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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



THANKING

MIN

WITH A FULL HEART AND DEVOTED TONGUE

وَقُنُ زَبَّ رِبْ كِيْ عِلْمُ ٥

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(CH2PPh2)3} LIGANDS.

A thesis submitted to the University of Wales, Bangor

by

Mutlaq Al-jahdali

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1999





To my parents, to my wife Fowzia

and my children Manar and Rakan

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Appendix for Chapter Two and Three

<u>Abstract :-</u>

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)(EtC₂Et) complexes of molybdenum(II) and tungsten(II), $[MI_2(CO) (NCMe)(\eta^2-EtC_2Et)_2]$. The crystal structures of the bis(PPh₃) complex $[WI_2(CO)(PPh_3)_2 (\eta^2-EtC_2Et)](4)$ and the PPh₂(CH₂)₃PPh₂ complex, $[WI_2(CO) \{Ph_2P(CH_2)_3PPh_2\}(\eta^2-EtC_2Et)](8)$ are discussed. The reaction of equimolar amounts $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and bipy to give the crystallographically characterised complex, $[MoI_2(CO)(bipy) (\eta^2-EtC_2Et)](12)$ is also described.

The third chapter describes the reactions of the complexes $[MI_2(CO) (NCMe)(\eta^2-EtC_2Et)_2]$ with one and two equivalents of phosphite ligands, $P(OR)_3$ (R = Me, Et, ⁱPr, ⁿBu and Ph) to give $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2-EtC_2Et)](R = Ph or ⁱPr), [WI_2(CO)\{P(OR)_3\}(\eta^2-EtC_2Et)_2](R = Me, Ph or ⁱPr) and <math>[MI_2(CO)\{P(OR)_3\}_2(\eta^2-EtC_2Et)](M = Mo, R = Me, Et, ⁱPr, and ⁿBu; M = W, R = Me, Et, ⁱPr, ⁿBu and Ph) respectively. The reactions of the crystallographically characterised complex <math>[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2-EtC_2Et)](13)$, with a series of neutral and anionic donor ligands is described. The crystal structures of one of the reaction products, $[MoI_2(CO)(dppe)(\eta^2-EtC_2Et)](24)$ is discussed. The structures of $[MI_2(CO)\{P(OⁱPr)_3\}_2(\eta^2-EtC_2Et)] \{M = Mo(31)$ 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(CH₂PPh₂)₃} seven-coordinate

didentate phosphine complexes of molybdenum(II) and tungsten(II), namely $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ (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, $[MI_2(CO)_2 \{MeC(CH_2PPh_2)_3-P,P',P''\}]$ (38 and 39) is also discussed. The reactions of 36 and 37 with $[MI_2(CO)_3(NCMe)_2](M = Mo \text{ or } W)$, $[MI_2(CO)_3(NCMe)L]\{L = PPh_3, AsPh_3, SbPh_3, P(OMe)_3, P(OEt)_3, P(OPh)_3\}$, $[MI_2(CO)_3(NCMe)_2](n = 1 \text{ or } 2)$, $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$, $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ (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 sevencoordinate dichloro complex [WCl₂(CO)₃(NCMe)₂], by reacting the complex [WI₂(CO)₃(NCMe)₂] with excess of NaCl in acetone/CH₂Cl₂ (50:50). The reaction of [WCl₂(CO)₃(NCMe)₂] with 3-hexyne gives [WCl₂(CO)(NCMe)(η^2 -EtC₂Et)₂](80), which reacts with a wide range of ligands, such as NPh₃, PPh₃, Ph₂P(CH₂)_nPPh₂, (n = 1 or 2), P(OPh)₃, cis-Ph₂PCH=CHPPh₂, bipy and NaS₂CNR₂ (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 [WCl₂ (CO)₃(NCMe)₂] towards the polymerisation of phenylacetylene, PhC₂H is briefly discussed.

Abbreviations

Ar	Aryl
^t Bu	Tertiary butyl C(CH ₃) ₃
Cod	Cyclooctadiene C ₈ H ₁₂
Ср	Cyclopentadienyl (η^5 -C ₅ H ₅)
Cp'	Methylcyclopentadienyl (η^5 -C ₅ H ₅ Me)
bipy	2.2'-bipyridyl
1,10-Phen	1,10-Phenanthroline, C ₁₂ H ₈ N 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 ₂ H ₅
Me	Methyl, CH ₃
Ph	Phenyl, C ₆ H ₅
ⁱ Pr	Isopropyl, (CH ₃) ₂ CH-
Ру	Pyridine, C5H5N
THF	Tetrahydrofuran, C4H8O

Linear triphos	$PhP(CH_2CH_2PPh_2)_2$
Tripodal triphos	MeC(CH ₂ Ph ₂) ₃
Х	Halide
НОМО	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
М	Transition Metal

Instruments :-

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

<u>Units :-</u>

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 $[Kr]4d^55s^1$, and it is an element in the second transition series , whereas tungsten has the electronic configuration $[Xe]5d^46s^2$, 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).

PROPERTY		MOLYBDENUM	TUNGSTEN
Symbol		Мо	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
I	V	65	66
1	ш	69	-
MP/ ⁰ C		1620	3380
BP/ºC		4650	5500
Density (20 °C)/g.cm ⁻³		10.28	19.3
Electrical resistivity (20 °C)/µohm.cm		~5	~5
Atomic Radius (A)		1.40	1.41
Δ H Ionization 1 st (kJ/Mol ⁻¹)		685	770

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

1.2-Preparation and Applications of Molybdenum and Tungsten:

Both molybdenum and tungsten have approximately the same abundance in nature ($\sim 10^{-10}$ %). 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 MoO₃ 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 [NH₄]₆[Mo₇O₂₄].4H₂O or [NH₄]₂[Mo₂O₇], 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 catalysts¹. Molybdenum is an integral part of the nitrogen fixing enzyme, nitrogenase². Tungstic acid is roasted to WO₃, which is reduced to the metal by heating with hydrogen at 850^oC, 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, Zeise⁴ described the synthesis of the first complex involving preparation of Zeise's salt, K[PtCl₃(η^2 -C₂H₄)].H₂O, by reacting ethene with K₂[PtCl₄] 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. $[PtCl_3(\eta^2-C_2H_4)]^2$

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 metal⁷. The earliest papers concerning the bonding of alkenes to metals were published by Dewar⁸, in 1951 and Chatt and Duncanson⁹ 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 $d\pi$ 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 sp² to sp³, 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 sp³ hybridisation.(see Figure1.2).



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

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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(η^2 -RC₂R)Cp₂] (M = Mo or W).

It has been suggested by King,¹⁰ that the π_{\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 π_{\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(C₆H₁₁)₃}₂](C₆H₁₁ = 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 [MX₂(CO)₂L₂](X = halogen; L = tertiary phosphine or arsine)¹¹ (see Figure 1.3).



Fig.1.3- A diagram to show the interaction between π_{\perp} alkyne orbitals

and metal d-orbitals.

In 1980, Templeton and Ward^{12,13} and Hoffman¹⁴ 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 π_{\perp} orbitals into vacant σ -metal acceptor orbitals, donation of electron density from π_{\perp} orbitals is restricted. Three-electron donation occurs because *cis*-alkyne ligands have $C_{2\nu}$ symmetry, giving rise to π_{\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 = PEt₃, PPh₃, py) with RC₂R (R = H and Me) to give the carbonyl displaced complexes [Mo X₂(CO)L₂(η^2 -RC₂R)] (where L = PEt₃, PPh₃, py).

The first molybdenum(II) and tungsten(II) alkyne complexes were synthesised by Otsuka *et al*¹⁶ in 1969 by refluxing [MoH₂Cp₂] with diphenylacetylene in toluene for three hours, to give the thermally stable but air-sensitive complex [Mo(η^2 -PhC₂Ph)Cp₂].

In 1973, Thomas¹⁷ prepared the bis(cyclopentadienyl)alkyne complexes $[M(\eta^2-RC_2R)(\eta^5-Cp)_2]$ (M = Mo and W; R = Ph, CF₃, Me)(see Equation 1.1), by reduction of the Mo(IV) and W(IV) complexes $[MCl_2(\eta^5-Cp)_2]$, in the presence of the alkyne in toluene.

$$[MCl_{2}(\eta^{5}-Cp)_{2}] + RC_{2}R \xrightarrow{Na/Hg, Toluene, 17h} [M(\eta^{2}-RC_{2}R)(\eta^{5}-Cp)_{2}] + 2NaCl + [MH_{2}(\eta^{5}-Cp)_{2}]$$

(Equation 1.1)

Irradiation of the complex $[Mo(CO)(\eta^5-Cp)_2]$ with UV light^{18,19} in the presence of RC₂R forms the molybdenum ethyne and butyne deravatives, $[Mo(\eta^2-RC_2R)Cp_2](R = H, Me)$. The easiest method to prepare cyclopentadienyl mono(alkyne) complexes is by heating $[MoCl(CO)_3Cp)]$ with internal alkynes in hexane to afford $[MoCl(CO)(\eta^2-RC_2R)Cp]$, (where $R = CF_3$, Me, Ph)²⁰

The dppe ligand can also be replaced by RC₂R (R = Me, Ph) from [Mo(dppe)₂Cp][X](X = BF₄ or PF₆) with RC₂R (R = Me, Ph) to give [Mo(dppe)(η^2 -RC₂R)Cp][X].²¹ The molybdenum and tungsten acyl complexes of the type [M(COR)(CO)(η^2 -R₁C₂R₂)(η^5 -Cp, Cp' or Cp*)] have also been prepared by Alt *et al*^{22,23}, by photolysis of [WR(CO)₃(η^5 -Cp, Cp' or Cp*)] with alkynes R₁C₂R₂ at low temperature to afford the complexes [W(COR)(CO)(η^2 -R₁C₂R₂)(η^5 -Cp, Cp' or Cp*)] (R = Me, Et, ⁿPr, ⁿBu, Ph; R₁ = R₂ = H,

Me and Ph; $Cp' = C_5H_4Me$; $Cp^* = C_5Me_5$). Acyl derivatives of the general complexes $[W(COR)(L)(\eta^2-R_1C_2R_2)(\eta^5-Cp)]^{25}$ are formed by reacting the alkyne complexes $[W(COR)(\eta^2-R_1C_2R_2)(\eta^5-Cp)]$ with two-electron donor ligands, (L) {L = PR₃, 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 coworkers²⁵ have prepared the cationic molybdenum complexes $[Mo(CO)(L)(\eta^2-RC_2R')(\eta^5-Ar)]^+$ by replacement of an alkyne ligand by phosphine ligands from $[Mo(CO)(\eta^2-RC_2R_1)_2(\eta^5-Ar)]^+$ (where R = 'Bu or 'Pr, R₁ = H; R = Ph, R₁ = Me, L = PEt₃, PPh₃ or PCy₃; Ar = Cp or In; R = R₁ = Me or *p*-tol). (see equation 1.2).

$$[Mo(CO)(\eta^{2}-RC_{2}R_{1})_{2}(\eta^{5}-Ar)][BF_{4}] + L \longrightarrow [Mo(CO)L(\eta^{2}-RC_{2}R_{1})(\eta^{5}-Ar)][BF_{4}] + RC_{2}R_{1}$$

The cationic complexes $[Mo(dppm)(\eta^2-RC_2R_1)(\eta^5-Cp)]^{+26}$ were prepared by reaction of $[Mo(NCMe)(\eta^2-RC_2R_1)_2(\eta^5-Cp)]^+$ (R, R₁ = H and Ph) with dppm involving displacement of both NCMe and an alkyne ligand in these reactions.

The cationic bis(phosphine) complexes, $[Mo(L_2 \text{ or } L^L)(\eta^2 - RC_2R_1)(\eta^5 - Ar)]^*$ can be synthesised by reaction of $[Mo(NCMe)(\eta^2 - RC_2R_1)_2(\eta^5 - Ar)]^+$ with two equivalents of L $(L = PMe_3, PEt_3 \text{ or } PMePh_2)$ or one equivalent of bidentate phosphine $\{L^L = dppe, dmpe\}$. In 1987, Bergman, *et al*²⁷ prepared the mono(alkyne) products by irradiating in Et₂O with the complex, $[W(\eta^1 - CH_2COEt)(CO)_3Cp]$ with UV light in the presence of PhC₂H to afford the oxallyl complex, $[W(\eta^1-CH_2COEt)(CO)_2(\eta^2-PhC_2H)Cp]$. In 1982, Umland and Vahrenkamp²⁸ reported the reactions of alkynes, RC₂R with the sevencoordinate complexes $[WI_2(CO)_4L]$ to afford $[WI_2(CO)_2L(\eta^2-RC_2R_1)]$ (L = PMe₃, AsMe₃, CN^tBu; R = R₁ = H; R = Ph, R₁ = H). In 1983, Templeton and co-workers²⁹ reported the synthesis and characterisation of complexes of the type $[MoBr_2(CO)L_2(\eta^2-RC_2R_1)](R = R'= Me and Ph)$ by refluxing seven-coordinate complexes $[MoBr_2(CO)_3(PEt_3)_2]$ with excess alkyne (see equation 1.3)

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

Equation (1.3)

In 1986³⁰, 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 = PPh₃, PEt₃, py, L₂ = dppe, R = R₁ = Me, Ph, Et, R = H, R₁ = 'Bu, ⁿBu, Ph), in refluxing CH₂Cl₂ for a period of many days to give $[MX_2(CO)L_2(\eta^2-RC_2R_1)]$. The preparation of mono(alkyne) complexes³¹ such as $[MX_2(CO)L_2(\eta^2-RC_2R_1)]$, by reaction of $[\{W(\mu-Br)Br(CO)_4\}_2]$ with RC₂R₁ (R = R₁= Me, Ph, Et; R = Me, R₁ = Ph) in hexane have been described. These react with four equivalents of nucleophilic ligands L {L = CN^tBu, PPh₃ and P(OMe)₃} (as shown in Equation 1.4), to give mono(alkyne) complexes.³¹

$$[W(\mu-Br)Br(CO)_{4}]_{2} + Excess RC_{2}R_{1} \longrightarrow [W(\mu-Br)Br(CO)(\eta^{2}-RC_{2}R_{1})_{2}]_{2} + 6CO T$$

$$\downarrow L$$

$$[WBr_{2}(CO)L_{2}(\eta^{2}-RC_{2}R_{1})] + RC_{2}R_{1}$$

Equation (1.4)

Reacting the seven-coordinate complex, $[MoBr_2(CO)_3(PEt_3)_2]$ with cyclooctyne was reported by Bennett and Boyd³² to give $[MoBr_2(CO)(PEt_3)_2(\eta^2-C_8H_{12})]$.

In 1978,³³ the alkyne complex, $[W(CO)(S_2CNEt_2)_2(\eta^2-HC_2H)]$ has been prepared by reacting the tungsten complex, $[W(CO)_2(PPh_3)(S_2CNEt_2)_2]$ with HC₂H, whereby the ethyne ligand replaces both the CO and PPh₃. The mixed alkene/alkyne cationic complex $[Mo(CO)(\eta^2-C_2H_4)(\eta^2-MeC_2Me)Cp][BF_4]$ has been prepared by Green *et al*³⁴, as shown in Equation(1.5)



Equation (1.5)

The alkyne complex $[WCl(CO)_2(acac)(\eta^2-HOC_2tol-p)]$ was prepared in 1979³⁵ by Fischer and Friedrich by photolysis of $[W(=Ctol-p)Cl(CO)_4]$ with excess Na[acac] in diethyl ether to give a coordinated hydroxy alkyne by replacement of a carbonyl ligand by acac. (see Equation 1.6). trans-[W(=Ctol-p)Cl(CO)₄] + Na[acac] $\xrightarrow{\text{Et}_2\text{O},\text{hv}}$ [WCl(CO)₂(acac)(η^2 -HOC₂tol-p)] +2CO1.

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 CH₂Cl₂ at room temperature to give $[Mo(\eta^2 - ethyne)_2(S_2P^iPr_2)_2]$. Complexes containing triphenylphosphine can be prepared by simple substitution of the carbonyl ligand. For example, reaction of the complex $[Mo(SC_6F_5)(CO)(\eta^2 - CF_3C_2CF_3)Cp]$ with PPh₃ at ambient temperature in diethyl ether gave the complex $[Mo(SC_6F_5)(CO)(PPh_3)(\eta^2 - CF_3C_2CF_3)Cp]$.³⁷ For the related tungsten complexes³⁸, 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 iodidebridges with NCMe in [{W(μ -I)I(CO)(NCMe)(η^2 -PhC₂R)₂}₂] (R = Me or Ph)³⁹ to give [WI₂(CO)(NCMe)(η^2 -PhC₂R)₂]. These complexes react with one equivalent of L (L = py, 3-Cl-Py, or 3,5-Me₂Py) in CH₂Cl₂ at room temperature to give the acetonitrile displaced products [WI₂(CO)L(η^2 -PhC₂R)₂]. [WI₂(CO)(NCMe)(η^2 -MeC₂Me)₂] was reacted with two equivalents of pyridine gave firstly, mono(alkyne) complex, [WI₂(CO)(py)(η^2 -PhC₂R)₂], which is reacted again with displaced but-2-yne ligand to afford the cationic bis(but-2-yne) complex, [WI(CO)(py)₂(η^2 -MeC₂Me)₂]I⁴⁰. Six coordinate bis(alkyne) complexes such as $[\{W(\mu-Br)Br(CO)(\eta^2-RC_2R)_2\}_2]$ can be prepared by addition of internal alkynes to $[\{W(\mu-Br)Br(CO)_4\}_2]$ in hexane at room temperature to yield the dimeric products $[\{W(\mu-Br)Br(CO)(\eta^2-RC_2R)_2\}_2]$, see Equation $(1.7)^{31}$.

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

(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 $[\{W(\mu-Br)Br(CO)(\eta^2-MeC_2Me)_2\}_2]$ and CN^tBu to afford $[WBr_2(CO)(CN^tBu)(\eta^2-MeC_2Me)_2]$.

In 1982⁴¹, 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 $[Mo(S_2CNEt_2)_2(\eta^2-RC_2R)_2]$. When the solvent was changed to toluene or benzene, the reaction takes one hour. Mixed alkyne complexes were synthesised by reaction of $[Mo(CO)(S_2CNR_2)_2(\eta^2-RC_2R)]$ with an amount equimolar of alkyne, see Equation (1.8).



(Equation 1-8)

R= Et, R¹= H, R²= Ph, R³= R⁴= Ph; R= Me, R¹= R²= Ph, R³= R⁴= CO₂Me; R= Me, R¹= H, R²= Ph, R³= R⁴= Et; R= Me, R¹= R²= Ph, R³= H, R⁴= ⁿBu.

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(η^2 -RC₂R')₂Cp] (M = Mo or W; R = R' = CF₃, Ph or Me; R = Me, R' = Ph), by reacting the complexes [MCl(CO)₃Cp] with internal alkynes in refluxing hexane. Mixed bis(alkyne) cyclopentadienyl⁴³ complexes have been prepared by refluxing the complexes [MCl(CO)(η^2 -PhC₂Ph)Cp] (M = Mo or W) with hexafluorobut-2-yne at 40^oC to produce [MCl(η^2 -CF₃C₂CF₃)(η^2 -PhC₂Ph)Cp].

In 1975, Davidson and Sharp⁴⁴ synthesised the complexes [MCl(η^2 -RC₂R)₂Cp](M = Mo or W; R = Me, CF₃, CO₂Me) by reacting [MoCl(CO)₃Cp] with MeC=CMe, CF₃C=CCF₃ and MeCH₂C=CCH₂Me in hexane. The molybdenum bromo and iodo derivatives, [MoX(CO)₃Cp] (X = Br or I) have been reported to react with the alkyne, (MeC₂Me) in THF (THF = Tetrahydrofurane) to give [MoX(CO)(η^2 -MeC₂Me)Cp], but the yields were very low⁴³. The same group also prepared mixed alkyne complexes, [MoCl(η^2 - RC_2R^1)(η^2 - $R^2C_2R^3$)Cp] from reaction of [MoCl(CO)(η^2 - RC_2Ph)Cp](R = H and Me), and an equivalent amount of alkyne at room temperature, see equation (1.9).

$$[MoCl(CO)(\eta^{2}-RC_{2}R^{1})Cp] + R^{2}C_{2}R^{3} \longrightarrow [MoCl(\eta^{2}-RC_{2}R^{1})(\eta^{2}-R^{2}C_{2}R^{3})Cp]$$

R= Me, R¹= Ph, R²= R³= CF₃; R= R¹= Ph, R²= R³= CF₃, R= R¹= Ph, R²= H, R³= CF₃.

Equation (1.9)

Davidson and Sharp⁴⁴ reported complexes of the type $[MoCl(\eta^2-ClCH_2C_2CH_2Cl)_2Cp]$ 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 $[Mo(CO)(\eta^2-HOCH_2C_2CH_2OH)_2Cp][Cl]$.

<u>1.5-Reactions of alkyne complexes of Molybdenum(II) and Tungsten(II):</u></u> <u>I.5a-Reactions of mono(alkyne) complexes:-</u>

One of the most common reactions of alkyne complexes is substitution. When the complexes $[M(SC_6F_5)(CO)(\eta^2-CF_3C_2CF_3)Cp]$ (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 = PEt₃, PPh₃, PMe₂Ph, P(OMe)₃}.

Electrophilic attack by $[OEt_3][BF_4]$ to the acyl oxygen on complexes of the type $[W(\eta^1 - COR)(CO)(\eta^2 - HC_2H)Cp]$ affords the cationic carbene complexes $[W\{(\eta^1 - C(R)OEt)\}$ (CO)($\eta^2 - HC_2H$)($\eta^5 - Cp$)][BF₄] (R= Me, Et, ⁿPr, ⁿBu)⁴⁵.

In 1984, Green *et al*⁴⁶ prepared the neutral complexes $[Mo(SR){P(OMe)_3}(\eta^2 - MeC_2Me)Cp]$ by replacement one of the phosphite ligands in the cationic complex $[Mo{P(OMe)_3}_2(\eta^2 - MeC_2Me)Cp][BF_4]$ with excess of RS⁻ (where R = Me, 4NH₂C₆H₄, 4-MeOC₆H₄, 4-MeC₆H₄, C₆H₅, 4-NO₂C₆H₄).

In 1985, Templeton *et al*⁴⁷ have synthesised the complexes $[Mo(S_2CNR_2)_2(\eta^2-alkene)(\eta^2-RC_2R)]$ by treating $[Mo(CO)(S_2CNR_2)_2(\eta^2-RC_2R)]$ (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 $[M(CO)(S_2CNR_2)_2(\eta^2-RC_2R)]$ with two equivalents of the two-electron donor ligands (L) {L = $P(OR)_3$, PR₃, RCN) which replaces the alkyne ligand, see Equation (1.10).

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

Equation (1.10)

Bennett *et al*⁴⁹ treated the complexes $[M(CO)(S_2CNR_2)_2(\eta^4-C_8H_{12})]$ (M = Mo or W, R = Me or Et) in presence of cyclooctyne to produce a mixture of $[M(CO)(S_2CNR_2)_2\{(\eta^4-C_8H_{12})_2CO\}]$ and $[M(S_2CNR_2)_2(\eta^4-C_8H_{12})_2(CO)]$ (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 $\{(\eta^4-C_8H_{12})_2CO\}$ 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 Vasapollo³¹ have described the reaction of the bis(alkyne) dimers, $[\{W(\mu-Br)Br(CO)(\eta^2-RC_2R^1)_2\}_2]$, with four equivalents of L {L = CN^tBu, P(OMe)_3, PPh_3} in dichloromethane to give monomeric alkyne complexes of the type [WBr₂(CO)L₂(η^2 -RC₂R¹)].

