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Recent Advances in the Chemistry of Nitrogen Fixation

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Contents

I. Introduction

A. Scope of the Review

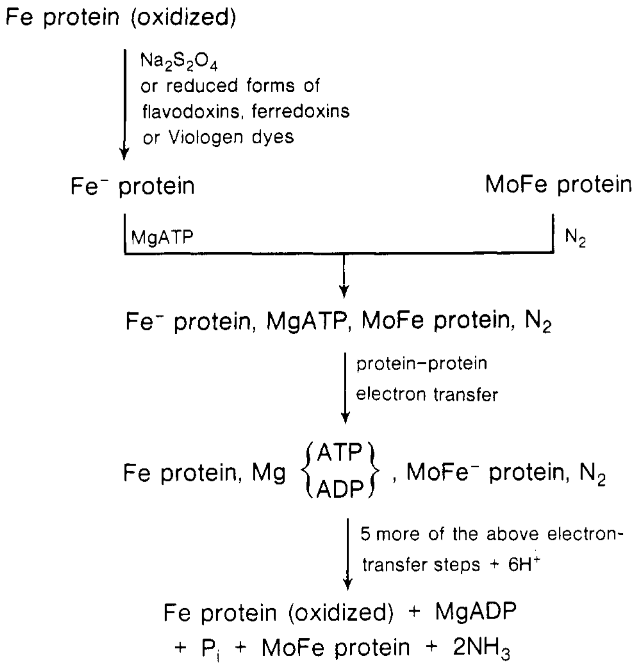
We have placed a number of restrictions upon the scope of this review. We have attempted to cover, in reasonable depth, developments relevant to the chemistry of nitrogen fixation which have been published during the last five years, up to about the end of 1976, but some important references from 1977 are included. The literature previous to this coverage has been extensively reviewed.[1-6] We have omitted heterogeneous catalysis and metal surface interactions almost entirely. We must also, of necessity, mention only very briefly the recent advances in the study of biological nitrogen fixation at the molecular level. This has provided the stimulus for most chemical investigations and the present position is summarized below.

B. Biochemical Investigations

Biochemical investigations have been mainly concerned with the preparation and characterization of nitrogenase proteins from a variety of microorganisms and investigation of the mechanism of their function.

Nitrogenase has been isolated from about 20 microorganisms and purified from about four. It consists of two nonheme, iron–sulfur proteins. The larger has a molecular weight of approximately 220 000 depending on its source and contains four subunits, two each of two types. It contains 2 molybdenum atoms, about 20–32 iron atoms, also depending on its source, and an approximately equal number of sulfide ions (acid-labile sulfur) per molecule. The smaller protein has a molecular weight of 55 000–70 000, with two equal subunits and four iron atoms and four sulfide ions per molecule. Both proteins are sensitive to dioxygen, especially the smaller which is destroyed irreversibly by the briefest exposure. Both are necessary for nitrogenase activity.

Cluster extrusion and Mossbauer and EPR spectroscopic studies indicate that at least half of the iron and sulfur atoms are associated in clusters.[7-9] The iron in the smaller protein has been extruded as a single Fe_4S_4 cluster, but the larger protein contains various clusters with a high proportion of the Fe_4S_4 type. Studies in several laboratories[7-9] using EPR, Mossbauer, stopped-flow, SCHEME I[a]



[a] This scheme shows the steps believed to be involved in nitrogenase action; but the sequence shown is not firmly established.

and UV spectroscopic techniques form the basis of the simplified scheme of nitrogenase action shown in Scheme I. The smaller protein (Fe protein) can be reduced by various reagents (Scheme I). In association with the monomagnesium salt of ATP, it undergoes a conformational change and its redox potential falls from −280 to −400 mV (relative to the hydrogen electrode), but whether this change is essential to its function in nitrogenase has not been established. In any case, the reduced Fe protein forms a complex with the MoFe protein and MgATP. It then transfers its reducing electron to the MoFe protein and so to the dinitrogen bound at the active site. Finally after a series of such electron transfer steps, with concomitant proton transfer from water to dinitrogen, MgADP, inorganic phosphate (P_i), and ammonia are produced with regeneration of the proteins at their original oxidation levels.

There is a long-established belief that molybdenum provides the site where molecular nitrogen (dinitrogen) is attached to the enzyme and reduced. The evidence is all circumstantial[10] and because the molybdenum gives no EPR or other signals detected by common methods of spectroscopic investigation, there is little knowledge of its state or environment. Recent X-ray absorption edge measurements (X-AFS) have, however, located a molybdenum-K edge arising from the MoFe protein of nitrogenase from *Clostridium pasteurianum.*[11] As yet the interpretation of the absorption edge parameters in terms of the state of molybdenum cannot be made with a high degree of confidence. Nevertheless, it indicates that nearest neighbors of the molybdenum are probably sulfur atoms and that there is no Mo═O linkage in the active enzyme.[12] Further application of this important technique should provide vital information toward an understanding of the function of the molybdenum.

The iron–sulfur clusters are believed to store the electrons for the reduction as in ferredoxin and related nonheme iron proteins, but there is also the possibility that some iron may interact with the dinitrogen.

The reaction catalyzed by nitrogenase is the reduction of dinitrogen to ammonia. No intermediate has been detected until recently when hydrazine has been found in significant quantity when the enzyme is destroyed by acid or alkali while it is functioning under dinitrogen.[13] No hydrazine is found under identical conditions under argon. These discoveries are consistent with the existence of a bound N_2H_x species during the fixation process.

C. Chemical Investigations

The major advances during the last five years form the subject of this review and derive from the search for both an understanding of the mode of action of iron and molybdenum in nitrogenase and for low-temperature (and pressure) catalysts for the production of nitrogen hydrides and organic nitrogen compounds. There has also been considerable activity in the pursuit of synthetic analogues for iron–sulfur cluster compounds (ferredoxins and related compounds). This work is relevant to the iron–sulfur content of nitrogenase and has recently been reviewed.[14,15]

During the course of investigations of the nature of metal–dinitrogen interactions, many dinitrogen complexes, exhibiting a variety of binding modes, have been synthesized and their physical properties have been studied. The discovery of reactions of dinitrogen complexes which lead to the formation of nitrogen hydrides and nitrogen–carbon bonded species, has been an important advance.

Systems based mainly on vanadium and molybdenum, which reduce molecular nitrogen to ammonia or hydrazine in aqueous conditions, have been developed. Attempts to deduce the nature of the species involved in these systems, and in nitrogenase, have led to considerable investigation of the chemistry of vanadium and more especially of molybdenum in their higher oxidation states. Although reference will be made to appropriate findings in this area, the reader is referred to a number of reviews for a detailed discussion.[16–19]

In the final part of this review we have discussed the possible biological implications of these discoveries and give some modest speculations on the likely future advances in the field of chemical nitrogen fixation.

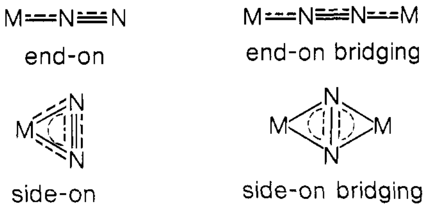
D. Abbreviations

acac	acetylacetato
ADP	adenosine diphosphate
Ar	η^6-arene ligand
ATP	adenosine triphosphate
bpy	1,1′-bipyridine
Bu^n	*n*-butyl
Bu^t	*tert*-butyl
depe	$Et_2PCH_2CH_2PEt_2$
diars	$1,2\text{-}(Me_2As)_2C_6H_4$
DMF	dimethylformamide (dmf as ligand)
dmpe	$Me_2PCH_2CH_2PMe_2$
dppae	$Ph_2AsCH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
dppey	$Ph_2PCH{=}CHPPh_2$
dppm	$Ph_2PCH_2PPh_2$
dppp	$Ph_2P(CH_2)_3PPh_2$
dpte	$PhSCH_2CH_2SPh$
Et	ethyl
EPR	electron paramagnetic resonance
IR	infrared
M	metal
Me	methyl
NMR	nuclear magnetic resonance
N-triphos	$N(CH_2CH_2PPh_2)_3$
oep	octaethylporphyrin
oxine	8-hydroxyquinolato
Ph	phenyl
pic	2-methylpyridine (picoline)
PR_3	mono(tertiary phosphine)
Pr^i	isopropyl
Pr^n	*n*-propyl

P-triphos	$P(CH_2CH_2PPh_2)_3$
THF	tetrahydrofuran (thf as ligand)
UV	ultraviolet
X-AFS	X-ray absorption edge fine structure analysis
X-PES	X-ray photoelectron spectroscopy

E. Nomenclature for Dinitrogen Bonding Modes

The nomenclature adopted for the various possible bonding modes for dinitrogen are shown below.



II. Preparation and Characterization of Dinitrogen Complexes

A. Introduction

Immediately following the discovery of $[Ru(NH_3)_5(N_2)]^{2+}$ in 1965 the number of elements known to form dinitrogen complexes grew rapidly (see earlier reviews).[1-6] By comparison, the last five years have been a period of consolidation, rather than dramatic developments. The full details of preparations previously only published as communications made welcome appearances, and a section of Volume XV of "Inorganic Syntheses" encompassed the preparation of some iron, ruthenium, and nickel dinitrogen complexes. The considerable technical difficulties presented by the bis(cyclopentadienyl)titanium–dinitrogen complexes and their reactions are being overcome and the complexities partially, if not completely, unravelled. A bis(pentamethylcyclopentadienyl)zirconium complex has provided the first well-characterized example of a complex with both bridging and terminally bound dinitrogen ligands.

The past five years has seen a shift in emphasis from group 8 metal complexes of dinitrogen to those of the earlier transition metals where the ligating dinitrogen molecule is apparently more reactive. In this context bis(dinitrogen) complexes of molybdenum and tungsten have proved invaluable precursors for the synthesis of derivatives with N-H or N-C bonds. However, the group 8 metals have not been neglected and osmium has provided the first example of a metal porphyrin dinitrogen complex. The ruthenium pentaammine dinitrogen system continues to be studied and is remarkable for the number of very different routes now available for its synthesis. Mention should also be made of the quite unprecedented nickel complex containing dinitrogen orthogonally bound in a side-on manner to a dinickel moiety. This unit is enclosed within a complex cluster of lithium atoms which are bound to phenyl groups.

The technique of matrix isolation has found increasing use during the period covered by this review, and a number of unusual transition metal dinitrogen species have been identified. As this field lies somewhat outside of the normal province of preparative inorganic chemistry, it has been allotted a separate section, II.D.

The preparations and characterizations of dinitrogen complexes included in this review are classified according to the metal to which the dinitrogen is bound (section II.C). The details of preparations, characterization, and spectroscopic measurements summarized in Tables I to VII are for those complexes first reported or completely described during the period covered by this review.

B. Methods of Preparation

The synthetic routes to dinitrogen complexes can be divided into three broad categories. Discussion of these is restricted to procedures that have appeared since the last comprehensive reviews, and references are given in the appropriate place in section C.

1. From Dinitrogen

These routes can either involve the reaction of dinitrogen with a preformed and isolated complex with replacement of labile neutral or anionic ligands by dinitrogen, or more conveniently, a single-stage reaction of a suitable complex with a reductant under dinitrogen. Respective examples are given in eq 1 and eq 2.

$$[MoCl_2(dppe)_2] \xrightarrow{NaBH_4} [MoH_4(dppe)_2] \xrightarrow{N_2} [Mo(N_2)_2(dppe)_2] \qquad (1)$$

$$[MoCl_3(thf)_3] \xrightarrow[dppe]{Mg/THF/N_2} [Mo(N_2)_2(dppe)_2] \qquad (2)$$

Selection of reducing agent is often all-important both in terms of a suitable reducing potential and convenience in workup procedures. Grignard magnesium turnings are especially convenient; they are readily available and separation of excess reducing agent is considerably easier than with a reductant such as sodium amalgam. Preliminary activation of the magnesium with iodine vapor in vacuo is often crucial.

Sometimes the reductant becomes assimilated into the final reaction product, as illustrated:

$$[CoCl_2(PMe_3)_2] \xrightarrow[PMe_3]{Mg/THF/N_2} [Mg\{(N_2)Co(PMe_3)_3\}_2(thf)_4] \qquad (3)$$

The preparation of molybdenum and tungsten monophosphine bis(dinitrogen) complexes of type $[M(N_2)_2(PR_3)_4]$ (Table II) may well involve analogous species, and treatment with methanol during workup is required to liberate the bis(dinitrogen) complexes free of magnesium.

The choice of reducible precursor is often also vital, as is again illustrated by the synthesis of molybdenum bis(dinitrogen) complexes, where better yields are obtained by the reduction of $[MoCl_3(thf)_3]$ rather than of other complexes such as $[MoCl_4(thf)_2]$. Such subtleties are not always easy to rationalize and account for the still essentially empirical state of the art of N_2-complex preparation. At present there is only an extremely limited range of coligands for N_2 complexes on which to base any really systematic approach to synthesis. Radically new types of N_2 complexes with, say, largely oxygen or sulfur environments for the metal will probably necessitate the development of quite new types of precursors and possibly new reducing agents.

2. Indirect Methods

There are a variety of routes to dinitrogen complexes involving generation of the dinitrogen ligand by reaction at a ligating N or N_2 moiety, or oxidation of a hydrazine. These are often specific for one metal, and few have any generality for the synthesis of dinitrogen complexes. Examples of this type of synthesis first reported during the period of this review are given in eq 4–8.

$$[M(\eta^5\text{-}C_5H_5)(CO)_2(N_2H_4)] \xrightarrow[-40\ ^\circ C]{H_2O_2/Cu^{2+}/THF} [M(\eta^5\text{-}C_5H_5)(CO)_2(N_2)] \qquad (4)$$

$$M = Mn, Re$$

$$[Mn(\eta^5\text{-}C_5H_5)(CO)_2(thf)] \xrightarrow{CF_3CHN_2/THF} [\{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}_2N_2] \qquad (5)$$

TABLE I. Dinitrogen Complexes of Titanium, Zirconium, and Niobium

complex	text no.	color	$\nu(N\equiv N)$,[a] cm^{-1}	preparation	comments	ref
$[\{Ti(\eta^5\text{-}C_5H_5)_2Pr^i\}_2(N_2)]$	**1**	dark blue		$[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2]$ + $2Pr^iMgCl + N_2$ in Et_2O at −80 °C	No elemental analyses reported; N_2 measured after reaction with HCl/MeOH	23
$[Ti(\eta^5\text{-}C_5H_5)_2(N_2)MgCl]$	**2**	dark blue	1255 (1215)	$[\{Ti(\eta^5\text{-}C_5H_5)_2Pr^i\}_2N_2]$ + Pr^iMgCl in Et_2O	Paramagnetic μ_{eff} = 1.1 BM/Ti; mode of attachment of Mg unknown	24
$[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$	**3**	dark blue	1280 (1240)	$[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2]$ + 2MeMgI + N_2 in Et_2O at −70 °C	Paramagnetic μ_{eff} (300 K) 1.45 BM; stable at 20 °C	25
$[\{Ti(\eta^5\text{-}C_5H_5)_2R\}_2(N_2)]$ (R = C_6H_5, *o*-, *m*-, *p*-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, C_6F_5, $C_6H_5CH_2$)	**4**	dark blue		$[Ti(\eta^5\text{-}C_5H_5)_2R]$ + N_2 in toluene at −20 °C in 47–60% yield	Complexes indefinitely stable in solid state under N_2 at −20 °C	28, 29
$[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$		dark blue		"$[Ti(\eta^5\text{-}C_5H_5)_2]$" + N_2 in toluene at −80 °C	No elemental analyses; N_2 measured after decomposition at −20 °C	30
$[\{Ti_2(\eta^5\text{-}C_5H_5)_3(C_5H_4)\}_2(N_2)]$		dark blue		$[(\eta^5\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1{:}\eta^5C_5H_4)Ti}\text{-}(\eta^5\text{-}C_5H_5)]$ in ether at −35 °C + N_2	Decompn at 20 °C in toluene; over 3d with loss of N_2	34
$[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$	**6**	blue-black needles		$[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2]$ + N_2 in pentane at 0 °C	Paramagnetic μ = 2.18 BM/Ti; X-ray structure (see text)	35, 36
$[\{Ti(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$	**7**	blue-purple	2023^h, 2056^h (−65 °C)	$[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2]$ + N_2 in toluene at −80 °C	Complex unstable above −80 °C in toluene	35
$[\{Zr(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)_3]$	**8**	red-purple	2041, 2006, 1556 (1972, 1937, 1515)	$[Zr(\eta^5\text{-}C_5Me_5)_2Cl_2]$ + Na/Hg + N_2 in toluene/20 °C/48 h, 30–40% yield	X-ray crystal structure (see text)	37, 38
$[\{Nb(\eta^5\text{-}C_5H_5)_2Bu^n\}_2(O_2)(N_2)]$		dark blue	1740 (ether)	$[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ + Bu^nLi in Et_2O under Ar with 0.1% N_2 and 0.1% O_2	Structure unknown, but as formulated would contain bridging O_2 and N_2 ligands	40
$[\{NbCl(dmpe)_2\}_2(N_2)]$		green		$[NbCl_4(dmpe)_2]$ + Mg + N_2 in THF in low yield		41

[a] $^{15}N_2$ values in parentheses; those labeled "h", in hexane solution.

$$[OsO_2(oep)] + N_2H_4 \cdot H_2O \xrightarrow[\text{reflux}]{\text{THF}} [Os(N_2)(thf)(oep)] \qquad (6)$$

$$[RuCl(N_3)(diars)_2] + [NO]PF_6 \xrightarrow{\text{MeOH}} [RuCl(N_2)(diars)_2]^+ \qquad (7)$$

$$\begin{tikzcd} {[Ru(NH_3)_5NO]^{2+} + OH^-} \arrow[dr] & \\ & {[Ru(NH_3)_5(N_2)]^{2+}} \quad (8) \\ {[Ru(NH_3)_6]^{3+} + NO} \arrow[ur] & \end{tikzcd}$$

References to and discussion of the reactions are given in section II.C under the heading of the metal concerned.

3. Metathesis

Equation 9, 10, and 11 illustrate the synthesis of new dinitrogen complexes from others by simple metathesis (see also Table XII). Such reactions again tend to be specific, and the high lability of many N_2 complexes, particularly those of titanium and the platinum group metals, almost entirely precludes any simple ligand exchange procedures.

$$[Mo(N_2)_2(dppe)_2] \xrightarrow[C_6H_6]{\text{RCN}} [Mo(N_2)(RCN)(dppe)_2] \qquad (9)$$

$$[OsCl_2(N_2)(PR_3)_3] \xrightarrow[\text{EtOH}]{NaBH_4} [OsHCl(N_2)(PR_3)_3] \qquad (10)$$

$$[ReCl(N_2)(PMe_2Ph)_4] \xrightarrow{\text{py}} [ReCl(N_2)(py)(PMe_2Ph)_3] \qquad (11)$$

The reactivity of the ligating N_2 is a very sensitive function of other coligands, and a simple metathetical reaction, such as eq 11, provides a convenient way of modifying the reactivity of the complex. This is shown in the rhenium system where replacement of tertiary phosphine by pyridine enormously increases the rate of acylation of the dinitrogen ligand (see section V.B.3).

C. Dinitrogen Complexes

1. Titanium, Zirconium, and Hafnium

Since the first report[20] of an uncharacterized but isolable dicyclopentadienyltitanium dinitrogen complex, this area has been intensively studied. At times considerable confusion has arisen over the nature of the dinitrogen complexes formed. Those which appear to be well characterized are included in Table I. This area has been reviewed in a recent book on the organometallic chemistry of titanium, zirconium, and hafnium[21] and is included in a review of nitrogen fixation.[22]

Shilov et al. reported[23] that $[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2]$ reacts with Pr^iMgCl in Et_2O at −80 to −100 °C in the presence of dinitrogen to give a dark blue complex formulated as $[\{Ti(\eta^5\text{-}C_5H_5)_2(Pr^i)\}_2(N_2)]$ (**1**). Two alternative structures were proposed for this compound with the Pr^i group attached either to titanium or to a cyclopentadienyl ring. Complex **1** was subsequently reported[24] to react further with Pr^iMgCl to give another paramagnetic, bridged dinitrogen complex, $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)MgCl]$ (**2**), which has $\nu(N_2)$ at 1255 cm^{-1} (1215 cm^{-1} for the $^{15}N_2$ derivative). If MeMgI, instead of Pr^iMgCl, were used in the first reaction above, only the paramagnetic complex $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ (**3**) was isolated.[25] Its proposed structure is based on partial analyses and the observation of $\nu(N_2)$ at 1280 cm^{-1} (1240 cm^{-1} for the $^{15}N_2$ derivative). Considerable doubt has now been cast on the formulation of complex **2** by the work of Teuben and co-workers[26,27] who have shown that reaction of N_2 complexes such as **1** with Grignard reagents causes loss of a cyclopentadienyl group. This is discussed in further detail in section V.B.1.

Titanium(III) complexes of the type $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2R]$ (R = Ph; *o*-, *m*-, or *p*-$CH_3C_6H_4$; 2,6-$Me_2C_6H_3$; 2,4,6-$Me_3C_6H_2$; CH_2Ph; or C_6F_5) react with dinitrogen in toluene at −20 °C to give $[\{\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2R\}_2(N_2)]$ (**4**). These compounds can be isolated as dark blue or purple, crystalline, diamagnetic materials which are sufficiently stable for complete characterization.[28,29]

The nature of the titanium(II) species "$[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2]$", presumed to be intermediate in the formation of the complex **3**, has been the subject of dispute, but the situation has been considerably clarified by recent work. Thus in an elegant study,[30] Brintzinger et al., have shown that hydrogenation of $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2Me_2]$ in benzene gives a polymeric hydride. On standing in ether at −60 °C it loses dihydrogen to give "$[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2]$" ("titanocene") which reacts rapidly with dinitrogen (eq 12). This

$$\begin{tikzcd}
{[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2Me_2]} \arrow[r, "H_2", "\text{benzene}"'] & {[\{\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2H\}_2]} \\
{} \arrow[r] & {[\{\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2H\}_x]} \arrow[d, "\text{ether, }-60\ ^\circ C"] \\
{[\{\mathrm{Ti}(\eta^5\text{-}C_5H_5)(C_5H_4)H\}_2]} & \text{"}[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2]\text{"} \arrow[l, "\text{toluene}"', "120\ ^\circ C"] \arrow[d, "N_2\ \text{toluene}\ -80\ ^\circ C"] \\
& {[\{\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]\quad (12)}
\end{tikzcd}$$

x is an unknown number>2

species, however, undergoes a rapid rearrangement in refluxing toluene to give a green product which is completely inert to dinitrogen. Recent spectroscopic studies[31] and an X-ray crystal structure of an analogous derivative with bridging hydroxy groups[32] suggest that this green material contains a bridging fulvalene ligand in addition to the bridging hydride groups. Thus a proton shift from a cyclopentadienyl ligand has occurred forming a dinitrogen-inert species from "titanocene". This effect probably accounts for much of the confusion, extant in the older literature, concerning the structure of the species in these systems which is responsible for binding dinitrogen.

Complexes of stoichiometry $[\{\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ are readily generated from "$[(\eta^5\text{-}C_5H_5)_2\mathrm{Ti}]$" and dinitrogen and, although superficially the same as complex **3** mentioned above, have somewhat different reported physical properties.

In a meticulous study, Pez has isolated and characterized by X-ray crystallography the compound $[(\eta^5\text{-}C_5H_5)_2\text{-}\underline{\mathrm{Ti}\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)\text{-}\mathrm{Ti}}(\eta^5\text{-}C_5H_5)]$, which, at least empirically, closely resembles the "titanocene" discussed above.[33] This dinuclear complex also reacts with dinitrogen, to give a deep blue compound of composition $[\{\mathrm{Ti}_2(C_5H_5)_3(C_5H_4)\}_2(N_2)]$ which appears to have a dinitrogen group bridging two metal dimer units.[34]

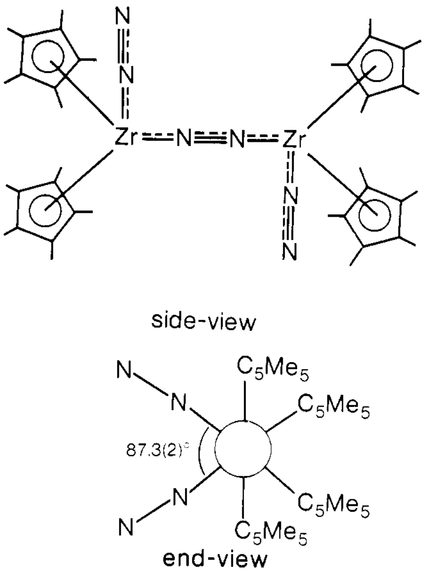
Whether some of these empirically similar compounds have the same structure is not clear, but obviously these titanium systems are complicated, partly as mentioned above because of the ease of hydrogen transfer from cyclopentadienyl groups. Substitution of (C_5H_5) by (C_5Me_5) gives more stable compounds which have been studied in a similar manner.

$$\begin{tikzcd}
{[\mathrm{Ti}(\eta^5\text{-}C_5Me_5)_2Me_2]} \arrow[r, "\text{toluene}", "110\ ^\circ C"'] & \text{"}[\mathrm{Ti}C_{10}Me_{10}CH_2]\text{"} \arrow[r, "\text{pentane}", "H_2\ 0\ ^\circ C"'] & {[\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)_2\}_2]\quad (13)} \\
& & \mathbf{5}
\end{tikzcd}$$

$$\begin{tikzcd}
{[\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)_2\}_2]} \arrow[r, "N_2", "0\ ^\circ C"'] \arrow[rd, "\text{toluene}", "-80\ ^\circ C\ N_2"'] & {[\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]} \\
\mathbf{5} \quad\quad \mathbf{6} & {[\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]\quad (14)} \\
& \mathbf{7}
\end{tikzcd}$$

Thus the analogue of titanocene with (C_5Me_5) ligands (**5**) has been prepared according to eq 13.[30a] Complex **5** is a red-brown, crystalline, dimeric compound which reacts with dinitrogen in two distinct stages (eq 14). The ^{15}N NMR spectrum of complex **7** shows a singlet and two doublets; this pattern was originally interpreted in terms of a mixture of complexes with end-on and side-on dinitrogen.[35] However, subsequent experiments[36] indicate that the formulation of **7** is probably incorrect and that it should be formulated $[\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$, similarly to its better characterized zirconium analogue (see below). Compound **6** has been shown by X-rays[36] to have a linear Ti—N═N—Ti unit with two independent molecules per unit cell (N-N distances 1.165 (14) and 1.155 (14) Å]. It is paramagnetic with $\mu_{\mathrm{eff}} = 2.18$ BM per titanium atom. The suggested bonding scheme for this compound and its zirconium analogue (below) resembles that already developed for such binuclear systems, the dominant interactions being between occupied titanium d-type orbitals and the vacant π^* dinitrogen orbitals and also between vacant titanium d-type orbitals and the filled π dinitrogen orbital. This leads to the observed weakening and lengthening of the N-N bond. The titanium electrons are placed singly into four molecular orbitals whose energy difference is estimated to be only 0.5 eV, but the reason for the low magnetic moment [about 2.87 BM is expected for high-spin Ti(II)] is not obvious, especially since its temperature dependence indicates little magnetic interaction between the titanium atoms.

