Hydrazido(2−)-complexes as Intermediates in the Conversion of Ligating Dinitrogen into Ammonia and Hydrazine

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The formation of hydrazido(2−)-complex intermediates in solution during the reaction of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (1) (M = Mo or W) with H_2SO_4 in tetrahydrofuran (thf) has been established by ^{15}N n.m.r. spectroscopy and the hydrazido(2−)-complexes $[M(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$ (2) isolated from these solutions. When treated with H_2SO_4 in methanol, the complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (3), $[MX(NNH_2)(PMe_2Ph)_3L]^+$ (4)(X = Cl, Br, or I; L = tertiary phosphine or substituted pyridine), and $[M(NNH_2)(quin)(PMe_2Ph)_3]X$ (5) (quin = quinolin-8-olate) give ammonia or hydrazine in varying yields depending upon the complex. Ammonia is also obtained by treating $[MX_2(NNH_2)(PMe_2Ph)_3]$ with $Na[BH_4]$ in thf or methanol, hydrides of the type $MH_n(PMe_2Ph)_3$ (M = W, n = 6; M = Mo, n unknown) which did not react with dinitrogen, being the metallic products. The tungsten hydrazido-(2−)-complexes, but not those of molybdenum, also give ammonia on treatment with aqueous K[OH]. The preparation and characterisation of the new hydrazido(2−)-complexes $[WBr(NNH_2)(NC_9H_7)(PMe_2Ph)_3]^+$ and $[W(NNH_2)L^1(PMe_2Ph)_3]^+$ (L^1 = $NC_5H_4CO_2$-2 or $NC_9H_6CO_2$-2) are also described.

OUR earlier studies of the reduction of dinitrogen at metal sites showed that the reactions of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (1; M = Mo or W) with acids such as H_2SO_4 in solvents such as methanol or tetrahydrofuran (thf) gave ammonia and hydrazine, the yield and ratio of the two products depending upon the metal, the solvent, and the acid used.[1] We have isolated a number of hydrazido-(2—)-complexes from these reactions and showed that they also react with further acid to give nitrogen hydrides,[2,3] again the yield of products and their ratio depended upon the metal and also upon the nature of the other ligands.[3] These studies clearly indicated hydrazido(2—)-complexes as intermediates in the protonation of dinitrogen complexes. In this paper we give full details of these protonation reactions and also present ^{15}N n.m.r. spectroscopic data which confirm the intermediacy of hydrazido(2—)-species in thf solution where complexes (1) are reacting with sulphuric acid.

RESULTS AND DISCUSSION

Nitrogen-15 N.M.R. Experiments.—(Performed in collaboration with Drs. J. Mason, Open University, and I. A. Stenhouse, P.C.M.U., Harwell). The reaction of an excess of sulphuric acid (20 : 1 mole ratio) with complexes (1) in thf was monitored by ^{15}N n.m.r. spectroscopy by adding the acid to a solution of the complex in the n.m.r. tube, allowing the reaction to proceed for suitable time intervals at 20 °C, but measuring the spectrum at −30 °C when the reaction rate was effectively zero. This cooling technique had to be employed because the necessarily long accumulation times would have exceeded the total reaction time if determined at 20 °C. In this way the degradation of the resonances of the starting complexes (1) and the formation of intermediate hydrazido(2—)-complexes were observed, making use of the ^{15}N n.m.r. parameters already established for these ligands.[4] The results are shown diagrammatically in Figure 1 and chemical shifts are tabulated in Table 1.

The reaction of complexes (1) with H_2SO_4 in thf involves the loss of one molecule of dinitrogen as the gas, followed by degradation of the second dinitrogen ligand to give ammonia.[1] This reaction course is clearly shown by the ^{15}N n.m.r. data to pass through the ligating hydrazido(2—)-stage in the reactions of both metal complexes (Figure 1). In both reactions the resonances

TABLE 1

^{15}N Chemical shifts of intermediate hydrazido(2−)-ligands in reaction of *cis*-$[M(^{15}N_2)_2(PMe_2Ph)_4]$ *with* H_2SO_4 in thf

Intermediate [a]	Chemical shift/ p.p.m.[b]	Assignment [c]
(*a*) For M = Mo		
I	−43.1	N_α
	−231.9	$N_\beta H_2$
II	−58.6	N_α
	−236.5	$N_\beta H_2$
(*b*) For M = W		
I	−78.2	N_α
	−243.0	$N_\beta H_2$
II	−87.3	N_α
	−254.8	$N_\beta H_2$
III	−232.4	$N_\beta H_2$
IV	−240.8	$N_\beta H_2$
V	−250.6	$N_\beta H_2$
VI	−235.2	$N_\beta H_2$

[a] See text and Figure 1. [b] Relative to external CH_3NO_2. [c] Gated broad-band proton decoupling employed to achieve maximum n.o.e. for protonated nitrogen.

characteristic of ligating dinitrogen [4] [Figure 1(*a*)] disappeared in *ca.* 10 min with the appearance of the resonance of free $^{15}N_2$ (−75 p.p.m.) and resonances characteristic of hydrazido(2—)-complexes,[4] which showed nuclear Overhauser effect (n.o.e.) inversion of the NH_2 resonance [Figure 1(*b*)] under broad-band proton decoupling. For both complexes, more than one hydrazido(2—)-resonance was observed, two for (1; M = Mo) and six for (1; M = W) (Figure 1, Table 1). These species were monitored by their NH_2 resonances which needed shorter accumulation times because of their enhancement by n.o.e. Although the order of appearance of these signals was uncertain they are clearly due

