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# Synthesis and reactions of the dichloro bis(3-hexyne) complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$

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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 $EtC_2Et$ in $CH_2Cl_2$ gives the bis(3-hexyne) complex $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**). Equimolar quantities of **1** and L {L = $NPh_3$, $PPh_3$, $L^{Mo}$ or $L^W$ $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo, $L^{Mo}$; W, $L^W$)} react in $CH_2Cl_2$ to give the acetonitrile replaced products, $[WCl_2(CO)L(\eta^2\text{-}EtC_2Et)_2]$ (**2**→**5**), in good yield. Reaction of **1** with $L_2$ {L = $PPh_3$, $L^{Mo}$, $L^W$, $L_2 = Ph_2P(CH_2)_nPPh_2$ (1,3,4,6), *cis*-$Ph_2PCH{=}CHPPh_2$} in $CH_2Cl_2$ at room temperature afforded the mono(3-hexyne) complexes, $[WCl_2(CO)L_2(\eta^2\text{-}EtC_2Et)]$ (**6**–**13**). Treatment of **1** with two equivalents of $P(OR)_3$ {R = Et, $^i$Pr} in diethyl ether gives $[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**14** and **15**), respectively. Equimolar amounts of **1** and 2,2′- bipyridyl (bipy) yields the cationic complex $[WCl(CO)(bipy)(\eta^2\text{-}EtC_2Et)_2]Cl$ (**16**). Reaction of equimolar quantities of **1** and $NaS_2CNR_2{\cdot}3H_2O$ (R = Me, Et) in $CH_2Cl_2$ at room temperature affords the mono-chloro complexes $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ (**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 $[\{M(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}RC_2R')\}_2]$ (M = Mo, W; R = R′ = Me, Ph, $CH_2Cl$; R = Ph, R′ = Me, $CH_2OH$; R = Me, R′ = PhS, *p*-tolS) [1] and the bis(alkyne) complexes, $[\{Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2\}_2]$ and $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (M = Mo, W; R = R′ = Ph; R = Me, R′ = Ph; for M = W only; R = R′ = Me, $CH_2Cl$, *p*-tol; R = Ph, R′ = $CH_2OH$) [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, $[WBr_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$. In 1989 [11], we described the synthesis and characterisation of the mixed-halide complexes $[\{W(\mu\text{-}Br)I(CO)(NCMe)(\eta^2\text{-}RC_2R)\}_2]$ (R = Me, Ph, $CH_2Cl$) and $[WBrI(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$, 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, $[WCl(CO)(2,2'\text{-}bipy)(\eta^2\text{-}MeC_2Me)_2]I$. 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, $[WCl_2(CO)(L_2)(\eta^2\text{-}PhC_2Ph)]$ (L = $PMe_3$, $PMe_2Ph$) [14], $[WCl_2(CO)(PMe_3)_2(\eta^2\text{-}PhC_2NH'Bu)]$ [15], $[WCl_2(CO)(PMe_3)_2(\eta^2\text{-}PhC_2R)]$ {R = OH, $OC(O)C_6H_4OMe$-4} [17] and $[WCl_2(=CHPh)(PMe_3)_2(\eta^2\text{-}PhC_2Ph)]$ [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 $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**), by the reaction of $[WCl_2(CO)_3(NCMe)_2]$ (prepared in situ) with 3-hexyne. The reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with neutral and anionic donor ligands is also described.

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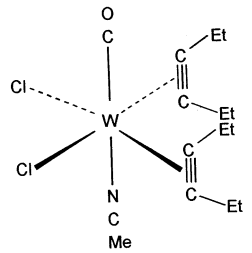



Fig. 1. Proposed structure of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**).

