Dinitrogen Complexes of the Transition Metals

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Contents

I. Introduction

The preparation of $[Ru(NH_3)_5(N_2)]^{2+}$ in 1965,[1] and the subsequent discovery that it can be prepared directly from dinitrogen gas,[2] led most chemists to assume that dinitrogen complexes of transition metals are involved, at some stage, in the biological "fixation" of dinitrogen. However, despite many attempts and one premature claim, no fully characterized dinitrogen complex has been reduced to ammonia. It may eventually be found that these complexes are not, after all, an intermediate in dinitrogen "fixation." However, like the organic diazonium salts, the dinitrogen complexes are of considerable interest in themselves and have already proved to be useful synthetic intermediates. Dinitrogen fixation as such has been reviewed recently.[3,4] This review will concern itself therefore with the preparation and properties of the dinitrogen complexes themselves.

The elements that have been reported to form mononuclear dinitrogen complexes are those left unshaded in Figure 1. The position of this group in the Periodic Table is significant for four reasons.

1. It coincides closely with the borderline regions between "class a" and "class b" metals, as defined by Ahrland and Chatt.[5]
2. It coincides fairly well with the group of metals which form carbonyls, suggesting a similarity between dinitrogen and carbon monoxide as ligands.
3. It includes the metals iron and molybdenum, which are believed to be the active sites in nitrogenase.
4. It includes the elements, again iron and molybdenum, used commercially as catalysts in the Haber synthesis of ammonia.

The mechanism of the Haber process was long believed to involve the adsorption of dinitrogen as nitrogen atoms.[6,7] However, Carra and Ugo recently argued that the kinetic results can be explained equally well by a mechanism involving the absorption of molecular nitrogen, followed by the transfer of an adsorbed hydrogen atom from an adjacent site.[8]

A large number of ligands can coexist with dinitrogen on a metal atom. Phosphines, halides, hydride, ammonia, carbon monoxide, and even water can all occur in dinitrogen complexes. Curiously, in view of the fact that nitrogenase contains a lot of sulfur, there has been only one report of a dinitrogen complex containing ligands donating through sulfur.[9]

II. Methods of Preparation

The various preparations will be presented with a minimum of discussion.

A. Preparations Using Dinitrogen Directly

1. $[Co(N_2)(PPh_3)_3]$,[10,11] $[RuH_2(N_2)(PPh_3)_3]$,[12] $[FeH_2(N_2)(PR_3)_3]$ (R_3 = $EtPh_2$, *n*-Bu),[13] and $[CoH(N_2)(PR_3)_3]$[14,15] have been prepared by reaction 1.

$$[MH_n(PR_3)_3] + N_2 \rightarrow [MH_{n-2}(N_2)(PR_3)_3] + H_2 \quad (1)$$

The reaction is interesting because it may provide a model for the first step in the "fixation" of dinitrogen by nitrogenase. The enzymic reaction is competitively inhibited by dihydrogen,[16] which is consistent with a rapid equilibrium reaction between a polyhydride and N_2 to give a dinitrogen complex, followed by some slow rate-determining step.

$$\text{"titanocene dimer"} + N_2 \rightarrow \text{"(titanocene dimer) }(N_2)\text{"} \quad (2)$$

2. $[(\pi\text{-Cp})_2TiN_2Ti(\pi\text{-Cp})_2]$[17] and the fully methylated derivative[18] have recently been synthesized in ether at −80° (eq 2). Prolonged exposure of a benzene solution

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TABLE I. Displacement of Water from Ruthenium(II) by Various Nucleophiles

Substrate	Nucleophile	Product	10^2K (25°), mol^{-1} sec^{-1}	$\Delta E‡$, kcal mol^{-1}	Ref
$[Ru(NH_3)_5H_2O]^{2+}$	CO	$[Ru(NH_3)_5CO]^{2+}$	12		27, 55, *a*
	RCN	$[Ru(NH_3)_5NCR]^{2+}$			*b–d*
	N_2	$[Ru(NH_3)_5(N_2)]^{2+}$	7.1, 7.97	22.0 ± 0.1	2, 83, *e*
	N_2O	$[Ru(NH_3)_5NNO]^{2+}$	7.21		68, 69
	Pyridine	$[Ru(NH_3)_5py]^{2+}$	11.8		*d*
	$[Ru(NH_3)_5(N_2)]^{2+}$	$[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$	4.2, 3.59	19.9 ± 0.5	*f*, *e*, 83
	$[Ru(NH_3)_4(H_2O)(N_2)]^{2+}$	$[(NH_3)_5RuN_2Ru(NH_3)_4H_2O]^{4+}$	2.72	20.4 ± 0.8	*e*
	$[Os(NH_3)_5(N_2)]^{2+}$	$[(NH_3)_5RuN_2Os(NH_3)_5]^{4+}$			73
	cis-$[Os(NH_3)_4(N_2)CO]^{2+}$	*cis*-$[(NH_3)_5RuN_2Os(NH_3)_4CO]^{4+}$			73
	cis-$[Os(NH_3)_4(N_2)_2]^{2+}$	*cis*-$[(NH_3)_5RuN_2Os(NH_3)_4(N_2)]^{4+}$			73
cis-$[Ru(NH_3)_4(H_2O)_2]^{2+}$	N_2	$[Ru(NH_3)_4(H_2O)(N_2)]^{2+}$	10.4	20.4 ± 0.2	*e*
	$[Ru(NH_3)_5(N_2)]^{2+}$	$[(NH_3)_4(H_2O)RuN_2Ru(NH_3)_5]^{4+}$	6.79	18.2 ± 0.1	*e*
	$[Ru(NH_3)_4(H_2O)(N_2)]^{2+}$	$[(NH_3)_4(H_2O)RuN_2Ru(NH_3)_4(H_2O)]^{4+}$	7.18	17.1 ± 0.2	*e*
$[Ru(H_2O)_6]^{2+}$	N_2	$[Ru(H_2O)_5(N_2)]^{2+}$ + $[(H_2O)_5RuN_2Ru(H_2O)_5]^{4+}$			*g*
$[Ru(trien)Br_2]Br$ + Zn/Hg + H_2SO_4[i]	N_2	$[(trien)XRuN_2RuX(trien)]X_2$ X = Br or I			*h*

[a] D. F. Harrison, Ph.D. Thesis, Stanford University, Jan 1969. [b] P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968). [c] P. C. Ford and R. E. Clarke, *Inorg. Chem.*, **9**, 227 (1970). [d] R. J. Allen and P. C. Ford, *ibid*, **11**, 679 (1972). [e] C. M. Elson, I. J. Itzkovitch, and J. A. Page, *Can. J. Chem.*, **48**, 1639 (1970). [f] D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968). [g] C. Creutz and H. Taube, *Inorg. Chem.*, **10**, 2664 (1971). [h] R. O. Harris and B. A. Wright, *Can. J. Chem.*, **48**, 1815 (1970). [i] Almost certainly $[Ru(trien)Br(H_2O)]^+$ is an intermediate.

of the titanocene to N_2 at 20–25° results in the formation of a complex formulated as $[(\pi\text{-}Cp)_2TiN_2]_2$.[19] Recently the molybdenum analogs have been prepared under 250 atm of N_2.[20]

3. Isopropylmagnesium chloride reacts with $[FeCl_3(PPh_3)_2]$ under N_2 to produce an incompletely characterized complex containing 1 mol of N_2 per 2 mol of iron.[21] Grignard reagents have also been used to prepare N_2 complexes of molybdenum[21] and titanium.[22]

$$[RuL_5H_2O]^{2+} + N_2 \rightarrow [RuL_5(N_2)]^{2+} + [L_5RuN_2RuL_5]^{4+} + H_2O \quad (3)$$

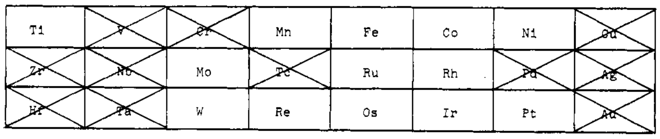
4. These displacement reactions, which are treated more fully in Table I, give both monomeric and dimeric products.

