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Preparation and properties of molybdenum and tungsten dinitrogen complexes

XXXV *. Synthesis of diazoalkane and hydrazido(2 –) complexes of tungsten containing a π-acceptor ligand

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Abstract

Diazoalkane complexes $[MCl_2(NNCRR')(PMe_2Ph)_3]$ (M = W or Mo; R, R′ = Me or Ph), derived from dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$, reacted with various π-acceptor molecules at 50°C to give a series of new diazoalkane complexes $[MCl_2(L)(NNCRR')(PMe_2Ph)_2]$ (L = olefins, CO, ^tBuNC, or aldehydes). Analogous substitution of ethylene or CO for one phosphine ligand occurred in the hydrazido(2 –) complex $[WCl_2(NNH_2)(PMe_2Ph)_3]$, which resulted in the formation of $[WCl_2(L)(NNH_2)(PMe_2Ph)_2]$. Condensation of this new hydrazido(2 –) complex (L = CO) with aldehyde or ketone gives the diazoalkane complexes of the type $[WCl_2(CO)(NNCRR')(PMe_2Ph)_2]$. The structures of $[WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)_2]$ (**4**) and $[WCl_2(\eta^2\text{-}p\text{-}CH_3C_6H_4CHO)(NNCMePh)(PMe_2Ph)_2]$ (**13**) were determined by single-crystal X-ray diffraction studies: **4** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.755(7)$, $b = 18.528(6)$, $c = 10.791(3)$ Å, $\beta = 93.25(4)°$, $Z = 4$, and $R = 0.036$ for 4199 reflections, while **13** crystallizes in the monoclinic space group $P2_1/n$ with $a = 31.519(13)$, $b = 11.360(5)$, $c = 9.348(3)$ Å, $\beta = 92.28(3)°$, $Z = 4$, and $R = 0.053$ for 3522 reflections. Both have an octahedral geometry with the diazoalkane and the π-acceptor ligands in mutual *cis* positions.

Introduction

Protonation reactions of a ligating dinitrogen in $[M(N_2)_2(P)_4]$ (M = Mo or W; P = tertiary phosphine) have been studied extensively with respect to the action of nitrogenase, and several hydrazido(2 –) ($MNNH_2$) complexes have been isolated as the key intermediates in the reduction of the coordinated dinitrogen into ammonia or hydrazine. Interestingly, detailed studies on the reactivities of the

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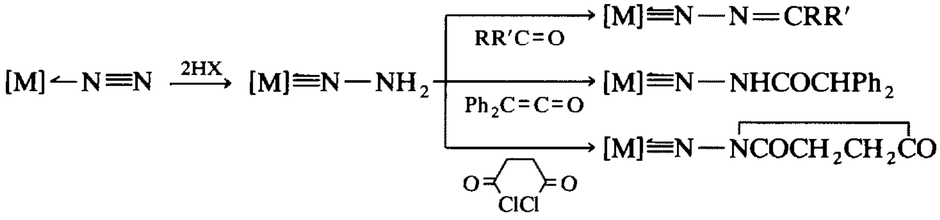
hydrazido(2 −) complexes such as $[MX_2(NNH_2)(PMe_2Ph)_3]$ and $[MF(NNH_2)(dppe)_2]BF_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have revealed that the terminal nitrogen atom of the hydrazido(2 −) ligands in these complexes shows a nucleophilic character enough to react with $\rangle$C=O groups and, as shown in eq. 1, a series of diazoalkane and organohydrazido(2 −) complexes is readily derived not only for the complexes with diphosphine ligands but also for those with monophosphine ligands [1–3]:



(1)

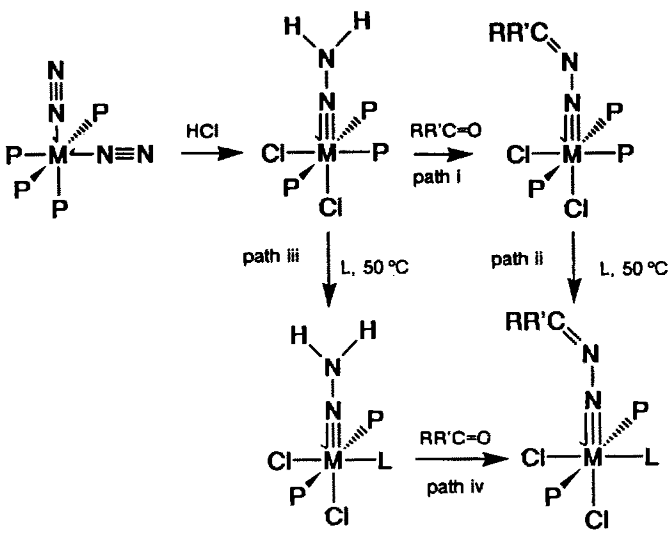
Formation of the diazoalkane complexes is of particular interest, because free diazoalkanes are not easily available despite their high synthetic utility in organic synthesis. This reaction provides a very convenient method to prepare a variety of diazoalkane ligands from molecular nitrogen. However, the reactivities of these diazoalkane complexes are still poorly explored except for the reaction of $[WBr_2(NNCRR')(PMe_2Ph)_3]$ with $LiAlH_4$ giving $RR'CHNH_2$ and NH_3 and the reaction with HBr forming azine and N_2H_4 [3c].

In order to develop a new reactivity of diazoalkane complexes, which may lead to intriguing synthesis of organonitrogen compounds from molecular nitrogen, we have investigated the reaction of the diazoalkane complexes $[MCl_2(NNCRR')(PMe_2Ph)_3]$ (**1** M = W, R = R' = Me; **2** M = W, R = Me, R' = Ph; **3** M = Mo, R = Me, R' = Ph) with olefins, CO, ᵗBuNC, or aldehydes (L). Interestingly, the phosphine ligand *cis* to the diazoalkane ligand and *trans* to the chloride ligand was preferentially replaced by the above substrates. Here we wish to report the details of preparation and characterization of these new diazoalkane complexes $[MCl_2(L)(NNCRR')(PMe_2Ph)_2]$ (**4**–**15**), together with the new hydrazido(2 −) complexes $[WCl_2(L)(NNH_2)(PMe_2Ph)_2]$ (**17**, **18**) derived analogously from $[WCl_2(NNH_2)(PMe_2Ph)_3]$ (**16**).

