Hydrazido(2−)-complexes of Tungsten-(V) and -(VI) and a Bis(diazenido)-complex of Tungsten(IV). *X*-Ray Crystal Structure of *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ †

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The hydrazido(2−)–hydride complexes $[WX_2H(NNH_2)(PMe_2Ph)_3]X$ (1; X = Cl or Br), $[WCl_3H(NNH_2)(PMe_2Ph)_2]$ (2), and $[WCl_3H(NNHPh)(PR_3)_2]$ (3) (PR_3 = PMe_2Ph, $PMePh_2$, or PPh_3) have been prepared by treatment of $[WX_2(NNH_2)(PMe_2Ph)_3]$ with HX in tetrahydrofuran and of $[WCl_4(PR_3)_2]$ with PhNHNH($SiMe_3$) respectively. The complexes (1; X = Cl) and (3; PR_3 = PMe_2Ph) convert into the hydrazido(2-) complexes *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ (4) and *trans*-$[WCl_3(NNHPh)(PMe_2Ph)_2]$ (5) respectively on slow recrystallisation. The *X*-ray structure of (4) (space group *Pnma*, *R* = 0.055) in which the N-*H* atoms have been located, shows the hydrazido(2-) ligand to have a planar $N-NH_2$ group [*d*(WN) = 1.752(10), *d*(NN) = 1.300(17), *d*(NH) = 1.08 and 0.78 Å; N–N–W = 178.7(9)°]. The preparation of the complexes $[WCl_4L_2]$ (L = pyridine, 2-, 3-, or 4-methylpyridine, or quinoline) from $[WCl_4(PPh_3)_2]$ is also described. $[WCl_4(C_5H_5N)_2]$ reacts with PhNHNH($SiMe_3$) to give the bis(diazenido)-complex $[WCl_2(NNPh)_2(C_5H_5N)_2]$ (6). Spectroscopic data for all new complexes are discussed in terms of their structures.

As part of our continuing interest in the reduction of dinitrogen at metal sites,[1,2] we have investigated the mechanism of conversion of dinitrogen to ammonia in the complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, as a result of protic attack, by characterisation of intermediate species and by spectroscopic studies (u.v., i.r., ^{15}N n.m.r.) of the reacting solutions.[3] During the course of this work we were able to isolate a series of hydrazido(2−)–hydride complexes. These compounds have been reported in a preliminary communication [4] and here we describe them, some analogues, and some of their reactions, in detail.

RESULTS

Preparation of Hydrazido(2−)–Hydride Complexes.—(*a*) *By addition of halogen acid.* We have already shown that the complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ reacts in methanol with an excess of halogen acid (HX) to give the hydrazido(2−) complexes $[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl, Br, or I).[5] However, in thf as solvent, a further protonation step occurs to give the hydrazido(2−)–hydride complexes as shown in equation (i) (thf = tetrahydrofuran).

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] + 4\,HX \xrightarrow[20\ °C]{thf} [WX_2H(NNH_2)(PMe_2Ph)_3]X\ (1) + [PMe_2PhH]X + N_2 \quad (X = Cl \text{ or } Br) \quad (i)$$

A cleaner synthesis of complexes (1) is achieved if $[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl or Br) are used as the starting materials instead of the dinitrogen complex. A pure iodo-complex (X = I) could not be isolated. A mixed-halide complex $[WBrCl(NNH_2)(PMe_2Ph)_3]Br$ has been similarly prepared by others and shown to be a hydrazido(2−)–hydride complex by *X*-ray and n.m.r. data [6] (see below).

Complexes (1) are characterised by analytical (Table 1) and spectroscopic data discussed below. Their conductivities in nitromethane (Table 1) show them to have a labile halogen and they are therefore formulated as seven-co-ordinate salts like their analogue $[WBrClH(NNH_2)(PMe_2Ph)_3]Br$.[6] Probably the halide anion is strongly hydrogen-bonded to the NNH_2 group as is commonly observed in hydrazido(2−) complex salts.[4,7] The complex (1; X = Cl) also contains a labile phosphine ligand which can be removed by treating it with a further mol of acid to give the bis(phosphine) complex (2) [equation (ii)] which is non-conducting in nitromethane (Table 1) and therefore is formulated as seven-co-ordinated. A similar reaction does

$$[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl + HCl \xrightarrow{thf} [WCl_3H(NNH_2)(PMe_2Ph)_2]\ (2) + [PMe_2PhH]Cl \quad (ii)$$

not occur for (1; X = Br) and therefore the driving force for phosphine loss in equation (ii) does not appear to be steric in origin.

(*b*) *By use of* PhNHNH($SiMe_3$). The phenylhydrazido(2−) analogue of (2) was prepared from PhNHNH($SiMe_3$) by the reaction shown in equation (iii).[4] This reaction was an attempt to prepare a hydrazido(1−) complex, but the spectroscopic properties of the product (3), as discussed below, show that it is a hydrazido(2−)–hydride complex. Clearly a proton shift from nitrogen to tungsten has occurred during the course of the reaction. The physical properties of (3) are shown in Table 1.

$$[WCl_4(PMe_2Ph)_3] + PhNHNH(SiMe_3) \xrightarrow[20\ °C]{thf} [WCl_3H(NNHPh)(PMe_2Ph)_2]\ (3) + PMe_2Ph + SiMe_3Cl \quad (iii)$$

Complexes (1), (2), and (3) are diamagnetic, thermally stable solids. Compounds (1) are pink in colour and (2) and (3) are yellow or yellow-green. Analogues of (3) were obtained from $[WCl_4(PR_3)_2]$ (PR_3 = PPh_3 or $PMePh_2$) but in a lower state of purity owing to their lability and air-sensitivity which made recrystallisation difficult.

Spectroscopic Properties.—The spectra of (1), (2), and (3) are shown in Table 2. The N–H stretching bands observed

† *cis*-Trichlorobis(dimethylphenylphosphine)[hydrazido(2−)]-tungsten(V).

