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Synthesis and reactions of the dichloro bis(3-hexyne) complex [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$]

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Abstract

Reaction of [WCl$_2$(CO)$_3$(NCMe)$_2$] (prepared in situ by reacting [WI$_2$(CO)$_3$(NCMe)$_2$] with two equivalents of NaCl in acetone) with an excess of EtC$_2$Et in CH$_2$Cl$_2$ gives the bis(3-hexyne) complex [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (**1**). Equimolar quantities of **1** and L {L = NPh$_3$, PPh$_3$, L^{Mo} or L^W [MI$_2$(CO)$_3$\{MeC(CH$_2$PPh$_2$)$_3$-*P*,*P'*\}] (M = Mo, L^{Mo}; W, L^W)} react in CH$_2$Cl$_2$ to give the acetonitrile replaced products, [WCl$_2$(CO)L(η^2-EtC$_2$Et)$_2$] (**2**→**5**), in good yield. Reaction of **1** with L$_2$ {L = PPh$_3$, L^{Mo}, L^W, L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (1,3,4,6), *cis*-Ph$_2$PCH=CHPPh$_2$} in CH$_2$Cl$_2$ at room temperature afforded the mono(3-hexyne) complexes, [WCl$_2$(CO)L$_2$(η^2-EtC$_2$Et)] (**6–13**). Treatment of **1** with two equivalents of P(OR)$_3$ {R = Et, ^{i}Pr} in diethyl ether gives [WCl$_2$(CO)\{P(OR)$_3$\}$_2$(η^2-EtC$_2$Et)] (**14** and **15**), respectively. Equimolar amounts of **1** and 2,2′- bipyridyl (bipy) yields the cationic complex [WCl(CO)(bipy)(η^2-EtC$_2$Et)$_2$]Cl (**16**). Reaction of equimolar quantities of **1** and NaS$_2$CNR$_2$·3H$_2$O (R = Me, Et) in CH$_2$Cl$_2$ at room temperature affords the mono-chloro complexes [WCl(CO)(S$_2$CNR$_2$)(η^2-EtC$_2$Et)$_2$] (**17** and **18**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tungsten; Alkyne; Carbonyl; Acetonitrile; Tertiaryphosphine

1. Introduction

Since our initial report in 1988 of the synthesis of the dimeric mono-alkyne complexes [{M(μ-I)I(CO)-(NCMe)(η^2-RC$_2$R')}$_2$] (M = Mo, W; R = R' = Me, Ph, CH$_2$Cl; R = Ph, R' = Me, CH$_2$OH; R = Me, R' = PhS, *p*-tolS) [1] and the bis(alkyne) complexes, [{Mo(μ-I)I(CO)(η^2-MeC$_2$Me)$_2$}$_2$] and [MI$_2$(CO)(NCMe)(η^2-RC$_2$R')$_2$] (M = Mo, W; R = R' = Ph; R = Me, R' = Ph; for M = W only; R = R' = Me, CH$_2$Cl, *p*-tol; R = Ph, R' = CH$_2$OH) [2], we have developed an extensive iodo-alkyne chemistry of molybdenum(II) and tungsten(II) [3–9]. More recently, in 1994 [10], we have described the synthesis and reactions with donor ligands of the dibromo-bis(2-butyne) complex, [WBr$_2$(CO)(NCMe)-(η^2-MeC$_2$Me)$_2$]. In 1989 [11], we described the synthesis and characterisation of the mixed-halide complexes [{W(μ-Br)I(CO)(NCMe)(η^2-RC$_2$R)}$_2$] (R = Me, Ph, CH$_2$Cl) and [WBrI(CO)(NCMe)(η^2-RC$_2$R)$_2$], and very

recently in 1998 [12], we described a series of mixed-chloroiodo alkyne complexes, including the X-ray structural characterisation of the cationic complex, [WCl(CO)(2,2′-bipy)(η^2-MeC$_2$Me)$_2$]I. Hitherto, far fewer dichloro alkyne complexes of molybdenum(II) and tungsten(II) have been reported. Templeton and co-workers [13], Brisdon et al. [14], Nielson and co-workers [15], and Mayr et al. [16–18] have described some new dichloro alkyne complexes, following which, [WCl$_2$(CO)(L$_2$)(η^2-PhC$_2$Ph)] (L = PMe$_3$, PMe$_2$Ph) [14], [WCl$_2$(CO)(PMe$_3$)$_2$(η^2-PhC$_2$NH^{t}Bu)] [15], [WCl$_2$(CO)-(PMe$_3$)$_2$(η^2-PhC$_2$R)] {R = OH, OC(O)C$_6$H$_4$OMe-4} [17] and [WCl$_2$(=CHPh)(PMe$_3$)$_2$(η^2-PhC$_2$Ph)] [18], have been crystallographically characterised.