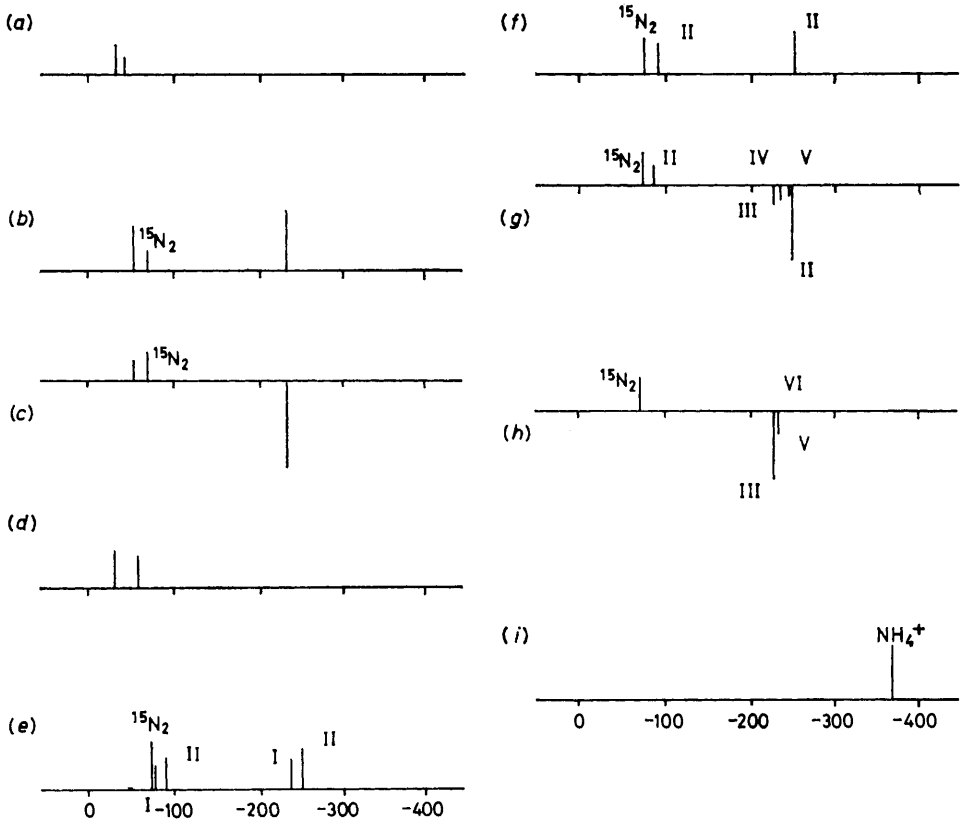


FIGURE 1 Nitrogen-15 n.m.r. spectra (schematic) of the reaction of *cis*-$[M(^{15}N_2)_2(PMe_2Ph)_4]$ with H_2SO_4 in thf. M = Mo for (*a*)—(*c*), M = W for (*d*)—(*i*). Sample temperature, −30 °C, except for (*i*), 20 °C. Reaction time: 0 (*a*) and (*d*); 10 (*b*) and (*e*); 25 (*f*); 55 (*g*); 90 (*h*); 120 (*i*); and 140 min (*c*)

to hydrazido(2—)-groups in different co-ordination environments. For (1; M = W) these signals also degraded and after *ca.* 120 min reaction time a resonance at −364 p.p.m. assignable to $^{15}NH_4^+$ was observed, the temperature being allowed to remain at 20 °C for this measurement to minimise precipitation of ammonium sulphate. In contrast, no signal due to ammonium was observed for (1; M = Mo) although the hydrazido(2—)-resonances had completely disappeared after *ca.* 4 h reaction time. Possibly the ammonium sulphate had precipitated from the reaction or paramagnetic product species (see below), which were shown to be present by e.s.r. measurement on the reaction solution, caused loss of signal.

In separate experiments, the complexes $[M(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$ (2) were precipitated from reacting solutions of (1) in thf–H_2SO_4 by rapid addition of pentane after *ca.* 30 min reaction at 20 °C. Complexes (2) are very sensitive to air and moisture and could not be recrystallised so that (2; M = Mo) was not obtained pure. Physical properties of (2; M = Mo) are shown in Table 2. Both complexes (2) gave ammonia on treatment with sulphuric acid in thf and most notably (2; M = W) gave ammonia in the same yield (1.9 mol NH_3 per mol W) on treatment with methanol alone as is obtained by treatment of (1; M = W) with H_2SO_4 in methanol. This behaviour contrasts with the properties of analogues of (2; M = W), where halide instead of HSO_4^- ligates the metal, which do not react with methanol [2,3] (see later). Evidently the π-releasing ability of the HSO_4^- ligand increases the susceptibility of the hydrazido(2—)-group to electrophilic attack.

Complexes (2) are poorly soluble except in pyridine, which caused displacement of phosphine, so that a reliable structural assignment cannot be made and ^{15}N n.m.r. data could not be obtained. Nevertheless, (2; M = W) is doubtless one of the intermediates observed in the ^{15}N n.m.r. experiment formed by protonation and phosphine displacement from (1; M = W). Further intermediates probably involve isomerisation and further phosphine displacement by sulphato-type ligands. Attempts to follow the reactions by ^{31}P n.m.r. spectroscopy under the same conditions as used for ^{15}N measurements showed the resonance due to free displaced phosphine, and other resonances typical of the meridional arrangement of phosphine ligands in hydrazido(2—)-complexes,[2] but the complexity of the spectra precluded detailed analysis.

