

Inorganic Nitrogen Fixation. Nitrogen Compounds of the Transition Metals

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Nitrogenpentaammineruthenium(II)

In the early spring of 1965 a pale yellow complex was defying the efforts of Senoff to tidy up his experimental work on ruthenium compounds for his Ph.D. at the University of Toronto, and preventing him from completing his thesis. It was not until 6 months later that we felt confident enough to claim, in Sept 1965, that we had prepared the first complex of a transition metal that contained the N_2 molecule as a neutral ligand.¹

For some years we had been using the standard procedure for preparing ammine complexes of ruthenium.² This involves the reaction between commercial ruthenium trichloride (a mixture of Ru(III) and Ru(IV)) and zinc dust in concentrated aqueous ammonia, followed by treatment with hydrochloric acid, to give $[Ru^{II}(NH_3)_6]ZnCl_4$. Mild oxidation of this gives $[Ru^{III}(NH_3)_6]^{3+}$ and treatment with strong hydrohalic acids gives the appropriate halopentaammine of ruthenium(III). We were intrigued by an unusual reaction in which chloropentaammineruthenium(III), $[Ru^{III}(NH_3)_5Cl]^{2+}$, had been prepared directly by refluxing an aqueous solution of potassium pentachloro-aquaruthenite(III), $K_2[Ru^{III}Cl_5H_2O]$, with hydrazine monohydrochloride.^{3,4}

We are beginning to investigate the course of these strange reactions, but in the first place we were interested in discovering whether simple reactions of this type were suitable for preparing other amines of ruthenium. We found that when hydrazine hydrate was used instead of the hydrochloride, without refluxing, commercial ruthenium trichloride (or $K_2[Ru^{III}Cl_5H_2O]$) yielded the new complex $[Ru^{II}(NH_3)_5N_2]X_2$, $X = Cl, Br, I, BF_4, PF_6$.

It is worth noting that, although the discovery of this compound has overshadowed our original aim to find simple methods for the preparation of ruthenium amines, this aim has been amply fulfilled. We now have rapid synthetic methods for the preparation of ammine complexes of ruthenium in high yield.⁵

Preparation and Properties

The properties of this nitrogen complex, which seemed so inexplicable at the time, are as follows.

(1) It is diamagnetic. We therefore assumed that it was ruthenium(II), a spin-paired d^6 system.

(2) The dihalo salts are 2:1 electrolytes in dimethyl sulfoxide, determined by comparison with $[Ru^{III}(NH_3)_5I]I_2$, over the concentration range $1-10 \times 10^{-5} M$.

(3) It contains only five molecules of ammonia per ruthenium. This means that a sixth ligand must be present, and it must be a neutral group to explain properties 1 and 2.

(4) Standard microanalyses for nitrogen gave varying results, but they were always much too high for five molecules of ammonia per ruthenium.

(5) The infrared spectrum showed NH_3 bands, but they resembled the bands in pentaamines of ruthenium(III) more closely than those of ruthenium(II). In addition the spectrum showed a very strong sharp band at between 2100 and 2170 cm^{-1} (depending upon the anion present) assigned to the N-N stretching vibration.

(6) Decomposition of the complex with 98% sulfuric acid gave a noncondensable gas (in 40% yield) which proved to be pure N_2 . It was later found that dry thermal decomposition *in vacuo* gave up to 90% of the theoretical amount of nitrogen gas based on the now accepted formula.

(7) Treatment with hydrochloric acid in the presence of air gives a very good yield of $[Ru^{III}(NH_3)_5Cl]Cl_2$, a reaction that is not found with any other known ruthenium(II) ammine.

(8) As our confidence increased in the possibility of its being an Ru- N_2 compound, we read the initial work of Vol'pin and Shur on the conversion of N_2 to ammonia using hydrides in the presence of transition metal compounds.⁶ Treatment of the complex with sodium borohydride in alkaline solution gave more ammonia than could be accounted for by the five molecules of ammonia per ruthenium. Repeated experiments indicate that one ammonia molecule is produced in this reaction for each N_2 ligand present. This behavior is at present under investigation.

