordinate halocarbonyl part of the molecule most likely has a distorted capped octahedral structure (see Fig.4.1.4.) as many structures of $[MX_2(CO)_3L_2]$ have distorted capped octahedral geometries[72,73,127,133,222].

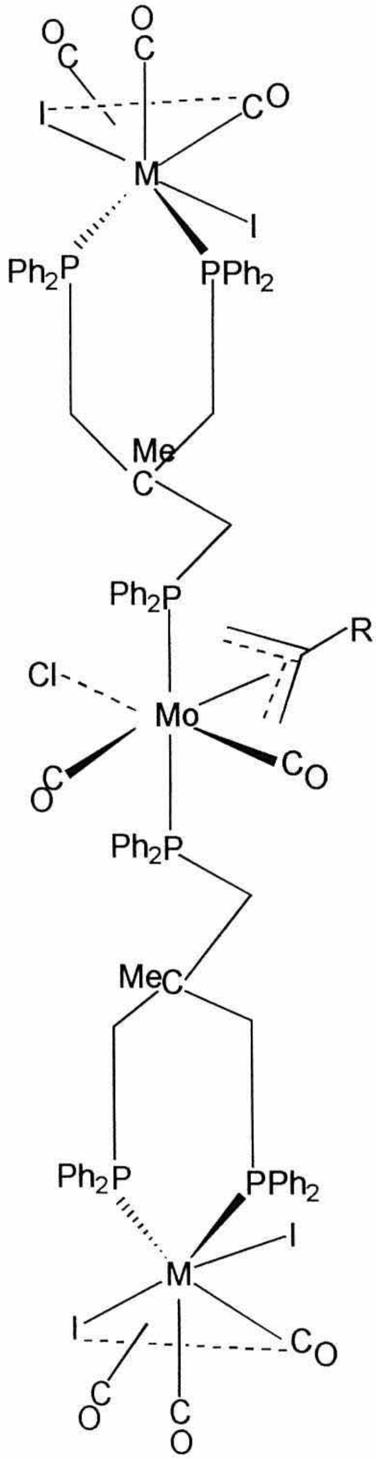


Fig.4.2. Proposed structure of [MoX(CO)$_2$(L^{Mo} or L^{W})$_2$(η^3-C$_3$H$_4$R)] **(67-72)**.

4.2.4-Synthesis and characterisation of the bimetallic complexes, $[Fe(CO)_4(L^{Mo}$ or $L^W)]$ (73 and 74) :-

Reaction of $[Fe_2(CO)_9]$ with two equivalents of L^{Mo} or L^W in CH_2Cl_2 at room temperature affords the bimetallic, tripodal triphos-bridged complexes, $[Fe(CO)_4(L^{Mo}$ or $L^W)]$ (**73** and **74**) in good yield. Complexes **73** and **74** have been characterised by elemental analysis (Table 4.2.1) IR (Table 4.2.2) and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Tables 4.2.3 and 4.2.4), Molecular weight studies by Rast's method[158] on selected complexes, confirmed the bimetallic nature of these complexes. Complexes **73** and **74** are soluble in CH_2Cl_2, less soluble in $CHCl_3$, and only sparingly soluble in diethyl ether and hydrocarbon solvents. The complexes are air-sensitive in solution, but can be stored in the solid-state under an inert atmosphere.

The IR spectra of **73** and **74** have as expected a number of carbonyl bands, there are four carbonyl ligands on the iron centre and three carbonyl groups on the molybdenum or tungsten centres. For example, complex **74** has carbonyl bands ($CHCl_3$) at 2030, 1955, 1928, 1912 and 1901 cm^{-1}. It is likely the bands at 2030, 1955 and 1901 cm^{-1} are due to the $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ fragment, but for the $[Fe(CO)_4]$ part of complex **74**, may have three carbonyl bands at 2030, 1928 and 1912 cm^{-1}.

It should be noted that the tungsten phosphine ligand, $[WI_2(CO)_3\{MeC\{CH_2PPh_2)_3\text{-}P,P'\}]$ has bands at $\nu(CO)(CHCl_3)$ = 2036, 1958 and 1904 cm^{-1}, and a related simple monodentate phosphine complex, $[Fe(CO)_4\{P(o\text{-}Tolyl)_3\}]$ has carbonyl bands at $\nu(CO)$ (hexane) = 2043, 1975 and 1947 cm^{-1} [223]. Hence, the bands are similar for the two complexes, which agrees with the broad overlapping carbonyl region of the IR spectra of **73** and **74**.

The $^{31}P\{^1H\}$ NMR spectra of **73** and **74**, both show two resonances due to the fluxional $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ units at δ = 17.58 and -16.35 ppm respectively. For example, complex **74** shows $^{31}P\{^1H\}$ NMR data for $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ at δ = -16.35 ppm (due to L^W) and 39.30 ppm due to the phosphorus atom which is coordinated to the iron centre, in an approximetly 2:1 intensity ratio. Several attempts were made to grow suitable single crystals for X-ray crystallography without success.

The X-ray crystal structures of the complexes $[Fe(CO)_4L]$ {L = P(p-tolyl)$_3$[223] and PPh$_3$[224]} have been reported, and both have an a very similar trigonal bipyramidal geometry , with the phosphine ligand in the axial position. In view of these studies, and the IR and $^{31}P\{^1H\}$ NMR spectral data of complexes **73** and **74**, the most likely structure for **73** and **74** is shown in Fig.4.2.3.

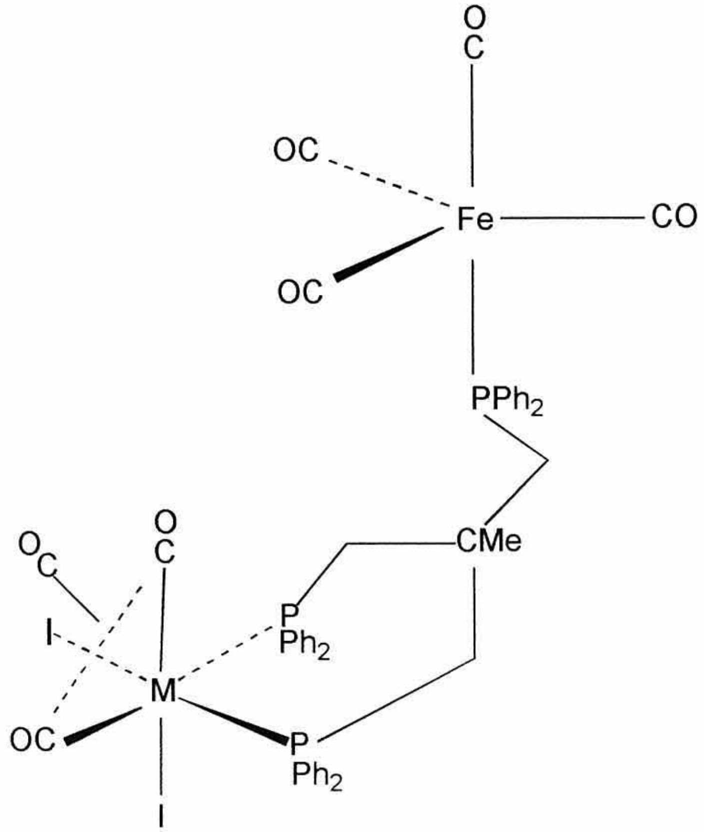


Fig.4.2.3- Proposed structure of $[Fe(CO)_4(L^{Mo}$ or $L^W)]$ (**73 and 74**).

4.2.5-Synthesis and characterisation of the cationic bimetallic complexes, $[Fe(CO)_2(L^{Mo}$ or $L^{W})(Cp$ or $Cp')]X$(75-79) :-

Equimolar quantities of $[FeI(CO)_2(Cp$ or $Cp')]$ and L^{Mo} or L^{W} react in warm CH_2Cl_2 to give the cationic iodide displaced bimetallic complexes $[Fe(CO)_2(L^{Mo}$ or $L^{W})(Cp$ or $Cp')]I$ **(75-78)** in high yield. The cationic nature of these complexes was confirmed by an iodide exchange reaction with $Na[BPh_4]$. Reaction $[Fe(CO)_2(L^{W})Cp]I$ **(76)** with one equivalent of $Na[BPh_4]$ in CH_2Cl_2 at room temperature furnished the iodide-exchanged complex, $[Fe(CO)_2(L^{Mo})Cp][BPh_4]$**(79)** in 35 % yield.

The cationic complexes **75-79** were characterised in the normal manner (Tables 4.2.1-4.2.5). The bimetallic nature of these complexes was confirmed by molecular weight measurements of **75-79** using Rast's method[158]. Complexes **75-79** are soluble in polar solvents such as CH_2Cl_2, $CHCl_3$ and acetone, but as expected completely insoluble in diethyl ether and hydrocarbon solvents. The complexes are stable in the solid state if stored under an inert atmosphere, but decompose in solution when exposed to air.

The IR spectra of **75-79** show the overlapping bands expected for the *cis*-$Fe(CO)_2$-units, and the $[MI_2(CO)_3]$ unit. For example, the IR spectrum for $[Fe(CO)_2(L^{Mo})Cp]I$ **(75)** has bands at $\nu(CO) = 2043, 2019, 1998, 1938$ and $1906\ cm^{-1}$. The two bands at 2043 and 1998 cm^{-1} are similar to the closely related monodentate phosphine complex, $[Fe(CO)_2(PPh_3)Cp]I$, which has carbonyl stretching bands at $\nu(CO) = 2045$ and $1995\ cm^{-1}$, [225]. The bands at 2019, 1938 and 1906 cm^{-1} are due to L^{Mo}. The $^{31}P\{^1H\}$ NMR spectra of complexes **75-79** show two resonances, and suggest a single isomer for the complexes in solution.

For example, complex **75** has a single resonance at δ = 52.71 ppm due to [Ph_2P-Fe] unit and at δ = 17.63 ppm for L^{Mo} in an approximately 1:2 intensity ratio. The likely structure of complexes **75-79** is as shown in Fig.4.2.4. A number of unsuccessful attempts were made to grow suitable single crystals for X-ray crystallography of complexes **75-79**.

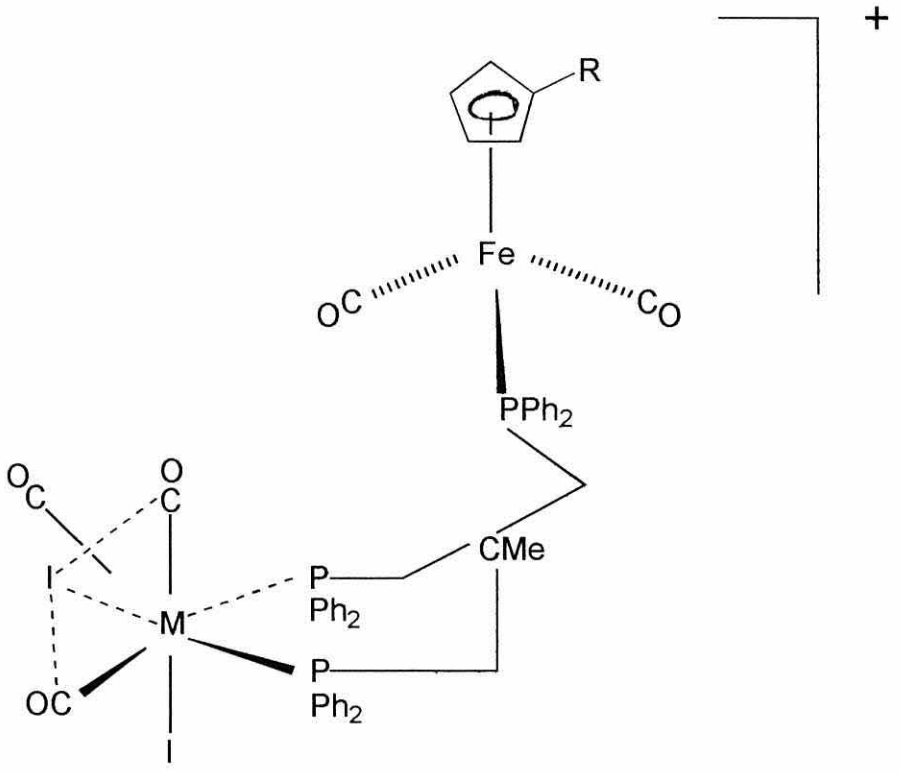


Fig.4.2.4-Proposed structure of the cationic complexes, $[Fe(CO)_2(L^{Mo}$ or $L^W)$(Cp or Cp')]X (**75-79**).

4.2.6-Conclusions :-

In conclusion, the preparation and characterisation of a range of new multimetallic complexes containing bridging-tripodal triphos, attached with two phosphorus atoms on $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$, and one phosphorus atom attached to a molybdenum(II) π-allyl unit, an iron(0) unit or an iron(II) moiety. These results are summarised in Scheme 4.2.1.

$$\begin{tikzcd}
 & {[\{Mo(\mu\text{-}X)(CO)_2(L^{Mo}\text{ or }L^{W})(\eta^3\text{-}C_3H_4R)\}_2]} & \\
{[Fe(CO)_4(L^{Mo}\text{ or }L^{W})]} & L^{Mo}\text{ or }L^{W} \arrow[l, "\mathbf{(iii)}"'] \arrow[r, "\mathbf{(ii)}"] \arrow[u, "(i)"'] \arrow[d, "\mathbf{(iv)}"] & {[MoX(CO)_2(L^{Mo}\text{ or }L^{W})_2(\eta^3\text{-}C_3H_4R)]} \\
 & {[Fe(CO)_2(L^{Mo}\text{ or }L^{W})(Cp\text{ or }Cp')]I} &
\end{tikzcd}$$

$L^{Mo} = [MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$

$L^{W} = [WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$

Reagents :- (i). One equivalent of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$.

(X= Cl, R= H or Me; X= Br, R= H) in CH_2Cl_2

(ii). Half an equivalent of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$.

(iii). Half an equivalent of $[Fe_2(CO)_9]$.

(iv). One equivalent of [FeI(CO)$_2$(Cp or Cp')].

Scheme 4.2.1

Reactions of L^{Mo} and L^{W} with $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$, $[Fe_2(CO)_9]$ or [FeI(CO)$_2$(Cp or Cp')].