Thus far, no other species appears to have sufficient concentration to be observed by ^{15}N n.m.r. or other spectroscopic means before or after the hydrazido(2—)-stage of reduction of dinitrogen. Nevertheless the characterisation of MNNH, MNH, and M≡N complexes by ^{15}N n.m.r. spectroscopy,[5] to be described separately,

TABLE 2

Physical properties of hydrazido(2−)-complexes and acid adducts

Complex	Yield/%	Colour	M.p. (θ_c/°C)	Analyses/% [a] C	H	N	Other	Molar conductance [b] $ClCH_2CH_2Cl$	CH_3NO_2
$[WBr(NNH_2)(NC_9H_7)(PMe_2Ph)_3]Br\cdot C_9H_7N$	56	Red	195—197	48.2 (48.2)	5.3 (4.7)	5.3 (5.3)		n.m.	n.m.
$[W(NNH_2)(NC_5H_4CO_2\text{-}2)(PMe_2Ph)_3]Cl$	48	Dark purple	190	45.7 (45.9)	5.1 (5.0)	5.4 (5.3)	6.2 (5.6) [c]	2	77
$[W(NNH_2)(NC_5H_4CO_2\text{-}2)(PMe_2Ph)_3]Br\cdot 0.5CH_2Cl_2$	66	Dark purple	110 (decomp.)	41.2 (41.9)	4.8 (4.6)	4.7 (4.8)		1	79
$[W(NNH_2)(NC_5H_4CO_2\text{-}2)(PMe_2Ph)_3]I$	42	Dark purple	154—156	40.6 (41.1)	4.7 (4.5)	4.7 (4.8)		8	109
$[W(NNH_2)(NC_9H_6CO_2\text{-}2)(PMe_2Ph)_3]Br$	44	Green	165 (decomp.)	45.3 (46.4)	4.6 (4.7)	4.7 (4.8)		4	93
$[W(NNH_2)(NC_9H_6CO_2\text{-}2)(PMe_2Ph)_3]I\cdot 2CH_2Cl_2$	53	Green	118 (decomp.)	41.2 (41.5)	4.6 (4.1)	3.7 (3.8)		14	108
$[W(NNH_2)(NC_5H_4CO_2\text{-}2)_2(PMe_2Ph)_3]\cdot NC_5H_4CO_2H\text{-}2$	43	Purple	90 (decomp.)	50.1 (50.7)	4.4 (4.7)	6.8 (7.0)		3	37
$[W(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$	51	Grey-brown	115 (decomp.)	34.4 (34.3)	4.6 (4.4)	3.0 (3.3)		*d*	*d*
$[W(NNH_2)(quin)(PMe_2Ph)_3]Cl\cdot H_2SO_4$	60	Red	90 (decomp.)	43.7 (43.7)	4.9 (4.8)	4.8 (4.6)		*d*	*d*
$[W(NNH_2)(quin)(PMe_2Ph)_3]Br\cdot H_2SO_4$	65	Red	134—136	42.3 (41.7)	4.8 (4.6)	4.4 (4.4)	3.5 (3.4) [c] 8.3 (8.4) [f]	*d*	*d*

[a] Calculated values are given in parentheses. [b] Values in S cm² mol⁻¹. n.m. = Not measured. [c] Cl analysis. [d] Decomposes in solution, molybdenum analogue could not be purified, see text. [e] S analysis. [f] Br analysis.

will aid in future attempts to gain more detailed information of the course of these reactions.

Protonation Reactions of Hydrazido(2−)-complexes.— This study was prompted by the solvent dependence of the reactions of complexes (1) with acids, which might involve co-ordination of solvent to the metal. We have therefore investigated the further protonation of the complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (3; X = Cl, Br, or I), $[MX(NNH_2)(PMe_2Ph)_4]X$ (4), $[M(NNH_2)(quin)(PMe_2Ph)_3]X$ (5) (quin = quinolin-8-olate), and $[MX(NNH_2)(py)(PMe_2Ph)_3]X$ (6) to see if variation of the co-ordination environment at the metal would affect the nature of the hydride products. These complexes when treated with H_2SO_4 in methanol under standard conditions gave the products shown in Table 3.

A number of effects are apparent from these data. First, as was originally observed in the reactions of complexes (1),[1] under these conditions there is a dependence of yield upon the metal. Thus hydrazine is only obtained in this series from tungsten complexes {although $[MoCl_2(NNH_2)(PMe_2Ph)_3]$ has been shown[6] to give hydrazine with HCl in dimethoxyethane} and the maximum yield of reduced nitrogen product for tungsten is twice that of molybdenum.

TABLE 3

Reaction of hydrazido(2−)-complexes with H_2SO_4–MeOH [a]