5. (a) This reaction may proceed through a solvated intermediate such as $[MH(s)(depe)_2]^+$.[23,24]

$$[MHCl(depe)_2] + NaBPh_4 \xrightarrow{N_2} [MH(N_2)(depe)_2](BPh_4) + NaCl \ (M = Fe, Ru, and Os) \quad (4)$$

(b) For $(\pi\text{-}Cp)Fe(dmpe)I$, the reaction with $TlBF_4$ in acetone under N_2 gives the dimeric species $[(\pi\text{-}Cp)Fe(dmpe)N_2Fe(dmpe)(\pi\text{-}Cp)](BF)_2{\cdot}2H_2O$ *via* an acetone coordinated intermediate.[25]

6. A few low-valent olefin complexes will react with N_2 if a tertiary phosphine is also present.[26,27] $[CoH(N_2)(PPh_3)_3]$, for example, has been obtained from $[Co(C_8H_{13})(C_8H_{12})]$ in this way.



Ti	~~V~~	~~Cr~~	Mn	Fe	Co	Ni	~~Cu~~
~~Zr~~	~~Nb~~	Mo	~~Tc~~	Ru	Rh	~~Pd~~	~~Ag~~
~~Hf~~	~~Ta~~	W	Re	Os	Ir	Pt	~~Au~~

Figure 1. Metals which form dinitrogen complexes.

7. Many metal acetylacetonates will react with N_2 in the presence of a tertiary phosphine and an aluminum alkyl (or $AlEt_2(OEt)$). Sometimes the product contains a hydride ligand as well as dinitrogen and phosphine. $[CoH(N_2)(PR_3)_3]$,[28,29] $[Co(N_2)(PPh_3)_3]$ (see section III.C and ref 10), $[NiH(N_2)(PEt_3)_2]$,[30] $\{[(C_6H_{11})_3P]_2NiN_2Ni[P(C_6H_{11})_3]_2\}$,[31] $[Mo(\pi\text{-toluene})(N_2)(PPh_3)_2]$,[32,33] and *trans*-$[Mo(N_2)_2(diphos)_2]$[33] have been obtained by this route.

8. (a) Metal amalgams have been used as reducing agents in place of the aluminum alkyls employed in reaction 7. In this manner, Chatt and his group have obtained *trans*-$[W(N_2)_2(diphos)_2]$,[34] *cis*-$[W(N_2)_2(PMe_2Ph)_4]$,[34] $[ReCl(N_2)(PMe_2Ph)_4]$,[35] $[OsX_2(N_2)(PR_3)_3]$,[36,37] *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$,[38] and *trans*-$[Mo(N_2)_2(diphos)_2]$.[38]

(b) Shilov, *et al*, have reduced a number of ruthenium and osmium halo complexes with zinc amalgam and obtained several dinitrogen complexes such as [Ru-

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$Cl_2(N_2)(H_2O)_2(THF)]$.[39-42]

9. (a) Zinc dust, in the presence of excess phosphine and dinitrogen in THF, reduces $[MoOCl_2(diphos)(THF)]$ to $[MoCl(N_2)(diphos)_2]$ and $[Mo(N_2)_2(diphos)_2]$.[43]

(b) Powdered sodium reduces cobalt(II) complexes under nitrogen to give monomeric and dimeric dinitrogen species.[44]

$$2CoCl_2(PR_3)_2 + 2PR_3 + 4Na \rightarrow (R_3P)_3CoN_2Co(PR_3)_3 + 4NaCl \quad (5)$$

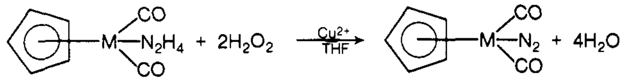
$$CoCl_2(PR_3)_2 + PR_3 + 3Na \rightarrow Na[Co(N_2)(PR_3)_3] + NaCl \quad (6)$$

$$R_3 = Ph_3,\ Et_2Ph$$

B. Preparation from Compounds Containing Chains of Nitrogen Atoms

1. A variety of ruthenium(III) and -(IV)[1,45-47] and osmium(III) and -(IV)[48,49] chloro and ammine complexes and even OsO_4 will react with aqueous hydrazine to give complexes of the type $[M(NH_3)_5(N_2)]X_2$. Unfortunately the products are often contaminated with hydrazine or bis dinitrogen complexes.[46-48] $[OsCl_3(PBu_2Ph)_3]$ gives a mixture of starting material and $[OsCl_2(N_2)(PBu_2Ph)_3]$,[50] while [Fe(dithiocarbamate)$_3$] with hydrazine gives an unknown product having $\nu(N_2)$ at 2045 cm^{-1}.[9]

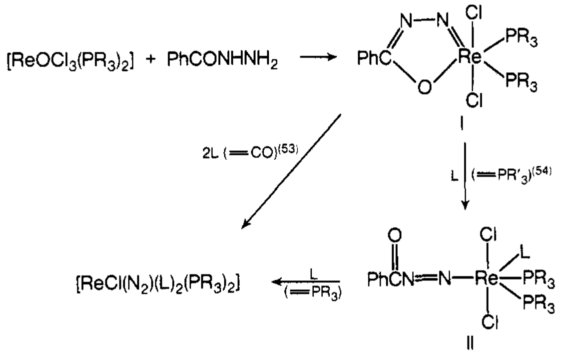
2. Oxidation of coordinated hydrazine (eq 7) has produced the first dinitrogen complex of manganese.[51,52]



(7)

M = Mn, Re

3. Intermediates I and II (eq 8) have both been isolated and characterized. The reverse of reaction 1 would be similar to a benzoylation and appears to be worth attempting.



(8)

4. There is evidence that reaction 9, which is the best way of preparing $[Ru(NH_3)_5N_2]^{2+}$, proceeds through a ruthenium(III) azido complex.[45] If *cis*-$[Ru(NH_3)_4X_2]X$ is used, the product is $[Ru(NH_3)_4(H_2O)(N_2)]^{2+}$ and not the bis dinitrogen complex.[55] If reaction 9 is done at pH 0, binuclear as well as mononuclear species are obtained. Kane-Maguire, *et al.*, have evidence that the dimers are formed by dimerization of the nitrene $[Ru(NH_3)_5NH]^+$ followed by the loss of two protons.[56,57]

$$[Ru(NH_3)_5L]^{n+} + N_3^- \xrightarrow{pH\ 4} [Ru(NH_3)_5N_2]^{2+} + L \quad (9)$$

$$(n = 2 \text{ or } 3)$$

5. Nitrous acid reacts with coordinated azide ligands to give dinitrogen complexes and nitrous oxide. $[RuCl(N_2)(diars)_2]PF_6$[58] and a mixture of $[Ru(en)_2(H_2O)(N_2)](BPh_4)_2$ and unstable $[Ru(en)_2(N_2)_2](BPh_4)_2$[59] have been prepared *via* this reaction.

