

Synthesis and Reactions of Polynuclear Polyhydrido Rare Earth Metal Complexes Containing “(C₅Me₄SiMe₃)LnH₂” Units: A New Frontier in Rare Earth Metal Hydride Chemistry

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A series of tetranuclear octahydrido rare earth metal complexes of general formula [(C₅Me₄SiMe₃)Ln(μ-H)₂]₄(THF)_n (Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, Lu; n = 0, 1, or 2) that contain C₅Me₄SiMe₃ as an ancillary ligand have been prepared and structurally characterized. These hydride clusters are soluble in common organic solvents such as THF, toluene, and hexane, and maintain their tetranuclear framework in solution. Such polynuclear polyhydrido complexes exhibit extremely high and unique reactivity toward a variety of unsaturated

substrates including CO, CO₂, and nitriles. The reaction of these neutral polyhydrides with one equivalent of [Ph₃C][B(C₆F₅)₄] affords the corresponding cationic hydride clusters [(C₅Me₄SiMe₃)₄Ln₄H₇(THF)_n][B(C₆F₅)₄], which can act as catalysts for the syndiospecific polymerization of styrene and regio- and stereospecific *cis*-1,4-polymerization of 1,3-cyclohexadiene.

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1. Introduction

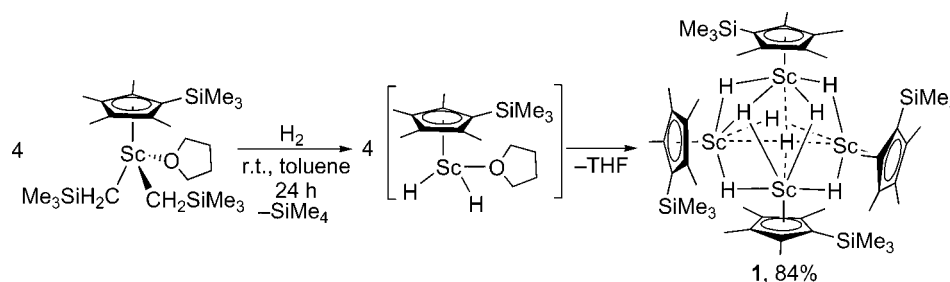
Metal hydrides are fundamental components in a wide range of stoichiometric and catalytic reactions, and their importance in modern inorganic and organic chemistry cannot be overemphasized.^[1,2] A large number of monohydride complexes of the rare earth (group 3 and lanthanide) metals of the general type “L₂MH” or “(L)(L')MH”, which are supported by two anionic ancillary ligands per metal, have been synthesized and studied^[2] since the first rare earth metallocene hydride complex was reported in the early 1980s.^[3] In contrast, dihydrido rare earth metal complexes of the type “LMH₂”, which bear one anionic ancillary ligand per metal, have been much less extensively investigated even though such complexes are of great interest both structurally and chemically. A major factor that has hampered the investigation of rare earth metal dihydride or polyhydride complexes is the difficulty in isolating structurally well defined complexes. Early attempts to prepare a dihydrido rare earth metal complex by reaction of dialkyl complexes such as [(C₅Me₅)Lu(CH₂CMe₃)₂(THF)]^[4] or [(C₅Me₄SiMe₃)Y(CH₂SiMe₃)₂(THF)]^[5] with H₂ did not afford a structurally characterized hydride species. The first structurally characterized dihydrido rare earth metal species was isolated as the Sm^{III}/K heteropolymetallic form

[(C₅Me₅)Sm(μ-H)₂]₆{KH(THF)₂]₃, which formally consists of six “(C₅Me₅)SmH₂” units and three “KH(THF)₂” units.^[6a] This complex was serendipitously obtained by the reaction (σ-bond metathesis and subsequent oxidation) of the Sm^{II} alkyl complex [(C₅Me₅)SmCH(SiMe₃)₂[(C₅Me₅-K(THF)₂)]_n]^[6] with an excess of PhSiH₃. Very recently, a series of salt-free polynuclear polyhydrido rare earth metal complexes that contain “(C₅Me₄SiMe₃)LnH₂” units has been synthesized from the C₅Me₄SiMe₃-ligated dialkyl complexes [(C₅Me₄SiMe₃)Ln(CH₂SiMe₃)₂(THF)] (Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, Lu). It has been found that these polyhydrido rare earth metal complexes show a unique reactivity that differs from that of conventional monohydride complexes. This article summarizes recent studies on this new class of rare earth metal hydride complexes.

2. Synthesis and Structures of Tetranuclear Octahydrido Rare Earth Metal Complexes

Hydrogenolysis of the C₅Me₄SiMe₃-ligated bis(trimethylsilylmethyl)scandium complex [(C₅Me₄SiMe₃)Sc(CH₂-SiMe₃)₂(THF)] with H₂ in toluene at room temperature gives the THF-free tetranuclear octahydride complex [(C₅Me₄SiMe₃)Sc(μ-H)₂]₄ (**1**) (Scheme 1).^[7] This complex can be viewed as being the result of a self-assembly of four “(C₅Me₄SiMe₃)ScH₂” units in a tetrahedron through “intermolecular” Sc–H interactions. There are a total of eight hydride ligands in the molecule, one of which is body-centered in a μ₄-H–Sc₄ fashion, one is face-capped in a μ₃-

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Scheme 1. Synthesis of a tetranuclear octahydrido scandium complex.

H–Sc₃ form, and six are edge-bridged in a μ_2 -H–Sc₂ style. The THF ligand bonded originally to the scandium metal center of the alkyl precursor is squeezed out in the hydride complex due to the formation of “intermolecular” Sc–H bonds.

Hydrogenolysis of the bis(trimethylsilylmethyl) complexes of larger rare earth metals such as Y, Er, and Tm in toluene affords the corresponding tetranuclear octahydride complexes [$\{(C_5Me_4SiMe_3)Ln(\mu-H)_2\}_4(THF)$] (**2**: Ln = Y;^[8] **3**: Ln = Er;^[9] **4**: Ln = Tm^[9]) where one of the four metal centers in these complexes bears an additional THF ligand (Scheme 2). The overall structure of the mono(THF)-containing polyhydride complexes **2–4** is almost the same as that of the THF-free Sc complex **1**. In the case of the analogous complexes of larger metals such as Gd (**5**),^[9] Dy (**6**),^[9] and Ho (**7**),^[9] an agostic interaction between the metal center and a methyl group of an adjacent C₅Me₄SiMe₃ ligand

is also observed, probably due to the greater steric unsaturation of these larger metal centers (Scheme 2).^[9,10] These results show that the fine structures of the tetranuclear octahydride complexes are, to some extent, dependent on the ionic radius of the metal centers.