Table.4.2.1-Physical and Analytical data[a] for a the multimetallic complexes 61-79 :-

Complex		Colour	Yield%	C%	H%
(61)	$[\{Mo(\mu\text{-}Cl)(CO)_2(L^{Mo})(\eta^3\text{-}C_3H_5)\}_2].CH_2Cl_2$	Brown	51	43.5	3.6
				(43.8)	(3.4)
(62)	$[\{Mo(\mu\text{-}Cl)(CO)_2(L^{W})(\eta^3\text{-}C_3H_5)\}_2]$	Green	54	42.8	3.6
				(42.8)	(3.2)
(63)	$[\{Mo(\mu\text{-}Cl)(CO)_2(L^{Mo})(\eta^3\text{-}C_3H_4Me)\}_2]$	Green	28	46.5	3.8
				(46.2)	(3.6)
(64)	$[\{Mo(\mu\text{-}Cl)(CO)_2(L^{W})(\eta^3\text{-}C_3H_4CH_3\text{-}2)\}_2]$	Green	21	43.1	3.6
				(43.2)	(3.3)
(65)	$[\{Mo(\mu\text{-}Br)(CO)_2(L^{Mo})(\eta^3\text{-}C_3H_5)\}_2]$	Green	22	44.3	3.7
				(44.2)	(3.3)
(66)	$[\{Mo(\mu\text{-}Br)(CO)_2(L^{W})(\eta^3\text{-}C_3H_5)\}_2]$	Green	50	41.8	3.5
				(41.5)	(3.1)
(67)	$[MoCl(CO)_2(L^{Mo})_2(\eta^3\text{-}C_3H_5)]$	Brown	64	47.2	4.2
				(47.6)	(3.6)
(68)	$[MoCl(CO)_2(L^{W})_2(\eta^3\text{-}C_3H_5)]$	Green	49	44.2	3.6
				(44.3)	(3.3)
(69)	$[MoCl(CO)_2(L^{Mo})_2(\eta^3\text{-}C_3H_4Me\text{-}2)]$	Green	75	48.5	4.1
				(47.9)	(3.6)

(70) $[\mathrm{MoCl(CO)_2(L^{W})_2(\eta^3\text{-}C_3H_4Me\text{-}2)}]$	Green	39	44.7	3.6
			(44.5)	(3.4)
(71) $[\mathrm{MoBr(CO)_2(L^{Mo})_2(\eta^3\text{-}C_3H_5)}].\mathrm{Et_2O}$	Green	48	47.8	3.9
			(47.3)	(3.8)
(72) $[\mathrm{MoBr(CO)_2(L^{W})_2(\eta^3\text{-}C_3H_5)}]$	Green	31	44.0	3.5
			(43.5)	(3.3)
(73) $[\mathrm{Fe(CO)_4(L^{Mo})}].\mathrm{CH_2Cl_2}$	Green	45	45.8	4.5
			(44.9)	(3.2)
(74) $[\mathrm{Fe(CO)_4(L^{W})}]$	Green	48	47.3	3.7
			(46.7)	(4.1)
(75) $[\mathrm{Fe(CO)_2(L^{Mo})Cp}]\mathrm{I}$	Green	32	45.4	3.8
			(45.0)	(3.3)
(76) $[\mathrm{Fe(CO)_2(L^{W})Cp}]\mathrm{I}$	Green	55	42.4	3.3
			(42.2)	(3.1)
(77) $[\mathrm{Fe(CO)_2(L^{Mo})Cp'}]\mathrm{I}$	Green	37	44.7	3.5
			(45.3)	(3.4)
(78) $[\mathrm{Fe(CO)_2(L^{W})Cp'}]\mathrm{I}$	Green	30	42.3	3.3
			(42.6)	(3.2)
(79) $[\mathrm{Fe(CO)_2(L^{W})Cp}][\mathrm{BPh_4}]$.	Green	35	54.3	5.7
			(54.8)	(3.9)

[a] Calculated values in Parentheses

Table.4.2.2-Infrared Data[a] for the multimetallic Complexes 61-79

Complex	$\upsilon(C\equiv O)(cm^{-1})$
(61)	2015 s, 1941 s, 1933 br, s, 1842 m.
(62)	2031 s, 1956 br, s, 1938 s, 1901 m.
(63)	2040 s, 1981 s, 1938 br, s, 1846 m.
(64)	2036 s, 1957 br, s, 1935 s, 1904 s, 1844 m.
(65)	2021 s, 1948 s, 1939 br, s, 1849 m.
(66)	2039 s, 1961 br, s, 1945 s, 1906 m.
(67)	2041 s, 1959 s, 1939 br, s, 1846 m.
(68)	2038 s, 1960 br, s, 1932 s, 1905 m.
(69)	2044 s, 1974 s, 1938 br, s, 1841 m.
(70)	2033 s, 1957 br, s, 1933 s, 1903 m, 1840 m.
(71)	2037 s, 1968 s, 1931 br, s, 1839 m.
(72)	2034 s, 1957 br, s, 1904 s, 1843 m.
(73)	2044 s, 2019 s, 1976 br, s, 1928 s, 1939 m.
(74)	2030 s, 1955 s, 1928 br, s, 1912 m, 1901 m.
(75)	2043 s, 2019 s, 1998 s, 1938 br, s, 1906 m.

(76)	2038 s, 1996 s, 1958 br, s, 1903 m.
(77)	2039 s, 1993 s, 1940 br, s, 1918 s, 1909 m.
(78)	2038 s, 1994 s, 1960 br, s, 1906 m.
(79)	2038 s, 2000 s, 1958 br, s, 1908 m.

[a]Spectra recorded in $CHCl_3$ as thin films between NaCl plates.

s = strong, m = medium, w = weak.

Table.4.2.3- ^{1}H NMR Data[a] (δ) for the multimetallic complexes 61-79

Complex	^{1}H NMR data (δ) ppm
(61)	7.4-6.5(m, 30H, 6Ph), 5.3(s, 2H, CH_2Cl_2); 3.6(m, not clear 1H, CH, allyl), 2.2(dd, 4H, $2CH_2$ of allyl), 1.9(s, 6H, $3CH_2$, tripodal triphos), 1.3(s, 3H, $1CH_3$, tripodal triphos).
(62)	8.0-7.2(m, 30H, 6Ph), 3.6(m, 1H, CH of allyl), 2.5- 2.2(dd, 4H, $2CH_2$ of allyl), 1.8-1.5(m, 6H, $3CH_2$ of tripodal triphos), 1.3(s, 3H, $1CH_3$, tripodal triphos).
(63)	7.9-7.0(m, 30H, 6Ph); 3.1(m, 1H, 1 CH allyl); 2.4-2.2(m, 4H, $2CH_2$, allyl); 1.5(m, 3H, $1CH_3$ allyl); 1.4(s, 6H, $3CH_2$, tripodal triphos); 1.1(m, 3H, $1CH_3$, tripodal triphos).
(64)	7.8-7.1(m, 30H, 6Ph), 3.7-3.4(m, 1H, 1CH, allyl), 2.5-2.1(m, 4H, $2CH_2$, allyl), 1.6(t, 3H, $1CH_3$, allyl), 1.7-1.4(m, 6H, $3CH_2$, tripodal triphos), 1.2(s, 3H, $1CH_3$, tripodal triphos).
(65)	7.8-7.1(m, 30H, 6Ph), 3.7-3.5(m, 1H, 1CH, allyl), 2.5-2.2(dd, 4H, $2CH_2$, allyl), 1.8-1.4(m, 6H, $3CH_2$, tripodal triphos), 1.3(s, 3H, $1CH_3$, hexyne).
(66)	7.8-7.2(m, 30H, 6Ph), 3.8-3.6(m, 1H, 1CH, allyl), 2.4-2.2(m, 4H, $2CH_2$, allyl), 1.9-1.4(m, 6H, $3CH_2$, tripodal triphos), 1.3(s, 3H, $1CH_3$, tripodal triphos).

(67)	7.8-7.0(m, 30H, 6Ph), 3.65(m, not clear 1H, CH, allyl), 2.3(dd, 4H, $2CH_2$, allyl), 2.0(s, 6H, $3CH_2$, tripodal triphos), 1.3(s, 3H, $1CH_3$, tripodal triphos).
(68)	8.1-7.1(m, 30H, 6Ph), 3.5(m, 1H, CH, allyl), 2.5- 2.2(dd, 4H, $2CH_2$, allyl), 1.8-1.5(m, 6H, $3CH_2$, tripodal triphos), 1.3(s, 3H, $1CH_3$, tripodal triphos).
(69)	7.9-7.0(m, 30H, 6Ph); 3.2(m, 1H, 1CH, allyl); 2.6-2.2(m, 4H, $2CH_2$, allyl); 1.5(s, 3H, $1CH_3$, allyl); 1.3(s, 6H, $3CH_2$, tripodal triphos); 0.9(s, 3H, $1CH_3$, tripodal triphos).
(70)	7.9-7.0(m, 60H, 12Ph); 3.7(br, 1H, 1CH, allyl); 2.5-2.1(m, 4H, $2CH_2$, allyl); 1.7-1.5(m, 3H, $1CH_3$, allyl); 1.3(s, 6H, $3CH_2$, tripodal triphos); 0.9(s, 3H, $1CH_3$, tripodal triphos).
(72)	7.9-7.1(m, 30H, 6Ph), 3.8-3.6(m, 1H, CH, allyl),2.6-2.2(dd, 4H, $2CH_2$, allyl), 1.7-1.4(br.m, 6H, $3CH_2$, tripodal triphos), 1.3(s, 3H, $1CH_3$, tripodal triphos).
(73)	7.8-7.0(m, 30H, 6Ph); 5.4(s, 2H, CH_2Cl_2); 1.3(s, 6H, $3CH_2$, tripodal triphos); 0.9(s, 3H, $1CH_3$, tripodal triphos).
(74)	7.7-6.8(m, 30H, 6Ph); 1.4(s, 6H, $3CH_2$, tripodal triphos); 0.9(s, 3H, $1CH_3$, tripodal triphos).
(75)	7.7-7.0(m, 30H, 6Ph); 5.1(s, 5H, cyclopentadienyl), 1.3(s, 6H, $3CH_2$, tripodal triphos), 0.9(s, 3H, $1CH_3$, tripodal triphos).

(76)	7.7-7.2(m, 30H, 6Ph); 5.1(s, 5H, cyclopentadienyl); 1.8-1.6(br, 6H, $3CH_2$, tripodal triphos); 1.3(s, 3H, $1CH_3$, tripodal triphos).
(77)	7.7-7.0(m, 30H, 6Ph); 4.9(d, 4H, cyclopentadienyl), 2.2(s, 3H, $1CH_3$, cyclopentadienyl); 1.3(s, 6H, $3CH_2$, tripodal triphos), 0.9(s, 3H, $1CH_3$, tripodal triphos).
(78)	7.8-7.0(m, 30H, 6Ph); 4.9(d, 4H, cyclopentadienyl), 2.2(s, 3H, methyl cyclopentadienyl); 1.3(s, 6H, $3CH_2$, tripodal triphos), 0.9(s, 3H, $1CH_3$, tripodal triphos).
(79)	7.9-7.1(m, 50H, 10Ph); 5.1(m, 5H, cyclopentadienyl); 1.3(s, 6H, $3CH_2$, tripodal triphos); 0.9(s, 3H, $1CH_3$, tripodal triphos).

[a]Spectra recorded in $CDCl_3$ (+25) and referenced to $SiMe_4$,

s = singlet, br = broad, d = doublet, m = multiplet

Table.4.2.4- ^{31}P NMR Data[a] (δ) for the multimetallic Complexes 61-79[a].

Complex	^{31}P (δ) data (ppm)
(61)	δ = 17.59 (s, 2P, L^{Mo}) and 31.84 (s, 1P, Ph_2P-Mo).
(62)	δ = -17.65 (s, 2P, L^{W}) and 27.30 (s, 1P, Ph_2P-Mo).
(63)	δ = 17.60 (s, 2P, L^{Mo}) and 28.96 (s, 1P, Ph_2P-Mo).
(64)	δ = -12.24 (s, 2P, L^{W}) and 32.04 (s, 1P, Ph_2P-Mo).
(65)	δ = 17.55 (s, 2P, L^{Mo}) and 34.62 (s, 1P, Ph_2P-Mo).
(66)	δ = -11.76 (s, 2P, L^{W}) and 24.99 (s, 1P, Ph_2P-Mo).
(67)	δ = 17.57 (s, 2P, L^{Mo}) and 32.85 (s, 1P, Ph_2P-Mo).
(68)	δ = -12.81 (s, 2P, L^{W}) and 25.28 (s, 1P, Ph_2P-Mo).
(69)	δ = 17.59 (s, 2P, L^{Mo}) and 29.45 (s, 1P, Ph_2P-Mo).
(70)	δ = -14.35 (s, 2P, L^{W}) and 25.05 (s, 1P, Ph_2P-Mo).
(71)	δ = 17.57 (s, 2P, L^{Mo}) and 27.53 (s, 1P, Ph_2P-Mo).
(72)	δ = -14.23 (s, 2P, L^{W}) and 25.14 (s, 1P, Ph_2P-Mo).
(73)	δ =17.58 (s, 2P, L^{Mo}) and 27.93 (s, 1P, Ph_2P-Fe).
(74)	δ = -16.35 (s, 2P, L^{W}) and 39.30 (s, 1P, Ph_2P-Fe).

(75)	$\delta = 17.63$ (s, 2P, L^{Mo}) and 52.71 (s, 1P, Ph_2P-Fe).
(76)	$\delta = -12.20$ (s, 2P, L^{W}) and 52.66 (s, 1P, Ph_2P-Fe).
(77)	$\delta = 17.64$ (s, 2P, L^{Mo}) and 52.30 (s, 1P, Ph_2P-Fe).
(78)	$\delta = -13.95$ (s, 2P, L^{W}) and 51.99 (s, 1P, Ph_2P-Fe).

[a] Spectra recorded in $CDCl_3$ (+25 °C) and referenced to 85% H_3PO_4.

Table.4.2.5-Molecular weight studies [a] using Rast's method for selected multimetallic complexes 61-79 :-

Complex	Molecular weight {Found(Calcd).}
(63)	1429(1300)
(69)	2667(2358)
(70)	2667(2534)
(71)	2222(2389)
(72)	2667(2565)
(73)	1333(1282)
(74)	1429(1370)
(75)	1429(1362)
(76)	1482(1450)
(77)	1333(1376)
(78)	1379(1464)

[a] Camphor was used as the solvent in these measurements.

CHAPTER FIVE

REACTIONS AND CATALYTIC ACTIVITY OF THE SEVEN-COORDINATE DICHLORO TRICARBONYL COMPLEX, $[WCl_2(CO)_3(NCMe)_2]$. SYNTHESIS AND REACTIONS OF $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$.

Chapter Five

Reactions and catalytic activity of the seven-coordinate dichloro tricarbonyl complex, [$WCl_2(CO)_3(NCMe)_2$];

Synthesis and reactions of [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$]

5.1-Introduction :-

Since the initial report in 1988[40] of the synthesis of the dimeric mono(alkyne) complex [{M (μ-I)I(CO)(NCMe)(η^2-RC_2R')}$_2$] (M = Mo, W; R = R' = Me, Ph, CH_2Cl; R = Ph, R' = Me, CH_3OH; R = Me, R = PhS, *p*-tolS), and the bis(alkyne) complexes, [{Mo(μ-I)I(CO)(η^2-MeC_2Me)$_2$}$_2$] and [$MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2$] (M = Mo, W; R = R' = Ph; R = Me, R' = Ph; for M = W only; R = R' = Me, CH_2Cl_2, *p*-tol, R = Ph, R' = CH_2OH)[92]. Baker *et al* have described an extensive iodo-alkyne chemistry of molybdenum(II) and tungsten(II)[39,92,102,127,133,147,152,226-229].

In 1994[148], Baker *et al* described the synthesis and reactions with donor ligands of the dibromo-bis(2-butyne) complex, [$WBr_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2$], and very recently in 1998[154], also they described a series of mixed chloro/iodo alkyne complexes, including the X-ray structural characterisation of the cationic complex, [$WCl(CO)(2,2'\text{-bipy})(\eta^2\text{-}MeC_2Me)_2$]I.

Far fewer dichloro alkyne complexes of molybdenum(II) and tungsten(II) have been reported. Templeton *et al*[15], Brisdon *et al*[135], Nielson *et al*[136], and Mayr *et al*[140,141,230] have described some new dichloro alkyne complexes, the following of which [$WCl_2(CO)(L_2)$

(η^2-PhC$_2$Ph)](L = PMe$_3$, PMe$_2$Ph)[135], [WCl$_2$(CO)(PMe$_3$)$_2$(η^2-PhC$_2$NHBu^t)][140], [WCl$_2$(CO)(PMe$_3$)$_2$(η^2-PhC$_2$R)] {R = OH, OC(O)C$_6$H$_4$OMe-4}[141], and [WCl$_2$(=CHPh)(PMe$_3$)$_2$(η^2-PhC$_2$R)](R = Me, H)[230] have been crystallographically characterised.

Very recently[231], the synthesis of the seven-coordinate dichloro-complex [WCl$_2$(CO)$_3$(NCMe)$_2$] by the reaction of [WI$_2$(CO)$_3$(NCMe)$_2$] with two equivalents of NaCl in acetone/CH$_2$Cl$_2$ has been described. The complex [WCl$_2$(CO)$_3$(NCMe)$_2$] has been shown to polymerise phenylacetylene[231].

The general aim for this chapter was to prepare and characterise a series of new dichloro complexes of tungsten(II). More specifically, the synthesis and characterisation of the bis(3-hexyne) complex, [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$]. Another aim was to investigate the chemistry of this complex with a series of neutral and anionic donor ligands.
Finally, a very important aim was to study the catalytic activity of the seven-coordinate complex, [WCl$_2$(CO)$_3$(NCMe)$_2$] towards the polymerisation of phenylacetylene.

5.2-Synthesis and characterisation of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (80):-

The starting material used in this work, namely [WCl$_2$(CO)$_3$(NCMe)$_2$], was prepared by reacting the seven-coordinate diiodo-complex, [WI$_2$(CO)$_3$(NCMe)$_2$][74], with two equivalents of NaCl in acetone at room temperature to give the halide-exchanged product, [WCl$_2$(CO)$_3$(NCMe)$_2$][231]. This unstable complex, has been characterised by IR, ^{1}H and ^{13}C NMR spectroscopy. It has been shown to be a highly active phenylacetylene polymerisation catalyst, but would be expected to initially form coordinated bis(alkyne) complexes before undergoing intramolecular oxidative-addition to give a metallocyclobutadiene intermediate, followed by insertion to give an arene or polymerisation products[231]. Reaction of [$WCl_2(CO)_3(NCMe)_2$] (prepared *in situ* as described before), with an excess of 3-hexyne eventually gives the new bis(alkyne) complex [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] **(80)**, which has been characterised by IR (Table 5.2), ^1H and ^{13}C NMR spectroscopy (Table 5.3 and 5.4). Complex **80** is very much less stable than its diiodo analogue [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$][155], and hence it was very difficult to obtain satisfactory elemental analysis results, even after many repeated attempts of preparing the complex from both reaction of [$WCl_2(CO)_3(NCMe)_2$] (prepared *in situ*) with EtC_2Et or treating [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] with NaCl.

