

**COMPLEXES OF MOLYBDENUM (II) AND TUNGSTEN (II) WITH 2-PENTYNE
CONTAINING PHOSPHITE LIGANDS**

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ABSTRACT

When reaction between equimolar quantities of $[\text{Mo}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ and one equivalent of phosphite groups $\text{P}(\text{OR})_3$, the yield will take different way, where $\text{M} = \text{Mo}$ the 2-pentyne displaced products, $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})]$ ($\text{R} = \text{Ph}, \text{Pr}$) (1) and (2) and with $\text{M} = \text{W}$ afforded the acetonitrile displaced products $[\text{W}_2(\text{CO})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Ph}$) (3-6). Reaction of $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with two equivalents of $\text{P}(\text{OR})_3$ gave the mono (2-Pentyne) complexes, $[\text{M}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-EtC}_2\text{Me})]$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}, \text{Ph}$)⁵⁻¹⁵.

Key words: Complexes, Molybdenum (II) and Tungsten(II), 2-pentyne and Phosphite ligands.

INTRODUCTION

Alkyne complexes of molybdenums (II) and tungsten (II) have received a huge attention over the years, and at least two extensive review articles have been published on this area^{1,2}. Many halo carbonyl alkyne complexes containing two phosphine or phosphite ligands of the type $[\text{MXY}(\text{CO})_2(\eta^2\text{-RC}_2\text{R}')]^+$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R}' = \text{alkyne}, \text{aryl}$) have been described³⁻³⁰. In 1982³, Umland and Vahrenkamp described the mono (ligand) complexes, $[\text{W}_2(\text{CO})_2\{\text{L}(\eta^2\text{-HC}_2\text{tBu})\}]$ ($\text{L} = \text{CN}^t\text{Bu}, \text{PMe}_3, \text{AsMe}_3$). The complexes of bis (3-hexyne) $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ($\text{M} = \text{Mo}$ or W)³⁰ were described and their reactions with phosphine donor ligands to give a series of bis (phosphine) complexes including the crystallographically characterized complexes, $[\text{W}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Et})]$ and $[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Et})]$. In 1989, Baker *et al*³¹ reported the preparation of the bis (phosphite) complexes $[\text{W}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-R}'\text{C}_2\text{R}'')]^+$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}$ and ^tBu ; $\text{R}' = \text{Me}$ or Ph), which was structurally characterized for $\text{R} = \text{R}' = \text{Me}$. In 1999, Baker *et al*³² described the synthesis and crystallographic characterization of the first mono (phosphite) complexes of the type $[\text{M}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OPh})_3\}(\eta^2\text{-R}'\text{C}_2\text{R}'')]^+$ ($\text{R}' = \text{R}'' = \text{Me}$ or Ph ; $\text{R}' = \text{Me}$; $\text{R}'' = \text{Ph}$), and also extended the series of bis (phosphite) complexes $[\text{M}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-R}'\text{C}_2\text{R}'')]^+$. In 2001³³, we described the reaction of 3-hexyne complexes of molybdenum (II) and tungsten (II) $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ with mono (phosphite) ligands $[\text{M}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Et})]$ and $[\text{W}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-EtC}_2\text{Et})_2]$ and

also in the same paper described many derivatives of bis (3-hexyne) complexes with ligands including crystallographically complexes. The reaction of $[\text{W}(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-MeC}_2\text{Me})]$ $[\text{BP h}_4]$ with L ($\text{L} = \text{Net}, \text{NC}^i\text{Pr}, \text{NC}^i\text{Bu}, \text{NCPh}, \text{NCCH}_2\text{Ph}, 1,2\text{-C}_6\text{H}_4(\text{NCCH}_2)_2, \text{NCCH}_2(\text{C}_4\text{H}_3\text{S-3})$) to produce the nitrile exchanged products, $[\text{W}(\text{CO})\text{L}\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-MeC}_2\text{Me})]$ $[\text{BPh}_4]^{34}$ and the complexes for $\text{L} = \text{NC}^i\text{Pr}, \text{NC}^i\text{Bu}, \text{NCCH}_2\text{Ph}, 1,2\text{-C}_6\text{H}_4(\text{NCCH}_2)_2$ have all been crystallographically characterized. In 2003, Demircan *et al*³⁵, were prepared the two stable endoproducts from pentacarbonyl $(\eta^2\text{-bis}(\text{trimethylsilyl})\text{ethyne})$ tungsten(0), $[\text{W}(\text{CO})_5(\eta^2\text{-btmse})]$ with tricyclohexylphosphine which could be isolated and fully characterized by using the single crystal x-ray diffractometry. In this paper we described the synthesis and structural characterization for the mono (2-Pentyne) complexes of phosphite $[\text{M}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})]$ and we preparation of 2-Pentyne bis(phosphite) complexes $[\text{M}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-tC}_2\text{Me})]$.