Complex	NH_3 [b,c]	N_2H_4 [b,c]	N_2 [b,d]	N_2 balance/% [e]
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	1.26(4)	0.12(4)	n.m.	75
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	1.58(3)	0.05(2)	0.0	84
$[WI_2(NNH_2)(PMe_2Ph)_3]$	1.88(2)	0.04(2)	0.0	94
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	0.61(4)	0.0	0.44	75
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	0.98(6)	0.0	0.38	87
$[MoI_2(NNH_2)(PMe_2Ph)_3]$	0.99(7)	0.0	0.40	90
$[WCl(NNH_2)(PMe_2Ph)_4]Cl$	1.46(3)	0.04(2)	0.0	77
$[WBr(NNH_2)(PMe_2Ph)_4]Br$	1.69(1)	0.01(0)	0.0	86
$[WI(NNH_2)(PMe_2Ph)_4]I$	1.90(0)	0.05(0)	0.0	100
$[MoCl(NNH_2)(PMe_2Ph)_4]Cl$	0.56	0.0	0.2	48
$[MoBr(NNH_2)(PMe_2Ph)_4]Br$	0.49	0.0	0.0	24.5
$[MoI(NNH_2)(PMe_2Ph)_4]I$	0.30	0.0	0.0	15
$[WCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	*f*	0.17(1)	n.m.	
$[WBr(NNH_2)(py)(PMe_2Ph)_3]Br$	1.38 [f]	0.09(0)	0.0	78 [g]
$[WI(NNH_2)(py)(PMe_2Ph)_3]I$	*f*	0.04(0)	n.m.	
$[MoCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	*f*	0.0	0.0	
$[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$	0.07(4)	0.30(4)	0.0	34
$[W(NNH_2)(quin)(PMe_2Ph)_3]Br$	0.0	0.38(1)	n.m.	38
$[W(NNH_2)(quin)(PMe_2Ph)_3]I$	0.0	0.39(0)	n.m.	39
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Cl$	0.58(7)	0.0	0.28	57
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Br$	0.55(0)	0.0	0.12	40
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]I$	0.55(0)	0.0	0.17	45

[a] Complex (*ca.* 0.1 mmol) treated with H_2SO_4 (*ca.* 2 mmol) in MeOH (40 cm³). The NH_3 and N_2H_4 were determined by colour tests, as in ref. 1, after distillation from an excess of K[OH]. [b] Mol per mol metal. [c] Error in last figure averaged over at least two measurements. [d] Evolved during protonation reaction. n.m. = Not measured. [e] Percentage nitrogen accounted for. [f] Pyridine interferes with indophenol test, ammonia inferred from oxidation of trap solution. [g] Sodium hypobromite oxidation of trapped ammonia–hydrazine solution.

Second are the marked ligand effects. We have already shown that the yield of ammonia from reactions of complexes (1) with various acids depend upon the anion of the acid.[1] Thus the reaction of (1; M = Mo) with H_2SO_4 in thf or methanol gives 0.7 mol NH_3 per mol Mo whereas HBr gives 0.9 mol.[1] This anion dependence can now be traced to the ligand environment at the hydrazido(2—)-stage since (Table 3) in the series (3; X = Cl, Br, or I) the yield of ammonia increases on passing from chloride to iodide (from 0.7 to 0.95 mol NH_3 per mol Mo, 1.26—1.88 mol NH_3 per mol W). There is thus a *trans* effect of the anion upon the further reaction of the hydrazido(2—)-group. A similar effect occurs in complexes (4) (Table 3) but a very dramatic effect is observed for complexes (5) which contain the quinolin-8-olate ligand, with oxygen *trans* to the hydrazido(2—)-group.[3] For (5; M = Mo) a moderate yield of ammonia (0.55 mol) is obtained, but no ammonia is observed for (5; M = W), instead hydrazine and dinitrogen are the only products. Presumably the production of hydrazine from $[MoCl_2(NNH_2)(PMe_2Ph)_3]$ specifically with HCl in dimethoxyethane is a consequence of co-ordination of this solvent to molybdenum.[6]

Because mechanistic details of these reactions have not yet been determined, it is premature to speculate on the reasons for the marked difference in behaviour of complexes (5) but *X*-ray structure determinations of (5; M = W, X = I; M = Mo, X = Br or I)[4] have shown that there is no marked structural difference for (5; M = W) compared to its molybdenum analogues. The co-ordination environment is the same for both Mo and W and the bond lengths of the M=N–NH_2 unit are, for both metals, not significantly different from those observed in related hydrazido(2—)-complexes.[3] There are some differences in the hydrogen-bonding schemes between the NH_2 group and the two anions for the various complexes, but these factors are unlikely to be significant in influencing the products of protonation reactions in solution. Thus it appears that the electronic condition of the hydrazido(2—)-group plays the dominant role in determining its further reactions.

Unfortunately pyridine (py) interferes with the indophenol test for ammonia and few determinations of ammonia were therefore carried out on complexes (6). The yield from (6; M = W, X = Br) was obtained by difference after oxidation of the products to dinitrogen with sodium hypobromite (Table 3).

In general, it appears that the different yields of nitrogenous products from protonation reactions of hydrazido(2—)-complexes are primarily determined by the metal. For tungsten, the production of a maximum of 2 moles of ammonia per metal is accommodated by a mechanism described elsewhere[1,7] involving stepwise terminal protonation and N–N bond cleavage *via* the intermediate W=N–NH_3^+. The yield of ammonia obtained from molybdenum complexes maximises at 1 mol per mol Mo atoms (Table 3). Thus if the reaction is stoicheiometric, the final oxidation state of molybdenum must be three. A mononuclear molybdenum(III) d^3 ion must be paramagnetic,[8] and hence it would produce the paramagnetic solution and loss of ^{15}N n.m.r. signals described above.

Confirmation of this view comes from the isolation of molybdenum(III) products from the related reactions of HX with $[Mo(N_2)\{PPh(CH_2CH_2PPh_2)_2\}(PPh_3)]$ (X = Br)[9] and *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (X = Cl, Br, or I)[10] in tetrahydrofuran. Yields lower than 1 mol NH_3 per mol Mo may be due to the general lability of the molybdenum complexes or possibly other mechanisms, such as diazene disproportionation,[1] may operate depending upon the conditions. Production of hydrazine and an equivalent amount of N_2 from complexes (5; M = W) probably involves hydrolysis of the hydrazido(2—)-complex to give hydrazine perhaps through a sideways-bound hydrazido(1—)-intermediate, such as has been characterised[11] in the complex cation $[Mo(NNMePh)(NHNMe_2)(S_2CNMe_2)_2]^+$. However, the nitrogen balance in these latter reactions and a few others is poor and further studies are in hand to elucidate the details of the mechanism of the reactions of hydrazido(2—)-complexes.