Recently [19], we have described the in situ synthesis 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. In this paper, we describe the synthesis of the bis(3-hexyne) complex [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (**1**), by the reaction of [WCl$_2$(CO)$_3$(NCMe)$_2$] (prepared in situ) with 3-hexyne. The reactions of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (**1**) with neutral and anionic donor ligands is also described.

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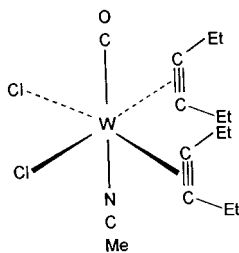
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Fig. 1. Proposed structure of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**).

2. Results and discussion

### 2.1. Synthesis and characterisation of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**)

Reaction of $[WCl_2(CO)_3(NCMe)_2]$ (prepared in situ as described previously [19]), with an excess of 3-hexyne eventually gives the new bis(3-hexyne) complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**), which has been characterised by IR (Table 2), ^{1}H- and ^{13}C-NMR spectroscopy (Tables 3 and 4). Complex **1** is very much less stable than its diiodo analogue $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ [20], 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 $[WCl_2(CO)_3(NCMe)_2]$ (prepared in situ) with EtC_2Et or treating $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with two equivalents of NaCl. It can be used for reactions if used very quickly, but during the preparation of a sample for elemental analysis, it decomposes before the pure sample is analysed. Complex **1** is also 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 a strong

carbonyl band at 2079 cm^{-1}, which is at higher wavenumber compared to $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ at 2056 cm^{-1}. 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 $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ (R = Me, R′ = Me, Ph [2]; R = Bu^t, R′ = Me [21]; R = Me, R′ = Ph [22]), which have all been crystallographically characterised, it is very likely that the structure of **1** will be very similar as shown in Fig. 1.

The room temperature ^{13}C{^{1}H}-NMR spectrum (CDCl$_3$) for complex **1** (Table 4), has alkyne contact carbon resonances at $\delta = 162.43$ and 167.50 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. The rest of this paper describes the reactions of the versatile complex, $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with both neutral and anionic donor ligands. These results are summarised in Scheme 1.

2.2. Reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with one equivalent of L to give $[WCl_2(CO)L(\eta^2\text{-}EtC_2Et)_2]$ (**2–5**)

Reaction of equimolar amounts of **1** and L {L = NPh$_3$, PPh$_3$ or $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$} (M = Mo or W)} in CH$_2Cl_2$ at room temperature gives the acetonitrile exchanged products, $[WCl_2(CO)L(\eta^2\text{-}EtC_2Et)_2]$ (**2–5**). All the new complexes have been characterised in the normal manner (see Tables 1–3) and ^{13}C-NMR for complex **2** (see Table 4). Complex **2** is less stable, and more soluble than the phosphine
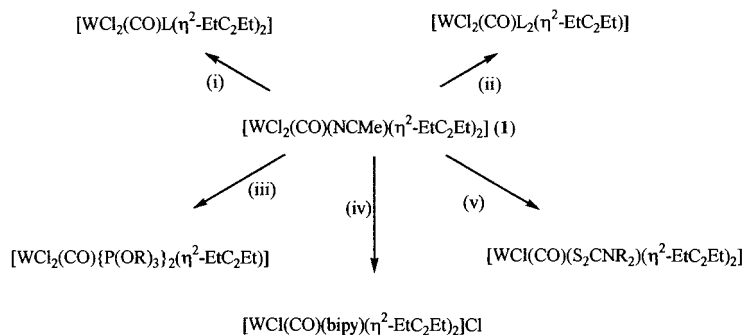
Scheme 1.

Table 1
Physical and analytical data [a] for the chlorocarbonyl 3-hexyne tungsten complexes (**1–18**)

