



PROPERTIES OF TRANSITION METAL CENTRES IN NITROGEN FIXATION

This work presents an attempt for the characterization of the dinitrogen-binding transition metal centres and a proposal for the way the activation of N_2 depends on their properties.

Although a few recent reviews are known [1-4] on dinitrogen complexes, the concept of the present work develops under a new perspective which relates properties and types of behaviour previously described individually in more detail.

Following a brief introduction on the current importance of the nitrogen fixation, the composition and structure of the transition metal centres which bind N_2 are presented, as well as their electronic properties (electron richness, σ acceptance and π back-bonding capacities, and polarisability) which play a fundamental role in the coordination of dinitrogen. The dependence of these properties on the periodic group of the central metal and on the effect of co-ligands is discussed.

The chemical behaviour of these centres (which is dependent mainly on electronic and structural factors such as the unsaturated character derived from the lability of the dinitrogen ligand) is then described, followed by the types of activation of N_2 upon coordination in poly- or mono-nuclear complexes. It is then analysed the dependence of this activation on the periodic group of the transition metal and on the presence of ions of the less electronegative non-transition metals.

The application of isocyanides as potential models for the coordination and reactivity of dinitrogen is also proposed, and structural models for the enzymatic nitrogen fixation centre are presented.

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1 — INTRODUCTION

Definition and interest

The current interest on the reactivity of dinitrogen, the most abundant gas of the earth atmosphere (formerly considered as an inert species) is justified mainly by the importance of the applications of its fundamental derivative, ammonia.

The reductive transformation of dinitrogen into ammonia is known as "nitrogen fixation", although in a broad sense all the types of studies which somehow may contribute to a better understanding of this process may be included under this topic.

Within the biological field, ammonia constitutes the basis of biosynthetical inclusion (assimilation) of the nitrogen element in organic molecules which form fundamental cellular components with proteins or nucleic acids.

The direct assimilation of N_2 from the air is not possible by upper organisms and plants get nitrogen from the soil usually after the formation of ammonia, whereas that element becomes available to animals (namely to Man) through the feed (plants or other animals).

The abovementioned reduction, in a catalytic way, may be performed biologically by the enzyme nitrogenase under ambient conditions, or in industry under drastic conditions. Moreover, the nitrogen fixation constitutes usually the limiting factor of the biological productivity; only in regions of high nitrogen concentration (due to decomposition processes or to the exaggerated application of nitrogen fertilizers) other nutrients, such as potassium, phosphorus or sulphur, become the limiting factors.

Within the industrial field, ammonia constitutes the starting material for the production of most of the nitrogen compounds: nitric acid, nitrogen fertilizers, acrylonitrile, amines and explosives.

Historical background

Although since a few thousand years Man discovered that the yield of the crops could be increased by the addition of legumes to the soil, only by the end of last century this problem started to be enlightened when, in 1887, Hellriegel and Wilfarth proved the nitrogen fixation capacity of nodulated legumes. In the following year, the first nodule bacte-

rium was isolated by Beijerinck and, in 1893, Winogradsky isolates the first soil bacterium which can fix nitrogen (it was later called *Clostridium pasteurianum*).

Meanwhile, by the end of last century and beginning of the current one, there occurred an increasing demand on nitrogen fertilizers (due to feed requirements) and on nitric acid (mainly after the invention of dynamite by Alfred Nobel in 1866). Nitrates from Chile were then the main natural resource for the starting materials, but they were insufficient for the requirements of an increasing consumption.

Dinitrogen, with a huge natural stock in the atmosphere, appeared as a potential alternative candidate, but the known industrial processes (oxidation to NO and reduction to calcium cyanamide), with high energy requirements, deserved only a weak popularity.

The problem appears to be solved in 1908 through the development of a distinct route: taking advantage of the use of high pressures and in the presence of a metal catalyst, Haber promotes the synthesis reaction of ammonia from dinitrogen and dihydrogen which becomes commercially profitable.

However, the industrial synthesis of ammonia requires a high energy consumption, not only by the synthesis reaction (which requires high pressures and temperatures) but also in the production of dihydrogen (which consumes reserves of fossil energy such as petroleum derivatives, natural gas or coal). It was estimated [5] that the production of nitrogen fertilizers corresponds roughly to 1 ~ 1.6% of the world consumption of fossil energy.

Hence, the nitrogen fixation appears as a fundamental chemical reaction to satisfy the increasing feed demands (due to the demographic expansion), but requiring a high and increasing energy consumption which is not compatible with the decrease of the fossil energy stocks. The required nitrogen supply to the biosphere has then to be balanced with the energy cost.

Excluding, for this problem, a drastic solution of control or reduction of the population, a few interdisciplinary proposals may be presented:

- Increasing the efficiency of the Haber synthesis with a decrease in the energy cost;
- Production of a new type of catalyst, model of the enzymatic activity, which may operate (preferably in the soil) in ambient conditions without

requiring fossil energy resources (water and sun light may behave as the hydrogen and energy sources, respectively);

— Promotion of the biological fixation namely through a wider distribution of nitrogen fixation bacteria and the extension, by genetic manipulation, of the fixing capacity to plants, such as cereals, with a high agricultural interest.

The first two routes, chemically in nature, require a better understanding of the metal centres which may activate dinitrogen, as shown below.

Although in 1930 it was shown by BORTELS [6] the essential role of molybdenum in the enzymatic fixation (e.g., *A. vinelandii* does not fix nitrogen in a medium without Mo and the growing is stimulated by the presence of this element), the explanation based on the recognition of the presence of Mo in a protein of the enzyme was based [7] only in 1966 when the two components of nitrogenase were sepa-

rated and one of them was shown to present this element.











Meanwhile, in 1964, the reduction of N_2 in solution by a transition metal system is reported by VOL'PIN [8] and the occurrence of a stable metal-dinitrogen bond is demonstrated (ALLEN and SENOFF [9]) in 1965 through the preparation of the first transition metal dinitrogen complex. It is, in this way, evidenced the possibility of occurrence of a similar metal-dinitrogen interaction in the natural system and in the industrial synthesis, i.e., the probable involvement of dinitrogen complexes as intermediates in the production of ammonia.

2 — STRUCTURAL AND ELECTRONIC PROPERTIES

The knowledge of the properties of a dinitrogen-binding metal centre is hampered by the common difficulty of isolation. It is usually present in the

Table 1

Common metal oxidation state and d^n electronic configuration, geometry, charge and examples of co-ligands in transition metal dinitrogen complexes

		d^n	Geometry	Charge	Co-ligands
IVB	Ti ^{II} Zr ^{II}	d^2	 	0	$\eta^5-C_5R_5^-$, R^-
VB	Nb ^{III(V)} Ta ^{III(V)}	$d^{2(o)}$	 	0	CHR(2-), R^- , X^-
VIB	M ⁰	d^6	 	0	PR_3 , $\eta^6-C_6R_6$, CO, PhS(CH ₂) ₂ SPh
VIIIB	M ^I	d^6		0	PR_3 , P(OR) ₃ , Cl^- , $S_2PR_2^-$, $S_2CNR_2^-$, H^- , CO, $\eta^5-C_5H_5$
VIII	Fe ^{II} Ru ^{II} Os ^{II}	d^6		+1 +2	PR_3 , H^- , Cl^- , R^- , $\eta^5-C_5H_5^-$, SR^- , NH_3 , H_2O , thf, porphinato
	Co ^I Rh ^I Ir ^I	d^8	 	0	PR_3 , H^- , Cl^-
	Ni ⁰	d^{10}		0	PR_3 Electropositive metal (polynuclear structures)
	Co ^{-I}			-1	

composition of coordinatively saturated complexes, and its properties are deduced from their expression in these complexes where the influence of other ligand(s) is present.

2.1. COMPOSITION

2.1.1. METAL AND LIGANDS

Fully characterized dinitrogen complexes prepared by conventional techniques are already known for the majority of transition metals as shown below:

IVB	VB	VIB	VII	VIII		
Ti		Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
	Ta	W	Re	Os	Ir	Pt

Moreover, some of the gaps may be filled if one considers species prepared by low temperature matrix isolation techniques — *e.g.*, $V(N_2)_6$ [10], $M(N_2)_n(O_2)$ ($M = Pd, Pt$; $n = 1, 2$) [11] and $Cu_n(N_2)_m$ [12].

Usually the dinitrogen complexes obey the 18-electron rule (except in the extreme groups), they are diamagnetic and neutral (with exceptions for those of the iron sub-group which are often cationic). They present the metal in a low oxidation state and co-ligands which are considerable electron donors and commonly weak π acceptors, namely tertiary phosphines and halides, or ammonia and amines in the case of Ru and Os (Table 1). The last two general features (low metal oxidation states and the presence of electron donor co-ligands) evidence an important property of the dinitrogen-binding transition metal centres: their high (or, at least, considerable) electron richness; this point will be treated below in more detail.

Examples of ligating atoms of co-ligands are known for any of the IVA to VIIA groups, the most common being underlined in Table 2.

Sulphur ligands are very rare although in the enzymatic system sulphur is an element which is present in the vicinity of molybdenum. The only well characterized examples are the Re(I) complexes *mer*-[Re (S-S) (N_2) (PMe_2Ph)₃] (S-S = $S_2PPh_2^-$, $S_2CNR_2^-$, $S_2(OEt)^-$) [13] and derived mixed dinitrogen-isocyanide species such as *mer*-[Re(η^1 - S_2PPh_2) (N_2) (CNMe)_x(PMe_2Ph)_{4-x}] ($x = 1$ or 2) [14], the Os(II) complex *mer*-[OsCl(SC₆F₅) (N_2) (PMe_2Ph)₃] [15] and the less well defined 1,2-bis(phenyl-

thio)ethane complex of Mo(0) *trans*-[Mo(N_2)₂ (PMe_2Ph)₂(S-S)] (S-S = $PhSCH_2CH_2SPh$) [16]. However, no reaction involving the N_2 ligand (apart from possible displacement) has yet been reported. Lighter metals (Fe, Co, Ni) appear to present a higher tendency to bind hydride relative to the heavier ones (Re, Os, Ir) which ligate preferentially halides as co-ligands in N_2 complexes.

A few other general observations are presented below, but the best choice of co-ligands, in N_2 complexes, is still guided by experience, their stability being strongly dependent on the composition. Hence, *e.g.*, although $[IrCl(N_2)(PPh_3)_2]$ is a known stable species, the analogues with PMe_2Ph or $P(C_6H_4CH_3-4)_3$ are not enough stable to be isolated without decomposition.

2.1.2. GEOMETRY

The geometry of the dinitrogen complexes appears to be determined by the d^n electronic state of the metal (see Table 1) which, for d^6 - d^{10} species (VIB — VIII groups), may be rationalised by extended Hückel theoretical calculations [17] based on the following assumptions: the N_2 bonding results mainly from the π -backbonding component; the molecular orbitals of the N-N₂ bond derived from overlap of the metal d orbitals with the dinitrogen $1\pi_g^*$ orbitals are fully occupied.

The former proposal may, however, fail in complexes of the group VIII (where the σ component may

Table 2
Ligand bonding atoms in dinitrogen complexes

Bonding atom Group	Ligand
IVC	C $\eta^5-C_5H_5^-$, $\eta^6-C_6H_6$ CO, CNR CHR(2-), R ⁻
VA	N P As NH_3 , $H_2N(CH_2)_2NH_2$, edta PR_3 (and chelating diphosphines), $P(OR)_3$ AsR_3
VIA	O S H_2O , thf, edta $S_2PPh_2^-$, $S_2CNR_2^-$, SR^- , $PhS(CH_2)_2SPh$
VIIA	X Halide(Cl^-)
IA	H Hydride

have a fundamental role, as shown below), whereas the latter assumption may not be followed by the group IVB metals since the expected strong π interaction with N_2 (see below) may result in a considerable stabilization of the $M-N_2$ bond even for an incomplete fulfilment of the $\pi(M-N_2)$ orbitals.

Group IVB d^2 metal complexes present either a trigonal — *e.g.*, $[(\eta^5-C_5Me_5)_2Ti](\mu-N_2)$ [18] — or a tetrahedral geometry — *e.g.*, $[(\eta^5-C_5H_5)_2Zr(N_2)(\mu-N_2)]$ [19].

However, group VB d^2 (or d^0 , depending on the formal charge on the ligand N_2 , as shown below) metal compounds display a trigonal bipyramid structure — *e.g.*, $[Ta(CH_2CMe_3)(CHCMe_3)(PPh_3)_2](\mu-N_2)]$ [20] where the axial positions are occupied by the two phosphines — or an octahedral-type geometry as in $[TaCl_3(Pb_3)(thf)_2](\mu-N_2)]$ ($bz = CH_2C_6H_5$) [21] where *thf* is in *trans* position relative to the bridging N_2 ligand.

Dinitrogen complexes of groups VIB and VIIB and of the iron sub-group usually present a metal d^6 centre (which corresponds to metal oxidation states of 0, +1 and +2, respectively) with either an octahedral-type geometry — such as $[M(N_2)_2L_4]$ ($M = Mo, W$; L = tertiary monophosphine or $\frac{1}{2}$ diphosphine [22], *trans*- $[ReCl(N_2)L_4]$ [23], *trans*- $[FeH(N_2)(tetraphos)]$ Br {tetraphos = $Ph_2PC_2H_4P(Ph)C_2H_4P(Ph)C_2H_4PPh_2$ } [24] and $[Ru(NH_3)_5(N_2)] Cl_2$ [25] — or, if a cyclic arene ligand is bound, a trigonal pyramid geometry is observed where this ligand coordinates the apical position — *e.g.*, $[Mo(\eta^6-C_6H_3Me_3)(dmpe)]_2(\mu-N_2)]$ [26] (where *dmpe* = $Me_2PC_2H_4PMe_2$) and $[Mn(\eta^5-RC_5H_4)(CO)_2](\mu-N_2)]$ [27].

Group VIB metal complexes with an electronic state different from d^6 (metal oxidation state other than zero) are also known and they may present a distinct geometry: $[WH(N_2)_2(dppe)_2]^+$ (where *dppe* = $Ph_2PC_2H_4PPh_2$) which is pentagonal bipyramid [28] (coordination number seven) with metal d^4 and $[Cl_4Mo](\mu-N_2)]$ [29] with a d^2 metal and coordination number five.

Metal d^8 complexes of the Co sub-group display either a trigonal bipyramid geometry — *e.g.*, $[CoH(N_2)(PPh_3)_3]$ [30] — or a square planar arrangement such as in $[RhH(N_2)(PPhBu_2)_2]$ [31] (in both cases, the hydride ligand is *trans* to N_2).

Metal d^{10} complexes of group VIII present either a trigonal planar geometry — $[(PCy_3)_2Ni]_2$

$(\mu, \eta^2-N_2)]$ [32] and $[Ph(NaOEt)_2(Ph_2Ni)_2(\mu, \eta^2-N_2)NaLi_6(OEt)_4OEt_2]$ [33] — or a trigonal pyramid structure as in the hexameric cluster $K[Co(N_2)(PMe_3)_3]$ [34] and in $[Co(PMe_3)_3(N_2)]_2Mg(thf)_4$ [35].

Polyhydridic complexes deviate from the above-mentioned geometric patterns, as observed, *e.g.*, for the double metal-metal bonded dinuclear compound $[RuH_2(PPh_3)_2](\mu-H)_4[Ru(N_2)(PPh_3)_2]$ [36].

