

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

MUTLAQ AL-JAHDALI

King Abdulaziz University, Science Faculty, Chemistry Department
P.O.Box 80203, Jeddah 21589, Kingdom of Saudi Arabia
E-mail: mutlaqaljhdali@hotmail.com

Preparation of $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ by reacting of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ with two equivalents of NaCl in acetone, followed with an excess of EtC₂Me (2-pentyne) in CH₂Cl₂ gives the 2-pentyne complex $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1).

Equimolar quantities of 1 with (L = NPh₃ and PPh₃) react in CH₂Cl₂ to give the acetonitrile replaced products, $[\text{WCl}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ (2) and $[\text{WCl}_2(\text{CO})(\text{NPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ (3) in good yield. Reaction of 1 with equimolar amount of bidentate of $\{L_2 = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2 (n = 1-5)\}$ in CH₂Cl₂ at room temperature afforded the mono-(2-Pentyne) complexes, $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ (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 complexes¹ $[\{\text{M}(\text{M}-\text{I})\text{I}(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R}^1)\}_2]$ (M = Mo, W; R = R¹ = Me, Ph, CH₂Cl; R = Ph, R¹ = Me, CH₂OH; R = Me, R¹ = PhS, P-tols) and the bis(alkyne) complexes² $[\{\text{Mo}(\text{M}-\text{I})\text{I}(\text{CO})(\eta^2\text{-MeC}_2\text{Me})_2\}_2]$ and $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R}^1)_2]$ (M = Mo, W; R = R¹ = Ph; R = Me, R¹ = Ph; for M = W only; R = R¹ = Me, CH₂Cl; P-tol; R = Ph, R¹ = CH₂OH). An extensive iodoalkyne chemistry of molybdenum(II) and tungsten(II) was developed³⁻⁹. In 1994, Baker *et al.*^{10,11} described the synthesis and reactions with donor ligands of dibromobis(2-butyne) complex, $[\text{WBr}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$. Baker *et al.*¹² reported a series of mixed chlorido-alkyne complexes, including the X-ray structural characterization of the cationic complex, $[\text{WCl}(\text{CO})(2, 2^1\text{-bipy})(\eta^2\text{-MeC}_2\text{Me})_2]^+$. Many papers have been published¹³⁻¹⁷ describing some new dichloro-alkyne complexes such as $[\text{WCl}_2(\text{CO})(\text{L}_2)(\eta^2\text{-PhC}_2\text{Ph})]$ (L = PMe₃, PMe₂Ph), $[\text{WCl}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-Ph}_2\text{C}_2\text{NH}^1\text{BU})]$, $[\text{WCl}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-PhC}_2\text{R})]$ (R = OH, OC(O)C₆H₄OMe-4) and $[\text{WCl}_2(=\text{CHPh})(\text{PMe}_3)_2(\eta^2\text{-PhC}_2\text{Ph})]$ which have been crystallographically characterized.

In 2000, the preparation of the seven-coordinate dichloro-complex $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ by the reaction of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ with two equivalents of NaCl in acetone has been reported¹⁸.

In 2001, Mutlaq and Baker¹⁹ described the synthesis of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ by the reaction of $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ 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 $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ with 2-pentyne following the reaction with mono-dentate and bidentate ligands.

EXPERIMENTAL

Reagents and general techniques: The starting material $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ was prepared *in situ* by reacting $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ 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, ¹³C and ³¹P NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer, and spectra were referenced to SiMe_4 for ¹H and ¹³C or 85% H_3PO_4 for ³¹P.

Preparation of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1): To a stirred solution of $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ {which were prepared *in situ* by reaction of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ (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 $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1), which was recrystallized several times (yield = 0.25 g, 47%).

Preparation of $[\text{WCl}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ (2): To a stirred solution of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (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 $[\text{WCl}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ (2) (yield of product = 0.15 g, 56%).

Similar reaction of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ with one equivalent of NPh_3 in CH_2Cl_2 at room temperature give the complex $[\text{WCl}_2(\text{CO})(\text{NPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ (3) (Table-1).

Preparation of $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ (4): To a stirred solution of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1) (0.2 g, 0.4 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was added $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$ (0.16 g, 0.4 mmol). Filtration and removal of solvent *in vacuo* after 24 h gave the green powder $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ (4) (yield of product = 0.18 g, 60%).

