Asian Journal of Chemistry Vol. 16, No. 2 (2004), 1051–1058

Preparation and Characterization of the Dichloro bis-(2-Pentyne) Complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$

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Preparation of $[WCl_2(CO)_3(NCMe)_2]$ by reacting of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of NaCl in acetone, followed with an excess of EtC_2Me (2-pentyne) in CH_2Cl_2 gives the 2-pentyne complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (**1**).

Equimolar quantities of **1** with ($L = NPh_3$ and PPh_3) react in CH_2Cl_2 to give the acetonitrile replaced products, $[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Me)_2]$ (**2**) and $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Me)_2]$ (**3**) in good yield. Reaction of 1 with equimolar amount of bidentate of $\{L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1–5)$\}$ in CH_2Cl_2 at room temperature afforded the mono-(2-Pentyne) complexes, $[WCl_2(CO)(Ph_2P(CH_2)_nPPh_2)(\eta^2\text{-}EtC_2Me)]$ (n = 1–5) (**4–8**).

Key Words: **Preparation, Characterization, Dimeric mono-alkyne complex, Tungsten(II).**

INTRODUCTION

In 1988 Baker *et al.* reported the synthesis of the dimeric mono-alkyne complexes[1] $[\{M(M\text{-}I)I(CO)(NCMe)(\eta^2\text{-}RC_2R^1)\}_2]$ (M = Mo, W; $R = R^1 = Me$, Ph, CH_2Cl; R = Ph, $R^1 = Me$, CH_2OH; R = Me, $R^1 = PhS$, P-tols) and the bis (alkyne) complexes[2] $[\{Mo(M\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2\}_2]$ and $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R^1)_2]$ (M = Mo, W; $R = R^1 = Ph$; R = Me, $R^1 = Ph$; for M = W only; $R = R^1 = Me$, CH_2Cl; P-tol; R = Ph, $R^1 = CH_2OH$). An extensive iodoalkyne chemistry of molybdenum(II) and tungsten(II) was developed[3–9]. In 1994, Baker *et al.*[10, 11] described the synthesis and reactions with donor ligands of dibromo-bis(2-butyne) complex, $[WBr_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$. Baker *et al.*[12] reported a series of mixed chloroido-alkyne complexes, including the X-ray structural characterization of the cationic complex, $[WCl(CO)(2, 2^1\text{-bipy})(\eta^2\text{-}MeC_2Me)_2]I$. Many papers have been published[13–17] describing some new dichloro-alkyne complexes such as $[WCl_2(CO)(L_2)(\eta^2\text{-}PhC_2Ph)]$ ($L = PMe_3$, PMe_2Ph), $[WCl_2(CO)(PMe_3)_2(\eta^2\text{-}Ph_2C_2NH^1BU)]$, $[WCl_2(CO)(PMe_3)_2(\eta^2\text{-}PHC_2R)]$ {R = OH, $OC(O)C_6H_4OMe\text{-}4$} and $[WCl_2({=}CHPh)(PMe_3)_2(\eta^2\text{-}PhC_2Ph)]$ which have been crystallographically characterized.

In 2000, the preparation of the seven-coordinate dichloro-complex $[WCl_2(CO)_3(NCMe)_2]$ by the reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of NaCl in acetone has been reported[18].

In 2001, Mutlaq and Baker[19] described the synthesis of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ by the reaction of $[WCl_2(CO)_3(NCMe)_2]$ with 3-hexyne and also described the above complex with neutral and anionic donor ligands.

In this paper, we used same methods to synthesize and characterize the seven-coordinate dichloro-complex $[WCl_2(CO)_3(NCMe)_2]$ with 2-pentyne following the reaction with mono-dentate and bidentate ligands.

EXPERIMENTAL

Reagents and general techniques: The starting material $[WCl_2(CO)_3(NCMe)_2]$ was prepared *in situ* by reacting $[WI_2(CO)_3(NCMe)_2]$ with two equivalents CH_2Cl_2 in acetone. The reactions were carried out by using standard vacuum/schlenk line techniques. The solvent CH_2Cl_2 was dried over calcium hydride and diethyl ether was dried over sodium wire. All chemicals used were purchased from commercial sources.