TABLE 1

Characterisation data for hydrido-, hydrazido(2−), diazenido-, and pyridine complexes

Complex	Colour	Yield (%)	M.p./°C (decomp.)	Analyses [a] (%) C	H	N	Halogen	Conductivity (Λ/S cm² mol⁻¹) CH_3NO_2 [b]	$ClCH_2CH_2Cl$
$[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl$ [c,d]	Yellow	10	106	39.3 (39.2)	5.4 (5.1)	3.9 (3.4)		31	1
$[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl\cdot C_6H_6$ [d,e]	Yellow	95	96	42.6 (42.4)	5.1 (4.9)	3.8 (3.8)	15.4 (14.5)	n.m.	n.m.
$[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$	Pink	70	123	33.2 (33.2)	4.1 (4.2)	3.2 (3.2)	27.7 (27.6)	57	1
$[WBr_2D(NND_2)(PMe_2Ph)_3]Br$	Pink	10		33.5 (33.2)	4.0 (4.2)	3.5 (3.2)		n.m.	n.m.
$[WCl_3H(NNH_2)(PMe_2Ph)_2]$	Yellow-green		190—195	31.4 (33.2)	4.0 (4.2)	4.3 (4.7)	18.3 (17.8)	1	*f*
$[WCl_3H(NNHPh)(PMe_2Ph)_2]$	Yellow-green	60	160—163	39.1 (39.2)	4.4 (4.3)	4.2 (4.2)		n.c.	
$[WCl_3H(NNHPh)(PMePh_2)_2]$	Green	44	160—163	45.1 (48.2)	4.1 (4.1)	3.6 (3.5)	13.0 (13.4)	n.c.	
$[WCl_3H(NNHPh)(PPh_3)_2]$	Green	40	135—160	53.5 (54.7)	4.4 (4.0)	2.7 (3.0)	11.1 (11.6)	n.c.	
$[WCl_2(NNPh)_2(C_5H_5N)_2]$	Violet	45	150	42.2 (42.1)	3.7 (3.8)	13.3 (13.4)		n.c.	
$[WCl_4(C_5H_5N)_2]$	Brown-orange	90		25.0 (24.8)	2.2 (2.1)	5.6 (5.8)			
$[WCl_4(2Me\text{-}py)_2]$	Yellow-orange	88		30.8 (28.1)	3.0 (2.7)	5.1 (5.5)			
$[WCl_4(3Me\text{-}py)_2]$	Orange	75		28.4 (28.1)	3.1 (2.7)	5.3 (5.5)	27.8 (27.7)		
$[WCl_4(4Me\text{-}py)_2]$	Orange	85		28.3 (28.1)	2.8 (2.7)	5.5 (5.5)	27.7 (27.7)		
$[WCl_4(C_9H_7N)_2]$	Red-orange	80		36.5 (37.0)	2.8 (2.4)	4.5 (4.8)			

[a] Calculated values are in parentheses. [b] Values of *ca.* 75—95 S cm² mol⁻¹ have been reported for 1 : 1 electrolytes in CH_3NO_2; n.m. = not measured, n.c. = non-conducting. [c] Precipitated from thf during reaction. [d] Decomposes by loss of one PMe_2Ph ligand at room temperature. [e] Prepared in benzene. [f] Insoluble.

for (1) are typical of hydrazido(2−) groups strongly hydrogen-bonded to an anion,[5] whilst in (2) the shift to higher frequency and sharpening of the ν(N–H) band are consistent with the expected weaker hydrogen bonding, which can only be intermolecular in these compounds. The bands assigned to W–Cl stretching for (1; X = Cl) are absent for (1; X = Br) and are in the appropriate region of the spectrum. A weak band at 1 825 cm^{-1} in the spectrum of (1; X = Br) is tentatively assigned to ν(W–H) by comparison with the spectrum of the deuterio-analogue (Table 2). Tungsten–hydride absorption bands are generally weak and occur in this region, *e.g.* ν(WH) = 1 760 and 1 820 cm^{-1} in $[WH_6(PMe_2Ph)_3]$.[8]

The ^{31}P, ^1H, and ^{15}N n.m.r. data for these compounds are shown in Table 3. The $^{31}P\text{-}\{^1H\}$ spectra of (1; X = Cl or Br) are both second-order ABX spectra arising from three phosphorus nuclei in different chemical and magnetic environments (tungsten satellites were not resolved). The spectra were analysed according to published procedures,[9] with the derived parameters being shown in Table 3. The singlet ^{31}P spectrum of (2) indicates two equivalent phosphine ligands.

The ^1H spectrum of (1; X = Cl) (Table 3) shows the presence of two chemically similar pairs of P–*Me* groups (δ 1.80 p.p.m.) and of another pair (2.12 p.p.m.). The double doublet splitting pattern of these resonances indicates that the methyl groups are magnetically inequivalent. The hydrazido(2−) resonance apparently lies beneath the P–*Ph* multiplet since the integration of this resonance decreased by 2 on addition of D_2O. The double doublet of doublets at 9.90 p.p.m., which integrated for one proton and did not exchange with D_2O, is assigned to the metal hydride. The ^1H spectrum of (1; X = Br) is essentially similar but the hydrazido(2−) resonance was clearly seen at 9.36 p.p.m. and disappeared instantly on addition of D_2O. The metal–hydride resonance occurs at δ = 9.22 p.p.m. Compounds (2) and (3; PR_3 = PMe_2Ph) give P–*Me*

TABLE 2

Infrared spectral parameters for hydrazido(2−)–hydride complexes and one partially deuteriated analogue

