

2-Pentyne Complexes of Molybdenum (II) and Tungsten (II)

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ABSTRACT. Treatment of $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$) with two equivalents of EtC_2Me in CH_2Cl_2 at 0C° yields the bis (2-Pentyne) complexes $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1 and 2). complexes. 1 and 2 react with two equivalents of PPh_3 in CH_2Cl_2 to give the complexes $[\text{M}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (3 and 4).

Reaction of 1 and 2 with an equimolar amount of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ to give $[\text{M}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (for $\text{M} = \text{MO}, \text{W}$; $n = 1-4$) (5-12).

Introduction

The ability of alkyne ligands to act as four-electron donor ligands to transition-metal centers has been well illustrated in the alkyne complexes of molybdenum (II) and tungsten (II)^[1,2]. Although a number of 2-butyne, methyl propyne, phenylacetylene and related alkyne complexes of molybdenum (II) and tungsten (II) have been prepared^[3-20].

Recently, many 3-hexyne derivatives have been reported^[21-26] these include the dimeric tungsten complex $[\{\text{W}(\mu\text{-Br})\text{Br}(\text{CO})(\eta^2\text{-EtC}_2\text{Et})_2\}_2]$ ^[21]; molybdenum dichloro and dibromophosphine complexes $[\text{MoX}_2(\text{CO})\text{L}_2(\eta^2\text{-EtC}_2\text{Et})]$ ($\text{X} = \text{Cl}, \text{L} = \text{PPh}_3, \text{X} = \text{Br}, \text{L} = \text{PEt}_3, \text{PPh}_3, \text{X} = \text{Cl}, \text{Br}, \text{L}_2 = \text{dppe}$)^[22] and the bis (diallyl dithiocarbamate) complexes $[\text{Mo}(\text{CO})(\text{S}_2\text{CNET}_2)_2(\eta^2\text{-EtC}_2\text{-Et})]$ ^[23] and $[\text{Mo}(\eta^2\text{-PhC}_2\text{H})(\eta^2\text{-EtC}_2\text{Et})(\text{S}_2\text{CNMe}_2)_2]$ ^[24].

In 1988, Baker and others reported the synthesis and x-ray crystal structures of the tungsten bis (alkyne) complexes $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}, \text{Ph}$), and also described the synthesis and crystal structures of the related

molybdenum complexes $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}, \text{Ph}$)^[25]. The chemistry of $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{Ph}$) with both neutral and anionic ligands has been studied in details^[27].

In 1999, crystal structures of $[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Et})]$ and $[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Et})]$ was determined and investigated^[28].

In 2000, Mutlaq and others synthesized many derivatives of 3-hexyne complexes including phosphines and phosphates groups with some crystal structures^[29-31]. P.K. Baker *et. al* prepared the nitrile exchanged products, $[\text{WI}(\text{CO})\text{L}\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\eta^2\text{-MeC}_2\text{Me})]$ $[\text{BPh}_4]$ from reaction of $[\text{WI}(\text{CO})(\text{NCMe})\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\eta^2\text{-MeC}_2\text{Me})]$ $[\text{BPh}_4]$ and L $\{\text{L} = \text{Net}, \text{NC}^i\text{Pr}, \text{NC}^i\text{Bu}, \text{NCPh}, \text{NCCH}_2\text{Ph}, 1,2\text{-C}_6\text{H}_4(\text{NCCH}_2)_2, \text{NCCH}_2(\text{C}_4\text{H}_3\text{S-3})\}$; 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^[32].

In 2003, Oktay and others, reacted pentacarbonyl (η^2 -bis(trimethylsilyl) ethyne) tungsten(0), $[\text{W}(\text{CO})_5(\eta^2\text{-btmse})]$ with tricycle hexylphosphine PCy_3 to yield two stable endoproduts which could be isolated and fully characterized by using the single crystal x-ray diffractometry^[33].

In this paper we described the first 2-Pentyne diiodo complexes $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ ($\text{M} = \text{Mo}, \text{W}$) and their reactions with phosphine groups.

Experimental

Physical Measurements and Instruments

Elemental analysis (C, H and N) were determined by department of chemistry, King Abdulaziz University of Jeddah. Using a Carlo Erba Elemental Analysis MOD 1108 (Using helium as carrier gas). Infrared spectra were obtained by CHCl_3 films between NaCl plates and recorded on a Perkin-Elmer 1430 ratio recording IR spectrophotometer.

