DOI: 10.1002/anie.201406677

Rare-Earth-Metal Hydrides

Molecular Rare-Earth-Metal Hydrides in Non-Cyclopentadienyl Environments

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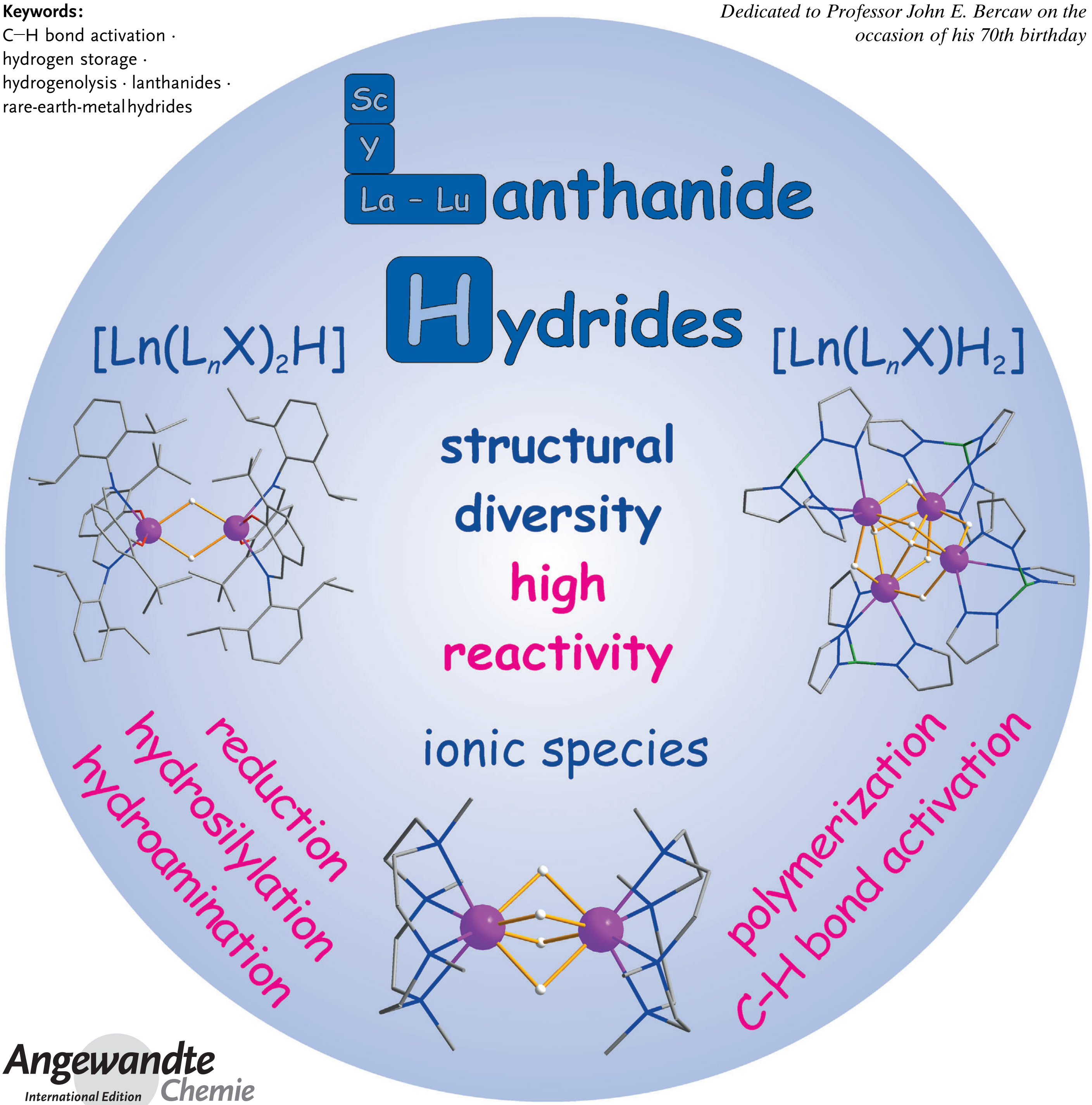
Keywords:
C–H bond activation ·
hydrogen storage ·
hydrogenolysis · lanthanides ·
rare-earth-metal hydrides

Dedicated to Professor John E. Bercaw on the occasion of his 70th birthday



Molecular hydrides of the rare-earth metals play an important role as homogeneous catalysts and as counterparts of solid-state interstitial hydrides. Structurally well-characterized non-metallocene-type hydride complexes allow the study of elementary reactions that occur at rare-earth-metal centers and of catalytic reactions involving bonds between rare-earth metals and hydrides. In addition to neutral hydrides, cationic derivatives have now become available.

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1. Introduction

The elegant use of cyclopentadienyl (Cp) ligands allowed the isolation and characterization of rare-earth-metal (Group 3 and the lanthanides) hydride complexes in the 1980s.[1] Molecular rare-earth-metal hydrides were mostly limited to those supported by the bis(η^5-cyclopentadienyl) or bent metallocene ligand frameworks.[2] Such complexes have played an essential role in studying σ-bond metathesis and developing homogeneous catalysts, for example, for α-olefin hydrogenation, hydroelementation, and polymerization. Following the great success of non-bis(cyclopentadienyl) ligand scaffolds ("post-metallocene catalysts") for polymerization catalysts based on Group 4 metals,[3] these new types of supporting ligands are increasingly applied to the Group 3 metals and lanthanides in order to expand their structural and reactivity patterns.[4] Electronic and steric control of the relatively large and highly electropositive rare-earth-metal centers is not straightforward, as intramolecular ligand fluxionality and intermolecular scrambling may preclude stable and inert compounds with a defined ligand sphere.[5] Furthermore, as lanthanide-based interstitial alloys such as $LaNi_5H_6$ have been studied as hydrogen-storage materials,[6] a search for molecular models for these solid-state systems appears warranted in order to understand the molecular mechanism of dihydrogen activation during uptake and release processes. Eventually the conceptual relationship between interstitial solid-state hydrides of the rare-earth metals of the type $[LnH_n]$ ($n = 2,3$) and molecular hydride complexes within a defined coordination sphere could be clarified.

Rare-earth-metal hydride complexes based on Cp ligands have been reviewed several times in the past decade.[2b,7] An overview of non-Cp rare-earth-metal hydrides was published in 2008,[4] followed by a review on rare-earth-metal alkyl and hydrido complexes supported by guanidinato and aminopyridinato ligands.[8] At that time, mainly neutral compounds of the type $[(L_nX)_2LnH]$ existed. Since 2008, there has been an increased interest in utilizing non-Cp ligands to obtain neutral and cationic hydride complexes with variable numbers of hydride ligands. The aim of the present review is to systematically survey structurally characterized trivalent neutral and cationic non-Cp rare-earth-metal hydride complexes reported since 2002.

2. Neutral Rare-Earth-Metal Hydrides

All lanthanide hydrides of the composition $[LnH_x]$ ($x = 2,3$) are interstitial compounds.[9] So far no molecular derivatives featuring only neutral donors $[(L_n)LnH_x]$ have been reported. Theoretical investigations on the binary hydrides $[LnH_3]_x$ (Ln = La and Gd) predict the possible existence of trinuclear and tetranuclear cores.[10]

2.1. Dihydrides of the Type $[(L_nX)LnH_2]$

Polynuclear hydride complexes were first stabilized using a substituted Cp ligand to give tetranuclear complexes of the composition $[(\eta^5\text{-}C_5Me_4SiMe_3)LnH_2(THF)_n]_4$.[7b,c,11] As an alternative to Cp ligands, polydentate, mostly nitrogen-based frameworks have recently been introduced in order to generate $[(L_nX)LnH_2]$ complexes. The structural diversity of these species is presented below.

2.1.1. Pyrazolyl Borate

Takats et al. employed monoanionic tris(pyrazolyl)borate scorpionate ligands ($Tp^{R,R'}$, $L_3^- = L_2X$-type, Scheme 1) for the isolation of rare-earth-metal dihydrides of the type $[(Tp^{R,R'})LnH_2]_n$.[12] To obtain these hydride complexes, the corresponding bis(alkyl) complexes, $[(Tp^{R,R'})Ln(CH_2SiMe_3)_2(THF)]$, were treated with a high pressure of dihydrogen (75 bar; Scheme 1). The requirement of high pressure is attributed to the stabilization of the Ln−alkyl bond by the hard scorpionate nitrogen donor set.

