Journal of Organometallic Chemistry, 239 (1982) 65—77
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Review

THE REACTIONS OF DINITROGEN IN ITS METAL COMPLEXES *

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(Received in India November 6th, 1981; in Amsterdam May 25th, 1982)

We are proud to dedicate this review to the honour of our old friend Professor R.C. Mehrotra on the occasion of his 60th birthday. Molybdenum and tungsten are versatile elements capable of displaying a great range of oxidation states and both class (a) and class (b) characters. Molybdenum is especially important to life as an essential element in a number of redox enzymes such as nitrate reductase and nitrogenase. Professor Mehrotra laid much of the foundation of the chemistry of its class (a) character in his well known researches into the molybdenum(V) alkoxides. In this review we complement his work by consideration of an aspect of the class (b) chemistry of molybdenum, tungsten and related elements in low oxidation states where they combine with and activate molecular nitrogen.

The major recent stimulus for the investigation of the reactions of dinitrogen at metal sites arose from knowledge of the function of the enzyme nitrogenase which catalyses the conversion of molecular nitrogen into ammonia under ambient conditions. Following Bortels' demonstration, some 50 years ago, that the presence of molybdenum was essential for the enzyme to function, chemists began to seek reactions of dinitrogen with molybdenum and other transition metal compounds which might throw light upon the enzyme mechanism [1].

These efforts were largely unsuccessful until about 15 years ago when Allen and Senoff prepared, fortuitously from hydrazine, the first metal complex containing dinitrogen as a ligand [2], $[Ru(NH_3)_5(N_2)]^{2+}$. Following that discovery, other syntheses of dinitrogen complexes followed, involving the degradation of a compound containing two or more linked nitrogen atoms such as a hydrazine or an azide, or directly from nitrogen gas [1—3]. This latter route has tended to dominate in more recent work and the large number of dinitrogen complexes, prepared from almost all of the transition metals, is constantly

* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

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increasing as a perusal of recent reviews will demonstrate [1—3]. It is not here our purpose to present the detailed chemistry of dinitrogen complexes, but rather to concentrate on their reactions. Nevertheless, a few of their properties should be stressed at this point, as follows.

By far the majority of dinitrogen complexes are of transition metals in their lower oxidation states. This arises because of the nature of the metal—dinitrogen bond, which in the case of mononuclear dinitrogen complexes, resembles the bonding of carbon monoxide to these metals i.e. a σ-donation of electrons to the metal (rather weak in the case of N_2) together with back-donation from occupied metal *d*-orbitals into vacant π^*-orbitals on dinitrogen. There is only one known example where the nitrogen molecule is probably bonded 'side-on' with both nitrogen atoms equally bonded to the metal. Dinitrogen can also bridge two metals, one attached to each nitrogen atom, and the bonding scheme again involves a strong π-interaction between metal-*d* and N_2-π orbitals, producing a linear M—N—N—M system as has been discussed in detail elsewhere. A few complex examples of side-on bridge bonding are also known [1—3].

Early investigations of the reactions of molecular nitrogen in its complexes were somewhat disappointing in that the dominant reaction of the complexes was the simple loss of dinitrogen as the gas, either by displacement by another ligand, or arising from the oxidation of the metal. Nevertheless, such loss of dinitrogen provides a route to new, and often catalytically active compounds [1—3].

Later were discovered reactions which involved dinitrogen itself. The simplest of such reactions is the formation of adducts in which the terminal nitrogen atom in a mononuclear complex acts as a Lewis base [1,3]. Following these observations was the development of reactions which lead to the formation of nitrogen—hydrogen and/or nitrogen—carbon bonds. Reactions of this type returns us to the general theme of present-day dinitrogen chemistry, in that they may have relevance to the mechanism of nitrogenase action. They also show great promise of leading to the development of cyclic and catalytic processes for the formation of ammonia, hydrazine, and their organic derivatives. We discuss these reactions of dinitrogen complexes below.

Displacement of dinitrogen

As mentioned above, this type of reaction was the first to be discovered and in many aspects is the least interesting in that no nitrogen-containing products, other than the gas, are obtained.

Oxidation of the central metal of a dinitrogen complex causes weakening of the metal—dinitrogen interaction because of the weakened capacity of the metal for back donation and the dinitrogen is usually evolved as gas; typical oxidising agents are halogens, halogen acids, organic acids, acyl chlorides etc. [1,3]. In a few cases the dinitrogen is weakly retained at the oxidized metal, e.g. *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ is oxidised by Cl_2 to *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$-Cl [4]. Examples of such oxidative reactions are shown in Table 1. The reactions involving dihydrogen are formal oxidations of the metal, despite the reduction in oxidation level of the complex by addition of hydrogen.