In all cases the yields of ammonia are determined after distillation from base (see Experimental section) because this gave the most reproducible results. It was not an essential step in ammonia production, however, since positive but somewhat variable indophenol tests could be carried out directly on the reaction solution and in some reactions in thf, ammonium sulphate separated from the solution. The molybdenum reactions are very sensitive to traces of dioxygen, however, which must be rigorously excluded at all stages otherwise very low yields of ammonia result.

Adducts of Hydrazido(2—)-complexes with Sulphuric Acid.—In an attempt to isolate further protonated species which might be formed during these reactions, the complexes (5; M = W) were treated with an excess of sulphuric acid in thf and red adducts were obtained by precipitation with diethyl ether. For (5; X = I), 8-hydroxyquinolinium hydrogensulphate precipitated from the red solution and no product could be isolated. No product could be isolated from similar reactions using other hydrazido(2—)-complexes.

The physical properties of the red, air-sensitive adducts are shown in Table 2. When dry, they dissociate in the few solvents in which they dissolve. Addition of any base, even water, to their suspensions regenerates the starting complexes (5) and thus they are characterised by analysis and i.r. spectra only. Their precise formulation is uncertain, but the occurrence of i.r. bands assignable to PH^+ and NH^+ suggest that they are phosphonium salts, possibly with the nitrogen of the quinolin-8-olate ligand protonated. Other reactions of halogen acids with hydrazido(2—)-complexes of tungsten, which give hydride hydrazido(2—)-complexes,[12] will be described elsewhere.

Reactions of Hydrazido(2—)-complexes with Base.—Treatment of the complexes (1) with 40% w/v K[OH] solution at *ca.* 100 °C results in the loss of all the co-ordinated dinitrogen as gas. Similar loss of dinitrogen

TABLE 4

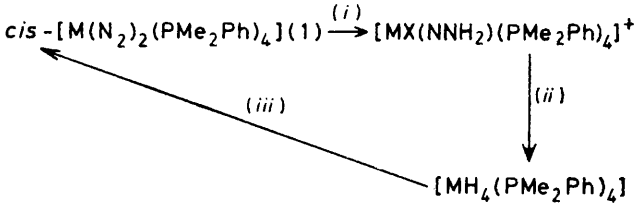
Reaction of hydrazido(2−)-complexes with 40% K[OH] [a] solution

Complex	NH_3 [b,c]	N_2H_4 [b,c]	N_2 [b,d]	N_2 balance/% [e]
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	1.40(3)	0.14(3)	n.m.	84
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	1.38(2)	0.13(3)	n.m.	82
$[WI_2(NNH_2)(PMe_2Ph)_3]$	1.30(1)	0.15(1)	n.m.	80
$[WCl(NNH_2)(PMe_2Ph)_4]Cl$	0.60(2)	0.18(0)	n.m.	48
$[WBr(NNH_2)(PMe_2Ph)_4]Br$	0.32(5)	0.19(1)	n.m.	35
$[WI(NNH_2)(PMe_2Ph)_4]I$	0.26(6)	0.11(3)	n.m.	24
$[WCl(NNH_2)(py)(PMe_2Ph)_3]Cl$		0.22(4)	n.m.	
$[WBr(NNH_2)(py)(PMe_2Ph)_3]Br$		0.13(1)	n.m.	
$[WI(NNH_2)(py)(PMe_2Ph)_3]I$		0.14(0)	n.m.	
$[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$	0.06(1)	0.13(1)	0.35	51
$[W(NNH_2)(quin)(PMe_2Ph)_3]Br$	0.03(1)	0.26(2)	0.43	70
$[W(NNH_2)(quin)(PMe_2Ph)_3]I$	0.03(1)	0.43(2)	0.45	89
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Cl$	0.02(0)	0.0		
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Br$	0.02(0)	0.0		
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]I$	0.0	0.0		

[a] Complex (*ca.* 0.1 mmol) treated with K[OH] (*ca.* 100 mmol) in H_2O (10 cm^3). The NH_3 and N_2H_4 were determined by colour tests. [b] Mol per mol metal. [c] Evolved during *in vacuo* base treatment. [d] n.m. = Not measured. [e] Percentage nitrogen accounted for.

occurs for the molybdenum hydrazido(2−)-complexes, and no ammonia or hydrazine is formed, but the tungsten complexes, surprisingly, give ammonia or hydrazine in yields which approach those obtained from protonation reactions (Table 4). The mechanism of these reactions is unlikely to be easily established because of the non-homogeneity and high temperature, but it may involve substitution at the metal of hydroxide after deprotonation of the hydrazido(2−)-ligand followed by abstraction of protons from water by diazenido- and hydrazido-(2−)-complexes which are rendered more basic by the *trans* hydroxide ligand. A similar process has been invoked to explain the production of ammonia from *trans*-$[MoX(NH)(Ph_2PCH_2CH_2PPh_2)_2]^+$ in basic methanol.[13] Alternative processes could involve proton transfer from ligating hydroxide to the N_2H_2 ligand, generating a tungsten oxide, or displacement of isodiazene as a consequence of hydroxide attack followed by its disproportionation.