2.2. DINITROGEN BONDING

2.2.1. BONDING MODES

A wide versatility of coordination to a transition metal is known for the dinitrogen ligand, and the modes shown in fig. 1 have already been clearly evidenced.

The terminal mode of coordination is the most common, either in mononuclear or in dinuclear complexes; in the latter, N_2 behaves as a di-hapto (η^2) ligand.

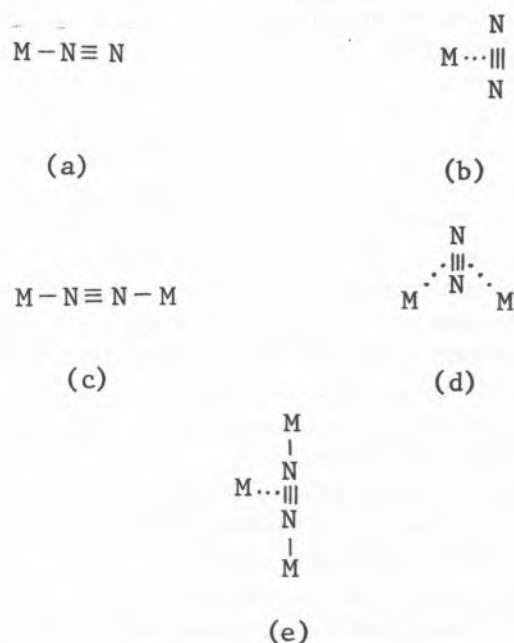


Fig. 1

Modes of dinitrogen bonding to transition metals.

- (a) η^1 -terminal. (b) η^2 -lateral. (c) μ^2, η^2 -bridging terminal. (d) μ^2, η^2 -bridging lateral. (e) μ^3, η^2 -bridging terminal-lateral

Only scant examples are known for the lateral (side-on) coordination and they may involve polinuclear species with high complexity.

The simplest known compound with a side-on N_2 ligand is $Co(\eta^2-N_2)$, prepared by co-condensation reaction of atomic cobalt with dilute nitrogen-argon matrices at 10K, the type of N_2 bonding being evidenced by i.r. studies with $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$ (only one stretching band is observed for the $^{29}N_2$ isotopic ligand) [37].

ESR electron-nuclear spin coupling studies on $[Zr(\eta^5-C_5H_5)_2(N_2)\{CH(SiMe_3)_2\}]$ with $^{28}N_2$ and $^{30}N_2$ and the absence, in the i.r. spectrum, of any band assigned to $\nu(N\equiv N)$, suggest a sideways-bound (type *b*) dinitrogen, although a fast zirconyl oscillation between the two nitrogen atoms of a corresponding end-on bonded N_2 complex cannot be ruled out [38].

Type (d) bonding is present, e.g., in the following complexes of $Ni(0)$: $[(LiPh)_3Ni]_2(\mu, \eta^2-N_2)(OEt_2)_2$ [39], prepared by reaction of $[Ni(CDT)]$ (where CDT = cyclododecatetraene) with $LiPh$ in Et_2O , and $[Ph(NaOEt)_2\{Ph_2Ni\}_2(\mu, \eta^2-N_2)NaLi_6(OEt)_4OEt_2]_2$ [33] which is formed when the reaction occurs also in the presence of $NaPh$; a partial view of the latter is depicted in fig. 2, the N_2 ligand lying in the intersection of two distorted trigonal planar $\{Ph_2Ni(\eta^2-N_2)\}$ units with each Ni atom above (by 0.05 Å) the plane approaching the

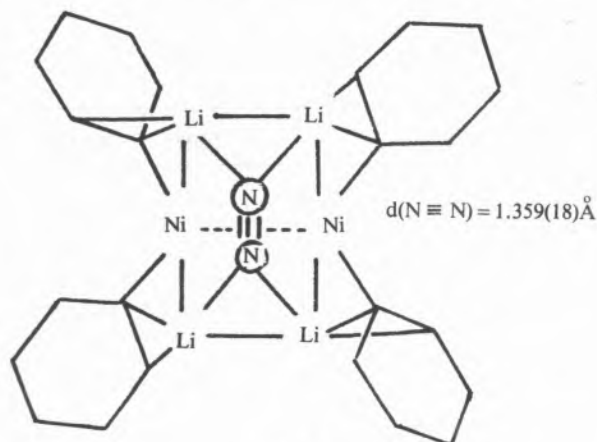


Fig. 2

Partial view of the internal skeleton of complex $[Ph(NaOEt)_2\{Ph_2Ni\}_2(\mu, \eta^2-N_2)NaLi_6(OEt)_4OEt_2]_2$

other transition metal atom. Each Ni atom and the N_2 ligand also interact with a few ions of electropositive non-transition metals (lithium and sodium) through multicentered electron-deficient bondings; the negative charge at the N_2 ligand is stabilized by its interaction with these metal atoms. Such a stabi-

lization with a promoting effect on the metal to dinitrogen back-bonding is also observed in other complexes where N_2 bridges a transition and non-transition metals such as K^+ in the hexameric $K^+[Co(N_2)(PMe_3)_3]^-$ complex [34] and Mg^{2+} in $[Co(PMe_3)_3(N_2)]_2Mg(thf)_4$ [35].

The effect of the cation of the electropositive species on the activation of dinitrogen will be considered later on.

Dinitrogen bridges three transition metal atoms (mode *e* of fig. 1) in $[(\mu_3-N_2)\{(\eta^5-\eta^5-C_{10}H_8)(\eta^5-C_5H_5)_2Ti_2\}\{(\eta^1-\eta^5-C_5H_4)(\eta^5-C_5H_5)_3Ti_2\}]\cdot[(\eta^5-C_5H_5)_2Ti(C_6H_{14}O_3)]\cdot C_6H_{14}O_3$ which is prepared by reaction of $[\mu-(\eta^1-\eta^5-C_5H_4)(\eta^5-C_5H_5)_3Ti_2]$ with N_2 in DME/diglyme; it is composed of two complex units (one with N_2 and the other without this species and presenting a molecule of diglyme, $H_3COC_2H_4OC_2H_4OCH_3$, bonded through two oxygen atoms) and diglyme of crystallization [40]; it is unknown if the two complex units are distinct molecules co-crystallized in the unit cell or if the compound is a complex ionic salt. The complex unit with N_2 and a fulvalene ($\eta^5-\eta^5-C_{10}H_8$) and cyclopentadienyl ($\eta^5-C_5H_5$ and $\eta^1-\eta^5-C_5H_4$) co-ligands is depicted in fig. 3.

Dinitrogen may also bridge three atoms in a terminal mode, but they are not all transition metals: $[WCl(PMe_2Ph)_3P_y(\mu_3-N_2)(AlCl_2)_2]_2$, formed in

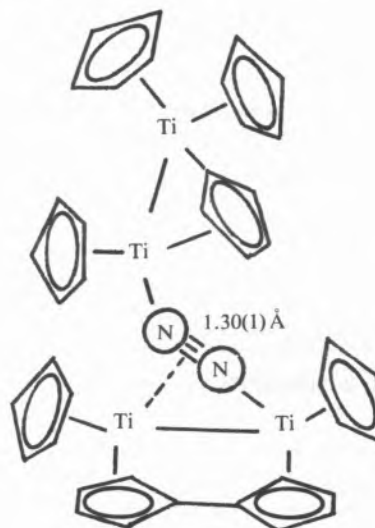
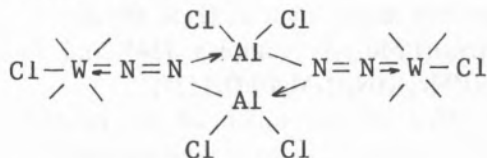


Fig. 3

Complex unit with a bridging terminal-lateral dinitrogen ligand, $[(\mu_3-N_2)\{(\eta^5-\eta^5-C_{10}H_8)(\eta^5-C_5H_5)_2Ti_2\}\{(\eta^1-\eta^5-C_5H_4)(\eta^5-C_5H_5)_3Ti_2\}]\cdot[(\eta^5-C_5H_5)_2Ti(C_6H_{14}O_3)]\cdot C_6H_{14}O_3$ (see text for the complete formulation of the complex)

the reaction of *cis*-[W(N₂)₂(PMe₂Ph)₄] with AlCl₃/P_y in C₆H₆, and presenting two AlCl₂ bridges between the N₂ ligands [41]:



2.2.2. BONDING PARAMETERS

A slight increase of the N-N bond length (relative to the value in the free ligand) [42] usually occurs upon ligation of dinitrogen to a mononuclear metal centre (Table 3), as observed, *e.g.*, in complex *mer*-[Re(η¹-S₂PPh₂)(N₂)(CNMe)(PMe₂Ph)₃] [44]. However, in some multinuclear complexes, a strong lengthening may result leading to a N-N distance which lies in the expected range intermediate between the values for a double (1.23 Å) [46] and a single (1.46 Å) [48] bond. This behaviour is observed, *e.g.*, in the abovementioned Ti complex [40] with a triple N₂ bridge (see fig. 3) where d(N-N)=1.30(1) Å, and in the dinuclear Ni species [33] with a bridging edge-on (side-on) N₂ (fig. 2) [d(N-N)=

=1.359(18) Å]. A long N-N distance [1.30(1) Å] also occurs in the known group VB dinuclear N₂ complexes, *e.g.*, [[Ta(CH₂Bu¹)(CHBu¹)(PPh₃)₂]₂(μ-N₂)] which displays a short metal-nitrogen bond corresponding to a considerable double bond character [20].

In these complexes with a long N-N distance, the ν(NN) stretching vibration, when it is observed, occurs at values which are also intermediate between the expected ones for a N-N double and single bond (Table 3). Moreover, at least a considerable lowering of ν(NN) upon N₂ coordination is always observed in agreement with a substantial participation of the metal to π* dinitrogen backbonding as shown below.

2.2.3. BONDING ORBITALS

The *terminal* mode of bonding of N₂ to a metal centre may be described as for CO by the Chatt-Dewar-Duncanson model; it is the result of a N₂ to metal σ electron donor component with concomitant π backbonding from a filled metal t_{2g} orbital to a π* N₂ antibonding orbital (fig. 4).

Table 3
Bonding parameters and i.r. (or Raman) ν (NN) data for dinitrogen ligand

Compound	d(N-N) Å	d(M-N) Å	ν (NN) cm ⁻¹	Ref.
N ≡ N(free)	1.0976(1)		2331 ^{a)}	[42,43] ^{b)}
[Re(η ¹ -S ₂ PPh ₂)(N ₂)(CNMe)(PMe ₂ Ph) ₃]	1.13(1)	1.83(1)	1980	[44]
[(η ⁵ -C ₅ Me ₅) ₂ Ti] ₂ (μ-N ₂)	1.16(1) ^{c)}	2.017(10) ^{c)}		[45]
Ph-N=N-Ph	1.23		1441 ^{a)}	[46,47] ^{b)}
[(μ ₃ -N ₂){(η ⁵ :η ⁵ -C ₁₀ H ₈)(η ⁵ -C ₅ H ₅) ₂ Ti ₂ }] [(η ¹ :η ⁵ -C ₅ H ₄)(η ⁵ -C ₅ H ₅) ₃ Ti ₂]. [(η ⁵ -C ₅ H ₅) ₂ Ti(C ₆ H ₁₄ O ₃)] · C ₆ H ₁₄ O ₃	1.30(1)	1.91(1) t 2.14(1) l	1282	[40]
[{Ta(CH ₂ Bu ¹)(CHBu ¹)(PPh ₃) ₂] ₂ (μ-N ₂)	1.30(1)	1.837(8) 1.842(8)		[20]
[{Ph(NaOEt) ₂ }[Ph ₂ Ni] ₂ (μ-N ₂)NaLi ₆ (OEt) ₄ OEt ₂] ₂]	1.359(18)	2.01(5)		[33]
H ₂ N-NH ₂	1.46		1111	[48,49] ^{b)}

a) In Raman spectroscopy

b) Corresponding to d(N-N) and ν (N-N), respectively

c) Average values for two independent molecules

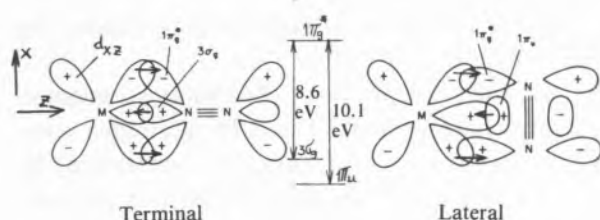


Fig. 4

Terminal and lateral (side-on) modes of N_2 bonding to a transition metal

The *side-on* N_2 bonding may be accounted for by the same model, but one of the π_u N_2 bonding orbitals is now the dinitrogen to metal donor orbital; the other π_u N_2 orbital which lies perpendicularly to the former may bind a second metal forming a dinuclear complex with side-on bonded N_2 , the two $M-N_2$ bonds being roughly perpendicular to one another, as known for the abovementioned dinuclear Ni complexes.

Although both π_g^* N_2 orbitals may π accept from filled metal t_{2g} orbitals when N_2 binds in a terminal mode, only one of the π_g^* orbitals can be involved in the bonding for a mononuclear side-on N_2 complex (fig. 4), in agreement with the rare occurrence of the latter type of complexes (another argument based on energy considerations will be mentioned below). Since the π backbonding occurs to a ligand antibonding orbital, a weakening of the N-N bond results leading to a decrease in $\nu(NN)$ relative to the value in free N_2 .

2.3. ELECTRON π -DONOR AND σ -ACCEPTOR CHARACTER OF THE METAL CENTRE

2.3.1. DEPENDENCE ON THE TRANSITION METAL PERIODIC GROUP

The high stability of the N_2 molecule towards coordination to a metal centre results mainly from the exceptionally low energy of the donor orbital (especially in the case of the side-on mode of bonding — see fig. 4) and the high energy difference relative to the acceptor π_g^* orbital.

Hence, in order to bind N_2 , a metal centre should present an empty σ orbital with low energy and fil-

led t_{2g} orbitals at a high energy level to overlap with the correspondent ligand orbitals.

In other words, due to the weak σ donor character of N_2 , the binding metal centre should display a considerable σ -acceptor character and/or a high π donor ability in order to compensate the weak σ component of the bond.

A high electron richness is also a common feature of the metal centre which favours the π backbonding. This component of the bond is also promoted by an energy increase of the metal filled d_{xz} and d_{yz} orbitals which are involved in the bond, since they become closer to the high energy acceptor π_g^* orbital of N_2 . However, the σ acceptance of the metal centre is favoured by an energy decrease of the metal acceptor orbital.

Hence, due to the known decrease of the energy level of the d orbitals along any transition series, the σ acceptor character is favoured by an increase in the atomic number of the metal whereas the π backbonding capacity is promoted by a decrease of this number, thus occurring preferably in the first groups (IVB and VB) which are also those which present orbitals with a more diffuse character; however, the latter groups present a low number of filled d orbitals. The increase of σ acceptance along a transition series also agrees with the known similar trend followed by the *effective nuclear charge* (as a result of the imperfect shielding of one d electron by another) and the *electronegativity* of the metal.