6. $[IrX(N_2)(PR_3)_2]$[60-63] and $[RhCl(N_2)(PPh_3)_2]$[64] have been prepared by eq 10.

$$trans\text{-}[MCl(CO)(PR_3)_2] + RCON_3 + EtOH \rightarrow trans\text{-}[MCl(N_2)(PR_3)_2] + RCONHCO_2Et \quad (10)$$

7. Another preparation is reaction 11.[65] The osmium tetrahydride will not react with free dinitrogen even under pressure (*cf.* reaction 1).

$$[OsH_4(PR_3)_3] + CH_3C_6H_4SO_2N_3 \rightarrow [OsH_2(N_2)(PR_3)_3] \quad (11)$$

8. Many of the systems which react with N_2 to give a dinitrogen complex can also react with nitrous oxide (N_2O) to give the same product.[36,37,66,67] Since nitrous oxide complexes have now been isolated,[68] it is almost certain that these reactions proceed through an N-bonded nitrous oxide complex which is subsequently reduced[69,70] (see also section IV).

$$[Ru(NH_3)_5Cl]Cl_2 + Zn/Hg \longrightarrow [Ru(NH_3)_5H_2O]^{2+} \xrightarrow{N_2O} [Ru(NH_3)_5NNO]^{2+} \xrightarrow[\text{or } Cr^{2+}]{Zn/Hg} [Ru(NH_3)_5NN]^{2+} \quad (12)$$

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C. Preparations in Which Two Nitrogen Atoms Are Combined to Give a Dinitrogen Group

1. Reaction 13 must be regarded as doubtful because the analogous reaction of $[RuClNO(diars)_2]Cl_2$ with hydrazine has been found to give an azide[58] and not $[RuCl_2(N_2)(diars)_2]$ as previously believed.[71]

$$[Fe(CN)_5NO]^{2-} + N_2H_4 \rightarrow [Fe(CN)_5(N_2)]^{2-\ 71} \qquad (13)$$

2. Reaction 14 is not fully understood.[72]

$$\begin{aligned} &RuCl_3 + Zn + NH_3\ (0.880\ \text{or liq}) \rightarrow \\ &\qquad \underset{90\%}{[Ru(NH_3)_6]Cl_2} + \underset{10\%}{[Ru(NH_3)_5(N_2)]Cl_2} \qquad (14) \end{aligned}$$

3. Attempts to apply reaction 15 to ammonia molecules bound to other metals, *e.g.*, molybdenum and ruthenium, have not been successful.[74,75]

$$\begin{aligned} &[Os(NH_3)_5L]^{2+} + HNO_2 \rightarrow cis\text{-}[Os(NH_3)_4(N_2)L]^{2+} + \\ &\qquad\qquad 2H_2O \qquad (15) \\ &\qquad L = CO^{73}\ \text{or}\ N_2\ ^{74} \end{aligned}$$

4. Reaction 16 probably proceeds *via* an amide complex of the metal.[76]

$$\begin{aligned} &[Ru(NH_3)_6]^{3+} + NO + OH^- \rightarrow [Ru(NH_3)_5(N_2)]^{2+} + \\ &\qquad\qquad 2H_2O \qquad (16) \end{aligned}$$

5. Ammonium salts react with coordinated nitro ligands to produce dinitrogen complexes of platinum[77] and rhodium[78] containing bridging N_2 ligands.

Reactions in which dinitrogen complexes are prepared from other dinitrogen complexes will be discussed in the next section.

III. Chemical Properties of Dinitrogen Complexes

A. Stability

The temperature at which pure, dry, dinitrogen complexes decompose varies from below 20° to above 200°. If impurities are present, or if the compound is in solution, even in a nonpolar solvent, decomposition usually occurs at a much lower temperature. Studies on $[Ru(NH_3)_5N_2]^{2+}$,[45] $[Os(NH_3)_5N_2]^{2+}$,[49] $[Co(N_2)(PPh_3)_3]$,[10] and $[CoH(N_2)(PPh_3)_3]$[15] show that essentially all the dinitrogen is released as gas. "Stability" is a function of many variables and it has not been possible to make any generally valid correlations between this property and $\nu(N_2)$ or position of the metal in the Periodic Table. For example, ammine-dinitrogen complexes of osmium are more stable than those of ruthenium and have a lower $\nu(N_2)$, while the iron analogs cannot be made at all. However, in complexes of the type $[MH_2(N_2)(PR_3)_3]$ this order of stability is reversed and becomes Fe > Ru > Os.[65] However, for complexes of the type *trans*-$[MH(N_2)(depe)_2]^+$, $\nu(N_2)$ and "ease of loss of dinitrogen" both fall in the order Ru > Os > Fe.[24] The one generally valid correlation is that a bis dinitrogen complex is less thermally stable than the "analogous" mono dinitrogen complex.

B. Oxidation

It is probably true to say that none of the dinitrogen complexes are indefinitely stable to air (dioxygen). However, the ammine-dinitrogen complexes of ruthenium and osmium are sufficiently stable, even in solution, to allow many laboratory operations to be performed in air. Solutions of the phosphine-containing complexes should always be handled in the absence of dioxygen.

There is only one example of a redox pair of nitrogen complexes in which both compounds have been reasonably well characterized.[35,79]

$$\begin{aligned} &\underset{\nu(N_2)\,=\,1980\ cm^{-1}\ (CHCl_3)}{[ReCl(N_2)(diphos)_2]} \underset{Zn/Hg\,+\,THF}{\overset{Cl_2\,+\,CCl_4}{\rightleftharpoons}} \\ &\qquad\qquad \underset{\nu(N_2)\,=\,2060\ cm^{-1}\ (CHCl_3)}{[ReCl(N_2)(diphos)_2]Cl} \qquad (17) \end{aligned}$$

Various metal salts, *e.g.*, $CuCl_2$, $FeCl_3$, or silver salts, can also be used as the oxidant in this reaction.

Treatment of $[Os(NH_3)_5(N_2)]^{2+}$ with easily reducible metal salts gives a number of products. Pratt, *et al.*, suggest that dimers of the type Os^{II}-N_2-M are formed.[80] Chatt suggests, by analogy to the reaction of eq 17, that monomeric osmium(III) and possibly osmium(IV) complexes are formed.[79] Support for Chatt's theory is provided by Page who finds that $[Os(NH_3)_5(N_2)]^{2+}$ can be cleanly and reversibly oxidized electrochemically (at ~ +0.3 V*; the asterisk denotes reaction at a rotating platinum electrode relative to a saturated calomel electrode) to an osmium(III)-dinitrogen complex, which subsequently decomposes to an osmium(III)-aquo complex at a first-order rate of $2 \times 10^{-2}\ sec^{-1}$ at 25°.[81] Further oxidation, at a higher potential, leads to decomposition at such a rate that no osmium(IV)-dinitrogen complex can be detected, even by rapid scan techniques.[82]

Similar experiments with $[Ru(NH_3)_5(N_2)]^{2+}$ show that it is oxidized irreversibly (at +0.72 V*) to $[Ru(NH_3)_5H_2O]^{3+}$.[82a] If any ruthenium(III) dinitrogen complex is formed, it must have a much shorter half-life than the osmium analog. By contrast the dimeric complex $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ can be reversibly oxidized (at ~0.5 V*) to a 5+ cation, which decomposes to $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$ ($k_1 = 1 \times 10^{-1}\ sec^{-1}$ at 25°).[81,83] As usual the osmium analog is more stable. Thus, $[(NH_3)_5RuN_2Os(NH_3)_5]^{5+}$ obtained by the reversible oxidation of the 4+ cation at ~0.1 V*,[84] or by chemical oxidation, can be isolated.[73] It is proving difficult to obtain an analytically pure sample. Further oxidation, at a higher potential, does not give a 6+ ion, but results in

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(72) J. Chatt and J. E. Fergusson, *Chem. Commun.*, 126 (1968).

