Dinitrogen Fixation by Transition Metal Hydride Complexes

Takanori Shima and Zhaomin Hou

Abstract This chapter describes the activation of dinitrogen by various transition metal hydride complexes. A number of mononuclear transition metal hydride complexes can incorporate dinitrogen, but they are usually difficult to induce N–N bond cleavage. In contrast, multimetallic hydride complexes can split and hydrogenate dinitrogen through cooperation of the multiple metal hydrides. In this transformation, the hydride ligands serve as the source of both electron and proton, thus enabling the cleavage and hydrogenation of dinitrogen without extra reducing agents and proton sources. Generally, the reactivity of the metal hydride complexes is significantly influenced by their composition (nuclearity) and metal/ligand combination.

**Keywords** Dinitrogen cleavage • Hydride • Hydrogenation • Multimetallic • Nitride

Contents

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1   Introduction

Dinitrogen (N_2) is an abundant and easily accessible resource, which occupies about 78% of Earth's atmosphere. However, N_2 molecule is chemically inert under ordinary conditions due to its strong N–N triple bond (944.84 ± 0.10 kJ/mol) [1], large HOMO-LUMO energy gap (10.82 eV) [2], and nonpolarity. Certain microbial organisms can reduce N_2 to NH_3 by using nitrogenase enzymes at ambient temperature and pressure. This process consumes eight protons (H^+) and eight electrons (e^-) to convert one molecule of N_2 to two molecules of NH_3 with release of one molecule of H_2. Recent studies revealed that the multiple metal centers having two hydrides and two sulfur-bound protons in the iron–molybdenum cofactor play a key role to promote H_2 release and N_2 reduction (Scheme 1a) [3–6]. However, the biological ammonia synthesis is not yet well understood and is difficult to mimic artificially. Industrially, ammonia is produced from N_2 and H_2 by the Haber–Bosch process under relatively harsh conditions (350~550°C, 150~350 atm) to activate N_2 on the solid catalyst surface. It was proposed that the reaction is initiated by dissociative absorption of N_2 and H_2 on low valent multiple iron metal sites to form metal hydrides and nitrides, followed by reversible hydrogenation of the nitride species to provide NH_3 (Scheme 1b) [7–11]. Both the biological and the Haber–Bosch processes are thought to take place through the cooperation of multiple metal sites bearing hydride ligands.
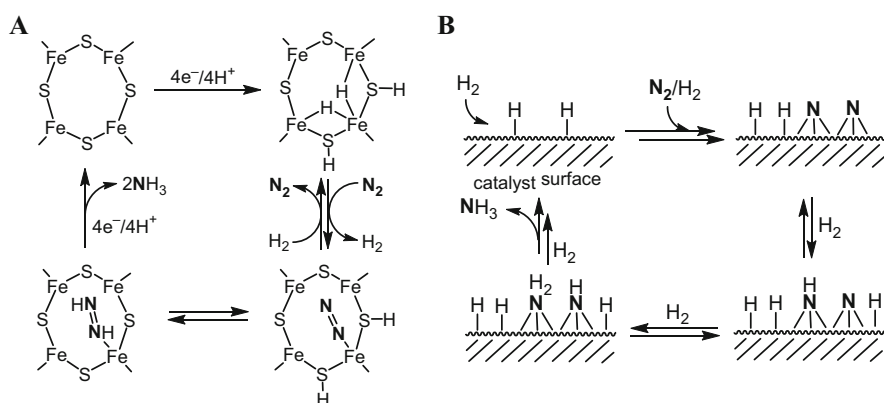

Scheme 1 Proposed pathways for catalytic ammonia formation by (**a**) nitrogenase enzyme (only the core structure is shown) and (**b**) the Haber–Bosch process (only part of the catalyst surface is shown)

In order to further explore the mechanism of N_2 reduction at the molecular level and thereby develop milder chemical processes for ammonia synthesis, extensive studies on the activation of N_2 with organometallic complexes have been carried out over the past decades [12]. As model reactions of the enzyme process, the use of strong metal reducing agents as an electron source in combination with transition metal complexes has been extensively studied, and the catalytic transformation of N_2 to ammonia has been achieved at ambient temperature and pressure by using carefully designed proton sources [13–15]. An alternative approach is the activation of N_2 by transition metal hydrides without the use of extra reducing agents or proton sources [16]. This approach is of particular interest, in view of the fact that both the biological and the industrial Haber–Bosch processes may involve metal hydrides as true active catalyst species. This chapter focuses on the activation and functionalization of N_2 by transition metal hydride complexes.

2 Dinitrogen Complexes Derived from Mononuclear Transition Metal Hydride Complexes

2.1 Group 9 Transition Metal Hydrides

The first dinitrogen complex $[(NH_3)_5Ru(N_2)]^{2+}$ was obtained serendipitously from the reaction of a ruthenium trichloride with hydrazine hydrate in 1965 [17]. Shortly after this discovery, the N_2-derived end-on coordinated cobalt dinitrogen complex $[(Ph_3P)_3Co(N_2)H]$ (**1**) was synthesized from the reaction of a cobalt acetylacetonate, diethylaluminium monoethoxide, and triphenylphosphine ligands in the presence of N_2 gas (Scheme 2) [18]. When **1** was kept under an atmosphere of H_2, the coordinated N_2 ligand was displaced by H_2 to afford the cobalt hydride complex $[(Ph_3P)_3CoH_3]$ (**2**) [19]. Complex **2** could also be prepared by the reaction of $[CoX_2(PPh_3)_2]$ (X = Cl, Br, I) with borohydride in the presence of H_2 and free PPh_3, and the reaction of **2** with N_2 easily took place to give **1** (Scheme 2) [20]. Thus, the hydrogenation/dinitrogen coordination reactions are reversible.
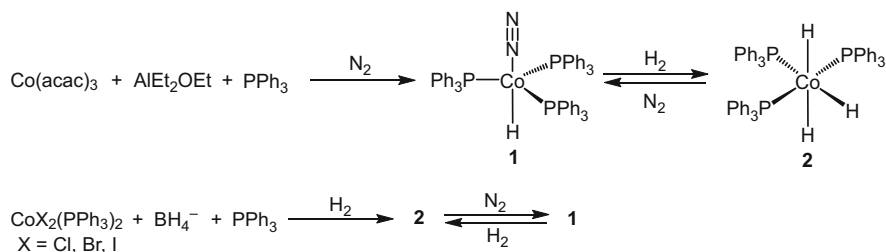
Scheme 2 Synthesis and reversible hydrogenation of the cobalt dinitrogen complex **1**
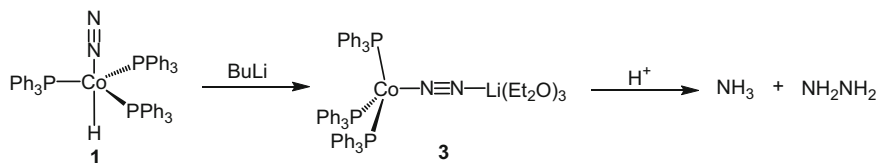
**Scheme 3** Protonation of the cobalt dinitrogen complex **1**
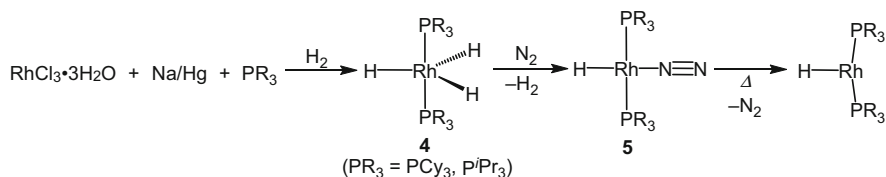
Scheme 4 Synthesis of the rhodium dinitrogen complex **5**