The nuclearity of the resulting rare-earth-metal hydride compounds is strongly influenced by the substituent R on the Tp ligand (Figure 1). Hexanuclear aggregates were obtained for Ln = Y, Lu using the sterically less demanding Tp^{H2} ligand. The solid-state structure of the isostructural yttrium and

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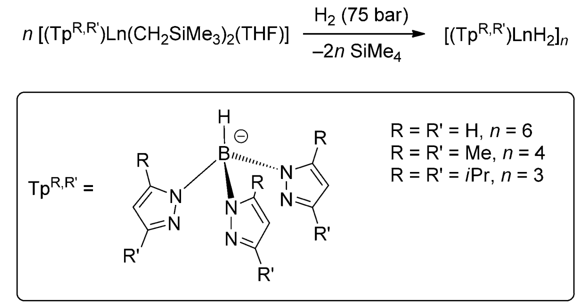


Scheme 1. Substituent-dependent nuclearity of tris(pyrazolyl)borate-supported hydrido complexes.

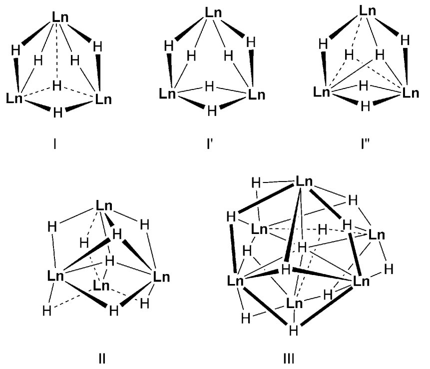
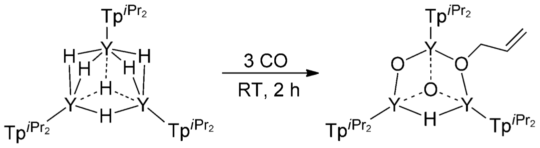


Figure 1. $[LnH_2]_n$ core structures of hydrido complexes $[(L_nX)LnH_2]$.

lutetium complexes indicate that the metal centers are positioned in a trigonal-antiprismatic manner (**III**). There are three μ_2-bridging, eight μ_3-bridging, and one μ_6-bridging hydride ligands. Tetranuclear aggregates for Ln = Y, Nd, Sm, and Lu were observed when Tp^{Me2} was used as ligand. In this type of aggregate (**II**), the metal atoms occupy the corners of a distorted tetrahedron. There is one μ_4-bridging hydride at the center of this tetrahedron, one face-capping μ_3-bridging hydride, and six μ_2-bridging hydrides (one μ_4, two μ_3, and five μ_2-bridging hydrides for Ln = Nd). By using Tp^{iPr2}, trinuclear aggregates for Ln = Y, Lu were obtained (**I**). Each of these complexes possesses five μ_2-bridging and one μ_3-bridging hydride ligands.

Efforts to obtain dihydride complexes using the sterically demanding $Tp^{tBu,Me}$ ligand have not been successful, although the alkyl groups bonded to the metal center were eliminated during hydrogenolysis. It is thought that the *t*Bu substituents of the ligand undergo metalation during the hydride synthesis.[12b] Recently, Anwander et al. stabilized a monomeric hydridoaluminate complex $[Tp^{tBu,Me}Ln\{(\mu\text{-}H)AlMe_2\}_2]$ (Ln = Y, Lu) with this bulky scorpionate ligand.[13]

Unique reactivity was observed when the yttrium compound $[(Tp^{iPr2})YH_2]_3$ was reacted with CO to give a trimeric mixed oxo/hydrido cluster with an additional propenolate that bridges two metal centers (Scheme 2).[12c] Apparently, CO is reduced by insertion into the metal–hydride bonds and coupled to give the propenolate group. Upon heating this complex, evolution of propene was detected by means of ^1H and ^{13}C NMR spectroscopy. It is not evident if an yttrium oxo cluster, similar to the oxo cubane reported for half-sandwich complexes, was formed after propene elimination.[14]



Scheme 2. Reaction of $[(Tp^{iPr2})YH_2]_3$ with CO.

Waldemar Fegler studied chemistry at RWTH Aachen University and at NTNU Trondheim. In 2009, he joined the group of Prof. Jun Okuda for his diploma and doctoral studies on the chemistry of molecular rare-earth-metal alkyl and hydride complexes. In 2011, he visited the group of Prof. Kazushi Mashima at Osaka University.

Mathias Kramer studied chemistry at Balliol College, Oxford. During his Part II thesis he was working with Prof. Dermot O'Hare on the chemistry of pentalene complexes. In 2005, he received his Master of Chemistry and subsequently started his doctoral studies on cationic alkyl and hydride complexes in the group of Prof. Jun Okuda in Aachen. Since 2009, he works at Continental AG in Hannover, Germany.

Ajay Venugopal is currently an assistant professor at IISER-TVM, India. His research is focused on the structure, bonding, and reaction mechanisms in organometallic chemistry. In 2008, he obtained his doctoral degree from the University of Münster, Germany, under Prof. Norbert W. Mitzel. He later moved to SINTEF Materials and Chemistry in Oslo, Norway, to work with Dr. Richard H. Heyn on gold-catalyzed C–H bond activation. In 2010, he received an Alexander von Humboldt fellowship to work with Prof. Jun Okuda at RWTH Aachen, Germany, on lanthanide hydrides.

Jun Okuda received his Dr. rer. nat. degree at RWTH Aachen University in 1984 with G. E. Herberich and was a Postdoctoral Associate at MIT with R. R. Schrock. After his habilitation at TU Munich, he held academic positions at the State University of New York at Albany and the universities of Marburg and Mainz before accepting the Chair of Organometallic Chemistry at his alma mater in 2003. His research interests include ligand design for reactive organometallic compounds, mechanistic study of homogeneous and energy-related catalysts, as well as artificial metalloenzymes.

2.1.2. *NNNN Macrocycle*

Amido triamine rare-earth-metal dihydrides of the type $[(Me_3TACD)LnH_2]_n$ ($n=3$: Ln = Y, Ho, Lu; $n=4$: Ln = La, Ce, Pr; $(Me_3TACD)H$ = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane; $L_{3+1}X$-type) were obtained by the reaction of the corresponding rare-earth-metal alkyls or allyls with H_2 or $PhSiH_3$ (Figure 2).[15] Single-crystal X-ray diffraction studies indicate that the trinuclear complexes contain only μ_2-bridging hydrides (**I′**) unlike those observed in $[(Tp^{iPr2})LnH_2]_3$ (**I**). Solution studies using NMR spectroscopy infer that there is no intermolecular exchange of the hydride ligands and the trinuclear framework remains intact.

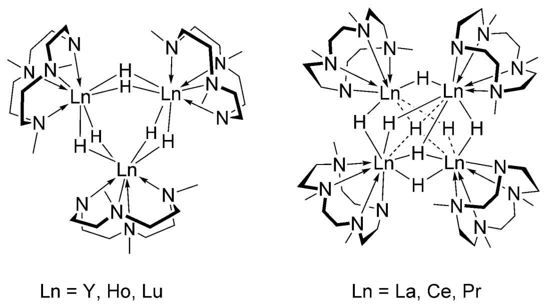
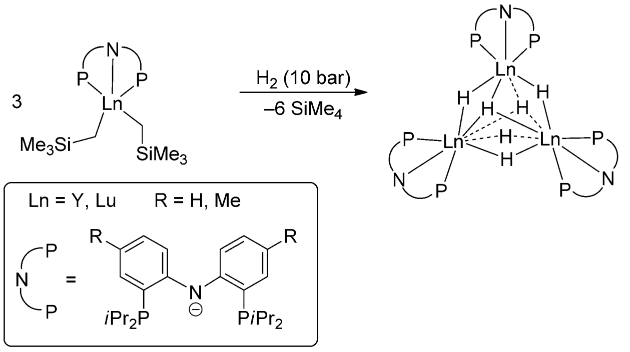


Figure 2. Tri- and tetranuclear hydrido complexes featuring the anionic Me_3TACD^- ligand.

