

Nitrogen Fixation

(Incorporating the Liversidge Lecture, delivered in London, 18th November, 1971)*

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Nitrogen fixation is topical and the subject of many detailed reviews. Here the intention is to give a concise account of the present state of the subject in the light of our experience and that of our colleagues with reference to reviews and very recent papers only. We shall be concerned with developments over the past decade, which has seen a great surge of interest in the fixation of molecular nitrogen (*i.e.* dinitrogen) under mild conditions such as might simulate those found in biological nitrogen-fixing systems. Active extracts were obtained from bacteria only eleven years ago and the past six years have seen the development of the whole of the co-ordination chemistry of dinitrogen. This chemistry has added remarkably little to our knowledge of how the natural system works, but there is sufficient circumstantial evidence to suggest that it is relevant.

There are two main approaches to the study of nitrogen fixation. One is to study the natural nitrogen-fixing systems found in bacteria and some other very simple forms of life. The other is to attempt to make chemical models of the natural system to see whether any fixation of nitrogen can be achieved under mild reaction conditions such as one would expect to find in bacteria.

1 Biological Nitrogen Fixation

This, the more direct approach, has yielded very important biochemical information and much of interest to the chemist. The biochemical literature is vast (references 1–8 are recent and representative†) and here we can only summarize that of interest to chemists.

Only very primitive bacteria and some blue-green algae⁸ fix nitrogen.^{1–9}

* The lecture was also given in St. Andrews, 11th November, Aberystwyth, 25th November, 1971, Aberdeen, 8th March, and Glasgow, 9th March, 1972.

† Phrases in square brackets in references are descriptions of the contents of review articles.

¹ 'The Chemistry and Biochemistry of Nitrogen Fixation', ed. J. R. Postgate, Plenum Press, London, 1971.

² R. W. F. Hardy and R. C. Burns, *Ann. Rev. Biochem.*, 1968, **37**, 331. [Enzymology and chemistry of biological nitrogen fixation.]

³ R. W. F. Hardy and E. Knight, in 'Progress in Phytochemistry', ed. L. Rheinhold and Y. Liwshitz, Wiley, London, 1968, p. 407. [Biochemistry of nitrogen fixation.]

⁴ J. R. Postgate, *Symposium Soc. Gen. Microbiol.*, 1971, **21**, 287; ref. 1, p. 161. [Physiological chemistry of nitrogen fixation.]

⁵ R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Adv. Chem. Ser.*, 1971, No. 100, 219. [Biochemistry of nitrogen fixation.]

The bacteria have yielded most biochemical information. They are of two main types, symbiotic and free-living. The symbiotic, *e.g.* rhizobium, are the more important.¹⁰ They have normal bacterial lives in the soil but they do not fix nitrogen there. However, certain plants, especially the legumes, grown in soil deficient in fixed nitrogen, exude some substance which attracts a specific species of rhizobium to the root hairs. The organisms enter along the axis of the hair infecting certain cells and causing nodules to grow on the roots. The bacteria multiply briefly within a membrane in the infected cells, then change shape, increase in volume up to 40 times, and lose the power of reproduction. In this altered state they are called 'bacteroids' and they can fix nitrogen, providing the plant with ammonia in exchange for carbohydrate.

In contrast, the free-living bacteria live and fix nitrogen in the soil but are only important ecologically in barren soils.¹¹ They are the more easily cultured in the laboratory and most of our information concerning the chemistry and biochemistry of the natural process of nitrogen fixation has been obtained from them.

In 1930, Bortells showed that molybdenum is essential for nitrogen fixation by bacteria and is closely associated with the metabolism of dinitrogen. The bacteria grow well in the absence of added molybdenum if they are provided with a source of ammoniacal nitrogen but are unable to metabolize dinitrogen in the absence of molybdenum in excess of impurity levels. Indeed, in the presence of ammoniacal nitrogen the bacteria do not produce nitrogenase, the nitrogen-fixing enzyme. However, if the source of ammonia is removed, the bacteria can develop nitrogenase and metabolize dinitrogen within 1–10 h. The amount of molybdenum required by the bacteria is often very small, for example the bacteria *Beijerinckia indica* require only 0.004–0.034 p.p.m. for half optimal growth, and in culture 0.1 p.p.m. is ample. Vanadium, but no other metal, can be used by some cultures of bacteria in place of molybdenum. Iron, like molybdenum, is an essential trace element and magnesium ions are also necessary for nitrogen fixation.

The low solubility of dinitrogen in water does not limit the rate of fixation in bacteria, which is independent of pressure down to 0.1 atm. It seems that the enzyme has an enormous affinity for molecular nitrogen. The temperature is also somewhat critical. Bacteria work best between 15 and 25 °C. They are very slow at 0 °C and most cut off sharply at about 35–40 °C.

Studies using ¹⁵N₂ show that the first recognisable product from the natural system is ammonia. There is no evidence for the intermediate formation of

* R. W. F. Hardy and R. C. Burns, in 'Inorganic Biochemistry', ed. G. Eichorn, Elsevier, Amsterdam, 1972. [Bioinorganic chemistry of nitrogen fixation.]

† R. H. Burris, *Proc. Roy. Soc.*, 1969, **B172**, 339; ref. 1, p. 105. [Fixation by free-living microbes: enzymology.]

‡ R. M. Cox and P. Fay, *Proc. Roy. Soc.*, 1969, **B172**, 357. [Fixation by blue-green algae.]

§ W. D. P. Stewart, 'Nitrogen Fixation in Plants', Athlone Press, London, 1966.

¹⁰ F. Bergerson, *Proc. Roy. Soc.*, 1969, **B172**, 401; H. J. Evans and S. A. Russell, ref. 1, p. 191. [Fixation in leguminous systems.]

¹¹ W. D. P. Stewart, *Proc. Roy. Soc.*, 1969, **B172**, 367.

hydroxylamine, hyponitrous acid, di-imine, hydrazine, or any of the other substances which, on the basis of thermodynamic studies, might be intermediates. The dinitrogen in its intermediate stages of reduction is held by the enzyme, only ammonia being freed. Indeed, hydrazine is not reduced by the enzyme but poisons it.

It is often said that the bacteria are very efficient nitrogen fixers because they operate under mild conditions of temperature and pressure, with carbohydrate or similar reducing agent. However, in normal laboratory culture, they consume enormous amounts of energy in the form of carbohydrate; by this criterion they are highly inefficient. The most efficient fix only about 15 mg of nitrogen per 1g of glucose consumed, but laboratory systems devised to simulate natural conditions more precisely suggest that bacteria may actually be up to three times more efficient than this. It is claimed that the treatment of soil with waste molasses stimulates nitrogen fixation.

The enzyme nitrogenase, when extracted and tested *in vitro*, requires considerable amounts of adenosine triphosphate (ATP) to function. Approximately 15 moles ATP are hydrolysed to reduce 1 mole of dinitrogen to 2 of ammonia, a free energy dissipation in the region of 105 kcal mole⁻¹ of dinitrogen. The seemingly high energy requirement of the reduction is puzzling. If dinitrogen and dihydrogen were to react to equilibrium at atmospheric pressure and temperature, heat would be evolved and the equilibrium concentration of ammonia would approach 100%. Thus only an efficient catalyst is necessary and no additional energy in any system which can generate dihydrogen. All nitrogen-fixing bacteria contain hydrogenase and can generate dihydrogen (although not all hydrogenase-containing bacteria fix nitrogen). The bacteria do not utilize dihydrogen as such, and indeed, dihydrogen is a competitive inhibitor of nitrogen fixation. Presumably dihydrogen can compete with dinitrogen for the active site in the enzyme.

The nitrogenase system is not as specific as most enzyme systems. It will reduce a number of dinitrogen-like molecules, such as acetylene, which are competitive inhibitors of nitrogen fixation. Carbon monoxide is not reduced, but is a strongly competitive inhibitor. Table 1 lists such 'dinitrogen analogues' and their reactions with the bacteria or enzyme extracts. In some of these the triple bond is reductively split as in dinitrogen, but acetylene is reduced to ethylene free from ethane or methane, and dideuterioacetylene yields *cis*-dideuterioethylene. All those substances in Table 1 which have a well-developed co-ordination chemistry also have a high affinity for class *b* transition-metal ions¹² although other such substances, *e.g.* C₂H₄ or P(CH₂OH)₃, do not interfere with the nitrogenase system, perhaps for steric reasons. Only small rod-like molecules interfere; methylacetylene is reduced more slowly than acetylene and ethylacetylene slower still. Dimethylacetylene and diphenylacetylene are not reduced at all.

¹² S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, 12, 265. [Class *a* and class *b* metal ions.]