These general features are summarized in fig. 5 where typical examples are shown, namely the dinuclear group VB centres with a high π backbonding capacity; as a result of the strong electron π -donation from these metals, an oxidation may result with reduction of the N_2 ligand and, e.g., in complexes of the type $[(TaCl_3(PR_3)(thf)_2(\mu-N_2)]$, ligating N_2 appears to behave formally as diimido [or dinitrito(4-)] species (N_2^{4-}) whereas the metal atoms display the +5 high oxidation state, as evidenced by chemical studies which will be mentioned later on (section 3.2.1.i).

In agreement with the general trends mentioned above, the transition metals of the first groups present common high oxidation states in their usual compounds, whereas low oxidation states are usual for high group transition metals.

The presence of a positive charge at the metal results in an increase of the electron acceptor ability

and in dicationic complexes of the iron sub-group (with Ru(II) and Os(II)) the N_2 ligand may bind a site which presents only σ donor co-ligands.

In the abovementioned dinuclear Ni (group VIII) complexes with a high σ -acceptor character, N_2 may bind in the more unfavourable side-on mode; in these complexes, both $N_2 \pi_g^*$ orbitals are involved in π backbonding which is enhanced by the interac-

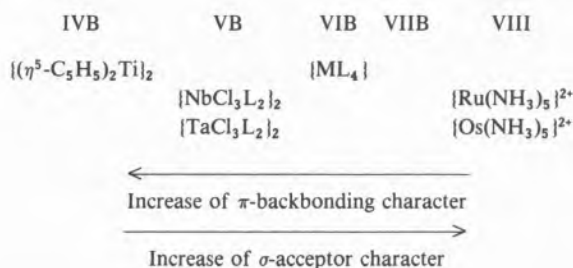


Fig. 5

Dependence of the π -backbonding and the σ -acceptor characters of a metal centre on the periodic group (L = tertiary phosphine)

tion of the N_2 ligand with cations of electropositive elements such as lithium and sodium, as it was mentioned earlier.

The implications of the abovementioned electronic properties of metal centres on the chemical reactivity of the N_2 ligand will be discussed in sections 3.2. and 5.

2.3.2. DEPENDENCE ON THE TRANSITION SERIES (ALONG EACH GROUP)

Although general correlations between the electronic properties of the transition metals (and, hence, the resulting stability of their N_2 complexes) and their position along each group are difficult to detect, a few comments may be mentioned.

For *high transition metal groups* with a weak π - and a strong σ -component in the metal-dinitrogen bond (see fig. 5), the stability of binary dinitrogen complexes may follow the order of the Allred-Rockow electronegativity (which corresponds to the electrostatic force exerted by the nucleus on the valence electrons, being proportional to the ratio between the effective nuclear charge and the covalent radius): first transition series > third transition series > second transition series metal (within each periodic group); the reversal of the second and third transition series order results from the known lanthanide contraction.

Hence, *e.g.*, the stability of the dinitrogen complexes $M(N_2)_n$ ($n = 1 - 3$) of the Ni subgroup (prepared by matrix co-condensation techniques) follows the order $Ni > Pt > Pd$ [50].

In agreement with these observations, unambiguously characterized Pd and Pt dinitrogen complexes are unknown at ambient temperature, although dinitrogen complexes of Ni (see previous sections) have been prepared.

However, in dinitrogen complexes with ligands other than N_2 or with metals of lower periodic groups (hence, with an important π -component in the $M-N_2$ bond), other factors (such as the energy of the t_{2g} metal orbitals and the dependence of the metal d orbitals energy on the co-ligands) may play a fundamental role and the abovementioned correlation fails often.

Hence, *e.g.*, within the Fe sub-group, although the stability of the complexes $trans-[MH(N_2)(dppe)_2]^+$ ($M = Fe, Ru, Os$) [51] follows the order of the Allred-Rockow electronegativity ($Fe > Os > Ru$), the monophosphinic species $[MH_2(N_2)L_3]$ [52] and the amino complexes do not obey the same trend (the former follow the order $Fe > Ru > Os$, whereas in the latter the observed order is $Os > Ru \gg Fe$, the aminocomplexes of iron being even unknown).

As discussed in the previous section, the transition metal basicity decreases along each series.

However, an *increase of the transition metal basicity on going down each periodic group* was proposed [53] on the basis of studies of the reactivity of transition metal complexes with Lewis acids. For N_2 complexes, this trend appears to be followed at least by some metals of the VIB and VIIB groups as evidenced by chemical studies which will be discussed in sections 3.2. and 5.

2.3.3. DINITROGEN COMPLEXES WITH REPRESENTATIVE METALS

From the considerations mentioned on sections 2.2.3. and 2.3., it is understandable the paucity of examples known with N_2 ligating a representative metal due to the unavailability of filled d orbitals to participate in metal to ligand π backbonding.

However, a few cases are known, the representative metal centre behaving as an electron acceptor (Lewis acid) towards N_2 or as a stabilizer of the negative charge at this ligand which may bind concomitantly a transition metal centre whose π backbonding donor capacity to N_2 is enhanced by the elec-

tron acceptor character (or the positive charge) of the representative metal site. The bond of N_2 to this site has a prominent σ character; however, electrostatic representative metal-reduced N_2 (nitride) interactions are possible.

Hence, *group IA* cations of electropositive metals (Li^+ , Na^+ , K^+) may ligate N_2 in polynuclear structures with electron deficient multicentered bonds also involving transition metals. Examples were already quoted (section 2.2.1.): the hexameric cluster $K[Co(N_2)(PMe_3)_3]$ and $[Ph(NaOEt)_2\{Ph_2Ni\}_2(\mu, \eta^2-N_2)NaLi_6(OEt)_4OEt_2]_2$.

Ionic nitrides of electropositive *IA* and *IIA* elements are known and some of them may be formed by direct reaction with N_2 . Hence, *e.g.*, the dinitride(1-) $Li^+N_2^-$ [$\nu(N_2) = 1800\text{ cm}^{-1}$] and the dinitride(2-) $Li_2^+N_2^{2-}$ [$\nu(N_2) = 1535\text{ cm}^{-1}$] are formed by low-temperature matrix co-deposition of Li atoms and dinitrogen [54].

Scant examples of dinitrogen compounds with a *group IIA* metal involve $Mg(NH_2)_2$ [$\nu(N_2) = 2160\text{ s}$, 2040 sh cm^{-1}] (prepared by thermolysis of the azide-hydrazine compound $Mg(N_3)_2(N_2H_4)_2$) [55] and some N_2 species of calcium, strontium and barium obtained by acid decomposition and oxidation (CH_3COOH or H_2O) of the corresponding pernitrides of metal(II), M_3N_4 [56].

Table 4

Values of P_L ligand parameter for a variety of ligands (see text)

L	P_L (volt) ^{a)}	L	P_L (volt) ^{a)}
NO^+	1.40	NH_3	-0.77
CO	0.00	CF_3COO^-	-0.78
N_2	-0.07	NCS^-	-0.88
$P(OPh)_3$	-0.18	CN^-	-1.00
$CNC_6H_5Cl_2-2,6$	-0.33*	NCO^-	-1.16
PPh_3	-0.35	I^-	-1.15
CNC_6H_4Cl-4	-0.37*	Br^-	-1.17
CNPh	-0.38	Cl^-	-1.19
$CNC_6H_4CH_3-2$	-0.38*	H^-	-1.22
$CNC_6H_4CH_3-4$	-0.39*	N_3^-	-1.26
$CNC_6H_4OCH_3-4$	-0.40*	OH^-	-1.55
NCPH	-0.40		
CNMe	-0.43		
CNBu	-0.44*		
NCMe	-0.58		
Py	-0.59		

a) Values in volt (*versus* s.c.e.), measured in $thf-[NBu_4]BF_4$ at a Pt electrode. All values taken from reference [59] except those denoted by * which are given by reference [60].

Dinitrogen may also bridge a transition metal and a $Mg(II)$ moiety such as in $[Co(PMe_3)_3(N_2)]_2Mg(thf)_4$ [35] and in various titanium and vanadium species, $[Ti(\eta^5-C_5H_5)_2(NNMgCl)]$ [$\nu(N_2) = 1255\text{ cm}^{-1}$] and possible $[(thf)ClM(NNMgCl)]$ ($M = Ti$ or V), which are intermediate in the reduction of N_2 to hydrazine, ammonia or organonitrogenated compounds (see section 3.2.1.i).

Electrophilic attack of a *group IIIA* Lewis acid to a dinitrogen ligand may lead to dinitrogen bridging species as shown in section 3.2.3.

Dinitrogen may also ligate a *group IVA* metal centre as in $[MX_2N_2]$ prepared in low temperature matrix studies by condensation of N_2 with the unsaturated dihalides MX_2 ($M = Sn, Pb$; $X = \text{halide}$) (an analogous reaction occurs for HgX_2 [57]). The prominent σ character of the metal- N_2 bonds evidenced by the positive shift of $\nu(CO)$ which occurs on coordination of carbon monoxide to form the analogous compounds $[MX_2(CO)]$.

2.4. — ELECTRON RICHNESS

2.4.1. ELECTROCHEMICAL QUANTIFICATION

The common high electron richness of a mononuclear dinitrogen binding metal centre (resulting, *e.g.*, from the low metal oxidation state and the presence of electron donor co-ligands) is patent since its generation. Hence, the most general preparative route of dinitrogen complexes from direct reaction with N_2 consists in the reduction of a metal species by a strong reducing agent until N_2 binds in a late stage of the reduction when an electron-rich centre is available — see, *e.g.*, the synthesis of *trans*- $[Mo(N_2)_2(dppe)_2]$ by reduction of $[MoCl_5]_2$ by $Na(Hg)$ or Mg in the presence of $dppe$ and under N_2 [58].

Although the i.r. $\nu(N_2)$ value may be considered as an indicator of the electron rich character of the binding metal centre [which is favourable to π back-bonding and, thus, to a decrease in $\nu(N_2)$], the coupling of the $N \equiv N$ to other group stretching vibrations and other effects (*e.g.*, dependence on the σ component) lead to a somewhat unreliable character in the use of this parameter.

The ready chemical or electrochemical oxidation of the dinitrogen complexes also results from the high electron richness of the metal centre and on the basis of the half-wave oxidation potential ($E_{1/2}^{ox}$) values, a criterium for the quantification of the elec-

tron rich character of the centre was proposed [59]. Square pyramid 16-electron metal sites $\{M_s\}$ were considered and their *electron-richness* (E_s) was defined [59] by the half-wave oxidation potential of the carbonyl complex:

$$E_s = E_{1/2}^{\text{ox}}[M_s(\text{CO})] \quad (1)$$

The greater the electron rich character of the site, the easier its oxidation and hence the lower the E_s value will be.

A linear correlation was observed [59] between $E_{1/2}^{\text{ox}}$ of the elements of a series of 18-electron octahedral-type complexes $[M_sL]$ (where L varies along the series) and $E_{1/2}^{\text{ox}}$ of their homologues in a isoelectronic and isostructural series of pentacarbonylchromium complexes:

$$E_{1/2}^{\text{ox}}[M_sL] - E_{1/2}^{\text{ox}}[M_s(\text{CO})] = \beta \cdot \{E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5L] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6]\} \quad (2)$$

The slope, β , of the line is a measure of the sensitivity of the energy of the HOMO orbital to a change of L ligand is called *polarisability* of the metal centre.

The difference between $E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5L]$ and $E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6]$ is a measure of the net electron donor character of the ligand and is denoted by P_L (*ligand parameter*) (equation 3): the higher this character, the lower $E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5L]$ is and, hence, the lower (usually the more negative) the P_L value becomes; high P_L values correspond to ligands which behave as strong net electron acceptors.

$$P_L = E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5L] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6] \quad (3)$$

Hence, since $E_{1/2}^{\text{ox}}[M_s(\text{CO})]$ is the E_s electron-richness parameter of the metal site, equation (2) becomes, upon rearrangement:

$$E_{1/2}^{\text{ox}}[M_sL] = E_s + \beta \cdot P_L \quad (4)$$

P_L values have already been quoted [59,60] for a variety of ligands (see Table 4) and, *e.g.*, CO, N_2 and CNR (isocyanides) behave, in this order, as strong net electron acceptors (high P_L values) whereas the anionic ligands such as thiocyanate (NCS^-), halides, hydride and hydroxide present a strong net electron donor character (low P_L values).

Linear relationships of the type of equation 4 have been experimentally observed [59,60] for a variety

of 16-electron dinitrogen binding metal centres and the estimated E_s and β values are shown in Table 5.

Table 5
Values of E_s and β for a variety of 16-electron square pyramid dinitrogen-binding metal sites

$\{M_s\}$	E_s (volt) ^{a)} (vs s.c.e.)	β
$\{\text{Mo}(\text{NO})(\text{dppe})_2\}^+$	+0.91	0.51
$\{\text{Mo}(\text{CO})(\text{dppe})_2\}$	-0.11	0.72
$\{\text{Mo}(\text{N}_2)(\text{dppe})_2\}$	-0.13	0.84
$\{\text{Mo}(\text{NCPh})(\text{dppe})_2\}$	-0.40	0.82
$\{\text{Mo}(\text{N}_3)(\text{dppe})_2\}^-$	-1.00	1.0
$\{\text{FeH}(\text{dppe})_2\}^+$	+1.04	1.0
$\{\text{Re}(\text{N}_2)(\text{dppe})_2\}^+$	+1.20	0.74
$\{\text{ReCl}(\text{dppe})_2\}$	+0.68*	3.4*

a) Values in volt (*versus* s.c.e.), measured in $\text{thf} \cdot [\text{NBu}_4]\text{BF}_4$ at a Pt electrode. All values taken from reference [59] except those denoted by * which are given by reference [60].

The Mo(0) centres present a higher electron richness (lower E_s values) than the Fe(II) and Re(I) sites and, within a group with a common metal, the anionic centres are more electron rich than the neutral ones. On the basis of these electrochemical parameters, it is possible to propose dinitrogen coordination and chemical reactivity criteria; the latter will be exemplified along the text but the former may now be considered.

Hence, metal sites with a high electron richness (low E_s values) bind strong electron acceptor ligands (with high P_L values) such as N_2 , CO or CNR as it is observed for the $\{\text{Mo}(\text{N}_2)(\text{dppe})_2\}$ metal centre ($E_s = -0.13$ V).

However, N_2 may bind sites with E_s values falling in the -1.3 to +1.3 V range, but when the centre presents a high E_s value, the ligand which is *trans* to N_2 behaves as a strong net electron donor (such as halide or hydride) thus presenting a low P_L value; it is then experimentally observed that such a metal site has a high polarisability (β). A typical example is given by $\{\text{ReCl}(\text{dppe})_2\}$ (with high E_s and β values of +0.68 V and +3.4, respectively) [60] which may bind N_2 in *trans*- $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ where the strong net electron donor chloride ligand ($P_L = -1.19$ V) is *trans* to N_2 .

Based on these observations, one may propose that *high electron-richness (low E_s value) and high polarisability (high β value) of a metal centre favour dinitrogen coordination* [59].

2.4.2. CO-LIGAND EFFECT

The dinitrogen bonding to a metal centre may be favoured by the presence, in *trans* position, of a strong net electron donor co-ligand.

The electron donating power of the ligand *trans* to N_2 enhances the metal to dinitrogen π backbonding, thus stabilizing the M- N_2 bond and promoting the coordination of dinitrogen.