Very few reports exist on hydride complexes of lanthanum.[16] The tetranuclear $[(Me_3TACD)LaH_2]_4$ represents the first Cp-free neutral lanthanum dihydrido complex.[15b] This compound was synthesized by hydrogenolysis of the allyl precursor, $[(Me_3TACD)La(\eta^3\text{-}C_3H_5)_2]$, as tris($\eta^3$-allyl) complexes of the larger rare-earth metals are more easily accessible and thermally stable than trimethylsilylmethyl derivatives. $[(Me_3TACD)LaH_2]_4$ is tetrameric in the solid state and the core structure of this aggregate resembles that found in $[(Tp^{Me2})LnH_2]_4$ (**II**), which differs from the cyclopentadienyl complex $[(\eta^5\text{-}C_5Me_4SiMe_3)LaH_2]_4$ by the bridging modes of the hydride ligands.[16a] These tri- and tetranuclear hydrido complexes were used as catalysts in the hydrosilylation of olefins and furfural, and in the copolymerization of cyclohexene oxide and carbon dioxide with a high degree of carbonate linkage.[15c]

2.1.3. *PNP Chelate*

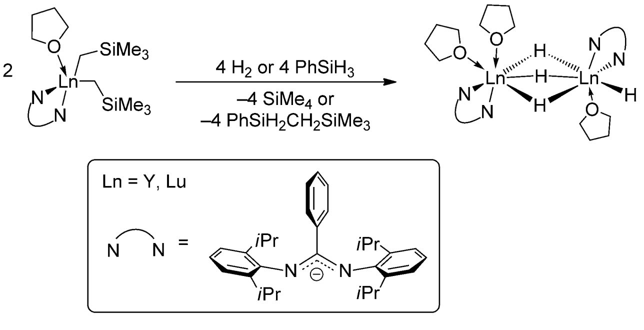
The monoanionic bis(phosphinophenyl) amido (PNP) ligand of the type $L_{2+1}X$ was adopted by Hou et al. to stabilize and isolate trimeric hexahydride complexes $[(Me\text{-}PNP^{iPr})LnH_2]_3$ (Ln = Y, Lu; $Me\text{-}PNP^{iPr} = \{4\text{-}Me\text{-}2\text{-}(iPr_2P)\text{-}C_6H_3\}_2N$; Scheme 3).[17] The outcome of the hydrogenolysis strongly depended on the substituents of the phosphine donors. Isopropyl groups were found to effectively stabilize the complex, whereas phenyl substituents gave only intractable products upon treatment with dihydrogen. The initially synthesized hexahydride $[(PNP^{iPr})YH_2]_3$ ($PNP^{iPr} = \{2\text{-}(iPr_2P)\text{-}C_6H_4\}_2N$) was identified by a quartet signal in the ^{1}H NMR spectrum (^{89}Y = 100 %, $I = {}^1/_2$). However, it proved to be too soluble in common solvents to be isolated. Thus, the ligand backbone was modified by adding methyl substituents in an attempt to decrease compound solubility. This change led to isolable trimeric hexahydride complexes $[(Me\text{-}PNP^{iPr})LnH_2]_3$ (Ln = Y, Lu; $Me\text{-}PNP^{iPr} = \{4\text{-}Me\text{-}2\text{-}(iPr_2P)\text{-}C_6H_3\}_2N$; Scheme 3). The $[Ln_3H_6]$ core, which is different from those found in $[(Tp^{iPr2})YH_2]_3$ and $[(Me_3TACD)LnH_2]_3$, possesses two μ_3-bridging and four μ_2-bridging hydride ligands (**I″**). One of the Y···Y distances (3.1648(7) Å) in $[(Me\text{-}PNP^{iPr})YH_2]_3$ is very short compared to values reported in the literature.[4] On the NMR time scale at ambient temperature, the fluxional structure contains equivalent hydride ligands.



Scheme 3. Preparation of trinuclear hydrido complexes supported by a PNP chelate ligand.

2.1.4. *Benzamidinate*

Amidinates of the type LX are common ligands. Amidinate-supported dialkyl complexes gave dimeric hydrido complexes $[(NCN)LnH_2]_2(THF)_3$ (Ln = Y, Lu; NCN = $PhC(NC_6H_3iPr_2\text{-}2,6)_2$) upon hydrogenolysis (Scheme 4).[18] The complexes contain three bridging and one terminal hydrido ligands of enhanced reactivity, for example, in the ring-opening of THF and insertion of unsaturated C–C and C–N bonds.



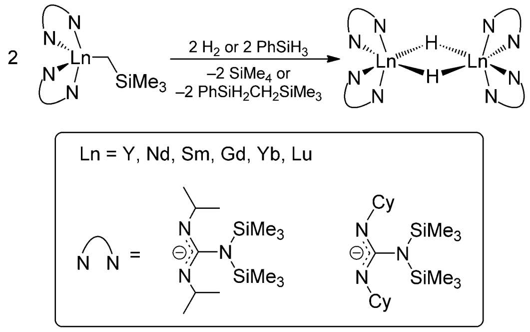
Scheme 4. Preparation of dimeric benzamidinato-supported hydrido complexes.

2.2. *Monohydrides of the Type [(L$_n$X$_2$)LnH]*

Complexes containing two sets of monoanionic ligands of the type L_nX show a certain similarity to metallocene hydrides with regard to their structure and reactivity, but offer more diverse structures and reactivity patterns than those of metallocene hydrides because of the harder donor atoms.

2.2.1. *Bis(guanidinate)*

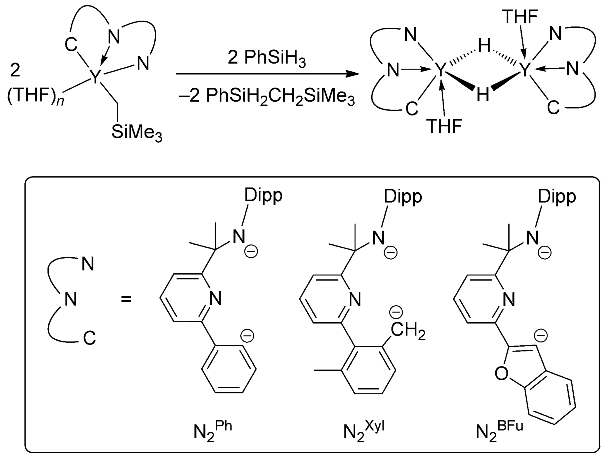
Bulky guanidinato ligands (LX-type) were utilized to prepare hydrides of the type $[\{(Me_3Si)_2NC(NR)_2\}_2LnH]_2$ (Ln = Y, Nd, Sm, Gd, Yb, Lu; R = *i*Pr, Cy (cyclohexyl); Scheme 5).[19] All complexes were dimeric in the solid state, similar to benzamidinate-supported complexes reported by Teuben et al.[20] The solution behavior of the yttrium compound $[\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2YH]_2$ was studied by NMR spectroscopy. In [D$_6$]benzene, the hydride signal in $[\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2YH]_2$ appears as a triplet ($^1J_{YH}$ = 26.2 Hz) in the ^{1}H NMR spectrum; hence, the structure is a dimer, as was observed in the solid state. In the presence of excess [D$_8$]THF, the hydride ligand appears as a doublet with a large coupling constant ($^1J_{YH}$ = 60.2 Hz), which the authors attribute to a monomeric hydride species, similar to other claims regarding terminal yttrium hydrides. Isolation of this complex was not possible and dissociation of the dimer was not achieved upon addition of excess PMe$_3$. A stoichiometric mixture of the bulky Y and Lu compounds $[\{(Me_3Si)_2NC(NCy)_2\}_2Ln(\mu\text{-}H)]_2$ in [D$_6$]benzene solutions also provided evidence for partial dissociation. After 24 h, a mixture of homo- and heterometallic dimers was identified from their chemical shifts and multiplicity patterns in the ^{1}H NMR spectrum. These guanidinato hydride complexes exhibit moderate catalytic activity toward ethylene polymerization and ring-opening polymerization of ε-caprolactone. The lutetium complex $[\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2LuH]_2$ reduced fullerene, resulting in a temperature-dependent equilibrium of a $C_{60}^{-\bullet}$ radical anion and a dianionic $(C_{60}^{-})_2$ dimer.[21]



Scheme 5. Preparation of dimeric bis(guanidinato) hydrido complexes.

2.2.2. *Aminopyridinate*

6-Aryl-substituted aminopyridinate ligands of the type $L_{1+1}X_2$ were investigated in order to stabilize rare-earth-metal hydride complexes. In attempts to obtain bis(alkyl) complexes with phenyl (Ph), xylyl (Xyl), and benzofuryl (BFu) substituted aminopyridines as starting compounds for hydrogenolysis, Trifonov et al. obtained cyclometalated mono(alkyl) species resulting from C−H bond activation of the substituent on the pyridine unit. These alkyl compounds reacted with PhSiH$_3$ to give dimeric hydride species $[N_2^{Ph}Y(\mu\text{-}H)(THF)]_2$, $[N_2^{Xyl}Y(\mu\text{-}H)(THF)]_2$, and $[N_2^{BFu}Y(\mu\text{-}H)(THF)]_2$ (Scheme 6).[22]



Scheme 6. Preparation of hydrido complexes bearing metalated aminopyridinato ligands.

