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THE REACTIONS OF DINITROGEN IN ITS MONONUCLEAR COMPLEXES

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Summary

Until recently dinitrogen in its mononuclear complexes was thought to be almost as inert as elementary nitrogen, but recently we have shown that in the bis-dinitrogen complexes of molybdenum and tungsten it reacts with acids in a protic medium under ambient conditions to yield up to 90% ammonia. With some organic halides it gives good yields of organonitrogen products and, with dimethylsulphate in methanol, methylamines and methylhydrazines. These reactions and events leading to their discovery are described.

I wish to thank the Editors and Publishers of this Journal for their invitation to contribute to their hundredth volume. I have chosen as my subject the recent work in my laboratory on the reactions of monoligating dinitrogen in stable complexes, because it may mark the beginning of a new era in the somewhat meagre chemistry of dinitrogen under ambient conditions.

Dinitrogen is a raw material for chemical industry and so inert that considerable energy is consumed during its processing. If new and more effective catalysts for its activation could be found they could have an enormous effect on the fertilizer and plastics industries. That such catalysts might exist is shown by the action of nitrogen-fixing bacteria. They produce ammonia from molecular nitrogen and water at ordinary temperature and pressure using chemically mild reducing agents such as sugars [1]. The reaction is catalysed by the enzyme, nitrogenase, which consists of two proteins. There is a large one containing two atoms of molybdenum and about 32 of iron, and another relatively small one, containing 4 atoms of iron. Associated with the iron atoms are an equal number of sulphide ions. Isolated from the nitrogen-fixing organism *Klebsiella pneumoniae*, the two proteins have molecular weights of about 220 000 and 68 000, respectively. In aqueous solution at around neutral pH, these two proteins, together with the monomagnesium salt of ATP and in presence of a suitable reducing agent ($Na_2S_2O_4$), convert molecular nitrogen to ammonia under ambient conditions [2]. There is evidence that the large protein probably binds the dinitrogen molecule which, with six electrons passed successively from the small protein, and six protons from the environment, becomes reduced to two molecules of ammonia.

Molybdenum is thought to provide the active site where dinitrogen is bound and reduced. The large protein as isolated from *Klebsiella pneumoniae* and purified, contains 1.3 to 2.0 atoms of molybdenum. Its activity is roughly proportional to its molybdenum content, not to the square or some such function. This, together with the fact that the large protein can be separated into identical pairs of sub-units, suggests that the molybdenum atoms act independently. Thus, if molybdenum provides the active site, nitrogenase may provide an example of a single metal centre at which the nitrogen molecule can be protonated and reduced to ammonia. If the two molybdenum atoms react with dinitrogen in concert they must be present as a tightly knit dimer so that both atoms are inserted into, or removed from, the enzyme together. It must be emphasised however that there is no concrete evidence that molybdenum is at the active site, nor whether the molybdenum interacts with dinitrogen singly, in tightly knit pairs, or in association with an iron atom, and none concerning the oxidation state of the molybdenum atom or types of ligating atoms surrounding it in the enzyme [3]. Nevertheless the strength of circumstantial evidence suggests that dinitrogen in its mononuclear complexes with molybdenum and related elements, might show an unusually high reactivity to protons. This reactivity might extend to organic reagents, and a study of such complexes could point the way to better catalysts for the activation of molecular nitrogen. The work to be summarised here was based on this conjecture.

Over the last decade a great number of mononuclear dinitrogen complexes derived from transition elements of Groups VI to VIII of the Periodic Table have been discovered, and most can be prepared from molecular nitrogen [4]. The general types are summarised in Table 1. The co-ligands with dinitrogen are mainly good electron-donor ligands such as tertiary phosphines, ammonia or hydride ions. Occasionally one or two halide ions are also present. The metal atoms are in low oxidation states or if they are not, they are ligated by a num-

TABLE 1

PRINCIPAL TYPES OF MONONUCLEAR DINITROGEN COMPLEXES[a]

L = tertiary monophosphine or sometimes the arsine, am = ammonia, amine or ½ diamine; ar = arene; bl = bidentate ligand, usually tertiary phosphines, e.g. $Ph_2PCH_2CH_2PPh_2$ or $Et_2PCH_2CH_2PEt_2$, L_2 in most of the complexes may be replaced by (bl); X = halide ion, sometimes one "X" may be replaced by H as in $[ReH(N_2)(PMe_2Ph)_4]$ and $[OsHCl(N_2)(PMe_2Ph)_3]$. There is one Zr complex $[(cp)_2Zr(N_2){-}N{\equiv}N{-}Zr(N_2)(cp)_2]$ with both terminal and bridging dinitrogen ligands.