As has been discussed above and elsewhere [1—3] dinitrogen is a relatively

TABLE 1

EXAMPLES OF OXIDATION OF DINITROGEN COMPLEXES [a]

Complex	Reagent	Product
a) N_2 loss		
trans-[$Mo(N_2)_2(dppe)_2$]	HCl	[$MoH_2Cl_2(dppe)_2$]
trans-[$Mo(N_2)_2(dppe)_2$]	RSH	[$Mo(SR)_2(dppe)_2$]
trans-[$Mo(N_2)_2(dppe)_2$]	H_2	[$MoH_4(dppe)_2$]
trans-[$ReH(N_2)(dppe)_2$]	H_2	[$ReH_3(dppe)_2$]
[$RuH_2(N_2)(PR_3)_3$]	H_2	[$RuH_4(PR_3)_3$]
[$OsCl_2(N_2)(PR_3)_3$]	Cl_2	[$OsCl_3(PR_3)_3$]
trans-[$IrCl(N_2)(PPh_3)_2$]	HCl	[$IrHCl_2(PPh_3)_2$]
b) N_2 retention		
trans-[$Mo(N_2)_2(dppe)_2$]	I_2/MeOH	*trans*-[$Mo(N_2)_2(dppe)_2$]I_3
trans-[$W(N_2)_2(dppe)_2$]	HCl	[$WH(N_2)_2(dppe)_2$]HCl_2
trans-[$ReCl(N_2)(PMe_2Ph)_4$]	Cl_2	*trans*-[$ReCl(N_2)(PMe_2Ph)_4$]Cl
trans-[$IrCl(N_2)(PPh_3)_2$]	$MeSO_3CF_3$	[$IrCl(Me)(SO_3CF_3)(N_2)(PPh_3)_2$]

[a] References 1, 2 and 3.

weak ligand of its class and consequently it may be displaced by related ligands such as carbon monoxide or methyl isocyanide, both of which bind better to metals in the σ- and/or π-sense than does dinitrogen in its mononuclear complexes. These ligands also interact with nitrogenase. Examples of dinitrogen displacement, in which the oxidation state of the metal remains unchanged, are shown in Table 2. In the sense that these reactions often lead to the preparation of new and interesting compounds, dinitrogen can be regarded as a good leaving group in preparative transition metal chemistry. There is a relatively small number of examples of reactions where other ligands are displaced in preference to

TABLE 2

EXAMPLES OF DISPLACEMENT REACTIONS OF DINITROGEN COMPLEXES [a]

Complex	Reagent	Product
a) Loss of N_2		
trans-[$Mo(N_2)_2(dppe)_2$]	CO	*cis*-[$Mo(CO)_2(dppe)_2$]
trans-[$Mo(N_2)_2(dppe)_2$]	MeNC	*trans*-[$Mo(CNMe)_2(dppe)_2$]
trans-[$ReH(N_2)(dppe)_2$]	C_2H_4	*trans*-[$ReH(C_2H_4)(dppe)_2$]
[$Mn(\eta$-$C_5H_5)(CO)_2(N_2)$]	THF	[$Mn(\eta$-$C_5H_5)(CO)_2(THF)$]
[$FeH_2(N_2)(PEtPh_2)_3$]	CO	[$FeH_2(CO)(PEtPh_2)_3$]
[$Ru(NH_3)_5(N_2)$]$^{2+}$	C_5H_5N	[$Ru(NH_3)_5(C_5H_5N)$]$^{2+}$
[$CoH(N_2)(PPh_3)_3$]	NCR	[$CoH(NCR)(PPh_3)_3$]
[$\{(\eta^5$-$C_5Me_5)_2Zr(N_2)\}_2N_2$]	CO	[$\{(\eta^5$-$C_5Me_5)_2Zr(CO)\}_2N_2$]
b) Retention of N_2		
cis-[$Mo(N_2)_2(PMe_2Ph)_4$]	$PhSCH_2CH_2SPh$	*trans*-[$Mo(N_2)_2(PMe_2Ph)_2(PhSCH_2CH_2SPh)$]
trans-[$W(N_2)_2(PMePh_2)_4$]	C_5H_5N	[$W(N_2)_2(C_5H_5N)(PMe_2Ph_2)_3$]
trans-[$ReCl(N_2)(PMe_2Ph)_4$]	C_5H_5N	[$ReCl(N_2)(C_5H_5N)(PMe_2Ph)_3$]
mer-[$OsX_2(N_2)(PR_2Ph)_3$] [b]	$NaBH_4$	*mer*-[$OsHX(N_2)(PR_2Ph)_3$]

[a] References 1, 2 and 3. [b] X = Cl or Br; R = Me, Et, Bu^n.

dinitrogen from the coordination sphere of a mononuclear dinitrogen complex, e.g. *trans*-$[W(N_2)_2(PMePh_2)_4]$ gives *trans*-$[W(N_2)_2(C_5H_5N)(PMePh_2)_3]$ on treatment with pyridine [5]. The bridging dinitrogen of the complex $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ remains intact when the complex is treated with CO, whereas the terminal dinitrogen ligands are displaced (Table 2), doubtless a reflection of the relative strength of the delocalised ZrN_2Zr bonding system [6].