Complex **80** is also less soluble in chlorinated solvents and diethyl ether and hydrocarbon solvents compared to its diiodo analogue[155]. The IR spectrum for **80** ($CHCl_3$) has a strong carbonyl band at 2079 cm^{-1}, which is at higher wavenumber compared to [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] at 2056 cm^{-1}. It also has a nitrile band, $\nu(N{\equiv}C) = 2305\ cm^{-1}$, and a very weak alkyne stretching band at 1630 cm^{-1}. The alkyne stretching band of the 3-hexyne is at lower wavenumber compared to the "free" alkyne, which is again due to a synergic bonding effect of the metal-alkyne bond. In view of the similar IR, ^1H and ^{13}C NMR spectral properties of the dichloro complex **80** to the related diiodo alkyne complexes [$WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2$] (R = Me, R' = Me, Ph[92]; R = Bu^t, R' = Me[87]; R = Me, R'= Ph[232]), which have all been crystallographically characterised, it is very likely the structure of **80** will be very similar as shown in Fig.5.1.

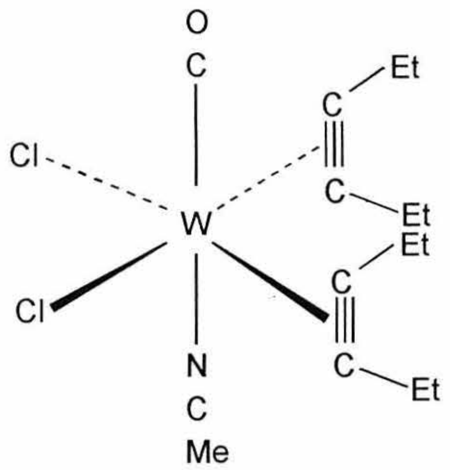
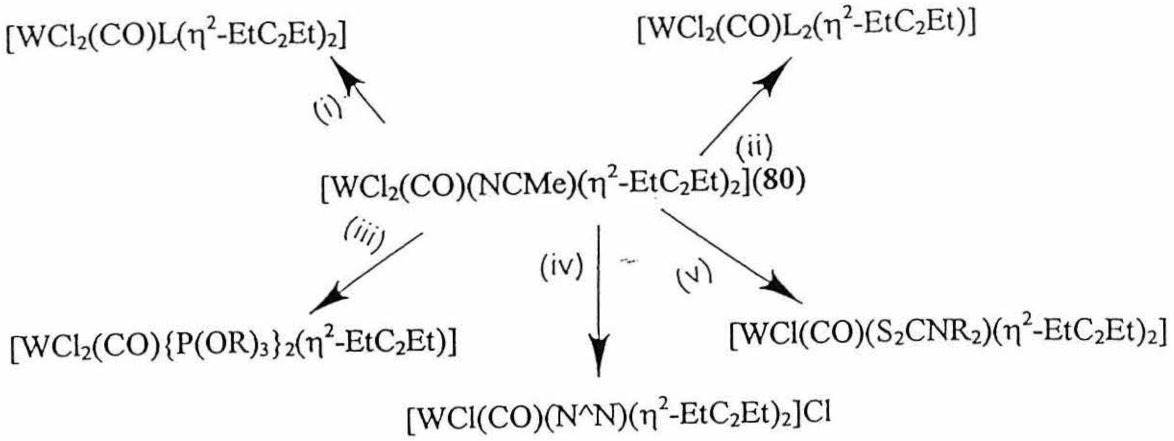


Fig.5.1. Proposed structure of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$](**80**).

The ^{1}H NMR (+25 °C, CDCl$_3$) spectrum for complex **80** has broad quartet at $\delta = 3.6$-3.2 ppm, due to coupling of the 3-hexyne methyl groups to the 3-hexyne CH$_2$ groups, a singlet at $\delta = 2.6$ ppm due to the acetonitrile and a triplet at $\delta = 1.3$ ppm due to the methyl of the 3-hexyne, which is coupled to the CH$_2$ groups in 3-hexyne. The integration conform with the formula, [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] for complex **80**.

The room temperature ^{13}C NMR spectrum (CDCl$_3$) for complex **80** (Table 5.5), has alkyne contact carbon resonances at $\delta = 162.43$ and 167.50 ppm, which from Templeton and Ward's[13] correlation suggests that the two 3-hexyne ligands are donating a total of six-electrons to the tungsten, this also enables complex **80** to obey the effective atomic number rule.

The rest of this chapter describes the reactions of the versatile complex, [WCl$_2$(CO) (NCMe)(η^2-EtC$_2$Et)$_2$](**80**) with both neutral and anionic donor ligands. These results are summarised in Scheme.5.1.



Reagents : (i). $\{L = NPh_3, PPh_3, L^{Mo}, L^{W}\}$.

(ii). $L_2 = 2PPh_3, 2L^{Mo}, 2L^{W}$; $L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4 and 6);

and *cis*-$Ph_2PCH{=}CHPPh_2$.

(iii). $2P(OR)_3$, (R = Et, ^iPr); (iv). N^N = bipy;

(v). NaS_2CNR_2, (R = Me, Et).

Scheme 5.1

5.3-Reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(80) with one equivalent of L to give $[WCl_2(CO)L(\eta^2\text{-}EtC_2Et)_2]$ (81-84) :-

Reaction of equimolar amounts of **80** and L {L = NPh_3, PPh_3 or $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo or W)} in CH_2Cl_2 at room temperature gives the acetonitrile exchanged products, $[WCl_2(CO)L(\eta^2\text{-}EtC_2Et)_2]$(**81-84**). All the new complexes have been characterised in the normal manner (see Tables 5.1-5.4 and ^{13}C NMR for complex **81** table 5.5). Complex **81** is less stable, and more soluble than the phosphine complexes **82-84**. All the complexes decompose very quickly when exposed to air in solution, and are also air-sensitive in the solid state, but can be stored under dinitrogen for several weeks.

Complex **81** has a single carbonyl band in its IR spectrum at 2081 cm^{-1} (Table 5.2), in a similar position to **80**, and would be expected to have a similar structure as the acetonitrile complex shown in Fig.5.1. Also, the room temperature ^{13}C NMR spectrum ($CDCl_3$) of the soluble complex $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$(**81**), shows alkyne contact carbon resonances at $\delta = 168.98$ and 162.30 ppm, which again indicates[13] that the two 3-hexyne ligands are donating a total of six-electrons to the metal in this complex, which enables the complex to obey the effective atomic number rule.

Similarly, the mono(triphenylphosphine) complex, $[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Et)_2]$(**82**) has a carbonyl band in its IR spectrum at 2064 cm^{-1} in the expected region for this type of complex with a similar structure to **80**, which has PPh_3 replacing the NCMe ligand in Fig.5.1. The $^{31}P\{^1H\}$ NMR spectrum has a single resonance at $\delta = -25.33$ ppm, due to the coordinated triphenylphosphine ligand.

The new organometallic phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo, W), have been prepared by reaction of equimolar amounts of $[MI_2(CO)_3(NCMe)_2]$ and $MeC(CH_2PPh_2)_3$ in CH_2Cl_2 at room temperature (see Chapter Four part I). The new bimetallic complexes, $[MCl_2(CO)(L^{Mo}$ or $L^{W})(\eta^2\text{-}EtC_2Et)_2]\{L^M = [MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(**83** and **84**)(M = Mo or W) have carbonyl bands at 2075 and 2079 cm^{-1} respectively. For example, for $[WCl_2(CO)L^{Mo}(\eta^2\text{-}EtC_2Et)_2]$(**83**), ν(CO) occurs at 2075, 2044, 1970 and 1934 cm^{-1}. The band at 2075 cm^{-1} will be due to the carbonyl ligand on the tungsten dichloro centre, which is similar to $[WCl_2(CO)(L^W)(\eta^2\text{-}EtC_2Et)_2]$(**5**) which has at 2079 cm^{-1}. The other three bands are due to the $[WI_2(CO)_3$-unit, which are related to the organometallic phosphine, [$WI_2(CO)_3\{MeC(CH_2PPh_2)_3$-*P,P'*}] which has ν(CO) at 2036, 1958, and 1905 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **83** has a single resonance at δ = 17.59 ppm due to the two phosphorus atoms of the tripodal triphos attached to the fluxional $MoI_2(CO)_3$ unit, and at 23.60 ppm due to the third phosphorus atom, which is coordinated to the tungsten bis(alkyne) unit, in an approximately 2:1 intensity ratio.

The structure of the seven-coordinate complex, [$MI_2(CO)_3\{MeC(CH_2PPh_2)_3$-*P,P'*}] part of the bimetallic complexes are most likely to be capped octahedral as many complexes have this type have this structure[72,73,222](see Fig.4.1.1 in Chapter Four). Hence, it is likely the structure of **83** and **84** will have L^{Mo} or L^W replacing the acetonitrile in Fig 5.1.

5.4-Reactions of (80) with two equivalents of L{L = PPh_3, L^{Mo} , L^W, or one equivalent of L_2, $L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4 or 6) or *cis*-$Ph_2PCH{=}CHPPh_2$} to give [$WCl_2(CO)L_2(\eta^2\text{-}EtC_2Et)$](85-92):-

Treatment of **80** with L_2 {L_2 = 2PPh_3, 2L^{Mo}, 2L^W, $Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4 and 6) or *cis*-$Ph_2PCH{=}CHPPh_2$} in CH_2Cl_2 at room temperature, eventually gave the mono(3-hexyne) complexes, [$WCl_2(CO)L_2(\eta^2\text{-}EtC_2Et)$](**85-92**).

All the new complexes **85-92** have been characterised by elemental analysis (C, H and N) (Table 5.1), IR (Table 5.2), ^1H NMR (Tables 5.3) and ^{13}C NMR for complex **85** (Table 5.5), and in selected complexes by $^{31}P\{^1H\}$ NMR spectroscopy (Table 5.4). Complex **89** was confirmed as an Et_2O solvate and **91** as a CH_2Cl_2 solvate by repeated elemental analyses and ^1H NMR spectroscopy. These bis(phosphine) complexes are considerably more stable than **(80-84)** , and can be stored for several weeks under a nitrogen atmosphere. They are also stable in the air in the solid state for a few hours.

The complexes are much less soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ compared to **80-84**. All the bis(phosphine) complexes **85-92** have carbonyl stretching bands in the region of 1940 cm^{-1}, which is typical for other dihaloalkyne complexes of the type, $[MXY(CO)L_2(\eta^2\text{- }RC_2R')]$[98,99,127,133,147,152]. They also have alkyne stretching bands at considerably lower wavenumber compared to the uncoordinated 3-hexyne ligand.

The $^{31}P\{^1H\}$ NMR spectrum of $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$(**85**), has a single resonance at $\delta = -9.71$ ppm, which suggests *trans*-PPh_3 groups, which would be expected due to the very large ligand cone angle[159] of PPh_3 (145°). This also agrees with all the crystal structures of $[MX_2(CO)L_2(\eta^2\text{-}RC_2R')]$ (M = Mo, X = Br, L = PEt_3, R = H, R'= Ph[15]; M = W, X = Cl, L = PMe_3 or PMe_2Ph, R = R'= Ph[136]; M = W, X = Cl, L = PMe_3, R = Ph, R'= $NHBu^t$ [141]; M = W, X = I, L = PPh_3, R = R'= Et[155]), which all have *trans*-phosphine ligands. Hence, the most likely structure of complex **85** will be as shown in Fig.5.2.

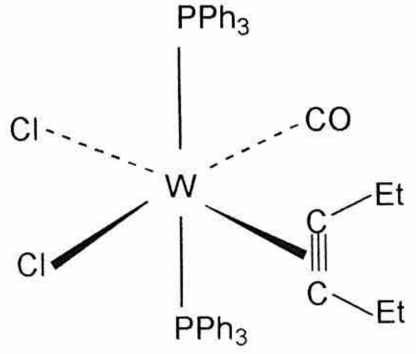


Fig.5.2. Proposed structure of $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$(**85**).

The IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopic properties of the trimetallic complexes, $[WCl_2(CO)(L^{Mo}$ or $L^W)_2(\eta^2$-$EtC_2Et)]$(**86** and **87**) show the two L^{Mo} or L^W moeities are in the same environment, and would also suggest a *trans*-arrangement of these very large monodentate phosphine ligands. For example, $[WCl_2(CO)(L^{Mo})_2(\eta^2$-$EtC_2Et)]$(**86**) has carbonyl bands at ν(CO) = 2044, 1972, 1938, 1904 cm^{-1}, the band at {ν(CO) = 1972 cm^{-1} is likely to be due to the $WCl_2(CO)$-unit, and the bands ν(CO) = 2044, 1938 and 1904 cm^{-1} due to the $\{MoI_2(CO)_3$-}unit in its IR spectrum (Table 5.2).

The ^1H NMR spectra for the complexes (**86-87**) are noising, due to the poor solubility of theses complexes. For example, complex **86** has 6 Ph groups as multiplet and 2 CH_2 of 3-hexyne which are not clear quartets and the same situation exists with the CH_3 groups, which are not the expected simple triplets.

The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, +25 °C) of **86** has resonances at δ = 17.58 and 30.76 ppm in a 2:1 intensity ratio. The resonance at δ = 17.58 is most likely to be due to the two phosphorus atoms on the fluxional organomolybdenum phosphine ligand, $[MoI_2(CO)_3\{MeC(CH_2\,PPh_2)_3$-*P,P'*}](**36**), which has a resonance at δ = 12.63 ppm at room temperature for the two coordinated phosphorus atoms. The lower field resonance at δ = 30.76 ppm will be due to the *trans*-phosphorus atoms attached to the $[WCl_2(CO)$-centre.

The bidentate phosphine ligand complexes $[WCl_2(CO)L_2(\eta^2$-$EtC_2Et)]\{L_2 = Ph_2P(CH_2)_n$ PPh_2 n = 1, 3, 4 and 6} or *cis*-$Ph_2PCH{=}CHPPh_2$}(**88-92**), are related to, for example, the diiodo complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2$-$EtC_2Et)]$(n = 1, 3, 4 and 6), which was has been structurally characterised for n = 3 (see Fig.2.7)[155]. In view of the similar spectroscopic properties of $[WX_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2$-$EtC_2Et)]$ (X = Cl(**89**),

$\nu(CO)$ = 1944 cm^{-1}; X = I **(8)**, $\nu(CO)$ = 1942 cm^{-1}}, $^{31}P\{^1H\}$ NMR (for X = Cl, δ = -18.14 and -17.62 ppm, for X = I, δ = -23.73 and -36.21 ppm}, it is likely they will have a similar structure as shown in Fig.5.3.

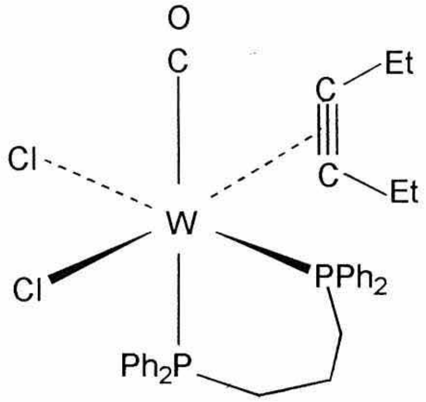


Fig.5.3. Proposed structure of [$WCl_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)$](89)

It is interesting to note that the reaction of equimolar amounts of [$MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] and $P(OR)_3$ (R = ^{i}Pr or Ph) gives the 3-hexyne displaced products, [$MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)$] which was crystallographically characterised for R = Ph (see Chapter Three). It was also reported in the same chapter, that the reaction of the diiodo-tungsten complex, [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] with one equivalent of $P(OR)_3$ (R = Me, Et, ^{i}Pr) gave the acetonitrile displaced products, [$WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2$].

It is very likely that these, and the related earlier reactions with phosphite and phosphine ligands proceed *via* an associative mechanism, with the 3-hexyne ligand being able to alter its mode of bonding from a four- to two-electron donor ligand during the formation of the complex, [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$], which can lose the acetonitrile ligand to give the four-electron donor 3-hexyne product, [$WCl_2(CO)(L)(\eta^2\text{-}EtC_2Et)_2$].

This type of associative mechanism has been proposed[25,48] for other reactions of this type. Many reactions were attempted to produce bis(3-hexyne) complexes, [WCl_2(CO) {$P(OR)_3$}(η^2-$EtC_2Et)_2$]. For example, reaction of equimolar amounts of [WCl_2(CO) (NCMe)(η^2-$EtC_2Et)_2$] and P($O^iPr)_3$ to give [WCl_2(CO){P($O^iPr)_3$}(η^2-$EtC_2Et)_2$] were unsuccessful, as the product was not isolated in a pure state.