Number	Complex	Colour	Yield (%)	Analysis (%)		
				C	H	N
1	$[WCl_2(CO)(NCMe)(\eta^2-EtC_2Et)_2]$	Green	39	37.2 (36.9)	3.6 (4.7)	1.0 (2.8)
2	$[WCl_2(CO)(NPh_3)(\eta^2-EtC_2Et)_2]$	Green	64	54.3 (53.8)	4.9 (5.1)	2.6 (2.0)
3	$[WCl_2(CO)(PPh_3)(\eta^2-EtC_2Et)_2] \cdot CH_2Cl_2$	Green	48	47.9 (48.3)	4.4 4.7	
4	$[WCl_2(CO)(L^{Mo})(\eta^2-EtC_2Et)_2]$, $L^{Mo} = [MoI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$	Brown	39	45.1 (45.4)	4.7 (4.0)	
5	$[WCl_2(CO)(L^{W})(\eta^2-EtC_2Et)_2]$, $L^{W} = [WI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$	Green	62	42.3 (42.9)	3.7 (3.7)	
6	$[WCl_2(CO)(PPh_3)_2(\eta^2-EtC_2Et)]$	Green	41	58.9 (58.1)	4.5 (4.5)	
7	$[WCl_2(CO)(L^{Mo})_2(\eta^2-EtC_2Et)]$	Brown	79	46.6 (45.9)	4.3 (3.6)	
8	$[WCl_2(CO)(L^{W})_2(\eta^2-EtC_2Et)]$	Green	30	42.4 (42.9)	3.7 (3.3)	
9	$[WCl_2(CO)(dppm)(\eta^2-EtC_2Et)]$	Green	53	50.9 (51.2)	4.6 (4.3)	
10	$[WCl_2(CO)(dppp)(\eta^2-EtC_2Et)] \cdot Et_2O$	Green	36	53.5 (53.6)	5.0 (5.4)	
11	$[WCl_2(CO)(dppb)(\eta^2-EtC_2Et)]$	Green	17	49.1 (49.3)	5.0 (4.6)	
12	$[WCl_2(CO)(dpph)(\eta^2-EtC_2Et)] \cdot CH_2Cl_2$	Green	17	51.0 (50.5)	5.0 (4.9)	
13	$[WCl_2(CO)(cis-dppethy)(\eta^2-EtC_2Et)]$	Green	80	52.9 (52.1)	4.8 (4.2)	
14	$[WCl_2(CO)\{P(OEt)_3\}_2(\eta^2-EtC_2Et)] \cdot CH_2Cl_2$	Green	63	30.7 (31.1)	5.4 (5.5)	
15	$[WCl_2(CO)\{P(O^iPr)_3\}_2(\eta^2-EtC_2Et)]$	Green	69	39.3 (38.4)	6.4 (6.7)	
16	$[WCl(CO)(2,2'-bipyridyl)(\eta^2-EtC_2Et)_2]Cl$	Green	49	42.1 (42.4)	4.4 (4.7)	4.9 (4.7)
17	$[WCl(CO)(S_2CNMe_2)(\eta^2-EtC_2Et)_2] \cdot CH_2Cl_2$	Green	39	31.3 (31.7)	4.3 (4.9)	3.2 (3.8)
18	$[WCl(CO)(S_2CNEt_2)(\eta^2-EtC_2Et)_2]$	Green	58	36.3 (36.5)	5.1 (5.5)	3.4 (3.4)

[a] Calculated values in parentheses.

Table 2
Infrared data [a] for the chlorocarbonyl 3-hexyne tungsten complexes (**1–18**)

Complex	$\nu(C\equiv O)$ (cm^{-1})	$\nu(C\equiv C)$ (cm^{-1})	$\nu(C\equiv N)$ (cm^{-1})
1	2079(s)	1630(w)	2305(w)
2	2081(s)	1587(w)	
3	2064(s)	1644(w)	
4	2075(s); 2044(s); 1970(s); 1934(s)	1619(w)	
5	2079(s); 2034(s); 1958(s); 1905(s)	1609(w)	
6	1995(s)	1640(w)	
7	2044(s); 1972(s); 1938(s); 1904(s)	1622(w)	
8	2038(s); 1990(s); 1962(s); 1907(s); 1901(s)	1625(w)	
9	1936(s)	1601(w)	
10	1944(s)	1604(w)	
11	1932(s)	1636(w)	
12	1935(s)	1635(w)	
13	1963(s)	1602(w)	
14	1958(s)	1621(w)	
15	1951(s)	1641(w)	
16	2052(s)	1605(w)	
17	2043(s)	1605(w)	
18	2041(s)	1646(w)	

[a] Spectra recorded in CHCl$_3$ as thin films between NaCl plates (s, strong; m, medium; w, weak).

complexes **3**–**5**. All the complexes 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 2081 cm^{-1} (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 $^{13}C\{^1H\}$-NMR spectrum (CDCl$_3$) of the most soluble complex

in this series, $[WCl_2(CO)(NPh_3)(\eta^2-EtC_2Et)_2]$ (**2**), shows alkyne contact carbon resonances at $\delta = 168.98$ and 162.30 ppm, which again indicates [23] 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.

The new organometallic phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3-P,P'\}]$ (M = Mo, W), have been prepared by the reaction of equimolar amounts of

Table 3
^{1}H-NMR data [a] for the chlorocarbonyl 3-hexyne tungsten complexes (**1–18**)

