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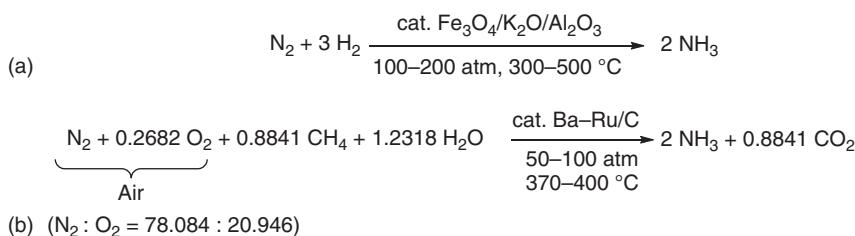
## Overviews of the Preparation and Reactivity of Transition Metal–Dinitrogen Complexes

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### 1.1 Introduction

Nitrogen, the fifth most abundant element in the solar system, is the most abundant element in the atmosphere of Earth [1] as well as the fourth most abundant element in cellular biomass [2]. However, it is rather a trace element in the lithosphere of Earth [3]. Thus, utilization of chemically inert gaseous molecular dinitrogen ( $N_2$ ) that exists in the atmosphere of Earth as the primary nitrogen source is inevitable in both biogeography and industry. Indeed, fixation of atmospheric nitrogen can be achieved by the conversion of molecular dinitrogen into ammonia ( $NH_3$ ) containing the most reduced form of nitrogen (−3) that can be a convenient precursor for several nitrogen-containing compounds and has been the most fundamental reaction pathway of the global nitrogen cycle [4, 5]. Industrially,  $NH_3$  is one of the 10 largest commodity chemical products and has been produced by the Haber–Bosch process in which atmospheric dinitrogen reacts with gaseous dihydrogen ( $N_2 + 3 H_2 \rightarrow 2 NH_3$ ) since the early twentieth century [6–14]. Haber and van Oordt in 1904 first succeeded in the conversion of the mixture of  $N_2$  and  $H_2$  into  $NH_3$  in the presence of transition metal catalyst (Fe or Ni) at a high temperature in a laboratory [15–17]. Later, modification of the reactors and catalysts was achieved, and 90 g of ammonia was shown to be obtained every hour by using an osmium-based catalyst with the total yield of ammonia up to 8 vol% at 550 °C and a total pressure of 175 atm of a stoichiometric mixture of dinitrogen and dihydrogen (1 : 3) in an experimental lecture held in Karlsruhe on 18 March 1909 [18–20]. Further modification of the catalysts for industrialization was investigated by Mittasch and coworkers in BASF, leading to the discovery of the combination of iron,  $K_2O$ , and  $Al_2O_3$  as one of the most active catalysts by 1910 [6, 21]. The first commercial plant for ammonia synthesis at Oppau began its operation by 1913 in collaboration with Bosch and coworkers at BASF, while the earlier commercial methods to fix atmospheric nitrogen such as Frank–Caro cyanamide process ( $CaC_2 + N_2 \rightarrow CaCN_2 + C$ ) and Birkeland–Eyde electric arc process ( $N_2 + O_2 \rightarrow 2 NO$ ) were gradually replaced by the Haber–Bosch ammonia process [6–14]. Typical reaction conditions of the Haber–Bosch process are

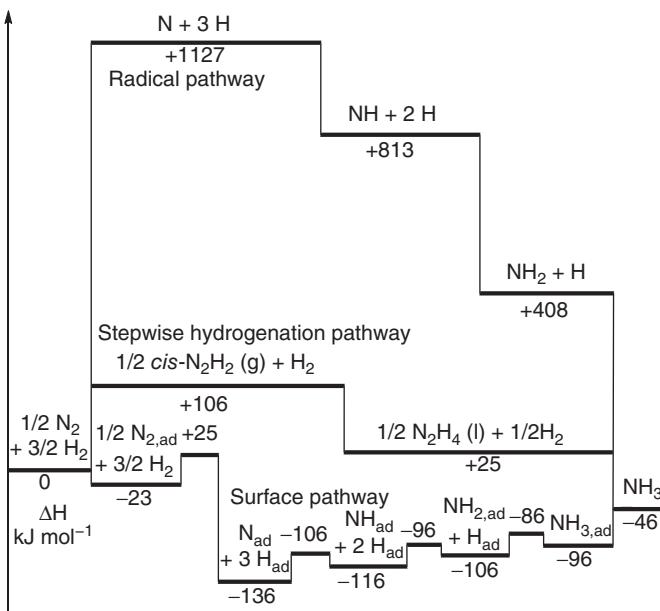


**Figure 1.1** (a) Prototype Haber–Bosch process operated at the first BASF's Oppau plant.  $\text{H}_2$  is originally obtained from steam reforming of coal. (b) Kellogg advanced ammonia process with methane steam reforming.

shown in Figure 1.1a [6], where the reaction is carried out under high temperature and high pressure in the presence of heterogeneous solid-state catalysts prepared from magnetite ( $\text{Fe}_3\text{O}_4$ ) with the addition of alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), or alkaline earth metal oxide ( $\text{CaO}$ ) as a “structural” promoter and alkaline metal oxide ( $\text{K}_2\text{O}$ ) as an “electronic” promoter.

Although formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  is thermodynamically favored under standard conditions ( $\Delta_rH^\circ = -45.90 \text{ kJ mol}^{-1}$ ,  $\Delta_rG^\circ = -16.37 \text{ kJ mol}^{-1}$  at 1 bar and 25 °C), this conversion can hardly occur at ambient reaction conditions because the dissociation energy of the dinitrogen triple bond is high ( $D_0^\circ = 945.37 \text{ kJ mol}^{-1}$ ) [22]. To lower and surmount the activation energy of this conversion, elevated pressure and temperature as well as heterogeneous solid-state catalysts are necessary, where bond-breakings upon chemisorption on the surface of solid-state catalysts were experimentally observed by Ertl and coworkers, who clarified the surface reaction pathway of the Haber–Bosch process as shown in Figure 1.2 [23–29]. Activation energy and turnover frequency of the catalytic ammonia synthesis are highly dependent not only on the catalyst but also on temperature, pressure, and the ratio of the substances and products, where the logarithm of the equilibrium constant for the reaction of  $\text{N}_2 + 3 \text{H}_2 = 2 \text{NH}_3$  at 1 bar becomes zero theoretically at 456 K [22]. For example, the apparent activation energy for the catalytic ammonia synthesis on the  $\text{Fe}(111)$  surface of an iron single crystal at around 748 K and a total pressure of 20 atm of a stoichiometric mixture of dinitrogen and dihydrogen (1 : 3) was determined by Somorjai and coworkers as  $81.2 \text{ kJ mol}^{-1}$  with an initial turnover frequency of  $12.7 \pm 2.0$  molecules of ammonia per  $\text{C}_4$  surface iron atom per second [30].

A more improved method such as Kellogg advanced ammonia process (KAAP) uses ruthenium-based catalyst supported on graphite-containing carbon copromoted with barium, cesium, or rubidium performed at comparably lower pressure and temperature, the stoichiometry of which can be expressed as Figure 1.1b, when natural gas steam reforming is applied to ammonia production without the separation of dinitrogen from air [8–14, 31–35]. In this reaction, methane is the main hydrogen source of ammonia, and the gaseous ammonia obtained from the stoichiometry in Figure 1.1b theoretically contains 20.8 GJ per metric ton or  $355 \text{ kJ mol}^{-1}$  as chemical energy calculated based on the heat of combustion of methane in the lower heating value (LHV) ( $\Delta_cH^\circ = -802.3 \text{ kJ mol}^{-1}$ ,  $\Delta_cG^\circ = -800.8 \text{ kJ mol}^{-1}$ ) or 18.6 GJ per metric ton



**Figure 1.2** Potential energy diagram for ammonia synthesis on the surface of iron, via stepwise hydrogenation or via formation of radicals.

based on that of ammonia ( $\Delta_c H^\circ = -316.8 \text{ kJ mol}^{-1}$ ,  $\Delta_c G^\circ = -326.5 \text{ kJ mol}^{-1}$ ) if full recovery of the reaction heat is assumed ( $\Delta_r H^\circ = -37.8 \text{ kJ mol}^{-1}$  and  $\Delta_r G^\circ = -27.5 \text{ kJ mol}^{-1}$  per  $\text{NH}_3$  for Figure 1.1b) [22]. A classical BASF-type Haber–Bosch process that uses coke consumes chemical energy of 100 GJ per metric ton of  $\text{NH}_3$  in 1920 [6], which is much more efficient than the Birkeland–Eyde electric arc process (600 GJ per metric ton of fixed nitrogen) or the Frank–Caro cyanamide process (190 GJ per metric ton of  $\text{NH}_3$  derived from the decomposition of  $\text{CaCN}_2$  with  $\text{H}_2\text{O}$ ) [12], whereas the most efficient ammonia plant with the ruthenium-based catalyst and methane steam reforming consumes as low as 27.2 GJ per metric ton or  $463 \text{ kJ mol}^{-1}$  of  $\text{NH}_3$ , where energy efficiency of around 75% with respect to the stoichiometric methane demand is achieved, which also means that additional chemical energy of  $108 \text{ kJ mol}^{-1}$  is required for the industrial synthesis of  $\text{NH}_3$  as represented in Figure 1.1b [13]. In an exergy analysis of a low-energy ammonia process to obtain the liquefied ammonia at  $-33^\circ\text{C}$  (20.14 GJ per metric ton or  $343 \text{ kJ mol}^{-1}$ ) by Dybkjaer under a model reaction at  $140 \text{ kgf cm}^{-2}$  in an indirectly cooled two-bed radial converter using pure methane, cooling water available at  $30^\circ\text{C}$ , a steam to the carbon ratio of 2.5, and so forth, a total exergy of  $30.69 \text{ GJ per metric ton}$  or  $523 \text{ kJ mol}^{-1}$  is consumed with an exergy loss of  $10.55 \text{ GJ per metric ton}$  or  $180 \text{ kJ mol}^{-1}$  corresponding to a thermodynamic efficiency of 66% for the production of  $\text{NH}_3$ , where the biggest loss of exergy occurs at methane steam reforming sections with rather a slight loss made during the actual ammonia synthesis (1.70 GJ per metric ton or  $29 \text{ kJ mol}^{-1}$ ) [13, 36]. Further improvement of Haber–Bosch catalysts is still in progress, especially in the development of electronic and structural promoters. For example, Hosono and coworkers have

developed ruthenium-loaded electrode catalysts, which show higher catalytic performance than the conventional ruthenium catalysts at lower temperatures and pressures [37–40].

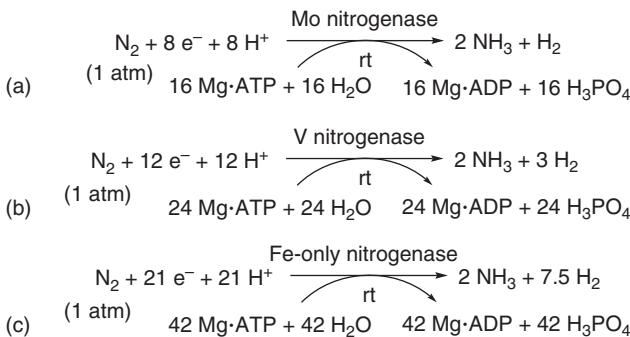
In total, the Haber–Bosch process annually produces more than 170 million metric tons of  $\text{NH}_3$  [41], consumes fossil fuels as the hydrogen source of  $\text{NH}_3$ , corresponding to 1–2% of the world's annual primary energy supply, and is responsible for the emission of more than 450 million metric tons of  $\text{CO}_2$  [42–44]. This pollution can be reduced by using renewable energy sources for producing dihydrogen from water, but it should be more convenient to use water as a proton source for ammonia without using dihydrogen gas in high pressure and temperature.

It must be noted that ammonia is attracting attention as a possible hydrogen carrier in the future, as well as a fuel for vehicles [45–49], which can minimize the use of fossil fuels. The present Haber–Bosch process requires a lot of reactors to obtain high pressure and temperature; thus, biological nitrogen fixation that can be carried out in small cells at ambient reaction conditions by using water as a proton source has been investigated as a model of an alternative method for the Haber–Bosch process [50–54].

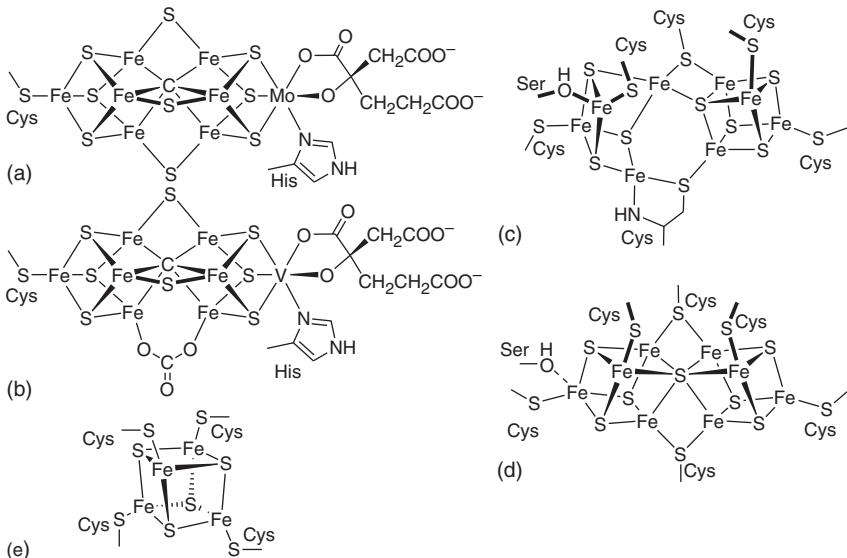
## 1.2 Biological Nitrogen Fixation

Atmospheric molecular dinitrogen has been fixed as ammonia via biological nitrogen fixation using electron carriers (ferredoxins or flavodoxins) as reducing reagents and water as a proton source under ambient pressure and temperature by some specific bacterial and archaeal organisms that possess nitrogen-fixing enzyme called nitrogenase [51, 52]. Based on the difference in transition metal (Mo, V, or Fe) included in its key cofactor (iron–molybdenum cofactor (FeMo-co), iron–vanadium cofactor (FeV-co), or iron–iron cofactor (FeFe-co)) consisting of an iron–sulfur cluster, nitrogenase can be classified into molybdenum nitrogenase, vanadium nitrogenase, or iron-only nitrogenase, among which molybdenum nitrogenase, the canonical form of this enzyme, works most efficiently, where 8 equiv of electrons and protons is consumed for reducing 1 equiv of dinitrogen to form 2 equiv of ammonia together with the formation of an equimolar amount of dihydrogen gas (Figure 1.3a), whereas vanadium nitrogenase (Figure 1.3b) or iron-only nitrogenase (Figure 1.3c) is less effective requiring more protons and electrons wasted to form more dihydrogen molecules [55, 56]. All the diazotrophic bacteria known to date encode molybdenum nitrogenase, whereas some diazotrophic bacteria especially living in soils possess the genes for alternative vanadium or iron-only nitrogenase. Few species such as *Azotobacter vinelandii*, an aerobic free-living microorganism in soils, are known to contain all the three types of nitrogenases, but utilization of alternative vanadium or iron-only nitrogenase occurs under molybdenum limitation or both molybdenum and vanadium limitations, respectively [57–59].

Structures of FeMo-co (Figure 1.4a) and FeV-co (Figure 1.4b) are determined both crystallographically and spectroscopically, where  $\text{Fe}_4\text{S}_3$  and  $\text{Fe}_3\text{MS}_3$  ( $\text{M} = \text{Mo}$  or  $\text{V}$ ) cuboidal units share one central carbon atom, and are further



**Figure 1.3** Proposed stoichiometry of biological nitrogen fixation by three types of nitrogenases: (a) molybdenum nitrogenase, (b) vanadium nitrogenase, and (c) iron-only nitrogenase.



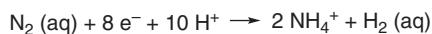
**Figure 1.4** Structures of (a) FeMo-co in MoFe protein, (b) FeV-co in VFe protein, (c) P-cluster in the oxidized state in MoFe protein, (d) P-cluster in the reduced state in MoFe protein, and (e) [4Fe-4S] cluster in Fe protein.

bridged by three sulfur atoms for FeMo-co [60–62] or a combination of two sulfur atoms and one carboxylate for FeV-co [63], respectively. The structure of FeFe-co has not yet been determined crystallographically but has been spectroscopically supposed to have a similar structure to FeMo-co or FeV-co, where molybdenum or vanadium atom is substituted for the corresponding iron atom [51, 52]. As shown in Figure 1.4a,b, molybdenum and vanadium atoms are coordinatively saturated by the chelation of homocitrate, whereas the iron atoms surrounding the carbon atom have vacant sites. Thus, recent theories on the reaction mechanism of nitrogen fixation prefer coordinatively unsaturated iron atoms to molybdenum or vanadium atom where conversion of dinitrogen

into ammonia occurs, whereas the precise reaction pathways for the conversion of dinitrogen into ammonia remain arguable [64–72].

Thermodynamic favorability of the formation of ammonia in aqueous solution changes depending on the pH of the solution because proton transfers are involved in the reaction, and ammonia exists as an ammonium cation ( $pK_a = 9.25$ ) in acidic or neutral conditions. Standard transformed Gibbs energy of the reaction of dinitrogen, electrons, and protons to form ammonium cation and dihydrogen in a ratio of 2 : 1 in an aqueous solution is given as  $-159.7 \text{ kJ mol}^{-1}$  per dinitrogen at pH 0 ( $\alpha_H^+ = 1$ ) and zero ionic strength, which corresponds to standard electrode potential of  $+0.276 \text{ V}$ . On the other hand, standard transformed Gibbs energy at pH 7 shifts to  $+239.8 \text{ kJ mol}^{-1}$ , corresponding to standard apparent reduction potential of  $-0.311 \text{ V}$  vs. SHE (standard hydrogen electrode) (Figure 1.5a) [73]. Thus, the reaction requires the introduction of appropriate reducing reagents such as ferredoxin ( $E^\circ$  value varies from  $-0.377$  to  $-0.434 \text{ V}$  at pH 7 from different biological sources) (Figure 1.5b) [74, 75] and hydrolysis of several ATPs (ATP = adenosine triphosphate; Figure 1.5c) [75–77].

The schematic shown in Figure 1.6 summarizes the key metabolic pathways related to nitrogen fixation by molybdenum nitrogenase, which consists of two component proteins: molybdenum–iron protein also called dinitrogenase or nitrogenase component 1 containing FeMo–co and P–cluster whose structures in different oxidation states are shown in Figure 1.4c,d [78] and iron protein also called dinitrogenase reductase or nitrogenase component 2 containing [4Fe–4S] cluster whose structure is shown in Figure 1.4e [79, 80]. An electron is transferred from ferredoxin or flavodoxin to the [4Fe–4S] cluster in iron protein, which docks with the aid of 2 M amount of ATP to molybdenum–iron protein to



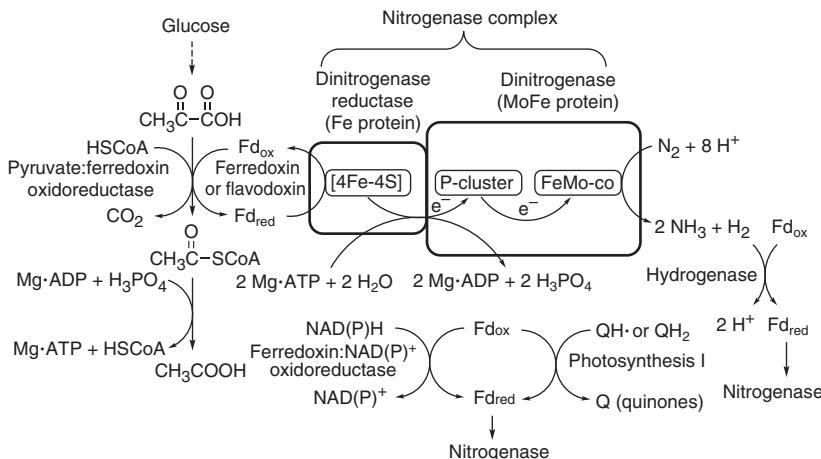
$$\begin{aligned} \Delta_r G^\circ &= +239.8 \text{ kJ mol}^{-1} \\ E^\circ &= -0.311 \text{ V} \end{aligned}$$

$$\begin{aligned} 8 \text{ Fd}_{\text{red}}^- &\rightarrow 8 \text{ Fd}_{\text{ox}} + 8 \text{ e}^- \\ \Delta_r G^\circ &= -304.6 \text{ kJ mol}^{-1} \\ E^\circ &= -0.395 \text{ V} \end{aligned}$$

$$\begin{aligned} 16 \text{ ATP}^{4-} + 16 \text{ H}_2\text{O (l)} &\rightarrow 16 \text{ ADP}^{3-} + 16 \text{ HPO}_4^{2-} + 16 \text{ H}^+ \\ \Delta_r G^\circ &= -602.2 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{N}_2 \text{ (aq)} + 8 \text{ Fd}_{\text{red}}^- + 16 \text{ ATP}^{4-} + 16 \text{ H}_2\text{O (l)} &\rightarrow 2 \text{ NH}_4^+ + \text{H}_2 \text{ (aq)} + 8 \text{ Fd}_{\text{ox}} \\ &\quad + 16 \text{ ADP}^{3-} + 16 \text{ HPO}_4^{2-} + 6 \text{ H}^+ \\ \Delta_r G^\circ &= -667.0 \text{ kJ mol}^{-1} \end{aligned}$$

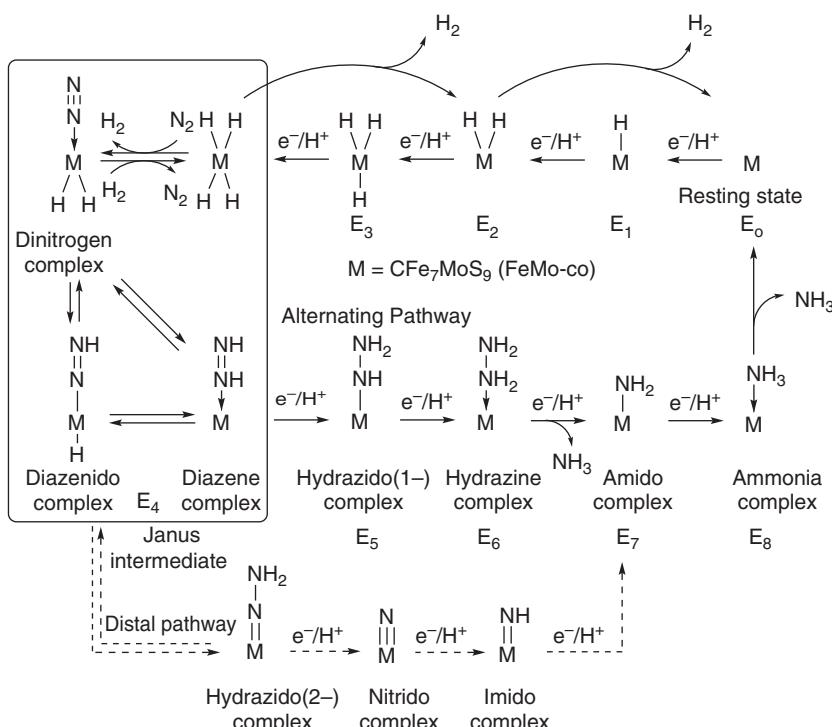
**Figure 1.5** Standard transformed Gibbs energies and standard apparent reduction potentials of reactions in molybdenum nitrogenase at  $25^\circ\text{C}$ , 0 ionic strength, and pH 7: (a) nitrogen fixation, (b) reduction of ferredoxin (reduction potential based on the data obtained from *Clostridium pasteurianum*), (c) hydrolysis of ATP, and (d) total reactions. Stoichiometry in (c) and (d) is shown ignoring  $\text{HATP}^{3-}$  ( $pK_a = 7.60$ ),  $\text{HADP}^{2-}$  ( $pK_a = 7.18$ ), and  $\text{H}_2\text{PO}_4^-$  ( $pK_a = 7.22$ ), but thermodynamic data in (c) and (d) are calculated considering these equilibria at pH 7 (not 16  $\text{H}^+$  but 11.9  $\text{H}^+$  for (c), not 6  $\text{H}^+$  but 1.9  $\text{H}^+$  for (d)).



