Nitrogen Fixation by Transition Metals: A Review

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Abstract

Within the background of biological nitrogen fixation mediated by the enzyme nitrogenase, transition-metal complexes capable of binding and activating dinitrogen towards protonation and reduction have been synthesized. Of particular interest in this research area has been the transition-metal mediated conversion of dinitrogen to ammonia (stoichiometric and catalytic) and the elucidation of the corresponding mechanistic pathways. Metal dinitrogen complexes can be used for molecular dinitrogen fixation. Most commonly used were Molybdenum, Tungsten and Iron as they form part of nitrogenase enzymes. But late transition metal complexes were also studied for their ability to catalytic reduction of molecular dinitrogen. The different metal complexes and their possible mechanisms from different research papers is discussed in this review.

Keywords: Nitrogen; Transition metals; Metal complexes

Introduction

Nitrogen is an essential element for living organisms & Industrial processes. Although, available abundantly in atmosphere, as gaseous molecular nitrogen, it is practically cannot be used by us. As nitrogen molecule is very stable chemically, it is unusable by most of living organisms. It must be converted to a usable form (fixed) by one or several routes. The commonly observed fixed forms of gaseous nitrogen are NH_3, NO_3^-, and $NH4^+$. Also, conversion of gaseous nitrogen to usable forms is very difficult but certain microorganisms can do it at very ambient conditions with the help of nitrogenase enzymes, which work as a catalyst in conversion of dinitrogen to ammonia [1-4].

$$N_2 + 8H^+ + 8e^- + 16ATP \circledR 2NH_3 + H_2 + 16ADP + 16Pi$$

Industrially, this is achieved by Haber- Bosch process, where molecular nitrogen is combined with hydrogen in the presence of heterogeneous solid state catalysts prepared from magnetite (Fe_3O_4) with small amounts of aluminum or potassium, which

act as promoters, to form ammonia **(FIG 1).**

Though, conversion of dinitrogen and dihydrogen into ammonia is favored thermodynamically, this reaction cannot proceed at ambient reaction conditions, because the dissociation of triple bond of dinitrogen requires high energy. To accomplish this, process requires harsh reaction conditions, like high temperature and pressure and catalyst for activation of dinitrogen. Even though the yield obtained is comparatively very low (10-20%) [1,2].
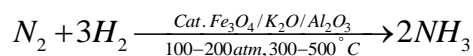
$$N_2 + 3H_2 \xrightarrow[\text{100--200}atm, 300-500^\circ C]{\text{Cat.}Fe_3O_4/K_2O/Al_2O_3} 2NH_3$$

FIG. 1. **Haber-Bosch Process.**

On the other hand, micro bacteria fix molecular nitrogen using nitrogenase enzymes, which under ambient temperature and pressures. Three types of nitrogenases are known, which are Molybdenum (Mo), Vanadium (V) & Iron (Fe) nitrogenases. Micro bacteria mediate nitrogen fixation with the help of these nitrogenases [2].

Therefore, to mimic the action of microorganisms, to fix the gaseous molecular nitrogen, several catalytic systems have been established which use transition metal dinitrogen complexes or their precursors to fix nitrogen under ambient reaction conditions. Transition metals have partially filled 'd' subshell, which can give rise to cations with an incomplete 'd' subshell. Several metals from transition metals family were used to design the dinitrogen complexes which contain dinitrogen (N_2) as a ligand. These ligands act as catalysts and catalyze the hydrogenation of Nitrogen to ammonia or its equivalent under mild conditions [3,5,6].

Synthetic model systems have been created which bind and activate N_2 towards protonation and further reduction. Although biomimetic nitrogen fixation schemes involve the stepwise addition of protons and electrons to coordinated N_2, it should be mentioned that some model systems also exhibit other reaction modes such as the spontaneous cleavage of N_2 into two nitrides or the hydrogen-mediated reduction of N_2 at ambient conditions which do not have a direct relevance to nitrogenase [7].

