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Preparation and properties of molybdenum and tungsten dinitrogen complexes

XLII *. Preparation and characterization of W(V) diazoalkane complexes *mer,trans*-$[WX_3(NN{=}CMeR)(PMe_2Ph)_2]$ (X = Br, I; R = Me, Ph) and hydrazido(2 −) complex $[WI_3(NNH_2)(PMe_2Ph)_2]$. X-ray structure of *mer,trans*-$[WBr_3(NN{=}CMePh)(PMe_2Ph)_2]$

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Abstract

Reactions of W(IV) diazoalkane complexes *cis,mer*-$[WX_2(NN{=}CMeR)(PMe_2Ph)_3]$ (X = Br, I; R = Me, Ph) and hydrazido(2 −) complex *cis,mer*-$[WI_2(NNH_2)(PMe_2Ph)_3]$ with five equivalents of CH_2X_2 in toluene at 80°C gave paramagnetic W(V) complexes, *mer,trans*-$[WX_3(NN{=}CMeR)(PMe_2Ph)_2]$ and $[WI_3(NNH_2)(PMe_2Ph)_2]$ respectively. The latter complex was also obtained upon hydrolysis of a W(V) disilylhydrazido(2 −) complex *mer,trans*-$[WI_3(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2]$ and was converted into *mer,trans*-$[WI_3(NN{=}CMeR)(PMe_2Ph)_2]$ by the subsequent condensation with RMeC=O. The structure of *mer,trans*-$[WBr_3(NN{=}CMePh)(PMe_2Ph)_2]$ (**6d**) was determined by X-ray analysis. Crystal data for **6d** are as follows: monoclinic, space group $P2_1/n$ with $a = 9.900(3)$ Å, $b = 21.029(4)$ Å, $c = 13.950(2)$ Å, $\beta = 96.80(2)°$, $V = 2883.9(11)$ Å^3, $Z = 4$ and $R = 0.060$ for 4567 reflections.

1. Introduction

Transformation of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**1**) and *trans*-$[M(N_2)_2(dpe)_2]$ (**2**) (M = Mo, W; dpe = $Ph_2PCH_2CH_2PPh_2$) into diazoalkane complexes *cis,mer*-$[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ (**3**) and *trans*-$[MF(NN{=}CRR')(dpe)_2][BF_4]$ reported previously provides one of the most usefully potential methods for preparing organo-nitrogen complexes from dinitrogen complexes [2,3]. Thus a dinitrogen ligand in **1** and **2** is readily converted into a variety of coordinated diazoalkanes by two steps: initial protonation of a coordinated dinitrogen to give a hydrazido(2 −) ligand (M = NNH_2) and successive condensation of the hydrazido(2 −) ligand with various aldehydes and ketones. In our past and continuing pursuit of the novel systems in which molecular nitrogen is converted into organo-nitrogen compounds under ambient conditions, efforts have been made to exploit the unique reactivities of these diazoalkane complexes.

Well-characterized reactions of the diazoalkane complexes of the type *trans*-$[MX(NN{=}CRR')(dpe)_2]^+$ are those with organic bases and $LiAlH_4$ [4] as well as the electrochemical reduction [5] and result in the formation of a series of diazenido complexes accompanied by the decrease in the formal oxidation state of the metal from +4 to +2. However, the conversion of the diazoalkane ligands into nitrogen-containing organic compounds has not yet been exploited. In contrast with the difficulty in cleaving the M–N and N–N bonds in these dpe complexes, the PMe_2Ph complex *cis,mer*-$[WBr_2(NN{=}CMe_2)(PMe_2Ph)_3]$ (**3c**) readily reacts with HBr or $LiAlH_4$ at room temperature, affording either a mixture of $Me_2C{=}NN{=}CMe_2$ and H_2NNH_2

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* For Part XLI, see ref. 1.

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or of $^{i}PrNH_2$ and NH_3 respectively [3]. In our continuous study on diazoalkane complexes, our attention has recently focused on exploitation of new reactivities of **3** as well as their mono-substituted derivatives such as *cis,trans*-$[WX_2(NN{=}CRR')(PMe_2Ph)_2(L)]$ (L = π-acceptor ligands) [6] and *mer*-$[WX(NN{=}CCR')(PMe_2Ph)_3(CO)]^+$ [7]. The preceding paper [1] dealt with a dinuclear W(II) complex with a bridging diazenido ligand *trans,trans*-$[ClW(CO)_2(PMe_2Ph)_2(N{=}NCMe_2CMe_2N{=}N)W(CO)_2(PMe_2Ph)_2Cl]$, which was prepared by the reduction of *mer*-$[WCl(NN{=}CMe_2)(PMe_2Ph)_3(CO)]^+$ by Mg under CO [7].