Table 1 *Substances which interact with the nitrogenase system*

<i>Substance</i>	<i>Interaction or reduction product</i>	<i>Relative rates^a</i>
N ₂	2NH ₃	1.0
C ₂ H ₂	C ₂ H ₄	4.0
N ₃ ⁻	NH ₃ , N ₂	3.0
N ₂ O	N ₂ , H ₂ O	3.0
MeNC	CH ₄ , MeNH ₂ , traces of C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , etc.	0.8
MeCN	C ₂ H ₆	0.004
EtCN	C ₃ H ₈ , NH ₃	0.003
CH ₂ =CHCN	C ₃ H ₆ , C ₃ H ₈ , NH ₃	0.2
CN ⁻	CH ₄ , NH ₃ , MeNH ₂	0.6
H ₂	Competitive inhibition of nitrogen fixation	
CO	Strong inhibition of nitrogen fixation	
NO	Inhibition	
N ₂ H ₄	Inhibition	

^a Obtained from the rate of formation of reduction products from an enzyme saturated with substrate⁵

The reduction of acetylene to ethylene provides a very quick quantitative test for nitrogen fixation because the ratio of the two gases is readily determined in minute concentration by gas-liquid chromatography. It is often useful to measure fixation in soil under natural conditions, or to screen bacteria for nitrogen-fixing activity, but positive acetylene tests on bacteria should always be confirmed by mass spectrometric tests of ¹⁵N₂ metabolism. No anomalous result has yet been reported from the acetylene test.

Before 1960 all attempts to obtain active nitrogen-fixing cell-free extracts from bacteria failed, leading to the view that nitrogenase was very unstable. Then Carnahan, Mortenson, Mower, and Castle, working with *Clostridium pasteurianum*, discovered that it was essential to exclude dioxygen from the bacterial extracts. Their discovery sparked the present phase of interest in nitrogen fixation. They also found that nitrogenase alone did not cause the reduction of dinitrogen. The system also needed an electron carrier, such as ferredoxin, and a reducing agent (sodium pyruvate) which appeared to be somewhat specific because, as later discovered, it activated an ATP-generating system. The whole had to be buffered to about neutral pH. Later Bulen, Burns, and LeComte showed that sodium dithionite is an excellent artificial reducing agent which can replace both the electron carrier and the more natural reducing agent. They produced a very simple method for the assay of nitrogenase. Sodium dithionite and an ATP-generating system (adenosine diphosphate, creatine phosphate, and creatine kinase) were added to the buffered bacterial extract under argon. This caused the evolution of dihydrogen at a rate which was measured. In a parallel experiment under dinitrogen the rate of dihydrogen evolution was lower. The decrease in rate of dihydrogen evolution was exactly

equivalent to the rate of nitrogen fixation. An assay by this method can be done in 20 min, and its discovery facilitated the concentration and purification of nitrogenase fractions, although it has now been superseded by the acetylene test.

The nitrogenase system produces electrons at a constant rate, regardless of the substrate, so that the total reduced product (*e.g.* dihydrogen plus ammonia or other reduction products, depending on the substrate) has the same chemical equivalence. Even under carbon monoxide, when the reduction of substrates is inhibited, dihydrogen is evolved as if no substrate were present. The relative rates of reduction in Table 1 indicate the efficiency of reduction. Thus acetylene, needing two electrons for reduction, should be reduced three times as fast as dinitrogen, which requires six. In fact it is reduced four times as fast, and proportionately less dihydrogen is produced. Thus it is reduced more efficiently.

Nitrogenase from several sources has now been examined and has been obtained from three genera of bacteria in a state of what is believed to be high purity. It can be separated into two proteins, one of molecular weight $2-3 \times 10^5$ and the other around 7×10^4 ; these may be broken down into sub-units. The larger protein contains molybdenum and iron, and the smaller only iron, as essential metallic constituents. There is still some doubt about the molecular weights and the exact metal content of the two proteins and of the character of the sub-units. Neither protein shows nitrogenase action on its own but a mixture is immediately active. There is obviously no winding together of protein chains or other slow process involved in their concerted action. The large protein from one species of bacteria can be activated by the small protein from another if the bacteria are sufficiently closely related, but the activity falls as the difference between the two types of bacteria increases. This would indicate that the two proteins are essentially the same but have peripheral differences which prevent their fitting together when they come from widely different bacteria.

The nomenclature of the proteins is somewhat confusing as almost every worker in the field appears to have developed his own. The larger protein has been variously called enzyme 1, protein 1, fraction 1, component 1, molybdo-ferredoxin, azofermo, Fe-Mo protein, and Mo-Fe protein; the smaller has been referred to as enzyme 2, protein 2, fraction 2, component 2, azo ferredoxin, azofer, and Fe protein. We shall call them the molybdenum-iron (or Mo-Fe) and the iron (or Fe) proteins. The Mo-Fe protein is brown in aqueous solution; it appears to contain 1 or, less probably, 2 atoms of molybdenum and around 15 atoms of iron per molybdenum atom. One mole of dihydrogen sulphide per iron atom is liberated by acid. A solution of the Fe protein is yellow and contains 2 atoms of iron and 2 ions of 'labile sulphide'. The proteins are unusual only in containing a somewhat higher than normal proportion of sulphur, leading to the suggestion that perhaps the iron and molybdenum are in a sulphur environment. There is no direct evidence as to how the metals are held, or even whether they are directly involved with dinitrogen during the fixation process. Mössbauer spectra of ^{57}Fe -labelled proteins under various conditions and with various

substrates have not given any definitive information, but they suggest that the iron atoms do not react directly with the dinitrogen and probably occur in pairs. It appears that, when all conditions for nitrogenase activity are satisfied (ATP, reductant *etc.*), the Fe protein catalyses a reduction of some of the iron in the Mo-Fe protein. E.s.r. spectra have shown signals typical of non-haem iron but no reproducible signals have been obtained from molybdenum. The electronic, o.r.d., *etc.* spectra have not yet given any useful information. The oxidation state of molybdenum is unknown and iron is probably present as iron(II) and iron(III) in the working enzyme.

Both proteins are oxidized by air. If not over-exposed to air, the Mo-Fe protein can be reactivated by sodium dithionite, but the Fe protein is destroyed irreversibly. The aerobes, azotobacter, have a high respiratory rate and it has been suggested that this is necessary to consume dioxygen, so as to protect their nitrogenase. There is a limit to this mechanism of protection and as soon as the dioxygen tension in the environment becomes too high they switch off their nitrogen-fixing activity as though they had pulled down shutters to keep out the dioxygen (and dinitrogen). When the dioxygen tension drops the azotobacters start to fix nitrogen again at the critical threshold tension of dioxygen.

The Mo-Fe protein has been obtained crystalline from *Azotobacter vinelandii*, but from no other source. The crystals are colourless and have curved faces, thus they are not suitable for X-ray structure determination. They must very readily to a brown, highly active solution of the large protein.

The two nitrogenase proteins have sometimes been attributed distinct functions, one as a dinitrogen-trapping agent and the other as the reducer, but apart from indications from Mössbauer spectroscopic methods, there is no definite evidence concerning their functions.

The absence of reactions with bulky molecules related to those in Table 1 suggests that access to the active site is probably restricted. The site appears to have extreme class *b* metal character. The production of C₂ hydrocarbons from the reduction of methyl isocyanide has been held to support the hypothesis of a bimetal site, the two adjacent metal atoms being necessary to bring together the two terminal carbon atoms of the isocyanide, but it is equally consistent with a free-radical mechanism and only one site of attack. Indeed, most transition-metal ions in the presence of reducing agent produce some C₂ hydrocarbons from isocyanides. Studies of the relative rates of reduction of various substrates and of dinitrogen by nitrogenase fractions, and of the effects of inhibitors on the reductions and on hydrogen evolution, have given much valuable information about the biochemistry of nitrogen fixation. This is summarized well by Burris;⁷ such studies give no hint as to the chemical mechanism of the reduction of dinitrogen on nitrogenase.

2 Chemical Nitrogen Fixation

Although such evidence as described above points to the activation of dinitrogen by metal ions in the natural system, it is conceivable that highly reactive or strained organic species might use their energy to activate dinitrogen. Thus the

phenylsulphenium ion (PhS^+) reacts with N_2 in trace amounts to form a material which may contain $[\text{PhSN}_2]^+$. Diazomethane is photolysed reversibly, carbene must therefore react with dinitrogen. Finally a salt, formulated $\text{Na}_4[\text{C}\{\text{CH}_2\text{P}(\text{S})\text{CS}\}_4]$, is said to react with dinitrogen 'greedily' to give a product in which the nitrogen atoms are still linked. We have failed to confirm this last. None of these routes is likely to provide a ready source of fixed nitrogen.

Studies of biological fixation suggest that it occurs at a metal site which is sensitive to dioxygen. The site may be in an anaerobic and/or anhydrous region of the enzyme, but there is no evidence concerning this. However, the rate of dihydrogen evolution from the enzyme increases in the absence of a substrate which indicates that protons can reach the reducing site. Most attempts to produce chemical model systems have been based on the assumption that molybdenum and iron are key elements. This has led, over the past quarter of a century, to the study of the interaction of dinitrogen with mixtures of transition-metal compounds and the development of three main types of chemical approach. These are now all being studied in various laboratories, and in chronological order of initiation they are as follows:

(a) Reduction with aqueous reducing agents. Dinitrogen is bubbled through, or compressed on to, mixtures of reducing agent and transition-metal catalysts dissolved or suspended in water, and after reaction, if any, the solution is tested for ammonia or other reduced products such as hydrazine.