Sodium amalgam reduction of $[\mathrm{Zr}(\eta^5\text{-}C_5Me_5)_2Cl_2]$ under dinitrogen gives $[\{\mathrm{Zr}(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$ (**8**) which is isolated as a diamagnetic red-purple solid.[37] The structure of this compound has been determined by X-rays,[38] and there are two terminal and one bridging dinitrogen ligands present in the molecule. The ^{15}N NMR spectrum of **8** prepared from $^{15}N_2$, in toluene at −28 °C, shows two doublets, assigned to the terminal dinitrogen ligands, centered 89.8 and 160.4 ppm upfield of a singlet due to the bridging dinitrogen ligand.[39]



8

In solution, the bridging and terminal dinitrogen groups give IR bands at 1556 (bridging) and 2006, 2041 (terminal) cm^{-1}, respectively, the assignment being confirmed by ^{15}N labeling. Treatment of **8** with $^{15}N_2$ gas shows that the terminal dinitrogen ligands can undergo rapid exchange, whereas the bridging dinitrogen ligand cannot.[39] So far, attempts to prepare the hafnium

TABLE II. Dinitrogen Complexes of Chromium, Molybdenum, and Tungsten

complex	text no.	color	$\nu(N\equiv N)$,[a] cm^{-1}	preparation	comments	ref
$[CrAr(CO)_2(N_2)]$ (Ar = C_6H_6, C_6Me_6, $C_6H_3Me_3$)	**9**	red-brown	2145^h (Ar = C_6H_6), 2112^h (Ar = C_6Me_6), 2132^h (Ar = $C_6H_3Me_3$)	For Ar = C_6H_6 by displacement of C_5H_8 from $[Cr(\eta^6\text{-}C_6H_6)(\eta^2\text{-}(C_5H_8)(CO)_2]$. For Ar = C_6Me_6, $C_6H_3Me_3$ by UV irradiation of tricarbonyl	Ar = C_6H_6, sublimable very air sensitive; Ar = C_6Me_6, $C_6H_3Me_3$ lose N_2 in solution to give dimers	42
$[\{CrAr(CO)_2\}_2(N_2)]$ (Ar = C_6Me_6, $C_6H_3Me_3$)	**10**	red		By solution of monomer	Not isolable	42
$[MoAr(N_2)(PR_3)_2]$ (Ar = C_6H_5Me, $C_6H_3Me_3$; PR_3 = PPh_3, PPh_2Me)	**12**	orange	1988^n, (Ar = C_6H_5Me, PR_3 = PPh_3), 1970^n (Ar = C_6H_5Me, PR_3 = PPh_2Me), 1975^n (Ar = $C_6H_3Me_3$, PR_3 = PPh_3)	(i) By $AlEt_3$ reduction of $[Mo(acac)_3]$ in toluene + N_2 + PPh_3 in ca. 10% yield; Ar = $C_6H_5CH_3$ only (ii) Displacement of H_2 from $[Mo(Ar)H_2(PR_3)_2]$ with N_2 in THF at 150 atm	Complexes decompose in benzene at 20 °C 50% yield	45, 46
cis-$[Cr(N_2)_2(PMe_3)_4]$	**11**	brown	1918, 1990^n	By Mg reduction of $[CrCl_2(PMe_3)_3]$ in THF at 25 °C under N_2	Decomposes at 20 °C with liberation of N_2 and PMe_3	43
$[\{Cr(dppe)_2\}_2(N_2)]$		brown		Mg reduction of $CrCl_2$ + dppe in THF at 20 °C, 7 days	Formulation based solely on analysis	44
$[\{Mo(\eta^6\text{-}C_6H_6)(PPh_3)_2\}_2(N_2)]$	**14**	maroon	1910 (R)	(i) Displacement of H_2 from $[Mo(\eta^6\text{-}C_6H_6)(H_2)(PPh_3)_2]$ with N_2 at 1 atm (ii) Bu^nLi reduction of $[\{Mo(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)Cl\}_2]$ in benzene under N_2 at 1 atm + PPh_3	Complexes moderately air stable as solids	46
$[\{Mo(\eta^6\text{-}C_6H_3Me_3)(dmpe)\}_2(N_2)]$	**15**	purple	1989^n (1923)	Na/Hg reduction of $[Mo(\eta^6\text{-}C_6H_3Me_3)(\eta^3\text{-}C_3H_5)\text{-}(dmpe)]PF_6$ in THF under N_2 at 1 atm, 40% yield	X-ray crystal structure shows N–N distance 1.145 (7) Å and Mo–N–N angle 175.6(4)° (see text)	47
$[\{Mo(\eta^6\text{-}C_6H_3Me_3)H(dmpe)\}_2\text{-}(N_2)]^{2+}$		red-brown	1937 vw^n	Protonation of dimeric dinitrogen complex 15 with HBF_4 in toluene/Et_2O at −95 °C	ν(Mo–H) at 1815 cm^{-1} Mo–H resonance at τ 14.62; BF_4^- salt water soluble	47
$[(\eta^6\text{-}C_6H_5Me)(PPh_3)_2Mo(N_2)Fe(\eta^5\text{-}C_5H_5)(dmpe)]BF_4$		brown	1930^n	$[Mo(\eta^6\text{-}C_6H_5Me)(N_2)(PPh_3)_2]$ + $[Fe(\eta^5\text{-}C_5H_5)\text{-}(dmpe)(Me_2CO)]BF_4$ in toluene	IR spectrum dependent on solvent of crystallization	46
trans-$[Mo(N_2)_2\{Ph_2P(CH_2)_n\text{-}PPh_2\}_2]$		orange	1995 ($n = 1$), 2020 w, 1970 ($n = 2$), 2010 w, 1975 $n = 3$	(i) $Mo(acac)_3$ + $AlEt_3$ + diphosphine + N_2 in toluene (ii) $[MoCl_2(diphosphine)_2]$ + Na/Hg + N_2 in THF (iii) $[MoCl_3(thf)_3]$ + Mg + 2 equiv of diphosphine + N_2 in THF up to 80% yield (iv) $[MoOCl_3(dppe)]$ + Zn + dppe + N_2 in THF	Complex with $n = 1$ not obtained pure X-ray crystal structure (see text)	50–56
$[Mo(N_2)_2\{(tol)_2PCH_2CH_2\text{-}P(tol)_2\}_2]$ (tol = *m*-$C_6H_4CH_3$)		orange	1960, $2017w^n$	$[MoH_4\{(tol)_2PCH_2CH_2P\text{-}(tol)_2\}_2]$ + N_2 (1 atm) in cyclohexane, 20 °C	*m*-Tolyl group confers good solubility	54
$[Mo(N_2)_2(Ph_2PCH{=}CHPPh_2)_2]$		orange	1970^n, 2002^n (cis), 2000^n (trans)	$[MoCl_3(thf)_3]$ + 2 equiv of diphosphine + Mg + N_2 (1 atm) in THF at 20°	Cis isomer formed initially, but rapidly rearranges to stable characterized trans isomer	56
$[Mo(N_2)_2(dppae)_2]$		yellow-orange	1964, $2032w^n$	$[MoCl_3(thf)_3]$ + Na/Hg + N_2 (1 atm) + $2Ph_2PCH_2CH_2AsPh_2$ in THF		59
trans-$[Mo(N_2)_2(dppae)_2]$		yellow	1971s, 2031w	$[MoCl_3(thf)_3]$ + Na/Hg + N_2 (1 atm) + $2Ph_2AsCH_2CH_2AsPh_2$ in THF	Much less stable than diphosphine analogues and too air-sensitive for complete characterization	59

TABLE II (*Continued*)

complex	text no.	color	$\nu(N{\equiv}N)$,[a] cm^{-1}	preparation	comments	ref
trans-$[MoX(N_2)(dppe)_2]$ (X = Cl, Br)	**17**	yellow	1966^n	(i) $[MoOCl_3(dppe)] + Zn + N_2$ + diphosphine in THF (ii) UV irradiation of MeX + $[Mo(N_2)_2(dppe)_2]$ in benzene at 40 °C, 62 h, X = Cl or Br	Paramagnetic μ_{eff} = 1.83 BM; may disproportionate in solution to *trans*-$[Mo(N_2)_2(dppe)_2]$ + $[MoX_2(dppe)_2]$	63
trans-$[Mo(N_2)_2(dppe)_2]A$ ($A = I_3^-, Br^-, Cl^-$)		red	2043^n (I_3^- salt)	$A = I_3^-$ from *trans*-$[Mo(N_2)(dppe)_2]$ + 1.5 mol of I_2 in MeOH	Paramagnetic μ_{eff} = 1.97 BM (I_3^- salt); Cl_2, Br_2 can be used as oxidants, but only I_3^- product characterized	60–62
trans-$[Mo(N_2)(p\text{-}XC_6H_4CN)(dppe)_2]$ (X = NH_2, OMe, Me, Cl, H, COMe)	**18**	orange	$1910–1965^n$ (depending on X)	*trans*-$[Mo(N_2)_2(dppe)_2]$ + nitrile (3 mol) in toluene at 20 °C/18 h	Linear plot for $\nu(N_2)$ vs ρ for X substituent; $\nu(C{\equiv}N)$ decreased by up to 125 cm^{-1} on coordination	67
trans-$[Mo(N_2)(CO)(dppe)_2]$	**19**	orange	$2080,^n 2110^n$	*trans*-$[Mo(N_2)_2(dppe)_2]$ $\xrightarrow[\text{reflux}]{DMF/C_6H_6}$ $[Mo(CO)(dmf)(dppe)_2]$ $\xrightarrow[C_6H_6]{N_2}$ $[Mo(CO)(N_2)(dppe)_2]$	$\nu(C{\equiv}O)$ 1812, 1791 cm^{-1}	69
$[Mo(N_2)_2(PR_3)_4]$ ($PR_3 = PMe_2Ph, PPh_2Me, PEt_2Ph$)		yellow-orange	$2025, 1940^b$ (PMe_2Ph), 1923^b (PEt_2Ph), 1925^b (PPh_2Me)	(i) $[MoCl_2(PR_3)_4]$ + Na/Hg + N_2 in THF at RT (ii) $[MoCl_4(PR_3)_2]$ + Na/Hg + $2PR_3$ + N_2 in THF (iii) $[MoCl_4(thf)_2]$ + Mg + N_2 + $4PR_3$ in THF	PMe_2Ph derivative has cis configuration; others are trans.	57, 58, 68, 72, 73
$[Mo(N_2)_2(PhSCH_2CH_2SPh)(PMe_2Ph)_2]$		red-purple		*cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ + $PhSCH_2CH_2SPh$ in toluene at −70 °C	Decomposes at 20 °C with evolution of N_2	68
trans-$[W(N_2)_2(dppe)_2]$		orange	1953^b	$[WCl_4(dppe)_2]$ + Mg + 1 dppe + N_2 in THF/20 °C	Probably isostructural with Mo analogue, 70–80% yield	57
trans-$[W(N_2)_2\{(tol)_2PCH_2CH_2P(tol)_2\}_2]$ (tol = $m\text{-}CH_3C_6H_4$)		orange	1930^n, $1992w^n$	$[WCl_4\{(tol)_2PCH_2CH_2P(tol)_2\}]$ + diphosphine + Mg + N_2 in THF/20 °C		58
$[WH(N_2)_2(dppe)_2][HCl_2]\cdot 2THF$		orange	1995^n	$[W(N_2)_2(dppe)_2]$ + 2 equiv HCl gas in THF	X-ray crystal structure shows pentagonal bipyramid with apical N_2 ligands	65, 66
cis-$[W(N_2)_2(PMe_2Ph)_4]$		orange	1931^b, 1998^b	$[WCl_4(PMe_2Ph)_3]$ + $1PMe_2Ph$ + N_2 + Mg in THF/20 °C	70% yield	58
trans-$[W(N_2)_2(PPh_2Me)_4]$		red	1910, $1975w^n$	$[WCl_4(PPh_2Me)_2]$ + $2PPh_2Me$ + Mg + N_2 in THF/20°C	20% yield	196

[a] (R) in parentheses indicates Raman, otherwise IR spectra; bands strong unless otherwise stated. b, benzene solution, n, Nujol mulls.

analogue have been unsuccessful and there are no reported hafnium dinitrogen complexes.

2. Vanadium, Niobium, and Tantalum

Although alkaline solutions of vanadium(II) in combination with magnesium(II) or catechol are efficient in reducing dinitrogen to hydrazine, there are no characterized vanadium dinitrogen complexes.

It was recently claimed[40] that reaction of $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ with Bu^nLi in ether under argon containing 0.1% of N_2 and O_2 gives the remarkable complex $[\{Nb(\eta^5\text{-}C_5H_5)_2Bu^n\}_2(O_2)(N_2)]$ in 40% yield. The presence of dinitrogen was confirmed by elemental analysis and an IR band at 1740 cm^{-1} is attributed to $\nu(N{\equiv}N)$, without confirmation by ^{15}N labeling. Mass spectroscopy is the only evidence advanced for the presence of the dioxygen ligand, a peak at *m/e* 296 being assigned to the $[Nb(\eta^5\text{-}C_5H_5)_2(Bu^n)O]^+$ ion. Reduction of $[NbCl_4(dmpe)_2]$ with magnesium in THF under nitrogen gives a complex formulated as $[\{NbCl(dmpe)_2\}_2(N_2)]$ which gives hydrazine in 20% yield on reaction with HCl in THF.[41]

3. Chromium, Molybdenum, and Tungsten

a. Chromium

Several of the dinitrogen complexes of chromium so far reported contain π-bonded, cyclic hydrocarbon ligands, and these are summarized in Table II. They are most generally prepared by replacement of a labile ligand such as cyclopentene:[42]

$$[Cr(\eta^6\text{-}C_6H_6)(CO)_2(\eta^2\text{-}C_5H_8)] \xrightarrow[\text{benzene}]{N_2} \underset{\mathbf{9}}{[Cr(\eta^6\text{-}C_6H_6)(CO)_2(N_2)]} \qquad (15)$$

The mesitylene and hexamethylbenzene analogues of **9** are best prepared by displacement of carbon monoxide from $[Cr(\eta^6\text{-}Ar)(CO)_3]$ (Ar = $C_6H_3Me_3$, or C_6Me_6) by dinitrogen under UV irradiation in THF. The IR and the UV changes that occur in solution during this reaction suggest that dinitrogen is lost from [Cr(η^6-Ar)(CO)$_2$(N$_2$)] to give the dinuclear species [{Cr(η^6-Ar)(CO)$_2$}$_2$(N$_2$)] (**10**) which were not isolated.[42]

Chromium N$_2$ complexes with tertiary phosphine ligands have been recently reported, reduction of [CrCl$_2$(PMe$_3$)$_3$] with magnesium in THF at 25 °C giving *cis*-[Cr(N$_2$)$_2$(PMe$_3$)$_4$] (**11**). The complex is rather unstable, decomposing at room temperature with loss of N$_2$ and PMe$_3$. The cis configuration is assigned on the basis of ^{1}H and ^{31}P NMR spectra and the presence of two strong IR bands at 1918 and 1990 cm^{-1} assignable to ν(N$_2$).[43] An analogous reduction using dppe produces a brown complex formulated as [{Cr(dppe)$_2$}$_2$(N$_2$)][44] which is considerably less well characterized than **11.** The formulation is based on elemental analysis and there are no IR bands assignable to ν(N$_2$). In view of the protracted time for the reaction the presence of nitride species cannot be ruled out.

b. Molybdenum and Tungsten

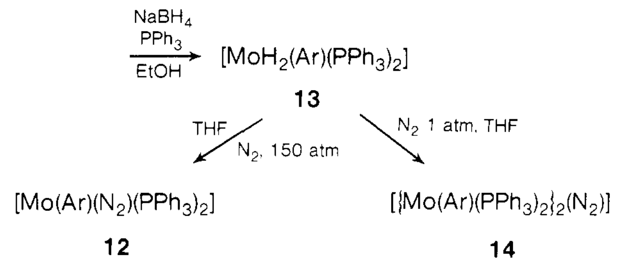
i. With Aromatic Hydrocarbon Ligands. The first reported dinitrogen complex of molybdenum, [Mo(η^6-C$_6$H$_5$Me)(N$_2$)(PPh$_3$)$_2$] (**12**), was prepared by the reduction of molybdenum tris(acetylacetonate) in toluene with triethylaluminum in the presence of a tenfold excess of triphenylphosphine.[45] The yield of this reaction was low (13%) and lower still if other aluminum compounds or less triphenylphosphine was used. No dinitrogen complexes at all were isolated if benzene or mesitylene were used as solvent. Subsequently, however, yields of about 50% were obtained by an indirect route which starts from bis(arene)molybdenum complexes (Scheme II).[46] These and other analogous complexes are summarized in Table II.

Treatment of the dihydride [Mo(C$_6$H$_6$)H$_2$(PPh$_3$)$_2$] (**13**) with dinitrogen at 1 atm gave the maroon dimeric complex **14** which has no IR bands in the 1800–2000-cm^{-1} region but shows a strong band at about 1970 cm^{-1} in its Raman spectrum. An analogue of **14** with a di(tertiary phosphine), [{Mo(η^6-C$_6$H$_3$Me$_3$)-dmpe}$_2$(N$_2$)] (**15**), has been prepared by sodium amalgam reduction of [Mo(η^6-C$_6$H$_3$Me$_3$)(η^3-C$_3$H$_5$)(dmpe)]PF$_6$ in THF under dinitrogen.[47] The structure of **15** has been determined by X-rays and pertinent bond distances are shown below.[48] Although dimeric, **15** shows an IR band at 1989 cm^{-1} which is shifted to 1923 cm^{-1} in its ^{15}N$_2$ derivative. Protonation of **15** with HBF$_4$ in toluene yields [{Mo(η^6-C$_6$H$_3$Me$_3$)H(dmpe)}$_2$(N$_2$)](BF$_4$)$_2$ which has ν(N–N) at 1937 cm^{-1} and ν(Mo–H) at 1815 cm^{-1} in its IR spectrum.[47]

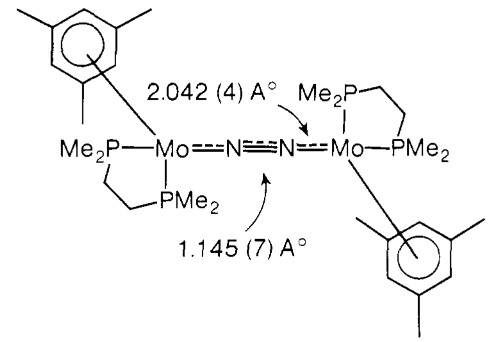
The mononuclear complex [Mo(η^6-C$_6$H$_5$Me)(N$_2$)(PPh$_3$)$_2$] (**12**) reacts with [Fe(η^5-C$_5$H$_5$)(Me$_2$CO)(dmpe)]BF$_4$ to give the heteronuclear complex [(η^6-C$_6$H$_5$Me)(PPh$_3$)$_2$Mo(N$_2$)Fe(η^5-C$_5$H$_5$)(dmpe)]BF$_4$ which has ν(N$_2$) at 1930 cm^{-1}.[46]

Sodium amalgam reduction of [Mo(η^5-C$_5$H$_5$)$_2$Cl$_2$] in THF under argon gives a 30% yield of polymeric "molybdenocene" [{Mo(η^5-C$_5$H$_5$)$_2$}$_n$]. Although this compound absorbs 1 mol of dinitrogen at low temperature, the resulting dinitrogen complex decomposes on warming the solution. The pentamethylcyclopentadienyl analogue of "molybdenocene" is a much more stable, yellow, crystalline, dimeric material but does not appear to form a stable dinitrogen complex.[49]

SCHEME II



Ar = C$_6$H$_6$ only for **13**



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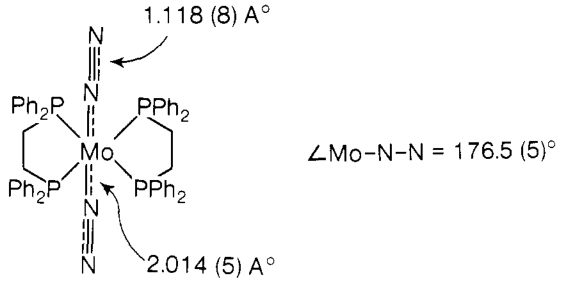
ii. With Tertiary and Ditertiary Phosphines and Related Ligands. If in the preparation of [Mo(η^6-C$_6$H$_5$Me)(N$_2$)(PPh$_3$)$_2$] from [Mo(acac)$_3$] mentioned above, a di(tertiary phosphine), dppe, is added instead of triphenylphosphine, the complex *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (**16**) can be isolated in low yield.[50] The trans configuration of complex **16** has been confirmed by X-rays, and the essential geometry and some bond lengths are shown in structure **16.**[51] Several different preparative routes to this complex and its analogues with variations in reducing agents and molybdenum precursor have been published[52–56] (see Table II). The tungsten analogues are best prepared by the magnesium reduction of [WCl$_4$(P–P)] [P–P = di(tertiary phosphine)] in THF under dinitrogen in the presence of 1 mol of the di(tertiary phosphine).[57,58]



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The stability of molybdenum complexes is highly dependent on the value of n in Ph$_2$P(CH$_2$)$_n$PPh$_2$, and pure compounds can be isolated only for n = 2 or 3 and with the diphosphine Ph$_2$PCH═CHPPh$_2$.[56] Substitution of phosphorus atoms by arsenic atoms decreases the stability of the resulting dinitrogen complex and although *trans*-[Mo(N$_2$)$_2$(dppae)$_2$] has been well characterized, *trans*-[Mo(N$_2$)$_2$(dpae)$_2$] is too unstable to be purified.[59]

The cationic molybdenum(I) complexes [Mo(N$_2$)$_2$(dppe)$_2$]$^+$ can be generated by halogen or electrochemical oxidation of **16**, and the triodide salt has been partially characterized.[60–62] [MoCl(N$_2$)(dppe)$_2$] (**17**) was first reported as a product of the zinc reduction of [MoOCl$_3$(dppe)] in the presence of dppe but was not characterized other than by observation of ν(N$_2$) at 2035 and 1985 cm^{-1} in its IR spectrum in chloroform solution.[52] It was later reported that complex **17** and its bromide analogue could be prepared analytically pure by UV irradiation of **16** in benzene in the presence of an alkyl halide.[63] However, since products with identical spectroscopic properties to **17** can be generated by mixing equimolar amounts of [MoCl$_2$(dppe)$_2$] and **16** in THF, it seems very probable that **17** is a cocrystallized mixture of the two.[64] Diazenido complexes can also be formed by the reaction of **16** with alkyl halides, and these reactions are discussed in more detail in section V.B.3.

Addition of 2 equiv of HCl gas to $[W(N_2)_2(dppe)_2]$ in THF gives the cationic hydride complex $[WH(N_2)_2(dppe)_2]HCl_2$ isolated as a THF solvate. The IR spectrum shows an intense band at 1995 cm^{-1} assigned to $\nu(N_2)$.[65] The X-ray crystal structure of the complex shows a pentagonal-bipyramidal structure with the N_2 ligands in apical sites.[66] Under similar conditions $[Mo(N_2)_2(dppe)_2]$ loses both N_2 ligands to give $[MoCl_2H_2(dppe)_2]$.

One of the dinitrogen ligands of **16** can be displaced by organonitriles to give *trans*-$[Mo(N_2)(RCN)(dppe)_2]$ (**18**) (R = Me, Et, *p*-$NH_2C_6H_4$, *p*-$OMeC_6H_4$, *p*-MeC_6H_4, C_6H_5, *p*-ClC_6H_4, *p*-$MeCOC_6H_4$). In these complexes the C≡N stretching frequency is lowered from that of the free ligand and $\nu(N_2)$ lies in the range 1915–1966 cm^{-1}. The complexes **18** have been assigned a trans structure on the basis of their single ^{31}P NMR resonance. Facile displacement of the organonitrile ligand makes these complexes convenient precursors for the formation of diazenido and related species by reaction with organic halides (section V.B.3).

Carbon monoxide displaces both N_2 ligands from **16** to give first *trans*- and then *cis*-$[Mo(CO)_2(dppe)_2]$.[68] The carbonyl–dinitrogen complex $[Mo(CO)(N_2)(dppe)_2]$ (**19**) is prepared by the following indirect route. Complex **16** reacts with DMF in benzene to give $[Mo(CO)(dmf)(dppe)_2]$, and the DMF ligand is displaced by dinitrogen to give **19**.[69] The dinitrogen can be removed in vacuo producing the five-coordinate carbonyl $[Mo(CO)(dppe)_2]$.[70]

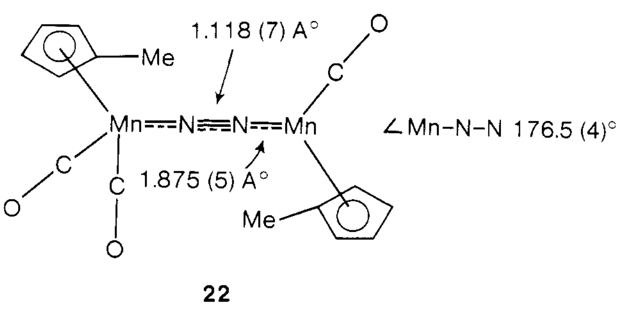
Molybdenum and tungsten bis(dinitrogen) complexes with mono(tertiary phosphines) have been prepared using a variety of precursors and reducing agents[57,58,68,72,73] (see Table II). $[MCl_2(PR_3)_4]$ or $[MCl_4(PR_3)_{2or3}]$ (M = Mo or W; PR_3 = PMe_2Ph, PEt_2Ph, or $PMePh_2$) have been used in THF with sodium amalgam, sodium sand, or magnesium as reductants in the presence of stoichiometric amounts of the tertiary phosphine. The presence of an excess of the phosphine lowers the yields. The range of complexes that can be prepared is limited and only complexes with PMe_2Ph, PEt_2Ph, and $PMePh_2$ have been characterized. Two of the phosphine ligands of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ can be replaced by the disulfide $PhSCH_2CH_2SPh$, but the resulting deep purple dinitrogen complex is only stable at low temperatures.[68] The observation of two strong IR bands assignable to $\nu(N_2)$ indicates a cis configuration for the dinitrogen complex with PMe_2Ph coligands, but the $PMePh_2$ and PEt_2Ph complexes show one strong and one very weak N_2 band, so presumably have trans dinitrogen ligands.

4. Manganese, Technetium, and Rhenium

The preparation and properties of the dinitrogen complexes of this group are summarized in Table III.

a. Manganese

All the reported dinitrogen complexes of manganese contain cyclopentadienyl ligands and the first, $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$ (**20**), was prepared by the action of dinitrogen at atmospheric or higher pressures on $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(thf)]$[74] (**21**) or by the controlled oxidation of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2H_4)]$ with hydrogen peroxide in the presence of copper(II) salts at −40 °C.[75] The binuclear complexes $[\{Mn(\eta^5\text{-}RC_5H_4)(CO)_2\}_2(N_2)]$ (**22**) (R = H or Me) have been obtained by reaction of **21** with 1,1,1-trifluorodiazoethane or diazoethane in an ether–THF mixture. The structure of **22** was confirmed by the X-rays as shown in the diagram.[76]



22

The authors suggest that the preparation of **22** does not involve simple thermal or catalytic cleavage of dinitrogen from the diazo compound since, as indicated above, **21** gives only the mononuclear complex **20** with dinitrogen. The initial formation of a terminally coordinated diazoethane complex is suggested and is supported by the isolation of a stable diazo complex from diethyl diazomalonate.

b. Rhenium

i. Mononuclear Complexes. The rhenium analogue of the manganese complex **20** above has been prepared by the controlled oxidation of $[Re(\eta^5\text{-}C_5H_5)(CO)_2(N_2H_4)]$ under similar conditions to those used for the preparation of **20**.[7778]

The full details of the preparation (Scheme III) of a series of rhenium(I)–dinitrogen complexes by the degradation of a chelated benzoyldiazenido complex have appeared.[70] A considerable range of complexes with both monodentate and bidentate tertiary phosphines, carbonyl and other ligands have been prepared and are summarized in Table III. Some typical preparative reactions are summarized in Scheme III.

The structure of complex **24** has been determined by X-rays.[80] Disordering of the Cl and N_2 ligands in the crystal prevented an accurate determination of the N–N bond length. However, despite the very low $\nu(N_2)$ value for **24** (1925 cm^{-1}), its N–N distance (1.06 Å) appears to be essentially the same as that found in other mononuclear dinitrogen complexes showing higher $\nu(N_2)$ values. The rhenium(I)–dinitrogen complexes are readily oxidized to provide a corresponding series of rather unstable paramagnetic salts.[79]

One of the phosphine ligands of **24** or its analogues can be replaced by pyridine or by substituted pyridines to give the complexes of type **25** (Scheme II).[81,82] Because of the lability of the heterocyclic ligand in these complexes they are suitable as precursors for a limited range of derivatives with N–C bonds (see section V.B.3). Treatment of **24** with the sodium salts of dithiocarbamates or related ligands gives complexes of the general type $[Re(S_2CNR'_2)(N_2)(PMe_2Ph)_3]$ (**26**) (R′ = Me, Et). Complexes **26** lose their dinitrogen on reaction with acids to give dithiocarbamato-hydrido complexes (see section IV.A).[83]

The ammonium salt of rhenium enneahydride, $[NH_4]_2[ReH_9]$, reacts with 2 equiv of dppe in propan-2-ol under dinitrogen to give the rhenium(I)–hydrido–dinitrogen complex $[ReH(N_2)$-

SCHEME III

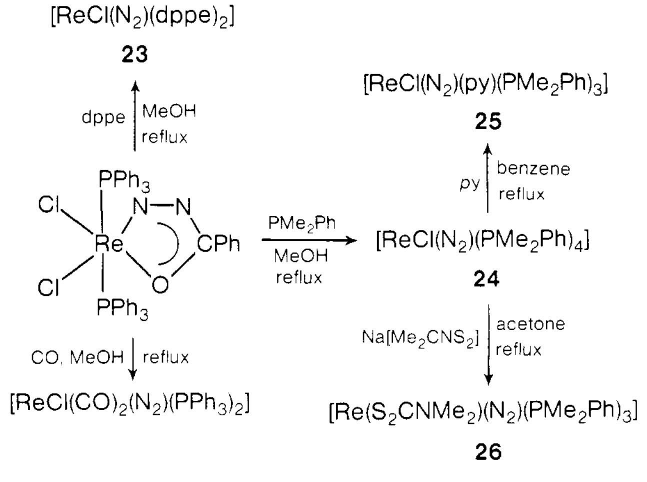


TABLE III. Dinitrogen Complexes of Manganese and Rhenium

complex	text no.	color	$\nu(\mathrm{N{\equiv}N})$,[a] cm^{-1}	preparation	comments	ref
[Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)]	**20**	red-brown	2169^h	[Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$H$_4$)] + H$_2$O$_2$ + Cu^{2+} in THF at −40 °C in 40% yield	Complex sublimable 10^{-4} mmHg/20 °C: ν(C≡O) 1980, 1923 cm^{-1}; N$_2$ reversibly displaced by THF; complex air stable	74, 75
[{Mn(η^5-C$_5$H$_4$R)(CO)$_2$}$_2$(N$_2$)] (R = H or CH$_3$)	**22**	light brown	1975 (R = H), 1971 (R = Me)	[Mn(η^5-C$_5$H$_4$R)(CO)$_2$thf] + CF$_3$CHN$_2$ at −80 °C in THF	X-ray structure for R = Me, yield low (see text)	76
[Re(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)]		yellow	2141^h	[Re(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$H$_4$)] + H$_2$O$_2$ + Cu^{2+} in THF at −20 °C/0.5 h	Complex sublimable 10^{-4} mmHg/20 °C: ν(C≡O) 1970, 1915 cm^{-1}; 30% yield, air stable	77, 78
[ReCl(N$_2$){Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$] (n = 1, 2, 3)	**23**	yellow	1980^c (n = 1, 2), 1950^c (n = 3)	[ReCl$_2$(N$_2$COPh)(PPh$_3$)$_2$] + 2 equiv of diphosphine in refluxing methanol, 60–70% yield	^{31}P NMR suggests N$_2$ trans to Cl	79
[ReCl(N$_2$)(Ph$_2$PCH═CH-PPh$_2$)$_2$]		yellow	1980^c	As above using Ph$_2$PCH═CHPPh$_2$		79
[ReCl(N$_2$)(dppae)$_2$]		yellow	1961^n	As above using dppae	Complexes with Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ or *o*-phenylenebis-(dimethylarsine) cannot be isolated pure	79
[ReCl(N$_2$)(PR$_3$)$_4$] (PR$_3$ = PMe$_2$Ph, PPh$_2$Me, Me$_2$NPF$_2$, PPh$_2$H, P(CH$_2$OH)$_3$)		yellow	1925^c (PMe$_2$Ph), 1925^c (PMePh$_2$), 2075^c (Me$_2$NPF$_2$), 2010^c (PPh$_2$H), 2000^n [P(CH$_2$OH)$_3$]	As above using 4 equiv of appropriate mono(tertiary or secondary phosphine)	P(CH$_2$OH)$_3$ complex not fully characterized, but indefinitely stable in water; X-ray crystal structure for PMe$_2$Ph complex; trans Cl and N$_2$ disordered (see text)	79
[ReCl(N$_2$)L$_2$(PPh$_3$)$_2$] (L = PF$_3$, PH$_2$Ph, P(OCH$_2$)$_3$CMe)		yellow	2090^c (PF$_3$), 2000^c (PH$_2$Ph), 2035^n [P(OCH$_2$)$_3$CMe]	As above using 2 equiv of PH$_2$Ph or P(OCH$_2$)$_3$CMe or with excess PF$_3$ in a sealed tube		79
[ReCl(N$_2$){P(OMe)$_3$}$_2$-(PMe$_2$Ph)$_2$]		yellow	2000^b	[ReCl$_2$(N$_2$COPh)(PMe$_2$Ph)$_3$] + P(OMe)$_3$ + Et$_3$N in refluxing methanol		79
[ReCl(CO)$_2$(N$_2$)(PR$_3$)$_2$] (PR$_3$ = PPh$_3$, PEtPh$_2$, PPh$_2$Pr^n)		yellow	2105^c (PPh$_3$),^{b} 2100^c (PEtPh$_2$), 2080^c (PPh$_2$Pr^n)	CO bubbled through refluxing methanol suspension of [ReCl$_2$(N$_2$COPh)(PPh$_3$)$_2$] or [ReCl$_2$(N$_2$COPh)(PR$_3$)$_3$]	ν(C≡O)^b 2020, 1935 (PPh$_3$); 2055, 1920 (PEtPh$_2$); 2005, 1920 (PPh$_2$Pr^n)	79
[ReCl(N$_2$)L(PMe$_2$Ph)$_3$] (L = py, 3-picoline, 4-picoline, pyridazine)		orange	1905^n (py), 1910^n (3-, 4-picoline), 1930, 1940^n (pyridazine)	[ReCl(N$_2$)(PMe$_2$Ph)$_4$] + L in benzene at reflux	Lability of L renders complexes good precursors for N–C bond formation	81, 82
[ReL(N$_2$)(PMe$_2$Ph)$_3$] (L = S$_2$CNMe$_2$, S$_2$CNEt$_2$, S$_2$COEt, S$_2$PPh$_2$)	**26**	red (except for S$_2$PPh$_2$, which is yellow)	1945^n (S$_2$CNMe$_2$, S$_2$CNEt$_2$), 1964^n (S$_2$COEt), 1940^n (S$_2$PPh$_2$)	[ReCl(N$_2$)(PMe$_2$Ph)$_4$] + L in acetone at reflux	N$_2$ readily displaced with acids to yield hydrido complexes	83
[ReH(N$_2$)(dppe)$_2$]	**27**	yellow	2006^n	[Et$_4$N][ReH$_9$] + 2dppe in propan-2-ol under N$_2$ at 25 °C	Reacts with alkyl halides, RX → [ReX(N$_2$)(dppe)$_2$] (X = Cl, Br, I); τ(Re–H) 19.94 (quartet)	84
[ReH$_2$(N$_2$)(dppe)$_2$]BF$_4$		yellow	2118^n	[ReH(N$_2$)(dppe)$_2$] + 1 equiv of HBF$_4$ in benzene	τ(Re–H) 19.40 (quartet)	84
[ReCl(N$_2$)(dppe)$_2$]A (A = Cl$^-$, Br$_3^-$, I$_3^-$, BF$_4^-$, PF$_6^-$, FeCl$_4^-$, CuCl$_2^-$)		pink-purple or green	2005^c	[ReCl(N$_2$)(dppe)$_2$] + halogen in CH$_2$Cl$_2$ or with AgNO$_3$, FeCl$_3$, or CuCl$_2$ in MeOH, followed by anion exchange for BF$_4$ and PF$_6$ salts	Paramagnetic; EPR in CHCl$_3$ glass shows 2 signals with *g* values 1.64 and 2.00; exist as green and purple isomers in the solid state	79
			Polynuclear Complexes			
[TiCl$_4${(N$_2$)ReCl(PMe$_2$Ph)$_4$}$_2$]	**28**	dark blue	1812^n	2[ReCl(N$_2$)(PMe$_2$Ph)$_4$] + TiCl$_4$ in dry CH$_2$Cl$_2$ at 20 °C	Crystallizes with 2 mol of CH$_2$Cl$_2$; very air sensitive, hydrolyses to regenerate Re(I)–N$_2$ complex	85

TABLE III. (*Continued*)

complex	text no.	color	$\nu(N{\equiv}N)$,[a] cm^{-1}	preparation	comments	ref
$[TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}(thf)]$	**29**	purple	1740^n	$[ReCl(N_2)(PMe_2Ph)_4]$ + $TiCl_4$ in CH_2Cl_2/THF at 20 °C	Very air sensitive	85
$[ReCl(N_2)(PMe_2Ph)_4{\cdot}Ti_2Cl_6O(Et_2O)]$	**30**	deep red	$1622w^n$	$[ReCl(N_2)(PMe_2Ph)_4]$ + excess $TiCl_4$ in CH_3Cl_2 at 20 °C precipitated with Et_2O	Structure and bonding of titanium moiety not known; O probably from Et_2O	85
$[CrCl_3\{(N_2)ReCl(PMe_2Ph)_4\}(thf)_2]$	**31**	dark violet	1860^n $(1815)^n$	$[ReCl(N_2)(PMe_2Ph)_4]$ + $[CrCl_3(thf)_3]$ in CH_2Cl_2 at 20 °C	Paramagnetic μ_{eff} 4.07 BM; adduct reacts with O_2 faster than parent N_2 complex → $[ReCl(N_2)(PMe_2Ph)_4]^+$	86
$[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$	**32**	purple	1660^n	$[ReCl(N_2)(PMe_2Ph_4]$ + $[MoCl_4(thf)_2]$ in CH_2Cl_2/MeOH at 20 °C	X-ray crystal structure (see text); air-sensitive; μ_{eff} 1.85 BM	87, 88
$[MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]$	**33**	green	1800^n	$2[ReCl(N_2)(PMe_2Ph)_4]$ + $[MoCl_4(PPh_3)_2]$ in CH_2Cl_2 at 20 °C	X-ray crystal structure (see text); diamagnetic	89

[a] Superscript n, Nujol mull; b, benzene solution; c, chloroform solution; h, hexane solution. [b] N≡N and C≡O vibrations are coupled.