In 1983, Templeton *et al*⁵⁰, synthesised the sulphur-bridged dimers $[Mo_2(\mu-S)(\mu-R^1C_2R^2)(S_2CNR_2)_3(SCNR_2)]$ (see Fig.1.6). by reaction of the complexes $[Mo(S_2CNR_2)_2(\eta^2-R^1C_2R^2)_2]$ with one equivalent of PEt₃ in refluxing toluene for 1.5hr (where R = Me, Et; R¹ = R² = Et; R¹ = H, R² = Ph, ⁿBu; R¹ = Me, R² = Ph).



Figure (1-6)

In 1985, Templeton *et al*⁵¹ protonated the complexes, $[W(S_2CNR_2)_2(\eta^2 - R^1C_2R^2)_2]$ (R, R¹, R² = H, Me and Ph respectively) with H[BF₄], which led to oxidative-coupling of the alkyne ligands to form a η^4 -C₄R₄H ligand, see equation (1.11)



Equation (1-11)

A number of "eighteen-electron" complexes of the type $[M(SC_6F_5)(\eta^2-RC_2R)_2Cp]$ were prepared by inserting TISC₆F₅ into the bis(alkyne) complexes $[MCl(\eta^2-RC_2R)_2Cp]$ (M = Mo or W, R = CF₃ or Ph). In 1974, Stone *et al*⁴², reacted the same complexes with KBHpz₃ (KBHpz₃ = tripyrazole hydro borate potassium) to give η^3 -allylic complexes, as shown in Figure (1-7).


Figure (1-7)

In 1980, Davidson⁵² prepared the cyclopentadienone complexes $[MoX(CO)(\eta^4 - Cyclopentadienone)Cp]$ (Fig.1.8a) by reacting $[MoX(\eta^2 - HFB)_2(\eta^5 - Cp)]$ (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 NaS₂CNMe₂ reacts with $[MoI(CO)(\eta^4 - cbd)Cp]$ to afford the complex without carbonyl and iodo groups, $[Mo(S_2CNMe_2)(\eta^4 - cbd)Cp]$.



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

In 1981, Green *et al*⁵³, have described substitution for both cations, { $[Mo(CO)_2(\eta^2 - RC_2R^1)(\eta^5 - Ar)]^+$ } and { $[Mo(NCMe)_2(\eta^2 - RC_2R^1)(\eta^5 - Ar)]^+$ }, one of them contains carbonyl with alkyne, and the other contains acetonitrile ligands. The complex, { $[Mo(NC Me)_2(\eta^2 - RC_2R^1)(\eta^5 - Ar)]^+$ } which contains acetonitrile, reacts with two equivalents of L (L₁ = monodentate phosphine such as PEt₃, PMe₃ and PMePh₂; L₂ = bidentate phosphorus, dppe or dmpe) to afford complexes of the type $[Mo(L)_2(\eta^2 - RC_2R^1)(\eta^5 - Ar)]^+$ or $[Mo(L_2)(\eta^2 - RC_2R^1)(\eta^5 - Ar)]^+$, which have carbonyl and alkyne reacts with one equivalent of L (L = monodentate phosphine) such as PEt₃, PPh₃ and PCy₃ to give the complexes $[Mo(CO)L(\eta^2 - RC_2R^1)(\eta^5 - Ar)]^+$ (where Ar = Cp or In).

Green and co-workers⁵⁴ reacted complexes of the type $[Mo(CO)(\eta^2-RC_2R^1)Cp]^+$ (R =R¹ = Me, R = H, R¹ = ^tBu) and dpps (o-diphenyl phosphino styrene) in refluxing CH₂Cl₂, where the dpps join through both phosphorus and the alkene ligands to give $[Mo(dpps)(\eta^2-RC_2R^1)Cp]$. Sodium dithiocarbamate replaces CO and alkyne from cationic complexes of the type $[Mo(CO)(\eta^2-RC_2R^1)_2Cp]^+$, to afford $[Mo(S_2CNMe_2)(\eta^2-RC_2R^1)Cp](R = R^1 = Me, R = ^tBu R^1 = H)$, but with $(SC_6H_4SPh-o)^-$ two products are formed with one alkyne and two alkynes, $[Mo(SC_6H_4SPh-o)(\eta^2-RC_2R^1)Cp]$ and $[Mo(SC_6H_4SPh-o)(\eta^2-RC_2R^1)Cp]$ and $[Mo(SC_6H_4SPh-o)(\eta^2-RC_2R^1)Cp]$.

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 1960⁵⁵. by the controlled oxidation of $[Mo(CO)_4(diars)]$ with iodine or bromine to give $[MoX_2(CO)_3(diars)]$, $\{diars = 1,2-Me_2As(C_6H_4)AsMe_2\}$.

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:-





Under similar conditions, the controlled oxidation of the tungsten complex $[W(CO)_4$ (diars)] with X₂ 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 isolated⁵⁵.

In 1971, Colton *et al*^{56,57} prepared dimeric complexes of the type $[\{M(\mu-X)X(CO)_4\}_2]$ (M = Mo, W; X = Cl, Br, I), and the first of this type of complex, $[\{Mo(\mu-Cl)Cl(CO)_4\}_2]$ 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, $[\{M(\mu-Br)Br(CO)_4\}_2]$ (M = Mo, W). The crystal structure of $[\{W(\mu-Br)Br(CO)_4\}_2]$ has been determined⁶⁰ and shows each tungsten atom to be a *fac*-[WBr₃(CO)₃] octahedron with a capping carbonyl on the tricarbonyl face, see Figure 1.9.



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

The complexes $[\{M(\mu-I)I(CO)_4\}_2]$ (M = Mo, W) were prepared by the photochemical reaction of I₂ with $[W(CO)_6]$ at ambient temperatures. There are many examples of reactions of these dihalide-bridged dimers, $[\{M(\mu-X)X(CO)_4\}_2]$ with a variety of donor ligands⁶¹⁻⁷⁰. 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):-



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 coordi--nate 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 [MI2(CO)3(NCMe)2] (M = Mo, W) :-

The seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ were reported in 1986⁷⁴ 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 I₂ 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 CH₂Cl₂.
- (2) $L = PPh_3$, AsPh_3, SbPh_3, py, P(OR)_3.
- (3) $L = PPh_3$, AsPh₃, SbPh₃, BiPh₃. (4) +(5) $L = P(OR)_3$ (R = Me, Ph) in CH₂Cl₂.
- (6) L = N-N = 2,2'- bipyridyl; 1,10-Phenanthroline.
- (7) $L = PPh_3$, AsPh₃, SbPh₃, in CH₂Cl₂ followed by Na[S₂CNR₂]. (R = Me, Et).

The seven-coordinate complexes molybdenum(II) and tungsten(II), $[MI_2(CO)_3(NC Me)_2]$ are soluble in CH₂Cl₂, CHCl₃, 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 ¹³C NMR spectra for the above complex. At low temperature (-70° C, CD₂Cl₂) 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 ¹³C 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 [WI₂(CO)₃(NCMe)₂].

1.9-Reactions of the Seven Coordinate complexes of the Molybdenum(II)

and Tungsten(II), [MI2(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, CH₂Ph, Ph), which react with one equivalent of L (L = PPh₃; AsPh₃; SbPh₃) 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 1987⁷⁷, 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 $[{M(\mu-I)I(CO)_3(py)}_2]$ by displacement of acetonitrile when $(M = Mo \text{ and } W; py = 2Me-py, 4Me-py, 3,5-Me_2-py, 3Cl-py, 3Br-py, 4Cl-py, 4Br-py).$ 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-HO₂CC₅H₄N in methanol afforded $[MI_2(CO)_3(NC_5H_4CO_2H-4)_2]$, which is soluble in water. When equimolar amounts of 3-NaO₃SC₅H₄N are added, the mixed ligand complexes of the type $[MI_2(CO)_3(NC_5H_4CO_2H-4)(3-NC_2H_4SO_3Na)]$ are obtained ⁷⁹.

In 1989, Baker *et al*⁸⁰ have synthesised the complexes $[MI_2(CO)_3(RN=CHCH=NR)]$ (M = Mo, W; R = Buⁱ, 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 Fraser⁸¹ 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 = PPh₃, AsPh₃, SbPh₃ 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, $[MI_2(CO)_3$ $\{Ph_2P(C H_2)_nPPh_2\}]$ (M = Mo or W; n = 1-6) have been reported in 1987⁸³, 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)(η^2 -dppf)] by reaction of *fac*-[W(CO)₃(NCMe)₃] with dppf then added I₂ to give [WI₂(CO)₃(η^2 -dppf)], which when reacted with H₂O₂ gave the P=O, oxidised complex [WI₂(CO)₃{ η^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, $[M_2I_4(CO)_6(\mu-Ph_2PC\equiv CPPh_2)_2]$ 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 $[MI_2(CO)_3(\eta^1-Ph_2PC\equiv CPPh_2)_2]$, are observed.⁸⁷

In 1994, Baker and Sherlock⁸⁸ synthesised complexes of the type $[MoI_2(CO)_2 \{\eta^3 - PhP(CH_2CH_2PPh_2)_2\}]$ and $[WI_2(CO)_3 \{\eta^2 - PhP(CH_2CH_2PPh_2)_2\}]$ (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 $[\{M(\mu-I)I(CO)_3L\}_2]$ {L = PPh₃, AsPh₃, SbPh₃, PPh₂Cy, 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(CH₂)₂SR to yield $[MI_2(CO)_3 \{RS(CH_2)_2SR\}]$ (M = W, Mo, R= Ph, 4-MeC₆H₄, 4-FC₆H₄), and they have reported the crystal structure for $[WI_2(CO)_3\{(4-MeC_6H_4)S(CH_2)_2S(4-MeC_6H_4)\}]$, and the reaction of MeS(CH₂)₂S (CH₂)₂SMe with $[MI_2(CO)_3\{(CO)_3(NCMe)_2]\}$ (NCMe)₂] to afford $[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe-S,S'\}]$ and $[MI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe-S,S',S'\}]$ (M = W, Mo).

1.10-Reactions of [MI2(CO)3(NCMe)2] with alkynes :-

for R = Me.

Reaction of one equivalent of alkyne, (RC_2R) , with the seven coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ gave $[MI_2(CO)(NCMe)_2(\eta^2-RC_2R')]$, which dimerizes to produce the iodo-bridged complexes, $[\{M(\mu-I)I(CO)(NCMe)(\eta^2-RC_2R')\}_2]$ (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, $[MI_2(CO)(NCMe)(\eta^2-RC_2R')_2]$, are obtained.

In 1988, Baker *et al*⁹² synthesised the above products by reaction of $[MI_2(CO)_3(NCMe)_2]$ with excess of RC₂R' to yield $[MI_2(CO)(NCMe)(\eta^2-RC_2R')_2]$, $(R = R' = Ph; R = Me, R' = Ph; for M = W; R = R' = Me, CH_2Cl_2; ptol; R = Ph, R' = CH_2OH)$, and the dimeric molybdenum complex, $[\{Mo(\mu-I)I(CO)(\eta^2-MeC_2Me)_2\}_2]$. The complexes $[WI_2(CO) (NCMe)(\eta^2-RC_2R)_2]$ (R = Me, Ph), were crystallographically characterised, (see Figure 1.16)



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

In 1994, Baker *et al*⁹³ have prepared bis(alkyne) complexes, $[WI_2(CO)(NCR)(\eta^2-R^1 C_2R^1)_2]$ by reaction of the complex, $[WI_2(CO)_3(NCR)_2]$ (R = Et, ^tBu, Ph and CH₂Ph) with excess R¹C₂R¹ (R¹ = Me, Ph), and they reported the crystal structure for $[WI_2(CO)(NCR)(\eta^2-MeC_2Me)_2]$.

1-11-Reactions of [MI₂(CO)(NCMe)(η^2 -RC₂R)₂] with donor ligands :-

The complexes $[WI_2(CO)(NCMe)(\eta^2-R'C_2R')_2]$ (R' = Me or Ph) react with one, two, three, four or five equivalents of CN'Bu to give $[WI_2(CO)(CN'Bu)(\eta^2-R'C_2R')_2]$, $[WI_2(CO)(CN'Bu)_2(\eta^2-R'C_2R')]$, $[WI_2(CN'Bu)_3(\eta^2-R'C_2R')]$, $[WI(CN'Bu)_4(\eta^2-R'C_2R')]I$, and $[W(CN'Bu)_5(\eta^2-R'C_2R')]2I$ respectively⁹⁴. In 1987, Baker, Drew and Armstrong⁹⁵ synthesised the crystallographically characterised complex $[WI_2(CO)_2(\eta^2-MeC_2Me)_2]$, by reaction of $[WI_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$ with carbon monoxide.

In 1992, Baker *et al*⁹⁶ refluxed the complex $[WI_2(CO)(NCMe)(\eta^2-PhC_2Ph)_2]$ in acetonitrile for 5 hours in the presence of PhC₂Ph to give the bis(acetonitrile) complex $[WI_2(NCMe)_2(\eta^2-PhC_2Ph)_2]$. 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 $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ by L (L = imidazole, pyrazole) to afford the complexes $[WI_2(CO)L(\eta^2-RC_2R)_2](M = W; R = Me, Ph)$.

Treatment of $[MI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ with one equivalent of L {L = bidentate phosphine such as Ph₂P(CH₂)_nPPh₂ (n = 1, 2, 3, 4, or 6)} gives the complexes $[MI_2(CO)$ {Ph₂P(CH₂)_nPPh₂}(η^2 -RC₂R)], whereas when one or two equivalents of monodentate phosphines such as PMe₃, PEt₃, PPh₃, is used the complexes, $[WI_2(CO)(L)(\eta^2-RC_2R)_2]$ or $[WI_2(CO)(L)_2(\eta^2-RC_2R)]$ 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 $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)]$. 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 $[MI_2(CO){P(OR^1)_3}_2(\eta^2-RC_2R)]$ (M = W, R = Me, Ph; R' = Me, Et, ⁱPr, ⁿBu), which were prepared by reaction of the complexes $[MI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me, Ph) with two equivalents of $P(OR^1)_3$. The X-ray crystal structure of the complex $[WI_2(CO){P(OMe)_3}_2(\eta^2-MeC_2Me)]$ has been determined, and has *cis*-phosphite ligands. (see Fig 1.18), which are *trans*-to a carbonyl group, and an iodo-ligand. The ¹³C 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 $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)]$



Fig.1.18-Crystal structure of *cis*-[WI₂(CO){P(OMe)₃}₂(η^2 -MeC₂Me)]

Organophosphine ligands are central to the coordination chemistry of organotransitionmetal complexes. Treatment of linear triphos {PhP(CH₂CH₂PPh₂)₂}, with [WI₂(CO) (NCMe)(η^2 -MeC₂Me)₂] was described by Baker *et al.*¹⁰⁰ in 1995 to yield the new organometallic phosphine ligand, [WI₂(CO)(η^2 -triphos)(η^2 -MeC₂Me)], 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 $[WI_2(CO)(\eta^2 - triphos)(\eta^2 - MeC_2Me)]$

In 1988, Armstrong and Baker¹⁰¹ have reacted anionic donor ligands such as Na[acac], with $[WI_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$ to give $[WI(CO)(acac)(\eta^2-MeC_2Me)_2]$, 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 $[WI(CO)(\eta^2-SC_5H_4N)(\eta^2-MeC_2Me)_2]$. In 1990, Baker *et al*¹⁰² have described the reactions of a series of dithiocarbamate type ligands, S_2CX^- {X = NMe₂, NEt₂, N(CH₂Ph)₂, OEt, NC₄H₈, or NC₅H₁₀} with [WI₂(CO)(NCMe)(η^2 -RC₂R)₂] in dichloromethane or diethyl ether to give either the new bis(alkyne) complexes [WI(CO)(S₂CX)(η^2 -RC₂R)₂], or the mono(alkyne) complexes, [W(CO)(S₂CX)₂(η^2 -RC₂R)].

The molecular structure of the complex [WI (CO)(S₂CNC₄H₈)(η^2 -MeC₂Me)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 [WI₂(CO) (NCMe)(η^2 -RC₂R)₂] with two equivalents of S₂CX⁻ to give the mono(alkyne) complexes [W(CO)(S₂CX)₂(η^2 -RC₂R)], and they reported from ¹³C NMR spectroscopy, that the alkyne ligands in the bis(alkyne) complexes [WI(CO)(S₂CX)(η^2 -RC₂R)₂] are donating an average of three electrons each to the metal, whereas the alkyne ligand in the complexes [W(CO)(S₂CX)₂(η^2 -RC₂R)] are donating four-electrons to the tungsten¹³.



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

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 [W₂Cl₃(CO)₆(η^3 -allyl)],[WBr(CO)₄(η^3 -allyl)] and [WI(CO)₄(η^3 -allyl)] respectively. In 1968, Hayter¹⁰⁴ 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 = C₃H₅, C₄H₇, C₃H₄Cl, C₆H₉, C₃H₄Ph), 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 = C₃H₅, 2MeC₃H₄, C₃H₄Cl)¹⁰⁴.

More recently, in 1986, Baker¹⁰⁵ described the reaction of fac-[Mo(CO)₃(NCMe)₃] with CH₂=C(CH₂Cl)₂ to give [MoCl(CO)₂(NCMe)₂{ η^{3} -C₃H₄(2-CH₂Cl)}].(the proposed structure is shown in Fig.1.21).

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

The reaction of $[Mo(CO)_4L_2]$ (L_2 = bipy, phen ,2,2'-bipyridylamine) with triphenyl cyclopropenyl bromide yield two types of complexes, namely, $[MoBr(CO)_2L_2(\eta^3-C_3Ph_3)]$ and $[MoBr(CO)_2L_2(\eta^3-C_3Ph_3O)]$. 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 $[MoX(CO)_2(NCMe)_2(\eta^3-C_5H_7)]$ (X = Cl, Br), and in the second step reacts these complexes with bidentate ligands such as dppe and dmpe to afford $[MoCl(CO)_2(dmpe)(\eta^3-C_5H_7)]$ and $[MoBr(CO)_2$ (dppe)($\eta^3-C_5H_7$)] respectively. The first successful synthesis of π -allyl complexes of molybdenum(II) and tungsten(II) was described in 1965 by Murdoch¹⁰⁷ by reaction of $[NEt_4][MX(CO)_5]$ with C₃H₅X to give $[NEt_4][M_2(\mu-X)_3(CO)_4(\eta^3-C_3H_5)_2]$, (see Figure 1.22).



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

Murdoch and Henzi¹⁰⁸ prepared a new complex $[MX(CO)_2(py)_2(\eta^3-C_3H_4CH_3)]$ (where M = Mo; X = Cl)(see Fig.1.23), which is prepared from $[NEt_4][M_2(\mu-X)_3(CO)_4(\eta^3-C_3H_4Me)_2]$ by splitting the bridge and reacting with nitrogen donor groups such as bipy, pyridine etc.



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

In 1977, Doyle¹⁰⁹ prepared the anionic π -allyl complexes of the type [MCl(CO)₂(diket) (η^3 -C₃H₅)]⁻ 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 [PPh₄][MoCl (CO)₃(bipy)] with ClCH₂C₂CH₂Cl to give [MoCl(CO)₂(bipy)(η^3 -CH₂-C(CO₂Me)= C=CH₂)] which has an η^3 -bonded *trans*-butadienyl ligand. Under anhydrous conditions the crystallographically characterised complex [MoCl(CO)₂(bipy){ η^3 -CH₂-C-(CO₂Me)-C(Me)(OMe)}] was isolated.

1.12b-Reactions of [MX(CO)2(NCMe)2(13-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 Friedel¹¹¹. The complexes $[MX(CO)_2(NCMe)_2(\eta^3-C_3H_5)]$, were prepared by reaction of $[M(CO)_6]$ and allyl halides (XC_3H_5) , (see Equation 1.15).

$$[Mo(CO)_{6}] + (\eta^{3}-C_{3}H_{5}X) \xrightarrow{CH_{3}CN, 80^{0}C, -4CO} [MoX(CO)_{2}(CH_{3}CN)_{2}(\eta^{3}-C_{3}H_{5})]$$

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

(Equation 1.15)

In 1974, King and Saran¹¹² prepared $[MoCl(CO)_2(CNR)_2(\eta^3-C_3H_5)]$ from $[MoCl(CO)_2(NCMe)_2(\eta^3-C_3H_5)]$, by reaction with two equivalents of CNR (R = Me, Et, ⁱPr, ⁱBu, Neopentyl, Cy). In 1981, Deaton and Walton¹¹³ have shown zero-valent complexes, $[Mo(CO)_2(CNR)_2L_2]$ can be prepared by reacting the complexes $[MoCl(CO)_2(CNR)_2(\eta^3-C_3H_5)]$ with two equivalents of $L(L = PEt_3, P^nPr_3, PMePh_2, PEtPh_2 etc)$.

The first reaction between $[MX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ with nitrogen donor ligands was described in 1976 by Hsieh and West¹¹⁴. They used R'N=CHCH=NR' to replace two acetonitrile ligands to yield $[MX(CO)_2(R'N=CHCH=NR')(\eta^3-C_3H_4R)]$ (M = Mo, W; X = Cl, Br, I, NCS; R = H, Me, Et, ⁱPr, ^tBu, Cy, Ph, *p*-MeC₆H₄, *p*-MeOC₆H₄), and the reactions of these complexes with a number of reagents including MeLi, C₅H₅Tl, SnCl₂, Ag⁺ and Lewis bases have been investigated.

Brisdon *et al*¹¹⁵ reacted bi-and tridentate nitrogen donor ligands with $[MX(CO)_2(NCMe)_2$ (η^3 -C₃H₄R)] to produce $[MoCl(CO)_2(N^N)(\eta^3$ -C₃H₄R)] (N^N = bipy; 2,2'-bipyridyl amine), or the cationic complexes $[Mo(CO)_2(N^N^N)(\eta^3$ -C₃H₄R)]^+ {N^N^N = dien, bis (2-pyridylmethyl) amine}. In 1969, Tom, Dieck and Friedel¹¹⁶ prepared the unstable zerovalent complexes, $[Mo(CO)_2(NCMe)_2(PPh_3)_2]$ by reaction of $[MoX(CO)_2(NCMe)_2(\eta^3$ allyl)] with PPh₃. Brisdon and Paddick¹¹⁷ have prepared the complexes $[MoX(CO)_2$ {Ph₂As(CH₂)₂AsPh₂}(η^3 -C₃H₅)] (X = Cl, Br, I), and the dimeric complexes $[MoX(CO)_2(\eta^3-C_3H_5)]_2$ { μ -Ph₂As(CH₂)_2AsPh₂}] by reacting the complexes $[MoX(CO)_2(\eta^3-C_3H_5)]_2$ { μ -Ph₂As(CH₂)_2AsPh₂.

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 $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$, with an equimolar amount of the semicarbazone to give $[MX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3-C_3H_4R)]$ (X = Cl, Br, I; R = H, 2Me; R',R'' = H or Me and Me, Et, Prⁿ, Ph), which are the first organotransition-metal complexes and also the first d⁴ compounds containing a semicarbazone as a bidentate ligand coordinated to molybdenum. In 1986, Campbell *et al*¹²⁰ have reacted the complexes $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ with thiosemicarbazide to give $[MoX(CO)_2(H_2NNHCSNH_2)(\eta^3-C_3H_4R)]$ (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 (η^3 -C₃H₅)], (see Figure 1.24).