As compared with the progressing chemistry of W^{IV} diazoalkane complexes shown above, the properties of W diazoalkane complexes of the oxidation state other than +4 have been unexplored. On the contrary, we have recently reported that a related W^{IV} disilylhydrazido(2 −) complex $[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$ (**4**) can be readily converted into W(V) disilylhydrazido(2 −) complexes $[WX_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$ (X = I (**5a**), Cl (**5b**)) by the reactions of **4** with CH_2X_2, which provide the first potential method for preparing W^{V} organo-nitrogen complexes from **1** (M = W) [8].

In this paper, we describe the reactions of **3** (M = W) with CH_2X_2 (X = Br, I) to give novel paramagnetic W(V) diazoalkane complexes of *mer,trans*-$[WX_3(NN{=}CMeR)(PMe_2Ph)_2]$ (**6**) (Scheme 1). Synthesis of a related hydrazido(2 −) complex $[WI_3(NNH_2)(PMe_2Ph)_2]$ (**7**) and the X-ray structure of *mer,trans*-$[WBr_3(NN{=}CMePh)(PMe_2Ph)_2]$ (**6d**) are also described.

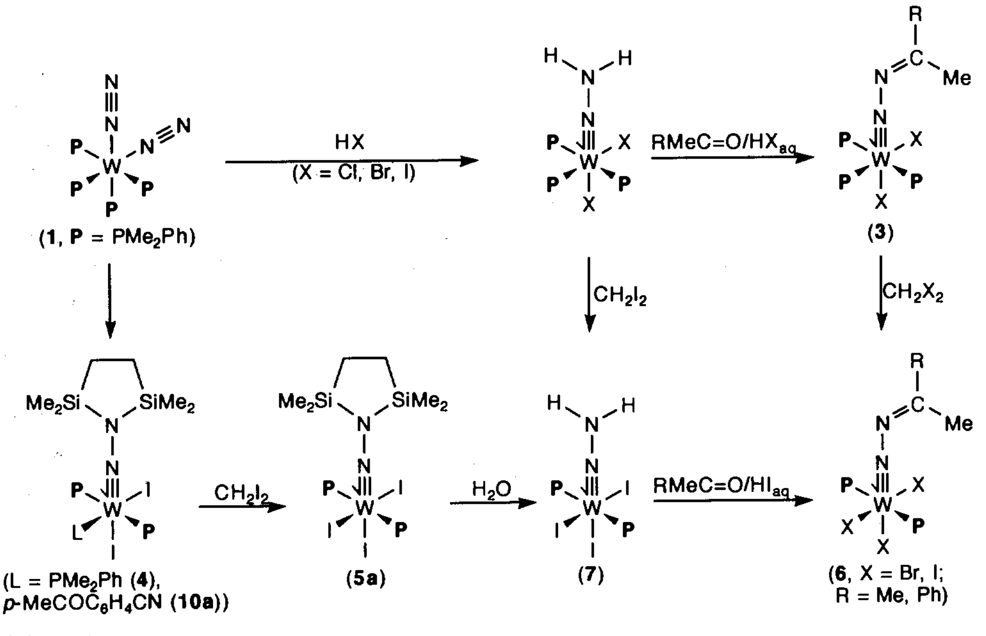
2. Experimental details

2.1. General remarks

All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk tube techniques. Complexes $[WI_2(NNH_2)(PMe_2Ph)_3]$ [9], $[WX_2(NN{=}CMeR)(PMe_2Ph)_3]$ (**3**) (X = Br, I; R = Me, Ph) [3] and $[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(L)(PMe_2Ph)_2]$ (L = PMe_2Ph, CO, $CH_2{=}CH_2$, t-BuNC, *p*-$MeCOC_6H_4CN$) [8] were prepared according to the methods given in the literature. Solvents were dried and distilled under N_2 before use. IR spectra were recorded on a Shimadzu FT-8100M spectrometer. Gas–liquid chromatography (GLC) analyses were carried out on a Shimadzu GC-14A gas chromatograph equipped with 0.2 mm × 25 m CBP-1 capillary column, while gas chromatography-mass spectroscopy (GC-MS) (70 eV) analyses were undertaken on a Shimadzu GC-MS QP-1000 spectrometer. Electron paramagnetic resonance (EPR) spectra were obtained at X-band frequencies using a JEOL JEX-FEIX spectrometer. Elemental analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

2.2. Preparation of mer,trans-$[WI_3(NN{=}CMe_2)(PMe_2Ph)_2]$ (6a)

(a) A mixture of $[WI_2(NN{=}CMe_2)(PMe_2Ph)_3]$ (**3a**) (200 mg, 0.217 mmol), CH_2I_2 (88 μl, 1.1 mmol) and toluene (10 ml) was stirred at 80°C for 2 h in the dark.



Scheme 1.