Results and discussion

Synthesis and characterization of diazoalkane and hydrazido(2 −) complexes containing a π-acceptor ligand

When a solution of the diazoalkane complex $[WCl_2(NNCMe_2)(PMe_2Ph)_3]$ (**1**) in toluene was stirred at 50°C under 1 atm of ethylene, butadiene, or CO, one phosphine ligand *trans* to one chloride ligand was preferentially displaced by the above substrate to give new diazoalkane complexes $[WCl_2(L)(NNCMe_2)(PMe_2Ph)_2]$ (**4** L = C_2H_4; **6** L = $CH_2{=}CHCH{=}CH_2$; **7** L = CO) in moderate yields (Scheme 1, path ii). Analogous reactions of **1** with excess methyl acrylate or PhCHO under N_2 also gave $[WCl_2(L)(NNCMe_2)(PMe_2Ph)_2]$ (**5** L = $CH_2{=}CHCO_2Me$; **8** L = PhCHO). By similar reactions, a series of new diazoalkane complexes



Scheme 1.

$[WCl_2(L)(NNCMePh)(PMe_2Ph)_2]$ (**9** L = C_2H_4; **10** L = CO; **11** L = ^tBuNC; **12** L = PhCHO; **13** L = p-$CH_3C_6H_4CHO$) and $[MoCl_2(L)(NNCMePh)(PMe_2Ph)_2]$ (**14** L = C_2H_4; **15** L = CO) was prepared from $[WCl_2(NNCMePh)(PMe_2Ph)_3]$ (**2**) and $[MoCl_2(NNCMePh)(PMe_2Ph)_3]$ (**3**) respectively, as summarized in Table 1:

$$\underset{\mathbf{1\text{–}3}}{[MCl_2(NNCRR')(PMe_2Ph)_3]} \xrightarrow[-PMe_2Ph]{L} \underset{\mathbf{4\text{–}15}}{[MCl_2(L)(NNCRR')(PMe_2Ph)_2]} \quad \mathbf{4}$$

Furthermore, ethylene or CO can also replace one phosphine ligand in the hydrazido(2 −) complex **16**. Thus, **16** reacted with ethylene or CO in THF at 50°C to afford the corresponding hydrazido(2 −) complexes $[WCl_2(L)(NNH_2)(PMe_2Ph)_2]$ (**17** L = C_2H_4; **18** L = CO) (path iii):

$$\underset{\mathbf{16}}{[WCl_2(NNH_2)(PMe_2Ph)_3]} \xrightarrow[-PMe_2Ph]{L} \underset{\mathbf{17,\ 18}}{[WCl_2(L)(NNH_2)(PMe_2Ph)_2]}$$

Subsequent condensation of this hydrazido(2 −) complex **18** with PhCHO produced the diazoalkane complex $[WCl_2(CO)(NNCHPh)(PMe_2Ph)_2]$ (**19**) (path iv). This provides another route to prepare diazoalkane complexes of the type $[WCl_2(CO)(NNCRR')(PMe_2Ph)_2]$ from **16**. It is noteworthy that **18** reacts readily with $Ph_2C{=}O$, a ketone with two bulky substituents, to give $[WCl_2(CO)(NNCPh_2)(PMe_2Ph)_2]$ (**20**). This is in sharp contrast to the fact that the condensation does not proceed between **16** and $Ph_2C{=}O$ [3c]. Replacement of one phosphine ligand in **16** by CO substantially decreases the steric crowding around the hydrazido(2 −) ligand in **18**, which presumably realizes the condensation with the bulky ketone:

$$\underset{\mathbf{18}}{[WCl_2(CO)(NNH_2)(PMe_2Ph)_2]} \xrightarrow[-H_2O]{RR'C=O} \underset{\mathbf{19,\ 20}}{[WCl_2(CO)(NNCRR')(PMe_2Ph)_2]}$$

However, treatment of **16** with excess PhCHO in THF at 50°C afforded an aldehyde–diazoalkane complex $[WCl_2(\eta^2\text{-}PhCHO)(NNCHPh)(PMe_2Ph)_2]$ (**21**) di-

Table 1

NMR parameters for hydrazido(2−) and diazoalkane complexes containing a π-acceptor ligand $[\mathrm{MCl_2(L)(E)(PMe_2Ph)_2}]$ [a]

Complex			Resonance
M	L	E	
(a) ^{1}*H NMR data*			
4 W	$\mathrm{C_2H_4}$	$\mathrm{NNCMe_2}$	1.04 (t, 3H, *J*(PH) = 0.9 Hz, NNC*Me*$_2$) 1.00 (s, 3H, NNC*Me*$_2$) 1.82, 1.98 (t, 6H each, *J*(PH) = 4.3 Hz, P*Me*$_2$) 2.10, 2.17 (m, 2H each, C$_2$*H*$_4$)
5 W	$\mathrm{CH_2{=}CHCO_2Me}$	$\mathrm{NNCMe_2}$	0.89, 1.03 (s, 3H each, NNC*Me*$_2$) 1.83, 1.95, 2.14, 2.31 (d, 3H each, *J*(PH) = 9.8 Hz, P*Me*$_2$) 2.24 (dt, 1H, *J* = 4.6, 9.8 Hz, WC*H*$_2$CHCO$_2$Me) 2.63 (m, 1H, WC*H*$_2$CHCO$_2$Me) 3.43 (m, 1H, WCH$_2$C*H*CO$_2$Me) 3.29 (s, 3H, WCH$_2$CHCO$_2$*Me*)
6 W	$\mathrm{CH_2{=}CHCH{=}CH_2}$	$\mathrm{NNCMe_2}$	1.00, 1.03 (s, 3H each, NNC*Me*$_2$) 1.75, 1.91, 1.99, 2.09 (d, 3H each, *J*(PH) = 9.5 Hz, P*Me*$_2$) 2.33 (m, 1H, WC*H*$_2$CHCHCH$_2$) 2.52 (dt, 1H, *J* = 9.8, 3.7 Hz, WC*H*$_2$CHCHCH$_2$) 3.80 (m, 1H, WCH$_2$C*H*CHCH$_2$) 4.76 (m, 2H, WCH$_2$CHCHC*H*$_2$) 6.22 (dt, 1H, *J* = 10.4, 17.4 Hz, WCH$_2$,CHC*H*CH$_2$)
7 W	CO	$\mathrm{NNCMe_2}$	0.90 (t, 3H, *J*(PH) = 0.9 Hz, NNC*Me*$_2$) 0.97 (s, 3H, NNC*Me*$_2$) 1.88, 1.90 (t, 6H each, J(PH) = 4.0 Hz, P*Me*$_2$)
8 W	PhCHO	$\mathrm{NNCMe_2}$	0.75, 1.36 (s, 3H each, NNC*Me*$_2$) 1.89, 2.04, 2.08, 2.13 (d, 3H each, *J*(PH) = 9.4 Hz, P*Me*$_2$) 4.73 (dd, 1H, *J* = 10.4, 1.4 Hz, PhC*H*O)
9 W	$\mathrm{C_2H_4}$	NNCMePh	1.40 (t, 3H, *J*(PH) = 0.9 Hz, NNC*Me*Ph) 1.84, 2.00 (t, 6H each, *J*(PH) = 4.3 Hz, P*Me*$_2$) 2.20, 2.27 (m, 2H each, C$_2$*H*$_4$)
10 W	CO	NNCMePh	1.36 (s, 3H, NNC*Me*Ph) 1.91, 1.92 (t, 6H each, *J*(PH) = 4.6 Hz, P*Me*$_2$)
11 W	^{t}BuNC	NNCMePh	1.10 (s, 9H, ^{t}*Bu*NC) 1.57 (t, 3H, *J*(PH) = 0.9 Hz, NNC*Me*Ph) 2.02, 2.07 (t, 6H each, *J*(PH) = 4.0 Hz, P*Me*$_2$)
12 W	PhCHO	NNCMePh	1.17 (s, 3H, NNC*Me*Ph) 1.83, 2.02, 2.04, 2.11 (d, 3H each, *J*(PH) = 10.1 Hz, P*Me*$_2$) 5.39 (dd, 1H, *J* = 10.1, 1.5 Hz, PhC*H*O)
13 W	*p*-$\mathrm{CH_3C_6H_4CHO}$	NNCMePh	1.14 (s, 3H, NNC*Me*Ph) 2.37 (s, 3H, *Me*C$_6$H$_4$CHO) 1.89, 2.06, 2.09, 2.16 (d, 3H each, *J*(PH) = 10.1 Hz, P*Me*$_2$) 4.88 (dd, 1H, *J* = 10.4, 1.2 Hz, PhC*H*O)
14 Mo	$\mathrm{C_2H_4}$	NNCMePh	1.58 (s, 3H, NNC*Me*Ph) 1.81, 2.02 (t, 6H each, *J*(PH) = 4.0 Hz, P*Me*$_2$) 2.45, 2.67 (m, 2H each, C$_2$*H*$_4$)
15 Mo	CO	NNCMePh	1.55 (s, 3H, NNC*Me*Ph) 1.82, 1.90 (t, 6H each, *J*(PH) = 4.0 Hz, P*Me*$_2$)
17 W	$\mathrm{C_2H_4}$	$\mathrm{NNH_2}$ [b]	0.88, 1.07 (m, 2H each, C$_2$*H*$_4$) 1.69, 1.76 (t, 6H each, *J*(PH) = 4.3 Hz, P*Me*$_2$) 5.54 (br, s, 2H, N*H*$_2$)
18 W	CO	$\mathrm{NNH_2}$ [c]	1.94, 2.04 (t, 6H each, *J*(PH) = 4.3 Hz, P*Me*$_2$) 3.97 (br, s, 2H, N*H*$_2$)