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(80) P. K. Das, J. M. Pratt, R. G. Smith, G. Swinden, and W. J. U. Woolcock, *ibid.*, 1539 (1968).

(81) C. M. Elson, J. Gulens, I. J. Itzkovitch, and J. A. Page, *ibid.*, 875 (1970).

(82) J. A. Page, *et al.*, unpublished work.

(82a) The exact nature of many of the "aquo" complexes is not certain. Many may be sulfato complexes in solutions containing the sulfate ion.

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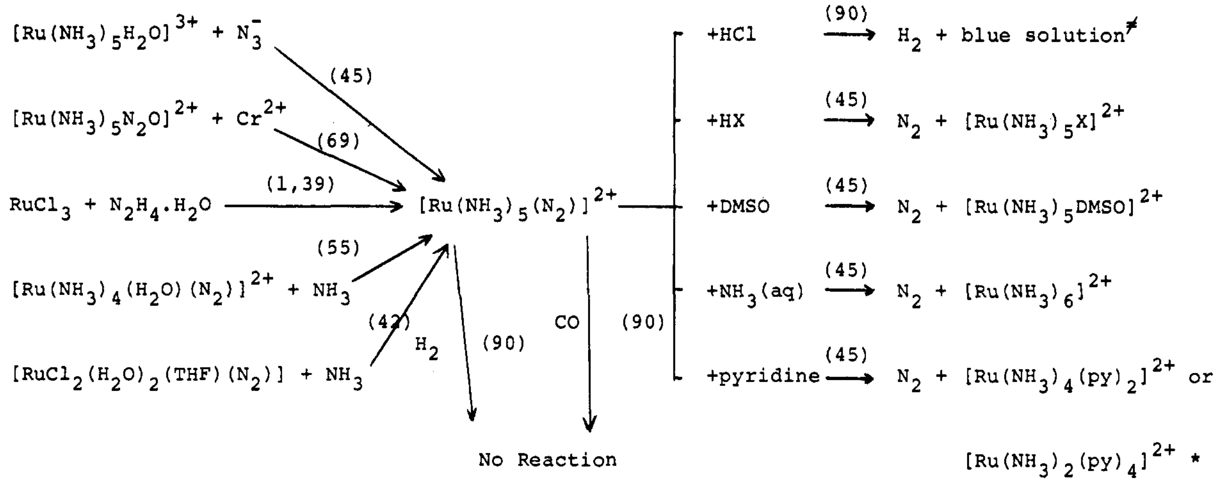

Figure 2. Some reactions of ruthenium ammines.

oxidative decomposition to $[Os(NH_3)_5(N_2)]^{3+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$.[84]

Sigwart and Spence irradiated $[Ru(NH_3)_5(N_2)]^{2+}$ and $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ with uv light' and observed photochemical oxidation of the metal to $[Ru(NH_3)_5Cl]^{2+}$ (in aqueous HCl) or to $[Ru(NH_3)_6]^{3+}$ (in aqueous NH_3). Since they could detect no dihydrogen after irradiation they proposed that the metal is oxidized by the dinitrogen, which must therefore itself be reduced.[85] However, Ford *et al.*, photolyzed $[Ru(NH_3)_5py]^{5+}$ and $[Ru(NH_3)_5NCCH_3]^{2+}$ and did observe evolution of dihydrogen, along with the oxidation of the metal.[86] This different behavior of such similar systems is surprising and suggests that further study is desirable.

C. Displacement Reactions

The displacement reactions of the ruthenium ammines are set out in Table I and Figure 2. Many of the reactions in which water is displaced from ruthenium(II) have been followed kinetically. Although the reactions follow overall second-order rate equations, the rate constant does not vary greatly with the attacking ligand. This suggests that the incoming ligand is only weakly bound to the metal in the "activated complex." The most interesting of these reactions are those in which water is reversibly displaced by a dinitrogen complex to give a binuclear complex containing a dinitrogen bridge. The equilibrium constants

$$K = \frac{[Ru(NH_3)_5(N_2)^{2+}][H_2O]}{[Ru(NH_3)_5H_2O^{2+}][N_2]}$$

$$K' = \frac{[(NH_3)_5RuN_2Ru(NH_3)_5{}^{4+}][H_2O]}{[Ru(NH_3)_5H_2O^{2+}][Ru(NH_3)_5(N_2)^{2+}]}$$

have the values of 3.3×10^4 and 7.3×10^3, respectively, at 25°.[87] This implies that, as far as reactivity toward $[Ru(NH_3)_5H_2O]^{2+}$ is concerned, dinitrogen is only slightly *deactivated* by coordination to ruthenium(II).

Thermochemists have only just begun to study dinitrogen complexes. To date the only enthalpy measurement from thermochemistry has been that of the overall reaction

$$2[Ru(NH_3)_5H_2O]^{2+} + N_2(aq) \rightarrow [Ru_2(NH_3)_{10}(N_2)]^{4+} + 2H_2O \qquad (18)$$

$$\Delta H = -22 \pm 2 \text{ kcal mol}^{-1} \ (25°)\ ^{88}$$

Figure 2 shows that dinitrogen is bound to the metal strongly enough for displacement reactions among the other ligands to be performed. However, it is a decidedly labile ligand. Sometimes only the dinitrogen is displaced by an incoming ligand (*e.g.*, ammonia), and sometimes other ligands are displaced as well (*e.g.*, by pyridine). Hydrohalic acids appear to cause simultaneous oxidation of the metal. However, since the reactions were carried out in air, it is possible that dioxygen or dihalogens (formed from HX and O_2) are responsible for the oxidation.

The chemistry of the osmium ammines is limited by the fact that $[Os(NH_3)_5H_2O]^{2+}$ apparently cannot be made. Thus $[Os(NH_3)_5(N_2)]^{2+}$ has not been prepared from dinitrogen, and $[(NH_3)_5OsN_2Os(NH_3)_5]^{4+}$ is unknown (*cf.* reaction 4). The Os–N_2 bond appears to be stronger than the Ru–N_2 bond, as shown by the failure of $[Os(NH_3)_5(N_2)]^{2+}$ to react with carbon monoxide, pyridine, ammonia, sulfur dioxide, dihydrogen, or hydrohalic acids (*cf.* Figure 2). If an oxidizing agent is present, the hydrohalic acids do react to give $[Os(NH_3)_5X]X_2$.[49]

Figure 3 depicts the chemistry of the cobalt-triphenylphosphine system. A controversy over the formulation of the "dinitrogen complex" (which appeared to have somewhat variable properties) was settled by Markó, *et al.*,[10] who demonstrated the existence of two distinct compounds, $[CoH(N_2)(PPh_3)_3]$ (III) and $[Co(N_2)(PPh_3)_3]$ (IV). III is prepared from $[CoH_3(PPh_3)_3]$ or $[Co(acac)_3]$ and IV, which has no hydridic hydrogen, is prepared from $[CoH_2(PPh_3)_3]$ or $[Co(acac)_2]$. The present authors find[89] that, in the solid phase at room temperature, III changes into IV within a few days. This implies that many of the reported reactions have been performed on mixtures of III and IV.