Elemental analyses (C, H and N) were determined by using a Carlo-Erba elemental analyser MoD 1108 (using helium as the carrier gas). IR spectra were recorded as thin $CHCl_3$ films on a Perkin-Elmer FT 1600 series IR spectrophotometer.

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer, and spectra were referenced to $SiMe_4$ for ^1H and ^{13}C or 85% H_3PO_4 for ^{31}P.

Preparation of $[WCl_2(CO)(NCMe)(\eta^2$-EtC2Me$)_2]$ (1): To a stirred solution of $[WCl_2(CO)_3(NCMe)_2]$ {which were prepared in situ by reaction of $[WI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.82 mmol) with two equivalents of NaCl (0.096 g, 1.6 mmol)} (0.5 g, 1.2 mmol) in CH_2Cl_2 (25 cm^3) was added excess of EtC_2Me (0.16 g, 0–14 mL, 1.2 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green oily product of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ **(1)**, which was recrystallized several times (yield = 0.25 g, 47%).

Preparation of $[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Me)_2]$ (2): To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ **(1)** (0.3 g, 0.65 mmol) in CH_2Cl_2 (20 cm^3) was added PPh_3 (0.17 g, 0.65 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green powder $[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Me)_2]$ **(2)** (yield of product = 0.15 g, 56%).

Similar reaction of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ with one equivalent of NPh_3 in CH_2Cl_2 at room temperature give the complex $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Me)_2]$ (3) (Table-1).

Preparation of $[WCl_2(CO)(Ph_2P(CH_2)PPh_2)(\eta^2\text{-}EtC_2Me)]$ (4): To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ **(1)** (0.2 g, 0.4 mmol) in CH_2Cl_2 (20 cm^2) at room temperature was added $Ph_2P(CH_2)PPh_2$ (0.16 g, 0.4 mmol). Filtration and removal of solvent *in vacuo* after 24 h gave the green powder $[WCl_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}EtC_2Me)]$ **(4)** (yield of product = 0.18 g, 60%).

Similar reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ **(1)** with one equivalent of $Ph_2P(CH_2)_nPPh_2$ (n = 2–5) in CH_2Cl_2 at room temperature gave the complexes $[WCl_2(CO)(Ph_2P(CH_2)_nPPh_2)(\eta^2\text{-}EtC_2Me)]$ (n = 2–5) **(5–8)** (Table-1).

TABLE-1
PHYSICAL AND ANALYTICAL DATA FOR THE CHLOROCARBONYL 2-PENTYNE TUNGSTEN COMPLEXES (1–8)

Complex No.	Complex	Colour (Yield %)	% Elemental analysis: Found (Calcd.)		
			C	H	N
1	$[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$	Green	35.30	3.8	2.6
		(47)	(35.6)	(4.0)	(2.9)
2	$[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Me)_2]$	Green	51.0	4.1	
		(56)	(51.1)	(4.5)	
3	$[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Me)_2]$	Green	52.0	4.4	1.9
		(54)	(52.4)	(4.6)	(2.1)
4	$[WCl_2(CO)(Ph_2P(CH_2)PPh_2)(\eta^2\text{-}EtC_2Me)]$	Green	50.2	3.9	
		(60)	(50.6)	(4.08)	
5	$[WCl_2(CO)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Me)]$	Green	50.9	4.3	
		(43)	(51.2)	(4.2)	
6	$[WCl_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Me)]$	Green	51.6	4.2	
		(56)	(51.9)	(4.4)	
7	$[WCl_2(CO)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}EtC_2Me)]$	Green	52.3	4.2	
		(28)	(52.5)	(4.6)	
8	$[WCl_2(CO)\{Ph_2P(CH_2)_5PPH_2\}(\eta^2\text{-}EtC_2Me)]$	Green	52.8	4.6	
		(32)	(53.1)	(4.8)	

RESULTS AND DISCUSSION

Synthesis and characterization $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (1): Reaction of $[WCl_2(CO)_3(NCMe)_2]$ (prepared *in situ* as described previously with an excess of 2-pentyne gives the new bis(2-pentyne) complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ **(1)** which has been characterized by IR (Table-2), ^1H and ^{13}C NMR (Tables 3 and 4).