In the case of lutetium, the reaction of the bisalkyl complex $[(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)]$ with H₂ did not give a single hydride complex.^[11] However, hydrogenolysis of the hydride-bridged dimeric mixed alkyl/hydride complex [$\{(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)(\mu-H)(THF)\}_2$] (**8**), which was prepared by reaction of $[(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)]$ with one equivalent of PhSiH₃, affords the tetranuclear mono(THF)-coordinated lutetium octahydride complex [$\{(C_5Me_4SiMe_3)Lu(\mu-H)_2\}_4(THF)$] (**9**) in THF (Scheme 3).^[12] The structure of **9** is identical with those of the analogous mono(THF)-containing complexes **2–4**. When the reaction of the alkyl/hydride complex **8** with H₂



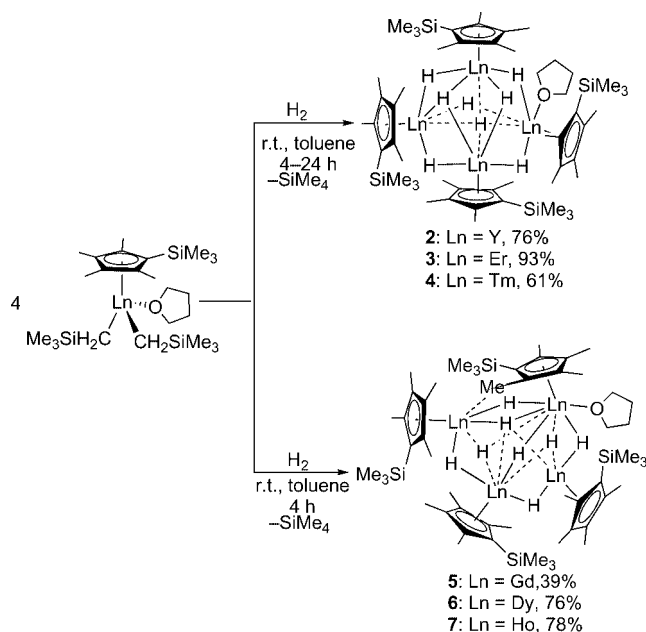
Zhaomin Hou was born in Shandong Province, China, in 1961. He received his B.Sc. from the China University of Petroleum (Shandong, China) in 1982, and his M.Sc. and Ph.D. from Kyushu University (Fukuoka, Japan) in 1986 and 1989, respectively. He joined RIKEN (The Institute of Physical and Chemical Research) in 1989, where he is now Chief Scientist and Director of the Organometallic Chemistry Laboratory. The current research activity in his group includes development of new catalysts for regio- and stereospecific olefin polymerization/copolymerization, new catalysts for efficient organic synthesis, and rare earth metal complexes with novel structures and reactivities, as well as synthesis of new functional materials. He is a recipient of the Japan Society of Coordination Chemistry Award for Young Scientists (1996), the Rare Earth Society of Japan Award for Young Scientists (1997), the Progress Award in Synthetic Organic Chemistry, Japan (2000), the JSPS Prize (2007), the Chemical Society of Japan Award for Creative Work for 2007, and the Mitsui Chemicals Catalysis Science Award (2007).



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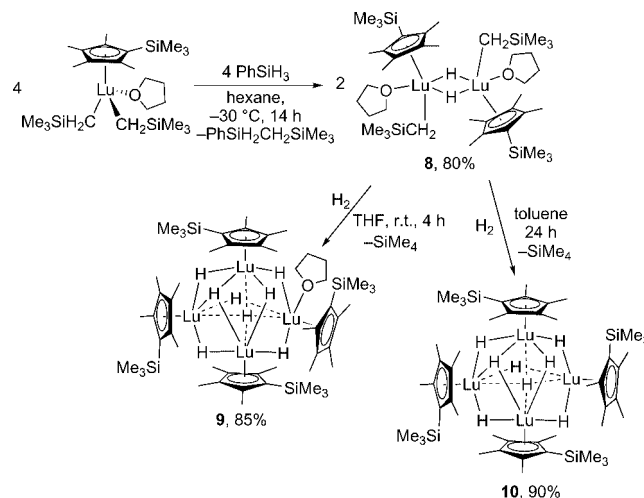


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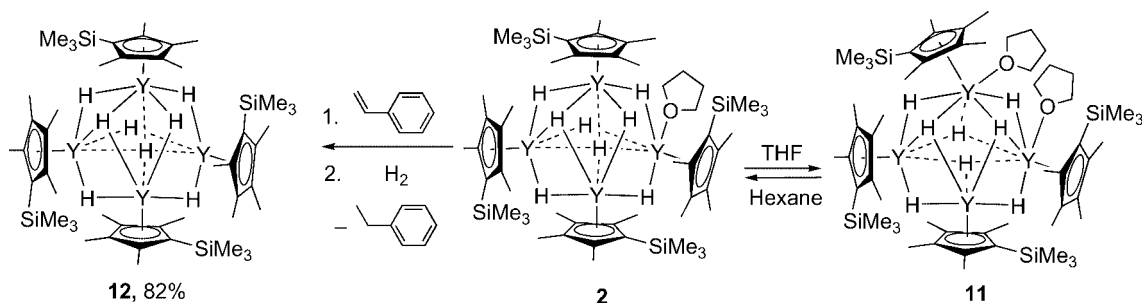
Scheme 2. Synthesis of mono(THF)-coordinated tetranuclear octahydrido rare earth metal complexes.

was carried out in toluene, the corresponding THF-free tetranuclear lutetium octahydride complex **10** was obtained (Scheme 3).^[12]



Scheme 3. Synthesis of THF-free and mono(THF)-coordinated lutetium polyhydride complexes.

The octahydride complexes **1–7**, **9**, and **10** are all soluble in common organic solvents such as THF, toluene, and hexane, and their tetranuclear frameworks are maintained in solution. In the case of yttrium, recrystallization of the mono(THF) complex **2** from THF gives the structurally characterizable bis(THF)-coordinated complex **11** (Scheme 4);^[9,12,13] formation of an analogous bis(THF)



Scheme 4. Formation of yttrium polyhydride complexes with and without THF ligands.

