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THE ACTIVATION OF MOLECULAR NITROGEN

R. MURRAY* AND D. C. SMITH

Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, The Heath, Runcorn Cheshire (Great Britain)

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CONTENTS

ABBREVIATIONS

acac = acetylacetonate
ADP = adenosine diphosphate
ATP = adenosine triphosphate
A. vinelandii = *Azotobacter vinelandii*
CoA-SH = Coenzyme A
C. pasteurianum = *Clostridium pasteurianum*
Cr-P = creatine phosphate
DMSO = dimethylsulphoxide
Fd = ferredoxin
HDS = hydrogen-donating system
NADH = reduced nicotinamide-adenine dinucleotide
NADPH = reduced nicotinamide-adenine dinucleotide phosphate
NAS = nitrogen-activating system
PCMS = *p*-chloromercurisulphonate
Ph_3P = triphenylphosphine
P_i = inorganic phosphate
Py = pyridine
TPP = thiamine pyrophosphate

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[*] Present address: School of Chemistry, Leicester College of Technology, Leicester.

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A. INTRODUCTION

The process whereby micro-organisms (either themselves or in association with certain plants) "fix" atmospheric nitrogen and convert it into nitrogeneous cell constituents has intrigued biologists and chemists alike for many years. Whereas this biochemical activation of the nitrogen molecule by the metallo-enzyme systems present in such organisms occurs under mild conditions, all industrial processes utilising gaseous nitrogen have used very forcing conditions[1].

The section of this review dealing with enzymatic nitrogen fixation is not intended to be exhaustive. It attempts to survey the findings of the many major investigations with particular reference to the involvement of metal centres, and thus highlights those sections of the work which may assist in imitating nature.

The developments in organometallic and coordination chemistry in recent years have given fresh hope that a metal complex will be found capable of activating nitrogen under ambient conditions so that it may readily react to give useful inorganic or organic compounds. Reaction of molecular nitrogen with organometallic species and the metal complexes of nitrogen are discussed in detail, and a number of metal compounds which contain nitrogen are considered as analogues of fixation intermediates.

Some consideration is given to nitrogen adsorbed on metal surfaces and Haber catalysts to compare heterogeneous, biological and possible homogeneous routes to ammonia synthesis. For completeness the reactions of "active" nitrogen are also mentioned.

This review thus attempts to gather together all the relevant literature information (although it must be remembered that this field must suffer more than most from unpublished negative results) in the hope that any rationalisation which may follow will help in the discovery of catalytic nitrogen fixation under mild conditions.

B. BIOLOGICAL SYSTEMS WHICH FIX MOLECULAR NITROGEN

The biological systems studied may be divided into two basic classes[2] (a) free-living (asymbiotic) micro-organisms which include certain aerobic, anaerobic and photosynthetic bacteria; blue-green algae; actinomycetes; some yeasts, and even certain hydrocarbon-oxidising bacteria[3]: (b) symbiotic associations in which bacteria are incorporated into the root systems of certain plants, to form nodules which are the sites of fixation, *e.g.* the legume-Rhizobium association.

(i) Asymbiotic systems

By far the greatest proportion of work has been carried out on cell-free extracts of two bacteria, namely the aerobic *Azotobacter vinelandii* and anaerobic *Clostridium pasteurianum*. As a consequence, this discussion is based mainly on the results obtained from these two systems. Results of studies on other micro-organisms lend support to the following conclusions[2,4].

Fixation of nitrogen by such enzyme extracts depends basically on the adsorption of the nitrogen molecule at a suitable "active site" on the enzyme surface, a source of energy, and the presence of a suitable reducing system, for conversion of tbe bound nitrogen to ammonia. It is the precise nature of, and role played by these components that have occupied biochemists for many years.

(a) *Clostridium pasteurianum*

Extraction of the nitrogen-fixing enzyme system from this organism has been achieved[5] either by (a) crushing the frozen cells in a Hughes press and centrifugation to obtain an active cell-free extract or (b) rapid drying (30–40°) of a cell paste and extraction of the powder with 0.05 M phosphate buffer under hydrogen (pH 6.8), followed by high-speed centrifugation at 0°.

Nitrogen-fixing activity may be determined by exposure of the extracts to ^{15}N-enriched nitrogen and Kjeldahl digestion following a suitable incubation period. Release of the nitrogen and analysis by mass spectrometry provides the atom-% excess of ^{15}N. Values greater than 0.015 atom-% excess (a conservative estimate for the sensitivity of the mass spectrometer) are accepted as a reliable indication of fixation[2,4c,6].

Requirements for activity

Pyruvate; ferredoxin; ATP or ADP; P_i; ATPase; coenzyme A; TPP; Mg; Fe; Mo.

The role of added pyruvate appears to be twofold, in that in addition to furnishing reducing power, it serves as a source of high energy phosphate (ATP), the latter being a key requirement for fixation[7–10]. Pyruvate metabolism produces a steady-state level of acetyl coenzyme A (an active acyl-transfer agent *in vivo*)[11a], acetyl phosphate and ATP *via* the phosphoroclastic reaction (Fig. 1). TPP could well be involved in the oxidative decarboxylation of pyruvate[11b].

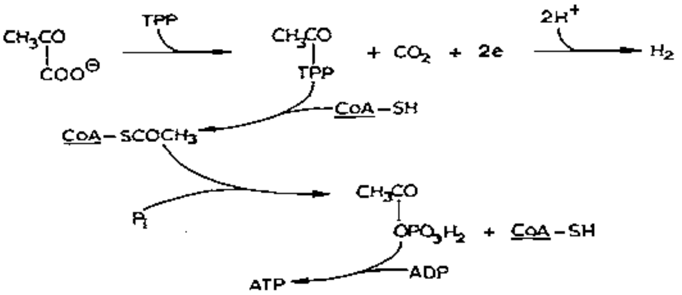


Fig. 1. The phosphoroclastic reaction.

In 1962, Mortenson *et al.*[12] reported the isolation of a non-haem iron/sulphur containing protein (Fd) from the pyruvate-utilising system of this organism[13]. This protein has a potential near that of the hydrogen electrode and it was realised that the pyruvate oxidation above is coupled to the reduction of ferredoxin, the latter being involved in the electron transport sequence from the electron donor to the nitrogen molecule[8,9b]:

$$H_2 + Fd \xrightleftharpoons{\text{hydrogenase}} Fd^{\text{reduced}} + 2H^+$$

Ferredoxin markedly stimulates the evolution of hydrogen from pyruvate[12].

Evidence that fixation requires high energy phosphate is supplied by the observation that arsenate inhibits fixation[7]. It competes with phosphate in the phosphoroclastic reaction, preventing build-up of acetyl phosphate, and hence indirectly inhibits ATP synthesis. One suggestion[8] for the role of ATP is to activate the enzyme such that combination with nitrogen occurs, with subsequent use of the energy derived from ATP for sufficient activation of nitrogen to allow reduction to take place[9a]. A reductant-dependent enzyme ATPase, and Mg^{2+} are required for ATP consumption[14]. The role of magnesium could well be to provide a centre around which ATP and the species utilising the derived energy can interact[15,16]. Other roles for ATP may be to initiate or maintain pyruvate metabolism, and when hydrogen is the electron donor, to aid in the generation of reduced ferredoxin[10]. In addition a hydrogenase function which liberates hydrogen from the active system in the absence of nitrogen is ATP dependent[14].

Pyruvate has to be replaced by a suitable ATP generator and a reductant, which confirms the dual role played by pyruvate. For example, KBH_4, H_2, NADH or NADPH can act in combination with an ATP generating system such as acetylphosphate (provided ADP is present), or creatine phosphate/creatine kinase[9].

Reduced ferredoxin can act as the electron carrier from the active reductants to nitrogen, but the dye methyl viologen can substitute[9b]. Recently Knight *et al.*[17] have isolated a metal-free flavoprotein from *Clostridium* extracts grown in an iron-deficient medium. This protein probably replaces ferredoxin as electron carrier under such circumstances.

Mortenson *et al.*[13] have separated the active extracts of *C. pasteurianum* into two fractions, designated as the nitrogen-activating (NAS) and hydrogen-donating (HDS) systems, which apart are inactive but in combination result in full fixation activity. The HDS was obtained by heating cell extracts at 60° under hydrogen, and contained the hydrogenase and pyruvate-metabolising activity. The NAS was obtained by treatment of extracts with protamine sulphate, followed by calcium phosphate gel at pH 6.5. Further work on the latter component has established[18] the presence of two components, one containing at the reported stage of purity (78%) 1 atom Mo, 1 atom Mg, 12 atoms Fe and 3 atoms sulphide per molecule, (named molybdoferredoxin) and the other containing Fe/sulphide (named azoferredoxin). Both components are inactivated by oxygen, and although the former component could be frozen anaerobically with little loss in activity, the latter lost partial activity under all examined conditions of storage.

(b) *Azotobacter vinelandii*

Active cell-free extracts can be obtained either by ultrasonic or lysozyme disruption of cells in the medium in which they are grown[19]. Successive high-speed centrifugations result in active particulate fractions sedimented between 25,000 and 144,000 g. Exposure of the extracts to ${}^{15}N$ or radioactive ${}^{13}N$ have confirmed fixation[20].

Requirements for activity

Non-haem iron (not ferredoxin); ATP (or generator); ATPase; flavin; cytochromes b, c, a; $S_2O_4^{2-}$; Mg; Mo.

The physiological source of reducing power in this organism is not pyruvate (*cf. C. pasteurianum*), and still remains to be identified[21].

In studies of this organism, dithionite has been extensively used as an exogenous electron donor[21], and creatine phosphate/creatine kinase as ATP generator[21,22]:

$$\mathrm{ADP} + \mathrm{Cr\text{-}P} \xrightleftharpoons{\text{Creatine kinase}} \mathrm{ATP} + \mathrm{Cr}$$

An ATP-dependent hydrogenase is also present (*cf. C. pasteurianum*), which liberates hydrogen from dithionite[21]. The cell-free preparations of *A. vinelandii* are routinely prepared in air, and in contrast to *Clostridium*[23] extracts they are not cold labile or unstable to dialysis[21].

The presence of a reductant-dependent ATPase has been established, which may function either in the activation of electrons for nitrogen reduction, or in energy-dependent hydrogen evolution in the absence of nitrogen[22]. Inorganic phosphate (P_i) elimination occurs from ATP *via* this ATPase in *A. vinelandii*, and although not proven, it is likely that a similar elimination occurs in *C. pasteurianum*.

Although Bulen *et al.*[24] succeeded in isolating a molybdenum-rich particulate fraction in 1956, it was not until almost 10 years later that the localisation of nitrogen-fixing activity in this fraction was reported. Purification[25] of the extracts by protamine precipitation and anaerobic chromatography has separated the active material into two enzyme components, one containing non-haem iron and molybdenum, and one containing non-haem iron only. The presence of both components is required for both nitrogen reduction and ATP-dependent hydrogen evolution.

The use of e.s.r. techniques has established the presence of both flavin and cytochromes b, c and a (containing haem-iron)[4b,26] which are components of the electron-transfer chain. In addition a reduced form of non-haem iron (not ferredoxin) is observed which may either act as yet another electron carrier, or perhaps as the endogenous source of reducing power. However, the precise nature of, and role played by this latter component awaits clarification.

(ii) Symbiotic systems

Until very recently, great difficulty had been experienced in attempts to obtain cell-free extracts from root nodules with nitrogen-fixing activity. Excised root nodules themselves, obtained from soybean plants, actively fix nitrogen and Bergersen in 1960[27] proposed a general theory of fixation, suggesting that in such plant cells, fixation occurred within a membrane envelope which encloses the bacteroids and leg-haemoglobin, a haem-iron component known for many years to be present in active nodules[28–32].

Then followed a report by Abel *et al.*[33] that ferrolegoglobin (when isolated under hydrogen) complexes with molecular nitrogen in preference to oxygen. Isolation of this haem-protein by conventional techniques results in a product (ferrilegoglobin) which preferentially complexes with oxygen. It was therefore considered that in "native" ferrolegoglobin, the haem group occupies a protected position within the protein folds, and on autoxidation, exposure of this haem group occurs (ferrilegoglobin)[34]. On this basis, a mechanism involving legoglobin as the active site of fixation was proposed (*vide infra*).

More recently, studies on an active *brei* (pulp) of soybean nodules[35] have shown that, in addition to a dependence on oxygen, fixation requires ATP.

However, in 1967 Koch *et al.*[36] successfully obtained cell-free extracts of bacteroids from soybean nodules, and demonstrated the additional requirements of an ATP generator, $S_2O_4^{2-}$ as electron donor and anaerobic conditions (*i.e.* very similar requirements to *A. vinelandii*): hydrogen evolution occurs during fixation. In this latest report, a non-haem iron protein was also isolated, but to date no consistent enzyme activity has been achieved with this component. It is also of interest to note that no mention was made of a legoglobin component in this study of a cell-free system.