Adduct formation

When bound at metal sites, dinitrogen gains electron density, to a varying extent, as a result of the *d*-electron-release from the metal to which it is attached. Thus ligating dinitrogen is more basic than is the free molecule, a property which can be demonstrated by the formation of adducts in which electron acceptor entities or molecules attach themselves to the terminal nitrogen atom. The first example of this type of reaction was provided by the displacement of ligating water from ruthenium(II) to give a binuclear, μ-dinitrogen complex [7] [eq. 1].

$$[Ru(NH_3)_5(H_2O)]^{2+} + [Ru(NH_3)_5(N_2)]^{2+} \rightleftharpoons [\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+} + H_2O \quad (1)$$

This bridging interaction involving two transition metal centres leads to a highly conjugated linear M—N—N—M π-system.

When the adduct atom comes from a Main Group such a conjugated system cannot be formed. Nevertheless, some Main Group adducts are stable, and the relative Lewis-base character of dinitrogen in a variety of dinitrogen compounds has been shown by measurement of the equilibrium constants K, of a series of equilibria of the type 2 [8].

$$[ReCl(N_2)(PMe_2Ph)_4] + Me_3Al\cdot OEt_2 \overset{K}{\rightleftharpoons} [Cl(PMe_2Ph)_4Re(\mu\text{-}N_2)AlMe_3] + Et_2O \quad (2)$$

An interesting consequence of the asymmetric bridge bonding of these latter adducts compared with the delocalised μ-N_2 binuclear complexes described earlier, is the range of chemical shifts recently observed in their ^{15}N NMR spectra. Because of the low-lying π-system, the chemical shifts of the delocalised compounds lie at low field e.g. 210.8 ppm for $[\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+}$, whereas removal of lone pair character from the terminal nitrogen atom of *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ [$\delta(N) = -67.6$ ppm] shifts in its resonance considerably upfield in $[ReCl(N_2AlMe_3)(PMePh)_4]$ [$\delta(N) = -133.2$ ppm] [9].

Formation of nitrogen—hydrogen bonds

Once the basicity of ligating dinitrogen had been established, it was an obvious extension to examine the reactions of ligating dinitrogen with other potentially electrophilic reagents to produce nitrogen—hydrogen and nitrogen—carbon bonds. In this section we discuss nitrogen—hydrogen bond formation and its possible relevance to the action of nitrogenase. Although the basicity of ligating dinitrogen might lead one to expect a widespread tendency for dinitrogen

complexes to protonate at nitrogen, in practice relatively few do so. This is because the metals themselves are relatively electron rich and receive the proton in preference to dinitrogen in many cases, eventually leading to loss of dinitrogen as gas by proton oxidation of the metal. However, in a few cases, stable hydrido-dinitrogen complexes are formed, e.g. *trans*-$[WH(N_2)_2(dppe)_2][HCl_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (Table 1) [10]. However, protonation of ligating dinitrogen does occur for a limited number of binuclear and mononuclear complexes, to give mainly hydrazine from binuclear complexes and hydrazine or ammonia from mononuclear ones, depending upon the conditions of reaction.

If we consider the binuclear complexes first, those well-characterised compounds which give hydrazine on treatment with acids such as HCl are: $[\{Ti(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ [6], $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ [6] and $[\{TaX_3L_2\}_2(\mu\text{-}N_2)]$ (X = Cl, OBu^t or H_2CCMe_3; L = THF, $P(CH_2Ph)_3$ or PEt_3) [11]. All these complexes contain linear dinitrogen bridges.

In the tantalum compounds the N—N bond is rather long and the Ta—N bond is somewhat short [N—N = 1.282(6), Ta—N = 1.796(4) Å; X = Cl, L_2 = THF + $P(CH_2Ph)_3$] which suggests that the electronic condition of the bridging dinitrogen has a high degree of N_2^{4-} character, allowing facile protonation to give hydrazine [11]. Nevertheless, the μ-N_2 distances of the other reactive binuclear complexes are not exceptionally long [1.182—1.155 Å] [1—3]. Mechanistic details of these reactions are not yet available but some interesting results have been obtained for the compound $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$. In this compound the terminal dinitrogen ligands were selectively labelled with ^{15}N and the hydrazine resulting from reaction with HCl was found to be 50% ^{15}N-enriched. Thus the terminal dinitrogen ligands take part in the reaction and it has been proposed that mononuclear intermediates such as $[Zr(\eta^5\text{-}C_5Me_5)_2(N_2H)$ ($^{15}N_2H$)] are involved in the reaction mechanism [6].

Some other less well-characterised binuclear complexes are also involved in reactions which lead to hydrazine or ammonia. Thus reduction of the compound $[\{Ti(\eta^5\text{-}C_5H_5)_2R\}_2(\mu\text{-}N_2)]$ (R = acyl or aryl) with sodium naphthalenide ($NaC_{10}H_8$) followed by hydrolysis, gives hydrazine or ammonia although the identity of the reduced metal species is not certain [12]. A niobium complex, tentatively formulated as $[\{NbCl(Me_2PCH_2CH_2PMe_2)_2\}_2(\mu\text{-}N_2)]$ could not be purified, but about 20% of its dinitrogen was converted into hydrazine on treatment with HCl [13]. Also in this class we mention the complex formulated as $[(Ph_3P)_2H(Pr^i)Fe(\mu\text{-}N_2)Fe(Pr^i)(PPh_3)_2]$ which is stable at —50°C, at which temperature it gives about 0.1 mol of hydrazine [14] per dinitrogen on treatment with HCl, and the complex $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$, which gives reduced nitrogen species on protonation, but whose detailed chemistry has not yet been explored [15].