## 2. Results and discussion

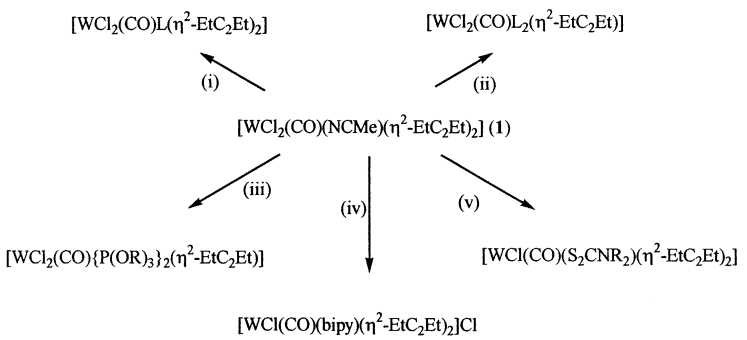
### 2.1. Synthesis and characterisation of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (1)

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 $^{13}C\{^1H\}$-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




Reagents: (i) {L = $NPh_3$, $PPh_3$. $L^{Mo}$, $L^{W}$}
(ii) $L_2 = 2PPh_2$, $2L^{Mo}$, $2L^{W}$; $L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4 and 6); and *cis*-$Ph_2PCH{=}CHPPh_2$
(iii) $2P(OR)_3$, (R = Et, $^i$Pr)
(iv) bipy
(v) $NaS_2CNR_2.3H_2O$ (R = Me, Et)