Complex	^{1}H-NMR (δ ppm)
1	3.4 (q, 8H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 2.6 (s, 3H, CH_3CN), 1.3 (t, 12H, J_{H-H} = 7.5 Hz; CH_3, hexyne)
2	7.4–6.9 (m, 15H, *Ph*), 3.35 (q, 8H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 1.3 (t, 12H, J_{H-H} = 7.5 Hz; CH_3, hexyne)
3	7.7–7.1 (m, 15H, Ph), 5.3 (s, 2H, CH_2Cl_2), 3.6–3.1 (mq, 8H, CH_2, hexyne), 1.3 (t, 6H, J_{H-H} = 8.5 Hz; CH_3, hexyne), 0.9 (t, 6H, J_{H-H} = 8.5 Hz; CH_3, hexyne)
4	7.7–7.0 (m, 30H, Ph), 3.25 (q, 8H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 2.25 (s, 6H, CH_2, tripodal triphos), 1.2 (t, 12H, J_{H-H} = 7.5 Hz; CH_3, hexyne), 0.9 (s, 3H, CH_3, tripodal triphos)
5	7.7–7.1 (m, 30H, Ph), 3.45 (q, 8H, J_{H-H} = 8.5 Hz; CH_2, hexyne), 2.7–2.2 (m, 6H, CH_2, tripodal triphos), 1.3 (s, 3H, CH_3, tripodal triphos), 0.9 (t, 12H, J_{H-H} = 8.5 Hz; CH_3, hexyne)
6	7.6–7.2 (m, 30H, *Ph*), 3.3 (q, 4H, J_{H-H} = 8.5 Hz; CH_2, hexyne), 1.1 (t, 6H, J_{H-H} = 8.5 Hz; CH_3, hexyne)
7	7.8–6.9 (m, 60H, *Ph*), 3.25 (q, 4H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 2.25 (s, 12H, CH_2, tripodal triphos), 1.2 (t, 6H, J_{H-H} = 7.5 Hz; CH_3, hexyne), 0.9 (s, 6H, CH_3, tripodal triphos)
8	8.0–7.1 (m, 60H, *Ph*), 3.4 (q, 4H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 2.3–2.0 (m, 12H, CH_2, tripodal triphos), 1.3 (t, 6H, J_{H-H} = 7.5 Hz; CH_3, hexyne), 0.9 (s, 6H, CH_3, tripodal triphos)
9	7.6–7.0 (m, 20H, *Ph*), 4.8 (m, 2H, CH_2, dppm), 3.6 (q, 4H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 1.1 (t, 6H, J_{H-H} = 7.5 Hz; CH_3, hexyne)
10	7.5–7.0 (m, 20H, *Ph*), 3.4 (q, 4H, J_{H-H} = 8.6 Hz; CH_2, ether), 3.3 (q, 4H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 2.3 (m, 2H, CH_2, propane), 2.2 (m, 2H, CH_2, propane), 1.9 (m, 2H, CH_2, propane), 1.1 (t, 6H, J_{H-H} = 7.5 Hz; CH_3, hexyne), 0.9 (t, 6H, J_{H-H} = 8.6 Hz; CH_3, ether)
11	7.7–6.9 (m, 20H, Ph), 3.3–2.7 (m, 4H, J_{H-H} = 8.2 Hz; CH_2, hexyne), 2.3 (m, 4H, CH_2PPh_2, dppb), 1.3 (s, 4H, CH_2, dppb), 0.9 (t, 6H, J_{H-H} = 8.2 Hz; CH_3, hexyne)
12	7.7–7.0 (m, 20H, Ph), 3.4 (q, 4H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 2.3 (brm, 4H, CH_2PPh_2-dpph), 1.4 (brm, 8H, CH_2, dpph), 0.9 (t, 6H, J_{H-H} = 7.5 Hz; CH_3, hexyne)
13	7.8–7.1 (m, 20H, *Ph*), 3.6 (q, 4H, J_{H-H} = 8.5 Hz; CH_2, hexyne), 3.3–3.0 (md, 2H, $CH = CH$), 1.2 (t, 6H, J_{H-H} = 8.5 Hz; CH_3, hexyne)
14	5.3 (s, 2H, CH_2Cl_2), 4.2–3.9 {dq, 12H, CH_2, $P(OEt)_3$}, 3.6 (q, 4H, J_{H-H} = 7.5 Hz; CH_2, hexyne), 1.9–1.2 {dt, 18H, CH_3, $P(OEt)_3$}, 1.1 (t, 6H, J_{H-H} = 7.5 Hz; CH_3, hexyne)
15	4.8–4.5 (m, 6H, CH, isopropyl), 3.6 (q, 4H, J_{H-H} = 8.5 Hz; CH_2, hexyne), 1.5–1.1 (md, 36H, CH_3, isopropyl), 1.2 (t, 6H, J_{H-H} = 8.5 Hz; CH_3, hexyne)
16	9.0–7.4 (m, 8H, 2,2'-bipyridyl), 3.7 (mq, 8H, J_{H-H} = 8 Hz; CH_2, hexyne), 1.2 (t, 12H, J_{H-H} = 8 Hz; CH_3, hexyne)
17	5.3 (s, 2H, CH_2Cl_2), 3.45 (q, 8H, J_{H-H} = 8.5 Hz; CH_2, hexyne), 3.1 (s, 6H, CH_3, $(Me)_2$–NCS_2), 1.2 (t, 12H, J_{H-H} = 8.5 Hz; CH_3, hexyne)
18	3.85 (q, 4H, J_{H-H} = 9 Hz; CH_2, $(Et)_2$–NCS_2), 3.5 (q, 8H, J_{H-H} = 8.5 Hz; CH_2, hexyne), (t, 6H, J_{H-H} = 9 Hz; CH_3, $(Et)_2$–NCS_2), 1.2 (t, 12H, J_{H-H} = 8.5 Hz; CH_3, hexyne)