**Figure 1.6** Metabolic relationship between nitrogen fixation by Mo nitrogenase and electron transfers from pyruvate degradation, hydrogen uptake, respiration, or photosynthesis by ferredoxin/flavodoxin.

transfer an electron from the [4Fe-4S] cluster to the P-cluster, from which the FeMo-co obtains electrons [81, 82]. The rate-determining step is the dissociation of iron protein from molybdenum-iron protein ( $6\text{ s}^{-1}$  at  $25^\circ\text{C}$ ,  $\text{pH} = 7.4$ ) [83], whereas the turnover of the formation of 1 M ammonia per molybdenum nitrogenase has been measured to be 1.5 seconds at  $23^\circ\text{C}$  by Thorneley and Lowe [84], who proposed a kinetic model of the catalytic cycle of nitrogenase reaction, where eight steps of reduction and protonation against dinitrogen occur for molybdenum nitrogenase (Figure 1.7) [64, 66, 69]. Although the amount of ATPs required for the reduction of 1 M dinitrogen has not been precisely determined by experiments, 16 ATPs are at least consumed by molybdenum nitrogenase (Figure 1.3a) based on the assumption that 2 ATPs are hydrolyzed for the transfer of one electron, whereas vanadium and iron-only nitrogenases consume at least 24 and 42 ATPs, respectively, based on the same assumption (Figure 1.3b,c) [51, 52, 55, 56]. In a typical stoichiometry by molybdenum nitrogenase, the standard transformed Gibbs energy of the reduction of dinitrogen is given as  $-667\text{ kJ mol}^{-1}$  at zero ionic strength (Figure 1.5d) [73, 75-77].

It must be noted that both diazene ( $\text{HN}=\text{NH}$ ) and hydrazine ( $\text{H}_2\text{N}-\text{NH}_2$ ) are the substrates of nitrogenase to afford ammonia and that hydrazine is obtained as a minor product from the reduction of dinitrogen in appropriate reaction conditions [85, 86]. Without dinitrogen, protons can work as substrates to afford only dihydrogen [64]. In addition, other substrates such as ethylene, cyclopropene, acetylene, propyne, 1- or 2-butyne, allene, propargyl alcohol or amine, cyanide, cyanamide, several nitriles or isocyanides, diazirine, dimethyl-diazenze, carbon monoxide, carbon dioxide, carbon disulfide, carbonyl sulfide, thiocyanate, cyanate [87], nitrite, hydroxylamine [88], or azide have been known to be reduced by nitrogenase [64]. Figure 1.7 denotes the Lowe-Thorneley kinetic model modified by Hoffman and coworkers [66, 69], where formation of at least an equimolar amount of dihydrogen is inevitable for the reduction



**Figure 1.7** Modified Lowe–Thorneley kinetic model of the conversion of  $\text{N}_2$  into  $\text{NH}_3$  and  $\text{H}_2$  on FeMo-co. Coordination of nitrogen- or hydrogen-containing ligands is shown as if they form mononuclear complexes, although M can be multimetallic centers and sulfur atoms where ligands may bridge or coordinate to different atoms.

of dinitrogen [89]. The first four reduction/protonation steps from  $E_0$ , the resting state of FeMo-co ( $\text{CFe}_7\text{MoS}_9$ ), give a  $(\text{CFe}_7\text{MoS}_9)(\text{H}^+)_2(\text{H}^-)_2$  species, where hydrido can bridge several transition metal centers in FeMo-co, whereas protonation likely occurs on bridging sulfur atoms. Reductive elimination of dihydrogen and coordination of dinitrogen occur in the  $E_4$  “Janus” intermediate and then pairs of reduction/protonation on dinitrogen take place to afford 2 M amounts of ammonia and the starting resting  $E_0$  state. Here, the “alternating” reaction pathway where both distal and proximal nitrogen atoms are protonated stepwise and the “distal” reaction pathway where the first three protonation reactions occur at the distal nitrogen atom to give the nitrido intermediate can be drawn as shown in Figure 1.7, but the “alternating” pathway is highly likely because similar intermediates are spectroscopically observed when diazene or hydrazine is used as a reactant, and formation of hydrazine as an intermediary product is also detected.

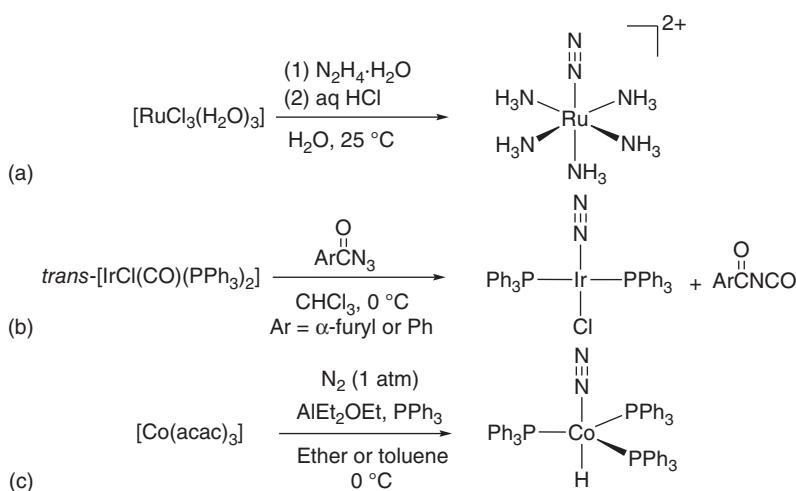
Ferredoxin or flavodoxin, the reducing reagent of nitrogenase, transfers electrons from several metabolites, but the main source of electrons is the degradation of pyruvate for both anaerobic and aerobic microorganisms (Figure 1.6). Hydrogenase can further recycle the dihydrogen produced in nitrogenase catalysis. Ferredoxin or

flavodoxin can also be reduced by NADH (nicotinamide adenine dinucleotide), NADPH (nicotinamide adenine dinucleotide phosphate), or quinones, which are produced by several metabolic pathways including both anaerobic and aerobic respiration or photosynthesis (Figure 1.6) [57–59, 90]. Cyanobacteria such as *Anabaena variabilis* perform oxygen-evolving photosynthesis and oxygen-inhibited nitrogen fixation in different cells (vegetative cells and heterocysts), or the former during day and the latter during night in the same cells, preventing the inactivation of nitrogenase by dioxygen gas [91, 92].

### 1.3 Historical Background of Transition Metal–Dinitrogen Complexes

Biological nitrogen fixation was experimentally confirmed by 1888 [93–95], and lithium was reported to react with dinitrogen at room temperature and an atmospheric pressure to form lithium nitride ( $\text{LiN}_3$ ) that can be easily converted to ammonia in 1892 [96–99]. However, formation of other nitrido complexes from the reaction dinitrogen requires higher temperature [100, 101], and further reactivities of metals with molecular dinitrogen under ambient reaction conditions have been limited in number. In 1964, Haight and Scott have reported the detection of a small amount of ammonia on prolonged cathodic reduction of dinitrogen or reduction by stannous chloride in the presence of aqueous solution of molybdate and tungstate at room temperature, although the pressure of dinitrogen gas is not well documented in the literature [102]. Conversion of dinitrogen into ammonia using transition metal complexes under ambient reaction conditions has been first reported in 1964 by Vol'pin and Shur, who obtained a small amount of ammonia when dinitrogen gas at atmospheric pressure was passed through a mixture of anhydrous  $\text{CrCl}_3$  and  $\text{LiAlH}_4$  or  $\text{EtMgBr}$  in ether at room temperature [103]. Other transition metal complexes such as  $[\text{Cp}_2\text{TiCl}_2]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) or  $\text{TiCl}_4$  in combination with  $\text{EtMgBr}$  or  $^i\text{Pr}_3\text{Al}$  also fixes dinitrogen [104–106]. Formation of aniline, *p*-toluidine, or aliphatic amines as a dinitrogen-derived nitrogen-containing compound has also been reported by bubbling dinitrogen through a mixture of  $[\text{Cp}_2\text{TiCl}_2]$  or  $[\text{Cp}_2\text{TiPh}_2]$ , with  $\text{PhLi}$ , *p*-TolLi,  $\text{EtMgBr}$ , or  $^n\text{BuLi}$  at an atmospheric pressure and room temperature, followed by further hydrolysis [107, 108].

Isolation of a series of transition metal–dinitrogen complexes where a molecular dinitrogen is coordinated to a transition metal was first reported in 1965 by Allen and Senoff [109, 110], who performed the reduction of  $[\text{RuCl}_3(\text{H}_2\text{O})_3]$  with hydrazine hydrate in water at room temperature to afford a ruthenium–dinitrogen complex  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  in the late 1963 (Figure 1.8a) [111]. At first, they mistakenly identified that they obtained a ruthenium–hydrido complex but later found that the compound was diamagnetic with a strong infrared band around  $2170\text{--}2100\text{ cm}^{-1}$  attributable to the coordinated  $\text{N}\equiv\text{N}$  stretching, liberating dinitrogen gas on treatment with sulfuric acid.  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$  also became the first transition metal–dinitrogen complex whose molecular structure was determined by a single-crystal X-ray analysis in 1966 [112].



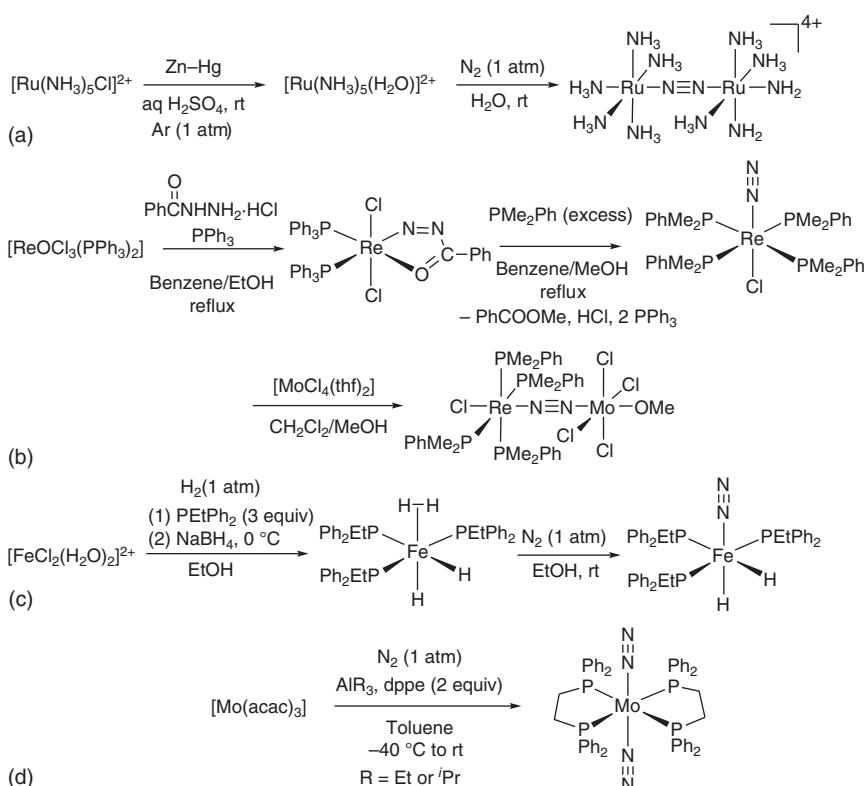
**Figure 1.8** Early reports of the preparation of transition metal–dinitrogen complexes by the reduction of metal centers in the presence of (a) hydrazine, (b) azide, and (c) dinitrogen.

The second example of transition metal–dinitrogen complexes was reported in 1966 by Collman and Kang, who obtained the iridium–dinitrogen complex *trans*-[IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] by the reaction of Vaska’s iridium complex *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with a variety of aromatic acyl azides in chloroform at 0 °C (Figure 1.8b) [113–115].

The first transition metal–dinitrogen complex with the direct fixation of gaseous molecular dinitrogen was reported in 1967 by Yamamoto et al. who obtained the cobalt–dinitrogen complex [CoH(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] by the reduction of [Co(acac)<sub>3</sub>] with AlEt<sub>2</sub>OEt under atmospheric pressure of dinitrogen in the presence of PPh<sub>3</sub> in ether or toluene (Figure 1.8c), which became the third example of isolated transition metal–dinitrogen complexes [116–118]. There was a confusion in the identification of its structure whether the compound contained a hydrido ligand or not, but it was later confirmed as a (hydrido)(dinitrogen) complex [119–124].

All the above three complexes are mononuclear complexes with a dinitrogen ligand coordinated to a metal center in an “end-on” manner. On the other hand, the binuclear transition metal–dinitrogen complex with a bridging dinitrogen was first reported in 1968 by Taube and coworkers, who prepared the diruthenium–dinitrogen complex *trans*-[{{Ru(NH<sub>3</sub>)<sub>5</sub>}<sub>2</sub>(μ-N<sub>2</sub>)}<sup>4+</sup>] by the reduction of *trans*-[Ru(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> with zinc amalgam in water under an atmospheric pressure of dinitrogen (Figure 1.9a) [125]. This compound was first identified in 1967 as the same complex with Allen and Senoff’s complex [Ru(NH<sub>3</sub>)<sub>5</sub>(N<sub>2</sub>)][BF<sub>4</sub>]<sub>2</sub>, which shows a strong IR absorption band at 2154 cm<sup>-1</sup> [109, 126], whereas a Raman band at 2100 cm<sup>-1</sup> was observed for {{Ru(NH<sub>3</sub>)<sub>5</sub>}<sub>2</sub>(N<sub>2</sub>)}[BF<sub>4</sub>]<sub>4</sub> [127], whose molecular structure was determined crystallographically [128].

Preparation of the heterobimetallic dinitrogen-bridged transition metal–dinitrogen complex [(PMe<sub>2</sub>Ph)<sub>4</sub>ClRe(μ-N<sub>2</sub>)MoCl<sub>4</sub>(PEtPh<sub>2</sub>)] was reported by Chatt et al. in 1969 via the ligand exchange reaction of a molybdenum phosphine



**Figure 1.9** Early reports of the preparation of transition metal–dinitrogen complexes of (a) dinuclear with bridging dinitrogen, (b) heterobimetallic dinuclear with bridging dinitrogen, (c) iron, and (d) molybdenum.

complex  $[\text{MoCl}_4(\text{PEtPh}_2)_2]$  with the mononuclear rhenium–dinitrogen complex *trans*- $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$  [129–131], the dinitrogen ligand of which is originated from benzoylhydrazine [132–134]. The IR band attributable to the  $\text{N}\equiv\text{N}$  triple bond shifts from  $1922 \text{ cm}^{-1}$  for mononuclear rhenium complex to  $1810 \text{ cm}^{-1}$  for the heterobimetallic complex [129]. The molecular structure of its analogous complex  $[(\text{PMe}_2\text{Ph})_4\text{ClRe}(\mu\text{-N}_2)\text{MoCl}_4(\text{OMe})]$  was later confirmed by an X-ray analysis (Figure 1.9b) [135, 136]. Preparation of another heterobimetallic dinitrogen-bridged transition metal–dinitrogen complex  $[(\text{NH}_3)_5\text{Os}(\mu\text{-N}_2)\text{Ru}(\text{NH}_3)_5]^{4+}$  was also reported in 1969 [137–140].

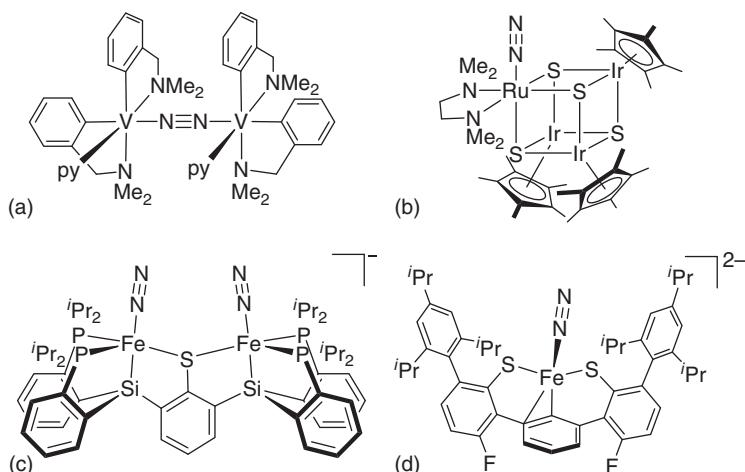
Preparation of iron– [141–145], molybdenum– [146–152], or vanadium–dinitrogen complexes [153–156] has been of great interest from the viewpoint of a model for the active site of nitrogenase. Sacco and Aresta reported the formation of the first iron–dinitrogen complex *cis,mer*- $[\text{FeH}_2(\text{N}_2)(\text{PEtPh}_2)_3]$  in 1968 by the reaction of dinitrogen with the dihydrogen complex *cis,mer*- $[\text{FeH}_2(\text{H}_2)(\text{PEtPh}_2)_3]$ , which was first formulated as a dihydrido complex  $[\text{FeH}_2(\text{PEtPh}_2)_3]$  [157], then reformulated as a tetrahydrido complex  $[\text{FeH}_4(\text{PEtPh}_2)_3]$  [158, 159], but later identified as the dihydrogen complex based on the  $T_1$  relaxation time measurement (Figure 1.9c) [160]. Thus, coordination of dinitrogen occurs by the

ligand exchange with a dihydrogen ligand rather than by the reductive elimination of two dihydrido ligands. The molecular structures of these complexes were later determined by X-ray and neutron diffraction studies [161].

Preparation of molybdenum–dinitrogen complex was first reported by Hidai et al. in 1969, who obtained the molybdenum–dinitrogen complex *trans*–[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] by the reaction of [Mo(acac)<sub>3</sub>] with aluminum-reducing reagents in the presence of dppe under atmospheric pressure of dinitrogen (Figure 1.9d) [162–164]. The structure of this compound was later determined by an X-ray crystallographic analysis [165].

It is very surprising that several transition metal–dinitrogen complexes have been prepared in the late 1960s within a few years since the first discovery of transition metal–dinitrogen complexes [166–168]. Preparation and identification of dinitrogen complex of vanadium, another important transition metal of nitrogenase, was reported comparably later, when Ihmels and Rehder have reported the preparation of the anionic vanadium–dinitrogen complex [V(CO)<sub>5</sub>(N<sub>2</sub>)]<sup>–</sup> by UV irradiation of [V(CO)<sub>6</sub>]<sup>–</sup> or [V(CO)<sub>5</sub>(acetone)]<sup>–</sup> in 2-methyltetrahydrofuran at 200 K in the presence of atmospheric dinitrogen in 1985 [169, 170]. The first vanadium–dinitrogen complex crystallographically analyzed was reported in 1989 by Gambarotta and coworkers, who succeeded in the preparation of dinitrogen-bridged divanadium complex [(V{*o*-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>})<sub>2</sub>(py)<sub>2</sub>( $\mu$ -N<sub>2</sub>)] (Figure 1.10a) [171].

For construction of biomimetic reactions based on the metal–sulfur clusters in metalloenzymes, a lot of sulfur-bridged transition metal clusters have been synthesized as models of nitrogenase [53, 141, 172–179], but the first dinitrogen complex [(Cp<sup>\*</sup>Ir)<sub>3</sub>{Ru(tmeda)(N<sub>2</sub>)}( $\mu$ <sub>3</sub>-S)<sub>4</sub>] (Cp<sup>\*</sup> =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) where dinitrogen is coordinated to sulfur-bridged transition metal cluster has been isolated rather recently by Mizobe and coworkers (Figure 1.10b) [180, 181].



**Figure 1.10** Selected examples of transition metal–dinitrogen complexes as models for cofactors in nitrogenase: (a) vanadium–dinitrogen complex, (b) cubane–dinitrogen complex, (c) multimetallic iron–dinitrogen complex with Fe–S bonds, and (d) iron–dinitrogen complex with Fe–S and Fe–C bonds.

Isolation of the sulfur-supported multimetallic iron complex  $[\{Fe(N_2)\}_2(\mu-SAr)]^-$  ( $Ar = 2,5-C_6H_4\{Si(C_6H_4P^iPr_2-o)_2\}_2$ ) has also been reported more recently by Creutz and Peters (Figure 1.10c) [182].

Recent analyses of nitrogenase have clarified that FeMo-co contains a carbide atom that constitutes the edge of two cuboidal clusters ( $[Fe_4S_3]$  and  $[Fe_3MoS_3]$ ) [60–62], where the carbon atom has been transferred from the methyl radical originated from *S*-adenosylmethionine to bridge the two clusters [183]. The iron–dinitrogen complex  $[Fe(N_2)(L)]^{2-}$  ( $LH_2 = 6,6''-F_2-3,3''-(2,4,6-iPr_3C_6H_2)_2-m$ -terphenyl-2,2''-(SH)<sub>2</sub>) bearing both Fe–S and Fe–C bonds has been prepared by Holland and coworkers in 2015 (Figure 1.10d) [179, 184].