(b) Nitriding. The aprotic reduction of dinitrogen is brought about by a transition-metal compound mixed with a very strong reducing agent such as an alkali metal. The product behaves as a nitride.

(c) Study of dinitrogen complexes. This is a fundamental study of the interaction of dinitrogen with transition-metal salts, which appears to be relevant to the functioning of the enzyme.

Obviously these three approaches are related. Thus dinitrogen complexes are probably precursors to nitrogen fixation by reduced transition-metal systems, and may be intermediates in the reduction of dinitrogen to ammonia in the biological system. However, the chemical work at present falls neatly into the three sections noted above. Because it provides fundamental background information, the chemistry of dinitrogen complexes will be taken first.

A. Dinitrogen Complexes.—Dinitrogen complexes are the only type of compound formed by elementary nitrogen under mild reaction conditions, *i.e.* in water or alcohols at ordinary temperature and pressure. There are two classes: terminal-dinitrogen complexes in which the dinitrogen molecule occupies one co-ordination place in a transition-metal complex, and bridging-dinitrogen complexes where dinitrogen bridges two metal atoms, one or both of which may be transition metals. Their general chemistry and their relation to biological and abiological nitrogen fixation have been reviewed in detail.¹³⁻²¹ In

¹³ J. Chatt, *Proc. Roy. Soc.*, 1969, **B172**, 327; *Pure Appl. Chem.*, 1970, **24**, 425. [Chemistry of nitrogen fixation.]

¹⁴ J. E. Fergusson and J. L. Love, *Rev. Pure Appl. Chem.*, 1970, **20**, 33. [Dinitrogen complexes.]

this outline we shall consider mainly those aspects relevant to nitrogen fixation.

Terminal-dinitrogen Complexes. The electronic structure of dinitrogen is similar to that of carbon monoxide. The filled orbital of highest energy in both molecules has σ -symmetry and low energy, but owing to the greater electronegativity of nitrogen relative to carbon, dinitrogen is a poorer electron donor. Its ionization potential of 15.6 eV is almost equal to that of argon and considerably higher than that of carbon monoxide (14.0 eV). Nevertheless, it forms a range of mononuclear complexes which are in many ways similar to those formed by carbon monoxide, and a similar bonding scheme has been postulated for them (Figure 1). The dinitrogen complexes are, however, far less numerous.

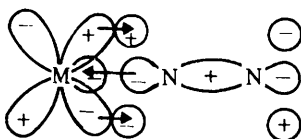


Figure 1 Bonding scheme for dinitrogen complexes. Electrons are donated from the dinitrogen $3\sigma_g$ -orbital into a hybrid acceptor orbital on the metal ion, and a d (or dp hybrid) orbital of the metal donates electrons back into the anti-bonding dinitrogen $1\pi_g$ -orbital

The first dinitrogen complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, was isolated by Allen and Senoff in 1965, during the attempted synthesis of $[\text{Ru}(\text{NH}_3)_6]^{2+}$ by the reaction of hydrazine with ruthenium trichloride trihydrate in water. Its solid salts were characterized by a very strong band in their i.r. spectra at about 2100 cm^{-1} , the precise frequency being dependent upon the counter-anion. About 25 mononuclear complexes of dinitrogen have now been characterized. All have the dinitrogen bound in end-on configuration (*i.e.* they are *monohapto*-complexes) with the M—N—N system essentially linear in all cases investigated by X-ray analysis (see Table 2). In the complexes, the N—N distance is increased by less than 0.015 \AA from that in N_2 itself (1.098 \AA). The elements italicized in Table 3 are those which are at present known to form crystalline mononuclear dinitrogen complexes. They lie about a line drawn from nickel to tungsten in the Periodic Table, the most stable complexes being formed by elements towards the tungsten end. All but a very few of the dinitrogen complexes obey the effective atomic number rule. A representative selection is shown in Table 4. It is evident that

¹⁶ Yu. G. Borodko and A. E. Shilov, *Russ. Chem. Rev.*, 1969, **38**, 355. [Dinitrogen complexes and nitrogen fixation.]

¹⁷ R. Murray and D. C. Smith, *Co-ord. Chem. Rev.*, 1968, **3**, 429. [Activation of molecular nitrogen.]

¹⁸ A. D. Allen and F. Bottomley, *Accounts Chem. Res.*, 1968, **1**, 360. [General review of dinitrogen complexes.]

¹⁹ G. J. Leigh, *Preparative Inorg. Reactions*, 1971, **7**, 165. [Synthesis of dinitrogen complexes.]

²⁰ J. Chatt and R. L. Richards, ref. 1, p. 57. [Dinitrogen complexes and nitrogen fixation.]

²¹ G. J. Leigh, ref. 1, p. 19. [Abiological nitrogen fixation.]

²² G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1969, **8**, 650. [Non-enzymatic nitrogen fixation.]

Table 2 X-Ray structural data on some dinitrogen complexes

Complex	N-N (Å)	M-N (Å)	M-N-N (°)
[CoH(N ₂)(PPh ₃) ₃] ₂ Et ₂ O	1.16	1.80	175
[CoH(N ₂)(PPh ₃) ₃] ^a	1.123(13)	1.829(12)	178(1)
	1.101(12)	1.784(13)	178(2)
[Ru(NH ₃) ₅ (N ₂)] [BF ₄] ₂	~ 1.03	2.10(04)	—
[Ru(NH ₃) ₅ (N ₂)]Cl ₂	1.12(08)	2.10(01)	~ 180
[Ru(NH ₃) ₅ (N ₂)Ru(NH ₃) ₅][PF ₆] ₄	1.124(15)	1.928(6)	178.3(5)
[Ru(N ₃)(N ₂)(en) ₂][PF ₆] ^b	1.106(11)	1.894(9)	179.3(9)
[ReCl(N ₂)(PMe ₂ Ph) ₄]	1.055(30)	1.966(21)	177(1)

^a Two crystallographically independent molecules in the unit cell; ^b en = ethylenediamine; distances and angles refer to the complexed dinitrogen

dinitrogen differs from carbon monoxide mainly in its tendency to form mono- or occasionally bis-dinitrogen complexes, and only with metals in moderately low oxidation states (0—II), whereas carbon monoxide also tends to form polycarbonyl complexes with metals in exceptionally low oxidation states (—II—0). In its behaviour as a ligand, dinitrogen is thus closer to organic isonitriles than to carbon monoxide.

The dinitrogen stretching frequencies, $\nu(\text{N}_2)$, in the i.r. spectra of dinitrogen complexes parallel those of $\nu(\text{CO})$ in the analogous carbonyl complexes, consistent with similar bonding systems for both carbon monoxide and dinitrogen in their complexes. Theoretical considerations, as well as i.r. and Mössbauer spectroscopy, suggest that dinitrogen is both a weaker σ -donor and a weaker π -acceptor than carbon monoxide. In its terminal complexes, the dinitrogen molecule is strongly polarized, as indicated by the strong $\nu(\text{N}_2)$ bands in their i.r. spectra. The charge difference between the two nitrogen atoms in [ReCl(N₂)-(Ph₂PCH₂CH₂PPh₂)₂] has been estimated from its X-ray-induced electron emission spectrum to be about 0.4 electrons.

Dinitrogen might also form side-on, or *dihapto*-complexes, but none have been characterized. The main evidence concerning their stability comes from a study of the isomerization of [Ru(NH₃)₅(¹⁴N¹⁶N)]²⁺ to [Ru(NH₃)₅(¹⁶N¹⁴N)]²⁺, which has an activation energy of about 21 kcal mol⁻¹ in aqueous solution. The aquation of this ion with loss of dinitrogen has an activation energy of 28 kcal mol⁻¹. The isomerization occurs by tumbling of the dinitrogen molecule, passing through the *dihapto*-position. The energetics of the process indicate that the activation energy of displacement of dinitrogen from the *dihapto*-position by water is of the order of 7 kcal mol⁻¹, i.e. the *dihapto*-dinitrogen is almost free. It thus seems unlikely that *dihapto*-complexes could be stable relative to *monohapto*-complexes at any temperature, although they might exist at very low temperatures.

