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Synthesis and Reactions of Polynuclear Polyhydrido Rare Earth Metal Complexes Containing “$(C_5Me_4SiMe_3)LnH_2$” Units: A New Frontier in Rare Earth Metal Hydride Chemistry

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Keywords: Rare earths / Hydride ligands / Cyclopentadienyl ligands / Cluster compounds / Hydrogenation

A series of tetranuclear octahydrido rare earth metal complexes of general formula $[(C_5Me_4SiMe_3)Ln(\mu\text{-}H)_2]_4(THF)_n$ (Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, Lu; n = 0, 1, or 2) that contain $C_5Me_4SiMe_3$ 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, CO_2, and nitriles. The reaction of these neutral polyhydrides with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ affords the corresponding cationic hydride clusters $[(C_5Me_4SiMe_3)_4Ln_4H_7(THF)_n][B(C_6F_5)_4]$, which can act as catalysts for the syndiospecific polymerization of styrene and regio- and stereospecific *cis*-1,4-polymerization of 1,3-cyclohexadiene.

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 “L_2MH” 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 “LMH_2”, 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 $[(C_5Me_5)Lu(CH_2CMe_3)_2(THF)]$[4] or $[(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)]$[5] with H_2 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 $[\{(C_5Me_5)Sm(\mu\text{-}H)_2\}_6\{KH(THF)_2\}_3]$, which formally consists of six “$(C_5Me_5)SmH_2$” 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 $[\{(C_5Me_5)SmCH(SiMe_3)_2[(C_5Me_5)K(THF)_2]\}_n]$[6] with an excess of $PhSiH_3$. Very recently, a series of salt-free polynuclear polyhydrido rare earth metal complexes that contain “$(C_5Me_4SiMe_3)LnH_2$” units has been synthesized from the $C_5Me_4SiMe_3$-ligated dialkyl complexes $[(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(THF)]$ (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 $C_5Me_4SiMe_3$-ligated bis(trimethylsilylmethyl)scandium complex $[(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)]$ with H_2 in toluene at room temperature gives the THF-free tetranuclear octahydride complex $[\{(C_5Me_4SiMe_3)Sc(\mu\text{-}H)_2\}_4]$ (**1**) (Scheme 1).[7] This complex can be viewed as being the result of a self-assembly of four “$(C_5Me_4SiMe_3)ScH_2$” 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 μ_4-H–Sc_4 fashion, one is face-capped in a μ_3-

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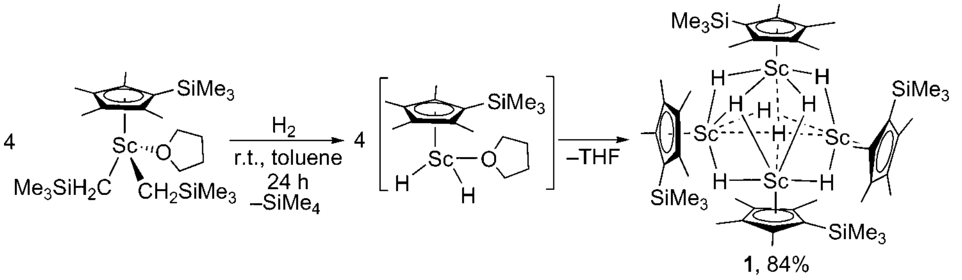

Scheme 1. Synthesis of a tetranuclear octahydrido scandium complex.

