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# Molecular Rare Earth Hydride Clusters

**Takanori Shima and Zhaomin Hou**

**Abstract** This chapter describes the synthesis, structure, and reactivity of molecular rare earth hydride clusters consisting of the dihydride species "(L)$LnH_2$" bearing one anionic supporting ligand per metal. Generally, hydrogenolysis of the dialkyl precursors [(L)$LnR_2$] with $H_2$ easily leads to formation of polynuclear rare earth hydride clusters through self-assembly of the resulting dihydride species. The molecular structure and reactivity of the hydride clusters are significantly influenced by both the bulkiness of the ancillary ligands and the size of the metal ions. Unique reactivities are observed with various substrates, including CO, $CO_2$, $H_2$, and unsaturated C–C and C–N bonds, because of the synergistic effects of the multiple metal-hydride sites.

**Keywords** Cluster • Heteromultimetallic • Hydride • Multimetallic • Synergistic effect

## Contents

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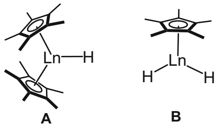
## 1 Introduction

Rare-earth metal hydrides play an important role in a wide range of catalytic and stoichiometric reactions. They are highly reactive and effective for a number of chemical transformations not only due to the nucleophilicity and basicity of the hydride species, but also due to the strong Lewis acidity and oxophilicity of the metal centers. Moreover, as rare-earth metals are constituents in materials which have high hydrogen storage capacities (e.g., $LaNi_5H_x$), molecular hydride clusters are expected to shed light on the chemistry of hydrogen in these systems.

Since the 1980s, well-defined rare-earth metal hydrides bearing two monoanionic cyclopentadienyl ligands per metal (such as **A**, Scheme 1) have been well investigated [1–3]. Such metallocene hydride complexes are highly reactive for a number of transformations including addition of the metal hydride to C=C, C=O, and C≡N bonds of organic compounds and reduction of carbon monoxide (CO) to an enediolate unit (OCH=CHO). Whilst such complexes have been shown to adopt bi- or polymeric structures in solid state, their reactions in solution tend to occur at a mononuclear metal center containing a single hydride ligand [4].

Recently, rare earth dihydrides of the type "(L)$LnH_2$" (**B**) (Ln = rare-earth metals) bearing one anionic supporting ligand per metal have received much attention. These species can undergo "self-assembly" to give the corresponding multimetallic rare earth hydride clusters, which show unique structures and reactivities that are different from those bearing two anionic supporting ligands per metal. This is a consequence of both synergistic effects among those metal atoms and the number of reactive hydrides present. This chapter focuses on the synthesis, structures, and reactivities of this new class of molecular rare earth hydride clusters [5, 6].



**Scheme 1** Rare earth hydride complexes bearing two (**A**) and one (**B**) cyclopentadienyl ligands

# 2 Synthesis and Structure of Neutral Rare Earth Hydride Clusters

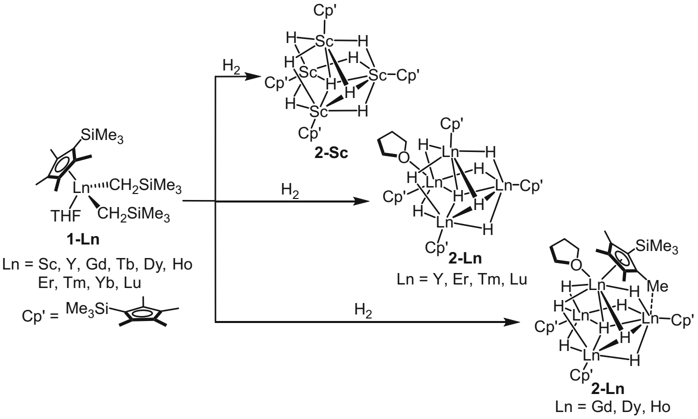
## *2.1 Cyclopentadienyl-Ligated Hydride Clusters*

Recently, a series of highly reactive half-sandwich type rare earth dialkyl complexes, $[(C_5Me_4R)LnR'_2(THF)_n]$ (**1-Ln**: R = $SiMe_3$; R′ = $CH_2SiMe_3$, *o*-$CH_2C_6H_4NMe_2$; **1-Ln$^{\mathbf{R}}$**: R = Me, H; R′ = $CH_2SiMe_3$, *o*-$CH_2C_6H_4NMe_2$), have been isolated and structurally characterized, which possess the monoanionic cyclopentadienyl ligands such as $C_5Me_4SiMe_3$ with the nucleophilic primary alkyl groups such as $CH_2SiMe_3$ or *o*-$CH_2C_6H_4NMe_2$. Treatment of those dialkyl complexes with one equivalent of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$ can generate the cationic monoalkyl species, which serve as excellent catalysts for the polymerization and copolymerization of various olefins as well as for other chemical transformations such as methylalumination of alkenes and alkynes and C–H alkylation of anisoles and pyridines with alkenes [7, 8]. Remarkably, hydrogenolysis of the half-sandwich dialkyl complexes with $H_2$ has led to the formation of a new family of rare earth hydride clusters consisting of the "$(C_5Me_4R)LnH_2$" units.

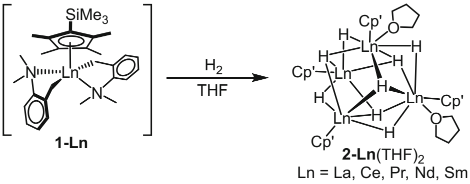
The structures of the rare earth hydride clusters are dependent, to some extent, on the size of the metal radius [9, 10]. For example, the reaction of the $C_5Me_4SiMe_3$-ligated scandium dialkyl complex $[Cp'Sc(CH_2SiMe_3)_2(THF)]$ (**1-Sc**) (Cp′ = $C_5Me_4SiMe_3$) with $H_2$ at room temperature provides the THF-free tetranuclear octahydride cluster $[\{Cp'Sc(\mu\text{-}H)_2\}_4]$ (**2-Sc**) (Scheme 2) [9, 10]. This complex can be considered a self-assembled architecture comprising four "$Cp'ScH_2$" units held together via "intermolecular" Sc–H interactions. Eight hydride ligands are present in the whole molecule; six of which are edge-bridged adopting a $\mu_2$-H–$Sc_2$ coordination mode, one of which is face-capped in a $\mu_3$-H–$Sc_3$ mode, and one of which is body-centered in a $\mu_4$-H–$Sc_4$ fashion. The THF ligand is no longer present in the hydride cluster **2-Sc**.

Hydrogenolysis of the dialkyl complexes of medium sized rare-earth metals such as Y, Er, Tm, and Lu in toluene gives the corresponding tetranuclear octahydride clusters $[\{Cp'Ln(\mu\text{-}H)_2\}_4(THF)]$ (Ln = Y, Er, Tm, Lu) (**2-Ln**), in which one THF molecule is ligated to one of the four metal centers (Scheme 2) [9–13]. Despite the presence of a coordinated solvent, the structures of **2-Ln** are remarkably similar to that of the THF-free Sc cluster **2-Sc**.