(figure 1.24)

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

(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 spectroscopy¹²². 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 (*v*) and wavelength (λ) is as following :-

$$E = hv$$
 (h = 6.63 x 10⁻²⁷ erg sec)
 $v = c/\lambda$ (c = 2.998 x 10¹⁰ 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), ¹H NMR, ¹³C NMR and ³¹P 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 (v), 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 regions¹²⁴ 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
$C \equiv C, C \equiv N$	2300-2000
С—Н, О—Н, N—Н	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 (¹H NMR) :-

The NMR phenomenon (first observed in 1946),¹²⁴ is observable because certain nuclei behave like bar magnets. Most important among such nuclei are ¹H, ¹³C, ¹⁹F and ³¹P. All having a nuclear spin (*I*) of ¹/₂; those with nuclear spin of 1 include deuterium ²H and ¹⁴N. 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 ¹²C and ¹⁶O. 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 (¹H NMR)¹²² spectra result from absorption of energy that affects the spins of the hydrogen nuclei. Chemical shifts¹²⁴ are very important in ¹H 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 (CH₃)₄Si (TMS). This has several advantages; it is chemically inert, symmetrical, volatile (bp. 27^{0} C), 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 ¹H 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 CH₂ and CH₃ 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.

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(Fig.1-25)

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

Carbon nuclear magnetic resonance (¹³C NMR)^{123,124} spectra are analogous to proton NMR spectra, from ¹³C 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 ¹²C nucleus is not magnetically "active" (spin number, *I*, is zero), but the ¹³C nucleus, like the ¹H nucleus, has a spin number of ¹/₂. However, since the natural abundance of ¹³C is only about 1.1% that of ¹²C, and its sensitivity is only about 1.6% that of ¹H, the overall sensitivity of ¹³C compared with ¹H is about 1/5700.

The earlier, continuous wave, slow-scan procedure requires a large sample and a prohibitively long time to obtain a ¹³C NMR spectrum, but the availability of FT instrumentation, which permits simultaneous irradiation of all ¹³C nuclei, has resulted in an increased activity in ¹³C NMR spectrometry, beginning in the early 1970s, comparable to the burst of activity in ¹H 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—H, nondecoupled ${}^{13}C$ NMR spectra usually show complex overlapping multiplets that are difficult to interpret.

As it is with ¹H 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 ¹³C spectra range about 240 ppm downfield from TMS; this is a range of about 20 times that of routine ¹H spectra (~12 ppm). Several cations have been recorded at approximately 335 ppm downfield, and CCl₄ absorbs at approximately 96 ppm (upfield from TMS).

The definition of chemical shift¹²⁴ 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 ¹³C 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 (H₃C-CH₂-C=C-CH₂-CH₃) 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 ¹³C NMR chemical shift is shown in Fig.2.4¹³.

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

(³¹P NMR) :-

The spin of ³¹P NMR¹²⁴ is $1/_2$ and has also 100% abundance, so that the multiplicities generated with other nuclei are usually easily interpreted in the ³¹P NMR spectra, first order splittings are normal, because of the wide range of chemical shifts. The most widely used reference for ³¹P NMR chemical shifts is an external sample of 85% aqueous phosphoric acid H₃PO₄. There is always a problem in correlating shifts to an external sample, but H₃PO₄ 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 1.26-³¹P NMR Chemical shifts.

The aims from using ³¹P NMR spectroscopy in this thesis were, firstly to study the cisand *trans*- isomerism of the bis(phosphite) complexes, $[MI_2(CO){P(OR)_3}_2(\eta^2-EtC_2Et)]$, 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, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$, so that these could be used as phosphine ligands to coordinate to other transition-metal centres. The ³¹P{H} NMR spectroscopy was also used to establish the multimetallic nature of the reaction products derived from reaction of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$, 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, structuredetermination 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^{e} combines a reflection and a translation. (see fig 1.27).




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.

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Complete lists of bond lengths and bond angles are also part of the output from the leastsquares 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

<u>3-HEXYNE COMPLEXES OF MOLYBDENUM(II)</u>

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(µ-Br)Br(CO)(η^2 -EtC₂Et)₂}]¹¹, molybdenum dichloro-and dibromo-phosphine complexes [MoX₂(CO)L₂(η^2 -EtC₂Et)] (X = Cl, L = PPh₃; X = Br, L =PEt₃, PPh₃; X = Cl, Br, L₂ = dppe)¹⁵ and the bis(dialkyldithiocarbamate) complexes [Mo(CO)(η^2 -EtC₂Et)(S₂CNEt₂)₂]¹³¹ and [Mo(η^2 -PhC₂H)(η^2 -EtC₂Et)(S₂CNEt₂)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 1989⁹², reported the synthesis and X-ray crystal structures of the tungsten bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me, Ph). Very recently, in 1998¹³² Baker and co-workers also described the synthesis and crystal structures of the related molybdenum complexes $[MoI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me, Ph). The chemistry of $[MI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (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 $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$, 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, $[MI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (M = Mo, W; R = Me or Ph).

2.2-Reactions of [MI2(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 I₂ at 0°C⁷⁴ (see equation 2.1)

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

(Equation 2.1.)

Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) with two equivalents of EtC₂Et in CH₂Cl₂ at room temperature gave good yields of the bis(3-hexyne) complexes $[MI_2(CO)$ (NCMe)(η^2 -EtC₂Et)₂] (1 and 2), (see equation 2.2).

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

(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 ¹³C 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 (CHCl₃) for 1 and 2 show carbonyl stretching bands at v(C=O) = 2055 and 2056 cm⁻¹ respectively.

These are in very similar positions to their related 2-butyne derivatives $[MI_2(CO)(NCMe) (\eta^2-MeC_2Me)_2] \{ \upsilon(C=O) = 2061 \text{ cm}^{-1} (M = Mo)^{132}, 2050 \text{ cm}^{-1} (M = W)^{92} \}$. The nitrile bands at $\upsilon(N=C)$ at 2305 and 2253 cm⁻¹ are typical of complexes where the acetonitrile is acting as a simple σ -donor ligand¹³⁴.

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 CHCl₃).



Fig.2.1b-(IR spectrum of 2 in CHCl₃).

The X-ray crystal structures of a number of these bis(alkyne) complexes, $[MI_2(CO)(NCR)(\eta^2-R'C_2R')_2]$ (M = W, R = Me, R' = Me, Ph⁹², M = Mo, R = Me, R' = Me, Ph¹³²) 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 $[MI_2(CO)(NCR)(\eta^2-EtC_2Et)_2](1 \text{ and } 2)$

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 CH₂ groups at $\delta = 3.15$ -3.4 ppm as quartet for 2CH₂ and at $\delta =$ 2.9-3.1 ppm for another 2CH₂, because they are in different environments and affected by different group which is CO and NCMe, and the spectrum shows triplet for CH₃ at $\delta =$ 1.2-1.35 ppm (see fig 2.3).



The room temperature ¹³C NMR spectra of 1 and 2 have alkyne carbon contact resonances at $\delta = 163.48$ 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 Ward¹³ have shown how the ¹³C 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 ¹³C 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 ¹³C NMR spectrum for 1 is shown in Fig.2.5.



Fig.2.4-A plot of ¹³C NMR alkyne chemical shift vs. Formal number of electrons donated per alkyne ligand (N)¹³



Fig.2.5-¹³C NMR spectrum of 1.

2.3-Reactions of [MI2(CO)(NCMe)(n²-EtC2Et)2] with PPh3. X-ray

crystal structure of [WI2(CO)(PPh3)2(n²-EtC2Et)](4) :-

Reactions of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (M = Mo, W) with two equivalents of PPh₃ in CH₂Cl₂ at room temperature gave the bis(PPh₃) complexes $[MI_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)]$ (3 and 4), (see equation 2.3).

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

(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 ³¹P 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 CH₂Cl₂ and CHCl₃, however it was difficult to obtain good ¹³C 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** { $\nu(C=O) = 1942 \text{ cm}^{-1}$ } in the same solvent.

The ¹H NMR for complex **4** which has been crystallographically characterised by X-ray crystallography shows that the resonances at $\delta = 7.2$ -7.65 ppm are for phenyl group (integration 30H), $\delta = 3.0$ -3.2 ppm for CH₂ groups(integration 4H) and at $\delta = 1.0$ -1.25 ppm for the CH₃ groups(integration 6H).

The ³¹P{H} NMR spectra for **3** and **4** have single resonances at $\delta = -2.69$ and -15.93 ppm respectively, this indicates a *trans*-arrangement of the PPh₃ groups, which is also shown by the X-ray crystal structure of the tungsten complex **4**.

J coupling between tungsten and phosphorus shown in ³¹P 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 Mo⁹⁶. 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 $[WI_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)]$ (4) were grown by cooling a CH_2Cl_2 /Et₂O (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 [MI₂(CO)(NCMe)(n²-EtC₂Et)₂] with

<u> $Ph_2P(CH_2)_nPPh_2$ (M = Mo, n = 1; M = W, n = 1 to 6) :-</u>

Equimolar quantities of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (M = Mo, W) and Ph₂P(CH₂)_n PPh₂ (M = Mo, n = 1; M = W, n = 1 to 6) react in CH₂Cl₂ at room temperature to yield the mono(3-hexyne) complexes $[MI_2(CO){Ph_2P(CH_2)_nPPh_2}(\eta^2-EtC_2Et)]$ (5-11), (see equation 2.4)

$$[MI_{2}(CO)(NCMe)(\eta^{2}-EtC_{2}Et)_{2}] \xrightarrow{Ph_{2}P(CH_{2})_{n}PPh_{2}, CH_{2}Cl_{2}}$$

$$[MI_{2}(CO)\{Ph_{2}P(CH_{2})_{n}PPh_{2}\}(\eta^{2}-EtC_{2}Et)]$$

$$+ EtC_{2}Et$$

$$(M = Mo, n = 1; M = W, n = 1 \text{ to } 6)$$

(Equation 2.4)

Complexes 5-11 were fully characterised except ¹³C 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(PPh₃) complexes 3 and 4. The colours and spectroscopic properties of 5-11 are analogous to their 2-butyne analogues, $[WI_2(CO){Ph_2P(CH_2)_nPPh_2}(\eta^2-MeC_2Me)]$ as previously reported ⁹⁸.

For example, the room temperature ¹³C NMR spectrum (CDCl₃) for complex **9** has alkyne contact carbon resonances about 205.02 ppm (see table 2.4) which indicates from Templeton and Ward's¹³correlation (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 ³¹P NMR spectra of [WI₂(CO){Ph₂P (CH₂)_nPPh₂}(η^2 -EtC₂Et)] (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 [WI₂(CO){Ph₂P(CH₂)₃PPh₂}(η^2 -EtC₂Et)](**8**) for X-ray analysis were grown by cooling a CH₂Cl₂/Et₂O 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 $[MoBr_2(CO)(PMePh_2)_2(\eta^2-MeC_2Me)]^{135}$ and $[WCl_2(CO)(PMe_3)_2(\eta^2-PhC_2Ph)]^{136}$.

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 $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)]^{98}$ and $[WI_2(CO)(dppm)(\eta^2-MeC_2Ph)]^{137}$, 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 [MoI₂(CO)(NCMe)(η²-EtC₂Et)₂] and 2,2'-bipyridyl :-

Complex 12, $[MoI_2(CO)(2,2^{\circ}-bipyridyl)(\eta^2-EtC_2Et)]$ was prepared by reacting $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with one equivalent of 2,2^{\circ}-bipyridyl in CH₂Cl₂ at room temperature. The IR spectrum shows a single carbonyl band at $v(CO)(CHCl_3) = 1946$ cm¹, 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 ¹³C NMR spectrum (CDCl₃) shows alkyne contact carbon chemical shifts above 200 ppm which suggests the 3-hexyne is utilising both its filled $p\pi$ -orbitals and donating 4-electrons to the molybdenum, { δ (C=C)(CDCl₃) = 211.95 ppm}. Complex **12** is soluble in chlorinated solvents such as CH₂Cl₂ and CHCl₃, 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 $[MI_2(CO)(NCMe)(\eta^2 - EtC_2Et)_2]$, 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 described¹²⁷. The reaction chemistry of $[MI_2(CO)(NCMe)(\eta^2 - EtC_2Et)_2]$ with neutral and anionic donor ligands is similar to their 2-butyne and diphenyl acetylene analogues.¹²⁷



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



Figure 2.7- The structure of [WI₂(CO){Ph₂P(CH₂)₃PPh₂}(η²-EtC₂Et)] (8) with the atom numbering scheme. Ellipsoids are shown at 30% probability.



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

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

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

^a Calculated values in Parenthesis.

Complex No.	υ(C≡O)cm ⁻¹	υ(N≡C)cm ⁻¹	υ(C≡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)	

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

^aSpectra recorded in CHCl₃ as thin films between NaCl plates.

s = strong, w = weak.

Complex No	¹ H NMR (δ) ppm		
(1)	3.15-3.4(br, m, 4H, CH ₂), 2.9-3.1(br, m, 4H, CH ₂), 2.75(s, 3H,		
	NCC <u>H</u> ₃), 1.2-1.35(t, 12H, C <u>H</u> ₃).		
(2)	3.2-3.4(m, 4H, CH ₂), 2.9-3.1(m, 4H, CH ₂), 2.85(s, 3H, NCCH ₃),		
	1.2(dt, 12H, C <u>H</u> ₃).		
(3)	7.1-7.65(br, m, 30H, Ph), 2.6-3.4(br, m, 4H, CH ₂), 0.95-1.3(dt, 6H, CH ₃)		
(4)	7.2-7.65(br, m, 30H, <u>Ph</u>), 3.1(dq, 4H, C≡CC <u>H</u> ₂), 1.0-1.25 (t, 6H, C <u>H</u> ₃).		
(5)	6.8-7.35(br, m, 20H, <u>Ph</u>), 4.6(q, 2H, C=CC <u>H</u> ₂ , J_{H-H} = 10Hz), 3.45		
	(q, 2H,C <u>H</u> ₂), 2.9-3.15(br, 2H, C=CC <u>H</u> ₂), 0.9-1.25(t, 6H, C <u>H</u> ₃ , J _{H-H}		
	= 7.5Hz).		
(6)	7.0-7.8(brm, 20H, Ph), 4.7(dt, 2H, J _{H-H} = 8Hz, PCH ₂), 3.6(q, 2H,		
	C≡CC <u>H</u> ₂ , $J_{H-H} = 7.5$ Hz), 3.2(q, 2H, C≡CC <u>H</u> ₂ , $J_{H-H} = 7.3$ Hz), 1.05-		
	1.25(t, 6H, C <u>H</u> ₃ , $J_{H-H} = 7.5$ Hz).		
(7)	7.5-8.1 (m, 20H, Ph), 3.7(brm, 4H, Ph ₂ PCH ₂), 3.4(q, 4H, C≡CCH ₂),		
	1.4 (t, 6H, C <u>H</u> ₃).		
(8)	7.4-8.0 (m, 20H, <u>Ph</u>), 3.5 (q, 4H, C≡CC <u>H</u> ₂), 3.3 (brm, 4H, Ph ₂ PC <u>H</u> ₂),		
	1.2 (t, 6H, CH ₃), 0.8 (brm, 2H, Ph ₂ PCH ₂ CH ₂).		
(9)	6.8-7.7(br, m, 20H, Ph), 3.4(q, 4H, PCH2CH2), 2.6-3.15(br, 4H,		
	PCH_2CH_2), 1.1(t, 6H, CH_3).		

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

- (10) 6.9-7.6(brm, 20H, Ph), 3.2-3.4(brm, 4H, PCH₂CH₂), 2.95-3.2(br, m, 6H, CCH₂, PCH₂CH₂), 0.8-1.35(t, 6H, CH₃), 0.8-1.35(brm, 2H, CH₂).
- (11) 7.2-7.7 (m, 20H, <u>Ph</u>), 3.4(q, 4H, C=CC<u>H</u>₂), 3.0 (brm, 4H, Ph₂PCH₂CH₂C<u>H</u>₂), 2.4 (brm, 4H, Ph₂PCH₂C<u>H</u>₂), 0.8 (t, 6H, C<u>H</u>₃), 0.5 (brm, 4H, Ph₂PCH₂CH₂C<u>H</u>₂).
- (12) 9.2-7.6(v.br, 8H, 2pyridyl), $3.8-3.4(q, 4H, 2CH_2)$, $1.4-1.1(t, 6H, 2CH_3)$.

^aSpectra recorded in CDCl₃ (+25^oC) and referenced to SiMe₄. s = singlet, br = broad, d = doublet, m = multiplet, t = triplet,

q = quartet.

¹³C (δ) ppm **Complex No.** 6.85(s, CH₃-CN), 12.37, 13.86, 14.109, 14.37(s, 4CH₃), 25.92, (1)29.19(s, 4CH₂), 129.55(s, C=N), 163.48, 172.18(C=C); 217.04 (s, C≡O). 5.03(s, CH₃-CN), 13.63, 13.75(s, 4CH₃), 25.73, 28.94, 29.35(s, (2) $4CH_2$), 128.63(C=N), 160.82, 171.44(C=C); 206.53(C=O). 12.53, 13.73, 14.53 (s, 2CH₃), 32.66, 33.18, 55.25 (s, 2CH₂), (3)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). 11.94, 13.15 (s, 2CH₃), 31.92 (s, 2CH₂), 127.48, 127.55, 127.62, (4)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). 12.49, 13.41, 13.77, 14.50 (s, 2<u>C</u>H₃), 28.13, 29.64, 31.68 (s, 2<u>C</u>H₂ (5)131.63, 131.85, 132.04, 132.29, 133.32, 133.67, 133.82 (s, 4Ph), 228,90(C≡O). 13.40(s, 4CH₃), 30.72, 31.32, 31.77(s, 4CH₂), 53.53(s, CH₂-P), (6)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). 12.27, 13.48, 14.35, 15.28 (s, CH₂CH₃), 22.66, 24.91, 25.39 (s, (9) PCH₂CH₂, CH₂CH₃), 28.87, 29.67, 30.97, 31.75, 34.21, 53.51, 65.84(s, PCH₂), 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).

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

^a Spectra recorded in CDCl₃ (+25 ⁰C) and referenced to SiMe₄, s = singlet, br = broad, d = doublet, m = multiplet.

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

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

^a Spectra recorded in CDCl₃ (+25 ⁰C) and referenced to H₃PO₄.

CHAPTER THREE

3-HEXYNE COMPLEXES OF MOLYBDENUM(II) AND

TUNGSTEN(II) CONTAINING PHOSPHITE

DONOR LIGANDS.

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

Chapter Three

3-Hexyne complexes of Molybdenum(II) and Tungsten(II) containing Phosphite donor ligands : X-ray crystal structures of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)], [MoI_2(CO)(dppe)(\eta^2-EtC_2Et)]$ and $[MI_2(CO){P(O^iPr)_3}_2(\eta^2-EtC_2Et)]$ (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)L₂(η^2 -RC₂R¹)] (M = Mo, W; X, Y = Cl, Br, I; R, R¹ = 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, [WI₂(CO)₂L(η^2 -HC₂Bu¹)] (L = CN⁴Bu, PMe₃, AsMe₃) described by Umland and Vahrenkamp in 1982²⁸.

In 1998¹⁵⁵, the preparation of the bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2 - EtC_2Et)_2]$ (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, $[WI_2(CO)(PPh_3)_2(\eta^2 - EtC_2Et)]$ and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2 - EtC_2Et)]$ (see chapter two). In 1989⁹⁹, the preparation of the bis(phosphite) complexes $[WI_2(CO)\{P(OR)_3\}_2(\eta^2 - R^*C_2R^*)]$ (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 [MoI₂(CO)(NCMe){P(OPh)₃}(η^2 -R'C₂R'')] (R' = R'' = Me or Ph; R' = Me, R'' = Ph) have been described, and also extended the series of bis(phosphite) complexes [MI₂(CO){P(OR)₃}₂(η^2 -R'C₂R'')] 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, ¹Bu, ⁱPr and Ph) with the 3-hexyne complexes of molybdenum(II) and tungsten(II), [MI₂(CO)(NCMe)(η^2 -EtC₂Et)₂]. The second aim was to study the chemistry of the structurally characterised complex [MoI₂(CO)(NCMe){P(OPh)₃}(η^2 -EtC₂Et)], 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, [WI₂(CO){P(OR)₃}₂(η^2 -EtC₂Et)] by NMR spectroscopy.

3.2-The Synthesis and X-ray crystal structure (R = Ph) of

$[MoI_2(CO)(NCMe){P(OR)_3}(\eta^2-EtC_2Et)](R = Ph \text{ or } {}^iPr):-$

The starting materials used in this research, $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (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 $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and P(OR)₃ (R = Ph or ⁱPr) in diethyl ether at room temperature gave the new mixed ligand complexes, $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2-EtC_2Et)]$ (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), ¹H, ¹³C NMR spectroscopy (Table 3.3-3.4) and ³¹P 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 CH₂Cl₂ and CHCl₃, 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^oC) without any significant decomposition.

The IR spectra (CHCl₃) (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, $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-R^2C_2 R^2)]$ (R²= R²= Me v(CO) = 1995 cm⁻¹, Ph v(CO) = 2013 cm⁻¹; R²= Me, R²= Ph v(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, $[MoI_2(CO)(NCMe){P(OPh)_3}$ (η^2 -EtC₂Et)] (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.





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)A⁰}, *trans*-to an acetonitrile {Mo(1)-N(300)2.212(13) A⁰}, and a phosphite ligand {Mo(1)-P(4) 2.485 (4) A⁰} *trans* to an iodide {Mo-I(2) 2.799 (3)A⁰}. The coordination sphere is completed by the hexyne Mo(1)-C(5) 2.007(12), Mo(1)-C(4) 2.040 (13) A⁰), *trans*-to iodide {I(3) at 2.862(3) A⁰}. 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 $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](M = Mo$ 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 ³¹P{¹H} NMR (CDCl₃ +25^oC) spectrum of **13** has a single resonance at $\delta = 114.44$ ppm (Table 3.5). The ¹H NMR (CDCl₃, +25^oC) spectrum shows the expected resonances for **13** and **14**, which is confirmed the crystal structure that there is NCMe in the complexes at $\delta = 2.20$ and 2.05 ppm respectively. The ¹³C NMR spectrum for the structurally characterised complex **13** and **14** show an alkyne contact carbon resonance at $\delta = 193$ and 196.85 ppm which from Templeton and Ward's¹³ correlation of the alkyne contact carbon resonances to the number of electron donated by the 3-hexyne is acting as a 4electron 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 $[WI_2(CO){P(OR)_3}(\eta^2-EtC_2Et)_2]$ (R = Me, ⁱPr and Ph) :-

It is interesting to consider the studies reported in 1989⁹⁹, that when equimolar quantities of [WI₂(CO)(NCMe)(η^2 -PhC₂Ph)₂] and P(OPh)₃ are reacted in CHCl₃ for 48hr a mixture of the mono(triphenylphosphite) complex [WI₂(CO){P(OPh)₃}(η^2 -PhC₂Ph)₂], {v(CO) = 2030 cm⁻¹}, the bis(triphenylphosphite) complex, [WI₂(CO){P(OPh)₃}₂(η^2 -PhC₂Ph)], {v(CO) = 1990 cm⁻¹} and the starting material, [WI₂(CO)(NCMe)(η^2 -PhC₂Ph)₂] {v(CO) = 2090 cm⁻¹} was obtained.