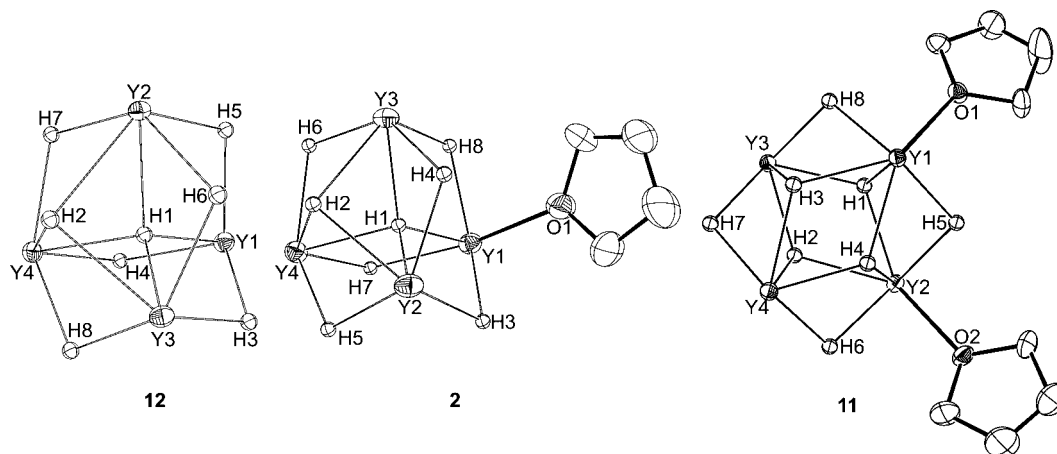
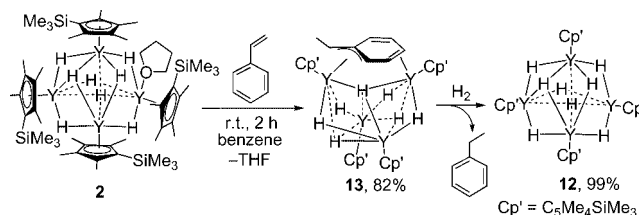


Figure 1. ORTEP drawings of the Y_4H_8 core structures of **12** (left, THF-free), **2** (middle, with one THF ligand), and **11** (right, with two THF ligands).

ethylbenzene and the THF-free yttrium octahydride complex $\{[(C_5Me_4SiMe_3)Y(\mu-H)_2]_4\}$ (**12**).^[14] Under 1 atm of H₂, styrene can be catalytically hydrogenated into ethylbenzene by **2** or **12**.



3. Reaction of Rare Earth Metal Polyhydrides with Unsaturated C–C Bonds

Reaction scheme showing the conversion of complex **2** to complex **14** (82% yield) under conditions: r.t., 1 h, benzene, -THF.

Reaction scheme showing the synthesis of cyclopentadienylidene complexes **15**, **16**, and **17** from complex **2**.

Complex **2** (a dimeric zirconium complex with two cyclopentadienylidene ligands and two cyclopentadienyl ligands) reacts with $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$ in benzene at room temperature (r.t.) for 4 days, with loss of H_2 and THF, to yield complex **15** (63% yield).

Complex **15** (a dimeric zirconium complex with two cyclopentadienylidene ligands and two cyclopentadienyl ligands) can be converted to complex **16** (63% yield) by loss of THF.

Complex **16** (a dimeric zirconium complex with two cyclopentadienylidene ligands and two cyclopentadienyl ligands) can be converted to complex **17** (63% yield) by loss of H_2 .

Complex **17** (a dimeric zirconium complex with two cyclopentadienylidene ligands and two cyclopentadienyl ligands) can be converted to complex **18** (63% yield) by loss of H_2 .

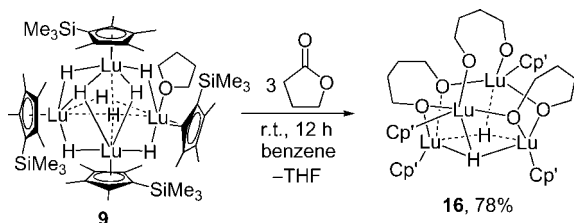
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The reaction of **2** with 1,3-cyclohexadiene (CHD) yields the 1,4-addition product **14** in which the resulting allyl unit interacts with two Y atoms through the two “terminal” carbon atoms, each of which bonds to one metal center in an η^1 -fashion (Scheme 6).^[9] As in the case of styrene, the use of an excess amount of CHD does not lead to further reaction.

The reaction of **2** with 1,4-bis(trimethylsilyl)-1,3-butadiyne affords the tetranuclear yttrium tetrahydride complex **15**, which formally consists of a $[(C_5Me_4SiMe_3)YH]_4^{4+}$ unit and a butene-tetraanion species (Scheme 7).^[8] This butene-tetraanion moiety is bonded to two yttrium atoms in a π, η^4 -“inverse-sandwich” fashion and to the other two yttrium atoms in a σ_1, μ_1 -terminal form at the two terminal carbon atoms. The formation of **15** can be explained as follows. Addition of two Y–H units of **2** to the two C≡C units of 1,4-bis(trimethylsilyl)-1,3-butadiyne in a “2,1” fashion yields the 1,3-butadiene-1,4-diyl (or butadiene-dianion)/hexahydride species **A** (Scheme 7). Subsequent 1,4-Y–H addition to the 1,3-butadiene unit in **A** could give the 2-buten-1,1'-4-triyl/pentahydride species **B**. Deprotonation at the C4 position of the butene species by a Y–H unit in **B** should afford the 2-buten-1,1',4,4'-tetrayl/tetrahydride species **C**. This species can be regarded as a resonance structure (a localized form) of **15** (cf. also **D** and **E**).

4. Reaction of Rare Earth Metal Polyhydrides with Unsaturated C–O Bonds

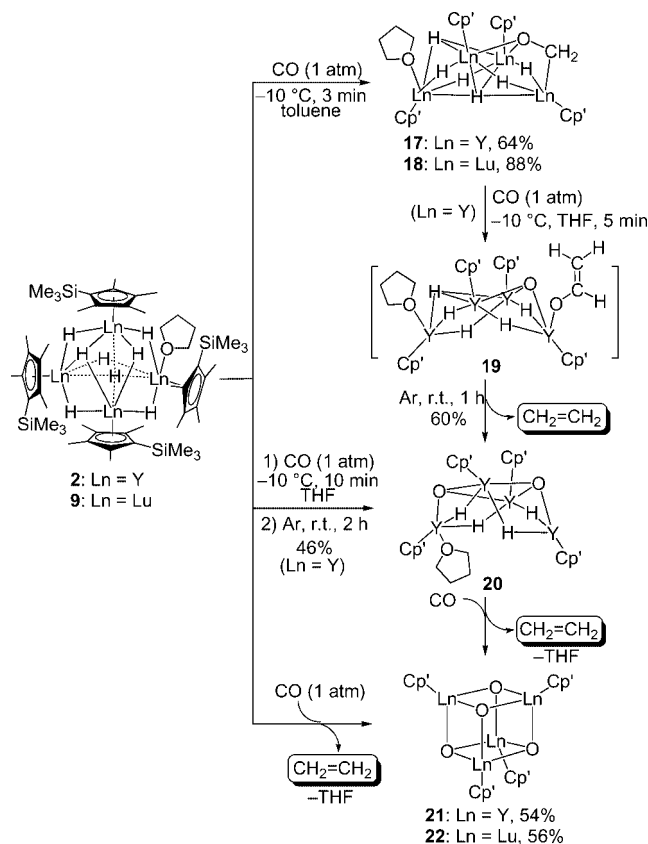
Reaction of the lutetium octahydride complex **9** with γ -butyrolactone gives the tetranuclear mixed alkoxido/dihydrido complex **16** (Scheme 8).^[8] γ -Butyrolactone is a stable, non-polymerizable cyclic ester. In this reaction, three molecules of γ -butyrolactone are completely reductively ring-opened by six of the eight hydride ligands in **9** to give the linear diolate species “-O(CH₂)₄O-”, thus demonstrating the unusually high reactivity of this rare earth metal polyhydride complex. Further reaction between **16** and γ -butyrolactone was not observed, even when an excess amount of γ -butyrolactone was present. However, both **9** and **16** show high activity for the ring-opening polymerization of ϵ -caprolactone.