The first, stable metal dinitrogen complex have been reported by Allen and Senoff in 1965, as a Ruthenium complex, $[Ru(NH_3)_5(N_2)]^{2+}$ **[FIG. 2]**. Ruthenium based catalysts can be operated at a comparatively lower temperature and pressure conditions as compared to Haber- Bosch process. Also, Metal dinitrogen complexes with Molybdenum, Iron, Tungsten etc. as catalysts were reported which can convert dinitrogen into ammonia or its equivalents [2-5].
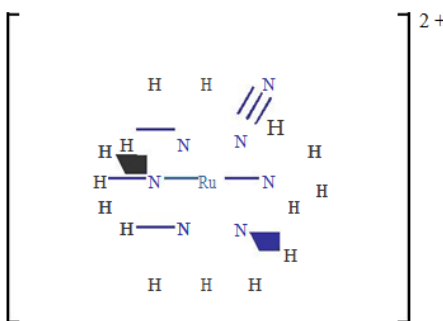

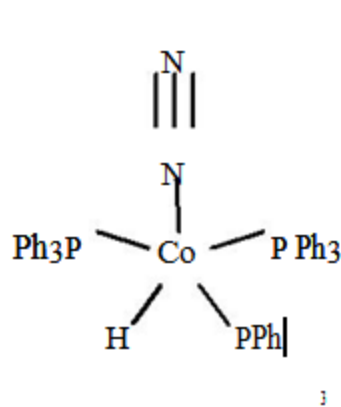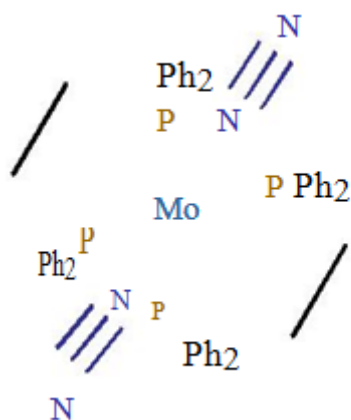FIG. 2. **Ruthenium Complex-The first reported metal-dinitrogen complex.**

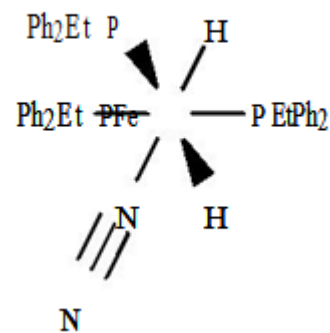FIG. 3. **Iron complex.**   FIG. 4. **Molybdenum Complex.**   FIG. 5. **Cobalt complex.**

Transition metal complexes

The available dinitrogen systems can be subdivided into those containing early transition metals, Mo & W, iron and late transition metals. Few example of each of these groups are summarized in this section.

Early transition metal complexes

Iron and Molebdenum are the most popular metals for the dinitrogen complexes, as they are found in FeMoco of the enzyme nitrogenase. Over the years Tungsten & Molybdenum complexes are being studied [8,9].

Molybdenum and tungsten dinitrogen complexes

Chatt & Hidai explored bidentate phosphine ligands such as dppe (bis(diphenylphosphino)ethane) and depe (bis(diethylphosphino)ethane) for synthetic nitrogen fixation [10,11]. Because of the softness of phosphine donors the metal-ligand bonding in such systems is considerably weakened in Mo-nitride complexes. Therfore, George et al used of tridentate phosphine ligands for formation of Mo-dinitrogen ligand complexes. They synthesized complexes of type $[Mo(N_2)(dpepp)(L_2)]$, where $L_2 = 2\ PMe_2Ph$ **(FIG 3)** which protonated by hydrochloric acid can produce a mixture of Hydrazine and Ammonia [12,13].

Svea et al. used tetradentate phosphine ligands for formation of Mo- dinitrogen ligand complexes which produced complexes of type $[Mo(N_2)2(prP_4)]$, which can then be reacted with HBF4 to produce hydrazido complexes $[Mo(NNH_2)F(prP_4)]^+$ [14].