^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Bruker AC 500 MHz NMR spectrometer. ^1H and ^{13}C NMR spectra were referenced to SiMe_4 , whereas ^{31}P NMR spectra were referenced to 85% H_3PO_4 .

Reagents and Materials

All reactions and purifications were carried out under an atmosphere of dry nitrogen using standard vacuum/chlenk line techniques. The complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$), were prepared by the published method^[27]. All solvents and chemicals used were of reagents grade quality and were purchased from commercial sources. The solvents used were dried and distilled before use.

Preparation of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1)

To a stirred solution of $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.5 g, 0.96 mmol) in 25 ml of CH_2Cl_2 at 0°C 2-Pentyne (0.13 g, 0.20 ml, 1.9 mmol) was added. The solution was stirred at room temperature for 24 h. Filtration and removal of the solvent in vacuum gave crystalline powder which was recrystallized from dichloromethane and diethyl ether giving pure $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (Yield = 0.35 g, 0.66%).

In a similar reaction of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ with two equivalents of 2-Pentyne in CH_2Cl_2 at 0°C gave the bis(2-Pentyne) complex $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (2). See Table 1 for physical and analytical data.

TABLE 1. Physical and analytical data^a for 2-Pentyne complexes. 1-12.

Compound no.	Colour	Yield %	Analytical data found (calcd)		
			C	H	N
$[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1)	Brown	66	27.9 (28.1)	3.2 (3.4)	2.1 (2.5)
$[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (2)	Yellow	72	24.6 (24.3)	3.1 (2.9)	2.4 (2.2)
$[\text{MoI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (3)	Green	66	51.2 (51.6)	4.3 (4.5)	
$[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (4)	Green	72	47.1 (47.3)	3.9 (4.1)	
$[\text{MoI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (5)	Green	55	47.8 (48.1)	4.2 (4.4)	
$[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (6)	Green	48	43.3 (43.0)	4.1 (3.9)	
$[\text{MoI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (7)	Green	57	48.6 (48.8)	4.1 (4.5)	
$[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (8)	Green	43	44.1 (43.9)	4.3 (4.1)	
$[\text{MoI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (9)	Green	61	49.7 (49.5)	4.9 (4.7)	
$[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (10)	Green	36	44.8 (44.6)	4.3 (4.2)	
$[\text{MoI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (11)	Green	52	49.8 (50.1)	4.6 (4.9)	
$[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (12)	Green	39	45.4 (45.2)	4.7 (4.4)	

^aCalculated values in parentheses.

Preparation of $[\text{MoI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (3)

To a stirred solution of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.2 g, 0.36 mmol) in CH_2Cl_2 (20 cm^3) PPh_3 (0.19 g, 0.7 mmol) was added for 48 h, then filtration and removal of solvent in vacuum yielded a brown crystalline powder which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give pure $[\text{MoI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (3); (yield = 0.23 g, 66%). A similar reaction of $(\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gave the complex $[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (4). See table 1 for physical and analytical data.

Preparation of $[\text{MoI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (5)

To a stirred solution of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (0.2 g, 0.36 mmol) in CH_2Cl_2 (15 cm^3) $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$. (0.14 g, 0.36 mmol) was added. After 24 h filtration and removal of solvent in vacuum gave a crystalline powder of $[\text{MI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (5) (yield = 0.15 g, 55%).

Similar reactions of equimolar quantities of $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ in CH_2Cl_2 at room temperature gave the complexes (M = Mo, n = 2-4; M = W, n = 1-4) (6-12). See table 1 for physical and analytical data (6-12).

Results and Discussion

The starting materials used in this research $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo,W) were prepared by treating the zero-valent complexes *fac*- $[\text{M}(\text{CO})_3(\text{NCMe})_3]$ (prepared *in situ*) with one equivalent of I_2 at 0°C ^[27]. Reaction of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo,W) with two equivalents of EtC_2Me in CH_2Cl_2 at room temperature gave good yields of the bis (2-Pentyne) complexes $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1 and 2).

Both complexes 1 and 2 were characterized by elemental analysis (C, H and N) (Table 1), I R (Table 2) and $^1\text{HNMR}$ spectroscopy (Table 3).