The reaction of **1** with MgEt$_2$, BuLi, or Na metal afforded the N$_2$-bridged hetero-bimetallic complex, [{(Ph$_3$P)$_3$Co(μ-N$_2$)}$_2$Mg(THF)$_4$], [(Ph$_3$P)$_3$Co(μ-N$_2$)Li(Et$_2$O)$_3$] (**3**), or [(Ph$_3$P)$_3$Co(μ-N$_2$)Na(THF)$_3$], respectively [21]. While the coordinated N$_2$ ligand in **1** is unable to react with protic acids, the coordinated N$_2$ ligand in the electron-rich heterobimetallic complexes such as **3** gives 20–30% of hydrazine and ammonia by addition of H$_2$SO$_4$ or HCl (Scheme 3). However, reaction of the Co-N$_2$-Li complex **3** with H$_2$ afforded an analogous hydrogen complex Co-H$_2$-Li, with quantitative evolution of N$_2$. Upon exposure to an N$_2$ atmosphere, the hydrogen complex Co-H$_2$-Li released H$_2$, and regenerated **3**, demonstrating the reversibility of the coordination of H$_2$ and N$_2$ to the Ph$_3$P-Co-Li moiety.

With regard to other group 9 metals, the reduction of RhCl$_3$·3H$_2$O with Na/Hg in the presence of sterically demanding phosphines and H$_2$ afforded the hydride complexes [(R$_3$P)$_2$RhH$_3$] (**4**) (R = Cy, ^{i}Pr), which upon reaction with N$_2$ gave the end-on coordinated dinitrogen/hydride complexes [(R$_3$P)RhH(N$_2$)] (**5**) (Scheme 4) [22, 23]. The dinitrogen ligands in these compounds were weakly activated and could readily be released by gentle heating.

2.2 Group 8 Transition Metal Hydrides

The iron hydride complexes [FeH$_2$(H$_2$)(PR$_3$)$_3$] (**6**, PR$_3$ = PEtPh$_2$, PBuPh$_2$), which were prepared by treating FeCl$_2$ with PR$_3$ and NaBH$_4$ under an H$_2$ atmosphere, could incorporate atmospheric nitrogen to give the end-on coordinated dinitrogen complexes [FeH$_2$(N$_2$)(PR$_3$)$_3$] (**7**) in an irreversible way (Scheme 5) [24–27]. Complex **7** released N$_2$ when heated under vacuum or upon addition of I$_2$, HCl, or CO.
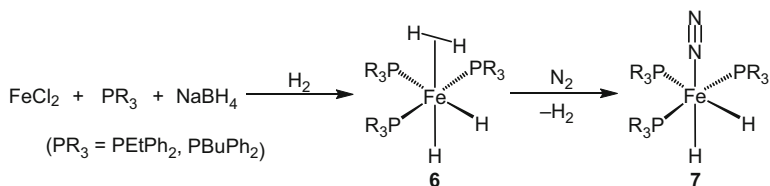
Scheme 5 Synthesis and dinitrogen coordination of the iron hydride complex **6**
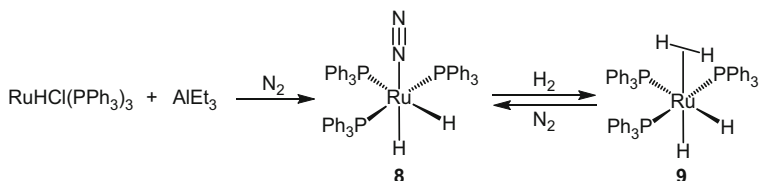

**Scheme 6** Synthesis and hydrogenation of the ruthenium dinitrogen complex **8**

The ruthenium dinitrogen compound $[RuH_2(N_2)(PPh_3)_3]$ (**8**) was obtained from the reaction of $[RuHCl(PPh_3)_3]$ [28] with $AlEt_3$ under an N_2 atmosphere (Scheme 6) [29]. Treatment of **8** with H_2 gave the corresponding dihydride/dihydrogen complex $[RuH_2(H_2)(PPh_3)_3]$ (**9**). This conversion was readily reversed by exposing **9** to N_2. It is worth noting that the reactions of $[RuH_2(PPh_3)_4]$ with N_2 and H_2 did not afford isolable **8** and **9** due to the presence of the dissociated free PPh_3 ligand [30]. The ruthenium dinitrogen complexes bearing sterically demanding phosphines [31], [PNP] pincer ligand [32], and tris(pyrazolyl)borate ligand [33], were also synthesized from the corresponding hydrogen complexes with N_2.

The reaction of $[FeCl_2(dmpe)_2]$ (**10**) bearing the bidentate dmpe (bis(dimethylphosphino)ethane) ligand with sodium borohydride ($NaBH_4$) afforded the hydride complex $[FeH(H_2)(dmpe)_2]^+$ (**11**) in high yield (Scheme 7) [34]. Complex **11** reacted with N_2 to give an end-on coordinated dinitrogen complex $[FeH(N_2)(dmpe)_2]^+$ (**12**). Deprotonation of **12** by KO^tBu provided an unstable iron (0) complex $[Fe(N_2)(dmpe)_2]$ (**13**). Treatment of **13** with HCl yielded ammonia (12%) and the chloride complex **10** (80%) with release of N_2 and H_2 [35–37]. The dichloride complex **10** could serve as a precursor to the hydride complex, and therefore, a synthetic cycle for the transformation of N_2 to ammonia could be realized.