Complex **1** is very much less stable than its diiodo analogue $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)]$[20] and $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$[19]. It was difficult to obtain pure powder even after many attempts, but it can be used for reaction if used very quickly. Complex **1** is also same for solubility of analogue complex of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$[19] but less soluble in chlorinated solvents and diethyl ether and hydrocarbon solvents compared to its diiodo analogue[20]. The IR spectrum for **1** ($CHCl_3$) has strong carbonyl band at 2073 cm^{-1}, which is at same number compared to $[WCl_2(CO)(NCMe)(\eta^2\text{-}Et_2C_2Et)_2]$ at 2079 cm^{-1}; but at higher wavenumber compared to diiodo of previous complex at 2056 cm^{-1}.

TABLE-2

INFRARED DATA[a] FOR THE CHLOROCARBONYL 2-PENTYNE TUNGSTEN COMPLEXES (1–8)

Complex No.	ν(C≡O) cm^{-1}	ν(C≡N) cm^{-1}	ν(C≡C) cm^{-1}
1	2073 s	1632 w	1609 w
2	2067 s	1642 w	—
3	2075 s	1603 w	—
4	1937 s	1604 w	—
5	1941 s	1601 w	—
6	1942 s	1598 w	—
7	1929 s	1607 w	—
8	1932 s	1611 w	—
9	1935 s	1600 w	—

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

TABLE-3

^{1}H NMR DATA[a] FOR THE CHLOROCARBONYL 2-PENTYNE TUNGSTEN COMPLEXES (1–8)

Complex No.	^{1}H NMR (δ) ppm
1	3.5 (q, 4H, CH_2, 2-Pentyne); 3.2 (s, 6H, CH_3, 2-Pentyne); 2.70 (S, 3H, CH_3, CN); 1.2 (t, 6H, CH_3-CH_2, 2-Pentyne)
2	7.8–7.2 (m, ^{1}SH, Ph); 3.6–3.2 (mq, 4H, CH_2 Pentyne); 3.1 (s, 6H, CH_3 Pentyne); 1.2 (t, 6H, CH_2CH_3 Pentyne)
3	7.3–6.8 (m, 15H, Ph); 3.3 (q, 4H, CH_2 Pentyne); 3.1 (s, 6H, Pentyne); 1.2 (t, 6H, $CH_2\underline{CH_3}$Pentyne).
4	7.5-7.1 (m, 20H, Ph); 4.7 (m, 2H, CH_2 dppm); 3.6 (q, 4H, CH_2 Pentyne); 3.0 (s, 6H, CH_2CH_3 Pentyne); 1.2 (t, 6H, CH_2CH_3 Pentyne)
3	7.5–7.1 (m, 20H, Ph); 3.4 (q, 4H, CH_2 Pentyne); 3.2 (s, 6H, $\underline{CH_3}$ Pentyne); 2.7–2.5 (t, 2H, 2H dpp); 2.7–2.5 (2t, 4H, dppe); 1.1 (t, 6H, $CH_2\underline{CH_3}$ Pentyne).
6	7.4–7.2 (m, 20H, Ph); 3.4 (q, 4H, CH_2 Pentyne); 3.1 (s, 6H, $\underline{CH_3}$ Pentyne); 2.6 (t, 2H, CH_2CH_2-CH_2 dppp); 2.4 (2t, 4H, $CH_2CH_2CH_2$ dppp); 1.2 (t, 6H, $CH_2\underline{CH_3}$ Pentyne).
7	7.6–7.2 (m, 20H, Ph); 3.5 (q, 4H, CH_2 Pentyne); 3.2 (s, 6H, CH_3 Pentyne); 2.4 (m, 4H, dppb); 2.1 (m, 4H, dppb); 1.3 (t, 6H,CH_2 $\underline{CH_3}$ Pentyne).
8	7.6–7.2 (m, 20H, Ph); 3.6 (q, 4H, CH_2 Pentyne); 3.3 (s, 6H, CH_3 Pentyne); 2.8 (m, 2H, dpppe); 2.6 (m, 4H, dpppe); 2.3 (m, 4H, dppe); 1.5 (t, 6H, $CH_2\underline{CH_3}$ Pentyne).