Table 1 (continued)

Complex			Resonance
M	L	E	
19 W	CO	NNCHPh [c]	1.92, 1.94 (t, 6H each, *J*(PH) = 4.2 Hz, P*Me*$_2$)
20 W	CO	$NNCPh_2$ [c]	1.76, 1.92 (t, 6H each, *J*(PH) = 4.1 Hz, P*Me*$_2$)
21 W	PhCHO	NNCHPh [c]	1.94, 2.13 (d, 3H each, *J*(PH) = 10.1 Hz, P*Me*$_2$) 2.18 (d, 6H, *J*(PH) = 10.1 Hz, P*Me*$_2$) 4.85 (dd, 1H, *J* = 10.7, 1.2 Hz, PhC*H*O) 5.75 (s, 1H, NNC*H*Ph)
(b) $^{13}C\{^1H\}$ *NMR data*			
4 W	C_2H_4	$NNCMe_2$	11.71, 11.74 (t, *J*(PC) = 15 Hz, P*Me*$_2$) 21.69, 23.50 (s, NNC*Me*$_2$) 42.03 (d, *J*(PC) = 3.7 Hz, C_2H_4) 175.77 (s, NN*C*Me$_2$)
5 W	CH_2=$CHCO_2Me$	$NNCMe_2$	11.39, 11.58, 11.69, 13.73 (d, *J*(PC) = 30 Hz, P*Me*$_2$) 21.75, 23.87 (s, NNC*Me*$_2$) 49.07 (d, *J*(PC) = 6 Hz, W*C*H$_2$CHCO$_2$Me) 49.16 (d, *J*(PC) = 12 Hz, WCH$_2$*C*HCO$_2$Me) 176.42, 177.42 (s, WCH$_2$CH*C*O$_2$Me or NN*C*Me$_2$)
6 W	CH_2=CHCH=CH_2	$NNCMe_2$	10.20, 11.24, 11.46, 12.09 (d, *J*(PC) = 31 Hz, P*Me*$_2$) 22.23, 23.63 (s, NNC*Me*$_2$) 48.58 (d, *J*(PH) = 6 Hz, W*C*H$_2$CHCHCH$_2$) 61.00 (d, *J*(PH) = 6 Hz, WCH$_2$*C*HCHCH$_2$) 111.06 (s, WCH$_2$CHCH*C*H$_2$) 147.89 (s, WCH$_2$CH*C*HCH$_2$) 177.33 (s, NN*C*Me$_2$)
(c) $^{31}P\{^1H\}$ *NMR data*			
4 W	C_2H_4	$NNCMe_2$	−9.03 (*J*(WP) = 236 Hz)
5 W	CH_2=$CHCO_2Me$	$NNCMe_2$	−6.87 (d, *J*(PP′) = 148, *J*(WP) = 231 Hz) −10.46 (d, *J*(WP) = 226 Hz)
6 W	CH_2=CHCH=CH_2	$NNCMe_2$	−8.55 (d, *J*(PP′) = 155, *J*(WP) = 226 Hz) −12.33 (d, *J*(WP) = 246 Hz)
7 W	CO	$NNCMe_2$	−9.85 (*J*(WP) = 286 Hz)
9 W	C_2H_4	NNCMePh	−9.26 (*J*(WP) = 232 Hz)
10 W	CO	NNCMePh	−10.25 (*J*(WP) = 287 Hz)

[a] Taken in C_6D_6 at 400 MHz (^1H), 101 MHz (^{13}C) and 162 MHz (^{31}P). [b] Taken in $CDCl_3$ with some drops of DMSO-d_6. [c] Taken in $CDCl_3$.

rectly. Since the reaction of **16** and PhCHO in THF at room temperature gave only a diazoalkane complex $[WCl_2(NNCHPh)(PMe_2Ph)_3]$ (**22**) in high yield and complex **22** was converted into **21** in the presence of PhCHO at more elevated temperatures, formation of **21** from **16** observed here might proceed through path i and path ii:

$$\underset{\mathbf{16}}{[WCl_2(NNH_2)(PMe_2Ph)_3]} \xrightarrow[-PMe_2Ph \atop -H_2O]{PhCHO} \underset{\mathbf{21}}{[WCl_2(PhCHO)(NNCHPh)(PMe_2Ph)_2]}$$

The structures of ethylene- and aldehyde-diazoalkane complexes **4** and **13** were determined by X-ray crystallography. The perspective views of **4** and **13** are shown in Figs. 1 and 2 respectively. Tables 2 and 3 contain bond lengths and angles for these compounds.