Yandulov and Schrock used Molybdenum complexes with triamidoamine ligands carrying large bulky substituents, which gave a complex complex $[Mo(HIPTN_3N)]$, Where HIPT=$(3,5-(2,4,6-i-Pr_3C_6H_2)2-C_6H_3)$. This complex was in turn converted to ammonia by stepwise addition of protons [15].

Schrock employed the anionic PCP pincer ligand (t-BuPOCOP=C_6H_3-1,3-$[OP(t-Bu)_2]_2$) for synthetic nitrogen fixation which was obtained by lithiation of 1-iodo-2,6-$[OP(t-Bu)_2]_2C_6H_3$ [16].

Iron dinitrogen complexes

Iron complexes play a special role in synthetic nitrogen fixation as the biological reduction of dinitrogen mediated by the enzyme nitrogenase is supposed to proceed at the iron atoms of the FeMoco. Also, the industrial production of NH_3 is performed at high temperature and pressure through the Haber–Bosch process where potassium promoted iron surface serves as catalyst to mediate the reaction between the extremely inert N2 molecule and H2. Peters et al. reported the phosphine/acetate iron (II) scaffold [Fe(PhB(CH$_2$P(CH$_2$Cy)$_2$)$_3$)(OAc)] **(FIG 4)** that is able to bind diazene, hydrazine and ammonia [17].

Other transition metal complexes

Many other transition metal-dintrogen complexes were also reported by various researchers' groups. Early transition metals like Titanium, Zirconium, Vanadium, and Chromium are the most common transition metals used for dinitrogen fixation. Some of the late transition metals like Ruthenium, Cobalt, and Iridium were studied in the view of synthetic products for dinitrogen fixation. Some of the complexes discussed in the literature are summarized below:

The end-on bridged titanium complexes [Ti(Z$_5$-C$_5$Me$_5$)(Z$_6$-C$_5$H$_4$CR$_2$)]$_2$(m-Z1:Z1-N2)R$_2$=(p-tolyl)$_2$ or adamantylidene and [TiCl((Me$_3$Si)$_2$N)(TMEDA)]$_2$(m-Z1:Z1-N2)(TMEDA=tetramethylethylenediamine) have been synthesized by Beckhaus et al [18].

The end-on bridged zirconocene complex is the indenyl-ligated dinitrogen complex [Zr(Z$_5$-C$_5$Me$_5$)(Z$_9$-C$_9$H$_5$-1-R$_1$-3-R$_2$)](m-Z1:Z1-N2) (R$_1$=Me, i-Pr, t-Bu; R$_2$=Me) that is obtained by treatment of [Zr(Z$_5$-C$_5$Me$_5$)(Z$_9$-C$_9$H$_5$-1-R$_1$-3-R$_2$)] with one atmosphere of N$_2$ [19,20]. Even though Ruthenium does not play any role in biological systems, it has high weightage for studies in synthetic nitrogen fixation as it produces more stable nitrogen-metal complexes in comparison with their iron analogues. Also, very first dinitrogen complex studied was a ruthenium complex, Ru (NH$_3$)$_5$(N$_2$)]$^{2+}$, studied by Allen & Senoff [3].

The iridium (I) compound [IrCl (N2)(PPh3)2] showed a moderate activation of N2. Though it was one of the first studied molecules in dinitrogen-metal complexes for nitrogen fixation, it is not studied much as compared to other metal complexes [21,22].

Activation of dinitrogen center for protonation

Only Lithium (Li) was known to react with dinitrogen to form Lithium Nitride (LiN3) at ambient conditions, which can react with water molecules to produce ammonia [23]. While it requires more elevated temperatures and pressure conditions for other metals to react with dinitrogen, to form metal nitrides [24].