Complex	Position (cm^{-1}) [a]	Assignment
$[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl$	3 060m, br 3 210m, br	ν(NH)
	240m, sp 258m, sp 288m, sp	ν(WCl)
$[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$	2 980— 3 110s, br	ν(NH)
	1 825w, sp	ν(WH) [b]
$[WBr_2D(NND_2)(PMe_2Ph)_3]Br$	2 118m, br 2 197m, br 2 200m, br	ν(ND)
$[WCl_3H(NNH_2)(PMe_2Ph)_2]$	3 118s, sp 2 197s, sp 3 375m, sp	ν(NH)
	267m, sp 304m, sp	ν(WCl)
$[WCl_3H(NNHPh)(PMe_2Ph)_2]$	3 230m, br	ν(NH)
	270m 300m	ν(WCl)
$[WCl_3H(NNHPh)(PMePh_2)_2]$	3 230m, br	ν(NH)
$[WCl_3H(NNH_2)(PMePh_2)_2]$ [c]	3 123w 3 197m 3 350w	ν(NH)
	260m 300m, br	ν(WCl)

[a] Mull spectra (Nujol or hexachlorobutadiene); sp = sharp, m = medium, br = broad, w = weak, s = strong. [b] Tentative assignment. [c] See ref. 11.

TABLE 3

Hydrogen-1, ^{31}P-{^1H}, and ^{15}N n.m.r. parameters for hydrazido(2−)-hydride complexes

Complex (solvent)	^1H δ [a]/p.p.m.	^1H Assignment [b]	^{31}P-{^1H} δ [c]/p.p.m.	^{31}P-{^1H} Assignment [b,d]	
$[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl$ (CD_2Cl_2)	1.60—2.35(12)	P–*Me*(m)	−151.4	PMe_2Ph_A	
	2.20(6)	P–*Me*(dd)	−145.3	PMe_2Ph_B	
	7.05—7.9(17)	P–*Ph*(m), N–H_2 [e]	−137.9	PMe_2Ph_X	
				$^2J(P_AP_B)$	50 Hz
				$^2J(P_AP_X)$	−156 Hz
	9.90(1)	W–*H*(ddd) ^2J(PH) 18, 84, and 96 Hz		$^2J(P_BP_X)$	−34 Hz
$[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$ (CD_2Cl_2)	1.20—1.75(12)	P–*Me*(m)	−149.7	PMe_2Ph_A	
	1.95(6)	P–*Me*(dd)	−150.3	PMe_2Ph_B	
	7.00—8.05(15)	P–*Ph*(m)	−160.8	PMe_2Ph_X	
	9.22(1) [f]	W–*H*(ddd)		$^2J(P_AP_B)$	37 Hz
		^2J(PH) 16, 84, and 89 Hz		$^2J(P_AP_X)$	−146 Hz
				$^2J(P_BP_X)$	52 Hz
	9.36(2) [e]	N–H_2(s)			
			^{15}N −226.4(t) [g]	β-NH_2, ^1J(NH)	86 Hz
			^{15}N −65.8(s) [g]	α-N	
$[WCl_3H(NNH_2)(PMe_2Ph)_2]$ ([$^2H_6$]dimethyl sulphoxide)	2.05(12)	P–*Me*(dt) $\lvert^2J(PCH) + {}^4J(PWPCH)\rvert$ = 6 Hz	135.5	PMe_2Ph(s)	
	7.35—7.80(10)	P–*Ph*(m)		*J*(WP)	161 Hz
	8.88(2)	N–H_2(s)		*J*(PH)	86 Hz
	11.15(1) [e]	W–*H*(t), *J*(PH) 89 Hz			
$[WCl_3H(NNHPh)(PMe_2Ph)_2]$	2.15(12)	P–*Me*(dt) $\lvert^2J(PCH) + {}^4J(PWPCH)\rvert$ = 6 Hz			
	7.2—8.4(17) [h]	P–*Ph*, N*Ph*(m), NH_2			
	11.2(1)	WH (t), ^2J(PH) 80 Hz			
$[WCl_3H(NNH_2)(PMePh_2)_2]$	2.49(6)	P–*Me*(m)			
	7.23—7.74	P–*Ph*(m)	124.69	$PMePh_2$	
	5.60	NH_2 (br, s)		*J*(WP)	153.8 Hz
	12.10	W–*H*(t) ^2J(PH) = 91.6 Hz			

[a] Relative to $SiMe_4$; integration in parentheses. [b] m = Multiplet, dd = doublet of doublets, ddd = double doublet of doublets, dt = doublet of triplets, t = triplet, s = singlet, br = broad. [c] Relative to $P(OMe)_3$; integration in parentheses. [d] From computer analysis. [e] Exchange rapidly with D_2O. [f] Not exchanged by D_2O after 18 h. [g] Relative to CD_3NO_2. [h] N–NH_2 resonance obscured by Ph resonances, could not be exchanged by D_2O because of instability of complex. [i] Data from ref. 11.

patterns typical of *trans* phosphine groups with a low-field non-exchangeable metal–hydride resonance at somewhat higher field than the NNH_2 resonances (Table 3), which in the case of (3; PR_3 = PMe_2Ph) is apparently obscured by Ph resonances.

The ^{15}N spectrum of (1; X = Br) enriched 95% in ^{15}N shows a high-field resonance (−226.4 p.p.m. relative to CD_3NO_2) in the region diagnostic of the NH_2 group [10] [^1J(NH) 86 Hz] and a singlet at lower field (−65.8 p.p.m.) due to the α-N. Under noise decoupling the high-field signal is inverted due to nuclear Overhauser enhancement as is usually observed.[10] These spectral data unambiguously show that this complex has a hydrazido(2−) ligand and therefore the site of attachment of the third proton cannot be at a nitrogen atom.

