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Preliminary communication

DIAZENIDO (IMINONITROSYL) (N_2H), HYDRAZIDO(2–) (N_2H_2), AND HYDRAZIDO(1–) (N_2H_3) LIGANDS AS INTERMEDIATES IN THE REDUCTION OF LIGATING DINITROGEN TO AMMONIA

JOSEPH CHATT*, ALAN J. PEARMAN and RAYMOND L. RICHARDS
Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ (Great Britain)

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Summary

Complexes of molybdenum and tungsten containing the ligands N_2H, N_2H_2 and N_2H_3, have been obtained from dinitrogen complexes, and probably represent intermediate stages in the reduction of ligating dinitrogen to ammonia.

We recently reported [1] the reduction of dinitrogen in *cis*-$[M(N_2)_2(PMe_2Ph)$ (A, M = Mo or W) to ammonia by reaction with sulphuric acid in methanol at 20°C. The reaction is rapid and no intermediate products of reduction could be isolated. However, by the use of halogen acids and other tertiary phosphines as co-ligands, we have been able to isolate complexes containing dinitrogen in intermediate stages of reduction, as detailed below.

Compounds B, containing the hydrazido(2–) form of the N_2H_2 ligand, have been obtained from A according to reaction 1.

$$\underset{(A)}{cis\text{-}[M(N_2)_2(PMe_2Ph)_4]} + HX(excess) \xrightarrow[20^\circ C]{MeOH} \underset{(B)}{[MX_2(=N{-}NH_2)(PMe_2Ph)_3]} + N_2 + [PHMe_2Ph]X \qquad (1)$$

(M = Mo, X = Cl; M = W, X = Cl or Br)

This reaction is complete in less than two minutes, a shorter time than for the reaction of A with sulphuric acid to give ammonia [(A, M = Mo) about 4 min; (A, M = W) about 30 min], and the N_2H_2 ligand is probably an intermediate on the route to ammonia.

In accord with this view the $MeOH/H_2SO_4$ treatment of the complex B (M = W) gives 1.3-1.6 mol NH_3 and 0.05-0.15 mol N_2H_4 per W atom, whereas B (M = Mo) gives about half as much NH_3 and only a trace of N_2H_4 per Mo atom, closely

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*To whom correspondence should be addressed.

paralleling the yields obtained by $MeOH/H_2SO_4$ treatment of the parent dinitrogen complexes A (M = W or Mo).

Ammonia is also obtained in good yield (1.4 mol per W atom) from B (M = W) on distillation from 40% KOH, but only in traces from B (M = Mo). It is surprising that strong alkali gives so much ammonia from B (M = W), because mild alkali (NEt_3 or aq. K_2CO_3) removes hydrogen halide from $[MX_2(N_2H_2)(dpe)_2]$ (M = Mo or W; X = Cl or Br; dpe = $Ph_2PCH_2CH_2PPh_2$) [2] to form complexes of the hitherto unknown diazenido* (or iminonitrosyl) ligand [3]. These are diamagnetic, of formula $[MX(N_2H)(dpe)_2]$ and when X = Br have $\nu(N_2)$ 1940 cm^{-1} (M = Mo) and $\nu(N_2)$ 1880 cm^{-1} (M = W). It appears that in B (M = W) which has only three phosphine molecules ligating the tungsten atom, the N_2H_2 ligand is too basic to be deprotonated by aqueous alkali, and protonation proceeds to ammonia almost as well with acid. On the other hand, the N_2H_2 ligand in B (M = Mo) is deprotonated, because strong alkali liberates it almost entirely as dinitrogen.

The diazenido complexes revert quantitatively to the parent N_2H_2 complexes on treatment with one mole of halogen acid in thf at 20°C and they probably represent the first step in the protonation of the dinitrogen ligand to N_2H_2.

The reaction of *trans*-$[W(N_2)_2(PMePh_2)_4]$ (C), containing a more bulky phosphine, with hydrogen chloride in methanol does not yield an analogue of B, but ammonia (1.9 mol/W atom) and hydrazine (0.02 mol/W atom). However, in dichloromethane, C reacts with hydrogen chloride to give D, a complex containing a hydrazido(1–) ligand (eqn. 2).

$$\underset{\text{(C)}}{trans\text{-}[W(N_2)_2(PMePh_2)_4]} + HCl(\text{excess}) \rightarrow$$

$$\underset{\text{(D)}}{trans\text{-}[WCl_3(NH{\cdot}NH_2)(PMePh_2)_2]} + N_2 + 2[PHMePh_2]Cl \qquad (2)$$

Compound D has ν(NH) at 3123, 3197 and 3356 cm^{-1} (Nujol) and δ(NH) at 5.6 ppm (β-protons, broad singlet) and 12.1 ppm (α-proton, triplet, ^3J(PH) 91.6 Hz) relative to tetramethylsilane ($CDCl_3$). Sulphuric acid treatment of D in methanol at 20°C gives ammonia (0.6 mol) and hydrazine (0.25 mol).