Hydrogenolysis of an iron chloride complex bearing the bidentate 1,2-bis(bis(methoxypropyl)phosphino)ethane ligands with H_2 gave the corresponding hydride/dihydrogen complex **14** (Scheme 8) [38]. The H_2 ligand in **14** could be substituted by N_2, quantitatively affording the dinitrogen complex **15**. The reaction with KO^tBu yielded a neutral Fe(0) complex **16**. Protonation of **16** with triflic acid produced NH_4^+ (15%) and trace $N_2H_5^+$ (2%), but did not give a characterizable iron complex [39].
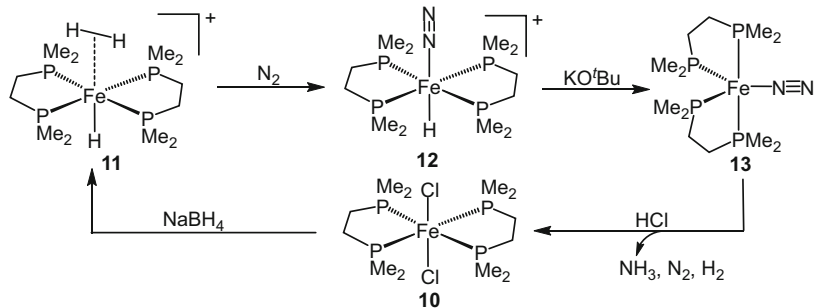
**Scheme 7** A synthetic cycle for transformation of dinitrogen to ammonia by the iron complexes **10–13**
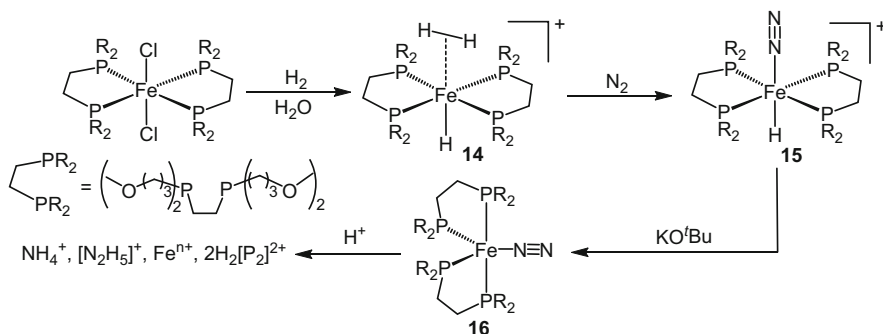
**Scheme 8** Dinitrogen activation by the iron hydride complex **14**

2.3 Group 7 Transition Metal Hydrides

Addition of $LiAlH_4$ to a suspension of $[MnBr_2(dmpe)_2]$ followed by hydrolysis with water afforded the hydride complex $[MnH(H_2)(dmpe)_2]$ (**17**) (Scheme 9) [40]. Complex **17** readily reacted with N_2 to give the corresponding end-on coordinated dinitrogen complex $[MnH(N_2)(dmpe)_2]$ (**18**) [41]. Half-sandwich manganase dihydride complex $[(C_5H_5)MnH_2(dfepe)]$ (dfepe = diperfluoroethylphosphinoethane) with N_2 afforded a binuclear end-on coordinated dinitrogen complex $[(C_5H_5)Mn(dfepe)]_2(N_2)$ via the formation of a mononuclear dinitrogen complex $[(C_5H_5)Mn(N_2)(dfepe)]$ [42].

The rhenium dinitrogen complex $[ReH(N_2)(dmpe)_2]$ (**20**) was obtained from the reaction of the nonahydride complex $[NEt_4]_2[ReH_9]$ (**19**) [43] with dppe (dppe = 1,2-bis(diphenylphosphino)ethane) under an N_2 atmosphere (Scheme 10) [44]. In contrast, the reactions of monodentate tertiary phosphines with **19** in an N_2 atmosphere gave only the hydride complexes. The dinitrogen complex **20** was readily protonated at the metal center by HBF_4 to form the cationic dihydro dinitrogen rhenium complex $[ReH_2(N_2)(dmpe)_2]BF_4$, while protonation at the N_2 ligand was not observed.
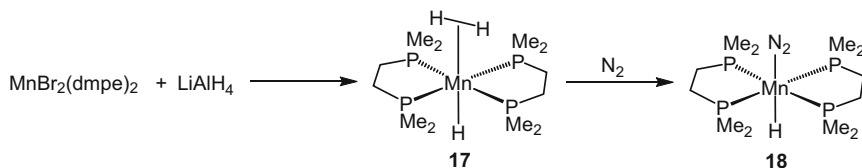
**Scheme 9** Synthesis of the manganese hydride complex **17** and its reaction with N_2
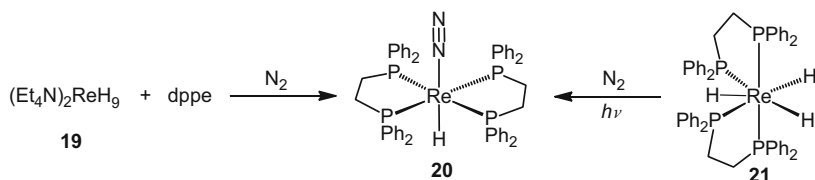
Scheme 10 Synthesis of the rhenium dinitrogen complex **19** from the reactions of rhenium hydride complexes with N_2

Synthesis of the dinitrogen complex **20** by photolysis of the trihydride complex [ReH$_3$(dmpe)$_2$] (**21**) with UV light in an N_2 atmosphere was also reported [45].

2.4 Group 6 Transition Metal Hydrides

The molybdenum and tungsten hydride complexes having bidentate phosphine ligands [MH$_4$(dppe)$_2$] (M = Mo (**22**), W) were obtained from the reactions of the chloride precursors [MCl$_4$(dppe)] and excess of dppe ligand with NaBH$_4$ [46, 47]. Photolysis of [MoH$_4$(dppe)$_2$] (**22**) with UV light gave an end-on coordinated dinitrogen complex [Mo(N$_2$)$_2$(dppe)$_2$] (**23**) in high yield (Scheme 11) [48], while irradiation of [MH$_4$(dppe)$_2$] (M = Mo, W) with γ-ray gave the dinitrogen complexes [M(N$_2$)$_2$(dppe)$_2$] together with ammonia and hydrazine [49–51]. Hydrogenolysis of [Mo(N$_2$)$_2$(dppe)$_2$] (**23**) with H$_2$ regenerated the tetrahydride complex [MoH$_4$(dppe)$_2$] (**22**) [52, 53]. The reaction of a C$_6$H$_6$-coordinated half-sandwich molybdenum dihydride complex [(C$_6$H$_6$)MoH$_2$(PPh$_3$)$_2$] (**24**) with N$_2$ afforded a binuclear end-on coordinated dinitrogen complex [(C$_6$H$_6$)Mo(PPh$_3$)$_2$]$_2$(N$_2$) (**25**) in quantitative yield with release of H$_2$ in a reversible fashion (Scheme 12) [54].