The reduction of terminal dinitrogen ligands in mononuclear complexes has been extensively studied, these reactions being confined almost exclusively to complexes of molybdenum and tungsten. One possible exception is the production of hydrazine on treatment of $[CoH(N_2)(PPh_3)_3]$ with $MgEt_2$ in THF followed by hydrolysis. It seems likely, however, that the dinitrogen is bridged between cobalt and magnesium in an intermediate adduct such as $[(PPh_3)_3Co(\mu\text{-}N_2)Mg(THF)_2]$. On treatment with an excess of sulphuric acid at room temperature, the complexes $[M(N_2)_2P_4]$ (M = Mo or W; P = PMe_2Ph or $PMePh_2$)

give ammonia or hydrazine, the yield being critically dependent upon the metal, the acid anion and the reaction solvent e.g. reactions 3 and 4 [1,17].

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow[MeOH]{H_2SO_4} [NH_4]_2SO_4 + N_2 + W^{VI} \text{ products} \quad (3)$$

$$cis\text{-}[Mo(N_2)_2(PMe_2Ph)_4] \xrightarrow[THF]{HBr} [NH_4]Br + 1.5N_2 + [MoBr_3(PMe_2Ph)_2(THF)] + 2[PMe_2PhH]Br \quad (4)$$

In both reactions, it has been established that hydrazido(2—)-complexes, i.e. containing the ligand $=N—NH_2$, are crucial and persistent intermediates in the reduction process [17]. These intermediates have been isolated from protonation reactions such as reaction 5 and also observed by their characteristic ^{15}N NMR resonances (Table 3) during analogous reactions, such as reactions 3 and 4, where isolation of intermediates is difficult [17].

$$cis\text{-}[M(N_2)_2(PMe_2Ph)_4] + 3HX \xrightarrow{MeOH} [MX_2(NNH_2)(PMe_2Ph)_3] + [PMe_2PhH]X + N_2 \quad (5)$$

(X = Cl, Br or I)

^{15}N NMR can therefore be used to follow the kinetics of such reactions by observation of the formation and disappearance of the labelled ($=NNH_2$) intermediate during the formation of nitrogen hydrides [17].

Complexes of the (diazenido)-ligand (—N=NH), which can be considered to represent the first step in the protonation and reduction of ligating dinitrogen, have also been prepared [reaction 6] and their ^{15}N NMR parameters established (Table 3).

$$[M(NNH_2)X(dppe)_2]X + NEt_3 \overset{THF}{\rightleftharpoons} [M(NNH)X(dppe)_2] + [NEt_3H]X \quad (6)$$

(X = F, Cl, Br or I)

Some examples of this type of complex may be fluxional in solution, with the proton labile between metal and dinitrogen, but under conditions of ^{15}N

TABLE 3

^{15}N NMR PARAMETERS OF COMPLEXES RELEVANT TO NITROGEN REDUCTION REACTIONS [a]

Complex	Chemical shift data [b]	
	N_α	N_β
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	—42.6	—34.9
trans-$[W(N_2)_2(dppe)_2]$	—63.5	—52.0
$[WBr(NNH)(dppe)_2]$	—25.9	—187.1
$[WBr(NNH_2)(dppe)_2]Br$	—78.5	—234.9
$[MoI_2(NNH_2)(PMe_2Ph)_3]$	—72.2	—248.3
$[WH(NNH_2)Br_2(PMe_2Ph)_3]Br$	—65.8	—266.4

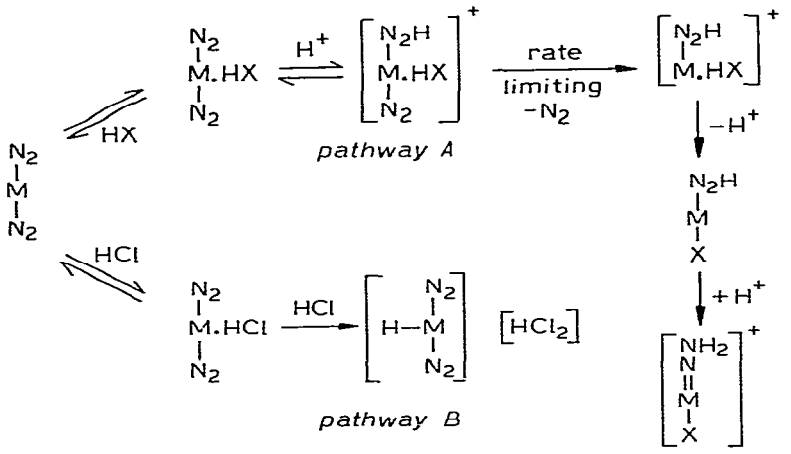
[a] Ref. 9, references therein and unpublished results. [b] Relative to $C^2H_3NO_2$ in THF solution, N_α = nitrogen atom adjacent to metal, N_β = terminal nitrogen atom. All ligands enriched to 95% in ^{15}N.