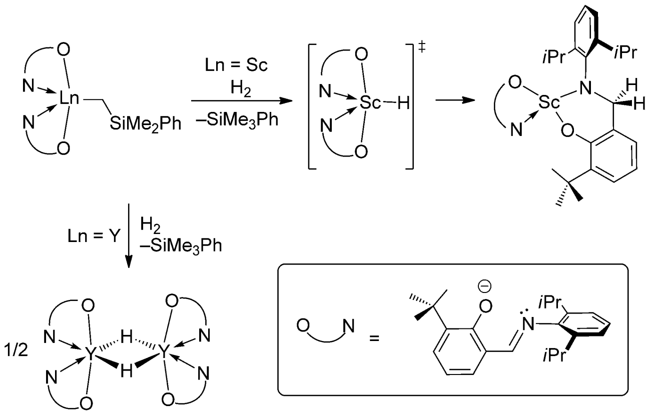
Notably, no hydrogenolysis of the metal−aryl or metal−benzyl bonds was observed, even with an excess of silane and longer reaction times. The use of dihydrogen resulted in the precipitation of an insoluble solid, which was not fully characterized. As a result of the steric bulk around the metal center, the presence of a coordinating solvent molecule and the inability to form reactive monomeric species by means of dissociation, no activity toward the polymerization of ethylene was detected when these hydride complexes were evaluated.

2.2.3. *Salicylaldiminate*

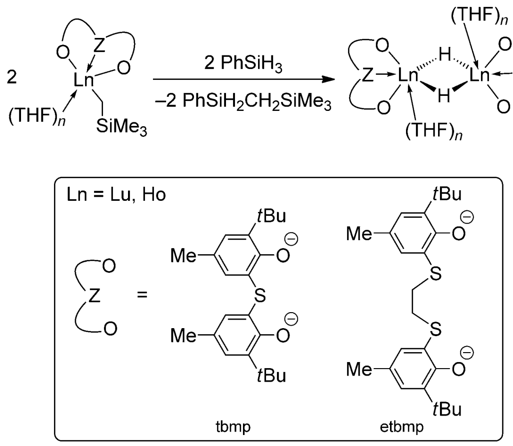
Rare-earth-metal hydrides of the type [(salicylaldiminato)$_2$LnH] (Ln = Y, Sc), supported by the bulky salicylaldimine ligand (LX-type), were investigated by Piers et al.[23] The yttrium hydride complex was obtained by hydrogenolysis of the corresponding alkyl complex using either H$_2$ or PhSiH$_3$ (Scheme 7). The resultant hydride complex is dimeric in both the solid state and solution. In the case of scandium, the hydride species was not observed, and it was thought to react with the ligand framework by nucleophilic attack of the hydride group at the aldimine carbon atom. This reactivity was attributed to the formation of a terminal Sc−H intermediate, which is unstable as a monomer, and too sterically encumbered to dimerize.

2.2.4. *Bis(phenolate)*

The variation of substituents on the phenyl rings of bis(phenolate) ligands and the incorporation of one or more donor atoms in the linker bridge led to a plethora of ligands of the type L_nX_2, differing in their steric demands and electronic properties. The rare-earth-metal alkyl complexes [(tbmp)Ln(CH$_2$SiMe$_3$)(THF)$_2$] and [(etbmp)Lu(CH$_2$SiMe$_3$)(THF)]



Scheme 7. Different reactivities of alkyl complexes of Y and Sc supported by salicylaldiminato ligands upon hydrogenolysis: formation of a stable hydrido complex versus hydride migration.



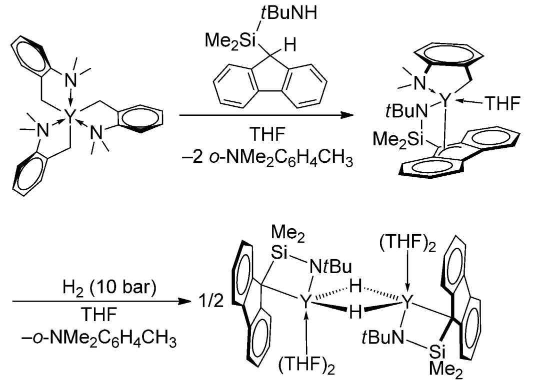
Scheme 8. Hydrido complexes stabilized by a bis(phenolato) ligand.

(Ln = Lu, Ho; tbmp = 6,6′-thiobis(2-*t*Bu-4-methylphenolate); etbmp = 6,6′-(ethane-1,2-diylbis(sulfanediyl))bis(2-*t*Bu-4-methylphenolate) reacted with $PhSiH_3$ to afford the corresponding hydrides (Scheme 8).[24] A dimeric structure of the type $[(tbmp)Ln(\mu\text{-}H)(THF)_2]_2$ was confirmed by X-ray diffraction methods (Lu···Lu distance 3.553(1) Å).[24a]

The lutetium hydrides catalyzed the highly regioselective hydrosilylation of various mono- and dienes with primary and secondary silanes. In addition, both the isolated and in situ generated hydrides were inactive in the polymerization of styrene, selectively affording a stable 2,1-insertion product. The lutetium hydrides showed moderate catalytic activity for the ring-opening polymerization of lactide.[24a]

2.2.5. *Fluorenyl Amide*

The homoleptic tris(*o*-dimethylaminobenzyl) rare-earth-metal complexes developed by Manzer[25] are known for most of the rare-earth metals.[26] Unlike the trimethylsilylmethyl complexes, they are accessible for the larger rare-earth metals. Recently, a range of differently substituted Cp-supported multinuclear hydrido complexes were obtained from *o*-aminobenzyl complexes.[27] Prior to this, Harder demonstrated that a heteroleptic yttrium complex, $[(9\text{-}tBuNSiMe_2C_{13}H_8)Y\{o\text{-}(NMe_2)CH_2C_6H_4\}]$, is hydrogenated using 10 bar of H_2 to give the dimeric hydride $[(9\text{-}tBuNSiMe_2C_{13}H_8)YH(THF)]_2$ (Scheme 9).[28] The fluorenyl ligand of the type LX_2 in this complex is coordinated to the metal center in an η^1 manner, in contrast to the family of so-called constrained-geometry hydride complexes with a linked Cp-amide ligand of the type $L_{2+1}X_2$.[2d,e]



Scheme 9. η^1-Bonded fluorenyl amido ligand bearing dinuclear hydrido complex synthesized from the *o*-dimethylaminobenzyl precursor.

2.2.6. *Bis(benzamidinate)*

A dianionic silylene-linked bis(benzamidinato) ligand has been recently used to obtain the hydride complex $[Me_2Si\{NC(Ph)N(Dipp)\}_2Y(\mu\text{-}H)]_2$ (Dipp = 2,6-$iPr_2C_6H_3$) from the corresponding alkyl complex through hydrogenolysis using $PhSiH_3$ (Figure 3).[29] Single-crystal X-ray analysis indicated a Y···Y distance of 3.4661(5) Å.

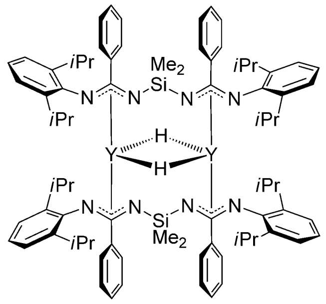
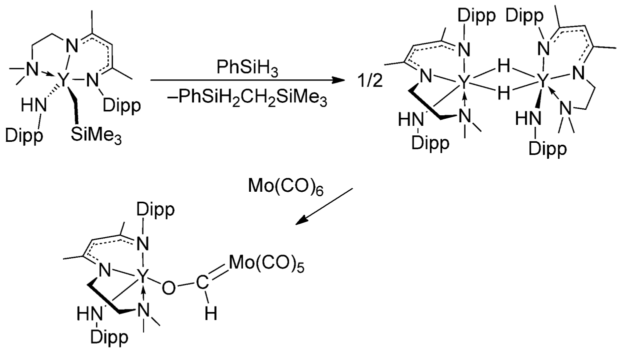


Figure 3. Dinuclear hydrido complex sterically encumbered by two linked benzamidinato ligands.

2.2.7. *β-Diketiminate*

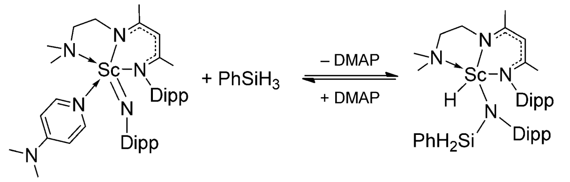
Chen et al. obtained a dimeric, bridging hydrido complex, $[(L')Y\{NH(Dipp)\}(\mu\text{-}H)]_2$, in which L′ is a β-diketiminato-based tridentate ligand of the type L_2X (L′ = (Dipp)N-(MeC)CH(CMe)$NCH_2CH_2NMe_2$; Scheme 10).[30] Insertion



Scheme 10. Preparation of a β-diketimininate and anilide supported dimeric hydrido complex.

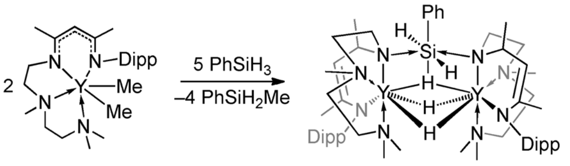
of C=N, N=N, N=C=N, and C=O functionalities across the Y–H bond was demonstrated. [(L)Y{NH(Dipp)}(μ-H)]$_2$ also reacted with Mo(CO)$_6$ resulting in a heterobimetallic yttrium molybdenum oxycarbene complex.

