

## Stepwise Conversion of Dinitrogen Co-ordinated to Molybdenum into an Amine and an Imido-complex. Relevance to the Reactions of Nitrogenase

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Conversion of dinitrogen bound terminally at a mononuclear molybdenum site into an imido-ligand (NH) and a secondary amine has been achieved by the reactions shown in Scheme 1; the mode of N–N cleavage and the retention of the four equatorial ligands may be characteristic of the reactions of nitrogenase.

Species containing Mo=N or Mo=NH groups have been postulated as intermediates in the sequential reduction of N<sub>2</sub> to NH<sub>3</sub> catalysed by the enzyme nitrogenase, and in the reactions of certain dinitrogen complexes or their derivatives with protic or hydridic reagents.<sup>1</sup> Here we describe the first example of a stepwise reaction sequence from dinitrogen co-ordinated end-on in a mononuclear molybdenum complex to an imido-complex with splitting of the N–N bond and concomitant generation of amine.

We have already shown that the dinitrogen complex [Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] (1) [dppe = 1,2-bis(diphenylphosphino)ethane] can be alkylated in a two-stage process to afford dialkylhydrazido(2–)-complexes *trans*-[MoBr(N<sub>2</sub>R<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> (2) (R = alkyl).<sup>2,3</sup> *Two-electron reduction* of complexes (2), either electrochemically or with LiBu<sup>t</sup>, in tetrahydrofuran (thf) under Ar gives dark red solutions containing an Mo<sup>II</sup> species identified as [Mo(N<sub>2</sub>R<sub>2</sub>)(dppe)<sub>2</sub>] (3) [R<sub>2</sub> = CH<sub>2</sub>–[CH<sub>2</sub>]<sub>n</sub>CH<sub>2</sub>, n = 2 or 3].<sup>4</sup> We now find that (3) (n = 3) reacts rapidly with anhydrous hydrogen bromide to give rose-coloured solutions from which [MoBr(NH)(dppe)<sub>2</sub>]Br (4) was isolated in 67% yield. Treatment of (4) with base converted it into the known nitrido-complex [MoBr(N)(dppe)<sub>2</sub>], the

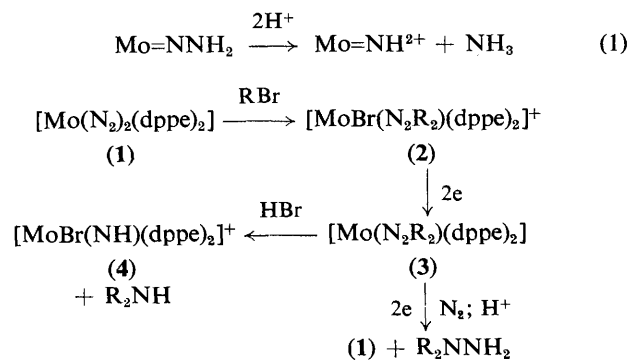
identity of which was confirmed by comparison with an authentic sample.<sup>5</sup>

The other major product of the reaction with hydrogen bromide is piperidine, isolated and determined by treatment with base, extraction, and gas–liquid chromatography. The yield of amine produced in solution by the reaction was 74% based on (2). About 30% of the amine could be recovered by our extraction procedure.

We have thus established two reduction pathways for the same mononuclear dialkylhydrazido(2–)-derivative: a *four-electron pathway* which yields a dialkylhydrazine and an Mo<sup>0</sup> complex<sup>4</sup> and a *two-electron pathway* which yields an amine and an Mo<sup>IV</sup> complex (Scheme 1).

Preliminary results suggest that alkylimido-complexes which are homologues of (4) undergo electrochemical reduction which parallels that of the hydrazido(2–)-complexes and which could lead to the regeneration of (1).

Various reported degradation reactions of dinitrogen, diazenido-, and hydrazido-complexes which give rise to ammonia or amines may also involve nitrido- or imido-complexes, but these have never been positively identified or characterised.<sup>1</sup> As yet we do not know the intimate mechanism



Scheme 1

of the N-N bond splitting in our reactions, but our results strongly support the idea that conversion of terminally coordinated dinitrogen, at a mononuclear molybdenum site such as may exist in nitrogenase, can occur *via* reaction (1).

Nitrogenase reactions need not incur any gross structural changes at the molybdenum site during turnover; all the conversions (1) → (2) → (3) → (4) occur with the conservation of the four ligands in the equatorial plane.

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