Similar reactions of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1) with one equivalent of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2-5$) in CH_2Cl_2 at room temperature gave the complexes $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ ($n = 2-5$) (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 | $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ | Green (47) | 35.30 (35.6) | 3.8 (4.0) | 2.6 (2.9) |
| 2 | $[\text{WCl}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ | Green (56) | 51.0 (51.1) | 4.1 (4.5) | |
| 3 | $[\text{WCl}_2(\text{CO})(\text{NPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ | Green (54) | 52.0 (52.4) | 4.4 (4.6) | 1.9 (2.1) |
| 4 | $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ | Green (60) | 50.2 (50.6) | 3.9 (4.08) | |
| 5 | $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ | Green (43) | 50.9 (51.2) | 4.3 (4.2) | |
| 6 | $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ | Green (56) | 51.6 (51.9) | 4.2 (4.4) | |
| 7 | $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ | Green (28) | 52.3 (52.5) | 4.2 (4.6) | |
| 8 | $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ | Green (32) | 52.8 (53.1) | 4.6 (4.8) | |

RESULTS AND DISCUSSION

Synthesis and characterization $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1): Reaction of $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$ (prepared *in situ* as described previously with an excess of 2-pentyne gives the new bis(2-pentyne) complex $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (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 $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ²⁰ and $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ 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 $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ ¹⁹ but less soluble in chlorinated solvents and diethyl ether and hydrocarbon solvents compared to its diiodo analogue²⁰. The IR spectrum for 1 (CHCl_3) has strong carbonyl band at 2073 cm^{-1} , which is at same number compared to $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-Et}_2\text{C}_2\text{Et})_2]$ 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. | $\nu(\text{C}\equiv\text{O}) \text{ cm}^{-1}$ | $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$ | $\nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$ |
|-------------|---|---|---|
| 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 | — |

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

TABLE-3
¹H 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, 5H, 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_2CH_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, CH_3 Pentyne); 2.7-2.5 (t, 2H, 2H dpp); 2.7-2.5 (2t, 4H, dppe); 1.1 (t, 6H, CH_2CH_3 Pentyne). |
| 6 | 7.4-7.2 (m, 20H, Ph); 3.4 (q, 4H, CH_2 Pentyne); 3.1 (s, 6H, CH_3 Pentyne); 2.6 (t, 2H, CH_2CH_2 - CH_2 dppp); 2.4 (2t, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$ dppp); 1.2 (t, 6H, CH_2CH_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_2CH_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_2CH_3 Pentyne). |

^aSpectra 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_2CH_3 , Pentyne); 20.30 (s, CH_3C_2) Pentyne; 27.95; 28.30 (s, CH_2CH_3 Pentyne); 130.45 (s, $\text{C}\equiv\text{N}$); 163.46, 167.50 (s, $\text{C}\equiv\text{C}$); 198.28 (s, $\text{C}\equiv\text{O}$) |
| 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, $\text{C}\equiv\text{C}$); 195.30 (s, $\text{C}\equiv\text{O}$) |
| 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, $\text{C}\equiv\text{N}$); 162.50, 166.26 (s, $\text{C}\equiv\text{C}$); 195.80 (s, $\text{C}\equiv\text{O}$) |

^aSpectra recorded in CDCl_3 (25°C) and referenced to SiMe_4 ; s = Singlet.

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

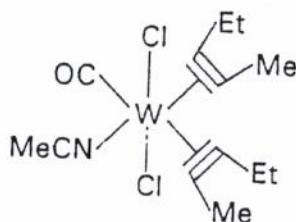
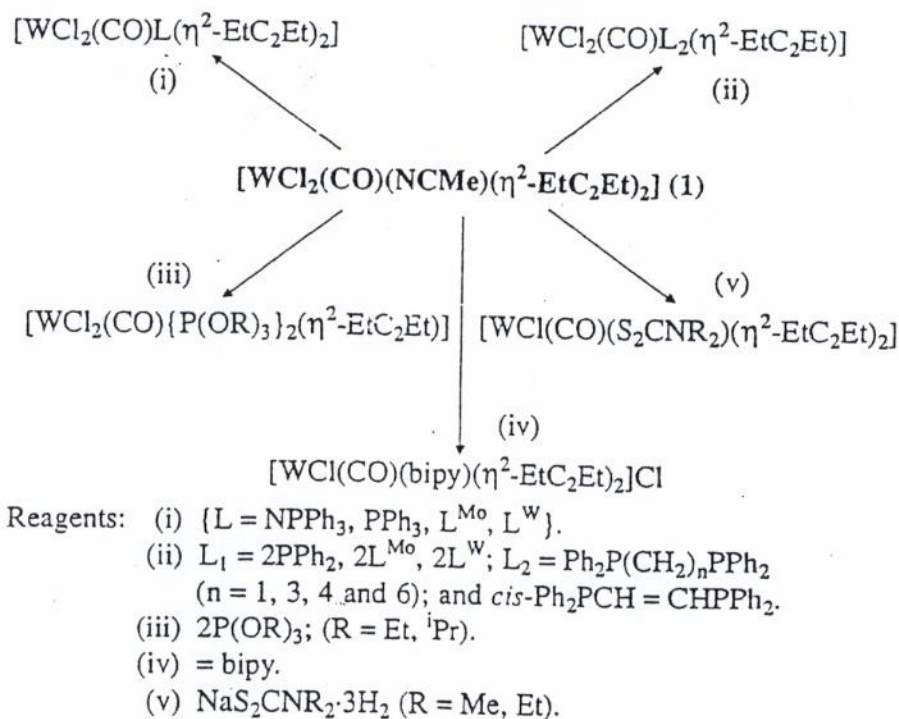