We have previously reported [11] the preparation of a poorly soluble hydrazide complex $[WCl_3(N_2H_3)(PMePh_2)_2]$ which was assigned a hydrazido(1−) structure on the basis of its low-field ^1H n.m.r. spectrum. The data presented in this paper for its more soluble analogues clearly show that it must be reformulated [4] as the hydride complex $[WCl_3H(NNH_2)(PMePh_2)_2]$. The spectral properties of this compound are also included in Tables 2 and 3 for comparison. The structure of $[WBrClH(NNH_2)(PMe_2Ph)_3]Br$, which was also originally formulated as a hydrazido(1−) complex,[12] has recently been re-formulated as that of a hydrazido(2−)–hydride complex.[6]

The hydride resonances of these complexes are at particularly low field, in the region 9.9—11.2 p.p.m. (relative to $SiMe_4$). More commonly, hydride complexes of molybdenum and tungsten absorb in the region 3.0 to −4.6 p.p.m. (Table 4). They are distinguished from the NH_2 group resonances, which occur in the same region, by their persistence in the presence of D_2O, which rapidly exchanges with NH_2 groups.

The reason for this particularly low-field chemical shift is not clear although the low symmetry of the molecules and the low formal number of *d* electrons (hence low-lying excited electronic states) are presumably major contributing factors. Other hydride complexes whose resonances fall in this region are the formally d^0 complexes $[M(\eta^5\text{-}C_5Me_5)_2H_2]$ [M = Ti (0.28), Zr (7.46), and Hf (15.6 p.p.m.)].[13]

Structures of the Hydrazido(2−)-Hydride Complexes.—The *X*-ray structure [6,12] of $[WBrClH(NNH_2)(PMe_2Ph)_3]Br$, which has very similar spectroscopic properties to those of complexes (1), clearly establishes a linear NNH_2 group with a *trans* halide in the molecule. The three phosphine groups lie essentially in a plane perpendicular to that of the X–W–NNH_2 (X = Cl or Br) axis but with one obtuse (115°) P–W–P angle.[6] It therefore appears that a likely location of the hydride in this complex and also by analogy in complexes (1) is in the face delineated by the obtuse P–W–P angle as shown in Figure 1(*a*). The singlet ^{31}P resonance of (2) and of $[WCl_3H(NNH_2)(PMePh_2)_2]$ (Table 3) and other spectroscopic properties are consistent with the structure proposed in Figure 1(*b*) for these complexes. Again, the location of the hydride ligand is likely to be on an edge or capping a face of a distorted octahedron. A similar geometrical arrangement has been discussed for the related series of complex cations $[MH(XY)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (XY = CO, N_2, or RNC).[14]

Reactions of the Hydrazido(2−)-Hydride Complexes.—

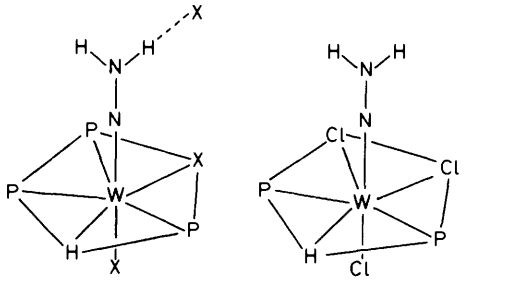
TABLE 4

N.m.r. data for some Group 6 hydrido-complexes

Complex [a]	Metal electron configuration	Hydride shift [b]/ p.p.m.	Coupling constants/Hz	Ref.
$[WH_6(PMe_2Ph)_3]$	$5d^0$	−1.94	^2J(PH) 37 J(WH) 28	8
$[MoH_4(PEtPh_2)_4]$	$4d^2$	−2.20	^2J(PH) 34	*c*
$[WH_4(PEtPh_2)_4]$	$5d^2$	−1.82		8
$[MoH_4(dppe)_2]$	$4d^2$	−2.79 [d]		8
$[WH_4(dppe)_2]$	$5d^2$	−3.65 [d]		8
$[WH_4(PMe_2Ph)_4]$	$5d^2$	−2.70	^2J(PH) 31 J(WH) 27	*e*
$[WH_2Cl_2(PMe_2Ph)_4]$	$5d^2$	−1.56	^2J(PH) 33, 41, 60	*f*
$[MoH_2Cl_2(dppe)_2]$	$4d^2$	−4.55	^2J(PH) 48	*g*
$[MoH_2(CO_2CF_3)_2(PMePh_2)_3]$	$4d^2$	−1.35	^2J(PH) 57	*h*
$[WH_2(CO_2CF_3)_2(PMePh_2)_3]$	$5d^2$	3.00	^2J(PH) 48	*h*
$[W(\eta^6\text{-}C_6H_6)_2H][PF_6]$	$5d^4$	1.07		*i*
$[WH(N_2)_2(dppe)_2]\cdot HCl$	$5d^4$	−3.50	^2J(PH) 72, 10	*g*

[a] dppe = 1,2-Bis(diphenylphosphino)ethane. [b] Relative to $SiMe_4$. [c] F. Penella, *Chem. Commun.*, 1971, 158. [d] Corrected value; originally reported relative to chlorobenzene taken as δ 7.05 p.p.m. [e] B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J. Chem. Soc., Chem. Commun.*, 1972, 34; B. Bell, D.Phil. Thesis, University of Sussex, 1971. [f] M. E. Fakley and R. L. Richards, *Transition Met. Chem.*, 1981, in the press. [g] J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074. [h] E. C. Guzman and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 1716. [i] F. G. N. Cloke, M. L. H. Green, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1978, 72.

Compounds (1; X = Cl or Br) are dehydrohalogenated by bases ($PMePh_2$, C_5H_5N, NEt_3 *etc.*), regenerating the starting hydrazido(2−) complexes. Treatment of complexes (1) and (2) with sulphuric acid in methanol or methanol alone yielded, after evaporation of solvent and base distillation, hydrazine and ammonia in the yields shown in Table 5. In general the yields of nitrogen hydrides obtained are lower,



(*a*) P = PMe_2Ph X = Cl or Br (*b*) P = PMe_2Ph or $PMePh_2$

FIGURE 1 Possible structures for hydrazido(2−)-hydride complexes of tungsten

and with a greater proportion of hydrazine than are obtained under identical conditions from the parent hydrazido(2−) complexes.[3,4] This is presumably due to the higher formal oxidation state of tungsten in the hydride complexes and these complexes may in fact represent intermediates on the route to hydrazine (see Discussion section).