In 1965, Allen and Senoff, prepared a transition meta- dinitrogen complex, by conducting an aqueous reaction of Ruthenium (III) Chloride with hydrazine and isolated first transition metal- dinitrogen complex Ru(NH$_3$)$_5$(N$_2$)]$^{2+}$, which in turn liberated dinitrogen gas on treatment with sulfuric acid [2-4,25,26]. Also, Cobalt- dinitrogen complex [CoH(N$_2$) (PPh$_3$)$_3$] **(FIG 5)** was reported by Yamamoto, which involved direct coordination of gaseous dinitrogen to the transition metal complex, by reduction of [Co(acac)$_3$] with AlEt2OEt under atmospheric pressure of dinitrogen in presence of PPh$_3$ in Ether [27].

Since then, various transition metal-dinitrogen complexes have been prepared with "terminal", "bridging", "endon", "sideon" and their combinations including biomimetic complexes where dinitrogen is co-ordinated to iron **[FIG 5]**,

molybdenum **[FIG 4]** simulating possible coordination of dinitrogen on FeMo-Cofactor [28-33].

Conversion of dinitrogen into ammonia or hydrazine

Proton rich source like brosted acids attack the electron rich centre dinitrogen ligand, to form ammonia. Chatt developed an approach to convert dinitrogen from dinitrogen-molybdenum/ tungsten complexes [10]. Later, Hidai & coworkers reported stoichiometric activation of dinitrogen to produce ammonia when reacted with brosted acids. Dinitrogen complex based on tungsten (W), [W(N$_2$)$_2$(PMe$_2$Ph)], on reaction with sulfuric acid, produced ammonia **[SCHEME 1]**. Stepwise protonation of nitrogen resulted in the formation of intermediates like Diazenido complex, Hydrazido complex and hydrazidium complex. Some of which produced ammonia on reaction with acids or bases [28-30]. Based on these several other metal complexes were also reported.
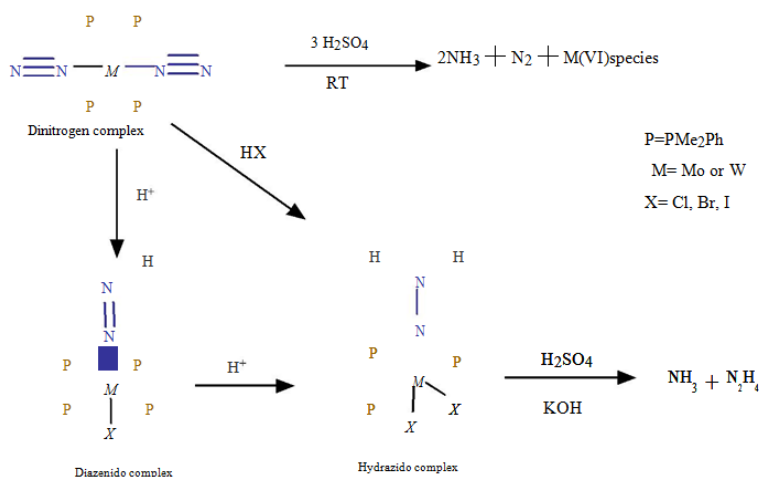
SCHEME 1. **Protonation of dinitrogen.**

Transformation of Hydrazine to Ammonia

Mulitmetallic dinitrogen bridges transition metal complexs **(FIG 4)** on reaction with brosted acids produce hydrazine [34]. Zirconium based dinitogen bridged complex, [{Cp*2Zr(N$_2$)}$_2$(l-N$_2$)], Cp*=C$_5$Me$_5$, on reaction with hydrochloric acid gave a micture of hydrazine and dinitrogen together with the formation of Zirconocene dichloride [Cp*2ZrCL$_2$] [19].
Multimetallic dinitrogen bridged complexes of transition metals like molybdenum, tungsten, or nickel give ammonia, rather than hydrazine, on reaction with acids [35].