(iii) Fixation intermediates

Ammonia is recognised as the key intermediate of fixation, namely "the inorganic compound at the end of fixation before assimilation of fixed nitrogen into carbon skeletons occurs"[37]. Support for this hypothesis stems from the observed fate of the tracer when active extracts are exposed to nitrogen containing $^{15}N_2$. Ammonia is the most heavily, and most rapidly labelled entity[2,38].

A reductive pathway, possibly *via* diimide (HN=NH) and hydrazine is preferred[39–41], although hydrolysis of diimide to hydroxylamine, and subsequent reduction of the latter to ammonia is also a possibility. However, no intermediates between nitrogen and ammonia have been observed. Diimide (generated by hydrolysis of dipotassium azodicarboxylate) proved inhibitory to fixation by *C. pasteurianum*. Use of ^{15}N-enriched nitrogen in the presence of hydrazine or hydroxylamine have failed to detect any labelling on subsequent isolation of their respective derivatives[41]. Hence whatever the intermediates are, they must remain tightly bound to the enzyme surface until the ammonia stage is reached. A recent report[42] of haem-protein/diimide interactions is the first piece of experimental evidence that such complexes can exist.

(iv) Metal requirements of nitrogen-fixing organisms

It is now well established that iron and molybdenum are required as trace metals by free-living organisms that fix nitrogen.

Strains of *Azotobacter* require iron and molybdenum whilst utilising molecular nitrogen as their nitrogen source for growth[2,4a,4b,4e,25a,43]. The nitrogenase systems of botb *A. vinelandii*[25] and *C. pasteurianum*[18] have been separated into an iron/molybdenum component and an iron component. The presence of molybdenum has also been established in other biological systems, *e.g.* Xanthine oxidase[44] and nitrate reductase[4b].

E.S.R. studies by Nicholas *et al.*[2,4b,26] also demonstrate the presence of iron and molybdenum in active organisms. In addition to the haem-iron components (cytochromes) necessary for cell metabolism, an e.s.r. signal (g 1.94) attributed to a reduced form of non-haem iron has been observed, although *A. vinelandii* does not contain ferredoxin. A g 1.97 signal also found in *Azobacter* particles is probably associated with Mo^V, for on oxidation or further reduction the signal disappears. It is of interest that particles from cells grown on NH_4^+ do not contain appreciable concentrations of molybdenum.

The g 1.94 iron signal also appears in the NAS component of *C. pasteurianum*[26,45] but Mo^V is not observed. However, the absence of Mo^V does not disprove the existence of molybdenum, since oxidation states other than Mo^V or Mo^{III} would not produce e.s.r. signals. In addition at least a 10 M^{-4} metal concentration is required for detection by this technique.

A Mn^{II} signal is observed in crude extracts of *C. pasteurianum*, but not in the separated NAS component. However, the significance of manganese, which is found in a number of bacteria, is not clear, although it may well be associated with the metabolism of hydrogen[26].

An apparent requirement for molybdenum is reported for fixation both in legumes[38] and non-legumes[46,47], and, as mentioned previously, the leg haemoglobin of legume symbiotic systems contains iron[28–32].

Cobalt (as Vitamin B_{12}) also appears to be essential to nitrogen fixing systems[2,4b,48], but because of the very low concentrations involved it is not considered to be an active component of the nitrogenase system, but may be involved in the biosynthesis of the enzyme systems.

In spite of tbe numerous papers published on the subject of biological nitrogen fixation, a great deal of speculation still exists as to the precise roles played by the iron and molybdenum components, and definitive proof is still awaited. At the present stage of the subject, enzyme purification is the major obstacle confronting the biochemist, and until the detailed examination of a highly purified enzyme is achieved, one can still only speculate.

Yakovlev and Gvozdev[49] have recently studied the kinetics of molybdenum and iron uptake by growing *A. vinelandii* cells, and find that the extent of molybdenum incorporation into cells utilising molecular nitrogen is directly proportional to their nitrogen-fixing activity. In contrast molybdenum incorporation into cells grown in an NH_4^+ medium is proportional to cell growth. The latter is also paralleled by hydrogenase activity and the extent of iron incorporation into cells growing on nitrogen gas. It is therefore postulated tbat molybdenum participates in the enzymic activation of nitrogen, rather than being associated with the hydrogenase function.

Il'ina[50] suggests that a similar correlation exists between molybdenum and the nitrogen-activating system of mycobacteria, in which molybdenum does not affect hydrogenase activity, but does stimulate certain dehydrogenases. It would appear, from analogous studies on *A. chroococcum*[51], that this organism adapts to a certain concentration of molybdenum, above which no further increase in nitrogen-fixing activity is observed.

In contrast to the above, Bulen *et al*[25a]. assume from the available evidence that iron is the metal site at which the nitrogen molecule is bound, with molybdenum (in cooperation with a flavin moiety) functioning as a single-electron transfer agent (*vide infra*).

The idea that fixation of nitrogen occurs at a metal site on the enzyme surface receives support from the observed inhibition of fixation by substrates other than nitrogen. H_2, CO, N_2O and NO competitively inhibit fixation in extracts of *C. pasteurianum*, at concentrations which do not markedly affect the rate of pyruvate metabolism[13,52]. Cyanide and azide are both weak inhibitors. However, although hydrogen inhibition is competitive at low concentrations of phosphate, it becomes noncompetitive at high concentrations[52]. The reason for this behaviour is unknown. Hydrogen is also a competitive inhibitor of fixation both in *A. vinelandii*[53] and cell-free extracts of soybean root nodules[36].

A number of studies have found that acetylene is also a competitive inhibitor in cell-free extracts of *C. pasteurianum*[54,55], *A. vinelandii*[55] and soybean root nodules[36].

Removal of the gaseous inhibitors by evacuation and replacement by nitrogen results in regeneration of fixation activity, thus indicating the reversible nature of inhibition. It also strongly suggests that the inhibitory site is identical with the nitrogen-binding site on the enzyme. A metal centre would seem to be a very attractive possibility as the site for facile attachment of such a number of low molecular weight gases of diverse properties.

In addition to these inhibitory effects, certain low molecular weight substrates also undergo reduction by the biological nitrogen-fixing systems. Nitrous oxide is reduced to ammonia by *C. pasteurianum*[52] at approximately 6% of the rate of nitrogen fixation. This presumably occurs *via* the conversion:

$$N_2O \rightarrow N_2 + H_2O$$

as evidence of this conversion has been reported from studies on nodule[56] and free-living[57] systems.

Acetylene is readily reduced to ethylene by *C. pasteurianum* extracts[54,55], the requirements being identical to those for nitrogen reduction, namely ATP, Mg and ferredoxin. In this connection, Moustafa and Mortenson[16] have recently found that Mg^{2+} ions are needed for ATP utilisation, and have suggested that two molecules of ATP participate in the rate-determining step(s) catalysed by the acetylene-reducing system. ADP appears to regulate the sequence of events by acting as a "negative modifier". When a low ATP:ADP ratio is present, acetylene reduction (*i.e.* nitrogen-fixation) is inhibited and the remaining ATP can be utilised for other cell functions.

Both the *brei* and cell-free extracts of soybean root nodules also reduce acetylene to ethylene[36]. Further reduction of the ethylene formed does not occur, apparently due to the olefin being readily released from the active site. The facile measurement of acetylene reduction has even been used[58] as an index of fixation *in situ*, in such habitats as lakes, soils and nodulated plants. It is a sensitive method, and is much more rapid and cheaper than the conventional ^{15}N technique.

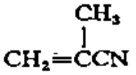
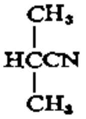
Other substrates reduced by the nitrogen-fixing organisms *C. pasteurianum*, *A. vinelandii* and *A. Chroococcum* include acetylene analogues[59], hydrogen cyanide[59,60], alkyl cyanides and isocyanides[4a,59], and azide ion[60,61]. The following table (Table 1) presents the substrates studied and the isolated reduction products in order of decreasing rates of reduction.

The overall conclusions drawn from these studies are that the conversions proceed by two-electron reductive steps; the requirements for reduction being ATP, and dithionite (or hydrogen or borohydride) as electron source. The substrates inhibit ATP-dependent hydrogen evolution from dithionite, and all the reductions are inhibited by carbon monoxide, although the latter is not reduced. The number of electrons involved are either two, four, six, eight, ten or twelve, thus demonstrating that if nitrogen is reduced to ammonia by the same mechanism, then diimide and hydrazine would be intermediate products. Since further reduction of ethylene to alkane is not observed, release of olefin from the binding site must be a facile process, in contrast to the nitrogen reduction intermediate at the same oxidation level, *i.e.* diimide.

Differences in the rates of reduction encountered between different substrates are assigned to either electronic or steric effects at the substrate binding site, *e.g.* $CH_3NC > CH_3CN$, due to better end-on bonding of the electron-rich terminal carbon of CH_3NC. The reduction of $CH_3CH{=}CHCN$ and $CH_2{=}CHCH_2CN$, *versus* the unreactivity of $CH_3CH_2CH_2CN$, may be attributed to the

TABLE I

SUBSTRATES REDUCED BY CELL-FREE EXTRACTS OF ASYMBIOTIC NITROGEN-FIXING BACTERIA

Substrate	*Isolated Products*
CH_3NC	$CH_4+CH_3NH_2$ [+traces of C_2H_6 and C_2H_4]
HCN	CH_4+NH_3 [+traces of CH_3NH_2]
$CH_2=CHCN$	$C_3H_6+C_3H_8$
CH_3CN	C_2H_6 [+trace NH_3]
CH_3CH_2CN	$C_2H_6+C_3H_8$
cis $CH_3CH=CHCN$	$CH_3CH_2CH=CH_2+C_4H_{10}+$ *cis* $CH_3CH=CHCH_3$
$CH_2=CHCH_2CN$	$CH_3CH_2CH=CH_2$
trans $CH_3CH=CHCN$	*trans* $CH_3CH=CHCH_3$
 $CH_2=C(CH_3)CN$	no reduction
$CH_3CH_2CH_2CN$	
 $(CH_3)_2CHCN$	
$HC\equiv CH$	$CH_2=CH_2$
$CH_3C\equiv CH$	$CH_3CH=CH_2$
$CH_3CH_2C\equiv CH$	$CH_3CH_2CH=CH_2$
$CH_3C\equiv CCH_3$	no reduction
$CH_2=CHCH=CH_2$	

possibility of interaction of the double bond at a second site thus enhancing the binding to the enzyme. Steric effects may be operative when the comparison of *cis*-$CH_3CH=CHCN$ *versus* *trans*-$CH_3CH=CHCN$ or $CH_2=C(CH_3)CN$ is considered. By using deuterium oxide as solvent for extracts and reagents during acetylene reduction by *C. pasteurianum*, Dilworth[54] found that *cis*-$C_2H_2D_2$ was the sole product. The reduction therefore appears to be completely stereospecific, with only *cis* addition of hydrogen occurring, which suggests that the substrate is both firmly and specifically bound to the enzyme during reduction.

(v) Mechanisms of fixation

Winfield in 1955[62] proposed that a multifunctional dinuclear metal site on the enzyme surface serves to bind the nitrogen molecule, for subsequent hydrogenation to ammonia, with ligand atoms (possibly carbon) facilitating the transfer of hydrogen atoms to the bound nitrogen (Fig. 2). Roberts[63] considered that initially a chemisorption of nitrogen occurs (analogous to that postulated to occur when clean metal surfaces are exposed to nitrogen, *vide infra*) and that maybe even polynuclear metal sites are involved (Fig. 3).

In these schemes, subsequent release of the product ammonia then regenerates the dinuclear site, and the catalytic cycle is repeated.

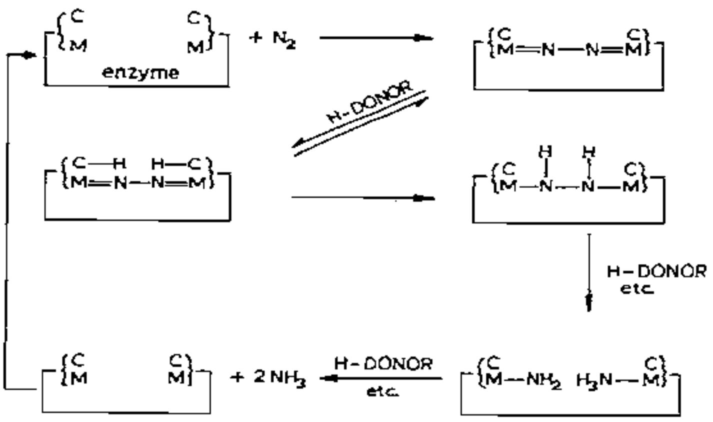


Fig. 2. Mechanism of fixation according to Winfield[62].