There are a number of important differences between the reactions outlined in Figures 2 and 3. Some of these are probably due to the fact that the ionic ruthenium complexes are studied in aqueous solutions, while the neutral cobalt complexes are soluble only in nonpolar solvents. The reversible displacement reaction between polyhydride and dinitrogen complexes is unknown in the ammine systems, possibly because the hydrides (which are

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(84) C. M. Elson, J. Gulens, and J. A. Page, *ibid.*, **49**, 207 (1971).

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(87) J. N. Armor and H. Taube, *ibid.*, **92**, 6170 (1970).

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(89) A. D. Allen and R. N. Whiteley, unpublished work.

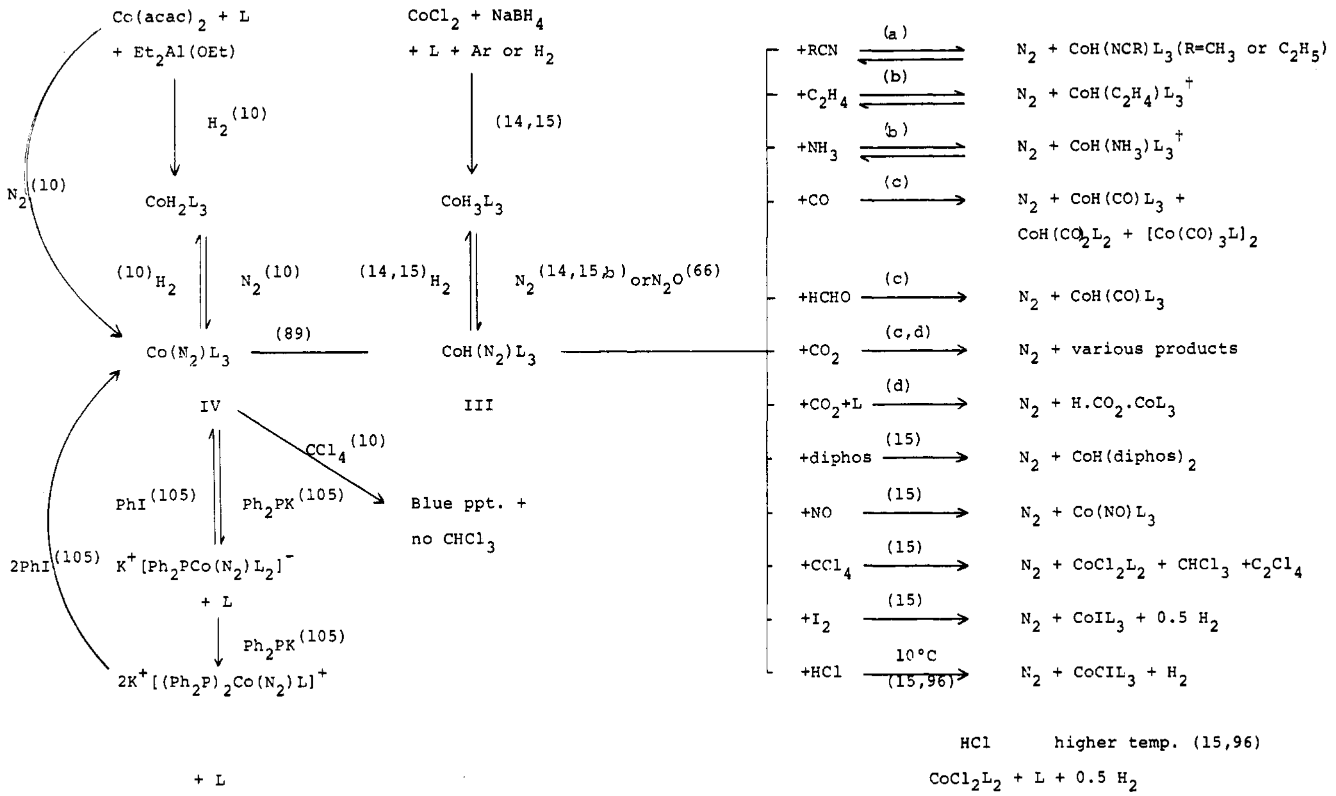
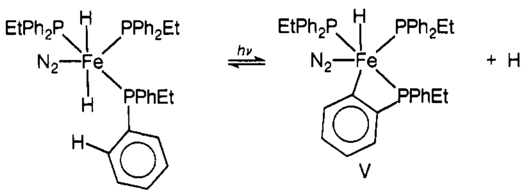


Figure 3. Reactions of cobalt tris(triphenylphosphine) complexes. L = triphenylphosphine. A dagger denotes that the products were not isolated, so the formulation is not certain. Letter reference designations are as follows: (a) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 208 (1969). (b) A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **89**, 3071 (1967). (c) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 981 (1968). (d) L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 3896 (1968).

unknown) are unstable in water.

Dinitrogen can reversibly displace ammonia bound to the cobalt system but cannot displace it from $[Ru(NH_3)_6]^{2+}$.[90] Since nitrogenase is not inhibited by ammonia,[16] and therefore must bind it rather weakly compared with other ligands, the phosphine complexes appear to be the better model of the biological system.

The chemistry of $[RuH_2(N_2)(PPh_3)_3]$[12,91,92] and $[FeH_2(N_2)(PR_3)_3]$[13] has been studied less thoroughly than that of the cobalt complexes, but appears to be very similar. The iron complex undergoes a reversible reaction in light which does not involve the dinitrogen group (*cf.* ruthenium ammines)[13,93] (eq 19). Species similar to V



+ H_2 (19)

V

are believed to be formed as intermediates in the thermal H/D exchange reactions of the ortho protons of $[RuH_2(N_2)(PPh_3)_3]$[94] and $[CoH(N_2)(PPh_3)_3]$.[95]

Complexes of the type *trans*-$[IrCl(N_2)(PR_3)_2]$ react with many reagents with loss of dinitrogen.[60,62,96,97] The products vary from planar iridium(I) complexes to five- or six-coordinate iridium(III) complexes. Surprisingly dihydrogen does not react at all. Some olefins (*e.g.*, diethyl maleate) form addition complexes without causing loss of dinitrogen.[60,62,97] These adducts have the highest $\nu(N_2)$ (2190 cm^{-1}) found among neutral dinitrogen complexes and merit more than the slight attention they seem to have received.