Chloride and *dithiophosphinate* (S_2PPh_2) *trans* to N_2 are strong M- N_2 bond stabilizers as evidenced, e.g., by the stability of the complexes *trans*-[ReCl(N_2) (dppe) $_2$], *mer*-[ReCl(N_2) (CNMe)(P(OMe) $_3$) $_3$] [61] and *mer*-[Re(η^1 - S_2PPh_2) (N_2) (CNMe) $_x$ (PMe $_2$ Ph) $_{4-x}$] ($x = 1$ or 2) [14], the N_2 ligand binding a site which may present up to two strong competitors (CNMe) for the π backbonding. Chloride is a known π donor and a weak field ligand: interaction of a filled p chloride orbital with a t_{2g} metal orbital results in a destabilization of the latter with a decrease of the energy difference (Δ) relative to the empty e_g^* orbitals; the increase in energy of the t_{2g} metal orbitals favours the electron π donor capacity (π backbonding ability) of the metal centre to the $\pi_g^*N_2$ orbitals. This stabilizing effect on the M- N_2 bond by a π donor ligand in *trans* position may also be rationalized by some simplified π -molecular orbital schemes: an increase of the number of filled M- N_2 bonding (and N-N antibonding) character orbitals results from the electron π release from the π donor ligand [62].

Hydride is also a ligand which tends to be in a *trans* position relative to N_2 in hydridic dinitrogen complexes such as the trigonal bipyramid [CoH(N_2) (PPh $_3$) $_3$] [30] and the square planar [RhH(N_2) (PPhBu $_2$) $_2$] [31] species.

It is a strong net electron donor ligand [$P_L(H^-) = -1.22$ V], comparable to chloride [$P_L(Cl^-) = -1.19$ V], although without a π donor capacity. It presents a high *trans* effect (through a σ mechanism) which favours the bonding, in *trans* position, of a weak σ donor (and strong π acceptor) ligand rather than a strong σ donor (and weak π acceptor) species which may compete with the hydride by the metal σ orbitals.

The higher tendency of the hydride ligand to be *trans* to N_2 rather than to a phosphine (see the abovementioned Co(I) and Rh(I) complexes) evidences the weaker σ donor (and stronger π acceptor) character of dinitrogen relative to a phosphine ligand.

The σ -donor hydride ligand may promote, through a synergic effect, the π -backbonding ability of the metal centre to the *trans* N_2 ligand.

In a high electron rich metal centre dinitrogen may also bind to the metal even in the presence, in *trans* position, of a strong electron acceptor competitor, such as carbonyl; however, the metal-dinitrogen bond then presents a high lability.

This behaviour is observed for the [Mo(CO) (dppe) $_2$] site ($E_s = -0.11$ V) which can bind reversibly N_2 to afford the labile *trans*-[Mo(N_2) (CO) (dppe) $_2$] species (the N_2 ligand is evolved by just bubbling argon through a solution of this complex) [63].

The effect of other co-ligands, such as the strong net electron donor methoxide anion (from methanol solvent dissociation), on the activation towards protonation of dinitrogen derived ligands (e.g., the hydrazido(2-) species, NNH $_2$) will be mentioned in later sections (3.2.).

3 — CHEMICAL PROPERTIES

The chemical behaviour of dinitrogen-binding metal centres is usually mainly dependent on their electronic properties which were discussed in the previous sections.

However, structural features related, e.g., to the geometry or to the unsaturation of the binding centre due to the lability of N_2 , may also play a role, as well as some stereochemical factors as shown by the following example.

Although the bis(diphosphinic) complexes [FeHX (depe) $_2$] and [FeHX (dppe) $_2$] are known, the penta-coordinated tetraphosphinic species [FeH (tetraphos)]X [tetraphos = Ph $_2$ PC $_2$ H $_4$ P(Ph)C $_2$ H $_4$ P(Ph)C $_2$ H $_4$ PPh $_2$; X $^-$ = Br $^-$, I $^-$] is ionic and does not bind the X $^-$ halide although N_2 may ligate the metal site to afford [FeH(N_2) (tetraphos)]X. As evidenced [24] by X-ray data the inability of the halide to bind is due to a stereochemical hindrance of the phenyl rings and N_2 (with an atomic radius which is smaller than the halide ionic radius) may ligate the metal site in preference to the halide.

3.1. — CHEMICAL REACTIVITY OF DINITROGEN BINDING METAL SITES

The evolution of N_2 from a dinitrogen complex (e.g., by photolysis) may constitute a convenient way to generate a dinitrogen binding metal centre;

this may also be formed by following the synthetic steps for a dinitrogen complex in the absence of N_2 , under argon atmosphere.

However, the direct study of the metal centre is usually hampered by its high reactivity which prevents its isolation, although a very limited number of examples are known where this isolation was achieved.

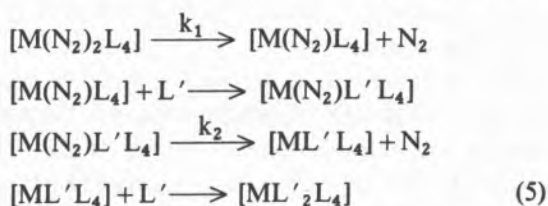
3.1.1. SIMPLE ADDITION REACTIONS

Simple addition reactions to a metal centre following N_2 evolution correspond to the replacement of this ligand in a dinitrogen complex.

In metal centres which present a *high π -backbonding capacity* (groups IVB to VIIB(Re)), the known examples of N_2 replacement involve preferably strong π acceptor ligands such as CO, CNR, NCR or C_2H_4 , as observed in the N_2 substitution reactions of $[M(N_2)_2L_4]$ ($M=Mo$ or W ; L =tertiary m o n o -

phosphine or $\frac{1}{2}$ dppe) by isocyanides [64,65] or carbon monoxide [66].

The mechanism of this type of reactions was studied [67] at the $Mo(0)$ and $W(0)$ phosphinic metal sites and N_2 loss was shown to be the rate limiting step followed by addition of the incoming ligand (L') to the unsaturated pentacoordinated $[M(N_2)L_4]$ centre; the replacement of the second N_2 ligand also

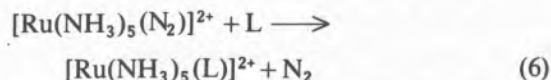


follows a dissociative mechanism with dinitrogen loss being the rate controlling step (equations 5).

Although N_2 is readily replaced by a strong π acceptor in complex $[Mo(N_2)_2(dppe)_2]$, the σ donor NH_3 species behaves as a labile ligand affording the unstable aminocomplex $[No(N_2)(NH_3)(dppe)_2]$ which was only detected in solution by electrochemical techniques [59].

However, when the metal centre presents a *lower electron π releasing character but a high σ -acceptor capacity* [mainly for groups VIIB (Mn) and VIII, although examples for group VIB are also known], N_2 may be replaced by σ -donor ligands without π withdrawing ability.

Hence, the pentaminoruthenium(II) moiety in $[Ru(NH_3)_5(N_2)]^{2+}$ may readily bind a sixth molecule of NH_3 to give $[Ru(NH_3)_6]^{2+}$ through an irreversible replacement of N_2 (reaction 6) [68].

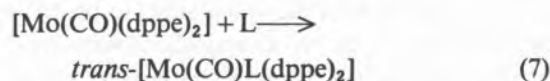


The N_2/NH_3 competition for a metal site presents some catalytic meaning since NH_3 , a product of reduction, has to be replaced by N_2 in order to complete the catalytic cycle of N_2 reduction to NH_3 .

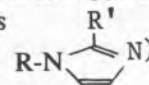
The unsaturated metal centres involved in these reactions were not isolated, but in the following examples the *isolation* was possible.

The square pyramid [63] pentacoordinated carbonyl species $[Mo(CO)(dppe)_2]$, generated, *e.g.*, by N_2 evolution from the dinitrogen parent complex, undergoes addition reactions with a variety of (electron donor) Lewis bases not only with π -acceptor ability (carbon monoxide, nitriles) but also without this capacity (ammonia, amines) or even with a π -donor character (amides*, imidazoles) (reactions 7) [69].

The presence of the strong electron π -acceptor CO ligand renders the $Mo(0)$ metal centre susceptible to π -acceptance from convenient π -donor ligands, although without complete loss of the π -backbonding ability and of the σ -acceptor character which, as shown previously, appear to be important features of the N_2 binding transition metal sites.



($L=CO, N_2, C_2H_4, NCR, NH_3$, amines, pyridines, amides $RR'NC(R'')O$, imidazoles

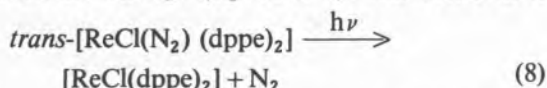


Another rare example of structural characterization of an unsaturated intermediate involved in N_2 substitution reactions, or related ones, was recently reported [70]. It is a trigonal bipyramid $Re(I)$ species, $[ReCl(dppe)_2]$, prepared by photolysis of the octa-

* The low i.r. $\nu(CO)$ values ($\sim 1680 \sim 1720 \text{ cm}^{-1}$) observed in the amide complexes suggest that these ligands are behaving not only as σ -donors but also as π -donors:



hedral parent N_2 complex, through N_2 loss and a structural change (equation 8). The reaction is



irreversible and it demonstrates another *fundamental requirement for binding of dinitrogen*: the *geometry* of the metal centre, *i.e.*, the presence of convenient co-ligands at a metal with a favourable oxidation state is not enough for N_2 coordination.

Although the $\{\text{ReCl(dppe)}_2\}$ centre is not susceptible to bind N_2 , it presents a high reactivity and can coordinate stronger ligands than N_2 such as isocyanides [70].

3.1.2. OXIDATIVE ADDITION REACTIONS

The N_2 binding metal centres are particularly susceptible to oxidative addition reactions, leading, *e.g.*, to the formation of metal-carbon or metal-hydrogen bonds. *These reactions are favoured by the electron-rich character and the unsaturation of the metal centres.

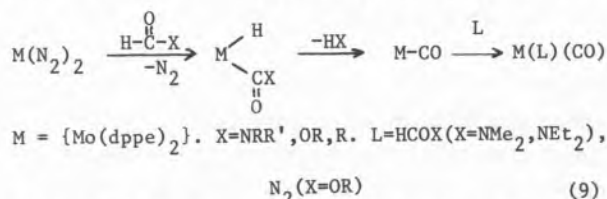
(i) Addition of C-H bond

Orthometalation reactions are known since long in the chemistry of dinitrogen complexes and they are believed to be involved, *e.g.*, in the $[\text{CoH(N}_2\text{)}(\text{PPh}_3)_3]$ plus D_2 system with exchange between deuterium atoms and the hydrogen atoms of the hydride ligand and of the *ortho* positions in the phosphinic phenyl rings. The postulated [72] mechanism involves a reversible oxidative addition of the *ortho* C-H bond of the phenyl groups to the unsaturated metal centre derived from N_2 evolution. This type of study may be of biological significance since HD formation occurs during the enzymatic N_2 reduction under an N_2/D_2 atmosphere.

Other more recent examples of orthometalation reactions of N_2 binding centres have been reported: the $\{\text{Mo(PMe}_3\text{)}_5\}$ site (generated by loss of PMe_3 from $[\text{Mo(PMe}_3\text{)}_6]$ with a high stereochemical tension among the phosphine ligands) which may ligate N_2 can undergo two reversible orthometalation

reactions (the second one upon loss of another phosphine ligand) [73]; the postulated $[\text{ReH(dppe)}_2]$ species, derived by N_2 evolution from the parent dinitrogen complex, undergoes orthometalation and other oxidative addition reactions such as C-D addition from C_6D_6 to yield $[\text{ReH(D)}(C_6D_5)(\text{dppe})_2]$ which, under N_2 , affords $[\text{ReD(N}_2\text{)}(\text{dppe})_2]$ upon C_6D_5H loss [74].

Oxidative addition of C-H bond is probably also involved in *decarbonylation* reactions of aldehyde-type species by $\text{trans-[Mo(N}_2\text{)}_2(\text{dppe})_2]$: formamides (HCONRR'), formate esters (HCOOR) and aldehydes (RCHO) are decarbonylated to amines ($\text{RR}'\text{NH}$), alcohols (ROH) and alkanes (RH), respectively, with formation of carbonyl complexes [75]. The proposed [75] reaction scheme is shown by equations (9), and it involves loss of N_2 and oxidative addition of C-H followed by reductive elimi-



nation of the decarbonylated species. The C-H bond addition is evidenced by the unreactivity of acetamides $\text{MeC(CO)NRR}'$ (which do not present such a bond) and the evolution of a small amount of H_2 , during the reactions, in agreement with the possible involvement of a hydridic species.

Primary alcohols may also undergo decarbonylation by the same Mo(0) metal centre and by the postulated [76] $[\text{ReCl(dppe)}_2]$ species derived by N_2 loss from the parent dinitrogen complex. The mechanism was not studied but may involve dehydrogenation of alcohol to aldehyde which then undergoes decarbonylation.

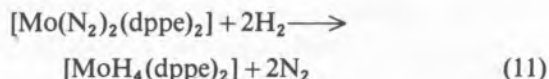
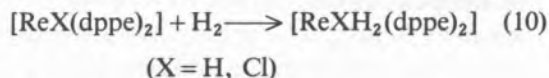
Decarbonylation and dehydrogenation of hydroaromatic compounds may also be achieved [75] by the $[\text{Mo(N}_2\text{)}_2(\text{dppe})_2]$ complex and, *e.g.*, $[\text{Mo(CO)}_2(\text{dppe})_2]$ and $[\text{MoH}_4(\text{dppe})_2]$ are formed from reaction of the dinitrogen complex with thf under heating; this reaction probably occurs *via* saturated carbon-hydrogen bond activation.

(ii) Hydrogenation

The ready hydrogenation of unsaturated centres with formation of polyhydridic species, illustrated by reaction (10) [74,76], corresponds to the known

* Other types of addition reactions are known and *e.g.*, $\text{trans-[Mo(NO)(NCO)(dppe)}_2\text{)]}$ is formed from the reaction of $\text{trans-[Mo(N}_2\text{)}_2(\text{dppe})_2]$ with *N*-methyl-*N*-nitrosourea, MeN(NO)C(O)NH_2 , which is postulated to occur via the intermediate $[\text{Mo(NO)[N(Me)C(O)NH}_2\text{]}(\text{dppe})_2]$ which, upon loss of NH_2Me , yields the final product [71].

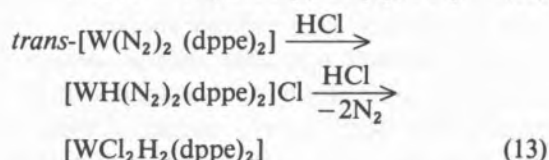
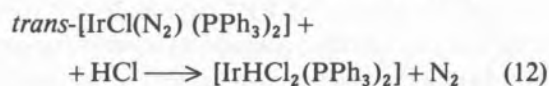
oxidative substitution (which may be reversible) of N_2 by H_2 , exemplified by reaction (11) [66,77].



This type of study may present some biological interest since H_2 is a competitive inhibitor of the enzymatic nitrogen fixation. Moreover, since NH_3 is industrially synthesized from N_2 and H_2 , it would be interesting to study the interaction between N_2 and hydride ligands bonded at a metal site with possible hydrogenation of the former which, however, was not yet achieved.