NMR measurements (Table 3) this ligand is clearly established [9]. A complex containing an adduct of the N_2H ligand [WHClBr{NN(BPh_3)H}(PMe_2Ph)$_3$] has been structurally characterised by X-rays [18].

A mechanism for the first two protonation steps in these reactions which accommodates the tendency of the metal to protonate, rather than the ligating dinitrogen, under certain conditions has been developed from a kinetic study of the reactions of *trans*-[M(N_2)$_2$($Et_2PCH_2CH_2PEt_2$)$_2$] with HX (X = Cl, Br, or HSO_4) in THF. This is shown in Scheme 1 [19].

SCHEME 1

MECHANISM OF CONVERSION OF LIGATING N_2 INTO NNH_2 [a]



[a] The $Et_2PCH_2CH_2PEt_2$ ligands are omitted for convenience.

Initial association of HX with the dinitrogen complex and protonation of dinitrogen occurs prior to the rate-limiting dissociation of dinitrogen. Rapid attack of HX on the 5-coordinate intermediate and subsequent loss of a proton generates [M(NNH)X($Et_2PCH_2CH_2PEt_2$)$_2$] which is rapidly protonated to yield the hydrazido(2—)-product (pathway A). When X = Cl, pathway B can come into operation at a rate which is first-order in the HCl concentration, whereas pathway A occurs at a rate which exhibits a second-order dependence on HCl concentration. Thus at low acid concentrations metal-hydride formation is the faster of the two reactions, but on increasing the concentration of acid the reaction leading to the formation of the hydrazido(2—)-complex rapidly becomes the dominant pathway [19].

The steps subsequent to the hydrazido (2—)-stage of reaction have not yet been clearly established for either molybdenum or tungsten complexes. For molybdenum, the stoichiometry of the further protonation of [$MoX_2(NNH_2)$-(PMe_2Ph)$_3$] (X = Br or I) is $NH_3 + \frac{1}{2}N_2$ per molybdenum atom; also the molybdenum(III) products, corresponding to the three electrons transferred to the ligating dinitrogen, have been isolated [see reaction 4] [15,20].

An analogous molybdenum(III) product, has also been isolated from reaction 7 [21].

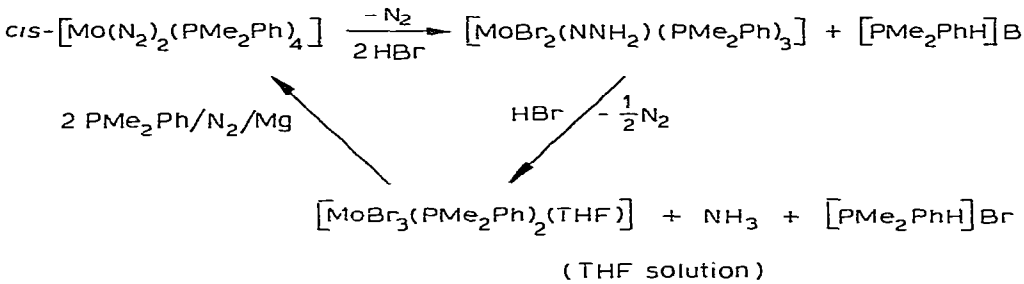
$$[Mo(N_2)_2\{PPh(CH_2CH_2PPh_2)_2\}(PPh_3)] \xrightarrow[THF]{HBr}$$

$$\tfrac{3}{2}N_2 + NH_3 + [PPh_3H]Br + [MoBr_3\{PPh(CH_2CH_2PPh_2)_2\}] \quad (7)$$

The molybdenum(III) products obtained from the reactions of $[MoX_2(NNH_2)(PMe_2Ph)_3]$ with HX and from reactions 4 and 7 can be reduced back to the starting dinitrogen complexes by Grignard magnesium under dinitrogen thus giving, for example, the cyclic but not catalytic scheme for the reduction of dinitrogen to ammonia shown in Scheme 2.

SCHEME 2

CYCLIC REDUCTION OF DINITROGEN TO AMMONIA



If the $[MoX_2(NNH_2)(PMe_2Ph)_3]$ complexes are treated with H_2SO_4, the product is ammonia, but the yield increases in the order Cl < Br < I, to a maximum of $1 NH_3$/Mo atom [17]. Other hydrazido(2—)-complexes which have a different coordination environment, e.g. [W(quinolin-8-olate)(NNH_2)-$(PMe_2Ph)_3]^+$ give hydrazine as the only product on treatment with sulphuric acid in methanol [17]. Such a coordination influence may explain the dependence of yield upon solvent, e.g. *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ gives essentially only NH_3 (0.33 mol/Mo atom) with anhydrous HCl in THF, but gives equal quantities of hydrazine and ammonia (0.32 N_2H_4/0.31 NH_3/Mo atom) in 1,2-dimethoxyethane. Presumably the solvent interacts with the metal and changes the electronic properties of the hydrazido(2—)-ligand thus affecting its subsequent reactions [18].