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 for 1 and 2 show carbonyl stretching bands at $\nu(\text{C} \equiv \text{O}) = 2053$ and 2057 cm^{-1} respectively. These are in very similar positions to their related 3-Hexyne derivatives $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ $\{\nu(\text{C} \equiv \text{O}) = 2059$ and 2056 cm^{-1} for M = Mo and W respectively^[28] and also similar to 2-butyne de-

rivatives $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ $\{\nu(\text{C}\equiv\text{O}) = 2061 \text{ cm}^{-1}$ and 2050 cm^{-1} for $\text{M} = \text{Mo}$ and W respectively $\}^{[2,25]}$.

The nitrile bands $\nu(\text{C}\equiv\text{N})$ at 2289 and 2256 cm^{-1} respectively, where the acetonitrile is acting as a σ -donor ligand $^{[34]}$, and the weak alkyne stretching bands at 1609 and 1629 cm^{-1} for 1 and 2 are lower than for the uncoordinated alkyne which is expected since there is back-donation of electron density from filled metal d-orbitals to empty π^* -orbitals on the 2-pentyne ligands. The structure of $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ is very likely the structure as shown in Fig. (1).

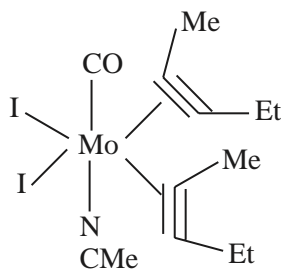


Fig. 1. Proposed structures of $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1 and 2).

Since the spectroscopic properties are closely related to the previously reported bis (alkyne) complexes of molybdenum (II) and tungsten (II) $^{[1,2,25,35,36]}$. The ^1H NMR spectra of 1 and 2 show two different sets of CH_2 groups, which confirmed the structure shown in Fig. 1. At room temperature ^{13}C NMR spectra of 1 and 2 show alkyne carbon contact resonance at $\delta = 175.12$ and 167.35 (for 1) and 161.30 and 172.45 (for 2).

The resonances observed for complexes 1 and 2 are in accord with two alkynes donating a total of four electrons to the metal centre, which also enables the complexes to obey the effective atomic number rule.

Treatment of $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ ($\text{M} = \text{Mo}, \text{W}$) with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gives the complexes $[\text{Ml}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-EtC}_2\text{Me})]$ (3 and 4).

Complexes 3 and 4 have also been characterized by elemental analysis (Table 1); IR (Table 2), ^1H NMR (Table 3) and ^{31}P .NMR spectroscopy (Table 4).

Complexes 3 and 4 are more stable in solution, but very much less soluble than bis (2-Pentyne) complexes (1 and 2). They are slightly soluble in CH_2Cl_2 and CHCl_3 . Hence, it was difficult to obtain the ^{13}C NMR spectra.

TABLE 2. Infrared data^a for 2-Pentyne complexes 1-12.

Compound no.	$\nu(\text{C} \equiv \text{O})$ cm^{-1}	$\nu(\text{C} \equiv \text{N})$ cm^{-1}	$\nu(\text{C} \equiv \text{C})$ cm^{-1}
(1)	2053(s)	2289(w)	1609(w)
(2)	2057(s)	2256(w)	1629(w)
(3)	1951(s)	1951(s)	1665(w)
(4)	1940(s)	–	1656(w)
(5)	1943(s)	–	1659(w)
(6)	1932(s)	–	1607(w)
(7)	1933(s)	–	1653(w)
(8)	1942(s)	–	1655(w)
(9)	1935(s)	–	1640(w)
(10)	1935(s)	–	1637(w)
(11)	1936(s)	–	1656(w)
(12)	1929(s)	–	1653(w)

^aspectra recorded in CHCl_3 as thin films between NaCl plates;
S = strong, W = weak.

TABLE 3. ¹H NMR data for selected 2-Pentyne complexes.