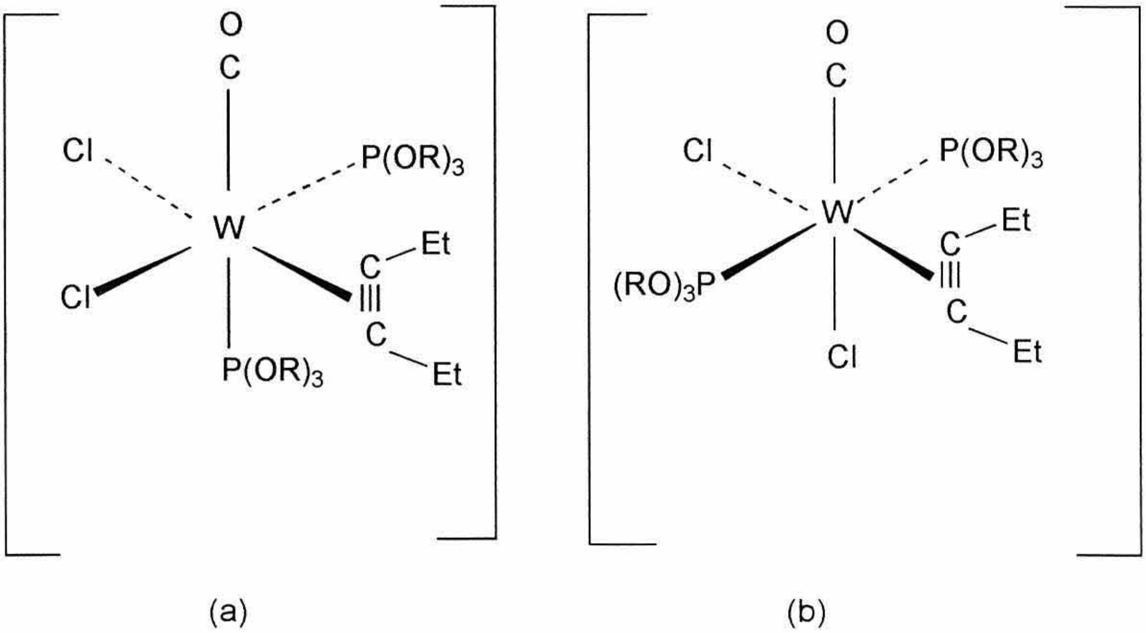
5.5-Reactions of [WCl_2(CO) (NCMe)(η^2-$EtC_2Et)_2$](80) with two equivalents of $P(OR)_3$ (R = Et, ^iPr) to give [WCl_2 (CO){$P(OR)_3$}$_2$(η^2-EtC_2Et)] (93 and 94) :-

Reaction of **80** with two equivalents of $P(OR)_3$ (R = Et, ^iPr) in diethyl ether gives the expected bis(phosphite) complexes, [WCl_2(CO){$P(OR)_3$}$_2$(η^2-EtC_2Et)] (**93** and **94**) in high yield. These complexes are very soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, and are also soluble in diethyl ether. The complexes have been fully characterised by elemental analysis (Table 5.1) and spectroscopic methods (see Tables 5.2-5.4). Complex **93** was confirmed as a CH_2Cl_2 solvate by repeated elemental analysis and ^1H NMR spectroscopy. They are very air-sensitive in solution when exposed to air, but can be stored for a few hours in the solid-state under dinitrogen. Complexes **93** and **94** are the most soluble complexes described in this chapter.

The synthesis and crystallographic characterisation of a large series of diiodo bis(phosphite) complexes have been described of the type, *cis*-[WI_2(CO) {$P(OMe)_3$}$_2$(η^2-MeC_2Me)][99], *trans*-[MoI_2(CO){$P(OEt)_3$}$_2$(η^2-MeC_2Me)][156] and *trans*-[WI_2(CO){P ($O^iPr)_3$}$_2$(η^2-EtC_2Et)](M = Mo or W)[234]. For The smallest cone angle phosphite[159],

$P(OMe)_3$ (cone angle $\theta = 107^0$) for the complexes $[MI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2 Me)]$ exist as a mixture of *cis*- and *trans*-isomers in solution, as observed from IR and $^{31}P\{^1H\}$ NMR studies. Whereas, for the largest phosphite ligand, $P(O^iPr)_3$ (cone angle $\theta = 128^0$), only the *trans*- isomer was observed in solution and the solid state[99,156,234]. The $^{31}P\{^1H\}$ NMR spectra of the dichloro complexes $[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**93** and **94**) show for R = Et, *cis* and *trans*-isomers.

The ^{31}P NMR spectrum of **93** shows a singlet resonance at $\delta = 100.40$ ppm, which is due to the *trans* isomer, and two doublets at $\delta = 107.26$ and 107.83 ppm due to the *cis* isomer ($J_{P\text{-}P} = 57.72$ Hz) (the ratio ≅ 40:60). Whereas, for R = ^{i}Pr (**94**) only a single resonance at $\delta = 94.80$ ppm ($J_{p\text{-}w} = 194.75$ Hz) due to the *trans*-isomer was observed. The proposed structures of the *cis*-and *trans*-isomers of **93** are shown in Fig.5.4 (a) and (b) respectively, which correspond with the crystal structures of related diiodo complexes[99,156,234].

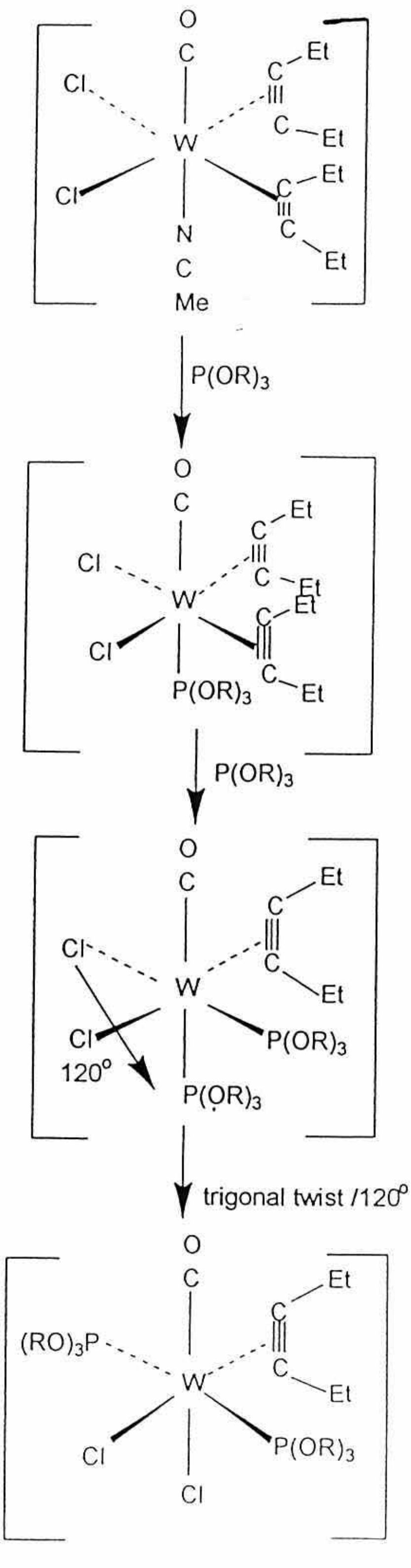


(a) (b)

Fig.5.4. Proposed structure of both the *cis*- (a) and *trans*- (b) isomers of

$[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**93** and **94**)

The most likely mechanism for the successive reactions of $P(OR)_3$ with $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ is as given in Scheme 5.2.



Scheme 5.2. Proposed mechanism for the reactions of $P(OR)_3$ with $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$.

5.6-Reaction of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$](80) with N^N (N^N = 2.2'-bipyridyl) to give [WCl(CO)(N^N)(η^2-EtC$_2$Et)$_2$]Cl (95) :-

Treatment of equimolar quantities of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] and N^N (N^N = 2,2'-bipyridyl) in CH$_2$Cl$_2$ at room temperature affords the cationic complex, [WCl(CO)(N^N)(η^2-EtC$_2$Et)$_2$]Cl (**95**) in high yield. Complex **95** has been characterised in the normal manner (see Tables 5.1-5.3 and 5.5), and is closely related to the crystallographically characterised complexes [WCl(CO)(bipy)(η^2-MeC$_2$Me)$_2$]I[154] and [WI(CO(bipy)(η^2-MeC$_2$Me)$_2$]I[40], and both have *cis*- and parallel 2-butyne ligands, which are in the equatorial plane with the 2,2'-bipyridine ligand, with the carbonyl and halide ligands occupying the axial sites.

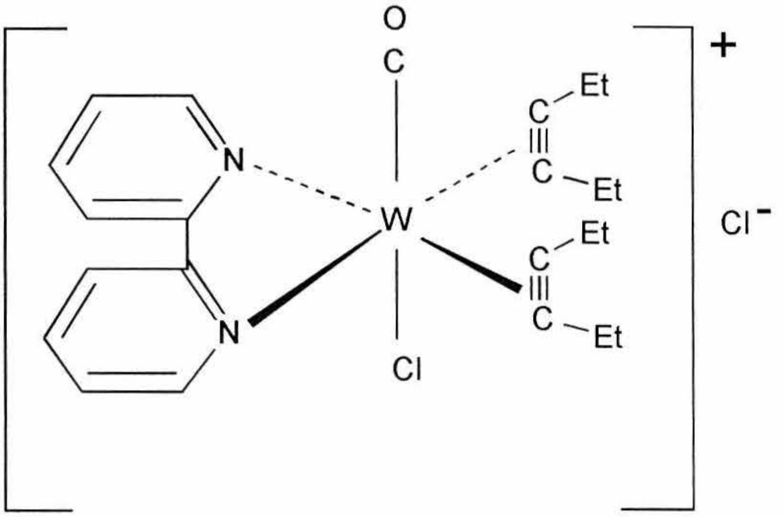


Fig.5.5. Proposed structure of [WCl(CO)(2,2'-bipy)(η^2-EtC$_2$Et)$_2$]Cl (**95**).

In view of the very similar spectroscopic properties of **95** to the crystallographically characterised complexes[39,154], it is likely to have the same structure as shown in Fig.5.5. For example, the IR spectrum of **95** (N^N = bipy) has a carbonyl band at 2052 cm^{-1}, which is very similar to the closely related 2-butyne complex $[WCl(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$[154], at 2051 cm^{-1}.

The ^1H NMR (+25 °C, $CDCl_3$) spectrum for complex 95 conformed the area for bipyridyl, which is at $\delta = 9.0\text{-}7.4$ ppm, the CH_2 groups were at $\delta = 3.7$ ppm as a quartet, and for the CH_3 groups at $\delta = 1.2$ ppm as triplets. The integration for the spectrum is concert for the formula, $[WCl(CO)(bipy)(\eta^2\text{-}EtC_2Et)_2]Cl$, of complex **95**.

The ^{13}C NMR spectrum (Table 5.5) of **95**, has alkyne contact carbon resonances at δ = 164.23 and 168.98 ppm due to the two alkyne ligands donating a total of six-electrons to the tungsten, which also enables the complex to obey the effective atomic number rule[13].

5.7-Reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(80) with one equivalent of $S_2CNR_2^-$ (R = Me, Et) to give $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ (96 and 97) :-

Reaction of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of NaS_2CNR_2 (R = Me, Et) gives the complexes, $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ (**96** and **97**) in high yield. These fully characterised complexes (Tables 5.1-5.3) are very similar to the crystallographically characterised complex, $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$[102], previously described. Complex **96** was confirmed as a CH_2Cl_2 solvate by repeated elemental analysis and ^1H NMR spectroscopy. The IR and NMR spectral properties of **96** and **97** are similar to the complex, $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$, and hence they are likely to have a similar structure as shown in Fig.5.6. For example, the IR spectrum of **97** (R = Et) has a carbonyl stretching band at 2041 cm^{-1}, which is similar to [WI(CO)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$], which has 2043 cm^{-1} in the same solvent, $CHCl_3$.

The ^1H NMR (+25 °C, $CDCl_3$) spectra for complexes 96 and 97 were difficult to interpret. For example, complex **97** shows the area for CH_2 groups from $CH_3\underline{CH_2}NCS_2$ group which were close to the area for the CH_2 groups of 3-hexyne, and similarly with CH_3 groups of both ligands. However, IR and elemental analysis results confirm the formula for **96** and **97**. Several unsuccessful attempts to obtain the ^{13}C NMR spectra (+25 °C, $CDCl_3$) for complexes **96** and **97**, were made as no carbonyl and alkyne contact carbons were observed in these spectra, these are not repeated in this thesis.

In conclusion, the synthesis of an unstable dichloro bis(alkyne) complex, [WCl_2(CO)(NCMe)(η^2-EtC_2Et)$_2$](**80**) has been described, and its reactions with a wide range of neutral and anionic donor ligands to give a series of products has been investigated as described in Scheme 5.1.

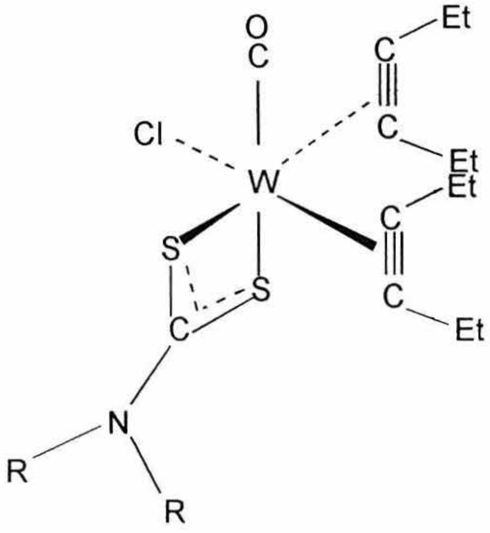


Fig.5.6. Proposed structure of [WCl(CO)(S_2CNR_2)(η^2-EtC_2Et)$_2$]

{R = Me (**96**); R = Et (**97**)}.

5.8-Homogeneous catalytic studies of the seven-coordinate dichloro complex, $[WCl_2(CO)_3(NCMe)_2]$:-

Homogeneous catalytic reactions have been investigated by using seven-coordinate halocarbonyl complexes, $[MXY(CO)_3(NCMe)_2]$ (M = Mo or W; X, Y = halide). One of the important reactions was the alkene metathesis polymerisation of norbornadiene by using $[MXY(CO)_3(NCMe)_2]$ (M = Mo or W) or $[MXY(CO)\{MeC(CH_2PPh_2)_3\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$[1].

In 1997, Buzar[235] has shown that the photochemical oxidation of $[W(CO)_6]$ with CCl_4 in cyclohexane/CCl_4 (10:1) eventually gives $[\{W(\mu\text{-}Cl)Cl(CO)_4\}_2]$, which reacts with NCMe to give $[WCl_2(CO)_3(NCMe)_2]$. During this section a different synthesis of $[WCl_2(CO)_3(NCMe)_2]$ is described, and its catalytic activity towards the polymerisation of phenyl acetylene is also discussed.

A previous study describes the trimerisation of MeC_2Ph by using the molybdenum(II) bis(phenylpropyne) complex, $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]$ in the presence of $P(O^iPr)_3$, gives 1,3,4-trimethyl-2,5,6-triphenylbenzene,[156] which has been crystallographically characterised. The diiodide complexes, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) catalyse the polymerisation of phenylacetylene. These reactions go *via* the bis (phenylacetylene) complex, $[MI_2(CO)(NCMe)(\eta^2\text{-}HC_2Ph)_2]$, which was crystallographically characterised for M = W (see Fig.5.7)[236].

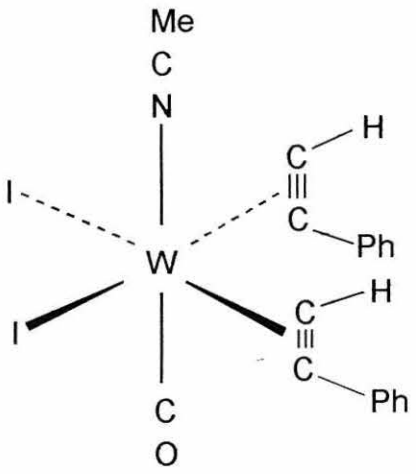


Fig. 5.7-Structure of [$WI_2(CO)(NCMe)(\eta^2\text{-}HC_2Ph)_2$]

In this section, preliminary studies of the polymerisation of HC_2Ph by using [$WCl_2(CO)_3(NCMe)_2$] is briefly discussed. The complex [$WCl_2(CO)_3(NCMe)_2$] was reacted with an excess of phenylacetylene to give orange to red polyphenylacetylene (PPA) in high yield (65%).