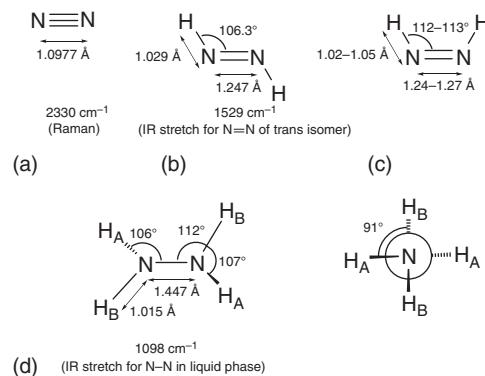
## 1.4 Coordination Chemistry of Transition Metal–Dinitrogen Complexes

### 1.4.1 Coordination Patterns of Dinitrogen and Mononuclear Transition Metal–Dinitrogen Complexes

Dinitrogen is a diatomic molecule with a Raman band at 2330, 2291, or 2252  $\text{cm}^{-1}$  for gaseous  $^{14}\text{N}_2$ ,  $^{14}\text{N}^{15}\text{N}$ , or  $^{15}\text{N}_2$ , respectively, because of the stretching vibration of the  $\text{N}\equiv\text{N}$  triple bond [185, 186]. The interatomic distance between two nitrogen atoms has been measured to be ranging from 1.09 to 1.11 Å by X-ray analyses of several different phases of solid-state dinitrogen ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - $\text{N}_2$ ) at very low temperatures or at extremely high pressures [187–198], whereas that of gaseous molecular dinitrogen calculated based on the spectroscopic data for the electronic ground state is 1.0977 Å (Figure 1.11a) [199, 200].

Three isomers are known for diazene or diimine: *trans*-diazene (Figure 1.11b), *cis*-diazene (Figure 1.11c), and isodiazene ( $\text{H}_2\text{N}^+=\text{N}^-$ ) [201, 202]. *trans*-Diazene is the most stable isomer among them, but *cis*-diazene, only 21 kJ mol<sup>-1</sup> higher in enthalpy than *trans*-diazene [202, 203], works as an hydrogenation reagent against unsaturated compounds with stereoselective syn addition of  $\text{H}_2$  [204] and is also regarded as an intermediary structure of the reduction of dinitrogen in nitrogenase reactions [205]. The interatomic distance between two nitrogen atoms in *trans*-diazene has been determined to be 1.247 Å based on the UV and

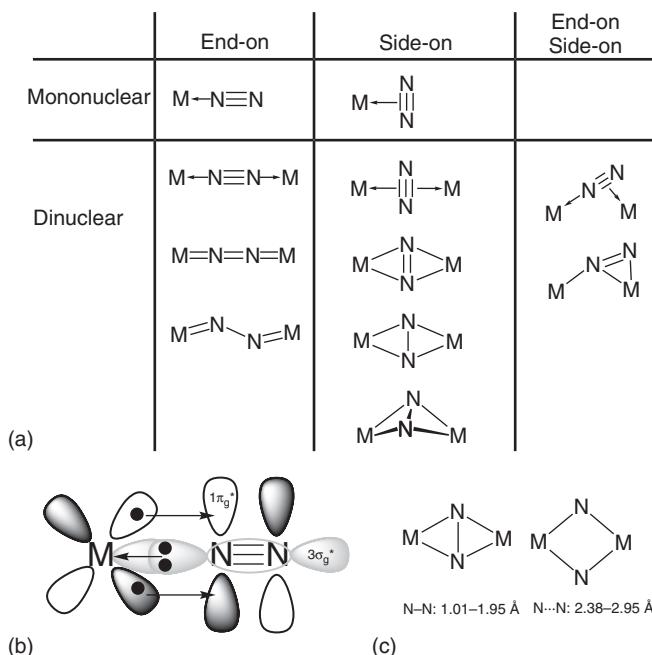
**Figure 1.11** Molecular structures of (a)  $\text{N}_2$ , (b) *trans*- $\text{N}_2\text{H}_2$ , (c) *cis*- $\text{N}_2\text{H}_2$ , and (d)  $\text{N}_2\text{H}_4$ .



IR spectroscopies (Figure 1.11b) [206, 207], whereas spectroscopic observations for *cis*-diazene that has not been isolated in the pure form have been problematic [208]. The bond lengths and angles of *cis*-diazene shown in Figure 1.11c are those taken from theoretical calculations [203, 209, 210].

The melting point of free hydrazine is not low (+1.4 °C), and the solid-state structure was analyzed by an X-ray analysis, which gave the N–N bond length at 1.46 Å at –15 °C [211], whereas the electron diffraction studies and microwave spectroscopies gave the N–N bond distance at 1.447 Å (Figure 1.11d) [212–215]. The Raman and IR spectra give the stretching vibration for N–N in the range of 1076–1126 cm<sup>–1</sup>, which can vary according to the phases of hydrazine (gas, liquid, or solid) [216–220]. It must be noted that the dihedral angle of the H–N–N–H is almost 90° because of the existence of lone pairs of nitrogen atoms, suggesting that the bond order of N–N in hydrazine is one. Based on the crystallographic data of compounds containing N–N bonds, bond distances of 1.10, 1.22, and 1.46 Å as reference values for triple-, double-, and single-bond orders are proposed [221].

Since 1965, a lot of transition metal–dinitrogen complexes have been prepared [166–168, 221–231], including both mononuclear dinitrogen complexes and dinitrogen-bridged multinuclear complexes. General bonding modes of dinitrogen in mononuclear and dinuclear transition metal–dinitrogen complexes are summarized in Figure 1.12a [221, 227].

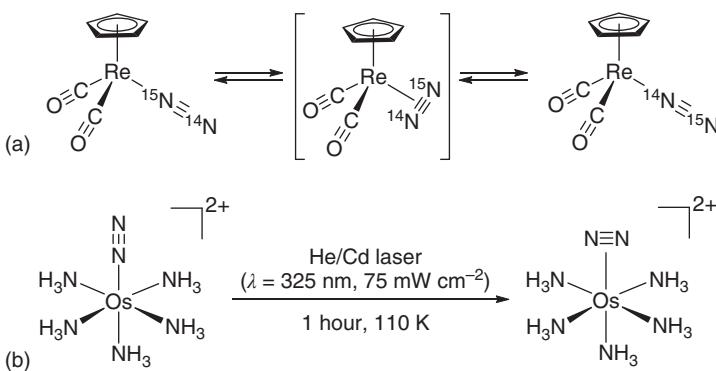


**Figure 1.12** (a) General bonding modes of dinitrogen in mononuclear and dinuclear transition metal–dinitrogen complexes. (b) Schematics of molecular orbital interactions of mononuclear end-on-bound transition metal–dinitrogen complex. (c) Metric difference of side-on-bridged dinuclear transition metal–dinitrogen complexes and bis(nitrido)-bridged complexes.

Dinitrogen is isoelectric with carbon monoxide, and the structure of dinitrogen complexes is closely similar to that expected for the corresponding carbonyl complexes, where dinitrogen works as a comparably weaker  $\sigma$  donor as well as a poorer  $\pi$  acceptor than carbon monoxide does [232, 233]. As shown in Figure 1.12b, coordination of dinitrogen to the transition metal center in an end-on manner can be described according to the Dewar–Chatt–Duncanson model where  $\sigma$  donation from the slightly antibonding filled  $3\sigma_g$  orbital (HOMO, highest occupied molecular orbital) of dinitrogen to the suitable empty d orbital of the transition metal, and the backbonding from the suitable filled d orbital of the transition metal to the empty  $1\pi_g^*$  orbital (LUMO, lowest unoccupied molecular orbital) of the dinitrogen [166–168]. End-on (or  $\eta^1$ )-coordinated dinitrogen in mononuclear dinitrogen complexes is roughly linear ( $M–N–N$  wider than  $164^\circ$ ) with an averaged bond distance of  $1.11(5)$  Å in general. Dinitrogen is a weak Lewis base; thus, the  $\pi$ -accepting character plays an important role in the variety of property and reactivity of the dinitrogen ligand [221]. By coordinating to the transition metal complexes in an end-on manner, the stretching frequency of the  $N\equiv N$  triple bond always shifts from  $2330\text{ cm}^{-1}$  [185] downward to the region of  $2250$ – $1800\text{ cm}^{-1}$ , depending on the  $\pi$ -donating character of the transition metal centers [143, 222–224]. The most investigated mononuclear transition metal–dinitrogen complexes have a  $d^6$  configuration in the metals (V(I–), Cr(0), Mo(0), W(0), Mn(I), Tc(I), Re(I), Fe(II), Ru(II), Os(II), and Ir(III)), whereas other mononuclear transition metal complexes include  $d^2$  (Ti(II), Zr(II)),  $d^3$  (Mo(III), W(III)),  $d^4$  (Mo(II), W(II), Re(III)),  $d^5$  (Mo(I), W(I), Re(II), Os(III)),  $d^7$  (Fe(I), Ru(I), Os(I)),  $d^8$  (Mn(I–), Fe(0), Ru(0), Os(0), Co(I), Rh(I), Ir(I), Ni(II)),  $d^9$  (Co(0), Rh(0)), and  $d^{10}$  (Mn(III–), Co(I–), Ni(0), Cu(I)) configurations [143, 221–224, 226]. In general, mononuclear transition metal–dinitrogen complexes have been well isolated and investigated for rather mid to late transition metals (groups 6–9) with rather low oxidation states enough to support backbonding with dinitrogen.

Counting the molecular orbitals of dinitrogen, side-on ( $\eta^2$ ) coordination of dinitrogen to the mononuclear transition metal center is possible in addition to the end-on ( $\eta^1$ ) coordination, whereas most of the reported mononuclear transition metal–dinitrogen complexes have the end-on-bound dinitrogen ligand. There was an early claim in which the side-on-bound dinitrogen was crystallographically identified for a Vaska-type rhodium–dinitrogen complex  $[\text{RhCl}(\eta^2\text{-N}_2)(\text{P}^i\text{Pr}_3)_2]$  [234], but a later study has suggested that the former X-ray analysis was in error and that the dinitrogen is actually end-on bound as  $[\text{RhCl}(\eta^1\text{-N}_2)(\text{P}^i\text{Pr}_3)_2]$  [235]. Similarly, a paramagnetic zirconium–dinitrogen complex with the side-on coordination of dinitrogen  $[\text{Cp}_2\text{ZrCH}(\text{SiMe}_3)_2(\eta^2\text{-N}_2)]$  has been proposed based on its ESR (electron spin resonance) measurement [236, 237], but the actual structure has been recently revised by Chirik and coworkers as the anionic mixed valence dizirconium–dinitrogen complexes  $[\text{Na}(\text{thf})_6][(\text{Cp}_2\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)]$  where a dinitrogen ligand bridges two zirconium atoms both in an end-on manner [238].

On the other hand, Armor and Taube have already reported a linkage isomerism for the  $^{15}\text{N}$ -labelled Allen and Senoff's complex  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  and have proposed an end-to-end rotation through the intermediacy of a side-on



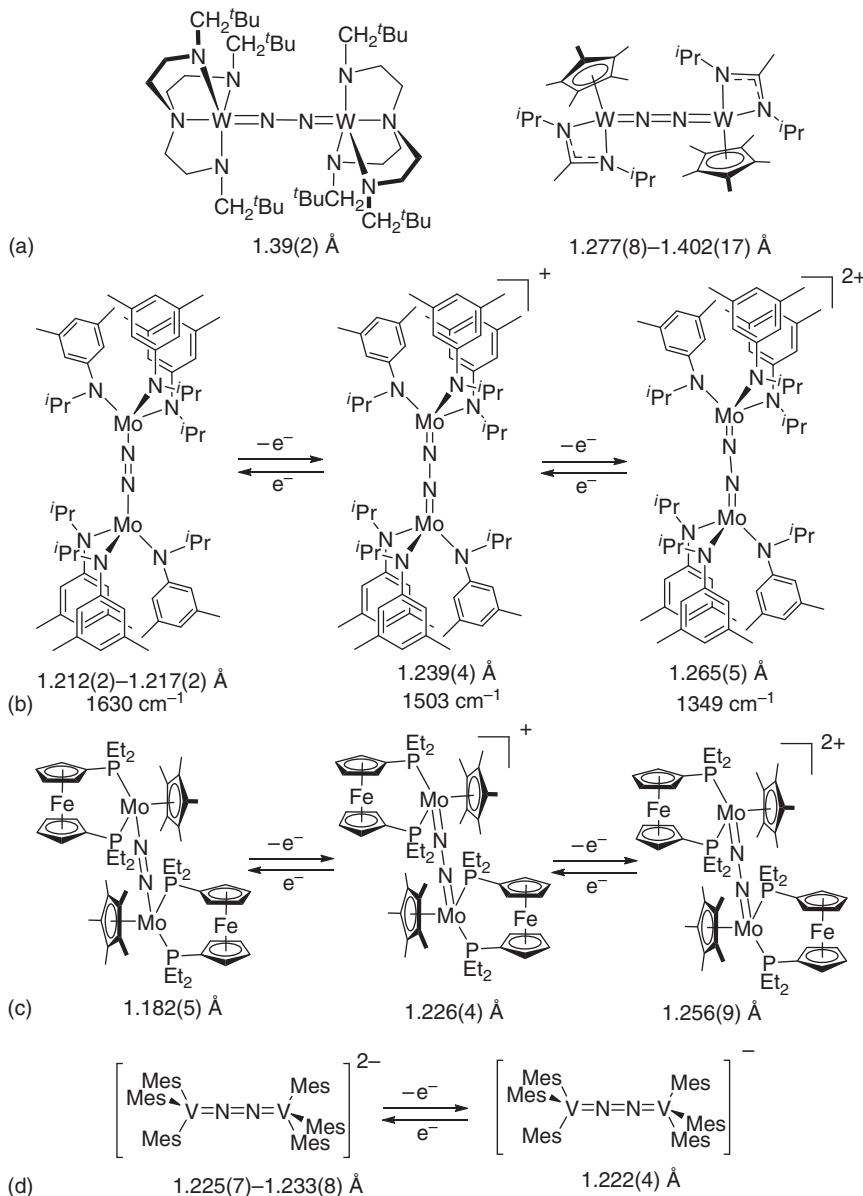
**Figure 1.13** Intramolecular linkage isomerism to form side-on-bound transition metal–dinitrogen complexes analyzed by (a) NMR and (b) X-ray crystallography.

dinitrogen complex in 1970 [239]. Cusanelli and Sutton have more firmly confirmed nondissociative and intramolecular linkage isomerization of the dinitrogen ligand for a series of rhenium–dinitrogen complexes (Figure 1.13a) [240]. More recently, side-on coordination of the dinitrogen to a single-metal center has been confirmed spectroscopically or crystallographically for Allen and Senoff's complex  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  [241] or its osmium analog  $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  [242], where irradiation of UV light to the solid-state crystals of  $[\text{M}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  ( $\text{M} = \text{Ru}$  [109–112] or  $\text{Os}$  [243, 244]) gave rise to the formation of metastable states of  $[\text{M}(\text{NH}_3)_5(\eta^2\text{-N}_2)]^{2+}$ , where the vibration of dinitrogen has shifted from  $2025$  to  $1838\text{ cm}^{-1}$  for the osmium–dinitrogen complex for instance (Figure 1.13b) [241, 242]. Anyway, both experimental and theoretical studies have confirmed that the side-on coordination is always higher in energy than end-on in mononuclear dinitrogen complexes [245–251].

#### 1.4.2 Multinuclear Transition Metal–Dinitrogen Complexes

In contrast to the mononuclear dinitrogen complexes, bridging dinitrogen complexes can be prepared for both early and late transition metals (group 4–10). The most investigated dinuclear transition metal–dinitrogen complexes with the end-on-bound bridging  $\mu\text{-}\eta^1\text{:}\eta^1\text{-dinitrogen}$  have a  $d^2$  (Ti(II), Zr(II), V(III), Nb(III), Ta(III), Mo(IV), W(IV)) or  $d^6$  (Cr(0), Mo(0), W(0), Mn(I), Tc(I), Re(I), Fe(II), Ru(II), Os(II), Ir(III)) configuration in the metals, whereas the other dinuclear transition metal complexes include  $d^1$  (Ti(III), Hf(III), Nb(IV), Ta(IV), Mo(V)),  $d^3$  (Ti(I), V(II), Nb(II), Ta(II), Mo(III), W(III)),  $d^4$  (V(I), Ta(I), Cr(II), Mo(II), W(II), Fe(IV)),  $d^5$  (V(0), Cr(I), W(I), Os(III)),  $d^7$  (Fe(I), Ru(I)),  $d^8$  (Fe(0), Ru(0), Co(I), Rh(I), Ir(I)),  $d^9$  (Co(0), Rh(0), Ni(I)), and  $d^{10}$  (Ni(0)) configurations [221–224]. Bridging end-on-coordinated dinitrogen in dinuclear dinitrogen complexes is roughly linear or slightly bent ( $\text{M–N–N}$  usually wider than  $160^\circ$  with exceptions [252]) and an averaged bond distance of  $1.19(7)\text{ \AA}$ , corresponding to rather a double bond, and the bond lengths of bridging dinitrogen that tend to be elongated in early transition metal complexes compared to those in late transition metal complexes [221]. The longest bond lengths up to  $1.40\text{ \AA}$  almost identical to those of a single bond were observed by X-ray analyses for dinitrogen-bridged tungsten(III)

complexes (Figure 1.14a) [253, 254]. Indeed, stretching vibration attributable to the NN bond is shifted sometimes drastically downward to the range of 2150 to 800 cm<sup>-1</sup> [143, 222–224], which is usually observed in Raman spectroscopies, for symmetric structures found in the dinitrogen-bridged dinuclear complexes that tend to make the molecules Raman active but IR inactive.

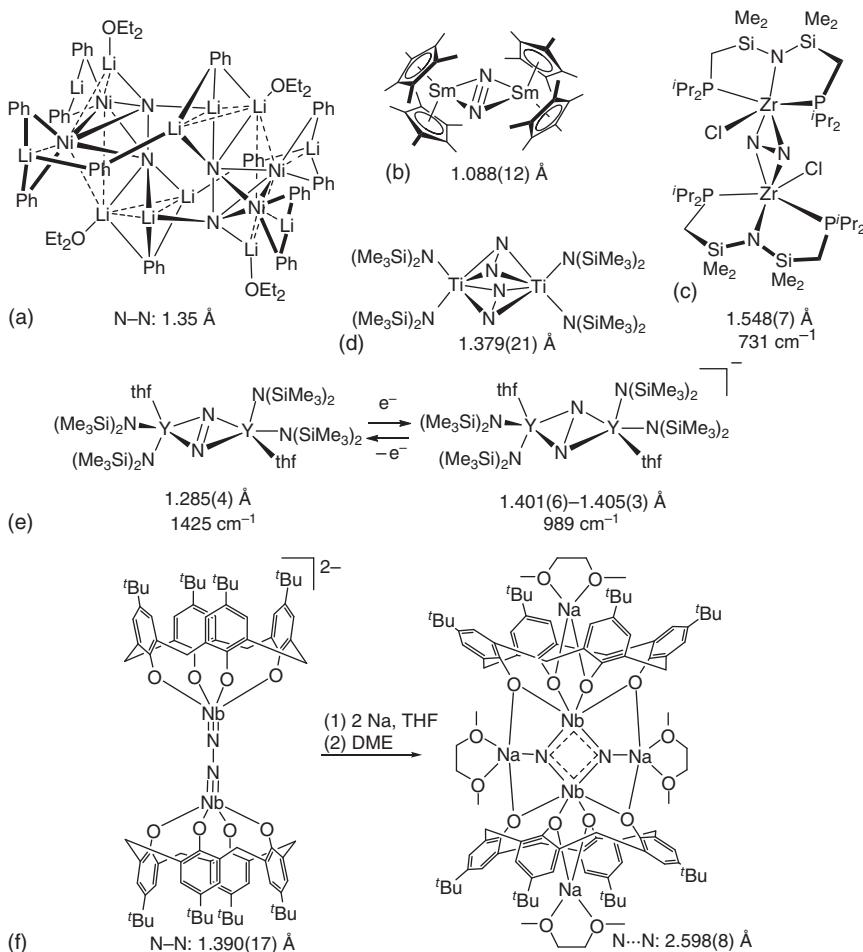


**Figure 1.14** Metric features of end-on-bridged dinuclear transition metal–dinitrogen complexes: (a) longest bond lengths found by X-ray analyses and (b–d) change in bond lengths of dinuclear end-on-bridged transition metal–dinitrogen complexes by redox.

Change of bond lengths in bridging dinitrogen by redox is significantly observed for molybdenum–dinitrogen complexes  $[(\text{Mo}\{\text{N}^t\text{Bu}(\text{C}_6\text{H}_3\text{Me}_2-3,5)\}_3)_2(\mu\text{-N}_2)]$  (Figure 1.14b) [255] and  $[\{\text{Cp}^*\text{Mo}(\text{depf})\}_2(\mu\text{-N}_2)]$  (depf, 1,1'-bis(diethylphosphino)ferrocene) (Figure 1.14c) [256], where stepwise oxidations can result in the elongation of bridging dinitrogen (1.21–1.27 Å or 1.18–1.26 Å) as well as the lowering of Raman band because of the NN bond stretching (1630 to 1349 cm<sup>-1</sup>) [255–257]. These complexes are also noteworthy that they give the corresponding nitrido complexes by thermal [258, 259] or photochemical methods [256]. On the other hand, bond lengths are shortened upon oxidation in cases for vanadium (Figure 1.14d) [260] or tantalum complexes [261, 262], thus are quite sensitive to the nature of the transition metal centers.

Side-on-bridged transition metal–dinitrogen complex was first characterized crystallographically by Jonas, Krüger, and Tsay for a nickel complex  $[\{\text{(PhLi)}_6\text{Ni}_2(\text{N}_2)(\text{OEt}_2)_2\}_2]$ , where each of the two dinitrogen ligands bridges two nickel atoms in side-on manners perpendicular to the Ni–Ni bond with two or three lithium atoms additionally coordinating to each of the nitrogen atoms (Figure 1.15a) [263, 264]. The same group has also revealed the similar structure for  $[\{\text{Ph}(\text{NaOEt}_2)_2\text{Ph}_2\text{Ni}_2(\text{N}_2)\text{NaLi}_6(\text{OEt}_4)\text{OEt}_2\}_2]$  [265], and the N–N bond lengths of these side-on-bound dinitrogen with end-on coordination to lithium atoms range between 1.35 and 1.36 Å [263–266].