(9) Preparation of the complex from fully deuterated reagents gave a product in which all the ammonia infrared bands had shifted in the predicted manner, but the band in the region of 2150 cm^{-1} had remained essentially unaffected. This confirmed that this band could not be attributed to a metal-hydrogen stretching vibration.

We were finally convinced of the correctness of our

(6) M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966), and references therein.

(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(2) F. M. Lever and A. R. Powell, Special Publication No. 13, The Chemical Society, London, 1959, p 135.

(3) V. I. Goremykin and T. D. Avtokratora, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 427 (1947).

(4) H. M. Powell and C. K. Prout, *J. Chem. Soc.*, 137 (1962).

(5) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

observations and conclusions, but it was with considerable apprehension that we submitted our result for publication in Sept 1965.

Support for our conclusions came in a quite unexpected way. One of the materials we attempted to make for purposes of comparison was $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{N}_3]^{2+}$, azidopentaammineruthenium(III). When we carried out a reaction between $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and sodium azide in neutral solution at room temperature or above, the (diamagnetic) product appeared to be identical with the nitrogen-ruthenium complex. For a while we were worried that the nitrogen complex was in fact the azidopentaammine of ruthenium(III), despite all the evidence to the contrary. Fortunately at that time Professor Fred Basolo visited Toronto and reported that he had made a paramagnetic material from the azide reaction at 0° , and that it seemed to be the genuine azidopentaammine. We repeated this and found that the reaction at 0° does give a red paramagnetic material (which can be unpredictably and violently explosive) that slowly decomposes on standing, decreasing in paramagnetic susceptibility and fading in color to off-white. Recrystallization of this off-white product gives the nitrogen complex. It seems that, when the azide reaction is carried out at room temperature or above, any azidopentaammineruthenium(III) initially formed decomposes rapidly to the nitrogen complex. We now use the azide preparation routinely for preparing the nitrogen-ruthenium complex, since it gives a purer product than that from the hydrazine reaction, which is contaminated with $[\text{Ru}^{\text{II}}(\text{NH}_3)_6]^{2+}$, the product obtained on refluxing the reaction.⁵

Meanwhile all our efforts at Toronto were directed toward the removal of the last vestiges of doubt concerning the structure of these complexes. It was clear that a crystal structure analysis had to be made, if the complexes were stable enough, but it was some months before we were able to prepare suitable crystals of all the halide salts. Once this was achieved the analysis of the structure of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$, under Dr. Nyburg's supervision, was completed by the end of 1966.⁷

The crystal is disordered, the nitrogen molecule randomly occupying any of the six octahedral positions around the ruthenium. The space-averaged result of this is six inner nitrogen atoms, comprising the five ammonia molecules and the inner nitrogen of the N_2 molecule (N(1) in Figure 1) and six outer nitrogens, each being one-sixth of a nitrogen atom (N(2)). This disorder makes it impossible to determine the Ru-N bond lengths accurately, and hence no comparison with molecular nitrogen can be made. Within the error imposed by the disorder the Ru-N-N group is linear. This was expected from the intensity and frequency of the infrared absorption band assigned to the N-N stretching vibration and indicates the similarity between N_2 and CO as ligands.

In addition to this structural work, we were investi-

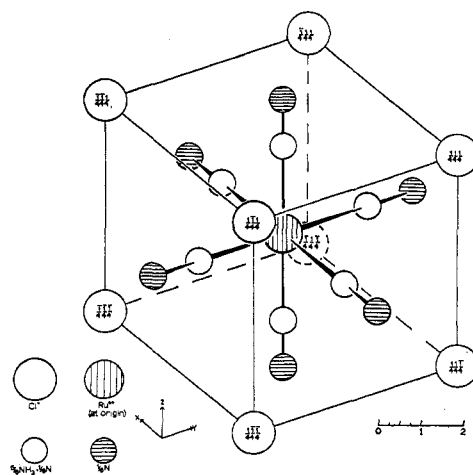


Figure 1. Disordered structure of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$.

gating the formation of the nitrogen complex in the ruthenium trichloride-hydrazine hydrate reaction. This work is not yet complete. We are now fairly certain that decomposition of a ruthenium(II) hydrazine complex leaves a bonded nitrogen molecule, but we have evidence that, in addition to this reaction, all of the known methods of preparing $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]^{2+}$ (see below and the azide reaction above) can, and probably do, take place as well.