Formation of nitrido complexes

Nitrido complexes are formed by forming a bond between two monoatomic nitrogen atoms and transition metal. Formation of transition metal-dinitrido complexes is another method of catalytic nitrogen fixation. **(FIG 1)** Laplaza and Cummins, in 1995, reported the formation of nitride complex with molybdenum [36]. Since then many products have been reported. The nitride bridges metal complexes serve as an intermediate which can bind and liberate dinitrogen. Similarly, cleavage of dinitrogen from netal-dinitrido complex produces ammonia on treatment with hydrogen chloride. Photochemical cleavage of dinitogen- dimetal ligand can produce ammonia. Triple bond in dinitrogen ligand bridging two molybdenum moieties in

dinitrogen- bridged dimolybdenum complex was cleaved under visible light irradiation at room temperature to give molybdenum nitride complex which on reaction with acid produced ammonia [2].

Activation of dinitrogen to react with dihydrogen

Direct reaction of dinitrogen with dihydrogen uses high temperature condition, as explained by Haber- Bosch process. It can be reacted under ambient conditions because of high dissociation energy of triple bond in dinitrogen. Substitution reaction between dihydrogen and dinitrogen are well studied for molybdenum and tungsten – dinitrogen metal complexes and dihydrogen. Therefore, appropriate activation of dinitrogen to react with dihydrogen is suggested for formation of ammonia. Tungsten complex was studied for the protonation by acidic Ruthenium dinitrogen complex, which was observed to produce hydrazido complex and further reaction with excess of acidic Ruthenium complex under atmospheric pressure and slightly elevated temperature produced ammonia. Heterolytic cleavage of dihydrogen is induced by nucleophilic attack of dinitrogen at ruthenium centre produces a proton which is used to produce ammonia from molecular dinitrogen under ambient conditions. Similarly, Tungsten dinitrogen complexes on treatment with dinitro molebdenum complex under atmospheric pressure produces ammonia, has been reported [27,37,38].

T. Shima and coworkers have reported similar type of reaction for trinuclear titanium compex, where partial hydrogenation and cleavage of dinitrogen was observed to give a polyhydrido tetra titanium complex [39].

Activation without using dinitrogen complexes

Shilov has reported the conversion of dinitrogen into mixture of hydrazine and ammonia using polynuclear molebdenum-magnesium complex using $[Mg(MeOH)_6][Mg_2\text{-}Mo_8O_22(OMe)_6(MeOH)_4]_6MeOH$ as a catalyst [40,41].

In another method, treatment of an aqueous methanol solution of sodium amalgam, L-a-dipalmitoylphosphatidylcholine (PC), and P^nBu_3 in the presence of a polynuclear molybdenummagnesium catalyst under atmospheric pressure of dinitrogen and room temperature produced hydrazine, in combination with ammonia [41,42].

Electrochemical reactions to synthesize ammonia from dinitrogen and dihydrogen or steam using transition metal complexes as catalysts were also studied [43]. Likewise, photochemical reduction of dinitrogen into ammonia using transition metal complexes as catalysts has been studied [44]. In both the cases, yields obtained were very low.

Catalytic Formation of Ammonia & Silylamine

Ammonia is the most common form of "fixed" dinitrogen which is utilised by most of the biological systems. Transition metals can be used for catalytic conversion of dinitrogen into ammonia. Also, Silylamine ($N(SiMe_3)_3$) can be easily transformed into ammonia by acid hydrolysis, reductive silylation of molecular dinitrogen can be used as an alternative way of nitrogen fixation. These both the reactions are studied in the view of metal-dinitrogen complexes.

Catalytic Formation of Ammonia

Two transition-metal elements Mo & Fe, constitute FeMo-co, the active site of nitrogenase. The Mo or Fe- dinitrogen

complexes have been found to catalyze the reduction of dinitrogen into ammonia under ambient reaction conditions [15,45].