Although products containing dinitrogen in the N_2H, N_2H_2 (two isomers) [2] and N_2H_3 stages of reduction have now been isolated, it is not clear how these are converted into ammonia rather than into hydrazine, or even whether the reduction occurs by the same mechanism in both the tungsten and the molybdenum series. It could be different, because the tungsten and molybdenum N_2H_2 complexes behave so differently with strong alkali, and the yields of ammonia from the $MeOH/H_2SO_4$ treatment of analogous complexes appear to be ideally two NH_3/W atom, but only one NH_3/Mo atom.

The above differences may reflect only the greater lability and poorer reducing power of molybdenum complexes in lower oxidation states, or a completely different mechanism. The possibility of a bridging N_2H_2 intermediate in the molybdenum case cannot be ignored, but seems unlikely in the case of

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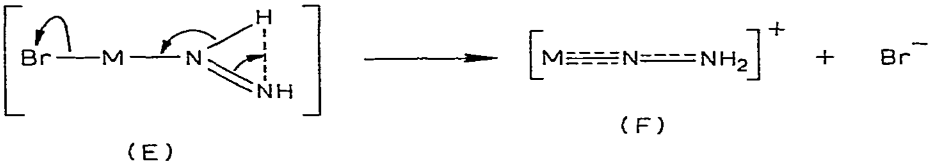
*The systematic name "diazenido" has been adopted, but the ligand is exactly analogous to nitrosyl and in these complexes will be linear as in the so-called NO^+ complexes.

tungsten because it is difficult to see how it could lead to a greater yield than only one NH_3/W atom.

The fact that hydrazine is a minor product even from the N_2H_2 and N_2H_3 complexes indicates a facile mechanism for the splitting of the N—N bond. The conversion [2] of the diazene ligand in $[WBr_2(NH{=}NH)(dpe)_2]$ (E) to the linear hydrazido(2–) form in $[WBr({=}N{-}NH_2)(dpe)_2]^+$ (F) indicates a mechanism of splitting as given below which may be pertinent to the reduction of dinitrogen to ammonia in these complexes and on nitrogenase.

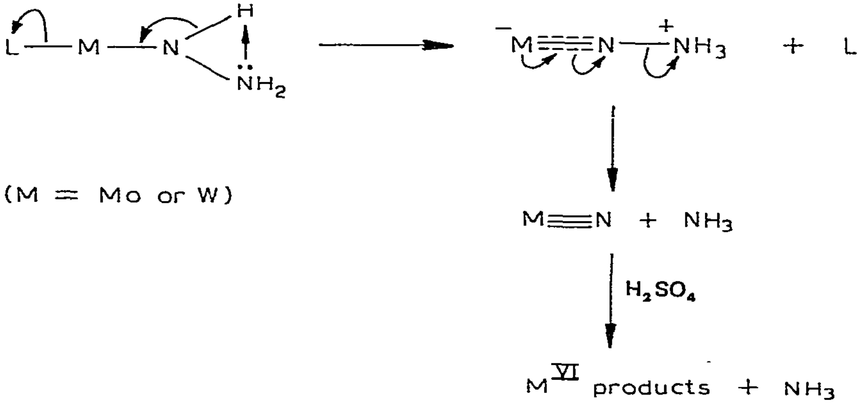
The conversion of E to F is controlled by the electron requirement of the metal [2]. The removal of a bromide ion from the closed shell complex E renders the metal electron-deficient, causing proton transfer as in reaction 3.



(3)

(M = Mo or W)

Similar conversion in an N_2H_3 complex such as D might also be induced by loss of a ligand leading to the formation of a hydrazinium(1–) complex (reaction 4a). Cleavage of the N—N bond would then be facilitated by the positive charge on the terminal nitrogen atom and easy supply of electrons from the metal atom (reaction 4b) to give ammonia and a nitride complex which would readily hydrolyse to produce the second molecule of ammonia (reaction 4c).



(4a)

(M = Mo or W)

(4b)

(4c)

References

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