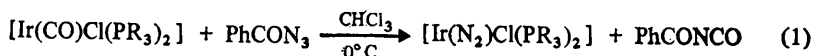
Terminal-dinitrogen complexes are usually prepared by the reduction of a transition-metal complex under dinitrogen, or from a two or three nitrogen atom chain in a ligand attached to the metal.^{18,19} Dinitrogen is very specific as

to the type of transition-metal site which it will occupy and this appears always to possess strong class *b* character. The stabilities of dinitrogen complexes are very dependent upon the co-ligands with dinitrogen, and it is critical to have the right co-ligands in the reduced complex. The only guide to their choice is experience. Thus, the ruthenium(II) and osmium(II) dinitrogen complexes are particularly stable with five ammonia molecules as co-ligands (*i.e.* [(Ru,Os)-(NH₃)₅(N₂)²⁺]) and not with many others, except ethylenediamine. All metals along the W—Ni line (Table 3) give isolable dinitrogen complexes with tertiary

Table 3 *The occurrence of dinitrogen complexes*

Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

organic phosphines, usually also with hydride or halide ions as co-ligands. The lighter transition elements (Fe, Co, and Ni) tend to use hydride and the heavier (Re, Os, and Ir) use halide. Molybdenum(0), tungsten(0), and nickel(0) give dinitrogen complexes with phosphines only as co-ligands (Table 4). Only rarely have tertiary arsines been satisfactory co-ligands, and never yet have organic sulphides. The critical nature of the co-ligands is well illustrated in the series of complexes [Ir(N₂)Cl(PR₃)₂] (PR₃ = tertiary phosphine). The complex is readily produced by reaction (1) when R = Ph, but analogous products containing



similar phosphines such as methyl-diphenylphosphine and tri-*p*-tolylphosphine are too unstable to be isolated in pure condition. Only two reasonably extensive series of stable dinitrogen complexes have been discovered. These are of the types [ReCl(N₂)(PR₃)₄] and [OsCl₂(N₂)(PR₃)₃]. The critical dependence of stability on co-ligands with dinitrogen explains why the discovery of dinitrogen complexes was so long delayed in spite of many attempts to obtain them during the 1940's and 50's, and also why there are so few relative to the numbers of the analogous carbonyl complexes. For example, the carbonyl analogues of the above iridium(I) complex can be prepared from almost any tertiary phosphine, and are relatively stable substances.

Typical reactions (2)—(7) of formation of dinitrogen complexes are as follows:

(a) By direct reduction:

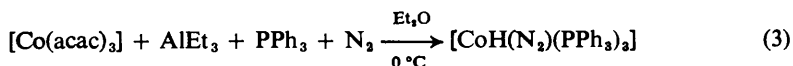
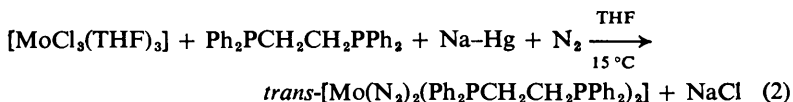


Table 4 Some typical terminal-dinitrogen complexes

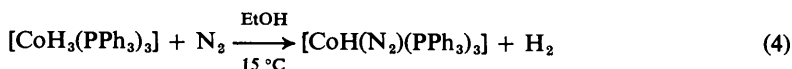
Compound	Colour	Metal electron con- figuration	$\nu(\text{N}_2)^a$ (cm ⁻¹)
<i>trans</i> -[Mo(N ₂) ₂ - (Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂]	Orange- yellow	<i>d</i> ⁶	2020, 1970(Nujol)
[Mo(π -PhMe)(N ₂)(PPh ₃) ₂]	Orange	<i>d</i> ⁶	2005(toluene)
<i>cis</i> -[W(N ₂) ₂ (PMe ₂ Ph) ₄]	Yellow	<i>d</i> ⁶	1931, 1998(benzene)
<i>trans</i> -[ReCl(N ₂)(PMe ₂ Ph) ₄]	Yellow	<i>d</i> ⁶	1925(chloroform)
[ReCl(N ₂)(Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂] ⁺	Green or purple	<i>d</i> ⁵	2060(chloroform)
[ReCl(N ₂)(CO) ₂ (PPh ₃) ₂] ^b	Yellow	<i>d</i> ⁶	2105, 2020, 1935 (chloroform)
[FeH ₂ (N ₂)(PEtPh ₂) ₃]	Yellow	<i>d</i> ⁶	2057(Nujol)
[FeH(N ₂)(Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂] ⁺	Orange	<i>d</i> ⁶	2090(Nujol)
[Ru(NH ₃) ₅ (N ₂) ²⁺	Pale yellow	<i>d</i> ⁶	2130(water)
[RuH ₂ (N ₂)(PPh ₃) ₃]	White	<i>d</i> ⁶	2147(Nujol)
<i>cis</i> -[Ru(N ₂) ₂ en ₂] ^{2+ c}	Pale yellow	<i>d</i> ⁶	2220, 2190 (not stated)
[OsCl ₂ (N ₂)(PMe ₂ Ph) ₃]	White	<i>d</i> ⁶	2082(benzene)
[OsHCl(N ₂)(PMe ₂ Ph) ₃]	White	<i>d</i> ⁶	2057(benzene)
[Co(N ₂)(PPh ₃) ₃]	Red	<i>d</i> ⁹	2093(THF)
[Co(N ₂)(PEt ₂ Ph) ₃] ⁻	Black	<i>d</i> ¹⁰	1875(THF)
[CoH(N ₂)(PPh ₃) ₃]	Red- orange	<i>d</i> ⁸	2096(Nujol)
[IrCl(N ₂)(PPh ₃) ₂]	Yellow	<i>d</i> ⁸	2105(chloroform)
[RhCl(N ₂)(PPh ₃) ₂]	Light yellow	<i>d</i> ⁸	2152 (not stated)
[NiH(N ₂)(PEt ₃) ₂]	Orange- yellow	<i>d</i> ⁹	2076(hexane)
<i>Some bridging dinitrogen complexes</i>			
[{Ti(π -C ₅ H ₅) ₂ Ph} ₂ (N ₂)]	Purple	<i>d</i> ¹	not i.r.-active
[{Mo(π -C ₆ H ₆)(PPh ₃) ₂] ₂ (N ₂)]	Maroon	<i>d</i> ⁶	1910 (solid state, Raman)
[{Ru(NH ₃) ₅] ₂ (N ₂) ⁴⁺	Yellow	<i>d</i> ⁶	2100 (solid state, Raman)
[(NH ₃) ₅ Ru(N ₂)Os(NH ₃) ₅] ⁴⁺	Not stated	<i>d</i> ⁶	2040 (not stated)
[{Co(PPh ₃) ₃] ₂ (N ₂)]	Dark red	<i>d</i> ⁹	not i.r.-active
[{Ni(PCy ₃) ₂] ₂ (N ₂) ^d	Dark red	<i>d</i> ¹⁰	2028(benzene)

^a Solvent or dispersion medium in brackets; ^b $\nu(\text{N}_2)$ and $\nu(\text{CO})$ are extensively coupled; ^c en = ethylenediamine; ^d Cy = cyclohexyl; i.r.-active $\nu(\text{N}_2)$ probably due to dissociation in solution to [Ni(PCy₃)₂(N₂)]

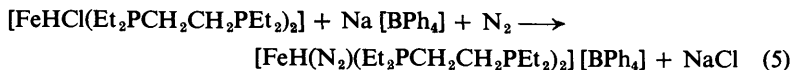
Nitrogen Fixation

(b) By displacement of other ligands:

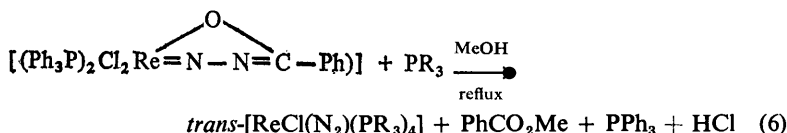
(i) hydride



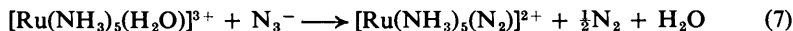
(ii) chloride



(c) By degradation of a nitrogen chain. Allen and Senoff's preparation and the formation of the iridium complex (see above) are of this type. A further example is:



The azide ion has also been used as a source of co-ordinated N_2 and provides the best preparation of Allen and Senoff's compound.



Many terminal-dinitrogen complexes which are formed as impure products by such reactions as the above and recognised by their strong i.r. bands are too unstable to be isolated.

Most reagents react with dinitrogen complexes with displacement of dinitrogen and formal oxidation of the metal, but certain ligand molecules such as carbon monoxide displace dinitrogen without the oxidation.

The reaction (8) of dihydrogen with $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$, and similarly with a number of related complexes, may be relevant to the natural process.

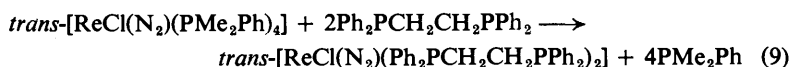


This reversible reaction occurs in ethanol and shows that dinitrogen and dihydrogen can compete for the same metal site. Also carbon monoxide, which is a strong inhibitor of nitrogen fixation in the natural system, displaces dinitrogen irreversibly from this cobalt complex. Thus, if nitrogenase contained a metal site of the type in the cobalt complex, the competitive inhibition of nitrogen fixation by dihydrogen and the strong inhibition by carbon monoxide would be allowed for. When diduterium is used in place of dihydrogen in reaction (8) it replaces all 18 *o*-hydrogen atoms from the phosphine ligands as well as the hydrogen on the metal, indicating that reversible formation of *o*-C-Co bonds with loss of dihydrogen occurs.