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

$[MI_2(CO)_3(NCMe)_2]$ and $MeC(CH_2PPh_2)_3$ in CH_2Cl_2 at room temperature [24]. For example, the complex $[WCl_2(CO)(L^{Mo})(\eta^2\text{-}EtC_2Et)_2]$ (**4**) has carbonyl bands 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 $[WCl_2(CO)(L^{W})(\eta^2\text{-}EtC_2Et)_2]$ (**5**) which has $v(CO)$ at 2079 cm^{-1}. The other three bands are due to the $WI_2(CO)_3$-unit, which are related to the organometallic phosphine, $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ which has carbonyl stretching bands at 2036, 1958 and 1904 cm^{-1} [24]. The $^{31}P\{^1H\}$-NMR spectrum of **4** has a single resonance at $\delta = 17.59$ ppm due to the two phosphorus atoms of the tripodal triphos attached to the fluxional $MoI_2(CO)_3$-unit, and at 23.60 ppm due to the third phosphorus atom, which is coordinated to the tungsten bis(alkyne) unit, in a ca. 2:1 intensity ratio. The structure of the seven-coordinate complexes, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ part of the bimetallic complexes are most likely to be capped octahedral as

many complexes of this type have this structure [25–27]. Hence, it is likely that the structure of **4** and **5** will have L^{Mo} or L^{W} replacing the acetonitrile in Fig. 1.

Table 4
$^{13}C\{^1H\}$-NMR data [a] (δ) for selected chlorocarbonyl 3-hexyne tungsten complexes

Complex	^{13}C (δ ppm)
1	9.50 (s, MeCN), 13.90 (s, CH_3, hexyne), 28.99, 29.8 (s, CH_2, hexyne), 129.5 (s, $C\equiv N$), 162.43, 167.50 (s, $C\equiv C$), 193.57 (s, $C\equiv O$)
2	13.84 (s, CH_3, hexyne), 28.96 (s, CH_2, hexyne), 122.68, 124.15, 129.184 (s, Ph), 147.84 (s, $C\equiv N$), 162.30, 168.98 (s, $C\equiv C$), 194.4 (s, $C\equiv O$)
16	14.06, 14.48, 14.87 (s, CH_3, hexyne), 27.92, 29.8, 33.72, 35.21 (s, CH_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, $C\equiv C$), 189.30 (s, $C\equiv O$)

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $SiMe_4$ (s, singlet).

Table 5
^{31}P{^{1}H}-NMR data ^{a} (δ) for selected chlorocarbonyl 3-hexyne tungsten complexes

Complex	^{31}P{^{1}H}(δ ppm)
3	−25.33 (s, PPh$_3$)
4	17.59 (s, 2P, L^{Mo}), 23.60 (s, 1P, Ph$_2$P–W)
6	−9.71 (s, *trans*, PPh$_3$)
7	17.58 (s, 2P, L^{Mo}), 30.76 (s, 1P, Ph$_2$P–W)
9	−23.99, −23.57 (d, J_{P-P} = 41.72 Hz, 2P of dppm)
10	−18.13, −17.62 (d, J_{P-P} = 52.22 Hz, 2P of dppp)
11	−10.39, −16.77 (d, J_{P-P} = 55.89 Hz, 2P of dppb)
12	−16.84, −10.27 (d, J_{P-P} = 66.54 Hz, 2P of dpph)
13	−23.83, −2.79 (d, J_{P-P} = 59.83 Hz, 2P of *cis* dppeth)
14	100.40 (s, *trans*), 107.26 (d, *cis*), 107.83 (d, *cis*)
	(J_{P-P} = 57.72 Hz)
15	94.80 (s, *trans*) (J_{W-P} = 194.75 Hz)

^{a} Spectra recorded in CDCl$_3$ (+25°C) and referenced to 85% H$_3$PO$_4$ (s, singlet; d, doublet).
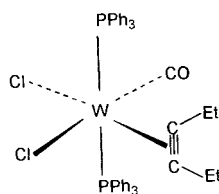
Fig. 2. Proposed structure of [WCl$_2$(CO)(PPh$_3$)$_2$(η^2-EtC$_2$Et)] (**6**).
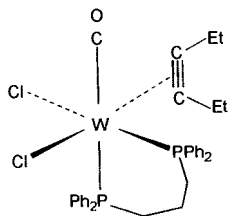
Fig. 3. Proposed structure of [WCl$_2$(CO){Ph$_2$P(CH$_2$)$_3$PPh$_2$}(η^2-EtC$_2$Et)] (**10**).