In this section, the successful synthesis and characterisation of the mono(phosphite) complexes, $[WI_2(CO){P(OR)_3}(\eta^2-EtC_2Et)_2]$, (R = Me, ⁱPr, Ph) (15-17), is described by changing the reaction solvent, and the alkyne in these reactions. Treatment of equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and $P(OR)_3$ (R = Me, ⁱPr or Ph) in diethyl ether at room temperature gave the acetonitrile replaced bis(3-hexyne) complexes, $[WI_2(CO){P(OR)_3}(\eta^2-EtC_2Et)_2]$ (15-17) in high yield. Complexes 15-17 have been fully characterised by elemental analysis (Table 3.1), IR (Table 3.2), ¹H, and ³¹P{¹H} NMR spectroscopy (Table 3.3 and 3.5). complex 16 characterised by ¹³C NMR as well, whereas the rest was difficult to obtain ¹³C 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 $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with one equivalent of P(OR)₃ is not unexpected, as we have previously observed similar differences. For example, reaction of equimolar amounts of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and 2,2'-bipy(bipy) gave the neutral molybdenum mono(2-butyne) complex,

 $[MoI_2(CO)(bipy)(\eta^2-EtC_2Et)]$ (see complex 12), whereas, the reaction of equimolar amounts of $[WI_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$ and bipy gave the cationic complex, $[WI(CO)(bipy)(\eta^2-MeC_2Me)_2]I$, 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, [WI₂(CO) $L(\eta^2-R^2C_2R^2)_2$]. 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 $[WI_2(CO)(NCMe)(\eta^2 - RC_2R)_2](R = Me \text{ or Ph})$ with a range of monodentate neutral donor ligands always go with retention of configuration, it is very likely the reactions of equimolar amounts of $[WI_2(CO)(NCMe)(\eta^2 - EtC_2Et)_2]$ 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 $[WI_2(CO){P(OR)_3}(\eta^2-EtC_2Et)_2](15-17)$

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 ¹³C NMR spectrum for complex **16** shows alkyne contact carbon resonances at $\delta = 166.8$ and 169.50 ppm, which suggests¹³, 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 [MoI2(CO)(NCMe){P(OPh)3}(n²-EtC2Et)](13) :-

In a previous very recent study¹⁵⁶ of the reactions of $[MoI_2(CO)(NCMe)(\eta^2-R'C_2R'')_2]$ with one equivalent of P(OPh)₃ to give the three crystallographically characterised complexes, $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-R'C_2R'')]$ (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, [MoI₂ (CO)(NCMe){P(OPh)₃}(η^2 -EtC₂Et)](13) is discussed. The first simple reaction was carried out by bubbling carbon monoxide through an Et₂O solution of 13, which gives the acetonitrile replaced product, [MoI₂(CO)₂{P(OPh)₃}(η^2 -EtC₂Et)](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 (CHCl₃) for [MoI₂(CO)₂{P(OPh)₃}(η^2 -EtC₂Et)] has a single carbonyl band at 2040cm⁻¹, which is as expected much higher than for 13 which has v(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 ¹³C NMR spectrum of **18** has a single alkyne, (C=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 indicates¹³, that the 3-hexyne is utilizing both of its filled p π -orbitals and donating 4-electrons to the molybdenum in this complex.

Equimolar quantities of 13 and L {L = PPh₃, P(OⁱPr)₃, [MI₂(CO)₃{MeC(CH₂PPh₂)₃-*P*,*P*'}](M = Mo, W)} in CH₂Cl₂ at room temperature gave the acetonitrile replaced products, [MoI₂(CO) L{P(OPh)₃}(η^2 -EtC₂Et)] (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 = PPh₃, [MI₂(CO)₃{MeC(CH₂PPh₂)₃-*P*,*P*'}] than 13-18, but more stable than these complexes. It should be noted that the organometallic phosphines, [MI₂(CO)₃{MeC(CH₂PPh₂)₃-*P*,*P*'}] (M = Mo or W) have been prepared by reacting equimolar quantities of [MI₂(CO)₃ (NCMe)₂] and MeC(CH₂PPh₂)₃ in CH₂Cl₂ at room temperature¹⁵⁷, as described in chapter four of this thesis.

The complexes (L = PPh₃)(19) and {L = P(OⁱPr)₃}(20) were confirmed as CH₂Cl₂ and Et₂O 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(PPh₃) complex, [WI₂(CO)(PPh₃)₂(η^2 -EtC₂Et)](4) (see chapter two), and other related bis(phosphite) complexes (see scheme 3.1).



Fig.3.3. Proposed structure of $[MoI_2(CO)L\{P(OPh)_3\}(\eta^2-EtC_2Et)](19-22)$ $\{L = PPh_3(19); P(O^iPr)_3(20); L^{Mo}(21); L^{W}(22)\}.$

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 $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ units. The IR spectrum for the complex $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ has bands at v(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 method¹⁵⁸.

The ³¹P{H} NMR spectra have two resonances due to every phosphorus in the complexes. For example, the triphenylphosphine complex **19** has two singlets at $\delta = 114.57$ ppm {P(OPh)₃}(J_{P-P}=227.94 Hz) and $\delta = 102.74$ ppm due to PPh₃.



Scheme. 3.1. Proposed mechanism for the stepwise reaction of two equivalents of phosphite ligands with $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$.
Reaction of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)](13)$ with an equimolar amount of L^L (L^L = bipy or dppe) afforded the new complexes $[MoI_2(CO)(L^L)(\eta^2-EtC_2Et)](23$ 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 ¹³C, ³¹P{¹H} NMR spectroscopy for complex 24 (tables 3.4 and 3.5) and X-ray crystallography for the bis(diphenylphosphino) ethane complex, $[MoI_2(CO)(dppe)(\eta^2-EtC_2Et)](24)$, 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 $[MI_2(CO)(L^L)(\eta^2-RC_2R')]$, including the following complexes $[MoI_2(CO) (5,6-Me_2-1,10-Phen)(\eta^2-PhC_2Ph)]^{132}$, $[WI_2(CO)(dppm)(\eta^2-MeC_2R)](R = Me^{98}, R = Ph^{137})$ and $[WI_2(CO) \{Ph_2P(CH_2)_3PPh_2\}(\eta^2-EtC_2Et)]^{155}$, which have been structurally characterised. Suitable single crystals for X-ray crystallography of $[MoI_2(CO)(dppe)(\eta^2-EtC_2Et)](24)$ were grown by cooling $(-17^\circ C)$ 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 $[MoI_2(CO)(dppe)(\eta^2-EtC_2Et)](24)$. 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 [MoI₂(CO)(dppe)(η²-EtC₂Et)](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 $[WI_2(CO) (dppm)(\eta^2-MeC_2Ph)]^{137}$ and $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)],^{98}$ 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, ⁱPr, 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 [MoI₂(CO)(dppe)(η^2 -EtC₂Et)] formulation. The ³¹P{¹H} NMR spectrum (CDCl₃, +25^oC) for 24 has a single resonance at $\delta = 31.35$ ppm. Equimolar quantities of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)](13)$ and NaS_2CNR_2 (R = Me or Et) react in CH₂Cl₂ at room temperature to give the dithiocarbamate complexes, $[MoI(CO){P(OPh)_3}(S_2CNR_2-S,S')(\eta^2-EtC_2Et)]$. CH₂Cl₂(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 CH₂Cl₂ 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)(S₂CNC₄H₈)(η^2 -MeC₂Me)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 ${}^{31}P{}^{1}H{}$ 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 $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2 - EtC_2Et)](13)$ with a variety of neutral and anionic ligands, such as 1,10-phenanthroline, AsPh₃, SbPh₃ were carried out, and although reactions occurred no pure products could be isolated from these reactions.



Fig.3.5 Proposed structure of $[MoI(CO){P(OPh)_3}(S_2CNR_2)(\eta^2-EtC_2Et)]$.CH₂Cl₂. (25 and 26).

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

$[MI_2(CO){P(OR)_3}_2(\eta^2 - EtC_2Et)] :-$

When the complexes $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ were reacted with two equivalents of $P(OR)_3$ in diethyl ether at room temperature, the bis(phosphite) complexes $[MI_2(CO){P(OR)_3}_2(\eta^2-EtC_2Et)]{M = Mo \text{ or } W; R= Me, Et, {}^{i}Pr, {}^{n}Bu, Ph (for M = W$ $only)}(27-35)$ were obtained in high yield, *via* displacement of an acetonitrile and a 3hexyne ligand.

Complexes 27-35 were characterised by elemental analysis (Table 3.1), IR (Table 3.2),¹H (Table 3.3), ³¹P (Table 3.5 except complex 29), and in selected cases ¹³C 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 $[WI_2(CO) \{P(OR)_3\}_2(\eta^2 - EtC_2Et)] \{R = Et(30) \text{ and } ^nBu(34)\}$ 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, $[WI_2(CO) \{P(OR)_3\}_2(\eta^2 - R^2C_2R^2)](R = Me, Et, ^{i}Pr, ^{n}Bu; R^2 = Me \text{ or } Ph)(structurally characterised for <math>R = R^2 = Me)^{99}$ and the large series of complexes, $[MI_2(CO) \{P(OR)_3\}_2(\eta^2 - R^2C_2R^2)] \{R = Ph, R^2 = Me, R^2 = Ph (M = Mo only); M = Mo or W, R = Me, R^2 = R^2 - R^2C_2R^2) \} \{R = Ph, R^2 = Me, R^2 = Ph (M = Mo only); R = Et, R^2 = R^2 - Me, Ph (M = Mo only); R^2 = Me, R^2 = Ph (M = W only); R = Et, R^2 = R^2 - Me, Ph (M = Mo only); R^2 = Me, R^2 - Ph (M = W only); R = R^2 - Me, Ph (M = Mo only); R^2 = Me, R^2 - Ph (M = Mo only); R = R^2 - Me, Ph (M = Mo only); R^2 = Me, R^2 - Ph (M = Mo only); R^2 = Me, Ph (M = Mo only); R = R^2 - Me, Ph (M = Mo only); R^2 = Me, R^2 - Ph (M = Mo only); R^2 = Me, Ph (M = Mo only); R^2 = Me, R^2 - Ph (M = Mo only); R^2 = Me, Ph (M = Mo only); R^2 = R^2 - Me, R^2 - Ph (M = Mo only); R^2 = Me, R^2 - R^2 - Me, R^2 - R^2 - Me; R^2 - R^2 - Me, R^2 - R^$

Suitable single crystals for X-ray analysis of $[MI_2(CO){P(O^iPr)_3}_2(\eta^2-EtC_2Et)](31)$ and (32) were grown by cooling (-17^oC) 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 [WI₂(CO){P(OⁱPr)₃}₂(η^2 -EtC₂Et)](**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)A⁰, Mo(1)-P(4) 2.566(5) A⁰}. 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) A⁰ respectively.

This *trans* configuration around the metal has been observed previously¹⁵⁶ with other alkynes phosphite complexes, for example, $[MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2-MeC_2Me)]$ (M = W, Mo) which are isostructural and $[MoI_2(CO)\{P(OPh)_3\}_2(\eta^2-MeC_2Me)]$, $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2-MeC_2Me)]$, $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2-MeC_2Ph)]$ which are not. Only two *cis* complexes have been prepared and structurally characterised *viz* $[MI_2(CO)\{P(OMP)_3\}_2(\eta^2-MeC_2Me)]$ (M = Mo) $_3\}_2(\eta^2-MeC_2Me)$] (M = Mo) $_3M_2(\eta^2-MeC_2Me)$] (M = Mo) (M = Mo) (M = MO)

The IR spectra of complexes 27-30, {P(OMe)₃} and {P(OEt)₃}, and 33 and 34 {P(OⁿBu)₃} complexes, have two carbonyl stretching bands in both their solution (CHCl₃) 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 $[MoI_2(CO){P(OEt)_3}_2(\eta^2-EtC_2Et)]$ (29) has carbonyl bands v(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 angles¹⁵⁹ for P(OR)₃ are { $R = Me(107^{0})$, Et \approx ⁿBu(109⁰), ⁱPr(128⁰)}, 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 ³¹P NMR data has been used to obtain the *cis* : *trans* isomer ratio of the series of phosphite ligands $[MI_2(CO){P(OR)_3}_2(\eta^2-EtC_2Et)]$ (R = Me, Et, ⁿBu or ⁱPr) and were found not in similar ratios to those previously observed for the closely related 2-butyne and 1-phenylpropyne complexes of the type, $[MI_2(CO) {P(OR)_3}_2(\eta^2-R^*C_2R^*)]$ (R' = R'' = Me; R' = Me, R'' = Ph)¹⁵⁶, which was for R = Me: Et: ⁿBu: ⁱPr 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 ¹³C 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 complxes¹³, 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 $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)]$ (13) has been described. The chemistry of 13 has been extensively studied, and one of the reaction products, $[MoI_2(CO)(dppe)(\eta^2-EtC_2Et)]$, has been crystallographically characterised.

The synthesis and structure (M = Mo and W; R = ⁱPr) of a series of bis(phosphite) complexes [MI₂(CO){P(OR)₃}₂(η^2 -EtC₂Et)] are also described. Finally, by considering the results of two previous papers describing the reactions of [MI₂(CO)(NCMe)(η^2 -R'C₂R'')₂] with phosphites^{99,156} and in particular the work described in this chapter, a detailed mechanism of the reactions of [MI₂(CO)(NCMe)(η^2 -R'C₂R'')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 [WI₂(CO){P(OⁱPr)₃}₂(η²-EtC₂Et)]((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 ${}^{31}P{}^{1}H$ NMR spectrum for the complex

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



Fig.3.8-The room temperature ${}^{31}P{}^{1}H$ NMR spectrum for the complex [WI₂(CO){P(OⁱPr)₃}₂(η^2 -EtC₂Et)](**32**).

Complexes	Colour	Yield%	С%	H%	N%
(13) [MoI ₂ (CO)(NCMe){P(OPh) ₃ }(η^2 -EtC ₂ Et)]	Brown	84	40.0	3.5	1.7
			(39.9)	(3.5)	(1.7)
(14) [MoI ₂ (CO)(NCMe){P(O ⁱ Pr) ₃ }(η^2 -EtC ₂ Et)]	Brown	76	30.1	4.7	2.0
			(30.5)	(4.8)	(2.0)
(15) [WI ₂ (CO){P(OMe) ₃ }(η^2 -EtC ₂ Et) ₂]	Green	79	24.1	4.2	-
			(24.3)	(3.9)	
(16) [WI ₂ (CO){P(O ⁱ Pr) ₃ }(η^2 -EtC ₂ Et) ₂]	Green	85	31.2	5.4	_
			(31.5)	(4.9)	
(17) [WI ₂ (CO){P(OPh) ₃ }(η^2 -EtC ₂ Et) ₂]	Green	80	38.2	3.5	-
			(38.8)	(3.8)	
(18) $[MoI_2(CO)_2{P(OPh)_3}(\eta^2-EtC_2Et)]$	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	-
$(\eta^2 - EtC_2Et)]$. CH ₂ Cl ₂			(47.3)	(3.8)	
(20) $[MoI_2(CO){P(O^iPr)_3}{P(OPh)_3}$	Brown	43	42.9	5.5	-
$(\eta^2 - EtC_2Et)].Et_2O$			(43.3)	(5.4)	
(21) [MoI ₂ (CO)(L){P(OPh) ₃ }(η^2 -EtC ₂ Et)]	Brown	62	44.5	3.6	-
{L= [MoI ₂ (CO) ₃ {MeC(CH ₂ PPh ₂) ₃ - P , P '}]}			(45.3)	(3.5)	

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

(22) [MoI ₂ (CO)(L){P(OPh) ₃ }(η^2 -EtC ₂ Et)]	Brown	36	42.5	3.4	_
{L= [WI ₂ (CO) ₃ {MeC(CH ₂ PPh ₂) ₃ - P,P' }]}			(43.2)	(3.4)	
(23) [MoI ₂ (CO)(2,2'-bipy)(η^2 -EtC ₂ Et)]	Brown	-	45.4	3.7	3.2
			(45.4)	(3.6)	(3.0)
(24) [MoI ₂ (CO){PPh ₂ (CH ₂) ₂ PPh ₂ }(η^{2} -EtC ₂ Et)]	Green	92	46.2	4.0	_
			(46.2)	(4.0)	
(25) [MoI(CO){(CH ₃) ₂ NCS ₂ } {P(OPh) ₃ }	Brown	36	40.3	4.1	1.9
$(\eta^2$ -EtC ₂ Et)].CH ₂ Cl 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
$(\eta^2$ -EtC ₂ Et)].CH ₂ Cl ₂			(42.5)	(4.3)	(1.6)
(27) $[MoI_2(CO){P(OMe)_3}_2(\eta^2-EtC_2Et)]$	Brown	78	22.1	4.0	
			(22.1)	(4.0)	
(28) [WI ₂ (CO){P(OMe) ₃ } ₂ (η^2 -EtC ₂ Et)]	Green	57	19.2	3.5	_
			(19.6)	(3.5)	
(29) [MoI ₂ (CO){P(OEt) ₃ } ₂ (η^2 -EtC ₂ Et)]	Brown	41	28.6	5.2	
			(28.8)	(5.1)	
(30) $[WI_2(CO){P(OEt)_3}_2(\eta^2-EtC_2Et)].Et_2O$	Green	49	27.8	5.0	-
			(28.9)	(5.2)	
(31) [MoI ₂ (CO){P(O ⁱ Pr) ₃ } ₂ (η^2 -EtC ₂ Et)]	Brown	77	33.9	5.9	-
			(34.3)	(6.0)	
(32) [WI ₂ (CO){P(O ⁱ Pr) ₃ } ₂ (η^2 -EtC ₂ Et)]	Green	91	31.4	5.6	-
			(31.1)	(5.4)	

(33) $[MoI_2(CO){P(O^nBu)_3}_2(\eta^2-EtC_2Et)]$	Brown	56	38.5	6.7	
			(38.8)	(6.7)	-
(34) [WI ₂ (CO){P(O ⁿ Bu) ₃ } ₂ (η^2 -EtC ₂ Et)]. Et ₂ O	Green	54	38.0	6.6	_
			(37.5)	(6.6)	
(35) [WI ₂ (CO){P(OPh) ₃ } ₂ (η^2 -EtC ₂ Et)]	Green	80	43.5	3.9	_
			(44.2)	(3.5)	

^a Calculated values in Parentheses.

Complex	υ(C≡O)	υ(C≡C)	υ(C≡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,	1648 wcm ⁻¹	-
	1938 s and 1859 s) cm	r ¹	
(22)	(2037 s, 1962 s,	1636 w cm ⁻¹	_
	1904 s,1852 s) 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	_

Table 3.2- Infrared Data for the phosphite complexes $13-35^{a}$

(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	a <u>-</u> :
(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	_

^aSpectra recorded in CHCl₃ as thin films between NaCl plates. s = strong,

sh = shoulder, w = weak, vw = very weak.

^bSpectra recorded in the solid state as KBr discs.

complex	¹ Η 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 <u>Me</u>), 1.9(d,
	9H, $J_{H-H} = 6.76Hz$, 3O-CH(<u>CH</u> ₃) ₂), 1.3(d, 9H, $J_{H-H} = 6.1Hz$, 3O-
	CH(<u>CH</u> ₃) ₂), 1.2(s, 6H, 2CH ₃).
(15)	$3.7(d, 3H, CH_3, J_{H-H}=7.35); 3.5(d, 6H, 2CH_3 J_{H-H}=5.34); 3.6$
	(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, <u>CH</u> 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 ⁱ Pr); 4.8(q, 4H, 2CH ₂ hexyne);
	$3.4(q, 4H, 2CH_2 \text{ ether}); 1.4(d, 18H, 6CH_3 \text{ of }^{i}\text{Pr}, J_{H-H} = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 6CH_3 \text{ of }^{i}\text{Pr}) = 5.60); 1.1(t, 6H, 18H, 18H, 18H, 18H, 18H, 18H, 18H, 18$
	2CH ₃); 0.9(t, 6H, 2CH ₃ ether).

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

- (21) 7.8-7.0(v.br, 30H, 6Ph); 3.5-3.2(q, 4H, 2CH₂); 2.4-2.1(m, 6H, 2CH₂);
 1.3(s, 3H, 1CH₃); 1.2(t, 6H, 2CH₃).
- (22) 7.7-6.7(v.br, 30H, 6Ph); 3.6-3.1(q, 4H, 2CH₂); 2.4-2.1(m, 6H, 2CH₂); 1.4-1.15(t, 6H, 2CH₃); 0.8(s, 3H, 1CH₃).
- (24) 7.3-7.1(v.br, 24H, 4Ph); 4.0(s, 4H, 2CH₂); 3.5(q, 4H, 2CH₂);
 0.85(t, 6H, 2CH₃).
- (25) 7.4-7.1(m, 15H, 3Ph); 5.3(s, 2H, <u>CH</u>₂Cl₂); 3.8(q, 4H, 2CH₂ hexyne);
 3.5(q, 6H, 2CH₃ of (<u>CH</u>₃)₂NCS₂); 1.4(t, 6H, 2CH₃ hexyne).
- (26) 7.5-7.1(m, 15H, 3Ph); 5.3(s, 2H, <u>CH</u>₂Cl₂); 4.1-3.8(m, 4H, 2CH₂
 (CH₃<u>CH</u>₂)₂NCS₂); 3.8-3.6(q, 4H, 2CH₂ of hexyne); 1.5(t, 6H, 2CH₃
 of (<u>CH</u>₃CH₂)₂NCS₂); 1.1(t, 6H, 2CH₃ hexyne).
- (27) $3.95(d, 9H, J_{H-H} = 9.91 \text{ Hz}, \text{OMe}), 3.65(q, 4H, 2CH_2), 3.6(d, 9H, J_{H-H} = 10.82, \text{OMe}), 1.35(t, 6H, 2CH_3).$
- (28) $3.95(d, 2H, J_{H-H} = 9.92Hz \text{ OMe}), 3.75(d, 3H, J_{H-H} = 11.9 \text{ Hz OMe}),$ $3.6(q, 4H, 2CH_2), 3.3(d, 9H, J_{H-H} = 10.7 \text{ Hz OMe}), 1.2(t, 6H, 2CH_3).$
- (29) $3.9-4.2(m, 12H, O-\underline{CH_2CH_3}), 3.1(q, 4H, 2CH_2), 1.0-1.25(m, 18H, J_{H-H} = 6.97, O-CH_2\underline{CH_3}), 0.9(t, 6H, CH_3).$
- (30) 4.75(m, 12H, 6CH₂), 3.1(q, 4H, 2CH₂), 1.4(t, 18H, O-CH₂CH₃),
 1.1(t, 6H, 2CH₃ of hexyne).
- (31) 4.75(m, 6H, O -<u>CH</u>), 3.65(q, 4H, 2CH₂), 1.3(t, 6H, 2CH₃ of hexyne). 1.2(d, 36H, J_{H-H} =1.21 Hz, 6O-CH(<u>CH₃)₂</u>).



^aSpectra recorded in CDCl3 (+25) and referenced to SiMe₄, s = singlet,

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

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

Comp.N	lo. 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, 2CH₃), 32.32, 32.41, 35.47 (s, 2CH₂), 65.44, 65.52, 67.38(s, O-CH₂CH₃), 195.0 (s, C=C), 200.99 (s, C=O).