During 1966 and 1967 transition metal complexes containing molecular nitrogen (which will be described later) had been prepared by other workers, and in one case N_2 gas had been used as the reagent.⁸ We tried unsuccessfully to prepare the ruthenium-nitrogen compound from gaseous N_2 , and only began to understand the reason for our failure when Professor Taube and his group began investigating these reactions. In the summer of 1967 Harrison and Taube⁹ investigated the behavior of reduced solutions of ruthenium(III) in an atmosphere of nitrogen. The reduction of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{Cl}_2]^{2+}$ with amalgamated zinc gives a solution believed to contain $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{OH}_2]^{2+}$. When N_2 is passed through this solution a strong absorption at $263 \text{ m}\mu$ slowly appears, with a weak shoulder at about $220 \text{ m}\mu$. On working up this solution Harrison and Taube obtained a material which showed a band at $221 \text{ m}\mu$ ($\epsilon_{\text{max}} 1.6 \times 10^4$) and which proved to be identical with our $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$. The material giving rise to the even stronger absorption at $263 \text{ m}\mu$ was finally characterized by Taube and his coworkers as a remarkable new nitrogen complex with the formula $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{N}_2\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$.¹⁰ A pure sample of this dimeric ion shows no infrared absorption in the region of 2100 cm^{-1} , as would be expected for a symmetrical N_2 environment. The Raman spectrum has not yet been studied. The remarkable thing about this compound is its stability with respect to

(8) A. B. Shilov, A. K. Shilova, and Yu. G. Borodko, *Kinetika i Kataliz*, **7**, 768 (1966).

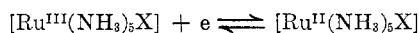
(9) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

(10) D. E. Harrison, H. Taube, and E. Weissberger, *Science*, **159**, 320 (1968).

(7) F. Bottomley and S. C. Nyburg, *Chem. Commun.*, 897 (1966).

hydrolytic dissociation. If equimolar (say 0.1 *M*) solutions of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]^{2+}$ and $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{OH}_2]^{2+}$ are mixed together, the dimeric ion is formed slowly in almost quantitative yield. This shows that the Ru-N₂ group is a very powerful nucleophile for Ru^{II}, replacing an aqua group almost completely, despite the 500-fold excess concentration of water over Ru-N₂. It appears that the reaction between nitrogen gas and $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ takes place by initial formation of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]^{2+}$, which then condenses with unreacted $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$. This unexpected reactivity of the bound N₂ molecule is very good indicator of the wide variety of reactions to be studied and is especially important in investigations of the biological nitrogen-fixation process.

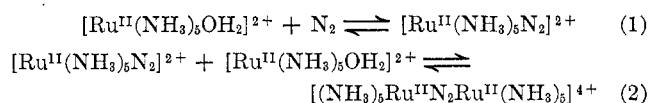
Itzkovitch and Page at Toronto have investigated the electrochemistry and kinetics of formation of these ruthenium-nitrogen complexes polarographically.¹¹ In an H₂SO₄-K₂SO₄ electrolyte the reaction (X is H₂O or HSO₄⁻)



is readily reversible, with well-defined one-electron reduction and oxidation waves, with $E_{1/2} = \pm 0.25$ V. This value compares well with earlier determinations.^{12,13}

In contrast, the monomeric and dimeric ruthenium(II)-nitrogen complexes are very much more resistant to oxidation. The half-wave potential of the monomer is 1.0 V more positive than that of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{X}]$, and the dimer is even more difficult to oxidize. On oxidation the N₂ complexes decompose with loss of the N₂ ligand.