As the size of the metal center increases to include Gd, Dy, and Ho, an agostic interaction between a methyl group of a $C_5Me_4SiMe_3$ ligand and an adjacent metal center is also observed, likely due to greater steric unsaturation caused by larger radius of the metal centers (Scheme 2) [9, 10]. It is worth noting that in the case of Dy and Y, the bis(THF)-coordinated clusters **2-Ln**$(THF)_2$ can also be isolated by recrystallization in THF solvent. In these cases, an interstitial $\mu_4$-H ligand is not observed, and the tetranuclear metal frame is thus connected by four $\mu_2$-H and four $\mu_3$-H ligands. One THF molecule in **2-Ln**$(THF)_2$ is labile and can easily be



**Scheme 2** Hydrogenolysis of dialkyl complexes **1-Ln**

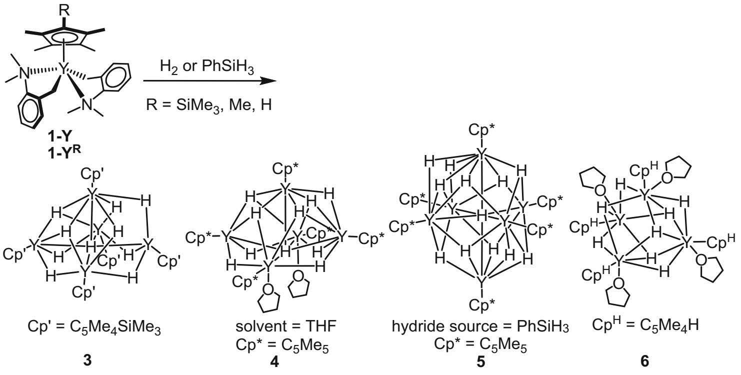


**Scheme 3** Hydrogenolysis of bis(*o*-dimethylaminobenzyl)complexes of early lanthanide metals

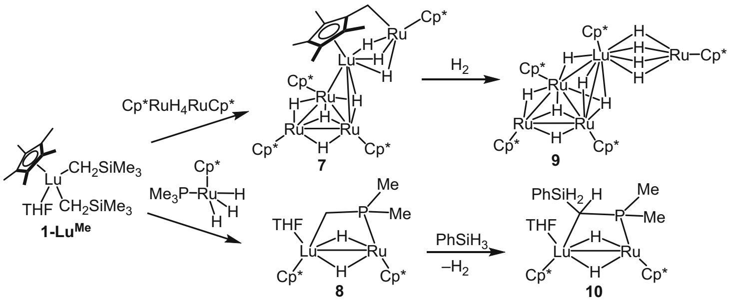
removed to give the mono(THF)-coordinated analogues through recrystallization in appropriate solvents, such as toluene.

Due to difficulties in the synthesis of the half-sandwich $CH_2SiMe_3$ complexes of early (larger) lanthanide metals (La, Ce, Pr, Nd, and Sm), the analogous *o*-dimethylaminobenzyl complexes [Cp′Ln(*o*-$CH_2C_6H_4NMe_2)_2$] were used for the synthesis of the corresponding hydride clusters, which upon hydrogenolysis in THF gave tetranuclear octahydride clusters [{Cp′Ln(μ-H)$_2$}$_4$(THF)$_2$] (**2-Ln**(THF)$_2$) bearing two THF ligands (Scheme 3) [10]. A mono(THF)-coordinated analogue was not obtained by recrystallization of bis(THF)-coordinated complexes **2-Ln** (THF)$_2$ of these larger metals in toluene, in contrast to **2-Y**(THF)$_2$ and **2-Dy** (THF)$_2$ described above.

The sterically less demanding pentamethylcyclopentadienyl-ligated samarium hydride cluster [{Cp*Sm(μ-H)$_2$}$_6${KH(THF)$_2$}$_3$] (Cp* = $\eta^5$-$C_5Me_5$) was obtained by the reaction of the $Sm^{II}$ alkyl complex [{Cp*SmCH(SiMe$_3$)$_2$}{Cp*K(THF)$_2$}] with $PhSiH_3$ [14]. Previous attempts to hydrogenate the $C_5Me_5$-ligated dialkyl complexes [Cp*Lu($CH_2CMe_3$)$_2$(THF)] or [Cp*Lu($CH_2CMe_3$){CH(SiMe$_3$)$_2$} (THF)] did not give a structurally characterizable hydride species [15]. However, hydrogenolysis of THF-free *o*-dimethylaminobenzyl *o*-$CH_2C_6H_4NMe_2$-ligated complexes [($C_5Me_4R$)Y(*o*-$CH_2C_6H_4NMe_2$)$_2$](**1-Y** and **1-Y$^{\mathbf{R}}$**) (R = $SiMe_3$, Me, H) with $H_2$ or $PhSiH_3$ in THF or toluene afforded the corresponding tetra-, penta-, and



**Scheme 4** Synthesis of tetra- (**6**), penta- (**3**, **4**), and hexanuclear (**5**) yttrium hydride clusters with different Cp ligands



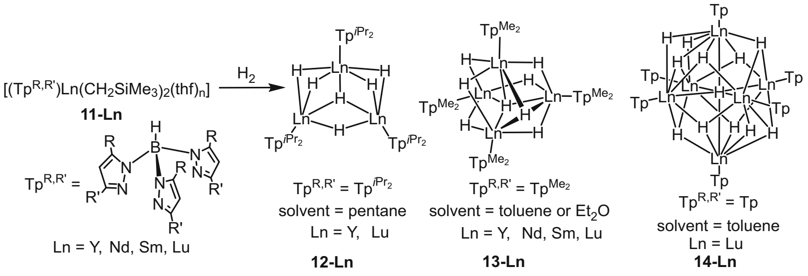
**Scheme 5** Synthesis of d-f heterometallic hydrides

hexanuclear yttrium hydride clusters [{Cp′Y(μ-H)$_2$}$_5$] (**3**), [{Cp*Y(μ-H)$_2$}$_5$(THF)$_2$] (**4**), or [{Cp*Y(μ-H)$_2$}$_6$] (**5**), and [{(C$_5$Me$_4$H)Y(μ-H)$_2$}$_4$(THF)$_4$] (**6**) (Scheme 4) [16]. The nuclearities of these clusters are dependent on the ligand size, the reaction solvent, and the source of hydride used in the synthesis.

By use of a half-sandwich rare earth dialkyl complex such as [Cp*Lu(CH$_2$SiMe$_3$)$_2$(THF)] (**1-Lu$^{Me}$**) as a building block to react with d-transition metal hydrides such as [Cp*Ru(μ-H)$_4$RuCp*] and [Cp*Ru(PMe$_3$)H$_3$], the corresponding heterometallic hydride compounds (**7** and **8**) were synthesized as shown in Scheme 5 [17, 18]. Hydrogenolysis of **7** with H$_2$ afforded a decahydride cluster **9** as a result of addition of two molecules of H$_2$, while the reaction of **8** with PhSiH$_3$ provided a dehydrogenative silylation product **10**.