2.3. Reactions of 1 with two equivalents of L {L = PPh$_3$, L^{Mo}, L^W}, or one equivalent of L$_2$ {L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1, 3, 4 or 6) or cis-Ph$_2$PCH=CHPPh$_2$} to give [WCl$_2$(CO)L$_2$(η^2-EtC$_2$Et)] (6–13)

Treatment of **1** with L$_2$ {L$_2$ = 2PPh$_3$, 2L^{Mo}, 2L^W, Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1, 3, 4 or 6) or *cis*-Ph$_2$PCH=CHPPh$_2$} in CH$_2$Cl$_2$ at room temperature, eventually gave the mono(3-hexyne) complexes, [WCl$_2$(CO)L$_2$(η^2-EtC$_2$Et)] (**6–13**). All the new complexes **6–13** have been characterised in the normal manner (Tables 1–5). Complex **10** was confirmed as an Et$_2$O solvate and **12** as a CH$_2$Cl$_2$ solvate by repeated elemental analyses and ^{1}H-NMR spectroscopy. These bis(phosphine) complexes are considerably more stable than **1–5**, 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$_2$Cl$_2$ and CHCl$_3$ compared to **1–5**.

The ^{31}P{^{1}H}-NMR spectrum of [WCl$_2$(CO)-(PPh$_3$)$_2$(η^2-EtC$_2$Et)] (**6**), has a single resonance at δ = −9.71 ppm, which suggests *trans*-PPh$_3$ groups, which would be expected due to the very large ligand cone angle [28] of PPh$_3$ (145°). This also agrees with all the crystal structures of [MX$_2$(CO)L$_2$(η^2-RC$_2$R')] (M = Mo, X = Br, L = PEt$_3$, R = H, R' = Ph [13]; M = W, X = Cl, L = PMe$_3$ or PMe$_2$Ph, R = R' = Ph [15]; M = W, X = Cl, L = PMe$_3$, R = Ph, R' = NH^{t}Bu [17]; M = W, X = I, L = PPh$_3$, R = R' = Et [20]), which all have *trans*-phosphine ligands. Hence, the most likely structure of complex **6** will be as shown in Fig. 2.

The IR, ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopic properties of the trimetallic complexes, [WCl$_2$(CO)(L^{Mo} or L^W)$_2$(η^2-EtC$_2$Et)] (**7** and **8**) show the two L^{Mo} or L^W moieties are in the same environment, and would also suggest a *trans*-arrangement of these very large monodentate phosphine ligands. For example, [WCl$_2$(CO)(L^{Mo})$_2$(η^2-EtC$_2$Et)] (**7**) has carbonyl bands at ν(CO) = 2044, 1972, 1938, 1904 cm^{-1}; the band at {ν(CO) = 1972 cm^{-1}} is likely to be due to the WCl$_2$(CO)-unit, and the bands ν(CO) = 2044, 1938 and 1904 cm^{-1} due to the MoI$_2$(CO)$_3$-unit in its IR spectrum (Table 2). The ^{31}P{^{1}H}-NMR spectrum (CDCl$_3$, +25°C) of **7** has resonances at δ = 17.58 and 30.76 ppm in a 2:1 intensity ratio. The resonance at δ = 17.58 is most likely to be due to the two phosphorus atoms on the fluxional organomolybdenum phosphine ligand, [MoI$_2$(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$-P,P'}], which has a resonance at δ = 12.63 ppm at room temperature for the two coordinated phosphorus atoms [24]. The lower field resonance at δ = 30.76 ppm will be due to the *trans*-phosphorus atoms attached to the WCl$_2$(CO)-centre.

The bidentate phosphine ligand complexes [WCl$_2$(CO)L$_2$(η^2-EtC$_2$Et)] {L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$; n = 1, 3, 4 or 6, or *cis*-Ph$_2$PCH=CHPPh$_2$} (**9–13**), are related to, for example, the diiodo complexes [WI$_2$(CO){Ph$_2$P(CH$_2$)$_n$PPh$_2$}(η^2-EtC$_2$Et)] (n = 1, 3, 4 or 6), which has been structurally characterised for n = 3 [20]. In view of the similar spectroscopic properties of [WX$_2$(CO){Ph$_2$P(CH$_2$)$_3$PPh$_2$}(η^2-EtC$_2$Et)] {X = Cl (**10**), ν(CO) = 1944 cm^{-1}; X = I [20], ν(CO) = 1942 cm^{-1}}, ^{31}P{^{1}H}-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. 3.

2.4. Reactions of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (1) with two equivalents of P(OR)$_3$ (R = Et, ^{i}Pr) to give [WCl$_2$(CO){P(OR)$_3$}$_2$(η^2-EtC$_2$Et)] (14 and 15)