Using this ligand, the first terminal imido complex of scandium was obtained, and remarkably reacted with phenylsilane to give a scandium anilido complex with a terminal hydrido ligand in a reversible manner (Scheme 11).[31] This hydrido complex inserted carbodiimide and catalyzed the hydrosilylation of imines selectively, giving silylamines.



Scheme 11. Equilibrium between a β-diketimininate imido and a mixed amide hydride complex.

Another β-diketiminate-derived ligand with two additional N donors was used to stabilize a dimeric yttrium hydride complex, which was obtained through hydrogenolysis of a dimethyl complex (Scheme 12).[32] Surprisingly, not only

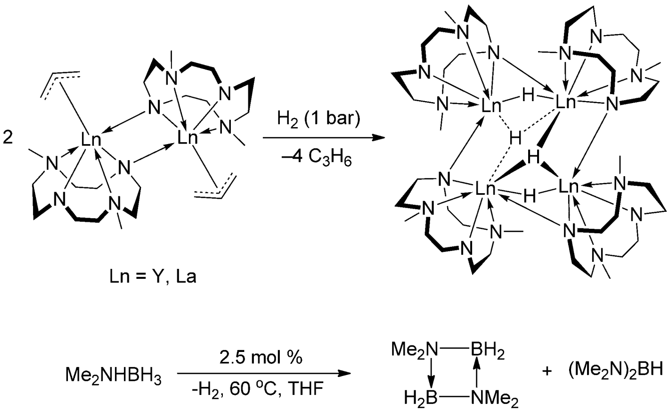


Scheme 12. Phenylsilane adduct formation during hydrogenolysis of a dimethyl β-diketiminato complex to give a diamine diamido stabilized dimeric hydrido complex.

one of the two intermediately formed hydrides was transferred to the ligand during hydrogenolysis making it dianionic, but also one molecule of phenylsilane was trapped inside the dimeric complex. One of the silyl hydrogen atoms is bridging the yttrium centers while two opposing nitrogen atoms coordinate to the hypervalent silicon atom. This unusual adduct was presented as a structural model for the σ-bond metathesis transition state between a Si–H bond and a d^{0}M–N bond.

2.2.8. NNNN Macrocycle

By using the dianionic NNNN-type macrocycle Me$_2$TACD (L$_{2+2}$X$_2$-type), dimeric lanthanum and yttrium allyl complexes were transformed into tetrameric tetrahydrido clusters that contain two μ_2- and two μ_3-bridging hydrido ligands (Scheme 13).[33a] Additionally, one amido group of each Me$_2$TACD ligand functions as a bridging unit between two of the metal centers. This type of bridging amido donor was also observed in heterobimetallic hydrido complexes of rare-earth/alkaline metals (Figure 5) and for the related mono(amido) ligand Me$_3$TACD in a cationic calcium hydrido cluster.[34]



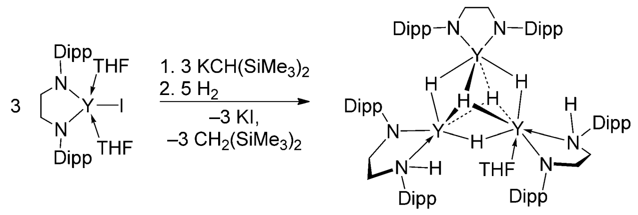
Scheme 13. Tetrameric Me$_2$TACD hydrido complexes.

These complexes were shown to catalyze the dehydrogenation of dimethylamine borane, a derivative of the potential hydrogen carrier ammonia borane.[33] The lanthanum complex was significantly more active than the yttrium homologue. To shed light on possible intermediate species, the lanthanum hydrido complex was treated with different amounts of dimethylamine borane. Two equivalents of the amine borane reacted with elimination of dihydrogen toward a bis(amido borane) adduct with retention of the tetrameric cluster framework. With more than two equivalents of amine borane, the tetrameric cluster was disintegrated to give different monomeric amido borane species with concomitant loss of dihydrogen. The basic amido functionalities of the macrocyclic ligands were found to assist the deprotonation of amine borane.[33a]

2.3. Neutral Rare-Earth-Metal Hydrides of Miscellaneous Types

2.3.1. Diamide

As early as 2004, Cloke et al. studied the hydrogenolysis of the diamido alkyl yttrium complex [{(Dipp)N(CH$_2$)}$_2$Y{CH(SiMe$_3$)$_2$}(THF)] using H$_2$ (Scheme 14).[35] A trinuclear yttrium hydride of the composition [{(Dipp)NH-

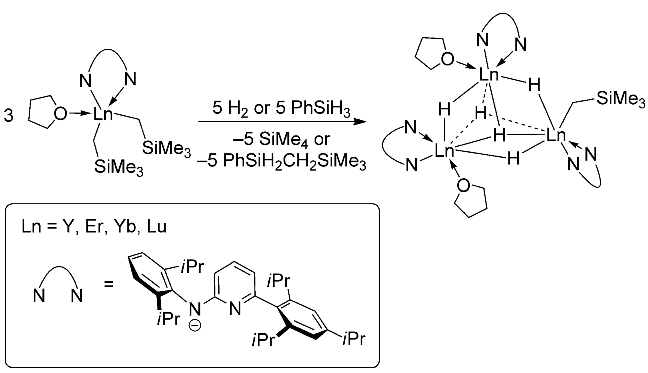


Scheme 14. In situ generation of a monoalkyl species and hydrogenolysis toward a trinuclear pentahydrido complex, isolated as a minor component of the product mixture.

$(CH_2)_2N(Dipp)\}_2\{(Dipp)N(CH_2)\}_2Y_3H_5(THF)]$ was isolated as a crystalline compound in a low yield. This product is believed to have formed from the addition of molecular hydrogen across Y−N bonds at two of the three yttrium centers. Single-crystal X-ray diffraction studies indicated that three hydride ligands are μ_2-bridging between the three metal centers, forming a hexagon, and the two other hydrides are μ_3-bridging the three metal atoms, thereby capping the hexagon. The hydrides are located in close vicinity to a pair of relatively acidic amine protons. The solid-state structure is, however, inconsistent with the solution NMR studies, which indicate that the major species is $[\{(Dipp)N(CH_2)\}_2YH(THF)_x]_n$.

2.3.2. *Aminopyridinate*

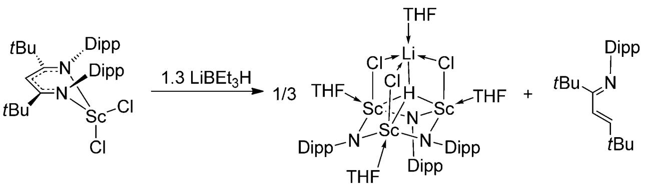
When bis(alkyl) complexes $[Ap^*Ln(CH_2SiMe_3)_2(THF)]$ (Ln = Y, Er, Yb, Lu), supported by a bulky aminopyridinato ligand of the type $L_{1+1}X$ (Ap*H = (Dipp){6-(2,4,6-triisopropylphenyl)pyridin-2-yl}amine), were treated either with $PhSiH_3$ or H_2 at elevated pressures, trinuclear alkyl hydrido aggregates of the type $[(Ap^*)_3Ln_3H_5(CH_2SiMe_3)(THF)_2]$ were obtained (Scheme 15).[36] Notably, this compound is the first example of a trinuclear alkyl hydrido aggregate stabilized by a non-Cp ligand. The Y_3H_5 core resembles the one found in $[\{(Dipp)NH(CH_2)_2N(Dipp)\}_2\{(Dipp)N(CH_2)\}_2Y_3H_5(THF)]$ depicted in Scheme 14. In addition to one aminopyridinato ligand, one of the yttrium atoms bears a CH_2SiMe_3 ligand, while each of the other two contain one coordinated THF molecule.



Scheme 15. Incomplete hydrogenolysis of an yttrium dialkyl supported by an aminopyridinato ligand to give a trinuclear mixed alkyl hydrido complex.

2.3.3. *β-Diketiminate*

When the β-diketiminato scandium dichloro complex [(Dipp-*t*Bu-nacnac)ScCl$_2$] (Dipp-*t*Bu-nacnac = CH{(C*t*Bu)-(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$) was reacted with $LiBEt_3H$, the scandium imido cluster $[(NDipp)ScCl(THF)]_3[LiH(THF)]$, featuring a central μ_4-bridging hydride, was formed along with an enamine by-product (Scheme 16).[37] The proposed mechanism, which included hydride migration to the ligand, subsequent C−N bond cleavage, and aggregation of three metal imide fragments with one LiH moiety, was supported by an analogous reaction with $LiAlH_4$. Intermediate products were identified by monitoring the reaction by ^1H NMR spectroscopy and GC-MS.