EXPERIMENTAL

All preparations described in this paper were carried out using standard vacuum / schlenk line techniques. The starting materials, $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by the published method³⁰. Diethyl ether was dried over sodium wire before use and CH_2Cl_2 over Calcium hydride before use. All chemicals used were purchased from commercial sources.

Elemental analysis (C, H and N) were determined by using a Carlo Erba Elemental

Table-1: Physical and analytical data for the complexes (1-15)

Complex (No)	Colour	Yield%	Analytical data		
			Found (Calcd)		
			C	H	N
[Mo ₂ (CO)(NCMe){P(oPh) ₃ }(η ² -EtC ₂ Me) ₂] (1)	Brown	85	38.9 (39.2)	3.0 (3.3)	1.6 (1.8)
[Mo ₂ (CO)(NCMe){P(o ⁱ Pr) ₃ }(η ² -EtC ₂ Me) ₂] (2)	Brown	76	29.1 (29.4)	4.3 (4.6)	1.8 (2.0)
[W ₂ (CO){P(oMe) ₃ }(η ² -EtC ₂ Me) ₂] (3)	Green	59	23.0 (23.1)	3.11 (3.4)	
[W ₂ (CO){P(oEt) ₃ }(η ² -EtC ₂ Me) ₂] (4)	Green	62	26.1 (26.5)	3.7 (4.0)	
[W ₂ (CO){P(o ⁱ Pr) ₃ }(η ² -EtC ₂ Me) ₂] (5)	Green	73	29.2 (29.6)	4.3 (4.6)	
[Mo ₂ (CO){P(oMe) ₃ }(η ² -EtC ₂ Me) ₂] (6)	Brown	61	20.5 (20.8)	3.5 (3.7)	
[W ₂ (CO){P(oPh) ₃ }(η ² -EtC ₂ Me) ₂] (7)	Green	46	37.9 (38.1)	3.1 (3.4)	
[W ₂ (CO){P(oMe) ₃ }(η ² -EtC ₂ Me) ₂] (8)	Green	54	8.0 (18.4)	3.1 (3.3)	
[Mo ₂ (CO){P(oEt) ₃ }(η ² -EtC ₂ Me) ₂] (9)	Brown	56	27.5 (27.8)	4.6 (4.9)	
[W ₂ (CO){P(oEt) ₃ }(η ² -EtC ₂ Me) ₂] (10)	Green	60	24.6 (24.4)	4.0 (4.4)	
[Mo ₂ (CO){P(oEt) ₃ }(η ² -EtC ₂ Me) ₂] (11)	Brown	72	33.2 (33.4)	5.4 (5.8)	
[W ₂ (CO){P(o ⁱ Pr) ₃ }(η ² -EtC ₂ Me) ₂] (12)	Green	76	14.9 (15.1)	5.0 (5.2)	
[Mo ₂ (CO){P(o ⁱ Bu) ₃ }(η ² -EtC ₂ Me) ₂] (13)	Brown	43	37.8 (38.1)	6.2 (6.6)	
[W ₂ (CO){P(o ⁱ Bu) ₃ }(η ² -EtC ₂ Me) ₂] (14)	Green	45	34.4 (34.8)	6.2 (6.0)	
[Mo ₂ (CO){P(oPh) ₃ }(η ² -EtC ₂ Me) ₂] (15)	Brown	70	47.1 (47.3)	3.4 (3.6)	
[W ₂ (CO){P(oPh) ₃ }(η ² -EtC ₂ Me) ₂] (16)	Green	58	43.2 (43.6)	3.0 (3.3)	