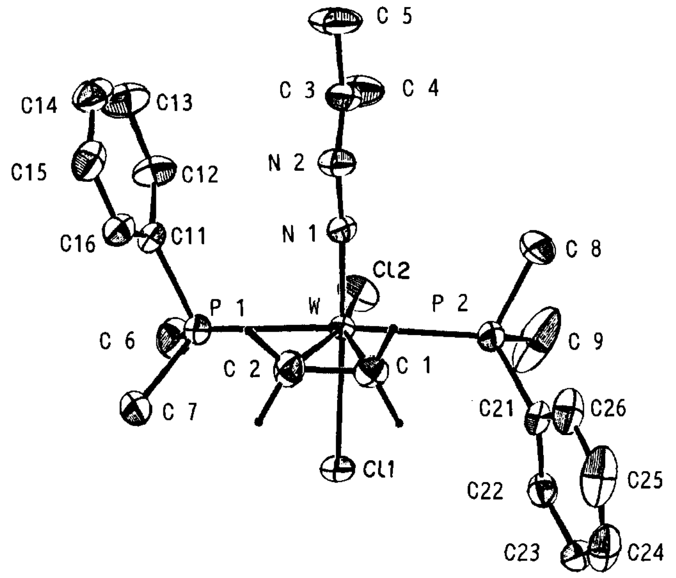


Fig. 1. Perspective view and atom numbering scheme of complex **4**.

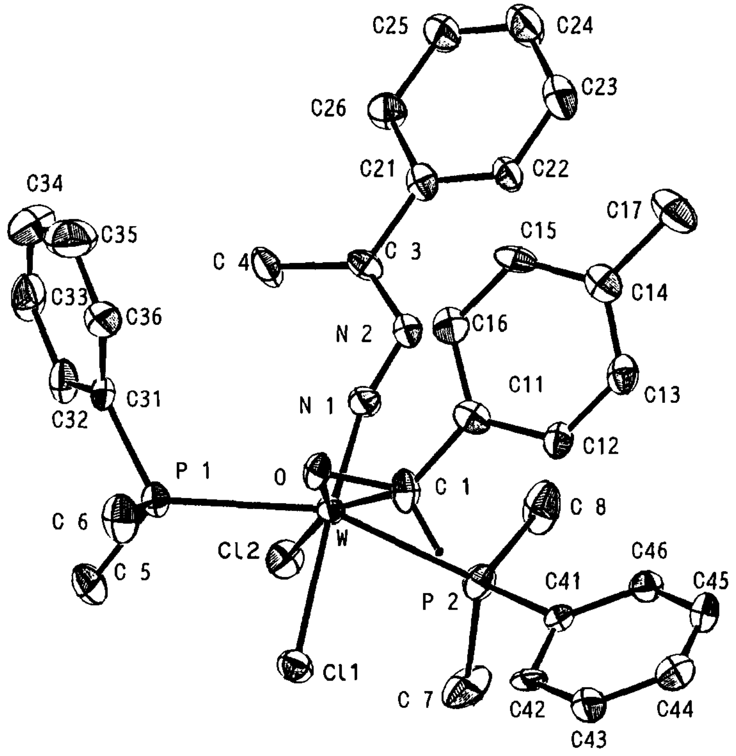


Fig. 2. Perspective view and atom numbering scheme of complex **13**.

Table 2

Selected bond lengths (Å) and angles (deg) for complex **4**

(a) In the coordination sphere of tungsten			
W-Cl1	2.479(2)	W-Cl2	2.475(3)
W-P1	2.540(2)	W-P2	2.536(2)
W-C1	2.217(9)	W-C2	2.228(10)
W-N1	1.750(6)		
Cl1-W-Cl2	87.39(8)	Cl1-W-P1	83.96(8)
Cl1-W-P2	87.43(9)	Cl1-W-C1	86.3(2)
Cl1-W-C2	85.7(3)	Cl1-W-N1	176.2(2)
Cl2-W-P1	82.70(9)	Cl2-W-P2	82.22(9)
Cl2-W-C1	160.0(2)	Cl2-W-C2	160.9(2)
Cl2-W-N1	96.0(2)	P1-W-P2	162.94(9)
P1-W-C1	115.4(2)	P1-W-C2	78.8(2)
P1-W-N1	94.7(2)	P2-W-C1	78.6(2)
P2-W-C2	115.2(2)	P2-W-N1	94.8(2)
C1-W-N1	91.1(3)	C2-W-N1	90.6(3)
(b) In the diazoalkane and ethylene ligands			
N1-N2	1.34(1)	N2-C3	1.29(1)
C3-C4	1.47(1)	C3-C5	1.50(2)
C1-C2	1.40(1)		
W-N1-N2	167.3(6)	N1-N2-C3	116.7(7)
N2-C3-C4	125.3(9)	N2-C3-C5	116.9(9)

Table 3

Selected bond lengths (Å) and angles (deg) for complex **13**

(a) In the coordination sphere of tungsten			
W-Cl1	2.501(4)	W-Cl2	2.475(4)
W-P1	2.596(4)	W-P2	2.554(4)
W-C1	2.19(1)	W-O	2.004(9)
W-N1	1.79(1)		
Cl1-W-Cl2	87.0(1)	Cl1-W-P1	79.0(1)
Cl1-W-P2	83.0(1)	Cl1-W-C1	87.7(4)
Cl1-W-O	87.4(3)	Cl1-W-N1	174.8(4)
Cl2-W-P1	82.2(1)	Cl2-W-P2	80.6(1)
Cl2-W-C1	163.5(4)	Cl2-W-O	158.3(3)
Cl2-W-N1	90.7(4)	P1-W-P2	155.7(1)
P1-W-C1	112.1(4)	P1-W-O	76.2(3)
P1-W-N1	105.3(4)	P2-W-C1	83.2(4)
P2-W-O	119.4(3)	P2-W-N1	92.1(4)
C1-W-N1	93.2(5)	O-W-N1	96.4(5)
(b) In the diazoalkane and aldehyde ligands			
N1-N2	1.29(2)	N2-C3	1.27(2)
C3-C4	1.49(2)	C3-C21	1.51(2)
C1-O	1.33(2)		
W-N1-N2	166 (1)	N1-N2-C3	121 (1)
N2-C3-C4	125 (1)	N2-C3-C21	115 (1)
O-C1-C11	119 (1)		

The coordination geometry around the tungsten centre is essentially the same for both **4** and **13**, where two phosphine and two chloride ligands occupy mutually *trans* and *cis* positions respectively, in the octahedron. Two phosphine ligands in **4** and **13** are distorted (angles P1–W–P2 are 162.94(9)° and 155.7(1)° for **4** and **13** respectively) by steric repulsion between the phosphine groups and both diazoalkane and π-acceptor ligands.