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** | $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ | Green | 39 | 37.2 (36.9) | 3.6 (4.7) | 1.0 (2.8) |
| **2** | $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$ | Green | 64 | 54.3 (53.8) | 4.9 (5.1) | 2.6 (2.0) |
| **3** | $[WCl_2(CO)(PPh_3)(\eta^2\text{-}EtC_2Et)_2]\cdot CH_2Cl_2$ | Green | 48 | 47.9 (48.3) | 4.4 4.7 | |
| **4** | $[WCl_2(CO)(L^{Mo})(\eta^2\text{-}EtC_2Et)_2]$, $L^{Mo} = [MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ | Brown | 39 | 45.1 (45.4) | 4.7 (4.0) | |
| **5** | $[WCl_2(CO)(L^{W})(\eta^2\text{-}EtC_2Et)_2]$, $L^{W} = [WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ | Green | 62 | 42.3 (42.9) | 3.7 (3.7) | |
| **6** | $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ | Green | 41 | 58.9 (58.1) | 4.5 (4.5) | |
| **7** | $[WCl_2(CO)(L^{Mo})_2(\eta^2\text{-}EtC_2Et)]$ | Brown | 79 | 46.6 (45.9) | 4.3 (3.6) | |
| **8** | $[WCl_2(CO)(L^{W})_2(\eta^2\text{-}EtC_2Et)]$ | Green | 30 | 42.4 (42.9) | 3.7 (3.3) | |
| **9** | $[WCl_2(CO)(dppm)(\eta^2\text{-}EtC_2Et)]$ | Green | 53 | 50.9 (51.2) | 4.6 (4.3) | |
| **10** | $[WCl_2(CO)(dppp)(\eta^2\text{-}EtC_2Et)]\cdot Et_2O$ | Green | 36 | 53.5 (53.6) | 5.0 (5.4) | |
| **11** | $[WCl_2(CO)(dppb)(\eta^2\text{-}EtC_2Et)]$ | Green | 17 | 49.1 (49.3) | 5.0 (4.6) | |
| **12** | $[WCl_2(CO)(dpph)(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$ | Green | 17 | 51.0 (50.5) | 5.0 (4.9) | |
| **13** | $[WCl_2(CO)(cis\text{-}dppethy)(\eta^2\text{-}EtC_2Et)]$ | Green | 80 | 52.9 (52.1) | 4.8 (4.2) | |
| **14** | $[WCl_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$ | Green | 63 | 30.7 (31.1) | 5.4 (5.5) | |
| **15** | $[WCl_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ | Green | 69 | 39.3 (38.4) | 6.4 (6.7) | |
| **16** | $[WCl(CO)(2,2'\text{-bipyridyl})(\eta^2\text{-}EtC_2Et)_2]Cl$ | Green | 49 | 42.1 (42.4) | 4.4 (4.7) | 4.9 (4.7) |
| **17** | $[WCl(CO)(S_2CNMe_2)(\eta^2\text{-}EtC_2Et)_2]\cdot CH_2Cl_2$ | Green | 39 | 31.3 (31.7) | 4.3 (4.9) | 3.2 (3.8) |
| **18** | $[WCl(CO)(S_2CNEt_2)(\eta^2\text{-}EtC_2Et)_2]$ | 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≡O) ($cm^{-1}$) | $\nu$(C≡C) ($cm^{-1}$) | $\nu$(C≡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, $[WCl_2(CO)(NPh_3)(\eta^2\text{-}EtC_2Et)_2]$ (**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, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (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 ($\delta$ ppm) |
|---|---|
| **1** | 3.4 (q, 8H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 2.6 (s, 3H, C$H_3$CN), 1.3 (t, 12H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne) |
| **2** | 7.4–6.9 (m, 15H, *Ph*), 3.35 (q, 8H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 1.3 (t, 12H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne) |
| **3** | 7.7–7.1 (m, 15H, Ph), 5.3 (s, 2H, C$H_2$Cl$_2$), 3.6–3.1 (mq, 8H, C$H_2$, hexyne), 1.3 (t, 6H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne), 0.9 (t, 6H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne) |
| **4** | 7.7–7.0 (m, 30H, Ph), 3.25 (q, 8H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 2.25 (s, 6H, C$H_2$, tripodal triphos), 1.2 (t, 12H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne), 0.9 (s, 3H, C$H_3$, tripodal triphos) |
| **5** | 7.7–7.1 (m, 30H, Ph), 3.45 (q, 8H, $J_{H-H} = 8.5$ Hz; C$H_2$, hexyne), 2.7–2.2 (m, 6H, C$H_2$, tripodal triphos), 1.3 (s, 3H, C$H_3$, tripodal triphos), 0.9 (t, 12H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne) |
| **6** | 7.6–7.2 (m, 30H, *Ph*), 3.3 (q, 4H, $J_{H-H} = 8.5$ Hz; C$H_2$, hexyne), 1.1 (t, 6H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne) |
| **7** | 7.8–6.9 (m, 60H, *Ph*), 3.25 (q, 4H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 2.25 (s, 12H, C$H_2$, tripodal triphos), 1.2 (t, 6H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne), 0.9 (s, 6H, C$H_3$, tripodal triphos) |
| **8** | 8.0–7.1 (m, 60H, *Ph*), 3.4 (q, 4H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 2.3–2.0 (m, 12H, C$H_2$, tripodal triphos), 1.3 (t, 6H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne), 0.9 (s, 6H, C$H_3$, tripodal triphos) |
| **9** | 7.6–7.0 (m, 20H, *Ph*), 4.8 (m, 2H, C$H_2$, dppm), 3.6 (q, 4H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 1.1 (t, 6H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne) |
| **10** | 7.5–7.0 (m, 20H, *Ph*), 3.4 (q, 4H, $J_{H-H} = 8.6$ Hz; C$H_2$, ether), 3.3 (q, 4H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 2.3 (m, 2H, C$H_2$, propane), 2.2 (m, 2H, C$H_2$, propane), 1.9 (m, 2H, C$H_2$, propane), 1.1 (t, 6H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne), 0.9 (t, 6H, $J_{H-H} = 8.6$ Hz; C$H_3$, ether) |
| **11** | 7.7–6.9 (m, 20H, Ph), 3.3–2.7 (m, 4H, $J_{H-H} = 8.2$ Hz; C$H_2$, hexyne), 2.3 (m, 4H, C$H_2$PPh$_2$, dppb), 1.3 (s, 4H, C$H_2$, dppb), 0.9 (t, 6H, $J_{H-H} = 8.2$ Hz; C$H_3$, hexyne) |
| **12** | 7.7–7.0 (m, 20H, Ph), 3.4 (q, 4H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 2.3 (brm, 4H, C$H_2$PPh$_2$-dpph), 1.4 (brm, 8H, C$H_2$, dpph), 0.9 (t, 6H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne) |
| **13** | 7.8–7.1 (m, 20H, *Ph*), 3.6 (q, 4H, $J_{H-H} = 8.5$ Hz; C$H_2$, hexyne), 3.3–3.0 (md, 2H, C$H$ = C$H$), 1.2 (t, 6H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne) |
| **14** | 5.3 (s, 2H, C$H_2$Cl$_2$), 4.2–3.9 {dq, 12H, C$H_2$, P(OEt)$_3$}, 3.6 (q, 4H, $J_{H-H} = 7.5$ Hz; C$H_2$, hexyne), 1.9–1.2 {dt, 18H, C$H_3$, P(OEt)$_3$}, 1.1 (t, 6H, $J_{H-H} = 7.5$ Hz; C$H_3$, hexyne) |
| **15** | 4.8–4.5 (m, 6H, C*H*, isopropyl), 3.6 (q, 4H, $J_{H-H} = 8.5$ Hz; C$H_2$, hexyne), 1.5–1.1 (md, 36H, C$H_3$, isopropyl), 1.2 (t, 6H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne) |
| **16** | 9.0–7.4 (m, 8H, 2,2′-bipyridyl), 3.7 (mq, 8H, $J_{H-H} = 8$ Hz; C$H_2$, hexyne), 1.2 (t, 12H, $J_{H-H} = 8$ Hz; C$H_3$, hexyne) |
| **17** | 5.3 (s, 2H, C$H_2$Cl$_2$), 3.45 (q, 8H, $J_{H-H} = 8.5$ Hz; C$H_2$, hexyne), 3.1 (s, 6H, C$H_3$, (Me)$_2$–NCS$_2$), 1.2 (t, 12H, $J_{H-H} = 8.5$ Hz; C$H_3$, hexyne) |
| **18** | 3.85 (q, 4H, $J_{H-H} = 9$ Hz; C$H_2$, (Et)$_2$–NCS$_2$), 3.5 (q, 8H, $J_{H-H} = 8.5$ Hz; C$H_2$, hexyne), (t, 6H, $J_{H-H} = 9$ Hz; C$H_3$, (Et)$_2$–NCS$_2$), 1.2 (t, 12H, $J_{H-H} = 8.5$ Hz; C$H_3$, 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$_2$PPh$_2$)$_3$ in CH$_2$Cl$_2$ at room temperature [24]. For example, the complex [WCl$_2$(CO)(L$^{Mo}$)($\eta^2$-EtC$_2$Et)$_2$] (**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$^{W}$)($\eta^2$-EtC$_2$Et)$_2$] (**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$_2$PPh$_2$)$_3$-*P*,*P*′\}] which has carbonyl stretching bands at 2036, 1958 and 1904 cm$^{-1}$ [24]. The $^{31}$P\{$^1$H\}-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$_2$PPh$_2$)$_3$-*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\{$^1$H\}-NMR data [a] ($\delta$) for selected chlorocarbonyl 3-hexyne tungsten complexes