The less-stable dinitrogen complexes readily lose dinitrogen to leave highly reactive metal-containing species, *e.g.* $[\text{CoH}(\text{PPh}_3)_3]$, often excellent olefin polymerization catalysts. Dinitrogen complexes are especially sensitive to

oxidation with loss of dinitrogen, but a few of the very stable complexes, *e.g.*, $trans\text{-[ReCl(N}_2\text{)(PMe}_2\text{Ph)}_4]$, are able to retain their dinitrogen and yield a pure product, *e.g.*, $trans\text{-[ReCl(N}_2\text{)(PMe}_2\text{Ph)}_4]^+$, when the metal is oxidized to the next highest oxidation state. The N–N stretching frequency is then raised by about 80–100 cm^{-1} , owing to weaker back-bonding from the more positive metal of the oxidized species.

All attempts to reduce well-defined terminal-dinitrogen complexes to ammonia have failed. Very strong reducing agents capable of producing nitride from elementary nitrogen in aprotic solvents are capable of producing nitride from the complexes, but this may occur through preliminary dissociation of the complex. A very few dinitrogen complexes are sufficiently stable for ligand exchange reactions without loss of dinitrogen. One of the most remarkable, reaction (9), occurs in boiling toluene.



Although the less stable dinitrogen complexes react with potential ligand molecules with irreversible displacement of dinitrogen, some react reversibly, *e.g.* reaction (10).



This reaction is important because it shows that if dinitrogen were to be reduced on some metal sites, the ammonia produced could be displaced by dinitrogen so that the cycle of reduction would continue.

The terminal nitrogen atom of co-ordinated dinitrogen in some of the more stable complexes is an electron donor, and reacts with various electron acceptor systems to form bridging-dinitrogen complexes (see below).

Stable analogues of the dinitrogen complexes are usually obtained from carbon monoxide, organic cyanides, or organic isocyanides. In all such cases the stretching frequency of the triple bond is considerably lower than in the usual run of complexes of these ligands, indicating a very strong back-donation of *d*-electrons from the metal atom into the π -anti-bonding orbitals of the triply bonded system. This appears to be the main characteristic of a dinitrogen-bonding site. It has a high *d*-electron density on the metal, and this is probably responsible for the weak bonding of normally strong ligands such as water and ammonia, which have no mechanism for accommodating the *d*-electronic charge.

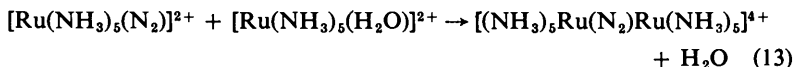
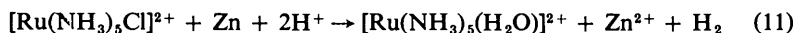
Since the donor orbital on dinitrogen has very low energy, the σ -acceptor on the metal will also have to be on a low energy for good mixing. Thus, for the binding of dinitrogen the metal must provide a very low energy σ -orbital to match the σ -orbital of the dinitrogen, and it must also have filled *d*-orbitals of sufficiently high energy to combine with the anti-bonding π -orbitals of the dinitrogen. These are conditions difficult to satisfy simultaneously. Their fulfillment depends critically on the metal, the co-ligands with dinitrogen, and their positions relative to dinitrogen. Minor changes in any of these render the site much less capable of holding dinitrogen.

Although the terminal nitrogen atom of some dinitrogen complexes serves as an electron donor to many acceptor systems, it does not appear to do so to the proton. If it did, the reduction of the dinitrogen ligand would be comparatively easy. However, since the electron density on the dinitrogen ligand is enhanced largely by electron drift from the *d*-orbitals of the metal, it is evident that the metal must also have a high electron density. Thus protic acids appear to protonate the metal, leading to its oxidation and the release of the dinitrogen.

It therefore appears unlikely that dinitrogen in terminal-dinitrogen complexes can be reduced as a consequence of attack by protons or by hydride ions. There is no evidence that dihydrogen is effective either. It may be that the electronic condition of bridging-dinitrogen is more favourable for reduction.

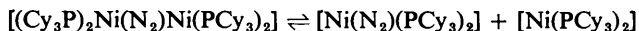
Bridging-dinitrogen Complexes. Dinitrogen is also like carbon monoxide in being capable of bridging between metal atoms. Carbon monoxide normally bridges between two class *b* transition-metal atoms through the carbon atom, as in the usual form of $[\text{Co}_2(\text{CO})_8]$. However, in a very few cases it bridges through carbon and oxygen in structures of the type $\text{M}-\text{C}\equiv\text{O}-\text{M}^1$, where *M* is a class *b* transition metal and *M*¹ a strong class *a* acceptor, e.g. Me_3Al . In contrast, only the $\text{M}-\text{N}\equiv\text{N}-\text{M}^1$ type of bridging has been found for dinitrogen and it occurs whether *M* and *M*¹ are both strong class *b* transition-metal acceptors, or only *M*, with *M*¹ a strong class *a* acceptor, e.g. Me_3Al , $\text{CrCl}_3(\text{THF})_2$, or PF_5 .

The first bridged complex was the ion $[(\text{NH}_3)_5\text{Ru}(\text{N}_2)\text{Ru}(\text{NH}_3)_5]^{4+}$, prepared in aqueous solution by a remarkable series of reactions:



In this bridged ion the $\text{Ru}(\text{N}_2)\text{Ru}$ system is essentially linear, but the N-N separation is insignificantly different from that in $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, and only marginally greater than in dinitrogen (see Table 2). In solid $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{[BF}_4\text{]}_2$, $\nu(\text{N}_2)$ (Raman spectrum) is only 31 cm^{-1} higher than in the corresponding salt of the dinuclear ion. Thus dinitrogen seems to have been altered very little on forming a bridge. A kinetic study of reaction (13) supports this by showing that the dinitrogen complex has about the same affinity for the aqua-complex as has dinitrogen itself.

Other similar bridged species where dinitrogen connects closed-shell atoms are $[(\text{NH}_3)_5\text{Ru}(\text{N}_2)\text{Os}(\text{NH}_3)_5]^{4+}$, $[(\text{C}_6\text{H}_6)(\text{PPh}_3)_2\text{Mo}(\text{N}_2)\text{Mo}(\text{PPh}_3)_2(\text{C}_6\text{H}_6)]^{2+}$ and $[(\text{Ph}_3\text{P})_3\text{Co}(\text{N}_2)\text{Co}(\text{PPh}_3)_3]$.²² They have had little study. There is also a nickel complex with tricyclohexylphosphine which dissociates in solution:



²² M. L. H. Green and W. E. Silverthorn, *Chem. Comm.*, 1971, 557.

²³ M. Aresta, C. F. Nobile, M. Rossi, and A. Sacco, *Chem. Comm.*, 1971, 781.

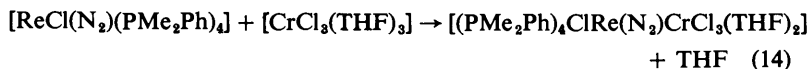
In addition to the above bridged complexes, there is a series of dinitrogen-bridged complexes derived from $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$, which has the lowest $\nu(\text{N}_2)$ (1925 cm^{-1}) so far observed in any neutral complex. This may be an indication of a greater back-donation of d -electrons in this complex than in any other, with consequent raising of the electron density on the dinitrogen ligand. It appears to have donor properties very similar to those of acetonitrile, and interacts with a great number of acceptor molecules of all types, sometimes with evolution of dinitrogen (*e.g.* with BCl_3), but often to form strongly coloured products which are essentially adducts. In these the N_2 molecule is believed to bridge between the rhenium atom of the original complex and the acceptor atom of the added reagent. Owing to the asymmetry of the product, $\nu(\text{N}_2)$ is i.r.-active and occurs at lower frequencies than in the parent rhenium complex. Table 5

Table 5 Adducts of $\text{trans-}[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ with various Lewis acids

Acid derivatives with configuration d^0-d^2	Colour	$\nu(\text{N}_2)$ (cm^{-1})	Ratio Re: acceptor atom
$[\text{TiCl}_3(\text{THF})_3]$	Blue	1805	1:1
TiCl_3	Red	not assignable	1:2
TaCl_5	Brown	1695	1:1
$[\text{MoCl}_4(\text{Et}_2\text{O})_2]$	Green	1795	1:1
	Blue	1680	1:2
$[\text{MoCl}_4(\text{PMe}_2\text{Ph})_2]$	Purple	not assignable	1:2
PF_5	Pale pink	1640	1:1
Acid derivatives with configurations d^3-d^{10} or without available d -orbitals			
$[\text{CrCl}_3(\text{THF})_3]$	Purple	1875	1:1
$\text{CoCl}_2(\text{THF})_{1-5}$	Blue	1855	<i>a</i>
$[\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2]$	Yellow	1890	<i>a</i>
AlMe_3	Pale yellow	1894	1:1

^a Dissociates upon work-up, pure adduct not obtained

lists some of the acceptor molecules which are known to react, together with $\nu(\text{N}_2)$ of the product and the number of acceptor atoms in the rhenium dinitrogen-bridged product. Combination may occur with displacement of a ligand, *e.g.* with $[\text{CrCl}_3(\text{THF})_3]$ (reaction 14), or by direct addition, as with PF_5 (reaction 15).