(iii) *Oxidation reactions by protic acid or organohalide*

Dinitrogen complexes usually react with protic acids which attack the metal centre (leading, e.g., to protonation or halogenation). Dinitrogen evolution occurs commonly as the result of the metal oxidation, and oxidative addition reactions are often involved as shown in equations (12) [78] and (13) [79].



If the metal centre presents a high reducing power as in $trans-[Mo(NCS)(N_2)(dppe)_2]^-$ with the strong net electron donor thiocyanate ligand [$P_L(NCS^-) = -0.88$ V], solvated protons may be reduced to dihydrogen with oxidation of the centre leading, in this example, to unidentified and unstable oxidized species [80].

Mechanistic studies performed on the reactions of $trans-[M(N_2)_2(dppe)_2]$ ($M = Mo$ or W) with weak acids in thf evidence the initial outer-sphere association of the acid electrophile to the metal centre which is followed by protonation at the N_2 ligand. However, since these reactions lead to attack at ligating dinitrogen they will be mentioned in section 3.2.1.ii.

Organohalides also present an oxidizing effect on the metal centre, e.g., $\{ML(dppe)_2\}$ ($M = Mo$ or W ; $L = NCS^-$, N_2 , NCR , N_3^-), the oxidation occurring through an outer-sphere electron transfer process if the centre presents a high reducing power (e.g., for $L = NCS^-$) or *via* an inner-sphere electron transfer mechanism for metal centres with a lower reducing power and presenting a labile L ligand (e.g., for $L = N_2$ or NCR); however these reactions involve the N_2 ligand and will be treated in section 3.2.2.i.

3.1.3. CATALYTIC REACTIONS

Due to the common high lability of the N_2 ligand, its complexes may behave as precursors for unsaturated metal centres; their chemical properties were already mentioned and they account for their active role in catalytic reactions such as hydrogenation, isomerization, oligomerization and polymerization of olefins. The subject has been reviewed [81] and only a few examples are now cited briefly.

$[RuH_2(N_2)(PPh_3)_3]$ catalyses the double bond migration of 1-pentene to 2-pentene, $[RuH_2(PPh_3)_3]$ being the active species; N_2 presents an inhibiting effect due to the competition with the olefin for this unsaturated site [82]. The reaction may possibly proceed through a hydrogen β -elimination to give an η^3 -allyl ligand or through a migratory insertion of hydride into the olefin double bond followed by an hydrogen β -elimination.

The lability of a co-ligand may also induce the catalytic activity and the *cis* to *trans* isomerization of 2-pentene by $[CoH(N_2)(PPh_3)_3]$ may involve the proposed active $[CoH(N_2)(\eta^2\text{-cis-2-pentene})(PPh_3)_2]$ species; the catalytic activity of the system is promoted by the presence of N_2 which favours dinitrogen coordination, the N_2 ligand presenting a labilizing effect on the *trans*-2-pentene ligating product [88,83]. The mechanism may conceivably involve a migratory insertion of hydride into the olefin double bond followed by a rearrangement and an hydrogen β -elimination.

Supported titanocene-type species (on a styrene-divinylbenzene polymer) which can reduce N_2 (at ca. 100 atm) to NH_3 , although in a non-catalytic low yield (<0.55 mol NH_3 /mol Ti) exhibit catalytic activity in the hydrogenation, isomerization and epoxidation of olefins, which appears to be promoted by the bonding, through substituted cyclopentadienyl moieties, of the Ti centres to the polymer

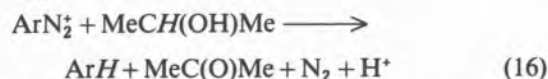
which prevents the formation of inactive dimers [84]. The activation of N_2 is postulated [84] to result from bonding to two Ti centres which are held in position by a methylene bridge between two cyclopentadienyl-type ligands (one at each Ti centre).

H-D exchange reactions between D_2O and aromatic hydrogens [of aromatic hydrocarbons PhX where $X = F, CH_3, OCH_3, COCH_3, N(CH_3)_2$] (equation 14) and between D_2O and H_2 (equation 15) are catalysed by $[RhH(PPR^i)_3]$ — which is isoelectronic and related to $[RhH(N_2)(PR_3)_2]$ — and $[Rh_2H_2(PCy_3)_4(\mu-N_2)]$ [85].



These reactions involve O-D and aromatic C-H (or H-H) bond activation and the mechanism, which was not studied in detail, is suggested [85] to be initiated by O-D oxidative addition to an unsaturated centre (formed by N_2 or phosphine loss) to give $[RhHDL_2]^+OD^-$ which, upon reductive elimination of DHO, affords $[RhDL_3]$; this species may then undergo oxidative addition of $C(Ar)-H$ or of $H-H$ bond (for reactions with ArH or H_2 , respectively) to give $[RhHD(Ar)L_2]$ or $[RhDH_2L_2]$; reductive elimination of the exchange products, ArD or HD , respectively, regenerate the active $[RhHL_3]$ centre [85].

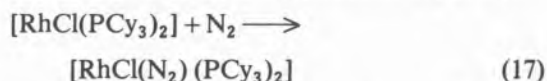
Aryldiazonium species $ArN_2^+Cl^-$ ($Ar = Ph, p-ClC_6H_4, p-MeC_6H_4, p-MeOC_6H_4, p-O_2NC_6H_4$) may be catalytically reduced to hydrocarbons ArH by primary or secondary alcohols ROH ($R = Me, Et, Pr^i$) in the presence of the catalyst precursor *trans*- $[W(N_2)_2(dppe)_2]$ [86]. The α -hydrogens of the alkyl group of the alcohol are the hydrogen source as evidenced by studies with deuterated alcohols and the C-H bond rupture appears to be the rate limiting step; a carbonyl group is formed and ketone was detected in the reaction with isopropanol (equation 16).



The reaction proceeds at ambient temperature and is selective; in the absence of catalyst, it only occurs with heating and also leads to the formation of phenolic ethers [86].

It is also possible to recognize, in various effective catalytic systems, the *involvement of N_2 binding* (or related species) *intermediates*.

Hence, the Rh(I) Wilkinson catalyst for the hydrogenation of olefins involves the active unsaturated centre $[RhClL_2]$ — formed, *e.g.*, by ligand evolution from $[RhClL_3]$ ($L =$ monophosphine such as PPh_3) — which may bind N_2 (reaction 17) [87a].



The $[RhClL_2]$ centre undergoes an oxidative addition reaction of H_2 to afford a dihydride complex which binds the olefin; a migratory insertion of hydride into the olefin double bond (to give an alkyl derivative) is followed by a reductive elimination of the alkane product with regeneration of the active $[RhClL_2]$ site [87b].

3.2. ACTIVATION AND REACTIVITY OF DINITROGEN

Although the free N_2 molecule is non-polar, on coordination it undergoes an *electronic polarization* (as a result of the different intensities of the σ and π components and of the distinct orbitals involved in the bond) as evidenced by the high intensity of the i.r. $\nu(N_2)$ band and by ESCA spectroscopic studies [88], *e.g.*, in $[ReCl(N_2)(dppe)_2]$ where the two nitrogen atoms exhibit distinct N-1s emissions at 397.9 and 399.9 eV (whereas the free N_2 molecule presents a single emission at 411 eV), suggesting a charge difference of 0.4 e between the two N atoms of the dinitrogen ligand.

When binding a *transition metal centre with a high π -backbonding capacity* [with a group IVB to VIB metal or with $Re(I)$], the N_2 molecule acquires a negative electronic charge density and is activated towards *attack by electrophiles* which occur at the *exo* nitrogen atom; i.r. $\nu(N_2)$ then occurs at a *low value* (typically below 1980 cm^{-1}) and the oxidation of the complex is observed at a *low $E_{1/2}^{ox}$* (below *ca.* 0 Volt vs. s.c.e., at a Pt electrode, in $thf-[NBu_4][BF_4]$); the electrophilic attack may also involve the metal centre [89,59].

However, when the metal site presents a *weak π -backbonding ability*, N_2 may be susceptible to attack by a *nucleophile* at the *endo* N atom, the i.r. $\nu(N_2)$ occurring at values (*e.g.*, $> 2100\text{ cm}^{-1}$) which lie above those reported for the previous type of activation and the complexes presenting higher $E_{1/2}^{ox}$ (above *ca.* +0.8 V); the nucleophilic attack may also occur at the metal centre [89,59].

These reactions may lead to the formation of N-H (hydrides of nitrogen) and N-C (organonitrogenated species) bonds which, generally, will be mentioned separately.

Our attention will be focussed mainly on the systems where intermediate species were isolated or which have been subject to mechanistic studies since they present the richest information on the involved metal sites.

Hence, aqueous systems (which have been reviewed) [90] will not be treated due to the yet so speculative nature and controversy of the hypotheses which have been put forward; no N_2 complex and no intermediate reduced species was isolated. The most effective catalytic systems at ambient temperature and pressure involve molybdenum (metal present in nitrogenase) and may be cited: MoO_4^{2-} /peptide chain component of bovine insuline/ $NaBH_4$ (yield of ca. 70 mol NH_3 /Mo) [91] and, more recently, $Mo(III)/Na(Hg)/Mg^+$ /phospholipid in alcoholic medium (yield of ca. 80 mol $NH_3 + N_2H_4$ /Mo) [92].

3.2.1. FORMATION OF HYDRIDES OF NITROGEN

(i) Polynuclear complexes

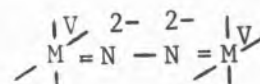
A high activation of dinitrogen towards protonation may result from its simultaneous coordination to two, or even more, metal centres. This behaviour appears to be observed typically for *the extreme transition metal groups (IVB, VB and VIII), and cations of the less electronegative elements* (Li^+ , Na^+ , K^+ and even Mg^{2+} or MgX^+) may be involved in the activation since they may stabilize the negative charge accumulated at dinitrogen from the transition metal electron π -release.

Hence, e.g., a high yield of ammonia (ca. 90%) and some hydrazine are formed by aqueous hydrolysis of complex $[(\mu_3-N_2)\{(\eta^5-\eta^5-C_{10}H_8)(\eta^5-C_5H_5)_2Ti_2\}\{(\eta^1-\eta^5-C_5H_4)(\eta^5-C_5H_5)_3Ti_2\}]\cdot[(\eta^5-C_5H_5)_2Ti(C_6H_{14}O_3)]\cdot C_6H_{14}O_3$ (see section 2.2.1. and fig. 3) in diglyme [40]; the N_2 ligand bridges three Ti centres and presents a long N-N bond.

Hydrazine (86% yield) is also obtained from the reaction of $[(Zr(\eta^5-C_5Me_5)_2(N_2))_2(\mu-N_2)]$ with HCl in toluene at $-80^\circ C$ and by using ^{15}N labelled terminal N_2 ligand it was shown that both terminal and N_2 generate the hydrazine [93].

Bridging N_2 in group VB dinuclear complexes present a high N-N bond elongation (which corresponds to a bond length which is intermediate bet-

ween a single and a double bond, as mentioned in section 2.2.) and, e.g., hydrazine is formed on protonation of $[(Cl_3L_2M)_2(\mu-N_2)]$ ($M=Nb, Ta$; $L=thf, PR_3$); the same complexes react with acetone to give dimethylketazine, $Me_2C=N-N=CMe_2^*$, and these results evidence the localization of four formal negative charges at the bridging N_2 ligand which is reduced as a result of the extensive π -backbonding from the metal atoms which then present a formal high oxidation state (+5) [94]. The ligating N_2 may then be viewed [94] as a diimido (or dinitride(4-)) species:



and the bonding and activation of N_2 may be rationalized by known simplified π -MO schemes [81].

In these systems a direct reduction of the N_2 ligand is observed without the addition of a reducing agent.

However, the activation of N_2 ligating group IVB or VB metal centres may not be enough to induce further protonation which often requires the help of an external reducing agent (such as a Grignard reagent or sodium naphthalene $NaC_{10}H_8$); this species may promote the reduction of the N_2 ligand by the transition metal centres through the direct reduction of the latter and/or by direct interaction with ligating N_2 thus enhancing the π -electron release from the transition metal centres.

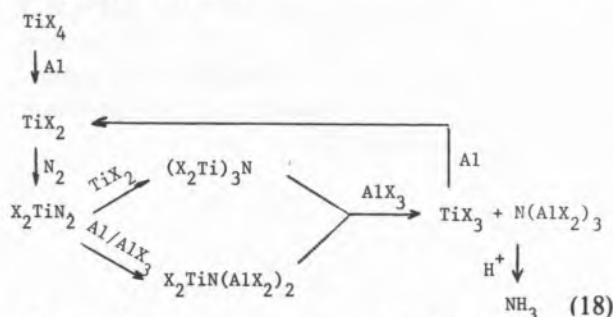
Interesting examples are provided by the following systems where the reduction of N_2 to hydrazine, ammonia or organonitrogenated compounds may occur:

$[(TiCl(\eta^5-C_5H_5)_2)_2] + Pr^iMgCl$ in ether where $[Ti(\eta^5-C_5H_5)_2(NNMgCl)]$ [$\nu(N_2)=1255\text{ cm}^{-1}$] was isolated and which on reaction with HCl gives hydrazine (ca. 80% yield) [95]; $[MCl_3(thf)_3]$ ($M=Ti$ or V) + Mg with possible formation of $[(thf)CIM(NNMgCl)]$ [96]. These $M-N=N-MgCl$ species are probable intermediates to transition metal-nitride-magnesium adducts, e.g., $[MN(MgCl)_2(thf)]$ ($M=Ti$ or V) which were isolated in the latter system and may lead to NH_3 (upon hydrolysis), to isocyanate ligand NCO (upon reac-

* This type of reaction is followed by organoimido ligands at group VB metal centres, $M=N-R$, which, by treatment with benzaldehyde, $PhCHO$, lead to $Ph(H)C=N-R + M=O$.

tion with CO) or to methylisocyanate MeNCO (upon alkylation by MeI) [96].

These systems are non-catalytic (they are at best stoichiometric) but a catalytic activity was developed since 1968 by VOL'PIN [97,98] through the addition of a Lewis acid (such as AlBr_3 or AlCl_3) to the abovementioned systems composed of a titanium compound (TiX_4) in the presence of a high excess of reducing agent (such as Al or LiAlH_4); as in the latter systems, N_2 binds a reduced Ti centre. The catalytic species appears to be TiX_2 (the Lewis acid adduct $\text{C}_6\text{H}_6 \cdot \text{TiCl}_2 \cdot 2\text{AlCl}_3$ was isolated in benzene in the absence of N_2 and it exhibits catalytic activity); the reduction of N_2 to nitride(3-) proceeds stepwise (as evidenced by the formation of hydrazine, on hydrolysis, when the reaction is carried out at lower temperatures) and conceivably involves polynuclear systems with N_2 and its reduced derivatives bridging Ti and Al centres such as AlX_3 or AlX_2 (reactions 18). The Lewis acid cleaves the Ti-nitride bond thus allowing the regeneration of the Ti(II) active species. Hydrolysis of the aluminum nitride leads to NH_3 with a yield of *ca.* 290 mol NH_3/Ti for the system $\text{TiCl}_4 + \text{Al} + \text{AlBr}_3$ (1:600:1000) at 130°C and $p(\text{N}_2) = 100$ atm.