In the diazoalkane ligand *trans* to one chloride ligand, the W–N1–N2 linkage is almost linear, while the N1–N2–C3 angle is 116.7(7)° for **4** or 121(1)° for **13**. The W, N1, N2 and C3 atoms lie nearly on the same plane and the observed N1–N2 (1.34(1) for **4** and 1.29(2) Å for **13**) and N2–C3 (1.29(1) for **4** and 1.27(2) Å for **13**) distances correspond well with those of the four-electron donor diazoalkane ligand in $[WF(NNCMeCH_2COMe)(dppe)_2]^+$ (N–N 1.32(3), N–C 1.30(3) Å) [3a] and $[WBr(NNCMe_2)(dppe)_2]^+$ (N–N 1.36(2), N–C 1.29(2) Å) [4] previously reported.

The ethylene and aldehyde ligands lie *cis* to the diazoalkane ligand by η^2-coordination mode and are oriented perpendicular to the tungsten–nitrogen triple bond. The observed C–C bond length (1.40(1) Å) for the ethylene ligand in **4** and C–O bond length (1.33(2) Å) for the aldehyde ligand in **13** are substantially longer than those of free ethylene (1.337(2) Å) and the C–O double bonds (1.22 Å) respectively. This indicates the presence of significant π-back donation from the tungsten(IV) centre to ethylene or aldehyde in **4** or **13** which is comparable with that of the zerovalent metal centres in *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (C–C 1.40(1) Å) [5] and $[Fe(CO)_2(PEt_3)_2(\eta^2\text{-}PhCHO)]$ (C=O 1.29(2) Å) [6a].

The NMR data for both **4** and **13** are diagnostic of the structures demonstrated by the X-ray crystallography shown above. Thus, the ^1H NMR spectrum of **4** shows the resonances assignable to the methyl protons in phosphine ligands as two triplets and those due to the protons in the ethylene ligand as two multiplets. The spectra recorded at 20 and 60°C are essentially the same as each other, indicating that the structure of **4** is rigid in this temperature region and the rotation of the ethylene ligand was not observed on the ^1H NMR time scale. In **13**, two phosphine ligands are not equivalent because of the η^2-coordination of $p\text{-}CH_3C_6H_4CHO$. This results in the appearance of the methyl protons in phosphine ligands as four doublets in the ^1H NMR spectrum. The aldehyde proton appears as a doublet of doublet due to the coupling with two inequivalent phosphorus atoms, which is consistent with the η^2-coordination of the aldehyde [6].

The ^1H, ^{13}C, and ^{31}P NMR data for all the other complexes **5–12**, **14**, **15**, and **17–21** are shown in Table 1. They are fully consistent with the same coordination geometry around tungsten or molybdenum for these complexes as for **4** and **13**. The butadiene ligand in the butadiene complex **6** is bound to tungsten through only one double bond, as indicated by its IR and NMR spectra. Thus, **6** showed an IR absorption at 1615 cm^{-1} assignable to ν(C=C) and two of four ^{13}C signals for the butadiene ligand appear in the usual olefinic region.

The diazoalkane complexes **4–15** and **19–21** and hydrazido(2 –) complexes **17** and **18** exhibited characteristic IR absorptions at 1582–1509 cm^{-1} assignable to ν(C=N) and 3289–3075 cm^{-1} assignable to ν(NH). The strong carbonyl and isonitrile stretching frequencies are observed at 1975–1940 cm^{-1} for **7**, **10**, **15**, and **18–20** and 1995 cm^{-1} for **11**, which is interpreted by the substantial metal to ligand π-back donation described above.

The hydrazido(2 –) and diazoalkane complexes containing π-acceptor ligands

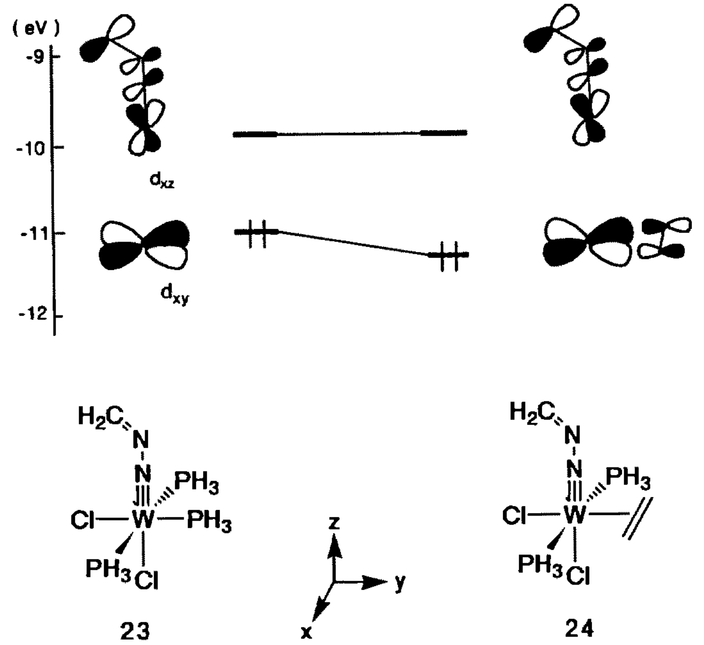


Fig. 3. Change in frontier level energy on going from $[WCl_2(NNCH_2)(PH_3)_3]$ (**23**) to $[WCl_2(C_2H_4)(NNCH_2)(PH_3)_2]$ (**24**).

obtained here are thermally stable and we have not yet observed the reaction between the nitrogen-containing ligand and the π-acceptor ligand. In contrast, Bergman and coworkers [7] have recently shown that imido and hydrazido(2 −) complexes such as $[Cp_2Zr{\equiv}NR]$, $[Cp^*Ir{\equiv}NR]$, and $[Cp_2Zr{\equiv}NNPh_2]$ undergo interesting reactions with substrates such as alkyne, CO, and CO_2, which results in the coupling between the imido or hydrazido(2 −) ligand and the substrate.