$[Cr(ar)(CO)_2(N_2)]$	$[Mn(cp)(CO)_2(N_2)]$	$[FeH_2(N_2)L_3]$ $[FeH(N_2)(bl)_2]^+$	$[CoH(N_2)L_3]$ $[Co(N)_2L_3]$ $[Co(N_2)L_3]^-$	$[NiH(N_2)L_2]$
$[Mo(ar)(N_2)L_2]$ $[Mo(N_2)_2L_4]$ $[Mo(N_2)_2(bl)_2]^+$	Tc	$[RuH_2(N_2)(L)_3]$ $[Ru(am)_5(N_2)]^{2+}$ $[RuCl(N_2)(bl)_2]^+$	$[RhX(N_2)L_2]$	Pd
$[W(N_2)_2L_4]$ $[W(N_2)_2(bl)_2]^+$	$[ReX(N_2)L_4]$ $[ReX(N_2)(bl)_2]^+$ $[Re(cp)(CO)_2(N_2)]$	$[OsX_2(N_2)L_3]$ $[Os(am)_5(N_2)]^{2+}$ $[Os(am)_4(N_2)_2]^{2+}$	$[IrX(N_2)L_2]$ $[Ir(Me)(CF_3SO_3)X(N_2)L_2]$	Pt

[a] For detailed references see ref. 4(c).

ber of hydride ions. All this indicates a high electron density on the metal [5]. Of the above ligands only hydride and ammonia are likely to ligate molybdenum in nitrogenase. There is an entrenched belief, but no definite evidence that the molybdenum in nitrogenase is ligated by sulphur. Sulphur has, to the present, been found remarkably rarely in dinitrogen complexes; when it is, it appears to impart no particular reactivity to the ligating dinitrogen [6].

The dinitrogen in all of its mononuclear complexes is bonded "end-on" analogously to carbon monoxide in its mononuclear complexes. It also develops, on coordination, sufficient electrical asymmetry to absorb strongly in the IR spectrum at 1900-2150 cm^{-1}. In some complexes such as *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ it is sufficiently dipolar for the binding energies of the 1*s*-electrons in the two nitrogen atoms to be resolved with a difference of about 1.7 eV [5]. Dinitrogen carries more negative charge than carbon monoxide in analogous complexes [7] and in *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ it carries, overall, about as much charge as the chlorine atom [5]. It should react, if at all, with the positive parts of other molecules. This is certainly so in complexes of low N—N stretching frequency. The terminal nitrogen atom in the above rhenium complex [$\nu(N_2)$ = 1925 cm^{-1}] is one of the most basic and adds to all types of Lewis acids [8], but not to the proton [9]. To triethylaluminium it is a much stronger base than ether, but weaker than tetrahydrofuran [7]. It forms particularly stable complexes with molecules containing as their acceptor centres, atoms from the early transition metal series, especially in their higher oxidation states. Typical examples of such stable complexes, extensively studied in my laboratory, are $[(PMe_2Ph)_4ClRe{-}N{\equiv}N{-}CrCl_3(thf)_2]$ [10], $[(PhMe_2P)_4ClRe{-}N{\equiv}N{-}MoCl_4(OEt)]$ [11] and the trinuclear species $[Cl_4Ti\{{-}N{\equiv}N{-}ReCl(PMe_2Ph)_4\}_2]$ [12] and $[MoCl_4\{{-}N{\equiv}N{-}ReCl(PMe_2Ph)_4\}_2]$ [13]. The structures of both the above molybdenum compounds have been determined by X-rays and each contains a linear arrangement of metal and nitrogen atoms [11,13]. The formation of dinuclear and trinuclear complexes from the mononuclear is perhaps the most general reaction of monoligating dinitrogen, but it is not universal, and not the type of reaction which particularly concerns us here. In bridged dinitrogen complexes the dinitrogen has generally shown no greater reactivity than in the mononuclear complex from which the bridged complex is derived; but certain dititanium and dizirconium μ-dinitrogen complexes readily protonate in ether at —60° to give excellent yields of hydrazine [14,15].

The dinitrogen in most of its mononuclear complexes is completely inert to chemical attack except by such strong reducing agents as would induce nitriding by molecular nitrogen in presence of suitable transition metal compounds [16,17]. The only exceptions have been the bis-dinitrogen complexes of molybdenum and tungsten of general formula $[M(N_2)_2L_4]$ (L = monotertiary phosphine or ½ ditertiary phosphine; M = Mo or W). These complexes are obtained by the reduction of $[MoCl_3(thf)_3]$ or $[WCl_4L_2]$ by Grignard magnesium in tetrahydrofuran in the presence of a slight excess of the phosphine, L, under atmospheric pressure of dinitrogen and at room temperature. Yields are 20-80% according to the phosphine, *trans*-$[W(N_2)_2(PMePh_2)_4]$ (20-30%) being the most difficult and *trans*-$[M(N_2)_2(dpe)_2]$ (M = W or Mo; dpe = $Ph_2PCH_2CH_2PPh_2$) being easiest (60-80%). The complexes $[M(N_2)_2(PMe_2Ph)_4]$ both have *cis*-configurations and are obtained pure in yields of 40-50%. The monophosphine complexes are the first well defined complexes in which monoligating dinitrogen has been reduced to produce almost quantitative yields of ammonia, or alkylated to produce high yields of organic products [18,19].