Reactions of Hydrazido(2−)-complexes with Hydrides.— We have already shown that treatment of the hydrazido-(2−)-complexes $[MoBr(NNH_2)(dppe)_2]Br$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $Na[BH_4]$ gives the hydride $[MoH_4(dppe)_2]$ from which dinitrogen can displace dihydrogen to give *trans*-$[Mo(N_2)_2(dppe)]$.[14] No ammonia



SCHEME (*i*) 2HX, $-N_2$; (*ii*) $Na[BH_4]$, $-NH_3$; (iii) $2N_2$, $-2H_2$

was produced in this reaction but we hoped that treatment of complexes (3) or (4) under the same conditions would give ammonia and allow us to regenerate the parent complexes (1) *via* a hydride, thus producing a cycle for dinitrogen reduction as shown in the Scheme.

Table 5 lists the yields of ammonia and hydrazine obtained from treatment of complexes (3) and (4) with $Na[BH_4]$ in methanol or thf solution under argon. Although ammonia was obtained, isolation of the metal hydride product was only successful for reaction of (2; M = W, X = Br) where $[WH_6(PMe_2Ph)_3]$ [15] was obtained in poor yield. Neither this compound nor impure hydrides obtained from other reactions showed any interaction with dinitrogen. Although the cycle of the Scheme appears to be sound in principle the correct choice of starting complex has not yet been achieved.

Preparation of New Hydrazido(2−)-complexes.— During the course of this work a number of new analogues of the hydrazido(2−)-complexes discussed above were prepared either from complexes (3; M = W) by ligand displacement *e.g.* equation (2), or directly from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ equation (3). Physical pro-

$$[WX_2(NNH_2)(PMe_2Ph)_3] + 2\ NC_5H_4CO_2H\text{-}2 \xrightarrow{CH_2Cl_2} [W(NNH_2)(NC_5H_4CO_2\text{-}2)(PMe_2Ph)_3]X + [HNC_5H_4CO_2H\text{-}2]X \quad (2)$$

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] + 4\ NC_5H_4CO_2H\text{-}2 \xrightarrow{thf} N_2 + [PMe_2PhH][NC_5H_4CO_2\text{-}2] + [W(NNH_2)(NC_5H_4CO_2\text{-}2)_2(PMe_2Ph)_3]\cdot NC_5H_4CO_2H\text{-}2\ (7) \quad (3)$$

perties of these complexes are shown in Table 2. The assignment of their structures is based upon these properties and spectroscopic data. Generally the meridional configuration of phosphine ligands shown by their analogues [2] and the presence of molecules of uncoordinated ligands in the crystal, which often occurs in these complexes,[2] are confirmed by their ^1H and ^{31}P n.m.r. spectra which, together with i.r. data, have been deposited as Supplementary Publication No. SUP 23089 (7 pp.).*

A problem arises over the assignment of the structure of complex (7) [equation (3)]. The ^{31}P-$\{^1H\}$ n.m.r. spectrum clearly shows the meridional phosphine arrangement, but the unique phosphine is at substanti-

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 5

Reactions of hydrazido(2−)- and other complexes of Mo and W with $Na[BH_4]$

Complex	Reaction atmosphere	Reducing agent	Solvent	NH_3 [a]	N_2H_4 [a]
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	Argon	$Na[BH_4]$	MeOH [b]	0.7—0.9	Trace [c]
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	Argon	$Na[BH_4]$	thf [b]	1.3	0.0
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	H_2		MeOH	0.0	0.0
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	Argon		MeOH	0.0	0.0
$[WBr(NNH_2)(PMe_2Ph)_4]Br$	Argon	$Na[BH_4]$	MeOH	0.9	Trace [c]
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	Argon	$Na[BH_4]$	MeOH	0.3	0.0
$[MoBr(NNH_2)(PMe_2Ph)_4]Br$	Argon	$Na[BH_4]$	MeOH	0.2	0.0
$[WCl_4(PPh_3)_2]$	Argon	$Na[BH_4]$	MeOH	Trace	0.0

[a] Determined colourimetrically and expressed as mol per mol metal. [b] $[WH_6(PMe_2Ph)_3]$ isolated on work up. [c] Trace amount, <0.05 mol per mol metal.

ally lower field (−130.3 p.p.m.) than in the other complexes of the series (*ca.* −145 p.p.m.). This may be due to the ligating atom being oxygen only *i.e.* as in Figure 2(*a*) but the alternative structure [Figure 2(*b*)] cannot

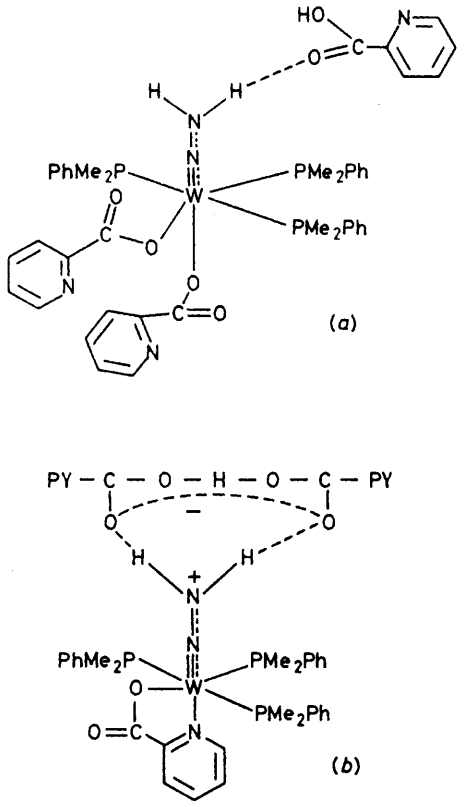


FIGURE 2 Two possible structures for compound (7)

be ruled out. This structure involves a formation of a hydrogenbis(pyridine-2-formate) anion, strongly hydrogen bonded to the hydrazido(2−)-groups. A similar anion has recently been proposed in the complexes $[WX(NNH_2)(dppe)_2]\cdot(CF_3CO_2)_2H$ (X = F, Br, or CF_3CO_2).[16]

Conclusions.—Hydrazido(2−)-complexes have been clearly demonstrated to be crucial intermediates in the reduction of ligating dinitrogen at molybdenum and tungsten. The final products of the reduction are then dependent upon the electronic condition of the hydrazido(2−)-group, which is determined by its coordination environment. This results in different mechanisms for further reduction of hydrazido(2−)-groups at molybdenum *versus* tungsten and future papers will examine this in more detail.