Scheme 16. Formation of a mixed metal chloro hydrido aggregate supported by THF and imido ligands resulting from ligand fragmentation upon hydride transfer.

2.3.4. *NNNN Macrocycle*

The stepwise hydrogenolysis of Me_3TACD-supported bis(allyl) complexes gave the mixed dimeric allyl hydrido complexes for neodymium and samarium (Figure 4).[15c] These dimeric structures are reminiscent of cyclopentadienyl-stabilized mixed hydrido alkyl complexes.[38]

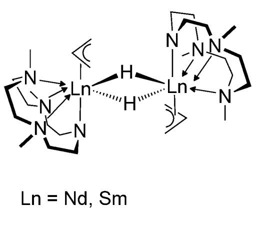


Figure 4. Dimeric mixed hydrido allyl complexes featuring the anionic Me_3TACD ligand.

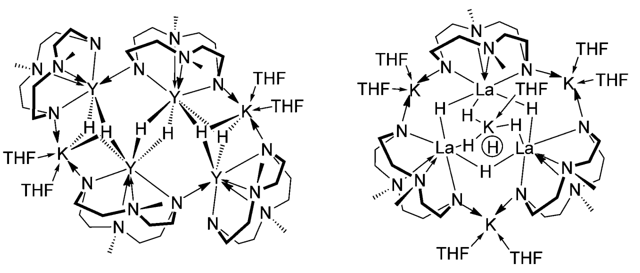
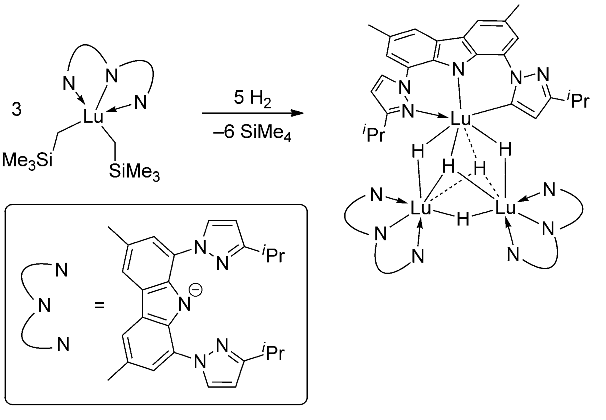


Figure 5. Polynuclear heterobimetallic hydrido complexes of rare-earth/alkaline metals stabilized by dianionic Me_2TACD ligands.

A similar tetradentate dianionic NNNN-type ligand, Me_2TACD, stabilizes heterobimetallic hydrido complexes of rare-earth/alkaline metals (Figure 5).[39] Intriguingly, amido nitrogen atoms of the macrocycle bonded to the rare-earth-metal centers additionally function as bridging units for the potassium atoms.

2.3.5. NNN Chelate

The lutetium hydrido complex reported by Hayes et al.[40] was synthesized by hydrogenolysis of a bis(alkyl) complex stabilized by an NNN pincer ligand of the type $L_{2+1}X$. It consists of a trinuclear metal core bridged by five hydrido ligands, in a manner similar to that shown previously.[35,36] Presumably, one hydrido ligand was lost through dehydrogenative metalation of the unsaturated backbone of a pyrazole moiety of one of the NNN pincer ligands (Scheme 17).



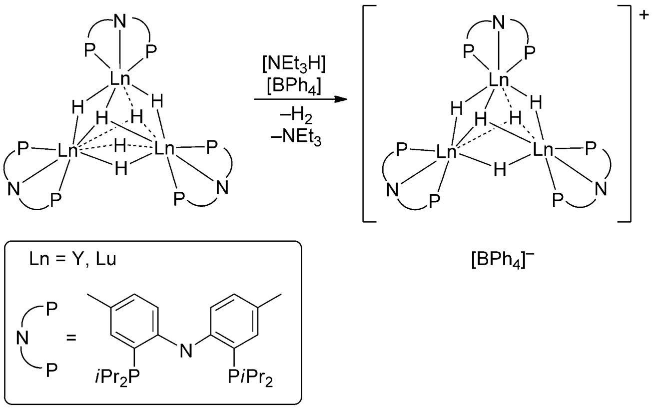
Scheme 17. A trinuclear lutetium hydrido complex that contains a metalated pyrazole functionality.

3. Cationic Rare-Earth-Metal Hydrides

The introduction of cationic charges was expected to reduce the nuclearity of rare-earth-metal hydrides, at the same time increasing the Lewis acidity. Only in 2011 was systematic access to ligand-supported rare-earth-metal hydrido cations reported.[17] These cationic complexes were obtained either by the protonation of hydride or alkyl ligands in the corresponding neutral hydride compounds (using weak Brønsted acids such as $[NEt_3H][BPh_4]$) or by hydrogenolysis of cationic rare-earth-metal alkyl precursors using H_2 or $PhSiH_3$.[2a]

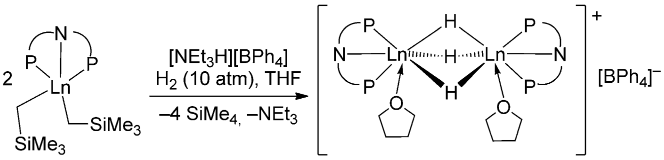
3.1. NNN Chelate

While probing the reactivity of the neutral $[(Me\text{-}PNP^{iPr})LnH_2]_3$ toward $[NEt_3H][BPh_4]$, monocationic trinuclear rare-earth-metal hydrides of the type $[(Me\text{-}PNP^{iPr})_3Ln_3H_5][BPh_4]$ (Ln = Lu, Y; Scheme 18) were isolated.[17] These complexes formed as a result of protonation of one of the hydride ligands by the Brønsted acid $[NEt_3H][BPh_4]$. The core structure of $[(Me\text{-}PNP^{iPr})_3Ln_3H_5][BPh_4]$ resembles the one found in neutral $[\{(Dipp)NH(CH_2)_2N(Dipp)\}_2\{(Dipp)N(CH_2)\}_2Y_3H_5(THF)]$ (Scheme 14). The Ln_3H_5 core is rigid even in solution with the hydride ligands giving rise to two different sets of resonances in the ^1H NMR spectrum. The $[BPh_4]^-$ anion does not appear to interact strongly with the cation either in the solid state or in solution. In the case of $[(\eta^5\text{-}C_5Me_4SiMe_3)_4Y_4H_7][B(C_6F_5)_4]$, a contact ion-pair structure was found in non-coordinating solvents.[41]



Scheme 18. Hydride abstraction from $[(Me\text{-}PNP^{iPr})LnH_2]_3$ through protonolysis with $[NEt_3H][BPh_4]$ to afford a cationic trimeric hydride complex.

In an alternative route, the dialkyl precursors $[(Me\text{-}PNP^{iPr})Ln(CH_2SiMe_3)_2]$ (Ln = Lu, Y) were reacted with H_2 in the presence of 0.5 equivalents of $[NEt_3H][BPh_4]$ to obtain dinuclear complexes with an Ln_2H_3 core $[(Me\text{-}PNP^{iPr})_3Ln_2H_3(THF)_2][BPh_4]$ (Scheme 19).

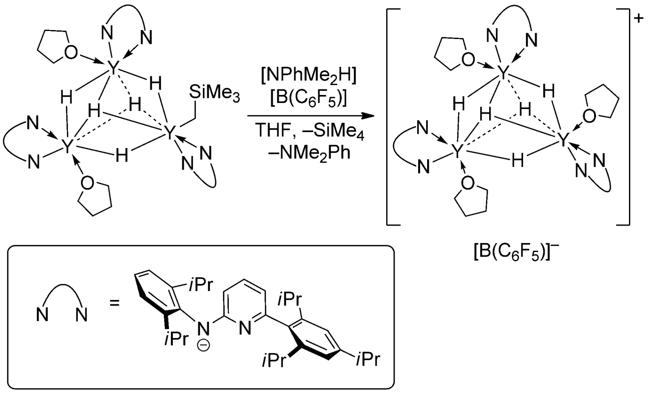


Scheme 19. Hydrogenolysis of a PNP pincer dialkyl complex in the presence of a Brønsted acid.