Interestingly, the protonation occurs in acid methanol to produce high yields of ammonia; hydrazine is only a very minor product. This suggests that the actual transfer of electrons from the metal to dinitrogen and its reduction to ammonia in these mononuclear complexes may approximate much more closely to the action of nitrogenase than does the protonation of bridging dinitrogen in dinuclear complexes. The latter produce hydrazine as the major product [14,15].

We obtained the first indication that monoligating dinitrogen might be reactive in these molybdenum and tungsten compounds from attempts in 1971 to acylate it with acetyl chloride in the complex *trans*-$[W(N_2)_2(dpe)_2]$. We used tungsten rather than molybdenum for our initial experiments because tungsten usually gives more tractible products. The reaction observed (eqn. 1) obviously involved fortuitous hydrogen chloride despite all attempts to keep the reagents dry and free from it [20].

$$[W(N_2)_2(dpe)_2] + CH_3COCl + HCl \rightarrow [WCl_2\{N_2H(COCH_3)\}(dpe)_2] \qquad (1)$$

The bis-dinitrogen compounds of tungsten and molybdenum were obvious candidates for such experiments because the four ligating phosphorus atoms, as good electron donors, must put excessive electron density on the metal(0) atom, and there are no anionic ligands to help accommodate it. That excess could be removed only by "back donation" mainly into the anti-bonding orbitals of the dinitrogen molecules. Thus the terminal atom of the dinitrogen should be rendered strongly basic, perhaps more so than in *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, because, although the rhenium atom is isoelectronic with tungsten in $[W(N_2)_2(dpe)_2]$, it has a higher nuclear charge to hold its electrons and also a chlorine atom to help accommodate them.

As mentioned above the terminal nitrogen atom in the rhenium compound is basic to all types of Lewis acids but not to the proton. Attempts to protonate the dinitrogen led to protonation of the metal (eqn. 2) [9]. This reaction indicated that the metal atom is more basic than the nitrogen molecule to which it is attached. However, because the more bulky Lewis acids, such as trimethylaluminium, are less able for steric reasons to insert themselves into the coordination sphere of the metal, they become attached to the terminal nitrogen atom. The ligating dinitrogen molecule obtains its charge from the metal by back donation. This requires a high electron density on the metal and so it seemed that the metal must always be the more basic. This reasoning accords with the observations that all of the mononuclear dinitrogen complexes then known, reacted with acid to give a mixture of dinitrogen and dihydrogen, or a metal hydride, but never hydrides of nitrogen. The evolution of dinitrogen and dihydrogen probably occurs because attack of the proton on the metal causes its oxidation with formation of a hydride complex and evolution of dinitrogen. This hydride complex may subsequently be attacked by more acid to liberate dihydrogen so affording a mixture of the gases and no nitrogen hydride. The metal in a few

$$[ReCl(N_2)(PMe_2Ph)_4] + HBF_4 \rightarrow [ReClH(N_2)(PMe_2Ph)_4]BF_4 \qquad (2)$$

especially stable dinitrogen complexes can be protonated and still retain its dinitrogen as in eqn. 2. The above reasoning suggested strongly that it was unlikely that any stable mononuclear dinitrogen complex could be protonated at the nitrogen molecule, but the fact that it appeared to occur in nitrogenase kept us persisting in the attempt.

Nevertheless this reasoning turned our attention from the possible reactions of ligating dinitrogen with hydrogen halides to those with reactive organic halides as providing a more attainable immediate goal. The bulky organic part of the molecule might, like the Lewis acids, attach itself to the terminal nitrogen of the ligating dinitrogen molecule; the chloride ion could displace another ligand from the metal, or remain outside the coordination shell. Organic acid chlorides were obvious candidates. J.R. Dilworth, during the investigation of the reactions of $[ReCl(N_2)(PMe_2Ph)_4]$ had seen some evidence that benzoyl chloride reacted to form $[ReCl_2(—N{=}N—COPh)(PMe_2Ph)_3]$ but could not isolate the pure product. Graham Heath, Overseas Research Scholar of Royal Commission for the Exhibition of 1851 (Dec. 1970-Sept. 1973), when he joined me, was given this problem. The more promising complex, *trans*-$[W(N_2)_2(dpe)_2]$ was now available [21] and its molybdenum analogue also in good yield [22]. Here the second dinitrogen molecule would form a perfect leaving ligand to admit the chloride ion. The addition to the tungsten complex was expected to give $[WCl(—N{=}N—COMe_2)(dpe)_2]$, but in fact it gave $[WCl_2\{N_2H(COMe)\}(dpe)_2]$ according to reaction 1 [20]. The additional hydrogen chloride had to be removed by base (NEt_3 or aqueous K_2CO_3) to afford the diazenato complex $[WCl(—N{=}N—COMe)(dpe)_2]$.