The resultant mixture was filtered to remove the dark-red solid deposited and the filtrate was concentrated *in vacuo*. Dark-red needles precipitated by addition of hexane were filtered off, washed with hexane and then dried *in vacuo* (133 mg; yield 67.0%). Anal. Found: C, 25.07; H, 3.10; N, 3.13. $C_{19}H_{28}N_2P_2I_3W$ calc.: C, 25.05; H, 3.10; N, 3.08%. IR (KBr): ν(C=N) 1572 cm^{-1}. EPR (CH_2Cl_2, room temperature): *g* 2.03.

(b) Into a mixture of CH_2Cl_2 (7.0 ml), acetone (136 μl, 1.85 mmol) and one drop of HI(aq) was added $[WI_3(NNH_2)(PMe_2Ph)_2]$ (**7**) (161 mg, 0.185 mmol). After stirring of the mixture overnight in the dark, the product solution was separated from a dark-blue solid by filtration and the filtrate was concentrated *in vacuo*. Addition of hexane gave a dark-red crystalline solid, which was filtrated off, washed with hexane and then dried *in vacuo* (97.3 mg; yield, 57.7%). Analogous treatment of $[WI_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$ (**5a**) with acetone in the presence of a catalytic amount of HI(aq) also gave **6a** in comparable yield.

2.3. *Preparation of mer,trans-[WI_3(NN=CMePh)($PMe_2Ph)_2$] (6b)*

Complex **6b** was obtained as a dark-red crystalline solid by the analogous methods to those for preparing **6a** with about 60–70% yields. Anal. Found: C, 29.53; H, 3.04; N, 2.66. $C_{24}H_{30}N_2P_2I_3W$ calc.: C, 29.63; H, 3.11; N, 2.88%. IR (KBr): ν(C=N) 1509 cm^{-1}. EPR (CH_2Cl_2, room temperature): *g* 2.02.

2.4. *Preparation of mer,trans-[WBr_3(NN=CMeR)($PMe_2Ph)_2$] (R = Me (6c), Ph (6d))*

Complexes **6c** and **6d** were obtained as orange crystals by treatment of $[WBr_2(NN{=}CMeR)(PMe_2Ph)_3]$ (R = Me (**3c**), Ph (**3d**)) with five equivalents of CH_2Br_2 in toluene at 80°C for 2 h, followed by the similar work-up of the reaction mixtures to that for preparing **6a** (method (a)). For **6c** the yield was 49.8%. Anal. Found: C, 30.08; H, 3.68; N, 3.93. $C_{19}H_{28}N_2P_2Br_3W$ calc.: C, 29.64; H, 3.67; N, 3.64%. IR (KBr): -(C=N) 1572 cm^{-1}. EPR (CH_2Cl_2, room temperature): *g* 1.95. For **6d**: the yield was 65.0%. Anal. Found: C, 35.18; H, 3.62; N, 3.71. $C_{24}H_{30}N_2P_2Br_3W$ calc.: C, 34.65; H, 3.63; N, 3.37%. IR (KBr): ν(C=N) 1514 cm^{-1}. EPR (CH_2Cl_2, room temperature): *g* 1.95.

2.5. *Preparation of [$WI_3(NNH_2)(PMe_2Ph)_2$] (7)*

(a) After a mixture of $[WI_2(NNH_2)(PMe_2Ph)_3]$ (250 mg, 0.282 mmol) and CH_2I_2 (114 μl, 1.42 mmol) in toluene (15 ml) was stirred at 80°C for 2 h, a dark-red solid was deposited on the wall of the reaction vessel. The mixture was filtered off, and addition of hexane on the filtrate concentrated *in vacuo* afforded dark-red microcrystals, which were washed with hexane and then dried *in vacuo* (94.4 mg; yield, 38.4%). Anal. Found: C, 21.46; H, 2.84; N, 2.99. $C_{16}H_{24}N_2P_2I_3W$ calc.: C, 22.07; H, 2.78; N, 3.22%. IR (KBr): ν(NH) 3318, 3198, 3125 cm^{-1}. EPR (CH_2Cl_2, room temperature): *g* 2.03.

(b) Complex *mer,trans*-$[WI_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$ (**5a**) (192 mg, 0.190 mmol) was dissolved in tetrahydrofuran (THF) (10 ml), and H_2O (10.3 μl, 0.572 mmol) was added. After the mixture was stirred overnight, the white powder deposited was filtered off and the filtrate was concentrated *in vacuo*. The addition of hexane afforded dark-red crystals of **7** together with a small amount of a grey solid. The former compound was collected, washed with hexane and then dried *in vacuo* (88.2 mg; yield, 53.2%).