Electronic structures of the hydrazido(2 −) and diazoalkane complexes

In connection with the experimental findings, we have performed model EHMO calculations for the hydrazido(2 −) and diazoalkane complexes [8]. The LUMO for the hydrazido(2 −) complex $[WCl_2(NNH_2)(PH_3)_3]$ is antibonding between W and N and that for the diazoalkane complex $[WCl_2(NNCH_2)(PH_3)_3]$ (**23**) is a combination of antibonding W–N, bonding N–N, and antibonding N–C orbitals. Two d electrons are paired in the d_{xy} orbital (HOMO) when the z axis is taken as coincident with the tungsten–nitrogen triple bond (Fig. 3) and thus π-back donation occurs predominantly to the ligand *cis* to the metal–nitrogen triple bond, which is consistent with our finding that the substitution of various π-acceptor ligands for one phosphine ligand in **1–3** and **16** occurs selectively in *cis* position with respect to the hydrazido(2 −) or diazoalkane ligands.

The general electronic features of d^2-oxo and related species have been well elucidated by several groups [8b,9,10]. Metal–ligand π bonding induces a splitting of the t_{2g} block: d_{xy} is essentially non-bonding, while d_{xz} and d_{yz} are destabilized by the antibonding interaction in C_{4v} symmetry when the z axis is taken as

Table 4

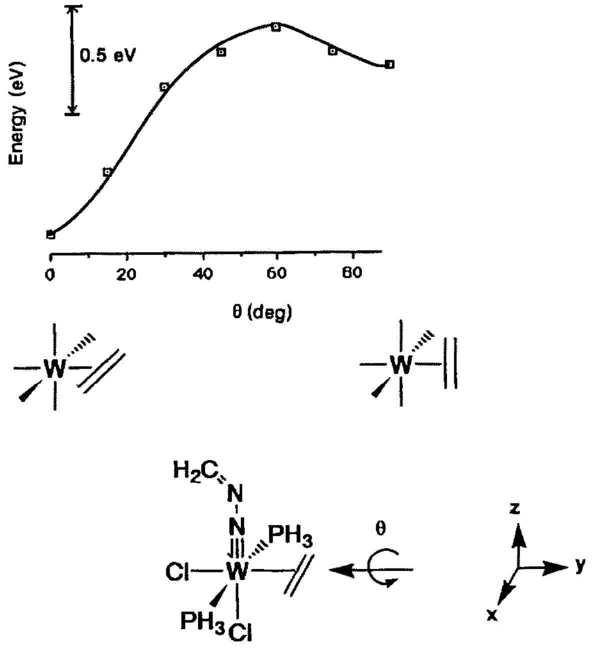
Parameters of electrochemical oxidation (W^{IV}/W^{V}) of diazoalkane complexes [a]

Complex	E^{ox} (V)
$[WCl_2(NNCMe_2)(PMe_2Ph)_3]$ (**1**)	0.13 (r)
$[WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)_2]$ (**4**)	1.20 (ir)
$[WCl_2(CH_2{=}CHCO_2Me)(NNCMe_2)(PMe_2Ph)_2]$ (**5**)	1.47 (ir)
$[WCl_2(CH_2{=}CHCH{=}CH_2)(NNCMe_2)(PMe_2Ph)_2]$ (**6**)	1.00 (ir)
$[WCl_2(CO)(NNCMe_2)(PMe_2Ph)_2]$ (**7**)	0.98 (ir)

[a] In CH_2Cl_2–0.1 M $[^nBu_4N][BF_4]$. Peak oxidation potential *vs.* SCE at a scan rate 200 mV s^{-1}; (r) reversible, (ir) irreversible.

coincident with the metal–ligand multiple bond. Mayer and coworkers [10] demonstrated that tungsten (IV) complexes $[WCl_2(E)(PR_3)_3]$ (E = O, S, or NR) react with π-acceptor ligands such as alkenes, alkyne, CO, isonitrile, or aldehyde to give $[WCl_2(E)(L)(PR_3)_2]$ (L = C_2H_4, $CH_2{=}CHMe$, $CH_2{=}CHCH_2OH$, $CH_2{=}CHCH{=}CH_2$, $PhC{\equiv}CH$, ^tBuNC, or $MeCH{=}O$) and concluded that this feature is a direct result of the electronic structure of the d^2 metal centre.

The EHMO calculation of the model complex $[WCl_2(C_2H_4)(NNCH_2)(PH_3)_2]$ (**24**) further demonstrates that, upon coordination of ethylene, the d_{xy} orbital (HOMO) is significantly stabilized by this π-back donation of the d_{xy} electrons

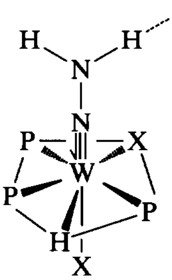


24

Fig. 4. Change in total energy for rotation of ethylene ligand around the *y* axis in $[WCl_2(C_2H_4)(NNCH_2)(PH_3)_2]$ (**24**).

into the C–C π^* orbital (Fig. 3). This correlates well with the electrochemical properties observed for **1** and **4**. Thus, the cyclic voltammogram of **4** showed an irreversible oxidation wave due to the tungsten(IV/V) couple at $E_p = 1.20$ V *vs.* SCE and this value is much more positive than that observed for **1** as a reversible process ($E_p = 0.13$ V *vs.* SCE) (Table 4). The effect of the rotation of the ethylene ligand around the y axis on the total energy of **24** is shown in Fig. 4. It is clear that the geometry in which the ethylene ligand is oriented perpendicular to the tungsten–nitrogen triple bond is most favourable because of the most effective bonding interaction of d_{xy} with π^* orbital of the ethylene ligand. The fact that the ethylene ligand in **4** does not rotate even at 60°C on the NMR time scale can be explained by this substantial π-back donation.

Previous study of the reactivities of hydrazido(2 –) complexes has demonstrated that the hydrido–hydrazido(2 –) complexes $[WX_2H(NNH_2)(PMe_2Ph)_3]X$ (**25**, X = Cl or Br) produced by the further protonation reaction of $[WX_2(NNH_2)(PMe_2Ph)_3]$ with HX, have a pentagonal bipyramidal structure, where the hydrazido(2 –) and hydrido ligands occupy one axial and one equatorial site respectively [11]. This seems consistent with the result that the two d electrons are paired in an orbital that lies perpendicular to the metal nitrogen bond:



P = PMe$_2$Ph
X = Cl or Br

25

Experimental

General procedure

All reactions were carried out in the absence of oxygen using standard Schlenk techniques. Solvents were dried and distilled just before use. Complexes **1–3** [3c] and **16** [12] were prepared by literature methods.