It has been shown that the dichloro complex is the most reactive , whereas the diiodo complex is the least reactive. Buzar *et al*[237] observed that the amount of dimers of Phenylacetylene such as dimer of phenylacetylene(dpha) and $(pa)_2$\{$(pa)_2$ = 1*H*-indene-1-Phenylmethylene)-from GC/MS results\} are higher than when using the tungsten dimers, such as [\{$W(\mu\text{-}Cl)Cl(CO)_4$\}$_2$]. In my research, significant amounts of these materials were found. The PPA which we observed in this reaction varies from orange to dark red, air-stable and completely soluble in chlorinated solvents such as CH_2Cl_2, $CHCl_3$ and aromatic hydrocarbons.

The structure was determined by studying IR and ^1H NMR spectra of the polymers. ^1H NMR shows peak at 6.9-7.3 ppm for the phenyl groups, which is very broad and shows a single resonance at $\delta = 2.7$ ppm for hydrogen atom which is coordinated with C=C. The structure was shown to be the *cis*-isomer, as there is a strong band at 740 cm^{-1} in the IR spectrum of high intensity which can be ascribed to the *cis*-isomer[235].

The mechanism of these polymerisation reactions almost certainly involves initial coordination of the alkynes to $[WCl_2(CO)_3(NCMe)_2]$ in a two step process, to eventually give the complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}HC_2Ph)_2]$. It is likely the two alkynes couple to give a metallocyclopentadiene intermediate. This metallocycle could insert an alkyne into a W-C bond to give a seven-membered ring, which could decompose to give the trimer, triphenylbenzene.

The diphenylbutadiene and triphenylbenzenes (1,3,5 and 1,2,4-tpb) detected by GS-MS in the residue obtained after separating the PPA with MeOH, also gives evidence for the formation of metallocyclopentadiene and metallocycloheptatrienes. Further studies of the catalytic activity of the complex $[WCl_2(CO)_3(NCMe)_2]$, and its derivatives in a wide range of catalytic reactions would be an interesting study for further work as described in Chapter Seven of this thesis.

Table 5.1-Physical and analytical data[a] for the chloro carbonyl 3-hexyne tungsten complexes80-97:-

Complex	Colour	Yield%	C%	H%	N%
(80) $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$	Green	39	27.2	3.6	1.0
			(36.9)	(4.7)	(2.8)
(81) $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$	Green	64	54.3	4.9	2.6
			(53.8)	(5.1)	(2.0)
(82) $[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Et)_2].CH_2Cl_2$	Green	48	47.9	4.4	-
			(48.3)	(4.7)	
(83) $[WCl_2(CO)(L^{Mo})(\eta^2\text{-}EtC_2Et)_2]$	Brown	39	45.1	4.7	-
$L^{Mo} = [MoI_2(CO)_3\{MeC(CH_2PPh_2)\text{-}P,P'\}]$			(45.4)	(4.0)	
(84) $[WCl_2(CO)(L^{w})(\eta^2\text{-}EtC_2Et)_2]$	Green	62	42.3	3.7	-
$L^{W} = [WI_2(CO)_3\{MeC(CH_2PPh_2)\text{-}P,P'\}]$			(42.9)	(3.7)	
(85) $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$	Green	41	58.9	4.5	-
			(58.1)	(4.5)	
(86) $[WCl_2(CO)(L^{Mo})_2(\eta^2\text{-}EtC_2Et)]$	Brown	79	46.6	4.3	-
			(45.9)	(3.6)	
(87) $[WCl_2(CO)(L^{w})_2(\eta^2\text{-}EtC_2Et)]$	Green	30	42.4	3.7	-
			(42.9)	(3.3)	

(88) $[WCl_2(CO)(dppm)(\eta^2\text{-}EtC_2Et)]$	Green	53	50.9	4.6	-
			(51.2)	(4.3)	
(89) $[WCl_2(CO)(dppp)(\eta^2\text{-}EtC_2Et)].Et_2O$	Green	36	53.5	5.0	-
			(53.6)	(5.4)	
(90) $[WCl_2(CO)(dppb)(\eta^2\text{-}EtC_2Et)]$	Green	17	49.1	5.0	-
			(49.3)	(4.6)	
(91) $[WCl_2(CO)(dpph)(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$	Green	17	51.0	5.0	-
			(50.5)	(4.9)	
(92) $[WCl_2(CO)(cis\text{-}dppethy)(\eta^2\text{-}EtC_2Et)]$	Green	80	52.9	4.8	-
			(52.1)	(4.2)	
(93) $[WCl_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)].$	Green	63	30.7	5.4	-
$.CH_2Cl_2$			(31.1)	(5.5)	
(94) $[WCl_2(CO)\{P(OPr^i)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Green	69	39.3	6.4	-
			(38.4)	(6.7)	
(95) $[WCl(CO)(2,2\text{'-}bipyridyl)(\eta^2\text{-}$	Green	49	42.1	4.4	4.9
$(\eta^2\text{-}EtC_2Et)_2]Cl$			(42.4)	(4.7)	(4.7)
(96) $[WCl(CO)(S_2CNMe_2)(\eta^2\text{-}Et\text{-}$	Green	39	31.3	4.3	2.2
$\text{-}C_2Et)_2].CH_2Cl_2$			(31.7)	(4.9)	(3.8)
(97) $[WCl(CO)(S_2CNEt_2)(\eta^2\text{-}EtC_2Et)_2]$	Green	58	36.3	5.1	2.4
			(36.5)	(5.5)	(3.4)

[a] **Calculated values in Parenthesis**

Table 5.2-Infrared data[a] for the chloro carbonyl 3-hexyne tungsten complexes 80-97

Complex	ν(C≡O)(cm^{-1})	ν(C≡C)(cm^{-1})	ν(C≡N)(cm^{-1})
(80)	2079 s	1630 w	2305 w
(81)	2081 s	1587 w	-
(82)	2064 s	1644 w	-
(83)	2075 s, 2044 s, 1970s, 1934 s, 1841 s	1619 w	-
(84)	2079 s, 2034 s, 1958 s, 1905 s	1609 w	-
(85)	1995 s	1640 w	-
(86)	2044 s, 1972 s, 1938 s, 1904s	1622 w	-
(87)	2038s, 1990 s, 1962 s, 1907 s, 1901 s	1625 w	-
(88)	1936 s	1601 w	-
(89)	1944 s	1604 w	-
(90)	1932 s	1636 w	-
(91)	1935 s	1635 w	-
(92)	1963 s	1602 w	-

(93)	1958 s	1621 w	-
(94)	1951 s	1641 w	-
(95)	2052 s	1605 w	-
(96)	2043 s	1605 w	-
(97)	2041 s	1646 w	-

[a]Spectra recorded in $CHCl_3$ as thin films between NaCl plates. s = strong, m = medium, w = weak.

Table 5.3-^{1}H NMR data[a] for the chloro carbonyl 3-hexyne tungsten complexes 80-97 :-

Complex	^{1}H NMR (δ, ppm)
(80)	3.6-3.2(q, 8H, 4CH_2, hexyne), 2.6(s, 3H, 1CH_3CN), 1.3(t, 12H, 4CH_3, hexyne).
(81)	7.4-6.9(m, 15H, 3Ph), 3.5-3.2(q, 8H, 4CH_2, hexyne), 1.3(t, 12H, 4CH_3, hexyne).
(82)	7.7-7.1(m, 15H, 3Ph); 5.3(s, 2H, 1CH_2Cl_2); 3.6-3.1(mq, 8H, 4CH_2, hexyne); 1.3(t, 6H, 2CH_3, hexyne); 0.9(t, 6H, 2CH_3, hexyne).
(83)	7.7-7.0(m, 30H, 6Ph); 3.5-3.0(q, 8H, 4CH_2, hexyne); 2.5-2.0 (s, 6H, 3CH_2 tripodal triphos); 1.2(t, 12H, 4CH_3, hexyne); 0.9(s, 3H, 1CH_3, tripodal triphos).
(84)	7.7-7.1(m, 30H, 4Ph), 3.6-3(q, 4H, 2CH_2, hexyne), 2.7-2.2(m, 6H, 3CH_2, tripodal triphos), 1.3(s, 3H, CH_3, tripodal triphos), 0.9(t, 6H, 2CH_3, hexyne).
(85)	7.6-7.2(m, 30H, 6Ph), 3.3(q, 4H, 2CH_2, hexyne), 1.1(t, 6H, 2CH_3, hexyne).
(86)	7.8-6.9(m, 60H, 12Ph); 3.5-3.0(q, 4H, 2CH_2, hexyne); 2.5-2.0 (s, 12H, 6CH_2, tripodal triphos); 1.2(t, 6H, 2CH_3, hexyne); 0.9(s, 6H, 2CH_3, tripodal triphos).

(87)	8.0-7.1(m, 60H, 12Ph); 3.6-3.2(q, 4H, 2CH$_2$, hexyne); 2.3-2.0 (m, 12H, 6CH$_2$, tripodal triphos); 1.3(t, 6H, 2CH$_3$, hexyne); 0.9(s, 6H, 2CH$_3$, tripodal triphos).
(88)	7.6-7.0(m, 20H, 4Ph), 4.8(m, 2H, 1CH$_2$, dppm), 3.6(q, 4H, 2CH$_2$, hexyne), 1.1(t, 6H, 2CH$_3$, hexyne).
(89)	7.5-7.0(m, 20H, 4Ph), 3.4(q, 4H, 2CH$_2$, ether), 3.3(q, 4H, 2CH$_2$, hexyne), 2.3(t, 2H, CH$_2$-, propane), 2.2(t, 2H, CH$_2$-, propane), 1.9(m, 2H, -CH$_2$-, propane), 1.1(t, 6H, 2CH$_3$, hexyne), 0.9(t, 6H, 2CH$_3$, ether).
(90)	7.7-6.9(m, 20H, 4Ph), 3.3-2.7(m, 4H, 2CH$_2$, hexyne), 2.3(t, 4H, 2CH$_2$-, PPh$_2$-dppb), 1.3(s, 4H, 2-CH$_2$-, dppb), 0.9(t, 6H, 2CH$_3$, hexyne).
(91)	7.7-7.0(m, 20H, 4Ph), 3.6-3.2(q, 4H, 2CH$_2$, hexyne), 2.3(br, 4H, 2CH$_2$-, PPh$_2$-dpph), 1.4(br, 8H, 4-CH$_2$-, dpph), 0.9(t, 6H, 2CH$_3$, hexyne).
(92)	7.8-7.1(m, 20H, 4Ph), 3.6(q, 4H, 2CH$_2$, hexyne), 3.3-3.0(md, 2H, CH=CH), 1.2(t, 6H, 2CH$_3$, hexyne).
(93)	4.2-3.9(dq, 12H, 6CH$_2$, P(OEt)$_3$); 5.3(s, 2H, CH$_2$Cl$_2$); 3.7-3.5 (q, 4H, 2CH$_2$, hexyne); 1.9-1.2(dt, 18H, 6CH$_3$, P(OEt)$_3$); 1.1 (t, 6H, 2CH$_3$, hexyne).

(94)	4.8-4.5(m, 6H, 6CH, isopropyl); 3.8-3.4(q, 4H, $2CH_2$, hexyne); 1.5-1.1(md, 36H, $12CH_3$, isopropyl); 1.2(t, 6H, $2CH_3$, hexyne).
(95)	9.0-7.4(m, 8H, 2,2'-dipyridyl), 3.7(mq, 8H, $4CH_2$, hexyne), 1.2(t, 12H, $4CH_3$, hexyne).
(96)	5.3(s, 2H, CH_2Cl_2); 3.6-3.3(q, 8H, $4CH_2$, hexyne); 3.1(s, 6H, $2CH_3$, $(Me)_2$-NCS_2); 1.3-1.1(t, 12H, $4CH_3$, hexyne).
(97)	4.0-3.7(q, 4H, $2CH_2$, $(Et)_2$-NCS_2); 3.6-3.4(q, 8H, $4CH_2$, hexyne); 1.5-1.3(t, 6H, $2CH_3$, $(Et)_2$-NCS_2); 1.3-1.1(t, 12H, $4CH_3$, hexyne).

[a]Spectra recorded in $CDCl_3$ (+25) and referenced to $SiMe_4$, s = singlet, br = broad, d = doublet, m = multiplet.

Table 5.4-$^{31}P\{^1H\}$ NMR data^a(δ) for selected chloro carbonyl 3-hexyne tungsten complexes 80-97 :-

Complex	^{31}P (δ) ppm
(82)	δ = -25.33 (s, 1P, PPh_3).
(83)	δ =17.59 (s, 2P, L^{Mo}) and 23.60(s, 1P, Ph_2P-W).
(85)	δ = -9.71 (s, 2P *trans*, PPh_3).
(86)	δ = 17.58 (s, 2P, L^{Mo}) and 30.76(s, 1P, Ph_2P-W).
(88)	δ = -23.99 and -23.57 (d, $J_{P\text{-}P}$ = 41.72 Hz, 2P of dppm).
(89)	δ = -18.13 and -17.62 (d, $J_{P\text{-}P}$ = 52.22 Hz, 2P of dppp).
(90)	δ = -10.39, -16.77 (d, $J_{P\text{-}P}$ = 55.89 Hz, 2P of dppb).
(91)	δ = -16.84, -10.27 (d, $J_{P\text{-}P}$ = 66.54 Hz, 2P of dpph).
(92)	δ = -23.83, -2.79 (d, $J_{P\text{-}P}$ = 59.83 Hz, 2P of *cis* dppeth).
(93)	δ = 100.40 (s, *trans*), and δ = 107.26(d, *cis*) and 107.83 (d, *cis*) ($J_{P\text{-}P}$ = 57.72 Hz)(ratio ≅40:60).
(94)	δ = 94.80, (s, 2P, *trans*) ($J_{W\text{-}P}$ = 194.75 Hz).

^{a}Spectra recorded in $CDCl_3$ (+25 °C) and referenced to 85% H_3PO_4

Table 5.5-^{13}C NMR data[a] (δ) for selected chloro carbonyl 3-hexyne tungsten complexes 80-97[a]

Complex	^{13}C (δ) ppm
(80)	9.50(s, MeCN), 13.896(s, CH_3, hexyne), 28.99, 29.8(s, CH_2 hexyne), 129.5(s, $C\equiv N$), 162.43, 167.50(s, $C\equiv C$), 193.573(s, $C\equiv O$).
(81)	13.84(s, $4CH_3$, hexyne), 28.957(s, $4CH_2$, hexyne), 122.68, 124.15, 129.184(s, 3Ph), 147.84(s, $C\equiv N$), 162.30, 168.98(s, $C\equiv C$), 194.4(s, $C\equiv O$).
(85)	11.96(s, $2CH_3$, hexyne), 31.94(s, $2CH_2$, hexyne), 128.19, 128.35, 128.85, 130.0, 130.81, 132.18, 133.51, 133.66, 134.64(s, 6Ph), 216.5(s, $C\equiv O$).
(95)	14.06, 14.48, 14.87(s, $4CH_3$, hexyne), 27.92, 29.8, 33.72, 35.21(s, $4CH_2$, hexyne),122.49, 125.15, 126.48, 128.49, 139.27, 139.60, 142.64, 148.01, 150.51, 152.04, 153.34 (s, 2,2'-dipyridyl), 164.23, 168.98(s, $C\equiv C$), 189.30(s, $C\equiv O$).

[a]Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$. s = singlet, br = broad, d = doublet, m = multiplet.

CHAPTER SIX

EXPERIMENTAL

FOR CHAPTERS TWO TO FIVE.