2.6. *Preparation of mer,trans-[$WI_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2$] (5a)*

Into a dark-blue suspension of *cis,trans*-$[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2(p\text{-}MeCOC_6H_4CN)]$ (**10a**) (804 mg, 0.779 mmol) in benzene (30 ml) was added CH_2I_2 (188 μl, 2.33 mmol). After the mixture had been stirred for 3 h at 50°C in the dark, the resultant dark-red suspension was concentrated. Addition of hexane gave **5a** [8] as a reddish-brown solid, which was washed with hexane and then dried *in vacuo* (505 mg, yield, 64.8%). If compared with the previous method for *cis,mer*-$[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$ (**4**) and CH_2I_2 in benzene [8], this alternative route via **10a**, which can be readily prepared by the reaction of **4** with *p*-$MeCOC_6H_4CN$ with about a 90% yield, is more convenient, because the latter method is free from concurrent precipitation of phosphonium salts with **5a**.

2.7. *Reaction of [WBr_2(NN=CMePh)($PMe_2Ph)_3$] (3d) with $PhCH_2Br$*

A mixture of **3d** (150 mg, 0.168 mmol) and $PhCH_2Br$ (146 mg, 0.856 mmol) in toluene (10 ml) was stirred at 80°C for 14 h. The GLC and GC–MS analyses of the resultant orange suspension showed that 2.0 mol of $PhCH_2Br$ per W atom was consumed during the reaction and 0.19 mol of $PhCH_2CH_2Ph$ per W atom was formed. A white solid was then separated from the reaction mixture by filtration, the IR and ^1H nuclear magnetic resonance (NMR) spectra of which are in good agreement with those of $[PMe_2Ph(CH_2Ph)]Br$ separately prepared from PMe_2Ph and $PhCH_2Br$ according to the method in the literature [10]. ^1H NMR data for $[PMe_2Ph(CH_2Ph)]Br$ ($CDCl_3$, 270 MHz): 7.5–7.9 (m, 5H, phenyl), 7.1–7.3 (m, 5H, phenyl), 4.42 (d, 2H, P-CH_2Ph, $J = 15.9$ Hz), 2.56 (d, 6H, P-CH_3, $J = 14.2$ Hz) ppm. The addition of hexane to the filtrate concentrated *in vacuo* gave orange crystals of **6d** (86.4 mg; 61.8%).

TABLE 1. Details of X-ray crystallography for *mer,trans*-[$WBr_3(NN{=}CMePh)(PMe_2Ph)_2$] (**6d**)

Crystal data	
Formula	$C_{24}H_{30}N_2P_2Br_3W$
Molecular weight	832.02
Crystal dimensions (mm × mm × mm)	0.58 × 0.33 × 0.24
Space group (crystal system)	$P2_1/n$ (monoclinic)
Crystal colour	Orange
a (Å)	9.900(3)
b (Å)	21.029(4)
c (Å)	13.950(2)
β (°)	96.80(2)
V (Å^3)	2883.9(11)
Z	4
d_{calc} (g cm^{-3})	1.916
$F(000)$ (electrons)	1548
μ_{calc} (cm^{-1})	83.35
Data collection	
Diffractometer	Rigaku AFC-5R
Monochromator	Graphite
Radiation; λ (Å)	Mo Kα; 0.7093
2θ range (°)	$5 < 2\theta < 60$
Scan method	ω–2θscan
Scan speed (° min^{-1})	16
Absorption correction method	ψ scan
Transmission factor	1.001–1.379
Reflections measured	$(+h, +k, \pm l)$
Number of unique data	9316
Number of data used	4567 ($\lvert F_o \rvert > 5\sigma(\lvert F_o \rvert)$)
Solution and refinement	
Number of parameters refined	290
R	0.060
R_w	0.066
Maximum residuals (electrons Å^{-3})	2.85 (around W atom)

TABLE 2. Positional parameters and equivalent temperature factors for *mer,trans*-[$WBr_3(NN{=}CMePh)(PMe_2Ph)_2$] (**6d**)

Atom	x	y	z	B_{eq} (Å^2)
W	7201.8(6)	1495.1(2)	7826.2(4)	2.7
Br(1)	9708(2)	1750(1)	7832(1)	4.9
Br(2)	7028(2)	1503(1)	5947(1)	5.2
Br(3)	4654(2)	1273(1)	7653(1)	4.6
P(1)	6706(4)	2681(2)	7541(3)	3.1
P(2)	7632(5)	327(2)	7571(3)	3.5
N(1)	7366(10)	1416(5)	9127(6)	2.6
N(2)	7438(11)	1232(6)	9997(7)	3.3
C(1)	6775(15)	1534(7)	10602(9)	3.4
C(2)	5904(23)	2088(9)	10354(13)	6.2
C(3)	6942(16)	1264(8)	11614(10)	4.2
C(4)	6659(15)	1657(7)	12378(10)	3.8
C(5)	6775(19)	1405(11)	13303(11)	5.9
C(6)	7114(17)	765(11)	13443(10)	5.6
C(7)	7382(19)	388(9)	12706(12)	5.3
C(8)	7286(16)	639(8)	11763(9)	4.1
C(11)	7908(16)	3079(7)	6877(11)	3.9
C(12)	5082(16)	2846(9)	6857(12)	4.8
C(13)	6750(16)	3169(7)	8635(10)	3.8
C(14)	5554(17)	3424(8)	8902(12)	4.6
C(15)	5657(23)	3762(10)	9804(14)	6.8
C(16)	6855(22)	3831(9)	10351(14)	6.1
C(17)	8038(21)	3571(10)	10055(13)	5.8
C(18)	7970(16)	3225(9)	9205(11)	4.5
C(21)	9222(22)	168(8)	7096(15)	6.6
C(22)	6357(24)	−69(8)	6725(12)	6.2
C(23)	7681(15)	−154(6)	8660(9)	3.2
C(24)	6451(17)	−254(7)	9049(11)	3.9
C(25)	6466(17)	−621(8)	9885(11)	4.3
C(26)	7663(17)	−889(7)	10319(10)	4.1
C(27)	8842(19)	−779(8)	9934(11)	4.7
C(28)	8861(16)	−408(8)	9113(11)	4.1