These adducts and the symmetrical, bridged compounds first discussed appear to be of very similar type. The rhenium-containing adducts fall into two distinct classes, those where $\nu(\text{N}_2)$ is lower than in the mononuclear rhenium complex by $< 100 \text{ cm}^{-1}$ (formed by d^3 – d^{10} acceptors), and those where the lowering is considerably greater, up to 350 cm^{-1} (formed by d^0 , d^1 , and d^2 acceptors). In some cases, *e.g.*, 1 : 2 adducts with titanium or molybdenum derivatives, it is not possible to assign a frequency to $\nu(\text{N}_2)$, presumably because it has been lowered into the region of the other ligand frequencies. The original rhenium complex can be recovered from all of these adducts by hydrolysis of the added molecule or otherwise, and so the N_2 molecule has remained intact.

The reason for the formation of two classes of adduct is apparent from the simplified π -molecular-orbital scheme for the $\text{Re}-\text{N}-\text{N}-\text{M}^1$ system given in Figure 2. The N_2 molecule provides the four electrons necessary to fill the $1e$ orbitals and the rhenium atom the six electrons necessary to fill the $1b_2$, and the $2e$ orbitals which are anti-bonding on N_2 . Thus when the acceptor atom M^1 is in

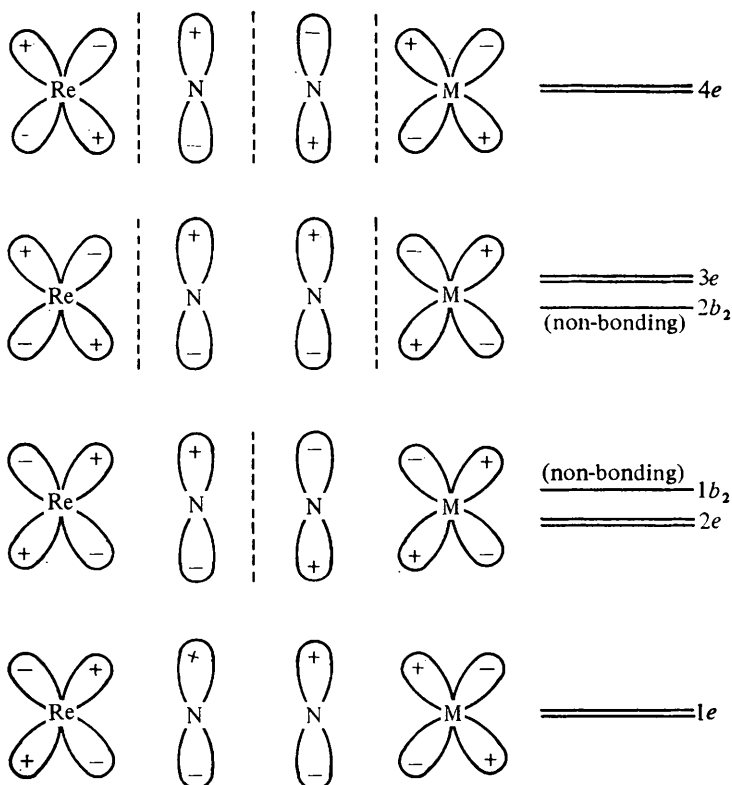


Figure 2 Suggested molecular-orbital scheme for the π -system of an adduct of $\text{trans}-[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ with a transition-metal derivative

a d^0 or d^1 state, it can, by withdrawing electrons from the bonding system of the N_2 and feeding none back into the π -orbital system, cause a great lowering of $\nu(N_2)$. However, when it is a d^3-d^{10} system, the additional electrons it contains must enter the $3e$ orbitals which are bonding on dinitrogen so compensating for any electron withdrawal from the N—N σ -system or $1e$ π -system, and causing very little lowering of $\nu(N_2)$ in the adduct. Thus, when both metals bridged by dinitrogen have closed electronic shells as in the complex $[(NH_3)_5Ru(N_2)Ru(NH_3)_5]^{4+}$, $\nu(N_2)$ is almost unchanged from that of the mononuclear analogue $[Ru(NH_3)_5(N_2)]^{2+}$.

One of the most interesting of the $[ReCl(N_2)(PMe_2Ph)_4]$ adducts is that with $MoOCl_3L$ ($L = Et_2O, PMe_2Ph, etc.$) attached to the terminal nitrogen atom (see Table 4). The low $\nu(N_2)$ may be a reflection of a weak N—N bond. It seems likely that, were it possible to attach two moieties of $MoOCl_3L$ type, one to each end of the dinitrogen molecule in a reducing medium, they might pull it apart. This is probably the basis of formation of nitride complexes from dinitrogen by transition-metal species which do not have closed electron shells. It suggests that transition metals with open electron shells should form dinitrogen complexes which might be unstable and reactive.

Evidence is now appearing that dinitrogen can indeed form complexes with d^1 electronic systems. Thus there is electrochemical evidence that titanium(III) chloride in dimethyl sulphoxide or propylene carbonate forms complexes with dinitrogen,²⁴ and more recently a d^1 complex, probably $[(\pi-C_5H_5)_2PhTi(N_2)-TiPh(\pi-C_5H_5)_2]$, has been isolated.²⁵ It is formed by reaction of $[TiPh(\pi-C_5H_5)_2]$ in toluene solution with dinitrogen. Reaction occurs at about $-80^\circ C$, and the solid complex is stable below $0^\circ C$.

None of the above dinitrogen complexes have been reduced to ammonia or to hydrazine. Indeed, since the $4e$ orbitals are on a higher energy than the corresponding anti-bonding orbitals in free dinitrogen (see Figure 2), the dinitrogen in the complexes is more difficult to reduce to nitride than is elementary nitrogen. Nevertheless, it is now becoming apparent that some very unstable bridging-dinitrogen complexes formed in aprotic media can be reduced to hydrazine and ammonia. These will be considered at the end of the next section.

3 Nitriding

Lithium, magnesium, the alkaline-earth metals, and most transition metals of Groups IV—VII form nitrides from dinitrogen exothermically, generally at a dull red heat; indeed, titanium is reported to burn with incandescence when so heated. At room temperature, nitriding occurs rapidly on chemically clean metal surfaces but it does not occur in the bulk metal or is very slow, except on lithium and the alkaline-earth metals. These build up a visible layer, or even nitride completely through the bulk of the metal (*e.g.* Ca). If fresh lithium metal is continually exposed to dinitrogen, for example, by very slow addition of ethyl bromide to lithium in boiling dry pentane under dinitrogen, yields of up to 40%

²⁴ T. C. Franklin and R. C. Byrd, *Inorg. Chem.*, 1970, 9, 986.

²⁵ J. H. Teuben and H. J. de Liefde-Meijer, *Rec. Trav. chim.*, 1971, 90, 360.

Nitrogen Fixation

Li_3N based on the metal can be obtained. Hydrolysis of the lithium nitride gives ammonia with traces of hydrazine.

Workers with Zeigler catalysts (*e.g.* $\text{TiCl}_4 + \text{AlEt}_3$ in petrol) for polymerization of olefins became aware of systems which nitride at room temperature during the 1950's. Dinitrogen can partially inhibit catalysis of olefin polymerization by some Ziegler-Natta systems. When the catalysts are formed under dinitrogen at atmospheric pressure and room temperature, the precipitated catalyst contains a small percentage of nitrogen which appears as ammonia when the catalyst is hydrolysed. This was discovered independently and developed mainly by the work of Vol'pin in Russia²⁶ and later, again independently, by Van Tamelen in the United States.²⁷

They showed that the reaction of a simple transition-metal compound, for example titanium tetrachloride or di-isopropoxydichloride, with a strong reductant such as a reactive organometallic compound or an alkali metal, in ethereal solution, yields products which react with dinitrogen. Details of the reaction are still uncertain, but generally when an organometallic reductant is used, there is an induction period after mixing the reagents before the absorption of dinitrogen begins, and during this period saturated and unsaturated hydrocarbons are evolved. Presumably organo-transition-metal compounds are formed and these decompose to form hydrides or lower-oxidation-state derivatives of the transition metal. It is one or more of these species which react with dinitrogen to produce complexes, which on solvolysis with protic solvents give ammonia, sometimes with hydrazine. Generally, the nitrogen-containing products behave as solutions or suspensions of highly reactive nitride complexes.

A highly active and much studied system which is homogenous is formed by the reaction of bis(π -cyclopentadienyl)dichlorotitanium with ethylmagnesium bromide. It shows an induction period, and the rate of reaction with dinitrogen is dependent on pressure. Russian workers have tended to use 100–150 atm, although others claim that $p\text{N}_2$ for half the maximum reaction rate is about 0.5 atm. Dinitrogen uptake is a maximum for rather over 4 mol of organometallic reagent or reductant per titanium atom in the above system and is partly inhibited by strongly solvating solvents. Generally, carbon monoxide, acetylene, olefins, and dihydrogen inhibit fixation as they do in the natural system, indicating that the fixation probably occurs on a class *b* metal site. However, some of the systems derived from titanium appear to show enhanced fixation in the presence of dihydrogen, which has been ascribed to the hydrogenation of dinitrogen. Dioxygen in small amounts is said not to affect the uptake of dinitrogen by some systems. The systems also reduce 'dinitrogen analogues' similarly to the reduction by nitrogenase.²⁸

Any very strong reducing agent appears to be able to activate the titanium

²⁶ M. E. Vol'pin and V. B. Shur, *Organometallic Reactions*, 1970, 1, 55. [General review of nitriding reactions.]