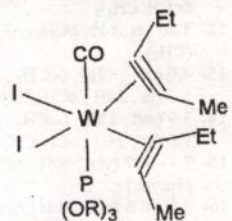
*Calculated values in parentheses

equimolar amounts of [M₂(CO)(NCMe)(η²-MeC₂Me)₂] and 2,2-bipy(bipy) gave the neutral molybdenum mono (2-butyne) complex [M₂(CO)(bipy)(η²-MeC₂Me)₂]²⁹ whereas, the reaction of equimolar amounts of [W₂(CO)(NCMe)₂] and bipy gave the cationic complex, [W₂(CO)(bipy)(η²-MeC₂Me)₂]⁺, which was crystallographically characterised as its [BPh₄]⁻ salt³⁸.

The IR spectra (Table 2) of (3-6) all have carbonyl bands above 2000 cm⁻¹ wave numbers, which would be expected for complexes of the type, [W₂(CO)L(η²-RC₂R)₂]. They also have, as expected, alkyne stretching bands at lower wave number compared to the uncoordinated 2-pentyne. Several unsuccessful attempts were made to grow single crystals for x-ray crystallography of (3-6) however, the most likely structures for (3-6) is shown in Fig. 1, since the crystal structures of a range of complexes, [M₂(CO)(NCMe)(η²-RC₂R)₂] have this geometry^{1,2,37,41}.

¹³C-NMR spectrum for complex 4 shows alkyne contact carbon resonances at δ = 165.3 and 167.5 PPM, which suggests³⁴ that the two 2-

Pentyne 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^{1,2,39}

Synthesis and characterisation of the bis (Phosphite) Complexes [M₂(CO){P(OR)₃}(η²-EtC₂Me)₂]⁷⁻¹⁵.

The complexes [M₂(CO)(NCMe)(η²-EtC₂Me)₂] were reacted with two equivalents of P(OR)₃ in diethyl ether at room temperature to give the bis (Phosphite) complexes [M₂(CO){P(OR)₃}(η²-EtC₂Me)₂] [M=Mo or W; R = Me, Et, ⁱPr, ⁿBu and Ph]⁷⁻¹⁵.