NMR spectra were taken on a JEOL GX-400 spectrometer. All chemical shifts are referred to residual proton or carbon signals in the deuterated solvents (^1H and ^{13}C NMR) or to external phosphoric acid (^{31}P NMR). IR spectra were obtained using either a Shimadzu IR-408 or DR-8000 spectrometer. Electrochemical measurements were made by Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) using a glassy carbon working electrode; potentials were measured *vs.* a saturated calomel electrode as reference.

$[WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)_2]$ (*4*)

A brown solution of **1** (500 mg) in toluene (24 ml) was stirred overnight at 50°C under 1 atm of ethylene. The resultant orange solution was concentrated to *ca.* 6 ml. Addition of hexane (12 ml) gave the orange crystals of the title compound, which were filtered and dried *in vacuo*. Yield 356 mg (84%). IR(KBr): ν(C=N) 1582 cm^{-1}. Anal. Found: C, 39.80; H, 5.10; N, 4.33. $C_{21}H_{32}N_2P_2Cl_2W$ calc.: C, 40.08; H, 5.14; N, 4.45%. **4** was also obtained in 51% yield by the analogous reaction of **1** with ethylene in the presence of $ZnCl_2$(dioxane) but at room temperature.

Other complexes $[WCl_2(CH_2{=}CHCO_2Me)(NNCMe_2)(PMe_2Ph)_2]$ (**5**), $[WCl_2(CH_2{=}CHCH{=}CH_2)(NNCMe_2)(PMe_2Ph)_2]$ (**6**), $[MCl_2(CO)(NNCRR')(PMe_2Ph)_2]$ (**7**, M = W, R = R' = Me; **10** M = W, R = Me, R' = Ph; **15** M = Mo, R = Me, R' = Ph), $[WCl_2(PhCHO)(NNCRR')(PMe_2Ph)_2]$ (**8** R = R' = Me; **12** R = Me, R' = Ph), $[WCl_2(C_2H_4)(NNCMePh)(PMe_2Ph)_2]$ (**9**), $[WCl_2(^tBuNC)(NNCMePh)(PMe_2Ph)_2]$ (**11**) and $[WCl_2(p\text{-}CH_3C_6H_4CHO)(NNCMePh)(PMe_2Ph)_2]$ (**13**), were prepared similarly, using the corresponding π-acceptor ligands (ethylene, methyl acrylate (10-fold molar excess), butadiene, CO, ^{t}BuNC (1-fold molar), ArCHO (4-fold molar excess)) at 50°C.

5: colour yellow, yield 30%. IR(KBr): ν(C=O) 1678, ν(C=N) 1575 cm^{-1}. Anal. Found: C, 39.89; H, 4.88; N, 4.02. $C_{23}H_{34}N_2O_2P_2Cl_2W$ calc.: C, 40.19; H, 5.00; N, 4.08%.

6: colour orange, yield 51%. IR(KBr): ν(C=N) 1575, ν(C=C) 1615 cm^{-1}. Anal. Found: C, 42.34; H, 5.14; N, 4.26. $C_{23}H_{34}N_2P_2Cl_2W$ calc.: C, 42.15; H, 5.24; N, 4.28%.

7: colour purple, yield 73%. IR(KBr): ν(CO) 1940, ν(C=N) 1578 cm^{-1}. Anal. Found: C, 38.10; H, 4.36; N, 4.44. $C_{20}H_{28}N_2OP_2Cl_2W$ calc.: C, 38.18; H, 4.49; N, 4.45%.

8: colour yellow, yield 54%. IR(KBr): ν(C=N) 1580 cm^{-1}. Anal. Found: C, 43.92; H, 4.89; N, 3.91. $C_{26}H_{34}N_2OP_2Cl_2W$ calc.: C, 44.15; H, 4.86; N, 3.96%.

9: colour orange, yield 75%. IR(KBr): ν(C=N) 1525 cm^{-1}. Anal. Found: C, 45.38; H, 4.99; N, 4.02. $C_{26}H_{34}N_2P_2Cl_2W$ calc.: C, 45.17; H, 4.97; N, 4.05%.

10: colour green, yield 77%. IR(KBr): ν(CO) 1950, ν(C=N) 1520 cm^{-1}. Anal. Found: C, 43.51; H, 4.44; N, 4.03. $C_{25}H_{30}N_2OP_2Cl_2W$ calc.: C, 43.44; H, 4.38; N, 4.05%.

11: colour dark orange, yield 72%. IR(KBr): ν(CN) 2075(sh), 1995(br), ν(C=N) 1530 cm^{-1}. Anal. Found: C, 46.69; H, 5.19; N, 5.43. $C_{29}H_{39}N_3P_2Cl_2W$ calc.: C, 46.66; H, 5.28; N, 5.63%.

12: colour orange, yield 63%. IR(KBr): ν(C=N) 1525 cm^{-1}. Anal. Found: C, 48.09; H, 4.62; N, 3.70. $C_{31}H_{36}N_2OP_2Cl_2W$ calc.: C, 48.39; H, 4.73; N, 3.64%.

13: colour red, yield 34%. IR(KBr): ν(C=N) 1509 cm^{-1}. Anal. Found: C, 48.22; H, 4.86; N, 3.67. $C_{32}H_{38}N_2OP_2Cl_2W$ calc.: C, 49.06; H, 4.90; N, 3.58%.

15: colour green, yield 50%. IR(KBr): ν(CO) 1975, ν(C=N) 1510 cm^{-1}. Anal. Found: C, 49.93; H, 5.04; N, 4.58. $C_{25}H_{30}N_2OP_2Cl_2Mo$ calc.: C, 49.76; H, 5.02; N, 4.64%.

$[MoCl_2(C_2H_4)(NNCMePh)(PMe_2Ph)_2]$ *(14)*

Formation of the title compound was confirmed by the ^1H NMR spectrum when **3** was treated with ethylene overnight at 50°C in toluene.

$[WCl_2(C_2H_4)(NNH_2)(PMe_2Ph)_2]$ *(17)*

A suspension of **16** (500 mg) in tetrahydrofuran (24 ml) was stirred overnight at 50°C under 1 atm of ethylene. The resultant green suspension was filtered and the filtrate was concentrated until a solid began to precipitate. Addition of hexane (20 ml) gave the greenish grey solid of the title compound, which was filtered and dried *in vacuo*. Yield 135 mg (32%). IR(KBr): ν(NH): 3289, 3189, 3110 cm^{-1}. Anal. Found: C, 36.49; H, 4.58; N, 4.68. $C_{18}H_{28}N_2P_2Cl_2W$ calc.: C, 36.69; H, 4.80; N, 4.76%. The complexes [$WCl_2(CO)(NNH_2)(PMe_2Ph)_2$] (**18**) and [$WCl_2(PhCHO)(NNCHPh)(PMe_2Ph)_2$] (**21**) were prepared similarly using CO and benzaldehyde (4-fold molar excess) respectively.