Fig. 1. Proposed structure of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1)

The room temperature ^{13}C -NMR spectrum (CDCl_3) for complex 1 (Table-4) has alkyne contact carbon resonances at $\delta = 162.57$ and 167.30 ppm, which from correlation of Templeton and Ward²³ suggests that the two η^2 -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 paper¹⁹ have been prepared many complexes starting from complex $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Et})_2]$ with both neutral and anionic donor ligands. These results are summarized in Scheme-1.

This paper describes the reactions of complex, $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (1) with monodentate such as PPh_3 and NPh_3 and bidentate ligands, such as $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$.

Reaction of $[\text{WCl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-EtC}_2\text{Me})_2]$ (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. $[\text{WCl}_2(\text{CO})(\text{PPh}_3 \text{ or } \text{NPh}_3)(\eta^2\text{-EtC}_2\text{Me})_2]$ (2 or 3).



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 ¹³C-NMR spectrum (CDCl₃) of the most soluble complex in this series, [WCl₂(CO)(PPh₃ or NPh₃)(η²-EtC₂Me)₂] (2, 3), shows alkyne contact carbon resonances at δ = 169.62 and 163.43 ppm for complex 2 and δ = 166.73 and 161.20 ppm for complex 3, which again indicates²⁵ 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 [WCl₂(CO)(NCMe)(η²-EtC₂Me)₂] (1) with one equivalent of bidentate of (Ph₂P(CH₂)_nPPh₂) n = (1-5): Treatment of 1 with Ph₂P(CH₂)_nPPh₂ (n = 1-5) in CH₂Cl₂ at room temperature eventually gave the mono (2-pentyne) complexes [WCl₂(CO)(Ph₂P(CH₂)_nPPh₂)(η²-EtC₂Me)] (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 CH₂Cl₂ and CHCl₃ 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, $J_{\text{P-P}} = 41.72$, H_2 2P, of dppm) |
| 5 | -19.14, -18.32 (d, $J_{\text{P-P}} = 53.23$, H_2 2P, of dppe) |
| 6 | -17.24, 16.65 (d, $J_{\text{P-P}} = 59.63$, 2P, of dppp) |
| 7 | -14.26, -13.95 (d, $J_{\text{P-P}} = 62.53$, 2P, of dppb) |
| 8 | -10.63, -10.45 (d, $J_{\text{P-P}} = 67.64$, H_2 2P, of dppe) |

^aSpectra recorded in CDCl_3 (25°C) and referenced to 85% H_3PO_4 (s, singlet, d, doublet).

The bidentate phosphine ligand complexes $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ ($n = 1-5$) (4-8), which has been structurally characterized for $n = 3$. In view of the similar spectroscopic properties of $[\text{WX}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Et})]$ ($X = \text{Cl}$, $\nu(\text{CO}) = 1944 \text{ cm}^{-1}$; $X = \text{I}^{20}$, $\nu(\text{CO}) = 1942 \text{ cm}^{-1}$); ^{13}P -NMR for $X = \text{Cl}$, $\delta = -18.13$ and -17.62 ppm, for $X = \text{I}^{20}$, $\delta = -23.73$ and -36.21 ppm), it is likely that they will have a similar structure as shown in Fig. 2.