## 2.2 *Pyrazolyl Borate-Ligated Hydride Clusters*

Hydrogenolysis of the rare earth dialkyl complexes bearing tris(3,5-dimethylpyrazolyl)borate (Tp$^{Me2}$) ligands [(Tp$^{Me2}$)Ln(CH$_2$SiMe$_3$)$_2$(THF)]



**Scheme 6** Hydrogenolysis of pyrazolyl borate-ligated dialkyl complexes **11-Ln** to tri- (**12-Ln**), tetra- (**13-Ln**), and hexanuclear (**14-Ln**) hydride clusters

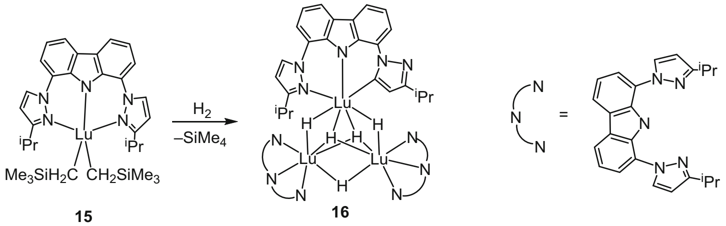
(**11-Ln**) with $H_2$ afforded the corresponding tetranuclear octahydride clusters $[\{(Tp^{Me2})Ln(\mu\text{-}H)_2\}_4]$ (**13-Ln**) (Ln = Y, Nd, Sm, Lu), in which the coordination modes of the hydride ligands are similar to those of the $C_5Me_4SiMe_3$-ligated analogues (see **2-Ln**). In contrast, hydrogenolysis of the more sterically demanding $^i$Pr substituted $Tp^{iPr2}$-ligated dialkyl complex $[(Tp^{iPr2})Ln(CH_2SiMe_3)_2(THF)]$ ($Tp^{iPr2}$ = tris(3,5-diisopropylpyrazolyl)borate) afforded the trinuclear hexahydride clusters $[\{(Tp^{iPr2})Ln(\mu\text{-}H)_2\}_3]$ (**12-Ln**) (Ln = Y, Lu) [19], while hydrogenolysis of the less sterically demanding non-substituted Tp-ligated dialkyl complexes $[(Tp)Ln(CH_2SiMe_3)_2(THF)]$ (Tp = tris(pyrazolyl)borate) gave the hexanuclear dodecahydride clusters $[\{(Tp)Lu(\mu\text{-}H)_2\}_6]$ (**14-Ln**) (Scheme 6) [20].

## 2.3 Bis(Pyrazolyl)Carbazole-Ligated Hydride Clusters

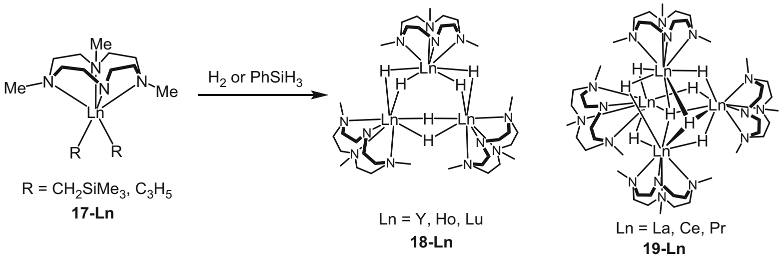
The pyrazole-based lutetium trinuclear pentahydride cluster $[\{(CzPz^{iPr})Lu\}_3(\mu\text{-}H)_5]$ (**16**) was obtained by hydrogenolysis of the bis(alkyl) complex $[(CzPz^{iPr})Lu(CH_2SiMe_3)_2]$ (**15**) ($CzPz^{iPr}$ = 1,8-bis(3-isopropylpyrazolyl)carbazol) with $H_2$ (Scheme 7) [21]. Notably, one C–H bond on the pyrazolyl substituent of the ligand was activated via dehydrogenative metalation. Attempts to prepare the sterically less hindered $CzPz^{Me}$-ligated analogue of hydride cluster were unsuccessful.

## 2.4 NNNN Macrocycle-Ligated Hydride Clusters

Hydrogenolysis of rare earth dialkyl or diallyl complexes **17-Ln** bearing a monoanionic macrocyclic [NNNN] ligand such as $Me_3TACD$ ($Me_3TACD$ = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) with $H_2$ or $PhSiH_3$ afforded the corresponding multinuclear hydride clusters $[\{(Me_3TACD)Ln(\mu\text{-}H)_2\}_n]$ ($n = 3$: Ln = Y, Ho, Lu (**18-Ln**); $n = 4$: Ln = La, Ce, Pr (**19-Ln**)) (Scheme 8) [22–24]. The trinuclear hydride clusters **18-Ln** contained only $\mu_2$-



**Scheme 7** Hydrogenolysis of a bis(pyrazolyl)carbazole-ligated dialkyl complex **15**



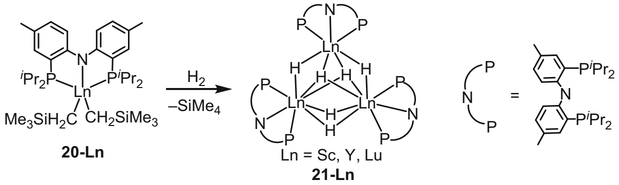
**Scheme 8** Hydrogenolysis of macrocyclic [NNNN]-ligated dialkyl complexes **17-Ln** to tri-(**18-Ln**) and tetranuclear (**19-Ln**) hydride clusters

bridging hydrides, in contrast with those found in the trinuclear yttrium hydrides [{(Tp$^{iPr2}$)Y(μ-H)$_2$}$_3$] (**12-Y**) [19] and [{(Me-PNP$^{iPr}$)Y(μ-H)$_2$}$_3$] (**21-Y**) (Me-PNP$^{iPr}$ = {4-Me-2-($^i$Pr$_2$P)-C$_6$H$_3$}$_2$N) [25]. The core structures of the tetranuclear hydride clusters **19-Ln** are similar to those found in [{(Tp$^{Me2}$)Ln(μ-H)$_2$}$_4$] (**13-Ln**) [20].

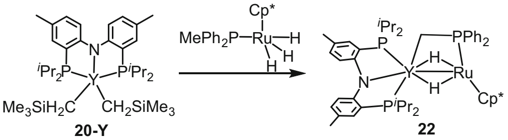
## 2.5 PNP-Ligated Hydride Clusters

Trinuclear rare earth hydride clusters [{(Me-PNP$^{iPr}$)Ln(μ-H)$_2$}$_3$] (**21-Ln**) (Me-PNP $^{iPr}$ = {2-($^i$Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$N) bearing the monoanionic bis(phosphinophenyl) amido ligands (PNP) were synthesized by hydrogenolysis of the dialkyl precursors **20-Ln** with H$_2$ (Scheme 9) [25]. The isolability of the hydride clusters is highly dependent on the substituents of the phosphine ligands. Hydrogenolysis of the dialkyl complex bearing the phenyl substituted phosphine (PNP$^{Ph}$) ligand gave a mixture of uncharacterized products, while hydrogenolysis of the dialkyl complex bearing an analogous diisopropyl-substituted ligand afforded the hydride cluster cleanly. The core structure of [{(Me-PNP$^{iPr}$)Y(μ-H)$_2$}$_3$] (**21-Y**) contains two μ$_3$-H capping ligands and four μ$_2$-H bridging ligands, which is contrast to those of other trinuclear hexahydrides such as [{(Me$_3$TACD)Y(μ-H)$_2$}$_3$] (**18-Y**) (all six μ$_2$-H) [22] or [{(Tp$^{iPr2}$)Y(μ-H)$_2$}$_3$] (**12-Y**) (one μ$_3$-H, five μ$_2$-H) [19].