2.8. X-ray crystallographic analysis of mer,trans-[$WBr_3(NN{=}CMePh)(PMe_2Ph)_2$] (6d) *

An X-ray diffraction study was carried out at room temperature using a single crystal of **6d** sealed in a glass capillary under N_2. The orientation matrices and unit-cell parameters were derived from a least-squares fit of 25 machine-centred reflections with 2θ values between 38 and 40°. No significant decay in the intensities of three standard reflections was observed during data collections. The intensity data were corrected for Lorentz and polarization effects, and absorption corrections were also performed. Details of the X-ray diffraction study of **6d** are summarized in Table 1. The positional parameters of the non-hydrogen atoms are listed in Table 2.

Structure solution and refinements were performed at The Computer Center, The University of Tokyo, using the UNIX-III program package. The W atom was found by the direct-method program SHELXS86. Subsequent cycles of difference Fourier syntheses and block-diagonal least-squares refinements revealed all non-hydrogen atoms, which were refined anisotropically. All hydrogen atoms were placed in calculated positions ($d_{C-H} = 1.09$ Å for methyl and methylene protons and $d_{C-H} = 1.08$ Å for phenyl protons). Anomalous dispersion effects were included, and the atomic scattering factors were taken from ref. 11.

3. Results and discussion

3.1. Preparation of W^V diazoalkane complexes 6 from the reactions of W^{IV} complexes 3 with CH_2X_2

When *cis,mer*-[$WI_2(NN{=}CMeR)(PMe_2Ph)_3$] (R = Me (**3a**); Ph (**3b**)) was treated with five equivalents of CH_2I_2 in toluene at 80°C, replacement of one PMe_2Ph ligand by the iodide ligand took place and W^V diazoalkane complexes *mer,trans*-[$WI_3(NN{=}CMeR)$

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* EPR spectra of complexes **6** and **7** (Figs. S1 and S2), tables of bond distances and angles, anisotropic thermal parameters and positional parameters for the hydrogen atoms, and listing of observed and calculated structure factors for **6d** (Tables S1–S4) are available from the authors.

$(PMe_2Ph)_2]$ (R = Me (**6a**), Ph (**6b**)) were produced in moderate yields:

$$\underset{\mathbf{3}}{cis,mer\text{-}[WX_2(NN{=}CMeR)(PMe_2Ph)_3]} + CH_2X_2 \longrightarrow$$
$$mer,trans\text{-}[WX_3(NN{=}CMeR)(PMe_2Ph)_2] \quad (1)$$
$$(X = I, Br;\ R = Me, Ph\ (\mathbf{6}))$$

Tribromo complexes *mer,trans*-$[WBr_3(NN{=}CMeR)(PMe_2Ph)_2]$ (R = Me (**6c**), Ph (**6d**)) were prepared analogously from the reactions of the corresponding bromo diazoalkane complexes *cis,mer*-$[WBr_2(NN{=}CMeR)(PMe_2Ph)_3]$ (R = Me (**3c**), Ph (**3d**)) with CH_2Br_2. The reactions undertaken both at room temperature and at 50°C resulted in the recovery of the starting W^{IV} complexes **3**. This presents a sharp contrast with the reaction of a disilylhydrazido(2 −) complex *cis,mer*-$[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$ (**4**) with CH_2I_2 previously reported, which proceeds smoothly even at room temperature to afford *mer,trans*-$[WI_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$ (**5a**) (*vide infra*) [8].