By following the increase in absorption at 221 mμ (for the monomer) and 263 mμ (for the dimer), Itzkovitch and Page were able to examine, using a closed-flow system, the kinetic form of the following reactions at 26°.



Taking the solubility of N₂ in the electrolyte as 6 × 10⁻⁴ *M*, they calculate the second-order rate coefficients for these two reactions to be (1) 7 × 10⁻² *M*⁻¹ sec⁻¹ and (2) 4 × 10⁻² *M*⁻¹sec⁻¹. Thus it seems that N₂ coordinated to ruthenium(II) reacts almost as readily with ruthenium(II) as does solvated N₂ in this electrolyte.

Bonding

These two characteristics of the monomeric Ru-N₂ complex, $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]^{2+}$, namely resistance to oxidation and reactivity toward a second ruthenium(II), provide important additional information concerning the metal-nitrogen bond. It is assumed, by analogy with the metal carbonyls, that there is extensive double bonding between the metal and the ligand. This can be considered as a σ bond formed by

donation of the lone pair of electrons on one of the nitrogen atoms to a vacant orbital on the metal, together with a π bond formed by donation of electrons in the previously nonbonding d (or hybrid) orbitals on the metal to an antibonding π orbital on the nitrogen molecule.

Consider first the situation if the bonding were simply σ donation from ligand to metal (no π back-bonding). If this were the case one would expect: (a) the N₂ stretching frequency to remain high, or even to increase, relative to free N₂; (b) the oxidation potential of the N₂ complex to be similar to other pentaammineruthenium(II) compounds; (c) the tendency of the terminal nitrogen atom to react with a second ruthenium(II) to be drastically reduced, since the coordinated N₂ would be strongly polarized toward the first ruthenium ion.

The formation of a second bond by π donation from metal to ligand affects all of the above: (a) donation of metal electrons into the antibonding π electron system of the N₂ ligand will reduce the over-all N-N bond order below 3, hence the reduction in the N₂ stretching frequency, as observed; (b) donation of metal electrons to the ligand orbitals will reduce the electron density on the metal and hence make further removal of electrons by oxidation more difficult (we have noted earlier that the NH₃ vibrations resemble those in ruthenium(III) complexes rather than ruthenium(II), indicating that π-electron withdrawal by N₂ is significant); (c) the reactivity of the terminal nitrogen toward a second ruthenium(II) site indicates that the electronic situation on this nitrogen atom is, on balance, not very different from that in the free N₂ molecule. If this is true we would expect the N₂ bond order in the Ru-N₂-Ru dimer to be further reduced, as π electrons from the second ruthenium are fed into the antibonding N₂ π-electron system. The N-N bond length in the dimer should also be longer than in the monomer.

The remarkable stability of the Ru^{II}-N₂ system is also indicated by the wide variety of ways in which it can be formed. In a recent article by Chatt and Fergusson¹⁴ it appears that it may even be formed from ammonia. They find that the original standard method of preparing ruthenium(II) ammines,² using ruthenium trichloride and zinc dust in concentrated ammonia, also gives a small yield of the nitrogen complex even in the absence of added gaseous nitrogen.

Our work began with the use of relatively exotic reagents to produce the N₂ ligand. One of the features of biological systems that impressed us most was their ability to extract nitrogen from the atmosphere, *i.e.*, in the presence of oxygen. For a while we assumed that this would be impossible in simple inorganic systems. It seems clear that only if the central metal ion has a high electron density is it capable of holding on to a neutral N₂ ligand—certainly N₂ is lost very rapidly when nitrogenpentaammineruthenium(II) is oxidized to ruthenium(III),¹¹ and ruthenium(II) com-

(11) I. J. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).

(12) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

(13) E. E. Mercer and R. R. Buckley, *ibid.*, **4**, 1692 (1965).