The $N_2H(COMe)$ ligand in the above product alerted us to the fact that the dinitrogen in $[W(N_2)_2(dpe)_2]$ might be protonated directly, and that it might react with alkyl halides. Also since the complex $[ReCl(py)(N_2)(PMe_2Ph)_3]$ had now been prepared, the way was again open to attempt to aroylate dinitrogen attached to rhenium. Here the strongly basic pyridine provided a more suitable leaving group than PMe_2Ph and compounds $[ReCl_2(N_2COR)(PMe_2Ph_3)_3]$ were readily obtained by reaction with RCOCl (R = alkyl or aryl). The molybdenum complex was found to react analogously to the tungsten one, and a number or alkyl- and aroyl-diazenato derivatives of tungsten, molybdenum and rhenium were prepared [20,23]. However, the osmium complex $[OsCl_2(N_2)(PR_3)_3]$ did not undergo addition of acetyl or benzoyl chlorides. Moreover, the rhenium products of the type $[ReCl_2(—N{=}N—COR)(PMe_2Ph)_3]$ unlike the tungsten and molybdenum N_2COR compounds did not add additional hydrogen chloride. Indeed $[ReCl_2(—N{=}N—COMe)(PMe_2Ph)_3]$ readily lost its acetyl group again at room temperature in the presence of an excess of the tertiary phosphine or pyridine by reversal of its reaction of formation. It was evident that the tendency of the dinitrogen ligand to react to form new stable nitrogen-containing ligands increased as one passed from osmium to tungsten. This led to renewed efforts to protonate the dinitrogen molecule in the bis-dinitrogen tungsten and molybdenum complexes.

Protonation of ligating dinitrogen

When we found that the acetyldiazenatotungsten complex avidly picked up hydrogen chloride according to reaction 1, G.A. Heath attempted the reaction of *trans*-[W$(N_2)_2$$(dpe)_2$] with hydrogen chloride using two moles of the acid in an attempt to obtain N_2H_2 complexes analogous to [WCl_2{$N_2H(COR)$}$(dpe)_2$]. However, reaction 3 was obtained and the hydride was eventually isolated as its $[HCl_2]^-$ salt (eqn. 3) [24]. Evidently the reaction had taken a "normal" course, exactly analogous to reaction 2. The result was a disappointment and quickly forgotten, although long after the events recorded below the cation was found to have an interesting pentagonal bipyramidal structure [25]. It was fortunate that the above result was not memorable, because about 3 months later, it led to my exhorting Dr. R.L. Richards, within whose remit the experiment lay, to try the reaction of hydrogen chloride on [W$(N_2)_2$$(dpe)_2$] once again. Fortunately he was not aware of the previous attempt and used a large excess (12 moles) of hydrogen chloride. Reaction 4 was achieved almost quantitatively. It was the first well defined protonation of mono-ligating dinitrogen to be achieved, and occurred very rapidly under ambient conditions [24]. The reaction stops at the N_2H_2 stage.

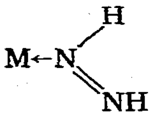
$$trans\text{-}[W(N_2)_2(dpe)_2] + 2HCl \rightarrow [WH(N_2)_2(dpe)_2][HCl_2] \qquad (3)$$

$$trans\text{-}[W(N_2)_2(dpe)_2] \xrightarrow[thf]{12\,HCl} [WCl_2(N_2H_2)(dpe)_2] + N_2 \qquad (4)$$

$$trans\text{-}[Mo(N_2)_2(dpe)_2] \xrightarrow{HCl} [MoH_n(dpe)_2] + N_2 \qquad (5)$$

(n = 2 or 4)