The complexes **6** are paramagnetic and the CH_2Cl_2 solutions of **6** show intense bands in their EPR spectra recorded at room temperature. The position of the isotropic *g* value and the shape of the resonance strongly depend on the nature of the halide ligands. Thus no phosphorus and iodine coupling was observed in the iodo complexes **6a** and **6b** ($g = 2.02$–2.03), while the splitting of the resonance due to the corresponding hyperfine coupling was detected in the bromo complexes **6c** and **6d** ($g = 1.95$). In the EPR spectra of the related disilylhydrazido(2 −) complexes **5**, a broad singlet at $g = 2.04$ was observed for the iodide complex **5a** and a 1:2:1 triplet coupled with two equivalent phosphorus atoms ($g = 1.92$) was obtained for its chlorine analogue **5b** respectively [8]. A similar phenomenon arising from the difference in the halide ligand was observed for the low spin ($S = \frac{1}{2}$) Mo(III) complexes $[CpMoX_2(dpe)]$ with X = Cl, Br or I [12]. The IR spectra of **6** exhibit the characteristic bands assignable to ν(C=N), the values of which indicate that the diazoalkane ligands in **6** remain intact after these oxidation reactions. This was confirmed by the X-ray analysis of **6d** as described below.

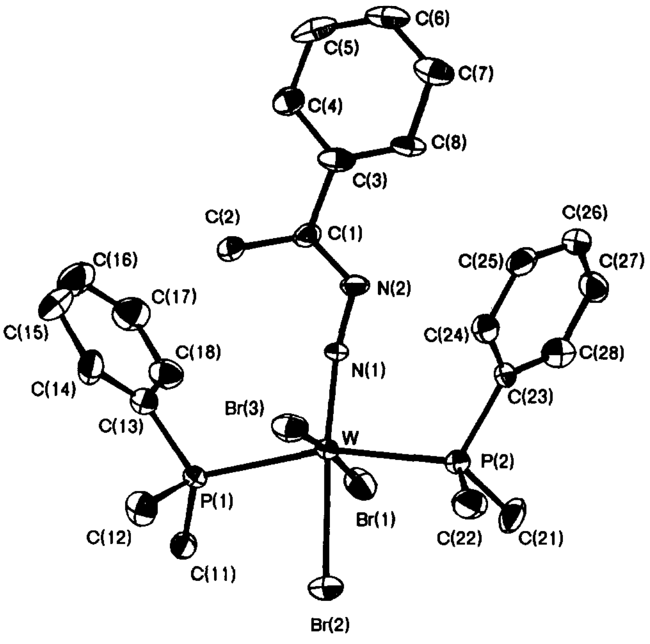

Fig. 1. ORTEP drawing of **6d**.

3.2. *Structure of mer,trans-*$[WBr_3(NN{=}CMePh)(PMe_2Ph)_2]$ *(6d)*

An X-ray analysis of **6d** was performed to clarify the detailed structure of these W(V) diazoalkane complexes. The ORTEP drawing of **6d** is shown in Fig. 1, while selected bond lengths and angles are summarized in Table 3. The pseudo-octahedral coordination geometry displays a *mer* arrangement of the three Br atoms and a *trans* disposition of the two PMe_2Ph ligands. A similar *mer,trans* configuration has been revealed in W^V disilylhydrazido(2 −) complex *mer,trans*-$[WCl_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$ (**5b**) [8] and hydrazido(2 −) complex *mer,trans*-$[WCl_3(NNHPh)(PMe_2Ph)_2]$ [13,14], while three Cl atoms and two

TABLE 3. Selected bond distances and angles in *mer,trans*-$[WBr_3(NN{=}CMePh)(PMe_2Ph)_2]$ (**6d**)

	Bond distance (Å)				Bond angle (°)		
W–Br(1)	2.537(2)	W–Br(2)	2.608(1)	Br(1)–W–Br(2)	87.1(1)	Br(1)–W–Br(3)	174.5(1)
W–Br(3)	2.548(2)	W–P(1)	2.563(4)	Br(1)–W–P(1)	88.0(1)	Br(1)–W–P(2)	91.4(1)
W–P(2)	2.525(4)	W–N(1)	1.810(9)	Br(1)–W–N(1)	92.6(3)	Br(2)–W–Br(3)	87.7(1)
N(1)–N(2)	1.27(1)	N(2)–C(1)	1.30(2)	Br(2)–W–P(1)	81.3(1)	Br(2)–W–P(2)	81.7(1)
C(1)–C(2)	1.47(2)	C(1)–C(3)	1.51(2)	Br(2)–W–N(1)	174.9(3)	Br(3)–W–P(1)	89.7(1)
				Br(3)–W–P(2)	89.4(1)	Br(3)–W–N(1)	92.8(3)
				P(1)–W–P(2)	163.1(1)	P(1)–W–N(1)	103.8(3)
				P(2)–W–N(1)	93.1(3)	W–N(1)–N(2)	167.5(10)
				N(1)–N(2)–C(1)	120.0(12)	N(2)–C(1)–C(2)	124.4(13)
				N(2)–C(1)–C(3)	114.6(12)	C(2)–C(1)–C(3)	121.0(13)