In 2003, Yandulov & Schrock reported a molybdenum- dinitrogen complex bearing tetradentate hexaisopropylterphenyl (HIPT)-substituted triamidoamine ligand as a catalyst, which can reduce dinitrogen into ammonia under ambient reaction conditions. Treatment of decamethylchromocene $(CrCp^*_2)$ as a reducing agent, and 2,6-lutidinium tetrakis [3,5-bis(trifluoromethyl)phenylborate] ([LutH]BArF$_4$) as a proton source, in the presence of the catalyst at room temperature for 7 h under atmospheric pressure of dinitrogen resulted in the formation of ammonia. During this reaction formation of hydrazine complex is not reported. Reactive Mo complex intermediates like diazenido, nitride, hydrido and ammonia complexes were identified. Whereas other transition metal complexes such as tungsten, chromium and vanadium produces stoichiometric ammonia [15] (**SCHEME 2**).
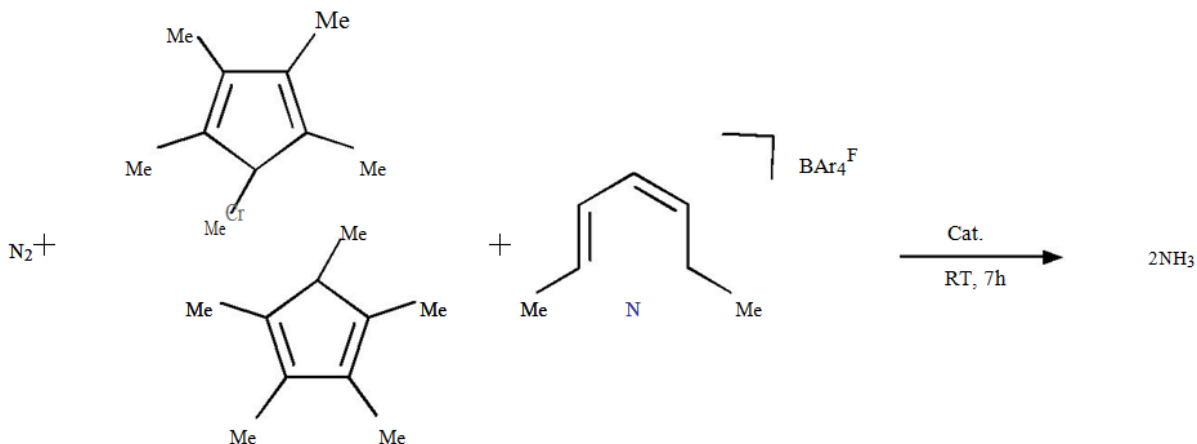
SCHEME 2. **Catalytic Nitrogen fixation.**

As per Schrock cycle, catalytic conversion of dinitrogen into ammonia is due to stepwise addition of protons and electrons occurs to release two ammonia molecules [15,16].

Another reaction in which involved dinitrogen-bridged dimolybdenum-dinitrogen complex, bearing a tridentate PNP-type pincer ligand, works as a catalyst, when the reaction of CoCp$_2$, employed as a reducing agent & 2,6-lutidiniumtrifluoromethane-sulfonate ([LutH]OTf), employed as the proton source, was carried out in the presence of a catalytic amount of [{Mo(N$_2$)$_2$(tBuPNP)}$_2$(N$_2$)] where (tBuPNP=2,6-bis[(di-tert-butylphosphinomethyl] pyridine) in toluene under atmospheric pressure of dinitrogen at room temperature, ammonia was obtained together with the formation of molecular dihydrogen [2,45].

Stoichiometric reaction of [{Mo(N$_2$)$_2$(tBuPNP)}$_2$(l-N$_2$)] with tetrafluoroboric acid in the presence of pyridine gave the corresponding hydrazido complex [MoF(N$_2$H$_2$)(py) (tBuPNP)] that produced ammonia on treatment with sulfuric acid, Though this complex did not show any catalytic activity. Similarly, Complexes prepared with the same pincer ligand, like dinitrogen bridged dimolybdenum tetrachloride complex [{MoCl$_2$(tBuPNP)}$_2$(l-N$_2$)] and molecular tungsten complex [W(N2)2(tBuPNP)(PMe3)], showed almost no activity towards the formation of ammonia. The reason being substitutions on the Phosphorous group is based on the new experimental studies, the maintenance of the dinuclear structure of {(tBuPNP)Mo(l-N$_2$)Mo(tBuPNP)} in PNP-type pincer ligand plays a crucial role in exhibiting catalytic activity for catalytic ammonia formation. A synergy exists between two Mo moieties linked with a bridging dinitrogen ligand at a protonation step, where one acts a ligand for other at the active site by donating an electron producing a ligand with a reductive activation to receive a proton to give hydrazido and hydrazidium complexes [46,47].