The reaction of the dinitrogen tungsten complex [W(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**26**) with the dihydrogen ruthenium complex [RuCl(H$_2$)(dppp)$_2$] (**27**) in the presence of H$_2$ generated NH$_3$ (55%) (Scheme 13) [55]. In this reaction, one H atom of the H$_2$ unit in **27** worked as a proton source, which protonated the coordinated N$_2$ in **26** to form initially a hydrazido (W≡N–NH$_2$) species, and the other H atom remained at the Ru atom as a hydride. Further protonation of the hydrazido units with **27** resulted in the formation of NH$_3$. Although the reaction allowed the formation of NH$_3$ from N$_2$ in
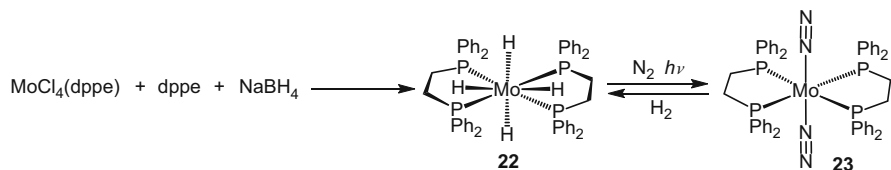
Scheme 11 Synthesis of the molybdenum hydride complex **22** and its reaction with N_2 under UV irradiation
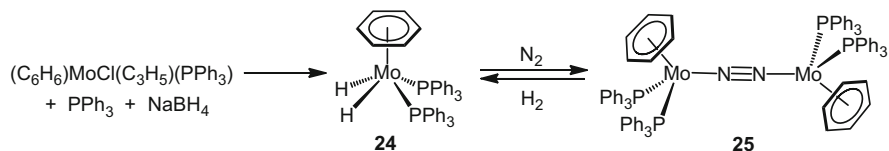
Scheme 12 Formation of a binuclear molybdenum dinitrogen complex **25**
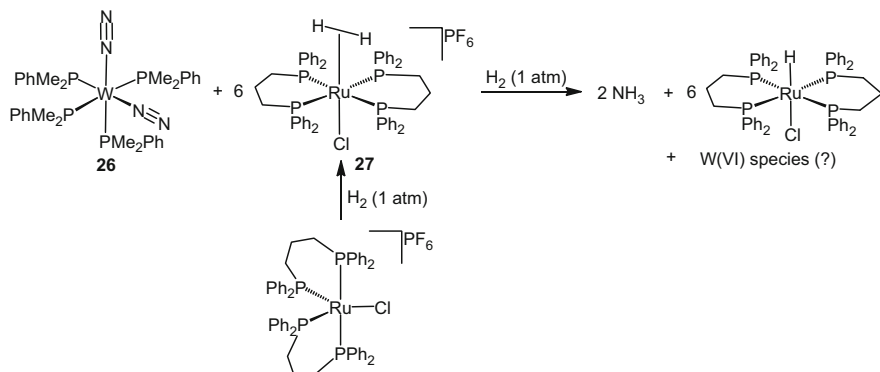
Scheme 13 Formation of ammonia from the reaction of the tungsten dinitrogen complex **26** with the ruthenium dihydrogen complex **27**

the presence of H_2, the electrons required for the cleavage of $N{\equiv}N$ bond were provided by the tungsten species.

As to group 5 transition metals, solid surface-supported tantalum hydrides were reported to cleave and hydrogenate N_2 [56]. However, the activation of dinitrogen by a well-defined mononuclear group 5 transition metal hydride complex remained unknown.
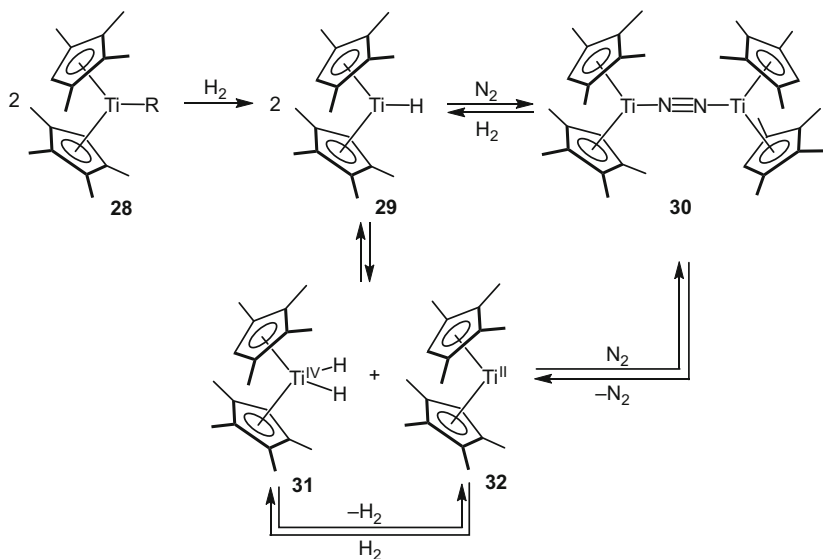
Scheme 14 Synthesis of the titanocene hydride complex **29** and the formation of an end-on bound dinitrogen complex **30**

2.5 Group 4 Transition Metal Hydrides

The activation of dinitrogen by titanium metallocene hydride complexes bearing different cyclopentadienyl ligands was investigated [57–59]. Acid hydrolysis of a reaction mixture of $(C_5H_5)_2TiCl_2$ and ethylmagnesium halide in the presence of N_2 was reported to yield NH_3 [59]. It was thought that a titanium hydride species was an active species for the reduction of N_2 in this reaction, though no structural evidence was available. Hydrogenolysis of $[(C_5Me_5)(C_5Me_4CH_2)TiCH_3]$ with H_2, followed by introduction of N_2 (1 atm), afforded an end-on coordinated N_2-bridged complex $[(C_5Me_5)_2Ti(\mu\text{-}N_2)Ti(C_5Me_5)_2]$ [60, 61]. This reaction was proposed to proceed through initial hydrogenolysis of the alkyl complex with H_2 to a dihydride species $[(C_5Me_5)_2TiH_2]$, followed by releases of H_2 and incorporation of N_2 to the resulting titanocene species $[(C_5Me_5)_2Ti]$. Similarly, hydrogenolysis of the trivalent titanium complexes $[(C_5Me_4H)_2TiR]$ (**28**) (R = Me, Ph) with H_2 followed by the reaction with N_2 afforded the corresponding N_2 complex $[(C_5Me_4H)_2Ti(\mu\text{-}N_2)Ti(C_5Me_4H)_2]$ (**30**) via the hydride complex $[(C_5Me_4H)_2TiH]$ (**29**) (Scheme 14) [62]. It was found that the Ti(III) metallocene hydride complex **29** could be disproportionated to the Ti(IV) dihydride **31** and the Ti(II) complex **32**. The dihydride **31** could lose H_2 to give **32** in a reversible fashion. The Ti(II) metallocene **32** reacted with N_2 to form the dinuclear titanium N_2 complex **30**. The N_2 ligand in **30** could be released under vacuum to give **32**.