Complex no.	¹ H NMR (δ) ppm
(1)	3.2-3.4 (m, 2H, $\text{C} \equiv \text{C} \text{CH}_2$); 2.8-3.1 (br, m, 2H, CH_2); 2.70 (S, 3H, $\text{NC} \text{CH}_3$); 2.5 (S, 3H, $\text{CH}_3\text{-C} \equiv \text{C}$); 1.1- 1.3(t, 6H, $\text{CH}_3 \text{CH}_2$).
(2)	3.1-3.4 (m, 2H, CH_2); 2.9-3.15 (m, 2H, CH_2); 2.8 (S, 3H, NCCH_3); 2.5 (S, 6H, $\text{CH}_3\text{-C} \equiv \text{C}$); 1.3 (t, 6H, CH_3CH_2).
(3)	7.0-7.65 (br, m, 30H, Ph); 2.6-3.4 (br, m, 2H, CH_2); 1.6-2.5 (S, 3H, CH_3); 0.8-1.3 (t, 3H, CH_2CH_3).
(4)	7.1-7.6 (br, m, 30H, Ph); 2.5-3.4 (br, m, 2H, CH_2); 1.5-2.5 (S, 3H, CH_3); 0.7-1.2 (t, 3H, CH_2CH_3).
(5)	6.9-7.3 (br, m, 20H, Ph); 4.5-4.8 (q, 2H, Ph.P-CH_2); 3.6-3.6 (q, 2H, CH_2); 2.9-3.1 (S, 3H, CH_3); 1.0-1.25 (t, 3H, CH_3CH_2).
(6)	6.8-7.2 (br, m, 20H, Ph); 4.4-4.7 (q, 2H, PhP-CH_2); 3.4-3.7 (q, 2H, CH_2); 2.9-3.2 (S, 3H, CH_3); 1.1-1.2 (t, 3H, CH_3CH_2).
(7)	6.9-7.3 (br, m, 20H, Ph); 4.4-4.6 (br, m, 4H, $\text{Ph.P, CH}_2\text{CH}_2$); 3.3-3.7 (q, 2H, CH_2); 2.8-3.2 (S, 3H, CH_3); 1.2-1.3(t, 3H, CH_3CH_2).
(8)	7.1-7.8 (br, m, 20H, Ph); 4.3-4.5 (br, m, 4H, $\text{PhP, CH}_2 \text{CH}_2$); 3.2-3.6 (q, 2H, CH_2); 2.5-3.1 (S, 3H, CH_3); 1.3-1.4 (t, 3H, CH_3CH_2).
(9)	7.3-7.9 (m, 20H, Ph); 3.4-3.6 (q, 2H, $\text{C} \equiv \text{C} \text{CH}_2$); 3.4 (br, m, 4H, Ph_2PCH_2); 2.6 (S, 3H, $\text{C} \equiv \text{C} \text{CH}_3$); 1.2 (t, 3H, CH_3); 0.9-1.1 (br, m, 2H, $\text{Ph}_2\text{PCH}_2 \text{CH}_2$).

TABLE 3. Contd.

Complex no.	¹ H NMR (δ) ppm
(10)	7.4-8.0 (m, 20H, Ph); 3.5-3.7 (q, 2H, C ≡ C CH ₂); 3.1-3.3 (br, m, 4H, Ph ₂ PCH ₂); 2.7 (S, 3H, C ≡ C CH ₃); 1.3 (t, 3H, CH ₃); 0.8-1.1 (br, m, 2H, Ph ₂ PCH ₂ CH ₂).
(11)	7.1-7.8 (br, m, 20H, Ph); 3.3-3.5 (m, 2H, Ph ₂ PCH ₂); 3.2 (q, 2H, C ≡ C CH ₂); 2.6-2.9 (br, m, 4H, Ph ₂ PCH ₂ CH ₂); 2.4 (S, 3H, C ≡ C-CH ₃); 1.0-1.3 (t, 3H, C ≡ C-CH ₂ CH ₃).
(12)	7.2-8.0 (br, m, 20H, Ph); 3.2-3.5 (m, 4H, PhPCH ₂); 3.3 (q, 2H, C ≡ C CH ₂); 2.7-3.0 (br, m, 4H, Ph ₂ PCH ₂ CH ₂); 2.3 (S, 3H, C ≡ C-CH ₃); 1.1-1.35 (t, 3H, C ≡ C CH ₂ CH ₃).

^aspectra recorded in CDCl₃ (25°C) and referenced to SiMe₄;
S = Singlet; br = broad; d = doublet; m = multiplet; t = triplet; q = quartet.

TABLE 4. ¹³C NMR data^a (δ) for selected 2-Pentyne complexes.