A further reaction of (2) and of $[WCl_3H(NNHPh)(PMe_2Ph)_2]$ occurred while they were being crystallised slowly from CH_2Cl_2–thf–diethyl ether under dinitrogen to obtain crystals for *X*-ray structure determination. Complex (2) gave yellow-green cubic crystals which analysed for $[WCl_3(NNH_2)(PMe_2Ph)_2]\cdot C_4H_8O$. Their molecular structure was determined (Figure 2) and the e.p.r. spectrum of the crystal showed it to be paramagnetic, with a multiplet signal at $g = 1.92(4)$. Thus the complex product of slow crystallisation is formed by loss of a hydrogen atom to give the formally W^V complex *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$. Selected structural details are given in the Experimental section (Tables 6 and 7); isotropic and anisotropic temperature factors and observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 23218 (11 pp.).*

TABLE 5

Ammonia and hydrazine produced by sulphuric acid–methanol–base distillation

Complex	NH_3 [a]	N_2H_4 [a]	%N reduced
$[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl$	0.97	0.42	90
$[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$	0.53	0.18	45
	(0.67) [b]	(0.14) [b]	48
	(0.72) [c]	(0.28) [c]	64
$[WCl_3H(NNH_2)(PMePh_2)_2]$ [d]	0.60	0.25	55

[a] Moles per tungsten atom. [b] Methanol alone, 48 h *in vacuo*; residue extracted into water. [c] Base distillation of complex without acid treatment. [d] Ref. 11; 0.3 mol H_2 evolved per tungsten atom.

An important feature of the structure (Figure 2) is the location of the hydrogen atoms of the hydrazido(2−) group, showing it to be essentially planar. This planarity and the bond lengths of the linear W=N–N system, which are close to those found in analogous complexes of tungsten(IV),[7,15] indicate very strong conjugation along the W–N–N chain. Structurally this ligand appears to be closer to isodiazene than hydrazido(2−) but we retain the latter name because of its common usage [3,4] and IUPAC recommendations.[16]

A mirror plane passes through Cl(2), W, N(1), and N(2) (Figure 2) about which a molecule of thf is disordered (not illustrated). A distortion from octahedral symmetry does occur in the molecule by an increase of P(1)–W–P(1)′ to 123.5(1)° and a concomitant decrease in the other angles about tungsten. Although this bond angle distortion would be compatible with the presence of a hydride ligand, the paramagnetism of the crystal rules this out. Moreover, in the paramagnetic phenyl analogue *trans*-$[WCl_3(NNHPh)(PMe_2Ph)_2]$ (see below) where the phosphine ligands are *trans* there is no distortion from octahedral symmetry.[4,17]

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Thus the distortion in the structure of *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ appears to be due to steric interaction of the *cis* PMe_2Ph ligands.

The nature of the reaction producing *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ is not established. It appears to be photo-initiated since u.v. irradiation of solutions of (3) produced an e.p.r. signal similar to that of *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$. Hydrogen gas was not detected over solutions of (2) and the fate of the hydride ligand is uncertain.

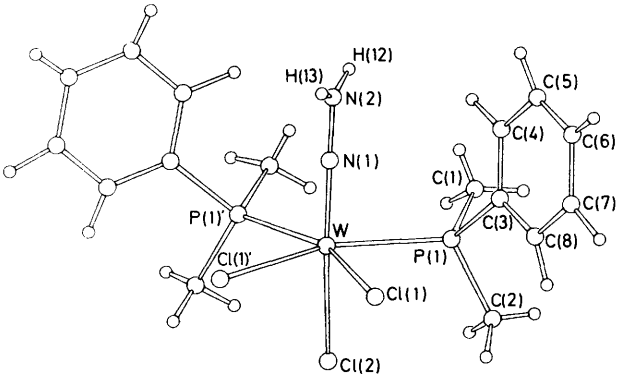


FIGURE 2 Structure of *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ (4) showing the atom numbering

A similar reaction occurs on recrystallisation of $[WCl_3H(NNHPh)(PMe_2Ph)_2]$ (3) to give paramagnetic *trans*-$[WCl_3(NNHPh)(PMe_2Ph)_2]$ [$g = 1.92(4)$], whose *X*-ray structure has also been determined.[4,17] As discussed above, it shows no deviation from octahedral symmetry, presumably because the *trans* arrangement of phosphine ligands precludes steric interactions.[17]

A Bis(diazenido)-complex of Tungsten(IV).—In an attempt to produce hydrazido-complexes of tungsten(IV) with pyridine rather than phosphine co-ligands, we treated the complex $[WCl_4(py)_2]$ (py = pyridine) with 2 mol of $PhNHNH(SiMe_3)$ in pyridine. This reaction produced a mixture of yellow and violet products of which the latter could be obtained pure and whose spectroscopic properties and analysis (Table 1 and Experimental section) were consistent with the formulation $[WCl_2(NNPh)_2(C_5H_5N)_2]$ (6). Probably the yellow product is the precursor to (4), *i.e.* $[WCl_3(NHNHPh)(C_5H_5N)_2]$ (5), and it analysed roughly for this formulation. The mechanism of formation of (4) is not clear but presumably it involves further attack by the excess of $PhNHNH(SiMe_3)$ on such a complex as (5) with deprotonation, perhaps by means of trace amounts of dioxygen, to give water.

During this work we incidentally prepared the series of complexes $[WCl_4L_2]$ (L = py, 2Me-py, 3Me-py, 4Me-py, or quinoline) in high yield by the displacement reaction (iv) which appears to be a cleaner and more general reaction than preparative methods previously employed.[18] Some

$$[WCl_4(PPh_3)_2] + 2\ L \xrightarrow[20\ °C]{CH_2Cl_2} [WCl_4L_2] + 2\ PPh_3 \quad \text{(iv)}$$

physical properties of these complexes are shown in Table 1.