PMe_2Ph ligands are mutually sited in the *fac* and *cis* positions respectively in *fac,cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ (**8**) [13]. In the diazoalkane ligand *trans* to one Br ligand, the W–N–N linkage is essentially linear, whereas the N–N–C bond angle is 120(1)°. The W, N(1), N(2), C(1), C(2) and C(3) atoms lie on nearly the same plane and the bonding parameters in the diazoalkane ligand of **6d** correspond well to those in the W^{IV} diazoalkane complex *cis,trans*-$[WCl_2(NN{=}CMePh)(PMe_2Ph)_2(\eta^2\text{-}p\text{-}MeC_6H_4CHO)]$ (W–N distance, 1.795(13) Å; N–N distance, 1.29(2) Å; N–C distance 1.27(2) Å; W–N–N angle, 166(1)°; N–N–C angle, 121(1)°) [6], indicating that the diazoalkane ligand in **6d** is considered to be a four-electron donor as reported for common W^{IV} diazoalkane complexes *trans*-$[WX(NN{=}CRR')(dpe)_2]X$ [2b,c,15] and *cis,trans*-$[WX_2(NN{=}CRR')(PMe_2Ph)_2(L)]$ [6].

Such a structural similarity of hydrazido(2 –) and disilylhydrazido(2 –) ligands between W^{IV} and W^{V} complexes has also been observed, in which these ligands have a planar structure with an essentially linear W–N–N linkage and function as a formal four-electron donor [8,13,14].

We have also carried out an X-ray analysis of **6a**, which unambiguously disclosed the similar coordination geometry around the W atom to **6d**. However, refinements of the structure of the diazoalkane ligand was not successful presumably because of the presence of a significant disorder in this ligand of **6a** [16*].

3.3. Preparation of W^V hydrazido(2 –) complex 7 and its conversion into 6a and 6b

A W^V hydrazido(2 –) complex $[WI_3(NNH_2)(PMe_2Ph)_2]$ (**7**) was similarly obtained when *cis,mer*-$[WI_2(NNH_2)(PMe_2Ph)_3]$ was allowed to react with CH_2I_2 at 80°C:

$$cis,mer\text{-}[WI_2(NNH_2)(PMe_2Ph)_3] + CH_2I_2 \longrightarrow \underset{\textbf{7}}{[WI_3(NNH_2)(PMe_2Ph)_2]} \quad (2)$$

Despite the formation of a substantial amount of undefined by-product(s) in this reaction, the yield of **7** was still moderate. Complex **7** can also be prepared from a W(V) disilylhydrazido(2 –) complex **5a** upon hydrolysis. Thus treatment of **5a** with three equivalents of H_2O in THF smoothly afforded **7** at room temperature:

$$\underset{\textbf{5a}}{[WI_3(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2]} + H_2O \longrightarrow \underset{\textbf{7}}{[WI_3(NNH_2)(PMe_2Ph)_2]} \quad (3)$$

Although characterization of a closely related chloro complex **8** has appeared already, this complex was produced from $[WHCl_3(NNH_2)(PMe_2Ph)_2]$ (**9**) by accidental loss of the hydride ligand during recrystallization and the details of preparation are not clear [13]. Two reaction courses described here therefore demonstrate more versatile methods to derive a W^V hydrazido(2 –) complex from the dinitrogen complex **1**.

Subsequent condensation of **7** with $Me_2C{=}O$ and $MePhC{=}O$ in the presence of a catalytic amount of HI(aq) afforded **6a** and **6b** respectively [17*]:

$$\underset{\textbf{7}}{[WI_3(NNH_2)(PMe_2Ph)_2]} + RMeC{=}O\ HI(aq) \longrightarrow mer,trans\text{-}[WI_3(NN{=}CMeR)(PMe_2Ph)_2] \quad (4)$$
$$(R = Me\ (\textbf{6a}),\ Ph\ (\textbf{6b}))$$

This as well as the fact that **7** is readily produced from **5** may strongly suggest the mutually *mer,trans* structure with respect to three iodide and two PMe_2Ph ligands for **7**, although the *fac,cis* geometry has been elucidated for the chloro complex **8** generated from the seven-coordinate complex **9** (*vide supra*) [13]. The EPR spectrum of **7** in CH_2Cl_2 at room temperature is quite analogous to those of **6a**, **6b** and **5a**, exhibiting a broad singlet at $g = 2.03$. In the IR spectrum, three characteristic bands appear at 3318, 3198 and 3125 cm^{-1} assignable to ν(NH).