CHAPTER SIX

EXPERIMENTAL FOR CHAPTER TWO TO FIVE

6.1-General Procedures :-

The preparation and purification of the complexes were carried out in an atmosphere of dry nitrogen using vacuum/Schlenk-line techniques. Dichloromethane was dried over P_2O_5 and distilled before use. The complexes, $[MI_2(CO)_3(NCMe)_2]$(M = Mo and W) were prepared according to literature methods[75] and $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4(2-R)]$(X = Cl or Br and R = H or CH_3; X = Cl or Br and R = H or CH_3)[104] were prepared by published methods. All chemicals used during the course of the research described in this thesis were purchased from commercial sources, 1,1,1-tris(triphenylphosphinomethane) ethane $\{MeC(CH_2PPh_2)_3\}$. Elemental Analysis (C, H, and N) were recorded on a Carlo Elemental Analyser MOD 1108 (Using helium as carrier gas) by Glyn Connolly or Jane Davies of the Department of Chemistry , University of Wales , Bangor. Infrared spectra were recorded on a Perkin-Elmer 1000 series FT Infrared spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker 250 AC NMR spectrometer by Eric. Lewis of the Department of Chemistry , University of Wales, Bangor. Spectra were generally recorded in $CDCl_3$ (+25), and referenced to $SiMe_4$ for ^1H and ^{13}C NMR, and 85% H_3PO_4 for ^{31}P NMR spectra. Crystallographic data were collected at 120K, on a FAST TV Area diffractometer following previously described procedures. The crystal structures of **4, 8, 13, 24** and **32** were determined by Professor Michael G. B. Drew, University of Reading and the structure [$MoI_2(CO)(2,2'$-bipy)(η^2-EtC_2Et)] (**12**) by Professor Michael B. Hursthouse, University of Southampton,

Southampton. Data for crystal structures determined by Professor Drew were collected at 293(2) K with Mo-Kα radiation (λ 0.71073 A^0) using the MAR-research Image Plate System. The default measurement and refinement procedure is presented first while variations for specific compounds are reported later. Each crystal was positioned 70 mm from the Image Plate. Ninety five frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program[238]. The structures were solved using direct methods with the SHELXS 86 program. The non-hydrogen atoms were refined with anisotopic thermal parameters[239]. Hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. Absorption corrections were carried out using the DIFABS program[240]. The structures were then refined using SHELXL[241]. All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading.

Data for crystal structure of complex, [$MoI_2(CO)(2,2'$-bipy)(η^2-EtC_2Et)](**12**) determined by Professor M. B. Hursthouse at Southampton University, and crystals were obtained by cooling (-17 °C) a concentrated CH_2Cl_2/Et_2O solution of **12** for 24hr. All measurements were made on a Delft Instruments FAST area detector diffractometer positioned at the window of a rotating anode generator with Mo-Kα radiation by following the procedures. The cell parameters were determined by least-squares refinement of the diffractometer angles for 250 reflections. The data were corrected for absorption effects (DIFABS). The structure was solved by direct methods (SHELXS-86) and refined by full- matrix least-squares on F^2 using all unique data with $F_o^2>0$ (SHELXL-93). The nonhydrogen atoms were refined with anisotropic temperature factors.

6.2-Experimental for Chapter Two :-

Preparation of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(1)

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.50gm, 0.968mmol) in 20ml of CH_2Cl_2 at 0 °C was added 3-hexyne (0.218ml, 0.158gm, 1.926mmol). The solution was slowly allowed to return to room temperature. Filtration and removal of solvent *in vacuo* gave a brown crystalline powder, which was recrystallised from dichloromethane and diethyl ether, giving pure $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**1**).(Yield of the product = 0.318g, 56%) For physical and analytical data see table 2.1.

Preparation of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(2)

To a solution of $[WI_2(CO)_3(NCMe)_2]$ (0.50gm, 0.827mmol) in 15ml of CH_2Cl_2 at 0 °C was added 3-hexyne(0.135gm, 1.6 mmol, 0.1867ml). The solution was allowed to return to room temperature after 2h, and was filtered after a further 15h. The solvent was removed *in vacuo* to give a yellow powder that was dissolved in the minimum quantity of CH_2Cl_2. A few drops of Et_2O added, and the solution was was cooled to -20 °C for 24h to give analytically pure yellow crystals of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**2**). (Yield of the product = 0.435g, 79%). For physical and analytical data see table 2.1.

Preparation of [$WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$](4).

To a stirred solution of [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] (0.50gm, 0.745mmol) in CH_2Cl_2 (20 cm^3) was added PPh_3 (0.39g, 1.48mmol). Filtration and removal of solvent *in vacuo* after 48h yielded a dark green crystalline powder, which was recrystallised from CH_2Cl_2 /Et_2O to give pure [$WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$](4). (Yield of product = 0.76g, 95.2%).

Similar reactions of [$MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gave the complex, [$MoI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$](**3**).

Preparation of [$WI_2(CO)(dppm)(\eta^2\text{-}EtC_2Et)$](6)

To a stirred solution of [$WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] (0.50g, 0.745mmol) in CH_2Cl_2 (15 cm^3) was added $Ph_2P(CH_2)PPh_2$ (0.286gm, 0.745mmol). After 24h filtration and removal of solvent *in vacuo* gave a green crystalline powder which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O, and cooled to -30 $^{\circ}C$ for 24h. This afforded analytically pure crystals of [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}EtC_2Et)$](**6**) (Yield of product = 0.61g , 87.89%).

Similar reactions of [$MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$](M = Mo or W) with one equivalent of L^L in CH_2Cl_2 at room temperature gave the complexes, [$MI_2(CO)(L\text{^}L)(\eta^2\text{-}EtC_2Et)$] {M = W, L^L = dppm(**5**); M = W, L = dppe (**7**), dppp(**8**), dppb (**9**), dpppen (**10**), dpph (**11**)}

Preparation of [$MoI_2(CO)(2,2'$-bipy)(η^2-EtC_2Et)](12)

To a stirred solution of [$MoI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (0.25g, 0.31mmol) in CH_2Cl_2 (15 cm^3) was added 2,2-bipyridyl (0.05gm, 0.32mmol). After 24h filtration and removal of solvent *in vacuo* gave a brown crystalline powder which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O, and cooled to -17 °C for 24h. This afforded analytically pure crystals of [$MoI_2(CO)(2,2'$-bipy)(η^2-EtC_2Et)](**12**) (Yield of product = 0.11g, 58.2%). Single crystals for X-ray analysis of **12** were grown from by CH_2Cl_2/Et_2O.

6.3-Experimental for Chapter Three :-

[$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2$-$EtC_2Et)$].(13)

To a stirred solution of [$MoI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (0.25g, 0.43mmol) in diethyl ether (20 cm^3) was added one equivalent of triphenylphosphite $P(OPh)_3$ (0.13g, 0.42 mmol, 0.11 ml). After 24hr, filtration and removal of solvent *in vacuo* gave the brown product, [$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2$-$EtC_2Et)$](**13**), which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to give small crystals of the product, suitable for X-ray crystallography. (Yield of pure product 0.29g, 84%)

A similar reaction of [$MoI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] with one equivalent of triisopropyl phosphite in diethyl ether at room temperature gave the complex, [$MoI_2(CO)(NCMe)$ $\{P(O^iPr)_3\}(\eta^2$-$EtC_2Et)$](**14**). For physical and analytical data see table 3.1.

Preparation of [$WI_2(CO)\{P(OMe)_3\}(\eta^2$-$EtC_2Et)_2$](15):-

To a stirred solution of [$WI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (0.25g, 0.37mmol) in diethyl ether (20 cm^3) was added trimethylphosphite, $P(OMe)_3$ (0.046g, 0.37 mmol, 0.044 ml), After 24hr filtration and removal of solvent *in vacuo*, gave an oily green product of

$[WI_2(CO)\{P(OMe)_3\}(\eta^2\text{-}EtC_2Et)_2]$, which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to gave small crystals of the pure product. (Yield of pure product 0.22g, 79%).

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $P(OR)_3$, {R= ^{i}Pr **(16)** and Ph **(17)**} in diethyl ether at room temperature gave the complexes $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$**(16)** and **(17)**. For physical and analytical data see table 3.1.

Preparation of $[MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$(18)

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.25g, 0.43mmol) in CH_2Cl_2 (20 cm^3) was added $P(OPh)_3$ (0.13g, 0.11ml, 0.43 mmol), and CO was bubble through the solution for 30 minutes. After 24hr filtration and removal of solvent *in vacuo* to gave an oily brown product of $[MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$**(18)**, and after repeated recrystallisation it was not possible to obtain satisfactory elemental analysis data for the product, which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to gave small crystals of the product, but due to sensitivity it was not possible to obtain satisfactory elemental analysis. (Yield of product 0.16g, 42%).

Preparation of $[MoI_2(CO)(PPh_3)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$. CH_2Cl_2 (19)

To a stirred solution of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (0.25g, 0.30 mmol) in CH_2Cl_2 (20 cm^3) was added PPh_3 (0.08g, 0.31 mmol). After 24hr filtration and removal of solvent *in vacuo* gave the brown product $[MoI_2(CO)(PPh_3)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$ **(19)**, which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to give small crystals of the product, (Yield of pure product 0.18g, 57%).

A similar reactions of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ with one equivalent of $P(O^iPr)_3$ in CH_2Cl_2 at room temperature and recrystallization by CH_2Cl_2/Et_2O gave the complex $[MoI_2(CO)\{P(O^iPr)_3\}\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)].Et_2O$ (**20**). For physical and analytical data see table 3.1.

Preparation of $[MoI_2(CO)L^{Mo}\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$(21)

$\{L^{Mo} = MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}\}$

To a stirred solution of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (0.18 g, 0.25 mmol) in CH_2Cl_2 (20 cm^3) was added at 0 °C $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (0.23g, 0.22 mmol), after 48hr filtration and removal of solvent *in vacuo* gave the brown product $[MoI_2(CO)(L^{Mo})\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$(**21**), which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to give small crystals of the product. (Yield of pure product = 0.25g, 62%).

Similar reactions of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of L $\{L^W = [WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]\}$ in CH_2Cl_2 at room temperature gave the complex, $[MoI_2(CO)(L^W)\{P(O\text{-}Ph)_3\}(\eta^2\text{-}EtC_2Et)]$(**22**). For physical and analytical data see table 3.1.

Preparation of $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$(24) :-

To a stirred solution of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (0.25g, 0.31 mmol) in CH_2Cl_2 (20 cm^3) was added dppe $\{Ph_2P(CH_2)_2PPh_2\}$ (0.12g, 0.30 mmol). After 3hrs filtration and removal of solvent *in vacuo* gave the green product $[MoI_2(CO)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Et)]$(**24**), which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to gave small crystals of the product, suitable for X-ray crystallographically. (Yield of pure product = 0.24g, 92%).

In a similar reaction of equimolar quantities of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ and 2,2'-bipyridyl in CH_2Cl_2 to gave the complex, $[MoI_2(CO)(2,2'\text{-bipy})(\eta^2\text{-}EtC_2Et)]$(**23**). See table 3.1 for physical and analytical data.

Preparation of $[MoI(CO)\{P(OPh)_3\}(S_2CNMe_2)(\eta^2\text{-}EtC_2Et)]$(25) :-

To a stirred solution of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (0.3g, 0.37 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was added of dimethyl dithiocarbamic acid, sodium salt dihydrate (0.07g, 0.39 mmol). After 24hr filtration and removal of solvent *in vacuo* gave the oily green product of $[MoI(CO)(S_2CNMe_2)\{P(OPh)_3(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$.(**25**), which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to gave small crystals of the product. (Yield of pure product = 0.1g, 36%).

Similar reactions of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $(C_2H_5)_2NCS_2Na$ in CH_2Cl_2 at room temperature gave the complex $[MoI(CO)(S_2CNEt_2)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)].CH_2Cl_2$ (**26**). See table 3.1 for physical and analytical data.

Preparation of $[MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)]$(27)

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.25g, 0.43 mmol) in diethyl ether (20 cm^3) at room temperature was added two equivalent of trimethylphosphite, $P(OMe)_3$ (0.11g, 0.86 mmol, 0.11 ml). After 24hr filtration and removal of solvent *in vacuo* gave the oily brown product of $[MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**27**), which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O and cooled to -17 °C for 24hr to gave small crystals of the product. (Yield of pure product = 0.24g, 78%)

Similar reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with $P(OR)_3$ {M = Mo, R = Et(**29**), R = ^{i}Pr(**31**), R = Bu^t(**33**); M = W, R = Me(**28**), R = Et(**30**), R = ^{i}Pr(**32**), R = Bu^t(**34**); R = Ph(**35**)} in diethyl ether at room temperature gave the complexes, $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**28** to **35**). For physical and analytical data see table 3.1. Suitable single crystal of the bis$\{P(O^iPr)_3\}$ complexes, $[MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$(**31** and **32**) were grown by cooling concentrated diethyl ether solution of **31** and **32** to -17 °C for 24hr.

6.4a- Experimental for Chapter four (Part I) :-

Preparation of $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(36):-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.50g , 0.97mmol) in CH_2Cl_2 (20 cm^3) at 0°C was added 1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$ (0.607g, 0.97 mmol). After stirring for 5 minutes, filtration and removal of solvent *in vacuo*, gave the brown crystalline powder of $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\}\text{-}P,P'\}]$(**36**), which was recrystalised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.82g, 79.7%).

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with one equivalent of L{L = 1,1,1-tris (diphenylphosphinomethyl)ethane} in CH_2Cl_2 at room temperature gave the complex, $[WI_2(CO)_3\{Me\ C(CH_2PPh_2)_3\text{-}P,P'\}]$(**37**). For physical and analytical data see table 4.1.1.

Preparation of $[MoI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$(38) :-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$(0.25g , 0.48mmol) in refluxing $CHCl_3$ (20 cm^3) at 60°C was added 1,1,1-tris(diphenylphosphinomethyl)ethane (0.30g, 0.48 mmol). After refluxing 15 hr, filtration and removal of solvent *in vacuo*, gave the brown crystalline powder $[MoI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$**(38)**, Which was recrystallised from $CHCl_3/Et_2O$ at -17°C. (Yield of pure product = 0.33g, 66.0%).

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with one equivalent of L{L= 1,1,1-tris (diphenylphosphinomethyl)ethane in refluxing $CHCl_3$ at 60°C, for 72 hours gave mainly the dicarbonyl complex, $[WI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$**(39)**. For physical and analytical data see table 4.1.1.

Preparation of $[MoI_2(CO)_3[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\}\text{-}P,P']_2]$(40) :-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.15g , 0.26 mmol) in CH_2Cl_2 (20 cm^3) at 0°C was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (0.54g, 0.51 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder of $[MoI_2(CO)_3[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]_2]$, which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.65g, 87%).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of L $\{L = [MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]\{M = W, L = L^{Mo}$ or $L^W\}$; $\{M = Mo, L = L^W\}$ in CH_2Cl_2 at room temperature, after 24hr gave the complexes, $[MI_2(CO)_2(L^{Mo}$ or $L^W)_2]$.**(41-43)**. For physical and analytical data see table 4.1.1.

Preparation of $[MoI_2(CO)_3(PPh_3)][MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]]$(44) :-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.3g , 0.58 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was firstly added triphenylphosphine (0.15g, 0.57 mmol), and left to stir for one minute. To this was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (0.62g, 0.58 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder of [MoI$_2$(CO)$_3$(PPh$_3$)[MoI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}]](**44**), which was recrystallised from CH$_2$Cl$_2$/Et$_2$O at -17 °C. (Yield of pure product = 0.92g, 90.2%).

Similar reactions of [MI$_2$(CO)$_3$(NCMe)$_2$] firstly, stirring with one equivalent of L, in CH$_2$Cl$_2$ at room temperature and then followed by (L = L^W or L^{Mo}) {M = Mo, L = L^{Mo}), R= AsPh$_3$ (**45**), R = SbPh$_3$ (**46**), {M = W, L = L^W, R = PPh$_3$ (**47**), R = AsPh$_3$ (**48**), R = SbPh$_3$ (**49**), R = P(OMe)$_3$ (**50**), R = P(OMe)$_3$ (**51**), R = P(OPh)$_3$ (**52**), and after 24hr gave the complexes, [MI$_2$(CO)$_3$(R)(L^{Mo} or L^W)]. (**45-52**). For physical and analytical data see table 4.1.1.

Preparation of [MoI(CO)$_3$(Ph$_2$P(CH$_2$)PPh$_2$)[MoI$_2$(CO)$_3$ {MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}]I(53) :-

To a stirred solution of [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.2g , 0.39 mmol) in CH$_2$Cl$_2$ (20 cm^3) at room temperature was firstly added dppm (0.15g, 0.39 mmol) and left to stir for 20 minutes. To this solution was added [MoI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}] (0.41g , 0.38 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder of [MoI$_2$(CO)$_3${Ph$_2$P(CH$_2$)PPh$_2$}[MoI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}](**53**), which was recrystallised from CH$_2$Cl$_2$/Et$_2$O at -17°C. (Yield of pure product = 0.47g, 64.4%).

Similar reactions of [MI$_2$(CO)$_3$(NCMe)$_2$], firstly, stirring with one equivalent of Ph$_2$P(CH$_2$)$_n$PPh$_2$ followed by (L = L^W or L^{Mo}) {M = W, L = L^W), n = 1(**54**), n = 2(**56**); {M = Mo, L = L^{Mo}, n = 2(**55**)} in CH$_2$Cl$_2$ at room temperature and after 24 hr gave the complexes, [MI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_n$PPh$_2$}(L^{Mo} or L^W)](n = 1 or 2)(**54-56**). For physical and analytical data see table 4.1.1.