| Complex | $^{13}$C ($\delta$ ppm) |
|---|---|
| **1** | 9.50 (s, MeCN), 13.90 (s, CH$_3$, hexyne), 28.99, 29.8 (s, CH$_2$, hexyne), 129.5 (s, C≡N), 162.43, 167.50 (s, C≡C), 193.57 (s, C≡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≡N), 162.30, 168.98 (s, C≡C), 194.4 (s, C≡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≡C), 189.30 (s, C≡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] ($\delta$) for selected chlorocarbonyl 3-hexyne tungsten complexes

| Complex | $^{31}P\{^{1}H\}$($\delta$ ppm) |
|---|---|
| **3** | −25.33 (s, $PPh_3$) |
| **4** | 17.59 (s, 2P, $L^{Mo}$), 23.60 (s, 1P, $Ph_2P$–W) |
| **6** | −9.71 (s, *trans*, $PPh_3$) |
| **7** | 17.58 (s, 2P, $L^{Mo}$), 30.76 (s, 1P, $Ph_2P$–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% $H_3PO_4$ (s, singlet; d, doublet).

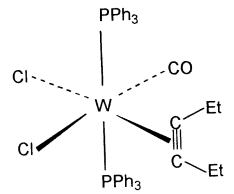



Fig. 2. Proposed structure of $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**6**).