We have been treating the activation of N_2 by polynuclear systems with low transition group metals which display a high π -backbonding ability although presenting a low number of available d valence electrons. The other known examples of N_2 activation towards protonation by polynuclear systems involve the other extreme transition group metals (VIII) which have a high number of d electrons but present a low π -electron release capacity. The dinuclear iron complexes $[(\text{PPh}_3)_2\text{H}(\text{Pr}^i)\text{FeN}_2\text{Fe}(\text{Pr}^i)(\text{PPh}_3)_2]$ [99] (prepared by reduction of $[\text{FeCl}_3(\text{PPh}_3)_2]$ with Pr^iMgBr in ether at -50°C under N_2) and $[(\text{FeMgCl}_3(\text{thf})_{1.5})_2(\text{N}_2)]$ [100] (isolated in the system $\text{FeCl}_3 + \text{Mg}$ in thf under N_2) give hydrazine (*ca.* 10% based on complex in the former

case, whereas the yield was not specified in the latter complex) on treatment with HCl .

The square planar $\text{Li}_4[\text{FePh}_4] \cdot (\text{Et}_2\text{O})_4$ complex was isolated in the system $\text{FeCl}_3 + \text{LiPh}$ in Et_2O under argon and it reacts with N_2 giving an unidentified species which, on treatment with acid, produces ammonia and/or hydrazine. The distances between the Li^+ ions and the Fe(0) centre suggest the possible interaction of the former with ligating N_2 at vacant axial coordination position [101].

The formation of hydrazine (20% based on the metal) has also been reported from treatment of $[\text{Co}(\text{N}_2)(\text{PPh}_3)_3\text{Mg}(\text{thf})_2]$ (produced in the reaction of $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$ with Et_2Mg in thf at 0°C) with sulphuric acid [102]. It is, however, unknown if the Mg centre binds to N_2 or to the Co site; a related complex with N_2 bridging cobalt and magnesium is known, $[(\text{Co}(\text{PMe}_3)_3(\text{N}_2))_2\text{Mg}(\text{thf})_4]$ [35], but it was not reported if N_2 is reduced in this species.

In the dinuclear nickel(0) complex, $[(\text{LiPh})_3\text{Ni}]_2(\mu, \eta^2\text{-N}_2)(\text{OEt}_2)_2$, the side-on bonded N_2 is also activated towards protonation and NH_3 (*ca.* 30–40% yield) is produced on hydrolysis in thf . Biphenyl and nickel(0) metal are the other products of the reaction, the phenyl anions behaving as the reducing agent; hence, in contrast to the abovementioned examples, the transition metal is not the source of electrons to the N_2 ligand [103].

(ii) Mononuclear complexes

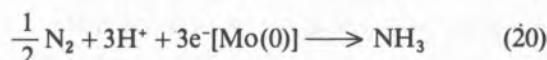
The most active mononuclear systems in the activation of N_2 towards protonation involve *electron-rich group VIB* transition metal (Mo and W) centres.

(ii.1) Reduction of N_2 to NH_3

When bound to $\{\text{ML}_4\}$ ($\text{M} = \text{Mo}$ or W ; $\text{L} =$ tertiary monophosphine) in complexes $[\text{M}(\text{N}_2)_2\text{L}_4]$, N_2 undergoes ready protonation by protic acid (HX) to afford NH_3 (and hydrazine) in MeOH at ambient temperature and pressure [104,105]. The reaction also proceeds without HX , under W-filament light, in MeOH which behaves as the protonating agent [104]*.

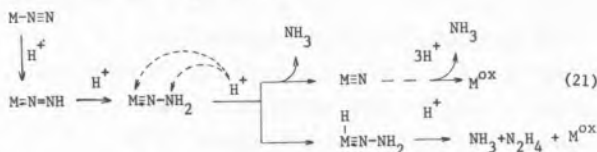
* Acidic transition metal hydrides, such as $[\text{H}_2\text{Fe}(\text{CO})_4]$, $[\text{HFeCo}_3(\text{CO})_{12}]$ or $[\text{HCo}(\text{CO})_4]$, may also be a proton source in these reactions, and NH_3 is obtained (although at lower yield than that obtained by using a mineral acid such as H_2SO_4) on treatment by aqueous KOH (basic distillation) [106].

The metal site behaves as the reducing agent, the maximum yield (2 mol NH₃/mol W) corresponding to the consumption of the six valence electrons of W(0) (equation 19); for the Mo(0) system, the maximum yield is *ca.* 1 mol NH₃/mol Mo, the molybdenum(0) being oxidized to the Mo(III) oxidation level (equation 20) [104].



The N₂ reduction/protonation proceeds stepwise with gradual weakening of the N-N bond until cleavage (reaction 21).

Hydrazido(2-) intermediate complexes, [MX₂(NNH₂)L₃], have been isolated [107]. They were also detected in solution by ¹⁵N n.m.r. [108] and they can undergo further protonation at the *exo* N atom to give NH₃ and a nitride complex which is protonated to NH₃; the metal of the hydrazido(2-) species is also susceptible to protonation to afford an hydrido-hydrazido(2-) complex, *e.g.*, [WHX₂(NNH₂)L₃]X [109], which, on protonation yields ammonia and hydrazine.



Complexes with other possible dinitrogen derived intermediate moieties have also been isolated, although with a more stable diphosphinic metal centre: the diazenido species of the type [MX(NNH)(dppe)₂] (from deprotonation of the hydrazido(2-) complex by base) [110] and complex [MoBr(NH)(dppe)₂]⁺ with an imido ligand (representing an intermediate stage of protonation of nitride to NH₃) which was derived from an organohydrazido(2-) precursor through an electrochemical 2e⁻/2H⁺ process [111] (see also reactions 26).

These systems, without an external reducing agent, are not catalytic, but the possibility to regenerate at the metal centre its N₂ binding capacity was demonstrated for Mo complexes. Hence, *e.g.*, protonation of the hydrazido(2-) complex [MoBr₂(NNH₂)(PMe₂Ph)₃], which was formed by reaction of [Mo(N₂)₂(PMe₂Ph)₄] with HBr, leads, as usually, to NH₃ and the Mo(III) complex [MoBr₃(thf)(PMe₂Ph)₂] was isolated; reduction of

the latter by sodium amalgam in the presence of phosphine and under N₂ regenerates the parent bis-dinitrogen complex [112], thus completing the N₂ reduction cycle although in a discontinuous way.

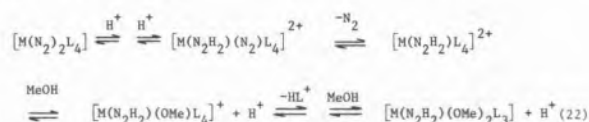
(ii.2) Mechanisms of the protonation reactions

Based on stopped-flow spectrophotometric and electronic spectroscopic studies and on product analysis the following mechanisms have been proposed for the initial steps of N₂ protonation. They are mentioned since they present important information on the properties of the involved transition metal centres.

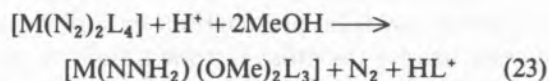
— Direct electrophilic attack at ligating N₂

The protonation of the monophosphinic complexes *cis*-[M(N₂)₂L₄] (M=Mo or W; L=PMe₂Ph) by strong acids (HCl, HBr, H₂SO₄) in methanol occurs by two successive direct proton attacks at the *exo* N atom of a ligand N₂ which is activated by the electron rich metal centre [113].

Dinitrogen evolution results from the oxidation of the metal and the vacant coordination position allows the strong net electron donor methoxide anion to bind, giving the cationic complex [M(N₂H₂)(OMe)L₄]⁺. The neutral [M(N₂H₂)(OMe)₂L₃] complex results from the coordination of a second MeO⁻ anion by replacement of a phosphine ligand which is removed as a phosphonium species HL⁺ (equation 22).



The overall stoichiometry of the reaction is shown by equation [23], one mole-equivalent of acid being consumed per mole-equivalent of complex as shown by spectrophotometric titration.



The kinetics exhibit a first-order dependence on complex concentration and a second-order dependence on acid concentration, but they are independent of the anion of the acid (which is strong in MeOH). The observed isotopic effect (*k_H*/*k_D* = 0.3) is consistent with a mechanism which involves protolytic equilibria before the rate limiting step [113].

The reaction is faster for W than for Mo on account of the higher basic character of the former which is then more effective in the activation of N_2 and derived ligands to protonation.

The strong electron donor ability of the methoxide ligands and the non-cationic character of the complexes $[M(N_2H_2)(OMe)_2L_3]$ favour the metal π -electron release to the hydrazido(2-) ligand which may undergo further protonation to NH_3 .* In agreement with these observations, complexes with chelating diphosphine ligands $[M(N_2)_2(LL)_2]$ [$LL = Ph_2PC_2H_4PPh_2$ (dppe), $Et_2PC_2H_4PEt_2$ (depe)], although undergoing ready protonation to $[M(N_2H_2)(OMe)(LL)_2]^+$, do not give NH_3 under mild conditions. The chelating effect of the diphosphine prevents its replacement by a stronger net electron donor anionic ligand, and the hydrazido(2-) species is not protonated.

Hence, the formation of ammonia requires the presence of a labile co-ligand (monophosphine), besides the other N_2 ligand, to allow the binding of a strong electron donor anionic species with a promoting effect on protonation.

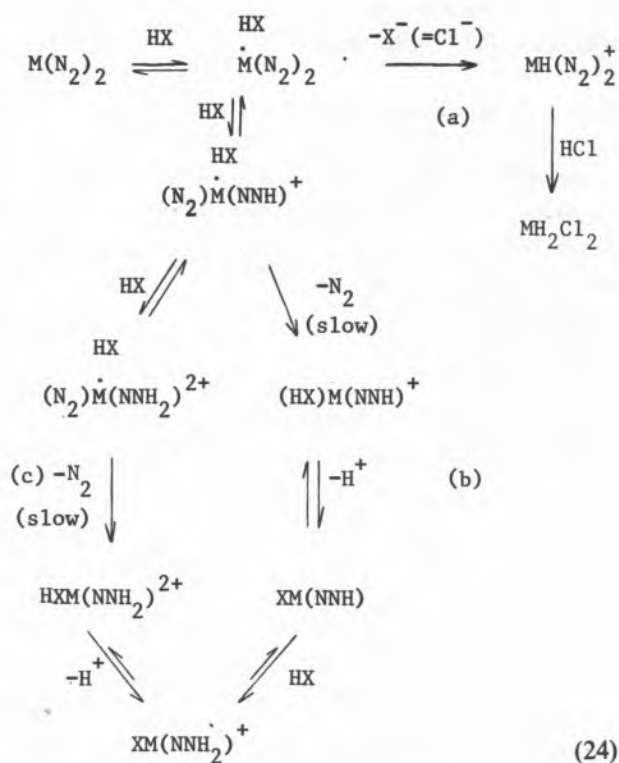
— Direct electrophilic attack at the metal centre

A distinct mechanism was proposed [114] for the protonation reactions of the diphosphinic complexes $trans-[M(N_2)_2(LL)_2]$ ($LL = dppe, depe$) by mineral acids ($HX = HCl, HBr, H_2SO_4$). However, solubility reasons precluded the use of MeOH and the studies were performed in thf, a solvent where the acids HX are *not* strong.

The kinetics of the reactions showed a first-order dependence on the concentration of complex whereas the dependence on the concentration of acid was a function of the nature of the acid: zero or first order on $[HCl]$; second or third order on $[HBr]$ and third order on $[H_2SO_4]$.

The data were interpreted by proposing the initial rapid formation of an adduct between HX and the complex followed by protonation of a ligating N_2 by another molecule of acid prior to the rate-limiting dissociation of N_2 (equations (24) where $M = M(LL)_2$).

* Another example of the strong methoxide activating power of a N_2 derived ligand towards protonation will be mentioned in section 3.2.2.



The postulated adduct may correspond to an outer-sphere association of the undissociated form of the acid electrophile (HX) with the electron-rich metal centre (the metal itself or a phosphorus atom); van der Waals interactions may also play an important role.

Although a direct spectroscopic evidence for the adduct formation is lacking, it corresponds to the best rationale of the available kinetic data.

Hence, *e.g.*, the adduct is most extensively formed with HCl which is the weakest acid of this study and the hydride complex $[WH(N_2)_2(dppe)_2]^+$ is formed by fast intramolecular electrophilic attack of HX on the metal within the edduct, following a zero order dependence on $[HCl]$ (route *a* of equations 24, observed for low $[HCl]$, not greater than twice the complex concentration).

However, for higher $[HCl]$ (greater than sixfold the complex concentration), the N_2 deactivating pathway (a) is replaced by the N_2 activating route (b), where ligating dinitrogen undergoes protonation to give the hydrazido(2-) complex, the kinetics following a first-order dependence on $[HCl]$.

The other acids studied (HBr and H_2SO_4) are stronger than HCl , the adduct is formed less extensively at a slower rate, and protonation proceeds through

a 2nd-order dependence on [HX] according to pathway (b) or a 3rd-order dependence on [HX] through route (c).

Hence, following an initial electrophilic attack of the protic acid at the metal centre, these reactions proceed through a further electrophilic attack at the metal (N₂ deactivating pathway *a*, for a weak acid) or further electrophilic attacks at a ligating dinitrogen (N₂ activating pathways *b* and *c*, for less undissociated acids).

These protonation reactions are faster for W than for Mo and for the depe ligand than for the dppe analogues as a consequence of the greater basicity of W and depe relative to Mo and dppe, respectively.

3.2.2. FORMATION OF ORGANONITROGENATED SPECIES

The formation of organonitrogenated species from a dinitrogen ligand has already been documented for the transition metal groups IV to VIIB.

However, group IVB transition metal systems involve reactions whose mechanisms are not yet known in detail and the metal centres have not been characterized.

Hence, *e.g.*, amines are formed in some Vol'pin type systems and the reactions are suggested [98] to proceed through an insertion of N₂ into a Ti-C(aryl) bond in mononuclear or dinuclear centres or through a nucleophilic attack of carbanion at the *endo* N of a N₂ ligand — *e.g.*, in the [TiCl₂(η⁵-C₅H₅)₂] (or [Ti(η⁵-C₅H₅)₂Ph₂]) + PhLi system — or through an insertion of N₂ into a Ti-benzene bond of an intermediate [115] — in the thermolysis of diphenyltitanocene.

Other examples, with possible involvement of intermediate species with the M-N=N-MgCl (M=Ti or V) moiety were already referred to (section 3.2.1.i).

An interesting reaction involving the dinuclear group VB Ta and Nb dinitrogen complexes (where the bridging N₂ ligand is strongly activated by the two high π electron release ability of the two metal centres) and acetone to give dimethylketazine was already mentioned (section 3.2.1.i) but the generality of this type of reaction has yet to be demonstrated.