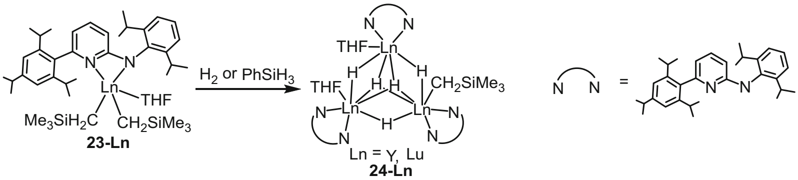
The reaction of the PNP-ligated yttrium dialkyl complex **20-Y** with the ruthenium hydride complex [Cp*Ru(PPh$_2$Me)H$_3$] afforded heterobimetallic hydride



**Scheme 9** Hydrogenolysis of PNP-ligated dialkyl complexes **20-Ln**



**Scheme 10** Synthesis of a Y/Ru heterobimetallic hydride compound consisting of a PNP-ligated rare earth unit



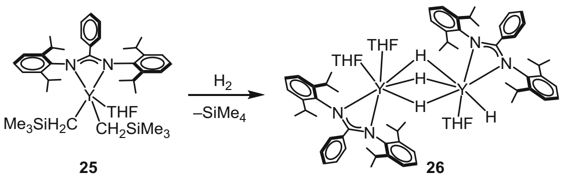
**Scheme 11** Hydrogenolysis of amidinate-ligated dialkyl complexes **23-Ln**

compound [(Me-PNP$^{iPr}$)Y(μ-H)$_2$(μ-CH$_2$PPh$_2$)RuCp*] (**22**) (Scheme 10) [26], similar to the Cp*-ligated lutetium analogue **8** [17].

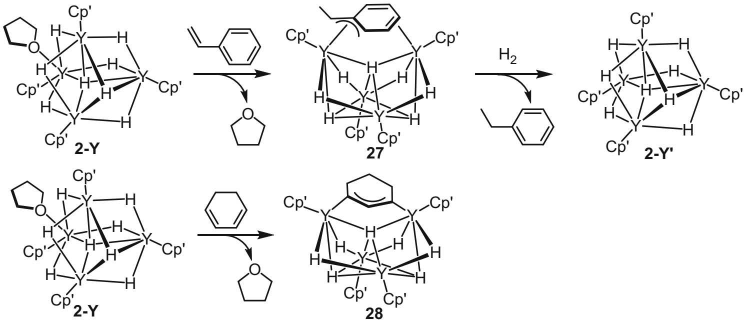
## *2.6 Amidinate-Ligated Hydride Clusters*

Hydrogenolysis of the amidopyridinate-ligated dialkyl complex [Ap*Ln(CH$_2$SiMe$_3$)$_2$(THF)] (**23-Ln**) (Ap* = ((2,6-diisopropylphenyl){6-(2,4,6)-triisopropylphenyl}pyridine-2-yl)amido) with H$_2$ or PhSiH$_3$ provided a partially hydrogenated trinuclear mixed alkyl/hydride cluster [(Ap*Ln)$_3$(μ-H)$_5$(CH$_2$SiMe$_3$)(THF)$_2$] (**24-Ln**) (Ln = Y, Lu) (Scheme 11) [27]. All attempts to remove the remaining alkyl group with hydride ligands to form polyhydride clusters consisting of Ap*LnH$_2$ units failed. Similar trinuclear alkyl/hydride clusters supported by the sterically less bulky analogous ligand, ((2,4,6-trimethylphenyl){6-(2,4,6)-triisopropylphenyl}pyridine-2-yl)amido ligand, were also recently reported [28].

Hydrogenolysis of the amidinate-ligated dialkyl complex **25** with H$_2$ gave the dinuclear hydride [{(NCN)YH$_2$}$_2$(THF)$_3$] (**26**) (NCN = PhC(NC$_6$H$_3$$^i$Pr$_2$-2,6)$_2$), which contains three μ$_2$-H ligands and one terminal hydride ligand (Scheme 12)



**Scheme 12** Hydrogenolysis of amidinate-ligated dialkyl complex **25**



**Scheme 13** Reactions of **2-Y** with styrene and 1,3-cyclohexadiene

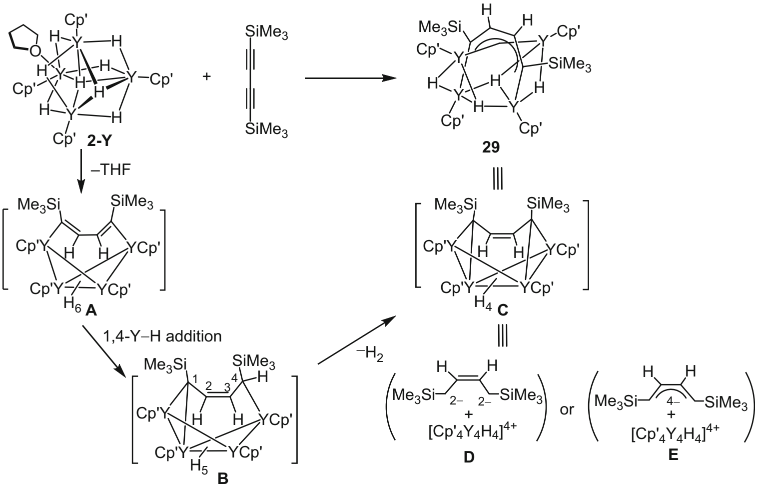
[29]. This represents the first example of a structurally characterized bi- or multimetallic rare earth complex bearing a terminal hydride ligand.

# 3 Reactivity of Neutral Rare Earth Hydride Clusters

## 3.1 *Reactions with Unsaturated C–C Bonds*

The reaction of the mono(THF)-coordinated tetranuclear yttrium octahydride cluster [{Cp′Y(μ-H)$_2$}$_4$(THF)] (**2-Y**) (Cp′ = $C_5Me_4SiMe_3$) with styrene afforded the benzylic allyl heptahydride cluster **27**, in which the allyl moiety is bonded to one Y atom in an η$^3$-fashion and the phenyl moiety is bonded to another Y atom in an η$^2$-form (Scheme 13) [11]. No further reaction was observed even in the presence of excess styrene. Hydrogenolysis of **27** with $H_2$ afforded the THF-free yttrium octahydride cluster [{Cp′Y(μ-H)$_2$}$_4$] (**2-Y′**) and ethylbenzene. Under atmospheric pressure of $H_2$, styrene can be catalytically hydrogenated into ethylbenzene by **2-Y** or **2-Y′**. Treatment of **2-Y** with 1,3-cyclohexadiene (CHD) provided the CHD insertion product **28**, in which the resulting allyl unit is bonded to two Y atoms in an η$^1$:η$^1$-fashion (Scheme 13). The addition of an excess of CHD to **28** did not lead to further reaction, as in the case of styrene [30].