DISCUSSION

The principal conclusion to be drawn from the content of this paper is that protons attached to nitrogen atoms ligating tungsten in its higher oxidation states are very labile. Thus although the tungsten(IV) centre was attacked by the silyl hydrazide group containing a potential α-NH bond, the preferential site for the proton was at the metal, from which it was eventually lost to give *trans*-$[WCl_3(NNHPh)(PMe_2Ph)_2]$. Similarly, protic attack on hydrazido(2—) complexes led ultimately to the formation of hydrides, rather than hydrazido(1—) complexes as had previously been suggested.[4,6] In this latter case, however, it is not clear whether or not protonation occurs at the metal directly. It is possible that initial attack could be at the α-N, giving a ' sideways bound ' (η^2)-$NHNR_2$ group from which proton transfer to the metal could occur. Examples of η^2-$NRNR_2$ groups have been structurally characterised in the complexes $[W(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}NPhNH_2)][BF_4]$[19] and $[Mo(NNMePh)(\eta^2\text{-}NHNMePh)(S_2CNMe_2)_2]^+$.[20] It is notable, however, that the precursor to $[W(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}NPhNH_2)]^+$ is a hydrazido(2—)–hydride complex,[21] $[W(\eta^5\text{-}C_5H_5)_2H(NNHPh)]^+$, in which the hydride ligand migrates to the hydrazido(2—) group, *i.e.* the reverse sequence to that suggested above. In this latter complex, the hydrazido(2—) ligand is noticeably bent (W–N–N = 146.3°), which would be consistent with considerable lone-pair character at the α-N (structure I) whereas the hydrazido(2—)–hydride complexes of this work have linear hydrazido-groups with an electron-deficient α-N (structure II). It is therefore tempting to suggest a correlation between NNR_2 geometry and proton migration, but the precursor to $[Mo(NNMePh)(\eta^2\text{-}NHNMePh)(S_2CNMe_2)_2]^+$, *i.e.* $[Mo(NNMePh)_2(S_2CNMe_2)_2]$,[22] has linear hydrazide groups and a rationale, in terms of geometry or electronic structure of hydrazide groups, for the preferred location of protons in these complexes is not at present obvious.

I II

A further point of interest is the role of the hydrazido(2—)–hydride complexes, reported here, in the formation of ammonia and hydrazine from dinitrogen complexes as a result of protic attack. The data detailed in Table 5, where the ratio of hydrazine to ammonia obtained from hydrazido–hydride complexes is much higher than observed from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ under the same conditions,[1,2] suggest that these hydrides lie on a side route to hydrazine rather than the main route to ammonia. This would be in keeping with their higher formal oxidation state, since fewer electrons are available for dinitrogen reduction, favouring hydrazine rather than ammonia as the final product.

EXPERIMENTAL

Air-sensitive materials were handled by standard dinitrogen-flow or vacuum techniques. Solvents were dried by standard methods and distilled before use. Hydrazido(2—) complex precursors were prepared by published

methods.[5] N.m.r. spectra were determined on JEOL PS100, PS100FT, FX90Q or Bruker WH180 instruments and i.r. spectra with Pye-Unicam SP1200 or SP2000 instruments. E.p.r. spectra were determined with a Varian E9 spectrometer, conductivities with a Portland Electronics conductivity bridge and melting points with an Electrothermal or Reichert hot-stage apparatus. Analyses were by Mr. & Mrs. A. G. Olney of these laboratories.

Crystallography.—Crystal data for compound (4). $C_{16}H_{24}Cl_3N_2P_2W{\cdot}C_4H_8O$, formula weight 668.7, Orthorhombic, $a = 20.057(3)$, $b = 18.581(3)$, $c = 6.971(1)$ Å, $U = 2\,597.9$ Å^3, $Z = 4$, $D_c = 1.71$ g cm^{-3}, $F(000) = 1\,316$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 51.5$ cm^{-1}. Space group *Pnma* from systematic absences of $0kl$ for $(k + l)$ odd, and $hk0$ for h odd, and successful structure refinement.

TABLE 6

Final atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
W	4 040.2(2)	2 500.0(0)	2 466.0(7)
P(1)	4 552(1)	1 315(1)	3 311(4)
Cl(1)	3 318(1)	1 640(1)	811(4)
Cl(2)	4 735(2)	2 500(0)	−527(5)
N(1)	3 683(5)	2 500(0)	4 759(14)
N(2)	3 431(5)	2 500(0)	6 477(20)
C(1)	5 208(5)	1 359(6)	5 131(17)
C(2)	4 951(6)	854(6)	1 327(18)
C(3)	3 982(3)	669(3)	4 357(9)
C(4)	3 827(3)	727(3)	6 301(9)
C(5)	3 384(3)	242(3)	7 142(9)
C(6)	3 096(3)	−302(3)	6 039(9)
C(7)	3 252(3)	−361(3)	4 094(9)
C(8)	3 695(3)	125(3)	3 254(9)
C(9)	1 633(27)	2 500(0)	3 770(74)
C(10)	1 353(20)	3 199(12)	4 639(37)
C(11)	2 066(11)	2 900(0)	6 541(33)
C(12)	1 713(24)	2 500(0)	6 977(63)
C(13)	1 893(28)	3 152(22)	5 817(53)
C(14)	1 728(30)	2 900(0)	3 829(65)

The data crystal of size 0.45 × 0.35 × 0.30 mm was sealed in a capillary tube. Cell dimensions were derived from the setting angles of 12 reflections measured on a Hilger and Watts Y290 diffractometer. Intensities of unique reflections with $2 < \theta < 25°$ were measured by an ω–2θ step scan of 50 steps, each of 0.02° and 0.5 s, with background counts of 12.5 s at each end of the scan. The intensities of three standard reflections remeasured every 100 reflections showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption and 1 890 reflections with $I > 3\sigma(I)$ were used in the structure analysis.