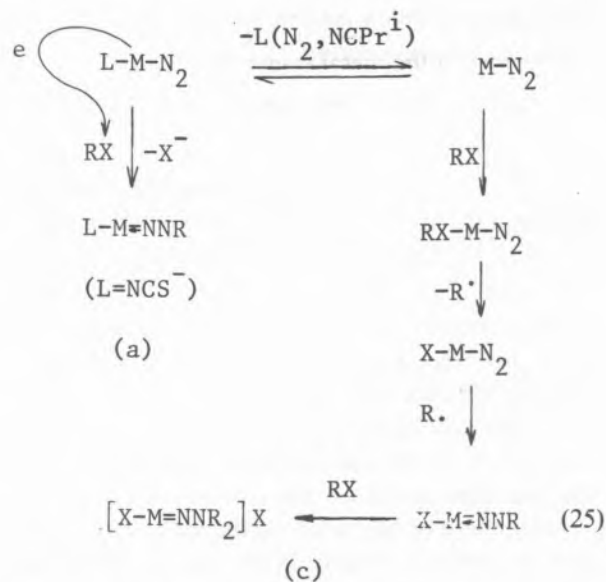
The behaviour of systems with transition metal VIB and VIIB groups is known in more detail and they may reflect opposing dinitrogen activating ways.

(i) Formation of *exo* nitrogen-carbon bonds

When N₂ binds an electron rich Mo(0) or W(0) metal centre {ML(LL)₂} (L=N₂, NCPrⁱ, NCS⁻; LL=dppe, depe or phenyl substituted dppe), of the type already mentioned, it may undergo attack by an organo (alkyl, aryl or aroyl) halide (RX).

However, this reaction does not occur *via* a direct electrophilic attack at the N₂ ligand, but it involves the previous oxidation of the metal centre.

If this centre presents a high electron donor co-ligand such as thiocyanate (P_L = -0.88 V), its resulting high reducing power leads to the reduction of the organohalide through an outer-sphere electron transfer reaction to afford a radical (R.) which attacks the *exo* N atom of the dinitrogen ligand (reaction 25a) leading to an organodiazenido species; the kinetics are first order on both complex and RX concentrations, and the reaction with MeI is *ca.* 38 times faster than with EtI in agreement with a S_N² type mechanism [116].



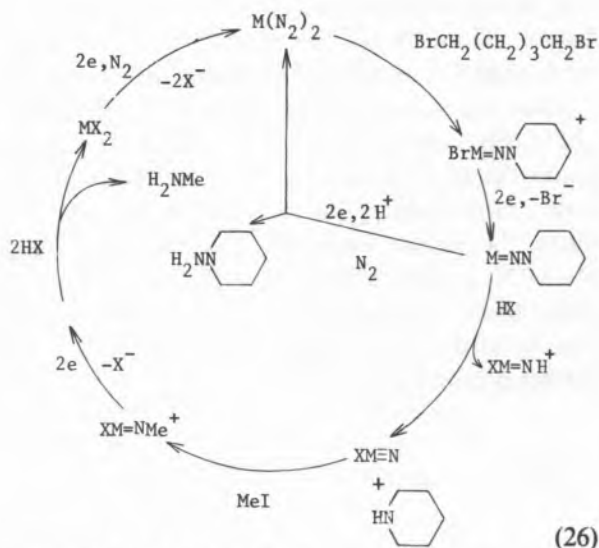
However, the mechanism of the reaction is different if the metal centre presents a lower reducing power and a labile co-ligand such as N₂ (P_L = -0.1 V) or NCPrⁱ (P_L = -0.6 V). Addition of the organohalide to the unsaturated species (formed upon loss of the labile ligand) is followed by homolytic cleavage of the halogen-carbon bond to afford, through an inner-sphere electron transfer process, a free radical (R.) which attacks the *exo* N atom of the ligating dinitrogen (reactions 25b) [116].

The diazenido product of these reactions, activated by the metal centre, may undergo a secondary alkylation [117] through a direct electrophilic attack at the *exo* N atom in a bimolecular reaction which is promoted by the factors which enhance the electron richness of the metal centre (increase of the electron donor character of the substituents on the phosphorus atoms, and use of W instead of Mo central metal). These factors also affect in the same way the primary alkylation through the outer-sphere electron transfer pathway (reactions 25a) but they hinder the inner-sphere pathway (b) since the labile ligand dissociation is hampered by an increase in the π -backbonding ability of the metal centre. From the above considerations one may conclude, however, that these reactions may occur only at a metal centre with, at least, the following features in a delicate balance: strong (route *a*) or considerable (route *b*) electron release power for the organohalide to lead to the C-X bond cleavage with formation of free or bonded X^- , respectively; high π -electron donor capacity to ligating N_2 which should stay coordinated to the metal even after its oxidation by reaction with the organohalide; coordinative unsaturation (for route *b*).

Hence, it is not surprising that these types of reactions are unknown for group VIII transition metals which present a high electronegativity. However, ligating N_2 in the heavy group VIIB metal complex $[ReCl(N_2)(PMe_2Ph)_4]$ (with a considerable electron π -releasing metal centre) may undergo acylation and arylation leading to $[ReCl_2(NNCOR)(PMe_2Ph)_3]$ ($R = \text{alkyl or aryl}$) [118].

Treatment of the Mo and W organohydrazido(2-) complexes with a reducing agent (such as $NaBH_4$ in methanol) leads to the formation of amines and ammonia [119,120] but with destruction of the N_2 binding ability of the metal centre. However the liberation of ligating organonitrogenated species with regeneration of the nitrogen fixation centre was already achieved by an electrochemical route in the cyclic organohydrazido complex $[MoBr\{NN-CH_2(CH_2)_3CH_2\}(dppe)_2]^+$ which was derived from double alkylation of N_2 ligand by 1,5-dibromopentane (reactions 26) [121,122].

The electrochemical reduction at a Pt electrode of this complex cation in thf confers on the metal centre such a high electron richness which promotes the protonation of that ligand (to afford an organohy-



drazine) and the N_2 binding ability with regeneration of the parent bisdinitrogen complex, as shown by the inner cycle of reactions 26.

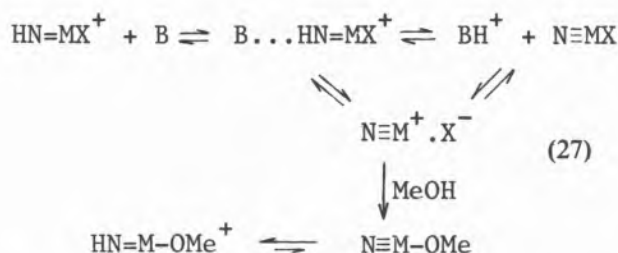
Other amines may be formed according to the outer cycle, *via* protonation of the neutral organohydrazido(2-) complex. Cleavage of the N-N bond occurs in a first step to afford piperidine, an imido and a nitrile species; the latter may undergo alkylation and the resulting organoimido species is susceptible to protonation, following a two electron electrochemical reduction, to give methylamine and the dihalide complex which, on reduction under N_2 , regenerates the parent dinitrogen complex.

The fundamentals of these cycles, based on the *promotion of the ligand nucleophilic character upon electrochemical reduction of the metal center*, is certainly susceptible to extension to other systems with different types of N_2 derived ligands, and it will be worthwhile to verify the generality of its application to the catalytic synthesis of nitrogenated species from dinitrogen ligand.

In contrast to the monophosphinic Mo and W complexes which activate N_2 towards reduction to NH_3 , the metal centres of the present cycles do not present a labile phosphine to be displaced by a stronger net electron donor ligand: *the electron releasing character of the centre is enhanced by electrochemical reduction*. However, replacement of the halide ligand by a stronger net electron donor species may also be used for a similar purpose as shown in the following example.

The imido complex *trans*- $[M(NH)X(dppe)_2]^+$ prepared in the sequence of the outer cycle (reactions

26), although unreactive in refluxing acidified methanol, affords NH_3 (70% yield for $\text{M} = \text{Mo}$) in basic methanol. The mechanism of this base catalysed reaction was studied [123] by stopped-flow spectrophotometry and is shown by the sequence (27): the imido ligand is deprotonated by the base (B) to form a nitride which, due to its high *trans* effect, induces the halide evolution and the ionic pair $\text{N} \equiv \text{M}^+ \text{X}^-$ is formed; binding of the strong electron donor MeO^- to the unsaturated centre promotes the basicity of the nitride ligand which then undergoes further protonation to NH_3 .



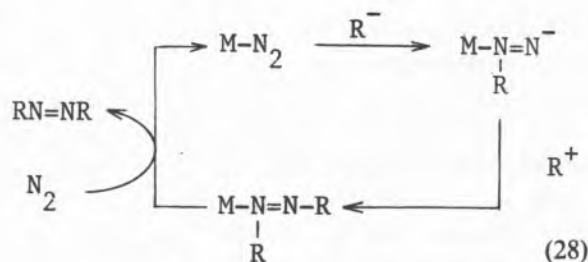
(ii) *Formation of endo nitrogen-carbon bond*

When N_2 binds a metal centre with a considerable lower electron-richness than those mentioned in the previous sections, the *endo* nitrogen atom may become susceptible to undergo a nucleophilic attack by a carbanion with formation of a N-C bond.

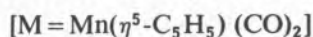
Although this type of attack has been postulated [98] in the formation of anilines from the reaction of N_2 with $PhLi$ in the presence of some high valent $Ti(IV)$ species such as $[TiCl_2(\eta^5-C_5H_5)_2]$ or $[Ti(\eta^5-C_5H_5)_2Ph_2]$, as mentioned in the previous section, the only well documented [124] system involves the dicarbonyl $Mn(I)$ complex $[Mn(\eta^5-C_5H_5)(CO)_2(N_2)]$.

This complex presents $E_{1/2}^{\text{ox}}$ and i.r. $\nu(\text{N}_2)$ at high values (+1.2 V vs. s.c.e. and 2160 cm^{-1} , respectively) in agreement with a relatively low electron-rich character of the metal centre and a low π -backbond ability to N_2 (the presence of the two strong π electron competitor CO co-ligands may well play a role in this behaviour).

The diazenido ligand (in the unisolated intermediate) derived from nucleophilic attack of carbanion (from MeLi or Ph Li) at the *endo* N atom of ligating N₂ can undergo reaction with an electrophile (carbocation or protic acid) to afford an organodiazene (reactions 28) which may be replaced by N₂ (at 100



atm pressure) thus regenerating the initial dinitrogen complex although with a low cyclic yield.



3.2.3. ADDUCT FORMATION

The Lewis basic nature of dinitrogen when ligating an electron-rich Mo(0), W(0) or Re(I) centre accounts for the formation of dinitrogen bridged di- and tri-nuclear complexes on reaction of $[M(N_2)_2L_4]$ ($M = Mo, W$) with $AlMe_3$ (or $AlEt_3$) or of *trans*- $[ReCl(N_2)(PMe_2Ph)_4]$ with a variety of representative or transition metal acceptor species such as $AlMe_3$, $TiCl_4$ or derived from $[CrCl_3(thf)_3]$ and $[MoCl_4L_2]$ ($L = thf$ or PPh_3).

Hence, e.g., the $[\text{Mo}(\text{NNAI}(\text{Et})_3)_2(\text{PMe}_2\text{Ph})_4]$ [125] and the $[\text{M}(\text{NNAI}(\text{Me})_3)(\text{N}_2)(\text{dppe})_2]$ ($\text{M} = \text{Mo}$ or W) [126] adducts are derived from reaction of AlEt_3 and AlMe_3 , respectively, with the parent N_2 complexes, whereas $[\{\text{WX}(\text{PMe}_2\text{Ph})_3(\text{Py})(\mu_3\text{-N}_2)(\text{AlX}_2)_2\}]_2$ (where Py = pyridine) (see section 2.2.1.) is derived from attack of AlX_3/Py at *cis*- $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ ($\text{X} = \text{Cl}$ or Br) [41].

Moreover, the following Re(I) complexes [127] are formed by reactions of *trans*-[ReCl(N₂)(PMe₂Ph)₄] with the appropriate acceptor species: [TiCl₄{(N₂) ReCl (PMe₂Ph)₄} (thf)], [TiCl₄{(N₂) ReCl (PMe₂Ph)₄}₂], [MoCl₄(OMe){(N₂) ReCl (PMe₂Ph)₄}] and [MoCl₄{(N₂) ReCl (PMe₂Ph)₄}₂].

3.3. ACTIVATION OF ISOCYANIDES AND THEIR APPLICATION AS PROBES IN THE STUDY OF DINITROGEN BINDING METAL CENTRES AND OF DINITROGEN REACTIVITY

After studying the reactivity of N_2 when activated by a transition metal centre, the difficulties encountered in its activation justify a brief reference to the attempts to apply other more reactive substrates of nitrogenase as probes in the study of N_2 binding centres.

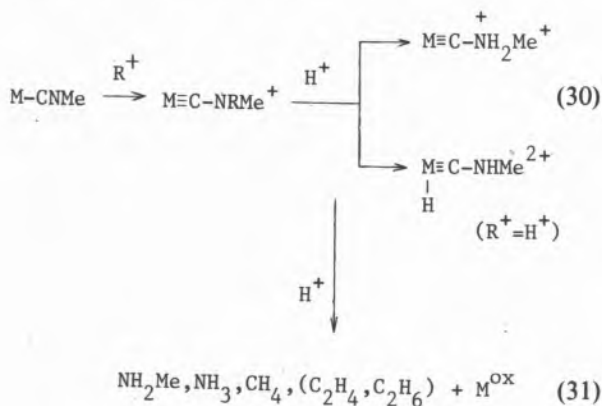
The isocyanides, organic species formulated as $C\equiv NR$, are isoelectronic with N_2 ; they are also

substrates of nitrogenase being reduced, as N_2 , with complete cleavage of the unsaturated bond in an overall process which requires 6 protons and 6 electrons per molecule (reaction 29, although C_2 and C_3 hydrocarbons are also produced in lower yields).

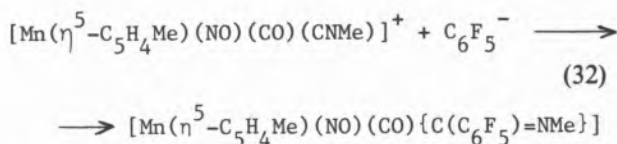


When bound to a nitrogen fixation group VIB Mo(0) or W(0) metal centre, with a high electron-richness, *e.g.*, as in *trans*-[M(CNMe)₂ (dppe)₂], isocyanides present, as a result of the extensive π -backbonding, very low i.r. $\nu(\text{CN})$ values (much lower than in the free ligands, by *ca.* 300 ~ 400 cm⁻¹) [64]; a high electron density is then localized at the N atom (it may present a bent geometry) [128] which becomes susceptible to undergo attack by electrophilic agents (a Lewis acid such as AlEt₃ [129], protic acids [129,130] or alkylating agents [131]) to give carbyne-type ligands (with a triple metal-carbon bond) as in *trans*-[M(CNRMMe) (CNMe) (dppe)₂]⁺ (reactions 30 where R⁺ = H⁺, Me⁺ or Et⁺); the metal site may also undergo protonation and hydrido-carbyne complexes, [MH(CNHMe) (CNMe) (dppe)₂]²⁺, are formed [132] in reactions which are related to those followed by the analogous dinitrogen complexes (equations 21).