The bis-dinitrogen molybdenum analogue reacted "normally" to evolve all of its dinitrogen and produce a hydride (eqn. 5). Fortunately we discovered that hydrogen bromide tended to protonate the dinitrogen in the tungsten complex much easier than the chloride, and with hydrogen bromide both molybdenum and tungsten N_2H_2 complexes were readily obtained. A whole range of these with different phosphines and halogens were prepared [24(b)]. Some of them, e.g. [$MoBr(N_2H_2)(depe)_2$]Br, were 6-coordinate. (depe = $Et_2PCH_2CH_2PEt_2$.) One of the halide ions (X) in the 7-coordinate N_2H_2 complexes can be replaced by non-coordinating ions such as BPh_4^- and ClO_4^- to give 6-coordinate complexes of the type [$MX(N_2H_2)$ $(dpe)_2$]BPh_4. By the use of ^{15}N and ^2H substitution, ^1H NMR and IR spectroscopy it was shown that, in the 7-coordinate complexes [$MX_2(N_2H_2)(dpe)_2$] (X = halogen), the N_2H_2 ligand has formally a diazene structure I, but in the 6-coordinated complexes $[MX(N_2H_2)(dpe)_2]^+$, it has the structure of a formal hydrazide (2—) ligand II [24]. This latter has been confirmed by X-ray structure determination [26]. In both structures the formal double bonds must be delocalised by conjugation with the *d*-orbital system of the metal, leading to considerable stabilisation of the N_2H_2 moiety. Indeed all our attempts to reduce the N_2H_2 complexes to ammonia or hydrazine failed despite the great variety of reagents tried, such as Adams catalyst/H_2, Zn/CH_3CO_2H, $SnCl_2$, $TiCl_3$/KOH, $TiCl_3$/HCl and $NaBH_4$. Attempts at further protonation of the N_2H_2 ligand by hydrogen bromide, sulphuric acid, methylsulphonic acid and trifluoroacetic acid also failed to give any ammonia or hydrazine at room temperature. The complex [$WCl_2(N_2H_2)(dpe)_2$] was recovered even from warm concentrated sulphuric acid.



(I)

$M{=}N{-}NH_2$

(II)

One molecule of hydrogen halide was extracted from the complexes $[WX_2(N_2H_2)(dpe)_2]$ (X = Cl or Br) by triethylamine or aqueous potassium carbonate. In this way, N_2H complexes were obtained (eqn. 6) [27]. The corresponding molybdenum complex $[MoBr(N_2H)(dpe)]$ is more difficult to prepare because it is sensitive to alkali which causes reversion to $[Mo(N_2)_2(dpe)_2]$ under dinitrogen.

$$[WX_2(N_2H_2)(dpe)_2] \xrightarrow{K_2CO_3} [WX(N_2H)(dpe)_2] + KX + KHCO_3 \qquad (6)$$

The *N*-hydrogen has not been found by either IR or ^1H NMR spectroscopy. The N_2H products are diamagnetic and are quantitatively reconverted to the N_2H_2 complex by exactly one mole of HX, and reaction with NO gives $[MX(NO)(dpe)_2]$; they can also be acetylated by acetyl halides to give the known $[MX_2\{N_2H(COCH_3)\}(dpe)_2]$ complexes. They presumably contain a new ligand, the iminonitrosyl or diazenato ligand bonded as $M \equiv N \equiv NH$, analogous to nitrosyl. Molybdenum and tungsten seem particularly prone to forming stable multiple bonds to nitrogen in such ligands as these; also the first thionitrosyl complexes were obtained from molybdenum [28]. This tendency to such multiple bonding correlates well with molybdenum's supposed role in nitrogenase.

The tungsten and molybdenum in the diazene complexes $[MCl_2(N_2H_2)(dpe)_2]$ have formal oxidation states of II. It should be possible to obtain further reduction of N_2H_2 by simple reaction with acid and concomitant oxidation of the metal, but it seems that the metal is too strongly stabilised in its lower oxidation state by the phosphine ligands to allow of this; also the chelate diphosphine ligands (dpe) are too strongly held to leave the metal as its oxidation proceeds. For this reason we turned to less strongly bonded monodentate phosphine ligands $[M(N_2)_2(PR_3)_4]$ (M = Mo or W; $PR_3 = PMe_2Ph$ or $PMePh_2$) and complexes of ligands with other donor atoms such as N, S or O.

However, before we had even prepared any N_2 complexes from other ligands, Alan Pearman (D.Phil. student) struck ammonia in an unprecedented 40-50% yield according to reaction 7 [18]. There was also ca. 15% hydrazine. The reaction proved very sensitive to solvent, and in methanol yields of up to 90% ammonia with only 2-3% of hydrazine, were obtained by reaction of sulphuric acid on the tungsten complex at room temperature. This is a remarkable yield of 1.8 moles NH_3 per mole of tungsten in a stoichiometric reaction. The electrons, in oxidation of the tungsten from 0 to VI, are passed 90% into the dinitrogen molecule to form ammonia despite the fact that the complex is dissolved in a medium as easily reducible as acid methanol; the reaction occurs even in wet methanol. The reaction demonstrates quite definitely that it is possible to reduce N_2 to ammonia in a protic medium with a very mild reducing agent; also that the reaction can occur at a single metal site. It has been argued that the reduction may occur through formation of a dinitrogen bridged species [29], but if this occurred the maximum yield of ammonia, according to reaction 8, would be half of that possible from reaction 7. Also only about 5% of the reducing power of the tungsten appeared as dihydrogen whereas reaction 8 requires 50% of it to be diverted into dihydrogen.