Regarding the bonding mode of dinitrogen, the side-on (η^2,η^2) bridging form is expected to enhance the reactivity of the dinitrogen ligand compared to the end-on
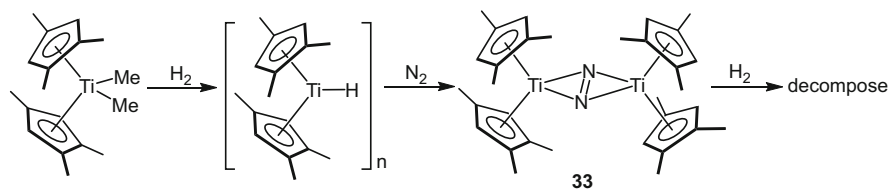
Scheme 15 Formation of the side-on bound dinitrogen complex **33** from the reaction of a less sterically hindered titanocene hydride complex with N_2
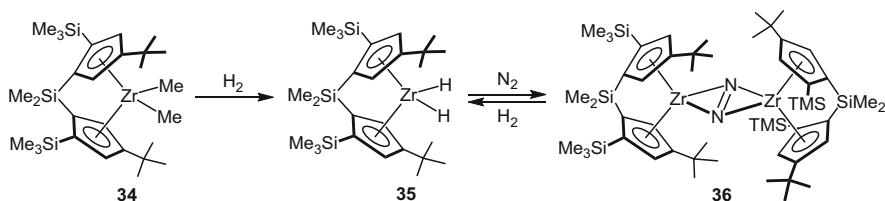
Scheme 16 Reversible formation of the side-on bound dinitrogen complex **36** from the reaction of the *ansa*-zirconocene hydride complex **35** with N_2

mode [63]. Metallocene complexes bearing less sterically demanding cyclopentadienyl ligands could provide a more sterically accessible and electron-poor metal center that potentially favors side-on η^2,η^2-N_2 coordination [64]. Indeed, hydrogenolysis of the 1,2,4-trimethylcyclopentadienyl-ligated titanocene dimethyl complex $[(C_5Me_3H_2)_2TiMe_2]$ with H_2 followed by reaction with N_2 afforded the side-on η^2,η^2-N_2 complex $[(C_5Me_3H_2)_2Ti]_2(\mu\text{-}\eta^2,\eta^2\text{-}N_2)$ (**33**) (Scheme 15) [65]. The reaction of the dinitrogen complex **33** with H_2 (1 atm) did take place, but a characterizable product was not obtained.

The *ansa*-zirconocene dihydride complex **35**, which was formed by hydrogenolysis of the dialkyl precursor **34**, reacted with N_2 reversibly to afford a side-on coordinated dinitrogen complex **36** (Scheme 16) [66]. In contrast, the zirconium metallocene dihydride complex bearing two C_5Me_5 ligands $[(C_5Me_5)_2ZrH_2]$ did not give an N_2-incorporated complex under similar conditions [67], suggesting that the *ansa* bridge structure of **35** should play an important role for the formation of the dinitrogen complex **36**.

3 Activation and Functionalization of Dinitrogen by Binuclear Transition Metal Hydride Complexes

The reaction of a tris(pyrazolyl)borate (^{iPr2}Tp)-ligated binuclear copper hydroxide $[^{iPr2}TpCu]_2(\mu\text{-}OH)_2$ (**37**) with triphenylsilane under an N_2 atmosphere afforded an end-on bridged dinitrogen complex $[^{iPr2}TpCu]_2(\mu\text{-}N_2)$ (**41**) (Scheme 17) [68]. A mixed valence Cu(I)/Cu(II) binuclear copper monohydride complex $[^{iPr2}TpCu]_2(\mu\text{-}H)$

(**40**) was isolated as a key intermediate. Complex **40** could be formed via combination of the highly reactive terminal Cu(II) hydride species [^{iPr2}TpCu-H] (**38**), which was produced by reaction between HSiPh$_3$ and the hydroxide **37**, with the unsaturated Cu (I) species [^{iPr2}TpCu] (**39**) generated by release of H$_2$ from **38**. Under an N$_2$ atmosphere, complex **40** changed to the dinitrogen complex **41** with release of H$_2$. Alternatively, the reaction of **39** with N$_2$ could also afford **41**. The N$_2$ ligand in **41** is quite labile, which could be replaced by ^{15}N$_2$, MeCN, or O$_2$.

The reaction of the sterically hindered β-diketiminate ligated iron chloride complex with KBEt$_3$H afforded the binuclear Fe(II) dihydride complex **42**, which upon UV irradiation under N$_2$ resulted in loss of H$_2$ and formation of the end-on dinitrogen complex **43** (Scheme 18) [69, 70].

The β-diketiminate-ligated cobalt and nickel hydride complexes **44** were obtained from the reaction of the chloride precursors with 1.0 equiv. of KBEt$_3$H (Scheme 19) [71, 72]. When 2.0 equiv. of KBEt$_3$H were used to react with the cobalt chloride complex, the potassium-bridged cobalt dihydride complex **45** was formed in high yield [71]. These binuclear dihydride complexes **44** and **45** readily reacted with N$_2$ at room temperature to afford the end-on bridged dinitrogen complexes **46** and **47**, respectively (Scheme 19). Attempts to reduce the dinitrogen ligand in the nickel dinitrogen complex with H$_2$ led to loss of N$_2$ [73].

The reaction of the PNP-ligated zirconium chloride complex [{P$_2$N$_2$}ZrCl$_2$] with KC$_8$ under N$_2$ yielded a side-on bound dinitrogen complex of zirconium, [{P$_2$N$_2$} Zr]$_2$(μ-η^2,η^2-N$_2$) (**48**) (P$_2$N$_2$ = PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh) (Scheme 20) [74].
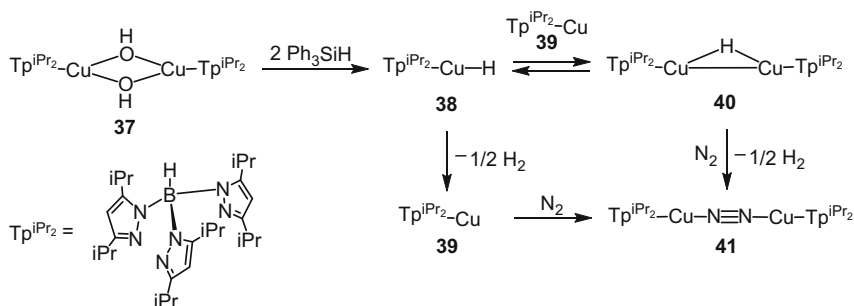
Scheme 17 Formation of a binuclear copper dinitrogen complex **41**
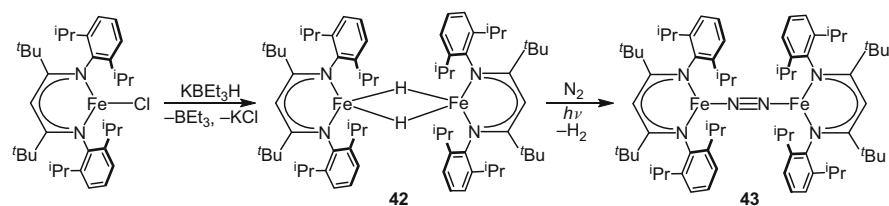
Scheme 18 Synthesis of the binuclear iron hydride complex **42** and its reaction with N$_2$ to generate the end-on dinitrogen complex **43**
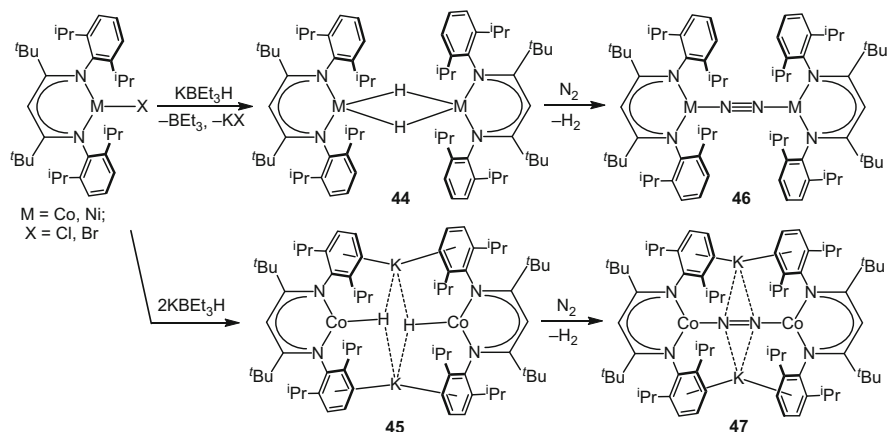
Scheme 19 Synthesis of binuclear cobalt and nickel hydride complexes **44** and **45** and their reactions with N_2 to generate the end-on dinitrogen complexes **46** and **47**