Scheme 8. Reaction of a lutetium polyhydride complex with γ -butyrolactone. Cp' = C₅Me₄SiMe₃.

The reaction of **2** with CO in toluene at -10°C occurs rapidly to give the hexahydrido/oxymethylene yttrium complex **17** (Scheme 9).^[15] When **17** is stirred at -10°C in the presence of CO for a few minutes and then at room temperature in the absence of CO for 1 h, the dioxo/tetrahy-

drido complex $[(C_5Me_4SiMe_3)Y_4(\mu_3-O)_2(\mu-H)_4(THF)]$ (**20**) is obtained with simultaneous release of ethylene. Complex **20** can also be isolated directly from the reaction of **2** with CO without isolating **17**. ¹H NMR monitoring of the reaction of **17** with CO in [D₈]THF at low temperatures revealed the formation of an enolate intermediate such as $[(C_5Me_4SiMe_3)Y_4(OCH=CH_2)(\mu-O)(\mu-H)_5(THF)]$ (**19**). Further reaction of the yttrium tetrahydrido/dioxo complex **20** with CO gives the corresponding tetraoxo complex **21** and ethylene.

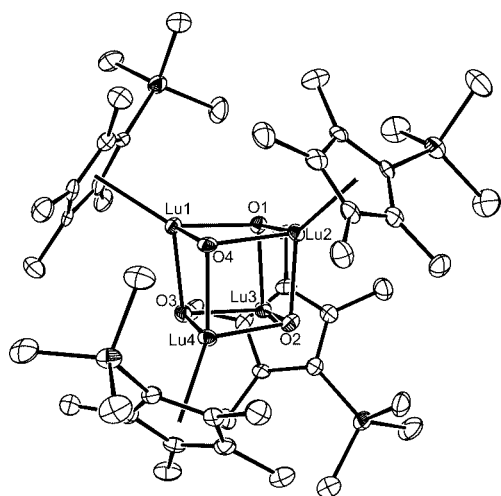


Scheme 9. Selective formation of ethylene by deoxygenative C–C coupling of carbon monoxide. Cp' = C₅Me₄SiMe₃.

Reaction of the lutetium octahydride complex **9** with CO (1 atm) affords the analogous lutetium hexahydrido/oxymethylene complex **18** and the tetraoxo lutetium cubane complex **22** with release of ethylene (Scheme 9); formation of a tetrahydrido/dioxo Lu chelate complex intermediate analogous to **20** was not observed. The solid-state structure of **22** is shown in Figure 2.

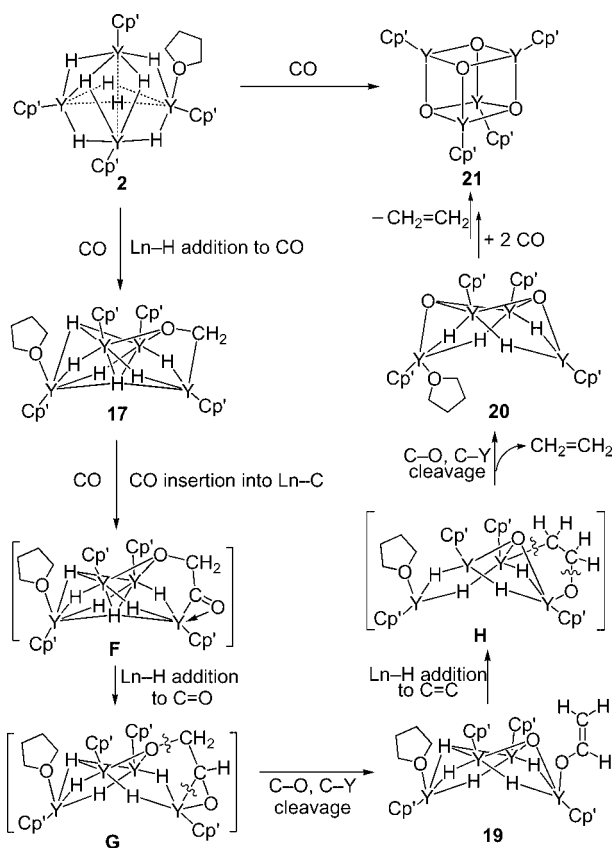
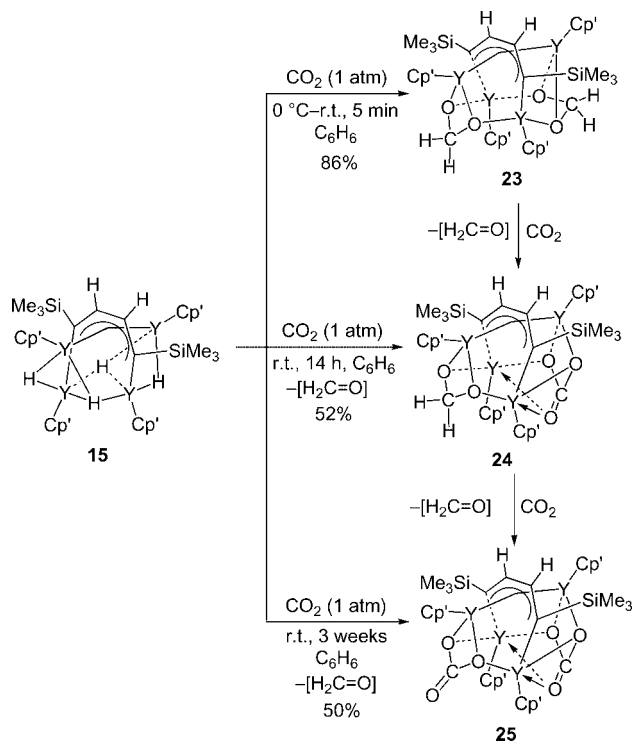
Although the reactions of CO with various transition metal hydrides, including lanthanide and actinide metallocene hydrides, have been reported,^[16] the selective formation of ethylene by reduction of CO is unprecedented. These results demonstrate again the unique reactivity of polyhydrido rare earth metal complexes.