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow[\text{thf}]{H_2SO_4} N_2 + 2NH_3 + W^{VI} \text{ products} \tag{7}$$

$$W{-}N{\equiv}N{-}W \xrightarrow[\text{MeOH}]{H_2SO_4} 2W^{VI} + 2NH_3 + 3H_2 \tag{8}$$

This reaction has been tried in various solvents and acids but so far none has bettered the methanol/sulphuric acid mixture. Methanol alone is sufficient to give an 85% yield of ammonia with 2% hydrazine at 60°, although it is inactive at room temperature except under irradiation (2 × 150 watt bulbs) when it yields 83% ammonia with 3% hydrazine.

The molybdenum complex *cis*-[Mo$(N_2)_2(PMe_2Ph)_4$] gives ammonia in 30-40% yield in methanol with sulphuric acid at room temperature, only slightly less in tetrahydrofuran, and always $<$ 1% hydrazine.

In the protonation experiments it appears that the ligating dinitrogen molecule is protonated directly and not via hydriding of the metal atom, because the complex $[WH(N_2)_2(dpe)_2]^+$ on treatment with an excess of hydrogen chloride in the manner needed to convert $[W(N_2)_2(dpe)_2]$ to $[WCl_2(N_2H_2)(dpe)_2]$, does not give the N_2H_2 product. It gives $[WH_2Cl_2(dpe)_2]$ instead, i.e., it reacts "normally" to give a hydride complex with loss of N_2 [24(b)].

The mechanism of the reduction of the dinitrogen ligand to ammonia is still to be determined. It could be that the dinitrogen in the molybdenum and tungsten complexes are reduced by different mechanisms. In the former, yields have never exceeded 50% on the basis of eqn. 7, which would allow of a μ-dinitrogendimolybdenum intermediate, according to eqn. 8. Against this is the fact that hydrazine is always a very minor product in the molybdenum complex reactions. Assuming a mononuclear mechanism it seems likely that the first step is protonation of one dinitrogen ligand to give a hydrazide (2—) N_2H_2 ligand with replacement of the second dinitrogen by sulphate or hydrogen sulphate anion. This first step is rapid; the evolution of dinitrogen is over within five minutes. The replacement of N_2 by HSO_4^- or SO_4^{2-} would increase the electron density at the metal. This alone, or by chelation of the sulphate ion, may cause a molecule of the phosphine to be displaced by more HSO_4^- or SO_4^{2-} with greater increase in electron density at the metal so promoting the protonation of the N_2H_2 ligand, as $M{=}N{-}NH_2 \rightarrow M{\equiv}N + NH_3$ or $M{-}NH{=}NH \rightarrow M{-}NH{-}NH_2$, and so on until the reaction is complete. With molybdenum the whole reaction is complete, so far as ammonia production is concerned, in 15 minutes at room temperature, but a little hydrogen gas is liberated for about 1 hour afterwards, suggesting that a hydride which slowly reacts with the acid has been formed as a by-product. The final stages of the reaction of the tungsten complex are rather slower, requiring about 1½ hours for the completion of ammonia production.

This work is still continuing with the aim of finding a cyclical reaction whereby N_2 can be converted to ammonia catalytically on a tungsten or molybdenum complex by electrolytic reduction.

Reactions to form nitrogen-to-carbon bonds

Before the acylation reactions mentioned above, there had been no evidence that carbon compounds would interact directly with ligating dinitrogen although they do so in nitriding reactions [16]. When Dr. A.A. Diamantis from the University of Adelaide joined my group on sabbatical leave (May 1972-May 1973) he also joined in our efforts to obtain nitrogen to sulphur bonds by the reaction of organic sulphonyl and sulphenyl halides with the bis-dinitrogen compound of tungsten. We expected to obtain reactions such as 9, but complete decomposition of the tungsten complex occurred with the formation of oxides of dpe and di-*p*-tolyldisulphide. This seemed an intersting reaction until we discovered that triphenylphosphine alone would reduce aromatic sulphonyl chlorides to the disulphides, and a literature search revealed that the reaction was already known. We then turned our attention to the reactions of alkyl halides with *trans*-$[W(N_2)_2(dpe)_2]$.

$$[W(N_2)_2(dpe)_2] + p\text{-TolSO}_nCl \rightarrow [WCl(-N{=}N-SO_n p\text{-Tol})(dpe)_2] \qquad (9)$$

$(n = 1 \text{ or } 2; p\text{-Tol} = p\text{-}C_6H_5CH_3)$

Methyl and ethyl bromides reacted slowly with $[W(N_2)_2(dpe)_2]$ but the isolation of small quantities of the products was both difficult and frustrating until it was found that the extent of the reaction depended upon the diffuse light of the laboratory, a somewhat variable quantity in our climate. The need for irradiation was discovered when Dr. Diamantis took two weeks vacation and left reaction mixtures in a closed cupboard so that they would produce him plenty of material to work with on his return. In fact he found no product whatsoever and so was alerted to the importance of light in this reaction. By irradiation with 2 × 150 watt bulbs, the reaction which had previously taken days and given miserable yields, now gave good yields within a few hours.