These dinuclear compounds can be regarded as a combination of a neutral dihydride and a cationic monohydride species formed during the hydrogenolysis of the corresponding neutral dialkyl and the monocationic alkyl species. Alkyl complexes were recently used to synthesize heterobimetallic hydrido complexes through protonation with ruthenium hydrides.[42]

3.2. Aminopyridinate

The reaction between the mixed alkyl hydrido aggregate $[(Ap^*)_3Y_3H_5(CH_2SiMe_3)(THF)_2]$ and one equivalent of $[NPhMe_2H][B(C_5F_5)_4]$ led to the protonation of the trimethylsilylmethyl group, resulting in the formation of the monocationic trinuclear hydride $[Ap^*_3Y_3H_5(THF)_3]$-

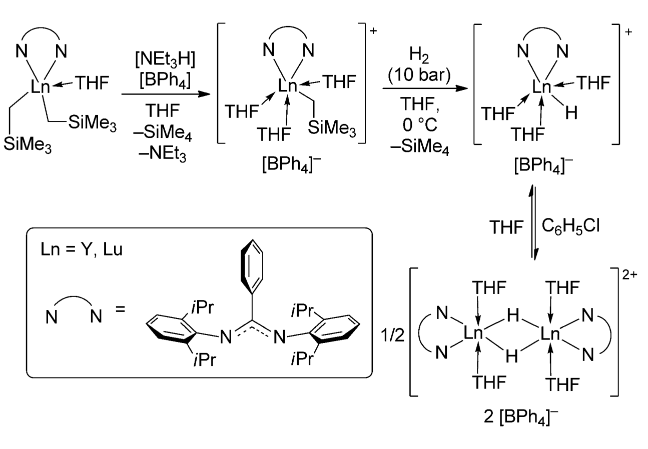


Scheme 20. Selective protonation of the alkyl moiety in the mixed alkyl hydrido complex $[(Ap^{*})_3Y_3H_5(CH_2SiMe_3)(THF)_2]$.

$[B(C_5F_5)_4]$ (Scheme 20).[36b] The Y_3H_5 core resembles that found in $[(Me\text{-}PNP^{iPr})_3Ln_3H_5][BPh_4]$ (Scheme 18). Notably, it was observed that the catalytic activity of this cation toward ethylene polymerization is appreciably higher than that of the corresponding mixed alkyl hydrido complex.

3.3. Benzamidinate

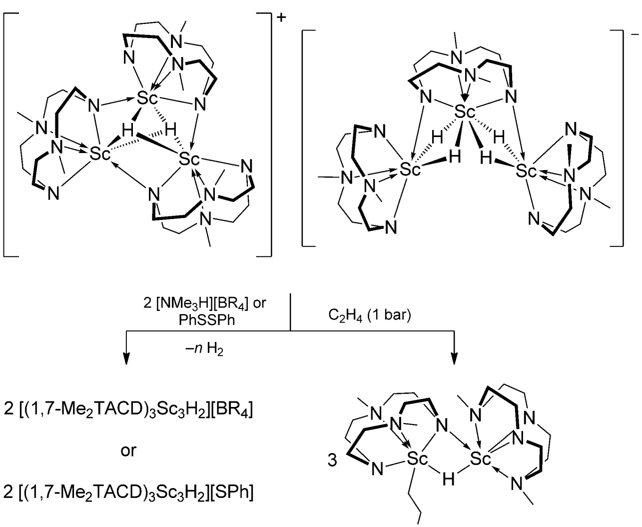
An example of cationic monohydrido complexes supported by bulky benzamidinate ligands has been reported by Hou et al.[43] In this case, synthesis of rare examples of terminal hydride complexes was achieved by hydrogenolysis of cationic alkyl species in THF. The ^{1}H NMR spectrum of the yttrium complex exhibited a characteristic doublet signal for the terminal hydrido ligand with a large Y–H coupling constant of $^1J_{YH} = 73.4$ Hz, which is comparable to those found in $[(\eta^5\text{-}C_5Me_5)_2YH(THF)]$ ($^1J_{YH} = 81.7$ Hz),[44] $[(Ind^{*})_2YH(THF)]$ ($^1J_{YH} = 82.0$ Hz, Ind* = heptamethylindenyl),[45] and $[(\eta^5\text{-}C_5Me_4SiMe_3)_2YH(THF)]$ ($^1J_{YH} = 74.8$ Hz).[46] Recrystallization of these complexes from chlorobenzene permitted the isolation of dimeric species featuring two bridging hydrido ligands, which could be transformed back into their mononuclear analogues upon dissolution in THF (Scheme 21).



Scheme 21. Preparation of cationic monohydrido complexes with amidinato ligands and their solvent-dependent dimerization.

3.4. NNNN and NNNC Chelate

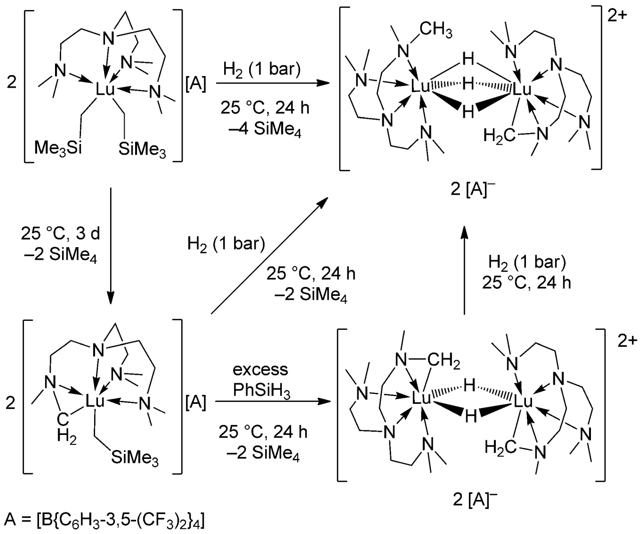
A scandium hydride ion pair, stabilized by the dianionic NNNN-type macrocyclic ligand 1,7-Me$_2$TACD, consists of a trimetallic dihydride cation and a trimetallic tetrahydride anion (Scheme 22).[47] The cyclic cationic part is similar to that in the monocationic calcium hydrido complex $[(1,4,7\text{-}Me_3TACD)_3Ca_3H_2][A]$ exhibiting two μ_3-bridging hydrides.[34] The anion is rather chain-like, featuring four μ_2-bridging hydrides.



Scheme 22. Scandium hydride ion pair stabilized by dianionic Me$_2$TACD ligands.

Enhanced reactivity was observed for the anion, which was doubly protonated by trimethylammonium borate or oxidized by diphenyldisulfide. In both cases, the cation with the C_3-symmetric core structure was obtained, charge-balanced by a borate or thiophenolate anion, respectively. Insertion of ethylene was accompanied by cluster rearrangement to give a bimetallic complex featuring one bridging hydrido ligand and a terminal ethyl group.

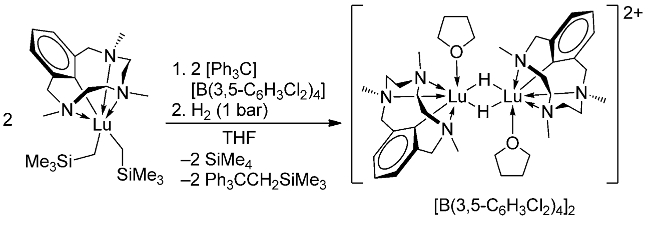
Neutral Me$_6$TREN (tris{2-(dimethylamino)ethyl}amine) was utilized to generate cationic dihydrido complexes starting from the cationic bis(alkyl) precursors $[(Me_6TREN)Ln(CH_2SiMe_3)_2][X]$ ($X = [B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]$). However, the adduct was thermally unstable, ultimately generating $[(Me_5TREN\text{-}CH_2)Lu(CH_2SiMe_3)][X]$ through C–H bond activation at one of the six methyl groups of Me$_6$TREN (Scheme 23).[48] Interestingly, upon reaction with PhSiH$_3$, $[(Me_5TREN\text{-}CH_2)Lu(CH_2SiMe_3)][X]$ converted into the dinuclear dicationic hydride complex $[(Me_5TREN\text{-}CH_2)Lu_2H_2][X]_2$. This dihydride species added H$_2$ to afford the dicationic trihydride $[(Me_5TRENCH_2)Lu(\mu_2\text{-}H)_3Lu(Me_6TREN)][X]_2$. This hydrido complex and an isostructural yttrium species, $[(Me_5TRENCH_2)Y(\mu_2\text{-}H)_3Y(Me_6TREN)][X]_2$, could also be formed directly by hydrogenolysis of the adducts $[(Me_6TREN)Ln(CH_2SiMe_3)_2][X]$ generated in situ. Attempts to prepare a tetrahydride by further hydrogenolysis were unsuccessful.