To enhance higher catalytic activity towards the catalytic nitrogen fixation, PPP-type pincer ligands were introduced with expectation of better activity over PNP- Pincer ligands. Because of lower Bronsted basicity and higher stability towards protonation in the catalytic reaction, and the p-accepting ability of the PPP-type pincer ligand can stabilize a variety of molybdenum complexes bearing a broad range of oxidation states of the Mo center in the catalytic reaction. The neutral molybdenum nitrido complex [MoCl(N)(tBuPPP)] and the cationic molybdenum nitrido complex [MoCl(N) (tBuPPP)]BAr$^F_4$ bearing a PPP-type pincer ligand (tBuPPP=bis[(di-tert butyl phosphino) ethyl]phenylphosphine) were prepared to study the enhancement of catalytic activity over PNP-pincer ligands.

When decamethylcobaltocene (CoCp$^*_2$), as the reducing agent, and 2,4,6-collidinium trifluoromethanesulfonate ([ColH]OTf) as the proton source, in the presence of a catalytic amount of the neutral molybdenum nitrido complex [MoCl(N)(tBuPPP)] in toluene under atmospheric pressure of dinitrogen at room temperature gave ammonia, with higher yield. This was the first reported Mo complex with PPP ligand as a catalyst. Many other complexes were reported after this, while catalytic reaction never reported to be happened using these ligands [45-48].

It has been known as an important element of FeMoco in nitrogenases. Peters and co-workers found iron-dintrogen complexes, which can be used as catalysts, as Mo-dinitrogen complexes, for the catalytic production of ammonia under ambient reaction conditions. In this reaction, an anionic iron- dinitrogen complex supported over tri-phoshine borane, used as catalyst, reduces molecular dinitrogen to ammonia, with a proton source [H(Et$_2$O)$_2$]BArF$_4$ under atmospheric pressure of dinitrogen through an iron-hydrazido complex as an intermediate [49].

When boron atom was substituted with silicon, in tetradentate ligand, only stoichiometric amount of ammonia was obtained, while an axial alkyl carbon in tetradentate ligand gave moderate yield. This study shows that the type of element (B or Si), does not have considerable effect on dinitrogen activation. The phosphine group is responsible for the activation of dinitrogen. Though the precise mechanism of Iron-dintrogen remains unclear, iron-dintrogen compelxes with an alkyl or carbine carbon atom has some resemblance to that of biological fixation of dinitrogen [50,51].

After studying Iron-dinitrogen complexes, Peters & co-workers reported stoichiometric reaction of molecular dinitrogen into ammonia under mild reaction conditions using Cobalt-dinitrogen complexes. In this reaction, anionic cobalt-dinitrogen complex supported on tris (phosphine) borane, produced ammonia [52].

Catalytic Formation of silylamine

Trimethylsilylamine (N(SiMe$_3$)$_3$) can be easily converted to ammonia by acid hydrolysis. It can be used for the formation of ammonia by silylation of molecular dinitrogen. In 1973, Shiina reported this method at room temperature using lithium as a reducing agent, trimethylsilyl chloride as a silylation reagent and transition metal salts like MnCl$_2$, FeCl$_3$ or CoCl$_2$ as catalysts [53] (**SCHEME 3**).

$$N_2 + 6Na + 6Me_3SiCl \xrightarrow[RT]{Cat.THF} 2N(SiMe_3)_3 \xrightarrow{H^+} 2NH_{4^+}$$
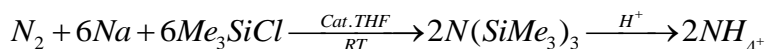
SCHEME 3. **Catalytic formation of silylamine.**