3.4. Mechanism for the conversion of W^{IV} diazoalkane and disilylhydrazido(2 –) complexes 3 and 4 into corresponding W^V complexes

As described above, related transformation of the W^{IV} disilylhydrazido(2 –) complex **4** into the W^V complex **5** has been reported in a preceding paper [8]. The significant difference observed in this reaction from that of **3** is that it readily proceeds at room temperature, while the latter requires more forcing conditions (*e.g.* 80°C). This tendency is quite analogous to the results of the substitution reactions of one PMe_2Ph ligand in **4** and **3** by π-acceptor ligands L such as CO and ethylene to give *cis,trans*-$[WX_2(E)(PMe_2Ph)_2(L)]$ ($E = N\overline{NSiMe_2CH_2CH_2Si}Me_2$ (**10**), $NN = CMeR$) [6, 8]. These findings may suggest that the dissociation of one PMe_2Ph ligand is presumably involved as the initial step in the conversion of **3** and **4** into corresponding W^V complexes. In fact, the recent study has revealed that the rate of the formation of **5** from a series of **10** and CH_2I_2 is greatly affected by the nature of L in the order of $PMe_2Ph > p\text{-}MeCOC_6H_4CN$ (**10a**) $\gg CO, CH_2{=}CH_2, {}^tBuNC$ and the reaction of **10a** with CH_2I_2 is significantly retarded upon the addition of excess $p\text{-}MeCOC_6H_4CN$.

To determine the stoichiometry of the reaction to give **6** from **3** and CH_2X_2, attempts were made to

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* Reference number with asterisk indicates a note in the list of references.

clarify the fate of CH_2X_2 consumed. However, full characterization of the organic products in these reaction mixtures was not successful. On the contrary, since we have found that $PhCH_2Br$ also reacts with **3d** in toluene at 80°C to give **6d** in moderate yield [18*], GC-MS and GLC studies were undertaken for this reaction system. This demonstrated that 2.0 mol of $PhCH_2Br$ per W atom was consumed during the reaction and 0.19 mol of $PhCH_2CH_2Ph$ per W atom was concurrently produced, whereas the white solid precipitated from the reaction mixture was characterized as $[PMe_2Ph(CH_2Ph)]Br$. Net stoichiometry to give **6d** in this reaction may therefore be described by the following equation, although the yield of $PhCH_2CH_2Ph$ is not satisfactory:

$$\underset{\mathbf{3d}}{[WBr_2(NN{=}CMePh)(PMe_2Ph)_3]} + 2PhCH_2Br \longrightarrow \underset{\mathbf{6d}}{[WBr_3(NN{=}CMePh)(PMe_2Ph)_2]} + [PMe_2Ph(CH_2Ph)]Br + \tfrac{1}{2}PhCH_2CH_2Ph \qquad (5)$$

These observations might indicate that the formation of the W(V) complexes **6** is accompanied by the generation of alkyl radical from RX [19*], where the R–X bond cleavage possibly takes place at the vacant site *cis* to the diazoalkane ligand resulting from the prior dissociation of a PMe_2Ph ligand. Electron transfer from a metal to RX to give MX and R· is not common for high valence metal centres [20]. However, the EHMO calculations for the model complexes *cis,mer*-$[WCl_2(NN{=}CH_2)(PH_3)_3]$, *cis,trans*-$[WCl_2(NN{=}CH_2)(PH_3)_2(CH_2{=}CH_2)]$, and *cis,mer*-$[WCl_2(NNH_2)(PH_3)_3]$ have elucidated the strong π-donating ability of the d electrons to the direction *cis* to the diazoalkane and hydrazido(2 –) ligands in these complexes [6] and this presumably enables the coordination and successive C–X bond cleavage of the alkyl halides at this site of the W^{IV} centre.

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16 Crystallographic data for *mer,trans*-$[WI_3(NN{=}CMe_2)(PMe_2Ph)_2]$ (**6a**): $C_{19}H_{28}N_2P_2I_3W$; $M = 910.95$; monoclinic; space group $P2_1/n$; $a = 9.166(2)$ Å, $b = 17.336(4)$ Å and $c = 17.512(4)$ Å; $\beta = 103.8(2)°$, $V = 2702(1)$ Å^3, $Z = 4$, $d_{calc} = 2.239$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 78.86$ cm^{-1}; $R = 0.057$; $R_w = 0.062$ for 3124 reflections ($I > 3.00\sigma(I)$).

17 Complexes **6a** and **6b** can be prepared directly from **5a** without isolation of **7**; treatment of **5a** in CH_2Cl_2 with $Me_2C{=}O$ and $MePhC{=}O$ in the presence of a catalytic amount of HI(aq) afforded **6a** and **6b** with good yields.

18 Treatment of **4** with various alkyl iodides such as EtI, ICH_2CH_2I and $PhCH_2CH_2I$ also resulted in the formation of **5a** with moderate yields at room temperature. Even the aryl iodides PhI and p-$MeOC_6H_4I$ can react with **4** analogously when heated to 50°C.

19 The mechanism involving the generation of benzyl radical from $PhCH_2Br$ is supported by the formation of $PhCH_3$ (0.39 mol per W atom) together with $PhCH_2CH_2Ph$ (0.067 mol per W atom) in the reaction of **3d** with $PhCH_2Br$ in *p*-xylene at 80°C, accompanied by the consumption of 2.0 mol of $PhCH_2Br$ per W atom.

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