- (30) 15,78, 15.89, 16.60 (s, 2CH₃), 31.41, 33.61 (s, 2CH₂), 61.74,
 61.82, 62.62, 63.29, 63.40, 63.50 (s, O-CH₂CH₃), 203.0, 205.0 (s, C≡C), 227.7(s, C≡O).
- (31) 21.93, 22.85, 24.02 (s, 2CH₃), 30.51, 30.98, 31.34, 32.20, 34.59
 (s, 2CH₂), 65.79, 67.39, 69.57, 70.59, 70.72, 71.77 2(s, O-CH(CH₃)₂), 207.82, 208.01 (s, C≡C), 236.21 (s, C≡O).
- (32) 23.58, 23.65, 23.94 (s, 2CH₃),31.15, 31.38 (s, 2CH₂),
 65.78, 67.35, 68.50 2(s, O-CH(CH₃)₂), 205.30 (s, C≡C),
 236.12 (s, C≡O).
- (33) 13.51, 13.68, 13.82 (s, 2CH₃), 32.33, 32.58, 32.67 (s, 2CH₂), 65.42,
 65.51, 66.12, 66.39, 66.73, 66.86 2(s, O-CH₂CH₂CH₂CH₃), 203.40 (s, C≡C), 236.29 (s, C≡O).
- (35) 12.56, 13.31, 14.22, 14.45 (s, 2CH₃); 29.13, 29.31, 29.76, 31.97
 (s, 2CH₂); 115.50, 117.38, 121.04, 121.12, 128.69, 129.50 (s, 6Ph); 204.69 (s, C≡C), 219.81 (s, C≡O).

^aSpectra recorded in CDCl₃ (+25 °C) and referenced to SiMe₄. s = singlet,

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

Complex	³¹ Ρ (δ) ppm
(13)	$\delta(P) = 114.44, (s).$
(15)	$\delta(P) = 104.98$, (s, J _{w-p} = 205.53 Hz).
(16)	$\delta(P) = 94.76$, (s, $J_{w-p} = 211.6 \text{ Hz}$
(17)	$\delta(P) = 92.26(s).$
(18)	$\delta(\mathbf{P}) = 111.216(\mathbf{s}).$
(19)	$\delta(P_1)\{PPh_3\}=102.74, (s)$
	$\delta(P_2){P(OPh)_3} = 114.57 \text{ (s, } J_{P-P} = 227.94 \text{ Hz}).$
(20)	$\delta(P) = 127.33$, {s, P(OPh) ₃ } and 110.88, {s, P(O ⁱ Pr) ₃ }.
(21)	$\delta(P) = (17.58, 2P \text{ of } L^{Mo} \text{ and } 32.17, 1P \text{ of } L^{Mo});$
	and 114.50, $\{s, P(OPh)_3\}$.
(24)	$\delta(P) = 31.35$, (s, dppe).
(25)	$\delta(P) = 128.01$, (J _{wp} = 72.70 Hz).
(26)	$\delta(P) = 127.26, \{P(OPh)_3\}(s).$
(27)	$\delta(P) = 115.35$, (<i>trans</i>)(s).
	$\delta(P) = 126.37$, (d, $J_{pp} = 53.66$ Hz)
	and 125.30, (d, $J_{pp} = 52.60 \text{ Hz})(cis)$.
(28)	$\delta(P) = 105.06$, (<i>trans</i>), (J _{p-w} = 259.14 Hz).
	$\delta(P) = 98.0$, (d, $J_{pp} = 61.97$ Hz)
	and 109.25, (d, $J_{pp} = 61.97$ Hz) (<i>cis</i>).

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

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

^aSpectra recorded in CDCl₃ (+25 $^{\circ}$ C) and referenced to H₃PO₄

<u>CHAPTER FOUR</u> <u>PART I :- TRIPODAL TRIPHOS {MeC(CH₂PPh₂)₃}</u> <u>SEVEN COORDINATE COMPLEXES OF</u> <u>MOLYBDENUM(II) AND TUNGSTEN(II)</u>

<u>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 $[FeI(CO)_2(Cp \text{ or } Cp')]$.</u>

Chapter Four

Tripodal triphos {MeC(CH₂PPh₂)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 described¹⁶⁰⁻¹⁷⁶, very few containing bridging-tridentate phosphines such as linear triphos {PhP(CH₂CH₂PPh₂)₂} and tripodal triphos {MeC(CH₂PPh₂)₃} have been reported. For example, in 1981 Hunt and Balch¹⁷⁷ described the synthesis, characterisation and reactions of [Pt₂(μ -dppm)₃] with different kinds of halogens and organic halides.

In 1986⁷⁴, the synthesis and characterisation of the highly versatile seven-coordinate complexes [MI₂(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 1994⁸⁸, the reactions of equimolar quantities of [MI₂(CO)₃(NCMe)₂] and linear triphos {PhP(CH₂CH₂PPh₂)₂}, to initially give the monodentate phosphines, [MI₂(CO)₃{PhP(CH₂CH₂PPh₂)₂-*P*,*P*'}], has been reported. These complexes eventually react intramolecularly to give [MI₂(CO)₂{PhP (CH₂CH₂PPh₂)₂-*P*,*P*',*P*''}]. Preliminary studies of the reactions of [WI₂(CO)₃{PhP (CH₂CH₂PPh₂)₂-*P*,*P*'}] as a monodentate phosphine ligand have been reported⁸⁸. Recently^{100,152,178}, the synthesis and crystallographic characterisation of the monodentate phosphine alkyne complexes, [WX₂(CO){PhP(CH₂CH₂PPh₂)₂-*P*,*P*'}(η²-RC₂R')] (X = I, R = R' = Me, Ph, R = Me, R' = Ph¹⁵²; X = Br, R = R' = Ph¹⁷⁸) 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 studied¹⁷⁸.

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

<u> Part I :-</u>

4.1.1-Reactions of the seven-coordinate complexes [MI2(CO)3(NCMe)2]

with tripodal triphos {MeC(CH₂PPh₂)₃} :-

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and tripodal triphos, $\{MeC(CH_2PPh_2)_3\}$ react in CH₂Cl₂ at room temperature for 5 minutes, to give the new complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (**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 ³¹P{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 CH₂Cl₂ and CHCl₃, 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, [WI₂(CO)₃{PhP(CH₂CH₂PPh₂)₂-*P*,*P*'}], which has three carbonyl bands in its IR spectrum⁸⁸.



Fig.4.1.1-The IR spectrum for complex (37) in CHCl₃.

The ³¹P{¹H} NMR(CDCl₃) 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, [MoI₂(CO)₃{MeC(CH₂PPh₂)₃-*P*,*P*'}]. At +25 °C, the ³¹P{¹H}NMR (CDCl₃) 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(CH₂PPh₂)₃ has a single resonance at $\delta = -26.32$ ppm in CDCl₃ at +25 °C, and the resonance at $\delta = -29.08$ ppm for the free phosphorus on **36** is, as expected, close to this value.



Fig.4.1.2. Variable temperature ³¹P{¹H} NMR spectra (CDCl₃) for [MoI₂(CO)₃{Me C(CH₂PPh₂)₃-*P*,*P*'}](36) at -50 °C, 25 °C and +50 °C.

Variable temperature ³¹P{¹H}NMR spectra in CDCl₃ 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-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-P} = 38.42 Hz, can be assigned to the coordinated *cis*- phosphorus atoms, and J_{W-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 ³¹P{¹H} NMR spectra (CDCl₃) for [WI₂(CO)₃{MeC(CH₂

PPh₂)₃-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 ³¹P{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 $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3 - P, P'\}]$.

(36 and 37)

The intramolecular reactions of $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ (36 and 37) in CHCl₃ to give $[MI_2(CO)_2 \{MeC(CH_2PPh_2)_3-P,P',P''\}]$ (38 and 39) were followed by IR spectroscopy. The reactions of 36 and 37 in refluxing CHCl₃ 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 CHCl₃ 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(CH₂CH₂PPh₂)₂}⁸⁸, with [MI₂(CO)₃(NCMe)₂] is much faster than with tripodal triphos to eventually give the dicarbonyl complexes, [MI₂(CO)₂{PhP (CH₂CH₂PPh₂)₂-*P*,*P*',*P*''}] and [MI₂(CO)₂{MeC(CH₂PPh₂)₃-*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 CHCl₃

For complex **38**, the reaction was totally completed in refluxing in CHCl₃ 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 CH₂Cl₂ and CHCl₃ 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 ³¹P{¹H} NMR data (Table 4.1.4).



Fig.4.1.6-The proposed structure of [MI₂(CO)₂{MeC(CH₂PPh₂)₃-*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 ³¹P{¹H} NMR spectra (CDCl₃) of **38** and **39** show one resonance for the phosphorus atoms at $\delta = 17.82$ 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 CDCl₃ and CD₂Cl₂ at low temperature. The rest of this chapter describes the reactions of the complexes [MI₂(CO)₃{MeC(CH₂PPh₂)₃-*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.



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, [MI2(CO)3(NCMe)2] with

2L^{Mo} or 2L^W to give [MI₂(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 $[MI_2(CO)_3(L^{Mo} \text{ or } L^W)_2]$ (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 method¹⁵⁸ (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 $[MI_2(CO)_3\{MeC(CH_2P Ph_2)_3-P,P'\}]$ 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 [MI₂(CO)₃(L^{Mo} or L^W)₂] (40 to 43)

The ¹H NMR (+25 °C, CDCl₃) 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 ³¹P{¹H} NMR (+25°C, CDCl₃) 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 $\delta = 19.36$ ppm, which is due to the same sets of two phosphorus atoms on the fluxional Mo unit of [MoI₂(CO)₃{MeC(CH₂P Ph₂)₃-*P*,*P*'}] {see complex **36**, $\delta = 16.67$ ppm}, and at $\delta = 24.99$ ppm, which is due for the phosphorus atoms bonded to the [MoI₂(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 [MI₂(CO)₃(L)(L^{Mo}

or L^{W}] {L = PPh₃, AsPh₃, SbPh₃, P(OR)₃ (R = Me, Et or Ph)}(44-52) :-

Treatment of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L {L = PPh₃, AsPh₃, SbPh₃, P(OR)₃ (R = Me, Et or Ph)} in CH₂Cl₂ 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 $[MI_2(CO)_3L(L^{Mo} \text{ or } L^W)](44-52)$ (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 ³¹P{¹H} NMR spectroscopy (Table 4.1.4). Complex 44 (M = Mo, L = PPh₃, L^{Mo}) was confirmed as a diethyl ether solvate by repeated elemental analysis and ¹H NMR spectroscopy. Molecular weight measurements by Rast's method¹⁵⁸ (Table 4.1.5) of selected 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 v(CO) = 2036, 1961 and 1910 cm⁻¹, which are likely to be due to the L^W, and bands at v(CO) = 2072, 2019 and 1844 cm⁻¹, which may be due to the [WI₂(CO)₃(PPh₃)...] unit. The ³¹P{¹H} NMR spectra of the AsPh₃ and SbPh₃ complexes show two different resonances due to tripodal triphos ligand. For example, complex **48** has two resonances; one at $\delta = -14.32$ ppm, which is due to the

two phosphorus atoms on the fluxional $[WI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P, P'\}]$ unit, and one at $\delta = 34.20$ ppm for the third phosphorus atom, which is attached to the $[WI_2(CO)_3$ $(AsPh_3)]$ unit. The resonances at $\delta = -14.32$ 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 $[MI_2(CO)_3(L)(L^{Mo} \text{ or } L^W)]$ {L = PPh₃, AsPh₃, SbPh₃, P(OR)₃ (R= Me, Et or Ph)}(44-52)

4.1.4-Reactions of the seven-coordinate complexes, [MI2(CO)3(NCMe)2] with

bidentate phosphines $\{Ph_2P(CH_2)_nPPh_2\}(n = 1 \text{ or } 2)$ followed by L^{Mo}

or L^W to give [MI(CO)₃(L^{Mo} or L^W){Ph₂P(CH₂)_nPPh₂}] [(53-56) :-

Reaction of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and Ph₂P $(CH_2)_nPPh_2$ (n = 1 or 2) in CH₂Cl₂ at room temperature afford the previously described⁸³ 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 $[MI(CO)_3(L^{Mo} \text{ or } L^W){Ph_2P(CH_2)_nPPh_2}]$ 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 ³¹P{¹H} NMR spectra have, as expected, four different resonances (see Table 4.1.4). For example, complex **54** has a resonance at $\delta = -14.41$ ppm, which is due to the two phosphorus atoms on fluxional L^W, and at $\delta = 24.97$ ppm due to the third phosphorus atom attached to the [WI(CO)₃(L^W){Ph₂P(CH₂)PPh₂}]I centre. Also complex **54** has two doublets at $\delta = -29.61$ and -36.19 ppm, due to the coordinated dppm ligand.



Fig.4.1.9. Proposed structure of $[MI(CO)_3(L^{Mo} \text{ or } L^W){Ph_2P(CH_2)_nPPh_2}]I$ (53-56)

4.1.5-Reactions of [MI₂(CO)(NCMe)(n²-EtC₂Et)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 $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](M = Mo \text{ or } W)$ 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_2Cl_2 at room temperature with one molar equivalent of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ to give the bis(3-hexyne) complexes, $[MI_2(CO)(L^{Mo} \text{ or } L^W)(\eta^2-EtC_2Et)_2](57 \text{ and } 58)$. Whereas, two equivalents of L^{Mo} or L^{W} react in CH_2Cl_2 at room temperature with one molar equivalent of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ to give the mono(3-hexyne) complexes, $[MI_2(CO)(L^{Mo} \text{ or } L^W)_2(\eta^2-EtC_2Et)]$ (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 $v(CO)(CHCl_3) = 2034$, 1980, and 1938 cm⁻¹, for the L^{Mo} unit, and one band at $v(CO)(CHCl_3) = 2046$ cm⁻¹ for the [MoI₂(CO)(L^{Mo})(η^2 -EtC₂Et)₂] part of the molecule. Since the structure of the acetonitrile bis(alkyne) complexes, [WI₂(CO)(NCMe)(η^2 -RC₂R)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 ³¹P{¹H}NMR spectrum of 57 has resonances at $\delta = 17.56$ and 38.95 ppm due to the [MoI₂(CO)₃{MeC(CH₂PPh₂)₃-*P*,*P*'}] unit and [MoI₂(CO)L^{Mo} (η^2 -EtC₂Et)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 [MI₂(CO)(η^2 -EtC₂Et)] unit.

For example, The IR spectrum of complex **59** has bands at v(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 [MoI₂(CO)(L^{Mo})₂(η^2 -EtC₂Et)] unit.

The room temperature ³¹P{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(CH₂PPh₂)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(CH₂PPh₂)₃-*P*,*P*'}]. The tricarbonyl complexes $[MI_2(CO)_3 {MeC(CH_2PPh_2)_3-P,P'}]$ (36) and (37) eventually react intramolecularly to give the dicarbonyl complexes, $[MI_2(CO)_2 {MeC(CH_2PPh_2)_3-P,P',P'')}]$ (38) and (39) respectively. The monodentate phosphine ligands, $[MI_2(CO)_3 {MeC(CH_2PPh_2)_3-P,P',P'')}]$ 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 $[MI_2(CO)(L^{Mo} \text{ or } L^W)(\eta^2-EtC_2Et)_2](57 \text{ and } 58).$



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

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Table 4.1.1-Physical and Analytical data^a for the tripodal triphos {MeC(CH₂PPh₂)₃} complexes of molybdenum(II) and tungsten(II) 36-60 :-

Complex		Colour	Yield%	С% Н	[%
(36)	$[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$	Brown	80	49.7	3.6
				(49.9)	(3.7)
(37)	$[WI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$	Orange	91	46.4	3.5
				(46.1)	(3.4)
(38)	[MoI ₂ (CO) ₂ {MeC(CH ₂ PPh ₂) ₃ - <i>P</i> , <i>P</i> ['] , <i>P</i> ^{''} }]	Brown	66	50.1	3.8
				(50.0)	(3.8)
(39)	$[WI_2(CO)_2 \{MeC(CH_2PPh_2)_3 - P, P', P''\}]$	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
	-P,P']2].2Et2O			(44.1)	(3.7)
(41)	$[WI_2(CO)_3[MoI_2(CO)_3\{MeC(CH_2PPh_2)$	3 Brown	78	41.1	3.0
	-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
	$-P, P'$ }]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
	-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
	$(CH_2PPh_2)_3 - P, P'\}$]].Et ₂ O			(46.0)	(3.9)

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(45)	[MoI ₂ (CO) ₃ (AsPh ₃)[MoI ₂ (CO) ₃ {MeC	Brown	81	43.0	3.2
	(CH ₂ PPh ₂) ₃ - <i>P</i> , <i>P</i> ['] }]]			(43.4)	(3.0)
(46)	$[MoI_2(CO)_3(SbPh_3)[MoI_2(CO)_3\{MeC$	Brown	70	42.0	3.2
	(CH ₂ PPh ₂) ₃ - <i>P</i> , <i>P</i> ['] }]]			(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 - <i>P</i> , <i>P</i> '}]]			(40.4)	(2.8)
(48)	$[WI_2(CO)_3(AsPh_3)[WI_2(CO)_3\{MeC$	Yellow	27	40.1	3.0
	(CH ₂ PPh ₂) ₃ - <i>P</i> , <i>P</i> '}]]			(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)	$[MoI(CO)_{3}{Ph_{2}P(CH_{2})PPh_{2}}[MoI_{2}(CO)_{3}$	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)	$[MoI(CO)_{3}{Ph_{2}P(CH_{2})_{2}PPh_{2}}[MoI_{2}(CO)_{3}$	Brown	74	45.8	3.3
	$\{MeC(CH_2PPh_2)_3-P,P'\}]I$			(46.2)	(3.3)

(56)	$[WI(CO)_3{Ph_2P(CH_2)_2PPh_2}[WI_2(CO)_3$	Yellow	66	42.4	3.1
	{MeC(CH ₂ PPh ₂) ₃ - P, P' }]I			(42.4)	(2.9)
(57)	$[MoI_2(CO)[MoI_2(CO)_3{MeC(CH_2P$	Brown	65	42.3	3.6
	$Ph_{2}_{3}-P,P'_{3}](\eta^{2}-EtC_{2}Et)_{2}]$			(42.7)	(3.7)
(58)	$[WI_2(CO)[WI_2(CO)_3{MeC(CH_2P$	Yellow	56	38.5	3.4
	$Ph_{2}_{3}-P,P'$](η^{2} -EtC ₂ Et) ₂]			(38.5)	(3.4)
(59)	$[MoI_2(CO)[MoI_2(CO)_3{MeC(CH_2P$	Brown	73	44.5	3.9
	$Ph_{2}_{3}-P,P'_{3}]_{2}(\eta^{2}-EtC_{2}Et)]$			(44.2)	(3.4)
(60)	$[WI_2(CO)[WI_2(CO)_3{MeC(CH_2P$	Orange	73	40.3	3.5
	$Ph_{2}_{3}-P,P'$] ₂ (η^{2} -EtC ₂ Et)]			(40.1)	(3.1)

^a Calculated values in Parenthesis.

Table	4.1.2	-Infrared	Data	for	Comp	leves	36-60 ^a
rabic	- T . T . W.	-init at cu	Data	101	Comp	ICACO	30-00

Complex	v(C≡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.

Compl	ex $v(C=O) \text{ cm}^{-1}$	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.

^aSpectra recorded in CHCl₃ as thin films between NaCl plates,

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

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Table 4.1.3-¹H NMR spectral data^a for the tripodal triphos {MeC(CH₂PPh₂)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 peak
	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
	ether; 2.4-2.0(br, 6H, 3CH ₂ , including single peak at 2.3 and smal
	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, 2CH₂ ether); 2.5(t, 6H, 2CH₃ ether); 2.3-1.9(br, 6H, 3CH₂, including. sharp peak at 2.2, and br peak at 2.0); 1.4-0.7(br 3H, free CH₃, including 3 peaks).
- (45) 7.7-7.25(45H, v.br, 9Ph); 2.15(6H, br, 3CH₂); 1.2(3H, br, free CH₃)
- (46) 7.8-7.0(v.br, 45H, 9Ph); 2.4-1.9(br, 6H, 3CH₂, including 2 sharp peaks); 1.4-0.9(br, 3H, CH₃).
- (47) 7.25(v.br, 45H, 9Ph); 2.6(br, 6H, 3CH₂, including 3 peaks);
 1.5-1.25(br, 3H, free CH₃).
- (48) 7.7-7.1(v.br, 45H, 9Ph); 2.65-2.2(br, 6H, 3CH₂); 1.9-1.4(br, 3H, free CH₃).
- (49) 7.7-7.1(v.br, 45H, 9Ph); 2.5-1.9(br, 6H, 3CH₂, including 3 peaks); 1.4-1.1(br, 3H, free CH₃).
- (50) 8.0-6.9(v.br, 30H, 6Ph); 3.8-3.5(d, 6H, 3 CH₂); 1.1(s, 3H, CH₃).
 1.3-1.0(ms, 9H, 3CH₃, phosphite).
- (51) 7.7-7.0(v.br, 30H, 6Ph); 4.2-4.0(br, 6H, 3 CH₂, phosphite); 2.4-2.0(v.br, 6H, 3 CH₂); 1.4-1.1(t, 9H, 3 CH₃, phosphite); 1.2(s, 3H, CH₃).
- (52) 7.8-6.7 (v.br, 45H, 9Ph); 2.4-1.9(br, 6H, 3 CH₂); 1.1(s, 3H, CH₃).
- (53) 7.6-6.8(v.br, 50H, 10Ph); 2.6(br, 2H, CH₂); 2.3-1.9(br, 6H, 3
 CH₂); 1.4-1.1(br, 3H, CH₃).

(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, 6CH₂ tripodal triphos); 1.2(t, 6H, 2CH₃); 1.1(s,

6H, 2CH₃, tripodal triphos);

(54)

(60) 7.8-7.1(v.br, 60H, 12Ph); 3.5-3.1(dq, 4H, 2CH₂, hexyne); 2.5-

2.1(m, 12H, 6CH₂, tripodal triphos); 1.4-1.1(t, 6H, 2CH₃, hexyne).

^aSpectra recorded in CDCl₃ (+25) and referenced to SiMe₄; s = singlet,

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

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7.6-7.1(v.br, 50H, 10Ph); 2.6(br, 2H, CH₂); 2.3-2.1(br, 6H, 3 CH₂);

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Table 4.1.4- ³¹ P NMR	R Data $(\delta)^a$ for selected tripodal triphos {MeC(CH ₂
PPh ₂) ₃ } c	complexes of molybdenum(II) and tungsten(II)
complexe	es (36-60) :-
Complex	³¹ P NMR data (δ) ppm
(36)	at -50 °C (tricarbonyl) complex :-
	$\delta(P) = 16.67$ due to 2 coordinated P,
	MeC(CH ₂ PPh ₂) ₃ atom
	$\delta(P) = -29.51$ due to free P,
	$MeC(CH_2PPh_2)_3$ atom.
	at 25 °C (tricarbonyl) complex :-
	$\delta(P) = 12.63$ due to 2 coordinated P,
	MeC(CH ₂ PPh ₂) ₃ atom and
	$\delta(P) = -29.51$ due to free P
	$MeC(CH_2PPh_2)_3$ atom
	at +50 °C (dicarbonyl) complex:-
	$\delta(P) = 17.82$ due to the P atom {MeC(CH ₂ PPh ₂ }
	of dicarbonyl complex (38).
(37)	at -50 °C (tricarbonyl) complex :-
	$\delta(P) = -14.55$ and -25.21 (d, 38.42 Hz) <i>cis</i> ,
	due to the coordinated P, MeC(CH ₂ PPh ₂) ₃ atoms
	and $\delta(P) = -31.25$ due to free uncoordinated P,
	MeC(CH ₂ PPh ₂) ₃ atom.