Reaction of **1** with two equivalents of P(OR)$_3$ (R = Et, ^{i}Pr) in diethyl ether gives the expected bis(phos-

phite) complexes, $[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**14** and **15**) in high yield. These complexes are very soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, and are also soluble in diethyl ether. These complexes have been fully characterised by elemental analysis (Table 1) and spectroscopic methods (see Tables 2–5). Complex **14** was confirmed as a CH_2Cl_2 solvate by repeated elemental analyses and ^{1}H-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 **14** and **15** are the most soluble complexes described in this paper. The synthesis and crystallographic characterisation of a large series of diiodo bis(phosphite) complexes have been described of the type, cis-$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ [6], $trans$-$[MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Me)]$ [29] and $trans$-$[MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (M = Mo or W) [30]. The ^{31}P{^{1}H}-NMR spectrum of **14** 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 ($J_{P-P} = 57.72$ Hz) (the ratio of cis- to $trans$-isomers is approximately 40:60). Whereas, for R = ^iPr (**15**) only a single resonance at $\delta = 94.80$ ppm ($J_{W-P} = 194.75$ Hz) due to the $trans$-isomer was observed. The proposed structures of the cis- and $trans$-isomers of **14** are shown in Fig. 4(a).
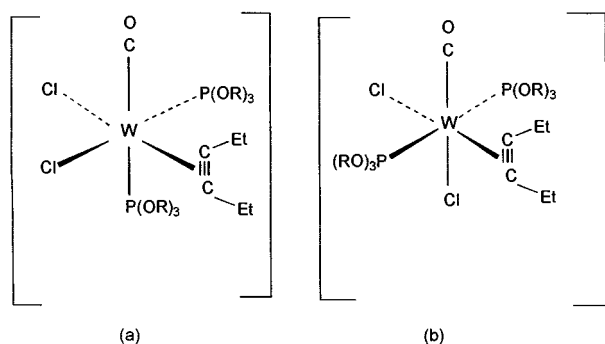

Fig. 4. Proposed structure of both the cis- (a) and $trans$- (b) isomers of $[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ {(**14**) and ^iPr (**15**)}.
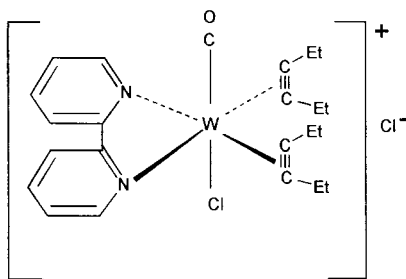

Fig. 5. Proposed structure of $[WCl(CO)(bipy)(\eta^2\text{-}EtC_2Et)_2]Cl$ (**16**).

and (b), respectively, which correspond with the crystal structures of related diiodo complexes [6,29,30].

2.5. Reaction of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (1) with 2,2′-bipyridyl (bipy) to give $[WCl(CO)(bipy)(\eta^2\text{-}EtC_2Et)_2]Cl$ (16)

Treatment of equimolar quantities of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and 2,2′-bipyridyl (bipy) in CH_2Cl_2 at room temperature affords the cationic complex, $[WCl(CO)(bipy)(\eta^2\text{-}EtC_2Et)_2]Cl$ (**16**) in high yield. Complex **16** has been characterised in the normal manner (see Tables 1–4), and is closely related to the crystallographically characterised complexes $[WI(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$ [4] and $[WCl(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$ [12], 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.

In view of the very similar spectroscopic properties of **16** to the crystallographically characterised complexes $[WI(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$ [4] and $[WCl(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$ [12], it is likely to have the same structure as shown in Fig. 5. The ^{13}C{^{1}H}-NMR spectrum (Table 4) of **16** has alkyne contact carbon resonances at $\delta = 164.23$ 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 rule [23].

2.6. Reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (1) with one equivalent of $NaS_2CNR_2 \cdot 3H_2O$ (R = Me, Et) to give $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ (17 and 18)

Reaction of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $NaS_2CNR_2 \cdot 3H_2O$ (R = Me, Et) in CH_2Cl_2 at room temperature gives the complexes, $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ (**17** and **18**) in high yield. These fully characterised complexes (Tables 1–4) are very similar to the crystallographically characterised complex, $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ [7], previously described. Complex **17** was confirmed as a CH_2Cl_2 solvate by repeated elemental analyses and ^{1}H-NMR spectroscopy. The IR and NMR spectral properties of **17** and **18** are similar to the complex, $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$, and hence they are likely to have a similar structure as shown in Fig. 6.

In conclusion, the synthesis of an unstable dichloro bis(alkyne) complex, $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) has been described, and its reactions with a wide range of neutral and anionic donor ligands to give a series of more stable products has been described, as shown in Scheme 1.
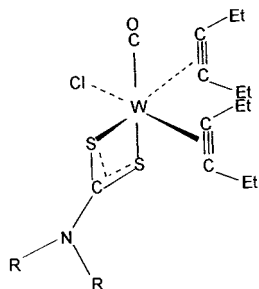
Fig. 6. Proposed structure of $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ {R = Me (**17**); R = Et (**18**)}.

3. Experimental

3.1. Reagents and general techniques

The reactions described in this research were carried out using standard vacuum/Schlenk line 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 of NaCl in acetone, as previously described [19]. 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 using a Carlo Erba Elemental Analyser MOD1108 (using helium as the carrier gas). IR spectra were recorded as thin $CHCl_3$ films on a Perkin–Elmer FT1600 series IR spectrophotometer. ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer, and spectra were referenced to $SiMe_4$ (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P).