In 1988, the side-on-bridged planar dinuclear dinitrogen complex analyzed crystallographically was first reported by Evans et al. for  $[(\text{Cp}^*_2\text{Sm})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ , which is also the first crystallographically analyzed f-block dinitrogen complex (Figure 1.15b) [267]. The bond length of the dinitrogen ligand in this compound is 1.09 Å, almost identical to a triple bond, whereas that of the second example of the side-on-bridged planar dinuclear dinitrogen complex analyzed crystallographically reported by Fryzuk et al. in 1990 for  $[\{\{\text{N}(\text{SiMe}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\}\text{ZrCl}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$  is 1.55 Å with a Raman band at 731 cm<sup>-1</sup>, even longer than the expected N–N single bond and enough to be assigned as (N<sub>2</sub>)<sup>4-</sup> (Figure 1.15c) [268–270]. In 1991, Gambarotta and coworkers reported the isolation of the unique bis(side-on)-bridged transition metal–dinitrogen complex  $[\{\{\text{Me}_2\text{Si}\}_2\text{N}\}_2\text{Ti}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)_2]$  where two dinitrogen ligands bridge two titanium atoms in side-on manners (Figure 1.15d) [271]. Since then, several side-on-bridged dinitrogen complexes have been prepared and characterized, especially for f-block lanthanide (Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu) and actinide (U) complexes [272–274]. Except for f-block elements, d<sup>1</sup> (Sc(II), Y(II), La(II), Zr(III)), d<sup>2</sup> (Y(I), Ti(II), Zr(II), Hf(II)), d<sup>3</sup> (Nb(II)), d<sup>5</sup> (Cr(I)), and d<sup>10</sup> (Ni(0)) configurations are known by counting dinitrogen as a neutral ligand, whereas the bond length of the dinitrogen ligand in the side-on-bound dinitrogen-bridged transition metal–dinitrogen complexes including f-block element–dinitrogen complexes ranges from 1.01 to 1.63 Å (Figure 1.12c) [221, 224, 229, 274]. Elongation of the bond length of the side-on-bound bridging dinitrogen ligand has been well observed for rare earth element–dinitrogen complexes, where the one-electron reduction of the dinuclear species assigned as with an (N<sub>2</sub>)<sup>2-</sup> ligand results in the formation of an anionic species assigned as with an (N<sub>2</sub>)<sup>3-</sup> ligand (Figure 1.15e) [275–277]. For the side-on-bridged dinuclear transition metal–dinitrogen complexes, the oxidation states of neutral (N<sub>2</sub>) to more reduced



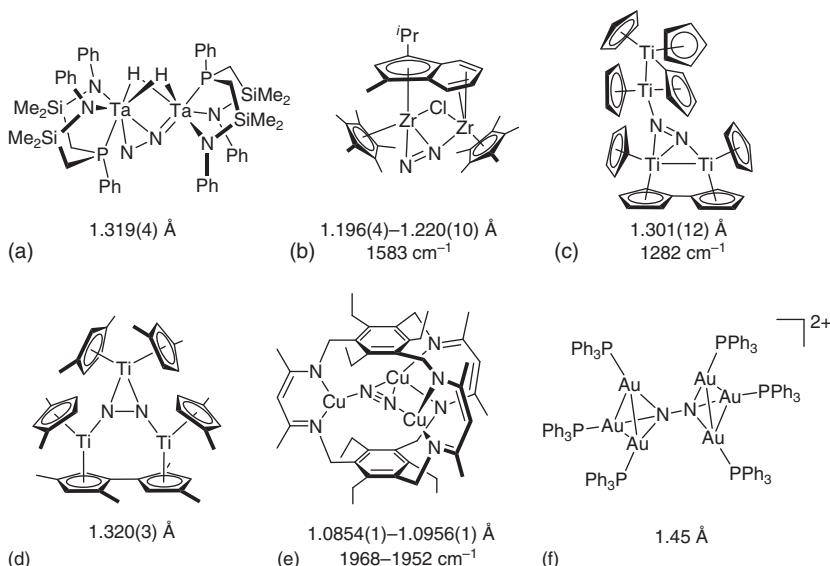
**Figure 1.15** Metric features of side-on-bridged dinitrogen complexes: (a) first crystallographically characterized side-on-bridged transition metal–dinitrogen complex, (b) first crystallographically characterized side-on-bridged dinuclear f-block element–dinitrogen complex, (c) first crystallographically characterized side-on-bridged dinuclear d-block element–dinitrogen complex, (d) first crystallographically characterized bis(side-on)-bridged dinuclear dinitrogen complex, (e) change in bond lengths of dinuclear bis(side-on)-bridged transition metal–dinitrogen complexes by redox, and (f) further reductive cleavage of the dinitrogen ligand.

forms ( $(\text{N}_2)^{2-}$ ,  $(\text{N}_2)^{3-}$ , and  $(\text{N}_2)^{4-}$ ) have been proposed based on the elongation of N–N bond lengths or vibration spectroscopies [221, 229, 274], whereas the N–N bond lengths determined by X-ray diffraction experiments can be sometimes underestimated and may not be appropriate to assess the level of dinitrogen reduction [278, 279].

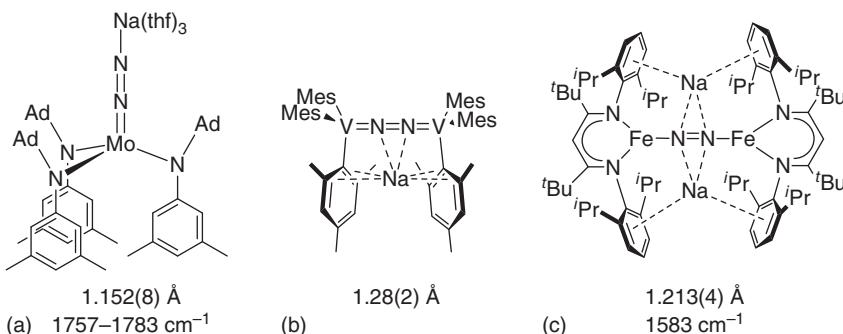
It must be noteworthy that further reduction of dinitrogen by bimetallic systems can result in the formation of bis(nitridido)-bridged complexes with two ( $\mu\text{-N}$ )<sup>3-</sup> bridging ligands [280–285]. For example, Floriani and coworkers have

reported that the two-electron reduction of the dianionic dinitrogen-bridged dinacobium complex  $[\text{Na}(\text{L})_x]_2\{(\text{p}-t\text{-Bu}-\text{calix}[4]\text{arene})\text{Nb}\}_2(\mu\text{-N}_2)$  ( $\text{L}$  = diglyme or thf) affords the corresponding bis(nitrido)-bridged complex [280] (Figure 1.15f). Bis(nitrido)-bridged complexes can be significantly distinguishable from the side-on-bridged dinitrogen complexes by metric features, for the two nitrido nitrogen atoms separated by 2.4–3.0 Å (Figure 1.12c) [221].

The third coordination mode of dinitrogen ( $\mu\text{-}\eta^1\text{:}\eta^2\text{-N}_2$ , Figure 1.12a) for a dinuclear complexes was reported in 1998 by Fryzuk et al. for a ditantalum complex  $[\text{Ta}_2(\mu\text{-H})_2\{\text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2\}_2](\mu\text{-}\eta^1\text{:}\eta^2\text{-N}_2)$ , where the bridging dinitrogen coordinates to the metal centers both in end-on and side-on manners (Figure 1.16a) [286, 287]. A similar structure was also found for a dizirconium complex (Figure 1.16b) [252], where the N–N bond lengths (1.20–1.32 Å) correspond to double or between double and single bonds. However, a similar coordination has been already reported by Pez et al. in 1982 for the fulvalene-bridged tetranuclear titanium complex  $[\{\text{Ti}_2(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Cp}_3\}\{\text{Ti}_2(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)\text{Cp}_2\}(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-N}_2)]$ , where the dinitrogen ligand bridges three titanium atoms in end-on, end-on, and side-on manners (Figure 1.16c) [288]. Dinitrogen as a bridging ligand coordinating to three transition metal centers has also been recently reported by Chirik's and Murray's groups for titanium (Figure 1.16d) [289] and copper (Figure 1.16e) [290] complexes, respectively. Furthermore, dinitrogen ligand coordinating to six transition metal centers has been reported for hexanuclear gold complex  $[(\text{AuPPh}_3)_6(\mu_6\text{-N}_2)]^{2+}$ ,



**Figure 1.16** Metric features of transition metal complexes with side-on-end-on-bridged or multidentate dinitrogen ligand: bidentate side-on-end-on-bridged dinuclear transition metal–dinitrogen complexes of (a) tantalum and (b) zirconium; tridentate side-on-end-on-bridged transition metal–dinitrogen complexes of (c) tetranuclear titanium, (d) trinuclear titanium, and (e) trinuclear copper; and (f) hexanuclear transition metal–dinitrogen complex of gold.



**Figure 1.17** Selected examples of transition metal–dinitrogen complexes containing (a) end-on, (b) side-on, and (c) bis(side-on) interactions with sodium.

which was prepared from the reaction with hydrazine [291]. However, the N–N bond length (1.45 Å) is long enough to be identified as a hydrazido(4–) complex ( $\text{N}_2$ )<sup>4–</sup> with the oxidation states of two gold atoms at +1.

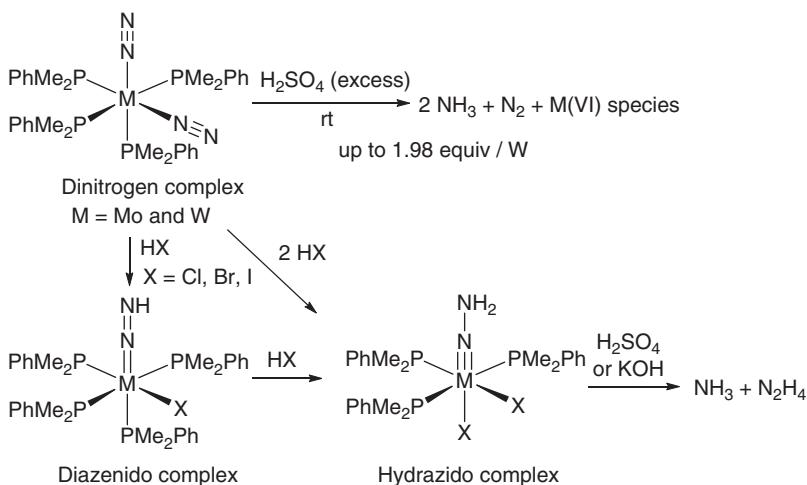
As already shown in Figure 1.15a [263–266], alkaline metal and alkaline earth metal elements can bind even to dinitrogen ligands coordinated to transition metal centers in both end-on and side-on manners, and its coordination chemistry is more complicated than that of transition metal–dinitrogen complexes [292, 293]. Selected examples of transition metal–dinitrogen complexes where sodium is coordinated in end-on [294], side-on [295], or bis(side-on) manners [296] are shown in Figure 1.17.

## 1.5 Chemical Activation and Reactivity of Dinitrogen Using Transition Metal Complexes

### 1.5.1 Protonation of Transition Metal-bound Dinitrogen

Since the first discovery of transition metal–dinitrogen complex [109], activation and transformation of dinitrogen into ammonia or other nitrogen-containing organic or inorganic compounds under ambient conditions using dinitrogen complexes have been a frontline topic in synthetic chemistry [50–54, 72, 141–156, 221–225, 227–231, 297–313].

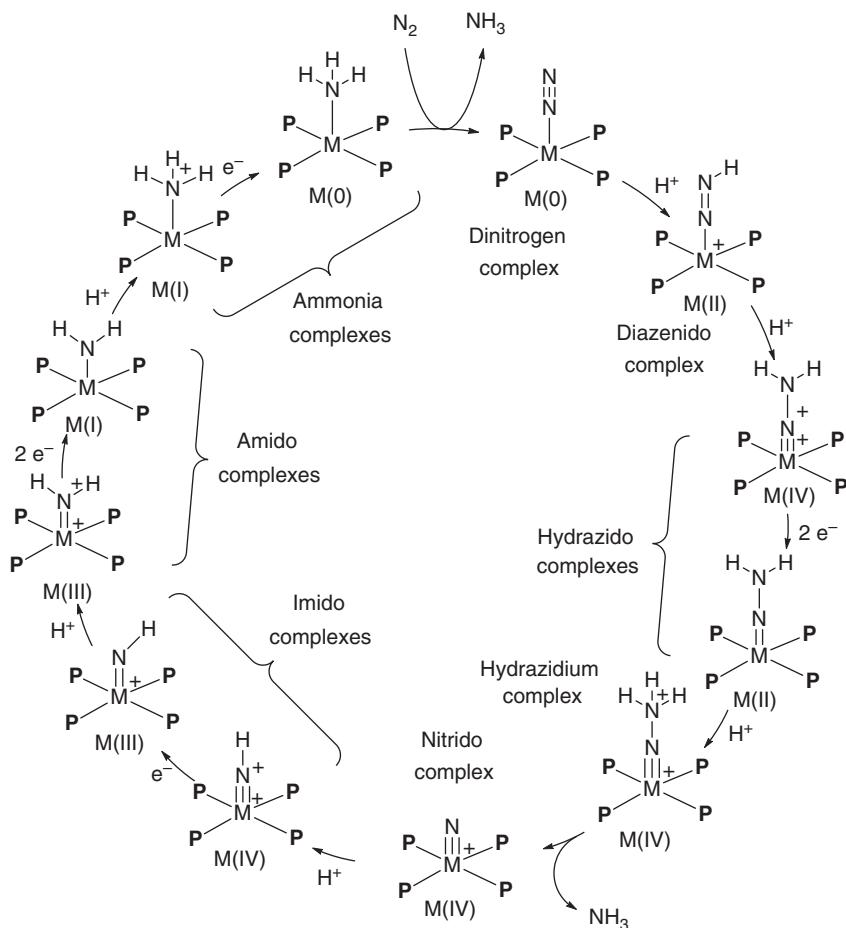
Formation of ammonia from dinitrogen by using transition metal complexes has already been reported by Vol'pin and Shur in 1960s [103–106], and several transition metal complexes where dinitrogen is not coordinated have been found to afford ammonia or hydrazine [314–322]. Ammonia formation from the decomposition of transition metal–dinitrogen complexes was first confirmed for titanium complexes in early 1970s, where small amounts of ammonia were obtained on treatment of reducing reagents or acids [320, 323–327]. In 1975, Chatt et al. have reported that the reaction of zero-valent group 6 transition metal (Mo and W)–dinitrogen complexes with sulfuric acid affords stoichiometric amount of ammonia (Figure 1.18) [328, 329], whereas Brûlet and van Tamelen have also reported the formation of ammonia for the molybdenum dinitrogen



**Figure 1.18** Protonation of dinitrogen bound to Mo or W centers to afford ammonia or hydrazine.

complex *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] on treatment with hydrobromic acid in the same year [330]. Since then, stoichiometric conversion of dinitrogen toward ammonia, hydrazine, or other nitrogen-containing compounds by the reaction of group 6 molybdenum- and tungsten–dinitrogen complexes with Brønsted acids, alcohols, or water has been surveyed by Chatt's [222] and Hidai's groups [223, 331–335]. As shown in Figure 1.12b, the dinitrogen ligand coordinated to the electron-rich transition metal centers is activated toward the attack by electrophiles, which leads to the formation of ammonia or hydrazine (Figure 1.18) [328–330, 336–344]. Stepwise protonation of the dinitrogen complexes leads to the formation of diazenido (MN=NH), hydrazido (MN—NH<sub>2</sub>), and hydrazidium (MN—N<sup>+</sup>H<sub>3</sub>) complexes, which gives ammonia as a major product sometimes with the formation of hydrazine as a minor product on further treatment with acids or bases (Figure 1.18) [345–360].

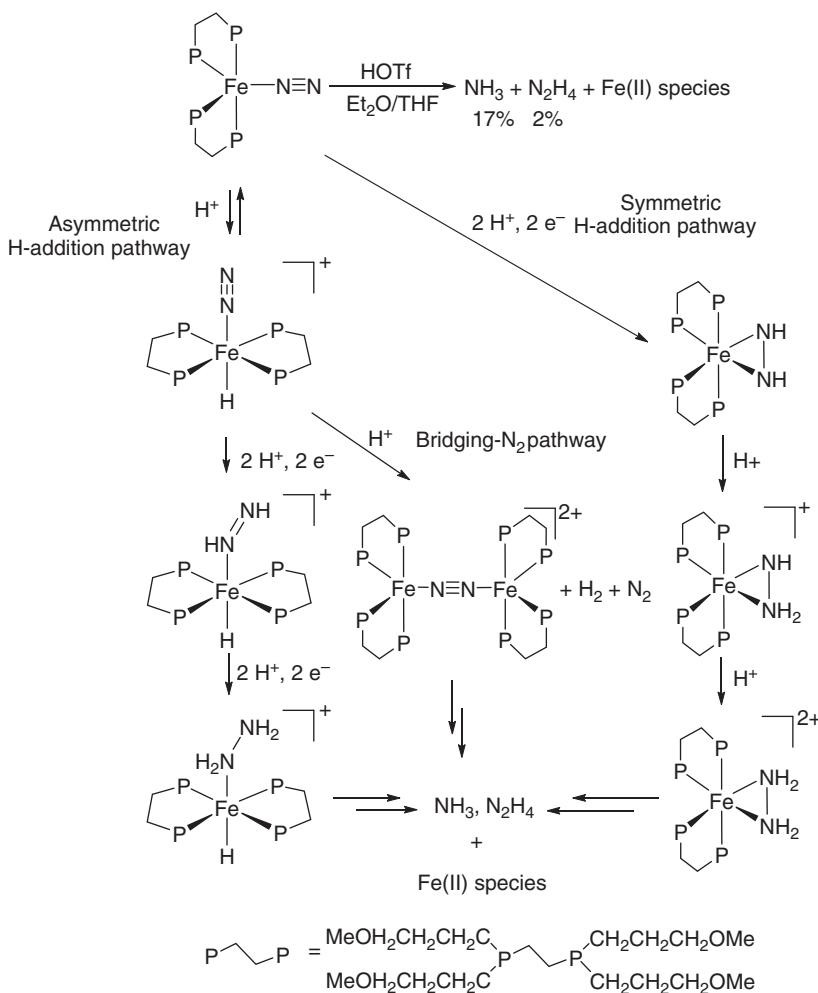
A hypothetical catalytic cycle called "Chatt cycle" (Figure 1.19) has been proposed based on these isolated intermediates in addition to nitrido (MN), imido (MNH), amido (MNH<sub>2</sub>), and ammonia (ammine) complexes (MNH<sub>3</sub>), whereas the definition of the Chatt cycle, especially explication of oxidation states of the transition metal centers, differs among researchers [150, 222, 361–366]. In a typical Chatt cycle based on the "distal" reaction pathway as drawn in Figure 1.19, an equimolar amount of ammonia is produced by protonation at the distal nitrogen atom of the end-on-coordinated dinitrogen and nitrogen–nitrogen bond split to afford nitrido complexes originated from the proximal nitrogen atom of the dinitrogen ligand, where the following protonation steps occur to afford another equimolar amount of ammonia. Thus, 2 M amount of dinitrogen is obtained per cycle, whereas six-electron reduction is necessary to recover the starting dinitrogen complex; thus, an appropriate choice of proton sources and reducing reagents is required. In the original paper by Chatt, this catalytic cycle was proposed for biological nitrogen fixation upon FeMo-co, while "alternating" pathway leading



**Figure 1.19** An example of proposed Chatt cycle.

to the formation of hydrazine was concluded to be rather a side reaction [222], although the alternating pathway is now more probable for nitrogenase reactions (Figure 1.7) [66, 69].

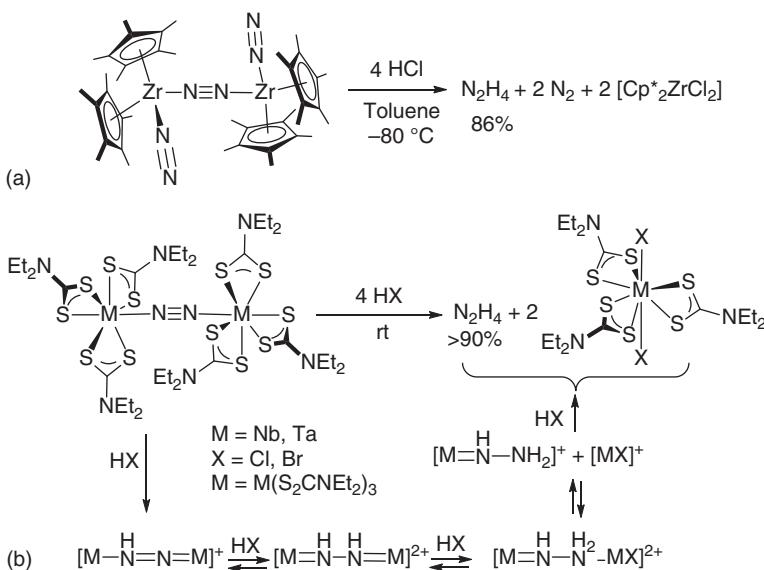
Other mononuclear dinitrogen complexes of vanadium [153–156, 367–370], chromium [371, 372], iron [142–145, 373–390], and cobalt [390–393] also gave but comparably lower yields of ammonia or hydrazine when treated with Brønsted acids or other proton sources. For instance, Tyler and coworkers have reported that the reaction of an iron-dinitrogen complex with trifluoromethanesulfonic acid (HOTf) affords a mixture of ammonia and hydrazine. Three possible reaction pathways (symmetric H-addition pathway, asymmetric H-addition pathway, and bridging- $N_2$  pathway) can be drawn by connecting all the isolated intermediary complexes as shown in Figure 1.20, where the asymmetric H-addition pathway is the most likely with both proximal and distal nitrogen atoms protonated stepwise based on the DFT calculations [143, 373–381].



**Figure 1.20** Three possible reaction pathways for the formation of ammonia and hydrazine by using an iron-dinitrogen complex.

Treatment of several dinitrogen-bridged early transition metal-dinitrogen complexes of zirconium [268, 269, 327, 394–397], niobium, or tantalum [398–402] with acids gives hydrazine as a major product. For example, the reaction of  $[\{\text{Cp}^*\text{Zr}(\text{N}_2)\}_2(\mu\text{-N}_2)]$  with hydrochloric acid was reported by Bercaw and coworkers to afford an equimolar amount of hydrazine and 2 M amount of  $[\text{Cp}^*\text{ZrCl}_2]$  (Figure 1.21a) [327, 394–397]. A similar reactivity has also been reported for tantalum- or niobium-dinitrogen complexes  $[\{\text{M}(\text{N}_2\text{S}_2\text{CNEt}_2)_3\}_2(\mu\text{-N}_2)]$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) where stepwise protonation reactions of the bridging dinitrogen ligand with hydrogen halide to afford an equivalents of hydrazine have been confirmed (Figure 1.21b) [398–401].