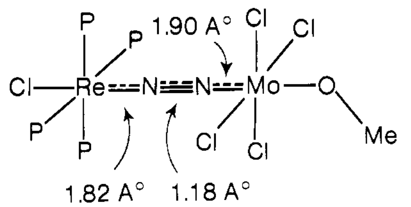
$(dppe)_2]$ (**27**).[84] This complex shows a hydride resonance in its NMR spectrum as a quartet at τ 19.94 and its $\nu(N_2)$ (2006 cm^{-1}) is some 20–30 cm^{-1} higher than those of analogous halido complexes. The protonation of **27** with HBF_4 occurs at the metal to give the Re(III)-dihydrido complex $[ReH_2(N_2)(dppe)_2]BF_4$ which has $\nu(N_2)$ at 2118 cm^{-1} and a quartet pattern at τ 19.40 in its ^1H NMR spectrum, assigned to the hydrido ligands.[84] The dinitrogen complexes **24** also undergo protonation at the metal with HBF_4, but the resulting compounds are too unstable to be satisfactorily characterized.[79]

ii. Polynuclear Complexes. The rhenium(I) complex $[ReCl(N_2)(PMe_2Ph)_4]$ (**24**) behaves as a ligand to other metal centers to give dinitrogen-bridged di- and trinuclear complexes. This is a general reaction with all types of metal acceptor species, but the most stable complexes are formed with the earlier transition metal centers in their higher oxidation states. Some of these latter complexes have now been fully characterized and are detailed in Table III.

Titanium tetrachloride reacts with 2 equiv of **24** in dichloromethane to give the deep-blue, very air-sensitive trinuclear complex $[TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]{\cdot}2CH_2Cl_2$ (**28**) which has $\nu(N_2)$ at 1812 cm^{-1} in its IR spectrum. The dinuclear $[TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}(thf)]$ (**29**) is obtained from equimolar mixtures of **24** and $TiCl_4$ in THF. Complex **29** is an intensely purple, very air-sensitive material with $\nu(N_2)$ at 1740 cm^{-1}. Treatment of an excess of $TiCl_4$ with **24** in dichloromethane, followed by the addition of diethyl ether, precipitates a red product of stoichiometry, $ReCl(N_2)(PMe_2Ph)_4Ti_2Cl_6OEt_2O$ (**30**), which has $\nu(N_2)$ at the exceptionally low value of 1622 cm^{-1}. The structure of **30** is unknown and it is not easy to visualize how the $Ti_2Cl_6O{\cdot}Et_2O$ unit is bound to the dinitrogen ligand.[85]

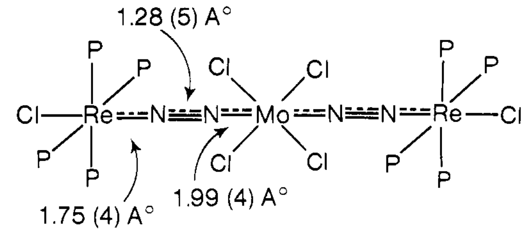
The dinitrogen ligand of **24** displaces one thf ligand from $[CrCl_3(thf)_3]$ to give paramagnetic, violet $[CrCl_3\{(N_2)ReCl(PMe_2Ph)_4\}(thf)_2]$ (**31**) with $\nu(N_2)$ at 1860 cm^{-1} (1815 cm^{-1} in the $^{15}N_2$ derivative).[86] Complex **31** is more oxygen sensitive than is the parent dinitrogen complex **24**, and it is rapidly cleaved in solution to give a cationic dinitrogen complex of rhenium(II). The UV spectrum of the dinuclear complex **31** shows an intense absorption at about 18 600 cm^{-1} which has been assigned on the basis of a simple four-center π-molecular-orbital model.[86] The application of this scheme to rationalize the spectroscopic properties of heteronuclear dinitrogen-bridged complexes has been discussed in detail in a previous review.[1]

Both binuclear and trinuclear complexes formed by reaction of **24** with acceptor moieties of molybdenum have been fully characterized by X-ray crystal structure determinations. Thus $[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$ (**32**) is prepared by the reaction of **24** with $[MoCl_4(thf)_2]$ in dichloromethane in the presence of methanol. It is isolated as air-sensitive, purple crystals with μ_{eff} = 1.85 BM and $\nu(N_2)$ at 1660 cm^{-1}. Its crystal structure[87,88] shows a considerable lengthening of the N–N bond relative to **24** (1.21 Å; cf. 1.06 Å in **24**). This lengthening is accompanied by a shortening of the Re–N and Mo–N bonds to 1.79 and 1.89 Å, respectively, compared to typical values of 1.97 Å for Re–N and 2.13 Å for Mo–N. The Re–N–N–Mo system is linear with a delocalized π system, and the structures of the titanium and chromium adducts **29** and **31** are probably analogous.



32, P = PMe_2Ph

Two equivalents of **24** react with $[MoCl_4(PPh_3)_2]$ in dichloromethane to give the dark green, diamagnetic, trinuclear product $[MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]$ (**33**) which has $\nu(N_2)$ at 1800 cm^{-1}. An X-ray crystal structure[89] has confirmed the presence of a linear $Re–N_2–Mo–N_2–Re$ system, and although the data were not sufficient for a detailed discussion of bond lengths, the N–N bond distances are significantly longer than that of the parent complex **24**. The titanium complex **28** and the analogous trinuclear tungsten complex, prepared from $[WCl_4(PPh_3)_2]$ and **24**, are presumably isostructural with **33**.



33, P = PMe_2Ph

Both **24** and its carbonyl analogue form 1:1 adducts with tri-

TABLE IV. Dinitrogen Complexes of Iron

complex	text no.	color	$\nu(N{\equiv}N)$,[a] cm^{-1}	preparation	comments	ref
$[\{Fe(\eta^5\text{-}C_5H_5)(dppe)\}_2(N_2)]^{2+}$	**34**	orange	2040 (R)	$[Fe(\eta^5\text{-}C_5H_5)(CO)(dppe)]^+$ irradiated in acetone under N_2 at −30 °C, 75% yield	N_2 readily displaced by acetone at 20 °C	93
$[\{Fe(\eta^5\text{-}C_5H_5)(dmpe)\}_2(N_2)]^{2+}$		orange	2054 (R)	$[Fe(\eta^5\text{-}C_5H_5)(dmpe)I] + TlBF_4 + N_2$ at 0 °C in acetone followed by NH_4PF_6 in H_2O		92
$[FeH_2(N_2)(PR_3)_3]$ ($PR_3 = PEtPh_2$, PBu^nPh_2, PPh_3, $PMePh_2$)	**35**	yellow	2058^n ($PMePh_2$), 2055^n ($PEtPh_2$), 2060^n (PBu^nPh_2), 2074 (PPh_3), (2008)	$FeCl_2 + 3PR_3 + NaBH_4 + N_2$ in EtOH at −10 °C in 70% yield; air also used as source of N_2 (30% yield)	$\nu(Fe{-}H)$ 1960w, 1855 cm^{-1} ($PEtPh_2$); 1950w, 1863 cm^{-1} (PBu^nPh_2); 1881w ($PMePh_2$)	94–97
$[FeH(N_2)L]BPh_4$ [L = $P(CH_2CH_2PPh_2)_3$, $N(CH_2CH_2PPh_2)_3$]		yellow-green	2100^n $[P(CH_2CH_2PPh_2)_3]$, 2090^n $[N(CH_2CH_2PPh_2)_3]$	$[FeXL]BPh_4$ (X = Cl, Br) + $NaBH_4 + N_2$ in EtOH at 20 °C	$\nu(Fe{-}H)$ 1945 cm^{-1} $[P(CH_2CH_2PPh_2)_3]$; 1925 cm^{-1} $[N(CH_2CH_2PPh_2)_3]$; complexes diamagnetic and probably octahedral	98
$[FeH(N_2)(dppe)_2][BPh_4]$			2130^ns	$[FeH(dppe)_2]BPh_4 + N_2$ in THF at 20 °C	Air can also be used as source of N_2; more stable than depe analogue, $\nu(Fe{-}H)$ 1880 cm^{-1}	
$[FeH(Pr^i)(PPh_3)_2(N_2)Fe(Pr^i)(PPh_3)_2]$		red	1761^nw (1704)	$[FeCl_3(PPh_3)_2] + Pr^iMgCl + N_2$ in Et_2O at −50 °C	Paramagnetic μ_{eff} 3.3 BM (20 °C); as isolated contains Et_2O of solvation; very air sensitive	104, 105
$[\{FeCl(depe)_2\}_2(N_2)][BPh_4]_2$		red-orange	2081^nw	$[FeCl_2(depe)_2] + NaBPh_4 + N_2$ in MeOH at 20 °C		101
$[Fe(N_2)(dppe)_2]$		red	2068^n	$[Fe(1,5\text{-}C_8H_{12})_2]$ + dppe + N_2 in Et_2O–methylcyclohexane at 0 °C	First reported Fe(0) N_2 complex	103

[a] (R), Raman spectrum; n, Nujol mulls; figures in parentheses for $^{15}N_2$ derivatives; s, strong.

methylaluminum, which are readily hydrolyzed to regenerate the dinitrogen or carbonyl complex. Competition with diethyl ether enabled the relative base strengths of the terminal nitrogen of a number of dinitrogen complexes to be determined, and this is discussed in more detail in section V.A.

With $[ReOCl_3(PPh_3)_2]$ and **24** the equilibrium

$$[ReCl(N_2)(PMe_2Ph)_4] + [ReOCl_3(PPh_3)_2] \rightleftharpoons [ReCl_3O\{(N_2)ReCl(PMePh)_4\}(PPh_3] + PPh_3 \quad (16)$$

is established in chloroform solution. The addition of triphenylphosphine displaces the equilibrium completely to the left. Two IR bands at 1820 and 1843 cm^{-1} were assigned to $\nu(N_2)$ in the dinuclear product and the equilibrium constant (K_{eq}) was calculated from integrated IR intensities to be 0.28 ± 0.03 at 27 °C. $[ReCl_2O(OMe)(PPh_3)_2]$ similarly forms a dinuclear complex, but K_{eq} is only 0.004 ± 0.002 at 27 °C.[91]

5. Iron, Ruthenium, and Osmium

a. Iron

i. With Cyclic Hydrocarbon Ligands. The dinitrogen-bridged complex $[\{Fe(\eta^5\text{-}C_5H_5)(dmpe)\}_2(N_2)]^{2+}$ is prepared by extraction of the iodide ligand from $[Fe(\eta^5\text{-}C_5H_5)(dmpe)I]$ with thallous tetrafluoroborate in acetone at 0 °C under dinitrogen.[92] The N-N stretching vibration is not IR active, but it appears in the Raman spectrum of the BF_4^- salt at 2054 cm^{-1}. The dppe analogue **34** of this salt is obtained by photochemical substitution of carbon monoxide by dinitrogen in the complex $[Fe(\eta^5\text{-}C_5H_5)(CO)(dppe)]PF_6$ in acetone at −30 °C. The dinitrogen ligand of **34** is labile and is readily replaced by acetone at room temperature.[93]

ii. With Tertiary Phosphine Ligands. The displacement by dinitrogen of two hydride ligands from $[FeH_4(PR_3)_2]$, prepared in situ by the borohydride reduction of iron(II) chloride in the presence of the tertiary phosphine, gives the dinitrogen complexes $[FeH_2(N_2)(PR_3)_3]$ ($PR_3 = PEtPh_2$, PBu^nPh_2, $PMePh_2$, and PPh_3) (**35**). Air can also be used as the source of dinitrogen in these preparations and the complexes can then be isolated in about 30% yield; their spectroscopic properties are summarized in Table IV. The potentially quadridentate ligands $P(CH_2CH_2PPh_2)_3$ (P-triphos) and $N(CH_2CH_2PPh_2)_3$ (N-triphos) form the cationic complexes $[FeXL]BPh_4$ (X = Cl or Br; L = P-triphos or N-triphos). These complexes can then be reduced to give the trihydrides $[FeH_3L]$ which in turn form the dinitrogen complexes $[FeH(N_2)L]$, presumably with L still functioning as a quadridentate ligand.[98]

The five-coordinate hydride complex $[FeH(dppe)_2]BPh_4$ adds dinitrogen at atmospheric pressure in THF to give $[FeH(N_2)(dppe)_2]BPh_4$ (**36**) and again air can be used as the source of dinitrogen.[99] Complex **36** is more stable than its depe analogue which has been prepared by extraction of halide ion from $[FeHCl(depe)_2]$ under dinitrogen.[100] One halide ion in the complexes $[FeCl_2(P{-}P)_2]$ (P-P = dmpe, depe) is readily displaced by methanol, and subsequent reaction with N_2 and tetraphenylborate ion yields $[\{FeCl(P{-}P)_2\}_2(N_2)][BPh_4]_2$. A weak IR band at 2081 cm^{-} is assigned to $\nu(N_2)$.[101]

Iron vapor reacts with cycloocta-1,5-diene in methylcyclohexane to give thermally unstable bis(cycloocta-1,5-diene)iron.[102] Addition of an ether solution of dppe to the iron bis(diene) complex in methylcyclohexane under argon gives a species which decomposes to iron metal at 0 °C. However, in the presence of dinitrogen, red, cyrstalline $[Fe(N_2)(dppe)_2]$ is formed,

TABLE V. Dinitrogen Complexes of Ruthenium and Osmium

complex	text no.	color	ν(N≡N),[a] cm^{-1}	preparation	comments	ref
$[RuH_2(N_2)(PPh_3)_3]$	**37**	off-white	2147^n	$[RuHCl(PPh_3)_3] + AlEt_3 + N_2$ in Et_2O at 20 °C in 76% yield	ν(Ru–H) 1947, 1917 cm^{-1}	106
$[RuH_2(N_2)(Ptol_3)_3]$ (tol = *p*-$CH_3C_6H_4$)		off-white	2130^n	$[RuCl_2(Ptol_3)_3] + NaBH_4 + N_2$ in EtOH at 20 °C in 35% yield	More soluble than PPh_3 analogue	106
$[RuCl(N_2)(diars)_2]BPh_4$	**38**	cream	2131^n	$[RuCl(N_3)(diars)_2] + NO^+PF_6^-$ or $NO_2^+SbF_6^-$ or dry HCl in methanol		107
$[\{Ru(H_2O)_5\}_2(N_2)][BF_4]_4$		gold-brown	2080^k	$[Ru(H_2O)_6]^{2+} + N_2$ at 5 atm in 1 N HBF_4		113
$[(H_2O)(NH_3)_4Ru(N_2)Os(NH_3)_5]^{4+}$				*cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+} + [Os(NH_3)_5(N_2)]^{2+}$ in aqueous solution	Dimer not isolable in absence of $[Ru(NH_3)_4(H_2O)_2]^{2+}$; Can be oxidized to 5+ cation	114, 115
$[OsHCl(N_2)(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph, $PEtPh_2$)		white	2049, 2024^n (PMe_2Ph); 2077, 2046^n (PEt_2Ph); 2070, 2044^n ($PEtPh_2$)	$[OsCl_2(N_2)(PR_3)_3] + NaBH_4$ in refluxing EtOH	ν(Os–H) 1912 cm^{-1} (PMe_2Ph), 1936 cm^{-1} (PEt_2Ph), 1934 cm^{-1} ($PEtPh_2$); bromide and deuterio analogues prepared	119
$[Os(N_2)(thf)$(octaethylporphyrin)], oep = octaethylporphyrin		dark violet	2030^n	(i) $[OsO_2(oep)] + N_2H_4{\cdot}H_2O$ in THF at reflux under N_2 (ii) $[OsO_2(oep)] + AlHBu^i_2 + N_2$ in THF at 20 °C	Air-stable as solid, but thermolabile in solution	120
$[(H_2O)(NH_3)_4Os(N_2)Os(NH_3)_5](tos)_5{\cdot}H_2O$		green	2005^k	$2[Os(NH_3)_5(N_2)]^{2+} + [Os(NH_3)_4(N_2)_2]^{2+}$ in H_2O at 70 °C under Ar; isolated as tosylate salts	Complexes produced as mixture from preparation, separated by ion-exchange chromatography; blue adduct not isolated, identified by UV	122
$[Cl(NH_3)_4Os(N_2)Os(NH_3)_5](tos)_4{\cdot}H_2O$		green	2115^k 1995(R)[a]			
$[(N_2)(NH_3)_4Os(N_2)Os(NH_3)_5]^{5+}$ (tos = *p*-$CH_3C_6H_4SO_2^-$)		blue				
$[\{OsCl(NH_3)_4\}_2(N_2)]Cl_2{\cdot}H_2O$		green	1999(R)[a]	$[Os(NH_3)_4(N_2)_2]^{2+}$ heated to 70 °C in water, purified by ion-exchange chromatography by elution with 3 N HCl		123

[a] n, Nujol mulls; k, KBr disk; a, aqueous solution.

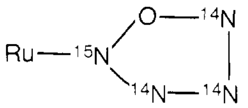
which has $\nu(N_2)$ at 2068 cm^{-1}.[103]

The reduction of $[FeCl_3(PPh_3)_2]$ with isopropylmagnesium chloride in diethyl ether at −50 °C under dinitrogen gives a dimeric complex formulated as $[(PPh_3)_2(Pr^i)HFe(N_2)Fe(Pr^i)(PPh_3)_2]$ which has $\nu(N_2)$ in its IR spectrum at 1761 cm^{-1} (1704 cm^{-1} in its $^{15}N_2$ derivative).[104] The integrated intensity of the Raman-active dinitrogen band is greater than the corresponding IR-active band, in accord with the proposed dinuclear structure. The complex is paramagnetic ((μ_{eff} at room temperature 3.3 BM), and the observed decrease in magnetic moment with decreasing temperature is attributed to an intramolecular exchange interaction.[105]

b. Ruthenium

i. With Tertiary Phosphine or Arsine Ligands. The ruthenium analogue of complexes **35**, $[RuH_2(N_2)(PPh_3)_2]$ (**37**), results from the triethylaluminum reduction of $[RuHCl(PPh_3)_3]$ in diethyl ether at room temperature under dinitrogen.[106] This off-white, diamagnetic complex is reasonably air stable and has $\nu(N_2)$ at 2147 cm^{-1} in its IR spectrum. Inner diazonium salts of $[B_{10}H_{10}]^{2-}$ such as $[N_2B_{10}H_8SMe_2]$ displace dinitrogen from **37** to give very stable derivatives of the type $[(PPh_3)_2H_2Ru(N_2)B_{10}H_8SMe_2]$ with a dinitrogen-bridged $Ru–N_2–B$ system. These yellow complexes are indefinitely air stable and have $\nu(N_2)$ between 2000 and 2135 cm^{-1} in their IR spectrum. The $Ru–N_2–B$ system is sufficiently inert to withstand attack by hydrogen chloride or sodium borohydride.[106]

The degradation of ligating azide ion by $NO^+PF_6^-$, $NO_2^+SbF_6^-$, or HCl has been utilized to prepare the very stable complex $[RuCl(N_2)(diars)_2)]^+$ (**38**) from $[RuCl(N_3)(diars)_2]$.[107] The mechanism of this reaction is not entirely clear, as $[RuCl(^{15}N^{14}N_2)(diars)_2]$ (ligated by the ^{15}N atom, prepared from $[RuCl(^{15}NO)(diars)_2]$ and hydrazine-^{14}N) gives an 80% yield of **38** with an $^{15}N^{14}N$ ligand and a 20% yield of **38** with $^{14}N_2$ as ligand. Although formation of the $^{15}N^{14}N$ species can be rationalized in terms of the cyclic transition state **39**, it is extremely



39

difficult to explain the formation of the Ru-($^{14}N_2$) species on this basis. The Ru-($^{15}N^{14}N$) complex is produced exclusively from the reaction of $[RuCl(^{15}N^{14}N_2)(diars)_2]$ with $NO_2^+SbF_6^-$, and it was proposed that the dinitrogen ligand is derived from an intermediate dinitrogen oxide complex which could not be isolated.[107] An analogous degradation of an $Ru–N_2O$ species to a dinitrogen complex is known for the ruthenium-pentaammine complex $[Ru(NH_3)_5(N_2O)]^{2+}$ (see section ii.)[108–110] The dinitrogen complex **48** can also be prepared, in low yield, together with $[RuCl(NH_3)(diars)_2]^+$, by the action of dry hydrogen chloride in methanol on $[RuCl(N_3)(diars)_2]$. The exclusive formation of the Ru($^{15}N^{14}N$) complex from the labeled azide derivative is consistent with protic attack at the nitrogen atom furthest from the metal, followed by elimination of the NH radical.[107]

ii. With Ammonia and Related Ligands. A remarkable feature of the chemistry of the dinitrogen complexes of the ruthenium-pentaammine series is the large number of quite different routes available for their preparation. Dinitrogen oxide can be used as the source of the dinitrogen ligand and $[Ru(NH_3)_5(H_2O)]^{2+}$ reacts with N_2O to give $[Ru(NH_3)_5(N_2)]^{2+}$ (**40**).[108,109] An intermediate, unstable dinitrogen oxide complex has now been isolated using high pressures of dinitrogen oxide, and its IR spectrum was interpreted in terms of an O-bonded dinitrogen oxide ligand.[110]

The reaction of the ligating nitrosyl of $[Ru(NH_3)_5(NO)]^{3+}$ with hydroxide ion gives a 25% yield of **40** together with *cis-* and *trans-*$[Ru(NH_3)_4(OH)(NO)]^{2+}$. The mechanism of this reacton is believed to involve the intramolecular interaction of bound NO and NH_2 as indicated in eq 17.[111]

$$[Ru(NH_3)_5(NO)]^{3+} \xrightarrow{OH^-} [Ru(NH_3)_4(NH_2)(NO)]^{2+}$$

$$\xrightarrow{[Ru(NH_3)_5(NO)]^{3+}} [(NH_3)_5Ru\{N(O)NH_2\}Ru(NH_3)_4(NO)]^{5+}$$

$$\xrightarrow{OH^-} [Ru(NH_3)_5(N_2)]^{2+} + [Ru(NH_3)_4(OH)(NO)]^{2+} \quad (17)$$

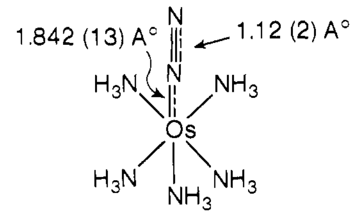
A related reaction is that of $[Ru(NH_3)_6]^{3+}$ with NO at pH 12, which gives a quantitative yield of **40** and is believed to proceed via an attack of NO on ligating NH_2.[112] The hexaaquoruthenium(II) cation can be generated in 0.1 M trifluoromethylsulfonic acid solution by the reduction of $[RuCl_5(H_2O)]^{3+}$ by dihydrogen. It reacts with dinitrogen under pressure to give the golden-brown cation $[\{Ru(H_2O)_5\}_2(N_2)]^{4+}$. This complex, isolated as its tetrafluoroborate salt, shows a weak IR band at 2080 cm^{-1} which is assigned to $\nu(N_2)$.[113]

The formation of the heterodinuclear complex $[(NH_3)_4(H_2O)Ru(N_2)Os(NH_3)_5]^{4+}$ in solution from $[Os(NH_3)_5(N_2)]Cl_2$ and $[Ru(NH_3)_4(H_2O)_2]^{2+}$ was followed spectrophotometrically by the appearance of a UV band at 257 nm. The dinuclear complex was not isolated, but it could be oxidized by one unit in solution at +0.10 V using a platinum electode. Ananation experiments indicated that the oxidation states of the metals within the oxidized complex were distributed in the sense $[(H_2O)(NH_3)_5Ru^{III}\text{-}N_2\text{-}Os^{II}(NH_3)_5]^{5+}$ because the aquo ligand was readily replaced by chloride at the ruthenium center, such a substitution being unlikely if the ruthenium were in oxidation state (II).[114,115] On chlorine oxidation of **40** chloride replaced the dinitrogen ligand to give $[Ru(NH_3)_5Cl]Cl_2$ which forms a series of solid solutions with **40** giving a modification of the cubic lattice of the dinitrogen complex. The considerable lowering of $\nu(N_2)$ (up to 20%) found in these solid solutions was attributed to a shortening of the Ru-N_2 bond length due to steric compression caused by the substitution of dinitrogen ligands by chloride.[116]

c. Osmium

The dinitrogen ligand of the complexes $[OsCl_2(N_2)(PR_3)_3]$[117,118] (PR_3 = PMe_2Ph, PEt_2Ph, or $PEtPh_2$) is inert to attack by sodium borohydride in refluxing ethanol, but chloride is replaced by hydride to give the hydrido-dinitrogen complexes $[OsHCl(N_2)(PR_3)_3]$.[119] The reaction of hydrazine with $[Os(O_2)(oep)]$ (oep = octaethylporphyrin) in tetrahydrofuran provides the first example of a complex in which dinitrogen has a porphyrin coligand, $[Os(N_2)(thf)(oep)]$. This complex can also be synthesized by the reduction of $[Os(O_2)(oep)]$ under dinitrogen with $AlHBu^i_2$.[120]

The osmium pentaammine-dinitrogen complexes, in contrast to their ruthenium analogues, have received little attention, but an X-ray structure (**41**) of $[Os(NH_3)_5(N_2)]Cl_2$ has been described.[116] It shows no particularly unusual features; the N-N distance is 1.12 Å and the Os-N-N angle is 178.3°, and, unlike its ruthenium analogue, there are no disorder problems.[121]



∠Os-N-N = 178.3 (1.3)°

41

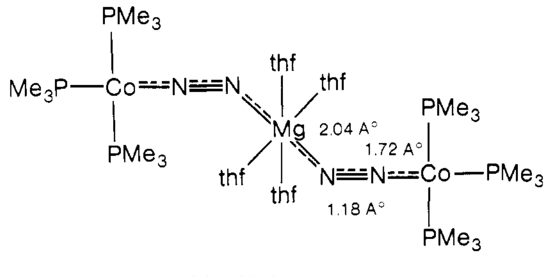
The green dinitrogen-bridged complex $[\{OsCl(NH_3)_4\}_2(N_2)]^{2+}$ [$\nu(N_2)$ 1999 cm^{-1} in its Raman spectrum] has been prepared by the elution, in 3 M HCl solution from an ion-exchange column,[122] of the product of heating $[Os(NH_3)_4(N_2)_2]Cl_2$[123] to 70 °C in water. Similar treatment of a 2:1 mixture of **41** and $[Os(NH_3)_4(N_2)_2]Cl_2$ gave a mixture of two further, dinuclear complexes, $[(NH_3)_4(H_2O)Os(N_2)Os(NH_3)_5]^{5+}$ and $[Cl(NH_3)_4Os(N_2)Os(NH_3)_5]^{4+}$, which were isolated as their 4-toluenesulfonate salts.[122]

6. Cobalt, Rhodium, and Iridium

a. Cobalt

The preparation of $[CoH(N_2)(PPh_3)_3]$ (**42**) by reduction of $[Co(acac)_3]$ with $AlBu^i_3$ in ether under dinitrogen has been described in detail.[124] There was initial controversy over the formulation of this dinitrogen complex which was previously given as $[Co(N_2)(PPh_3)_3]$,[125,126] but it appears to have been resolved by the confirmation of the presence of the hydrido ligand by ^1H NMR spectroscopy. The assignment of an IR band at 2088 cm^{-1} in the IR spectrum of the dinitrogen complex to $\nu(N_2)$ has been proved by its shift to 2026 cm^{-1} in the $^{15}N_2$ analogue. Analogues can also be obtained by hydrolysis of the anionic complexes $Na[Co(N_2)(PR_3)_3]$ (**43**) (PR_3 = PEt_2Ph or PEt_3). The latter were prepared by reduction of $[CoCl_2(PR_3)_2]$ with sodium sand in THF under dinitrogen in the presence of an excess of the tertiary phosphine. Without the excess of phosphine, dark brown dinuclear complexes $[\{Co(PR_3)_3\}_2(N_2)]$ were obtained, presumably via a disporportionation reaction. The presence of a single, bridging dinitrogen ligand was confirmed by the liberation of dinitrogen (0.5 mol/Co atom) by thermal decomposition of the complexes.[127] The IR spectra of the cobalt-dinitrogen complexes are summarized in Table VI.