The reaction of **2-Y** with 1,4-bis(trimethylsilyl)-1,3-butadiyne gave the tetranuclear yttrium tetrahydride cluster **29**, which consists formally of a



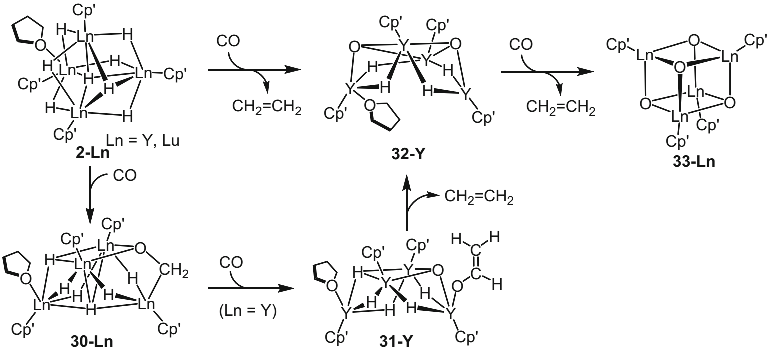
**Scheme 14** Reactions of **2-Y** with 1,4-bis(trimethylsilyl)-1,3-butadiyne

$[\{Cp'YH\}_4]^{4+}$ unit bonded to a butene-tetraanion species (Scheme 14) [11]. The butene-tetraanion moiety in **29** is bonded in an "inverse sandwich" fashion, in which the butene-tetraanion adopts a planar structure with $\mu_4$-coordination to two Y atoms and $\sigma{:}\eta^1$-coordination to the other two Y atoms. The formation of **29** can be explained by the following reaction paths. First, the two C≡C units of 1,4-bis(trimethylsilyl)-1,3-butadiyne react with two Y–H units of **2-Y** to afford the 1,3-butadiene-1,4-diyl hexahydride cluster **A**. Subsequently 1,4-Y–H addition to the 1,3-butadiene unit in **A** gives the 2-butene-1,1′,4-triyl/pentahydride species **B**. Deprotonation at the C4 position of the butene species by a Y–H unit affords the 2-butene-1,1′,4,4′-tetrayl/tetrahydride species **C** which can be described by the resonance structures **29**, **D**, and **E**.

The formation of a 2-butene-1,1′,4,4′-tetrayl species in the present reaction is in sharp contrast with the reaction of the binuclear ytterbium dihydride complex $[\{(Tp^{tBu,Me})Yb(\mu\text{-}H)\}_2]$ or the binuclear yttrium tetrahydride complex $[\{(NCN)Y(\mu\text{-}H)_2\}_2(THF)_3]$ (**26**) with 1,4-bis(trimethylsilyl)-1,3-butadiyne or 1,4-diphenyl-1,3-butadiyne, which yielded the enyne species $[(Tp^{tBu,Me})Yb(Me_3SiC{\equiv}C{-}C{=}CHSiMe_3)]$ [31] or 1,4-diphenyl-2-butyne-1,4-diyl species $[\{(NCN)YH(THF)\}_2(PhCH{-}C{\equiv}C{-}CHPh)]$ [29], respectively.

## 3.2 Reactions with Carbon Monoxide and Carbon Dioxide

Previous studies have shown that the reaction of rare earth metallocene monohydride complexes with CO mostly gave enediolate species [CpLnOCH=CHOLnCp]. In contrast, the reaction of the rare-earth metal-hydride

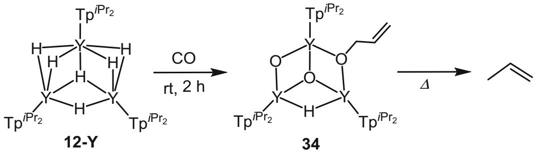


**Scheme 15** Reactions of **2-Ln** with CO

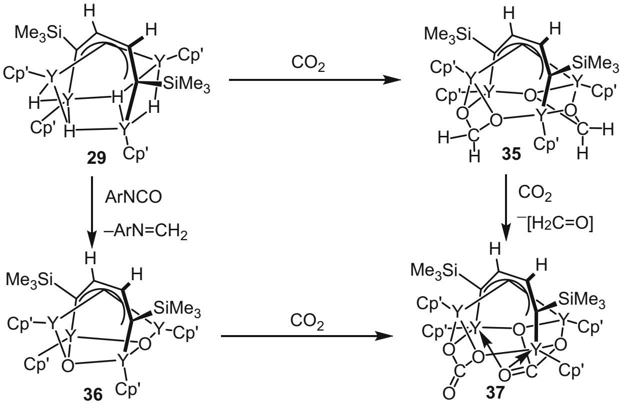
clusters [{Cp′Ln(μ-H)$_2$}$_4$(THF)] (Ln = Y, Lu) (**2-Ln**) with CO resulted in unprecedented selective formation of ethylene and the corresponding tetraoxo cluster [{Cp′Ln(μ$_3$-O)}$_4$] (**33-Ln**) under mild conditions (Scheme 15). Stepwise formation of some key reaction intermediates, such as the oxymethylene [(Cp′Y)$_4$(μ-OCH$_2$)(μ-H)$_6$(THF)] (**30-Ln**), the enolate [(Cp′Y)$_4$(OCH=CH$_2$)(μ-O)(μ-H)$_5$(THF)] (**31-Y**), and the dioxo species [(Cp′Y)$_4$(μ$_3$-O)$_2$(μ-H)$_4$(THF)] (**32-Y**), has been confirmed, some of which have been isolated and structurally characterized by X-ray diffraction studies. These results may shed light on the mechanistic aspects of the Fischer–Tropsch processes, which produce hydrocarbons and oxygenates by hydrogenation of CO on heterogeneous transition metal catalysts [32].

With regard to non-Cp-ligated rare earth polyhydrides, the reaction of the tris(3,5-diisopropylpyrazolyl)borate-ligated trinuclear yttrium hydride cluster [{(Tp$^{iPr2}$)Y(μ-H)$_2$}$_3$] (**12-Y**) with CO at room temperature was reported to afford the trinuclear hydride/oxo/propanolate cluster [(Tp$^{iPr2}$Y)$_3$(μ-H)(μ-O)$_2$(μ-OCH$_2$CHCH$_2$)] (**34**) through hydrogenation and coupling of three CO molecules (Scheme 16) [19]. Heating a toluene solution of this complex released only propene with no observed formation of ethylene.

Reactions of the rare earth hydride clusters [{Cp′Ln(μ-H)$_2$}$_4$(THF)] (Ln = Y, Lu) (**2-Ln**) with CO$_2$ took place immediately, but no characterizable products could be obtained. In contrast, their action of the butene-tetraanion/tetrahydride cluster **29** with CO$_2$ afforded the structurally characterizable bis(methylene diolate) complex **35** in high yield (Scheme 17) [33]. In this reaction, both C=O double bonds in CO$_2$ are reduced to C–O single bonds, in contrast with the reactions of most transition metal hydrides, which usually give formate MOCHO species. The reaction of an aryl isocyanate compound ArNCO with **29** afforded the μ$_3$-oxo cluster **36**. The methylene diolate **35** and the oxo cluster **36** can undergo CO$_2$ insertion to give the structurally characterizable carbonate cluster **37**.