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

plexes are in general fairly easily oxidized.¹² Despite these expectations of failure we decided, early in 1968, to repeat Taube's experiments using air instead of pure nitrogen. $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ was prepared by Taube's method,⁹ but the excess amalgamated zinc was not removed from the solution. When the solution had become neutral, indicating no further reduction was taking place, air was drawn through the mixture. The appearance of a red color after a short while indicated that ruthenium(III) was being produced (we assume this red color is due to $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{OH}]^{2+}$).¹⁵ The air was removed from the system with argon and a further portion of acid added, thus accomplishing reduction of ruthenium(III) under argon. When the solution was again neutral air was drawn through. It was encouraging to find that as these steps were repeated the time required to produce the red coloration lengthened, until finally no color was observed after the air had been drawn through for 45 min. These steps took place over a 7-hr period and the product was a high yield of Taube's dimeric ion. This was easily converted to the monomer, $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]^{2+}$, and identified unambiguously.¹⁶

At this stage it seemed to be desirable to make the process continuous by drawing air through a solution of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ in the presence of amalgamated zinc and furnishing a continuous supply of acid to keep the zinc "active." This system was a failure, no nitrogen fixation being observed. At present, we are uncertain as to the reason for this. However, the combination of experiments show that there is a true competition between N_2 and O_2 , *i.e.*, the O_2 is not being removed by a large excess of reducing agent. In this competition it seems that N_2 can easily hold its own.

Shortly after we reported this work van Tamelen and his group described a second system which would fix nitrogen from the atmosphere¹⁷ (see below).

Nitrogen Fixation by Inorganic Systems

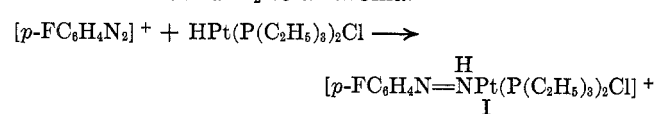
Beginning with the work of Vol'pin and Shur in 1964⁶ there are now several examples of transition metal systems that are capable of converting gaseous N_2 to ammonia under relatively mild conditions. The system that has been studied most completely^{6,18-21} is a solution of dicyclopentadienyltitanium dichloride and an ethylmagnesium halide in an inert solvent such as ether or tetrahydrofuran. Gaseous nitrogen reacts with such a solution to produce up to 1 mole of ammonia for each mole of titanium. The precise mechanism of this system is in some dispute,¹⁹⁻²¹ although it appears possible that a nitride intermediate may be involved. At present it can be said only that the es-

sential requirements of the system are a nitrogen fixer (that is, some ingredient which will form a complex, however transient, with molecular nitrogen), a reductant, and a source of protons.

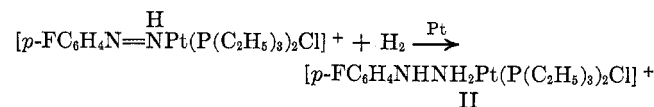
van Tamelen has extended the work on this system, first producing a very efficient cyclic process whose over-all stoichiometry was essentially catalytic²² and recently modifying the ingredients to produce a system that can fix atmospheric nitrogen.¹⁷ In this latest development naphthalide is used both as the reductant and to produce the nitrogen fixer by reacting with titanium tetraisopropoxide, $\text{Ti}((\text{CH}_3)_2\text{CHO})_4$, presumably generating a reduced titanium species. Isopropyl alcohol is the proton source. Since oxygen will react with naphthalide the precise course of the fixation of atmospheric nitrogen is not clear yet.

The implications of the discovery of atmospheric nitrogen fixation are very great. Clearly all one has to do is provide an environment for the metal ion that holds it in an appropriately reduced oxidation state. There are many ways in which this can be done in both biological and normal chemical systems. Nitrogen from the atmosphere can then be entrapped by a metal complex and is thereby rendered capable of reaction. There seems little difficulty in imagining several possible reactions that could then lead to the formation of ammonia or a derivative of ammonia, with eventual assimilation into a biological system.

In the search for inorganic analogs of the biological nitrogenase system, a clearly defined process has been described by Parshall.²³ In this system an aryldiazonium salt is used as a model for a metal-nitrogen compound, and a complex platinum hydride is used to convert the bound N_2 to ammonia.