EXPERIMENTAL

Air-sensitive materials were handled under dinitrogen, argon, or high vacuum techniques as appropriate; non-condensible gases were determined by Toepler pump. N.m.r. spectra were recorded using JEOL PS100 (in the Fourier-transform mode for ^{31}P) or Bruker WH180 (^{15}N, P.C.M.U., Harwell) instruments. E.s.r. measurements were made with a Varian E9 spectrometer and mass spectra with an A.E.I. MS10 instrument. A Unicam SP2000 spectrometer was used for i.r. measurements, conductivities were determined with a Portland Electronics conductivity bridge, magnetic susceptibilities with a Faraday balance, and molecular weights with an Hitachi–Perkin-Elmer 115 osmometer. Analyses were by Mr. A. G. Olney of the University of Sussex. The dinitrogen [1] and hydrazido(2-)[2]-complexes used as starting materials were prepared by published methods. Solvents were dried and distilled before use; pyridines and quinolines were analytical grade and used without further purification.

Nitrogen-15 N.M.R. Experiments.—Sulphuric acid (*ca.* 10 molar excess) was added to a solution of *cis*-$[M(^{15}N_2)_2(PMe_2Ph)_4]$ (0.5 g) in thf (15 cm) in a 25-mm diameter n.m.r. tube under argon. When rapid evolution of $^{15}N_2$ had ceased the anti-vortex plug and capillary reference tube containing $C^2H_3NO_2$ were inserted and the tube was sealed. The solution was then cooled to −30 °C and the ^{15}N n.m.r. spectrum recorded at that temperature. The tube was then removed from the instrument, warmed to 20 °C for an appropriate reaction time, re-cooled to −30 °C, and a further spectrum recorded. A similar procedure was adopted for ^{31}P n.m.r. measurements.

Preparation of Tris(dimethylphenylphosphine)[hydrazido(2−)]bis(hydrogensulphato)tungsten, $[W(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$.—Sulphuric acid (1.0 mol equivalent) dissolved in tetrahydrofuran (10 cm^3) was slowly added to a stirred solution of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.55 g) in tetrahydrofuran (10 cm^3). After rapid evolution of dinitrogen (1.0 mol equivalent), the red solution was stirred for a further 30 min when it was filtered. Addition of pentane (40 cm^3) to the filtrate precipitates the title complex as an unstable grey-brown *solid* (0.3 g, 51%), which was washed with pentane and dried in a vacuum at 20 °C. The molybdenum analogue was similarly isolated but could not be obtained pure.

Identical procedures but employing phosphoric acid or fluoroboric acid gave no isolable materials.

Reaction of $[W(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$ *with Methanol.*—Methanol (10 cm^3) was added to the complex (0.033 g) and the resulting solution stirred under dinitrogen for 48 h at 20 °C. The solvent was then removed under reduced pressure and the remaining oil extracted with water (20 cm^3) for 0.5 h. The green precipitate was filtered off and the filtrate made up to 60 cm^3 with distilled water and tested for ammonia and hydrazine by standard techniques.

Reactions of Hydrazido(2−)-complexes with Sulphuric Acid in Methanol.—Methanol (35 cm^3) and concentrated sulphuric acid (15 molar excess) were added to an accurately known amount of the hydrazido(2−)-complex (*ca.* 0.15 g) in an inert atmosphere or under vacuum. After stirring for 48 h any evolved gases were measured (vacuum experiments) and the solvent removed under reduced pressure. The resulting oil was treated with 40% K[OH] solution (15 cm^3) and distilled into 0.5 mol dm^{-3} H_2SO_4 (10 cm^3) which was then analysed for ammonia and hydrazine as usual.

Reaction of $[W(NNH_2)(quin)(PMe_2Ph)_3]Br$ *with Sulphuric Acid in thf.*—Concentrated H_2SO_4 (0.3 cm^3) was added to a solution of $[W(NNH_2)(quin)(PMe_2Ph)_3]Br$ (0.18 g) in thf (25 cm^3) and the mixture stirred under dinitrogen for 1 h. The resulting red *precipitate* was filtered off, washed with thf (5 cm^3), diethyl ether (5 cm^3), and dried in a vacuum. The properties of this diamagnetic (e.s.r.) compound are shown in Table 2.

A similar red product was obtained from $[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$ but the iodide analogue gave initially a red solution which after 45 min deposited a yellow precipitate of 8-hydroxyquinolinium hydrogensulphate (0.03 g) (Found: C, 42.6; H, 4.1; N, 5.9. Calc. for $C_9H_9NO_5S$: C, 44.5; H, 3.7; N, 5.8%), identical m.p., i.r., and n.m.r. spectra to an authentic sample.

Treatment of suspensions of these complexes in CH_2Cl_2 with a small quantity of base (H_2O, NEt_3, or pyridine) immediately regenerated the dark purple starting material.