Mori and coworkers carried out similar reaction of TiCl$_4$, granular lithium and trimethylsilyl chloride in THF under atmospheric pressure of dinitrogen at room temperature which further hydrolysed and acylated with PhCOCl to give PhCONH$_2$. Similar reaction using magnesium was also reported with a good yield of PhCONH$_2$. [54-57]

The Molybdenum- dinitrogen complex prepared by Hidai and coworkers, cis-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$], worked as catalyst for

transformation of dinitrogen into silylamine with sodium as a reducing agent and trimethylsilyl chloride as a silylation reagent [11,28-31].

Another metal complex, molybdenum, with two ancillary ferrocenyldiphosphine ligands, trans-[Mo(N$_2$)$_2$(depf)$_2$], was used as a catalyst, in the reaction of sodium and trimethylsilyl chloride was carried out in THF under atmospheric pressure of dinitrogen at room temperature to give silylamine [2].

Other group of researchers, found iron carbonyl complex [Fe(CO)$_5$] **(FIG 6)**, catalysing the same type of reaction. They observed silylation of molecular dinitrogen with this catalyst when sodium and trimethylsilyl chloride were reacted under ambient conditions to give silylamine with THF as solvent. Other iron carbonyl complexes like [Fe(SiMe$_3$)$_2$(CO)$_4$] **(FIG 7)** or [CpFe(CO)$_2$]$_2$, were also reported to be effective in catalysis [58].
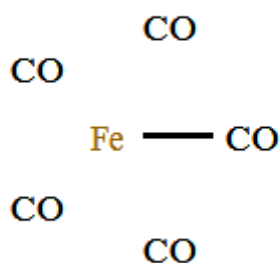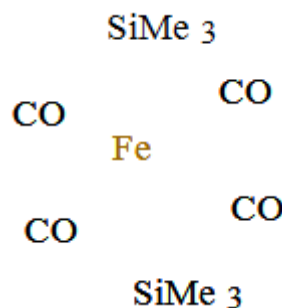

FIG. 6. **Iron carbonyl complex.**   FIG. 7. **Iron- Trimethylsilyl carbonyl complex.**

Cobalt has been shown to catalyse the transformation of molecular dinitrogen into silylamine. Cobalt carbonyl complexes such as [Co$_2$(CO)$_8$], [Co(SiMe$_3$)(CO)$_4$], [CpCo(CO)$_2$], and cobaltocene (CoCp$_2$) were used to effect the catalysis to give silylamine. The cobalt carbonyl complexes have shown similar catalytic activity as that of cobalt transition metal dinitrogen complexes, under similar conditions to yield silylamine. Mechanism of this reaction is explained by *in situ* model. A trimethylsilyl radical adds to the dinitrogen complex and gives a diazenido complex, which is further attacked by another trimethylsilyl radical, followed by the migration of a trimethylsilyl moiety on the Co atom to produce a hydrazido complex. Then, one of two trimethylsilyl ligands on the Co atom moves to the proximal N atom to give a hydrazine complex. The hydrazine molecule can be readily transformed into two molecules of N(SiMe$_3$)$_3$ in the reaction solution [27,59].

Conclusion

The dinitrogen molecule acts as a ligand towards appropriate transition metal centres, which produces complexes, some of, which can reduce molecular dinitrogen into ammonia. Thus, synthetic nitrogen fixation plays a key role in organometallic chemistry. Even though two difficulties, chemical inertness of nitrogen molecule and unsolved pathway of biological nitrogen fixation remain to be a challenge in quantitative success. Numbers of spectacular results were obtained using "d" block elements, show the significant progress of finding alternative pathways related to enzymatic reactions. Ammonia is finding its new significance as hydrogen carrier and an option for fossil fuels. This can be used for as a requirement of developing more convenient reactions for fixation of molecular nitrogen. Also, there is a great scope in realizing the existing reactions under ambient conditions.

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