The first step involves the condensation of the reagents to give a substituted diimide complex (I), the hydride being transferred from platinum to the adjacent nitrogen atom. The product (I) reacts rapidly with hydrogen (25°, 1 atm, Pt catalyst) to give a substituted hy-



drazine complex, II. Prolonged hydrogenation of this regenerates the platinum hydride and frees the *p*-fluorophenylhydrazine, which in turn eventually gives *p*-fluoroaniline and ammonia.

Other Transition Metal N_2 Compounds

In the past 2 years a surprisingly small number of other transition metal- N_2 compounds has been prepared. The first one to follow the ruthenium complex

(15) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

(16) A. D. Allen and F. Bottomley, *Can. J. Chem.*, **46**, 469 (1968).

(17) E. E. van Tamelen, G. Boche, and R. Greeley, *J. Am. Chem. Soc.*, **90**, 1677 (1968).

(18) G. N. Nechiporenko, G. M. Talerina, A. K. Shilova, and A. E. Shilov, *Dokl. Akad. Nauk SSSR, Otd. Khim. Nauk*, **164**, 977 (1965).

(19) H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966).

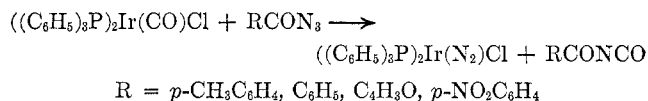
(20) H. Brintzinger, *ibid.*, **88**, 4307 (1966).

(21) R. Maskill and J. M. Pratt, *Chem. Commun.*, 950 (1967).

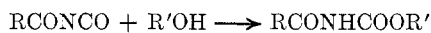
(22) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967).

(23) G. W. Parshall, *ibid.*, **89**, 1822 (1967).

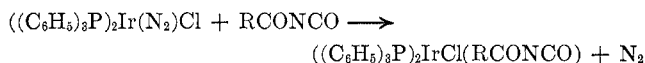
was reported by Collman and Kang^{24,25} as a product of the reaction between Vaska's iridium compound²⁶ and an acyl azide.



Small amounts of water or ethanol are necessary to remove RCONCO since RCONCO displaces N₂ from



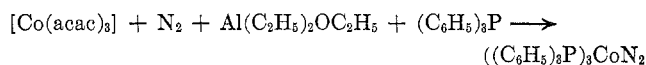
the complex.



The structure of this complex has not yet been reported, but it is assumed to be the *trans* complex by analogy with Vaska's compound. The corresponding but much less stable rhodium complex was reported in 1967 by Ukhin, *et al.*²⁷

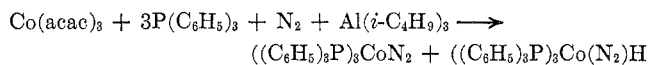
The preparation of a transition metal complex containing molecular nitrogen, using gaseous nitrogen as the reagent, was reported by three separate groups of workers early in 1967.

Yamamoto, *et al.*,²⁸ first reported the following reaction.



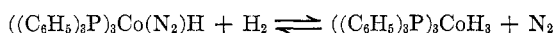
The yellow, air-sensitive product was thought to be the result of the formation of an unstable ethylcobalt compound which reacts with N₂ to give the final product.

Within a month Misono, *et al.*,²⁹ also working in Tokyo, reported that the same reaction, but using triisobutylaluminum in place of the diethylaluminum ethoxide, gave a mixture of products.



The presence of the hydride-nitrogen complex, in addition to the simple nitrogen compound, was inferred from the fact that thermal decomposition gives a mixture of nitrogen and hydrogen in the ratio 9:1.

The hydride-nitrogen compound received confirmation by Sacco and Rossi,³⁰ who found that a readily reversible equilibrium exists.



Thermal decomposition of the hydride-nitrogen compound gave 1.5 moles of gas/mole of compound, consisting of nitrogen and hydrogen in the ratio 2:1. Other evidence was presented for the presence of hydride in this compound, but no metal-hydrogen

(24) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).