Reactions of Hydrazido(2−)-complexes with Potassium Hydroxide.—Method I (*under argon*). An accurately weighed quantity (*ca.* 0.05 g) of the complex was treated with 40% aqueous K[OH] solution (15 cm^3) under argon and the mixture distilled into 0.5 mol dm^{-3} H_2SO_4 (10 cm^3) in an all-glass apparatus.[1] Analysis for ammonia and hydrazine was then as usual.

Method II (*in a vacuum*). An accurately weighed quantity of complex (*ca.* 0.05 g) and 40% K[OH] solution were placed in separate limbs of a glass U-tube apparatus; after degassing, the vessel was sealed under vacuum and the contents combined in one limb. The mixture was carefully heated with a bunsen flame until no further colour change occurred. The vessel was then cooled to −196 °C, opened *via* a break-seal, and the evolved gas determined. The apparatus was then filled with argon, the solution transferred to the distillation apparatus and analysed for ammonia and hydrazine as usual.

Reactions of Hydrazido(2−)-complexes with Sodium Tetrahydroborate.—Sodium tetrahydroborate (*ca.* 0.2 g) and methanol (20 cm^3) were added to a known amount of complex (*ca.* 0.2 g) under argon. The flask was immediately connected to an acid trap (0.5 mol dm^{-3} H_2SO_4, 10 cm^3) through which the evolved volatiles were swept with an argon stream for 16 h. The trap was then analysed for ammonia and hydrazine and the reaction solution was reduced to dryness in a vacuum, the distillate being collected in 0.5 mol dm^{-3} H_2SO_4 (5 cm^3) which was also analysed for ammonia and hydrazine after combination with aqueous washings of the crude residual reaction solid. After the above procedure was followed for $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (0.29 g) and sodium tetrahydroborate (0.3 g), the final crude solid was extracted with hexane (20 cm^3) which was then concentrated to *ca.* half volume under reduced pressure and allowed to stand at −15 °C. Careful filtration of the solution at 0 °C gave white needles (0.05 g) which were washed with cold hexane, dried in a vacuum, and identified (i.r., n.m.r.) as $[WH_6(PMe_2Ph)_3]$ [15] (Found: C, 47.1; H, 6.7. $C_{24}H_{39}P_3W$ requires C, 47.7; H, 6.5%).

Similar reactions without $Na[BH_4]$, or using $[WCl_4(PPh_3)_2]$ as starting material or a dihydrogen atmosphere, gave negligible amounts of ammonia and hydrazine.

Preparation of Bromotris(dimethylphenylphosphine)[hydrazido(2−)]quinolinetungsten Bromide, $[WBr(NNH_2)(NC_9H_7)(PMe_2Ph)_3]Br$.—An excess of quinoline (20 cm^3) was added to $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (0.19 g) and the resulting suspension stirred vigorously for 2 h at 20 °C. Diethyl ether (80 cm^3) was carefully added, mixed, and the solution quickly filtered. On standing at 4 °C for several days, red *crystals* were deposited, which were filtered off, washed with water (5 cm^3), and dried in a vacuum (0.14 g, 56%).

Preparation of Tris(dimethylphenylphosphine)[hydrazido(2−)](pyridine-2-carboxylato)tungsten Chloride, $[W(NNH_2)(NC_5H_4CO_2\text{-}2)(PMe_2Ph)_3]Cl$.—Pyridine-2-carboxylic acid (0.14 g) was added to a suspension of $[WCl_2(NNH_2)(PMe_2Ph)_3]$ (0.36 g) in dichloromethane (30 cm^3) and the mixture was stirred overnight at 20 °C. The resulting purple solution was concentrated under reduced pressure to *ca.* 15 cm^3 and diethyl ether (50 cm^3) was carefully added and the mixture filtered immediately. Upon standing, the filtrate deposited very dark *crystals* (0.14 g, 48%) which were filtered off, washed with diethyl ether, and dried in a vacuum at 20 °C. The bromo- and iodo-analogues were similarly prepared.

Preparation of Tris(dimethylphenylphosphine)[hydrazido(2−)](quinoline-2-carboxylato)tungsten Bromide, $[W(NNH_2)(NC_9H_6CO_2\text{-}2)(PMe_2Ph)_3]Br$.—In an analogous procedure to that described above, addition of quinoline-2-carboxylic acid (0.3 g) to a suspension of $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (0.49 g) in dichloromethane (35 cm^3) gave, after 24 h and subsequent work-up, the title compound as a green *solid* (0.24 g, 44%) which was recrystallised from dichloromethane–diethyl ether. The iodo-analogue was similarly prepared but the choro-compound could not be obtained pure.

Preparation of Tris(dimethylphenylphosphine)[hydrazido(2−)]bis(pyridine-2-carboxylato)tungsten, $[W(NNH_2)(NC_5H_4CO_2\text{-}2)_2(PMe_2Ph)_3]$.—Tetrahydrofuran (30 cm^3) was distilled onto *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.22 g) and pyridine-2-carboxylic acid (0.14 g) at −196 °C in a vacuum. On warming to room temperature a reaction occurred, producing initially a yellow-green and finally, after 16 h, a purple solution. Dinitrogen (1.0 mol) was evolved together with a trace of dihydrogen. Concentration of the solution under reduced pressure (to *ca.* 10 cm^3) and addition of pentane (10 cm^3) followed by rapid filtration gave a purple solution from which the title compound gave a purple

precipitate (0.12 g, 45%). The solid was washed with pentane and dried in a vacuum at 20 °C.

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