On the other hand, a mixture of ammonia and hydrazine is obtained for other dinitrogen-bridged early transition metal-dinitrogen (titanium [288] and

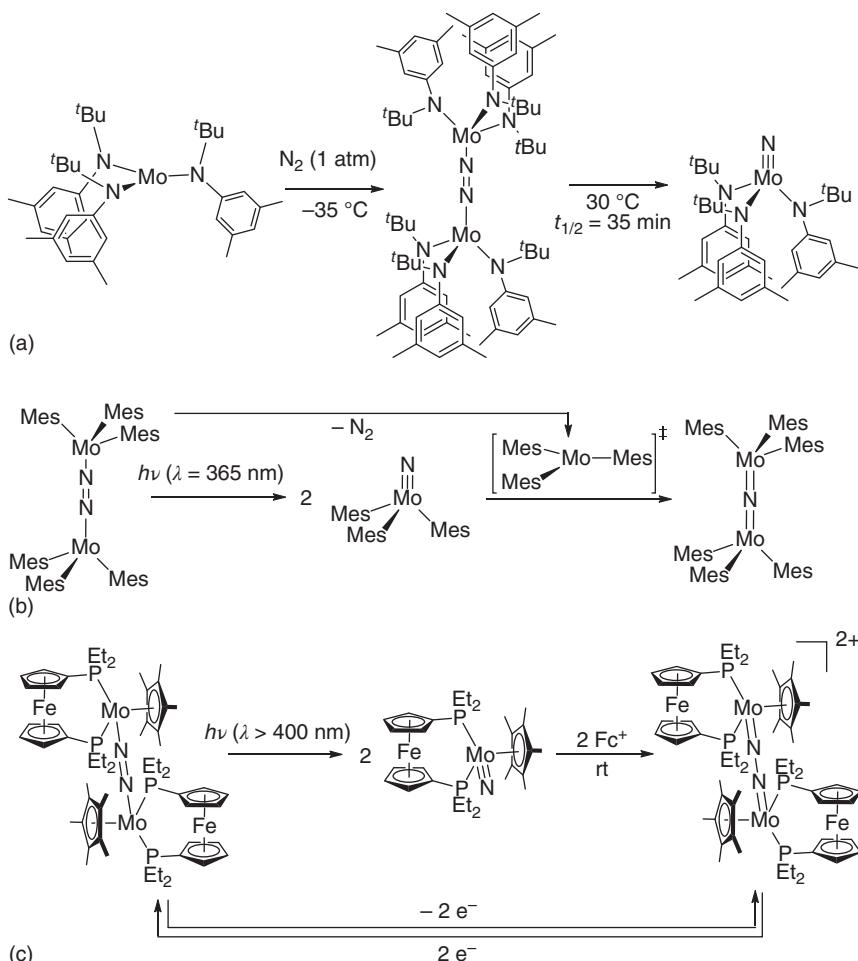


**Figure 1.21** Reaction of dinitrogen-bridged early transition metal-dinitrogen complexes with hydrogen halide to afford hydrazine for (a) zirconium and (b) niobium or tantalum complexes.

vanadium [260, 295, 403]) or heterobimetallic dinitrogen complexes [404, 405], whereas the dinitrogen-bridged dinitrogen complexes of middle-to-late transition metals (molybdenum, tungsten [406, 407], or nickel [266]) afford ammonia as the major product.

### 1.5.2 Cleavage of Transition Metal-bound Dinitrogen

In 1995, Laplaza and Cummins have reported that the dinitrogen-bridged molybdenum complex  $[(\text{Mo}\{\text{N}^t\text{Bu}(\text{C}_6\text{H}_3\text{Me}_2-3,5)\}_3)_2(\mu\text{-N}_2)]$  as already shown in Figure 1.14b [255] affords a pair of nitrido complexes with thermal cleavage of dinitrogen (Figure 1.22a) [258, 259]. As shown in Figure 1.15f, dinitrogen can be cleaved to afford the nitrido complexes by reduction [280]. Furthermore, photochemical cleavage of dinitrogen has been reported by Floriani and coworkers, where cleavage of the dinitrogen-bridged dimolybdenum complex  $[\{\text{Mo}(\text{Mes})_3\}_2(\mu\text{-N}_2)]$  occurs under irradiation of UV light to give the corresponding nitrido complex  $[\text{Mo}(\text{N})(\text{Mes})_3]$  [408], which reacts with  $[\text{Mo}(\text{Mes})_3]$  species to afford the nitrido-bridged dimolybdenum complex  $[\{\text{Mo}(\text{Mes})_3\}_2(\mu\text{-N}_2)]$  (Figure 1.22b) [409]. Since then, several transition metal-nitrido complexes [410, 411] have been prepared by thermal, reductive, or oxidative cleavage of the nitrogen ligand coordinated to transition metals [254–256, 261, 280–285, 294, 389, 412–435]. Further treatment of the nitrido complexes with acids leads to the formation of ammonia [256, 284, 285, 389, 412–416, 436, 437]. Reversely, coupling of nitrido complexes can lead to the regeneration of dinitrogen complexes [256, 438–448]. For example, irradiation of visible light to the neutral dinitrogen-bridged dimolybdenum complex  $[\{\text{Cp}^*\text{Mo}(\text{dpf})\}_2(\mu\text{-N}_2)]$  leads to the formation of the nitrido

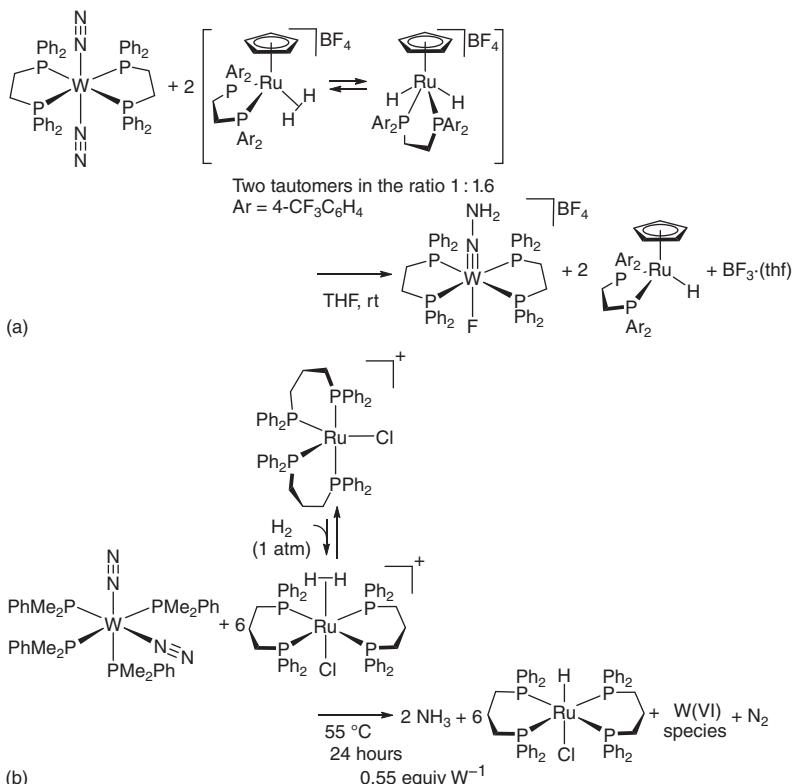


**Figure 1.22** Cleavage of dinitrogen by (a) thermal or (b) photochemical methods. (c) Regeneration of the dinitrogen ligand by coupling of the nitrido complexes.

complex  $[\text{Cp}^*\text{Mo}(\text{N})(\text{defp})]$ , which can be coupled to afford the dicationic dinitrogen-bridged dimolybdenum complex  $[\{\text{Cp}^*\text{Mo}(\text{defp})\}_2(\mu\text{-N}_2)]^{2+}$  by the oxidation with ferrocenium cation (Figure 1.22c) [256]. As already shown in Figure 1.14c, the electron configurations of the dinitrogen-bridged core can be changed stepwise by redox processes; thus, the starting neutral dinitrogen complex can be regenerated by redox processes from the cleaved nitrido complex (Figure 1.22c) [256, 449]. Thus, both cleavage and reformation of molecular dinitrogen are induced by a pair of two different external stimuli (photochemistry and redox) under ambient reaction conditions.

### 1.5.3 Reaction of Transition Metal-bound Dinitrogen with Dihydrogen

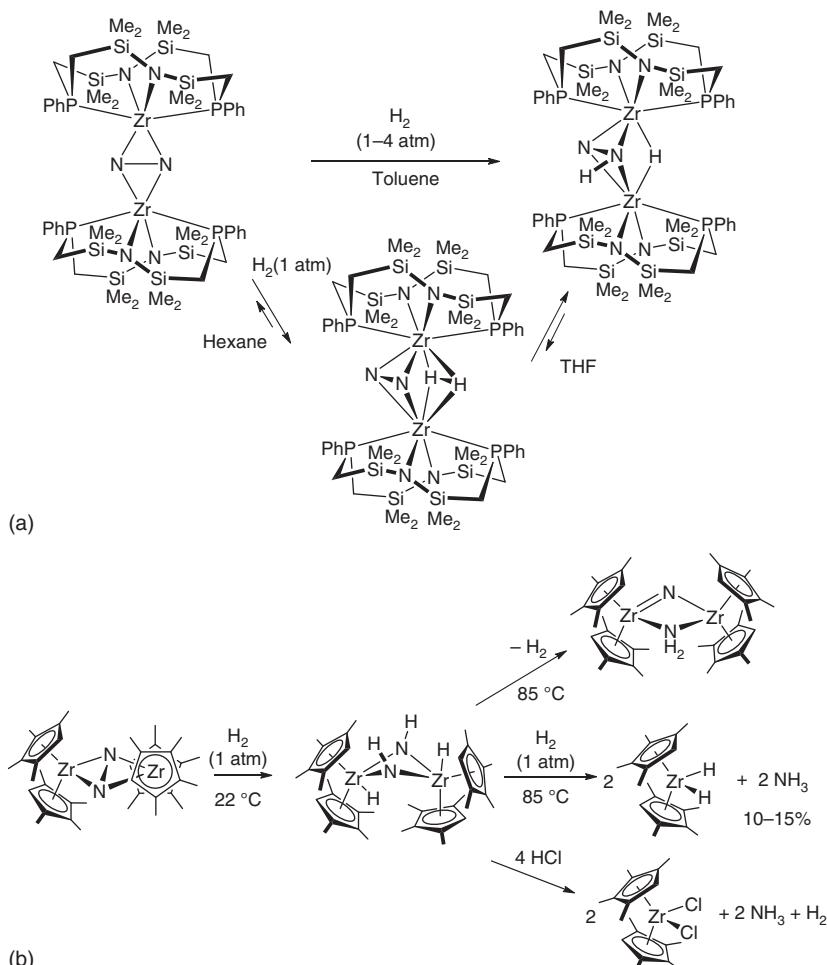
Reaction of gaseous dihydrogen with dinitrogen complexes has been apt to lead to the loss of dinitrogen to form hydride complexes [450–452]; thus,



**Figure 1.23** Reaction of tungsten–dinitrogen complex with acidic ruthenium– $\eta^2$ -dihydrogen complexes to form (a) hydrazido complex or (b) ammonia.

appropriate activation of dihydrogen was required for the direct reaction of transition metal-bound dinitrogen and dihydrogen under ambient reaction conditions. Indeed, Morris and coworkers have reported that the dinitrogen ligand of the tungsten–dinitrogen complexes *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})_2]$  can be protonated by the acidic ruthenium– $\eta^2$ -dihydrogen complex to afford the hydrazido complex (Figure 1.23a) [453]. When the tungsten–dinitrogen complex *cis*- $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$  was treated with an excess amount of the cationic ruthenium– $\eta^2$ -dihydrogen complex  $[\text{RuCl}(\eta^2\text{-H}_2)(\text{dppp})_2]^+$  under the atmospheric pressure of dihydrogen at  $55^\circ\text{C}$ , 0.55 equiv of ammonia was obtained based on the tungsten atom, with the dinitrogen ligand likely protonated by the proton ( $\text{H}^+$ ) formed from the heterolytic cleavage of dihydrogen on the ruthenium center, affording the stoichiometric amount of hydrido ruthenium complex  $[\text{RuHCl}(\text{dppp})_2]$  (Figure 1.23b) [454, 455]. Ammonia has also been obtained by the reaction of the tungsten–dinitrogen complexes and their derivatives with the sulfido-bridged dinuclear molybdenum complex  $[(\text{Cp}_2\text{Mo})_2(\mu\text{-S})(\mu\text{-SH})(\mu\text{-S}_2\text{CH}_2)]^+$  under the atmospheric pressure of dihydrogen [456, 457].

Reaction of dihydrogen gas with the side-on-coordinated dinitrogen-bridged dizirconium complex to afford the (diazenido)(hydrido)-bridged dizirconium



**Figure 1.24** Reaction of dinitrogen-bridged zirconium complex with gaseous dihydrogen to afford (a) diazenido-bridged complex or (b) ammonia.

complex has been reported by Fryzuk and coworkers, where the (dinitrogen)-(dihydrogen)-bridged complex has been isolated as an intermediary complex (Figure 1.24a) [458–460], whereas formation of ammonia has not been successful. Similar diazenido-bridged dizirconium or dihafnium complexes have been isolated by Sita and coworkers from the reaction of dinitrogen-bridged complexes with dihydrogen gas [461].

The reaction of side-on-coordinated dinitrogen-bridged dizirconium complex  $\{(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Zr}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$  with gaseous dihydrogen has also been reported by Chirik and coworkers, where 10–15% yield of ammonia is obtained via the formation of the bis(imido)-bridged dizirconium complexes  $\{(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Zr}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ , from which stoichiometric amount of ammonia is obtained on treatment with hydrochloric acid (Figure 1.24b) [462–464]. This result is perfectly in contrast to that obtained for  $[(\text{Cp}^*\text{Zr})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ .

which affords a stoichiometric amount of hydrazine on treatment with hydrogen chloride (Figure 1.21a) [394–397], demonstrating that the small difference in the design of auxiliary ligands can drastically affect the reactivity of the coordinated dinitrogen [465–468].

Stepwise hydrogenation of dinitrogen by using poly(titanium) system has been reported by Hou and coworkers [416]. Hydrogenation of nitride to afford ammonia has also been recently reported by using a ruthenium complex with a PNP-type pincer ligand [469, 470].

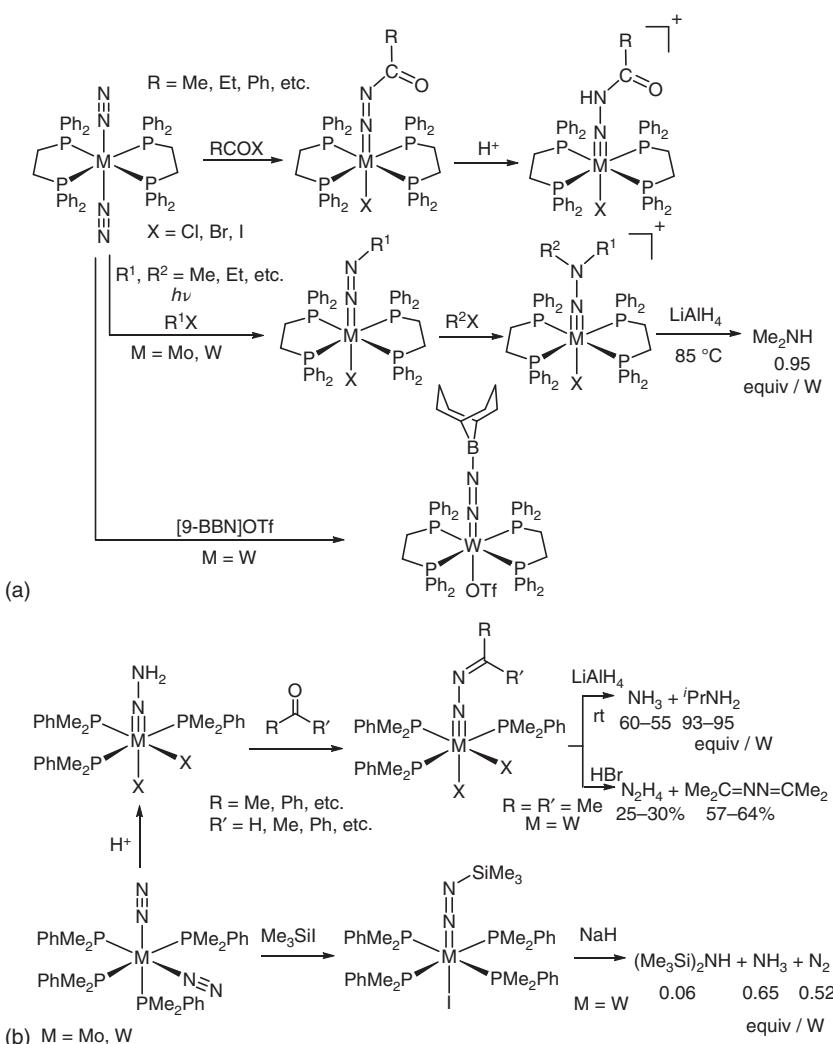
#### 1.5.4 Functionalization of Transition Metal-bound Dinitrogen

Functionalization of dinitrogen into nitrogen-containing compounds has been first reported by Vol'pin and Shur, who obtained amines by reaction with electrophiles [107, 108]. However, most of the conversion of dinitrogen into nitrogen-containing compounds has been remaining substoichiometric based on the amount of transition metals except for the catalytic formation of ammonia [471–473], hydrazine [474, 475], and silylamines [476–479].

As the dinitrogen ligand coordinated to the electron-rich transition metal centers is activated toward the electrophiles (Figure 1.12b), the reaction of dinitrogen with electrophiles has been well investigated [147, 222, 223, 227, 331–334, 465, 480–484]. Acylation of dinitrogen complex to afford acyldiazenido or acylhydrazido complexes was first reported by Chatt et al. in 1972 [485, 486], whereas alkylation of the dinitrogen complexes to afford alkyl diazenido or alkylhydrazido complexes has also been reported by the groups of Chatt and George (Figure 1.25a) [487–490]. Further destructive decomposition of the dialkylhydrazido complexes with reducing reagents, acids, or bases affords a stoichiometric amount of amines or alkylhydrazines (Figure 1.25a) [491–493].

Hidai and coworkers have revealed that the hydrazido complexes obtained from the corresponding dinitrogen complexes give diazoalkane complexes on treatment with ketones or aldehydes, which liberate a stoichiometric amount of ammonia, hydrazine, alkylamines, or ketone azines via decomposition by reducing reagents, acids, or bases (Figure 1.25b) [494–497]. Isolation of silyldiazenido complexes by silylation of dinitrogen complexes has also been successful for the group 6 transition metals, where a stoichiometric amount of silylamines or ammonia is obtained by further treatment with reducing reagents [477, 498–501] (Figure 1.25b). Similarly, boryldiazenido complexes have been isolated by the borylation reaction of the group 6 transition metal–dinitrogen complexes (Figure 1.25a) [502], where alumination [503–505], gallation [506], or germylation [501] of the dinitrogen ligand are also possible to afford the corresponding isolable group 6 transition metal complexes. Hydrosilylation, hydroboration, and hydroalumination of transition metal–dinitrogen complexes have been investigated by Fryzuk and coworkers for tantalum complexes [507–509].

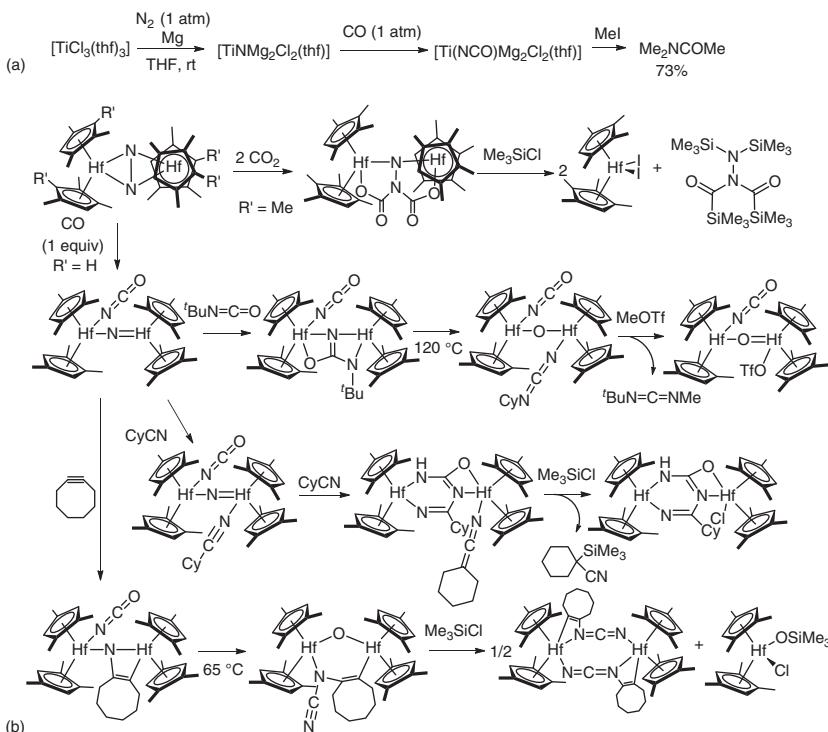
The reaction of carbon monoxide with dinitrogen to afford isocyanate ( $N=C=O$ ) was first reported by Sobota and Janas [510], who obtained  $N,N$ -dimethylacetamide on the treatment of titanium complex with iodomethane (Figure 1.26a) [510–512]. Chirik and coworkers have achieved dinitrogen functionalization with carbon dioxide or carbon monoxide by using dinitrogen–



**Figure 1.25** Functionalization of dinitrogen: (a) acylation, alkylation, and borylation and (b) condensation with ketones/aldehydes and silylation.

bridged dihafnium complexes [430, 465–467, 484]. For example, insertion of carbon dioxide into the dinitrogen-bridged dihafnium complex occurs to afford the hydrazido-1,1-dicarboxylato-bridged dihafnium complex, which liberates dicarboxyl silylsubstituted hydrazine by the reaction with trimethylsilyl chloride (Figure 1.26b) [513, 514]. On the other hand, insertion of carbon monoxide gives the nitrido-bridged isocyanato complex, where insertion of isocyanates, nitriles, or alkynes occurs to afford the corresponding ligand-coordinated complexes (Figure 1.26b) [430, 464, 515, 516].

