

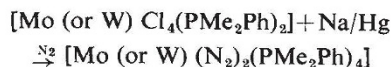
A hundred years ago



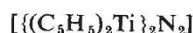
A RARE phenomenon, says the *Malta Times*, occurred in the forenoon of Monday, the 21st ult. During a strong wind from the south-west, which had prevailed for two days previously, the sea suddenly rose several feet and flooded the moles and roads surrounding the harbours, causing four or five steamers, moored between the Custom House and Calcare Rise, to snap their stern hawsers like packthreads, and carrying away boats that were hauled ashore in the French and other creeks. The sea then receded as suddenly as it rose, leaving portions of the bottom of the harbour exposed, upon which men and boys might be seen collecting fish and other marine animals that had been left aground by the retiring water. Shortly afterwards the sea resumed its ordinary level. Similar phenomena have been noticed occasionally during the course of many years.

From *Nature*, 11, 196, January 7, 1875.

from the Agricultural Research Council Unit of Nitrogen Fixation at the University of Sussex were first to devise a reaction based, appropriately, on a molybdenum complex (Bell, Chatt and Leigh, *Chem. Commun.*, 482, 1970).

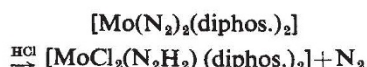


Subsequently, both Soviet and American teams succeeded in preparing



from gaseous nitrogen under mild conditions (Yu *et al.*, *Chem. Commun.*, 1178, 1972; Bercaw, Marvich, Bell and Brintzinger, *J. Am. Chem. Soc.*, 94, 1219, 1972; van Tamelen, Cretney, Klaentschi and Miller, *Chem. Commun.*, 481, 1972).

The second step required in the fixation process, the reduction of coordinated nitrogen to ammonia, has proved exceedingly difficult to achieve in any of the characterised complexes. Most attempts at reduction led to displacement of nitrogen. For example, solvolysis of $[\{(\text{C}_5\text{H}_5)_2\text{Ti}\}_2\text{N}_2]$ with methanolic HCl yields mainly nitrogen although ammonia and hydrazine appear as minor products. The first step in a well characterised partial reduction was achieved by Chatt, Heath and Richards in a reaction of their molybdenum (or tungsten) bis-dinitrogen complex with concentrated HCl (*Chem. Commun.*, 1010, 1972).



Now the persistence of the Sussex team has been rewarded. A report appearing in this issue of *Nature* (page 39) shows the room temperature reduction of *cis* or *trans*- $[\text{Mo (or W) (N}_2)_2(\text{PR}_3)_4]$ to two molecules of ammonia and one of nitrogen. The yields of ammonia go as high as 90% per nitrogen molecule reduced for a *cis* tungsten complex. Recently an interesting parallel development occurred in the United States, with the demonstration of the partial reduction of dinitrogen bound to a zirconium analogue of the cyclopentadienyl complex (Manriquez and Bercaw, *J. Am. Chem. Soc.*, 96, 6229, 1974). $[\text{C}_5(\text{CH}_3)_5]_2\text{ZrCl}_2$ undergoes reversible binding of nitrogen slowly at atmospheric pressure in the presence of sodium amalgam to form a binuclear species $[\{(\text{C}_5(\text{CH}_3)_5)_2\text{Zr}\}_2(\text{N}_2)_3]$. At -80°C , this product undergoes reaction with 10 M excess HCl in toluene releasing two molecules of nitrogen gas and forming a white solid, $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$.

There is an interesting contrast between the British and American reactions. The former seems to involve a metal ion oxidation state change of +6 to supply the reducing equivalents to produce two molecules of ammonia from one of nitrogen. In the American scheme, however, a dimeric metal complex supplies only four reducing equivalents to lower the oxidation state of N_2 to N_2H_4 . It has been thought extremely unlikely that the six reducing equivalents could be supplied by a single metal centre. It is a basic tenet of the theory of electron-transfer reactions, borne out by experiment, that probabilities of simultaneous transfers of two or more electrons are very low and indeed, there is now a general doctrine of compulsory one-electron steps in true electron transfer (as opposed to atom transfer) reactions. If reduction is brought about by a cluster of metal ions, a dimer for example, this difficulty is partially overcome. Thus the zirconium complex apparently involves only a two-electron transfer per metal atom. Such electron transfer processes are well known although taking place sequentially. The fact that nitrogenase contains a large number of metal ions lends some credence to the view that a multi-metal centre is responsible for reduction. A somewhat similar hypothesis persists for the terminal oxidases which supply four electrons for the reduction of oxygen to water. The presence of a number of metal redox sites in the enzymes again suggests a cooperative interaction between the centres to supply the necessary reducing equivalents without any one centre undergoing a large change in oxidation state.

For these reasons the claim by the Sussex group to have shown "that molecular nitrogen can be reduced at a single metal centre in a protic medium"

is important. It is clear that, according to the overall stoichiometry of the reaction, each metal ion supplies six reducing equivalents. But since no kinetic or mechanistic evidence is presented in this report, it is surely not yet possible to conclude that reduction has gone on at a single metal centre. The low oxidation states of molybdenum and tungsten are well known for a tendency to form clusters. A recent report (Cotton, Frenz and Webb, *J. Am. Chem. Soc.*, 95, 4431, 1973) describes the structures of two dimers of molybdenum, $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ and $[\text{Mo}_2(\text{SO}_4)_4]^{4-}$. Apparently sulphate ion, the medium used in the Sussex experiments, can bridge two molybdenum ions. Professor Chatt and his colleagues have themselves suggested that the difference between the susceptibility to solvolysis of the diphosphine and monophosphine complexes may reside in the lability towards substitution by sulphate ion of the latter ligand. In addition, they note the escape of one molecule of nitrogen on mixing the reagents. Thus, consideration should be given to the possibility that metal clusters are involved at some stage in multi-step reduction of nitrogen. Some mechanistic studies will clearly be necessary to resolve this problem. Although one may start a reaction with a "well-defined complex" and be able to write down the overall stoichiometry not all the intermediates are thereby defined. Undoubtedly these latest two reactions are going to provide useful models for exploration of the mechanisms and the intermediates by which multi-step reductions can occur.

Future for thin films

from A. G. Holmes-Siedle

THE table shown on page 9 was composed to stimulate discussion on the limitations and requirements for electronically active thin films when used for making solid-state devices. At present, almost all such devices are dependent on the use of major circuit elements made from single-crystal ingots (for example, most thin-film hybrid circuits contain a silicon transistor chip). The crystal must be grown with immense care, then sliced, polished, diffused and diced. More than 50 processing steps may thus be involved before a minute 'chip' with the required electronic functions is produced. The chip then has to be attached to a header and contacted by thin wires. Techniques are now available to produce many of the same electronic functions in the same volume of material using only thin layers which are deposited on an inert surface and then etched into complex patterns to form minute active circuit elements (see, for example, Maissel, *Handbook of Thin Film Technology*; McGraw-Hill, 1972).