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

TABLE-4

^{13}C NMR DATA[a] (δ) FOR SELECTED CHLOROCARBONYL 2-PENTYNE TUNGSTEN COMPLEXES

Complex No.	^{13}C NMR (δ) PPm
1	9.7 (s, Me, CN); 12.8 (S, $CH_2\underline{CH_3}$, Pentyne); 20.30 (s, CH_3C_2) Pentyne; 27.95; 28.30 (s, $\underline{CH_2}CH_3$ Pentyne); 130.45 (s, C≡N); 163.46, 167.50 (s, C≡C); 198.28 (s, C≡O)
2	12.93 (S, CH_3 Pentyne); 28.63 (s, CH_2 Pentyne); 25.72 (s, CH_3CH_2); 123.53, 124.17, 129.30 (s, Ph); 163.20, 165.65 (s, C≡C); 195.30 (s, C≡O)
3	13.25 (s, CH_3 Pentyne); 27.25 (s, CH_2 Pentyne); 26.37 (s, CH_3CH_2); 122.67, 123.18, 123.60 (S, Ph); 148.96 (s, C≡N); 162.50, 166.26 (s, C≡C); 195.80 195.80 (s, C≡O)

[a]Spectra recorded in $CDCl_3$ (25°C) and referenced to $SiMe_4$; s = Singlet.

In view of the similar IR, ^{1}H and ^{13}C-NMR spectral properties of the dichloro complex **1** to the related diiodo alkyne complexes [$WI_2(CO)(NCR)(R^1C_2R^1)_2$] (R = Me, R^1 = Me, Ph[2]; R = But, R^1 = Me[21]; R = Me, R^1 = Ph[22]), which have all been crystallographically characterized. It is very likely that the structure of **1** will be very similar as shown in Fig. 1.

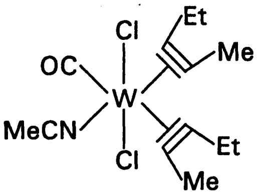
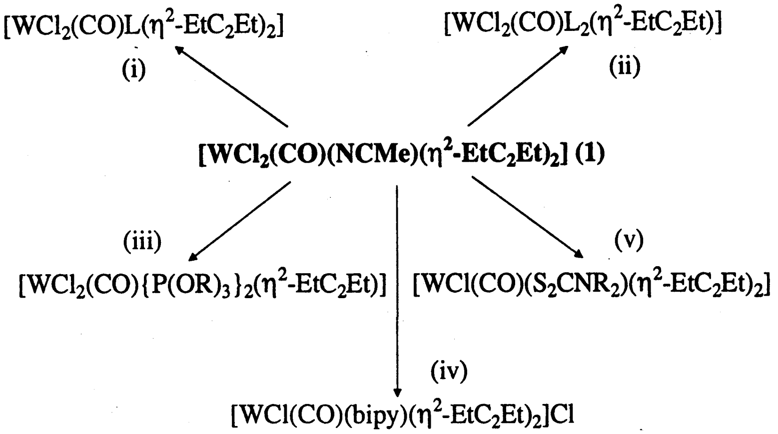


Fig. 1. Proposed structure of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Me)$] (1)

The room temperature ^{13}C-NMR spectrum ($CDCl_3$) for complex **1** (Table-4) has alkyne contact carbon resonances at δ = 162.57 and 167.30 ppm, which from correlation of Templeton and Ward[23] suggests that the two 3-hexyne ligands are donating a total of six electrons to the tungsten, which also enables complex **1** to obey the effective atomic number rule. From previous paper[19] have been prepared many complexes starting from complex [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] with both neutral and anionic donor ligands. These results are summarized in **Scheme-1.**

This paper describes the reactions of complex, [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Me)_2$] **(1)** with monodentate such as PPh_3 and NPh_3 and bidentate ligands, such as $Ph_2P(CH_2)_nPPh_2$.

Reaction of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Me)_2$] (1) with one equivalent of PPh_3 and NPh_3 (23): Reaction of equimolar amounts of **1** and PPh_3 and NPh_3 in CH_2Cl_2 at room temperature gives the acetonitrile exchanged products. [$WCl_2(CO)(PPh_3$ or $NPh_3)(\eta^2$-$EtC_2Me)_2$] (2 or 3).



Reagents: (i) {L = $NPPh_3$, PPh_3, L^{Mo}, L^{W}}.
(ii) $L_1 = 2PPh_2$, $2L^{Mo}$, $2L^{W}$; $L_2 = Ph_2P(CH_2)_nPPh_2$
(n = 1, 3, 4 and 6); and *cis*-$Ph_2PCH = CHPPh_2$.
(iii) $2P(OR)_3$; (R = Et, ^{i}Pr).
(iv) = bipy.
(v) $NaS_2CNR_2{\cdot}3H_2$ (R = Me, Et).