Formation of nitriles from nitrido complexes has been investigated, where nitrido ligands are not derived from dinitrogen [517, 518]. On the other hand,

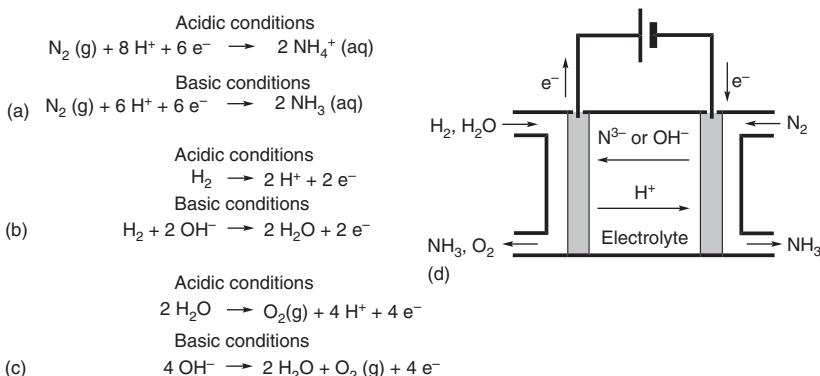


**Figure 1.26** Functionalization of dinitrogen via the reaction with carbon monoxide or carbon dioxide by using (a) titanium complex or (b) hafnium complexes.

formation of nitriles from the nitrido complex derived from molecular dinitrogen has been investigated by Cummins and coworkers for niobium and molybdenum–nitrido complexes [424, 519], and more recently by Schneider and coworkers for a rhenium–nitrido complex [520].

## 1.5.5 Electrochemical and Photochemical Conversion of Dinitrogen Using Transition Metal Complexes

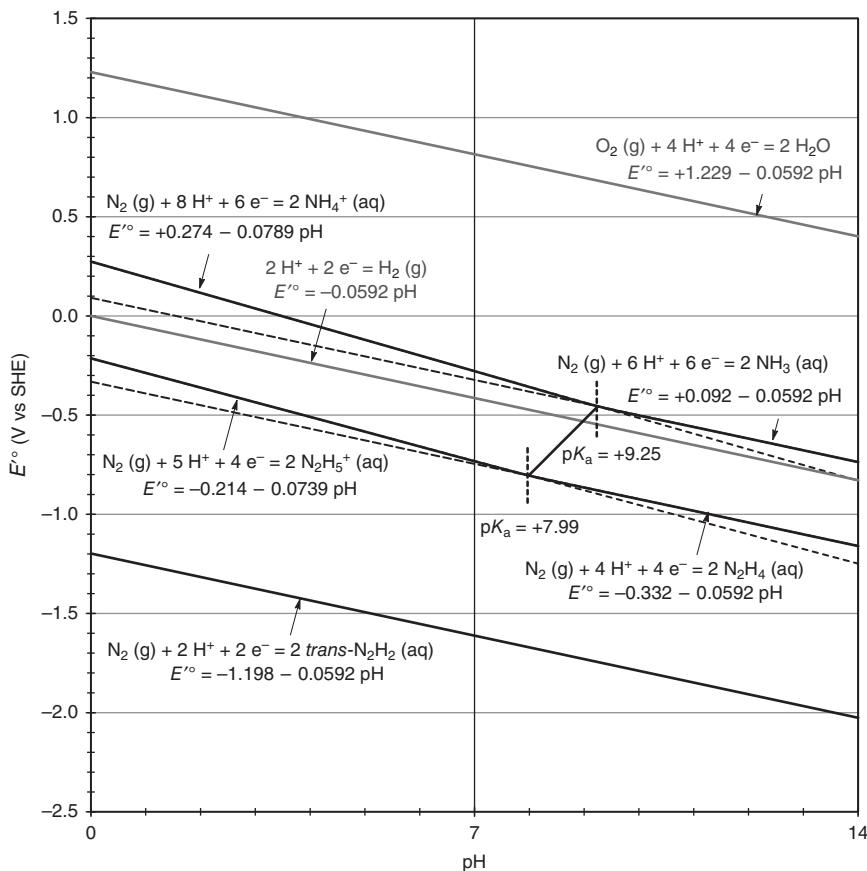
The electrochemical synthesis of ammonia- or nitrogen-containing compounds from dinitrogen under ambient reaction conditions has been investigated since the late 1960s [102, 521–523], around the same years that the transition metal–dinitrogen complexes were first isolated. Theoretically, cathodic reduction of dinitrogen in aqueous solution is dependent on pH, where ammonium cation ( $\text{NH}_4^+$ ) in acidic conditions or ammonia ( $\text{NH}_3$ ) in basic conditions is obtained (Figure 1.27a). In the Haber–Bosch process, this reaction is coupled with the oxidation of dihydrogen (Figure 1.27b), whereas the more attractive method to obtain protons and electrons to reduce dinitrogen is the oxidation of water (Figure 1.27c). A schematic of the representative cell for ammonia synthesis from dinitrogen is shown in Figure 1.27d, where water or dihydrogen can be used as the proton sources for ammonia [306, 524–529].



**Figure 1.27** Basic half-reactions for (a) the reduction of dinitrogen into ammonia, (b) oxidation of water into dioxygen, and (c) oxidation of dihydrogen. (d) Schematic ammonia synthesis cell from dinitrogen and dihydrogen or water under ambient reaction conditions.

The calculated standard apparent reduction potential of dinitrogen into ammonia in water (V vs. SHE) plotted against pH is shown in Figure 1.28 together with the Pourbaix diagram for water, including equilibrium regions for water, dioxygen, and dihydrogen under the standard conditions (1 bar, 25 °C, 0 ionic strength) [73]. As shown in Figure 1.28, reduction of dinitrogen to form ammonia is thermodynamically favored over the production of dihydrogen, whereas usage of water as a proton source for the production of ammonia requires power supply from the outside. However, both oxidation and reduction of dinitrogen are kinetically hindered, and most of the electrode reactions of nitrogen compounds are practically irreversible [530]. Indeed, formation of hydrazine ( $N_2H_4$ ) or hydrazidium cation ( $N_2H_5^+$ ) is thermodynamically disfavored over the production of dihydrogen [531], whereas formation of diazene ( $N_2H_2$ ) is unlikely to be observed under electrocatalytic conditions because of its extremely unfavorable reduction thermodynamics and rapid disproportionation to more easily reduced hydrazine (Figure 1.28) [22, 532, 533]. Thus, the electrochemical synthesis of ammonia by the reduction of dinitrogen under ambient reaction ambient conditions requires appropriate catalysts, such as transition metal complexes [102, 521–523, 534–553], transition metal–dinitrogen complexes and their derivatives [554–560], solid-state heterogeneous catalysts [561–571], or nonmetal catalysts [572, 573], whereas electrical efficiency or yield of ammonia have not yet been high enough.

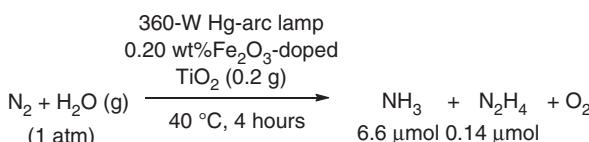
It must be noted that the reverse reaction of the electrosynthesis of ammonia from water and dinitrogen compromises the basis of the ammonia fuel cells; i.e. ammonia and dioxygen are supplied into anode and cathode, respectively, to afford dinitrogen and water as exhausted reactants ( $4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2O$ ) [45–49, 574–577]. Theoretically, the ammonia fuel cell has an electrical potential of 1.172 V at 25 °C and 1 bar, corresponding to the thermal efficiency of 88.6% (HHV, higher heating value) [22], whereas the most efficient ammonia-fed solid oxide fuel cells are operated at much higher temperatures [576, 577]. Indeed, the idea of using ammonia as a fuel for engines goes back to



**Figure 1.28** Pourbaix diagram for water with theoretical apparent standard reduction potentials for dinitrogen reduction to form ammonia, hydrazine, and *trans*-diazene under standard conditions (1 bar, 298.15 K, 0 ionic strength).

the nineteenth century [578], and several preproduction ammonia-fed motors have been constructed. For example, Norway's Norsk Hydro has constructed a small truck with an ammonia reformer that extracted dihydrogen from ammonia to burn in its internal combustion engines in 1933 [579]. Later, ammonia was commercially utilized as a fuel for motor buses in Belgium during WWII [580]. Ammonia is now gaining attention as a possible candidate for hydrogen storage and as a direct fuel that does not exhaust carbon dioxide [45–49, 575].

In 1977, Schrauzer and Guth have reported the photoinduced reaction of dinitrogen equilibrated with water vapor to afford a mixture of ammonia, hydrazine, and dioxygen by using transition metal-doped titanium dioxide powder as a photosensitizer as well as a catalyst for the dinitrogen reduction under the irradiation of UV or sunlight (Figure 1.29) [581]. Typical titanium dioxide materials are known to absorb UV light to give a bandgap of 3.0–3.2 eV, where the valence band at around +3 V vs. NHE (normal hydrogen electrode) is positive enough to oxidize water, whereas the conductance band edge at -0.2 to +0.1 V vs. NHE is



**Figure 1.29** Photoinduced reduction of dinitrogen and oxidation of water to afford ammonia, hydrazine, and dioxygen.

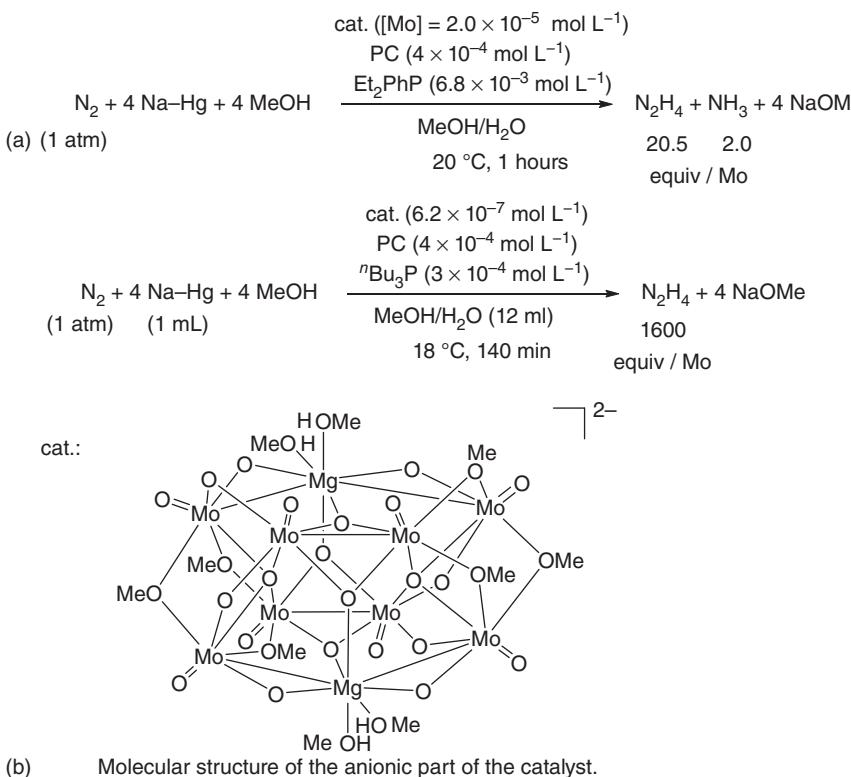
comparable to or slightly negative than the theoretical reduction potential of dinitrogen into ammonia (Figure 1.28) [22, 582, 583]. Since then, several works have been reported for the photochemical reduction of dinitrogen into ammonia or hydrazine using transition metal compounds [534, 584–598] or nonmetal compounds as catalysts [599, 600], where decomposition of ammonia to give dinitrogen is sometimes rather preferred, and yields of dinitrogen and hydrazine are still low [601, 602]. Photoinduced catalytic conversion of dinitrogen into ammonia can be achieved in combination of catalytic water oxidation and catalytic dinitrogen fixation [603]. As already shown in Figure 1.22b,c, direct photolytic splitting of dinitrogen to nitrides [255, 256, 409, 427, 428, 431, 435] has been clarified, which may be the key route to realize photosynthesis of ammonia from dinitrogen [449].

## 1.6 Catalytic Conversion of Dinitrogen into Ammonia Using Transition Metal Complexes

### 1.6.1 Catalytic Formation of Ammonia or Hydrazine Using Molybdenum Complexes

Early examples of catalytic conversion of dinitrogen or hydrazine in solution by using transition metal complexes were reported by groups of Vol'pin [314] and Shilov [318], although the reactions required higher temperatures or higher pressures. Catalytic conversion of dinitrogen into hydrazine under ambient reaction conditions (atmospheric pressure and room temperature) was first reported by Shilov and coworkers, who obtained 20.5 equiv of hydrazine and 2.0 equiv of ammonia based on the molybdenum atom of the polynuclear mixed valence Mo(V)–Mo(VI) molybdenum–magnesium complex as a catalyst, when the reaction was carried out in the presence of sodium amalgam, L- $\alpha$ -dipalmitoylphosphatidylcholine (PC), Et<sub>2</sub>PhP, and the catalyst at room temperature under 1 atm of dinitrogen (Figure 1.30a) [474]. The structure of the catalyst was later identified as the anionic octanuclear molybdenum complex [Mg(MeOH)<sub>6</sub>]<sub>2</sub>[Mg<sub>2</sub>Mo<sub>8</sub>O<sub>22</sub>(OMe)<sub>6</sub>(MeOH)<sub>4</sub>]·6MeOH [604, 605], where up to 1600 equiv of hydrazine based on the molybdenum atom was reported to be obtained when the reaction was carried out in the presence of sodium amalgam, PC,  $^7\text{Bu}_3\text{P}$ , and the catalyst at room temperature under 1 atm of dinitrogen (Figure 1.30b) [475]. Ammonia was also reported to be formed together with hydrazine in the case of Figure 1.30b, although the precise amount ammonia was not reported in later papers [475, 606–610].

Catalytic reduction of dinitrogen into ammonia under ambient reaction conditions by using transition metal–dinitrogen complex as a catalyst was first



**Figure 1.30** Catalytic formation of ammonia or hydrazine under ambient reaction conditions using anionic octanuclear molybdenum complex as a catalyst.

reported in 2003 by Yandulov and Schrock, who used decamethylchromocene ( $\text{CrCp}_2^*$ ) as a reducing agent and 2,6-lutidinium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate ( $[\text{LutH}]^+\text{BAr}_4^-$ ) as a proton source to afford 7.56 equiv of ammonia based on the molybdenum dinitrogen complex bearing a tetradentate hexaisopropylterphenyl (HIPT)-substituted triamidoamine ligand, or in 63% yield based on  $\text{CrCp}_2^*$  (Figure 1.31) [471]. Reactive intermediates such as diazenido, nitrido, ammonia, and hydrido complexes have also been isolated, where almost the same catalytic activities are reproduced (c. 8 equiv of ammonia based on the molybdenum atom of the catalyst, corresponding to 63–66% yield based on  $\text{CrCp}_2^*$ ) (Figure 1.31) [471, 611–614], whereas analogous dinitrogen, imido, and nitrido complexes of vanadium, chromium, and tungsten have only given stoichiometric amounts of ammonia [370, 615, 616]. On the other hand, similar molybdenum complexes bearing tetradentate triamidoamine ligands with different substituents on the amido nitrogen atoms have shown less catalytic activities [471, 613, 617–619], whereas some nitrido complexes have shown catalytic activities comparable to those of the molybdenum complexes bearing HIPT-substituted triamidoamine ligands (Figure 1.31) [613].

Both experimental and theoretical studies have confirmed the reaction pathway of the catalytic transformation of dinitrogen toward ammonia, which is called

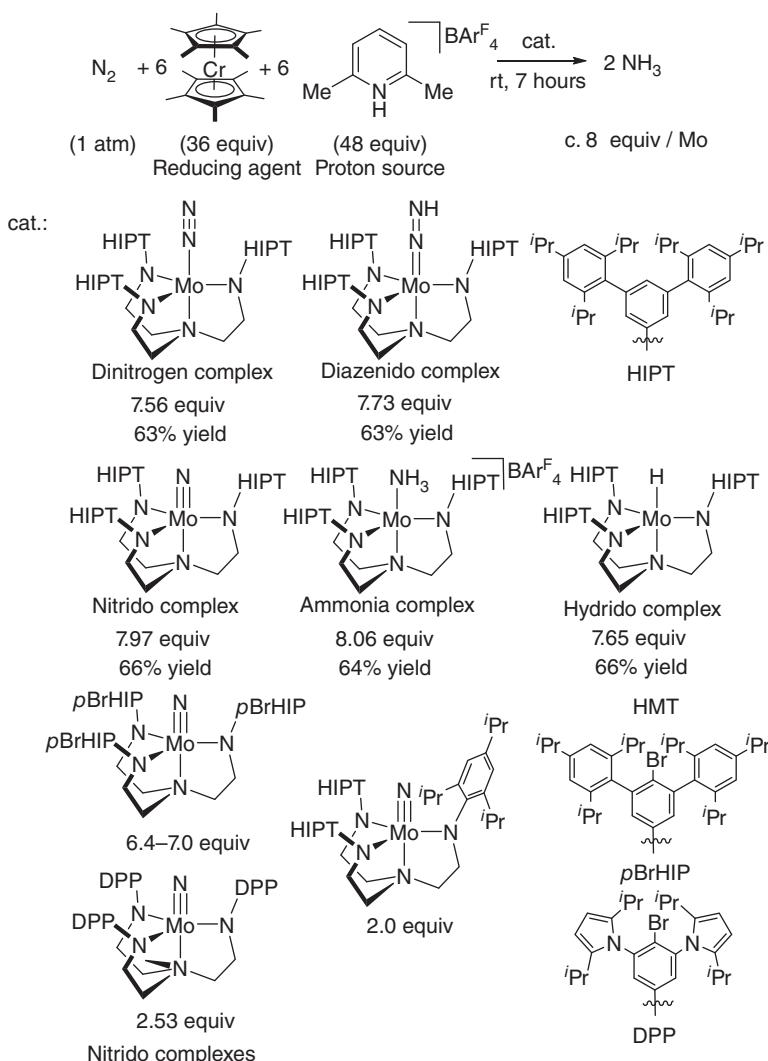
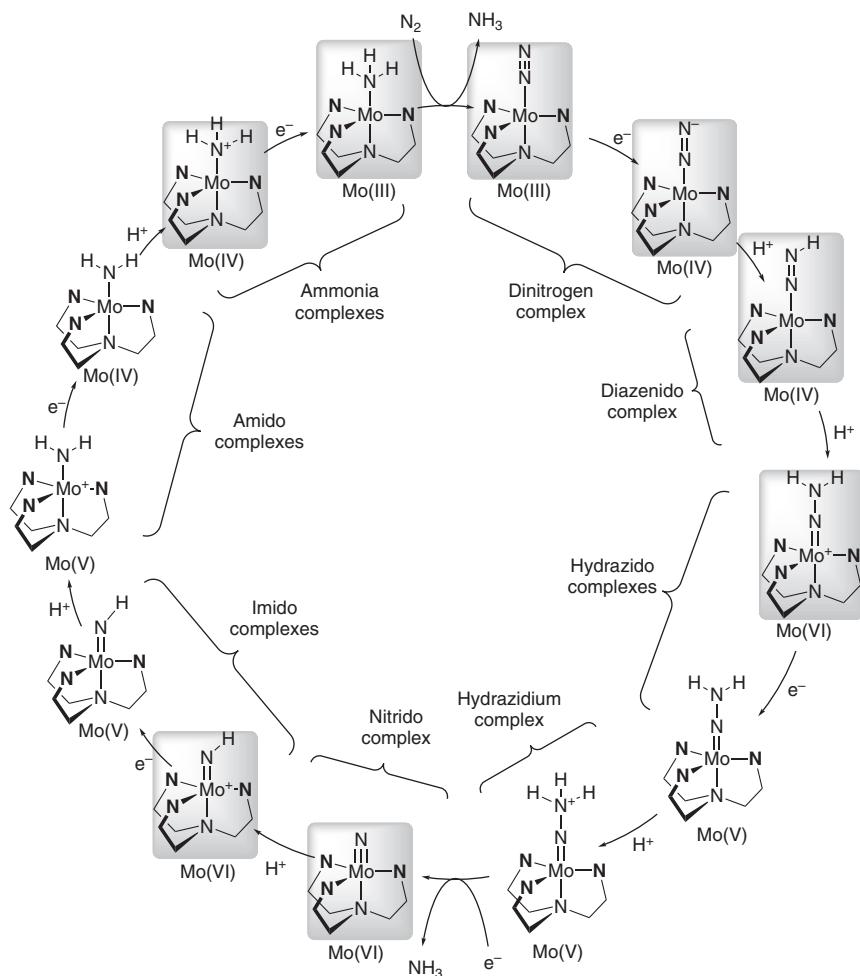


Figure 1.31 Catalytic nitrogen fixation using Schrock's catalysts.

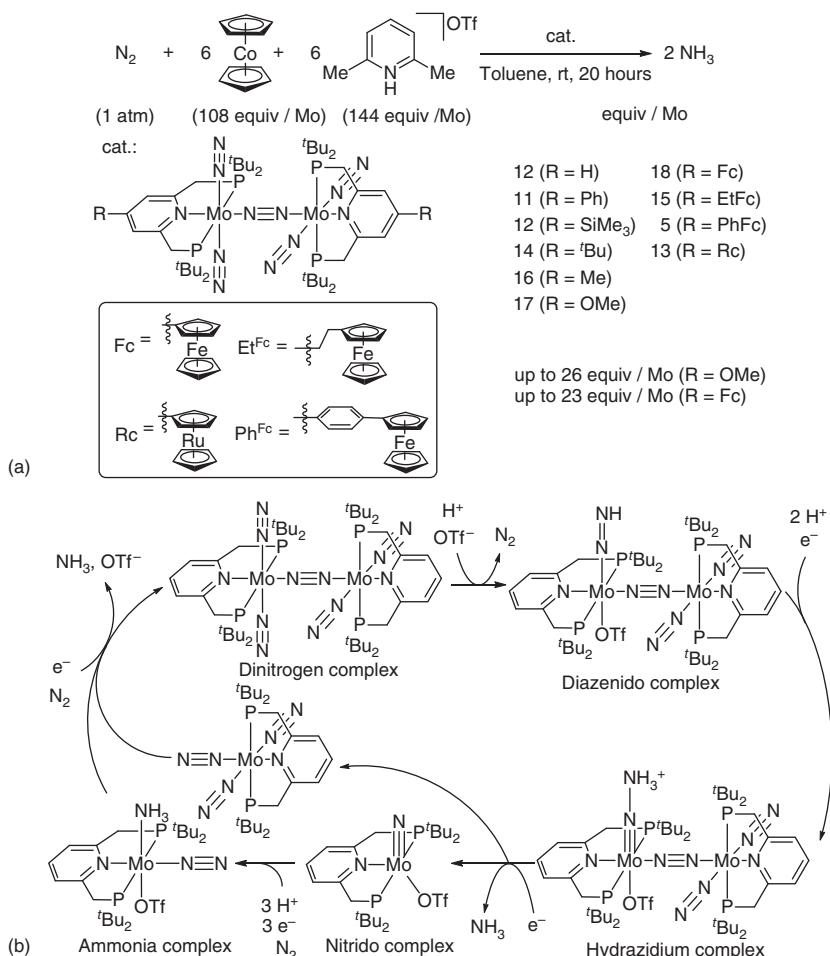
“Schrock cycle,” where the addition of protons and electrons occurs stepwise in the “distal” way to release 2 M amount of ammonia molecules with the retention of higher oxidation states of the molybdenum center (Figure 1.32) [471, 611, 612, 614, 620–622].