**Scheme 16** Reaction of **12-Y** with CO



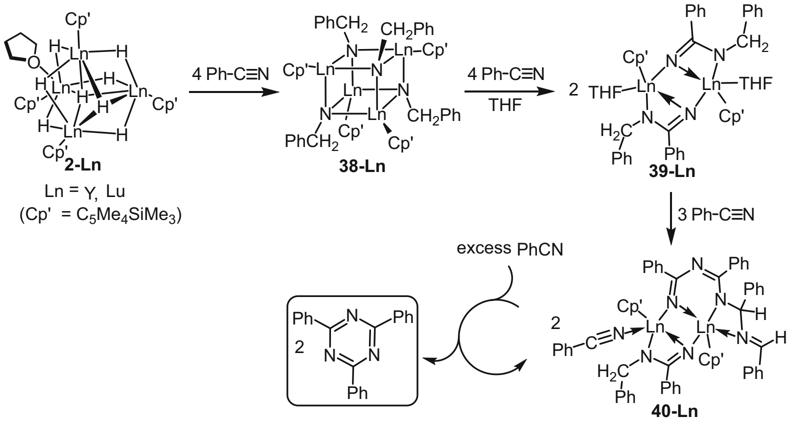
**Scheme 17** Reactions of **29** with $CO_2$

## 3.3 Reactions with Nitriles

The reaction of the rare earth hydride clusters [{Cp′Ln(μ-H)$_2$}$_4$(THF)] (**2-Ln**) (Ln = Y, Lu) with 4 equiv. of benzonitrile gave the corresponding tetranuclear cubane-like imido clusters [{Cp′Ln(μ$_3$-NCH$_2$Ph)}$_4$] (Ln = Y, Lu) (**38-Ln**) (Scheme 18) [11]. In these reactions, the C≡N triple bond of the nitrile compound is completely reduced to a C–N single bond following double Ln–H addition. This is in contrast to the previously reported reduction of nitriles by rare earth metallocene hydride complexes or group 4 metallocene dihydride complexes, which afforded only single-insertion products.

The reaction of an excess amount of benzonitrile with the benzylimido clusters **38-Ln** gave the benzonitrile tetramerization products **40-Ln**, via the benzamidinate-dianion compound **39-Ln** (Scheme 18). The direct reaction of compound **39-Ln** with three equivalents of benzonitrile also gave **40-Ln** in high yield. These results indicate that **39-Ln** should be an intermediate in the formation of **40-Ln** from **38-Ln**. The one step reaction of **2-Y** with 14 equivalents of benzonitrile also yielded **40-Y**.

When an excess of benzonitrile was added to a toluene solution of **40-Ln**, the cyclotrimerization product of benzonitrile, namely triphenyl triazine $C_3N_3Ph_3$, was obtained selectively (Scheme 18).The recovery of **40-Ln** from the reactions confirms that the benzonitrile-tetramerized complex **40-Ln** is the active catalyst. The



**Scheme 18** Reactions of **2-Ln** with nitriles

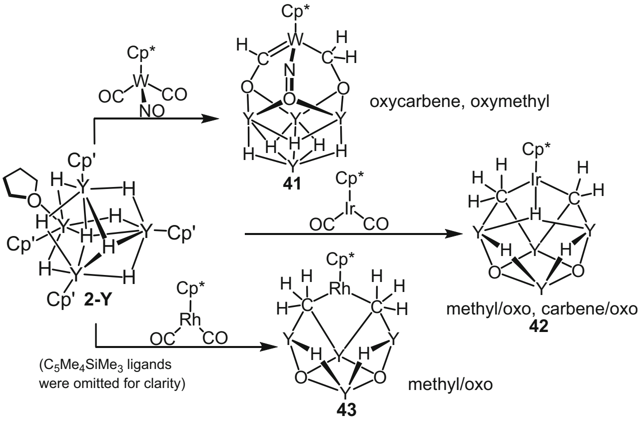
polyhydride clusters [{Cp′Ln(μ-H)$_2$}$_4$(THF)] (**2-Ln**), the imido clusters **38-Ln**, and the benzamidinate-dianion compounds **39-Ln** are also active for the catalytic cyclotrimerization of benzonitrile [34].

## 3.4 Reactions with d-Transition Metal Carbonyl Complexes

The reduction of metal carbonyl complexes M(CO) by rare earth hydrides has hardly been studied. Until recently, the only precedent was the reaction of scandocene hydride complex [Cp*$_2$ScH(THF)] with [CpCo(CO)$_2$], which yielded the scandoxycarbene species [CpCo(CO) = CH–O–ScCp*$_2$] [35]. On the other hand, the reactions of the yttrium hydride cluster [{Cp′Y(μ-H)$_2$}$_4$(THF)] (**2-Y**) with various transition metal carbonyl complexes such as [Cp*W(CO)$_2$(NO)], [Cp*Ir(CO)$_2$], or [Cp*Rh(CO)$_2$] were examined, which afforded selectively oxycarbene/oxymethyl (**41**), oxo/carbene/methyl (**42**), or oxo/methyl (**43**) clusters, with the reaction patterns being dependent on the nature of the transition metal carbonyls (Scheme 19) [36]. In the reaction of **2-Y** with [Cp*Rh(CO)$_2$], two C≡O triple bonds of the carbonyl ligands were completely reduced and cleaved by addition of six Y–H bonds from **2-Y**. These reactions not only provide a novel series of heteromultimetallic clusters bearing a robust tetranuclear yttrium frame, but they can also afford the mechanistic aspects of the Fischer–Tropsch synthesis, which involves the hydrogenation of CO in the presence of transition metal catalysts.

## 3.5 Reactions with d-Transition Metal Hydrides

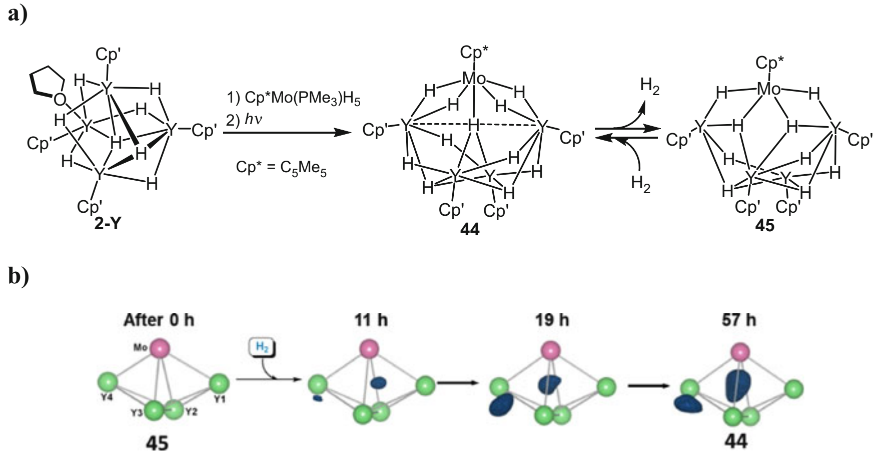
Heteromultimetallic hydride clusters containing both d-transition metals and rare-earth metals (including f-block metals) are of substantial interest, since they may