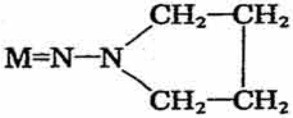
The product was a mixture of $[WBr(N_2R)(dpe)_2]$ (III) and $[WBr(N_2HR)(dpe)_2]Br$ (IV). Analogously to the acetyl chloride reaction, the primary product III had taken up hydrogen bromide; perhaps produced by the irradiation. Since the hydrobromide product was the more easily isolated, it became standard practice to add hydrogen bromide to the final reaction mixture and to isolate the N_2HR complex; overall reaction 10 was achieved [32]. The product IV was converted to III by reaction with a base such as triethylamine in benzene or, better, aqueous potassium carbonate. The product IV was shown to be an alkylazo or alkyldiazenato complex containing the ligand $-N{=}N-R$. Compounds with R = Me, Et or t-Bu were prepared; all have strong N—N stretching bands in their IR spectra at 1500-1520 cm^{-1}. The structure of $[WBr(N_2HMe)(dpe)_2]Br$ has been determined [32]. It contains the system W—N—NHMe with angles W—N—N 176° and N—N—C 120°. Obviously the W—N—N system is delocalised. From the ^{13}C NMR spectra, it appears that in this particular compound at least, the ligand is present in tautomeric forms —NH=NMe and =N—NHMe, corresponding to the two known forms of N_2H_2 and suggesting by analogy an equilibrium as reaction 11 which lies well to the right.

$$[W(N_2)_2(dpe)_2] + HBr \xrightarrow[C_6H_6]{h\nu} \underset{(III)}{[WBr(N_2R)(dpe)_2]} \xrightarrow{HBr} \underset{(IV)}{[MBr(N_2HR)(dpe)_2]Br} \qquad (10)$$

$$[\mathrm{WBr_2(NH{=}NR)(dpe)_2}] \rightleftharpoons [\mathrm{WBr({-}N{=}NHR)(dpe)_2}]\mathrm{Br} \qquad (11)$$

Many attempts were made to obtain dialkyl derivatives but only one was found, $[\mathrm{WBr({=}N{-}NMe_2)(dpe)_2}]\mathrm{Br}$ obtained by using an excess of methyl bromide.

When Dr. Diamantis returned home in 1973, the work was carried on together with Dr. G.J. Leigh, Dr. G.A. Heath and W. Hussain. The latter meticulously worked out the reactions of *trans*-$[\mathrm{Mo(N_2)_2(dpe)_2}]$ with methyl and ethyl bromides. These occurred in exactly analogous fashion to those of $[\mathrm{W(N_2)_2(dpe)_2}]$ except that the molybdenum compound would not undergo two methylations to give $[\mathrm{MoBr({=}N{-}NMe_2)(dpe)_2}]^+$ *. In fact the only other derivative of dialkyl type to be obtained was $[\mathrm{WBr\{N_2(CH_2)_4\}(dpe)_2}]$ from the bis-dinitrogen tungsten complex and $\mathrm{Br(CH_2)_4Br}$. It contained the ligand V. The dihalide, $\mathrm{Br(CH_2)_3Br}$, gave the open chain compounds analogous to III and IV with $\mathrm{R = CH_2(CH_2)_2Br}$. This work, completed in early 1974, was not published because of the difficulty of accounting for a mysterious green product from tetrahydrofuran.



(V)

