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Preliminary communication

HYDRAZIDO(2–) (OR ISODIAZENE) COMPLEXES OF TUNGSTEN

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Summary

The complexes $[WX_2(NNH_2)(PMe_2Ph)_3]$ (A, X = Cl or Br) react with HX in tetrahydrofuran to give hydride complexes $WX_3H(NNH_2)(PMe_2Ph)_3$ (B) B (X = Cl) loses PMe_2Ph with more HCl to give $WCl_3H(NNH_2)(PMe_2Ph)_2$, which on slow recrystallisation gives $[WCl_3(NNH_2)(PMe_2Ph)_2]$ whose X-ray structure has been determined $[WCl_3\{NNH(Ph)\}(PMe_2Ph)_2]$ has also been prepared and structurally characterised by X-rays In both structures the *N*-hydrogen atoms have been located and the hydrazido(2–) ligands are essentially planar, indicative of very strong conjugation along the M—N—N chain

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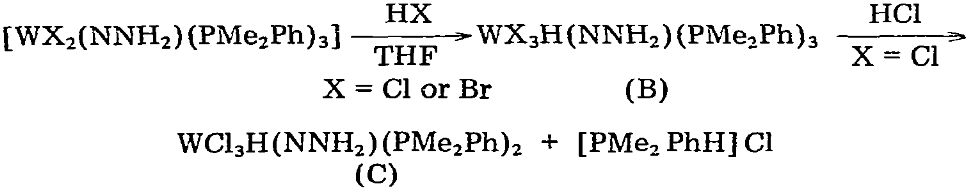
The complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (A, M = Mo or W, X = Cl, Br or I) represent a stable intermediate stage in the reduction of dinitrogen in *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ to ammonia [1] In order to learn more of the mechanism of the reduction, we have investigated the further protonation of compounds A The course of the protonation reaction is dependent upon the solvent, the metal and the ligand environment [2] but by use of anhydrous halogen acid in THF, we have isolated the tungsten complexes B and C (reaction 1), whose spectroscopic properties etc , are shown in Table 1 On the basis of these data and the lack of proton splitting of the $^{15}N_\alpha$ resonance in the ^{15}N spectrum of B (X = Br) [2], B and C are formulated as hydrazido(2–)-hydride complexes



$$[WX_2(NNH_2)(PMe_2Ph)_3] \xrightarrow[\substack{THF \\ X = Cl\ or\ Br}]{HX} \underset{(B)}{WX_3H(NNH_2)(PMe_2Ph)_3} \xrightarrow[X = Cl]{HCl} \underset{(C)}{WCl_3H(NNH_2)(PMe_2Ph)_2} + [PMe_2PhH]Cl \qquad (1)$$

TABLE 1

HYDRAZIDO(2–)-HYDRIDO COMPLEXES OF TUNGSTEN(VI)

	Colour	Yield (%)	γ(NH) (cm^{-1})^{a}	δ {WH} (ppm)^{b}	δ {N(2)H$_2$} (ppm)$^{b\ c}$	Λ/S (cm^{2}mol^{-1})
$WCl_3H(NNH_2)(PMe_2Ph)_3$	yellow	95	3060 3210	8 96—10 80 ddd ^2J(PH) 18 84 96 Hz	n.o	31^{d}, 1^{e}
$WCl_3H(NNH_2)(PMe_2Ph)_3$	yellow-green	10	3118 3197	11 15t^{f} ^2J(PH) 80 Hz	8 88s(br)	1^{e}
$WBr_3H(NNH_2)(PMe_2Ph)_3$	pink	70	2980—3110	9 22 ddd ^2J(PH) 16, 84 89 Hz	9 36s(br)	57^{d} 1^{e}
$WBr_3D(NND_2)(PMe_2Ph)_3$	pink	70	2118 2198 2200^{g}	n.o	n.o	
$WCl_3H\{NNH(Ph)\}(PMe_2Ph)_2$	green	30	3230	11 2 t ^2J(PH) 80 Hz	n.o	1^{e}