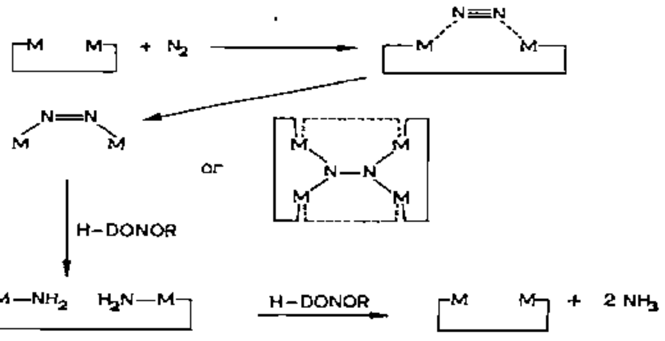


Fig. 3. Mechanism of fixation according to Roberts[63].

In 1963, following the observation that ferrolegoglobin present in legume root nodules preferentially complexes with nitrogen[33], Abel[64] expanded a mechanism put forward by Hoch *et al.*[56], and incorporated a role for legoglobin as the site of fixation in symbiotic systems (Fig. 4). The assumptions made were (a) that two legoglobin components form a complex (I) *in vivo*, thus providing a dinuclear metal site, and (b) that configuration changes occurred within the complex, to provide for the increase in N–N bond length from 1.09 Å in nitrogen gas to 1.47 Å in the postulated enzyme-bound hydrazine intermediate. The reversible valency change of $Fe^{II} \rightleftharpoons Fe^{III}$, which can occur with the central haem-iron of such components, also plays an important role.

The postulate of a transient bound $[N_2]^{2-}$ intermediate(II) receives some theoretical support from the electron affinity estimates of Bauer[65], who reported that the $[N_2]^{-}_{aq}$ anion may become moderately stable when situated near sufficient positive charges (*i.e.* metal cations), and that such an ion would show a great affinity for a proton in an aqueous environment. In fact Bauer had previously

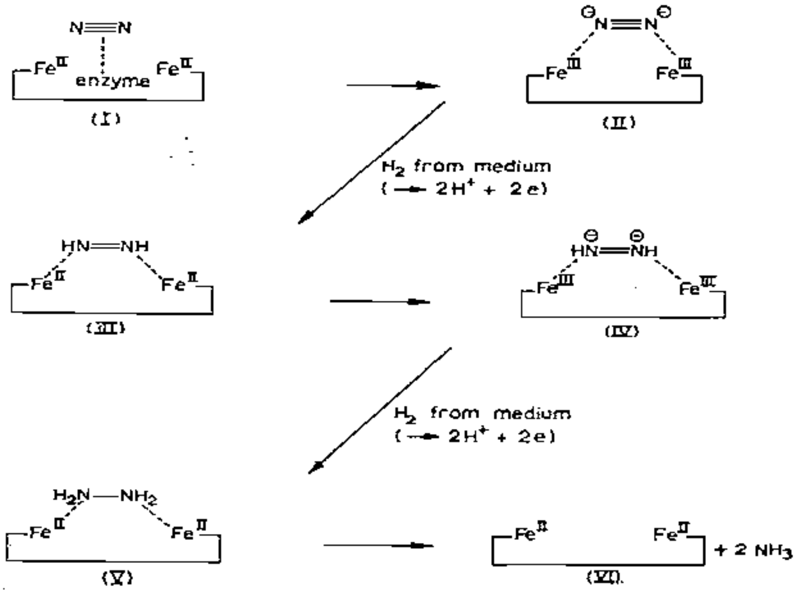


Fig. 4. Mechanism of fixation according to Abel[64].

proposed[66] a free-radical mechanism for symbiotic fixation at a mononuclear legoglobin site, involving the hypothetical N_2H radical, formed either from $[N_2]^-$ by proton capture, or by attack of a hydrogen radical on a legoglobin-bound nitrogen molecule.

In order to allow for the increase in N–N bond length in the diimide and hydrazine intermediates, Abel suggested that an enzymic configuration change occurs (II → III and IV → V in Fig. 4) *via* removal of protons (to produce hydrogen) from the immediate vicinity of the binding site, with a resultant increase in pH. During the final stage of the cycle, following release of ammonia from the active site, back-diffusion of protons is assumed to occur, to re-establish the original pH with a consequent configuration change (VI → I) necessary to bind a further molecule of nitrogen.

The effect of gaseous inhibitors would be to compete with nitrogen for the metal centres, with, for example, carbon monoxide being preferentially bound, since it need only react with one metal atom to block the dinuclear site required by nitrogen. The presence of excess hydrogen would prevent the necessary configuration changes by inhibition of the conversion of protons to hydrogen. The latter would thus inhibit fixation.

In 1965, without recourse to Abel's work, Bulen *et al.*[25a] suggested a working hypothesis for nitrogen fixation in free-living organisms. In the light of work by Koch *et al.*[36] on cell-free extracts from root nodules this might also be applicable to symbiotic systems. This mechanism (Fig. 5) envisages that one of the roles of

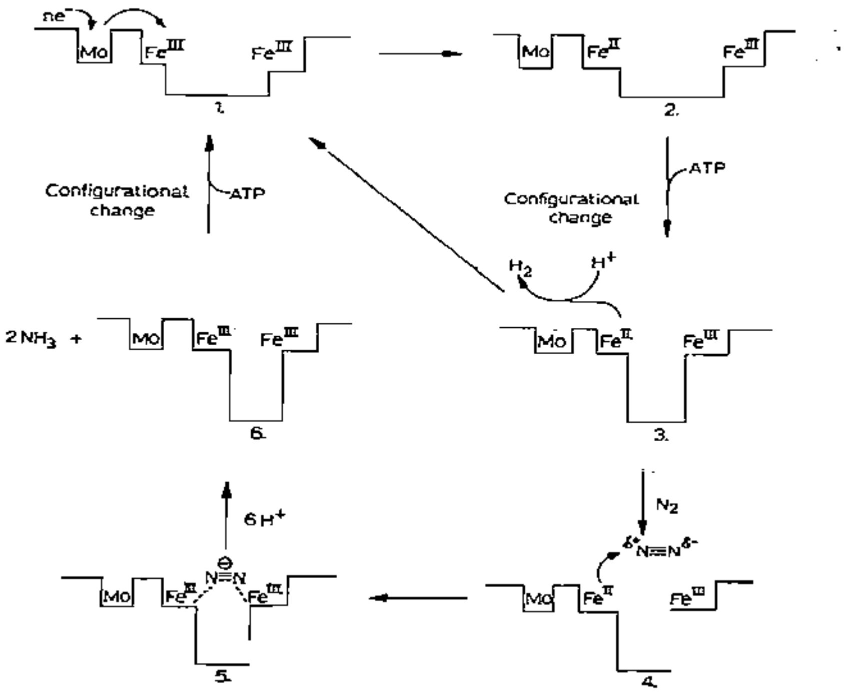


Fig. 5. Mechanism of fixation according to Bulen *et al.*[25a].

ATP is to effect configurational changes of the enzyme, akin to those envisaged by Abel as occurring *via* changes in pH. It was thought that ATP might also function in providing low potential electrons when an endogenous electron donor is used. The scheme again assumes an iron dinuclear active site, but in contrast to Abel's mechanism, a possible role for molybdenum is suggested (by analogy with molybdenum participation in other enzymes), namely as a one-electron transfer agent in conjunction with a flavin moiety. This could facilitate reduction of the iron from Fe^{III} to Fe^{II} (1 → 2) before attachment of nitrogen occurs. Subsequent re-oxidation to Fe^{III}, transfer to the bound nitrogen molecule (4 → 5), and proton capture (5 → 6), leads to the initial reduced form of nitrogen at the oxidation level of diimide and ultimately to ammonia. It will be noted that the $[N_2]^-$ anion is postulated as a transition state. It is also recognised that the possibility of polynuclear metal sites should not be overlooked.

At stage (3) in the absence of nitrogen, interaction with protons could regenerate the ferric state with evolution of hydrogen. The idea of only one iron atom undergoing reduction (2), is to provide polarisation of the nitrogen molecule once bound (4), and hence facilitate electron transfer (5). Carbon monoxide could also interact with metal centres at the nitrogen binding site (3), but although it would inhibit fixation, hydrogen evolution would be unaffected, since carbon monoxide would not accept electrons. Nitrous oxide inhibits both fixation and hydrogen evolution, and it may be that this molecule is bound before the configurational change occurs (2).

Hardy *et al.*[22,67] also consider the mechanism of fixation as involving two active metal sites on the enzyme (Fig. 6), namely an electron-activating site and a substrate-binding site. However they do not necessarily consider a dinuclear metal site for binding the nitrogen molecule prior to reduction. Although the mechanism is based on results obtained with *C. pasteurianum* and *A. vinelandii*, it is likely that an analogous pathway could be applicable to the nitrogen-fixing systems of symbiotic associations.

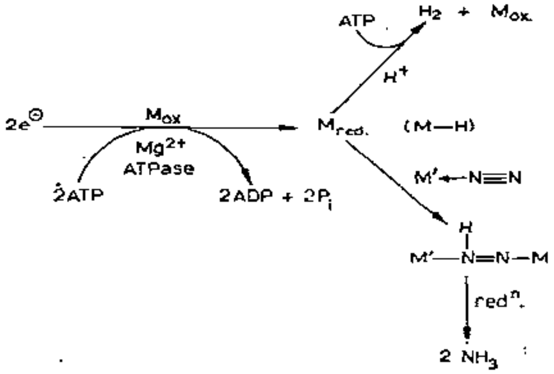
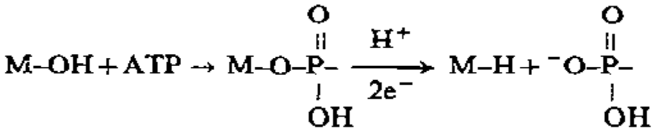


Fig. 6. Mechanism of fixation according to Hardy *et al.*[22,67].

Electrons from a suitable donor *e.g.* dithionite, or hydrogen *via* hydrogenase and ferredoxin (or other electron transport proteins) are activated by ATP *via* the reductant-dependent ATPase. Reduction of a metal site ($M_{ox.}$) occurs to produce $M_{red.}$ which could exist as a metal hydride. It may be that ATP assists in metal hydride formation by providing a good leaving group:



$$\text{M–OH}+\text{ATP} \rightarrow \text{M–O–}\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{OH}}{|}}{\text{P}}}\text{–} \xrightarrow[2e^-]{H^+} \text{M–H}+{}^-\text{O–}\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{OH}}{|}}{\text{P}}}\text{–}$$

The observation that the reductant-dependent ATPase is inhibited by chelating agents suggests metal involvement, and the presence of thiol is suggested by the inhibition obtained with PCMS. This electron-activation sequence is not inhibited by CO, H_2, N_2O, CN^- or N_3^- and in the absence of an electron acceptor the activated electrons are released as hydrogen.

The substrate-binding site (M′), probably a metal-protein complex, accommodates the substrates undergoing reduction, and is sensitive to carbon monoxide and hydrogen which can block the site, thus inhibiting fixation. Subsequent use of the activated electrons ($M_{red.}$) results in the reduction of nitrogen to ammonia.

The sites (M) and (M′) which may involve iron or molybdenum, must be distinct from each other for the former is insensitive to competitive inhibitors of fixation, in contrast to the latter. However it is likely that coupling of the two sites occurs in some way during fixation to increase the efficiency of the process.

C. REACTION OF NITROGEN WITH ORGANOMETALLIC SPECIES

The discovery of the first transition metal systems to react with nitrogen under mild conditions was made by Volpin, Shur *et al.*[68] Their work has established a basis for attempts at the catalytic fixation of nitrogen. Using mild conditions, room temperatures and pressures from 1 to 150 atmospheres, they successfully observed the reaction of nitrogen with the two-component system consisting of a transition metal halide and a reducing agent (*i.e.* RMgX, AlR_3, LiR, $LiAlH_4$). Subsequent hydrolysis of the products from these reactions liberated ammonia.