When tetrahydrofuran was the solvent for the alkylation reaction 10, a green product was found mixed with the normal products III and IV. Methyl and ethyl bromides gave the same green product which was obtained in greatest yield when methyl bromide was used. In this peculiar reaction the ligating dinitrogen appeared to have replaced the oxygen from tetrahydrofuran to give a new heterocyclic ligand. Spectroscopic evidence, collected from $^{15}\mathrm{N}$ and $N{-}^{2}\mathrm{H}$ substitution products as well as the normal complex, suggested that it contained a chain of four carbon atoms attached to the dinitrogen in the form e.g. $\mathrm{{-}CH_2(CH_2)_2CH{=}NH{-}N}$. This was either cyclised to form a coordinated tetrahydropyridazine ring VI or through the oxygen to tungsten to form the ring VII. Oxygen analysis in the presence of phosphorus and tungsten is notoriously unreliable but we could not ignore the fact that it indicated the presence of one oxygen atom corresponding to the formula $[\mathrm{WBrON_2C_4H_8(dpe)_2}]\mathrm{Br}$. Magnetic and other properties did not fit. Nevertheless it seemed very difficult to account for the loss of oxygen from the tetrahydrofuran unless it had become attached to tungsten. $[\mathrm{Mo(N_2)_2(dpe)_2}]$ gave analogously a dark brown salt of corresponding composition. Eventually the problem was solved by removal of hydrogen bromide from the green tungsten salt by alkali. This gave a non-ionic substance from which it was possible to get a mass spectrum which showed a cluster of peaks in the range m/e 1138-1148, the most intense peak being at m/e 1143 ± 1. There were no higher peaks and this corresponds to the substance VIII. The hydrobromide salts would then have the structure IX (M = Mo or W). The spec-

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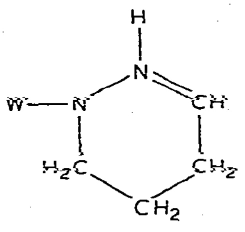
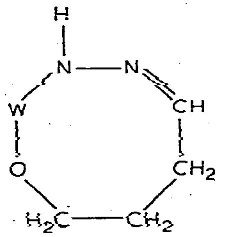
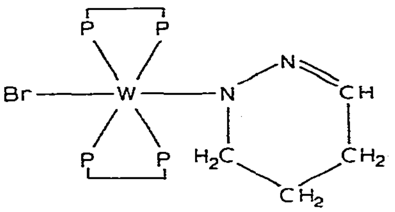
* In June 1974 I learnt that George and Iske, Jr. [33] had obtained results analogous to ours from $[\mathrm{Mo(N_2)_2(dpe)_2}]$ and methyl halides by UV irradiation.



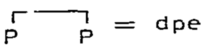
(VI)

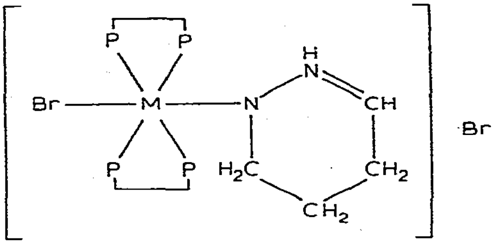


(VII)



(VIII)





(IX)

tral studies (IR and NMR) show all features of the tetrahydropyridazido ring except the link between the two central carbon atoms, they establish the presence of —N=CH—CH_2—, —CH_2—CH_2—, and NH groups in IX; and presumably these groups are joined as shown, although it is not certain which of the two nitrogen atoms is attached to the tungsten and which carries the hydrogen atom [31,34].

It is not at all clear how complex IX is formed during this reaction and what is the role of the alkyl bromide. It possibly leads to the elimination of the oxygen from the tetrahydrofuran as the alcohol ROH. Tetrahydrothiophene does not give an analogous reaction.

The observation that ligating dinitrogen can displace oxygen from a heterocyclic ring is unique. It indicates that the bis-dinitrogen, molybdenum and tungsten complexes are surprisingly reactive. They are quite different in reactivity from the mononuclear dinitrogen complexes formed by metals to the right of the molybdenum group in the periodic table.

As in the protonation reaction, we find that the monophosphine complexes $[M(N_2)_2(PR_3)_4]$ (M = Mo or W; PR_3 = PMe_2Ph or $PMePh_2$) are more reactive than the diphosphine ones. Thus $[Mo(N_2)_2(PMe_2Ph)_4]$ reacts in methanol with dimethylsulphate in presence of light to form a mixture of methylamines and methylhydrazines [35].

The high reactivity of mono-coordinated dinitrogen in these molybdenum and tungsten complexes and of bridging dinitrogen in the binuclear complexes of titanium and zirconium [14,15] heralds the beginning of possibly useful discovery in the complex chemistry of dinitrogen. I like to think of its chemistry as being in the same stage of development now as that of olefin complexes when the nature of their bonding was elucidated about 20 years ago [36]. It seems unlikely that it can be as prolific as the last 20 years of olefin complex chemistry because "olefin" represents a great number of substances and "dinitrogen" is only one. Nevertheless it is just as likely to throw up new and interesting chemistry and perhaps one or two useful industrial processes.

Finally I would like to thank all my co-workers and assistants in the laboratory and office without whose help in every sphere so little could have been achieved. Also those who have shown sufficient confidence in the aims of my research to have given it their continued sponsorship through the lean as well as the fat years. I thank them all for their loyal support and the exciting and rich research experience to which they have contributed so fully.

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