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(38)
$$\delta(P) = 17.80$$
 {Three P,

 $MeC(CH_2PPh_2)_3$ coordinated}.

(39)
$$\delta(P) = 15.72$$
, {Three P, MeC(CH₂PPh₂)₃

 $(J_{P-W} = 222.46 \text{ Hz}).$

(40)
$$\delta(P) = 19.36 \{s, 2P, MeC(CH_2PPh_2)_3\};$$

and 24.99 {s, 1P,
$$MeC(CH_2PPh_2)_3$$
}

(41)
$$\delta(P) = 17.45 \{s, 2P, MeC(CH_2PPh_2)_3\};$$

and 35.19 {s, 1P,
$$MeC(CH_2PPh_2)_3$$
}.

(42)
$$\delta(P) = -12.38 \{s, 2P, MeC(CH_2PPh_2)_3\},$$

and 32.61 {s, 1P,
$$MeC(CH_2PPh_2)_3$$
}.

(43)
$$\delta(P) = -15.83 \{s, 2P, MeC(CH_2PPh_2)_3\},$$

(44)
$$\delta(P) = 17.51 \{s, 2P, MeC(CH_2PPh_2)_3\},\$$

 $\delta(P) = 71.45 (PPh_3).$

(45)
$$\delta(P) = 17.51 \{s, 2P, MeC(CH_2PPh_2)_3\}, and 41.14$$

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

(46)
$$\delta(P) = 17.55 \{s, 2P, MeC(CH_2PPh_2)_3\}$$

 $(J_{p-p} = 180.13 \text{ Hz})$; and 25.94

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

(47)
$$\delta(P) = -13.76 \{s, 2P, MeC(CH_2PPh_2)_3\},$$

and 25.16 {s, 1P, MeC(CH₂PPh₂)₃}.

 $\delta(P) = 35.47$ (s, PPh₃).

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

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

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

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

 $\delta(P) = -22.50$ and -29.75 (s, dppm).

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

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

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

dppm}.

(55)
$$\delta(\mathbf{P}) = 17.52 \{ s, 2P, MeC(CH_2PPh_2)_3 \},$$

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

and 25.63 {s, 1P, MeC(CH₂PPh₂)₃}.

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

dppe}.

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

and 25.17 {s, 1P, MeC(CH₂PPh₂)₃},

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

 $\delta(P) = -13.16$ and -29.50 (s, dppe).

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

and 38.95 {s, 1P, MeC(CH₂PPh₂)₃}.

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

and 49.80 {s, 1P, MeC(CH₂PPh₂)₃}.

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(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}.

^aSpectra recorded in CDCl₃ (+25 $^{\circ}$ C) and refer to H₃PO₄.

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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)

Table.4.1.5-Molecular weights of selected complexes^a

^a Calculated values in parentheses.

Chapter Four-Part II

<u>Reactions of $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ with</u> [MoX(CO)_2(NCMe)_2(η^3 -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 reported¹⁹⁸⁻²⁰⁸. In 1986⁷⁴, 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 $[WI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2-P,P'\}]^{88}$, $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2-P,P'\}$ (η^2 -RC₂R')] (R = R' = Me or Ph; R = Me, R' = Ph)^{152} and $[MXY(CO)\{PhP(CH_2CH_2PPh_2)_2-P,P'\}$ (η^2 -RC₂R)] (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, $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ (X =

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

4.2.2-Preparation and characterisation of the tetrametallic complexes

 $[{M_0(\mu-X)(CO)_2(L^{M_0} \text{ or } L^W)(\eta^3-C_3H_4R)}_2](61-66):-$

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The starting materials used in this research, $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}](M = Mo$ 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 temperature²¹⁰, as described earlier in this Chapter. Equimolar amounts of $[MoX(CO)_2$ $(NCMe)_2(\eta^3-C_3H_4R)]$ (X = Cl, R = H or Me; X = Br, R = H) and $[MI_2(CO)_3\{MeC$ $(CH_2PPh_2)_3-P,P'\}]$ (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 $[\{Mo(\mu-X)(CO)_2(L^{Mo} \text{ or } L^W)(\eta^3-C_3H_4R)\}_2](61-66)$ 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 ³¹P{¹H} NMR spectroscopy (Table 4.2.3 and 4.2.4).

Molecular weight measurements were determined using Rast's method¹⁵⁸, 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 CH₂Cl₂ 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 CHCl₃ and CH₂Cl₂, 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 $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ 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(η^3 -C₃H₅)] has carbonyl bands at v(CO)(CHCl₃) = 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 [MoI₂(CO)₃{MeC(CH₂PPh₂)₃-*P*,*P*'}] part of the molecule. The complex [MoI₂(CO)₃ and 1917 cm⁻¹.

The molecular structures of several π -allyl complexes of the type [MoX(CO)₂L₂(η^3 -allyl)] (L₂ = nitrogen donor ligands) have been crystallographically determined²¹¹⁻²²⁰, 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(η^3 -C₃H₅)]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 ³¹P{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 ³¹P{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 ³¹P{¹H} NMR spectra were due to the expected resonances of the phosphine ligands [MI₂(CO)₃{MeC(CH₂PPh₂)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, $[MoX(CO)_2(NCMe)(L^{Mo} \text{ or } L^W)(\eta^3-C_3H_4R)]$, 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 method¹⁵⁸ 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 $[{Mo(\mu-X)(CO)_2(L^{Mo} \text{ or } L^W)(\eta^3-C_3H_4R)}_2](61-66).$

4.2.3-Synthesis and characterisation of the trimetallic complexes,

$[MoX(CO)_2(L^{M_0} \text{ or } L^W)_2(\eta^3-C_3H_4R)](67-72):-$

Reaction of $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ (X = Cl, R = H or Me; X = Br, R = H) with two equivalents of L^{Mo} or L^W in CH₂Cl₂ at room temperature affords the trimetallic, tripodal triphos-bridged complexes, $[MoX(CO)_2(L^{Mo} \text{ or } L^W)_2(\eta^3-C_3H_4R)]$ (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 ³¹P{¹H} NMR spectroscopy (Tables 4.2.3 and 4.2.4), and molecular weight studies using Rast's method¹⁵⁸ (Table 4.2.5).

The complex $[MoBr(CO)_2(L^{Mo})_2(\eta^3-C_3H_5)]$.Et₂O (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 method¹⁵⁸ 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 $\nu(CO) = 2041$, 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 MI₂(CO)₃ unit), are due to the L^{Mo} part of the molecule.

The room temperature ¹H NMR spectrum for complex 67, may be due to the different CH₂Cl₂ 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 ³¹P{¹H} NMR spectrum for complex 67 shows a resonance due to the equivalent phosphine atoms attached to the fluxional [MoI₂(CO)₃ {MeC(CH₂PPh₂)₃-*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(η^3 -C₃H₅)]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 ³¹P{¹H} 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 sevencoordinate halocarbonyl part of the molecule most likely has a distorted capped octahedral structure (see Fig.4.1.4.) as many structures of $[MX_2 (CO)_3 L_2]$ have distorted capped octahedral geometries^{72,73,127,133,222}.



Fig.4.2.Proposed structure of $[MoX(CO)_2(L^{Mo} \text{ or } L^W)_2(\eta^3-C_3H_4R)]$ (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, $[Fe(CO)_4(L^{MO} \text{ or } L^W)]$ (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 ³¹P{¹H} NMR spectroscopy (Tables 4.2.3 and 4.2.4), Molecular weight studies by Rast's method¹⁵⁸ 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 (CHCl₃) 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 $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ 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, $[WI_2(CO)_3 {MeC {CH_2PPh_2}_3-P,P'}]$ has bands at v(CO)(CHCl₃) = 2036, 1958 and 1904 cm⁻¹, and a related simple monodentate phosphine complex, $[Fe(CO)_4 {P(o-Tolyl)_3}]$ has carbonyl bands at v(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 ³¹P{¹H} NMR spectra of **73** and **74**, both show two resonances due to the fluxional $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ units at $\delta = 17.58$ and -16.35 ppm respectively. For example, complex **74** shows ³¹P{¹H} NMR data for $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ at $\delta = -16.35$ 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 $[Fe(CO)_4L] \{L = P(p-tolyl)_3^{223} \text{ and } PPh_3^{224}\}$ 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 ³¹P{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 $[Fe(CO)_4(L^{Mo} \text{ or } L^W)]$ (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 $[FeI(CO)_2(Cp \text{ or } Cp')]$ and L^{Mo} or L^W react in warm CH_2Cl_2 to give the cationic iodide displaced bimetallic complexes $[Fe(CO)_2(L^{Mo} \text{ or } L^W)(Cp \text{ or } Cp')]I$ (75-78) in high yield. The cationic nature of these complexes was confirmed by an iodide exchange reaction with Na[BPh₄]. Reaction $[Fe(CO)_2(L^W)Cp]I$ (76) with one equivalent of Na[BPh₄] 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 method¹⁵⁸. 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 [MI₂(CO)₃] unit. For example, the IR spectrum for [Fe(CO)₂(L^{Mo})Cp]I (75) has bands at v(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(PPh₃)Cp]I, which has carbonyl stretching bands at v(CO) = 2045 and 1995 cm^{-1, 225}. The bands at 2019, 1938 and 1906 cm⁻¹ are due to L^{Mo}. The ³¹P{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 $\delta = 52.71$ ppm due to [Ph₂P-Fe] unit and at $\delta = 17.63$ 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 $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$, 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.

$$[\{Mo(\mu-X)(CO)_{2}(L^{Mo} \text{ or } L^{W})(\eta^{3}-C_{3}H_{4}R)\}_{2}]$$

$$[Fe(CO)_{4}(L^{Mo} \text{ or } L^{W})] \text{ (iii)} \leftarrow L^{Mo} \text{ or } L^{W} \longrightarrow \text{ (ii) } [MoX(CO)_{2}(L^{Mo} \text{ or } L^{W})_{2}(\eta^{3}-C_{3}H_{4}R)]$$

$$\downarrow \text{ (iv)}$$

$$[Fe(CO)_{2}(L^{Mo} \text{ or } L^{W})(Cp \text{ or } Cp')]I$$

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

 $L^{W} = [WI_{2}(CO)_{3} \{MeC(CH_{2}PPh_{2})_{3}-P,P'\}]$

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

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

- (ii). Half an equivalent of $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$.
- (iii). Half an equivalent of [Fe2(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(η³-C₃H₄R)],

[Fe₂(CO)₉] or [FeI(CO)₂(Cp or Cp')].

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

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

(70) [MoCl(CO) ₂ (L^{W}) ₂ (η^{3} -C ₃ H ₄ Me-2)]	Green	39	44.7	3.6
			(44.5)	(3.4)
(71) [MoBr(CO) ₂ (L^{Mo}) ₂ (η^3 -C ₃ H ₅)].Et ₂ O	Green	48	47.8	3.9
	(e		(47.3)	(3.8)
(72) [MoBr(CO) ₂ (L^{w}) ₂ (η^{3} -C ₃ H ₅)]	Green	31	44.0	3.5
			(43.5)	(3.3)
(73) [Fe(CO) ₄ (L^{Mo})].CH ₂ Cl ₂	Green	45	45.8	4.5
			(44.9)	(3.2)
(74) [Fe(CO) ₄ (L^W)]	Green	48	47.3	3.7
			(46.7)	(4.1)
(75) $[Fe(CO)_2(L^{Mo})Cp]I$	Green	32	45.4	3.8
			(45.0)	(3.3)
(76) $[Fe(CO)_2(L^w)Cp]I$	Green	55	42.4	3.3
			(42.2)	(3.1)
(77) [Fe(CO) ₂ (L^{Mo})Cp']I	Green	37	44.7	3.5
			(45.3)	(3.4)
(78) [Fe(CO) ₂ (L^{W})Cp']I	Green	30	42.3	3.3
			(42.6)	(3.2)
(79) $[Fe(CO)_2(L^W)Cp][BPh_4].$	Green	35	54.3	5.7
			(54.8)	(3.9)

^a Calculated values in Parentheses

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Complex	$v(C=O)(cm^{-1})$
(61)	2015 s 1941 s 1933 br s 1842 m
(62)	2013 s, 1941 s, 1953 bi, s, 1842 m. 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.

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

(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.

^aSpectra recorded in CHCl₃ as thin films between NaCl plates.

s = strong, m = medium, w = weak.
Table.4.2.3- ¹H 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 ₂ Cl ₂); 3.6(m, not clear 1H, CH,
	allyl), 2.2(dd, 4H, 2CH2 of allyl), 1.9(s, 6H, 3CH2, 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, 2CH₂, allyl), 2.0(s, 6H, 3CH₂, tripodal triphos), 1.3(s, 3H, 1CH₃, tripodal triphos).
- (68) 8.1-7.1(m, 30H, 6Ph), 3.5(m, 1H, CH, allyl), 2.5- 2.2(dd, 4H, 2CH₂, allyl), 1.8-1.5(m, 6H, 3CH₂, tripodal triphos), 1.3(s, 3H, 1CH₃, tripodal triphos).
- (69) 7.9-7.0(m, 30H, 6Ph); 3.2(m, 1H, 1CH, allyl); 2.6-2.2(m, 4H, 2CH₂, allyl); 1.5(s, 3H, 1CH₃, allyl); 1.3(s, 6H, 3CH₂, tripodal triphos);
 0.9(s, 3H, 1CH₃, tripodal triphos).
- (70) 7.9-7.0(m, 60H, 12Ph); 3.7(br, 1H, 1CH, allyl); 2.5-2.1(m, 4H, 2CH₂, allyl); 1.7-1.5(m, 3H, 1CH₃, allyl); 1.3(s, 6H, 3CH₂, tripodal triphos);
 0.9(s, 3H, 1CH₃, tripodal triphos).
- (72) 7.9-7.1(m, 30H, 6Ph), 3.8-3.6(m, 1H, CH, allyl), 2.6-2.2(dd, 4H, 2CH₂, allyl), 1.7-1.4(br.m, 6H, 3CH₂, tripodal triphos), 1.3(s, 3H, 1CH₃, tripodal triphos).
- (73) 7.8-7.0(m, 30H, 6Ph); 5.4(s, 2H, CH₂Cl₂); 1.3(s, 6H, 3CH₂, tripodal triphos); 0.9(s, 3H, 1CH₃, tripodal triphos).
- (74) 7.7-6.8(m, 30H, 6Ph); 1.4(s, 6H, 3CH₂, tripodal triphos);
 0.9(s, 3H, 1CH₃, tripodal triphos).
- (75) 7.7-7.0(m, 30H, 6Ph); 5.1(s, 5H, cyclopentadienyl), 1.3(s, 6H, 3CH₂, tripodal triphos), 0.9(s, 3H, 1CH₃, tripodal triphos).

- (76) 7.7-7.2(m, 30H, 6Ph); 5.1(s, 5H, cyclopentadienyl); 1.8-1.6(br, 6H, 3CH₂, tripodal triphos); 1.3(s, 3H, 1CH₃, tripodal triphos).
 (77) 7.7-7.0(m, 30H, 6Ph); 4.9(d, 4H, cyclopentadienyl), 2.2(s, 3H, 1CH₃, cyclopentadienyl); 1.3(s, 6H, 3CH₂, tripodal triphos), 0.9(s, 3H, 1CH₃, 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, 3CH₂, tripodal triphos), 0.9(s, 3H, 1CH₃, tripodal triphos).
- (79) 7.9-7.1(m, 50H, 10Ph); 5.1(m, 5H, cyclopentadienyl); 1.3(s, 6H, 3CH₂, tripodal triphos); 0.9(s, 3H, 1CH₃, tripodal triphos).

^aSpectra recorded in CDCl₃ (+25) and referenced to SiMe₄,

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

Table.4.2.4- ³¹P NMR Data^a (δ) for the multimetallic

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

Complexes 61-79^a.

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

^aSpectra recorded in CDCl₃ (+25 °C) and referenced to 85% H₃PO₄.

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Table.4.2.5-Molecular weight studies ^a using Rast's method

S. in

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)	

for selected multimetallic complexes 61-79 :-

^a Camphor was used as the solvent in these measurements.

CHAPTER FIVE

REACTIONS AND CATALYTIC ACTIVITY OF THE SEVEN-COORDINATE DICHLORO TRICARBONYL COMPLEX, [WCl₂(CO)₃(NCMe)₂]. SYNTHESIS AND REACTIONS OF [WCl₂(CO)(NCMe)(η²-EtC₂Et)₂].

Chapter Five

<u>Reactions and catalytic activity of the seven-coordinate</u> <u>dichloro tricarbonyl complex, [WCl₂(CO)₃(NCMe)₂];</u> <u>Synthesis and reactions of [WCl₂(CO)(NCMe)(η²-EtC₂Et)₂]</u>

5.1-Introduction :-

Since the initial report in 1988⁴⁰ of the synthesis of the dimeric mono(alkyne) complex $[\{M (\mu-I)I(CO)(NCMe)(\eta^2-RC_2R')\}_2]$ (M = Mo, W; R = R' = Me, Ph, CH₂Cl; R = Ph, R' = Me, CH₃OH; R = Me, R = PhS, *p*-tolS), and the bis(alkyne) complexes, $[\{Mo(\mu-I)I(CO)(\eta^2-MeC_2Me)_2\}_2]$ and $[MI_2(CO)(NCMe)(\eta^2-RC_2R')_2]$ (M = Mo, W; R = R' = Ph; R = Me, R' = Ph; for M = W only; R = R' = Me, CH₂Cl₂, *p*-tol, R = Ph, R' = CH₂OH)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 1994¹⁴⁸, Baker *et al* described the synthesis and reactions with donor ligands of the dibromo-bis(2-butyne) complex, $[WBr_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$, and very recently in 1998¹⁵⁴, also they described a series of mixed chloro/iodo alkyne complexes, including the X-ray structural characterisation of the cationic complex, $[WCl(CO)(2,2'-bipy)(\eta^2-MeC_2Me)_2]I$.

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 $[WCl_2(CO)(L_2)]$

 $(\eta^2 - PhC_2Ph)](L = PMe_3, PMe_2Ph)^{135}, [WCl_2(CO)(PMe_3)_2(\eta^2 - PhC_2NHBu^t)]^{140}, [WCl_2(CO)(PMe_3)_2(\eta^2 - PhC_2R)]$ $(R = OH, OC(O)C_6H_4OMe-4\}^{141}, and [WCl_2(=CHPh)(PMe_3)_2(\eta^2 - PhC_2R)](R = Me, H)^{230}$ have been crystallographically characterised.

Very recently²³¹, the synthesis of the seven-coordinate dichloro-complex [WCl₂(CO)₃ (NCMe)₂] by the reaction of [WI₂(CO)₃(NCMe)₂] with two equivalents of NaCl in acetone/CH₂Cl₂ has been described. The complex [WCl₂(CO)₃(NCMe)₂] has been shown to polymerise phenylacetylene²³¹.

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, $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$. 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 [WCl2(CO)(NCMe)(n2-EtC2Et)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, ¹H and ¹³C NMR spectroscopy. It has been shown to be a highly active phenylacetylene polymerisation catalyst, but would be expected to initially form coordinated bis(alkyne)

intramolecular oxidative-addition undergoing give complexes before to a metallocyclobutadiene intermediate, followed by insertion to give an arene or polymerisation products²³¹. Reaction of [WCl₂(CO)₃(NCMe)₂] (prepared in situ as described before), with an excess of 3-hexyne eventually gives the new bis(alkyne) complex $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (80), which has been characterised by IR (Table 5.2), ¹H and ¹³C NMR spectroscopy (Table 5.3 and 5.4). Complex 80 is very much less stable than its diiodo analogue [WI₂(CO)(NCMe)(η^2 -EtC₂Et)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 [WCl2(CO)3(NCMe)2] (prepared in situ) with EtC₂Et or treating [WI₂(CO)(NCMe)(η^2 -EtC₂Et)₂] with NaCl.

Complex **80** is also less soluble in chlorinated solvents and diethyl ether and hydrocarbon solvents compared to its diiodo analogue¹⁵⁵. The IR spectrum for **80** (CHCl₃) has a strong carbonyl band at 2079 cm⁻¹, which is at higher wavenumber compared to [WI₂(CO) (NCMe)(η^2 -EtC₂Et)₂] at 2056 cm⁻¹. It also has a nitrile band, ν (N=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 ¹³C NMR spectral properties of the dichloro complex **80** to the related diiodo alkyne complexes [WI₂(CO)(NCR)(η^2 -R'C₂R')₂] (R = Me, R' = Me, Ph⁹²; R = Bu¹, R' = Me⁸⁷; R = Me, R'= Ph²³²), 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 $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$.

The ¹H NMR (+25 °C, CDCl₃) 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 CH₂ 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 CH₂ groups in 3-hexyne. The integration conform with the formula, [WCl₂(CO)(NCMe)(η^2 -EtC₂Et)₂] for complex **80**.

The room temperature ¹³C NMR spectrum (CDCl₃) for complex **80** (Table 5.5), has alkyne contact carbon resonances at $\delta = 162.43$ and 167.50 ppm, which from Templeton and Ward's¹³ 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, $[WCl_2(CO) (NCMe)(\eta^2-EtC_2Et)_2](80)$ with both neutral and anionic donor ligands. These results are summarised in Scheme.5.1.

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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-Ph2PCH=CHPPh2 .

(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 [WCl2(CO)(NCMe)(n²-EtC2Et)2](80) with

one equivalent of L to give [WCl2(CO)L(n²-EtC2Et)2] (81-84) :-

Reaction of equimolar amounts of **80** and L {L = NPh₃, PPh₃ or [MI₂(CO)₃{MeC(CH₂P Ph₂)₃-*P*,*P*'}] (M = Mo or W)} in CH₂Cl₂ at room temperature gives the acetonitrile exchanged products, [WCl₂(CO)L(η^2 -EtC₂Et)₂](**81-84**). All the new complexes have been characterised in the normal manner (see Tables 5.1-5.4 and ¹³C 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

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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 ¹³C NMR spectrum (CDCl₃) of the soluble complex [WCl₂(CO)(NPh₃)(η^2 -EtC₂Et)₂](**81**), shows alkyne contact carbon resonances at $\delta = 168.98$ and 162.30 ppm, which again indicates¹³ 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, $[WCl_2(CO)(PPh_3)(\eta^2-EtC_2Et)_2](82)$ 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 PPh₃ replacing the NCMe ligand in Fig.5.1. The ³¹P{¹H} NMR spectrum has a single resonance at $\delta = -25.33$ ppm, due to the coordinated triphenylphosphine ligand.