The second example of the catalytic formation of ammonia by using transition metal–dinitrogen complexes has been reported in 2010 by Nishibayashi and coworkers, who obtained 12 equiv of ammonia based on the Mo atom of the dinitrogen-bridged dimolybdenum–dinitrogen complex bearing a tridentate PNP-type pincer ligand  $[\{Mo(N_2)_2(^tBuPNP)\}_2(\mu\text{-}N_2)]$  ( $^tBuPNP = 2,6\text{-bis}[(\text{di-}tert\text{-butylphosphino)methyl]pyridine}$ ) on treatment with cobaltocene ( $CoCp_2$ ) as a reducing agent and 2,6-lutidinium trifluoromethanesulfonate



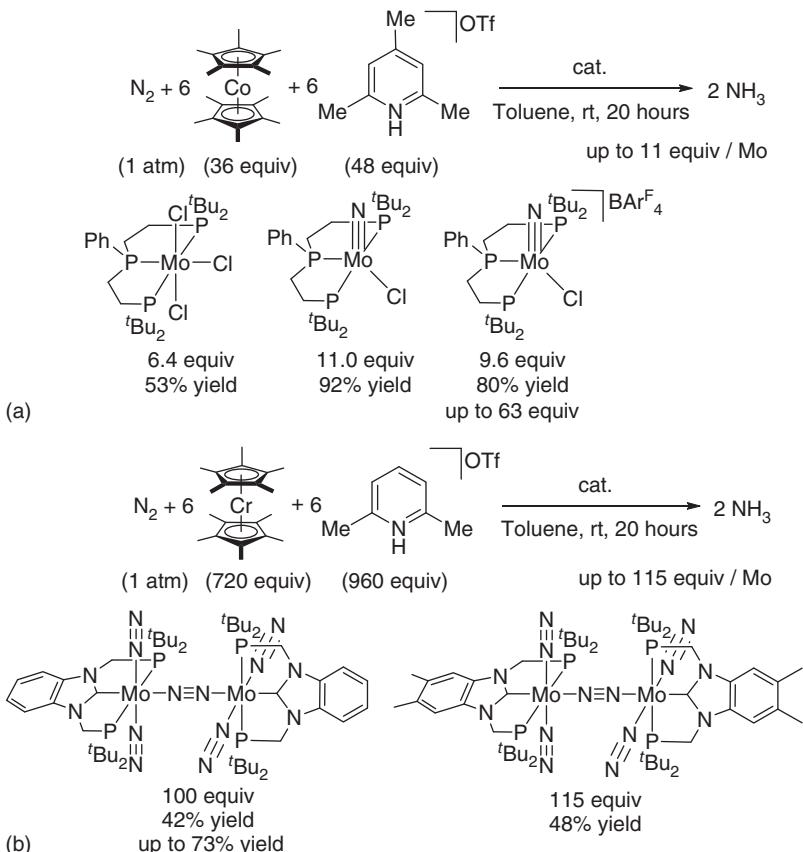
**Figure 1.32** Proposed Schrock cycle for the catalytic formation of ammonia. Compounds shown on light gray backgrounds are isolated or spectroscopically observed intermediates.

([LutH]OTf) as a proton source in the presence of the catalyst at room temperature for 20 hours under the atmospheric pressure of dinitrogen, where the yield of ammonia was 49% based on the amount of  $\text{CoCp}_2$  (Figure 1.33a) [472]. Introduction of electron-donating groups at the 4-position of the pyridine ring of the PNP-type pincer ligands has increased the catalytic activity where up to 26 equiv of ammonia has been obtained based on the molybdenum atom when methoxy group is introduced to the 4-position of the pyridine ring [623], whereas introduction of ferrocenyl or ruthenocenyl moieties has also been effective (Figure 1.33a) [624]. Changing substituents on the phosphorous atom, for example, introduction of adamantly (Ad) group instead of *tert*-butyl group to the phosphorous atom, has been less effective [625], whereas the corresponding complex of tungsten [626], dinitrogen-bridged tetrachloride complex [627], or



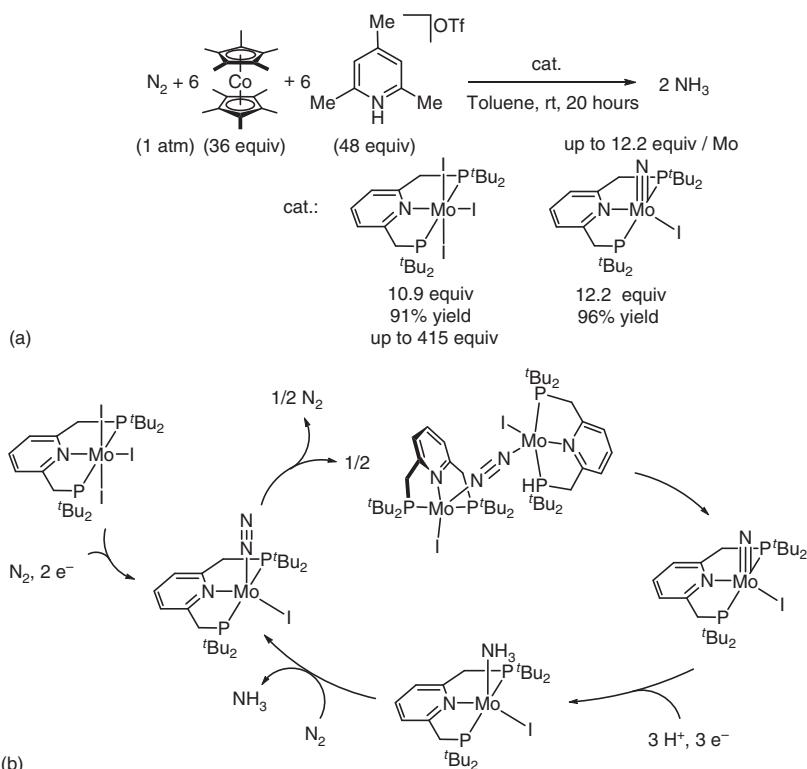
**Figure 1.33** (a) Catalytic formation of ammonia using dinitrogen-bridged dimolybdenum-dinitrogen complexes as catalysts and (b) its proposed catalytic reaction pathway.

the corresponding molybdenum complex with the analogous pincer-type ligand containing arsenic [628] has not worked as catalysts. The hydrazido complex obtained by stoichiometric protonation of the dinitrogen complex also has not worked as a catalyst for the reduction of dinitrogen to afford ammonia [626], whereas several nitrido complexes have worked as catalysts [629, 630]. Based on the experimental results and DFT calculations, a catalytic cycle during which the structure of dinitrogen-bridged core is maintained for the protonation of terminally coordinated dinitrogen and reduction of the molybdenum center to afford 1 M amount of ammonia and the corresponding nitrido complex, which is further protonated and reduced to afford ammonia and the starting dinitrogen-bridged dimolybdenum-dinitrogen complex via ligand exchange of ammonia with dinitrogen (Figure 1.33b) [629, 631, 632].



**Figure 1.34** Catalytic formation of ammonia using molybdenum complexes with (a) PPP-type or (b) PCP-type pincer ligands.

Ligation of PNNNP-, PNN-, or PNP-type pincer ligands to the molybdenum moieties has failed to reduce dinitrogen catalytically [630, 633], whereas the molybdenum nitrido complexes with PPP-type pincer ligands (Figure 1.34a) [634] or the dinitrogen-bridged dimolybdenum–dinitrogen complexes with N-heterocyclic carbene-based PCP-type pincer ligands (Figure 1.34b) [635] have been successful, where up to 63 or 115 equiv of ammonia is obtained based on the molybdenum atom of the catalyst, respectively. Furthermore, the molybdenum iodide complexes bearing a PNP-type pincer ligand have been found to have higher catalytic activities than the corresponding dinitrogen complexes, where up to 415 equiv of ammonia is produced based on the molybdenum atom of the catalyst (Figure 1.35a) [636]. Experimental details and DFT calculations have suggested that the reaction pathway includes the formation of a dinitrogen-bridged dimolybdenum iodide complex, where the splitting of the bridging dinitrogen ligand occurs to afford the nitrido complex (Figure 1.35b) [636]. This is the first example of the catalytic conversion of



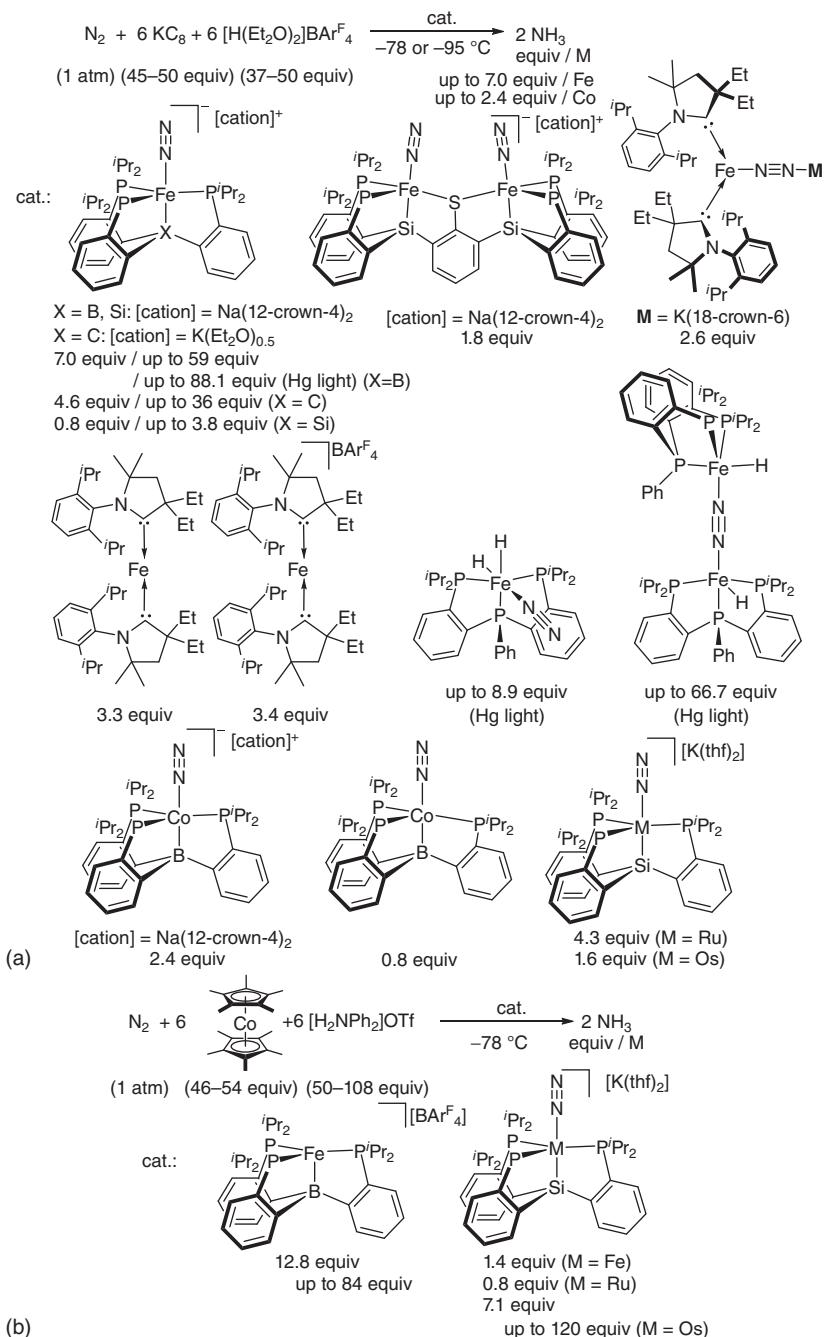
**Figure 1.35** (a) Catalytic formation of ammonia using dinitrogen-bridged dimolybdenum-dinitrogen complexes as catalysts and (b) its proposed catalytic reaction pathway.

molecular dinitrogen into ammonia via the direct cleavage of dinitrogen on a molecular catalyst as the key reaction step under ambient reaction conditions.

The molybdenum nitrido complex bearing pyridine- and diimido-based NNN-type pincer ligand has also been reported by Schrock and coworkers to work as a catalyst, where up to 10.3 equiv of ammonia is obtained based on the catalyst [637].

### 1.6.2 Catalytic Formation of Ammonia or Hydrazine Using Transition Metal Other than Molybdenum (Iron, Ruthenium, Osmium, Cobalt, and Vanadium) Complexes

In 2013, Peters and coworkers have reported the catalytic system producing ammonia by using iron–dinitrogen complexes as catalysts, where  $\text{KC}_8$  and the Brookhart's acid ( $[\text{H}(\text{OEt}_2)_2]\text{BAr}_4^{\text{F}}$ ) are employed as the reducing reagent and the proton source, respectively, to afford 7.0 equiv of ammonia based on the iron atom of the anionic iron–dinitrogen complex bearing a tris(phosphine)borane ligand used as the catalyst (Figure 1.36a) [473]. In order to prevent the formation of dihydrogen gas by the direct reaction of  $\text{KC}_8$  with Brookhart's acid, the reaction must be carried out at sufficiently low temperatures. The yield of



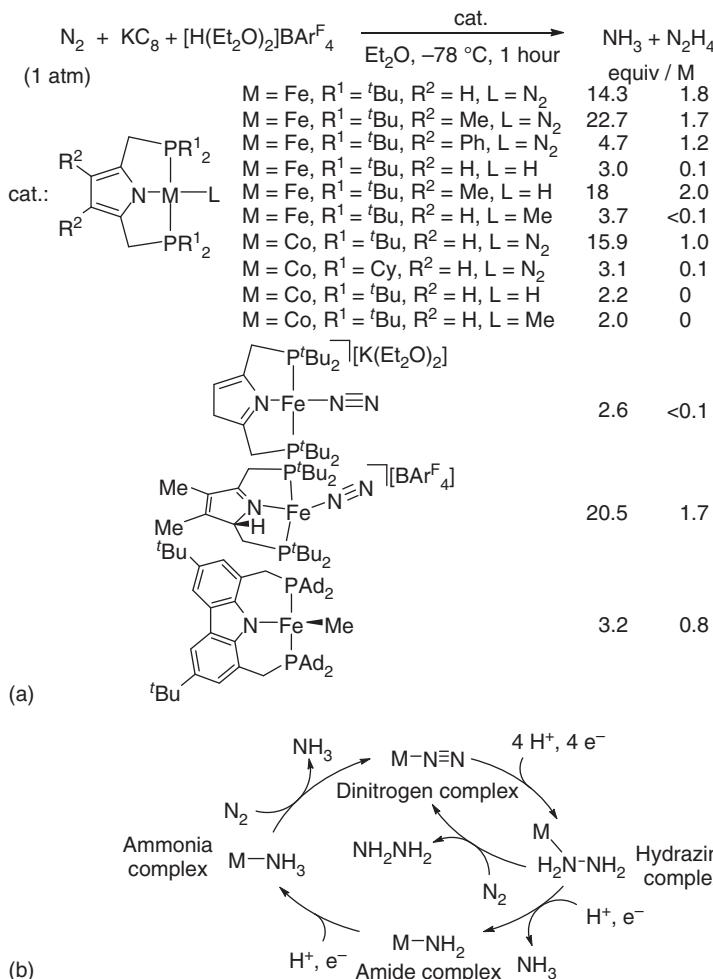
**Figure 1.36** Catalytic formation of ammonia using iron, ruthenium, osmium, and cobalt complexes by using (a) Brookhart's acid or (b) diphenylammonium trifluoromethanesulfonate as the proton source.

ammonia has been found to increase up to 59 equiv based on the iron atom with an estimate of the initial turnover frequency of  $1.2 \pm 0.1 \text{ min}^{-1}$  by increasing the amount of  $\text{KC}_8$  and the acid [638], or up to 88 equiv by further irradiation of UV light [639], whereas formation of catalytic amounts of ammonia has been found for other iron complexes [638–642], cobalt–dinitrogen complexes [643], or ruthenium– and osmium–dinitrogen complexes [644] as shown in Figure 1.36a. Spectroscopic observation and isolation of reaction intermediates or their derivatives lead to the conclusion that the conversion by using these iron complexes proceeds rather via the Chatt-type distal mechanism [645–649]. Switching the proton source from Brookhart’s acid to diphenylammonium trifluoromethanesulfonate has been effective especially for the osmium complex, where up to 120 equiv of ammonia has been obtained [644, 650].

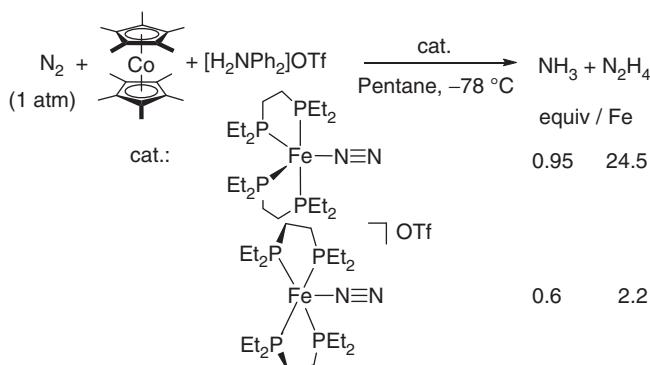
Catalytic formation of hydrazine in addition to ammonia has been recently reported by Nishibayashi and coworkers, up to 22.7 equiv of ammonia and 1.7 equiv of hydrazine, corresponding to 26.1 equiv of nitrogen atoms based on the iron atom of the iron–dinitrogen complex bearing the anionic pyrrole-based, PNP-type pincer ligand [651, 652] (Figure 1.37a). The cobalt–dinitrogen complex bearing the anionic pyrrole-based, PNP-type pincer ligand has also been found to be effective in fixing up to 17.9 equiv of nitrogen (15.9 equiv of ammonia and 1.0 equiv of hydrazine) based on the cobalt atom of the catalyst (Figure 1.37a) [653]. Several iron and cobalt complexes bearing anionic pyrrole-based, PNP-type pincer ligands or an anionic carbazole-based, PNP-type pincer ligand are active toward the catalytic fixation of dinitrogen into ammonia and hydrazine (Figure 1.37a) [651–654], whereas iron complexes bearing azaferrocene-based, PNP-type pincer ligands [655] or iron– and cobalt–dinitrogen complexes bearing PSiP-type pincer ligands [656] are not active toward the catalytic reduction of dinitrogen into ammonia or hydrazine. A catalytic cycle is proposed where alternating protonation at the distal and proximal positions of dinitrogen occurs to afford an intermediary hydrazine complex, where both hydrazine and ammonia can be produced (Figure 1.37b) [651].

More selective production of hydrazine has been recently achieved by Ashley and coworkers who have fixed up to 50 equiv of nitrogen atom in the forms of 0.95 equiv of ammonia and 24.5 equiv of hydrazine based on the iron atom, when  $\text{CoCp}_2^*$ , diphenylammonium trifluoromethanesulfonate, and the iron–dinitrogen complex  $[\text{Fe}(\text{N}_2)(\text{depe})_2]$  are employed as a reducing agent, a proton source, and a catalyst, respectively (Figure 1.38) [657]. Related iron complexes also give stoichiometric amounts of ammonia and hydrazine on treatment with acids, but not all of them work as catalysts [657, 658].

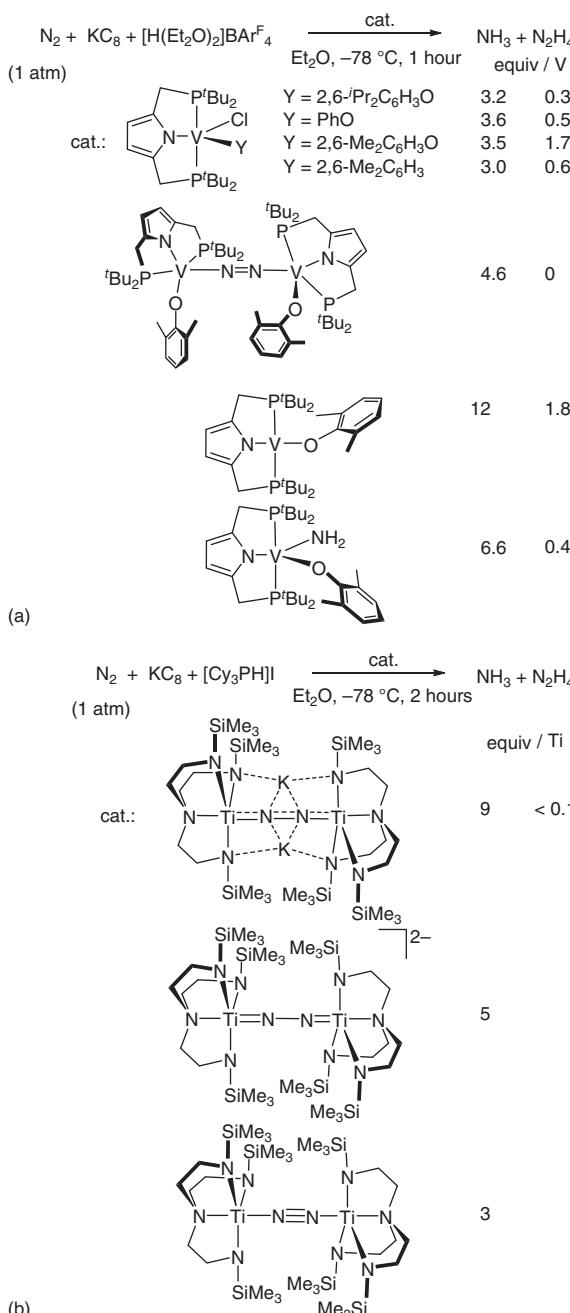
In addition to molybdenum– and late transition metal–dinitrogen complexes, earlier transition metal–dinitrogen complexes (vanadium and titanium) have been found to work as effective catalysts for the reduction of dinitrogen into ammonia [659, 660]. Indeed, Nishibayashi and coworkers have reported that up to 16 equiv of fixed nitrogen (12 equiv of ammonia and 1.8 equiv of hydrazine) has been obtained based on the vanadium atom of the catalyst, when a mononuclear vanadium complex bearing an anionic pyrrole-based, PNP-type pincer ligand and an aryloxy ligand in equilibrium with the formation of dinitrogen-bridged divanadium complex under atmospheric dinitrogen as a catalyst (Figure 1.39a) [659].



**Figure 1.37** (a) Catalytic formation of ammonia and hydrazine using iron and cobalt complexes and (b) proposed reaction mechanism for the formation of ammonia and hydrazine using iron or cobalt complexes as catalysts.