TABLE 2

THE REACTION OF NITROGEN WITH TRANSITION METAL COMPOUNDS AND REDUCING AGENTS

Transition metal Compound	*Reducing agent*	*Solvent*	*Nitrogen pressure (in atmospheres)*	*Ammonia produced on hydrolysis (in moles/mole of transition metal)*
$TiCl_4$	$Mg+I_2$	Ether	90	1.30
$(\pi\text{-}C_5H_5)_2TiCl_2$	C_2H_5MgBr	Ether	150	0.93
$(\pi\text{-}C_5H_5)_2TiCl_2$	LiC_6H_5	Ether	100	0.65 (+0.15 moles $C_6H_5NH_2$)
$(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$	–	Ether	80*	0.20
$TiCl_4$	$Al(Bu^i)_3$	Heptane	150	0.25
$TiCl_4$	C_2H_5MgBr	Ether	150	0.104
$VO(acac)_2$	$LiBu^n$	Toluene	83	0.35
$CrCl_3$	C_2H_5MgBr	Ether	150	0.20
$CrCl_3$	C_2H_5MgBr	Ether	150	0.168
$MoCl_5$	C_2H_5MgBr	Ether	150	0.075
WCl_6	C_2H_5MgBr	Ether	150	0.147
$Mn(acac)_3$	$Al(Bu^i)_3$	Toluene	100	0.09
$FeCl_3$	C_2H_5MgBr	Ether	150	0.088
$CoCl_2$ $NiCl_2$ $PdCl_2$ $(Ph_3P)_2PtCl_2$ Cu_2Cl_2	C_2H_5MgBr	Ether	150	0.00

* At 100 °C; all other reactions carried out at room temperature.

Table 2 indicates the range of elements, types of complexes and yields of ammonia that Volpin and Shur were able to obtain. Experiments[69] using $^{15}N_2$ proved that fixation was occurring since at least 97% of the ammonia produced came from the gaseous nitrogen.

The use of hydrogen/nitrogen gas mixtures[68b] showed that in most cases hydrogen caused a slight inhibition of fixation or had no effect at all. However, with the $Ti(acac)_4/AlBu^{i}_{3}$ system there was a significant increase in ammonia produced on hydrolysis when a $N_2:H_2$ ratio of 3:1 was employed.

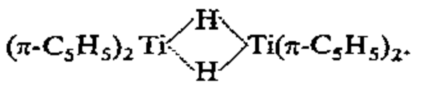
By depositing ferric chloride on various carriers (alumina, silica gel etc.) Khidekel and Grebenshchikov[70] were able to overcome the slight inhibition which hydrogen causes when ferric chloride is used alone. The presence of the carrier does not increase the yield of ammonia but seems to prevent attack of the reactive species by hydrogen.

Nitrogen was also shown to react with single organometallic species; $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ and $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$[71]. On heating these compounds with nitrogen at 80–90 atmospheres pressure, reaction occurred and subsequent hydrolysis yielded ammonia. Heating will convert both these compounds to titanocene, but further experiments showed that although titanocene would react with nitrogen the yield of ammonia was less than for either titanium(IV) compound. It is perhaps significant that the presence of hydrogen increases the yield of ammonia with all three compounds.

Careful investigation of the products from the system $(\pi\text{-}C_5H_5)_2TiCl_2/LiPh/N_2$ after hydrolysis showed aniline (0.15 mole/mole) as well as ammonia (0.65 mole/mole)[72]. Use of the *p*-tolyl lithium reagent gave *p*-toluidine. Volpin and Shur offer two alternative mechanisms: nitrogen insertion into a metal-aryl bond, forming intermediates such as $Ti{-}N{=}N{-}Ar$ (*vide infra*) or direct attack of phenyl lithium on a nitrogen molecule activated through coordination.

Carbon monoxide and hex-1-ene inhibit the nitrogen fixing ability of these systems[73] and this lends support to the theory that nitrogen coordinates at an active site on the transition metal—a site that is effectively blocked by carbon monoxide or an olefin.

In general the above experiments are probably suggestive of hydride intermediates being important[68a] and Brintzinger[74] has carried out e.s.r. work on the system $(\pi\text{-}C_5H_5)_2TiCl_2/C_2H_5MgBr$ to show conclusively the presence of hydridotitanium species. Addition of excess Grignard to $(\pi\text{-}C_5H_5)_2TiCl_2$ under argon gives rise to a complex signal near $g = 2$ which transforms in about one hour into a symmetric signal at $g = 1.993$, which deuteration studies confirm as being due to two equivalent protons coupling to titanium. Brintzinger has since[74b] reassigned the spectra as being due to a monomeric dihydride anion $[(\pi\text{-}C_5H_5)_2TiH_2]^-$, rather than his original formulation of a hydride bridged dimer,



$$(\pi\text{-}C_5H_5)_2Ti\langle\begin{smallmatrix}H\\H\end{smallmatrix}\rangle Ti(\pi\text{-}C_5H_5)_2.$$

This new formulation is based on the fact that only ten equivalent cyclopentadienyl protons can be seen coupling to each titanium nucleus. Brintzinger receives support from Maskill and Pratt[75] in stating that this initial species is indefinitely stable in the absence of air, whereas Shilov *et al.*[76] state that a delay in introducing nitrogen will result in less fixation. It is conceivable that an unidentified titanium complex (perhaps the species with $g = 2$) is the reactive intermediate and is in equilibrium with the observed hydride prior to reaction with nitrogen. Brintzinger also examined the final reaction solution before hydrolysis after a mixture of $(\pi\text{-}C_5H_5)_2TiCl_2$ and a ten fold excess of C_2H_5MgBr had been kept under 150 atmospheres pressure of nitrogen for 15 days. Only weak and complex e.s.r. signals were seen; however, slight acidification produced a strong signal at $g = 1.987$. Although Brintzinger originally claimed[74a] that the hyperfine pattern was due to two equivalent nitrogen atoms, he later showed[74b] that it was due to the four methylene protons of $[(\pi\text{-}C_5H_5)_2Ti(C_2H_5)_2]^-$, formed by the action of excess Grignard reagent on the halide species resulting from acidification of the nitrogen containing complex.

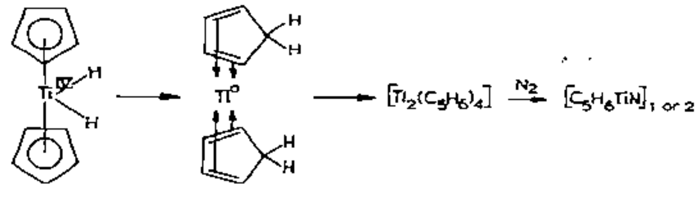
An important contribution to the mechanism of the $(\pi\text{-}C_5H_5)_2TiCl_2/C_2H_5MgBr$ system was made by Shilov *et al.*[76], using deuterated Grignard and solvent ether. It was first noted that about 1/3 of the gaseous products were liberated in the first five minutes after mixing and this occurs prior to any nitrogen fixation. The reactive intermediate formed at this stage is unstable (*cf.* Brintzinger[74] and Maskill and Pratt[75]) and any delay in introducing nitrogen reduces the amount of fixation. Hydrolysis at this stage with D_2O liberates HD which would be anticipated from the hydrolysis of a metal hydride. When nitrogen is present less hydrogen is liberated since less of the hydride species will be present. This may be due to reaction of the hydride species with nitrogen or due to the precursor of the hydride preferentially reacting with nitrogen. Ethylene and ethane are evolved and a complete breakdown of the ligand system occurs. Using C_2D_5MgBr the ethane is substantially C_2D_6, showing that the solvent is not taking part. Again if the system $(\pi\text{-}C_5H_5)_2TiCl_2/C_2D_5MgBr$ is hydrolysed with H_2O then HD is liberated showing that the hydride ligand originates from the Grignard.

In the system $(\pi\text{-}C_5H_5)_2TiCl_2/C_2D_5MgBr/(C_2D_5)_2O$, if the final hydrolysis is carried out using H_2O, no deuterium is found in the ammonia. Since ND_3 introduced at the beginning of the reaction retains deuterium Shilov *et al.* conclude that no hydrogen is attached to nitrogen prior to hydrolysis and that a nitride is formed from finely divided titanium metal and nitrogen.

Maskill and Pratt[75] carried out some kinetic measurements on the $(\pi\text{-}C_5H_5)_2TiCl_2/C_2H_5MgBr$ system, taking the amount of nitrogen fixed after one hour as a measure of rate. Despite the complexity of the reaction, several interesting points emerged based on this assumption. Using nitrogen-argon gas mixtures (to a total pressure of one atmosphere), the rate of nitrogen fixation is dependent on the partial pressure of nitrogen (pN_2) when the latter is low, but becomes independent at high pN_2 values. Thus the reactive intermediate is in excess at low pN_2 whereas its formation is the rate-determining step at high pN_2

i.e. $2\,Ti^x \xrightarrow{A} Ti_2{}^x \xrightarrow[N_2]{B}$ Products

Process A (which other results suggest may be a dimerisation) is rate determining at high pN_2, and B at low pN_2. Ti^x and Ti_2^x are unidentified monomeric and dimeric species. If Brintzinger's intermediate dihydride anion is a major constituent of the solutions, it cannot then be the reactive intermediate. Maskill and Pratt postulate a zero-valent titanium species as a possible intermediate:



This species could be analogous to a metal surface but not finely divided metal as suggested by Shilov *et al.*

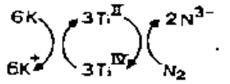
Olivé and Olivé[77] have worked on metal halide systems with lithium naphthalide in THF as reducing agent. Under argon the products of this reaction probably have σ- and π-naphthalene residues coordinated to the metal, and are good starting materials for a variety of complexes[77a]. These reduced species can store up to six electrons per transition metal and will react with nitrogen[77b]. The electrons are transferred to nitrogen so that it is bound as two nitride entities, *i.e.* $N_2 \xrightarrow{6e} 2N^{3-}$. Hydrolysis will liberate ammonia.

The ability of the complex to fix nitrogen depends on the capacity of the reduced species to store electrons, and this can be estimated by hydrolysis prior to reaction with nitrogen—the amount of hydrogen liberated being dependent on the electrons available. In the most favourable case (VCl_3 with a seven-fold excess of lithium naphthalide at 120 ats. of nitrogen for a reaction time of 30 minutes at 20 °C) 2.0 moles of ammonia/mole of vanadium are produced on hydrolysis. This is an improvement on any system studied by Volpin and Shur—their maximum yield was 1.30 mole/mole for $TiCl_4/Mg/MgI_2$ system.

Olivé and Olivé also found that $CrCl_3$ and $TiCl_4$ would fix nitrogen under their conditions but $NiCl_2$, although yielding a reduced species useful for preparing nickel complexes, was inactive.

The major objection to the above systems is that hydrolysis is necessary to produce any useful nitrogen-containing products. Recently van Tamelen *et al.*[78] published details of a system similar to those of Volpin and Shur but with a significantly different result in that ammonia is evolved without recourse to hydrolysis. Titanium tetrachloride was added to potassium *t*-butoxide in diglyme under nitrogen to give $TiCl_2(OBu^t)_2$. Addition of two equivalents of potassium resulted in reduction of titanium(IV) to titanium(II) and ammonia was evolved. The ammonia was identified in exit traps 48 hours after the addition of the potassium and evolution continued for several weeks. Yields of ammonia were 10–15 % based on titanium, and more was obtained by hydrolysis of the reaction mixture. Various titanium alkoxides were used successfully but a change in solvent markedly reduced the amount of ammonia produced. It is concluded that hydrogen abstraction from the diglyme occurs.

The oxidation-reduction steps may be written in the following way:



The ability of the titanium species to be indefinitely cycled is perhaps the key factor here—if it can be recycled there is a potentially important catalytic process. However, hydrolysis does yield more ammonia and this may be coming from a titanium nitride species which would be a termination sequence in the above process.

It should also be mentioned that Yatsimirskii and Pavlova[79] achieved nitrogen fixation in aqueous systems. Metal salts in acidic media were reduced with zinc or zinc amalgam and found to react with nitrogen—alkali was needed to liberate ammonia. Active compounds included $TiCl_4$, $VOSO_4$, $NbCl_5$, $K_2Cr_2O_7$, Na_2MoO_4, Na_2WO_4 and $KReO_4$, and were those considered to be reducible by zinc or zinc amalgam. $KMnO_4$, $CrCl_3$, $TaCl_5$, $HfOCl_2$ and $ZrOCl_2$ were found to be inactive. $CrCl_3$ is clearly an exception to the rationalisation since it is inactive but readily reduced by zinc amalgam.

D. NITROGEN COMPLEXES OF TRANSITION METALS

The work of Volpin and Shur has shown without any doubt that nitrogen will react with certain organometallic compounds, but the appearance of a paper in December 1965 by Allen and Senoff[80] represents the point at which a new interest was taken in the field of nitrogen fixation. The limitation of Volpin and Shur's work, in that hydrolysis is necessary to produce ammonia, is always apparent and Allen and Senoff's paper showing that molecular nitrogen could function as a ligand to a transition metal seemed to open up new areas for work and speculation.

There are now several examples of nitrogen complexes and these will be treated element by element:

Ruthenium: Allen and Senoff's contribution was to recognise the existence of $[Ru(NH_3)_5N_2]^{2+}$ (isolated as chloride, bromide, iodide, tetrafluoroborate and hexafluorophosphate, from the reaction of ruthenium trichloride* and hydrazine hydrate) and thus establish for the first time molecular nitrogen as a ligand.