(25) J. P. Collman, M. Kubota, J.-Y. Sun, and F. Vastine, *ibid.*, **89**, 169 (1967).

(26) L. Vaska, *Science*, **140**, 809 (1963).

(27) L. Yu. Ukhin, A. Yu. Shvetzov, and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 957 (1967).

(28) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

(29) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967).

(30) A. Sacco and M. Rossi, *Chem. Commun.*, 316 (1967).

stretching vibration could be detected in the infrared spectrum. Similar results were also obtained by the Japanese workers using $((C_6H_5)_3P)_3CoN_2$.³¹ In addition it has also been shown that reversible exchange of N₂ with ammonia and ethylene and irreversible exchange with carbon monoxide and carbon dioxide occurs.³²

Final proof of the existence of the hydride-nitrogen compound came with a report by Enemark, *et al.*, of the crystal structure of the product of the original reaction, this time using triethylaluminum instead of diethylaluminum ethoxide.³³ The structure (Figure 2)

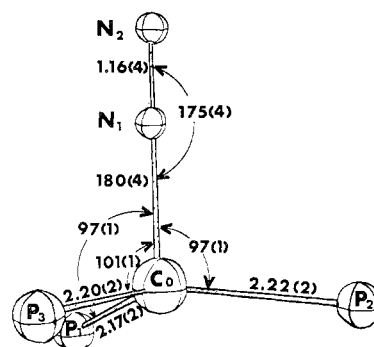
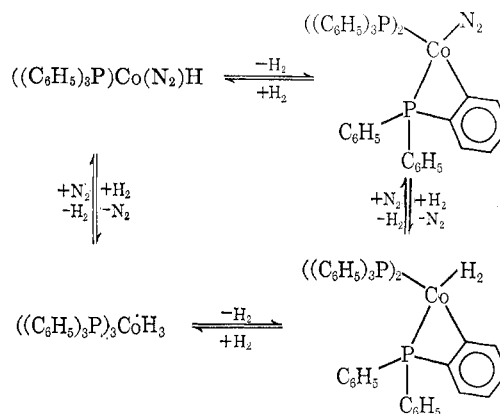


Figure 2. Structure of $((C_6H_5)_3P)_3Co^I(N_2)H$.³³

is a trigonal bipyramid, with a vacant site (presumably occupied by the hydride ion) *trans* to the N₂ molecule.

Parshall has recently investigated the deuterium exchange of $((C_6H_5)_3P)_3Co(N_2)H$ ³⁴ and finds that 19 hydrogen atoms exchange. To explain this an intermediate involving bonding between the *ortho* carbon atom of one of the phenyl rings and cobalt is postulated. It appears possible that this intermediate and the compound $((C_6H_5)_3P)_3CoN_2$ may be identical. If so, in our opinion, all of the reported data²⁸⁻³⁴ may be rationalized by the following scheme. Diagonal equilibria are also possible.



(31) A. Misono, Y. Uchida, T. Saito, and K. M. Song, *Chem. Commun.*, 419 (1967).

(32) A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

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The only other metal-mononitrogen compound that has been isolated and adequately characterized is remarkable because of its great stability. It was prepared by Stevens³⁵ at Toronto by the careful addition of ammonium hexachloroosmate to hydrazine hydrate, followed by heating under reflux until the product precipitates from the hot solution.

The N₂ stretching frequency is about 100 cm⁻¹ lower than that in the Ru-N₂ compounds, indicating a very considerable degree of metal-nitrogen double bonding. It is very difficult to decompose thermally, cannot be reduced to ammonia, and can be recovered unchanged after boiling in concentrated hydrohalic acids. It appears to form a dimeric compound when allowed to react with [Ru^{II}(NH₃)₅OH₂]²⁺, but this has not been fully characterized yet.