The rhenium complexes of the type $[ReX(N_2)(PR_3)]$ (X = Cl, Br) represent the opposite extreme, having the lowest reported $\nu(N_2)$ (1920–1980 cm^{-1}). The dinitrogen appears to be more strongly bound to the metal than in other phosphine complexes. For example, reaction with diphos results in the displacement of phosphines rather than dinitrogen.[35]

$$[ReCl(N_2)(PMe_2Ph)_4] + 2diphos \xrightarrow[14\,hr]{109°C} [ReCl(N_2)(diphos)_2] \quad (20)$$

Similarly oxidation by halogen does not break the $Re-N_2$ bond (see eq 17).[35,79] The most interesting reaction of these rhenium complexes is with certain class a metal compounds (A) and one class b metal complex $[Pt_2Cl_4(PEt_3)_2]$ to give colored asymmetric dimers probably containing a dinitrogen bridge.[98-100]

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TABLE II. Metal Complexes (A) Forming Adducts with $[ReCl(N_2)(PMe_2Ph)_4]$

A	A:Re	$\nu(N_2)$, cm^{-1}	Electronic config of A
$ScCl_3$	1	1870	d^0
$[CrCl_3(THF)_3]$	1	1860	d^3
$FeCl_2(THF)_{1.5}$	1	1860	d^6
$[Pt_2Cl_4(PEt_3)_2]$	?	1890	d^8
$[TiCl_3(THF)_3]$	1	1805	d^1
$ZrCl_4$	1	1790	d^0
$[MoCl_4(THF)_2]$	1	1795	d^2
$[MoCl_4(THF)_2]$	2	1680	d^2

Many of these dimers have been characterized only by their uv and ir spectra. The dimers are destroyed by "hard" ligands such as methanol, and $[ReCl(N_2)L_4]$ can sometimes be recovered almost quantitatively. Stronger Lewis acids, such as BCl_3 and $AlCl_3$, give transient colors with $[ReCl(N_2)(PMe_2Ph)_4]$ but then evolve dinitrogen.

Dinitrogen complexes in which $\nu(N_2)$ is greater than $\sim$1970 cm^{-1} do not form dimers with class a metal complexes. For example, triethylaluminum forms a dimer with $[ReCl(N_2)(PMe_2Ph)_4]$ ($\nu(N_2)$ = 1925 cm^{-1}) but ignores the dinitrogen group in $[FeH_2(N_2)(PEtPh_2)_3]$ ($\nu(N_2)$ = 2055–2060 cm^{-1}). Instead a phosphine molecule is abstracted to leave an apparently five-coordinated iron complex.[93]

$$[FeH_2(N_2)(PEtPh_2)_3] + AlEt_3 \rightarrow [FeH_2(N_2)(PEtPh_2)_2] + Et_3AlPEtPh_2 \quad (21)$$
$$\nu(N_2) = 1989\ cm^{-1}$$

The analogous $[ReCl(CO)(PMe_2Ph)_4]$ only forms a dimer with $AlEt_3$.[99]

Molybdenum(IV) complexes, in addition to forming the usual 1:1 adduct with the rhenium complexes, also form an adduct in which the Mo:Re ratio is 2:1. The A:Re ratio was not determined for all the adducts, so it is not known if this behavior is unique. The structure of these apparently trinuclear complexes has yet to be determined.

D. Reduction of Dinitrogen Complexes

Mortenson, in his review of biological dinitrogen fixation,[101] suggested that the enzymatic reaction proceeds in two distinct steps: firstly, the absorption, and presumably "activation" of dinitrogen on one "site;" and, secondly, the reduction of this "activated" dinitrogen on a second site. Inorganic chemists have certainly coordinated dinitrogen to a transition metal, but they seem to have achieved very little "activation." The resistance of dinitrogen complexes to reduction was demonstrated by a polarographic investigation of $[Os(NH_3)_5(N_2)]^{2+}$. No reduction waves could be found up to the limits of study (−1.3 V at pH 2 and −2.0 V at pH 9).[80] A whole range of reducing agents has been allowed to react with dinitrogen complexes,[1,36,45,90,96,101-103] including dimeric complexes, and, with only one possible exception, the NN triple bond remains intact. Dithionite, which is the only inorganic reducing agent capable of supplying electrons to nitrogenase, does not reduce it. A report that the dinitrogen in $[Ru(NH_3)_5(N_2)]^{2+}$ can be reduced to ammonia by sodium borohydride[1,45] was proved wrong by isotopic labeling experiments.[102-104] The high ammonia analysis obtained after treatment with sodium borohydride was explained by the discovery that the preparation of $[Ru(NH_3)_5(N_2)]^{2+}$ from ruthenium trichloride and hydrazine hydrate gives a product contaminated with $[Ru(NH_3)_5(N_2H_4)]^{2+}$ and $[Ru(NH_3)_6]^{2+}$.[102,103]

Treatment of $[Co(N_2)L_3]$ (L = various phosphines) with excess $KPPh_2$ or lithium alkyls gives solutions which are reported by Markó[105] to contain complexes of the type $[Co(PR_2)_2(PR_3)(N_2)]^{2-}$. Apparently the dinitrogen has again escaped reduction. However $\nu(N_2)$ has been reduced to 1864–1904 cm^{-1} which is even lower than $\nu(N_2)$ in $[ReCl(N_2)L_4]$. Markó found that the very weak Lewis acid iodobenzene attacks the dianion at the phosphorus atoms and regenerates $[Co(N_2)L_3]$. It is possible that other Lewis acids, *e.g.*, class a metal complexes, will attack the dinitrogen group to give a dinitrogen-bridged dimer.

In all the systems examined so far where a dinitrogen group has definitely been reduced, the extreme instability of the intermediate dinitrogen complexes has made their characterization difficult. van Tamelen[106-108] has reported that in the presence of "titanocene dimer" dinitrogen is reduced by sodium naphthalide to products which were subsequently hydrolyzed to ammonia. Unfortunately the intermediate "dinitrogen complex" was not isolated. Shilov, *et al.*,[109] isolated an unstable blue binuclear titanium complex which on further reduction with excess Grignard reagent produced hydrazine. This complex is stabilized with respect to loss of N_2 in the presence of triphenylphosphine.

$$(\pi\text{-}Cp)_2TiCl_2 + RMgCl + N_2 \rightarrow [(\pi\text{-}Cp)_2TiR]_2N_2 \quad (22)$$

The iron complex prepared *via* reaction 3 reacts with HCl in ether to produce hydrazine (10% yield).[110] This represents incomplete reduction of the N_2.

Brintzinger, *et al.*,[111] have successfully reduced their dimer $[(\pi\text{-}Cp)_2TiN_2Ti(\pi\text{-}Cp)_2]$ with lithium naphthalide, and upon hydrolysis NH_3 was released. These workers believe that the dinitrogen ligand is bonded edge-on to the titanium centers similar to acetylene in complexes where it functions as a bidentate ligand. It is possible that the structures of these titanium species are not analogous to those of other known dinitrogen complexes.