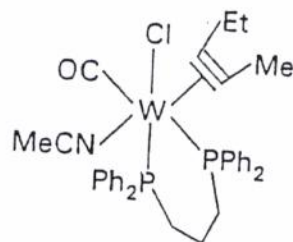


Fig. 2. Proposed structure of $[\text{WCl}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^2\text{-EtC}_2\text{Me})]$ (6).

ACKNOWLEDGEMENTS

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

REFERENCES

1. E.M. Armstrong, P.K. Baker and S.G. Fraser, *J. Chem. Res.*, 52 (1988); *J. Chem. Res. (M)*, 410 (1988).
2. E.M. Armstrong, P.K. Baker and M.G.B. Drew, *Organometallics*, 7, 319 (1988).
3. P.K. Baker, M.G.B. Drew, S. Edge and S.D. Ridyard, *J. Organomet. Chem.*, 409, 207 (1991).
4. P.K. Baker, E.M. Armstrong and M.G.B. Drew, *Inorg. Chem.*, 27, 2287 (1988).
5. E.M. Armstrong, P.K. Baker, M.E. Harman and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, 295 (1989).
6. P.K. Baker, E.M. Armstrong and M.G.B. Drew, *Inorg. Chem.*, 28, 2406 (1989).
7. E.M. Armstrong, P.K. Baker, K.R. Flower and M.G.B. Drew, *J. Chem. Soc. Dalton Trans.*, 2535 (1990).
8. P.K. Baker, *Adv. Organomet. Chem.*, 40, 45 (1996) and references cited therein.
9. ———, *Chem. Soc. Rev.*, 27, 125 (1998) and references cited therein.

10. P.K. Baker, D.J. Muldoon, A.J. Lavery and A. Shawcross, *Polyhedron*, **13**, 2915 (1994).
11. P.K. Baker, A. Bury and K.R. Flower, *Polyhedron*, **8**, 2587 (1989).
12. P.K. Baker, M.G.B. Drew, M.M. Meehan, H.K. Patel and A. White, *J. Chem. Res. (S)*, 379 (1998); *J. Chem. Res. (M)*, 1461 (1998).
13. P.B. Winston, S.J.N. Burgmayer and J.L. Templeton, *Organometallics*, **5**, 1707 (1986).
14. B.J. Brisdon, A.G.W. Hodson, M.F. Mahon, K.C. Molloy and R.A. Walton, *Inorg. Chem.*, **29**, 2701 (1990).
15. G.R. Clark, A.J. Nielson, A.D. Rae and C.E.F. Rickard, *J. Chem. Soc. Dalton Trans.*, 1783 (1994).
16. A. Mayr, C.M. Bastos, *J. Am. Chem. Soc.*, **112**, 7797 (1990).
17. A. Mayr, C.M. Bastos, R.T. Chang, J.X. Haberman, K.S. Robinson and D.A. Belle-Oudry, *Angew. Chem. Int. Ed. Engl.*, **31**, 747 (1992).
18. M. Al-Jahdali, P.K. Baker, A.J. Lavery, M.M. Meehan and D.J. Muldoon, *J. Mol. Catal.*, **159**, 5 (2001).
19. M. Al-Jahdali and P.K. Baker, *J. Organomet. Chem.*, **628**, 91 (2001).
20. M. Al-Jahdali, P.K. Baker and M.G.B. Drew, *Z. Naturforsch.*, **54B**, 171 (1999).
21. P.K. Baker, M.E. Harman, M.B. Hursthouse, A.J. Lavery, K.M.A. Malik, D.J. Muldoon and A. Shawcross, *J. Organomet. Chem.*, **484**, 189 (1994).
22. M.G.B. Drew, P.K. Baker, D.J. Muldoon, A.J. Lavery and A. Shawcross, *Gazz. Chim. Ital.*, **126**, 625 (1996).
23. J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc.*, **102**, 3288 (1980).

(Received: 20 September 2003; Accepted: 23 December 2003)

AJC-3316

**13th INTERNATIONAL SYMPOSIUM ON SUPRAMOLECULAR
CHEMISTRY**

INDIANA, USA

JULY 25-30, 2004

Contact:

<http://www.issc-xiii.org/>

**TETRAPYRROLES, CHEMISTRY AND BIOLOGY OF
(GORDON RESEARCH CONFERENCE)**

NEWPORT, RI, USA

JULY 25-30, 2004

Contact:

<http://www.grc.uri.edu/04sched.htm>