This reaction had been tried much earlier by Goremykin[81] using hydrazine

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* Ruthenium trichloride as supplied commercially contains ruthenium(IV) as well as ruthenium(III) species.

hydrochloride, and he reported a red compound which on treatment with acid gave a yellow crystalline material. Both were formulated as hydrazine complexes but Prout and Powell[82] showed by X-ray analysis that the yellow compound was $[Ru(NH_3)_5Cl]Cl_2$. The red compound has not been properly characterised and may contain coordinated nitrogen. A known reaction of the nitrogen complex (see Fig. 7) is to form $[Ru(NH_3)_5Cl]Cl_2$ with hydrochloric acid.

The presence of nitrogen in Allen and Senoff's compound was confirmed by a series of experiments whereby various ligands were used to displace the nitrogen, which was collected and analysed by mass spectrometry (see Fig. 7). Decomposition of the compound by concentrated sulphuric acid yielded pure nitrogen but only in 40% of the theoretical amount.

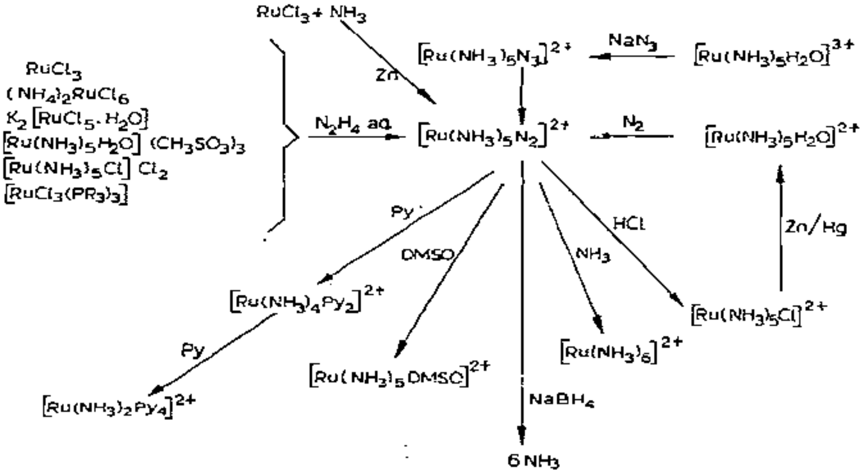


Fig. 7. Preparations and reactions of $[Ru(NH_3)_5N_2]^{2+}$.

Examination of the i.r. spectra of these compounds revealed a very characteristic strong absorption band at *ca.* 2100 cm^{-1} which must be assigned to the $N{\equiv}N$ stretching frequency if nitrogen is a ligand. This would represent a lowering on coordination of about 200 cm^{-1} compared with the Raman active band in molecular nitrogen which is observed at 2331 cm^{-1}. An alternative explanation was that nitrogen had been eliminated from a hydrazine or diimide ligand and that the 2100 cm^{-1} band was due to a metal hydride. This was dispelled by deutero-hydrazine experiments[83]: the compound prepared from $N_2D_4 . D_2O$ had an i.r. spectrum in which all the bands characteristic of N–H in the original sample had shifted whereas the 2100 cm^{-1} band was virtually unchanged.

Subsequently Allen and his co-workers[83] discovered two better routes to this compound—from the decomposition of $[Ru(NH_3)_5N_3]^{2+}$, which provides further proof of the structure of the compound, and by the reduction of $[Ru(NH_3)_5H_2O]_3{}^+$ with hydrazine hydrate. There is, in fact, a wide range of ruthenium complexes, including $RuCl_3(PR_3)_3$[84], which will give Allen's compound on treatment with hydrazine hydrate.

Allen *et al.*[83] speculate on the mechanism of formation of the nitrogen complex; when ruthenium(IV) species are treated with hydrazine hydrate it is possible to detect coordinated azide as an intermediate, but this does not occur when a pure ruthenium(III) compound is used. Azide ion is only formed by a 2 electron oxidation of hydrazine. However, the recent work of Harrison and Taube[85] has shown that the nitrogen compound can be formed from nitrogen gas, which would be produced by the action of a one electron oxidant on hydrazine. Simple treatment of $[Ru(NH_3)_5H_2O]^{2+}$ (prepared *in situ* by zinc amalgam reduction of $[Ru(NH_3)_5Cl]Cl_2$) with nitrogen at atmospheric pressure will give Allen's compound. A second compound was formed in this reaction, as evidenced by a peak in the u.v. but it was not identified. A solid was isolated which showed a weak absorption near 2100 cm^{-1} and liberated nitrogen on oxidation. Very recently Taube and his co-workers[86] were able to identify this new species as $[(NH_3)_5Ru N_2Ru(NH_3)_5]^{4+}$ (isolated as the tetrafluoroborate). This represents a new class of nitrogen complexes with molecular nitrogen acting as the single bridging group between two metal atoms. As would be expected from such a symmetrical arrangement, the i.r. absorption is weak and is centred at 2060 cm^{-1}. An alternative preparation is by addition of $[N_2Ru(NH_3)_5]^{2+}$ to $[(H_2O)Ru(NH_3)_5]^{2+}$ *i.e.* both molecular nitrogen and the nitrogen complex are capable of displacing water from the first coordination sphere of ruthenium.

Even more surprising is a report by Chatt and Fergusson[87] of a $[Ru(NH_3)_5 N_2]Cl_2$ preparation which apparently involves oxidation of ammonia to nitrogen in a strongly reducing environment. Hexammineruthenium(II) dichloride is prepared by the action of zinc on ruthenium chloride in concentrated aqueous ammonia. However it was noticed that the product was always contaminated by 1–3% of $[Ru(NH_3)_5N_2]Cl_2$. The use of anhydrous ammonia followed by hydrolysis increased the yield of the nitrogen complex to 10–15%. The experiments were carried out under argon thus leaving ammonia as the only source of nitrogen. The yields of $[Ru(NH_3)_5N_2]Cl_2$ were not, in fact, increased by bubbling nitrogen through the solution.

The decomposition of ammonia to nitrogen occurs readily on some metal surfaces (*vide infra*) but is a surprising reaction in a strongly reducing medium. Chatt and Fergusson suggest that a ruthenium hydride species may form which reacts with nitrogen liberating hydrogen.

Taube *et al.*[88] had previously made efforts to prepare nitrogen complexes by attacking coordinated azide with nitrosonium ion, *e.g.*

$$
\begin{aligned}
(NH_3)_5CoN_3{}^{2+} + NO^+ \rightarrow [(NH_3)_5CoNNNNO]^{3+} &\rightarrow (NH_3)_5CoN_2{}^{3+} + N_2O \\
\searrow [(NH_3)_5CoN(NO)NN]^{3+} &\rightarrow (NH_3)_5CoN_2O^{3+} + N_2
\end{aligned}
$$

Despite using $[(NH_3)_5CoN_3]^{2+}$, $[Pt(dien)N_3]^+$, $[Ru(phen)_2(py)N_3]^+$ and

$[(CN)_5CoN_3]^{3-}$ no evidence could be gathered for either nitrogen or nitrous oxide complexes.

Fig. 7 summarises the methods of preparation of $[(NH_3)_5RuN_2]^{2+}$ and the uses to which this compound has been put. In particular Allen[89] has prepared a variety of compounds $[Ru(NH_3)_5X]^{2+}$ which cannot easily be obtained by other routes.

Allen and Senoff[80] also report the sole example of enhanced reactivity of the coordinated nitrogen; reduction by sodium borohydride followed by alkali treatment liberates 6 moles ammonia/mole of ruthenium. It is not explained why only half of the coordinated nitrogen should give ammonia, nor is it clear why sulphuric acid treatment gives only 40% of the theoretical amount of nitrogen.

A crystal structure determination[90] of $[Ru(NH_3)_5N_2]I_2$ has shown the ruthenium atom and the two nitrogen atoms to be linear. Disorder in the crystal unfortunately prevented accurate determination of bond lengths: the approximate values being Ru–N $\simeq$ 2.11 Å and N–N $\simeq$ 1.12 Å.

Shilov *et al.*[91] reduced a THF solution of ruthenium trichloride with zinc in an atmosphere of nitrogen and isolated, but could not characterise, the first nitrogen complex to be prepared from molecular nitrogen. The solid product obtained on evaporation of the THF was shown to contain coordinated nitrogen by an i.r. band at 2140 cm^{-1} which shifted to 2070 cm^{-1} when the experiment was repeated using nitrogen-15.

Yamamoto *et al.*[92] report the formation of a hydridoruthenium species, possibly $(Ph_3P)_4RuH_2$, which reacts reversibly with molecular nitrogen to give a nitrogen complex. In contrast to the stable $[(NH_3)_5RuN_2]^{2+}$, the coordinated nitrogen is extremely labile and can even be displaced by argon as well as hydrogen and ammonia.

Osmium: Allen[93] has prepared the osmium analogue of his nitrogen ruthenium complex by reacting ammonium hexachloroosmate(IV) with hydrazine hydrate. Borod'ko *et al.*[94] have also published some observations on the reaction of $OsCl_3$ and $OsCl_3OH$ with hydrazine hydrate. In the product the i.r. band observed at 2010 cm^{-1} shifts to 1950 cm^{-1} when nitrogen-15 hydrazine hydrate is used.

The osmium complex $[Os(NH_3)_5N_2]^{2+}$ is much more stable than its ruthenium analogue, and can be refluxed in 50% hydrochloric acid without decomposition. Thermal decomposition of the solid yields 87% of the theoretical amount of nitrogen.

Iridium: Collman and Kang[95] prepared the complex $(Ph_3P)_2Ir(N_2)Cl$ by attacking the carbonyl group of Vaska's compound $[(Ph_3P)_2IrCOCl]$ with an acyl azide: it is necessary to have alcohol or water present for the reaction to go to completion and Collman later proposed a mechanism (Fig. 8)[96].

The presence of an alcohol removes the acyl isocyanate(II) and enables the nitrogen complex (I) to be isolated in good yield rather than further reaction to a π-bonded isocyanate (III) occurring.

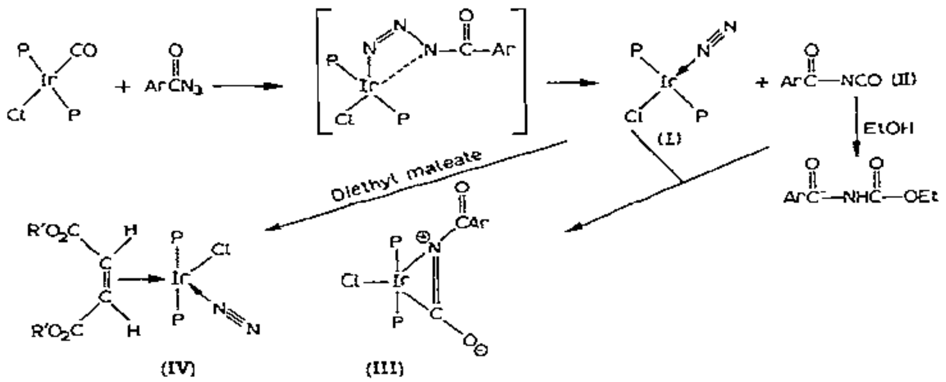


Fig. 8. Mechanism of formation of $(Ph_3P)_2Ir(N_2)Cl$[96].

The complex $(Ph_3P)_2Ir(N_2)Cl$ exhibited a characteristic sharp absorption at 2095 cm^{-1} together with an "impurity" band at 1970 cm^{-1} (*cf.* cobalt complexes). The olefin adduct (IV) showed a large shift in $N{\equiv}N$ stretching frequency to 2190 cm^{-1}.

This preparation is very similar to a reaction carried out by Beck[97] in which azide ion was used to attack a coordinated carbonyl group with the evolution of nitrogen and the retention of isocyanate:

$$W(CO)_6 + N_3^- \rightarrow W(CO)_5NCO^- + N_2$$

This approach may give a general method for preparing nitrogen complexes.

Rhodium: An analogous compound $(Ph_3P)_2Rh(N_2)Cl$ was prepared by Khidekel *et al.*[98] using Collman's route, but is considerably less stable and must be kept below room temperature in an inert atmosphere.