IV. Structural Studies

X-Ray crystallographers have studied seven dinitrogen complexes (Table III) and found that dinitrogen is bound end-on to the metal in each case. $[Ru(NH_3)_5(N_2)]Cl_2$ is octahedral; unfortunately, the cations are disordered, so it is impossible to determine accurate molecular parameters.[112,113]

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TABLE III. Molecular Parameters of Dinitrogen Complexes

Complex	M—N_2, Å	N≡N, Å	MNN, deg	Ref
N_2 gas		1.09758 (10)		*a*
$[Ru(NH_3)_5(N_2)]Cl_2$	2.10 (1)	1.12 (9)	180	112, 113
$[CoH(N_2)(PPh_3)_3]\cdot Et_2O$	1.80 (4)	1.16 (4)	175 (4)	114
$[CoH(N_2)(PPh_3)_3]$ (a)	1.784 (13)	1.101 (12)	178 (2)	116, 117
(b)	1.892 (12)	1.123 (13)	178 (1)	
$[(NH_3)_5RuN_2Ru(NH_3)_5](BF_4)_4\cdot 2H_2O$	1.928 (6)	1.124	178.3 (5)	118
$[Ru(N_3)(N_2)(en)_2]PF_6$	1.894 (9)	1.106 (11)	179.3 (9)	119
$[ReCl(N_2)(PMe_2Ph)_4]$	1.966 (21)	1.055 (30)	177 (1)	120
$[\{(C_6H_{11})_3P\}_2Ni(N_2)Ni\{(C_6H_{11})_3P\}_2]$	1.77	1.12	178.2	*b*
	1.79		178.3	
trans-$[Mo(N_2)_2(diphos)_2]$	2.01 (1)	1.10 (2)	171.8 (1.1)	*c*
$CH_3N{=}NCH_3$	1.47 (6)	1.24 (5)	110 (10)	*d*

[a] B. P. Stoicheff, *Can. J. Phys.*, **82**, 630 (1954). [b] P. W. Jolly, K. Jonas, C. Kruger, and Y.-H. Tsay, *J. Organmetal. Chem.*, **33**, 109 (1971). [c] T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, *Bull. Chem. Soc. Jap.*, **44**, 2883 (1971). [d] H. Boersch, *Sitzungsber. Akad. Wiss. Wien*, **144**, 1 (1935).

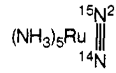
A preliminary study of $[CoH(N_2)(PPh_3)_3]$, crystallized in the presence of diethyl ether, showed that the complex is trigonal bipyramidal with three equatorial phosphines, and that a molecule of diethyl ether is included in the lattice.[114] Nmr studies show that the structure is the same in solution.[115] Exhaustive studies on a crystal of the cobalt complex grown in di-*n*-butyl ether showed the existence of two slightly different molecules of $[CoH(N_2)(PPh_3)_3]$ in the unit cell and that di-*n*-butyl ether is not included in the lattice.[116,117]

Treitel, *et al.*, have determined the structure of $[(NH_3)_5RuN_2Ru(NH_3)_5](BF_4)_4\cdot 2H_2O$ and confirmed the existence of a linear dinitrogen bridge.[118] The structural study of $[Ru(N_3)(N_2)(en)_2]PF_6$ revealed the complex to have a trans stereochemistry and has provided improved values of the Ru-N and N-N bond lengths of ruthenium(II)-dinitrogen complexes.[119]

The structure of $[ReCl(N_2)(PMe_2Ph)_4]$ is disordered between the chlorine atom and the N_2 group, and this has made a precise determination of the N-N bond length impossible.[120] This is unfortunate since $\nu(N_2)$ is the lowest in this complex of all those studied to date and thus would have provided the best opportunity of observing a lengthening of the N-N bond on coordination.

The most notable feature of these data is that, although all the metal complexes except the rhenium complex do have a longer NN bond than free dinitrogen, the lengthening and hence reduction in NN bond strength is very small. Addition of a second metal atom to form a dimer seems to make even less difference. The linearity of MNNM and the NN distance sharply differentiates the metal dimer from an organic azo complex such as azomethane. The nitrogen atoms in the azo compounds have a free lone pair which gives them a chemical reactivity not shared by the (almost) cylindrically symmetrical nitrogen atoms of the metallic dimer.

Although there have been no reports of the isolation of a complex containing a dinitrogen group bound edge-on to a metal, there is evidence that such a species can exist as an intermediate. An intermediate such as VI is



$$(NH_3)_5Ru\begin{matrix}{}^{15}N^{2+}\\ \Vert\!| \\ {}^{14}N\end{matrix}$$

VI

postulated to be formed in the intramolecular conversion of $[Ru(NH_3)_5{}^{15}N^{14}N]^{2+}$ (prepared by reducing $[Ru(NH_3)_5{}^{15}N^{14}NO]^{2+}$) to a 50:50 mixture of $[Ru(NH_3)_5{}^{15}N^{14}N]^{2+}$ and $[Ru(NH_3)_5{}^{14}N^{15}N]^{2+}$.[121]

A species such as VI would be analogous to $[Pt(Ph_3P)_2(PhC{\equiv}CPh)]$.[122]

V. Magnetochemistry

Most dinitrogen complexes are diamagnetic.[45] The only exceptions are $[Co(N_2)(PPh_3)_3]$ (μ = 2.2 BM at 25°[10]), $[ReCl(N_2)(diphos)_2]Cl$ (μ = 1.9 BM[35]), and $[(NH_3)_5RuN_2Os(NH_3)_5](BF_4)_5$ (μ = 1.8 BM[73]). The molybdenum(I) complex, $[MoCl(N_2)(diphos)_2]$,[43] should also be paramagnetic. The paramagnetism of $[Co(N_2)(PPH_3)_3]$, contrasting with the diamagnetism of $[CoH(N_2)(PPh_3)_3]$,[10] was one of the properties used to distinguish the two molecules.

VI. Bonding and Spectra

The bonding between dinitrogen and a metal is believed to involve donation from the slightly antibonding $3\sigma_g$ to the metal and back-bonding from the filled metal d orbitals to the empty $1\pi_g{}^*$ orbital of the dinitrogen. This is formally analogous to the bonding in metal carbonyls (Figure 4).

The evidence for this bonding scheme is as follows.

1. The metal -N-N system is linear.

2. The NN stretching frequency ($\nu(N_2)$) in complexes is 100-400 cm^{-1} lower than it is in free dinitrogen (2330 cm^{-1} in the Raman), and it is strongly infrared active. If there were no π back-bonding $\nu(N_2)$ would be expected to rise, as does $\nu(CO)$ in BH_3CO or $\nu(CN)$ in most nitrile complexes.

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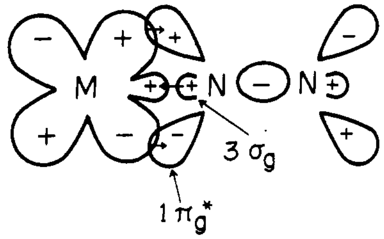

Figure 4. Diagram of the bonding between dinitrogen and a metal atom.

3. Replacement of ligands on a metal bound to dinitrogen by more strongly π-accepting ligands causes ν(N_2) to rise due to the increased competition for the metal d electrons (ref 123 includes many tables illustrating this).

4. Replacement of ammonia by dinitrogen in $[Os(NH_3)_5CO]^{2+}$ or $[Os(NH_3)_5(N_2)]^{2+}$ causes both ν(CO) or ν(N_2) to move to higher energy. This is a special case of (3) and shows that dinitrogen is a better π acceptor than ammonia.

5. Oxidation of the metal (reaction 17) or oxidative addition to the metal (*e.g.*, olefins to $[IrCl(N_2)(PPh_3)_2]$), causes ν(N_2) to shift to much higher energy.

6. Most of the known dinitrogen complexes contain metal ions with spin-paired octahedral d^6 and square-planar d^8 configurations, which are known to be good π donors.