[a] Nujol mulls [b] In CD_2Cl_2 solution unless otherwise indicated relative to $SiMe_4$. [c] N(2)$\underline{H}_2$ rapidly exchanges with D_2O [d] In ca 10^{-2} mol l^{-1} CH_3NO_2 solution [e] In ca. 10^{-2} mol l^{-1} $C_2H_4Cl_2$ solution. [f] In $(CD_3)_2SO$ solution [g] γ(ND) values ddd double doublet of doublets t triplet s(br) broad singlet n o not observed

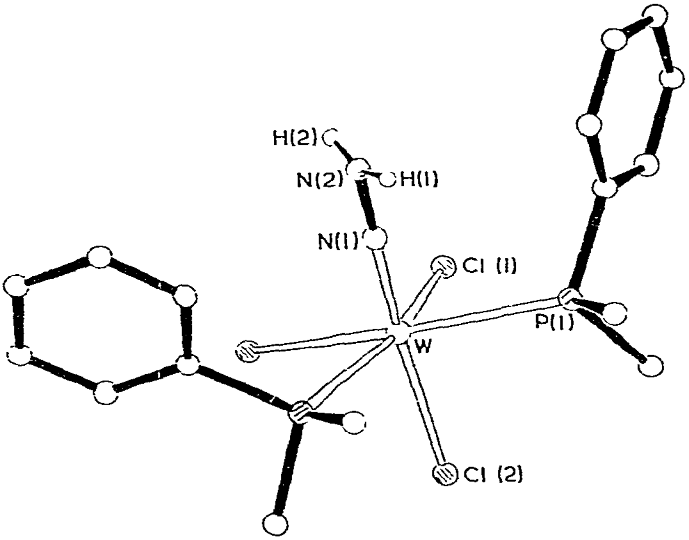


Fig 1 X-ray structure of cis $[WCl_3(NNH_2)(PMe_2Ph)_2]$ (E) Crystal data $C_{16}H_{24}Cl_3N_2P_2W \cdot C_4H_8O$, (molecular weight 668 8), orthorhombic, space group *Pnma* a 20 057(3), b 18 581(3) c 6 971(1) Å U 2598 1 Å^3 $Z = 4$ $F(000) = 1270$ μ(Mo-K_α) 46 7 cm^{-1} Cell dimensions and intensities measured on a Hilger and Watts Y290 diffractometer with monochromated Mo-K_α radiation No absorption correction was applied All hydrogen atoms of the complex were located in a difference map and one molecule of tetrahydrofuran was discovered disordered in the lattice 1890 reflections with $I > 3\sigma(I)$, θ_{max} 25° R = 0 055 $R' = 0\ 072$ with $w = 2\ 16/(\sigma_F^2 + 0\ 0018\ F^2)$

The figure shows the hydrazido(2–) hydrogen atoms but an intermolecular hydrogen bond H(1) Cl(2) is not illustrated Bond distances and angles W—N(1) 1 752(10) N(1)—N(2) 1 300(17) N(2) Cl′(2) 3 351 Å ∠W—N(1)—N(2) 178 7(9)°

A substance, apparently the phenyl analogue of C and formulated $WCl_3H\{NN(H)Ph\}(PMe_2Ph)_2$ (D) has been prepared by reaction 2, which could involve simple α-H shift from N to W

$$[WCl_4(PMe_2Ph)_2] + PhNHNHSiMe_3 \xrightarrow{THF} \underset{(D)}{WCl_3H\{NNH(Ph)\}(PMe_2Ph)_2} + SiMe_3Cl \qquad (2)$$

The complexes B, C and D are poor electrolytes in $C_2H_4Cl_2$ or CH_3NO_2, but they could be salts with the anion strongly hydrogen bonded to the NNH_2 group [1] They are diamagnetic and show a low field resonance, inert to exchange with D_2O, assigned to hydride (Table 1) A complex of this type was previously formulated as a hydrazido(1–) complex [3], but in view of the ^{15}N spectrum of B (X = Br), it is most probably $[WHCl_3(NNH_2)(PMePh_2)]$