A possible reaction mechanism for the formation of ethylene is shown in Scheme 10. Addition of two Y–H bonds in **2** across the C–O triple bond of one molecule of CO could give the oxymethylene complex **17**. Subsequent inser-

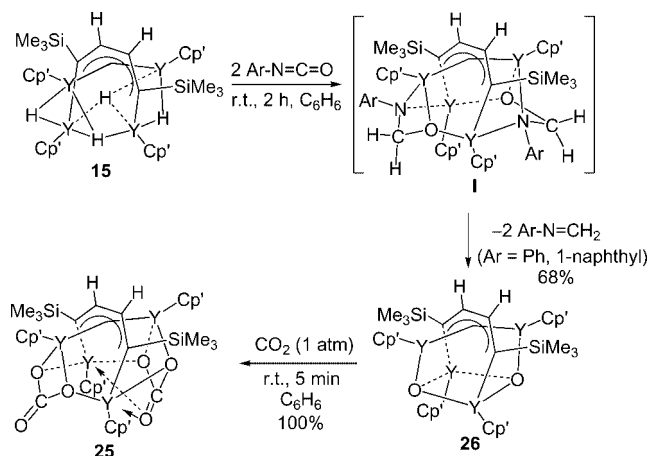
Figure 2. ORTEP drawing of **22**.

tion of another molecule of CO into the Y–CH₂ bond in **17** would afford an α -oxyacetyl species such as **F** (or its carbenoid isomer). Y–H bond addition across the acyl C=O double bond in **F** could yield the oxametallacyclopropane species **G**, which would produce the enolate species **19** by rupture of a C–O and the C–Y bond. Addition of another Y–H bond across the C=C double bond of the enolate unit might give the β -oxyethylene species **H**, which, after cleavage of the C–Y and the C–O bond, yields the dioxo complex **20** with release of ethylene. Formation of the tetraoxo complex **21** and ethylene from the reaction of **20** with CO could follow an analogous process, although intermediate species analogous to the oxymethylene **17** or an enolate species **19** have not been observed.

Reaction of the octahydride complex **2** with CO₂ also takes place very rapidly, although a characterizable product could not be isolated from this reaction. However, the structurally characterizable bis(methylene diolate) complex **23** was obtained in high yield from the reaction of the butene-tetraanion/tetrahydrido complex **15** with CO₂, (Scheme 11).^[17] In this reaction, the two C=O double bonds of CO₂ are completely reduced to C–O single bonds. This reaction takes place only at the hydride sites and the butene-tetraanion unit remains unchanged. Although a large number of studies on the hydrogenation of CO₂ with both homogeneous and heterogeneous systems have been reported, the observation of formation of a methylene diolate species remains rare.^[18] The present formation of the methylene diolate species is in sharp contrast with what was observed previously in the case of other transition metal polyhydride complexes such as [(C₅H₅)Ti(μ -H)₂(C₁₀H₈)],^[19] [(C₅H₅)₂Zr(H)(μ -H)(μ -N*i*Bu)Ir(C₅Me₃)],^[20] [H₂Ru(dmpe)₂],^[21] and [H₄Mo(dmpe)₂],^[22] [dmpe = 1,2-bis(dimethylphosphanyl)ethane] which yield either bis(formate),^[18,21] mixed hydride/formate,^[19,20] or mixed hydride/carbonate complexes^[21] upon reaction with CO₂. Further insertion of CO₂ into the metal-diolate bonds in **23** could also take place to give the mono- and dicarbonate complexes **24** and **25** in a stepwise manner, with possible release of formaldehyde (HCHO; Scheme 11).

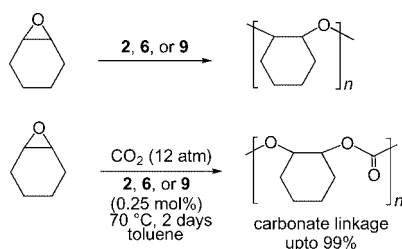
Scheme 10. A possible mechanism for the reaction of an yttrium polyhydride complex with carbon monoxide. Cp' = C₅Me₄SiMe₃.Scheme 11. Reduction of CO₂ into methylene diolate species and subsequent CO₂ insertion reactions. Cp' = C₅Me₄SiMe₃.

To see how complex **15** would behave toward an isocyanate, which is a commonly accepted model for CO₂ with respect to reaction patterns,^[23] the reactions of **15** with aryl isocyanates have been studied.^[17] When **15** was allowed to react with two equivalents of phenyl isocyanate or 1-naphthyl isocyanate, the dioxo complex **26** was formed together with the corresponding aromatic imine compounds, probably via the bis(methyleneolate/amido) intermediate **I** (Scheme 12). Exposure of the di-μ₃-oxo complex **26** to an atmosphere of CO₂ at room temperature led to immediate formation of the dicarbonate complex **25** (Scheme 12). Although formation of metal oxo complexes, such as [$\{\text{Cp}_2\text{ZrCl}\}_2(\mu\text{-O})$],^[24] [$\{\text{Cp}_2\text{Zr}(\mu\text{-O})\}_3$],^[25] and [$\{\text{C}_5\text{H}_4\text{-SiMe}_3\}_3\text{U}\}_2(\mu\text{-O})$],^[26] has been observed in various CO₂ reduction reactions, the insertion of CO₂ into such a metal oxo species has not been reported previously. The present reaction of **26** with CO₂ may provide, at a molecular level, a nice piece of evidence for interactions of CO₂ with metal oxides.^[27]



Scheme 12. Formation of a μ₃-oxo yttrium complex and its reaction with CO₂. Cp' = C₅Me₄SiMe₃.

Polyhydride complexes such as **2**, **6**, and **9** can also act as single-component catalysts for the ring-opening homopolymerization of cyclohexene oxide (CHO) and the alternating copolymerization of CHO and CO₂. The homopolymerization of CHO in bulk takes place much more rapidly than in solution and affords the corresponding polyethers [$M_n = (60\text{--}80) \times 10^3$ and $M_w/M_n \approx 2$] in high yields in most cases. The copolymerization of CHO and CO₂ at 70–110 °C under 12 atm of CO₂ yields the corresponding polycarbonates [$M_n = (20\text{--}40) \times 10^3$, $M_w/M_n = 4\text{--}5$; carbonate linkages

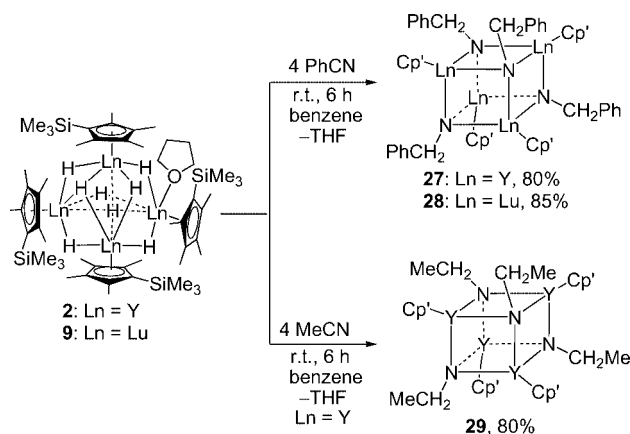


Scheme 13. Homopolymerization of cyclohexene oxide (CHO) and copolymerization of CHO with CO₂.