Preparation of $[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}](\eta^2\text{-}EtC_2Et)_2]$(57) :-

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.25g ,0.43 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (0.45g, 0.42 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder $[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}](\eta^2\text{-}EtC_2Et)_2]$(**57**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.42g, 65%),

A similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of L^W in CH_2Cl_2 gives $[WI_2(CO)(L^W)(\eta^2\text{-}EtC_2Et)_2]$(**58**). For physical and analytical data see table 4.1.1.

Preparation of $[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]_2(\eta^2\text{-}EtC_2Et)]$(60) :-

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.125g ,0.21 mmol) in CH_2Cl_2 (20 cm^3) at 0°C was added two equivalents of $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (0.45g, 0.42 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder $[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2\ PPh_2)_3\text{-}P,P'\}_2](\eta^2\text{-}EtC_2Et)]$ (**59**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.45g, 73%).

A similar reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with two equivalents of L^W in CH_2Cl_2 gives $[WI_2(CO)(L^W)_2(\eta^2\text{-}EtC_2Et)]$(**60**). For physical and analytical data see table 4.1.1.

6.4b-Experimental for Chapter Four (Part II) :-

Preparation of [{Mo(μ-Cl)(CO)$_2$(L^{Mo})(η^3-C$_3$H$_5$)}$_2$](61):-

To a stirred solution of [MoCl(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_5$)] (0.08g, 0.32 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added [MoI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}](L^{Mo}) (0.3g, 0.26 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green crystalline powder [{Mo(μ-Cl)(CO)$_2$(L^{Mo})(η^3-C$_3$H$_5$)}$_2$]**(61)**, which was recrystallised from CH$_2$Cl$_2$/Et$_2$O at -17 °C. (Yield of pure product = 0.22g, 54%).

Similar reactions of [MoX(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_4$R)] (X = Cl and Br) with one equivalent of L {L = [MI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}] in CH$_2$Cl$_2$ at room temperature gave the complexes [{Mo(μ-X)(CO)$_2$(L^{Mo} or L^{w})(η^3-C$_3$H$_4$R)}$_2$] {X = Cl, R = H, L^{w} **(62)**; R = Me, L^{Mo}**(63)**; L^{w} **(64)**}; {X = Br, R = H, L^{Mo}**(65)**, L^{W}**(66)**}. For physical and analytical data see table 4.2.1.

Preparation of [MoCl(CO)$_2$(L^{Mo})$_2$(η^3-C$_3$H$_5$)](67):-

To a stirred solution of [MoCl(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_5$)] (0.05g, 0.16 mmol) in CH$_2$Cl$_2$ (25cm^3) at 0°C was added [MoI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}](0.34g, 0.32 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green crystalline powder [MoCl(CO)$_2$(L^{Mo})$_2$(η^3-C$_3$H$_5$)]**(67)**, which was recrystallised from CH$_2$Cl$_2$/Et$_2$O at -17°C. (Yield of pure product = 0.24g, 64%).

Similar reactions of [MoX(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_4$R)] (X = Cl and Br) with two equivalents of L {L = [MI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-*P,P'*}] in CH$_2$Cl$_2$ at room temperature gave the complexes, [MoX (CO)$_2$(L^{Mo})$_2$(η^3-C$_3$H$_4$R)] {X= Cl, R = H, L^{w} **(68)**; R = Me,

L^{Mo}**(69)**; L^{w} **(70)**}; {X=Br, R = H, L^{Mo}**(71)**, L^{W}**(72)**}. For physical and analytical data see table 4.2.1.

Preparation of [Fe(CO)$_4$(L^{Mo})](73) :-

To a stirred solution of [$Fe_2(CO)_9$] (0.05g ,0.13 mmol) in CH_2Cl_2 (25cm^3) was added [$MoI_2(CO)_3${$MeC(CH_2PPh_2)_3$-*P,P'*}](0.3g, 0.28 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder [$Fe(CO)_4(L^{Mo})$]**(73)**, which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.08g, 45%).

A similar reaction of [$Fe_2(CO)_9$] with two equivalents of L {L = [$WI_2(CO)_3$ {MeC(CH$_2$ PPh$_2$)$_3$-*P,P'*}] in CH_2Cl_2 at room temperature gave the complex, [$Fe(CO)_4(L^{W})$] **(74)**. For physical and analytical data see table 4.2.1.

Preparation of [Fe(CO)$_2$(L^{Mo})(Cp]I (75) :-

To a stirred solution of [$FeI(CO)_2(\eta^5\text{-}C_5H_5)$] (0.05g ,0.16 mmol) in warm CH_2Cl_2 (25 cm^3) was added [$MoI_2(CO)_3${$MeC(CH_2PPh_2)_3$-*P,P'*}](0.17g , 0.16 mmol). Filtration and removal of solvent *in vacuo* after 24hr gave [$Fe(CO)_2(L^{Mo})(\eta^5\text{-}C_5H_5)$]I**(75)**, which was recrystallised from CH_2Cl_2/Et_2O (Yield of pure product = 0.07g, 32%).

A similar reaction of [$FeI(CO)_2(\eta^2\text{-}C_5H_4R)$] (R = H or Me) with one equivalent of L {L = [$MI_2(CO)_3${$MeC(CH_2PPh_2)_3$-*P,P'*}](M = Mo or W) in warm CH_2Cl_2 at room temperature gave the complex [$Fe(CO)_2$(L^{Mo} or L^{W})(η^2-C_5H_4R)]I, {R = H, L^{W} **(76)**; R = Me, L^{Mo} **(77)**, L^{W} **(78)**}. For physical and analytical data see table 4.2.1.

Preparation of $[Fe(CO)_2(L^W)(\eta^5\text{-}C_5H_5)][BPh_4]$(79) :-

To a stirred solution of $[Fe(CO)_2(L^W)(\eta^5\text{-}C_5H_5)]I$(0.05g, 0.43 mmol) in CH_2Cl_2 (25 cm^3) was added one equivalent of $Na[BPh_4]$ (0.012g, 0.42 mmol). Filtration and removal of solvent *in vacuo* after 24hr, gave the green complex, $[Fe(CO)_2(L^W)(\eta^5\text{-}C_5H_5)][BPh_4]$(**79**), which was recrystallised from CH_2Cl_2/Et_2O at -17 °C. (Yield of pure product = 0.02g, 35%).

6.5- Experimental for Chapter Five :-

Preparation of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(80) :-

To a stirred solution of $[WCl_2(CO)_3(NCMe)_2]$ {prepared in situ by reaction of $[WI_2(CO)_3(NCMe)_2]$ (0.5g, 0.82mmol) with two equivalents of NaCl(0.096g, 1.6 mmol)} (0.5g,1.2 mmol) in CH_2Cl_2 (25 cm^3) was added excess of EtC_2Et (0.19g , 0.27ml, 2.3mmol). Filtration and removal of solvent in vacuo after 24 hrs, gave the green oily product of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**80**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.23g, 39%).

Preparation of $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$(81) :-

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**80**) (0.2g, 0.41mmol) in CH_2Cl_2 (25 cm^3) was added NPh_3 (0.10g, 0.40 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, to gave the green powder $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$(**81**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.18g, 64%).

Similar reactions of [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] with one equivalent of L in CH_2Cl_2 at 0°C gave the complexes, [$WCl_2(CO)(L)(\eta^2\text{-}EtC_2Et)_2$] {L = PPh_3(**82**), L^{Mo}(**83**). L^W (**84**). For physical and analytical data see table 5.1.

Preparation of [$WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$](85) :-

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$](**80**) (0.1g, 0.20mmol) in CH_2Cl_2 (25 cm^3) was added two equivalents of PPh_3 (0.10g , 0.38 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder of [$WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)$](**85**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.08g, 41%).

Similar reactions of [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$](**80**) with two equivalents of L in CH_2Cl_2 at 0°C gave the complexes, [$WCl_2(CO)(L)_2(\eta^2\text{-}EtC_2Et)$] {L = L^{Mo}(**86**), L^W (**87**)}. For physical and analytical data see table 5.1.

Preparation of [$WCl_2(CO)(dppm)(\eta^2\text{-}EtC_2Et)$](88) :-

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$](**80**) (0.1g, 0.20mmol) in CH_2Cl_2 (25 cm^3) at room temperature was added $Ph_2P(CH_2)PPh_2$ (0.078g, 0.20 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder [$WCl_2(CO)$ $(dppm)(\eta^2\text{-}EtC_2Et)$](**88**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.09g, 53%).

Similar reactions of [$WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$](**80**) with one equivalent of L^L {L^L = $Ph_2P(CH_2)_nPPh_2$, n = 3(**89**), n = 4(**90**), n = 6(**91**), L^L = *cis*-$Ph_2PCH{=}CH\ PPh_2$ (**92**)} in CH_2Cl_2 at room temperature gave the complexes, [$WCl_2(CO)(L\text{^}L)(\eta^2\text{-}EtC_2Et)$]. For physical and analytical data see table 5.1.

Preparation of [$WCl_2(CO)\{P(OEt)_3\}_2(\eta^2$-$EtC_2Et)$](93) :-

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$](**80**) (0.1g, 0.20 mmol) in Et_2O (25 cm^3) was added $P(OEt)_3$ (0.068g, 0.07ml, 0.40 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder of [$WCl_2(CO)\{P(OEt)_3\}_2(\eta^2$-$EtC_2Et)$](**93**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.09g, 63%).

A similar reaction of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] with two equivalents of $P(O^iPr)_3$ in Et_2O at 0°C gave the complex, [$WCl_2(CO)\{P(O^iPr)_3\}_2(\eta^2$-$EtC_2Et)$](**94**). For physical and analytical data see table 5.1.

Preparation of [$WCl(CO)$(2,2'-bipyridyl)$(\eta^2$-$EtC_2Et)_2$]Cl(95) :-

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$](**80**)(0.15g, 0.30 mmol) in CH_2Cl_2 (25 cm^3) was added 2,2'-bipyridyl (0.045g , 0.28 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder of [$WCl(CO)$(2,2'-bipyridyl)$(\eta^2$-$EtC_2Et)_2$]Cl(**95**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.09g, 49%).

Preparation of [$WCl(CO)(S_2CNMe_2)(\eta^2$-$EtC_2Et)_2$](96) :-

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$](**80**) (0.15g, 0.30 mmol) in CH_2Cl_2 (25 cm^3) was added $NaS_2CNMe_2.3H_2O$ (0.023g, 0.3mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder [$WCl(CO)(S_2CNMe_2)$ $(\eta^2$-$EtC_2Et)_2$](**96**), which was recrystallised from CH_2Cl_2/Et_2O at -17°C. (Yield of pure product = 0.07g, 39%).

A similar reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**80**) with one equivalent of L = $NaS_2CNEt_2.3H_2O$ in CH_2Cl_2 at room temperature gave the complex, $[WCl(CO)(S_2CNEt_2)(\eta^2\text{-}EtC_2Et)_2]$(**97**). For physical and analytical data see table 5.1.

6.6- Experimental for Polymerisation of HC_2Ph(PA) :-

The toluene solution of PA(2g, 2.15ml, 0.0195mmol) and the internal standard (ortho-xylene) was added to the catalyst(0.118g, 0.19mmol) and the formation of PPA was monitored by gas chromatography. The reactions were continued for 24 hr and methanol was added to precipitate the polymer, which was collected, recrystallised from CH_2Cl_2/MeOH, dried in *vacuo* and analysed by IR and ^1H NMR spectroscopy(the yield of product = 1.3g, 65%). The filtrate which was obtained after precipitation of the various polymers was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 and then analysed by GC-MS. Analysis of the products showed that there were mainly diphenylbutadiene and triphenylbenzenes(very small amount of yield, 0.07g, 3.5% and 0.18g, 9% respectively).

CHAPTER SEVEN

CONCLUSIONS AND SCOPE FOR FURTHER WORK

Chapter Seven

Conclusions and Scope for Further Work

In conclusion, chapter two of this thesis described the preparation, characterisation and reactions of the 3-hexyne complexes, $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo and W). The crystal structures of the complexes, $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$**(4)** and $[WI_2(CO)\{PPh_2(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$**(8)** are also discussed.

Chapter three describes the reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with a wide range of phosphite ligands, $P(OR)_3$ (R = Me, Et, ${}^iPr$, ${}^nBu$ and Ph). The crystal structures of four complexes, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$**(13)**, $[MoI_2(CO)\{PPh_2(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Et)]$**(24)**, $[MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$**(31)** and $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$**(32)** were also described. The interesting complex, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$**(13)**, was reacted with a wide range of neutral and anionic donor ligands to give a series of new organomolybdenum complexes.

Chapter four is in two parts; the first part describes the reactions of $MeC(CH_2PPh_2)_3$ with the seven-coordinate complexes of molybdenum(II), and tungsten(II), $[MI_2(CO)_3(NCMe)_2]$ to give the complexes, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(**36** and **37**)(M = Mo and W respectively). The intramolecular reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ to give the dicarbonyl complexes $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ are described. The reactions of the organometallic phosphines, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(M = Mo, L^{Mo}; M = W, L^W) with a series of molybdenum(II) and tungsten(II) complexes is discussed. The second part of chapter four described the reactions of the π-allyl complexes, $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X = Cl or Br; R =

H or Me) with $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$(**36** and **37**)(M = Mo and W respectively) to give $[\{Mo(\mu\text{-}X)(CO)_2(L^{Mo}$ or $L^{W})(\eta^3\text{-}C_3H_4R)\}_2]$ or $[MoX(CO)_2(L^{Mo}$ or $L^{W})_2(\eta^3\text{-}C_3H_4R)]$, and reactions of the iron complexes $[Fe_2(CO)_9]$ and $[FeI(CO)_2(\eta^5\text{-}C_5H_5)]$ with L^{Mo} or L^{W} to give $[Fe(CO)_4(L^{Mo}$ or $L^{W})]$ or $[Fe(CO)_2(L^{Mo}$ or $L^{W})(\eta^5\text{-}C_5H_5)]I$, respectively.

Chapter five described the preparation of a series of dichloro and monochloro complexes of tungsten(II). For example, the synthesis and reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$(**80**) with a wide range of ligands is described. Finally, the catalytic activity of the seven-coordinate dichloro complex $[WCl_2(CO)_3(NCMe)_2]$ as a catalyst for the polymerisation of phenylacetylene has been studied.

Further work could be involve polymerisation of other alkynes by using seven-coordinate complexes of molybdenum(II) and tungsten(II) and their derivatives described in this thesis, as homogeneous catalysts. Using the methodology described in chapter five for preparing the dichloro complexes, $[WCl_2(CO)_3(NCMe)_2]$ a series of other different halide complexes could be prepared including fluoride complexes.

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APPENDIX

FOR CHAPTER TWO AND THREE

APPENDIX FOR CHAPTER TWO

Appendix for chapter Two

2.6a-Crystal data and structure refirement for 8 and 4.

		No.**8**	No.**4**
Formula		$[WI_2(CO)\{dppp\}(\eta^2$- -$EtC_2Et)]$	$[WI_2(CO)(PPh_3)_2(\eta^2$- -$EtC_2Et)]$
Empirical formula		$C_{35}H_{38}I_2OP_2W$	$C_{43}H_{40}I_2OP_2W$
Formula weight		1045.14	1072.34
Temperature (K)		293(2)	293(2)
Wavelength (Å)		0.71073	0.71073
Crystal system, space group		Monoclinic, P21/c	Orthorhombic P21/c
Cell dimension (Å °)	a	18.90 (2)	9.823 (9)
	b	9.632 (9)	16.378 (17)
	c	21.63 (2)	25.10 (3)
	β	107.98 (10)	(90)
Volume $Å^3$		3746 (7)	4039(7)

Z, Calculated density (Mgm^{-3})	4, 1.853	4, 1.764
Absorption coefficient (mm^{-1})	4.986	4.500
F (000)	2000	2064
Crystal size (mm)	0.25 * 0.30 * 0.30	0.15 *0.25 * 0.25
θ range for data collection (°)	2.40 to 25.93	2.42 to 25.94#
Index ranges	$0\le h\le 23$,	$0\le h\le 9$
	$-10\le k\le 10$,	$-19\le k\le 19$
	$-26\le l\le 25$	$-30\le l\le 30$
Reflections collected /unique	12362 / 6637	7410 / 5006
R (int)	0.0477	0.0615
Data / restraints / parameters	6637 / 0 / 391	5006 / 36 / 405
Final R indices [I>2σ(I)] R1	0.0504	0.0785
wR2	0.1227	0.1883
R indices (all data) R1	0.0717,	0.0911
wR2	0.1401	0.1959
Extinction coefficient	0.00018 (10)	0.00065 (10)
Largest diff. peak, hole (eÅ^{-3})	1.950, -1.843	4.124, -1.985

Table 2.6b-Crystal data and structure refinement for 12.