Further studies on the protonation of tungsten hydrazido(2—)-complexes have given hydride-hydrazido(2—)-complexes (reaction 8). Thus the hydrazido-(2—)-complexes are still ambivalent concerning the position of the next protonation site because of the basic character of the metal.

$$[WX_2(NNH_2)(PMe_2Ph)_3] \xrightarrow{HX} [WHX_2(NNH_2)(PMe_2Ph)_3]X$$

$$\downarrow HX\ (X = Cl)$$

$$[WHCl_3(NNH_2)(PMe_2Ph)_2] + [PMe_2PhH]Cl \quad (8)$$

The X-ray structure of one member of this series $[WHClBr(NNH_2)(PMe_2Ph)_3]$-Br suggests that the hydride ligand occupies one face of a distorted octahedron [18]. The compound $[WHCl_3(NNH_2)(PMe_2Ph)_2]$ loses a hydrogen atom on standing in CH_2Cl_2 solution to give the paramagnetic hydrazido(2—)-complex,

cis-$[WCl_3(NNH_2)(PMe_2Ph)_2]$, whose X-ray structure has been determined at sufficient resolution to show the planarity of the W=N—N$\lessdot^{H}_{H}$ system [22]. The linearity of this group in this and in other structurally characterised analogues and the relatively short M—N and N—N distances show that the hydrazido(2—)-group is strongly conjugated within itself and to the metal, acting as a 4-electron donor. The M—N multiple bonding appears to be an essential component of the reduction sequence. Thus the energy for the degradation of the strong N≡N bond is obtained by forming an M≡N and new N—H bonds [1,3].

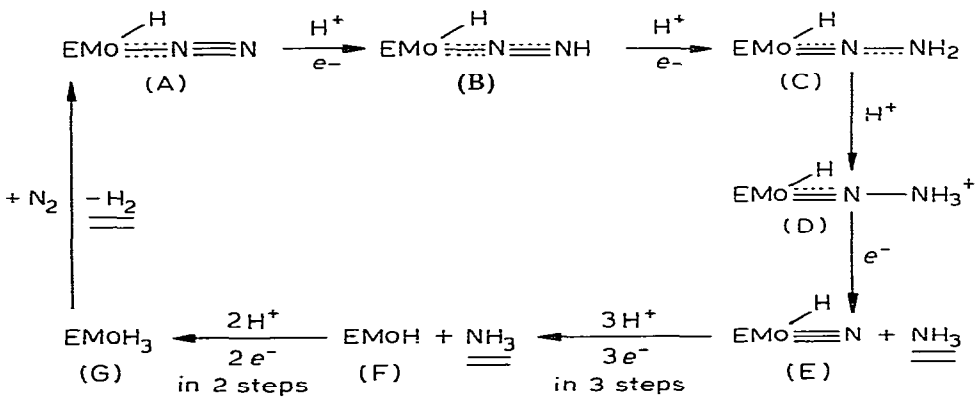
The mechanism of degradation of the hydrazido(2—)-ligand is still uncertain. Where tungsten is the central metal, the necessity for it to transfer six electrons to one of its dinitrogen ligands makes a binuclear intermediate step unlikely. It is not clear whether the hydride-hydrazido(2—)-complexes are on a direct route to ammonia but if they were, to obtain $2NH_3$ per W atom clearly implies complete hydrogen migration from metal to nitrogen and it seems more likely that the hydride-hydrazido(2—) compounds lie on the route to hydrazine [18,22].

In the molybdenum case, kinetic data show that the degradation of the hydrazido(2—)-complex stage is at least a biphasic process and may involve electron transfer between molybdenum atoms. The possibility of intermediates involving coupling of nitrogen species is excluded, because experiments using mixtures of $Mo^{28}N_2$ and $Mo^{30}N_2$ dinitrogen or corresponding hydrazido(2—)-complexes have shown that no $^{29}N_2$ formation occurs [23].

It is a reasonable proposition that the chemistry of dinitrogen at metal sites relates to that at the metal site of nitrogenase. Although a binuclear mechanism for nitrogenase action cannot be excluded, the lack of ammonia formation from well-characterised binuclear complexes and accumulating evidence which indicates that molybdenum atoms in nitrogenase act separately, led us to propose the cycle of Scheme 3 for the reduction of dinitrogen at the molybdenum site of nitrogenase [3,24].

SCHEME 3

DINITROGEN REDUCTION ON NITROGENASE INVOLVING A HYDRAZIDO(2—) INTERMEDIATE (Products double underlined)



This scheme accommodates the observation that rapidly quenching the nitrogenase reaction in vitro with acid or base gives hydrazine [25]. The hydrazido(2—)-stage of reduction (C) (Scheme 3) is so stable, that if it occurs

in the natural system, it is the most likely intermediate species to be caught by acid or base quench, and the source of the hydrazine. In Scheme 3 it is envisaged that molybdenum is maintained in some intermediate oxidation state, capable of binding dinitrogen and of transferring electrons to it from the iron-sulphur electron storage and transfer system of the enzyme.