If magnesium is employed as the reductant for $[CoCl_2(PMe_3)_2]$, a novel heteronuclear complex (**44**) is produced. It contains a cobalt dinitrogen-magnesium bridging unit which is bent at the nitrogen atom ligating the magnesium.[128]

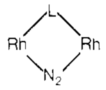


∠Mg-N-N = 158°

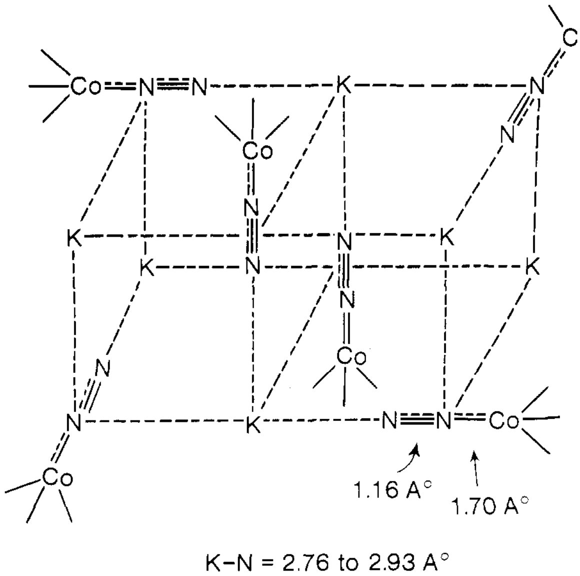
44

A potassium salt of **43** (**45**) can be obtained either by reaction of the complexes $K[Co(olefin)(PMe_3)_3]$ with N_2 or by potassium reduction of the trinuclear complex **44**. In **45** the monoclinic unit cell contains four $K[Co(N_2)(PMe_3)_3]$ molecules. Each dinitrogen molecule is bound terminally to a cobalt atom and also interacts in both an end-on and side-on fashion with potassium ions as

TABLE VI. Dinitrogen Complexes of Cobalt, Rhodium, and Iridium

complex	text no.	color	$\nu(N{\equiv}N)$,[a] cm^{-1}	preparation	comments	ref
$[CoH(N_2)(PPh_3)_3]$	**42**	orange	2088^t (2026)	$[Co(acac)_3] + PPh_3 + AlBu^i_3 + N_2$ in Et_2O at −50 °C, yield 69%	Previously formulated $[Co(N_2)(PPh_3)_3]$; X-ray crystal structure	124
$Na[Co(N_2)(PR_3)_3]$ ($PR_3 = PEt_2Ph, PPh_3$)	**43**	black	1840^n	$[CoCl_2(PR_3)_2] + PR_3 +$ Na sand $+ N_2$ in THF at 20 °C	Diamagnetic, reacts with water to give $[CoH(N_2)(PPh_3)_3]$	127
$K[Co(N_2)(PMe_3)_3]$	**45**	orange	1795s, $1758m^n$, 1868s, $1843m^{THF}$	$K[Co(olefin)(PMe_3)_3] + N_2$ in ether at 20 °C in 85% yield	X-ray crystal structure (see text)	129
$[\{Co(PR_3)_3\}_2(N_2)]$ ($PR_3 = PEt_2Ph, PPh_3$)		dark brown		$2[CoCl(PR_3)_3]$ + Na sand $+ N_2$ in THF at 20 °C	Liberates 0.5 mol of N_2/Co on thermal decomposition	127
$[\{Co(PMe_3)_3(N_2)\}_2Mg(thf)_4]$		orange	2068^h, 2058^t	$CoCl_2 + PMe_3 + Mg$ in THF under N_2, 3 days, 20 °C 70% yield	X-ray crystal structure (see text)	128
$K_2[\{Rh(NO_2)_3(NH_3)(OH)\}_2(N_2)]$		white	2070 (R), (2045)	$K[Rh(NO_2)_4(NH_3)_2]\cdot\frac{1}{2}H_2O + (NH_4)_2SO_4$ in H_2O at pH 1–2 at 100 °C for ½h in 20–30% yield	Liberates 0.5 mol of N_2/Rh on thermal decomposition at 180 °C	135
$[RhCl(N_2)(Pcy_3)_2]$ (cy = cyclohexyl)			2103^n	$[RhCl(Pcy_3)_2S]$ (S = solvent molecule) $+ N_2$ in THF at 20 ° for 5 days	Much more stable than PPh_3 analogue	130, 131
$[RhCl(\eta^2\text{-}N_2)(PPr^i_3)_2]$		orange	2100^n	$[\{RhCl(C_8H_{12})_2\}_2] + N_2 + PPr^i_3$ in pentane at 20 °C	X-ray crystal structure (see text)	134
$[Rh_2(L_3)_2(R_1CONCO)(L_1)(N_2)]$		white		Dimeric complexes of type $[\{Rh(CO)L_3\}_2L_1]$ + furoyl azide in $CHCl_3$ at 20 °C	Doubly bridged systems of the  type proposed where $L = L_1$ or L_2	136
$[Rh_2(L_3)_2(R_1CONCO)(L_2)(N_2)]$		white				
$[Rh_2(L_4)_2(R_1CONCO)(L_1)(N_2)]$						
$[L_3Rh(N_2)(L_1)Rh(N_3)_2(R_2CONCO)\text{-}L_3]$			2030^n	Complexes of type $[\{Rh(CO)\text{-}L_3\}_2L_1]$ + butyric azide in $CHCl_3$ at 20 °C	$\nu(N_3)$ 2070 cm^{-1}; terminal N_2 ligands postulated; bands assigned to $\nu(N_2)$ and $\nu(N_3)$ shift in 50 cm^{-1} to lower frequency using ^{15}N labeled azide	136
$[L_3Rh(N_2)(L_2)Rh(N_3)_2(R_2CONCO)\text{-}L_3]$ (L_1 = 1,4-$(Ph_2PCH_2)_2$-C_6H_4, L_2 = 1,3-$(Ph_2P)_2C_6H_4$, L_3 = acac, L_4 = oxine; R_1 = furoyl, $R_2 = Pr^n$)			2030^n			
$[RhH(N_2)(PPhBu^t_2)_2]$		yellow	2155^n	$[RhCl_3\,3H_2O] + PPhBu^t$ + Na/Hg(1%) $+ N_2$ in THF (15 h, 20 °C)	Air sensitive; $\nu(Rh\text{–}H)$ 1977 cm^{-1}; X-ray crystal structure (see text)	133
$[IrCl(N_2)(P\text{-polymer})_2]$ (P-polymer = polymer–PPh_2)		yellow	2095^n	$[IrCl(CO)(P\text{-polymer})_2]$ + p-$O_2NC_6H_4CON_3$ in $CHCl_3$	Polymer = cross-linked polystyrene	138

[a] t, solution in toluene; n, Nujol mull; ^{15}N in parentheses; R, Raman.



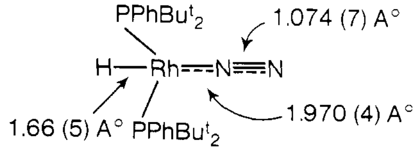
K–N = 2.76 to 2.93 A°

45

illustrated in the structure **45**. The IR spectrum of a Nujol mull of **45** shows bands at 1795 and 1758 cm^{-1} assigned to $\nu(N{\equiv}N)$, which shift to 1868 and 1843 cm^{-1} on solution in THF.[129] The IR spectrum of complex **43** shows a band at 1840 cm^{-1} in a Nujol mull, suggesting that the alkali cation–dinitrogen interactions do not occur in the solid state in the sodium salt.

b. Rhodium

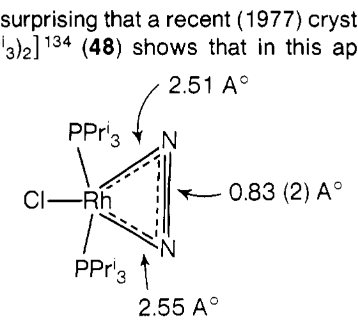
The square-planar complex $[RhCl(N_2)(Pcy_3)_2]$ (**46**) (Pcy_3 = tricyclohexylphosphine) has been prepared by displacement of a solvent molecule (S) from $[RhCl(Pcy_3)_2(S)]$ by dinitrogen at atmospheric pressure.[130,131] That complex **46** is considerably more stable than its triphenylphosphine analogue[132] is attributed to steric shielding of reactive sites at the rhodium atom. The complex $[RhH(N_2)(PPhBu^t_2)_2]$ (**47**) has been prepared by sodium



47

amalgam reduction of $RhCl_3 \cdot 3H_2O$ under N_2 in the presence of the phosphine. Some of its X-ray structural parameters are shown, the H-Rh-N-N system being essentially linear.[133] If Pcy_3 is used in this reaction $[\{RhH(Pcy_3)_2\}_2(N_2)]$ is obtained, and the analogue of **47** with Pcy_3 as ligand can only be obtained by reaction of $[RhH_3(Pcy_3)_2]$ with N_2. Surprisingly the Pcy_3 derivative is less stable than **47** and loses N_2 in solution.

In view of the structural confirmation of end-on dinitrogen in **47** it is rather surprising that a recent (1977) crystal structure of $[RhCl(N_2)(PPr^i_3)_2]$[134] (**48**) shows that in this apparently very similar complex the dinitrogen molecule is side-on. Disorder problems between chloride and N_2 prevented accurate N-N bond distance determination, but important bond lengths are shown in structure **48.** This is the first mononuclear side-on dinitrogen complex, and it is somewhat unexpected that $\nu(N_2)$ should be so close in frequency in the complexes **47** and **48** (2155 and 2100 cm^{-1}). This difference is about that normally found in substitution of trans chloride by hydride without a change in coordination of the N_2. Complex **48** was prepared by the action of dinitrogen on $[\{RhCl(C_8H_{14})_2\}_2]$ in pentane at room temperature in the presence of PPr^i_3. The dioxygen and ethylene complexes $[RhCl(O_2)(PPr^i_3)_2]$ and $[RhCl(C_2H_4)(PPr^i_3)_2]$ were prepared analogously. On the basis of this one example, it appears that the IR spectroscopic properties of side-on and end-on bound dinitrogen are very similar and that only relatively small changes in the dinitrogen binding site are necessary to change the dinitrogen binding mode.



48

The well-known interaction of nitrite ion with ammonium salts to give dinitrogen has been used as the basis for the preparation of some extraordinary rhodium complexes. A complex formulated as $K_2[\{Rh(NO_2)_3(NH_3)(OH)\}_2(N_2)]$ is obtained from treatment of $K[Rh(NO_2)_4(NH_3)_2]$ with ammonium sulfate at pH 1 and 100 °C for 12 h.[135] A band in its IR spectrum at 2070 cm^{-1} was assigned to the bridging dinitrogen ligand and if $(^{15}NH_4)_2SO_4$ was used as reagent this band was shifted to 2045 cm^{-1}, the shift corresponding to that calculated for an $^{15}N{\equiv}^{14}N$ ligand. These complexes are not fully characterized and together with some analogous platinum derivatives must, in the absence of further data, be regarded with considerable reservation.

A number of equally unusual compounds (see Table VI) have been reported as the products of reactions of rhodium(I) carbonyl complexes, such as $[\{Rh(CO)L_3\}_2L_1]$ (L_3 = acac and L_1 = 1,4-$Ph_2PCH_2C_6H_4CH_2PPh_2$) with aroyl azides in chloroform,[136] an analogous reaction to that used to prepare $[IrCl(N_2)(PPh_3)_2]$.[137] The product obtained from this reaction depends on the azide used: with furoyl azide the complex products are assigned the structure (**49**) which contains bridging L_1 and bridging dinitrogen. In view of the geometric requirements of the two bridging ligands, such a structure seems highly unlikely. With butyric azide, products containing terminal dinitrogen ligands such as $[L_3Rh(N_2)L_1Rh(N_3)_2(Pr^nCONCO)L_3]$ were postulated. Bands at 2030 and 2070 cm^{-1} in the IR spectra of these products were assigned to $\nu(N_2)$ and $\nu(N_3)$, respectively, both bands being shifted some 50 cm^{-1} to lower frequency in the product obtained by using ^{15}N-labeled butyric azide. However, in the absence of further characterization, these products all seem highly questionable, and it is possible that the IR bands assigned to $\nu(N_2)$ may in fact be due to azido ligands.

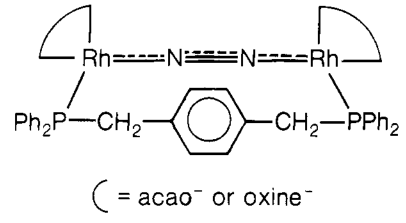
c. Iridium

Diphenylphosphino groups can be attached to a polystyrene cross-linked polymer by sequential bromination and lithiation, followed by reaction with Ph_2PCl, giving about a 10% substitution of the diphenylphosphino group on to the polymer. The resulting resin reacts with $[IrCl(CO)(PPh_3)_2]$ to release 2 mol of PPh_3 per iridium and give a resin-bonded Ir(I) carbonyl derivative.[138] This derivative reacts with *p*-nitrobenzoyl azide to give a resin-bound dinitrogen complex which has $\nu(N_2)$ at 2095 cm^{-1} compared to the value of 2105 cm^{-1} for the long-established complex *trans*-$[IrCl(N_2)(PPh_3)_2]$. The supported dinitrogen complex shows the expected IR spectral changes when it undergoes oxidative-addition reactions with reagents such as dihydrogen. The iridium(III) dinitrogen complex $[Ir(Me)Cl(SO_2CF_3)(N_2)(PPh_3)_2]$ has been prepared from *trans*-$[IrCl(N_2)(PPh_3)_2]$ and CF_3SO_2Me.[139]

7. Nickel, Palladium, and Platinum

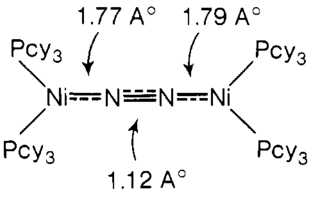
a. Nickel

The preparation, in 50% yield, of the dark red complex $[\{Ni(Pcy_3)_2\}_2N_2]$ (**50**) by the reduction with $AlMe_3$ of $[Ni(acac)_2]$ in toluene in the presence of Pcy_3 and dinitrogen has been described in detail.[140] Complex **49** dissociates readily in solution to give $[Ni(N_2)(Pcy_3)_2]$ (**51**) and $[Ni(Pcy_3)_2]$. Compound **51** has an IR band at 2028 cm^{-1} which is assigned to $\nu(N_2)$. An X-ray crystal structure of **50** revealed a linear Ni-N-N-Ni system which has essentially trigonal-planar nickel atoms. The N-N distance is close to that found in terminal dinitrogen complexes.[140] The dinitrogen ligand is surrounded by a cage of cyclohexyl rings which help to stabilize the formally coordinatively unsaturated complex. This same complex (**50**) was prepared by the sodium sand reduction of $[NiBr_2(Pcy_3)_2]$ under nitrogen in about 50% yield.[141] Reduction of $[NiX_2(PR_3)_2]$ under argon (X = Cl or Br; PR_3 = PEt_3, PEt_2Ph, or PBu^n_3) produces yellow $[Ni(PR_3)_4]$ which reacts with dinitrogen to give $[Ni(N_2)(PR_3)_3]$.[142] These N_2 complexes were, however, not isolated and they were characterized only by the observation of bands in the 2063–2070-cm^{-1} region, assigned to $\nu(N_2)$, in the IR spectra of their solutions (see Table VII). The similarity of the IR spectrum of $[Ni(N_2)(PEt_3)_3]$ to that previously reported for the complex $[NiH(N_2)(PEt_3)_2]$ suggests that the latter formulation is almost certainly incorrect.[142]



= acao$^-$ or oxine$^-$

49



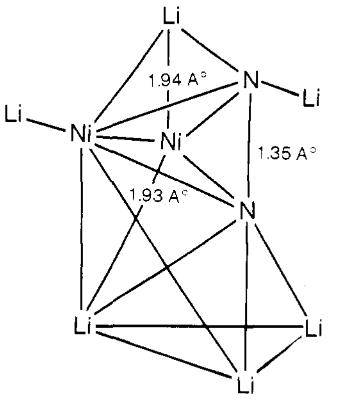
50, one of two independent molecules in unit cell

Some very unusual nickel–dinitrogen complexes have been prepared by the reaction of [Ni(CDT)] (CDT = *all-trans*-1,5,9-cyclodecatriene) with phenyllithium and dinitrogen in diethyl ether.[143] The essential feature of the extremely complex X-ray crystal structure (**52**) of the complex which has the stoichiometry

TABLE VII. Dinitrogen Complexes of Nickel, Palladium, and Platinum

complex	text no.	color	$\nu(N\equiv N)$,[a] cm^{-1}	preparation	comments	ref
$[\{Ni(Pcy_3)_2\}_2(N_2)]$	**50**	dark red		(i) $[Ni(acac)_2] + AlMe_3 + Pcy_3 + N_2$ in toluene at −20 °C, 50% yield (ii) $[NiBr_2(Pcy_3)_2]$ + Na sand + toluene + N_2 (20 °C), 50% yield	Complex dissociated in solution to $[Ni(Pcy_3)_2N_2]$, $\nu(N\equiv N)$ 2028 cm^{-1}; X-ray crystal structure (see text)	140
$[Ni(N_2)(PR_3)_3]$ ($PR_3 = PEt_3$, PBu^n_3, PEt_2Ph)		purple	2070[h] (PEt_3), 2065[b] (PEt_2Ph), 2060[t] (PBu^n_3)	$[NiX_2(PR_3)_2]$ (X = Cl, Br) + Na sand in toluene under Ar → $[Ni(PR_3)_4] \xrightarrow{N_2} [Ni(N_2)(PR_3)_3]$	Pure N_2 complexes not isolated, only $[Ni(PR_3)_4]$ obtained on workup	142
$[\{[(PhLi)_3Ni]_2(N_2)2Et_2O\}_2]$	**52**	dark red		$2[Ni(CDT)] + 6PhLi + N_2$ in Et_2O at 0 °C; CDT = all *trans*-1,5,9-cyclodecatriene	X-ray crystal structure (see text)	143, 144
$[\{Ph[NaOEt_2]_2[Ph_2Ni]_2(N_2)NaLi_6(OEt)_4OEt_2\}_2]$	**53**	orange		PhLi/PhNa mixture in 1:3.4 ratio added to $[Ni(CDT)]$ at −80 °C under N_2	X-ray crystal structure (see text)	145
$[(OH)_2Pd(N_2)(N_2H_4)Pd(OH)(NH_3)]^+$		dark green	2100 mw (2070 $^{29}N_2$)	$[Pd(NH_3)_2(NO_2)_2]$ + $N_2H_4H_2SO_4$ at pH 1 at 20 °C in 40–50% yield	Structure with bridging N_2 and N_2H_4 groups proposed, on basis of IR, analysis, and N_2 evolved on decomposition	146
$[(OH)(NH_3)Pd(N_2)(N_2H_4)Pd(H_2O)(NO_2)]^{2+}$		red	2100 mw (2070 $^{29}N_2$)	As above using 2 equiv of N_2H_4–H_2SO_4	Similar structure of above proposed	146
$K_2[\{Pt(OH_2)(NO_2)_2(NH_3)\}_2N_2]\cdot 2H_2O$		yellowish white	2034 (R) (2009 $^{29}N_2$)	$K_2[Pt(NO_2)_4] + (NH_4)_2SO_4$ at pH 2 at 70 °C (15–20% yield)	0.5 mol of N_2/Pt liberated with water; IR shifts when $(^{15}NH_4)_2SO_4$ used corresponds to $^{29}N_2$; elemental analysis	147
$K_2[\{Pt(ClO_4)_2(NO_2)_3(NH_3)\}_2(N_2)]\cdot 2KClO_4$		yellow	2065 (R)	$K_2[\{Pt(OH)_2(NO_2)_2(NH_3)\}_2N_2]\cdot 2H_2O + (NH_4)ClO_4$ in water	Not clear if ClO_4 groups bonded to Pt; bridging N_2 group apparently retained	147
$K_2[\{Pt(ClO_4)(NO_2)_3(NH_3)\}_2(N_2)]\cdot 0.5K_2SO_4$		yellowish white	2055 (R)	$K_2[\{Pt(ClO_4)(NO_2)_3(NH_3)\}_2N_2] + KClO_4 + (NH_4)ClO_4$ then acidified with H_2SO_4	Bridging N_2 group retained but overall structure not established; as with above species, N_2 binding to Pt(II) most surprising	147

[a] h, hexane solution; (R), Raman spectrum; t, THF solution; b, benzene solution.

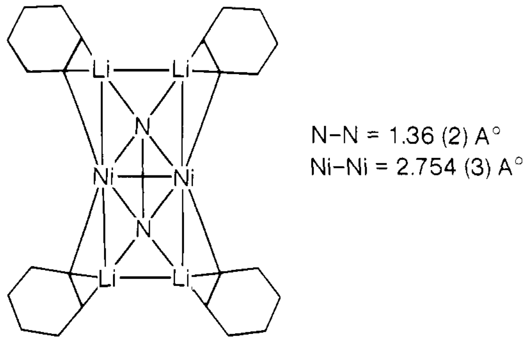


52

part of internal skeleton showing interactions of Li's with Ni and N

$[\{(C_6H_5Li)_6Ni_2(N_2)(Et_2O)_2\}_2]$ is that the dinitrogen is bound almost at right angles to a pair of nickel atoms which are connected by a long Ni-Ni bond. Two such Ni_2N_2 units are linked by a complex network of C_6H_5Li groups in the complex. This was the first authenticated example of side-on dinitrogen. The N-N bond length of 1.35 Å is the longest yet observed in any dinitrogen complex, which is attributed to the electron-acceptor properties of the bridging lithium atoms, enhancing the back-bonding from nickel into antibonding orbitals of dinitrogen.[144]

If a mixture of phenyllithium and phenylsodium is used in the above preparation, a product with the empirical formula $[\{C_6H_5(NaOEt_2)_2(C_6H_5)_2Ni_2(N_2)NaLi_6(OEt)_4OEt_2\}_2]$ (**53**) is ob-



53

part of internal skeleton showing interaction of N_2 with Ni and Li

TABLE VIII. N_2 Complexes Obtained by Matrix Isolation

species	$\nu(N{\equiv}N)$,[a] cm^{-1}	comments	ref
$Rh(N_2)$	2154	$Rh(N_2)_4$ has distorted tetrahedral D_{2d} symmetry in solid α-N_2	163
$Rh(N_2)_2$	2188		
$Rh(N_2)_3$	2196		
$Rh(N_2)_4$	2179, 2203		
$Ni(N_2)$	2088	$Ni(N_2)_4$ has regular tetrahedral structure in Ar matrix	150
$Ni(N_2)_2$	2104		151
$Ni(N_2)_3$	2137, 2187 (R), 2232 (R)		
$Ni(N_2)_4$	2174, 2246 (R)		
$Ni(O_2)(N_2)$	2243	O_2 side-on bonded, ν(O–O) 977 and 972 cm^{-1} for mono and bis N_2, respectively	152
$Ni(O_2)(N_2)_2$	2260, 2282		
$Ni(N_2)(CO)_3$	2264	By condensation of Ni atoms with N_2/CO/Ar mixtures or UV photolysis of $Ni(CO)_4$ in N_2/Ar matrix	153, 154
$Ni(N_2)_2(CO)_2$	2240, 2270		
$Ni(N_2)_3(CO)$	2210, 2258		
$Pd(N_2)$	2211	$Pd(N_2)_2$ has end-on bonded N_2's with $D_{\alpha h}$ structure symmetry	151
$Pd(N_2)_2$	2234, 2267 (R)		
$Pd(N_2)_3$	2241, 2251, 2274, 2274 (R)		
$Pd(O_2)(N_2)$	2288	ν(O–O) 1014 cm^{-1}	152
$Pd(O_2)(N_2)_2$	2310, 2304	ν(O–O) 998 cm^{-1}	
$Pt(N_2)$	2168, 2173	$Pt(N_2)_3$ has end-on bonded N_2's with regular trigonal-planar geometry	
$Pt(N_2)_2$	2150		
$Pt(N_2)_3$	2148, 2177, 2206, 2217, 2258 (R)		
$Pt(O_2)(N_2)$	2209	ν(O–O) 909 cm^{-1}	152
$Pt(O_2)_2(N_2)$	2267, 2260	ν(O–O) 897 cm^{-1}	
$Fe(CO)(N_2)(NO)_2$	2262, 2268, 2270	ν(CO) 2048, 2050, 2054 cm^{-1}; ν(NO) 1760, 1762, 1804, 1806 cm^{-1}	156
$Fe(N_2)_2(NO)_2$	2241, 2256	ν(NO) 1748, 1750, 1792, 1795 cm^{-1}; by photolysis of $[Fe(CO)_2(NO)_2]$ in N_2 matrix at 20 K	
$Co(CO)_2(N_2)(NO)$	2256, 2264	ν(CO) 2016, 2019, 2070, 2072 cm^{-1}; ν(NO) 1797, 1804 cm^{-1}	157
$Co(CO)(N_2)_2(NO)$	2226	ν(CO) 2018 cm^{-1}; ν(NO) 1782, 1786 cm^{-1}; by photolysis of $[CO(CO)_3(NO)]$ in N_2 matrix at 20 K	
$Cr(N_2)$	2215	Side-on bonding of N_2 may be involved for species with low coordination numbers	158
$Cr(N_2)_2$	2253		
$Cr(N_2)_3$	2178		
$Cr(N_2)_4$	2130		
$Cr(N_2)_5$	2035, 2068, 2195		
$Cr(N_2)_6$	2120		
$V(N_2)_6$	2100	Optical spectrum of $V(N_2)_6$ analogous to that of $V(CO)_6$	159
$V_2(N_2)_{12}$	2048, 2056, 2080, 2176		
$Nb(N_2)$	1926, 1931	These were two species tentatively assigned from a large number of IR bands in 1850–2200-cm^{-1} region.	162
$Nb(N_2)_4$	2073		

[a] $^{14}N{\equiv}^{14}N$ values; (R) indicates Raman.

tained. Its X-ray crystal structure (**53**) shows the same side-on dinitrogen as was seen for **52,** but in this case two $[(C_6H_5)_2Ni]_2N_2$ units are linked by two Na atoms and two $Li_6(OEt)_4OEt_2$ groupings. The N-N distance of 1.359 (18) Å is very similar to that observed in complex **52.**[145]

b. Palladium and Platinum

A number of palladium and platinum complexes, postulated to contain either bridging or terminal dinitrogen ligands, have been prepared by the reaction of nitrito complexes with hydrazinium or ammonium salts (see Table VII).[146,147] An analogous preparative route has already been discussed for some rhodium derivatives (section II.C.6), and the formulation of the Pd and Pt products as dinitrogen complexes depends on the assignment of bands at 2030–2100 cm^{-1} in their Raman spectra, to $\nu(N_2)$. Without any further evidence these formulations, like those of the analogous rhodium complexes, must remain very doubtful.

D. Matrix Isolation Studies

The cocondensation of metal atoms with pure dinitrogen or dinitrogen/argon mixtures at temperatures in the range 6–25 K enables unusual species, with dinitrogen bound to the metal, to be trapped in a solid matrix. Structures can then be assigned to these species on the basis of IR, Raman, and occasionally optical spectroscopy. Isotopic substitution, coupled with matrix annealing techniques permits complete assignments of the observed spectra to be made in some cases and the geometries of the species can be deduced. Species that have been identified by these techniques are summarized in Table VIII together with IR assignments. Details of the experimental methods have been given in a review[148] and are included in a recent book on the reactions of metal atoms.[149]

The most intensively studied element to date is nickel, and the species $Ni(N_2)_x$ (x = 1, 2, 3, or 4) can all be identified when nickel atoms are condensed with various mixtures of dinitrogen and argon.[150,151] $[Ni(N_2)_4]$ appears to have a regular tetrahedral structure in an argon matrix with terminal dinitrogen groups. If mixtures of dinitrogen and dioxygen are used, $Ni(O_2)(N_2)$ and $Ni(O_2)(N_2)_2$ are observed and are believed to contain side-on dioxygen and end-on dinitrogen ligands, $\nu(O_2)$ appearing in the range 972–977 cm^{-1} and $\nu(N_2)$ at 2242–2282 cm^{-1}.[152] The overall bonding picture for these mixed species is that the dinitrogen is weakly bound end-on to an $Ni^+O_2^-$ moiety, the O_2^- ligand being between oxide and superoxide in character.

Nickel species with both dinitrogen and carbon monoxide ligands can be obtained by co-condensation of nickel atoms with carbon monoxide/dinitrogen mixtures or by UV photolysis of $[Ni(CO)_4]$ in a dinitrogen/argon matrix.[153,154] Infrared or Raman bands have been assigned to all three members of the series $[Ni(N_2)_x(CO)_{4-x}]$ (x = 1, 2, or 3). Calculations which attempt to correlate changes in the π- and σ-orbital populations suggest that carbon monoxide is a better σ donor and π acceptor than is dinitrogen. Palladium and platinum both give the species $M(N_2)_x$ (M = Pd or Pt; x = 1, 2, or 3). The species $Pd(N_2)_2$ is assigned a linear $D_{\infty h}$ structure with terminal dinitrogen groups,[151] whereas the corresponding species $Pt(N_2)_2$ is postulated to contain two side-on dinitrogen ligands.[155] The general order of stability of the dinitrogen derivatives for this subgroup is Ni > Pt > Pd. The inversion of stability for Pd and Pt follows the Allred-Rochow electronegativity values and probably results from the lanthanide contraction. The N-N stretching frequencies for the matrix-isolated species are noticeably lower than those observed for species obtained by chemisorption of dinitrogen on elements of the nickel triad. Typical $\nu(N_2)$ values for chemisorbed dinitrogen are Ni, 2202 cm^{-1}; Pd, 2260 cm^{-1}. The weaker bonding of dinitrogen in the chemisorption process is attributed to the diversion of some of the electrons of the surface metal atoms into metallic conduction bands rather than into the π orbitals of dinitrogen.

Photolysis of $[Fe(CO)_2(NO)_2]$ in an N_2 matrix at 20 K gives species identified by IR spectroscopy as $[Fe(CO)(N_2)(NO)_2]$ and $[Fe(N_2)_2(NO)_2]$.[156] Analogous experiments with $[Co(CO)_3(NO)]$ produce $[Co(CO)_2(N_2)(NO)]$ and $[Co(CO)(N_2)_2(NO)]$.[157] If an argon and methane matrix is employed, the identification of the highly reactive intermediate $[Fe(CO)(NO)_2]$ and $[Co(CO)_2(NO)]$ suggests that the primary photochemical process is ejection of a carbonyl ligand.

The lighter transition metals are now also receiving attention, and chromium has been shown to form all the binary species $[Cr(N_2)_x]$ (x = 1–6). Tentative structures were advanced for all of these species but in some cases the spectral data were consistent with the occurrence of more than one geometry for each species.[158] The lack of monotonic increasing coordination-number-frequency correlation was attributed to the possibility of side-on dinitrogen bonding in species with low coordination numbers. The co-condensation of vanadium atoms and pure dinitrogen in a ratio of about 1:10^4 at 20–25 K gave a matrix with an IR spectrum suggesting the formation of $[V(N_2)_6]$ and $[V_2(N_2)_{12}]$. A reasonable correlation was found between the observed optical spectrum and that previously observed for $[V(CO)_6]$ and for $[V_2(CO)_{12}]$. If the condensation is carried out at 8–12 K, a UV spectrum characteristic of atomic vanadium is observed. This suggests that there is a very delicate balance between the activation energy required for binding of dinitrogen and the available thermal energy of the matrix at the condensation temperature.[159]

Condensation of titanium atoms with N_2 at 10–15 K gave species with optical and IR spectra consistent with $Ti(N_2)_6$; with carbon monoxide $Ti(CO)_6$ was identified.[160] An analysis of the optical spectra of the $M(N_2)_6$ species (M = Ti, V, Cr) has been made and both d-d and charge-transfer bands have been assigned.[161]

Analogous reactions of the niobium atoms with dinitrogen in an argon mixture at 14 K gave somewhat different results from those of the above metals, as a large number of IR bands assignable to $\nu(N_2)$ were observed over the extended range 1850–2200 cm^{-1}.[162] Some of these IR bands (see Table VIII) were tentatively assigned to $Nb(N_2)$ and $Nb(N_2)_4$ on the basis of isotopic labeling and matrix annealing techniques. The large number of observed IR bands is without precedent and possible explanations for them are the presence of species with different geometries, [e.g., $Nb(N_2)_3$ with either C_{3v} or D_{3h} symmetry] both side- and end-on dinitrogen, and interactions with the matrix.