Scheme 1.

Complex **(2)** is more stable than **(1)** but less than **(3)**. Complex **(3)** more soluble than complex **(2).**

All two complexes **2** and **3** decompose very quickly when exposed to air in solution, and are also air-sensitive in the solid state, but can be stored under dinitrogen for several weeks. Complex **2** has a single carbonyl band in its IR spectrum at 2067 cm^{-1} and 2075 cm^{-1} for complex **3** (Table-2) in a similar position to **1** and would be expected to have a similar structure as the acetonitrile complex shown in Fig. 1.

Also the room temperature ^{13}C-NMR spectrum ($CDCl_3$) of the most soluble complex in this series, $[WCl_2(CO)(PPh_3$ or $NPh_3)(\eta^2\text{-}EtC_2Me)_2]$ **(2, 3)**, shows alkyne contact carbon resonances at $\delta = 169.62$ and 163.43 ppm for complex **2** and $\delta = 166.73$ and 161.20 ppm for complex **3**, which again indicates[23] that the two 2-pentyne ligands are donating a total of six electrons to the metal in this complex, which enables the complexes to obey the effective atomic number rule.

Reaction of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (1) with one equivalent of bidentate of ($Ph_2P(CH_2)_nPPh_2$) n = (1–5): Treatment of **1** with $Ph_2P(CH_2)_nPPh_2$ (n = 1–5) in CH_2Cl_2 at room temperature eventually gave the mono (2-Pentyne) complexes $[WCl_2(CO)(Ph_2P(CH_2)_nPPh_2)(\eta^2\text{-}EtC_2Me)]$ **(4–8)**.

All the new complexes have been characterized in the normal manner (Table-5). These bis(phosphine) complexes are more stable than **1–3,** and can be stored for several weeks under a nitrogen atmosphere, and they are also stable in air in the solid state for 5 h. The complexes **4–8** are much less soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ compared to **1–3**.

TABLE-5

^{31}P NMR DATA[a] (δ) FOR SELECTED CHLOROCARBONYL 2-PENTYNE TUNGSTEN COMPLEXES

Complex No.	^{31}P NMR (δ) ppm
2	–26.73 (s, PPh_3)
4	–23.25, –23.65 (d, J_{P-P} = 41.72, H_2 2P, of dppm)
5	–19.14, –18.32 (d, J_{P-P} = 53.23, H_2 2P, of dppe)
6	–17.24, 16.65 (d, J_{P-P} = 59.63, 2P, of dppp)
7	–14.26, –13.95 (d, J_{P-P} = 62.53, 2P, of dppb)
8	–10.63, –10.45 (d, J_{P-P} = 67.64, H_2 2P, of dppe)

[a]Spectra recorded in $CDCl_3$ (25°C) and referenced to 85% H_3PO_4 (s, singlet, d, doublet).

The bidentate phosphine ligand complexes [$WCl_2(CO)(Ph_2P(CH_2)_nPPh_2)(\eta^2$-$EtC_2Me)$] (n = 1–5) (**4–8**), which has been structurally characterized for n = 3. In view of the similar spectroscopic properties of [$WX_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2$-$EtC_2Et)$] {X = Cl, ν(CO) = 1944 cm^{-1}; X = I^{20}, ν(CO) = 1942 cm^{-1}}; ^{13}P-NMR for X = Cl, δ = –18.13 and –17.62 ppm, for X = I^{20}, δ = –23.73 and –36.21 ppm}, it is likely that they will have a similar structure as shown in Fig. 2.

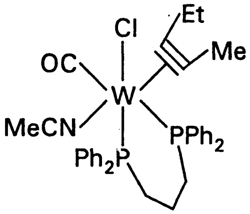


Fig. 2. Proposed structure of [$WCl_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2$-$EtC_2Me)$] (**6**).

ACKNOWLEDGEMENTS

Many thanks to all technicians at Chemistry Department, K.A.A. University, Jeddah, Saudi Arabia.

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(*Received*: 20 September 2003; *Accepted*: 23 December 2003) AJC-3316