The new organometallic phosphine ligands, $[MI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ (M = Mo, W), have been prepared by reaction of equimolar amounts of $[MI_2(CO)_3(NCMe)_2]$ and MeC(CH₂PPh₂)₃ in CH₂Cl₂ at room temperature (see Chapter Four part I). The new bimetallic complexes, $[MCl_2(CO)(L^{Mo} \text{ or } L^W)(\eta^2-EtC_2Et)_2]\{L^M = [MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (83 and 84)(M = Mo or W) have carbonyl bands at 2075 and 2079 cm⁻¹ respectively. For example, for $[WCl_2(CO)L^{Mo}(\eta^2-EtC_2Et)_2](83)$, v(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 $[WCl_2(CO)(L^W)(\eta^2-EtC_2Et)_2](5)$ 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 v(CO) at 2036, 1958, and 1905 cm⁻¹. The ³¹P{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 MoI₂(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-Ph2PCH=CHPPh2} to give [WCl2(CO)L2(n2-EtC2Et)](85-92):-

Treatment of **80** with L_2 { $L_2 = 2PPh_3$, $2L^{M_0}$, $2L^W$, $Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4 and 6) or *cis*-Ph_2PCH=CHPPh_2} in CH_2Cl_2 at room temperature, eventually gave the mono(3hexyne) complexes, [WCl_2(CO)L_2(\eta^2-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 ¹³C NMR for complex **85** (Table 5.5), and in selected complexes by ${}^{31}P{}^{1}H{}$ NMR spectroscopy (Table 5.4). Complex **89** was confirmed as an Et₂O solvate and **91** as a CH₂Cl₂ 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, $[MXY(CO)L_2(\eta^2 - RC_2R^2)]^{98,99,127,133,147,152}$. They also have alkyne stretching bands at considerably lower wavenumber compared to the uncoordinated 3-hexyne ligand.

The ³¹P{¹H} NMR spectrum of $[WCl_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)](85)$, has a single resonance at $\delta = -9.71$ ppm, which suggests *trans*-PPh₃ groups, which would be expected due to the very large ligand cone angle¹⁵⁹ of PPh₃ (145°). This also agrees with all the crystal structures of $[MX_2(CO)L_2(\eta^2-RC_2R')]$ (M = Mo, X = Br, L = PEt₃, R = H, R'= Ph¹⁵; M = W, X = Cl, L = PMe₃ or PMe₂Ph, R = R'= Ph¹³⁶; M = W, X = Cl, L = PMe₃, R = Ph, R'= NHBu^{t, 141}; M = W, X = I, L = PPh₃, R = R'= Et¹⁵⁵), 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 $[WCl_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)]$ (85).

The IR, ¹H and ³¹P{¹H} NMR spectroscopic properties of the trimetallic complexes, [WCl₂(CO)(L^{Mo} or L^W)₂(η^2 -EtC₂Et)](**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, [WCl₂(CO)(L^{Mo})₂(η^2 -EtC₂Et)](**86**) has carbonyl bands at v(CO) = 2044, 1972, 1938, 1904 cm⁻¹, the band at {v(CO) = 1972 cm⁻¹ is likely to be due to the WCl₂(CO)-unit, and the bands v(CO) = 2044, 1938 and 1904 cm⁻¹ due to the {MoI₂(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 ³¹P{¹H} NMR spectrum (CDCl₃, +25 °C) of **86** has resonances at $\delta = 17.58$ and 30.76 ppm in a 2:1 intensity ratio. The resonance at $\delta = 17.58$ is most likely to be due to the two phosphorus atoms on the fluxional organomolybdenum phosphine ligand, [MoI₂(CO)₃{MeC(CH₂ PPh₂)₃-*P*,*P*'}](**36**), which has a resonance at $\delta = 12.63$ ppm at room temperature for the two coordinated phosphorus atoms. The lower field resonance at $\delta = 30.76$ ppm will be due to the *trans*-phosphorus atoms attached to the [WCl₂(CO)-centre.

The bidentate phosphine ligand complexes $[WCl_2(CO)L_2(\eta^2-EtC_2Et)]\{L_2 = Ph_2P(CH_2)_n$ PPh₂ n = 1, 3, 4 and 6} or *cis*-Ph₂PCH=CHPPh₂}(**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 $[WX_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2-EtC_2Et)](X = Cl(89),$

at -

 $v(CO) = 1944 \text{ cm}^{-1}$; X = I (8), $v(CO) = 1942 \text{ cm}^{-1}$ }, ${}^{31}P{}^{1}H$ NMR (for X = Cl, $\delta = -18.14$ and -17.62 ppm, for X = I, $\delta = -23.73$ 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 [WCl₂(CO){Ph₂P(CH₂)₃PPh₂}(η²-EtC₂Et)](89)

It is interesting to note that the reaction of equimolar amounts of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and $P(OR)_3$ ($R = {}^iPr$ or Ph) gives the 3-hexyne displaced products, $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2-EtC_2Et)]$ 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, $[WI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with one equivalent of $P(OR)_3$ (R = Me, Et, iPr) gave the acetonitrile displaced products, $[WI_2(CO)\{P(OR)_3\}(\eta^2-EtC_2Et)_2]$.

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, $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$, which can lose the acetonitrile ligand to give the four-electron donor 3-hexyne product, $[WCl_2(CO)(L)(\eta^2-EtC_2Et)_2]$.

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, [WCl₂(CO) $\{P(OR)_3\}(\eta^2-EtC_2Et)_2$]. For example, reaction of equimolar amounts of [WCl₂(CO) (NCMe)(\eta^2-EtC_2Et)_2] and P(OⁱPr)_3 to give [WCl₂(CO) $\{P(OⁱPr)_3\}(\eta^2-EtC_2Et)_2$] were unsuccessful, as the product was not isolated in a pure state.

5.5-Reactions of [WCl₂(CO) (NCMe)(η²-EtC₂Et)₂](80)

with two equivalents of $P(OR)_3$ (R = Et, ⁱPr) to give [WCl₂

$(CO){P(OR)_{3}_{2}(\eta^{2}-EtC_{2}Et)}$ (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, [WCl₂(CO){P(OR)₃}₂(η^2 -EtC₂Et)] (**93** and **94**) in high yield. These complexes are very soluble in chlorinated solvents such as CH₂Cl₂ and CHCl₃, 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 CH₂Cl₂ 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*-[WI₂(CO) {P(OMe)₃}₂(η^2 -MeC₂Me)]⁹⁹, *trans*-[MoI₂(CO){P(OEt)₃}₂(η^2 -MeC₂Me)]¹⁵⁶ and *trans*-[WI₂(CO){P(OEt)₄}₂(η^2 -MeC₂Me)]¹⁵⁶ and *trans*-[WI₂(Q){P(OEt)₄}₂(η^2 -MeC₂Me)]¹⁵⁶ and *trans*-[WI₂(η^2 -MeC₂Me)]¹⁵⁶ and *trans*-[

P(OMe)₃ (cone angle $\theta = 107^{0}$) for the complexes [MI₂(CO){P(OMe)₃}₂(η^{2} -MeC₂ Me)] exist as a mixture of *cis*- and *trans*-isomers in solution, as observed from IR and ³¹P{¹H} NMR studies. Whereas, for the largest phosphite ligand, P(OⁱPr)₃ (cone angle $\theta = 128^{0}$), only the *trans*- isomer was observed in solution and the solid state^{99,156,234}. The ³¹P{¹H} NMR spectra of the dichloro complexes [WCl₂(CO){P(OR)₃}₂(η^{2} -EtC₂Et)](**93** and **94**) show for R = Et, *cis* and *trans*-isomers.

The ³¹P 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 $(J_{P-P} = 57.72 \text{ Hz})$ (the ratio ≈ 40.60). Whereas, for $R = {}^{i}Pr$ (**94**) only a single resonance at $\delta = 94.80$ ppm ($J_{P-W} = 194.75$ 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}.



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

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

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





 $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2].$

5.6-Reaction of [WCl₂(CO)(NCMe)(η²-EtC₂Et)₂](80) with N^N

$(N^{N} = 2.2'-bipyridyl)$ to give $[WCl(CO)(N^{N})(\eta^{2}-EtC_{2}Et)_{2}]Cl(95) :-$

Treatment of equimolar quantities of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ and N^N (N^N = 2,2'-bipyridyl) in CH₂Cl₂ at room temperature affords the cationic complex, $[WCl(CO)(N^N)(\eta^2-EtC_2Et)_2]Cl$ (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 $[WCl(CO)(bipy)(\eta^2-MeC_2Me)_2]I^{154}$ and $[WI(CO(bipy)(\eta^2-MeC_2Me)_2]I^{40}$, 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)(η²-EtC₂Et)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)(η^2 -MeC₂Me)₂]I¹⁵⁴, at 2051 cm⁻¹.

The ¹H NMR (+25 °C, CDCl₃) spectrum for complex 95 conformed the area for bipyridyl, which is at $\delta = 9.0$ -7.4 ppm, the CH₂ groups were at $\delta = 3.7$ ppm as a quartet, and for the CH₃ groups at $\delta = 1.2$ ppm as triplets. The integration for the spectrum is concert for the formula, [WCl(CO)(bipy)(η^2 -EtC₂Et)₂]Cl, of complex 95.

The ¹³C 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 rule¹³.

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

(η²-EtC₂Et)₂] (96 and 97) :-

Reaction of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with one equivalent of NaS₂CNR₂ (R = Me, Et) gives the complexes, $[WCl(CO)(S_2CNR_2)(\eta^2-EtC_2Et)_2]$ (96 and 97) in high yield. These fully characterised complexes (Tables 5.1-5.3) are very similar to the crystallographically characterised complex, $[WI(CO)(S_2CNC_4H_8)(\eta^2-MeC_2Me)_2]^{102}$, 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, $[WI(CO)(S_2CNC_4H_8)(\eta^2-MeC_2Me)_2]$, 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) $(S_2CNC_4H_8)(\eta^2-MeC_2Me)_2$], which has 2043 cm⁻¹ in the same solvent, CHCl₃.

The ¹H NMR (+25 °C, CDCl₃) spectra for complexes 96 and 97 were difficult to interpret. For example, complex 97 shows the area for CH₂ groups from CH₃<u>CH₂NCS₂</u> group which were close to the area for the CH₂ groups of 3-hexyne, and similarly with CH₃ groups of both ligands. However, IR and elemental analysis results confirm the formula for 96 and 97. Several unsuccessful attempts to obtain the ¹³C NMR spectra (+25 °C, CDCl₃) 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, [WCl₂ (CO)(NCMe)(η^2 -EtC₂Et)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)(S₂CNR₂)(η²-EtC₂Et)₂]

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

5.8-Homogeneous catalytic studies of the seven-coordinate

dichloro complex, [WCl2(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 $[MXY(CO)\{MeC(CH_2PPh_2)_3-P,P'\}(\eta^2-RC_2R')]^1$.

In 1997, Buzar²³⁵ has shown that the photochemical oxidation of $[W(CO)_6]$ with CCl₄ in cyclohexane/CCl₄ (10:1) eventually gives $[\{W(\mu-Cl)Cl(CO)_4\}_2]$, 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 MeC₂Ph by using the molybdenum(II) bis(phenylpropyne) complex, [MoI₂(CO)(NCMe)(η^2 -MeC₂Ph)₂] in the presence of P(OⁱPr)₃, gives 1,3,4-trimethyl-2,5,6-triphenylbenzene,¹⁵⁶ which has been crystallographically characterised. The diiodide complexes, [MI₂(CO)₃(NCMe)₂] (M = Mo, W) catalyse the polymerisation of phenylacetylene. These reactions go *via* the bis (phenylacetylene) complex, [MI₂(CO)(NCMe)(η^2 -HC₂Ph)₂], which was crystallographically characterised for M = W (see Fig.5.7)²³⁶.



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

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 $(pa)_2\{(pa)_2 = 1H\text{-indene-1-Phenylmethylene}\}$ -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*-isomer²³⁵.

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 $[WCl_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]$. 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.

Colour Yield% C% H% N% Complex (80) $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ 27.2 3.6 1.0 Green 39 (36.9)(4.7) (2.8) (81) $[WCl_2(CO)(NPh_3)(\eta^2-EtC_2Et)_2]$ Green 64 54.3 4.9 2.6 (53.8)(5.1) (2.0) (82) $[WCl_2(CO)(PPh_3)(\eta^2-EtC_2Et)_2].CH_2Cl_2$ Green 48 47.9 4.4 -(48.3) (4.7) (83) $[WCl_2(CO)(L^{Mo})(\eta^2-EtC_2Et)_2]$ 39 45.1 4.7 Brown - $L^{Mo} = [MoI_2(CO)_3 \{MeC(CH_2PPh_2)-P, P'\}]$ (45.4) (4.0) (84) $[WCl_2(CO)(L^w)(\eta^2-EtC_2Et)_2]$ Green 62 42.3 3.7 $L^{W} = [WI_{2}(CO)_{3} \{MeC(CH_{2}PPh_{2})-P, P'\}]$ (42.9)(3.7)(85) $[WCl_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)]$ Green 41 58.9 4.5 (58.1)(4.5)(86) $[WCl_2(CO)(L^{Mo})_2(\eta^2-EtC_2Et)]$ Brown 79 46.6 4.3 (45.9) (3.6) (87) [WCl₂(CO)(L^{w})₂(η^{2} -EtC₂Et)] Green 30 42.4 3.7 (42.9) (3.3)

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

(88) [WCl ₂ (CO)(dppm)(η^2 -EtC ₂ Et)]	Green	53	50.9	4.6	æ
			(51.2)	(4.3)	
(89) [WCl ₂ (CO)(dppp)(η^2 -EtC ₂ Et)].Et ₂ O	Green	36	53.5	5.0	-
			(53.6)	(5.4)	
(90) [WCl ₂ (CO)(dppb)(η^2 -EtC ₂ Et)]	Green	17	49.1	5.0	
			(49.3)	(4.6)	
(91) [WCl ₂ (CO)(dpph)(η^2 -EtC ₂ Et)].CH ₂ Cl ₂	Green	17	51.0	5.0	1.
			(50.5)	(4.9)	
(92) [WCl ₂ (CO)(cis-dppethy)(η^2 -EtC ₂ Et)]	Green	80	52.9	4.8	-
			(52.1)	(4.2)	
(93) [WCl ₂ (CO){P(OEt) ₃ } ₂ (η^2 -EtC ₂ Et)].	Green	63	30.7	5.4	
.CH ₂ Cl ₂			(31.1)	(5.5)	
(94) [WCl ₂ (CO){P(OPr ⁱ) ₃ } ₂ (η^2 -EtC ₂ Et)]	Green	69	39.3	6.4	-
			(38.4)	(6.7)	
(95) [WCl(CO)(2,2'-bipyridyl)(η^2 -	Green	49	42.1	4.4	4.9
$(\eta^2 - EtC_2Et)_2]Cl$			(42.4)	(4.7)	(4.7)
(96) [WCl(CO)(S_2CNMe_2)(η^2 -Et-	Green	39	31.3	4.3	2.2
$-C_2Et)_2$].CH ₂ Cl ₂			(31.7)	(4.9)	(3.8)
(97) [WCl(CO)(S_2CNEt_2)(η^2 -EtC ₂ Et) ₂]	Green	58	36.3	5.1	2.4
			(36.5)	(5.5)	(3.4)

^a Calculated values in Parenthesis

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Complex	$v(C=O)(cm^{-1})$	$v(C=C)(cm^{-1})$	$\nu(C=N)(cm^{-1})$
	14) 1		
(80)	2079 s	1630 w	2305 w
(81)	2081 s	1587 w	-
(82)	2064 s	1644 w	5 .
(83)	2075 s, 2044 s, 1970s,	1619 w	-
	1934 s, 1841 s		
(84)	2079 s, 2034 s,	1609 w	Ŧ
	1958 s, 1905 s		
(85)	1995 s	1640 w	-
(86)	2044 s, 1972 s,	1622 w	-
	1938 s, 1904s		
(87)	2038s, 1990 s, 1962 s,	1625 w	-
	1907 s, 1901 s		
(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	-

Table 5.2-Infrared data^a for the chloro carbonyl 3-hexyne tungsten

complexes 80-97

			•
(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	·=

^aSpectra recorded in CHCl₃ as thin films between NaCl plates. s = strong,

m = medium, w = weak.

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complexes 80-97 :-		
Complex	¹ Η NMR (δ, ppm)	
(80)	3.6-3.2(q, 8H, 4CH ₂ , hexyne), 2.6(s, 3H, 1CH ₃ CN), 1.3(t, 12	
	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 ₂ Cl 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.	
	(s, 12H, 6CH ₂ , tripodal triphos); 1.2(t, 6H, 2CH ₃ , hexyne);	
	0.9(s, 6H, 2CH ₃ , tripodal triphos).	

Table 5.3-¹H NMR data^a for the chloro carbonyl 3-hexyne tungsten

(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, 2CH₃, hexyne).

- (91) 7.7-7.0(m, 20H, 4Ph), 3.6-3.2(q, 4H, 2CH₂, hexyne),
 2.3(br, 4H, 2CH₂-, PPh₂-dpph), 1.4(br, 8H, 4-CH₂-, dpph),
 0.9(t, 6H, 2CH₃, hexyne).
- (92) 7.8-7.1(m, 20H, 4Ph), 3.6(q, 4H, 2CH₂, hexyne), 3.33.0(md, 2H, CH=CH), 1.2(t, 6H, 2CH₃, hexyne).
- (93) 4.2-3.9(dq, 12H, 6CH₂, P(OEt)₃); 5.3(s, 2H, CH₂Cl₂); 3.7-3.5
 (q, 4H, 2CH₂, hexyne); 1.9-1.2(dt, 18H, 6CH₃, P(OEt)₃); 1.1
 (t, 6H, 2CH₃, hexyne).

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(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 ₂ Cl 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).

^aSpectra recorded in CDCl₃ (+25) and referenced to SiMe₄, s = singlet, br = broad, d = doublet, m = multiplet.

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Table 5.4-³¹P{¹H} NMR data^a(δ) for selected chloro carbonyl

Complex	³¹ Ρ (δ) ppm
(82)	$\delta = -25.33$ (s, 1P, PPh ₃).
(83)	$\delta = 17.59 \text{ (s, 2P, L}^{Mo} \text{) and } 23.60 \text{ (s, 1P, Ph}_2\text{P-W} \text{)}.$
(85)	$\delta = -9.71$ (s, 2P <i>trans</i> , PPh ₃).
(86)	$\delta = 17.58$ (s, 2P, L ^{Mo}) and 30.76(s, 1P, Ph ₂ P-W).
(88)	$\delta = -23.99$ and -23.57 (d, $J_{P-P} = 41.72$ Hz,
	2P of dppm).
(89)	$\delta = -18.13$ and -17.62 (d, $J_{P-P} = 52.22$ Hz,
	2P of dppp).
(90)	δ = -10.39, -16.77 (d, J _{P-P} = 55.89 Hz, 2P of dppb).
(91)	$\delta = -16.84, -10.27$ (d, $J_{P-P} = 66.54$ Hz, 2P of dpph).
(92)	$\delta = -23.83, -2.79$ (d, J _{P-P} = 59.83 Hz,
	2P of cis dppeth).
(93)	$\delta = 100.40$ (s, <i>trans</i>), and $\delta = 107.26$ (d, <i>cis</i>)
	and 107.83 (d, <i>cis</i>) ($J_{P-P} = 57.72 \text{ Hz}$)(ratio $\cong 40.60$).
(94)	$\delta = 94.80$, (s, 2P, <i>trans</i>) (J _{W-P} = 194.75 Hz).

3-hexyne tungsten complexes 80-97 :-

^aSpectra recorded in CDCl₃ (+25 °C) and referenced to 85% H₃PO₄

Table 5.5-¹³C NMR data^a (δ) for selected chloro carbonyl

3-hexyne tungsten complexes 80-97^a

Complex	¹³ C (δ) ppm
	-é
(80)	9.50(s, MeCN), 13.896(s, CH ₃ , hexyne), 28.99, 29.8(s, CH ₂
	hexyne), 129.5(s, C≡N), 162.43, 167.50(s, C≡C), 193.573(s, C≡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=N), 162.30, 168.98(s, C=C),
	194.4(s, C≡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≡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=C), 189.30(s, C=O).

^aSpectra recorded in CDCl₃ (+25 °C) and referenced to SiMe₄. 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 P2O5 and distilled before use. The complexes, $[MI_2(CO)_3(NCMe)_2](M = Mo \text{ and } W)$ were prepared according to literature methods⁷⁵ and $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4(2-R))](X =$ Cl or Br and R = H or CH₃; X = Cl or Br and R = H or CH₃)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(CH₂PPh₂)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, ¹³C, and ³¹P 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 CDCl₃ (+25), and referenced to SiMe₄ for ¹H and ¹³C NMR, and 85% H₃PO₄ for ³¹P 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,

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University of Reading and the structure $[MoI_2(CO)(2,2'-bipy)(\eta^2-EtC_2Et)]$ (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-K α radiation (λ 0.71073 A⁰) 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 program²³⁸. The structures were solved using direct methods with the SHELXS 86 program. The non-hydrogen atoms were refined with anisotopic thermal parameters²³⁹. 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 program²⁴⁰. The structures were then refined using SHELXL²⁴¹. All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. Data for crystal structure of complex, [MoI₂(CO)(2,2'-bipy)(η²-EtC₂Et)](12) determined by Professor M. B. Hursthouse at Southampton University, and crystals were obtained by cooling (-17 °C) a concentrated CH₂Cl₂/Et₂O 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-Ka 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 leastsquares on F^2 using all unique data with $F_0^2 > 0$ (SHELXL-93). The nonhydrogen atoms were refined with anisotropic temperature factors.

6.2-Experimental for Chapter Two :-

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

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.50gm, 0.968mmol) in 20ml of CH₂Cl₂ 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 $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](1)$.(Yield of the product = 0.318g, 56%) For physical and analytical data see table 2.1.

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

To a solution of $[WI_2(CO)_3(NCMe)_2]$ (0.50gm, 0.827mmol) in 15ml of CH₂Cl₂ 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 CH₂Cl₂. A few drops of Et₂O added, and the solution was was cooled to -20 °C for 24h to give analytically pure yellow crystals of $[WI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](2)$. (Yield of the product = 0.435g, 79%). For physical and analytical data see table 2.1.

Preparation of [WI₂(CO)(PPh₃)₂(η²-EtC₂Et)](4).

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.50gm, 0.745mmol) in CH₂Cl₂ (20 cm³) was added PPh₃ (0.39g, 1.48mmol). Filtration and removal of solvent *in vacuo* after 48h yielded a dark green crystalline powder, which was recrystallised from CH₂Cl₂ /Et₂O to give pure $[WI_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)](4)$. (Yield of product = 0.76g, 95.2%).

Similar reactions of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with two equivalents of PPh₃ in CH₂Cl₂ at room temperature gave the complex, $[MoI_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)](3)$.

Preparation of [WI2(CO)(dppm)(n²-EtC2Et)](6)

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.50g, 0.745mmol) in CH₂Cl₂ (15 cm³) was added Ph₂P(CH₂)PPh₂ (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 CH₂Cl₂/Et₂O, and cooled to -30 °C for 24h. This afforded analytically pure crystals of $[WI_2(CO){Ph_2P(CH_2)PPh_2}(\eta^2-EtC_2Et)](6)$ (Yield of product = 0.61g, 87.89%).