3.2. Preparation of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (1)

To a stirred solution of $[WCl_2(CO)_3(NCMe)_2]$ {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 cm³) was added excess of EtC_2Et (0.19 g, 0.27 ml, 2.3 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green oily product of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**), which was recrystallised several times from CH_2Cl_2–Et_2O at −17°C (yield of product = 0.23 g, 39%).

3.3. Preparation of $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$ (2)

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) (0.2 g, 0.41 mmol) in CH_2Cl_2 (25 cm³) was added NPh_3 (0.10 g, 0.40 mmol). Filtration and re-

moval of solvent in vacuo after 24 h, gave the green powder $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$ (**2**), which was recrystallised from CH_2Cl_2–Et_2O at −17°C (yield of pure product = 0.18 g, 64%).

Similar reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of L in CH_2Cl_2 at room temperature (r.t.) gave the complexes $[WCl_2(CO)(L)(\eta^2\text{-}EtC_2Et)_2]$ {L = PPh_2 (**3**), L^{Mo} (**4**), L^W (**5**)}. For physical and analytical data see Table 1.

3.4. Preparation of $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (6)

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) (0.1 g, 0.20 mmol) in CH_2Cl_2 (25 cm³) was added PPh_3 (0.10 g, 0.38 mmol). Filtration, and removal of solvent in vacuo after 24 h, gave the green powder of $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**6**), which was recrystallised from CH_2Cl_2/Et_2O at −17°C (yield of pure product = 0.08 g, 41%).

Similar reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with two equivalents of L in CH_2Cl_2 at r.t. gave the complexes, $[WCl_2(CO)(L)_2(\eta^2\text{-}EtC_2Et)]$ {L = L^{Mo} (**7**), L^W (**8**)}. For physical and analytical data see Table 1.

3.5. Preparation of $[WCl_2(CO)(dppm)(\eta^2\text{-}EtC_2Et)]$ (9)

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) (0.1 g, 0.20 mmol) in CH_2Cl_2 (25 cm³) at r.t. was added $Ph_2P(CH_2)PPh_2$ (0.078 g, 0.20 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green powder, $[WCl_2(CO)(dppm)(\eta^2\text{-}EtC_2Et)]$ (**9**), which was recrystallised from CH_2Cl_2–Et_2O at −17°C (yield of pure product = 0.09 g, 53%).

Similar reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with one equivalent of $L^\wedge L$ {$L^\wedge L = Ph_2P(CH_2)_n$-$PPh_2$, $n = 3$ (**10**), $n = 4$ (**11**), $n = 6$ (**12**), $L^\wedge L = cis\text{-}Ph_2PCH{=}CHPPh_2$ (**13**)} in CH_2Cl_2 at r.t. gave the complexes, $[WCl_2(CO)(L^\wedge L)(\eta^2\text{-}EtC_2Et)]$ (**10–13**). For physical and analytical data see Table 1.

3.6. Preparation of $[WCl_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (14)

To a stirred solution of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) (0.1 g, 0.20 mmol) in Et_2O (25 cm³) was added $P(OEt)_3$ (0.068 g, 0.007 ml, 0.40 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green powder of $[WCl_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**14**), which was recrystallised from CH_2Cl_2–Et_2O at −17°C (yield of pure product = 0.09 g, 63%).

A similar reaction of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with two equivalents of $P(O^iPr)_3$ in Et_2O at r.t. gave the complex, $[WCl_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**15**). For physical and analytical data see Table 1.

3.7. Preparation of [WCl(CO)(bipy)(η^2-EtC$_2$Et)$_2$]Cl (16)

To a stirred solution of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (1) (0.15 g, 0.30 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added bipy (0.045 g, 0.28 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green powder, [WCl(CO)(bipy)(η^2-EtC$_2$Et)$_2$]Cl (16), which was recrystallised from CH$_2$Cl$_2$–Et$_2$O at -17°C (yield of pure product = 0.09 g, 49%).

3.8. Preparation of [WCl(CO)(S$_2$CNMe$_2$)(η^2-EtC$_2$Et)$_2$] (17)

To a stirred solution of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (1) (0.15 g, 0.3 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added NaS$_2$CNMe$_2$·3H$_2$O (0.023 g, 0.3 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green powder [WCl(CO)(S$_2$CNMe$_2$)(η^2-EtC$_2$Et)$_2$] (17), which was recrystallised from CH$_2$Cl$_2$–Et$_2$O at -17°C (yield of pure product = 0.07 g, 39%).

A similar reaction of [WCl$_2$(CO)(NCMe)(η^2-EtC$_2$Et)$_2$] (1) with one equivalent of NaS$_2$CNEt$_2$·3H$_2$O in CH$_2$Cl$_2$ at r.t. gave the complex [WCl(CO)-(S$_2$CNEt$_2$)(η^2-EtC$_2$Et)$_2$] (18). For physical and analytical data see Table 1.

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