The systematic absences were consistent with either space group $Pn2_1a$ or *Pnma*, the latter choice implying that the complex has molecular mirror symmetry. The positions of non-hydrogen atoms of the complex were first derived by routine heavy-atom methods and refined in space group $Pn2_1a$ with the phenyl rings as rigid bodies (C–C 1.395 Å) and anisotropic temperature factors. A difference map revealed a set of peaks which were interpreted as a molecule of thf solvent and were included in the refinement assigned as carbon atoms and given anisotropic temperature factors. This refinement converged at $R = 0.053$ but did not give reasonable bond lengths for the thf molecule which appeared to be disordered. At this point, the geometries of both the complex and the solvent molecules were consistent with the presence of a crystallographic mirror plane perpendicular to the b axis, so refinement was continued in space group *Pnma* with the solvent molecule occupying two overlapping orientations both lying across the mirror plane. Continued refinement with anisotropic temperature factors for the atoms of the complex and with isotropic temperature factors and bond length constraints (C–C 1.5 Å) for the solvent atoms converged at $R = 0.058$. Since the geometry of the molecules in the latter refinement appeared chemically acceptable and there was only a small difference in R value, the space group *Pnma* was assumed to be correct. An angle-weighted difference map revealed the positions of the hydrogen atoms of the complex and these were then held fixed with a common isotropic temperature factor which refined to 0.059 Å^2. The stereochemical reasonableness of the phenyl and methyl hydrogen atom positions (Figure 2) reinforces the identification of the hydrazido-hydrogen atoms. There was no sign on the difference map of a hydrogen attached to N(1) and this, coupled with the essential linearity of the W–N–N chain, makes it very unlikely that there is in fact any hydrogen at N(1). Further least-squares refinement with the weighting scheme $w = 2.16/[\sigma^2(F) + 0.0018(F^2)]$ converged at $R = 0.055$, $R' = 0.072$), with a maximum positional shift/error of 0.23. A final difference map had peaks of up to 0.8 e Å^{-3} near the tungsten atom and 0.5 e Å^{-3} near the solvent molecule but was elsewhere featureless. An attempt was made to apply an absorption correction but owing to difficulties in defining the crystal shape it gave no improvement in R or R' and was finally omitted.

Complex scattering factors for neutral atoms were taken from ref. 23, and the structure solution and refinement were carried out with the SHELX program system. Final atom positions are listed in Table 6, with hydrogen atoms in Table 7. Listings of temperature factors and structure factors have been deposited in the Supplementary Publication.

TABLE 7

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

W–P(1)	2.500(2)	P(1)–C(2)	1.812(12)
W–Cl(1)	2.446(2)	P(1)–C(3)	1.812(6)
W–Cl(2)	2.508(4)	N(1)–N(2)	1.300(17)
W–N(1)	1.752(10)	N(2)–H(12)	1.08
P(1)–C(1)	1.829(11)	N(2)–H(13)	0.78

(*b*) Angles

P(1)′–W–P(1)	123.5(1)	N(1)–W–Cl(1)	100.9(2)
Cl(1)–W–P(1)	77.2(1)	N(1)–W–Cl(2)	170.4(14)
Cl(2)–W–P(1)	88.2(1)	N(2)–N(1)–W	178.7(9)
N(1)–W–P(1)	87.3(2)	C(2)–P(1)–C(1)	103.5(5)
C(1)–P(1)–W	114.8(3)	C(3)–P(1)–C(1)	101.8(4)
C(2)–P(1)–W	114.7(3)	C(3)–P(1)–C(2)	105.8(4)
C(3)–P(1)–W	114.8(2)	H(12)–N(2)–N(1)	110
Cl(1)–W–P(1)′	158.4(1)	H(13)–N(2)–N(1)	107
Cl(1)′–W–Cl(1)	81.6(1)	H(13)–N(2)–H(12)	143
Cl(2)–W–Cl(1)	85.4(1)		

The deviation from the co-ordination plane defined by P(1), P(1)′, Cl(1), Cl(7), (Figure 2) is 0.11 Å for W and 1.83 Å for N(1), indicating a small displacement of the tungsten towards the hydrazido(2−) group.

The only intermolecular contact to be significantly less than the combined van der Waals radii of the interacting atoms is 2.27 Å for Cl(2) • • • H(12) at (x, y, z − 1). (The sum of van der Waals radii is in the range 2.90—3.35 Å.)[24]

Dibromotris(dimethylphenylphosphine)[hydrazido(2−)]hydridotungsten(VI) *Bromide* $[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$.—

Anhydrous hydrogen bromide (1 mol) was condensed on to a frozen solution of $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (1.3 g) in thf (5.0 cm^3) *in vacuo* and the reaction mixture was allowed to warm to room temperature with vigorous stirring. The product suddenly precipitated from the red–brown reaction solution after about 1 h as a fine pink solid which was filtered off, washed with thf, ether, and dried *in vacuo* at 20 °C (yield 1.1 g, 70%). A similar reaction using *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.4 g) in thf (40 cm^3) with HBr (4 mol equivalents) evolved dinitrogen (1.0 mol equivalent) and precipitated the title compound which was isolated as described above. Substitution of DBr for HBr gave the deuterio-complex.

Dichlorotris(dimethylphenylphosphine)[hydrazido(2−)]-hydridotungsten(VI) *Chloride Benzene*, $[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl{\cdot}C_6H_6$ (2).—Anhydrous hydrogen chloride (1 mol equivalent) was condensed onto a frozen solution of $[WCl_2(NNH_2)(PMe_2Ph)_3]$ (0.5 g) in benzene (30 cm^3) *in vacuo*. After stirring at room temperature for 2 h the yellow precipitate was filtered off, washed with benzene, and dried *in vacuo* at 20 °C (yield 0.05 g, 96%).