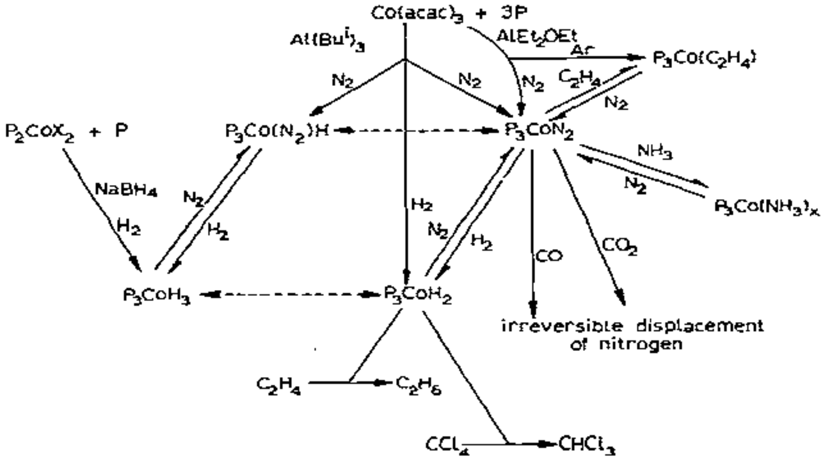


Fig. 9. Preparations and reactions of $(Ph_3P)_3Co(N_2)H$.

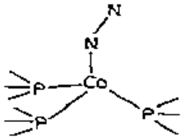
Cobalt: The entity $(Ph_3P)_3Co$ may be considered analogous to a metal surface in its ability to bind a number of small molecules, including nitrogen, hydrogen, ammonia, ethylene, etc. The scheme in Fig. 9 represents the interesting reactions that have been published on this system. This should be compared to $(Ph_3P)_2Pt$ which will coordinate a range of small molecules[99], although not nitrogen, and the work which has been done on metal surfaces. Eischens and Jacknow[100] found an i.r. band at 2202 cm^{-1} for nitrogen adsorbed on a nickel surface and postulate species such as $\mathrm{Ni}\overset{\mathrm{H}^-}{\diagup}\!\!\!-\mathrm{N}\equiv\mathrm{N}^+$ when hydrogen is introduced into the system. This is interesting in view of the compounds $(Ph_3P)_3CoN_2$ and $(Ph_3P)_3Co(N_2)H$ which are claimed to exist. In Fig. 9 double headed arrows link those compounds that could be identical.

The first paper to appear on this system was by Yamamoto *et al.*[101], who isolated a yellow crystalline complex which analysed for $(Ph_3P)_3CoN_2$, by the reaction of cobalt *tris*-acetylacetonate with diethylaluminium ethoxide in the presence of triphenylphosphine and nitrogen. The i.r. spectrum exhibited a strong band at 2088 cm^{-1} and the product evolved the theoretical amount of nitrogen on heating. Subsequently, Yamamoto *et al.*[102] reported on some exchange reactions of this complex and were able to establish reversible equilibria with hydrogen, ethylene, etc. An unexplained band at 1940 cm^{-1} was reported in the infra-red spectrum of the dihydride complex $(Ph_3P)_3CoH_2$.

Misono *et al.*[103] were working simultaneously on an identical system except that tri-*iso*butylaluminium was used as the alkylating agent. Thermal decomposition of their product yielded hydrogen as well as nitrogen and they concluded that two products, $(Ph_3P)_3CoN_2$ and $(Ph_3P)_3Co(N_2)H$, were formed. By working under an atmosphere of hydrogen rather than nitrogen Misono *et al.*[104] were later able to isolate a dihydride complex $(Ph_3P)_3CoH_2$ which on thermal decomposition yielded hydrogen and benzene. A dimeric structure was proposed for this complex to account for the observed diamagnetism. The high field quartet in the ^1H n.m.r. was attributed to three equivalent ^{31}P nuclei coupling to the two equivalent hydride ligands. The dimeric formulation could not be confirmed by molecular weight measurements, and i.r. spectra show three bands at 1755 cm^{-1}, 1900 cm^{-1} and 1935 cm^{-1}, whereas the symmetrical dimeric structure requires only one i.r. active band. The above details are more consistent with a cobalt(III) trihydride structure *i.e.* $(Ph_3P)_3CoH_3$, since the n.m.r. spectrum of $(Et_2PhP)_3IrH_3$ has been shown to contain a high field quartet[105].

Sacco and Rossi[106] prepared such a cobalt(III) trihydride by treating $(Ph_3P)_2CoX_2$ with sodium borohydride and one mole of phosphine in an atmosphere of hydrogen or argon. However, the i.r. spectrum exhibited only two bands in the metal-hydrogen stretch region, at 1745 cm^{-1} and 1933 cm^{-1}. This complex readily (and reversibly) reacts with nitrogen to form a nitrogen hydrido complex with elimination of hydrogen (see Fig. 9).

Sacco and Rossi were able to produce good evidence that hydrogen was present in their nitrogen complex, and this has been confirmed by a crystal structure determination. Using Yamamoto's method of preparation, Ibers *et al.*[107] were once able to obtain crystals which were suitable for an X-ray study. The complex crystallised as $(Ph_3P)_3Co(N_2)H \cdot Et_2O$ and showed i.r. bands at 2085 and 2105 cm^{-1}, which may be due to resolution of the metal-hydride band from the $N{\equiv}N$ stretch. Unfortunately the complex decomposed before sufficient data could be obtained for a very refined structure. However there seems no doubt that nitrogen is coordinated in an approximately linear manner, and that there is sufficient space, *trans* to the nitrogen for a hydride ligand to reside without any steric interference, (see Fig. 10).



Co—N = 1.80 Å
N—N = 1.36 Å
∠ Co—N—N = 175°

Fig. 10. Crystal structure of $(Ph_3P)_3Co(N_2)H$[107].

As is to be expected the cobalt atom is raised slightly out of the plane of the three phosphorus atoms, and the nitrogen bond length is increased slightly. More surprisingly the $<$Co–N–N is 175° rather than 180° as observed in the structure[90] of $[Ru(NH_3)_5N_2]I_2$.

Manganese: Johnson and Beveridge[108] reported a nitrogen complex which did not show any characteristic i.r. absorption in the 2100 cm^{-1} region. The compound *N,N*-disalicylaldehyde-1,3-propanediiminemanganese(II) in benzene solution was reported to absorb either nitrogen, carbon monoxide or oxygen at less than 1 atmosphere pressure to form 1:1 adducts. The absence of i.r. bands around 2000 cm^{-1} in both nitrogen and carbon monoxide adducts is very unusual.

Nature of the bonding in nitrogen complexes

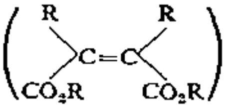
The i.r. spectra provide the most obvious physical parameter for a consideration of the bonding of nitrogen in these complexes. The intensity of the band associated with the $N{\equiv}N$ stretching vibration suggests that the nitrogen molecule is coordinated in a linear fashion, rather than in a symmetrical "π" arrangement. This has subsequently been confirmed for two complexes by X-ray crystallography[90,107]. Table 3 lists the $N{\equiv}N$ stretching frequencies and in some cases the $M{-}N_2$ stretching frequency in the complexes prepared to date.

Within the two series, $[Ru(NH_3)_5N_2]X_2$ and $[Os(NH_3)_5N_2]X_2$, the $\nu(N{\equiv}N)$ band varies markedly with the anion, moving to higher frequency with increasing size of the anion.

Allen *et al.*[83] suggest that extensive back donation from filled metal d orbitals to the empty antibonding π orbitals of nitrogen must occur to give these com-

TABLE 3

THE I.R. SPECTRA OF NITROGEN COMPLEXES

Complex	*$\nu(N\equiv N)$*	*$\nu(M\text{–}N_2)$*	*Ref.*
$(Ph_3P)_2Ir(N_2)(Cl)$ 	2190		95
$(Ph_3P)_2Ir(N_2)Cl$	2095		95
$[Ru(NH_3)_5N_2](PF_6)_2$	2167	474	83
$[Ru(NH_3)_5N_2]\ (BF_4)_2$	2144	487	83
$[Ru(NH_3)_5N_2]I_2$	2129	489	83
$[Ru(NH_3)_5N_2]Br_2$	2114	499	83
$[Ru(NH_3)_5N_2]Cl_2$	2105	508	83
$Ru/THF/N_2$	2140		91
$(Ph_3P)_3Co(N_2)H$	2088		106
$(Ph_3P)_3Co(N_2)$	2088		101
$[Os(NH_3)_5N_2]\ (BPh_4)_2$	2061	520	93
$[Os(NH_3)_5N_2]\ (BF_4)_2$	2055	529	93
$[Os(NH_3)_5N_2]\ (ClO_4)_2$	2051	531	93
$[Os(NH_3)_5N_2]I_2$	2033	533	93
$[Os(NH_3)_5N_2]Br_2$	2028	540	93
$[Os(NH_3)_5N_2]Cl_2$	2010	546	93
Os/N_2	2010		94

plexes their stability. This is supported by Collman and Kang's observation[95] that the $\nu(N\equiv N)$ frequency is increased *ca.* 100 cm^{-1} by the coordination of an olefin to $(Ph_3P)_2Ir(N_2)Cl$. Coordination of the olefin will reduce the extent of d orbital "backbonding" into nitrogen and hence decrease metal-nitrogen bond order with a consequent change in $\nu(N\equiv N)$ nearer to that in free nitrogen.

The strength of the metal nitrogen bond is well reflected in the $^{\nu}N\equiv N$ frequency; in the osmium series the nitrogen is only displaced with difficulty whereas in the ruthenium series the nitrogen is very readily displaced.

Nitrogen and carbon monoxide are isoelectronic but significant differences occur in molecular orbital schemes for the two molecules, which to some extent explain the different chemical properties[109].

The highest filled orbital of carbon monoxide contains the lone pair on the carbon atom which has considerable p character, and a directional bond is readily formed to metals. Back bonding from filled metal d orbitals into empty π^* antibonding orbitals enhances the stability of the complex. In nitrogen the highest filled orbital is a σ orbital[110] but it is concentrated between the nitrogen atoms. However the strongly bonding π orbitals shield this σ orbital and inhibit donation to a metal. The lone pairs are contained in s orbitals of low energy and are thus unsuitable for forming bonds with metals. Because of the much greater difference in energy between s and p orbitals for nitrogen as compared to carbon, little mixing occurs. The major contribution to the stability of the nitrogen complexes must therefore be due to back bonding into the lowest empty orbital which again is a π^* antibonding orbital. Any concentration of electron density in this orbital tends to destabilise the nitrogen molecule and should in fact render it more susceptible to attack. The bond length of coordinated nitrogen is somewhat longer than that observed in free nitrogen, as is to be expected since it is really an excited state of nitrogen attached to the metal.

It is interesting to compare those elements which are active in reacting with nitrogen after treatment with a reducing agent, and those which form stable nitrogen complexes. The Periodic Table (Fig. 11) shows that elements on the left react with nitrogen while those on the right, having more d electrons, are capable of forming stable nitrogen complexes.

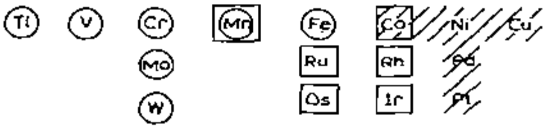


Fig. 11. Periodic Table showing those elements that are active, *e.g.* $\textcircled{\text{Ti}}$ and those that are inactive, *e.g.* $\cancel{\text{Cu}}$ in the nitrogen fixation systems of Volpin and Shur. Also shown are those elements which form stable nitrogen complexes, *e.g.* $\boxed{\text{Ru.}}$

E. INTERACTION OF NITROGEN WITH METAL SURFACES

In 1964 Eischens and Jacknow[100] successfully observed the infra-red absorption of nitrogen chemisorbed on a nickel surface. The band at 2202 cm^{-1} is only *ca.* 100 cm^{-1} lower than the Raman active band of nitrogen itself and suggests a structure similar to that found in nitrogen-metal complexes; *i.e.* only one of the nitrogen atoms is attached to the surface, and that to a single metal atom.

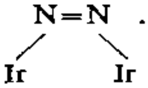
In view of this work it is obviously relevant to consider some of the work and theories concerning nitrogen chemisorbed to various metal surfaces. Mechanisms for the heterogeneous catalysis of ammonia formation from nitrogen and hydrogen arise from these studies, and their relevance towards possible homogeneous reactions is discussed. No attempt is made to make a full coverage of the literature on this topic, but rather a few important papers are cited to establish the major trends. Detailed reviews of the catalytic synthesis of ammonia have been presented[111].

Nitrogen can adsorb on a tungsten surface in at least three different states[112]. Below 200 °K the γ-state forms but this is a typical physically adsorbed state (*i.e.* it can be removed by evacuation at -78 °C). The primary chemisorbed state (β), which requires temperatures in excess of 2000 °K to desorb, is considered by Ehrlich[112] to be atomic. However Yates and Madey[113] using $^{28}N_2$ and $^{30}N_2$ adsorbed on polycrystalline samples of tungsten suggest that there are two β-states of very different binding energy, β_1 being molecular and β_2 atomic. Both these states undergo complete isotopic exchange *i.e.* treatment of the surface with a mixture of $^{28}N_2$ and $^{30}N_2$ and subsequent desorption yields $^{29}N_2$, in contrast to adsorption in the γ-state where the original $^{28}N_2$ and $^{30}N_2$ are obtained without mixing. Exchange in the β_1-state is explained by suggesting complex formation between two adsorbed nitrogen molecules; mixing thus occurs *via* a

adsorbed species.