Hydrogenolysis of **48** with H_2 afforded $[\{P_2N_2\}Zr]_2(\mu-\eta^2,\eta^2-N_2H)(\mu-H)$ (**49**) containing both a bridging hydride and a bridging hydrazido unit through addition of one molecule of H_2 across to a Zr–N bond. Theoretical studies suggested that addition of a second equivalent of H_2 is feasible, but this reaction was not observed experimentally [75].

The analogous side-on bound dinitrogen metallocene complex $[(C_5M_4H)_2Zr]_2(\mu-\eta^2,\eta^2-N_2)$ (**50**), which was formed by the reaction of the chloride precursor $[(C_5M_4H)_2ZrCl_2]$ with Na/Hg under N_2, underwent the addition of 2 equiv. of H_2 to furnish a dihydrido/diazenido complex $[(C_5M_4H)_2ZrH]_2(\mu-\eta^2,\eta^2-N_2H_2)$ (**51**) (Scheme 21) [64, 76, 77]. The reaction proceeded through a concerted, highly ordered transition state, in which the H–H bond is simultaneously cleaved with Zr–H and N–H bond formation. Thermolysis of the dihydrido/diazenido complex **51** caused H_2 loss and N–N bond cleavage to give the nitrido/amido complex $[(C_5M_4H)_2Zr]_2(\mu-N)(\mu-NH_2)$ (**52**). In this sequence of the reaction, H_2 worked as both proton and electron sources. It is also worth noting that thermolysis of the dihydrido/diazenido complex under an H_2 atmosphere yielded the dihydride complex $[(C_5M_4H)_2ZrH_2]$ with release of trace amount of ammonia [64].

A binuclear tantalum tetrahydride complex $([NPN]Ta)_2(\mu-H)_4$ (**53**) ($[NPN] = PhP(CH_2SiMe_2NPh)_2$), which was obtained from hydrogenolysis of the trimethyl precursor $[NPN]TaMe_3$, reacted spontaneously with N_2 to give a side-on, end-on bound dinitrogen complex $([NPN]Ta)_2(\mu-\eta^1,\eta^2-N_2)(\mu-H)_2$ (**54**) with elimination of H_2 (Scheme 22) [78, 79]. In this transformation, [N≡N] was formally reduced to $[N–N]^{4-}$ by four electrons generated by the reductive elimination of one molecule of H_2 and the oxidation state change of the two Ta ions from Ta(IV) to Ta(V). The unique side-on end-on coordination fashion of the bridging N_2 resulted in substantial reactivity of the N_2 fragment, leading to its cleavage and functionalization. While no apparent reaction of **54** with H_2 was observed, complete cleavage of the N–N bond in **54** was achieved by
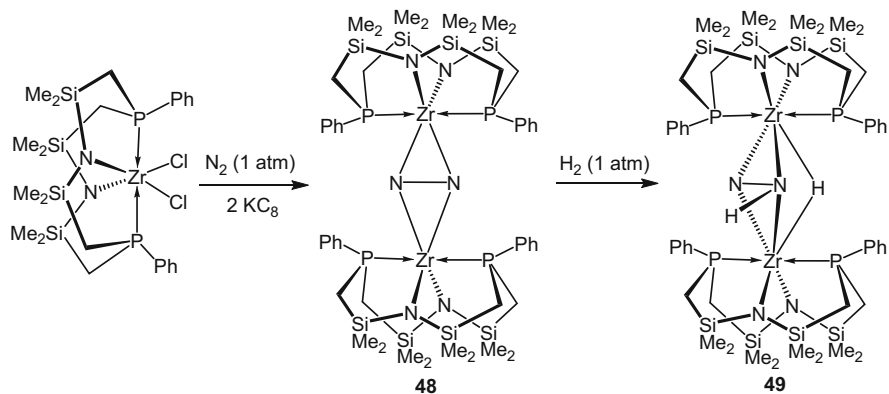
Scheme 20 Hydrogenation of the binuclear zirconium dinitrogen complex **48** with H_2
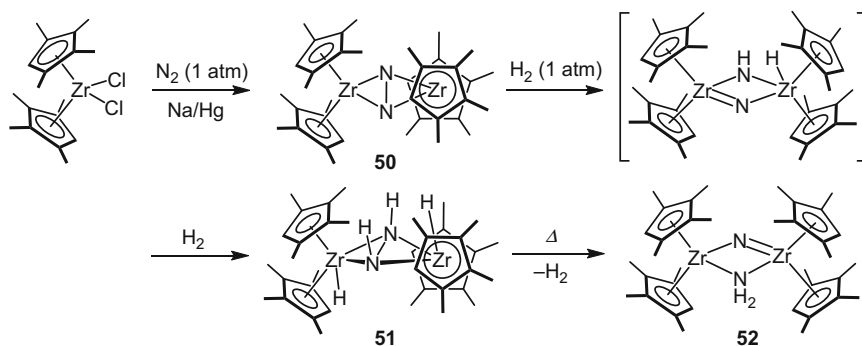
Scheme 21 Cleavage and hydrogenation of the side-on bound dinitrogen ligand in complex **50** by H_2

reaction with a variety of hydride reagents (E-H = R_2BH, R_2AlH, $RSiH_3$) (Scheme 22) [80–82].