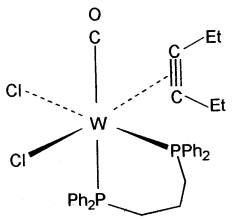



Fig. 3. Proposed structure of $[WCl_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**10**).

### 2.3. Reactions of **1** with two equivalents of L {$L = PPh_3$, $L^{Mo}$, $L^{W}$}, or one equivalent of $L_2$ {$L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4 or 6) or cis-$Ph_2PCH{=}CHPPh_2$} to give $[WCl_2(CO)L_2(\eta^2\text{-}EtC_2Et)]$ (**6**–**13**)

Treatment of **1** with $L_2$ {$L_2 = 2PPh_3$, $2L^{Mo}$, $2L^{W}$, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 3, 4 or 6) or *cis*-$Ph_2PCH{=}CHPPh_2$} in $CH_2Cl_2$ at room temperature, eventually gave the mono(3-hexyne) complexes, $[WCl_2(CO)L_2(\eta^2\text{-}EtC_2Et)]$ (**6**–**13**). All the new complexes **6**–**13** have been characterised in the normal manner (Tables 1–5). Complex **10** was confirmed as an $Et_2O$ solvate and **12** as a $CH_2Cl_2$ 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 $CH_2Cl_2$ and $CHCl_3$ compared to **1**–**5**.

The $^{31}P\{^{1}H\}$-NMR spectrum of $[WCl_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**6**), has a single resonance at $\delta = -9.71$ 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 $[MX_2(CO)L_2(\eta^2\text{-}RC_2R')]$ (M = Mo, X = Br, L = $PEt_3$, R = H, R′ = Ph [13]; M = W, X = Cl, L = $PMe_3$ or $PMe_2Ph$, 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 $L^{W})_2(\eta^2\text{-}EtC_2Et)]$ (**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, $[WCl_2(CO)(L^{Mo})_2(\eta^2\text{-}EtC_2Et)]$ (**7**) has carbonyl bands at $\nu(CO) = 2044$, 1972, 1938, 1904 $cm^{-1}$; the band at $\{\nu(CO) = 1972\ cm^{-1}\}$ is likely to be due to the $WCl_2(CO)$-unit, and the bands $\nu(CO) = 2044$, 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 $\delta = 17.58$ and 30.76 ppm in a 2:1 intensity ratio. The resonance at $\delta = 17.58$ is most likely to be due to the two phosphorus atoms on the fluxional organomolybdenum phosphine ligand, $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$, which has a resonance at $\delta = 12.63$ ppm at room temperature for the two coordinated phosphorus atoms [24]. The lower field resonance at $\delta = 30.76$ ppm will be due to the *trans*-phosphorus atoms attached to the $WCl_2(CO)$-centre.

The bidentate phosphine ligand complexes $[WCl_2(CO)L_2(\eta^2\text{-}EtC_2Et)]$ {$L_2 = Ph_2P(CH_2)_nPPh_2$; $n =$ 1, 3, 4 or 6, or *cis*-$Ph_2PCH{=}CHPPh_2$} (**9**–**13**), are related to, for example, the diiodo complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Et)]$ ($n = 1$, 3, 4 or 6), which has been structurally characterised for $n = 3$ [20]. In view of the similar spectroscopic properties of $[WX_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ {X = Cl (**10**), $\nu(CO) = 1944\ cm^{-1}$; X = I [20], $\nu(CO) = 1942\ cm^{-1}$}, $^{31}P\{^{1}H\}$-NMR (for X = Cl, $\delta = -18.13$ and $-17.62$ ppm, for X = I [20], $\delta = -23.73$ and $-36.21$ ppm}, it is likely that they will have a similar structure as shown in Fig. 3.

### 2.4. Reactions of $[WCl_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) with two equivalents of $P(OR)_3$ (R = Et, $^i$Pr) to give $[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**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 $^{31}P\{^1H\}$-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 = $^i$Pr (**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) and (b), respectively, which correspond with the crystal structures of related diiodo complexes [6,29,30].