²⁷ E. E. Van Tamelen, *Accounts Chem. Res.*, 1970, 3, 361. [Systems for chemical modification of dinitrogen.]

²⁸ E. E. Van Tamelen, H. Rudler, and C. Bjorkland, *J. Amer. Chem. Soc.*, 1971, 93, 3526; G. J. Leigh, unpublished observations.

and other early transition-metal systems; Grignard reagents in ether, triethyl-aluminium, metallic sodium in diglyme, lithium-naphthalene in tetrahydrofuran, or reduction at a nichrome cathode have been used. The fixed nitrogen in the system behaves as nitride, and can be so reactive that even tetrahydrofuran solvolyses it slowly to ammonia. Undoubtedly dinitrogen complexes, possibly bridged-dinitrogen species, $M-N\equiv N-M$ ($M = \text{metal}$), are formed as intermediates.²⁹⁻³¹ In titanium systems, titanium(II) is believed to be the active species, and e.s.r. studies certainly suggest that the principal species in titanium systems is diamagnetic.³² However, titanium complexes are so labile that any oxidation state which may be needed for nitrogen fixation could be produced by disproportionation of oxidation states, e.g. $2Ti^{II} \rightleftharpoons Ti^0 + Ti^{IV}$. Despite much work and speculation, the mechanism of the reactions involved in the conversion of dinitrogen into nitride are still uncertain, but it is not now thought that hydridic species are important in the system.

Most of the systems are not catalytic in the true sense, because solvolysis with destruction of the active species is needed to liberate ammonia. However, by controlled solvolysis followed by removal of the ammonia, a further cycle of reduction, dinitrogen absorption, and solvolysis can be made. Van Tamelen and co-workers have shown that the titanium retains activity through about nine cycles in the 2-propoxydichlorotitanium-diglyme-sodium system using propan-2-ol for solvolysis.

Vol'pin and co-workers, using a non-protic Lewis acid, aluminium tribromide, were able to demonstrate the truly catalytic effect of titanium by treating dinitrogen with a mixture of titanium tetrachloride, metallic aluminium, and aluminium tribromide at 50°C, either in the absence or in the presence of a solvent, e.g. benzene. As much as 200 mol of ammonia per mol of $TiCl_4$ was obtained after hydrolysis. It is clear that a system for the catalytic nitridding of aluminium had been evolved, since aluminium is not nitrided in the presence of its bromide alone. Circumstantial evidence suggests that titanium(II) halides produced by the reaction with aluminium form an active adduct $TiX_2 \cdot nAlBr_3$, and that this takes up dinitrogen to form eventually a nitride which, with aluminium tribromide, generates titanium tribromide and forms aluminium nitride. The titanium(III) is then reduced again to titanium(II) and recycled.

The above nitridding systems are also capable of producing nitrogen-containing organic compounds. Thus the bis(π -cyclopentadienyl)dichlorotitanium system with an excess of phenyl-lithium in ether solution under dinitrogen at room temperature gives, after hydrolysis, 0.15 mol of aniline per atom of titanium, as well as ammonia (0.65 mol) and trace amounts of *o*-aminobiphenyl; both formation of a benzyne intermediate and insertion of N_2 into a titanium-carbon

²⁹ M. O. Broitman, N. T. Denisov, N. I. Shuvalova, and A. E. Shilov, *Kinetika i Kataliz*, 1971, 12, 504, and references therein.

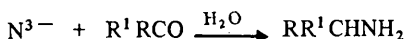
³⁰ E. E. Van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Amer. Chem. Soc.*, 1970, 92, 5251, and references therein.

³¹ J. E. Bercaw and H. Brintzinger, *J. Amer. Chem. Soc.*, 1971, 93, 2045; R. H. Marvich and H. Brintzinger, *J. Amer. Chem. Soc.*, 1971, 93, 2046.

³² E. Bayer and V. Schurig, *Chem. Ber.*, 1969, 102, 3378.

bond have been suggested as a mechanism, but dinitrogen has not yet been inserted into any stable transition-metal—carbon bonds.

An alternative synthesis of organonitrogen compounds also supports the idea that the reduced titanium systems contain nitride. Thus when bis(π -cyclopentadienyl)titanium dichloride is reduced with magnesium metal in tetrahydrofuran under dinitrogen, and the resultant mixture is allowed to react with ketones, secondary amines are formed upon subsequent hydrolysis:³³



Apparently only titanium systems react in this way. Di-*n*-butyl ketone gives 5-nonyl- and di-(5-nonyl)-amines in about 25% yield based on the total amount of nitrogen originally fixed. Benzaldehyde yields benzylamine and dibenzylamine. This reaction may be compared with that of lithium nitride with acid anhydrides to give nitriles or with benzoyl chloride to give tribenzamide.³⁴ In these cases, nitride ions are almost certainly involved. Probably some combination of catalytic nitridation with this kind of nitride ion reaction could lead to the large-scale synthesis of organonitrogen compounds direct from molecular nitrogen.

By careful control of the working-up, Van Tamelen and his co-workers³⁰ have been able to catch the reduced complexed dinitrogen before the N—N bond has been completely severed. Under these conditions, hydrazine is also a solvolysis product. Lithium and barium nitrides are also known to produce some hydrazine upon solvolysis. Recently, from the Shilov school,²⁹ have come some related developments concerning some very unstable, presumably bridging-dinitrogen, complexes of both early and late transition metals. The complexes may be related to $[(\pi\text{-C}_5\text{H}_5)_2\text{PhTi}(\text{N}_2)\text{TiPh}(\pi\text{-C}_5\text{H}_5)_2]$ discussed in the previous section. Apparently, however, that complex cannot be solvolysed to ammonia or hydrazine.²⁵ The Shilov school has prepared a bright-blue solution by the reaction of $[\text{TiCl}_2(\pi\text{-C}_5\text{H}_5)_2]$ with an excess of isopropylmagnesium chloride in ether at -60°C under dinitrogen. As with the phenyl complex²⁸ this solution does not take up dinitrogen at room temperature but, on cooling, dinitrogen is absorbed and on warming is evolved again. However, if the cold solution containing dinitrogen is solvolysed with hydrogen chloride, hydrazine is obtained. Similarly $[\text{TiCl}_2\text{Et}_2]$ on treatment with ethylmagnesium bromide in ether at -80°C produces a solution which contains a dinitrogen-trapping species. At -60°C dinitrogen is released, but treatment with hydrogen chloride at -60°C before the dinitrogen is released produces hydrazine.

Interestingly, the later transition metals also appear to undergo this type of reaction. When isopropylmagnesium chloride is added to ferric chloride in the presence of triphenylphosphine in ether, it also produces a solution which does not absorb dinitrogen at room temperature, but at -40°C and atmospheric pressure it does so to produce a red solution. This red solution, on solvolysis at

³³ E. E. Van Tamelen and H. Rudler, *J. Amer. Chem. Soc.*, 1970, **92**, 5253.

³⁴ P. E. Koenig, J. M. Morris, E. J. Blanchard, and P. S. Mason, *J. Org. Chem.*, 1961, **26**, 4777.

-40 °C with hydrogen chloride, gives up to 10% of its complexed dinitrogen as hydrazine and the remainder as dinitrogen. On the other hand, if the red solution is allowed to warm to room temperature it becomes brown, the complex decomposes and dinitrogen is evolved, $\frac{1}{2}\text{N}_2$ per iron atom. Hydrazine is obtained only in the presence of triphenylphosphine. In its absence there is only very slight formation of a dinitrogen complex, but if the reaction is run at 90 °C and at over 20 atm pressure of dinitrogen in absence of triphenylphosphine, nitriding occurs, and yields of ammonia after hydrolysis reach 30% based on FeCl_3 , assuming one nitrogen atom per iron atom. The addition of triphenylphosphine reduces the yield of ammonia from the above reaction. The reaction of molybdenum(v) chloride with isopropylmagnesium chloride in ether at low temperatures similarly yields, on hydrolysis, ammonia and hydrazine.

The above work has only just appeared and has not had appraisal in other laboratories. It is interesting in showing that easily dissociable, but nonetheless reactive, dinitrogen complexes can be formed at very low temperatures, although they are not formed at room temperature, and that they can be derived from transition metals whether at the beginning or near the end of the transition-metal series. It appears also that the formation of a dinitrogen complex precedes nitridation, but no well-characterized dinitrogen complex has been degraded to nitride, and the exact requirements for such a reaction of complexed dinitrogen are not yet clear.²⁰

4 Reduction by Aqueous Reducing Agents

This has often been attempted, and many strong reducing agents in the presence of derivatives of transition metals such as molybdenum have been reported to produce minute traces of ammonia from dinitrogen. Typical aqueous systems are dihydrogen with platinum black or in the presence of reduced molybdenum compounds, fresh metallic iron rusting in dinitrogen with traces of dioxygen, and acidic solutions of sodium molybdate, sodium borohydride, and thioorganics, with or without ferrous salts. The apparent production of traces of ammonia from dinitrogen must always be checked by reduction of $^{15}\text{N}_2$, and this relatively recent method of testing has been applied to very few systems. Spurious results are likely because the Nessler test for ammonia is not sufficiently specific and, where large volumes of dinitrogen are used, the system may scavenge from the gas phase traces of ammonia, or oxides of nitrogen which are subsequently reduced. The apparent production of ammonia has even been traced to the rubber tubes used to convey the dinitrogen.