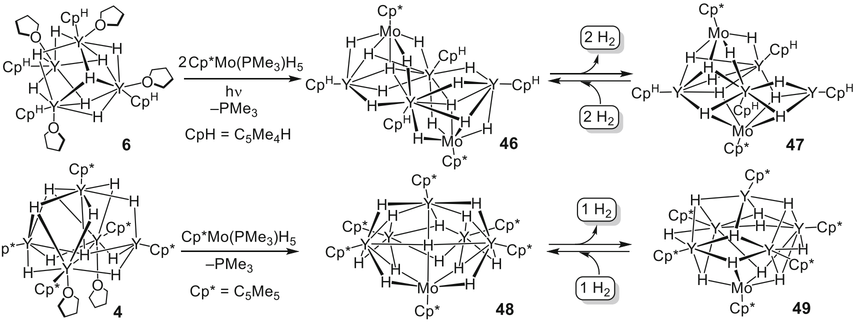
**Scheme 19** Reactions of **2-Y** with transition metal carbonyl complexes

demonstrate unique reactivity as a result of the multimetallic synergistic effect between the two substantially different metal types. Well-defined hydride clusters of this type are also of great interest as molecular models for hydrogen storage alloys such as $LaNi_5$. However, such heteromultimetallic clusters have not yet been deeply explored due to difficulty in their synthesis and structural characterization. The reaction of the yttrium hydride cluster $[\{Cp'Y(\mu\text{-}H)_2\}_4(THF)]$ (**2-Y**) with the molybdenum hydride $[Cp^*Mo(PMe_3)H_5]$ easily afforded the corresponding heteromultimetallic polyhydride cluster $[(Cp'Y)_4(\mu\text{-}H)_{11}MoCp^*]$ (**44**) (Scheme 20a) [37]. Cluster **44** released one $H_2$ molecule under vacuum condition to give a new cluster $[(Cp'Y)_4(\mu\text{-}H)_9MoCp^*]$ (**45**). Unprecedented structural features including a trigonal bipyramidal $\mu_5$-H atom in **44** and unique reactivities such as hydrogen addition/release reactions between **44** and **45** have been clarified. Monitoring of $H_2$ addition to the cluster **45** in a single-crystal-to-single-crystal process by X-ray diffraction has been achieved (Scheme 20b) [37]. Density functional theory (DFT) studies have demonstrated that the hydrogen addition process is cooperatively promoted by the Y/Mo heteromultimetallic sites, thus offering unprecedented insight into the hydrogen addition and release process of metal-hydride clusters.

Changing the steric bulk of the ancillary ligands on the Y atom could also allow the construction of the corresponding heteromultimetallic hydride clusters in the reaction with $[Cp^*Mo(PMe_3)H_5]$. The structural features and hydrogen uptake and release properties of the resulting heteromultimetallic hydride clusters are significantly influenced by the supporting ligands. The reaction of the $C_5Me_4H$-ligated tetranuclear yttrium hydride cluster **6** (see Sect. 2.1) with $[Cp^*Mo(PMe_3)H_5]$ afforded a hexanuclear heterometallic hydride cluster **46** consisting of 4 yttrium, 2 molybdenum, and 14 hydride ligands (Scheme 21) [38]. Cluster **46** released two



**Scheme 20** (**a**) Synthesis of the d-f heteromultimetallic hydride cluster **44** by the reaction of **2-Y** with the molybdenum hydride complex Cp*Mo(PMe$_3$)H$_5$, and its reversible H$_2$ release and uptake. (**b**) X-ray monitoring of the solid **45** with H$_2$ in a single-crystal to single-crystal process. Gradual increase of the electron density in the metal frame is observed, which represents the formation of the hydride ligands through H$_2$ addition to **45**



**Scheme 21** Synthesis and reversible H$_2$ release/uptake of d-f heteromultimetallic hydride clusters

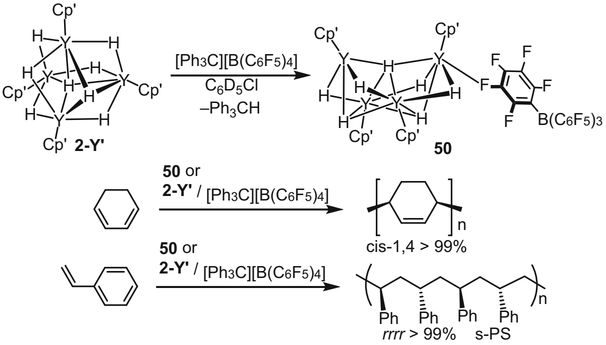
molecules of H$_2$ to give a new hydride cluster **47**, which could take up two molecules of H$_2$ to regenerate **46**. On the other hand, the reaction of the Cp*-ligated pentanuclear yttrium hydride cluster **4** with [Cp*Mo(PMe$_3$)H$_5$] afforded a d-f heterometallic hydride cluster **48** containing 5 yttrium, 1 molybdenum, and 11 hydride ligands (Scheme 21). Cluster **48** could lose only one molecule of H$_2$ and gave **49**. Addition of one molecule of H$_2$ to **49** could easily regenerate **48**.

## 4 Synthesis and Reactivity of Cationic Rare Earth Hydride Clusters

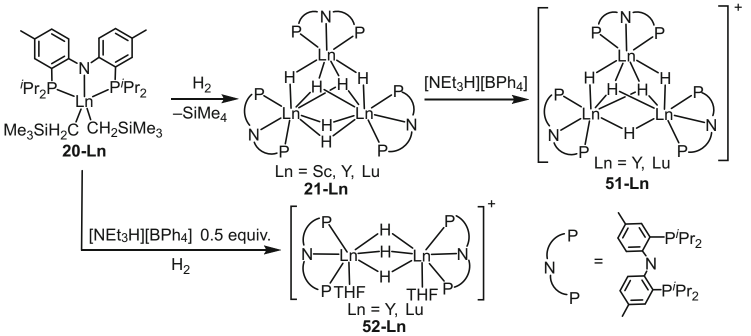
Cationic rare earth hydride clusters differ in their structure and reactivity from their neutral analogues. However, cationic clusters of this type have not been extensively studied. The reaction of the cyclopentadienyl-ligated yttrium octahydride cluster $[\{Cp'Y(\mu\text{-}H)_2\}_4]$ (**2-Y′**) with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ afforded the structurally characterized cationic heptahydride cluster, $[(Cp'Y)_4(\mu\text{-}H)_7][B(C_6F_5)_4]$ (**50**), in which a bonding interaction between one of the yttrium atoms in the $[Cp'_4Y_4H_7]^+$ cation and one fluorine atom in the $[B(C_6F_5)_4]^-$ anion is observed (Scheme 22). This is the first example of a well-defined cationic rare earth hydride cluster [30]. The cationic cluster **50** or the in-situ combination of **2-Y′** and $[Ph_3C][B(C_6F_5)_4]$ showed moderate activity for the regiospecific polymerization of either 1,3-cyclohexadiene or styrene (Scheme 22). This is in contrast with the reactions of the neutral hydride **2-Y** or **2-Y′** with 1,3-cyclohexadiene and styrene, which gave only the 1:1 addition products **28** and **27**, respectively.