The high stability of osmium complexes containing molecular nitrogen is further indicated by the recent preparation of the first dinitrogen complex, [Os^{II}(NH₃)₄(N₂)₂]X₂,³⁶ by the reaction of nitrous acid with [Os^{II}(NH₃)₅N₂]²⁺. This reaction is unusual in that it appears to involve the diazotization of a coordinated ammonia, and it illustrates yet another method by which N₂ complexes of transition metals may be formed. The N₂ stretching frequencies in this compound are higher than in [Os^{II}(NH₃)₅N₂]²⁺, consistent with a sharing of the π-donor capacity of the osmium(II) between the two nitrogen ligands.

In addition to these complexes a number of others have been described, but not so fully characterized. Shilov, *et al.*, have obtained a complex containing molecular nitrogen from the reaction between RuCl₃ and RuCl₃OH and zinc in tetrahydrofuran in the presence of nitrogen gas.^{8,37} The nature of this complex is uncertain. These workers have also prepared osmium³⁸ and ruthenium³⁷ complexes containing molecular nitrogen in a manner similar to that given earlier.

Johnson and Beveridge have described the reversible coordination of molecular nitrogen with N,N-disalicylaldehyde-1,3-propanediiminemanganese(II).³⁹ In this case it is postulated that the coordination of N₂ in-

Table I
Infrared Frequencies of Bands Assigned to ν_{N-N} in Transition Metal Complexes Containing Molecular Nitrogen

Compound	ν _{N-N} , cm ⁻¹	Ref
[Ru(NH ₃) ₅ N ₂]X ₂	2105-2169	1, 5
[Os(NH ₃) ₅ N ₂]X ₂	2010-2060	a
[Os(NH ₃) ₄ (N ₂) ₂]X ₂	2120, 2175	b
((C ₆ H ₅) ₃ P) ₂ Ir(N ₂)Cl	2095	25
C ₂ H ₅ O ₂ CCH=CHCOOC ₂ H ₅		
↓		
((C ₆ H ₅) ₃ P) ₂ Ir(N ₂)Cl	2190	25
((C ₆ H ₅) ₃ P) ₂ Rh(N ₂)Cl	2152	27
((C ₆ H ₅) ₃ P) ₃ Co(N ₂)H	2080-2084	29-31
((C ₆ H ₅) ₃ P) ₃ Co(N ₂)	2088	28, 29
((C ₆ H ₅) ₃ P) ₃ Ru(N ₂)	2143	c
Molecular N ₂ (Raman)	2330	d

^a A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

^b H. A. Scheidegger, J. N. Armor, and H. Taube, *J. Am. Chem. Soc.*, **90**, 3263 (1968). ^c A. Yamamoto, S. Kitazume, and S. Ikeda, *ibid.*, **90**, 1089 (1968). ^d K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, Inc., New York, N. Y., 1963, p 142.

volves "sideways-on" bonding found in ethylene complexes of transition metals.

Yamamoto and coworkers have described a complex formulated as ((C₆H₅)₃P)₃RuN₂, prepared from ((C₆H₅)₃P)₄Ru and N₂ gas. This complex has not been isolated from solution. A similar reaction with iridium failed to yield a complex containing molecular nitrogen.⁴⁰

The transition metal complexes containing molecular nitrogen which have been characterized are listed in Table I together with the frequency of the N₂ stretching vibration.

Conclusion

The nitrogen molecule acts as ligand toward appropriate transition metal centers in a manner very similar to the isoelectronic carbon monoxide molecule. The compounds formed vary from the very air-stable osmium(II) compound to the very air-sensitive cobalt(I) compound. In some of these compounds the N₂ can be reduced, at least partly, to ammonia. There seems to be no conceptual obstacle now to the development of an inorganic system capable of converting atmospheric nitrogen to ammonia at least as easily as it is done in biological systems.

(40) See Table I, footnote c.

(35) See Table I, footnote a.

(36) See Table I, footnote b.

(37) Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, *Dokl. Akad. Nauk. SSSR*, **176**, 1297 (1967).

(38) Yu. G. Borod'ko, V. S. Bukreev, G. I. Kozub, M. L. Khidkel, and A. E. Shilov, *Zh. Strukt. Khim.*, **8**, 542 (1967).

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