The anionic binuclear niobium tetrahydride complex **55** bearing triaryloxide ligands readily reacted with N_2 (1 atm) to afford the dinitrido complex **56** via N–N bond cleavage without using external reducing agent (Scheme 23) [83, 84]. This process corresponds to an overall six-electron reduction of N_2, in which four electrons are provided by formation of two molecules of H_2 from four hydride ligands and two electrons generated by oxidation of the metal–metal bond. The methylation of the nitride units in **56** by MeI proceeded in a stepwise fashion to give the bisimide complex **57** (Scheme 23). A reaction of **56** with H_2 did not take place.
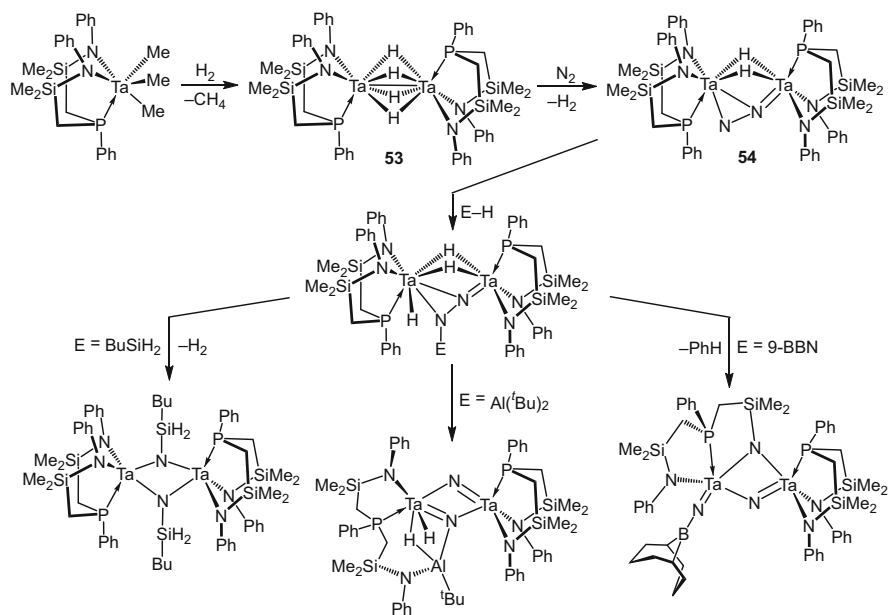
Scheme 22 Reaction of a binuclear tantalum tetrahydride complex **53** with N_2 to give a side-on, end-on dinitrogen complex **54** whose N–N bond could be cleaved upon reaction with hydride reagents
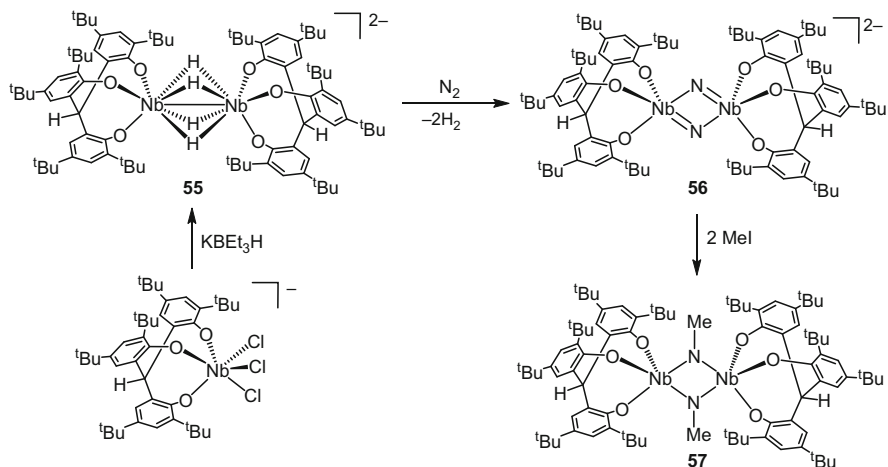
Scheme 23 Dinitrogen cleavage by a binuclear niobium tetrahydride complex

4 Activation and Functionalization of Dinitrogen by Tri- and Tetranuclear Transition Metal Hydride Complexes

Hydrogenolysis of the half-sandwich titanium trialkyl complex [Cp'Ti(CH$_2$SiMe$_3$)$_3$] (Cp' = C$_5$Me$_4$SiMe$_3$) with H$_2$ afforded the mixed valence Ti(III)/Ti(IV) heptahydride complex [(Cp'Ti)$_3$(μ_3-H)(μ-H)$_6$] (**58**) (Scheme 24) [85, 86]. This hydride cluster readily reacted with atmospheric pressure of N$_2$ at room temperature, giving an imido/nitrido complex [(Cp'Ti)$_3$(μ_3-N)(μ-NH)(μ-H)$_2$] (**61**) via N–N bond cleavage and N–H bond formation without the need of extra reducing agent or proton source. Monitoring the reaction by ^{1}H and ^{15}N NMR revealed the initial formation of a dinitrogen complex [(Cp'Ti)$_3$(μ_3-η^1, η^2, η^2-N$_2$)(μ-H)$_3$] (**59**) with release of two molecules of H$_2$, followed by N–N bond cleavage to give a dinitrido (N^{3-}) complex [(Cp'Ti)$_3$(μ_3-N)(μ-N)(μ-H)$_3$] (**60**), and hydride migration from titanium to the μ_2-nitrido unit to give the imido/nitrido complex **61**. The six electrons for the cleavage of the N–N bond were supplied by the reductive elimination of two molecules of H$_2$ and the oxidation of two Ti(III) species to two Ti(IV) species. The proton (H$^+$) for the formation of the N–H bond was generated by oxidation of a bridging hydride (H$^-$) by two Ti(IV) species which were both reduced to Ti(III). Obviously, the hydride ligands in **58** served as the source of both electron and proton for the dinitrogen cleavage and hydrogenation, resembling in part the industrial Haber–Bosch process at the molecular level.