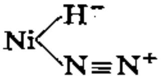
The third distinct state (α) of chemisorbed nitrogen which is populated at room temperature is thought to be molecular[112]. This adsorption only occurs where a β-state exists.

The Field Ion Microscope provides some interesting information about the nature of the adsorbed species[114]. Two distinct sites of nitrogen adsorption were observed on tungsten and iridium. In the case of adsorption as atoms, field desorption removed the underlying tungsten or iridium atom as an MN complex. Field desorption of chemisorbed molecules did not produce any corrosion of the metal. Iridium favours molecular chemisorption and it was suggested that the surface complex was



However the iridium atoms are 7.15 Å apart which leads to a very elongated N–N distance. Syrkin[115] has suggested a 3-centre bond with the nitrogen molecule symmetrically disposed to a single surface atom. However, there seems no need to postulate a structure other than that now accepted for nitrogen metal complexes, particularly since iridium forms such a complex.

A large number of atomic and molecular arrangements for nitrogen on a metal surface have been suggested as the above brief summary indicates. Eischens and Jacknow[100] go some way towards identifying one surface species as $Ni{-}N{\equiv}N^+$. Their experimental findings are supported by Nakata and Mansushita[116]. Use of $^{29}N_2$ and $^{30}N_2$ confirmed that the observed infra-red band was due to a $N{\equiv}N$ stretch since the heavier isotopes lowered the frequency from 2202 to 2160 and 2128 cm^{-1} respectively. Admission of hydrogen to the system at -100°C gave rise to a band at 2254 cm^{-1} which it was suggested arose from the species



which is of interest in view of the recent cobalt complex $(Ph_3P)_3Co(N_2)H$.

Some recent studies[117] concerning i.r. and electron microscopy suggest that the nitrogen on nickel, palladium and platinum surfaces which gives rise to i.r. bands around 2000 cm^{-1} is physically adosrbed. It is suggested that the diameter of the metal catalyst particles is the significant parameter. Physical adsorption occurs on the surface but only at certain small crystallites is the nitrogen i.r. active. Here, large electric fields exist and a preferred orientation of the nitrogen molecule can occur. A further point put forward to support physical adsorption is the non-specific nature of the adsorption *i.e.* occurring on palladium and platinum as well as nickel.

The significance of these different chemisorbed states towards the catalytic processes which occur have been considered. Ehrlich and his co-workers[118] suggest that the weakly bound molecular species may be catalytically significant and its conversion to a strongly chemisorbed species may be crucial. Carbon monoxide which behaves similarly to nitrogen in many situations does not have a weakly bound γ-state and does not dissociate to atoms on the metal surface. Roberts[119], working with molybdenum films, has estimated a value of 0.18 kcal mole^{-1} for E_1–E_2 where E_1 and E_2 are the activation energies for desorption of precursor molecules and their conversion to a chemisorbed state respectively. The first state is considered to be adsorption on the external surface of the metal, and a transfer occurring to the interior of the film where the molecules can truly be said to be chemisorbed.

Field emission microscopy has been used[120] to study nitrogen adsorbed on an iron tip, and shows that preferential adsorption occurs on the 111 face of the iron crystal. The nitrogen molecules are aligned with their axes perpendicular to the 111 face, and the model proposed for the bonding to the surface suggests that the 4π electrons are transferred to suitable atomic orbitals on the iron atoms, thus substantially weakening the bond between the nitrogen atoms. This may be the first step in the synthesis of ammonia.

The mechanism of ammonia synthesis on a metal surface seems most likely to involve reaction between adsorbed atomic nitrogen and adsorbed atomic hydrogen[121]. The surface species are thus $\equiv$N, $=$NH, —NH_2, —NH_3 and H. The affinity of the surface for nitrogen atoms must not be so great as to form a stable nitride.

Hydrogenated species containing the two nitrogen atoms still bonded together are rarely postulated[111a,111b,121], and there would seem to be no analogy between the heterogeneous and the biological nitrogen fixing systems, except perhaps in the initial molecular nitrogen complex.

In this context it is interesting to note that atomic hydrogen and molecular nitrogen do not give ammonia whereas atomic nitrogen and molecular hydrogen do. However, this fact is to some extent contradicted by some nitrogen isotope exchange work on various iron catalysts[122]. Exchange of $^{28}N_2$ and $^{30}N_2$ occurs on iron catalysts which are only feebly active for ammonia synthesis, but *no* exchange is observed on promoted iron catalysts which are good for ammonia synthesis. It is thus concluded that dissociation into nitrogen atoms is not a requirement for ammonia synthesis.

There is still debate about the rate determining step in ammonia synthesis. Chemisorption of nitrogen, or perhaps the conversion from a weak to a strongly adsorbed species was thought to be the rate determining step[123].

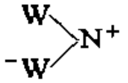
The major theoretical work[124], interpreting the rate data from many laboratories, assumed the rate determining step as chemisorption of nitrogen molecules onto a catalyst surface covered by nitrogen atoms.

Some kinetic measurements[125] utilising H_2/N_2 and D_2/N_2 mixtures over doubly promoted iron at 218–302 °C and 1/3 to 1 atmosphere, supported the postulate that the chemisorption of nitrogen was the rate determining step but concluded that the surface was covered by NH radicals. It was pointed out that the extent of reduction of the surface could give rise to very different mechanisms. A well reduced surface could result in dissociation of the chemisorbed molecule into atoms, whereas a moderately well reduced surface may give rise to an adsorbed species of the type (HN–NH) which will dissociate into NH radicals.

It was later shown[126] during work on ammonia synthesis on tungsten that the dissociative adsorption of nitrogen is accelerated by the presence of hydrogen. Experiments which separately determined nitrogen adsorption rate and ammonia synthesis rate and then equated the two, were not valid. Azuma[126] considered the rate determining step to be NH (or possibly NH_2) formation from adsorbed atomic species. Surface potential measurements[127] on nickel and iron support Azuma in that the important step is the formation of $=NH$ or $-NH_2$ adsorbed states. Evidence was obtained for a $Fe\equiv N$ species but not the corresponding $Ni\equiv N$. Tamaru[128] emphasises the enhanced rate of chemisorption of nitrogen due to the presence of hydrogen using a commercial doubly promoted iron catalyst. At 250 °C the chemisorption and hydrogenation of chemisorbed nitrogen proceed at comparable rates. Very recently the use of field ionization mass spectrometry[129] has shown that nitrogen enters the surface only in the molecular form. No evidence for atomic nitrogen was obtained by absorbing N_2/H_2 mixtures or ammonia on an iron tip.

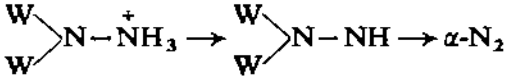
It should be emphasised that the commercial catalyst will give rise to a more complex system than that encountered on using extremely pure metal surfaces and tips etc., and different mechanisms may operate.

Experiments have also been performed on the decomposition of ammonia on metal surfaces. Simultaneous measurement of adsorption and reaction rate on a nickel catalyst showed[130] large amounts of NH_2 on the surface and the desorption of nitrogen as the rate determining step. Studies of ammonia decomposition on tungsten films enabled Dawson and Hansen[131] to propose a new mechanism. Ammonia was adsorbed below 300 °K and complete decomposition to nitrogen and hydrogen occurred by 500 °K. The nitrogen residue does not desorb until 1200 °K. From data obtained using the field emission microscope it was postulated that the formation of α-nitrogen (chemisorbed molecules) is the rate determining step for the decomposition of the bulk of the ammonia. The following mechanism was suggested:



$$\mathrm{W}(^{-}\mathrm{W})\mathrm{N}^{+}$$

(*i.e.* β-nitrogen) is the first stable surface species formed on admitting ammonia to the clean tungsten tip. This picks up ammonia from the gas phase:



$$\mathrm{W_2N-\overset{+}{N}H_3} \rightarrow \mathrm{W_2N-NH} \rightarrow \alpha\text{-}\mathrm{N_2}$$

There are stable metal complexes analogous to these intermediates (*vide infra*).

It may be possible to draw further analogies:

(i) between the weakly adsorbed molecular species and the more labile nitrogen complexes (*e.g.* $(Ph_3P)_3Co(N_2)H$ and $(Ph_3P)_2Ir(N_2)Cl$).

(ii) between a more strongly adsorbed nitrogen molecule and the more robust nitrogen complexes *e.g.* $[(NH_3)_5RuN_2]^{2+}$ and $[(NH_3)_5OsN_2]^{2+}$, which seem to retain one nitrogen atom during many reactions. A surprising reaction in the ruthenium system appears to be the formation of nitrogen from an ammonia ligand[87] which may proceed by a mechanism similar to that given above for a tungsten surface.

(iii) between the adsorbed, reactive nitrogen atom and the nitrogen containing intermediate in Volpin and Shur's system. No suitable hydrogen radical source seems to have been found for these systems and hydrolysis is required to produce ammonia. Perhaps in the modification of van Tamelen *et al.*[78] the hydrogen abstracted from the solvent is in the correct state for direct reaction with nitrogen.

F. "ACTIVE" NITROGEN

The term "active nitrogen" generally refers to nitrogen gas which has been subjected to some form of ionising radiation or electric discharge. The subject was reviewed in 1958[132] and in nearly all instances reactions are due to nitrogen atoms in the ground state. Considerable effort has been devoted to determining the spectroscopic state of the atomic nitrogen. Also active nitrogen can be used to transfer energy to other systems which subsequently decompose. Neither of these aspects are relevant to the present discussion and the reaction of active (atomic) nitrogen with hydrocarbons[133] or even organometallics[134] is only of marginal interest since molecular nitrogen is not involved.

Since nitrogen coordinated to a transition metal must be considered to be in an excited state (with electron density forced into high energy orbitals) the reactions of active nitrogen may give a clue as to suitable reactions to be attempted on co-ordinated nitrogen.

Discrepancies in the nitrogen atom concentration, as measured by HCN produced from ethylene and by the disappearance of NO, have been attributed[135] to the reaction of excited nitrogen molecules (produced by atomic recombination) with nitrix oxide. Subsequently Elias[136] measured nitrogen atom concentration by the pressure drop when recombination to molecules occurred, and concluded that the nitric oxide method was correct and low values were obtained from the ethylene reaction. The situation is further complicated by the finding[137] than an excited molecular state of nitrogen will react with nitric oxide. The species is produced by resonance capture of an excited electron and subsequent decomposition of the unstable negative excited molecular ion.

The reaction of active nitrogen with metal carbonyls[138] gives rise to the emission spectra of the metal atoms; carbonyl groups being stripped from the metal in a stepwise manner:

$$M(CO)_n + N \rightarrow M(CO)_{n-1} + NCO$$

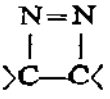
Metastable nitrogen molecules are considered to be involved in this reaction, in that collision with the metal atoms gives rise to the emission spectra of the metal.

Dodonova[139] successfully activated nitrogen with vacuum-u.v. radiation. Circulation of a nitrogen-methane mixture for 8–10 hours at 5–8 mm past a u.v. light produces a small yield of hydrogen cyanide which could be trapped out and identified. Presumably dissociation into atomic nitrogen occurred.

Getoff[140] was able to use u.v. light or γ-radiation to fix nitrogen. Ammonia was produced by reaction of nitrogen with water, provided acid or iron(II) ions were present. The u.v. lamp that was used emitted at 1495 Å and 1745 Å only.

Only e.s.r. investigations have been carried out on the species N_2^-. X-ray bombardment of a sodium azide crystal[141] or u.v. irradiation of a potassium azide crystal[142] produces N_2^- trapped in the crystal lattice. The lattice has a big influence on the spectra and the anisotropy is such that only one of the π^* levels is populated.