No crystals of members of this series of complexes have yet proved suitable for X-ray structure determination but slow crystallisation of complexes C and D gives, by further reaction, hydrazido(2–) complexes of tungsten(V) The X-ray structures of these compounds, *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ (E) (from C, *g* value by EPR of X-ray crystal = 1 92(4)) and *trans*-$[WCl_3\{NNH(Ph)\}(PMe_2Ph)_2]$ (F) (from D, *g* value of X-ray crystal = 1 92(4)) are shown in Fig 1 and 2 They are particularly interesting because the hydrogen atoms attached to nitrogen have been located

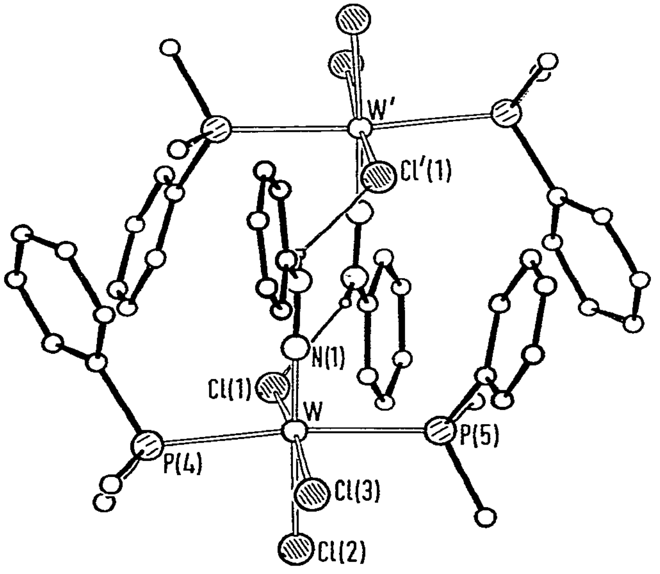


Fig 2 X-ray structure of *trans* $[WCl_3\{NNH(Ph)\}(PMe_2Ph)_2]$ (F) Crystal data $C_{22}H_{28}Cl_3N_2P_2W$, (molecular weight 672 6), monoclinic space group $P2_1/a$ a 26 048(4) b 10 773(4) c 19 529(2) Å β 104 53(1)° U 5304 9 Å $Z = 9$ (i.e two independent molecules in the crystal) $F(000) = 2632$ $\mu(Mo\text{-}K_\alpha)$ 39 3 cm^{-1} Cell dimensions and intensities measured on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation A semi-empirical absorption correction (using the method of Sheldrick et al [5]) was applied The hydrogen atom of one hydrazido(2–) group was found in a difference map, the position of the other was calculated both atoms included in the refinement 7065 reflections with $I > 2\sigma(I)$, θ_{max} 25°, final R = 0 036 R = 0 041 with $w = 1/\sigma_F^2$

The figure shows the two molecules related by a pseudo-centre of symmetry the hydrazido(2–) hydrogen atoms and their hydrogen bonds are included Bond distances and angles (molecule of W followed by that of W) W—N(1) 1 737(5), N(1)—N(2) 1 325(8) 1 316(8) N(2) ·Cl (1) 3 316 N'(2) Cl(1) 3 330 Å ∠W—N(1)—N(2) 174 4(5) 170 5(6)°

The bond lengths of the linear W=N—N system in both compounds are close to those found in analogous complexes of tungsten(IV) [4], indicating very strong conjugation along the W—N—N chain. This is further emphasised by the essential planarity of the W—N—NH$_2$ group of atoms in E and of the total atomic grouping W—N—NH(C_6H_5) in F Structurally this ligand appears to be closer to isodiazene than hydrazido(2–), but we retain the latter, commonly used name. Crystals of the complex *trans*-[WCl_3{NNH(Ph)}($PMe_2Ph)_2$] have two independent molecules which are connected in dimer pairs by intermolecular N—H····Cl hydrogen bonding interactions about a pseudo-centre of symmetry. The complex *cis*-[$WCl_3(NNH_2)(PMe_2Ph)_2$] has only one half molecule per asymmetric unit but again there is intermolecular hydrogen bonding, in chains through the crystal

The precise conditions necessary to effect this reaction and more rational routes to the tungsten(V) complexes are under investigation

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