III. Physical and Theoretical Studies of Dinitrogen and Related Complexes

In this section we summarize recent developments in our understanding of the bonding of dinitrogen to metal centers and the new physical data pertinent to that problem. The original considerations of the essentials of dinitrogen bonding occurred before the period of this review and are summarized in earlier reviews.[1,4,5] The main new developments have been the discovery of side-on bonded dinitrogen complexes, a number of X-ray crystal structures, the estimate of the charge carried by ligating dinitrogen and of the separation of charge within the ligating dinitrogen molecule, the application of ^{15}N NMR spectroscopy, and accumulation of new electrochemical data.

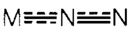
A. Bond Lengths

A large number of X-ray structural studies of transition metal–dinitrogen complexes has been made, as already indicated in section II. Here we summarize some of the main features. A selection of the more recently determined bond lengths is given in Table IX. Dinitrogen usually binds end-on to transition metals either terminally (**54**) or bridging (**55**), but three examples of side-on bonding, one of which is terminal (**56**) and the other two bridging (**57**), have been reported.

TABLE IX. Metal–Nitrogen and Nitrogen–Nitrogen Bond Distances in Representative Dinitrogen Complexes

compound	M–N, Å	N–N, Å	ref
N_2		1.0976	*a*
$[Mo(N_2)_2(dppe)_2]$	2.014 (5)	1.118 (9)	51
$[ReCl(N_2)(PMe_2Ph)_4]$	1.97 (2)	1.06 (3)	80
$[Os(NH_3)_5(N_2)]Cl_2$	1.842 (13)	1.12 (2)	116
$[RhH(N_2)(PPhBu^t{}_2)_2]$	1.970 (4)	1.074 (7)	133
$[RhCl(N_2)(PPr^i{}_3)_2]$ [b]	2.51 (1) 2.55 (1)	0.83 (2)	134
$[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$	2.005 (10) [c] 2.016 (10) 2.033 (10) 2.013 (10)	1.165 (14) [c] 1.155 (14)	36
$[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$	2.097 (3) [d] 2.188 (4) [f]	1.116 (8) [e] 1.182 (5) [g]	38
$[\{Mo(\eta^6\text{-}C_6H_3Me_3)(dmpe)\}_2(N_2)]$	2.042 (4)	1.145 (7)	48
$[\{Mn(\eta^5\text{-}C_5H_4Me)(CO)_2\}_2(N_2)]$	1.875 (5)	1.118 (7)	76
$[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$	1.90 (1) 1.82 (2)	1.18 (3)	88
$[\{Ru(NH_3)_5\}_2(N_2)](BF_4)_4$	1.98 (6)	1.12 (2)	116
$[\{Ni(PCy_3)_2\}_2(N_2)]$	1.77, 1.79	1.12	140
$[MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]$	1.99 (4) [h] 1.75 (4) [i]	1.28 (5)	89
$[\{Co(PMe_3)_3(N_2)\}_2Mg(thf)_4]$	2.04,[j] 1.72 [k]	1.18	128
$[\{(C_6H_5Li)_6Ni_2(N_2)(Et_2O)_2\}_2]$	1.91 (1) [l]	1.35 (2)	144

[a] P. G. Wilkinson and N. B. Houk, *J. Chem. Phys.*, **24**, 528 (1956). [b] Side-on bound dinitrogen, disordered structure (see text). [c] Data from two independent molecules in unit cell. [d] Zr–N (bridge). [e] Terminal N_2. [f] Zr–N (terminal). [g] Bridging N_2. [h] Mo–N. [i] Re–N. [j] Mg–N. [k] Co–N. [l] Ni–N.



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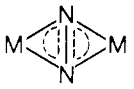

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In general, the N–N distances observed in complexes of type **54** (1.10–1.12 Å) are only slightly different and often within experimental error of that of free dinitrogen (1.0976 Å) (Table IX). Type **55** compounds also show little N–N bond lengthening when there are sufficient electrons available from the two metal atoms to fill all the molecular orbitals which are bonding on dinitrogen. This happens when the bridge occurs between "closed shell" complex centers. However, when there are too few electrons for this, e.g., as in $[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$, then the highest energy N–N bonding orbitals are unoccupied and the N–N distances are considerably longer; the value of $\nu(N_2)$ is then also low.

There are too few pertinent structures for any general conclusion to be drawn concerning side-on bonding (**56** and **57**), but surprisingly the one complex containing terminal side-on bonded dinitrogen (**56**) for which we have a structure appears to have a slightly shorter N–N distance (0.83 Å) than has free dinitrogen.[134] This is unlikely and is doubtless in error, being a consequence of the high degree of disorder in the crystal. Nevertheless, it would appear that terminal side-on, like terminal end-on dinitrogen is little altered in length by coordination. In the two examples containing side-on bridging dinitrogen the N–N bond length is excessively long (1.35 Å), but the dinickel compound in which it occurs has a very complex structure and the N_2 appears to be behaving as a ligating anion.

No compound which has an azobenzene-like structure, such as was postulated for $[(\eta^5\text{-}C_5H_5)_2Ti(N_2)Ti(\eta^5\text{-}C_5H_5)_2]$[25] and related complexes (see section II.C.1), has yet been structurally characterized.

TABLE X. X-PES Data for Dinitrogen and Related Complexes

complex	n(1s) binding energies (eV)	ref
[Mo(N$_2$)$_2$(dppe)$_2$]	399.6, 398.6	170
[MoCl(N$_2$)(dppe)]^a	399.9, 399.1	170
[MoBr(N$_2$)(dppe)$_2$]^a	400.1, 398.9	170
[Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)]	403.0, 401.8	169
[ReCl(N$_2$)(PMe$_2$Ph)$_4$]	400.1, 398.4	81
	400.0, 398.6	165
	400.3, 398.2	166
[ReCl(N$_2$)(PMe$_2$Ph)$_4$][FeCl$_4$]	400.1	81
[ReCl(N$_2$)(dppe)$_2$]	400.9, 398.8	81
	400.4, 398.5	166
[ReCl(N$_2$)(dppe)$_2$]FeCl$_4$	400.3	81
[ReCl(N$_2$)(py)(PMe$_2$Ph)$_3$]	399.8, 398.3	81
[FeH$_2$(N$_2$)(PPh$_3$)$_3$]	400.1, 399.0	167
[Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$	399.6 (2.0)^b	166
[RuCl(N$_2$)(diars)$_2$]SbF$_6$	402.3, 400.7	168
[Os(NH$_3$)$_5$(N$_2$)]Cl$_2$	399.5 (2.2)^b	166
[IrCl(N$_2$)(PPh$_3$)$_2$]	400.4, 399.1	166
[MoI(N$_2$Me)(dppe)$_2$]	399.7	170
[MoCl$_4$(OMe){(N$_2$)ReCl(PMe$_2$Ph)$_4$}]	398.6	81

[a] Now known to be equimolecular mixture of [Mo(N$_2$)$_2$(dppe)$_2$] and [MoX$_2$(dppe)$_2$]. [b] Broad unresolved line, half-width in parentheses where quoted.

B. Distribution of Electronic Charge within Ligating Dinitrogen

There is no direct method of measuring this property, and mostly it has been inferred from IR absorption intensities and X-PE spectra. The few dinitrogen complexes examined by this latter technique are with one exception mononuclear and contain end-on dinitrogen (Table X). Generally they are stable complexes with low ν(N$_2$) where back-bonding should be strong. On the basis of binding energy correlations and a comparison with dipole moment and electrochemical data, it has been concluded that in these particular complexes the dinitrogen ligand is overall negatively charged. The two nitrogen atoms also often carry sufficiently different charges for their clear resolution in the X-PE spectrum, but it seems unlikely that the charge difference will be so great in the less stable complexes of higher ν(N$_2$) formed by metals at the right of the transition metal series. Some evidence of this is provided by the comparison of the spectrum of the very stable complex *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$] [ν(N$_2$) 1925 cm^{-1}] with that of its less stable cation in the salt [ReCl(N$_2$)(PMe$_2$Ph)$_4$][FeCl$_4$] [ν(N$_2$) 2055 cm^{-1}] where the resolution is lost and the average N(1s) binding energy is higher. Also broad bands with no clear resolution were observed in the spectra of [M(NH$_3$)$_5$(N$_2$)]Cl$_2$ (M = Ru or Os) (Table X).

It seems unlikely that the charge difference between the two nitrogen atoms in any bridging dinitrogen ligand will be sufficient for resolution in the X-PE spectrum. The evidence is that neither of the following two highly asymmetric complexes shows any N(ls) resolution. They are the methyldiazenido complex [MoI(N$_2$Me)(dppe)$_2$],[171] where strong conjugation to the metal is known to occur but only weak conjugation to the methyl group is possible, and [MoCl$_4$(OMe){(N$_2$)ReCl(PMe$_2$Ph)$_4$}], where strong conjugation occurs along the straight Re–N–N–Mo chain[88] and the metals are widely different in oxidation state (Table X).

In the mononuclear complexes where resolution has been observed, it has not been possible to determine unequivocally by physical methods whether the nitrogen atom adjacent to the metal or the terminal nitrogen atom is the more negatively charged. Folkesson,[174] after a study of the intensities of the ν(N$_2$) absorption in the IR spectrum concluded that the ligating dinitrogen atom is the more negative, but in view of its more strongly basic character toward Lewis acids in general (see sections II and IV) the terminal nitrogen atom is usually assumed to carry the greater negative charge.

Attempts to compare the relative tendencies of the isostructural ligands CO, N$_2$, and NO to withdraw negative charge from the metal indicate that generally NO is about as electron withdrawing as the chlorine atom and that N$_2$ and CO are about equal and negative, but rather less so than NO. This conclusion was drawn on the basis of the apparent effective oxidation state of rhenium (determined by X-PE spectroscopy) in a closely related series of rhenium complexes,[81] but a similar conclusion was reached for analogous complexes of other metals using mainly IR spectroscopic data.[74,172] It seems likely that the relative tendencies to withdraw charge will vary slightly from one type of complex to another. Thus, for example, the Mn 2p$_{3/2}$ binding energy (642.1 eV) decreases on passing from [Mn(η^5-C$_5$H$_5$)(CO)$_3$] to [Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)], (641.8 eV) implying that in this case CO > N$_2$ in its ability to remove electron density from the manganese(I).[169]

C. Other Spectroscopic Investigations and Relative σ and π Properties of Ligating Dinitrogen

Many spectroscopic studies of dinitrogen and related complexes have been concerned with the relative σ-donor and π-acceptor properties of dinitrogen and analogous ligands such as carbon monoxide, and organic cyanides and isocyanides.

The intensities of the N$_2$ and CO stretching absorptions (I_{XY}, XY = CO or N$_2$) in their analogous complexes have been used to assess the degree of electron release from the metal d$_\pi$ to XY p$_\pi$* orbitals.[173,177] The stretching of the XY bond during a vibration increases the p$_\pi$* component of the bond. This process may be regarded as a flow of electron density from the metal d$_\pi$ orbitals into the p$_\pi$* orbitals of XY. The vibration thus induces a change in the dipole moment of the M–XY (M = metal) group, and its rate of change is proportional to the absorption intensity (I_{XY}). A linear correlation has been found between ν(N$_2$) and I_{N_2} for a series of complexes of molybdenum, tungsten, rhenium, ruthenium, osmium, and iridium, such that the lower is ν(N$_2$), the higher is I_{N_2}. Thus complexes which have particularly low ν(N$_2$) values have especially high I_{N_2} values and therefore a strong d$_\pi$–p$_\pi$* interaction,[173,174] as would be expected. For example, *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$] has one of the lowest ν(N$_2$) values (1925 cm^{-1}), a high I_{N_2} value (10.85 × 10^4 M^{-1} cm^{-2}),[173] and its particularly strong d$_\pi$–p$_\pi$* interaction results in a pronounced polarity of the Re–N–N group (see section III.B). The values of I_{CO} for a number of carbonyl complexes are higher than those of I_{N_2} in analogous complexes (e.g., for *mer*-[OsCl$_2$(XY)(PEt$_2$Ph)$_3$], I_{N_2} = 6.46 × 10^4 M^{-1} cm^{-2}, analogous I_{CO} = 9.05 × 10^4 M^{-1} cm^{-2});[173] therefore it has been argued that N$_2$ is a weaker π acceptor than is CO. Since ligating N$_2$ can only increase its intrinsically weaker σ-donor property over that of CO by a synergic process, it follows that it is also a weaker σ donor than is CO.[173] These conclusions had been reached earlier from consideration of the relative fractional lowering of ν(XY) in analogous complexes of iridium[175] and are supported by more recent determination of the force constants of the XY vibration in the complexes *trans*-[RuCl(XY)(diars)$_2$]Cl[172] and [Mn(η^5-C$_5$H$_5$)(CO)$_2$(XY)].[74]

The relative σ-donor and π-acceptor properties of dinitrogen have also been compared with those of analogous ligands using Mössbauer spectroscopy. Thus the ^{57}Fe isomer shifts of the complexes *trans*-[FeH(L)(dppe)$_2$]BPh$_4$ (L = N$_2$, CO, Bu^{t}NC, *p*-MeOC$_6$H$_4$NC, PhNC, or MeCN) depend on the s-electron density at the nucleus, which is affected by both the σ-donor and π-acceptor ability of L. Therefore the isomer shifts reflect the σ-donor plus π-acceptor ($\pi + \sigma$) properties of the ligands (L), and they indicate that dinitrogen is a weaker ($\pi + \sigma$) ligand than CO or RNC (R = Bu^t or *p*-MeOC$_6$H$_4$) but is comparable with PhCN and MeCN.[176] The quadruple splittings (QS) observed in these spectra become more positive as the π-acceptor property of

L increases, but more negative as its σ-donor ability increases; thus QS values are proportional to the relative ($\pi-\sigma$) abilities of L. The values obtained show dinitrogen to have the highest ($\pi-\sigma$) value.[176]

Thus, on the basis of the above data, dinitrogen has a σ-donor ability which is less than that of any other ligand but a π-acceptor ability which is moderate and lies between carbon monoxide and organic cyanides and isocyanides.

The data of sections III.B and III.C indicate that because dinitrogen is a particularly poor σ donor but a moderate π acceptor, its overall effect is to withdraw electronic charge from the metal to an extent about equal to that of carbon monoxide whose π-acceptor and σ-donor capacities are individually both greater than those of dinitrogen. The relative extent of withdrawal of charge by these two ligands appears to vary slightly from one type of complex to another.

The very weak σ-donor function of dinitrogen is accommodated only with difficulty by metal sites and, as was suggested earlier,[175] is probably responsible for the relative scarcity of complexes of dinitrogen as compared with those of other ligands.

D. ^{15}N NMR Spectra

^{15}N NMR spectroscopy provides a potentially useful tool for the study of nitrogen fixation and dinitrogen complexes, but owing to the very weak absorption by the ^{15}N nucleus and the consequent need for highly sensitive spectrometers, it has been little used. It was first applied to the labile, bridged $^{15}N_2$ complex $[\{Ti(\eta^5\text{-}C_5Me_5)_2(^{15}N_2)\}_2(^{15}N_2)]$ at −18 °C in toluene.[35] This complex was originally formulated as $[Ti(\eta^5\text{-}C_5Me_5)_2(^{15}N_2)]$ containing side-on dinitrogen and the spectrum was interpreted on that basis[30a,35] but later corrected.[36] The spectrum shows a doublet from the terminal nitrogen molecules at 520 and 569 ppm downfield from $NH_4^+(aq)$ and a singlet from the bridging dinitrogen at 653 ppm. These are slightly downfield from the range of organic diazenes such as *trans*-RN=NR (R = Ph, 431; R = Et, 505 ppm).[177] The value of the coupling constant $^1J|NN|$ of the terminal $^{15}N_2$ ligand is 7 ± 2 Hz and close to that of its zirconium analogue $[\{Zr(\eta^5\text{-}C_5Me_5)_2(^{15}N_2)\}_2(^{15}N_2)]$ (6.2 Hz).[39] The resonance pattern of the zirconium complex closely resembles that of its titanium analogue, but the shift data have not yet been referred to a standard.

Similarly $^1J|NN|$ values, 5.4 and 6.2 Hz, respectively, have been observed[178] for the only two other compounds to have been examined, *trans*-$[W(^{15}N_2)_2(dppe)_2]$ and *cis*-$[W(^{15}N_2)_2(PMe_2Ph)_4]$, but their chemical shifts (295.9, 307.5, and 298.3, 323.6 ppm, respectively) are to higher field and close to the values reported for $^{15}N_2CH(CO_2Et)$ (242.69, 358.92 ppm; $^1J|NN|$, 5.65 Hz).[177]

The titanium and tungsten complexes are structurally and electronically distinct, and so it seems that a wide range of ^{15}N chemical shifts will be found from dinitrogen complexes as a whole. The interpretation of the shifts awaits the production of more empirical data.

E. Electrochemical Data

There has been little systematic electrochemical work in the area of dinitrogen complexes. It is particularly useful for the study of unstable oxidized dinitrogen complex species to gain information on the energies of the redox orbitals and their bearing on the interpretation of molecular orbital structure. Systematic study has been limited to only two series of compounds, *trans*-$[ReX(N_2)L_4]$ [X = Cl or Br; L_4 = $(PMe_2Ph)_4$, $(dppe)_2$, $\{(PPh_3)_2(CO)_2\}$, $\{CO(PMe_2Ph)_3\}$, or $\{(PMe_2Ph)_3py\}$] and trans-$[M(N_2)(A)(dppe)_2]$ (M = Mo or W; A = N_2 or organic cyanide).[61,185] Typical electrochemical data are shown in Table XI.

TABLE XI. Electrochemical Data for Oxidation of Representative Dinitrogen Complexes

complex	$^1E_{1/2}$ [a]	$^2E_{1/2}$	ref
trans-$[Mo(N_2)_2(dppe)_2]$	−0.16 [b]	+0.78 [b]	185
	−0.24 [c]		61
trans-$[Mo(N_2)(PhCN)(dppe)_2]$	−0.48 [b]	+0.37 [b]	185
trans-$[Mo(N_2)(MeCN)(dppe)_2]$	−0.58 [b]	+0.33 [b]	185
trans-$[Mo(N_2)(SiCN)(dppe)_2]$ [d]	−0.59 [b]	+0.34 [b]	185
trans-$[W(N_2)_2(dppe)_2]$	−0.15 [b]	+0.79 [b]	185
trans-$[W(N_2)(PhCN)(dppe)_2]$	−0.48 [b]	+0.38 [b]	185
trans-$[W(N_2)(MeCN)(dppe)_2]$	−0.57 [b]	+0.32 [b]	185
trans-$[W(N_2)(SiCN)(dppe)_2]$ [d]	−0.55 [b]	+0.31 [b]	185
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	+0.048 [e]		81
$[ReCl(N_2)(py)(PMe_2Ph)_3]$	−0.085 [e]		81
$[ReBr(N_2)(py)(PMe_2Ph)_3]$	−0.053 [e]		81
$[ReCl(N_2)(CO)(PMe_2Ph)_3]$	+0.567 [e]		81
$[ReCl(N_2)(CO)_2(PPh_3)_2]$	+0.910 [e]		81
trans-$[ReCl(N_2)(dppe)_2]$	+0.121 [e]		81
$[Re(S_2CNMe_2)(N_2)(PMe_2Ph)_3]$	−0.260 [e]		81

[a] $^1E_{1/2}$ = half-wave potential (volts) for first one-electron oxidation vs. standard calomel electrode; $^2E_{1/2}$ = corresponding value for second one-electron oxidation. [b] In THF solution, $[NBu^n{}_4]BF_4$ supporting electrolyte. [c] In Me_2NCHO solution, $[NEt_4][ClO_4]$ supporting electrolyte. [d] SiCN = $Si(OMe)_3\{(CH_3)_2CN\}$. [e] In CH_2Cl_2/MeOH solution, $[NBu^n{}_4]BF_4$ supporting electrolyte.

The members of the latter series and *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ undergo a reversible one-electron oxidation in such solvents as THF or DMF but are not reducible under those conditions. Further oxidation steps are generally irreversible.[61] These observations have been complemented by chemical preparation of the unstable singly oxidized species, e.g., $[Mo(N_2)_2(dppe)_2]I_3$ by iodine oxidation of its neutral analogue (see sections II and IV.A).[61] The complexes $[M(N_2)(RCN)(dppe)_2]$ (M = Mo or W; R = Me, Pr^n, or Ph) are exceptional in that they show two successive one-electron polarographic oxidation waves, corresponding to the formation of species with the metal in oxidation states 0, I, and II.[185] Clearly the replacement of dinitrogen by the organic cyanide stabilizes the higher oxidation states because the organic cyanide, being a poorer π-electron acceptor than dinitrogen, raises the energy of the redox orbital (HOMO). This above type of N_2–nitrile complex has been formed on a tin oxide electrode surface by reaction of $NC(CH_2)_3SiCl_3$ with the surface to give a high surface coverage of $\equiv O_3Si(CH_3)CN$ groups, followed by treatment with *trans*-$[M(N_2)_2(dppe)_2]$.[185] The bound complexes $[M(N_2)\{NC(CH_3)_3SiO_3\ \text{electrode}\}(dppe)_2]$ show very similar electrochemical behavior to the above complexes and particularly to the analogous free complex $[M(N_2)\{NC(CH_3)_3Si(OMe)_3\}(dppe)_2]$.[185]

Studies of the reversible one-electron oxidation of the series *trans*-$[ReCl(N_2)L_4]$ [L_4 = $(PMe_2Ph)_4$, $(dppe)_2$, $\{(PPh_3)_2(CO)_2\}$, $\{CO(PMe_2Ph_3\}$, or $\{(PMe_2Ph)_3pyridine\}$] and of $[Re(S_2CNMe_2)(N_2)(PMe_2Ph)_3]$ (Table XI) lead to the conclusion that the redox orbital (HOMO) is essentially a metal nonbonding d orbital whose energy is affected by the binding of the various ligands at the metal.[184] Thus the above dimethyldithiocarbamato complex has a lower oxidation potential than $[ReCl(N_2)(PMe_2Ph)_4]$ indicating the greater general electron-releasing character of the dithiocarbamato ligand, compared with the chloride–tertiary phosphine combination which it has replaced.

The decomposition of *trans*-$[Mo(N_2)_2(dppe)_2]^+$ with the loss of both dinitrogen ligands (in THF/MeOH, with lithium chloride) has been monitored electrochemically.[186] The rate of dinitrogen loss has a first-order dissociation rate constant of $2.4 \pm 0.2 \times 10^{-1}\ s^{-1}$ at 25 °C.

F. Theoretical Considerations

The fundamental character of the bonding of dinitrogen in transition metal complexes was clear as soon as the structure of the first dinitrogen complex had been established and its discussion falls outside the period of this review. Later studies

TABLE XII. Oxidation Reactions of Dinitrogen Complexes

complex	ox agent/solvent	product	ref
	I. Dinitrogen Lost		
trans-$[\mathrm{Mo(N_2)(dppe)_2}]$	$\mathrm{Br_2/THF}$	$[\mathrm{MoBr_2(dppe)_2}]\mathrm{Br_3}$	187
trans-$[\mathrm{Mo(N_2)_2(PPh_2Me)_4}]$	$\mathrm{I_2/MeOH}$	u[a]	61
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	PhSCl/THF	$[\mathrm{MoCl(SPh)(dppe)_2}]$	187
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	RSH[b]/THF	$[\mathrm{Mo(SR)_2(dppe)_2}]$	187
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	HCl/THF	$[\mathrm{MoH_2Cl_2(dppe)_2}]$	58
trans-$[\mathrm{Mo(N_2)_2(dmtpe)_2}]$	$\mathrm{H_2/C_6H_6}$	$[\mathrm{MoH_4(dmtpe)_2}]$	54
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$[\mathrm{CH_3C_6H_4N_2}]\mathrm{BF_4}$	u[a]	188
mer-$[\mathrm{Re(S_2CNMe_2)(PMe_2Ph)_3(N_2)}]$	HCl/THF	$[\mathrm{ReH_2(S_2CNMe_2)Cl(PMe_2Ph)_2}]\mathrm{Cl}$	83
mer-$[\mathrm{OsCl(N_2)(PEt_2Ph)_3}]$	$\mathrm{Cl_2/CHCl_3}$	$[\mathrm{OsCl_3(PEt_2Ph)_3}]$	117
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{HCl/CH_3C_6H_5}$	$[\mathrm{IrHCl_2(PPh_3)_2}]$	189
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{R^1COCl}$[c]$/\mathrm{C_6H_6}$	$[\mathrm{IrCl_2(R)(CO)(PPh_3)_2}]$	190
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{R^2CO_2H}$[d]$/\mathrm{C_6H_6}$	$[\mathrm{IrCl(O_2CR)H(PPh_3)_2}]$	191
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{(R^3CO_2)_2O}$[e]$/\mathrm{C_6H_6}$	$[\mathrm{IrCl\{C(O)R\}(O_2CR)(PPh_3)_2}]$	192
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{R^4SO_2Cl}$[f]$/\mathrm{C_6H_5}$	$[\mathrm{IrCl_2(SOR)(PPh_3)_2}]$	193
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{CS_2}$	$[\mathrm{IrCl(C_2S_5)(PPh_3)_2}]$	194
	II. Dinitrogen Retained		
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$\mathrm{I_2/MeOH}$	*trans*-$[\mathrm{Mo(N_2)_2(dppe)_2}]\mathrm{I_3}$[g,h]	61
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$\mathrm{I_2/C_6H_6}$	$[\{\mathrm{MoI(C_6H_6)(dppe)_4}\}_2\mathrm{(N_2)}]$[i]	55
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$\mathrm{I_2/MeC_6H_5}$	$[\mathrm{Mo_2I_3(dppe)_4(N_2)}]$[i]	55
		$[\mathrm{Mo_2I_2(dppe)_4(N_2)}]$[i]	55
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$\mathrm{CH_3Cl/C_6H_6}/h\nu$	*trans*-$[\mathrm{MoCl(N_2)(dppe)_2}]$	63
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$\mathrm{PhSCl/MeC_6H_5}$ (−20 °C)	$[\mathrm{Mo_2(N_2)(SPh)_2(dppe)_2}]\mathrm{Cl_2}$	195
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$	$\mathrm{HClO_4/EtOH}$	$[\mathrm{MoH(N_2)(dppe)_2}]\mathrm{ClO_4}$[j]	195
$[\{\mathrm{Mo(Me_3C_6H_3)(dmpe)}\}_2\mathrm{(N_2)}]$	$\mathrm{HBF_4/MeC_6H_5}$	$[\{\mathrm{MoH(Me_3C_6H_3)(dmpe)}\}_2\mathrm{(N_2)}]$	47
trans-$[\mathrm{W(N_2)_2(dppe)_2}]$	HCl/THF	$[\mathrm{WH(N_2)_2(dppe)_2}]\mathrm{HCl_2}$[k]	58
trans-$[\mathrm{W(N_2)_2(PMePh_2)_4}]$	$\mathrm{FeCl_3/THF}$	*trans*-$[\mathrm{W(N_2)_2(PMePh_2)_4}]\mathrm{FeCl_4}$	196
trans-$[\mathrm{ReCl(N_2)(PMe_2Ph)_4}]$	$\mathrm{Cl_2/CCl_4}$	*trans*-$[\mathrm{ReCl(N_2)(PMe_2Ph)_4}]\mathrm{Cl}$[g]	79
trans-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$	$\mathrm{MeSO_3CF_3/C_6H_6}$	$[\mathrm{IrCl(Me)(SO_3CF_3)(N_2)(PPh_3)_2}]$	139

[a] u = uncharacterized product. All dinitrogen evolved as gas. [b] R = Me, Et, $\mathrm{Pr^n}$, $\mathrm{Bu^n}$, or $\mathrm{C_6H_5}$. [c] $\mathrm{R^1}$ = Me, Et, $\mathrm{C_6H_5CH_2}$, $\mathrm{C_6H_5}$, or $\mathrm{C_6F_5}$. [d] $\mathrm{R^2}$ = H, Me, Et, $\mathrm{Pr^n}$, $\mathrm{C_6H_5}$, or $\mathrm{CF_3}$. [e] $\mathrm{R^3}$ = Me, $\mathrm{CF_3}$, or $\mathrm{C_2F_5}$. [f] $\mathrm{R^4}$ = Me, Et, $\mathrm{Pr^n}$, or $\mathrm{C_6H_5}$. [g] Also prepared with other anions. [h] Cation also prepared electrochemically.[186] [i] Proposed formulas. [j] Via a compound formulated $[\mathrm{Mo_2H_2(N_2)_3(dppe)_4}](\mathrm{ClO_4})_2\cdot 2.5\mathrm{C_7H_8}$. [k] Pentagonal bipyramid with apical $\mathrm{N_2}$ groups (section II.C.3, Table II).

have been concerned mainly with the relative importance and magnitudes of the σ and π contributions to the bonding and the relative stabilities of dinitrogen complexes. Qualitative and semiquantiative molecular orbital schemes have been derived for terminal dinitrogen and bridging dinitrogen complexes. In general the observed spectroscopic properties and chemical reactions accord with the theoretical schemes.

A four-center π molecular orbital bonding scheme originally suggested for the dinitrogen-bridged complexes $[\{\mathrm{Ru(NH_3)_5(N_2)}\}_2\mathrm{(N_2)}]^{4+}$,[164] and $[\mathrm{CrCl_2}\{\mathrm{(N_2)ReCl(PMe_2Ph)_4}\}\mathrm{(thf)_2}]$[86] has been applied to the dimeric complexes $[\{\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{(N_2)}\}_2\mathrm{(N_2)}]$[38] and $[\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})\}_2\mathrm{(N_2)}]$.[36] This scheme was thoroughly discussed before the period of this review.[86] It accounts for the low $\nu(\mathrm{N_2})$ values and the long N-N distances observed in the above zirconium compound and such complexes as $[\mathrm{MoCl_4(OMe)}\{\mathrm{(N_2)ReCl(PMe_2Ph)_4}\}]$[88] which have too few electrons to occupy all highest energy π orbitals which are bonding on dinitrogen (3e in C_{4v} symmetry) but have filled levels which are π^*-$\mathrm{N_2}$ in character (2e in C_{4v} symmetry) (see also sections II and III.A).

Molecular orbital schemes for mononuclear complexes have also been constructed, in some cases semiquantitatively.[180,181] Thus LCAO-MO[180] and extended Hückel[181] calculations, applied to mono-dinitrogen complexes, are consistent with a predominant π-acceptor behavior of the dinitrogen ligand which, on ligation, becomes negatively charged with respect to the metal. One set of calculations[181] indicates charge separation between the nitrogen atoms with the terminal atom the more negative, consistent with the formation of adducts of the type, M-N-N Lewis acid, described in section II and V.A. Increasing positive charge on the metal atom weakens the M-$\mathrm{N_2}$ bonding interaction and strengthens the N-N bond,[182,183] consistent with the observation that dinitrogen complexes easily lose dinitrogen on oxidation (sections II and V.A).