= 95–99%] with a TOF of up to 2000 g polymer/(mol Ln h)^{−1} (Scheme 13).^[28] The first step in the copolymerization could be the formation of a methylene diolate species by insertion of one molecule of CO₂ into two Ln–H bonds.

5. Reaction of Rare Earth Metal Polyhydrides with Nitriles

The reaction of the yttrium or lutetium octahydride complex (**2**, **9**) with four equivalents of benzonitrile or acetonitrile affords the corresponding tetranuclear cubane-like imido complexes [$\{\text{C}_5\text{Me}_4\text{SiMe}_3\}\text{Ln}(\mu_3\text{-NCH}_2\text{Ph})\}_4$] (Ln = Y (**27**), Lu (**28**)) or [$\{\text{C}_5\text{Me}_4\text{SiMe}_3\}\text{Y}(\mu_3\text{-NCH}_2\text{Ph})\}_4$] (**29**), respectively (Scheme 14).^[8] The solid-state structure of the yttrium complex **27** is shown in Figure 3. In these reactions, the C–N triple bond of a nitrile compound is completely reduced to a C–N single bond by double Ln–H addition. This is in sharp contrast to the previously reported reactions of rare earth metallocene hydride complexes^[29] or zirconocene dihydride complexes^[30] with nitriles, which yielded only single-insertion products such as [$\{\text{C}_5\text{H}_5\}_2\text{-Y}(\mu\text{-N=CH}t\text{Bu})\}_2$] or [$\{\text{C}_5\text{Me}_5\}_2\text{Zr}(\text{H})(\text{N=CHR})$] (R = C₆H₄Me-*p*). The reaction of polyhydrido rare earth metal complexes with nitriles may offer a convenient salt-free route to the corresponding rare earth metal imido complexes, a class of compounds that are of considerable current interest but still remain very limited in number.^[31]



Scheme 14. Formation of cubane-type imido complexes by reduction of nitriles. Cp' = C₅Me₄SiMe₃.

Further reactions of the rare earth metal imido complexes with nitriles can also take place. The reaction of the benzylimidolutetium complex [$\{\text{C}_5\text{Me}_4\text{SiMe}_3\}\text{Lu}(\mu_3\text{-NCH}_2\text{Ph})\}_4$] (**28**) with four equivalents of benzonitrile at room temperature, for instance, gives the benzamidinate-dianion complex **30** (Scheme 15).^[32] An X-ray analysis showed that **30** possesses a dimeric structure in which the two Lu atoms are bridged by the ketimido nitrogen atom and the amido nitrogen atom is bonded terminally to one Lu atom. The formation of **30** apparently proceeds by nucleophilic addition of the imido unit in **28** to the CN group of benzonitrile, which demonstrates that a rare earth metal imido bond, even in a bridging form, is very reactive. This

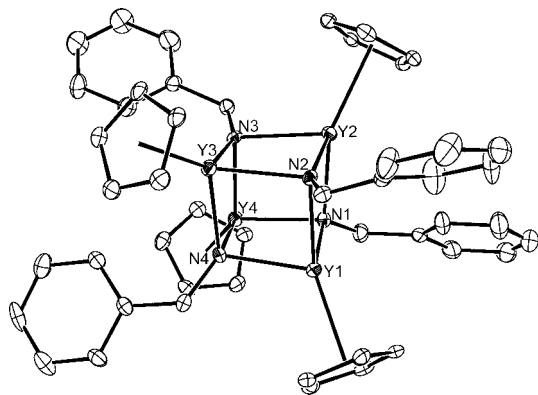
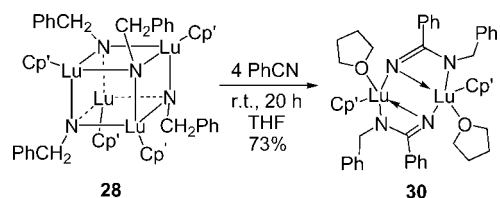


Figure 3. ORTEP drawing of **27**. The Me_3Si and Me groups in $\text{C}_5\text{Me}_4\text{SiMe}_3$ have been omitted for clarity.

contrasts with what was observed previously for transition metal imido bridging bonds, which are usually robust and unreactive.^[33]

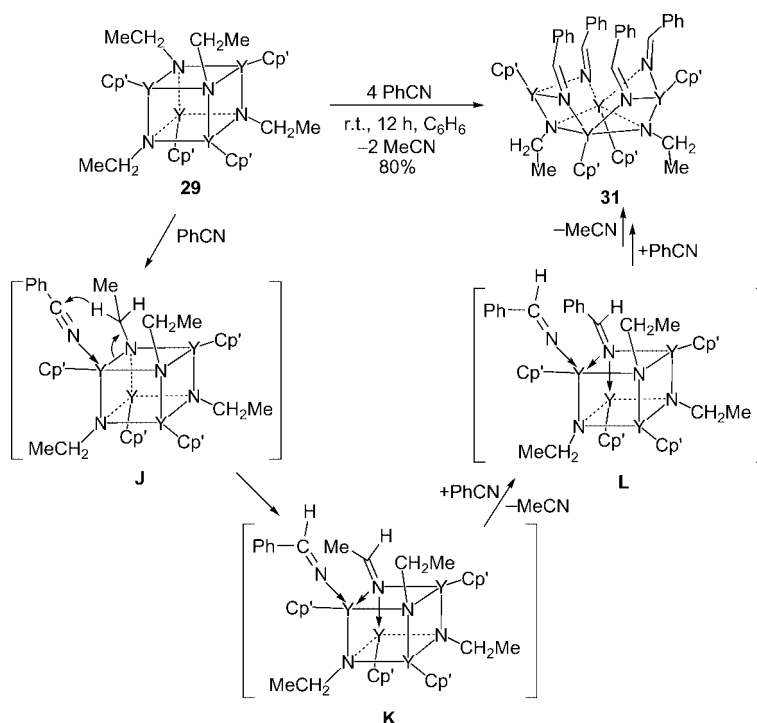


Scheme 15. Nucleophilic addition of an imido complex to benzonitrile. $\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$.