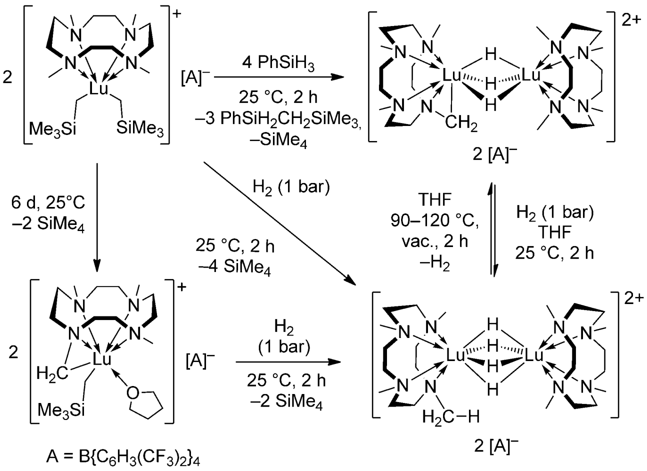
Scheme 23. Preparation of dicationic dinuclear hydrido complexes bearing neutral and metalated TREN ligands through hydrogenolysis of alkyl complexes.

The Lu···Lu distance in trihydride $[(Me_5TRENCH_2)Lu(\mu_2\text{-}H)_3Lu(Me_6TREN)][X]_2$ (3.2775(4) Å) is reduced by 0.24 Å compared to the dihydride (3.5147(2) Å). DFT calculations infer that a LUMO localized along the Lu···Lu axis in the dihydride facilitates the σ-bond metathesis reaction that gives the trihydride complex. Reactions of the di- and trihydrido complexes with benzophenone resulted in quantitative conversion of the hydrides and metal-bonded carbon atoms to the corresponding alkoxides. Analogous gadolinium and dysprosium hydrido complexes were shown to be single-molecule magnets.[49]

By using a *meta*-cyclophane-derived NNNC-type macrocyclic ligand, a dicationic dilutetium hydrido complex was obtained (Scheme 24).[50] The Lu···Lu distance is 3.4565(8) Å.



Scheme 24. Hydrogenolysis of an alkyl lutetium cation featuring a *meta*-cyclophane-derived NNNC-type ligand to afford a dicationic dihydrido complex.

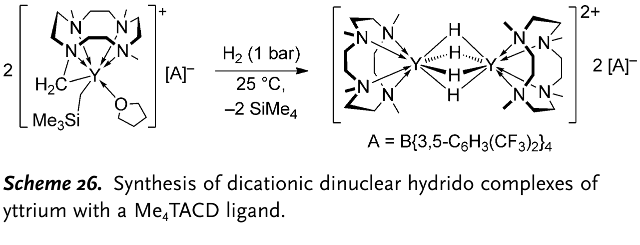


Scheme 25. Generation of dicationic dinuclear hydrido complexes bearing neutral and metalated TACD ligand through hydrogenolysis of alkyl complexes; reversible hydrogen addition and elimination.

Similar to Me$_6$TREN, neutral Me$_4$TACD (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) was used to stabilize cationic lutetium alkyl and hydrido complexes (Scheme 25).[51] As for the TREN ligand, the methyl substituents of the TACD ligand were prone to C–H bond activation. Using phenylsilane as hydride source, a triply hydride-bridged bimetallic Me$_4$TACD complex was obtained, which contains a metalated methyl group (Lu···Lu distance of 3.1747(5) Å).

This metal–carbon bond can add dihydrogen under mild conditions to give the first quadruply hydride-bridged bimetallic rare-earth-metal complex with a very short Lu···Lu distance of 2.9270(6) Å. Notably, a reverse C–H bond activation toward the trihydride is achieved by heating the tetrahydride complex under vacuum. Mechanistic investigations through theoretical calculations, kinetic studies, and isotope-labelling experiments indicate that the addition and release processes involve several steps, including labile dihydrogen adducts. Hydrogenolysis of the trihydride and the alkyl complexes in the solid state and in a single-crystal-to-single-crystal transformation corroborate that these findings might shed light on hydrogen-storage mechanisms involved in bulk materials containing metal–carbon bonds.[52c]

Using crystallography, the homologous quadruply hydride-bridged bimetallic complex of yttrium, $[(Me_4TACD)_2Y_2H_4]$, was shown to exhibit a Y···Y distance of 3.0615(9) Å, the shortest value reported in the literature (Scheme 26, Figure 6).[52c]



Scheme 26. Synthesis of dicationic dinuclear hydrido complexes of yttrium with a Me$_4$TACD ligand.

4. Summary and Outlook

Leaving behind the sterically protecting cyclopentadienyl ligand environment did not originally bode well for coordination of a highly polarizable, soft hydride at a large Lewis acidic center, such as a rare-earth metal. Since the first

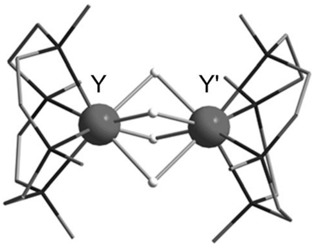
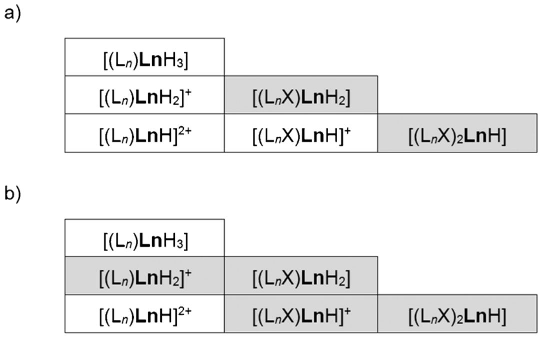


Figure 6. Molecular structure of the quadruply hydride bridged dinuclear cation $[(Me_4TACD)_2Y_2H_4]^{2+}$.[52c]



a)

$[(L_n)\mathbf{Ln}H_3]$		
$[(L_n)\mathbf{Ln}H_2]^+$	$[(L_nX)\mathbf{Ln}H_2]$	
$[(L_n)\mathbf{Ln}H]^{2+}$	$[(L_nX)\mathbf{Ln}H]^+$	$[(L_nX)_2\mathbf{Ln}H]$

b)

$[(L_n)\mathbf{Ln}H_3]$		
$[(L_n)\mathbf{Ln}H_2]^+$	$[(L_nX)\mathbf{Ln}H_2]$	
$[(L_n)\mathbf{Ln}H]^{2+}$	$[(L_nX)\mathbf{Ln}H]^+$	$[(L_nX)_2\mathbf{Ln}H]$

Figure 7. a) Types of rare-earth-metal hydrides without cyclopentadienyl ligands compiled in 2008[4] (grey). b) Currently known types of rare-earth-metal hydrides (grey).

overview on non-metallocene hydrides of rare-earth metals was published in 2008 (Figure 7 a),[4] a considerable number of new examples have been reported (Figure 7 b). Synthetic methods using σ-bond metathesis of the alkyl precursors without any stabilizing cyclopentadienyl ligand as well as characterization methods are now well established. Clearly, while metallocenes and half-sandwich hydrides led the way in this field, non-cyclopentadienyl ligands offer broader scopes of structures and reactivity. Non-metallocenes of Group 4 metals created a new dimension in the area of homogeneous olefin polymerization catalysts,[3] as new design principles allowed access to unprecedented rare-earth-metal hydrides. Although a neutral trihydride complex $[(L_n)LnH_3]$ that only contains a neutral ligand set remains elusive, cationic derivatives of the type $[(L_n)LnH_2]^+$ have become known, even with coordinated solvent molecules such as L = THF.[52] Pronounced tendency to form aggregates is common.

Non-metallocene hydrides of the rare-earth metals show novel reactivity patterns hitherto unknown for the well-studied metallocene hydride complexes. This becomes particularly evident in the reactivity toward so-called small molecules, such as dihydrogen, carbon monoxide, or ethylene. Remarkably, despite the tendency to aggregate into dimers and larger units, evidence has indicated that these clusters can act as active species in catalytic reactions such as olefin hydrosilylation.[15a]

Finally, molecular hydrides form a link to the interstitial hydride compounds $[LnH_x]$ ($x = 2,3$) of interest as hydrogen storage materials. A variety of metal-hydride bonds from terminal mode to μ_m-mode ($m = 2, 3, 4, 6$) have been observed. It is evident that the gap to the solid-state hydrides, some of which, such as the transparent semiconductor $[YH_x]$ ($x = 2,3$), show intriguing material properties,[53] has started to narrow.

Although early reports on THF-soluble dihydrides of the formula $[YbH_2]$ exist,[54] no systematic study on divalent hydride compounds has been conducted. With the current surge in divalent lanthanide complexes,[55] molecular rare-earth-metal hydrides with reduced metal centers having an oxidation state of $< +III$ probably offer a new area of study, in particular in the context of small-molecule activation.

We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support through the International Research Training Group "Selectivity in Chemo- and Biocatalysis (SeleCa)" (GRK 1628), the Cluster of Excellence "Tailor-Made Fuels from Biomass", and the Alexander von Humboldt Foundation for providing a postdoctoral fellowship to A.V. We are grateful to Professor Paul G. Hayes, University of Lethbridge, Canada, for numerous valuable comments.

Received: June 28, 2014

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