The semiquantitative MO scheme for mononuclear trans bis(dinitrogen) complexes reveals that the lowest unoccupied orbital ($\mathrm{e_u}$ in D_{4h} symmetry) is essentially π^*-$\mathrm{N_2}$ in character.[181] It has therefore been suggested that the promotion of an electron to this level, perhaps by photolysis, from a lower level ($\mathrm{b_{2g}}$) would weaken the N-N bonding without disturbing the M-$\mathrm{N_2}$ interaction. Thus, such complexes as *trans*-$[\mathrm{Mo(N_2)_2(dppe)_2}]$ would have enhanced reactivity toward electrophilic attack at nitrogen upon irradiation.[181,182] While this argument appears to be sound in principle, in fact, the loss of dinitrogen from *trans*-$[\mathrm{Mo(N_2)_2(dppe)_2}]$ is induced by irradiation. This gives rise to other possible reaction paths, and it accounts for the interesting free radical mechanism of alkylation of the remaining ligating $\mathrm{N_2}$ by alkyl halides and related reactions as discussed in section V.B.

Calculations on M-$\mathrm{N_2}$ interactions[180] have led to the conclusions that to the left of the transition series, those complexes in which the M-N-N system carries a positive charge are favored, whereas to the right of the series the M-N-N system must have essentially zero charge for stability. Reference to the compounds described in section II raises some doubts about these conclusions since, for example, $[\mathrm{Os(NH_3)_5(N_2)}]^{2+}$ and *trans*-$[\mathrm{Mo(N_2)_2(dppe)_2}]$ are thermally very stable. Clearly the nature of the coligands must also affect the M-$\mathrm{N_2}$ interaction to a large extent although it has not yet been quantified. It has also been suggested on the basis of similar calculation that reduction of dinitrogen to nitrogen hydrides may proceed via its protonation for complexes of the $\mathrm{d^{4-6}}$ configurations[180,183] (as has been observed, section V), but by nucleophilic attack in $\mathrm{d^{0-2}}$ complexes, should they exist. No example of nucleophilic attack at dinitrogen is yet known.

A qualitative bonding scheme for side-on dinitrogen has appeared and resembles that used to describe the bonding of un-

TABLE XIII. Ligand Displacement Reactions of Dinitrogen Complexes

compound	ligand/solvent	product	ref
	I. Dinitrogen retained		
trans-$[Mo(N_2)_2(dppe)_2]$	$4\text{-}XC_6H_4CN$[a]$/MeC_6H_5$	*trans*-$[Mo(N_2)(4\text{-}C_6H_4CN)(dppe)_2]$[a]	67
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	dpte/MeC_6H_5/20 °C	*trans*-$[Mo(N_2)_2(PMe_2Ph)_2(dpte)]$	68
trans-$[Mo(N_2)_2(PMePh_2)_4]$	dppe/THF	*trans*-$[Mo(N_2)_2(PMePh_2)_2(dppe)]$	196
trans-$[W(N_2)_2(PMePh_2)_4]$	py[b]/THF	*trans*-$[W(N_2)_2(PMePh_2)_3(py)]$[b]	196
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	dppe/MeC_6H_5/120 °C	*trans*-$[ReCl(N_2)(dppe)_2]$	79
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	$Na[S_2CNR_2]$[c]$/Me_2CO$	*mer*-$[Re(S_2CNR_2)(N_2)(PMe_2Ph)_3]$[c]	83
trans-$[ReX(N_2)(PMe_2Ph)_4]$[d]	py/C_6H_6[b]	*mer*-$[ReX(N_2)(PMe_2Ph)_3py]$[b,d]	81
mer-$[OsX_2(N_2)L_3]$[d,e]	L^1/MeC_6H_5[e]	$[OsX_2L_3(L^1)]$[d,e]	197
mer-$[OsCl_2(N_2)(PMe_2Ph)_3]$	$NaBH_4$/THF	*mer*-$[OsHCl(N_2)(PMe_2Ph)_3]$	119
	II. Dinitrogen Lost		
trans-$[Mo(N_2)_2(dppe)_2]$	CO/THF or MeC_6H_5	*cis*-$[Mo(CO)_2(dppe)_2]$	45, 60
trans-$[Mo(N_2)_2(PMePh_2)_4]$	CO/THF	*mer*-$[Mo(CO)_3(PMePh_2)_3]$	60
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	CO/THF or MeC_6H_5	*fac*-$[Mo(CO)_3(PMe_2Ph)_3]$	60,68
trans-$[M(N_2)_2(dppe)_2]$[f]	RNC/THF[g]	*trans*-$[M(RNC)_2(dppe)_2]$[f,g]	198
$[Mo(\eta^5\text{-}C_5Me_5)_2(N_2)]$	CO/MeC_6H_5	$[Mo(\eta^5\text{-}C_5Me_5)_2(CO)]$	49
$[Mo(Me_3C_6H_3)(N_2)(PPh_3)_2]$	CO/THF	$[Mo(Me_3C_6H_3)(CO)(PPh_3)_2]$	46
$[FeH(N_2)L^2]BPh_4$[h]	L^3/CH_2Cl_2[h]	$[FeH(L^2)L^3]BPh_4$[h]	98, 99
$[FeH_2(N_2)(PEtPh_2)_3]$	C_6H_{10}/THF	$[FeH(C_6H_{11})(PEtPh_2)_2(thf)]$	199
$[\{Fe(\eta^5\text{-}C_5H_5)(dmpe)\}_2(N_2)_2]^{2+}$	CO/Me_2CO	$[Fe(\eta^5\text{-}C_5H_5)(CO)(dmpe)]^{2+}$	92
$[\{Fe(\eta^5\text{-}C_5H_5)(dmpe)\}_2(N_2)_2]^{2+}$	$LiAlH_4$/THF	$[Fe(\eta^5\text{-}C_5H_5)H(dmpe)]$	92
$[RuH_2(N_2)(PPh_3)_3]$	L^4/THF[i]	$[RuH_2(L^4)(PPh_3)_2]$[i]	106
$[Os(oep)(N_2)(thf)]$	CO/THF	$[Os(oep)(CO)(thf)]$	120
$[Os(oep)(N_2)(thf)]$	C_5H_5N/THF	$[Os(oep)(C_5H_5N)_2]$	120
$[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$	$CO/C_6H_5CH_3$	$[\{Zr(\eta^5\text{-}C_5Me_5)_2(CO)\}_2(N_2)]$	200
$[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$	$H_2/C_6H_5CH_3$	$[ZrH_2(\eta^5\text{-}C_5Me_5)_2]$	200

[a] X = NH_2, MeO, Me, H, Cl, or COMe. [b] py = C_5H_5N, $2\text{-}MeC_5H_4N$, or $4\text{-}MeC_5H_4N$. [c] R = Me or Et. [d] X = Cl or Br. [e] L = PEt_2Ph; L^1 = PMe_2Ph, PEt_2Ph, or $P(OMe)_2Ph$. [f] M = Mo or W. [g] R = Me, Bu^t, or aryl. [h] L^2 = PEt_2Ph, $P(OMe)_3$, $P(OMe)_2Ph$, or PMe_2Ph; L^3 = CO, MeCN, PhCN, NH_3, C_5H_5N, Me_2CO, or thf. [i] L^4 = CO, PhCN, NH_3, PPh_3, or $P(4\text{-}MeC_6H_4)_3$.

saturated molecules such as olefins and acetylenes to transition metals.[144]

IV. Reactions of Dinitrogen Complexes

Since the discovery of dinitrogen complexes, the reaction of ligating dinitrogen has held the prime interest of chemists in this field, their major aim being to reduce ligating dinitrogen to ammonia. This goal has now been unambiguously achieved (section V.B.2) and a variety of other reactions of dinitrogen complexes have been investigated. They may be broadly divided into those which involve the reaction of ligating dinitrogen and those which do not. In this section we shall consider the latter under two headings.

A. Oxidation

The oxidation reactions are summarized in Table XII. Oxidation of the central metal atom even by only one unit is usually sufficient to cause the loss of dinitrogen, especially from the complexes of the lighter transition metals (Table XII). The oxidizing agents can typically be halogens, hydrogen halides, dihydrogen, or thiols. Electrochemical oxidation has also been used (section IV.E). Some dinitrogen complexes are able to retain their dinitrogen, albeit rather weakly, on oxidation by one unit; the factors determining whether dinitrogen is retained or lost may be fairly small; e.g., *trans*-$[Mo(N_2)_2(dppe)_2]$ retains dinitrogen on oxidation with diiodine but *trans*-$[Mo(N_2)_2(PMe_2Ph)_4]$ loses all of it, probably because *trans*-$[Mo(N_2)_2(PMe_2Ph)_4]I_3$ is soluble whereas its dppe analogue precipitates from methanol. In general, the retention of dinitrogen is more common with complexes of metals of the second and more especially the third transition periods and near the centers of the periods, e.g., Mo, W, Re, and Os.

B. Ligand Substitution

This type of reaction may involve the replacement of dinitrogen by another ligand without change of oxidation state of the metal or the replacement of one or more of its co-ligands with retention of dinitrogen. The reactions are summarized in Table XIII. Generally, ligands which displace dinitrogen are those of similar bonding characteristics particularly carbon monoxide, nitriles and isonitriles (see section IV). Substitution of both neutral and anionic coligands can occur without loss of dinitrogen and again generally such substitution is found among the more stable complexes of the second and third transition period metals.

C. Catalysis of Olefin Reactions

In addition to the isolation and characterization of the products listed in Tables XII and XIII, dinitrogen complexes have been used as catalyst precursors. Thus $[CoH(N_2)(PPh_3)_3]$ is a catalyst precursor for the hydrogenation, isomerization, and polymerization of olefins. The active cobalt species involved in these processes is unknown, but the EPR spectrum of a species derived by reaction of $[CoH(N_2)(PPh_2)_3]$ with styrene has been interpreted to indicate the formation of a binuclear cobalt compound.[201]

$[CoH(N_2)(PPh_3)_3]$ hydrogenates vinyl methyl ether and vinyl acetate; and treatment with sodium naphthalene gives a paramagnetic, apparently binuclear compound which is an effective olefin hydrogenation catalyst.[202] It also catalyzes the polymerization of vinyl compounds such as acrylonitrile and methyl methacrylate,[203] and the isomerization of 1-pentene to 2-pentene.[204] This isomerization is promoted by dinitrogen, which also affects the isomer distribution of the products. The isomerization of *cis*-2-pentene to *trans*-2-pentene under similar conditions is also enhanced by dinitrogen. It has been suggested that substitution of product olefin by reactant olefin at the metal site is promoted by dinitrogen so enhancing the rate of isomerization.[204]

A less surprising effect of dinitrogen is its inhibition of the isomerization of 1-pentene by $[RuH_2(N_2)(PPh_3)_2]$.[205] The catalytic process has two stages. In the first, the active species, considered to be $RuH_2(PPh_3)_3$ produces 1 mol of pentane/mol of catalyst. The second is slower and follows first-order kinetics;

TABLE XIV. $\nu(N_2)$ and Relative σ-Donor Strengths K [Reaction Type 19] of the Substances A against $AlMe_3$ ($Et_2O = 1$) in Benzene[a]

A	$\nu(N_2)$, cm^{-1}	K
Tetrahydrofuran		70
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	1923	20.6
trans-$[Mo(N_2)_2(dppe)_2]$	1979	33
	2020 w	(16.5)[b]
trans-$[W(N_2)_2(dppe)_2]$[c]	1948	15
	2015 w	(7.5)[b]
trans-$[ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2]$	2000	5.5
trans-$[ReCl(CO)(PMe_2Ph)_4]$		3.3
Et_2O		1
mer-$[OsCl_2(N_2)(PEt_2Ph)_3]$[c]	2063	0.3

[a] At 34 ± 2°, ref 90. [b] Halved for comparative purposes to account for two basic sites on the molecule. [c] Adduct slowly decomposes in solution.

the catalytic species is considered to be $Ru(PPh_3)_3$. The inhibition is attributed to the competiton between dinitrogen and olefin for the metal site.[205] Thus care must be taken when interpreting kinetic data for reactions of this type operating under dinitrogen.

V. Reactions of Ligating Dinitrogen

In this section the reactions of ligating dinitrogen which lead to the formation of N–H and N–C bonds are described. As a preamble, the demonstration and measurement of the basic nature of ligating dinitrogen is presented, followed by a description of those reactions which lead to the formation of ligating N_2R, N_2R_2 or $NN{=}CR_2$ (R = H or organic group) groups or ammonia, hydrazine, or amines. Finally the mechanisms which have been proposed for the variety of reactions involved in this section are discussed.

A. Basicity

When bound at a metal site dinitrogen withdraws electron density from the metal and generally acquires a weakly basic character (see section III). The first demonstration of this property was provided by the displacement of ligating water from ruthenium(II) to give a binuclear, μ-dinitrogen complex;[206]

$$[\mathrm{Ru(NH_3)_5(H_2O)}]^{2+} + [\mathrm{Ru(NH_3)_5(N_2)}]^{2+} \rightleftharpoons [\{\mathrm{Ru(NH_3)_5}\}_2(\mathrm{N_2})]^{4+} + \mathrm{H_2O} \quad (18)$$

This type of reaction is the basis of a number of syntheses of bi- and trinuclear μ-dinitrogen complexes (see section II), the bonding of which has already been discussed (sections II and III). Such bonding may involve a σ- or $(\sigma + \pi)$ donor behavior of ligating dinitrogen toward an acceptor molecule. The $(\sigma + \pi)$ behavior was discussed in sections II and III and here we discuss the σ-donor ability alone. The relative σ-donor strengths of the terminal nitrogen atom in a few robust mononuclear dinitrogen complexes and oxygen in an analogous carbonyl have been measured in benzene solution by determining the equilibrium constants, K, of a series of equilibria of the type:[90]

$$[\mathrm{ReCl(N_2)(PMe_2Ph)_4} + \mathrm{Me_3AlOEt_2} \xrightleftharpoons{K} [\mathrm{Cl(PMe_2Ph)_4ReN{\equiv}NAlMe_3}] + \mathrm{Et_2O} \quad (19)$$

Table XIV lists the complexes examined in order of σ-donor strength toward trimethylaluminum, relative to diethyl ether. The values of K follow the order of $\nu(N_2)$ values qualitatively but not exactly and the basicity of the dinitrogen ligand depends upon its coligands; e.g., if two PMe_2Ph ligands of *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ are replaced by the less basic $P(OMe)_3$, $\nu(N_2)$ is raised and K is lowered. Thus the greater the transfer of electron density from the metal into the π^* orbitals of the dinitrogen ligand, the more basic is the terminal nitrogen atom.[90]

B. Protonation and Reduction

The previous section has indicated that ligating dinitrogen, in certain complexes, is susceptible to electrophilic attack. Such attack has recently been extensively investigated, leading to the formation of nitrogen hydrides from both terminal and bridging dinitrogen and to the formation of nitrogen–carbon bonds.

1. In Binuclear and Related Complexes

This type of reaction, presently confined to titanium, zirconium, and iron, stems historically from the observation in 1964 by Vol'pin that ammonia was obtained by treatment, under dinitrogen, of metal halido compounds with a Grignard reagent, followed by hydrolysis of the product.[151]

a. Reactions

A detailed investigation of such systems containing iron, titanium, and zirconium has led to the isolation of a number of binuclear dinitrogen complexes (see section II), some of which can be protonated to give hydrazine and/or ammonia.

Shilov and his co-workers have isolated, from the reaction of $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ with Pr^iMgBr under dinitrogen, a binuclear complex whose very low $\nu(N_2)$ value (1255 cm^{-1}) suggests a greatly weakened N–N bond. It reacts at −60 °C with hydrogen chloride to give dinitrogen together with hydrazine or ammonia depending upon the solvent.[25]

In related work by Brintzinger and co-workers,[30] the compound $[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$ has been prepared. In contrast to its C_5H_5 analogue above, no band due to dinitrogen was observed in its IR spectrum, but after treatment of it with lithium naphthalene (2 equiv) at −80 °C, followed by application of about 150 atm of dinitrogen at 20 °C, then hydrolysis, it gives ammonia, possibly via a nitride species. It was also observed that reaction of $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ with EtMgCl in ether at 20 °C gives a yellow solid of stoichiometric formulation $[\{Ti(\eta^5\text{-}C_5H_5)_2(Et)\}_2 \cdot 6MgCl_2 \cdot 7Et_2O]$.[30] This material reacts directly with dinitrogen (130 atm) in 1,2-dimethoxyethane at 20 °C to give a black solid, formulated $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_3(N)_2]$ which gives 0.66 mol of NH_3 per Ti and $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$, when treated with HCl.[30] These observations are similar to those of Shilov et al., who envisage the reduction of their $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ complex by an excess of Grignard reagent as producing the compound $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2\{N_2MgCl\}]$ followed by $[Ti(\eta^5\text{-}C_5H_5)_2\{N(MgCl)_2\}]$.[25] The latter compound, a nitride derivative related to the one described above, liberates ammonia upon hydrolysis. Similar, but not identical species, $[(\eta^5\text{-}C_5H_5)_2Ti\text{-}N(Li)\text{-}N(Li)\text{-}Ti(\eta^5\text{-}C_5H_5)_2]$ and $[Ti(\eta^5\text{-}C_5H_5)_2(NLi_2)]$, have been postulated by other workers as intermediates during the reduction of dinitrogen by the $[TiCl_2(\eta^5\text{-}C_5H_5)_2]/Li/Hg$ system.[208]

In contrast to the above proposed intermediates, which retain all the ligating cyclopentadienyl groups, it has been recently suggested that treatment of the compounds $[\{Ti(\eta^5\text{-}C_5H_5)_2R\}_2(N_2)]$ (R = C_6H_5, *m*- or *p*-$CH_3C_6H_4$, C_6F_5, or $CH_2C_6H_5$) with sodium naphthalene causes the removal of one C_5H_5 group per titanium atom, to give the diazene precursor $[\{Ti(\eta^5\text{-}C_5H_5)R\}_2(N_2)]$ which reacts with hydrogen chloride in ether to give ammonia and dinitrogen (via diazene disproportionation). Alternatively the diazene precursor complex reacts with two further equivalents of sodium naphthalene to give the anionic compound $[\{Ti(\eta^5\text{-}C_5H_5)R\}_2(N_2)]^{2-}$ which with hydrogen chloride at −78 °C in ether gives hydrazine directly. It is proposed that this anionic compound, on warming, disrupts to give such a complex as $[Ti(\eta^5\text{-}C_5H_5)(R)N]^-$, which gives ammonia on acid hydrolysis.[26]

The complexity and lability of the above titanium systems has made the characterization of intermediates and the development of a unifying mechanism difficult (see section V.B.1.b), but greater stability occurs in some zirconium analogues, which has been turned to good account by Bercaw et al.[37-39] Thus the binuclear complex $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$ is sufficiently stable

SCHEME IV

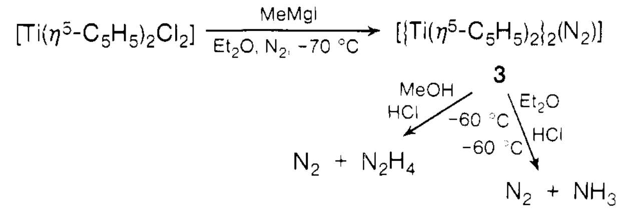
$$[\{Zr(\eta^5\text{-}C_5Me_5)_2(^{15}N_2)\}_2(N_2)] \xrightarrow{HCl} {}^{15}N_2 + [Zr(\eta^5\text{-}C_5Me_5)_2Cl_2]$$

$$+ [Zr(\eta^5\text{-}C_5Me_5)_2(^{15}N_2H)(N_2H)]$$

$$\xrightarrow{HCl} [Zr(\eta^5\text{-}C_5Me_5)_2Cl_2] + {}^{1}/_{2}{}^{15}N_2H_4 + {}^{1}/_{2}N_2H_4$$

$$+ {}^{1}/_{2}{}^{15}N_2 + {}^{1}/_{2}N_2$$

SCHEME V



for the determination of its X-ray structure (see section II), and it reacts with anhydrous hydrogen chloride in toluene at −80 °C to give hydrazine (0.86 mol):

$$[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)] + 4HCl$$

$$\rightarrow 2[Zr(\eta^5\text{-}C_5Me_5)_2Cl_2] + 2N_2 + N_2H_4 \text{ (+ a little } H_2) \tag{20}$$

It is notable that this type of binuclear complex and the related titanium compound above, but not higher oxidation-state compounds such as $[\{Ti(\eta^5\text{-}C_5H_5)_2(R)\}_2(N_2)]$ (R = alkyl or aryl),[23,29] give hydrazine. In the former, all four electrons needed to produce hydrazine from one dinitrogen molecule are available in the two zirconium(II) atoms; in the latter only two electrons are available and hydrazine could be achieved only through disproportionation of a diazene intermediate. The small amount of dihydrogen which is evolved during the reaction accounts for the remaining reducing equivalents of the zirconium atoms.

b. Mechanisms

Extensive investigations in a number of laboratories have resulted in several suggested mechanisms of reduction; all involve binuclear intermediates, and the poorly defined titanium compounds allow a wider range of possibilities.

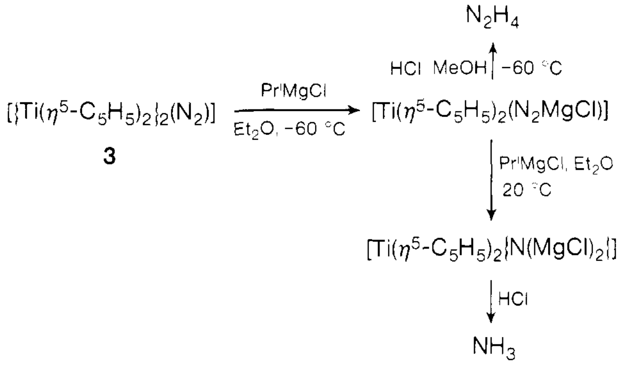
The zirconium system has been carefully studied by Bercaw, who has fully characterized the complexes $[\{Zr(\eta^5\text{-}C_5Me_5)_2\text{-}{}^{15}N_2\}_2(N_2)]$ and $[\{Zr(\eta^5\text{-}C_5Me_5)_2CO\}_2(N_2)]$. When treated with hydrogen chloride in toluene at −80 °C, the ^{15}N-labeled complex gives an equal mixture of $^{15}N_2H_4$ and $^{14}N_2H_4$ in near-quantitative yield, whereas no hydrazine is obtained from the carbonyl. It therefore appears that the terminal dinitrogen ligands are essential for hydrazine production and the mechanism shown in Scheme IV is proposed.[39]

The related titanium complex $[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$ (see section II.A) apparently gives, at best, only small amounts of ammonia, whereas the direct analogue of the zirconium compound $[\{Ti(\eta^5\text{-}C_5Me_5)_2N_2\}_2(N_2)]$ gives an almost quantitative yield of hydrazine,[36] presumably by a similar mechanism to that of Scheme IV.

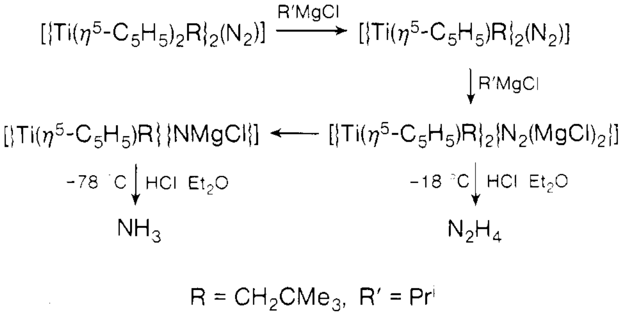
A more complicated situation arises when C_5H_5, rather than C_5Me_5 ligates titanium, because one C_5H_5 can apparently be lost during the reaction, or it can take part in hydrogen transfer reactions, whereas C_5Me_5 does not appear to do either. Thus Pez has prepared $[\{(\eta^5\text{-}C_5H_5)Ti(\eta^1{:}\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ (section II.C.1) which, after treatment with potassium naphthalene and hydrolysis by HCl, gives ammonia.[34]

Other workers have prepared the compounds $[\{Ti(\eta^5\text{-}C_5H_5)_2R\}_2(N_2)]$ (section II.C.1) and also obtained hydrazine and/or ammonia from them, after treatment with sodium or potassium naphthalene followed by acid hydrolysis. Shilov has suggested that the compound $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ (**3**) is the immediate precursor to hydrazine or ammonia formation (Scheme V).[25]

SCHEME VI



SCHEME VII



Thus **3** is regarded as forming diazene upon protonation, which disporportionates to dinitrogen and hydrazine or ammonia depending on the conditions. It has been suggested that **3** is nonlinear[24,25] (structurally analogous to diphenyldiazene), to account for its infrared active N–N stretching vibration, whereas the pentamethylcyclopentadienyl analogue (**6**) discussed above, which does not give ammonia or hydrazine in appreciable yield, is linear.[36] Such a structural difference may account for the different modes of reaction, but there is no direct evidence for the existence of nonlinear end-on bridged dinitrogen complexes.

Further treatment of **3** with Grignard reagent is suggested to proceed according to Scheme VI.[24,25]

Throughout the above schemes, the cyclopentadienyl ligands remain bound to the metal. Teuben et al., however, using a similar series of reactions to Scheme VI consider that the loss of a cyclopentadienyl ligand is a crucial step and have proposed Scheme VII. A similar scheme is thought to apply when sodium naphthalenide is the reducing agent.[26,27]

Clearly, these systems are labile and complicated; further meticulous work is necessary to determine the mechanism of hydrazine and ammonia production with any certainty.

The less well studied iron systems appear to involve binuclear intermediates but are as difficult to define as those of titanium. The reaction of $[FeCl_3(PPh_3)_2]$ with Pr^iMgBr in ether under dinitrogen at −50 °C produces a complex which has been formulated $[(Ph_3P)_2H(Pr^i)Fe(N_2)Fe(Pr^i)(PPh_3)_2]$. It decomposes rapidly in solution at 20 °C but is stable at −50 °C at which temperature it reacts with anhydrous HCl in ether to give about 0.1 mol of hydrazine per dinitrogen ligand; the rest of the dinitrogen is evolved as gas. A diazene-containing species such as $L_nFe^{+}\cdots NH\cdots NH\cdots FeL_n$ (L = ligand) which is protonated by the acid is suggested as an intermediate.[104] Similarly, from kinetic and EPR data,[209,210] the formation of an intermediate binuclear complex has been postulated from the reagents $FeCl_3/LiPh/N_2/Et_2O$ at −40 °C; it also gives hydrazine on treatment with acid. The yield originally observed was 0.28 mol per added $FeCl_3$ together with 0.15 mol of ammonia; dinitrogen was also liberated by this hydrolysis. More ammonia (0.37 mol) and less hydrazine

(0.03 mol) were obtained if the reaction temperature was raised from −40 to 90 °C (presumably in a sealed vessel).[209] The production of ammonia was subsequently shown to depend on the presence in the reaction solution of LiBr, formed during the preparation of LiPh. When lithium halides are excluded from the system, only hydrazine (0.2–0.22 mol/Fe atom) and dinitrogen (0.28–0.3 mol/Fe atom) are obtained.[210]

In a related study, using the system $FeCl_3/Mg/N_2/THF$, an intermediate dinitrogen complex formulated $[\{FeMgCl_3(thf)_{1.5}\}_2(N_2)]$ has been claimed, and this compound gives hydrazine on treatment with aqueous hydrochloric acid; the yield, however, was not quoted.[211]

2. *In Mononuclear Complexes*

Reactions which lead to the production of good yields of free or ligating dinitrogen hydrides from mononuclear dinitrogen complexes have so far been confined to the molybdenum and tungsten series.

a. Reactions

When treated with an excess of halogen acid at 20 °C the compounds *trans*-$[M(N_2)(dppe)_2]$ (M = Mo or W) give complexes of the N_2H_2 ligand:[58]

trans-$[M(N_2)_2(dppe)_2] + 2HX$
$= [MX_2(N_2H_2)(dppe)_2] + N_2$ (21)

(M = W, X = Cl, Br, or I; M = Mo, X = Br or I)

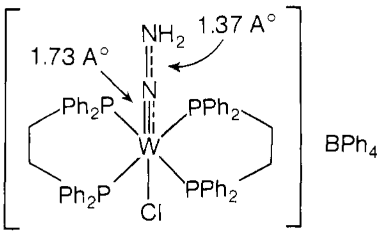
On the basis of a wide splitting of the N–H stretching IR bands and a single, rather low-field N–H resonance in these apparently seven-coordinate products, the N_2H_2 ligand has been assigned a diazene structure and considered to act as a two-electron donor to give an 18-electron configuration.[58] More recent evidence, however, suggests that the splitting and large chemical shift may be caused by asymmetric hydrogen bonding of the N_2H_2 ligand in the hydrazido(2-) form (:N–NH_2) to halogens (see complex **56** and Table XVI.)

One halide is labile and in the salt produced on its replacement by a noncoordinating anion such as BPh_4, the N_2H_2 ligand certainly has the hydrazido(2-) form in which it acts as a four-electron donor ligand, so that the metal retains an 18-electron configuration:[58]

$[MX_2(N_2H_2)(dppe)_2] + NaY$
$= [MX(NNH_2)(dppe)_2]Y + NaX$ (22)

M = W, X = Cl or Br, Y = BPh_4, ClO_4, PF_6, or BPh_4;
M = Mo, X = Br, Y = BF_4

The structure of *trans*-$[WCl(NNH_2)(dppe)_2]BPh_4$ (**58**) shows that the M–N–N unit is essentially linear, and the N–N bond distance indicates a bond order rather greater than unity; the short W–N distance confirms the expected essentially triple bond character of the bond[212] (see also Table XVI).