	No.**12**
Formula	[MoI$_2$(CO)(2,2'-dipyridyl)(η^2- -EtC$_2$Et)]
Empirical formula	$C_{17}H_{18}I_2ON_2Mo$
Formula weight	616.07
Temperature (K)	150(2) K
Wavelength (Å)	0.71073 A
Crystal system,	Monoclinic
space group	P21/c
Unit Cell dimension (A°)	a = 8.012 (2) A
	b = 16.760 (3) A
	c = 14.216 (3) A
	β = 95.28 (3) deg.
Volume Å3	1900.8 (7) A^3
Z	4

Calculated density (Mgm^{-3})	2.153 Mg/mm^{3}
Absorption coefficient (mm^{-1})	3.943 mm^-1
F (000)	1160
Crystal size (mm)	0.2 x 0.05 x 0.05 mm
Theta(θ) range for data collection (°)	2.43 to 30.49 deg.
Index ranges	$-11 \le h \le 11$, $-23 \le k \le 23$, $-19 \le l \le 20$.
Reflections collected /unique	30893
Independent reflections	5638 [R (int) = 0.0781]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5638 / 0 / 210
Goodness-of-fit on F^2	0.822
Final R indices [$I>2\sigma(I)$]	R1 = 0.0383, wR2 = 0.1010
R indices (all data)	R1 = 0.0562, wR2 = 0.1169
Largest diff. peak, hole (eÅ^{-3})	2.006 and -1.496 eÅ^{-3}.

Table 2.7a-Dimension in the Metal Coordination Spheres. Distances (Å), angles (°) :-

In complex No. (4) :-

W(1)-C(10)	1.93(2)
W(1)-C(200)	2.03(3)
W(1)-C(201)	2.03(3)
W(1)-P(1)	2.584(5)
W(1)-P(2)	2.599(6)
W(1)-I(2)	2.843(3)
W(1)-I(3)	2.900(3)
C(100)-W(1)-C(200)	110.2(11)
C(100)-W(1)-C(201)	72.9(11)
C(200)-W(1)-C(201)	37.3(11)
C(100)-W(1)-P(1)	91.9(7)
C(200)-W(1)-P(1)	95.3(6)
C(201)-W(1)-P(1)	98.6(7)

C(100)-W(1)-P(2)	89.2(7)
C(200)-W(1)-P(2)	95.3(6)
C(201)-W(1)-P(2)	92.9(7)
P(1)-W(1)-P(2)	168.2(2)
C(100)-W(1)-I(2)	71.9(8)
C(200)-W(1)-I(2)	177.9(8)
C(201)-W(1)-I(2)	144.8(8)
P(1)-W(1)-I(2)	84.34(15)
P(2)-W(1)-I(2)	84.88(15)
C(100)-W(1)-I(3)	162.9(8)
C(200)-W(1)-I(3)	87.0(8)
C(201)-W(1)-I(3)	124.2(8)
P(1)-W(1)-I(3)	85.91(15)
P(2)-W(1)-I(3)	89.57(16)
I(2)-W(1)-I(3)	90.95(7)

Table 2.7b-for Complex No. (8):

W(1)-C(100)	1.967(10)
W(1)-C(54)	2.006(10)
W(1)-C(53)	2.023(9)
W(1)-P(1)	2.545(3)
W(1)-P(5)	2.633(3)
W(1)-I(3)	2.824(2)
W(1)-I(2)	2.862(3)

C(100)-W(1)-C(54)	109.7(4)
C(100)-W(1)-C(53)	72.1(4)
C(54)-W(1)-C(53)	37.7(4)
C(100)-W(1)-P(1)	96.8(3)
C(54)-W(1)-P(1)	86.4(3)
C(53)-W(1)-P(1)	91.7(3)
C(100)-W(1)-P(5)	160.0(3)
C(54)-W(1)-P(5)	88.6(3)

C(53)-W(1)-P(5)	125.6(3)
P(1)-W(1)-P(5)	92.15(11)
C(100)-W(1)-I(3)	83.9(3)
C(54)-W(1)-I(3)	102.3(3)
C(53)-W(1)-I(3)	97.4(3)
P(1)-W(1)-I(3)	170.54(6)
P(5)-W(1)-I(3)	84.39(10)
C(100)-W(1)-I(2)	82.5(3)
C(54)-W(1)-I(2)	162.3(3)
C(53)-W(1)-I(2)	151.8(3)
P(1)-W(1)-I(2)	79.22(7)
P(5)-W(1)-I(2)	81.74(7)
I(3)-W(1)-I(2)	91.55(6)

Table 2.7c-Bond length (A) and angles (deg) for complex 12 :-

I(1)-Mo(1)	2.8701(6)	I (2)-Mo(1)	2.8113(8)
Mo(1)-C(17)	1.949(4)	Mo(1)-C(14)	2.006(4)
Mo(1)-C(13)	2.056(4)	Mo(1)-N(1)	2.189(3)
Mo(1)-N(2)	2.244(3)	N(1)-C(1)	1.343(5)
N(1)-C(5)	1.346(5)	N(2)-C(10)	1.345(5)
N(2)-C(6)	1.349(5)	O(1)-C(17)	1.152(5)
C(1)-C(2)	1.376(6)	C(2)-C(3)	1.378(6)
C(3)-C(4)	1.384(5)	C(4)-C(5)	1.394(5)
C(5)-C(6)	1.474(5)	C(6)-C(7)	1.401(5)
C(7)-C(8)	1.377(5)	C(8)-C(9)	1.384(6)
C(9)-C(10)	1.388(5)	C(11)-C(12)	1.504(6)
C(12)-C(13)	1.486(5)	C(13)-C(14)	1.310(5)
C(14)-C(15)	1.495(5)	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)-C(1)	98.85(14)
C(14)-Mo(1)-N(14)	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(14)-Mo(1)-I(2)	166.29(8)
N(2)-Mo(1)-I(2)	95.11(8)	C(17)-Mo(1)-I(2)	81.72(12)
C(14)-Mo(1)-I(2)	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)	C(1)-N(1)-C(5)	119.1(3)
C(1)-N(1)-Mo(1)	123.2(3)	C(5)-N(1)-Mo(1)	117.7(2)
C(10)-N(2)-C(6)	118.8(3)	C(10)-N(2)-Mo(1)	125.5(2)
C(6)-N(2)-Mo(1)	115.7(2)	N(1)-C(1)-C(2)	123.2(4)
C(1)-C(1)-C(3)	118.4(4)	C(2)-C(3)-C(4)	119.0(4)
C(3)-C(4)-C(5)	120.0(4)	N(2)-C(5)-C(4)	120.3(3)
N(1)-C (5)-C(6)	116.3(3)	C(4)-C(5)-C(6)	123.3(3)
N(2)-C (6)-C(7)	121.2(3)	N(2)-C(6)-C(5)	116.3(3)
C(7)-C(6)-C(5)	122.5(3)	C(8)-C(7)-C(6)	119.5(4)

C(7)-C(8)-C(9)	119.2(3)	C(8)-C(9)-C(10)	118.7(4)
N(2)-C(10)-C(9)	122.6(4)	C(13)-C(12)-C(11)	114.0(3)
C(14)-C(13)-C(12)	144.4(4)	C(14)-C(13)-Mo(1)	69.1(2)
C(12)-C(13)-Mo(1)	146.5(3)	C(13)-C(14)-C(15)	145.2(4)
C(13)-C(14)-Mo(1)	73.3(2)	C(15)-C(14)-Mo(1)	141.5(3)
C(14)-C(15)-C(16)	114.2(4)	O(1)-C(17)-Mo(1)	179.4(3)

APPENDIX FOR CHAPTER THREE

Appendix for Chapter Three

Table 3.6-Crystal data and structure refinement for (13) and (24).

	No.**13**	No.**24**
Formula	$[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	$[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$
Empirical formula	$C_{27}H_{28}I_2MoNO_4P$	$C_{33}H_{34}I_2MoOP_2$
Molecular weight	811.21	858.28
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system,	Monoclinic P21/c	Orthorhombic
space group	P21/c	pnam(No 62)
Unit Cell dimension (a Å)	16.36 (2)	15.555(17)
(b Å)	12.484(14)	10.058(12)
(c Å)	16.604(17)	21.59(2)
β(⁰)	113.78(1)	105.5(1)

Volume	Å^3	3102	1570
Z		4	4
Calculated density (Mgm^{-3})		1.737	1.688
Absorption coefficient (mm^{-1})		2.495	2.334
F (000)		1568	1672
Crystal size (mm)		0.25 * 0.25 * 0.10	0.25 *0.17 * 0.10
θ range for data collection(deg)		2.11 to 26.01	2.41 to 25.91
Index ranges		$-20 \le h \le 20$,	$-16 \le h \le 16$
		$0 \le k \le 15$,	$0 \le k \le 12$
		$-20 \le l \le 20$	$-26 \le l \le 26$
Reflections collected /unique		10520	7369
Independent reflections[R(int)]		5631/0.0845	2375/0.0701
Data/restraints/parameters		5631/0/328	2375/0/118
Final R indices [I>2σ(I)]	R1	0.0728	0.0806
	wR2	0.1845	0.2205
R indices (all data)	R1	0.1834	0.1262
	wR2	0.2286	0.2494
Largest diff. Peak and hole(eÅ^{-3})		1.495, -0.790	1.365, -0.856

Table 3.6-Crystal data and structure refinement for (31) and (32).

		No.**31**	No.**32**
Formula		$[MoI_2(CO)\{P(O^iPr)_3\}_2$ $(\eta^2\text{-}EtC_2Et)]$	$[WI_2(CO)\{P(O^iPr)_3\}_2$ $(\eta^2\text{-}EtC_2Et)]$
Empirical formula		$C_{25}H_{52}I_2MoNO_7P_2$	$C_{25}H_{52}I_2WO_7P_2$
Molecular weight		876.35	964.26
Temperature (K)		293(2)	293(2)
Wavelength (Å)		0.71073	0.71073
Crystal system,		Orthorhombic	Orthorhombic
space group		P21/c	P21/c
Unit Cell dimension	(a Å)	9.628 (9)	9.689(9)
	(b Å)	14.087(17)	13.983(17)
	(c Å)	14.073(17)	14.015(17)
	$\beta(^0)$	(90)	(90)

Volume	Å^3	1909	2683
Z		2	2
Calculted density (Mgm^{-3})		1.525	1.687
Absorption coefficient (mm^{-1})		2.078	4.785
F (000)		872	936
Crystal size (mm)		0.25 * 0.25 * 0.10	0.25 *0.20 * 0.05
θ range for data collection(deg)		2.94 to 26.04	2.10 to 26.08
Index ranges		0≤ h≤10,	0≤h≤11
		-17≤k≤17,	-16≤k≤17
		-17≤1≤17	-17≤1≤17
Reflections collected /unique		6568	6083
Independent reflections[R(int)]		3472/0.0719	3581/0.1118
Data/restraints/parameters		3472/45/117	3581/46/117
Final R indices [I>2σ(I)]	R1	0.0741	0.0797
	wR2	0.2017	0.2162
R indices (all data)	R1	0.1495	0.1620
	wR2	0.2388	0.2607
Largest diff. Peak and hole(eÅ^{-3})		0.846, -0.589	1.297, -0.9

Table 3.7-Bond lengths [A] and angles [deg] in the metal coordination spheres for 13, 24, 31 and 32 :-

For complex (13) :-

Mo(1)-C(200)	1.948(14)
Mo(1)-C(5)	2.007(12)
Mo(1)-C(4)	2.040(13)
Mo(1)-N(300)	2.212(13)
Mo(1)-P(4)	2.485(4)
Mo(1)-I(2)	2.799(3)
Mo(1)-I(3)	2.862(3)

C(100)-Mo(1)-C(3)	112.5(5)
C(100)-Mo(1)-C(4)	74.0(5)
C(3)-Mo(1)-C(4)	38.5(5)
C(100)-Mo(1)-N(100)	166.0(5)
C(3)-Mo(1)-N(200)	80.6(5)
C(4)-Mo(1)-N(200)	118.8(5)

C(100)-Mo(1)-P(4)	87.1(4)
C(3)-Mo(1)-P(4)	90.3(3)
C(4)-Mo(1)-P(4)	89.0(4)
N(200)-Mo(1)-P(4)	98.2(3)
C(100)-Mo(1)-I(3)	90.4(4)
C(3)-Mo(1)-I(3)	99.1(3)
C(4)-Mo(1)-I(3)	99.0(4)
N(200)-Mo(1)-I(3)	82.3(3)
P(4)-Mo(1)-I(3)	170.6(1)
C(100)-Mo(1)-I(2)	83.9(4)
C(3)-Mo(1)-I(2)	160.7(4)
C(4)-Mo(1)-I(2)	155.8(4)
N(200)-Mo(1)-I(2)	84.3(3)
P(4)-Mo(1)-I(2)	80.0(1)
I(3)-Mo(1)-I(2)	90.7(1)

For complex (24) :-

Mo(1)-C(100)	2.00(4)
Mo(1)-C(3)	2.01(2)
Mo(1)-C(4)	2.08(3)
Mo(1)-P(2)	2.545(4)
Mo(1)-I(1)	2.759(3)
Mo(1)-I(2)	2.853(4)

C(100)-Mo(1)-C(3)	112.4(10)
C(100)-Mo(1)-C(4)	70.9(12)
C(3)-Mo(1)-C(4)	41.7(8)
C(100)-Mo(1)-P(4)#1	160.1(10)
C(3)-Mo(1)-P(4)#1	85.6(5)
C(4)-Mo(1)-P(4)#1	127.2(4)
C(100)-Mo(1)-P(2)	92.7(9)
C(3)-Mo(1)-P(2)	85.6(5)

C(4)-Mo(1)-P(2)	91.0(7)
P(4)#1-Mo(1)-P(2)	80.0(2)
C(100)-Mo(1)-I(1)	88.3(9)
C(3)-Mo(1)-I(1)	101.4(4)
C(4)-Mo(1)-I(1)	96.9(7)
P(4)#1-Mo(1)-I(1)	96.4(1)
P(2)-Mo(1)-I(1)	171.9(1)
C(100)-Mo(1)-I(2)	79.2(1)
C(3)-Mo(1)-I(2)	163.1(6)
C(4)-Mo(1)-I(2)	148.8(7)
P(2)-Mo(1)-I(2)	81.5(1)
P(4)-Mo(1)-I(2)	80.0(1)
I(1)-Mo(1)-I(2)	90.8(1)

#1 Symmetry element x,y,.5-z

For complexes (31) and (32) :-

	(31) M= Mo	(32) M= W
M(1)-C(11)	1.89(3)	1.92(2)
M(1)-C(21)	1.96(2)	1.95(2)
M(1)-C(100)	2.10(2)	2.02(3)
M(1)-P(4)	2.566(5)	2.541(8)
M(1)-I(2)	2.872(2)	2.853(3)
C(11)-M(1)-C(21)	40.5(6)	40.0(5)
C(11)-M(1)-C(100)	105.5(11)	107.1(14)
C(21)-M(1)-C(100)	65.2(9)	67.2(11)
C(11)-M(1)-P(4)	87.7(15)	89.2(2)
C(21)-M(1)-P(4)	92.2(1)	92.2(2)
C(100)-M(1)-P(4)	92.0(4)	91(3)
C(11)-M(1)-P(4)#1	96.0(15)	94(2)
C(21)-M(1)-P(4)#1	92.6(2)	92.3(2)
C(100)-M(1)-P(4)#1	90.0(4)	91(3)
P(4)-M(1)-P(4)#1	175.2(3)	175.6(4)

C(100)-M(1)-I(2)	159.9(8)	157.5(11)
C(11)-M(1)-I(2)	94.5(5)	95.4(5)
C(21)-M(1)-I(2)	134.8(1)	135.3(1)
P(4)-M(1)-I(2)	88.8(4)	89.6(6)
P(4)#2-M(1)-I(2)	87.8(3)	87.3(6)
C(11)-M(1)-I(2)#1	173.5(11)	174.4(13)
C(21)-M(1)-I(2)#1	134.9(1)	135.6(1)
C(100)-M(1)-I(2)#1	69.7(7)	68.5(11)
P(4)-M(1)-I(2)#1	88.1(3)	87.3(6)
I(2)-M(1)-I(2)#1	90.3(1)	89.0(1)

#1 Symmetry element x, .5-y, 1-z