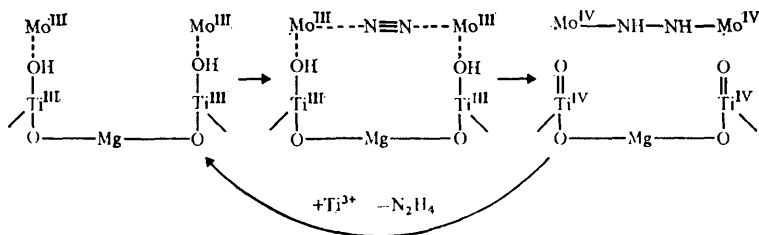
Two types of aqueous system are now known to reduce dinitrogen, the one to hydrazine and the other to ammonia. The essential catalyst to produce hydrazine is a reduced molybdenum or vanadium salt in the presence of a substantial proportion of magnesium ions.³⁵ Typically, dinitrogen is reduced by an aqueous or aqueous-alcoholic solution of sodium molybdate or molybdenum(v) tri-

³⁵ A. Shilov, N. Denisov, O. Efimov, N. Shuvalov, N. Shuvalova, and A. Shilova, *Nature*, 1971, 231, 460.

Nitrogen Fixation

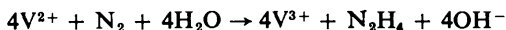
chloride oxide, mixed with titanium(III) chloride, at pH greater than or equal to 10.5. The mole ratio of magnesium to titanium for optimum reduction is 1:2.

Hydrazine is produced at room temperature and atmospheric pressure of dinitrogen, but at elevated temperatures and pressures (50—100 °C, 50—150 atm) yields of hydrazine as high as 100 mol per molybdenum atom have been obtained, and at the higher temperatures some systems produce ammonia. The reductant titanium(III) can be replaced by vanadium(II) or chromium(II). The system is poisoned by carbon monoxide, and indirect evidence suggests that carbon monoxide forms a 1:1 adduct with the molybdenum, which is in the oxidation state III. The mixture is heterogeneous. It has been suggested that the function of the magnesium is to keep the Ti^{III} ions in the hydroxide gel apart so that their oxidation with dihydrogen evolution is retarded by the formation of Ti—O—Mg—O—Ti species. The following scheme has been proposed:



This system parallels the natural system in many respects. However, its efficiency, as measured by the yield of reduced dinitrogen per molybdenum atom, is at best about 1% that of the natural system.

Vanadium(II) can take the place of both the molybdenum and the titanium in the above system and at alkaline pH rapidly reduces the dinitrogen to hydrazine. At 10 atm pressure, essentially quantitative reduction based on vanadium according to the following equation is claimed:



The rate of reduction is faster than in the molybdenum system. Both systems also reduce acetylene to ethylene (and further to ethane).

The molybdenum and vanadium systems apparently contain active metal compounds in the d^3 -configuration. They are thus more deficient in electrons than those systems forming non-reducible stable dinitrogen complexes, in which at least one metal atom has a closed electron shell. They also differ from systems which nitride, in that the latter contain the metal atoms in exceptionally low oxidation states and even as finely divided metal.

The second type of system known to reduce dinitrogen is the result of an attempt to produce chemical models on the basis of the scanty knowledge that nitrogenase contains iron, molybdenum, sulphide, and thiol groups. Schrauzer

and his co-workers³⁶ have reported that organic thiols, sodium molybdate, and ferrous sulphate in the presence of a reducing agent, *e.g.* $\text{Na}_2\text{S}_2\text{O}_4$ or NaBH_4 , give good reduction of those dinitrogen analogues which are reduced by the natural system. There is a close similarity to the natural system except that reduction is not strongly inhibited by carbon monoxide. By optimizing conditions for acetylene reduction, they have produced a system which gives trace amounts of ammonia from dinitrogen at 2000 p.s.i. pressure, *e.g.*, 3–5 μmol of NH_3 from about 5 mmol Na_2MoO_4 + 2.5 mmol thioglycerol + 0.1 mmol $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.25 g NaBH_4 in 50 ml water. The optimum ratio of molybdenum to iron is 2:1, and no ammonia is obtained in the absence of molybdenum. Copper, nickel, or palladium could not be used in place of iron.

Working with $^{15}\text{N}_2$, Hill and Richards³⁷ have been able to demonstrate the production of 2–3 μmol of $^{15}\text{NH}_3$ under Schrauzer's conditions using cysteine, molybdate, and ferrous sulphate, but at 1 atm of $^{15}\text{N}_2$. No $^{15}\text{NH}_3$ was obtained when no ferrous sulphate was added. Further, using 2-aminoethanethiol and one hundredth the quantity of catalyst Na_2MoO_4 (60 μmol), FeSO_4 (1 μmol), NaBH_4 (0.39 mmol) in water (1.5 ml) they have produced about 90 μmol of $^{15}\text{NH}_3$ from $^{15}\text{N}_2$ at atmospheric pressure.

Shilov's, Schrauzer's, and the results from our laboratory are all very new. They demonstrate unequivocally that dinitrogen can be reduced catalytically in an aqueous environment to give substantial yields of hydrazine or ammonia and, with further development, may provide important and useful methods of nitrogen fixation.

POSTSCRIPT. One of us has learnt more about the aprotic reduction of dinitrogen in the interesting system developed by the Shilov school, in discussion with Professor A. E. Shilov. The bright-blue solution mentioned above is obtained in a more concentrated state from $[\text{TiCl}(\pi\text{-C}_5\text{H}_5)_2]$ than from the dichloride, because the former is more soluble in ether. A blue solid complex $[\{\text{Ti}(\text{Pr}^i)(\pi\text{-C}_5\text{H}_5)_2\}_2(\text{N}_2)]$ has been isolated from it. Like its phenyl analogue, hydrogen chloride solvolyses it to give dinitrogen and not hydrazine in ether at -100°C . However, if it is first treated with an ethereal solution of isopropylmagnesium chloride, and then with hydrogen chloride at -100°C , hydrazine is obtained from it quantitatively (see *Chem. Comm.*, 1971, 1590).

The active complex $[\text{Fe}_2(\text{Pr}^i)_2(\text{PPh}_3)_4(\text{N}_2)\text{H}(\text{Et}_2\text{O})_n]$ has been isolated as a red solid from the ferric chloride system (see above). This decomposes slowly at 0°C , and at -40 to -100°C it is solvolysed by hydrogen chloride in ether to give a 10% yield of hydrazine, the remaining dinitrogen being evolved. Similar solvolysis at 0°C gives only dinitrogen as does solvolysis by cold methanol. Pretreatment with Grignard reagent is not necessary for the production of hydrazine from this complex (see *Chem. Comm.*, 1971, 1185).

By treating ferric chloride in very cold ether with phenyl-lithium (10–20 mol)

³⁶ G. N. Schrauzer, G. Schlesinger, and P. H. Doemeny, *J. Amer. Chem. Soc.*, 1971, **93**, 1803, and references therein.

³⁷ R. E. E. Hill and R. L. Richards, *Nature*, 1971, **233**, 114.

under dinitrogen, a red complex is formed in solution, which by cold solvolysis with hydrogen chloride yields about 56% of hydrazine based on iron, assuming two iron atoms per molecule of bound dinitrogen. Ammonia and dinitrogen are produced together with the hydrazine. This work will be published in *Kinetika i Kataliz.*

Fleischer and Krishnamurthy (personal communication) report that sodium *meso*-tetra(*p*-sulphonatophenyl)porphinatocobalt(III) in aqueous solution yields 0.6—0.8 mol NH₃ by passage of air through its aqueous solution and with one addition of sodium hydroborate every 24 h; we have confirmed this. They claim that most of the ammonia is derived from the dinitrogen of the air, and some from the porphin.

Hill and Richards (personal communication) report that their 2-aminoethanethiol system depends for its action on some unknown factor, and that pure reagents give only marginal fixation, if any. When the fixation of ¹⁵N₂ occurs on an appreciable scale, one third to one half as much ¹⁴NH₃ is formed as ¹⁵NH₃. It appears that some catalytically initiated condensation with elimination of ammonia from 2-aminoethanethiol is necessary to produce the ligand which forms the nitrogen-fixing catalyst complex, but the conditions for its formation are obscure.

Sellmann (*Angew. Chem. Internat. Edn.*, 1971, **10**, 919) has reported a dinitrogen manganese complex, [(CO)₂(π-C₅H₅)(N₂)Mn].