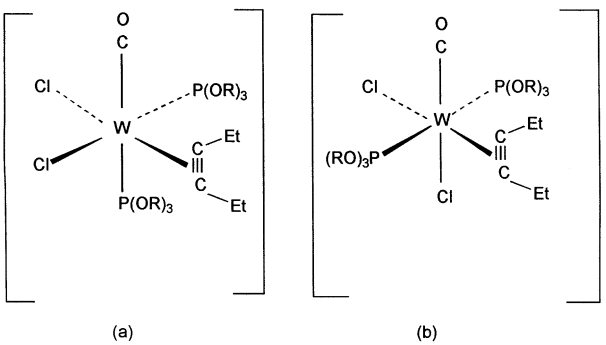



Fig. 4. Proposed structure of both the *cis*- (a) and *trans*- (b) isomers of $[WCl_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ {(**14**) and $^i$Pr (**15**)}.

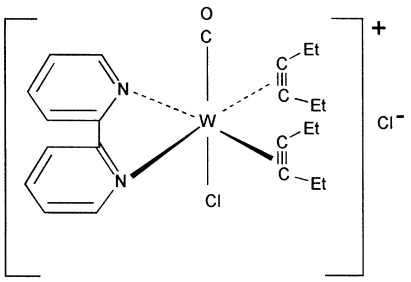



Fig. 5. Proposed structure of $[WCl(CO)(bipy)(\eta^2\text{-}EtC_2Et)_2]Cl$ (**16**).

### 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 $^{13}C\{^1H\}$-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.

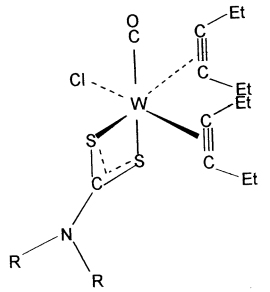



Fig. 6. Proposed structure of $[WCl(CO)(S_2CNR_2)(\eta^2\text{-}EtC_2Et)_2]$ {R = Me (**17**); R = Et (**18**)}.

## 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. $^1$H-, $^{13}$C{$^1$H}- and $^{31}$P{$^1$H}-NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer, and spectra were referenced to $SiMe_4$ ($^1$H 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 cm$^3$) 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 cm$^3$) was added $NPh_3$ (0.10 g, 0.40 mmol). Filtration and removal 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 cm$^3$) 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 cm$^3$) 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^L {L^L = $Ph_2P(CH_2)_n$-$PPh_2$, $n = 3$ (**10**), $n = 4$ (**11**), $n = 6$ (**12**), L^L = *cis*-$Ph_2PCH{=}CHPPh_2$ (**13**)} in $CH_2Cl_2$ at r.t. gave the complexes, $[WCl_2(CO)(L^L)(\eta^2\text{-}EtC_2Et)]$ (**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 cm$^3$) 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)(η²-EtC₂Et)₂]Cl (16)

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (**1**) (0.15 g, 0.30 mmol) in $CH_2Cl_2$ (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, [$WCl(CO)(bipy)(\eta^2$-$EtC_2Et)_2$]Cl (**16**), which was recrystallised from $CH_2Cl_2$–$Et_2O$ at −17°C (yield of pure product = 0.09 g, 49%).

### 3.8. Preparation of [WCl(CO)(S₂CNMe₂)(η²-EtC₂Et)₂] (17)

To a stirred solution of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (**1**) (0.15 g, 0.3 mmol) in $CH_2Cl_2$ (25 $cm^3$) was added $NaS_2CNMe_2 \cdot 3H_2O$ (0.023 g, 0.3 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the green powder [$WCl(CO)(S_2CNMe_2)(\eta^2$-$EtC_2Et)_2$] (**17**), which was recrystallised from $CH_2Cl_2$–$Et_2O$ at −17°C (yield of pure product = 0.07 g, 39%).

A similar reaction of [$WCl_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (**1**) with one equivalent of $NaS_2CNEt_2 \cdot 3H_2O$ in $CH_2Cl_2$ at r.t. gave the complex [$WCl(CO)(S_2CNEt_2)(\eta^2$-$EtC_2Et)_2$] (**18**). For physical and analytical data see Table 1.

## Acknowledgements

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