In sharp contrast to the above-mentioned nucleophilic addition reaction of the benzylimido complex **28**, the reaction of the ethylimido complex $[\{(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Y}(\mu_3\text{-}$

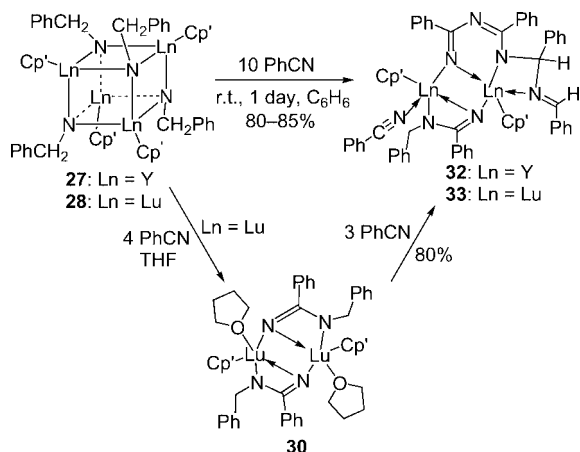
$\text{NCH}_2\text{CH}_3\}_4]$ (**29**) with benzonitrile gives the mixed benzaldimido/ethylimido complex **31** rather than an insertion product (Scheme 16). An X-ray analysis established that **31** adopts a tetranuclear crown-like core structure in which the four Y atoms are unsymmetrically bridged by four μ_2 -benzaldimido and two μ_3 -ethylimido ligands. Four molecules of benzonitrile are hydrogenated in this reaction to give four benzaldimido species ($\text{PhCH}=\text{N}^-$) by abstraction of four methylene hydrogen atoms from two of the four ethylimido units ($\text{CH}_3\text{CH}_2\text{N}^{2-}$) in **29** with the release of two molecules of acetonitrile (CH_3CN); the other two ethylimido units remain unchanged (Scheme 16). This formation of an aldimido species through hydrogen transfer from an alkyl imido species to a nitrile compound is, as far as we are aware, unprecedented.

The reaction of 10 equivalents of benzonitrile with the benzylimido complexes **27** or **28** gives the benzonitrile tetramerization products **32** or **33**, respectively (Scheme 17). The reaction of the benzamidinate-dianion complex **30** with three equivalents of benzonitrile also affords **33** in high yield. These results suggest that **30** should be an intermediate in the formation of **33** from **28**. The reaction of the polyhydride complex **2** with 14 equivalents of benzonitrile also affords **32**. A possible reaction mechanism for the formation of the benzonitrile tetramerization product **32** or **33** is shown in Scheme 18. The coordination of one molecule of benzonitrile to each metal atom in **30** should yield **M**. Hydrogen transfer from a methylene group to a coordinated PhCN in **M** (path *a*) should then afford **N**. Nucleophilic addition of the newly formed benzaldimido unit to the aldimine group (path *b*) could yield **O**, which gives **P** upon coordination of one molecule of PhCN . Migration of the

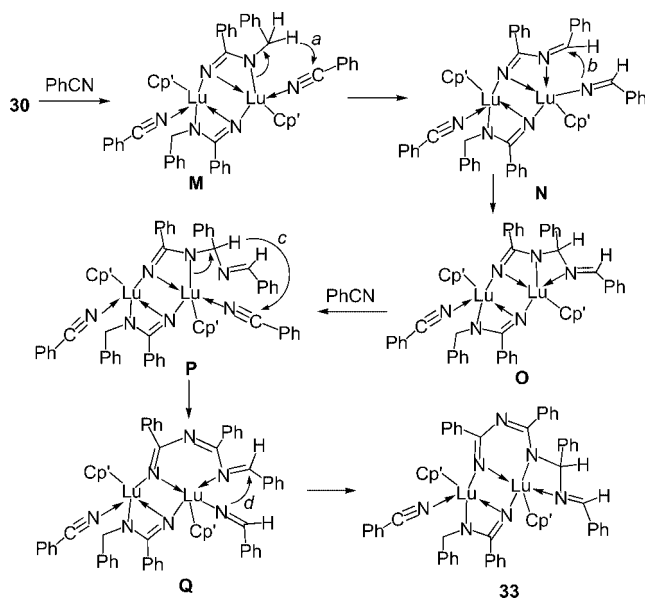


Scheme 16. Unique hydrogen transfer from ethyl imido species to benzonitrile. $\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$.

methine hydrogen to the PhCN unit in **P** (path *c*), followed by addition of the resulting aldimido unit to the aldimine group in the resultant **Q** (path *d*), should give **33**.



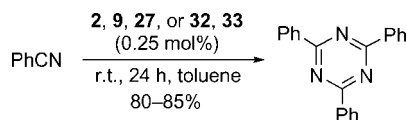
Scheme 17. Tetramerization of benzonitrile. Cp' = C₅Me₄SiMe₃.



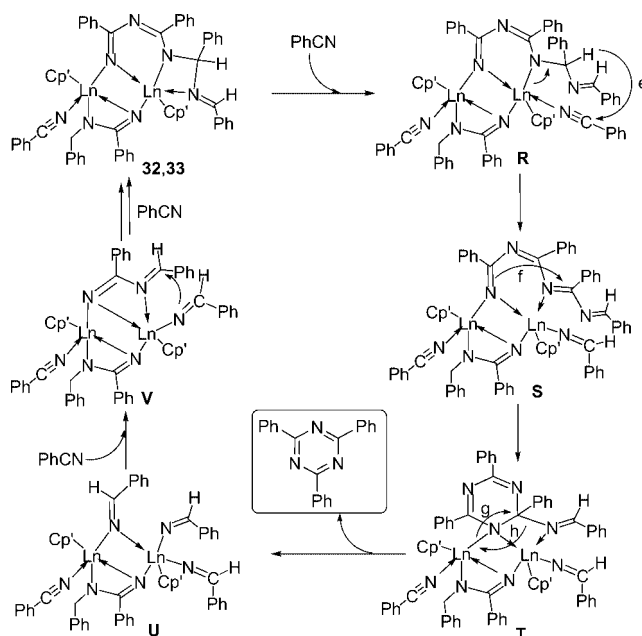
Scheme 18. Possible mechanism for the formation of **33**. Cp' = C₅Me₄SiMe₃.

When an excess amount of benzonitrile was added to a toluene solution of **32** or **33**, the benzonitrile-cyclotrimerization product, namely triphenyl triazine (PhCN)₃, is formed selectively (Scheme 19).^[32] The recovery of **32** or **33** from these reactions confirms that these benzonitrile-tetramerized complexes are true catalysts. The polyhydride complexes **2** and **9**, the imido complexes **27** and **28**, and the benzamidinate-dianion complex **30** are also active for the catalytic trimerization of benzonitrile. A possible mechanism for the catalytic cyclotrimerization of benzonitrile by **32** or **33** is shown in Scheme 20. The coordination of one molecule of benzonitrile to a metal center in **32** (or **33**) could give **R**, and methine hydrogen transfer (step *e*) to coordinated benzonitrile would afford **S**. Subsequent intramolecular nucleophilic addition of the ketimido unit to the

newly formed imine moiety (step *f*) could give **T**, and aromatization of the resultant six-membered ring in **T** (step *g*, Ln–N bond cleavage and C=N bond formation and step *h*, C–N bond cleavage and Ln–N bond formation) should release the triazine and generate **U**. Insertion of benzonitrile into **U** would then give **V**, which resembles intermediate **N** in Scheme 18 and could regenerate **32** (or **33**) as described above. Thus, the combination of C–N bond formation, hydrogen transfer, and C–N bond cleavage steps constitutes a unique catalytic cycle for the cyclotrimerization of benzonitrile.^[34]



Scheme 19. Catalytic cyclotrimerization of benzonitrile. Cp' = C₅Me₄SiMe₃.