There is only a single example in which both nitrogen atoms of the molecule are incorporated into an organic compound[143]. A mixture of perchlorocarbon compounds and nitrogen were subjected to ionizing radiation (γ-radiation from a ^{60}Co source). A mass spectrum of the products contained several peaks which were 28 mass numbers higher than blank experiments with argon replacing nitrogen. Also u.v. and i.r. measurements could tentatively be assigned to the $-N{=}N-$ grouping. Since reduction gives rise to a single NH band a cyclic structure is proposed in which nitrogen has added across the double bond:



$$\begin{array}{c} N{=}N \\ |\quad\;\; | \\ {>}C{-}C{<} \end{array}$$

G. MISCELLANEOUS REACTIONS OF MOLECULAR NITROGEN

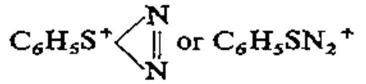
In 1964[144] it was reported that molybdate ions would catalyse the cathodic reduction of nitrogen to ammonia. Nitrogen was bubbled through an electrolytic cell (platinum or porous graphite cathode) containing hydrochloric acid and molybdate ions. Ammonia was produced, 10^{-4} to 10^{-3} moles/litre, after current had been passing for several days. Haight and Scott suggest interaction of nitrogen with molybdenum(IV) or molybdenum(V) and weakening of the N–N bond. Although there has been a report confirming these findings[145], there have been no further papers exploiting the possibility of electrochemical nitrogen fixation.

Anbar[146] has successfully oxidised molecular nitrogen at 100 atmospheres in aqueous solution to nitrate using singlet state excited oxygen. The latter was generated *in situ* by the reaction of sodium permanganate and hydrogen peroxide and it was found that nitrate was produced in yields of .05–.5% based on nitrogen.

Much earlier, Virtanen and Ellfolk reported[147] on the oxidative fixation of nitrogen in ultrasonic fields. The ultrasonic vibration causes cavitation bubbles which result in large fields and high pressures. Nitrite (at high pH) and nitrate (at low pH) ions are produced in amounts depending on the oxygen concentration in solution. Nitrogen is activated in the bubbles, either to N_2^+ or atomic nitrogen, and reacts with oxygen or hydrogen peroxide.

Volatile substances (*e.g.* ether) can inhibit this oxidative fixation, and although it is not yet proved that cavitation is responsible for fixation, Virtanen and Ellfolk consider[148] that the effect on the surface tension of the aqueous medium is more important than the earlier consideration that the volatile substance filled the cavity and prevented the establishment of high fields.

A most remarkable and facile reaction of nitrogen with an organic substrate has been described by Helmkamp and Owsley[149]. If the benzene-sulphenium cation ($C_6H_5S^+$) is generated in the presence of nitrogen gas, reaction occurs and although no pure compounds have yet been isolated, the products contain nitrogen as confirmed by elemental analysis, mass spectrometry, infra-red and ultra-violet measurements. The most likely product from this reaction is



$$C_6H_5S^+\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. \text{ or } C_6H_5SN_2^+$$

which would be expected to undergo the observed diazonium coupling reaction to give $(C_6H_5SN{=}NAr)H^+$.

Borod 'ko and Krylova[150] were able to observe some interaction between nitrogen and BF_3 and postulate the existence of a weak complex

$$N_2+BF_3 \rightleftharpoons \overset{\delta}{N_2}{}^{+}\cdots\cdots\overset{\delta-}{BF_3}$$

Borod 'ko *et al.*[151] speculate on the methods of activating molecular nitrogen and report on the exchange of labelled nitrogen with diazomethane:

$$CH_2N_2 + {}^{15}N_2 \rightleftharpoons CH_2{}^{15}N_2 + N_2.$$

The thermodynamics of diazomethane formation have been discussed by von Buenau *et al.*[152]

It is worthwhile to report on some reactions of nitrous oxide which are being investigated by Pratt[153] and his co-workers. Several complexes of cobalt either directly reduce or act as catalysts for the sodium borohydride reduction of nitrous oxide to nitrogen.

It has also been found that nitrous oxide can be electrochemically reduced to hydrazine—the suggested[154] mechanism is that nitrous oxide is adsorbed by the electrode surface and then reacts with protons. Adsorption *via* M–O–N–N would probably lead to evolution of nitrogen and an oxide film on the electrode. Adsorption must therefore occur as M–N–N–O with subsequent weakening of the N–N bond and easier reduction to hydrazine. This may be analogous to nitrogen on a metal surface.

Since only nitrogen is obtained by Pratt *et al.*[153] from the reaction of nitrous oxide with cobalt complexes, it must be assumed that the oxygen attaches to the metal. Any variation which could produce hydrazine from nitrous oxide using a simple metal catalyst would be an exploitable reaction.

H. MODEL SYSTEMS FOR NITROGEN FIXATION INTERMEDIATES

The work with biological systems has established that ammonia is the first identifiable product of nitrogen fixation[2,37,38]. It is very reasonable that nitrogen will first coordinate to a transition metal and will be converted by a reductive pathway to ammonia. Attempts to identify free diimide and hydrazine in the biological systems have failed[41] and it is probable that these species remain coordinated throughout their lifetime. Their reactivity when coordinated can be expected to be very different from that in the free state.

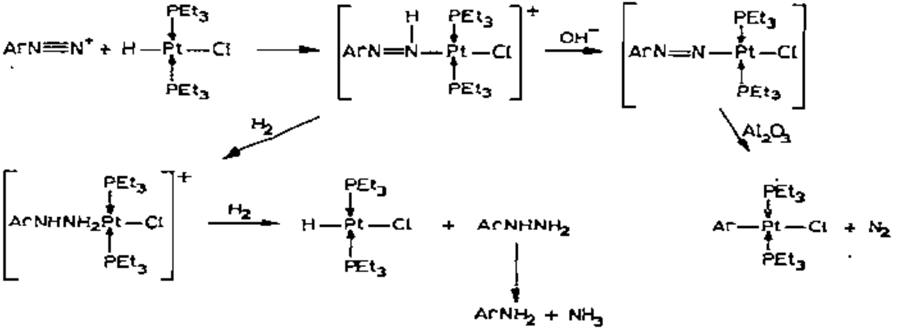


Fig. 12. An inorganic analogue of nitrogen reductase[155].

It is worthwhile considering some of the recent organometallic systems containing coordinated nitrogen compounds to see their relevance to nitrogen fixation.

Parshall[155] has successfully formulated an inorganic analogue of nitrogen reductase. Using a diazonium salt as a model for coordinated nitrogen and a metal hydride as the reducing agent, the reaction sequence shown in Fig. 12 was observed.

Stepwise reductions can be performed in a manner which may be analogous to the biological reduction. This model assumes that two centres are needed for fixation—one to bind the nitrogen and the other to provide reduction *via* a metal hydride. This is substantiated by the fact that the hydrogen evolution which goes on continually from the hydrogenase enzymes is not affected by a monodentate ligand such as carbon monoxide (although nitrogen reduction is inhibited), but is prevented when a chelating ligand is added.

Green and Sanders[156] have worked on an interesting series of molybdenum and tungsten compounds with a hydrazone ligand which can easily be protonated or alkylated (Fig. 13). The anionic compound is prepared from the cyclopentadienyltricarbonylmolybdenum anion and diazoacetic ester. It can be seen that a large number of reactions can be carried out on the nitrogen function which is attached to molybdenum.

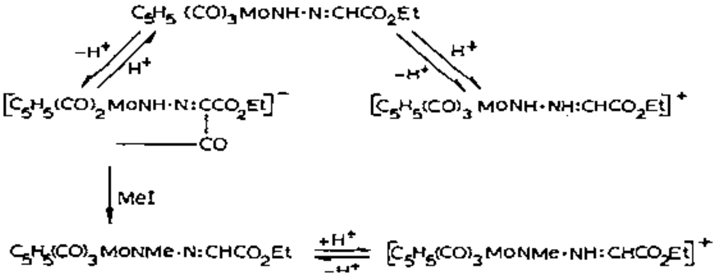
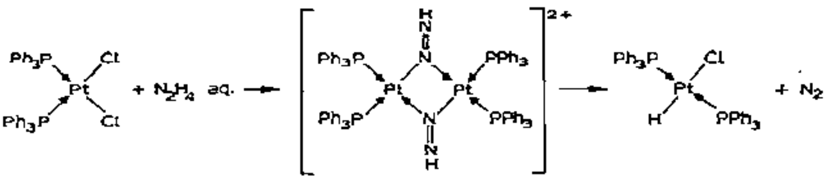
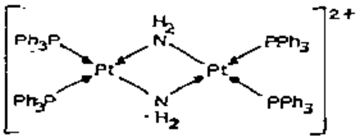


Fig. 13. Reactions of a coordinated hydrazone ligand[156].

An interesting dehydrodiimide complex of platinum has been prepared and its structure determined[157]. The complex is prepared from $(Ph_3P)_2PtCl_2$ and aqueous hydrazine and is the intermediate in the formation of $(Ph_3P)_2PtHCl$:



An accurate estimate of the N–N bond length could not be obtained since a second compound was considered to be present,

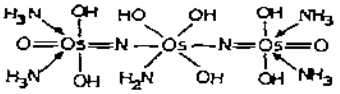


(This was deduced since the intensity peak for the nitrogen atom in the bridge was twice as great as that for the other nitrogen.) A value of 1.18 ± 0.09 Å was obtained. This reaction is, in effect, the reverse of a desired reaction of molecular nitrogen, *viz.* insertion into a metal-hydride bond.

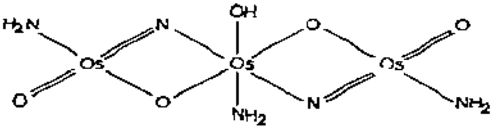
Of interest are the stable nitrido-complexes with a single nitrogen atom attached to a metal, for these may be analogues for some of the surface species formed in the Haber process. Most important are the rhenium complexes[158], $[ReNCl_2(PPh_3)_2]$ and $[ReNCl_2(PEt_2Ph)_3]$ prepared by hydrazine dihydrochloride reduction of potassium per-rhenate in the presence of phosphine. These have recently been studied by X-ray analysis[159], and have a short metal-nitrogen bond length.

Chatt and Heaton[160] have likened the nitrogen atom in these complexes to that in organic nitriles and have successfully used the electron-donor properties to prepare complexes of the type $[(PEt_2Ph)_3Cl_2Re{\equiv}N \rightarrow PtCl_2(PEt_3)]$, with a single nitrogen atom bridging tw ometals.

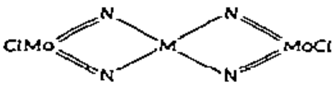
A trinuclear osmium complex has been prepared[161] by ammonia treatment of osmium tetroxide, in which similar bonding is proposed:



Pyrolysis of this compound gives ammonia, water and a complex which is formulated with nitrido-groups bridging in conjunction with oxo bridges:



A Patent[162] claims complexes in which two nitrido-groups bridge metal atoms:



where the central metal atom (M) can be Fe, Co, Ni, Pt, Pd, Ru, Rh and Mn.

Iridium also forms a nitrido complex in which it appears as though three metal atoms are attached to the single nitrogen[163]:

$K_4[N\{IrH_2O(SO_4)_2\}_3]$

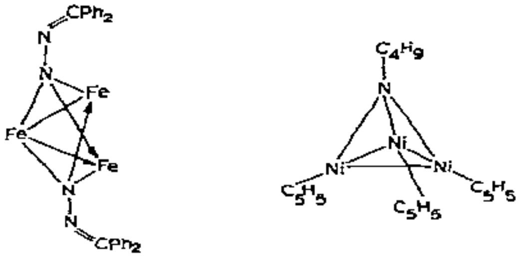


Fig. 14. Crystal structure of two complexes which have three metal atoms bound to a single nitrogen atom[164,165].

This type of bonding has been confirmed by X-ray analysis for an iron[164] and a nickel complex[165], (Fig. 14).

This opens up the field of nitrogen compounds bonded to transition metals, the scope of which is too great to be entered upon here. Suffice it to mention[166] a rhenium complex, $[Re(NPh)Cl_3(PEt_2Ph)_3]$, and to comment on the fact that there is considerable interest now being shown in the variety of bonding arrangements which can be obtained from the reaction of organometallic complexes with organo-nitrogen compounds[167].

I. SUMMARY

The problem of nitrogen fixation now commands intense effort and interest. We know that nitrogen and hydrogen[168] will coördinate to a metal; the change in reactivity of organic and inorganic substrates by coordination is a basic premise of organometallic chemistry[169]. Hydrazine[170,171] and ammonia[171] complexes are well known and now a diimide[42] complex has been reported. A pathway from nitrogen to ammonia is thus established.

Complexes representing plausible structures for intermediates, such as the dehydrodiimide platinum complex[157] and the arylazo complex[155,172], have been prepared.

Reactions of nitrogen with organometallic species will rupture the triple bond and ammonia can be liberated on hydrolysis[68]. This type of reaction has been developed until it gives ammonia in 100% yield based on transition metal[77b]; and now it has been shown that ammonia can come directly from such systems although in small amounts[78]. Reaction of nitrogen with an organic compound has occurred[149] although the products have not been fully characterised.

The scene is therefore set for the discovery of the vital reaction—the catalytic production of ammonia from nitrogen and hydrogen at room temperature and atmospheric pressure.

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