Complex no.	¹³ C NMR (δ) ppm
(1)	6.65 (S, CH ₃ , CN); 12.36, 12.80, 13.4, 14.23, 14.57, (S, CH ₂ CH ₃); 16.7, 17.53, 17.85 (S, CH ₃ , C ≡ C); 24.60, 27.32 (S, CH ₂); 129.85 (S, C ≡ N); 165.36, 173.2 (S, C ≡ C); 216.08 (S, C ≡ O).
(2)	5.7 (S, CH ₃ , CN); 12.6, 12.76, 13.06, 13.9, 14.2 (S, CH ₂ CH ₃); 16.3, 16.7, 17.02 (S, CH ₃ , C ≡ C); 25.3, 26.7 (S, CH ₂); 128.50 (S, C ≡ N); 163.62, 172.15 (S, C ≡ C); 210.03 (S, C ≡ O).

^aspectra recorded in CDCl₃ (25°C) and referenced to SiMe₄.
S = Singlet.

The IR and ¹HNMR spectral properties of 3 and 4 are similar to their 3-hexyne and 2-butyne tungsten and molybdenum analogue, [MI₂(CO)(PPh₃)₂(η²-MeC₂Me)]^[35] and [MI₂(CO)(PPh₃)₂(η²-EtC₂Et)]^[28], which have a carbonyl stretching band at 1951 and 1940 cm⁻¹ in the same solvent for (M = Mo and W) respectively.

The ³¹PNMR spectra for 3 and 4 have single resonances at δ = -2.56 and -13.36 respectively; similar to complexes of 3-hexyne which exhibit resonances at δ = -2.89 and -15.93 respectively. This suggests a trans arrangement of PPh₃ ligands^[28].

Equimolar quantities of [MI₂(CO)(NCMe)(η²-EtC₂Me)₂] (M = Mo, W) and Ph₂P(CH₂)_nPPh₂; (n = 1-4) react in CH₂Cl₂ at room temperature to yield the

mono (2-Pentyne) complexes $[\text{Ml}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (5-12) were fully characterized (See Tables 1 to 4).

They are intermediate in solubility between 1,2 and 3,4 and similar in sensitive to air as the previous complexes .

The colours and spectroscopic properties resemble that to 3-hexyne complexes $[\text{Ml}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Et})]$ ^[28] as well as for 2-butyne $[\text{Ml}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ ^[37].

The ³¹P NMR spectra of $[\text{Ml}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Me})]$ (n = 1-4) have two resonances (Table 5) expected for a single isomer from crystal structure of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\eta^2\text{-EtC}_2\text{Et})]$ ^[28].

TABLE 5. ³¹P NMR data^a (δ) for selected 2-Pentyne complexes.

Complex no.	³¹ P NMR (δ) ppm
(3)	δ (P) = -2.56
(4)	δ (P) = -13.36
(6)	δ (P _A) = -24.36; δ (P _B) = -35.27
(9)	δ (P _A) = -27.72; δ (P _B) = -36.75
(10)	δ (P _A) = -22.85; δ (P _B) = -31.24
(11)	δ (P _A) = -24.13; δ (P _B) = -29.72

^aspectra recorded in CDCl₃ (25°C) and referenced to H₃PO₄.

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مركبات تناسقية من 2-Pentyne مع الموليبيدينوم (II) والتنجستن (II)

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جدة - المملكة العربية السعودية

المستخلص. إن التفاعل الكيميائي بين المركبات التناسقية مع المركبات العضوية التي تحمل الرابطة الثلاثية هي محل اهتمام اصطناع عضو فلزي ، ومن هذه المعقدات تفاعل $[Ml_2(CO)_3(NCMe)_2]$ (عضو فلزي) مع (2-Pentyne) لتعطي $[Ml_2(CO)(NCMe)_2]$ (1 and 2) (M=Mo, W) $(\eta^2-EtC_2Me)_2]$ ثم يتم تفاعل المركبان 1 و 2 مع متصلات أخرى مثل: $Ph_2P(CH_2)_nPPh_2$ أو Ph_3P لتعطي على التوالي: $[Ml_2(CO)(PPh_3)_2(\eta^2-EtC_2Me)]$ (3 and 4) & $[Ml_2(CO)\{Ph_2P(CH_2)_n PPh_2\}(\eta^2-EtC_2Me)]$ (for M=Mo, W, n=1-4) (5-12).