The reaction of the PNP-ligated trinuclear rare earth hydride cluster $[\{(Me\text{-}PNP^{iPr})Ln(\mu\text{-}H)_2\}_3]$ (**21-Ln**) (see Sect. 2.5) with one equiv. of $[NEt_3H][BPh_4]$ afforded the cationic pentahydride cluster $[(Me\text{-}PNP^{iPr})_3Ln_3(\mu\text{-}H)_5][BPh_4]$ (**51-Ln**). Hydrogenolysis of the dialkyl complex $[(Me\text{-}PNP^{iPr})Ln(CH_2SiMe_3)_2]$ (**20-Ln**) with $H_2$ in the presence of 0.5 equiv. of $[NEt_3H][BPh_4]$ provided the cationic rare earth binuclear trihydride clusters $[(Me\text{-}PNP^{iPr})_2Ln_2(\mu\text{-}H)_3(THF)_2][BPh_4]$ (**52-Ln**) (Scheme 23). This is in sharp contrast with the hydrogenolysis of **20-Ln** in the absence of $[NEt_3H][BPh_4]$, which yielded the neutral hydride cluster **21-Ln** (see Scheme 9). The binuclear trihydride clusters **52-Ln** could be viewed as a combination of a monomeric dihydride "$(Me\text{-}PNP^{iPr})LnH_2$" and a cationic monohydride "$[(Me\text{-}PNP^{iPr})LnH]^+$"species.

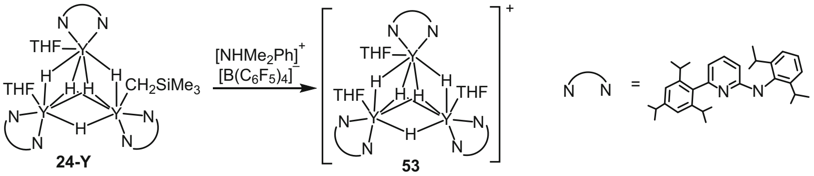
Protonation of the amidopyridinate-ligated trinuclear alkyl/hydride cluster $[(Ap^*Y)_3(\mu\text{-}H)_5(CH_2SiMe_3)(THF)_2]$ (**24-Y**) with $[NHMe_2Ph][B(C_6F_5)_4]$ afforded an alkyl-free cationic pentahydride cluster **53**, in which the core structure $Y_3H_5$



**Scheme 22** Synthesis of a cationic yttrium hydride cluster **50** and its catalysis for the polymerization of 1,3-cyclohexadiene and styrene



**Scheme 23** Synthesis of cationic di- and trinuclear rare-earth metal-hydride clusters **51-Ln** and **52-Ln** bearing PNP ligands

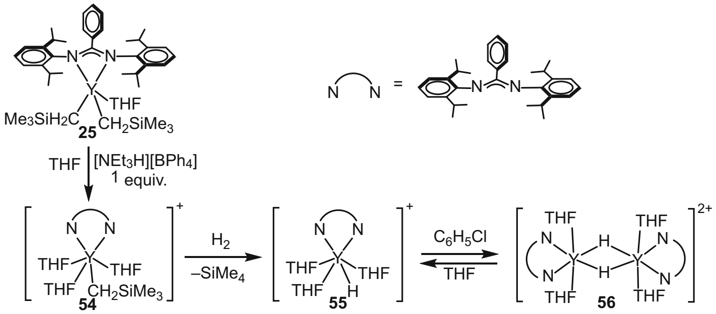


**Scheme 24** Synthesis of a monocationic yttrium hydride cluster **53** bearing an amidopyridinate ligands

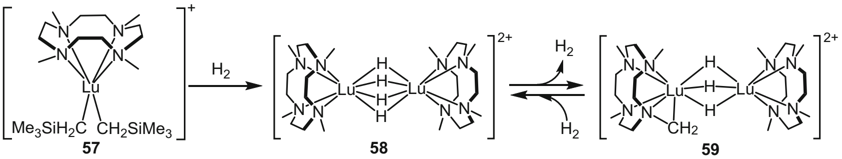
resembles that found in $[(\text{Me-PNP}^{i\text{Pr}}\text{Y})_3(\mu\text{-H})_5]^+$(**51-Y**) (Scheme 24) [39]. DFT calculations on the neutral cluster **24-Y** demonstrate that the Y–alkyl bond should possess enhanced reactivity compared to the Y–H bonds, thus accounting for the observation that the reaction occurred selectively through protonolysis of the Y–C bond rather than the Y–H bond.

Although hydrogenolysis of the cationic alkyl precursors such as $[\text{Cp}'\text{Ln}(\text{CH}_2\text{SiMe}_3)]^+$ and $[(\text{Me-PNP}^{i\text{Pr}})\text{Ln}(\text{CH}_2\text{SiMe}_3)]^+$ did not give a characterizable cationic hydride species, the hydrogenolysis of the amidinate-ligated cationic alkyl species $[(\text{NCN})\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_3]^+$ (**54**) ($\text{NCN} = \text{PhC}(\text{NC}_6\text{H}_3{}^i\text{Pr}_2\text{-2,6})_2$), generated in situ from the reaction of the dialkyl precursor **25** with 1 equiv. of $[\text{NEt}_3\text{H}][\text{BPh}_4]$, afforded a cationic terminal hydride compound $[(\text{NCN})\text{YH}(\text{THF})_3]^+$ (**55**) in good yield. Crystallization from a chlorobenzene solution provided the dicationic dihydride species $[\{(\text{NCN})\text{YH}(\text{THF})_2\}_2]^{2+}$ (**56**), while dissolution of this dimer in THF quantitatively regenerated the monomeric hydride **55** (Scheme 25) [40].

In a manner similar to the synthesis of the cationic hydride compound **55**, hydrogenolysis of the macrocyclic [NNNN]-ligated cationic dialkyl precursor $[(\text{Me}_4\text{TACD})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2]^+$(**57**) ($\text{Me}_4\text{TACD} = $ 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) with $H_2$ afforded the cationic bimetallic lutetium tetrahydride cluster $[(\text{Me}_4\text{TACD})\text{Lu}(\mu\text{-H})_4\text{Lu}(\text{Me}_4\text{TACD})]^{2+}$ (**58**). One of the methyl substituents on the $\text{Me}_4\text{TACD}$ ligand in **58** was found to undergo



**Scheme 25** Synthesis of a cationic terminal hydride compound **55** bearing an amidinate ligand and the interconversion between monomeric (**55**) and dimeric (**56**) yttrium hydrides



**Scheme 26** Synthesis of dicationic lutetium hydride clusters and its reversible hydrogen uptake and release

dehydrogenative C–H bond activation with Lu–H bond to give the cyclometalated trihydride **59** and one $H_2$ molecule. This species undergoes reversible $H_2$ uptake to regenerate the tetrahydride **58** under $H_2$ atmosphere (Scheme 26) [41].

## 5 Concluding Remarks and Outlook

Polynuclear rare earth hydride clusters with well-defined molecular structures can be obtained by hydrogenolysis of the dialkyl precursors bearing one anionic ancillary ligand such as $C_5Me_4SiMe_3$ per metal, through self-assembly of the resulting dihydride species. By using these hydride clusters as a building block, novel heteromultimetallic hydride clusters can also be prepared. It is now clear that the rare earth hydride clusters bearing one anionic ancillary ligand per metal can show more diverse and richer chemistry than those of monohydride relatives with two anionic ancillary ligands such as conventional metallocene compounds, because of the cooperation of multiple metals and hydrides. Recently, remarkable progress was found in the synthesis and chemistry of the analogous group 4 transition metal-hydride clusters bearing the $C_5Me_4SiMe_3$ ligands, which showed unique reactivity for the activation of inert molecules such as $N_2$ [42] and benzene [43]. As more hydride clusters are prepared and further investigations proceed, the diverse chemistry and applications available from rare earth and other transition metal elements will definitely be further extended. An exciting and rich future in this area can be expected.

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