Similar reactions of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](M = Mo \text{ or } W)$ with one equivalent of L^L in CH₂Cl₂ at room temperature gave the complexes, $[MI_2(CO)(L^L)(\eta^2-EtC_2Et)]$ $\{M = W, L^L = dppm(5); M = W, L = dppe (7), dppp(8), dppb (9), dpppen (10), dpph (11)\}$

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

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.25g, 0.31mmol) in CH₂Cl₂ (15 cm³) 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 CH₂Cl₂/Et₂O, and cooled to -17 °C for 24h. This afforded analytically pure crystals of $[MoI_2(CO)(2,2^2-bipy)(\eta^2-EtC_2Et)](12)$ (Yield of product = 0.11g, 58.2%). Single crystals for X-ray analysis of 12 were grown from by CH₂Cl₂/Et₂O.

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 cm³) 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 CH₂Cl₂/Et₂O 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 cm³) 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

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

Preparation of [MoI₂(CO)₂{P(OPh)₃}(η²-EtC₂Et)](18)

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.25g, 0.43mmol) in CH₂Cl₂ (20 cm³) 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 $[MoI_2(CO)_2{P(OPh)_3}(\eta^2-EtC_2Et)](18)$, 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 CH₂Cl₂/Et₂O and cooled to -17 ^oC 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 [MoI₂(CO)(PPh₃){P(OPh)₃}(η²-EtC₂Et)]. CH₂Cl₂(19)

To a stirred solution of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)_2]$ (0.25g, 0.30 mmol) in CH₂Cl₂ (20 cm³) was added PPh₃ (0.08g, 0.31 mmol). After 24hr filtration and removal of solvent *in vacuo* gave the brown product $[MoI_2(CO)(PPh_3){P(OPh)_3}(\eta^2-EtC_2Et)]$.CH₂Cl₂ (19), which was dissolved in the minimum quantity of CH₂Cl₂/Et₂O 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 $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)]$ 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 $[MoI_2(CO){P(O^iPr)_3}{P(OPh)_3}(\eta^2-EtC_2Et)]$.Et₂O (20). For physical and analytical data see table 3.1.

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

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

To a stirred solution of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)_2]$ (0.18 g, 0.25 mmol) in CH₂Cl₂ (20 cm³) was added at 0 °C $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (0.23g, 0.22 mmol), after 48hr filtration and removal of solvent *in vacuo* gave the brown product $[MoI_2(CO)(L^{Mo}){P(OPh)_3}(\eta^2-EtC_2Et)]$ (21), which was dissolved in the minimum quantity of CH₂Cl₂/Et₂O and cooled to -17 °C for 24hr to give small crystals of the product. (Yield of pure product = 0.25g, 62%).

Similar reactions of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)_2]$ with one equivalent of L { $L^W = [WI_2(CO)_3 \{MeC(CH_2PPh_2)_3-P,P'\}]$ } in CH₂Cl₂ at room temperature gave the complex, $[MoI_2(CO)(L^W){P(O-Ph)_3}(\eta^2-EtC_2Et)](22)$. For physical and analytical data see table 3.1.

Preparation of [MoI₂(CO)(dppe)(η²-EtC₂Et)](24) :-

To a stirred solution of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)_2]$ (0.25g, 0.31 mmol) in CH₂Cl₂ (20 cm³) 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 $[MoI_2(CO)$ $\{Ph_2P(CH_2)_2PPh_2\}(\eta^2-EtC_2Et)]$ (24), which was dissolved in the minimum quantity of CH₂Cl₂/Et₂O 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 $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2 - EtC_2Et)_2]$ and 2,2'-bipyridyl in CH₂Cl₂ to gave the complex, $[MoI_2(CO)(2,2'-bipy)(\eta^2 - EtC_2Et)]$ (23). See table 3.1 for physical and analytical data.

Preparation of [MoI(CO){P(OPh)₃}(S₂CNMe₂)(n²-EtC₂Et)](25) :-

To a stirred solution of $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)_2]$ (0.3g, 0.37 mmol) in CH_2Cl_2 (20 cm³) 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 $[MoI(CO)(S_2CNMe_2){P(OPh)_3(\eta^2-EtC_2Et)].CH_2Cl_2.(25)}$, 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 $[MoI_2(CO)(NCMe){P(OPh)_3}(\eta^2-EtC_2Et)_2]$ with one equivalent of $(C_2H_5)_2NCS_2Na$ in CH_2Cl_2 at room temperature gave the complex $[MoI(CO)(S_2CNEt_2)]$

Preparation of [Mol₂(CO){P(OMe)₃}₂(η²-EtC₂Et)](27)

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.25g, 0.43 mmol) in diethyl ether (20 cm³) 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 $[MoI_2(CO){P(OMe)_3}_2(\eta^2-EtC_2Et)](27)$, 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 $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with $P(OR)_3$ {M = Mo, R = Et(29), R = ⁱPr(31), R = Bu^t(33); M = W, R = Me(28), R = Et(30), R = ⁱPr(32), R = Bu^t(34); R = Ph(35)} in diethyl ether at room temperature gave the complexes, $[MI_2(CO){P(OR)_3}_2(\eta^2-EtC_2Et)](28 \text{ to } 35)$. For physical and analytical data see table 3.1. Suitable single crystal of the bis{P(OⁱPr)₃} complexes, $[MI_2(CO){P(OⁱPr)_3}_2(\eta^2-EtC_2Et)](31 \text{ and } 32)$ 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 [MoI2(CO)3 [MeC(CH2PPh2)3-P,P'] [(36):-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.50g, 0.97mmol) in CH₂Cl₂ (20 cm³) at 0°C was added 1,1,1-tris(diphenylphosphinomethyl)ethane, MeC(CH₂PPh₂)₃ (0.607g, 0.97 mmol). After stirring for 5 minutes, filtration and removal of solvent *in vacuo*, gave the brown crystalline powder of $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\}-P,P'\}]$ (36), which was recrystalised from CH₂Cl₂/Et₂O 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 CH₂Cl₂ at room temperature gave the complex, $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (37). For physical and analytical data see table 4.1.1.

Preparation of [MoI₂(CO)₂{MeC(CH₂PPh₂)₃-P,P',P''}](38) :-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2](0.25g, 0.48mmol)$ in refluxing CHCl₃ (20 cm³) 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 $[MoI_2(CO)_2 \{MeC(CH_2PPh_2)_3 - P, P', P''\}]$ (38), Which was recrystallised from CHCl₃/Et₂O 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 CHCl₃ at 60°C, for 72 hours gave mainly the dicarbonyl complex, $[WI_2(CO)_2\{MeC(CH_2PPh_2)_3-P,P',P'''\}]$ (39). For physical and analytical data see table 4.1.1.

Preparation of [MoI2(CO)3[MoI2(CO)3{MeC(CH2PPh2)3}-P,P']2](40) :-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.15g , 0.26 mmol) in CH₂Cl₂ (20 cm³) at 0°C was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (0.54g, 0.51 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder of $[MoI_2(CO)_3[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]_2]$, which was recrystallised from CH₂Cl₂/Et₂O 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 = $[MI_2(CO)_3$ {Me $C(CH_2PPh_2)_3$ -P,P'}]{M = W, L = L^{Mo} or L^W}; {M = Mo, L = L^W} in CH₂Cl₂ at room temperature, after 24hr gave the complexes, $[MI_2(CO)_2(L^{Mo} \text{ or } L^W)_2].(41-43)$. For physical and analytical data see table 4.1.1.

Preparation of [MoI2(CO)3(PPh3)[MoI2(CO)3{MeC(CH2PPh2)3-P,P'}]](44) :-

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.3g, 0.58 mmol) in CH₂Cl₂ (20 cm³) at room temperature was firstly added triphenylphosphine (0.15g, 0.57 mmol), and left to stir for one minute. To this was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (0.62g, 0.58 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline

powder of $[MoI_2(CO)_3(PPh_3)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]](44)$, which was recrystallised from CH_2Cl_2/Et_2O 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_2Cl_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, $[MI_2(CO)_3(R)(L^{Mo} \text{ or } L^W)]$. (45-52). For physical and analytical data see table 4.1.1.

Preparation of [MoI(CO)3(Ph2P(CH2)PPh2)[MoI2(CO)3

<u>{MeC(CH₂PPh₂)₃-P,P'}]I(53) :-</u>

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.2g , 0.39 mmol) in CH₂Cl₂ (20 cm³) at room temperature was firstly added dppm (0.15g, 0.39 mmol) and left to stir for 20 minutes. To this solution was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (0.41g , 0.38 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder of $[MoI_2(CO)_3\{Ph_2P(CH_2)PPh_2\}[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (53), which was recrystallised from CH₂Cl₂/Et₂O 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 $Ph_2P(CH_2)_nPPh_2$ followed by $(L = L^W \text{ or } L^{Mo})$ $\{M = W, L = L^W)$, n = 1(54), n = 2(56); $\{M = Mo, L = L^{Mo}, n = 2(55)\}$ in CH_2Cl_2 at room temperature and after 24 hr gave the complexes, $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}(L^{Mo} \text{ or } L^W)](n = 1 \text{ or } 2)(54-56)$. For physical and analytical data see table 4.1.1.

Preparation of [MoI2(CO)]MoI2(CO)3{MeC(CH2PPh2)3-P,P'}]

$(\eta^2 - EtC_2Et)_2$ (57) :-

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.25g ,0.43 mmoł) in CH₂Cl₂ (20 cm³) at room temperature was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (0.45g, 0.42 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder $[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}](\eta^2-EtC_2Et)_2](57)$, which was recrystallised from CH₂Cl₂/Et₂O at -17°C. (Yield of pure product = 0.42g, 65%),

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

Preparation of [MoI2(CO)[MoI2(CO)3{MeC(CH2PPh2)3-P,P'}]2

$(\eta^2 - EtC_2Et)](60) :-$

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ (0.125g ,0.21 mmol) in CH₂Cl₂ (20 cm³) at 0°C was added two equivalents of $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (0.45g, 0.42 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the brown crystalline powder $[MoI_2(CO)[MoI_2(CO)_3\{MeC(CH_2 PPh_2)_3-P,P'\}_2](\eta^2-EtC_2Et)]$ (59), which was recrystallised from CH₂Cl₂/Et₂O at -17°C. (Yield of pure product = 0.45g, 73%).

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

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

Preparation of $[{Mo(\mu-Cl)(CO)_2(L^{Mo})(\eta^3-C_3H_5)}_2](61):-$

To a stirred solution of $[MoCl(CO)_2(NCMe)_2(\eta^3-C_3H_5)]$ (0.08g, 0.32 mmol) in CH₂Cl₂ (25 cm³) was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}](L^{Mo})$ (0.3g, 0.26 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green crystalline powder $[\{Mo(\mu-Cl)(CO)_2(L^{Mo})(\eta^3-C_3H_5)\}_2](61)$, which was recrystallised from CH₂Cl₂/Et₂O at -17 °C. (Yield of pure product = 0.22g, 54%).

Similar reactions of $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ (X = Cl and Br) with one equivalent of L {L = $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ in CH₂Cl₂ at room temperature gave the complexes $[\{Mo(\mu-X)(CO)_2(L^{Mo} \text{ or } L^w)(\eta^3-C_3H_4R)\}_2]$ {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 $[MoCl(CO)_2(L^{M_0})_2(\eta^3-C_3H_5)](67):-$

To a stirred solution of $[MoCl(CO)_2(NCMe)_2(\eta^3-C_3H_5)]$ (0.05g, 0.16 mmol) in CH₂Cl₂ (25cm³) at 0°C was added $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}](0.34g, 0.32 mmol)$. Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green crystalline powder $[MoCl(CO)_2(L^{Mo})_2(\eta^3-C_3H_5)](67)$, which was recrystallised from CH₂Cl₂/Et₂O at -17°C. (Yield of pure product = 0.24g, 64%).

Similar reactions of $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)]$ (X = Cl and Br) with two equivalents of L {L = $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ in CH₂Cl₂ at room temperature gave the complexes, $[MoX(CO)_2(L^{Mo})_2(\eta^3-C_3H_4R)]$ {X= Cl, R = H, L^w(68); R = Me, $L^{M_0}(69)$; $L^w(70)$ }; {X=Br, R = H, $L^{M_0}(71)$, $L^w(72)$ }. For physical and analytical data see table 4.2.1.

Preparation of [Fe(CO)4(LMo)](73) :-

To a stirred solution of $[Fe_2(CO)_9]$ (0.05g ,0.13 mmol) in CH₂Cl₂ (25cm³) 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 CH₂Cl₂/Et₂O 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 CH₂Cl₂ 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(LMo)(Cp]I (75) :-

To a stirred solution of $[FeI(CO)_2(\eta^5-C_5H_5)]$ (0.05g ,0.16 mmol) in warm CH₂Cl₂ (25 cm³) 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 $[Fe(CO)_2(L^{Mo})(\eta^5-C_5H_5)]I(75)$, which was recrystallised from CH₂Cl₂/Et₂O (Yield of pure product = 0.07g, 32%).

A similar reaction of $[FeI(CO)_2(\eta^2-C_5H_4R)]$ (R = H or Me) with one equivalent of L {L = $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}](M = Mo \text{ or } W)$ in warm CH_2Cl_2 at room temperature gave the complex $[Fe(CO)_2(L^{Mo} \text{ or } L^W)(\eta^2-C_5H_4R)]I$, {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 $[Fe(CO)_2(L^w)(\eta^5-C_5H_5)][BPh_4](79) :-$

To a stirred solution of $[Fe(CO)_2(L^W)(\eta^5-C_5H_5)]I(0.05g, 0.43 \text{ mmol})$ in $CH_2Cl_2(25 \text{ cm}^3)$ was added one equivalent of Na[BPh₄] (0.012g, 0.42 mmol). Filtration and removal of solvent *in vacuo* after 24hr, gave the green complex, $[Fe(CO)_2(L^W)(\eta^5-C_5H_5)][BPh_4](79)$, 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 [WCl2(CO)(NCMe)(n²-EtC2Et)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 CH₂Cl₂ (25 cm³) was added excess of EtC₂Et (0.19g , 0.27ml, 2.3mmol). Filtration and removal of solvent in vacuo after 24 hrs, gave the green oily product of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$, which was recrystallised from CH₂Cl₂/Et₂O at -17°C. (Yield of pure product = 0.23g, 39%).

Preparation of [WCl2(CO)(NPh3)(n²-EtC2Et)2](81) :-

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ (0.2g, 0.41mmol) in CH₂Cl₂ (25 cm³) was added NPh₃ (0.10g, 0.40 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, to gave the green powder $[WCl_2(CO)(NPh_3)(\eta^2-EtC_2Et)_2](81)$, which was recrystallised from CH₂Cl₂/Et₂O at -17°C. (Yield of pure product = 0.18g, 64%).

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Similar reactions of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with one equivalent of L in CH₂Cl₂ at 0°C gave the complexes, $[WCl_2(CO)(L)(\eta^2-EtC_2Et)_2]$ {L = PPh₃(82), L^{Mo}(83). L^W (84). For physical and analytical data see table 5.1.

Preparation of [WCl2(CO)(PPh3)2(n²-EtC2Et)](85) :-

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ (0.1g, 0.20mmoł) in CH_2Cl_2 (25 cm³) was added two equivalents of PPh₃ (0.10g , 0.38 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder of $[WCl_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)](85)$, which was recrystallised from CH_2Cl_2/Et_2O at $-17^{\circ}C$. (Yield of pure product = 0.08g, 41%).

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

Preparation of [WCl₂(CO)(dppm)(η²-EtC₂Et)](88) :-

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ (0.1g, 0.20mmol) in CH₂Cl₂ (25 cm³) at room temperature was added Ph₂P(CH₂)PPh₂ (0.078g, 0.20 mmol). Filtration and removal of solvent *in vacuo* after 24 hrs, gave the green powder $[WCl_2(CO)$ (dppm)(η^2 -EtC₂Et)](88), which was recrystallised from CH₂Cl₂/Et₂O at -17°C. (Yield of pure product = 0.09g, 53%).

Similar reactions of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ 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, $[WCl_2(CO)(L^L)(\eta^2-EtC_2Et)]$. For physical and analytical data see table 5.1.

Preparation of [WCl2(CO){P(OEt)32(12-EtC2Et)](93) :-

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ (0.1g, 0.20 mmol) in Et₂O (25 cm³) 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 $-17^{\circ}C$. (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 Et₂O 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)(7²-EtC2Et)2]Cl(95) :-

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)(0.15g, 0.30 mmol)$ in $CH_2Cl_2 (25 \text{ cm}^3)$ 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 $-17^{\circ}C$. (Yield of pure product = 0.09g, 49%).

Preparation of [WCl(CO)(S2CNMe2)(n2-EtC2Et)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 cm³) was added NaS₂CNMe₂.3H₂O (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 $-17^{\circ}C$. (Yield of pure product = 0.07g, 39%).

A similar reactions of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ with one equivalent of L = NaS₂CNEt₂.3H₂O in CH₂Cl₂ at room temperature gave the complex, $[WCl(CO)(S_2CNEt_2)(\eta^2-EtC_2Et)_2](97)$. For physical and analytical data see table 5.1.

6.6- Experimental for Polymerisation of HC2Ph(PA) :-

The toluene solution of PA(2g, 2.15ml, 0.0195mmol) and the internal standard (orthoxylene) 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, $[MI_2(CO)(NCMe)(\eta^2 - EtC_2Et)_2]$ (M = Mo and W). The crystal structures of the complexes, $[WI_2(CO)(PPh_3)_2 (\eta^2 - EtC_2Et)](4)$ and $[WI_2(CO) \{PPh_2(CH_2)_3PPh_2\}(\eta^2 - EtC_2Et)](8)$ are also discussed.

Chapter three describes the reactions of $[MI_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$ with a wide range of phosphite ligands, $P(OR)_3$ (R = Me, Et, ⁱPr, ⁿBu and Ph). The crystal structures of four complexes, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2-EtC_2Et)](13)$, $[MoI_2(CO) \{PPh_2(CH_2)_2PPh_2\}(\eta^2-EtC_2Et)](24)$, $[MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2-EtC_2Et)](31)$ and $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2-EtC_2Et)](32)$ were also described. The interesting complex, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2-EtC_2Et)](13)$, 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, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}](36$ and 37)(M = Mo and W respectively). The intramolecular reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ to give the dicarbonyl complexes $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3-P,P'\}]$ to give the dicarbonyl complexes $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3-P,P'\}]$ are described. The reactions of the organometallic phosphines, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ are described. The reactions of the organometallic phosphines, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}](M = Mo, L^{Mo}; M = W, L^W)$ 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, $[MoX(CO)_2(NCMe)_2(\eta^3-C_3H_4R)](X = Cl or Br; R =$

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

Chapter five described the preparation of a series of dichloro and monochloro complexes of tungsten(II). For example, the synthesis and reactions of $[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2](80)$ 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, [WCl₂(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}(η ² -	$[WI_2(CO)(PPh_3)_2(\eta^2 -$
		-EtC ₂ Et)]	-EtC ₂ Et)]
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,		Monoclinic, P21/c	Orthorhombic P21/c
space group			
Cell dimension (Å °)	a	18.90 (2)	9.823 (9)
	b	9.632 (9)	16.378 (17)
	с	21.63 (2)	25.10 (3)
	β	107.98 (10)	(90)
Volume Å ³		3746 (7)	4039(7)

Z, Calculated density (Mgn	n ⁻³) 4	, 1.853	4, 1.	764
Absorption coefficient (mm	n ⁻¹) 4	986	4.50	0
F (000)	2	:000	2064	ŧ.
Crystal size (mm)	0.25 *	0.30 * 0.30	0.15 *0	.25 * 0.25
θ range for data collection	(°) 2	2.40 to 25.93	2.4	2 to 25.94#
Index ranges		0≤ h≤23,	į	0≤h≤9
		-10≤k≤10,		-19≤k≤19
		-26≤1≤25	yo .	-30≤1≤30
Reflections collected /uniqu	ue	12362 / 6637		7410 / 5006
R (int	t)	0.0477		0.0615
Data / restraints / parameter	ers	6637 / 0 / 391	5	006 / 36 / 405
Final R indices [I>2 σ (I)]	R1	0.0504		0.0785
	wR2	0.1227		0.1883
R indices (all data)	R 1	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

	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
	$\beta = 95.28$ (3) deg.
Volume Å3	1900.8 (7) A^3
Z	4

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

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	2.43 to 30.49 deg.
collection (°)	
Index ranges	-11≤ h≤11, -23≤k≤23, -19≤1≤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)

I(2)-W(1)-I(3)

89.57(16)

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)

.

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)
		-

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

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(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)

164.45(14) C(14)-Mo(1)-N(2)

C(17)-Mo(1)-N(2)

82.68(13)

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)

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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 }	[MoI ₂ (CO)(dppe)		
	$(\eta^2$ -EtC ₂ Et)]	$(\eta^2-EtC_2Et)]$		
Empirical formula	$C_{27}H_{28}I_2Mo N O_4P$	$C_{33}H_{34}I_2MoOP_2$		
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	on (a Å) 16.36(2)	15.555(17)		
	(b Å) 12.484(14)	10.058(12)		
	(c Å) 16.604(17)	21.59(2)		
	$\beta(^{0})$ 113.78(1)	105.5(1)		

Volume Å ³	b	3102			1570	
Z		4			4	
Calculated density (Mg	m ⁻³)	1.73	7		1.688	
Absorption coefficient	(mm ⁻¹)	2.49	5		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 collect	tion(deg)	2.11	to 26.01		2.41 to 25.91	
Index ranges		-20	≤ h≤20,	-	16≤h≤16	
		0≤	k≤15,		0≤k≤12	
		-20≤	:1≤20	-	26≤1≤26	
Reflections collected /u	inique	10:	520		7369	
Independent reflections	s[R(int)]	56	31/0.0845		2375/0.070	
Data/restraints/parame	ters	56	31/0/328		2375/0/118	
Final R indices [I>2o(I	[)] R1	0.0)728		0.0806	
	wR2	0.1	845		0.2205	
R indices (all data)	R1	0.1	834		0.1262	
	wR2	0.2	2286		0.2494	
Largest diff. Peak and	hole(eÅ ⁻³)	1.4	95, -0.790		1.365, -0.85	6

No.31			No. 32		
Formula	$[MoI_2(CO){P(O^iPr)_3}_2$		[WI2(CO	$O)\{P(O^{i}Pr)_{3}\}_{2}$	
	(1	$\int^2 -EtC_2Et$	(η^2 -EtC ₂ Et)]	
Empirical formula	C ₂₅ H	52 I2 Mo N O7 P2	($C_{25} H_{52} I_2 W O_7 P_2$	
Molecular weight	876.35			964.26	
Temperature (K)	293(2)		2	93(2)	
Wavelength (Å)		0.71073		0.71073	
Crystal system,	Orthorhombic		Or	horhombic	
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)	
	β(⁰)	(90)		(90)	

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

Volume Å	³ 19	09		2683	
Z	2			2	
Calculted density (Mg	m ⁻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 collect	ction(deg)	2.94 to	26.04	2.10 to 20	5.08
Index ranges		0≤ h≤	10,	0≤h≤11	
		-17≤k	≤17,	-16≤k≤	17
		- 17≤1≤	s17	<i>-</i> 17≤1≤	17
Reflections collected /unique		6568		6083	
Independent reflections[R(int)]		3472	3472/0.0719		.1118
Data/restraints/parameters		3472	3472/45/117		16/117
Final R indices [I> $2\sigma(I)$] R1		0.074	0.0741		7
	wR2	0.201	7	0.2162	2
R indices (all data)	R1	0.149	5	0.1620)
	wR2	0.238	88	0.260	7
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)

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

	(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)

For complexes (31) and (32) :-

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