18: colour brown, yield 64%. IR(KBr): ν(NH) 3225, 3150, 3075, ν(CO) 1940 cm^{-1}. Anal. Found: C, 34.68; H, 4.14; N, 4.58. $C_{17}H_{24}N_2OP_2Cl_2W$ calc.: C, 34.66; H, 4.11; N, 4.76%.

21: colour orange, yield 50%. IR(KBr): ν(C=N) 1535 cm^{-1}. Anal. Found: C, 48.03; H, 4.76; N, 3.56. $C_{30}H_{34}N_2OP_2Cl_2W$ calc.: C, 47.70; H, 4.55; N, 3.71%. **21** was also obtained in 59% yield by the reaction of **22** with benzaldehyde (4-fold molar excess) at 50°C.

[$WCl_2(NNCHPh)(PMe_2Ph)_3$] (22)

Complex **22** was prepared from **16** and benzaldehyde (4-fold molar excess) at room temperature in 55% yield as brown crystals using a procedure analogous to that used for **17**. ^{1}H NMR($CDCl_3$): δ 1.61, 1.85 (t, 6H each, J(PH) = 3.7 Hz, P*Me*$_2$Ph), 1.47 (d, 6H, J(PH) = 8.2 Hz, P*Me*$_2$Ph). IR(KBr): ν(C=N) 1535 cm^{-1}. Anal. Found: C, 46.78; H, 4.95; N, 3.48. $C_{31}H_{39}N_2P_3Cl_2W$ calc.: C, 47.29; H, 4.99; N, 3.56%.

[$WCl_2(CO)(NNCHPh)(PMe_2Ph)_2$] (19)

Complex **19** was prepared from **18** and benzaldehyde (4-fold molar excess) at room temperature in CH_2Cl_2 in 47% yield as green crystals using a procedure analogous to that used for **17**. IR(KBr): ν(CO) 1940, ν(C=N) 1535 cm^{-1}. Anal. Found: C, 42.29; H, 4.25; N, 4.01. $C_{24}H_{28}N_2OP_2Cl_2W$ calc.: C, 42.56; H, 4.18; N, 4.14%. In a similar way complex [$WCl_2(CO)(NNCPh_2)(PMe_2Ph)_2$] (**20**), was prepared from **18** and benzophenone in the presence of one drop of concentrated (*ca.* 35%) hydrochloric acid in 81% yield, colour green. IR(KBr): ν(CO) 1950, ν(C=N) 1510 cm^{-1}. Anal. Found: C, 47.41; H, 4.36; N, 3.76. $C_{30}H_{32}N_2OP_2Cl_2W$ calc.: C, 47.83; H, 4.29; N, 3.72%.

Collection of the X-ray diffraction data for [$WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)_2$] (4) and [$WCl_2(p\text{-}CH_3C_6H_4CHO)(NNCMePh)(PMe_2Ph)_2$] (13)

An orange cubic crystal of **4** with dimensions 0.49 × 0.30 × 0.20 mm^3 and a red cubic crystal of **13** with dimensions 0.63 × 0.18 × 0.10 mm^3 were sealed in a Pyrex glass capillary and used for data collection. Accurate cell dimensions were determined by least-squares refinement of 20 and 19 machine-centred reflections for **4** and **13** respectively. Intensities were measured with a MAC MXC-18 diffractometer using graphite monochromatized Mo-K_α radiation (λ = 0.71069 Å). Analysis of the systematic absences observed for $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$) indicated the space group $P2_1/n$ for both compounds. No significant decay was observed for three intensity standard reflections measured every 100 reflections. Intensity data were corrected for the Lorentz-polarization effect, and absorption corrections were performed. Selected crystallographic data are shown in Table 5.

Table 5

Details of X-ray crystallography for $[WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)_2]$ (**4**) and $[WCl_2(p\text{-}CH_3C_6H_4CHO)(NNCMePh)(PMe_2Ph)_2]$ (**13**)

	4	**13**
(a) Crystal data		
Empirical formula	$WCl_2P_2N_2C_{21}H_{32}$	$WCl_2P_2ON_2C_{32}H_{38}$
Formula weight	629.24	783.41
Colour	Orange	Red
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.755(7)	31.519(13)
b (Å)	18.528(6)	11.360(5)
c (Å)	10.791(3)	9.348(3)
β (deg)	93.25(4)	92.28(3)
V (Å^3)	2546.2	3344.2
Z	4	4
d_{calc} (g cm^{-3})	1.641	1.556
$F(000)$	1240	1560
Crystal size (mm)	0.49×0.30×0.20	0.63×0.18×0.10
μ (cm^{-1})	49.80	38.10
(b) Data collection		
Diffractometer	MXC 18	MXC 18
Monochromator	Graphite	Graphite
Scan range (deg)	$3.0 < 2\theta < 55.0$	$3.0 < 2\theta < 50.0$
Scan method	$\omega-2\theta$ $(3.0 < 2\theta < 55.0)$	$\omega-2\theta$ $(3.0 < 2\theta < 50.0)$
Scan speed (deg min^{-1})	16	16
Number of unique data points collected	6480	6844
Number of data points used ($F_o > 5\sigma(F_o)$)	4199	3522
(c) Solution and refinement		
Number of parameters refined	382	514
R, R_w [a]	0.036, 0.041	0.053, 0.061
Maximum residual peak (e Å^{-3})	0.75 (around W)	2.73 (around W)

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.

Structure solution and refinement for $[WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)_2]$ (4) and $[WCl_2(p\text{-}CH_3C_6H_4CHO)(NNCMePh)(PMe_2Ph)_2]$ (13) *

Structure solution and refinement were performed using the UNICS-III program at the computer centre of the University of Tokyo [13]. The tungsten atom in the asymmetric unit was found by the direct-methods program MULTAN-78 [14] or SHELXS86 [15] for **4** and **13** respectively. Subsequent block-diagonal least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms, which were refined anisotropically. Some hydrogen atom positions were visible in a final difference Fourier map, remaining hydrogen atoms being placed at the calculated positions. These hydrogen atoms were refined isotropically.

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* Tables of positional parameters, anisotropic thermal parameters, bond distances and angles for **4** and **13**, and listings of observed and calculated structure factors for **4** and **13** are available from the authors.

Calculations

The extended Hückel method [8] was employed in this study. The parameters used for W, Cl, O, N, C and H [8b] and P [8c] are taken from published sources. The structural data were idealized octahedral, with all *cis* angles 90°.

Acknowledgment

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