Table-4: ^{13}C -NMR data for selected complexes

Complex	^{13}C - NMR (& PPM)
1	5.30 (s, NCMe); 15.46 (s, CH_2CH_3), 15.16.32 (s, CH_3), 18.20 (s, CH_2CH_3), 115.65, 121.42, 122.06, 123.60, 129.17 (s, oph); 148.72, 149.66 (s, $\text{C}\equiv\text{N}$); 195.30 (s, $\text{C}\equiv\text{C}$); 207.60 (s, $\text{C}=\text{O}$).
2	6.2 (s, NCMe), 15.40, 15-95 (s, CH_2CH_3); 32.40 (s, CH_2CH_3); 36.20 (s, CH_3); 65.83 - 67.32 (2s, $\text{oCH}(\text{CH}_3)_2$); 136.20 (s, $\text{C}\equiv\text{N}$), 192.68 (s, $\text{C}\equiv\text{C}$); 223.60 (s, $\text{C}=\text{O}$).
3	13.73 (br, s, 2CH_3); 21-38 (br, s, 2CH_3); 32.56 (br, s, 2CH_2); 56.12, 57.71 (br, s, 2oCH_3); 207.6 (br, s, $\text{C}\equiv\text{C}$), 226.6 (br, s, $\text{C}=\text{O}$).
4	18.76, 21.30 (br, s, 2CH_3), 24.60, 31.25 (br, s, 2CH_2), 36.20, 38.65 (br, s, 2CH_3), 66.65, 67.93 (br, s, oCH_2CH_3), 189.43 (br, s, $\text{C}\equiv\text{C}$); 203.53 (s, $\text{C}=\text{O}$).
5	14.01, 15.42 (2s, 2CH_3); 18.23, 19.73 (2s, 2CH_3 pentyne), 24.61, 25.36 (2s, 3CH_3 phosphite) 32.50, 33.02 (2s, 2CH_3 pentyne), 67.62 (s, 3CH Phosphite), 171.67, 173.45 (s, $\text{C}\equiv\text{C}$), 205.39 (s, $\text{C}=\text{O}$).
8	13.36 (br, s, CH_2CH_3), 15.63 (br, s, CH_3); 33.65 (br, s, CH_2CH_3), 56.95 (br, s, oCH_3), 196.23 (br, s, $\text{C}\equiv\text{C}$), 223.65 (br, s, $\text{C}=\text{O}$).
12	8.32 (s, $1\text{CH}_2\text{CH}_3$), 21.72 (s, CH_3 pentyne), 30.53, 31.16 (s, CH_2CH_3); 66.43, 67.39, 69.57, 70.21, 70.73, 71, 96 (s, $\text{oCH}(\text{CH}_3)_2$); 205.84, 206.67 (s, $\text{C}\equiv\text{C}$); 238.41 (s, $\text{C}=\text{O}$).
15	13.56, 13.95 (s, CH_2CH_3), 16.63, 17.14 (s, CH_3 pentyne), 29.16, 29.84, 30.67 (s, CH_2CH_3); 114.56, 115.34, 116.02, 117.46, 118.21, 122.43, 125.67 (s, 6ph), 203.6 (s, $\text{C}\equiv\text{C}$), 226.31 (s, $\text{C}=\text{O}$).

Table-5: ^{31}P -NMR data (ppm) for complexes (1-16)

Complex	^{31}P .NMR & (PPm) .
(1)	115.65 (s, $\text{P}(\text{oPh})_3$).
(2)	108.70 (s, $\text{P}(\text{o}i\text{Pr})_3$).
(3)	103.65 (s, $\text{P}(\text{o}i\text{Pr})_3$).
(5)	97.24 (s, $\text{P}(\text{o}i\text{Pr})_3$).
(6)	124.65 (s, $\text{P}(\text{oPh})_3$).
(7)	101.3 (s, trans, $J_w - P = 264.74 \text{ H}_7$, $\text{P}(\text{o}i\text{Pr})_3$); 106.39 (d, cis, $J_p - p = 21.23 \text{ H}_7$, $\text{P}(\text{o}i\text{Pr})_3$); 94.52 (d, cis, $J_p - p = 22.34 \text{ H}_7$, $\text{P}(\text{o}i\text{Pr})_3$).
(9)	103.43 (s, trans, $J_w - P = 254.37$, $\text{P}(\text{o}i\text{Pr})_3$); 108.63 (d, cis, $J_p - p = 24.65 \text{ H}_7$, $\text{P}(\text{o}i\text{Pr})_3$); 97.27 (d, cis, $J_p - p = 20.92 \text{ H}_7$, $\text{P}(\text{o}i\text{Pr})_3$).
(11)	108.46 (s, trans, $\text{P}(\text{O}i\text{Pr})_3$).
(12)	104.63 (s, trans, $\text{P}(\text{O}i\text{Pr})_3$).
(13)	107.34 (s, trans, $\text{P}(\text{O}n\text{Bu})_3$); 126.27 (d, cis, $J_p - p = 36.43 \text{ H}_7$, $\text{P}(\text{O}n\text{Bu})_3$); 115.76 (d, cis, $J_p - p = 36.43 \text{ H}_7$, $\text{P}(\text{O}n\text{Bu})_3$).
(15)	93.66 (s, trans, $J_p - p = 206.57 \text{ H}_7$, $\text{P}(\text{O}i\text{Pr})_3$).
(16)	96.25 (s, trans, $J_p - p = 209.63 \text{ H}_7$, $\text{P}(\text{O}i\text{Pr})_3$).