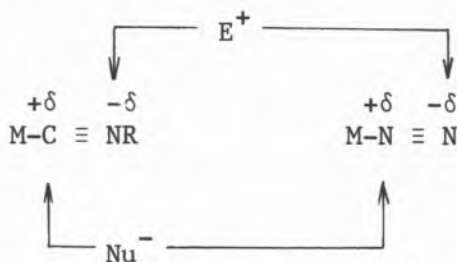
If the metal centre presents labile monophosphines, the isocyanide ligand may undergo a more extensive protonation until complete cleavage of the unsaturated bond (as it was observed in the related N_2 complexes with monophosphines) to afford amine, ammonia and hydrocarbon (reactions 31) [133]. The metal is also the reducing agent, the maximum yield corresponding to the consumption of its six valence electrons as observed for $[W(CNMe)_3(PMe_2Ph)_3]$ [133].



In contrast, if the isocyanide binds a low electron-rich metal centre, such as of the abovementioned Mn(I) type which activates N₂ towards attack by a nucleophile, the i.r. $\nu(\text{CN})$ may occur at higher values than those observed for the free ligand, and the ligating isocyanide carbon is susceptible to attack by a nucleophilic agent (see, *e.g.*, reaction 32) [134].



We may then propose that both isocyanide $\nu(\text{CN})$ and dinitrogen $\nu(\text{NN})$ reflect the electron-richness of the metal centre and the possibility of electrophilic attack (at the β atom) for high electron-rich sites or of attack by a nucleophile (at the α atom) for metal centres with a much lower electron-rich character:



Since isocyanides present a much easier coordination (they are better σ -donors and π -acceptors) than N_2 , and a higher reactivity, it would be interesting to extend the comparison between their electronic and chemical properties to a variety of metal centres in order to attempt the development of coordination and reactivity criteria for N_2 on the basis of the known behaviour of the isocyanides bound to the common sites.

4 — INORGANIC CLUSTERS AS STRUCTURAL MODELS FOR THE ENZYMATIC CENTRE

Following the consideration of the isocyanide potential models for the N_2 activating properties of transition metal centres, let us illustrate the attempts to develop structural models of the N_2 binding enzymatic centre, which fall within a general aim of bioinorganic chemistry: the proposal of synthetic models for the metalloenzyme and metalloprotein active centres.

Nitrogenase is formed by two iron-sulphur proteins and the presence of both of them is required for catalytic activity.

The heavier protein, called component 1, has molecular weight of *ca.* 220 000, 1 ~ 2 Mo atoms and 24-34 Fe atoms, whereas the smaller protein (component 2) presents molecular weight of *ca.* 60 000 and 4 Fe atoms (without Mo); in both proteins, iron is associated with a similar amount of sulphur, conceivably forming [4Fe-4S] cubane type clusters (the so-called P centres which have not yet been fully characterized) [135].

It was possible the isolation [136], from component 1, of a Mo and Fe co-factor (FeMoco) (the so-called M centre in the intact protein) with the Mo:Fe:S stoichiometry of 1:6 ~ 8:4 ~ 6 (two of these centres may be present in the Mo-Fe protein) and which generates an active Mo-Fe protein when added to a defective form of nitrogenase (without Mo) produced by a mutant bacterium.

The Mo-Fe protein, in the resting state, presents an EPR resonance [137] which is associated to six iron atoms (as evidenced by Mössbauer studies [138]) in a total electron spin $S = 3/2$ metal centre present in the FeMoco.

^{95}Mo and ^1H ENDOR (Electron Nuclear Double Resonance) spectroscopic studies on the resting state of the Mo-Fe protein evidence (from the observed hyperfine coupling to Mo) the presence of a single Mo atom in the $S = 3/2$ centre (which is redox active during the N_2 reduction) and suggest (from the magnitude of the ^{95}Mo hyperfine coupling) that this Mo atom presents a pair oxidation state, possibly tetrahedral Mo(II) or Mo(VI) [139].

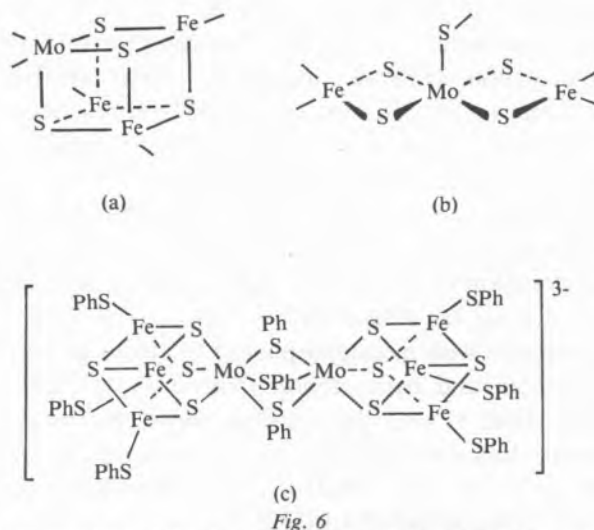
XAS (X-ray Absorption Spectroscopy) and EXAFS (Extended X-ray Absorption Fine Structure) studies evidence that the numbers of Fe (3-4) and S(2-3) atoms in the vicinity of Mo and their distances to this atom in the co-factor are analogous to those observed in the Mo-Fe protein (the Mo-S distances are 2.35 and 2.36 Å in the co-factor and in the protein, respectively, whereas the Mo-Fe distances are 2.66 and 2.68 Å, respectively) [140].

Based on these properties, a few Mo-Fe-S clusters have been proposed as structural models for the active site, namely these shown in fig. 6: the single cubane MoFe_3S_4 with a cubic arrangement of the metal and sulphur atoms, the double cubane (dimer with two single cubane units linked by sulphur or

thiolate bridges) and the linear model where the metal atoms follow a straight line [141]; other models have been proposed such as the complex "string bag" [142] arrangements which are composite clusters of hepta (h-type) and nona (n-type) simpler structures (with 7 and 9 atoms, respectively).

However, only recently it was demonstrated the nitrogen fixation ability of one of these clusters: the reduced (5-) form of the double cubane $[\text{Mo-Fe}]^{3-}$ of fig. 6, prepared by controlled potential electrolysis of the latter at a Hg electrode (-1.3 V vs. s.c.e.) in a protic solvent, MeOH/thf or an aqueous alkaline suspension [143].

The maximum yield was *ca.* $2\text{NH}_3/\text{complex}$ in an aqueous suspension during 4 days, although with a low current efficiency (lower than 0.1%, defined by the ratio between the charge which reduced N_2 to NH_3 and the total charge which passed through the cell) due to the high consumption in the protic reduction to H_2 .



Structural model clusters for the enzymatic Mo centre of nitrogenase. (a) Single cubane MoFe_3S_4 . (b) Linear $\text{Fe}_2\text{S}_2\text{MoS}_2\text{Fe}$ (c) Double cubane $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_9]^{3-}$ or $[\text{Mo-Fe}]^{3-}$

The same reduced $[\text{Mo-Fe}]^{5-}$ cluster also reduces other substrates of nitrogenase such as methylisocyanide [to CH_4 and other C_2 and C_3 hydrocarbons and MeNH_2 , CO_2 also being formed probably through oxidation, by an oxidized form of the complex, of HCOOH which is obtained by hydrolysis of the isocyanide] [144], acetonitrile [to $\text{NH}_3 + \text{C}_2\text{H}_6$ and C_2H_4] and acetylene [which is stereoselectively reduced to ethylene: *cis*- $\text{C}_2\text{D}_2\text{H}_2$ is formed from C_2D_2] [145].

In these systems the role of the Mo centre is yet unknown since the 3- and 4- reduced forms of the Fe-S cluster (without Mo) $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$, also exhibit reducing activity.

Moreover, in the double cubane structure the Mo atoms are coordinatively saturated and present thiolate bridges which are resistant to displacement; the substrate activation may then occur from coordination to iron. Hence, structures, *e.g.*, of the single cubane type, with an unsaturated Mo centre, may become more favourable.

This type of structure (fig. 6a) has been prepared [146] and authenticated by X-rays [147], the Mo(III) centre presenting a quelating catecholate ligand and an unsaturated character [the sixth coordination position is occupied by a labile solvent (*e.g.*, NCMe) ligand which undergoes ready replacement by a variety of neutral (CO , PEt_3) and anionic (CN^- , OPh^- , SR^-) species]. An electron spin $S=3/2$ is observed as in the resting FeMoco.

The solvated cluster undergoes a reversible single electron electrochemical reduction, and the reduced form adds CO to give a 1:1 adduct, and the low observed i.r. $\nu(\text{CO})$ value (1810 cm^{-1}) which is comparable to that known for $[\text{Mo}(\text{N}_2)(\text{CO})(\text{dppe})_2]$ (1799 cm^{-1}) suggests that the reduced single cubane cluster species presents an electron π releasing power similar to that of $[\text{Mo}(\text{N}_2)(\text{dppe})_2]!$ The study of the interaction of this cluster with enzymatic substrates is conceivably under progress but has not yet been reported.

5 — FINAL COMMENTS

The topic of this work possibly initiated in 1965 with the accidental preparation of the first dinitrogen complex. Since then, important developments on the search for N_2 activating metal centres have occurred: catalytic conversion of the Vol'pin system (Vol'pin 1968); development of aqueous systems (Shilov, Schrauzer, 1970); conversion of N_2 into organonitrogenated species and hydrides of nitrogen in isolated complexes (Chatt, Leigh, Richards, 1972, 1975); the isolation of FeMoco (Shah 1977); the electrochemical quantification of the electronic properties of the metal centres (Pickett 1980); application of Mo-Fe-S clusters as structural models for the enzymatic metal centre; use of isocyanides as coordination and reactivity models and as probes in

the study of the activating properties of the metal centres.

The third, fifth and seventh topics, which were covered in this work, are those which have given more information on the electronic properties of the N_2 activating centres: high electron-richness (E_s), high polarisability (β), high π -backbonding capacity and/or high σ -acceptor character. The convenient geometry and the coordinative unsaturation (due to the lability of N_2 and/or other ligands) are also features of the involved metal centres and all these properties, in variable intensity, rationalize the stabilization of unstable π -acceptors (such as organodiazenido and carbyne-type species), as well as the chemical reactivity: ready oxidation, addition and oxidative addition reactions, involvement in catalysis, susceptibility to electrophilic attack and activation of π -acceptor ligands such as N_2 and isocyanides. The half-wave oxidation potential of the complex and the i.r. stretching vibration associated to the triple bond of the unsaturated ligand reflect the type of activation it undergoes which promotes attack by a nucleophile or, more usually, by an electrophile. The reactions of N_2 ligand with electrophiles involve a fundamental electron density transfer from the metal centre to the electrophile through a direct way [*e.g.*, in alkylation and protonation reactions of dinitrogen at diphosphinic group VIB Mo(0) or W(0) metal centres] or an indirect pathway, *via* dinitrogen [*e.g.*, in the protonation reactions of ligating N_2 at monophosphinic Mo(0) or W(0) complexes by strong acids, and in the attack by Lewis acids].

The activation of N_2 towards electrophilic attack depends concomitantly on the tendency to π -backbonding donation of the metal centre and on its available number of d electrons: transition metals of the lower periodic groups have a high π -electron release ability but present a small number of d electrons, whereas the metals in high periodic groups, with a high number of d electrons, have a weak π -backbonding capacity. Fig. 5 can now be extended to the central groups, typically to Mo and W group VIB transition metals, with a privileged localization which corresponds to a compromise between those two tendencies, presenting the maximum known N_2 activating power in mononuclear complexes (fig. 7).

For the central transition metal groups (VIB and VIIB) the activation of ligating N_2 towards electrophiles appears to increase down the group as eviden-



Group		IVB Ti ...	VB V ...	VIB Cr ...	VIIB Mn ...	VIII Fe,Co,Ni ...
π -Backbonding ability		High				
Number of <i>d</i> electrons		Low				
N ₂ activation	Mononuclear centres	High				Low
	Polynuclear centres	<div>$M-N=N-M'$</div> <div>$\begin{array}{c} \text{Ti} \\ \vdots \\ \text{Ti}-N \equiv N-\text{Ti} \end{array}$</div>				<div>$M-N \equiv N-M'$</div> <div>$\begin{array}{c} \text{Li} \quad \text{Li} \\ \diagdown \quad \diagup \\ \text{N} \\ \vdots \\ \text{Ni} \text{---} \text{Ni} \\ \vdots \\ \text{N} \\ \diagup \quad \diagdown \\ \text{Li} \quad \text{Li} \end{array}$</div>

Fig. 7

Activation of N₂ along the periodic groups. M-Transition metal centre. M'-Transition or representative metal centre

ced by the higher rates of the protonation and alkylation (by an outer-sphere electron transfer mechanism) reactions of N₂ when bound to W rather than to Mo, *e.g.*, in [M(N₂)₂(dppe)₂] (the W centre appears to display a higher basicity than the Mo one). Moreover, when N₂ binds a Re(I) centre, in *trans*-[ReCl(N₂)(PMe₂Ph)₄], it undergoes attack by a Lewis acid, an acyl- and aroyl-halide, whereas when bound to a lighter Mn(I) centre, in [Mn(η^5 -C₅H₅)(CO)₂(N₂)], it reacts with a nucleophile; however, a direct comparison between the two transition metals is precluded by the different electronic properties of their ligands.

However, N₂ may also be activated towards reduction by transition metals of the extreme periodic group in polynuclear complexes where the N₂ activation results from the combined effect of two or more metal centres with a possible promoting role of cations of less electronegative non-transition metal atoms (fig. 7).

In the reduction of N₂ to NH₃ or to organonitrogenated species by group VIB metal centres, it is also fundamental the enhancement of the electron releasing ability of the binding centre through replacement of a labile co-ligand by a stronger net electron

donor ligand or through an electrochemical reductive pathway.

The current knowledge on the rationalization of the N₂ binding metal centres is yet incipient but already promising, namely on attempting to design N₂ activating systems which may reduce, in mild conditions, N₂ to compounds with industrial or agricultural interest.

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RESUMO

O presente trabalho constitui uma tentativa de caracterização dos centros de metais de transição com capacidade coordenadora de diazoto e uma reflexão sobre o modo como se manifestam as suas propriedades na activação desta espécie. Embora existam publicados vários artigos recentes de revisão sobre complexos de diazoto [1-4] não foi ainda nenhum elaborado sob esta perspectiva, pelo que o trabalho complementa, deste modo, assuntos tratados, necessariamente com mais pormenor, nesses artigos. Após um breve introdução à importância e actualidade da fixação de azoto, descreve-se a constituição dos centros de metais de transição coordenadores de diazoto, procede-se à sua caracterização estrutural e são apresentadas as suas propriedades electrónicas (riqueza electrónica, capacidade aceitadora σ e retrodoadora π , polarizabilidade) fundamentais àquela coordenação e é discutida a sua dependência em relação ao grupo periódico do metal central e ao efeito de co-ligandos.

Descreve-se em seguida o comportamento químico destes centros, em geral determinado por factores electrónicos e estruturais (nomeadamente o carácter insaturado derivado da labilidade do ligando diazoto), após o que são tratadas as formas de activação de N_2 por coordenação, em complexos poli-ou mono-nucleares. É analisada a dependência desta activação em relação ao grupo periódico do metal de transição e à presença de iões de metais representativos de baixa electronegatividade. É ainda proposto o uso de isonitrilos como modelos potenciais de coordenação e reactividade do diazoto e apresentados modelos estruturais e de reactividade do centro enzimático fixador de azoto.

NOTA DO EDITOR

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