7. Ruthenium(II) ammines are greatly stabilized by coordination of dinitrogen. For example, the half-wave potential for the one-electron oxidation of $[Ru(NH_3)_5H_2O]^{2+}$ is −0.25 V (at dme relative to sce) whereas that for $[Ru(NH_3)_5(N_2)]^{2+}$ is +0.72 V (at rpe relative to sce).[83]

8. The N-H bands in the infrared spectrum of $[Ru(NH_3)_5(N_2)]^{2+}$ are more like those of a ruthenium(III) ammine than a ruthenium(II) ammine.[45] Both (7) and (8) suggest that, relative to ammonia and water, the dinitrogen ligand either donates less charge to, or accepts more charge from, the $Ru^{II}(NH_3)_5$ moiety, or both.

9. An infrared absorption in the region 450-550 cm^{-1} in the spectra of the ruthenium and osmium ammine complexes has been tentatively assigned to the $M-N_2$ stretching frequency. Its frequency increases as ν(N_2) decreases which is consistent with a "synergic" type of bonding between dinitrogen and the metal.

Several workers have tried to compare the σ and π bonding properties of dinitrogen with those of carbon monoxide.[124,125] The MO diagram for dinitrogen shows that its π-acceptor orbitals ($1\pi_g{}^*$) are of higher energy than the analogous orbitals ($2\pi^*$) of carbon monoxide, which suggests that dinitrogen should be the weaker π acceptor. The σ-donor orbital of dinitrogen ($3\sigma_g$) is at a lower energy than that of carbon monoxide (5σ) which suggests that dinitrogen is also the poorer σ donor. Both of these effects are enhanced by the shape of the molecular orbitals. The $3\sigma_g$ and $1\pi_g{}^*$ are symmetrically placed between the two nitrogen atoms, while the 5σ and π* are distorted toward the carbon atom. Provided that the carbon monoxide is bonded end-on through the carbon atom, this distortion increases the overlap between the ligand orbitals and the appropriate metal orbitals. Conversely, the overlap between ligand and metal orbitals is decreased if carbon monoxide is bound end-on through the oxygen atom. This distortion may explain why no oxygen-bonded transition metal carbonyls are known, and why $[ReCl(N_2)L_4]$ forms more dimers with other metals than $[ReCl(CO)L_4]$.

TABLE IV. Infrared Spectra of Some Osmium Complexes

Compound	ν(N_2) or ν(CO), cm^{-1}	Ref
$[Os(NH_3)_5CO]Br_2$	ν(CO) 1883 vs	73
$[Os(NH_3)_5(N_2)]Br_2$	ν(N_2) 2028 vs, 2035 sh	49
cis-$[Os(NH_3)_4(N_2)CO]Br_2$	ν(CO) 1956 vs ν(N_2) 2177 s	73
cis-$[Os(NH_3)_4(N_2)_2]Br_2$	ν(N_2) 2102 s, 2169 s	73

Unfortunately, no measurement fully separates σ from π effects. Bancroft, *et al.*, have studied the Mossbauer spectra of a series of complexes of the type *trans*-$[FeHL(depe)_2]^+$ where L is a variety of ligands including dinitrogen.[23,24] Measurements of the center shift suggest that dinitrogen is a weaker σ donor and/or a weaker π acceptor than carbon monoxide, which does not contradict the theory. The ligand L which gives a center shift closest to that found in the dinitrogen complex is benzonitrile. This implies that the overall σ- and π-bonding properties of dinitrogen and benzonitrile are very similar, at least in this particular series of compounds.

The quadrupole splittings in these complexes indicate that π acceptance relative to σ donation is most important in the N_2 complex.[126]

Studies of the infrared spectra of dinitrogen and carbonyl complexes have led workers to conclude that dinitrogen is the better π acceptor,[62] but this has been disputed.[124]

Intensity measurements of ν(CO) in $[Ir(PPh_3)_2(CO)Cl]$ and ν(N_2) $[Ir(PPh_3)_2(N_2)Cl]$ indicate that CO is a much better π acceptor and σ donor than N_2.[127,128] Darensbourg also observed a correlation between the frequency, ν(N_2), and the integrated intensity of the infrared absorption.[128]

All the dinitrogen complexes lose dinitrogen more readily than the analogous carbonyls lose carbon monoxide, which is certainly consistent with the theory that dinitrogen is both the weaker σ donor and the weaker π acceptor.

The electronic spectra of the water-insoluble phosphine complexes have received very little attention, whereas those of the ruthenium and osmium ammines have been much used to follow the kinetics of reactions. Treitel, *et al.*,[118] consider that the intense band at 263 nm in the spectrum of the dimer $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ and the band at 221 nm in the spectrum of $[Ru(NH_3)_5(N_2)]^{2+}$ can be assigned to charge transfer from the metal d_π orbitals to the antibonding orbitals of dinitrogen. The metal d_π orbitals are at a higher energy in the dimer than in the monomer because the effective nuclear charge on each metal atom is increased less (than in the monomer) by having to provide only half of the back-bonding to the dinitrogen. This explains why charge transfer occurs at lower energy in the dimer.

As we have seen, the infrared spectra of these complexes can tell us a lot about bonding, but ν(N_2) in the phosphine-containing complexes can vary by up to 30

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cm^{-1} depending on the conditions of measurement. Furthermore, $\nu(N_2)$ in the ionic ammines decreases steadily as the size of the anion decreases.[45] Thus in $[Ru(NH_3)_5(N_2)](PF_6)_2$, $\nu(N_2)$ is 2167 cm^{-1}, whereas in the chloride salt $\nu(N_2)$ is 2115 cm^{-1}. This effect has been attributed to electrostatic interaction of the anions with the coordinated ammonia.[129] In the case of $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ $\nu(N_2)$ is only very weakly infrared active but is found in the Raman at 2100 cm^{-1}.[102,130] Since $\nu(N_2)$ in free dinitrogen is 2330 cm^{-1}, it seems that the second metal atom has less effect on the dinitrogen than the first. Possibly, since both metals are trying to donate charge into the $1\pi_g{}^*$ orbital of the dinitrogen, they act against each other.

Those dimers in which one of the metals has a low-lying empty orbital (*e.g.*, d^2, d^1, and d^0 systems) have an exceptionally low $\nu(N_2)$. Chatt has suggested[100] that the bonding is different in this case. The class b metal (Re(I)) donates charge into the $1\pi_g{}^*$ orbitals of the dinitrogen, while the class a metal accepts charge from the bonding $1\pi_u$ orbitals of dinitrogen into its empty orbital. (The σ bonding is as usual.) Both effects would weaken the NN bond and, since they would probably enhance each other, the lowering of $\nu(N_2)$ should be large.

VII. Abbreviations

M	any metal atom
R	any alkyl or aryl group
L	any ligand
X	any halide
Me	methyl
Et	ethyl
Bu	butyl
Ph	phenyl
THF	tetrahydrofuran
DMSO	dimethyl sulfoxide
depe	1,2-bis(diethylphosphino)ethane
diphos	1,2-bis(diphenylphosphino)ethane
diars	*o*-phenylenebisdimethylarsine
en	ethylenediamine
trien	triethylenetetramine
acac	acetylacetonate
nic	nicotinamide
py	pyridine
Cp	cyclopentadienyl
dmpe	1,2-bis(dimethylphosphino)ethane

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