$\text{R}'' = \text{Ph}$ (M = Mo only); M = Mo or W, R = Me, R' = R'' = Me, Ph (M = Mo only); R' = Me; R'' = Ph (M = W only); R = Et, R' = R'' = Me, Ph (M = Mo only); R' = Me, R'' = Ph (M = W only); R = Pr, R = R'' = Me, Ph (M = Mo only); R = nBu, R' = R'' = Me, Ph (M = Mo only for both complexes)³². The I.R. spectra of complexes⁷⁻¹⁵ have two carbonyl stretching bands in both their solution (CHCl_3) and solid state (KBr disc) spectra and it is very likely the carbonyl band at higher wave number will be due to the cis-isomer. For example, for the complexes $[\text{Mol}_2(\text{CO})\{\text{P}(\text{OEt})_3\}_2(\eta^2\text{-EtC}_2\text{Me})_2]$ has carbonyl

bands $\nu(\text{CO})$ at 1953 and 1982 cm^{-1} in liquid state and 1972 and 1991 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 group³², whereas in the trans-isomer the carbonyl is trans to an iodo group, which could conform with the lower carbonyl stretching bands in both the solid and solution state.

The ^{31}P -NMR data has been used to obtain the cis : trans isomer ratio of the series of phosphite ligands $[\text{Ml}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-EtC}_2\text{Me})_2]$ (R = Me,

Et, ⁿBu, ⁱPr or Ph) and here found to be similar ratios to those previously observed for the closely related 3-hexyne, 2-butyne and 1-phenyl propyne complexes of the type, $[M_2(CO)_2\{P(OR)_3\}_2(\eta^2-R^1C_2R^2)]$ ($M=Mo, W$) ($R^1=R^2=Me$; Et, $R^1=Me, R^2=Ph$)³², which was for $R=Me, Et, ^nBu, ^iPr$; 80:20, 40:60, 40:60 and 0:100 respectively.

The ratio between the cis and trans-isomers for the bis $\{P(OMe)_3\}$ complex is approximately 50:50. For the bis $\{P(O^iBu)_3\}$ complex, the ratio was

10:90 and the ratios for the bis $\{P(O^iPr)_3\}$ complexes were as expected 0:100.

The ¹³C-NMR spectra of complexes⁶⁻¹⁵ all generally show alkyne contact carbon resonances above 200 ppm, which conform with 2-Pentyne ligand donating 4 electrons to the molybdenum or tungsten in these complexes³⁷, which also enables the complexes to obey the effective atomic number rule.

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Table-2: Infrared data for phosphite complexes 1-16

Complex	V(C=O)(cm ⁻¹)	V(C=C)(cm ⁻¹)	V(C=N)(cm ⁻¹)
1	1979(s)	1642	2287(vw)
2	1982(s)	1598	2276(vw)
3	2043(s)	1663	
4	2038(s)	1642	
5	2053(s)	1592	
6	2038(s)	1602	
7	1998(s),1983(sh)	1684	
8	1982(s),1965(sh)	1585	
9	1982(s),1953(sh),1991(s),1972(sh)	1643(w)	1629(w)
10	1981(s),1941(sh),1937(s),1982(sh)	1638(w)	1632(w)
11	1963(s)	1609	
12	1954(s)	1698	
13	1967	1639	
14	1972	1646	
15	1953	1625(w)	
16	1972	1635(w)	