58

When sulfuric acid replaces halogen acids in eq 21, cationic, hydrazido(2-) complexes $[M(NNH_2)(SO_3H)(dppe)_2]HSO_4$ (M = Mo or W) are the only products.[213] If HBF_4 is used, fluorohydrazido(2-) compounds, $[MF(NNH_2)(dppe)_2]BF_4$ (M = Mo or W) result,[214] the molybdenum analogue having also been prepared by use of $[Et_3O]BF_4$ instead of HBF_4 (for structure, see Table XVI).[215]

The hydrazido(2-) complexes may be dehydrohalogenated with weak base to give diazenido complexes:[214]

trans-$[MX(NNH_2)(dppe)_2]BF_4 + NEt_3$
$=$ *trans*-$[MX(N_2H)(dppe)_2] + [NEt_3H]BF_4$ (23)

M = Mo or W; X = F, Cl, or Br

The diazenido ligand is isoelectronic with nitrogen oxide and is quantitatively displaced by it:[214]

trans-$[MX(N_2H)(dppe)_2] + 2NO$
$= [MX(NO)(dppe)_2] + N_2 +$ 'HNO' (24)

Treatment of the diazenido complexes with acids regenerates the hydrazido(2-) compounds.[214]

Attempts to reduce the N_2H_2 grouping in the above complexes by a variety of reducing agents failed,[58] but moderate yields of ammonia (0.24 mol/Mo atm) were obtained if $[MoBr_2(N_2H_2)(dppe)_2]$ together with *trans*-$[Mo(N_2)_2(dppe)_2]$ were treated with aqueous HBr in *N*-methylpyrrolidone or propylene carbonate followed by removal of solvent and Kjeldahl distillation.[216] Protonation and reduction beyond the N_2H_2 stage is probably the result of phosphine ligand displacement at the relatively high temperatures of solvent removal. On the other hand, the complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ or *trans*-$[M(N_2)_2(PPh_2Me)_4]$ (M = Mo or W) give, on treatment with sulfuric acid in methanol at 20 °C, then base distillation for M = Mo, high yields of ammonia (with a little hydrazine in some cases).[213,217] The reaction is illustrated in eq 25 and typical yields are shown in Table XV.

cis-$[M(N_2)_2(PR_3)_4] \xrightarrow[\text{base distillation for M=Mo}]{H_2SO_4/MeOH} N_2 + 2NH_3$
$+$ M(VI) products $+ 4[PR_3H]HSO_4$ (25)

M = Mo or W; PR_3 = PMe_2Ph or $PMePh_2$

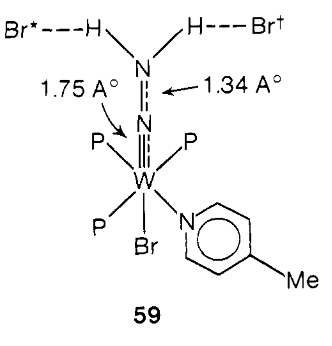
The yield of ammonia, according to eq 25 is essentially quantitative for M = W, but only ~0.66 mol/metal atom for M = Mo. The final tungsten product appears to be essentially a W(VI) oxide species, but the nature of the molybdenum-containing product has not yet been elucidated.[217] Some indication of probable intermediates in these reactions has been gained by variation of the reagents in reaction 14. Thus by using HX (X = Cl, Br, or I) instead of sulfuric acid, dihalidohydrazido(2-) complexes may be isolated:[218]

cis-$[M(N_2)_2(PMe_2Ph)_4] + HX(excess)$

$\xrightarrow{MeOH} [MX_2(NNH_2)(PMe_2Ph)_3] + N_2 + [PHMe_2Ph]X$ (26)

M = Mo or W; X = Cl, Br, or I

Various neutral ligands will displace one halide ion to give salts (eq 27),[219] the X-ray structure of one of which (**59** and Table XV)



P = PMe_2Ph
Br* = bromide in another complex cation
Br† = bromide in lattice

59

TABLE XV. Yields of Ammonia and Hydrazine from Dinitrogen, Hydrazido(2-) and Hydrazido(1-) Complexes[a]

compound	solvent	reagent[b]	NH_3	N_2H_4	N_2[c]
cis-$[W(N_2)_2(PMe_2Ph)_4]$	THF	H_2SO_4 (15)	0.89	0.20	0.98
cis-$[W(N_2)_2(PMe_2Ph)_4]$	MeOH	H_2SO_4 (15)	1.86	0.02	0.97
cis-$[W(N_2)_2(PMe_2Ph)_4]$	MeOH/H_2O	H_2SO_4 (15)	1.26	0.03	0.98
trans-$[W(N_2)_2(PMePh_2)_4]$	THF	H_2SO_4 (19.5)	0.72	0.15	1.0
trans-$[W(N_2)_2(PMePh_2)_4]$	MeOH	H_2SO_4 (20)	1.80	0.07	0.99
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	THF	H_2SO_4 (7)	0.55	trace	1.06
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	MeOH	H_2SO_4 (12)	0.64	trace	1.23 (0.21)[d]
trans-$[Mo(N_2)_2(PMePh_2)_4]$	THF	H_2SO_4 (12)	0.08	0.02	1.87
trans-$[Mo(N_2)_2(PMePh_2)_4]$	MeOH	H_2SO_4 (12)	0.66	0	1.64
trans-$[Mo(N_2)_2(dppe)_2]$[e]	n.m.p.[j]	HBr/H_2O (~100)	0.37		n.d.
trans-$[Mo(N_2)_2(dppe)_2]$[e]	p.c.[k]	HBr/H_2O (~100)	0.19		n.d.
cis-$[W(N_2)_2(PMe_2Ph)_4]$	MeOH[f]		1.56	0.03	1.03 (0.02)[d]
cis-$[W(N_2)_2(PMe_2Ph)_4]$	MeOH[g]		1.64	0.02	1.0 (0.04)[d]
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	MeOH		0	0	1.9 (1.1)[d]
$[WX_2(NNH_2)(PMe_2Ph)_3]$[l]	MeOH	H_2SO_4 (20)	1.54[h] (X = Cl)	0.06	n.d.[i]
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	H_2O	KOH (~250)	1.4	0.14	n.d.
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	MeOH	H_2SO_4 (20)	0.67	0.01	0.61
$[MX_2(NNH_2)(PMe_2Ph)_3]$[l]	H_2O	KOH (~250)	trace	trace	n.d.
$[WCl_3(NHNH_2)(PMePh_2)_2]$	MeOH	H_2SO_4 (20)	0.38	0.66	0.63
$[WCl_3(NHNH_2)(PMePh_2)_2]$	H_2O	KOH (~250)	0.76	0.08	n.d.

[a] References 196, 217–219. [b] Moles of reagent in parentheses. [c] Gas evolved. [d] H_2 gas. [e] Reference 161. [f] Irradiated with 2 × 150 W tungsten filament lamps for 42 h. [g] At 60 °C for 4 h. [h] 1.72, X = Br; 1.88, X = I. [i] n.d. = not determined. [j] n.m.p. = *N*-methylpyrrolidone, [k] p.c. = propylene carbonate. [l] X = Cl, Br, or I.

confirms the presence of the hydrazido(2-) ligand.[220] The N–H stretching IR band is broad and split (170 cm^{-1}) and the N–H resonance is at low field (8–10 ppm relative to Me_4Si) owing to asymmetric hydrogen bonding from $:NNH_2$ to bromide (**56**). Evidently the above spectroscopic parameters are not diagnostic of a monodentate diazene complex.

$$[MX_2(NNH_2)(PMe_2Ph)_3] + L \xrightarrow{CH_2Cl_2} [MX(NNH_2)L(PMe_2Ph)_3]X \quad (27)$$

M = Mo or W; L = substituted pyridine or tertiary phosphine

On reaction with H_2SO_4/MeOH, then distillation from base, the $[MX_2(NNH_2)(PMe_2Ph)_3]$ compounds provide ammonia in essentially similar yields to those obtained from the parent dinitrogen complexes under the same conditions.[218] These reactions are quicker and give higher yields, in the presence of Tl_2SO_4 (Table XV). They reach completion quicker (~2–3 min) than reaction 25, and so the hydrazido(2-) ligand is probably an intermediate on the route to ammonia, common to both molybdenum and tungsten. In contrast to its cis isomer, *trans*-$[W(N_2)_2(PPh_2Me)_4]$ on treatment with HCl in methanol gives ammonia (1.9 mol/W atom) and hydrazine (0.02 mol/W atom) but not a hydrazido(2-) complex. In dichloromethane, however, a hydrazido(1-) complex is formed[196] as in eq 28, which, in turn, gives ammonia and hydrazine on treatment with sulfuric acid and base distillation (Table XV).

$$\textit{trans-}[W(N_2)_2(PPh_2Me)_4] + HCl(excess) \xrightarrow{CH_2Cl_2} \textit{trans-}[WCl_3(NHNH_2)(PPh_2Me)_2] + N_2 + 2[PPh_2MeH]Cl \quad (28)$$

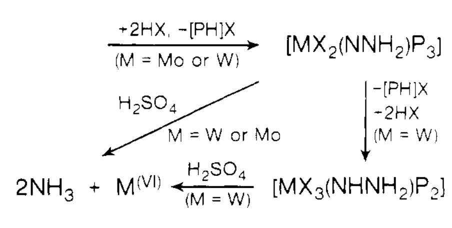
Although the hydrazido(1-) ligand could be a further step toward ammonia, the yield of hydrazine is relatively high compared with that obtained from the dinitrogen complex and more probably the hydrazido(1-) stage is on a side route to hydrazine. The mechanistic implication of these stepwise protonations, $M\text{–}N_2H$, $M\text{–}N_2H_2$, $M\text{–}N_2H_3$, are discussed later (section V.D.2.b). It should be noted that ammonia is also produced, in high yield, from the complexes $[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl, Br, or I), on their distillation from 40% KOH solution alone, but under these alkaline conditions their molybdenum analogues give only traces of ammonia at best (examples in Table XV). Moreover, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ gives almost as high a yield of ammonia (1.7 mol/W atom), but more slowly, on treatment with methanol alone, either at reflux (3–4 h) or under tungsten-filament irradiation (30 h at 20 °C).[217,221] A lower yield of ammonia is given by reaction with ethanol (0.4 mol/W atom) but the molybdenum analogue gives virtually no ammonia with either alcohol (0.08 mol/Mo at best).[217,221]

b. Mechanisms

As has been described above, the treatment of bis(dinitrogen) complexes with sulfuric and some other acids at 20 °C gives ammonia from molybdenum and tungsten complexes and varying, but substantially lower yields of hydrazine, barely detectable in the case of molybdenum complexes. A number of complexes have been isolated which contain the dinitrogen ligand in intermediate stages of reduction which, although they are not all prepared with the same phosphine or anionic ligand, can be used as a reasonable basis for Scheme VIII.

Some further comments on Scheme VIII are necessary. First, the complex containing the N_2H_3 ligand has been isolated only when M = W, but this is not surprising; complexes of the third long period metals usually are more robust than those of the second. The yield of ammonia for M = Mo is less than that obtained for M = W and close to 0.67 NH_3 per Mo atom. If the compounds $[MX_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W) are treated with sulfuric acid in methanol, they give ammonia (~1.8 mol/W atom; ~0.67 mol/Mo atom together with ~0.67 mol N_2/Mo atom) in similar yields to those obtained from the parent dini-

SCHEME VIII

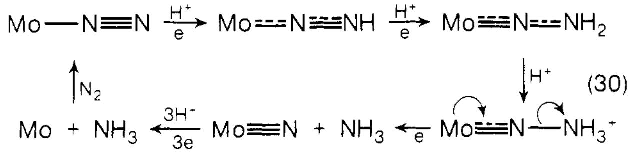


P = mono(tertiary phosphine); X = halide ion trogen complexes. Thus the mechanism appears to diverge for the two metals at the N-NH$_2$ stage.[217,219] The yield of ammonia obtained for M = Mo is consistent with a disporportionation step as in the equation

$$\text{Mo}{=}\text{N}{=}\text{NH}_2 \rightarrow \text{'Mo'} + \tfrac{2}{3}\text{N}_2 + \tfrac{2}{3}\text{NH}_3 \qquad (29)$$

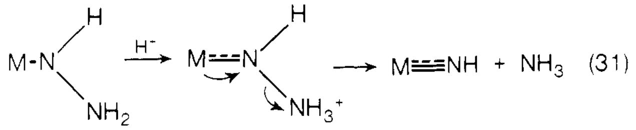
perhaps via release of isodiazene, whereas further protonation must occur when M = W to account for the very high yields (90% NH$_3$, 5% N$_2$H$_4$). The possibility that the N$_2$H$_2$ ligand is released from molybdenum but held by tungsten for further protonation and reduction may be a reflection of (a) the greater lability of molybdenum complexes and/or (b) the poorer reducing power of molybdenum in its lower oxidation states. Incidentally neither of these factors need have any relevance to the nitrogenase reaction if it occurs by a mechanism deduced from Scheme VIII, such as is represented by reactions 30 or 31. Property (a) could be overcome by the greater rigidity of the protein ligand and (b) by the continuous transfer of electrons into molybdenum from the electron-storage system of the enzyme.

If the M-NH-NH$_2$ stage represents a side reaction on the route to hydrazine, which seems likely, the protonation steps of [W(N$_2$)$_2$(PR$_3$)$_4$] (PR$_3$ = PMe$_2$Ph or PMePh$_2$) suggests the cyclic system in eq 30 for the mechanism of reduction of molecular



nitrogen on a molybdenum atom in nitrogenase. The electrons (e) would be provided from the reduced iron-sulfur clusters of nitrogenase and protons from the aqueous environment. The scheme indicates how the energy for the degradation of the strong triple bond of molecular nitrogen is provided by formation of the new Mo≡N bond and simultaneous formation of three N-H σ bonds.

Even if the M-NH-NH$_2$ stage of reduction is on the route to ammonia the above scheme needs little modification to accommodate it as in (31) which represents only the N≡N bond-splitting part of the cyclic scheme.



Compounds containing the grouping M≡N or its protonated form M≡NH should hydrolyze readily to ammonia, and indeed compounds such as [MoCl$_2$(N)(PMePh$_2$)$_2$], prepared indirectly, have been observed to do so.[222]

The involvement of dinitrogen-bridged complexes has usually been invoked to explain the reduction of dinitrogen to ammonia or hydrazine in metal complexes or by metal complexes as catalysts. The high yields of ammonia obtained from the bis(dinitrogen)tungsten complexes and the isolation of monomeric reduced complexes up to the NHNH$_2$ stage make the involvement of dimeric species highly improbable in their case. Similarly monomeric species are probably involved in all the stages of the reactions of the bis(dinitrogen)molybdenum compounds, but as yet the involvement of dimeric species cannot be completely excluded.

The production of hydrazine or ammonia from stable dinitrogen complexes, whether mono- or dinuclear, appears to involve the replacement of coligands such as dinitrogen, tertiary phosphines, or cyclopentadienyl groups, which stabilize the lower oxidation states of the metals. They are replaced by anionic ligands such as halide or sulfate ions which stabilize the higher oxidation states. This process promotes electron transfer from the metal to the dinitrogen or derived dinitrogen hydride ligand, promoting, in turn, further attack by protons to give hydrazine or ammonia as final major products. Clearly only tungsten or molybdenum, with their ability to undergo facile oxidation by six units could give 2 mol of ammonia from a mononuclear complex without being coupled to an external reducing agent.

3. *Formation of Nitrogen-Carbon Bonds*

Of potential industrial importance is the production of organo-nitrogen compounds from dinitrogen and a relatively cheap organic feedstock. The first steps in the development of such a process appear to have been taken. Some years ago Vol'pin reported that low yields of aniline were obtained after hydrolysis of solutions obtained by treating [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] with LiPh in ether under dinitrogen. Insertion of dinitrogen into a titanium-carbon bond was suggested as a mechanism, but no authenticated examples of such a reaction have yet been found.[223] Another early and related reaction, apparently involving the insertion of a ketone, with reduction, into a strongly reduced cyclopentadienyltitanium nitride complex, gave amines R$_2$CHNH$_2$ (R = Bu^n or PhCH$_2$) in up to 25% yield based on the nitrogen fixed by the titanium system.[224] The nitride was produced by the magnesium reduction of dichlorobis(cyclopentadienyl)titanium in tetrahydrofuran under dinitrogen.

a. Reactions

The first unambiguous formation of a nitrogen-carbon (and nitrogen-hydrogen) bond from ligating dinitrogen in almost quantitative yield is shown:[225,226]

$$\textit{trans}\text{-}[\text{W(N}_2)_2(\text{dppe})_2] + \text{CH}_3\text{COCl} + \text{HCl} = [\text{WCl}\{\text{N}_2(\text{H})\text{COCH}_3\}(\text{dppe})_2]\text{Cl} + \text{N}_2 \qquad (32)$$

This type of reaction occurs at room temperature. Similar reactions also occur with various alkyl halides to give organodiazenido compounds which can subsequently be protonated to the organohydrazido(2-) complexes (eq 33). This latter conversion is often used to isolate the product of a particular reaction because the organohydrazido(2-) complexes are more easily crystallized and are readily converted to organodiazenido complexes by weak base.[67,226-229]

$$\textit{trans}\text{-}[\text{M(N}_2)_2(\text{dppe})_2] + \text{RX} \rightarrow [\text{MX(N}_2\text{R)(dppe)}_2] + \text{N}_2 \xrightarrow{\text{HX}} [\text{MX}\{\text{NN(H)R}\}(\text{dppe})_2]\text{X} \qquad (33)$$

M = Mo or W; R = Me, Et, Pr^n, Pr^i, Bu^t, C$_6$H$_{11}$, C$_8$H$_{17}$, MeCO, EtCO, Bu^{t}CO, C$_6$H$_5$CO, CH$_3$C$_6$H$_4$CO, or CH$_2$CO$_2$Et

Reactions involving alkyl halides are catalyzed by daylight or by tungsten-filament light; indeed irradiation is essential when M = W, but the molybdenum complexes react slowly in the dark. The structures of several complexes of the above types have been established by X-rays (Table XVI).

When α,ω-dibromoalkanes, (CH$_2$)$_n$Br$_2$, are used as reagents, the products depend on the length of the alkyl chains as shown in Table XVII.[232] The product when n = 1 is a diazomethane complex.[233] Other *gem*-dibromoalkanes give analogous products. The reactions when n = 4 or 5 are the only ones yet known to attach two carbon atoms to the terminal nitrogen atom, except when M = W, when reaction with an excess of MeBr produces [WBr(N-NMe$_2$)(dppe)$_2$].[226] Benzyl bromide is anomalous; it produces [MBr$_2$(dppe)$_2$] and bibenzyl.[234]

All the above reactions occur in inert solvents such as toluene. However, certain solvents, e.g., tetrahydrofuran, can interfere in the reaction with the lower alkyl halides, particularly methyl bromide, to give organonitrogen products derived from the sol-

TABLE XVI. X-Ray Parameters for Hydrazido(2-) and Related Complexes

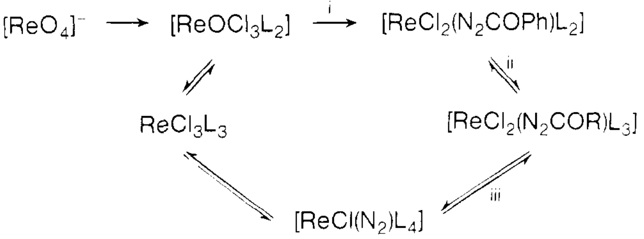
complex	M–N(1), Å[a]	N(1)–N(2), Å[a]	M–N(1)–N(2), deg	ref
$[WCl(NNH_2)(dppe)_2]BPh_4$	1.73 (1)	1.37 (2)	171 (1)	212
$[MoF(NNH_2)(dppe)_2]BF_4$	1.762 (12)	1.333 (24)	176.4 (13)	215
$[WBr(NNH_2)(PMe_2Ph)_3(MeC_5H_4N)]Br$	1.75	1.34	177	220
$[MoI\{NN(H)C_8H_{17}\}(dppe)_2]I$	1.801 (11)	1.259 (14)	174 (1)	228
$[WBr\{NN(H)Me\}(dppe)_2]Br$	1.768 (14)	1.32 (2)	174 (1)	230
$[MoCl\{NN(COPh)\}(dppe)_2]$	1.81	1.24	171.7	67
$[MoI\{NN(C_6H_{11})\}(dppe)_2]$	1.95 (1)[b]	0.91 (1)[b]	176 (1)[b]	228a
$[ReCl_2(N_2COC_6H_5)(PMe_2Ph)_3]$	1.74 (2)	1.22 (3)	170 (2)	231
$[WBr\{N_2CH(CH_2)_3OH\}(dppe)_2]PF_6$	1.778 (14)	1.306 (22)	172 (1)	237

[a] Atoms labeled M–N(1)–N(2). [b] Inaccurate value because of poor crystals.

TABLE XVII

n	products
1	$[MBr(N_2CH_2)(dppe)_2]^+ + N_2$
2	$[MBr_2(dppe)_2] + C_2H_4 + N_2$
3	$[MBr\{N_2(CH_2)_3Br\}(dppe)_2] + N_2$
4 or 5	$[MBr\{N{-}\overline{N(CH_2)_{(n-1)}C}H_2\}(dppe)_2]Br + N_2$
>5	$[(dppe)_2BrM\{N_2(CH_2)_nN_2\}MBr(dppe)_2]$ $+ [MBr\{N_2(CH_2)_nBr\}(dppe)_2] + N_2$

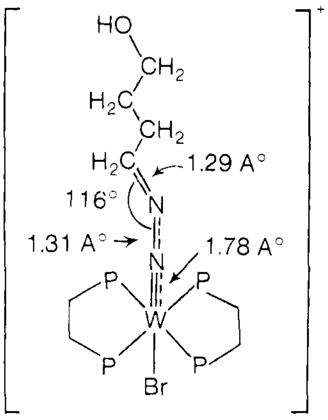
SCHEME IX



vent. The most studied of these is the reaction of methyl bromide with *trans*-$[Mo(N_2)_2(dppe)_2]$ in tetrahydrofuran:

$$trans\text{-}[Mo(N_2)_2(dppe)_2] + MeBr + THF \\ \rightarrow [MBr\{N{=}N{-}\overline{CH_2(CH_2)_3O}\}(dppe)_2] + MeH + N_2 \quad (34)$$

The heterocyclic ligand is very sensitive to acid, which opens the ring to give diazobutanol complexes $[MBr\{N{-}N{=}CH(CH_2)_3OH\}(dppe)_2]Br$. These were originally formulated, on the basis of spectroscopic data, as tetrahydropyridazido complexes,[236] but their composition and structure were finally established by X-rays (**60** and Table XV).[235,237] They are the



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usual products isolated when reaction 34 is catalyzed by irradiation, the acid being produced by photolysis of the methyl bromide. An alternative route to diazoalkane complexes is the condensation reaction, eq 35, which is catalyzed by acid (aqueous HBF_4).[238]

$$trans\text{-}[MoF(NNH_2)(dppe)_2]BF_4 + RR'C{=}O \\ \xrightarrow{HBF_4} H_2O + [MoF(NNCRR')(dppe)_2]BF_4 \quad (35)$$

$$R = CH_3CH_2,\ R' = H;\ R = C_6H_5,\ R' = H;\ R = R' = CH_3$$

The reactions of organic halides with molybdenum and tungsten dinitrogen complexes which have monodentate tertiary phosphine coligands, e.g., *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W), are less well studied but appear to lead to the complete destruction of the complex.[239] However, complexes of the type $[MCl_2(N_2CRR')(PMe_2Ph)_3]$ can be prepared by the condensation of organic carbonyl compounds with the complexes $[MCl_2(NNH_2)(PMe_2Ph)_3]$,[240] cf. eq 35.

Acyl- and aroyldiazenido complexes $[ReCl_2(N_2COR)(PMe_2Ph)_3]$ (R = Me or Ph) have been prepared by the treatment of $[ReCl(N_2)(PMe_2Ph)_3(C_5H_5N)]$ (or, less effectively, *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$) with RCOCl (R = Me or Ph).[241]

This synthesis of benzoyldiazenido complexes is essentially the reverse of the original preparation of rhenium(I)-dinitrogen complexes and thus a formally cyclic process with well-defined steps (Scheme IX) has been realized. Most of these steps are reversible, although not all can be carried out using the same phosphine. (Step i is only for L = PPh_3; steps ii and iii require other ligands such as L = PMe_2Ph, which allows all steps except i[226]). In all the reactions of dinitrogen complexes in Scheme IX, whether of rhenium, molybdenum, or tungsten, a neutral ligand (dinitrogen, tertiary phosphine, or pyridine) is displaced when N-C (or N-H) bond formation occurs. It was not possible to acylate, aroylate, protonate, or alkylate dinitrogen in *trans*-$[ReCl(N_2)(dppe)_2]$, where the chelating dppe ligand is not displaced. Also *mer*-$[OsCl_2(N_2)(PMe_2Ph)_3]$ is not acylated or aroylated, but in this case, in addition to the fact that the phosphine ligands are inert to displacement, the dinitrogen has little affinity for electrophiles (see Table XIII).

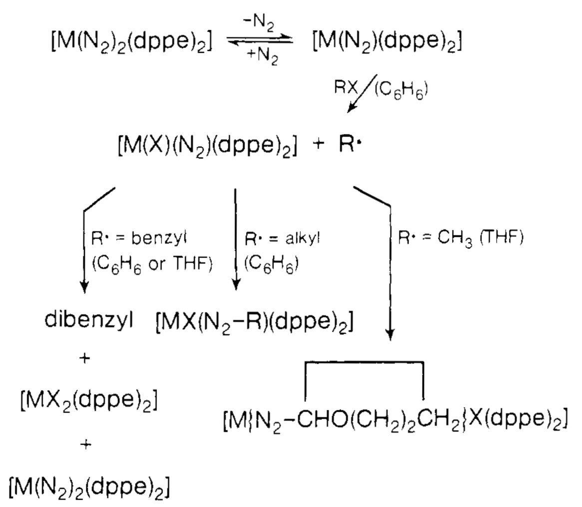
b. Mechanisms

The mechanism of the first step of the protonation of ligating dinitrogen discussed in section V.B.2.b has not yet been examined in detail. The first protonated product is clearly formed rapidly at room temperature in the presence of acid and does not appear to need irradiation. In the case where methanol alone is the reagent, light is necessary for complete reduction of dinitrogen at room temperature.

The mechanism of the alkylation of ligating dinitrogen by alkyl halides has, however, been established and involves the formation and reactions of free alkyl radicals in the manner of Scheme X.[234]

The first step, loss of dinitrogen, is rate controlling. It occurs in the dark when M = Mo (rate constant ca. $1.5 \times 10^{-4}\ s^{-1}$ by ^{15}N exchange) but is accelerated by light and needs light when M = W. The alkyl halide, RX, then becomes attached by the X atom to the metal and homolytic RX bond cleavage occurs to release an R· radical which attaches itself to the terminal nitrogen atom of the residual N_2 ligand. The reaction has pseudo-first-order kinetics in the presence of 100-fold excess of alkyl halide

SCHEME X



(M = Mo or W, RX = alkyl halide, solvent in parentheses)

(rate constants ca. 10^{-4} s^{-1} in the dark when M = Mo). The radicals have been identified by the ESR spectrum after trapping on nitrosodurene. In THF solution signals assignable to $O(CH_2)_3CH\cdot$ were observed as well as methane evolution when $R = CH_3$. The occurrence of free radicals was confirmed by the reaction of $[W(N_2)_2(dppe)_2]$ with $CH_2{=}CH(CH_2)_4Br$ which produces $[WBr\{N_2CH_2\overline{CH(CH_2)_3CH_2}\}(dppe)_2]$ in high yield and none of its $N_2(CH_2)_4CH{=}CH_2$ analogue. The rearrangement of the hex-5-enyl radical into the cyclopentylmethyl radical has a first-order rate constant of ca. 10^5 s^{-1}.[234]

The variety of products from different halides depends on the fate of the radicals. At room temperature, alkyl chlorides and aryl halides generally produce no radicals and there is no reaction.[234] Alkyl bromides in benzene or toluene give the normal alkyldiazenido products (eq 33), but in THF and a few related solvents, solvent radicals are produced and the diazenido complex derived from them is the first product (e.g., eq 34). This type of reaction has been observed in dioxan, tetrahydropyran, 2-methyltetrahydrofuran, tetrahydrothiophene, and *N*-methylpyrrolidine.[242] The solvent reactions occur best when methyl bromide is the alkyl halide; higher alkyl bromides give the normal alkyldiazenido product or a mixture of the normal and solvent derived products. The benzyl radical, which is not sufficiently reactive to attack the residual dinitrogen in $[MBr(N_2)(dppe)_2]$, dimerizes, and the unstable monobromo complex disproportionates to $[MBr_2(dppe)_2]$ and $[M(N_2)_2(dppe)_2]$ (see Scheme X).

The reactions of α,ω-dibromoalkanes $(CH_2)_nBr_2$ appear to proceed analogously through the radicals $Br(CH_{2(n-1)}CH_2\cdot$. When $n = 1$ the "normal product" containing the diazenido group $M{-}N{=}N{-}CH_2Br$ is presumably first formed but ionizes to give the diazomethane complex cation $[MBr(N_2CH_2)(dppe)_2]^+$. When $n = 2$ the radical $BrCH_2CH_2\cdot$ decomposes to give $Br\cdot + C_2H_4$. When $n = 3$ the normal product results, but when $n = 4$ or 5 cyclic products are obtained probably by intramolecular quaternization of the normal product on the terminal nitrogen atom.

The diazoalkane complexes containing the grouping $M(N{-}N{=}CRR')$ (M = Mo or W, R and R′ = H or alkyl) do not react with acids to give the organodiazenido complexes $[MBr(N_2CHR{-}R')(dppe)_2]^{2+}$, but their uncharged analogues are obtained by quantitative reaction with hydridic reagents, e.g., $LiAlH_4$.[233] On the other hand, the organodiazenido complexes $[MBr(NMR)(dppe)_2]$ react with acids to give organohydrazido(2-) complexes $[MBr(NNHR)(dppe)_2]^+$ quantitatively.

Amines are not obtained easily from the dppe–alkyldiazenido complexes, either by reaction with acids or with hydrides. However, the dialkylhydrazido complexes of the type $[MBr(N_2R_2)(dppe)_2]Br$ [M = W, $N_2R_2 = N_2Me_2$ or $N_2(CH_2)_4$; or M = Mo, $N_2R_2 = N_2(CH_2)_4$] give secondary amines in yields of up to 95% on treatment with an excess of $LiAlH_4$ in ether at 80 °C in a sealed tube.[243] Smaller, but still substantial yields (25–60%) are obtained by distillation of the complexes from 40% KOH.[243]

VI. Nitrogen Fixation in Aqueous Solution

A. Introduction

Reactions producing ammonia from well-characterized dinitrogen complexes have generally been carried out in nonaqueous media, although aqueous methanol has been used. However two research groups, those of A. E. Shilov and G. N. Schrauzer, have focused their attention on reactions of dinitrogen in predominantly aqueous media, both commencing their extensive series of publications in 1970.

Schrauzer's systems were initially based on the premise that the enzyme contains inter alia iron, molybdenum-, and sulfur-containing amino acids. He reduced mixtures of iron and molybdenum salts and sulfur ligands such as cysteine or mercaptoethanol with sodium borohydride in buffered solutions in the presence of dinitrogen. The iron was later found to be unnecessary and additional reagents such as ATP were incorporated. Ultimately the most successful system does not involve biological ligands, but utilizes molybdenum cyano complexes. By contrast Shilov has not attempted such direct simulation of the enzyme, but has undertaken a systematic study of the reactivity of the d^3 metal ions, vanadium(II) and molybdenum(III) toward dinitrogen in water.

Unfortunately, it is not in general possible to isolate intermediates from these systems, and the proposed mechanisms are based on kinetic measurements, overall stoichiometry, and, not least, chemical intuition. This can lead, as in the case of hydrazine formation from alkaline vanadium(II)–magnesium(II) mixtures, to quite different mechanistic postulates. Shilov favors a tetranuclear vanadium(II) binding site with one electron from each vanadium giving hydrazine, whereas Schrauzer is a proponent of diazene as an intermediate and its subsequent disproportionation to hydrazine and dinitrogen. The diazene is postulated to be generated on a mononuclear vanadium(II) entity which gives two electrons to a side-on bound dinitrogen.

The use of ^{15}N-labeling unequivocably establishes that many aqueous systems are capable of reducing dinitrogen to hydrazine and/or ammonia, although the overall yields can be very low. However, the major problem often encountered when working with aqueous nitrogen-fixing systems is that of irreproducibility. A reaction that apparently generates ammonia one day inexplicably fails to do so the next. The operation of these aqueous systems at low metal ion concentrations doubtless increase the possibility that impurities may be crucially involved. A further complication is the difficulty of controlling all the reaction parameters with precision in such complex mixtures. The literature is voluminous and often confusing. We have made no attempt at a critical appraisal of the various contradictions that it contains, and our brief summary is mainly intended to direct readers to the appropriate areas of the literature. Hopefully time and further work will define the essential factors which determine the reduction of dinitrogen in aqueous solution.

Discussion of the aqueous systems can conveniently be divided into those based on molybdenum, those based on vanadium, and the much smaller number based on other metals. A comparatively recent development has been the use of electrolysis or photolysis in nitrogen-fixing systems and a brief account is included.