The displacement of dihydrogen at the dinitrogen pick-up stage (G → A) accords with the observation that under optimum conditions of fixation one hydrogen molecule is evolved for each molecule of nitrogen reduced. The third hydrogen in (G) and single hydrogen in (A) and subsequently, is necessary to explain the production of HD in the presence of dideuterium.

Nitrogen—carbon bond formation

The formation of nitrogen—carbon-bonded organic compounds from dinitrogen is potentially of great industrial importance and has been investigated in parallel with nitrogen—hydrogen bond formation. Such reactions are confined to complexes of tantalum, molybdenum, tungsten, manganese and rhenium.

The first demonstration of N—C bond formation from ligating dinitrogen was the acylation of tungsten dinitrogen complexes shown in reaction 9.

$$\textit{trans}\text{-}[W(N_2)_2(dppe)_2] + CH_3COCl \rightarrow [WCl(N_2COCH_3)(dppe)_2] + 2H_2$$
$$\downarrow H^+$$
$$[WCl\{N_2H(COCH_3)\}(dppe)_2]^+ \qquad (9)$$

The resulting acyldiazenido-complex readily protonates to give a hydrazido-(2—)-complex as shown in reaction 9 but no further [26]. Subsequently, it was shown that alkyl halides react with *trans*-$[M(N_2)_2(dppe)_2]$ to give diazenido- and hydrazido(2—)-complexes; more recent work has elucidated the mechanism of these reactions.

Electrochemistry, EPR data and IR studies have been used to show that these reactions involve the initial rate-determining step of loss of dinitrogen to give the unstable, reactive species $M(N_2)(dppe)_2$; irradiation (tungsten filament lamp) is necessary to induce this dissociation step when M = W. This intermediate then binds the alkyl halide via the halide to give $M(RX)(N_2)(dppe)_2$, in which homolysis of the RX bond occurs, followed by attack of $R^{\cdot}$ on the remaining ligating dinitrogen to give $[M(N_2R)X(dppe)_2]$ [27]. The resultant diazenido-complexes protonate readily to give hydrazido(2—)-complexes, $[M(NHHR)X(dppe)_2]^+$, or alkylate to give $[M(NNRR')X(dppe)_2]^+$, (R = Me), but very slowly. The rate of introduction of the second alkyl group is first-order in the diazenido-complex and in methyl iodide; it corresponds to a classical S_N2 substitution [28].

The complexes *trans*-$[M(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$ are more electron-rich than their dppe analogues and when they are alkylated the second S_N2 step is faster than the first radical alkylation, so that dialkyl hydrazido(2—)-complexes are the only isolable products. The complex anion $[Mo(NCS)(N_2)(dppe)_2]^-$ reacts with Bu^nI to give the diazenido-product but apparently radical generation occurs via an outer-sphere electron transfer, consistent with the highly electron-rich nature of the anionic dinitrogen complexes [28].

α,ω-dibromoalkanes, $Br(CH_2)_nBr$ react to give products which depend upon the value of n. For $n = 2$, $[MBr_2(dppe)_2]$ is formed because the radical $BrCH_2$-$CH_2^{\bullet}$ is unstable, losing ethylene. Open chain products result when $n = 3$ to avoid steric strain, whereas for $n = 4$ or 5, cyclic hydrazide products $[MBr\{NN(CH_2)_n\}(dppe)_2]Br$ result. For $n = 6$ to 12 open-chain products are again preferred, but probably with admixture of oily ring products [29].

Diazoalkane complexes $[MX(NN{=}CRR')(dppe)_2]^+$ can be prepared either by the reaction of *gem*-dihalides on the $[M(N_2)_2(dppe)_2]$ complexes, or by condensation of hydrazido(2—)-complexes with aldehydes or ketones under protic catalysis. To date, the only route to prepare N=C bonds in the monophosphine series is by the latter route, e.g. $[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ from $[MX_2(NNH_2)(PMe_2Ph)_3]$ [30].

Protic and hydridic attack on diazoalkane complexes has been investigated. Thus hydrazine and ammonia (0.3 mol: 0.2 mol/metal atom) result when $[MX_2(NNCMe_2)(PMe_2Ph)_3]$ (X = Cl or Br) are treated with anhydrous HX in CH_2Cl_2 or THF [18]. In contrast, the complex $[WBr(NNCH_2)(dppe)_2]Br$ does not react with acids, but gives substituted diazenido-complexes with organo-Grignard or -lithium reagents (reaction 10).