Table-3: ¹H-NMR data for the complexes 1-16

Complex	¹ H-NMR(Sppm)
1-	7.36-7.55(m, 3ph), 3.5-3.65(q, 2H, CH ₂), 2-30 (S, 3H, No Me), 1.25 (t, 3H, CH ₃).
2-	4.3-4.7 (m, 3H, oCH; 3.5 (q, 2H, 1CH ₂), 2.1 (S, 3H, NoMe), 1.8 (d, 4H, 3 oCH (CH ₂) ₂ , 1.4 (t, 3H, CH ₃), 1.2 (S, 3H, CH ₃).
3-	3.7(d, 3H, CH ₃), 3.5 (d, 6H, 2CH ₃); 3.6 (q, 4H, 2CH ₂), 1.3 (t, H, 2CH ₃). 1.15 (S, 6N, 2CH ₃).
4-	3.8-4.3 (m, 12H, oCH ₂ CH ₃), 3.2 (m, 4H, 2CH ₂); 1.0-1.3 (m, 18H, oCH ₂ CH ₃), 1.1(m, 6H, 2CH ₃), 0.9 (S, 6H, 2CH ₃).
5-	4.1-4.5 (m, 3H, oCH), 3.6 (q, 4H, 2CH ₂), 1.5 (t, 6H, 2CH ₃). 1.2 (t, 18H, 6 CH ₃). 1.1 (s, 6H, 2CH ₃).
6-	7.6-7.2 (vbr, 1SH, 3Ph), 3.6-3.2 (3, 4H, 2CH ₂), 1.5-1.2 (t, 6H, 2CH ₃), 1.1 (S, 6H, 2CH ₃).
7-	3.8 (br, m, 6H, OMe), 3.6 (br, m, 3H, OMe) 3.5 (q, m, 2H, 1CH ₂), 3.3 (br, m, 9H, OMe), 1.3 (br, m, 3H, 1CH ₃), 1.1 (S, 3H, 1CH ₃).
8-	3.7 (br, m, 6H, oMe), 3.5 (br, m, 3H, oMe), 3.4 (q, 2H, 1CH ₂), 3.2 (brm, 9H, oMe), 1.35 (brm, 3H, 1CH ₃), 1.2 (S, 3H, 1CH ₃).
9-	3.8-4.2 (m, 12H, oCH ₂ CH ₃), 3.2 (m, 2H, 1CH ₂), 1.1-1.3 (m, 18H, oCH ₂ CH ₃), 1.0 (m, 3H, CH ₃), 0.9 (S, 3H, CH ₃).
10-	3.9-4.1 (m, 12H, oCH ₂ CH ₃), 3.2 (m, 2H, 1CH ₂), 1.0-1.2 (m, 18H, oCH ₂ CH ₃), 0.9 (m, 3H, CH ₃), 0.8 (S, 3H, CH ₃).
11-	4.70 (m, 6H, oCH ₂), 3.6 (q, 2H, 1CH ₂), 1.4 (t, 3H, 1CH ₃ of Pentyne), 1.2 (m, 36H, 6oCH(CH ₃) ₂).
12-	3.85 (m, 6H, oCH ₂), 3.7 (q, 2H, 1CH ₂), 1.45 (t, 3H, 1CH ₃ of pentyne), 1.3 (md, 36H, 6 oCH (CH ₃) ₂).
13-	4.0 (md, 12H, 6oCH ₂ , oCH ₂ CH ₃), 3.7(m, 4H, 2CH ₂ CH ₂ CH ₂ CH ₃), 3.3 (q, 2H, 1CH ₂), 1.9-1.7 (m, 24H, oCH ₂ CH ₂ CH ₃), (m, 18H, 6CH ₃), 1.2 (m, 3H, 1CH ₃), 0.9 (S, 3H, CH ₃).
14-	3.9 (md, 12H, 6oCH ₂ , oCH ₂ CH ₃), 3.8 (m, 4H, 2CH ₂ CH ₂ CH ₂ CH ₃), 3.2 (q, 2H, 1CH ₂), 1.9-1.6 (m, 24H, oCH ₂ CH ₂ CH ₃), 1.4 (m, 18H, 6CH ₃); 1.1 (m, 3H, CH ₃), 1.0 (S, 3H, CH ₃).
15-	7.4-6.7 (vbr, 30H, 6Ph), 3.6-3.2 (q, 2H, 1CH ₂), 1.3-1.2 (t, 3H, CH ₃), 1.0 (S, 3H, CH ₃ pentyne).
16-	7.5-6.6 (vbr, 30H, 6pH), 3.5-3.2 (q, 2H, CH ₂), 1.2-1.0 (t, 3H, CH ₃); 0.9 (S, 3H, CH ₃ pentyn).

cia displacement of an acetonitrile and a 2-pentyne ligand.