When the hydrogenolysis of the trialkyl titanium complex [Cp'Ti(CH$_2$SiMe$_3$)$_3$] with H$_2$ was carried out in the presence of N$_2$, a tetranuclear diimido/tetrahydrido complex [(Cp'Ti)$_4$(μ_3-NH)$_2$(μ-H)$_4$] (**62**), instead of the trinuclear heptahydride complex [(Cp'Ti)$_3$(μ_3-H)(μ-H)$_6$] (**58**), was obtained in high yield (Scheme 25) [85]. The formation of **62** could also be achieved by hydrogenolysis of [Cp'Ti(CH$_2$SiMe$_3$)$_3$] in the presence of 1 equiv. of the trinuclear imido/nitrido complex **61**, suggesting that the hydrogenation of **61** with a mononuclear titanium hydride species such as "Cp'TiH$_3$"
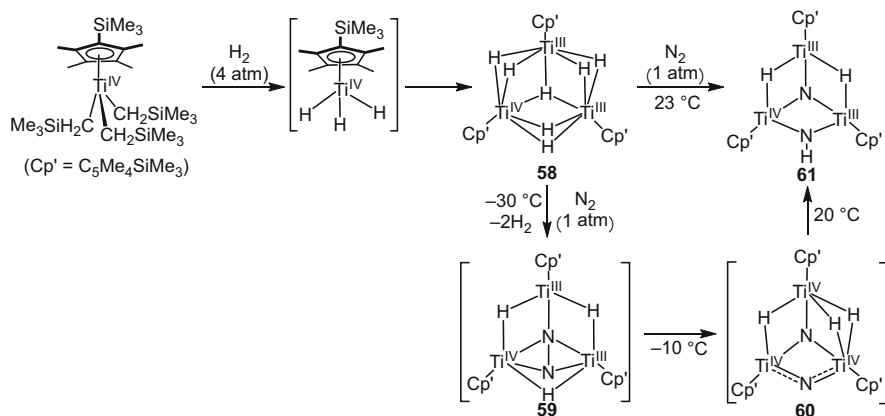
Scheme 24 Dinitrogen cleavage and hydrogenation by a trinuclear titanium heptahydride complex **58**
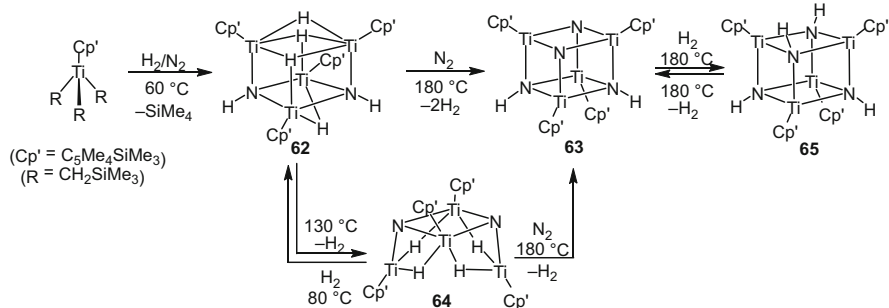
Scheme 25 Dinitrogen activation and hydrogenation by a tetranuclear titanium diimido/tetrahydrido complex **62**
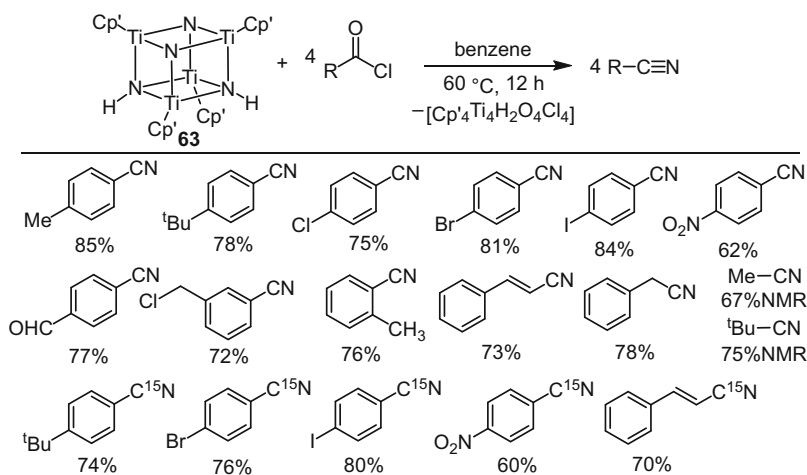
Scheme 26 Transformation to nitriles by reaction of **63** with acid chlorides

generated in situ by the hydrogenolysis of [Cp'Ti(CH$_2$SiMe$_3$)$_3$] may take place. No apparent reaction between **61** and H$_2$ was observed at room or higher temperatures.

Complex **62** reacted with atmospheric pressure of N$_2$ at 180°C to afford a mixed diimido/dinitrido complex [(Cp'Ti)$_4$(μ_3-N)$_2$(μ_3-NH)$_2$] (**63**) with release of two molecules of H$_2$ (Scheme 25) [87]. When **62** was heated at 130°C, one molecule of H$_2$ was released to give the dinitrido/tetrahydrido complex [(Cp'Ti)$_4$(μ_3-N)$_2$(μ-H)$_4$] (**64**). Exposure of **64** to H$_2$ (1 atm) at 80°C regenerated **62** quantitatively, demonstrating that **62** and **64** are facilely interconvertible through dehydrogenation and hydrogenation of the imido/nitrido ligands. When the dinitrido/tetrahydrido complex **64** was heated at 180°C in the presence of N$_2$ (1 atm), the diimido/dinitrido complex **63** was formed quantitatively. The hydrogenation of **63** with H$_2$ to give the tetraimido complex [(Cp'Ti)$_4$(μ_3-NH)$_4$] (**65**) took place in a reversible way at 180°C (Scheme 25).

Remarkably, the imido and nitride species in **63** could be easily converted to nitriles through reaction with acid chlorides at 60°C (Scheme 26) [87]. This

transformation did not require any extra reagents (either reducing agents or bases) and was compatible with functional groups such as aromatic C−X (X = Cl, Br, I) bonds, nitro group, aldehyde and chloromethyl moieties. ^{15}N-isotope labeled nitriles could also be efficiently prepared by using the ^{15}N-enriched analogue [(Cp'Ti)$_4$(μ_3-^{15}N)$_2$(μ_3-^{15}NH)$_2$] (**63-^{15}N**) derived from ^{15}N$_2$ gas.

5   Concluding Remarks and Outlook

It is clear from the results described above that molecular transition metal hydride complexes can serve as a platform for dinitrogen activation. Mononuclear transition metal hydride complexes can bind N$_2$ to form end-on dinitrogen complexes with loss of H$_2$. This process is generally reversible and N–N bond cleavage is difficult. Binuclear transition metal hydride complexes can show higher reactivity and induce N–N bond cleavage in some cases. A trinuclear titanium polyhydride complex has demonstrated even higher activity for the activation of dinitrogen, which enabled both N–N bond cleavage and N–H bond formation without the need of an external reducing agent or proton source. Obviously, the hydride ligands can serve as the source of both electron and proton for the reduction and hydrogenation of dinitrogen, and the cooperation of multiple metal hydride sites may play an important role in this process. A few functionalization reactions of the nitrogen species generated by the activation of dinitrogen with transition metal hydrides have been reported, among which the recent conversion of a tetranuclear titanium imido/nitrido complex to nitriles is particularly noteworthy. Despite recent progress in this area, the study on the activation and functionalization of dinitrogen by molecular transition metal hydrides, especially multimetallic polyhydride complexes, is still in infancy. The direct use of dinitrogen as a feedstock for organic synthesis remains a challenge.

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