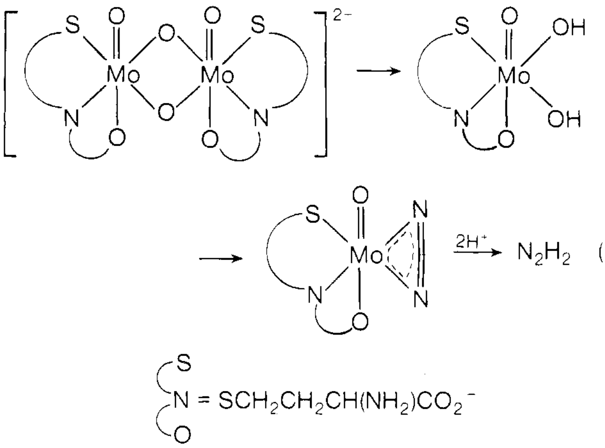
B. Systems Using Molybdenum

Schrauzer and co-workers have developed a number of systems which mimic certain aspects of the behavior of nitrogenase. For example, acetylene is reduced to ethylene, isonitriles to methane (and other hydrocarbons) and amines, and nitriles to hydrocarbons and ammonia. A typical system comprises sodium molybdate, thioglycerol or L(+)-cysteine and sodium borohydride held at pH 9–10 in a borate buffer. Other reagents are also added to enhance the yields of reduced substrate and their role is discussed below. In a recent review Schrauzer has summarized his mechanistic proposals for the reduction of a range of substrates in different systems.[244]

Although these molybdenum-thiol systems have been intensively investigated,[245–247] particularly with acetylene as substrate, no intermediate species have been isolated, and it is difficult to say with any certainty what active species are involved in the reduction steps. Schrauzer has repeatedly suggested that with cysteine as ligands a coordinatively unsaturated Mo(IV) complex is formed (eq 36) to which dinitrogen or acetylene binds in a side-on manner in the first stages of reduction.

However, it has also been suggested, on the basis of electrochemical measurements, that the reduction of acetylene to ethylene by molybdenum–cysteine systems is mediated by a molybdenum(III) species.[248]

Side-on bonding of dinitrogen is followed by transfer of two electrons from molybdenum and protonation to give diazene[249] (eq 36). The latter subsequently disproportionates to hydrazine, dihydrogen, and dinitrogen (eq 37) and the hydrazine is then reduced to ammonia (eq 38). The disproportionation of a diazene intermediate to give dihydrogen is suggested by Schrauzer as an explanation for the maximum of 60–70% inhibition of hydrogen evolution by dinitrogen in the enzyme system.



(36)

$$3N_2H_2 \rightarrow 2N_2 + H_2 + N_2H_4 \qquad (37)$$

$$N_2H_4 \xrightarrow[2H^+]{Mo} 2NH_3 \qquad (38)$$

The intermediacy of diazene is based on kinetic data, the inhibitory effect of olefinic substrates such as allyl alcohol and sodium fumarate, and ^{15}N-labeling experiments. If reactions are carried out in the presence of ATP under an atmosphere of $^{30}N_2$ and the system is then oxidized with sodium hypobromite, the yields of both $^{30}N_2$ and $^{29}N_2$ are a maximum after about 40 min and thereafter decrease. The $^{29}N_2$ yield provides a measure of the $^{15}NH_3$ generated, as the oxidation is carried out in the presence of a large excess of $^{14}NH_3$. The $^{30}N_2$ peak can only arise from species with intact N-N bonds such as protonated dinitrogen derivatives. Assignment of the origin of the $^{30}N_2$ peak to diazene is based on two observations. First, the $^{30}N_2$ yield is halved if the solution is made alkaline and distilled prior to oxidation; this is consistent with disproportionation of the diazene to dinitrogen and hydrazine, the latter being detected in the distillate. Second, the addition of diazene-trapping agents, such as fumarate anion, significantly reduces the $^{30}N_2$ peak. The maximum in the yield of $^{29}N_2$ is puzzling, as any $^{15}NH_3$ formed would be expected to accumulate during the reaction. This apparent anomaly may be due to the presence of ATP, or be an artifact of the analytical procedure employed.

Because the reduction of substrates such as CN^- and C_2H_2 are stimulated by the addition of ATP,[250] Schrauzer believes that the ATP facilitates the release of OH groups from molybdenum to generate the active site (eq 35) for binding dinitrogen. The iron–sulfur cluster $[Fe_4S_4(SPr^n)_4]^{2-}$ also accelerates the reduction of acetylene to ethylene by facilitation of electron transfer. However it is difficult to compare the efficiency of systems containing the iron–sulfur clusters as the latter are slowly decomposed by sodium borohydride, and, therefore sodium dithionite was employed as an alternative reductant.[247,249]

More recently the complex $[MoO(CN)_4(H_2O)]^{2-}$ has been used as the source of molybdenum.[251,252] Schrauzer suggests that when this compound is reduced with $NaBH_4$, ligating cyanide groups are converted to methane and ammonia, creating Mo(IV) dinitrogen-binding sites analogous to those proposed for the cysteine system. The yields of ammonia (see Table XVI) are considerably higher than those from systems based upon thiol-type ligands and approach those from dinitrogen complexes reported in section V.B. The starting molybdenum complex $[MoO(CN)_4(H_2O)]^{2-}$ decomposes slowly in mildly acidic media to liberate HCN and generate a species again reminiscent of the active species in the molybdenum–cysteine systems (eq 36). Dinitrogen can be reduced to ammonia in these systems without addition of reducing agent but only at levels of the order of 0.0003 mol of ammonia per molybdenum.[253] The molybdenum–cysteine dimer also undergoes dissociation in alkaline media to generate a solution capable of reducing acetylene but not dinitrogen.[254] The failure of this system to reduce dinitrogen and the low yields in previous systems are attributed to the instability of the presumed diazene intermediate.

Many of the features of the reducing behavior of nitrogenase have been mimicked by these systems of Schrauzer's to the extent that the same products are obtained from substrates as are produced by nitrogenase action.[244] However, the turnover numbers are much lower than for the enzyme (e.g., 1.7 mol min^{-1} mol^{-1} for C_2H_2 reduction vs. ~200 mol min^{-1} mol^{-1} for nitrogenase) and with the notable exception of the borohydride reduction of cyano complexes the yields of ammonia (Table XVI) are very low indeed.

Aqueous and aqueous-methanolic molybdenum systems were also developed by Shilov and his co-workers,[255] and, again, many of the features of the action of nitrogenase have been reproduced. They used as reductant a heterogeneous mixture of hydrated oxides produced from a molybdenum compound (e.g., $MoCl_5$, $MoOCl_3$, or MoO_4^{2-}), a reducing agent such as titanous chloride or chromous chloride, and magnesium salts brought to pH 10–14 by addition of sodium hydroxide. This mixture reduces dinitrogen to hydrazine, although some ammonia is also formed at high temperatures[256] (Table XVIII). Optimum yields of hydrazine are obtained at 90–110 °C, dinitrogen pressure of 100–150 atm, and a Mg/Ti ratio of 0.5. Up to 100 hydrazine and ammonia molecules can be formed per molybdenum atom.[257] Neither the titanium nor the reduced molybdenum compounds are capable of reducing dinitrogen alone.

The titanium-containing molybdenum system has been studied in the most detail. It appears that in the presence of dinitrogen, rather than argon, the oxidation of Ti(III) by water with production of dihydrogen is inhibited. It is assumed that this inhibition is caused by the formation of a dinitrogen complex of molybdenum whose dinitrogen ligand is reduced by Ti(III). It is suggested that the magnesium function is partly structural but also that the formation of Mg-O-Ti bonds adjusts the reduction potential of Ti(III) so that dinitrogen, rather than water, is reduced.[257]

TABLE XVIII. Nitrogen Fixation in Aqueous Solution

metal complex (moles)	reducing agent (moles)	other components (moles)	sub-strate	P_{N_2}, atm	Temp, °C	time, h	product	yield[c]	ref
$Na_2[Mo_2O_4(cys)_2]$[a,b] (9.5×10^{-5})	$NaBH_4$ (8.3×10^{-4})[a]	ATP (1.3×10^{-4}), borate buffer (0.2 F), pH 9.6[a]	CN^-	—	27	5 h	CH_4 NH_3 (C_2H_6, C_2H_4, CH_3NH_2)	0.00026 n.d. trace	250
$Na_2[Mo_2O_4(cys)_2]$[a,b] (2.4×10^{-5})	$S_2O_4^{2-}$ (5×10^{-4})[a]	$[Fe_4S_4(SPr^n)_4]^{2-}$ (4.8×10^{-5}) in 2 mL 1:1 MeOH borate buffer pH 9.6[a]	C_2H_2	—	27	5 h	C_2H_4	0.42	247
$Na_2[Mo_2O_4(cys)_2]$[a,b] (2.4×10^{-5})	$NaBH_4$ (6.0×10^{-4})[a]	In borate buffer (0.2 M) pH 9.6[a]	N_2	1	27	116 h	NH_3	0.04	246
$Na_2[Mo_2O_4(cys)_2]$[a,b] (2.4×10^{-5})	$NaBH_4$ (6.0×10^{-4})[a]	ATP (6×10^{-4}) borate buffer (0.2 M) pH 9.6[a]	N_2	1	27	40 min	NH_3	0.007	249
$K_2[MoO(CN)_4(H_2O)]$[a,b] (2.2×10^{-5})	$NaBH_4$ (3.2×10^{-4})[a]	ATP (1.6×10^{-4}) borate buffer (0.2 M) pH 6.5 $[Fe_4S_4(SPr^i)_4]^{2-}$ (2.2×10^{-5})[a]	N_2	1	27	3 h	NH_3 N_2H_4	0.29 0.029	252
$K_2[MoO(CN)_4(H_2O)]$[a,b] (10.5×10^{-3})	—	Acetate buffer, initial pH 4.3[a]	N_2	1	75	48 h	NH_3	0.00028	253
Mo (3×10^{-6})[d]	Ti(III) (3.0×10^{-4})	$MgCl_2$ ($1,5 \times 10^{-4}$), 85 °C, pH 10–12	N_2	100	85	10 min	N_2H_4	2.0	256
Mo (6×10^{-4})[e]	Ti(III) (*f*)	$MgCl_2$ (3×10^{-4}), 90 °C pH 10–14	N_2	40	90	15 min	N_2H_4	1.2	257
$VSO_4 \cdot 7H_2O$ (1×10^{-4})		$MgCl_2$ (5×10^{-4}), KOH (4.2×10^{-2}), in H_2O	N_2	100	20	1 min	N_2H_4	0.22	256
$VSO_4 \cdot 7H_2O$ (1×10^{-4})		$MgCl_2$ (5×10^{-3}), KOH (4.2×10^{-2}), in H_2O	N_2	0.9	70	1 min	N_2H_4	traces	256
Mo (3.4×10^{-10})[e]	Na/Hg > 3.4×10^{-7}	In $MeOH/H_2O$	N_2	40	20	15	N_2H_4	12 000	257
$VSO_4 \cdot 7H_2O$ (5.0×10^{-4})		Catechol (50×10^{-4}), NaOH (5.5×10^{-3}) in MeOH (10 mL), pH 10, no Mg^{2+}	N_2	1	25	*f*	NH_3	0.16	267

[a] Moles of components in parentheses assuming reaction solution volume of 4–6 mL. [b] cys = $[SCH_2CH(NH_2)CO_2]^{2-}$. [c] Expressed as moles of NH_3 or N_2H_4/metal atom. Maximum yields are generally quoted. [d] $MoOCl_3$ or $[MoO_4]^{2-}$ added to system in aqueous methanol. [e] Mo(III) carbonyl cluster complex (see text). [f] not given.

Carbon monoxide inhibits the reduction of dinitrogen by Shilov's molybdenum systems, and a carbonyl compound, considered to be a molybdenum(III) carbonyl cluster complex based on a tetrahedron of molybdenum atoms, has been isolated.[256,258] This observation has led Shilov to suggest that a polynuclear or at least a dinuclear molybdenum unit is the center of the dinitrogen-reduction process. Thus, in the absence of knowledge of any other intermediates, the reduction is envisaged as involving transfer of electrons along a chain formed from Ti(III), Mg(II), and hydroxide ions to the polynuclear Mo(III) reaction site.[257] Unlike Schrauzer's systems, ATP, Fe(II), and thiols have no beneficial effect. Acetylene and other substrates are reduced to give the same products as they give on nitrogenase, but less effectively; the production of hydrazine also differs from the biological process, which gives only ammonia.

Sodium amalgam can be used as an alternative to Ti(III) to transfer electrons to the molybdenum-bound dinitrogen. The molybdenum cluster carbonyl mentioned above can be used as the source of molybdenum catalyst provided the carbonyl ligands are first displaced. Hydrazine is produced by solution of the carbonyl in methanol, removal of carbon monoxide in a stream of argon, and addition of sodium amalgam, magnesium ion, and dinitrogen at 40 atm.[258] This catalytic system appears to provide the greatest turnover based on molybdenum, but the reaction has to be performed at very low concentrations of molybdenum (10^{-7}–10^{-10} M) to avoid catalytic formation of dihydrogen. Shilov has reported[255] that the results from this system are not reproducible and suggests that this is due to the participation of impurities at the amalgam surface.

C. Systems Using Vanadium

These are aqueous-methanolic systems developed by Shilov et al. The original vanadium(II) system (Table XVIII) is heterogeneous.[255,256] It resembles and was derived from the heterogeneous molybdenum systems described above. As in the molybdenum systems, the presence of magnesium and a high pH are necessary for the production of hydrazine (20 °C) or ammonia (70 °C),[256] but here the vanadium(II) takes over the dual role of binding and reducing the dinitrogen. By a study of the inhibitory effect of the addition of vanadium(III), Shilov concludes that the dinitrogen reduction involves oxidation of a tetranuclear cluster of vanadium(II) to vanadium(III) with transfer of four electrons to the dinitrogen which then protonates to give hydrazine (eq 36).[255,259] At higher temperatures, further reaction of the hydrazine with more vanadium(II) gives ammonia and dihydrogen. The vanadium atoms are trapped in a magnesium hydroxide host lattice, which both holds them at the requisite distances and prevents polymerization into larger aggregates.[259] A rather puzzling feature of this system is that carbon monoxide does not inhibit the formation of ammonia. This implies an unusual highly specific dinitrogen binding site, as carbon monoxide usually bonds more strongly than dinitrogen at nearly all the sites at present known to coordinate dinitrogen (see sections III.C and IV.B).

$$4V^{2+} + N_2 \rightarrow V_2^{2+}\cdots N{\equiv}N\cdots V_2^{2+} \xrightarrow{4H^+} 4V^{3+} + N_2H_4 \qquad (39)$$

Schrauzer has also examined the system based on alkaline suspensions of $V(OH)_2$ in $Mg(OH)_2$. He generally agrees with the observations of Shilov above, and quotes similar yields of hydrazine the maximum being about 15% based on the total vanadium(II) present.[260] However, he interprets the kinetics of the reaction and the observed reduction of allyl alcohol to 1-propanol or fumarate to succinate as supporting a mechanism involving monomeric vanadium(II) units which transfer two electrons to a side-on bound dinitrogen to give diazene. Subsequent disproportionation gives hydrazine which can then be further reduced to ammonia and dinitrogen at higher temperatures.

More recently a homogeneous system has been developed which utilizes vanadium(II) and catechol in aqueous or alcoholic solutions. It operates at atmospheric pressure and 20 °C.[256,261] In the absence of dinitrogen the solvent is reduced, giving dihydrogen, the yield of which falls as dinitrogen is added, the reducing equivalents of vanadium being diverted to ammonia production. The yield of ammonia is strongly pH dependent and rises to a sharp maximum at pH 10. Only aromatic diols with two *o*-hydroxy groups are capable of keeping the vanadium in solution and providing the appropriate site for binding and activating dinitrogen. If one or both of the hydroxyl groups are replaced by SH the systems are no longer active toward dinitrogen.[255]

The detailed nature of the active vanadium–catechol species has not been determined, but it appears to be a tetramer and the yield of ammonia (see Table XIII), obtained in the optimum pH range, corresponds to oxidation of about 75% of the V(II) present in the system to V(III); the remaining 25% is involved in the production of dihydrogen. The reduction of dinitrogen is inhibited by carbon monoxide and also by acetylene which is reduced to *cis*-ethylene, as shown by deuterium labeling. Thus several important aspects of nitrogenase action are qualitatively reproduced. Shilov suggests that analogously to the heterogeneous vanadium(II)/magnesium(II) system, the proposed tetrameric complex forms a dinitrogen-bridged compound as a precursor to ammonia formation. Two tetramers are necessary to provide the electrons required for the production of two ammonia and one dihydrogen molecules.[261]

D. Systems Using Group 8 Metals

Low yields of ammonia (~0.014 mol/mol of Fe) and hydrazine (~0.003 mol/mol of Fe) have been observed by Schrauzer et al. when alkaline suspensions of $Fe(OH)_2$ are prepared under dinitrogen. They suggest that the active agent is elemental iron, which is precipitated as a result of the disproportionation of $Fe(OH)_2$.[262]

Kahn and Martell have reported the production of ammonia, in aqueous solution, at 25 °C from a mixture of dinitrogen and dihydrogen (1:3 proportion) using rhodium, iridium, ruthenium, or osmium ions in hydrochloric acid solution.[263] The reacting gas mixture was circulated through a solution containing the metal ion and a reducing agent such as $TiCl_3$ or $SnCl_2$ (10 molar excess relative to metal ion). $^{15}N_2$ gas was used and the ammonia yield determined (after Kjeldahl distillation of the reaction mixture) by mass spectroscopy. Some yields of ammonia based on the group 8 metal ion present are shown in Table XIX. No ammonia was formed in the absence of dihydrogen; hence it must be concerned in the reduction process. The species involved in this reaction have not yet been described and the mode of action is obscure, although triphenylphosphine appears to be a poison (Table XIX). There have been attempts to repeat this work in other laboratories, but as yet unsuccessfully.[264]

TABLE XIX. Nitrogen Fixation by Group 8 Metal Ions[a]

reducing agent	metal ion[b]	NH_3 yield[c]
$TiCl_3$	Ru(II) (1.6×10^{-3})	0.4
$TiCl_3$	Rh(III) (1.0×10^{-3})	0.36
$SnCl_2$	Rh(III) (5.0×10^{-4})	0.4
$SnCl_2 + PPh_3$	Rh(III) (5.0×10^{-4})	0.06
$TiCl_3$	Ir(III) (2.7×10^{-3})	0.20
$TiCl_3$	Os(II) (2.7×10^{-3})	0.10

[a] 3 M hydrochloric acid solution at 25 °C; ($N_2 + 3H_2$) gas at 1 atm. [b] Molar concentration in parentheses. [c] Moles/mole of group 8 metal ion.

E. Electrochemical or Photochemical Reduction of Dinitrogen

Although not in aqueous solution, the involvement of electrochemical reduction in the formation of ammonia from dinitrogen was reported in 1969.[265] A mixture of titanium(IV) isopropoxide and aluminum isopropoxide was electrolyzed at 40 V for 11 days and ammonia was liberated on hydrolysis. More recently, Shilov and co-workers have reported the generation of small quantities of hydrazine by dinitrogen reduction at a mercury cathode in the presence of molybdenum complexes. However, the results are very variable, probably due to the participation of impurities at the interface between the cathode and the molybdenum complex.[266]

Ammonia and traces of hydrazine have also been produced photocatalytically from dinitrogen and water by passing moist dinitrogen over an iron-doped titanium dioxide catalyst at 30 °C with solar irradiation. Yields are at present low, the solar cell typically producing about 5×10^{-6} mol of ammonia after 3 h exposure.[267]

VIII. Nitrogen Fixation via Nitride Formation

The discovery of new reactions in this area stimulated the present phase of interest in the chemistry of dinitrogen under ambient conditions. These reactions led to nitrides by the strong reduction of certain transition metal compounds in an aprotic solvent in the presence of dinitrogen. Such complexes are sometimes sufficiently reactive to abstract hydrogen from solvents such as THF, but are usually converted to ammonia by addition of alcohols or water. Much of this work was performed in the laboratories of Vol'pin and van Tamelen prior to the period of this review and has been extensively reviewed elsewhere.[268-270] This section covering the relatively small amount of recent work is restricted to reactions giving nitrides as primary products. The formation of nitrides as intermediates in the reduction or protonation of characterized dinitrogen complexes has been discussed in section V.B.2.

The systems that have recently received the most attention are the magnesium reductions of titanium or vanadium halides in THF under N_2. The products of these reactions are black, benzene-soluble materials of stoichiometry $[MMg_2Cl_2N(thf)]$[271,272] (**61**) (M = Ti, V). Treatment of the titanium species with bipyridyl removes 1 equiv of magnesium as $Mg(bpy)_3$ to leave a product of composition $[TiMg_{1.5}NCl_2(bpy)_{1.5}]$. Complete removal of magnesium was achieved with benzoyl chloride leaving $TiClN(PhCO)_{1.5}$, suggesting that the nitrogen is bound to titanium rather than being present as magnesium nitride. A titanium(II) species is proposed for the initial binding and activation of dinitrogen in accord with earlier mechanistic proposals.[268,270] The mode of bonding of the magnesium in **61** remains unexplained, but Ti–N–Mg bridging systems may be present. The nitrides **61** react with CO_2 to give isocyanate derivatives formulated $[MMgCl_2(NCO)(O)(thf)_3]$ (**62**) which show ν(NCO) at 2235 and 2197 cm^{-1} in the IR. Subsequent hydrolysis of **62** gives stoichiometric amounts of CO_2 and NH_3, and methyl iodide gives methyl isocyanate in unspecified yield.

The group at Wroclaw in Poland has carried out investigations of the magnesium reduction of first-row transition metal compounds.[274,275] A typical reaction is the magnesium reduction of ferric chloride under dinitrogen which gives a yellow product formulated as $\{FeMgCl_3(thf)_{1.5}\}_2N_2$. This generates an unspecified amount of hydrazine on hydrolysis. However, no IR or Raman bands assignable to $\nu(N_2)$ were observed for this product, so it could well be an iron or magnesium nitride or contain the Fe–N–Mg group. The fixation of nitrogen by the magnesium reduction of $CrCl_2$ in THF has been discussed in section II.D.3 and probably also involves a nitride species.

The reaction mechanisms in this area are purely speculative and the ultimate nitride products are often ill-defined. Presently there are no fully characterized transition metal nitride complexes prepared directly from dinitrogen, although they have been prepared from hydrazines,[276] or by degradation of coordinated azide.[277,278] The presence of nitride ligands in reactions such as those above is usually inferred from the nitrogen analyses of the product and their hydrolysis to ammonia. However, nitrides can also give substantial amounts of hydrazine on hydrolysis,[279] so identification of the latter at low levels is not diagnostic for the intermediacy of dinitrogen species bound to a metal.

IX. Conclusions and Future Trends

The current phase of interest in nitrogen fixation started in the early 1960's when bacterial nitrogenase was first extracted in active form,[280] and the chemistry of nitrogen fixation received a further boost in 1965 when the first stable and well-characterized dinitrogen complexes were isolated.[281] Since then there has been a great outpouring of chemistry in the areas delineated by the previous sections. In some areas such as that involving the nitriding of transition metal complexes by strong reduction under dinitrogen in aprotic media, very little new work appeared during the period of this review (section VII). In others such as the fixation of nitrogen by contact with transition metal salts in aqueous or aqueous alcoholic solutions, where yields are often very low and the work is notoriously difficult to repeat, there is now an air of uncertainty which only further work in other laboratories can resolve (section VI).

Perhaps the most important developments during the period of this review has been the discovery of stoichiometric reactions of dinitrogen in some of its *stable* complexes (section V). This work has demonstrated the important fact that when dinitrogen is suitably attached to a metal atom in a low oxidation state it can be protonated by acid and reduced to give hydrazine or ammonia in substantial yields based on the reducing power of the reagents. In two cases dinitrogen attached to tungsten(0) in mononuclear complexes was reduced in 90% yield to ammonia by contact with acid; a small amount of the reducing power appeared as hydrazine and the remainder as dihydrogen. This demonstrates that when the bonding state is correct, a highly efficient reduction of dinitrogen to ammonia on a metal atom is possible even in an acid medium. It points to the possibility of electrolytic processes for the reduction of dinitrogen, if the right type of nitrogen binding site could be attached to the surface of a cathode. Perhaps the very efficient reductions of dinitrogen to hydrazine which occur in binuclear complexes of titanium and zirconium hold promise of electrolytic processes for the production of hydrazine. The production of ammonia by photolysis of dinitrogen with water on a suitable catalyst is potentially important, but its efficiency needs to be raised by some powers of 10.

The work of the past 10 years has made an enormous contribution to our knowledge of the chemistry of dinitrogen especially in its complex compounds. It has not produced any reactions leading to the formation of nitrogen hydrides or organonitrogen compounds which could possibly compete with existing processes, but it has indicated direction and potentiality. It is now certain that the reduction of dinitrogen at ordinary temperatures and pressures can be a very efficient process on the right transition metal site, but it is doubtful whether there is any chemical process which will compete with the Haber process so long as methane and oil are available as low priced raw materials for the production of hydrogen. When hydrogen must be obtained from water, an electrolytic or photolytic process for the fixation of nitrogen in aqueous solution could become economic. These seem to be the directions in which chemists should look.[282]

The problem of the production of ammonia for agricultural purposes is not necessarily a chemical one. Considerable effort is being expended in microbial genetics, to map the genes responsible for nitrogen fixation and its control in bacteria with the ultimate goal that they may be transferred to other bacteria to create more nitrogen fixers, or even to plants or animals themselves. Although this presents enormous difficulties, there appears at present to be no theoretical reason why it cannot be done, and it could provide an ideal solution to the nitrogen problem. Other biological solutions are also possible.[283]

When scientists toward the end of the last century saw the end of Chilean saltpeter as heralding the beginning of famine in the Western world, the problem of producing nitrogenous fertilizer was placed fairly and squarely on the shoulders of the chemists. It was solved around the end of the first decade of this century by the Haber process. Now when the problem is arising again as the world's oil and gas reserves are being depleted, it has returned to the scientists, either chemists or biologists, for solution. The problem is no easier and no less acute than before; all projections indicate that a new solution must be found within the next 30 years if our grandchildren and perhaps even our children are not to go hungry.

X. Appendix

The following papers appeared while the manuscript was in preparation, and their inclusion brings the literature coverage up to September 1978. The sequence of presentation follows that of the review.

Further information about EXAFS studies has appeared, and both the methods of data analysis and the limitations of the technique have been delineated.[284] Two further papers[285,286] have given accounts of EXAFS studies on a number of molybdenum complexes, on nitrogenase, and on the iron–molybdenum cofactor. The results indicate that in nitrogenase the molybdenum is ligated by three or four sulfurs at 2.49 ± 0.03 Å and one or two sulfurs at 2.72 ± 0.05 Å and two or three irons at 2.72 ± 0.05 Å. The Fe–Mo cofactor has similar parameters, showing that the Mo environment is maintained during the extraction process. The method is clearly immensely valuable in the elucidation of the structures of the active sites of nitrogenase and other metalloenzymes.

The Zr^{III} complex $[Zr(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}(N_2)]$ has been isolated as a brown paramagnetic solid by the sodium amalgam reduction of $[Zr(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$ in THF under N_2.[287] The EPR spectrum shows a 1:2:3:2:1 quintet (1:2:1 triplet for the $^{15}N_2$ analogue) and no IR bands in the 1500–2200 cm^{-1} region; these data are interpreted in terms of side-on bound N_2. The complex loses N_2 at 20 °C in vacuo to give $[\{Zr(\eta^5\text{-}C_5H_5)_2CH(SiMe_3)_2\}_2(N_2)]$, and protonation gives a 20% yield of hydrazine. The solution structure and dynamics of $[\{M(\eta^5\text{-}C_5Me_5)_2L\}_2(N_2)]$ ($M = Ti$, $L = N_2$; $M = Zr$, $L = N_2$, CO, PF_3) have been studied by variable-temperature ^1H and ^{15}N NMR spectroscopy.[288] For $M = Zr$, $L = N_2$, the C_5Me_5 groups exchange slower by a factor of 5–10 than the dissociative exchange of the terminal N_2 ligands with dissolved N_2. The ring interchange mechanism may involve stepwise dissociation and association of N_2 ligands with inversion at the Zr centers.

A one-step synthesis of *trans*-$[Mo(N_2)_2(dppe)_2]$ has been reported by sodium amalgam reduction of $MoCl_5$ in THF in the presence of dppe and N_2.[289] The complex $[OsCl(N_2)(diars)_2]Cl$

[$\nu(N_2)$ 2080 cm^{-1}] has been prepared in 25% yield by direct treatment of [OsCl(N$_3$)(diars)$_2$] with concentrated hydrochloric acid.[290] The tetraphenylporphyrin (TPP) analogue of [Os(oep)-(N$_2$)(thf)] has been prepared by reaction of [OsO$_2$(TPP)] with hydrazine hydrate. The red-violet N$_2$ complex was obtained in 84% yield and has $\nu(N{\equiv}N)$ at 2050 cm^{-1} (Nujol).[291]

The dinitrogen species [ML(CO)$_2$(N$_2$)] [ML = Cr(η^6-C$_6$H$_6$), Mn(η^5-C$_5$H$_5$), Fe(η^4-C$_4$H$_4$)] have been generated by UV photolysis of [ML(CO)$_3$] in nitrogen matrices at 12 K.[292] The complex [Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)] has also been prepared by conventional chemical methods.[74] The species M(CO)$_5$(N$_2$) (M = Mo, Cr, N) are generated by photolysis of matrix-isolated M(CO)$_6$ in the presence of N$_2$ and show a weak IR band at about 2253 cm^{-1} due to $\nu(N{\equiv}N)$.[293] Analogous UV photolysis of [Mn(CO)$_4$(NO)] in a nitrogen matrix at 20 K gives a species [Mn(CO)$_3$(N$_2$)(NO)] identified by IR with $\nu(N{\equiv}N)$ at 2264 cm^{-1}.[294]

Treatment of [MoBr(N$_2$Bu^n)(dppe)$_2$] with sodium methoxide in benzene–methanol at 100 °C for 10 h under N$_2$ in an autoclave gave a total yield of 58% of base comprising approximately equal amounts of *n*-butylamine and ammonia.[295] By contrast the organohydrazido(2−) complexes [MBr(NNMe$_2$)(dppe)$_2$]Br (M = Mo, W) give good yields of Me$_2$NH by reactions with LiAlH$_4$ or KOH, but no ammonia.[243] The full details of the X-ray crystal structure of [MoCl(N$_2$COPh)(dppe)$_2$] have been reported[296] and show a linear Mo–N–N system with Mo–N and N–N distances of 1.813 (17) and 1.255 (10) Å, respectively. The Mo–O distance of 4.02 Å indicates that the carbonyl oxygen does not interact in any way with the metal.

The first example of nucleophilic attack on coordinated N$_2$ (at the nitrogen adjacent to the metal) is provided by the reaction of [Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)] with PhLi to give Li[Mn(η^5-C$_5$H$_5$)-(CO)$_2${N(Ph)N}] (6% yield) which can be protonated to [Mn(η^5-C$_5$H$_5$)(CO)$_2${N(Ph)NH}].[297] This work has subsequently been extended to the preparation of [Mn(η^5-C$_5$H$_5$)(CO)$_2${N(Me)-NMe}] by sequential reaction of the N$_2$ complex with MeLi and Me$_3$OBF$_4$. The MeN=NMe ligand can be displaced from the complex by dinitrogen under pressure to regenerate the N$_2$ complex, forming the basis of a cyclic process for the preparation of dimethyldiazene from N$_2$.[298]

The mechanism of reduction of N$_2$ in the V(OH)$_2$–Mg(OH)$_2$ system has been further investigated[299] and the role of the host Mg(OH)$_2$ lattice assigned to permitting the accumulation of the presumed N$_2$H$_2$ intermediate without base-catalyzed disproportionation. The system behaves as a two-electron reductant for a range of substrates and the yield of N$_2$H$_4$ is proportional to $P_{N_2}{}^2$, ruling out direct reduction of N$_2$ to N$_2$H$_4$.

XI. References

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