Complexes⁷⁻¹⁵ were characterized by elemental analysis (Table 1), IR (Table 2), ¹H-NMR (Table 3), ³¹P-NMR (Table 5) and in selected cases ¹³C-NMR spectroscopy (Table 4). All the bis (Phosphite) complexes were extremely soluble in polar solvents, such as CH₂Cl₂ and CHCl₃ and also in diethyl ether. They are very air-sensitive in

solution, but can be stored under nitrogen in the solid state -17°C for several days.

These bis(Phosphite)-2-pentyne complexes [M₂(CO){P(OR)₃}₂(η²-EtC₂Et)] {M = Mo or W; R = Me, Et, ⁱPr, ⁿBu, Ph (for M = W)}³³, and [W₂(CO){P(OR)₃}₂(η²-R'₂C₂R'')] {R = Me, Et, ⁱPr, ⁿBu; R' = Me or Ph} (structurally characterized for R = R' = Me)³¹ and the large series of complexes, (M₂(CO){P(OR)₃}₂(η²-R'-C₂R'')) {R = Ph, R' = Me,

Analysed MOD 1108 (using helium as the carrier gas). IR spectra were recorded as thin CHCl_3 films between NaCl plates or in the solid state as KBr discs. ^1H , ^{13}C and ^{31}P -NMR spectra were recorded on a Burkert AC 250 MHz NMR spectrometer. ^1H and ^{13}C -NMR spectra were referenced to SiMe_4 and ^{31}P -NMR spectra were referenced to 85% H_3PO_4 .

Synthesis of $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ (1)- To a stirred solution of $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\eta^2\text{-EtC}_2\text{Me}\}_2]$ (0.25g, 4.5×10^{-4} mmol) in diethyl ether (20cm^3) was added $\text{P}(\text{O}^i\text{Pr})_3$ (0.14g, 4.5×10^{-4} mmol, 0.15 ml). After 24h, filtration and removal of solvent in vacuo gave the brown product, $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ ¹. (yield of pure product = 0.3g, 85%).

A similar reaction of $[\text{Mo}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with one equivalent of $\text{P}(\text{O}^i\text{Pr})_3$ in diethyl ether at room temperature gave the complex, $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ ². For physical and analytical data see table 1.

Preparation of $[\text{W}_2(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ (3)- To a stirred solution of $[\text{W}_2(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.25 g, 3.4×10^{-4} mmol) in diethyl ether (20cm^3) was added $\text{P}(\text{O}^i\text{Pr})_3$ (0g, 4.2×10^{-2} mmol, 0.45 ml). After 24h, filtration and removal of solvent in vacuo, gave an oily green product. $[\text{W}_2(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ ³ (yield of pure product = 0.16g, 59%).

A similar reaction of $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with one equivalent of $\text{P}(\text{OR})_3$ (R = ⁱPr (4) and Ph (5)) in diethyl ether at room temperature gave the complexes $[\text{W}_2(\text{CO})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ (4) and (5). For physical and analytical data see table 1.

Preparation of $[\text{Mo}_2(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\eta^2\text{-EtC}_2\text{Me})_2]$ (6)- To a stirred solution of $[\text{Mo}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.25g, 3.9×10^{-4} mmol) in diethyl ether (20cm^3) at room temperature was added $\text{P}(\text{O}^i\text{Pr})_3$ (4.8×10^{-4} g, 3.9×10^{-2} mmol, 5.0×10^{-2} ml). After 24h, filtration and removal of solvent in vacuo gave the oily brown product of $[\text{Mo}_2(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\eta^2\text{-EtC}_2\text{Me})_2]$ ⁶, (yield of pure product = 0.17g, 61%). Similar reactions of $\text{P}(\text{OR})_3$ (M = Mo, R = Et, ⁱPr, ⁿBu, Ph). M=W, R=Me, Et, ⁱPr, ⁿBu, Ph. In diethyl ether at room temperature gave the complexes $[\text{M}_2(\text{CO})\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-EtC}_2\text{Me})_2]$ ⁷⁻¹⁵. For physical and analytical data see table 1.