**Figure 1.38** Predominant formation of hydrazine using iron-dinitrogen complexes as catalysts.



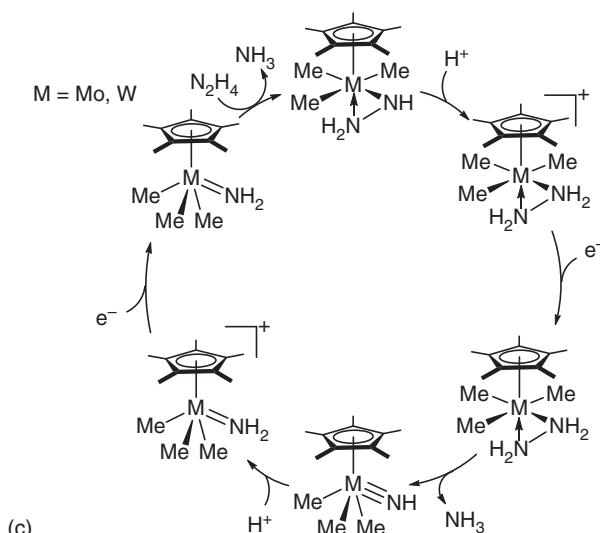
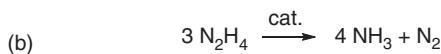
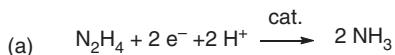
**Figure 1.39** Catalytic formation of ammonia and hydrazine using (a) vanadium or (b) titanium complexes.

On the other hand, catalytic reduction of dinitrogen into ammonia by using an anionic dinitrogen-bridged dititanium–dinitrogen complex bearing a tri-amidoamine ligand has been reported by Liddle and coworkers, who obtained up to 9 equiv of ammonia based on the titanium atom of the catalyst when phosphonium cation is employed as a proton source (Figure 1.39b) [660]. The

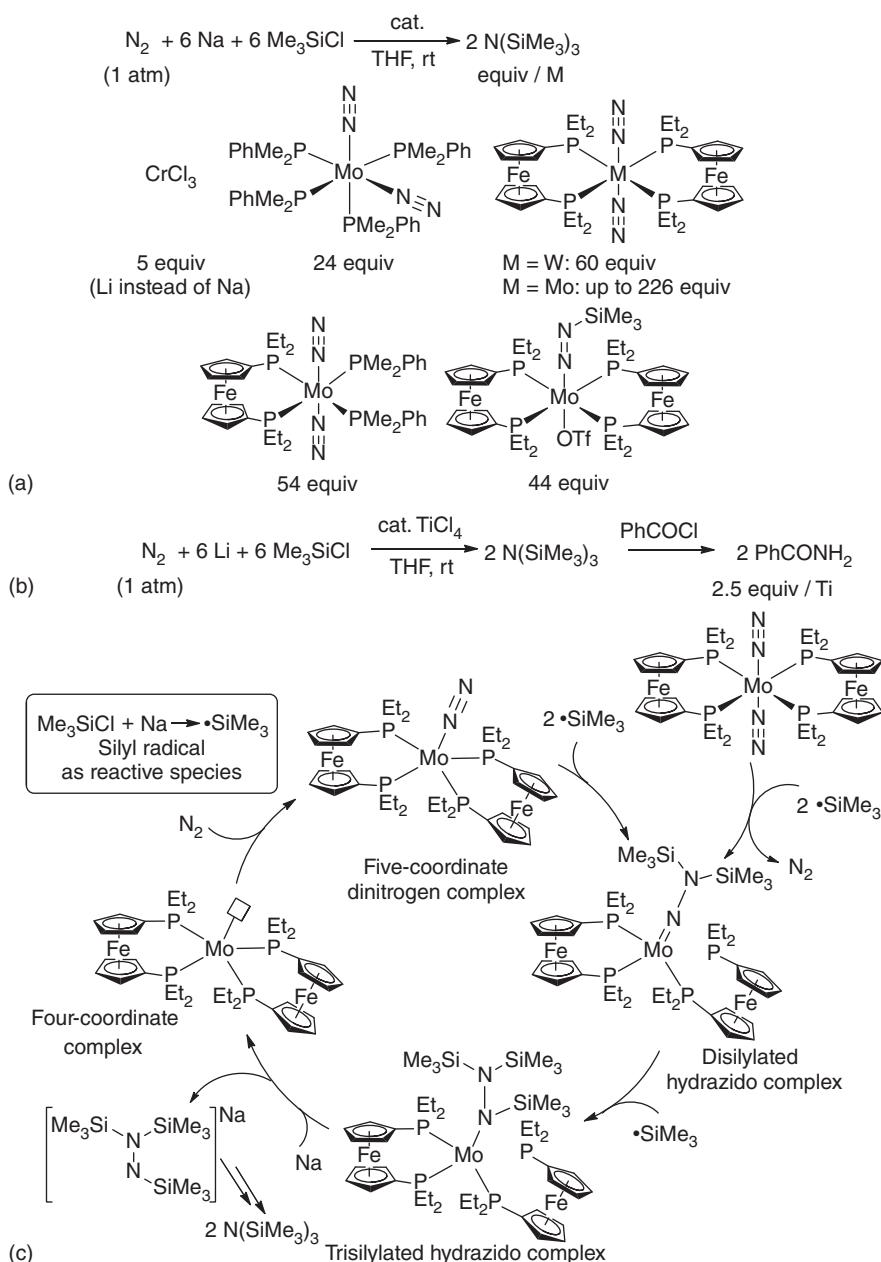
catalytic activity has also been investigated for vanadium–dinitrogen complexes bearing tetradentate triamidoamine ligands [661].

### 1.6.3 Catalytic Transformation of Hydrazine into Ammonia

Hydrazine is supposed to be the reactive intermediate for biological nitrogen fixation as well as the substrate for nitrogenase that converts hydrazine into ammonia [85, 86]. Ammonia can be formed either by the reduction of hydrazine (Figure 1.40a) or by disproportionation of hydrazine (Figure 1.40b), whereas several iron–molybdenum–sulfur clusters or similar cuboidal clusters prepared as the model compounds that mimic to FeMo-co have been found to work as catalysts to convert hydrazine into ammonia [662–670]. Dinuclear molybdenum [671, 672], iron [182, 673–677], or ruthenium [678, 679] complexes; heterobimetallic titanium–cobalt [680] or iron–ruthenium [681] complexes; or mononuclear vanadium [682], molybdenum [683–687], tungsten [683, 684, 688], iron [689, 690], or ruthenium [691, 692] complexes were also reported to act as catalysts for the decomposition of hydrazine into ammonia either reductively or disproportionately. An example of the catalytic reduction of hydrazine into ammonia reported by Schrock and coworkers is shown in Figure 1.40c, where stepwise protonation and reduction occur to afford 2 M amounts of ammonia [683, 684, 688].



**Figure 1.40** (a) Reduction of hydrazine into ammonia, (b) disproportionation of hydrazine into ammonia, and (c) an example of the proposed reduction pathway of hydrazine into ammonia for a mononuclear molybdenum or tungsten complex.

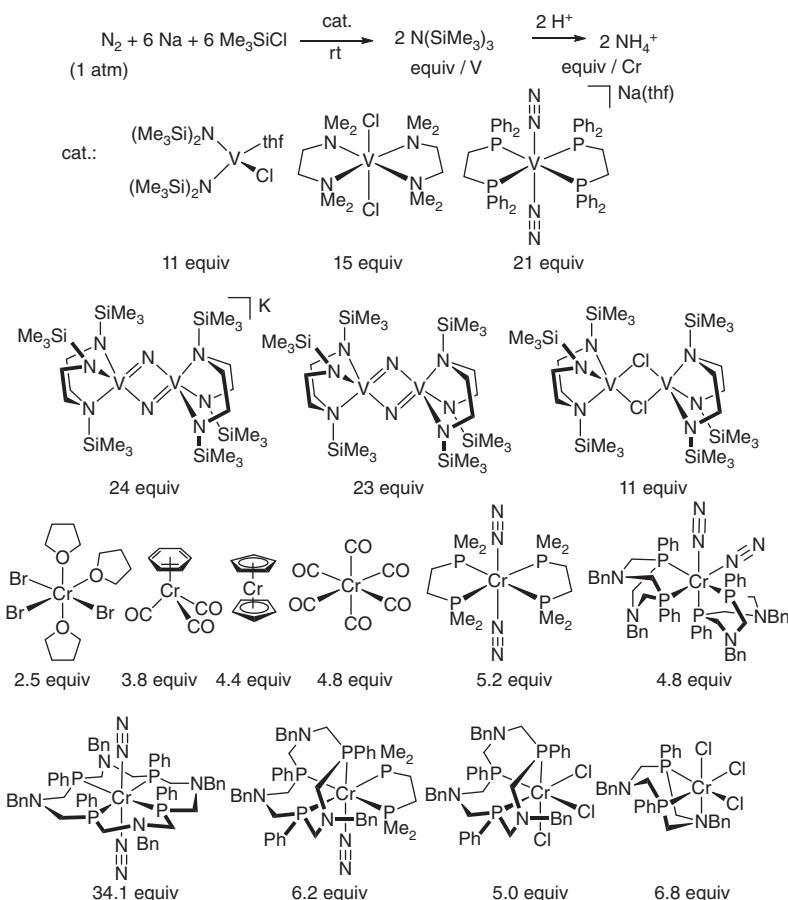


**Figure 1.41** Catalytic formation of silylamine from molecular dinitrogen (a) to afford ammonia after hydrolysis or (b) to afford benzamide via acylation. (c) An example of the proposed reaction pathway for the catalytic silylation of dinitrogen.

#### 1.6.4 Catalytic Formation of Silylamine

Catalytic formation of tris(trimethylsilyl)amine ( $\text{N}(\text{SiMe}_3)_3$ ) by the reductive silylation of molecular dinitrogen by trimethylsilyl chloride under ambient reaction conditions was first reported in 1972 by Shiina, who obtained  $\text{N}(\text{SiMe}_3)_3$  using lithium, trimethylsilyl chloride, and various transition metal compounds ( $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{FeCl}_3$ , or  $\text{CoCl}_3$ ) as a reducing agent, a silylation reagent, and a catalyst, respectively (Figure 1.41a) [476]. Later, Mori and coworkers have found that the titanium chloride ( $\text{TiCl}_4$ ) can also work as the catalyst (Figure 1.41b) [693, 694].  $\text{N}(\text{SiMe}_3)_3$  can be hydrolyzed to afford ammonia (Figure 1.41a) [477], or further acylated with benzoyl chloride to afford benzamide (Figure 1.41b) [693–700].

In 1989, Hidai and coworkers have found more effective catalytic formation of silylamine by using an isolated dinitrogen complex, where up to 24 equiv of silylamine is obtained based on the molybdenum–dinitrogen complex *cis*-[Mo(N<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>] (Figure 1.41a) [223, 477, 497–500]. A much more

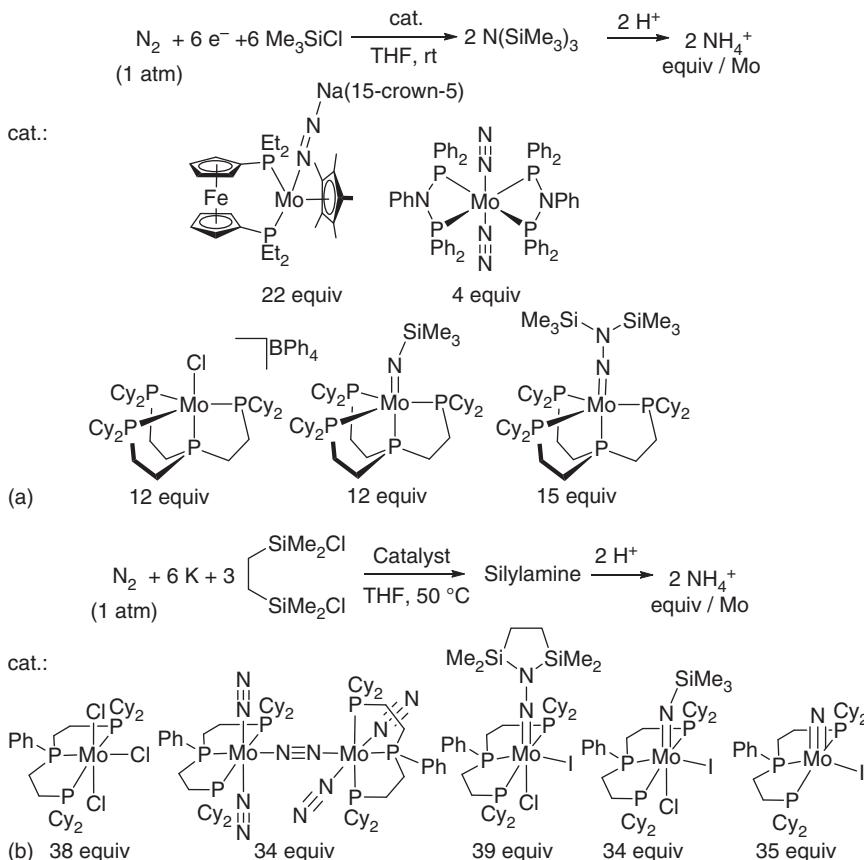


**Figure 1.42** Examples of catalytic silylation of dinitrogen into silylamine by using vanadium and chromium complexes.

effective catalytic system has been reported by Nishibayashi and coworkers for *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(depf)<sub>2</sub>] [701–703], where up to 226 equiv of ammonia is obtained based on the molybdenum atom of the catalyst [478] (Figure 1.41a). The catalytic cycle for the silylamine formation has been proposed based on the experimental details and DFT calculations as shown in Figure 1.41c [478].

Several catalytic systems to form silylamine via the silylation of dinitrogen by using transition metal complexes have now reported for this decade. For example, vanadium–dinitrogen complex or dinitrogen-derived nitrido-bridged divanadium complexes have been found to work as the catalysts for the formation of silylamine (Figure 1.42) [704]. For group 6 transition metal compounds, catalytic silylation of dinitrogen using chromium–dinitrogen complexes or their related compounds have been reported very recently (Figure 1.42) [705].

For molybdenum complexes, not only catalytic formation of silylamine via the silylation of dinitrogen by trimethylsilyl chloride (Figure 1.43a) [706–708]



**Figure 1.43** Examples of molybdenum-catalyzed silylation of dinitrogen into silylamines by using (a) trimethylsilyl chloride or (b) bis(chlorodimethylsilyl)methane.

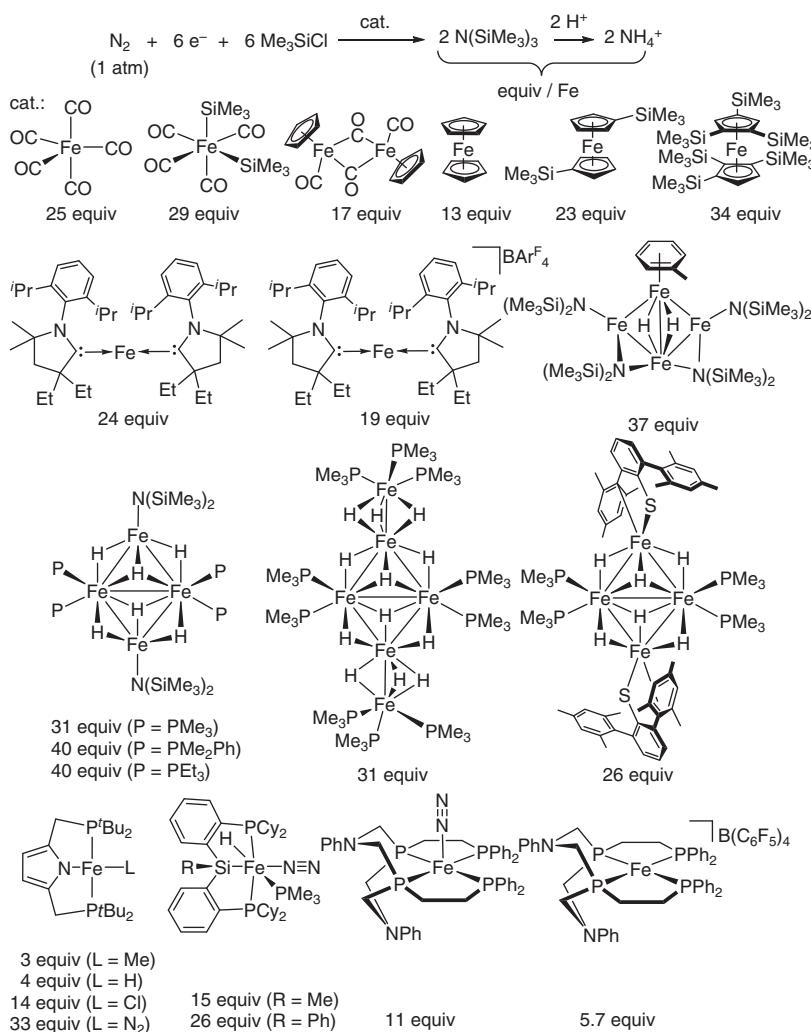


Figure 1.44 Examples of iron-catalyzed silylation of dinitrogen into silylamine.

but also catalytic formation of silylamine via the silylation of dinitrogen by 1,2-bis(chlorodimethylsilyl)methane has also been reported (Figure 1.43b) [709].

For the late transition metal complexes, several iron compounds including iron–dinitrogen complexes, ferrocenes, or iron carbonyl compounds are found to work as catalysts for the silylation of dinitrogen as shown in Figure 1.44 [479, 651, 656, 710–712].

Cobalt complexes also work as catalysts, where up to 200 equiv of ammonia has been obtained based on the cobalt atom of the catalyst after hydrolysis of the produced silylamine (Figure 1.45) [656, 713–716].

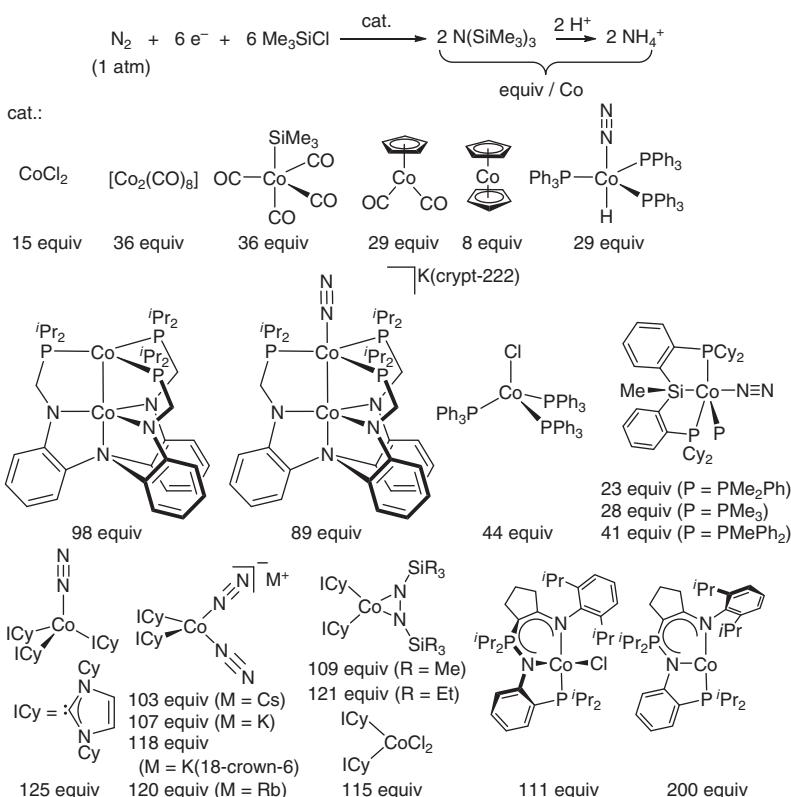


Figure 1.45 Examples of cobalt-catalyzed silylation of dinitrogen into silylamine.

## 1.7 Conclusion and Perspectives

It was more than a century ago that the Haber–Bosch process was industrially utilized [6–14] and has been still one of the most important chemical processes to fix atmospheric dinitrogen. However, this process requires dihydrogen mainly generated from fossil fuels; thus, utilization of water as a hydrogen source by using renewable energy has been expected from the viewpoint of resource protection and reduction of carbon dioxide emissions. At the same time, the Haber–Bosch process requires high pressure and temperature; thus, the miniaturization of reactors is problematic.

Ammonia attracts attention as a possible candidate for a hydrogen carrier in the near future nowadays, so it is important to develop more convenient preparation method of ammonia without using high-pressure and high-temperature reactors or gas cylinders in order to minimize the use of fossil fuels [45–49], although chemical nitrogen fixation using transition metal complexes under ambient reaction conditions still stands at the starting line for the development of more efficient catalysts. However, it cannot be too exaggerated to claim that the goal is not so far.

For example, one of the best turnover frequency observed for homogeneous catalytic formation of ammonia in solution under ambient reaction conditions is  $2\text{ min}^{-1}$  at  $-78^\circ\text{C}$  and 1 atm of dinitrogen by using an osmium–dinitrogen complex [644], whereas the molybdenum nitrogenases have exhibited a turnover frequency of approximately  $40\text{--}200\text{ min}^{-1}$  (or  $20\text{--}100\text{ min}^{-1}$  per FeMo-co) at  $23\text{--}30^\circ\text{C}$  and 1 atm of dinitrogen [84, 595, 717], nearly 2 orders of magnitude faster than that of the best homogeneous catalyst, and the ideal surface iron atom of the Haber–Bosch catalyst has exhibited a turnover frequency of approximately  $800\text{ min}^{-1}$  at  $525^\circ\text{C}$  and 20 atm of the mixture of dinitrogen and dihydrogen [30], one or more orders of magnitude faster than that of molybdenum nitrogenases.

On the other hand, one of the best turnover numbers observed for homogeneous catalytic reaction in solution under ambient reaction conditions is 415 equiv based on the catalyst at room temperature and 1 atm of dinitrogen by using a molybdenum complex [636]. One of the longest half-lives of molybdenum nitrogenases has been measured as long as 98 hours under anaerobic conditions in nitrogen-limited culture [718], corresponding to a turnover number of 2–3 orders of magnitude larger than that of the best homogeneous catalyst, whereas the half-lives of the molybdenum–iron proteins of molybdenum nitrogenases in aerobic conditions are as short as 10 minutes [719], corresponding to a turnover number of 1,000 or less per FeMo-co [84, 595, 720], approximately twice or comparable to the amount obtained by the best homogeneous catalyst.

Looking at these numerical values on catalyses, some solid progress to approach to the nitrogenase activities has been clearly made recently compared to the early days when the transition metal–dinitrogen complex was first discovered more than half a century ago. Catalytic nitrogen fixation under mild reaction conditions that is much more effective than that of nitrogenase or even comparable to that of the Haber–Bosch process shall be realized in the not so distant future.

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