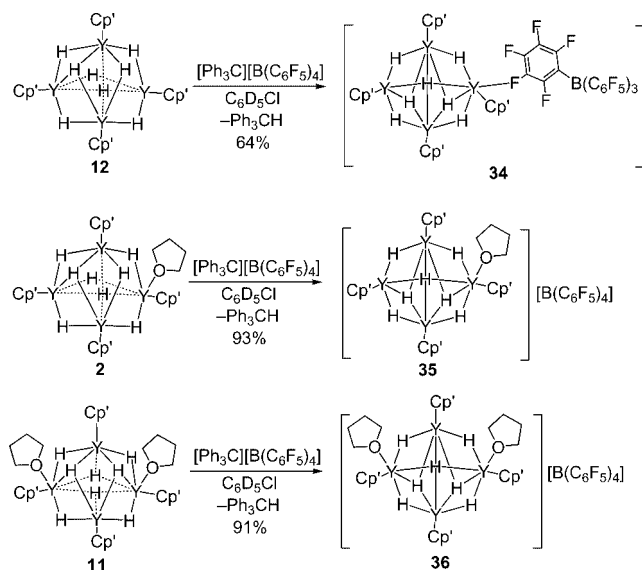


Scheme 20. A possible mechanism for the catalytic cyclotrimerization of benzonitrile. Cp' = C₅Me₄SiMe₃.

6. Cationic Rare Earth Metal Polyhydride Complexes

In contrast to cationic rare earth metal alkyl complexes, which have received much interest as novel polymerization catalysts,^[35,36] cationic hydrido rare earth metal complexes remain almost unexplored. It has recently been found that tetranuclear rare earth metal octahydride complexes such as **1–7** and **9–12** are suitable precursors for the preparation of cationic hydrido rare earth metal species.^[9] For example, the reactions of the yttrium octahydride complexes **2**, **11**, and **12** with one equivalent of [Ph₃C][B(C₆F₅)₄] afford the corresponding cationic heptahydride complexes **35**, **36**, and **34**, respectively, in high yields (Scheme 21). An direct bonding interaction between the [(C₅Me₄SiMe₃)₄Y₄H₇]⁺ cation and

the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion via a Y–F bond is observed in the THF-free complex **34**, while complexes **35** and **36** are solvent (THF)-separated ion pairs. The X-ray structures of **34** and **36** are shown in Figures 4 and 5, respectively. These complexes are the first examples of well-defined cationic hydrido rare earth metal complexes.



Scheme 21. Synthesis of cationic yttrium polyhydride complexes. $\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$.

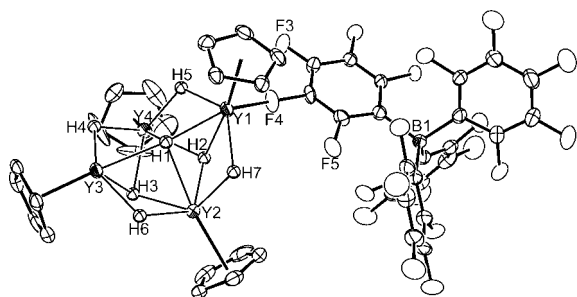


Figure 4. ORTEP drawing of **34**. The Me_3Si and Me groups in $\text{C}_5\text{Me}_4\text{SiMe}_3$ have been omitted for clarity.

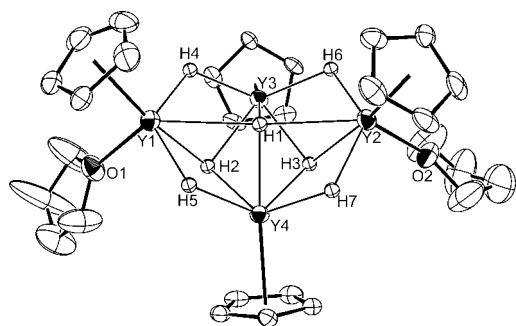
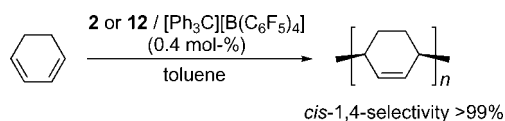


Figure 5. ORTEP drawing of **36**. The Me_3Si and Me groups in $\text{C}_5\text{Me}_4\text{SiMe}_3$ and the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion have been omitted for clarity.

In contrast to the neutral hydride cluster **2**, which yields a single Y–H addition product **13** or **14** on reaction with styrene or 1,3-cyclohexadiene (CHD), respectively, as de-

scribed above, the THF-free or mono(THF)-coordinated cationic hydride clusters such as **34** or **35** (either isolated or generated in situ) are active catalysts for the syndiospecific polymerization of styrene and the regio- and stereoselective *cis*-1,4-polymerization of CHD (Scheme 22).^[9] The bis(THF)-coordinated cationic complex **36**, however, is not catalytically active under the same conditions, probably due to the occupation of the active metal centers by two strongly coordinative THF ligands.



Scheme 22. *cis*-1,4-Selective polymerization of 1,3-cyclohexadiene by cationic yttrium polyhydride complexes.

7. Conclusion and Perspective

Hydrogenolysis of the bisalkyl complexes $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ leads to the formation of a series of structurally characterizable polyhydrido polynuclear rare earth metal complexes. These polyhydride complexes show a unique reactivity towards various substrates, such as hydrogenation of the C–N triple bond of a nitrile compound into a C–N single bond, reduction of carbon dioxide into a methylene diolate species, and deoxygenative C–C coupling of CO into ethylene. These reactions are in sharp contrast with what has been observed for the analogous monohydrido metallocene complexes. A new class of polynuclear rare earth metal complexes, such as cubane-type imido and oxo complexes, has also been derived from the polyhydride complexes. Abstraction of a hydride ligand from the neutral hydride clusters leads to the formation of structurally characterizable cationic polyhydrido rare earth metal complexes.

It should also be noted, however, that the synthesis and reactivity studies of polyhydrido rare earth metal complexes is still in its infancy, and well defined polyhydrido rare earth metal complexes reported in the literature are limited essentially to those bearing a $\text{C}_5\text{Me}_4\text{SiMe}_3$ ligand. As the expertise in this field increases and more complexes with new ligand systems are prepared,^[37] the diverse chemistry of polyhydrido rare earth metal complexes will certainly be further extended. An exciting and prosperous future in this area can therefore be expected.

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