RESULTS AND DISCUSSION

The synthesis of $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ R=Ph₂ or ⁱPr (1) and (2)- The starting materials used in this research, $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (M = Mo or W) were prepared by reacting the seven-coordinate complexes, $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ with 2-Pentyne. Reaction of equimolar quantities of $[\text{Mo}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ and $\text{P}(\text{O}-\text{R})_3$ (R =

Ph or ⁱPr) in diethyl ether at room temperature gave the new mixed ligand complexes, $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ ^{1,2} in high yield, via displacement of one of the 2-Pentyne ligands. Complexes 1 and 2 have been fully characterized by elemental analysis (Table 1). IR (Table 2) ^1H -NMR (Table 3) and ^{31}C -NMR (Table 4). Both complexes 1 and 2 are very soluble in polar chlorinated solvents such as CH_2Cl_2 and CHCl_3 , and also soluble in diethyl ether. The complexes are very air-sensitive in solution but can be stored under dinitrogen for several months (-17 °C) without any significant decomposition. The IR spectra (CHCl_3) (Table 2) for both complexes have as expected single carbonyl bands at 1979 and 1982 cm^{-1} respectively. These are similar to the three closely related crystallographically characterised complexes, $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{OR})_3\}(\eta^2\text{-RC}_2\text{R}')]$ [R = R' = Me, $\nu(\text{CO}) = 1995\text{ cm}^{-1}$; Ph, $\nu(\text{CO}) = 2013\text{ cm}^{-1}$; R = Me, R' = Ph, $\nu(\text{CO}) = 2000\text{ cm}^{-1}$].³²

In 2001³³ as well similar to carbonyl bands for the complexes $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Et})]$ $\nu(\text{CO}) = 1983\text{ cm}^{-1}$ and for complex, $[\text{Mo}_2(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}(\eta^2\text{-EtC}_2\text{Et})]$ $\nu(\text{CO}) = 1986\text{ cm}^{-1}$. The IR spectra of 1 and 2 also show weak nitrile bands at 2287 and 2276 cm^{-1} respectively, and alkyne stretching bands at 1642 and 1598 cm^{-1} respectively. These alkyne stretching bands are at lower wavenumber compared to the uncoordinated 2-pentyne ligand, due to the back-donation of electron density from the filled d-orbitals to empty π^* antibonding orbitals on the 2-pentyne ligand, which lowers the bond order and hence the alkyne stretching frequency.

The ^1H -NMR (CDCl_3 , 25 °C) spectrum shows the expected resonances for 1 and 2 for NCMe at $\delta = 2.35$ and 2.26 ppm, respectively. The ^{13}C -NMR spectra for the complexes 1 and 2 show alkyne contact carbon resonances at $\delta = 195.30$ and 197.70 ppm, respectively, which from Templeton and Ward's³⁴ Correlton of the alkyne contact carbon resonances to the number of electrons donated by the 2-pentyne is acting as a 4- electron donor to the molybdenum centre. This also confirms with complexes 1 and 2 obeying the effective atomic number rule

The synthesis of the bis (2-pentyne) tungsten complexes $[\text{W}_2(\text{CO})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ (R = Me, Et, ⁱPr, Ph)^{3,5}

Treatment of equimolar quantities of $[\text{W}_2(\text{CO})\{\text{P}(\text{OR})_3\}(\eta^2\text{-EtC}_2\text{Me})_2]$ ^{3,5} in high yield.

Complexes 3-6 have been fully characterised by elemental analysis (Table 1), IR (Table 2), ^1H -NMR and ^{31}P -NMR spectroscopy (Table 3 and 5). The solubilities of 3-6 are similar to complexes 1 and 2. They are slightly more soluble and stable than 1 and 2. This differing reactivity of the molybdenum and tungsten complexes $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with one equivalent of $\text{P}(\text{OR})_3$ is not expected, as we have previously observed similar differences. For example, reaction of