Trichlorobis(dimethylphenylphosphine)[hydrazido(2−)]-hydridotungsten(VI) *Tetrahydrofuran* (2/1), $[WCl_3H(NNH_2)(PMe_2Ph)_2]{\cdot}0.5C_4H_8O$.—Anhydrous hydrogen chloride (3 mol equivalents) was condensed onto a frozen solution of $[WCl_2(NNH_2)(PMe_2Ph)_3]$ (0.4 g) in thf–CH_2Cl_2 (1 : 1, 30 cm^3) *in vacuo*. The reaction was stirred for 22 h during which time the product precipitated as a yellow solid. It was filtered off, washed with degassed water, and ether, and dried *in vacuo* at 20 °C (yield 0.1 g, 23%).

Trichlorobis(dimethylphenylphosphine)hydrido[phenylhydrazido(2−)]tungsten(VI), $[WCl_3H(NNHPh)(PMe_2Ph)_2]$ (3).—$[WCl_4(PMe_2Ph)_3]$ (4.3 g) in suspension/solution in thf (50 cm^3) was treated with $PhNHNH(SiMe_3)$ (1.05 g) and the mixture stirred for 16 h to give a brown suspension in a yellow-green solution. The suspension was filtered and discarded and removal of solvent and treatment with hexane gave a mixture of orange-yellow and green solids which was filtered off, dried *in vacuo*, then recrystallised from CH_2Cl_2–hexane followed by CH_2Cl_2–ether to give yellow-green *crystals* (yield 2.8 g, 60%). The orange-yellow material which was originally obtained mixed with the yellow-green product was never obtained pure but had a similar analysis to (3) and was probably $[WCl_3(NHNHPh)(PMe_2Ph)_2]$.

Analogues of (3) were prepared by a similar route using *trans*-$[WCl_4(PR_3)_2]$ (PR_3 = $PMePh_2$ or PPh_3). In solution these compounds easily transformed into blue solids which have not yet been characterised. This transformation was inhibited by the presence of free phosphine and therefore their purification was carried out with phosphine present.

Trichlorobis(dimethylphenylphosphine)[hydrazido(2−)]-tungsten(V) *Tetrahydrofuran*, $[WCl_3(NNH_2)(PMe_2Ph)_2]{\cdot}C_4H_8O$ (4).—Anhydrous hydrogen chloride (4 mol equivalents) was condensed onto a frozen solution of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.4 g, 0.5 mmol) in thf–CH_2Cl_2 (1 : 1, 30 cm^3) *in vacuo*. The reaction mixture was stirred at 20 °C for 48 h, when it evolved dinitrogen (0.98 mol). The brown solution was concentrated under reduced pressure to approximately 10 cm^3 and ether (5 cm^3) was added until the solution became cloudy. After rapid filtration the solution was set aside at room temperature and yellow-green oily crystals were slowly deposited over 76 h and were filtered off, washed with ether, thf, degassed water, and finally with more ether. The clean, yellow-green *crystals* were dried *in vacuo* at 20 °C (yield 0.2 g, 60%) (Found: C, 35.7; H, 4.9; N, 4.2. Calc. for $C_{20}H_{32}Cl_3N_2OP_2W$: C, 35.9; H, 4.8; N, 4.2%). A single crystal of the batch was used for *X*-ray structural determination as discussed earlier.

cis-*Trichlorobis(dimethylphenylphosphine)[phenylhydrazido(2−)tungsten*(V), $[WCl_3(NNHPh)(PMe_2Ph)_2]$, was obtained from (3) upon slow recrystallisation under the same conditions as its hydrazido(2−) analogue above.

$[WCl_4L_2]$ (L = py, 2-, 3-, *or* 4-Me-py *or Quinoline*).—*trans*-$[WCl_4(PPh_3)_2]$ was treated with the appropriate py ligand (2.2 mol equivalent) in CH_2Cl_2 and the mixture stirred for 24 h, by which time the $[WCl_4(py)_2]$ complex had precipitated in high yield. It was filtered off, washed with CH_2Cl_2, and dried *in vacuo*.

Dichlorobis(phenyldiazenido)bis(pyridine)tungsten(IV), $[WCl_2(NNPh)_2(C_5H_5N)_2]$.—$[WCl_4(C_5H_5N)_2]$ (2.25 g) was treated with $PhNHNH(SiMe_3)$ (0.83 g, 2 mol) in pyridine (70 cm^3) and the red suspension was stirred for 24 h. The resulting suspension was filtered free of a brown-yellow solid (0.8 g). This solid could be obtained in better yield by similar treatment of $[WCl_4(C_5H_5N)_2]$ with 1 mol equivalent of $PhNHNH(SiMe_3)$ and it appeared to be $[WCl_3(NHNHPh)(C_5H_5N)_2]$ but it could not be purified and turned violet on attempted crystallisation (Found: C, 32.6; H, 4.1; N, 10.1. $C_{16}H_{17}Cl_3N_4W$ requires C, 35.7; H, 4.5; N, 10.0%); i.r. spectrum, ν(NH) 3 230 cm^{-1}.

The maroon supernatant liquid from the above reaction was concentrated *in vacuo* and hexane was added to give a violet solid which was recrystallised (CH_2Cl_2–hexane) as violet *plates* (yield 1.3 g, 45%).

Reaction of $[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$ *with* NEt_3.—Triethylamine (1 drop, excess) was added to a suspension of $[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$ (0.05 g) in thf–CH_2Cl_2 (1 : 1, 10 cm^3). An immediate colour change from pink to brown occurred and the reaction was stirred overnight at 20 °C. Removal of the solvent under reduced pressure gave a brown solid which was washed with methanol, water, and ether, dried *in vacuo*, and identified as $[WBr_2(NNH_2)(PMe_2Ph)_3]$ by comparison of its i.r. spectrum with that of an authentic sample. A similar dehydrohalogenation occurred if pyridine, 8-hydroxyquinoline, or dimethylphenylphosphine were used in the above reaction instead of triethylamine.

Reactions of Hydrazido(2−)–Hydrido Complexes with H_2SO_4–MeOH. These reactions follow established procedures [2] and the results are shown in Table 5.

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