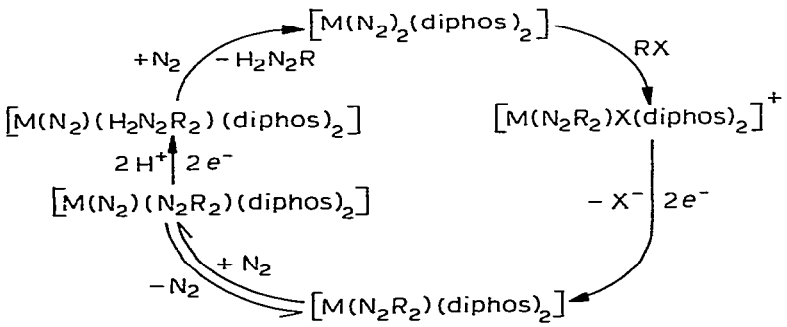
$$[WBr(NNCH_2)(dppe)_2]Br + LiMe \rightarrow [WBr(NNCH_2CH_3)(dppe)_2] + LiBr \qquad (10)$$

Lithium aluminium hydride analogously produces the methyl-diazenido-complex [29].

Attempts have been made to obtain simple organonitrogen products from the above organodiazenido- and organohydrazido(2—)-complexes. In general, treatment with acids leads to considerable N—C bond cleavage and overall yields are poor, but significant yields of secondary amines as well as primary amines and ammonia were obtained using sodium borohydride in methanol [31]. These conditions seem altogether too vigorous to form a basis of a catalytic process, but a recently developed cycle for the formation of organic hydrazines (Scheme 4) appears to hold promise as the basis of an electrochemical method for the production of these organic compounds [32].

SCHEME 4

CYCLIC REDUCTION SCHEME FOR THE CONVERSION OF LIGATING DINITROGEN INTO ORGANIC HYDRAZINES

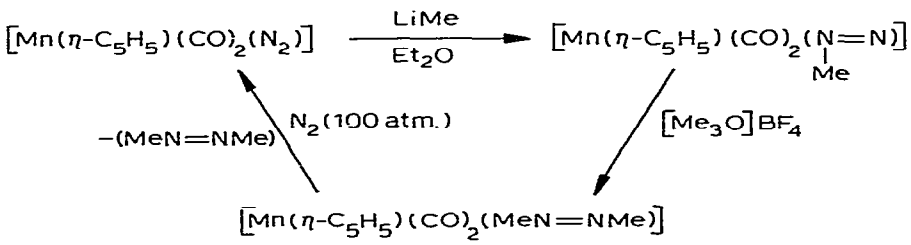


M = Mo or W; diphos = $R'_2PCH_2CH_2PR'_2$; R = alkyl; R' = alkyl or aryl

Although the N—C bond-forming chemistry is now extensive for Mo and W, other metals can be used, as noted above, which can lead to different types of mechanistic processes. Thus although the dinitrogen complexes of rhenium such as $[ReCl(N_2)(C_5H_5N)(PMe_2Ph)_3]$ acylate and aroylate with the appropriate carboxylic chloride in a reaction essentially similar to reaction 9, to yield $[ReCl_2(N_2COR)(PMe_2Ph)_3]$ (R = alkyl or aryl) [26], the manganese complex $[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$ is electron deficient relative to the phosphine-dinitrogen complexes and might be expected to be more susceptible to nucleophilic attack. This is found to be the case and its reaction with phenyllithium gives, after treatment with acid, a phenyldiazene complex. It reacts equally well with LiMe and subsequent treatment with $[Me_3O]^+$ gives a dimethyl diazene complex which on treatment with dinitrogen under pressure generates the starting dinitrogen complex (Scheme 5). Although side reactions prevent the cycle being repeated extensively, nevertheless it does demonstrate the possibility of designing a cyclic process for the formation of organonitrogen compounds using the complex-forming capability of dinitrogen [33].

SCHEME 5

CYCLIC CONVERSION OF LIGATING DINITROGEN INTO MeNNMe ON MANGANESE



The reaction of Scheme 5 does not appear to be generally applicable. For example treatment of the related rhenium compound $[ReCl(CO)_2(N_2)(PPh_3)_2]$ with LiMe results in attack on ligating CO rather than at N_2, to give the hydroxy carbene complex $[ReCl\{C(Me)OH\}(CO)(N_2)(PPh_3)_2]$ on treatment with acid [34].

A remarkably facile reaction occurs between $[\{TaCl_3(PEt_2)_2\}_2(\mu\text{-}N_2)]$ or $[\{TaCl(C_2H_4)(PMe_3)_3\}_2(\mu\text{-}N_2)]$ and acetone to give $Me_2C{=}N{-}N{=}CMe_2$ in high yield, the oxygen being presumably taken up by the tantalum [11]. So far this is the only reported reaction of these compounds to give N—C bonds but clearly much new and interesting chemistry will soon emerge from this region of the periodic table.

General conclusions

Since the discovery, about six years ago, of reactions of ligating dinitrogen which give nitrogen hydrides and organo-nitrogen products, this area of chemistry has advanced through study of detailed mechanisms of these reactions towards development of cyclic systems for the production of ammonia, hydrazine and their organic derivatives. A reasonable proposal for the mechanism of reduction of dinitrogen at the metallic site of nitrogenase has been made but what remains of paramount importance is to develop dinitrogen complexes,

stable or otherwise, where the environment of the metal is closer to that expected to pertain in nitrogenase. In particular the known sulphur environment of iron and molybdenum in this enzyme makes the preparation of dinitrogen complexes with sulphur ligation a primary research objective.

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