$H–Sc_3$ form, and six are edge-bridged in a μ_2-$H–Sc_2$ 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 $[\{(C_5Me_4SiMe_3)Ln(\mu\text{-}H)_2\}_4(THF)]$ (**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 $C_5Me_4SiMe_3$ 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 H_2 did not give a single hydride complex.[11] However, hydrogenolysis of the hydride-bridged dimeric mixed alkyl/hydride complex $[\{(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)(\mu\text{-}H)(THF)\}_2]$ (**8**), which was prepared by reaction of $[(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)]$ with one equivalent of $PhSiH_3$, affords the tetranuclear mono(THF)-coordinated lutetium octahydride complex $[\{(C_5Me_4SiMe_3)Lu(\mu\text{-}H)_2\}_4(THF)]$ (**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 H_2

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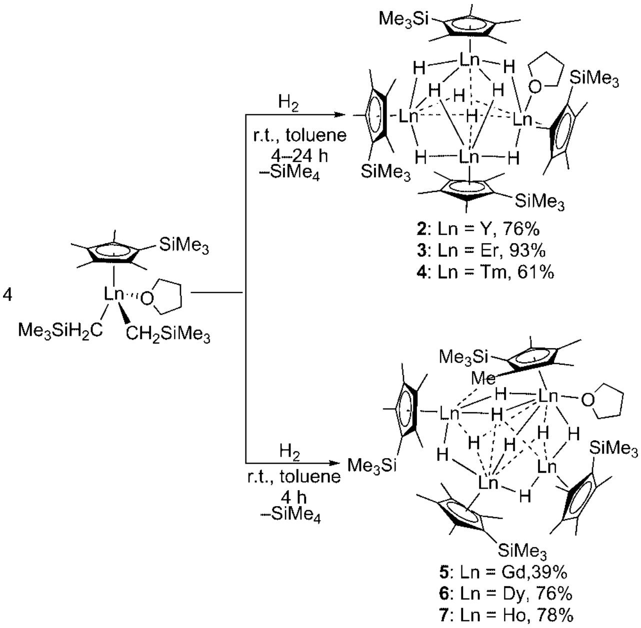
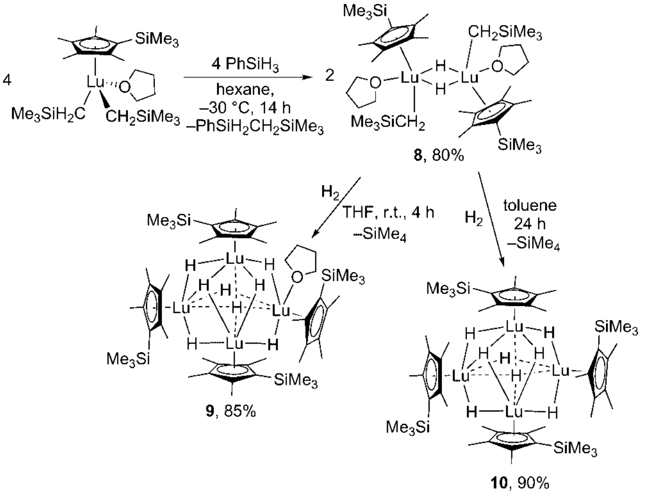


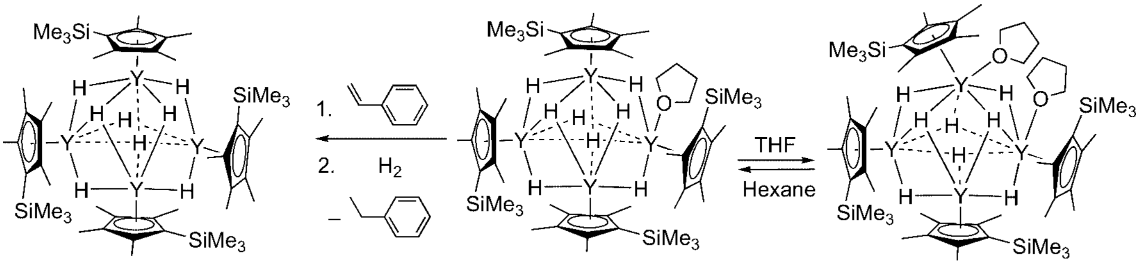
Scheme 2. Synthesis of mono(THF)-coordinated tetranuclear octahydrido rare earth metal complexes.

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)



12, 82% **2** **11**

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

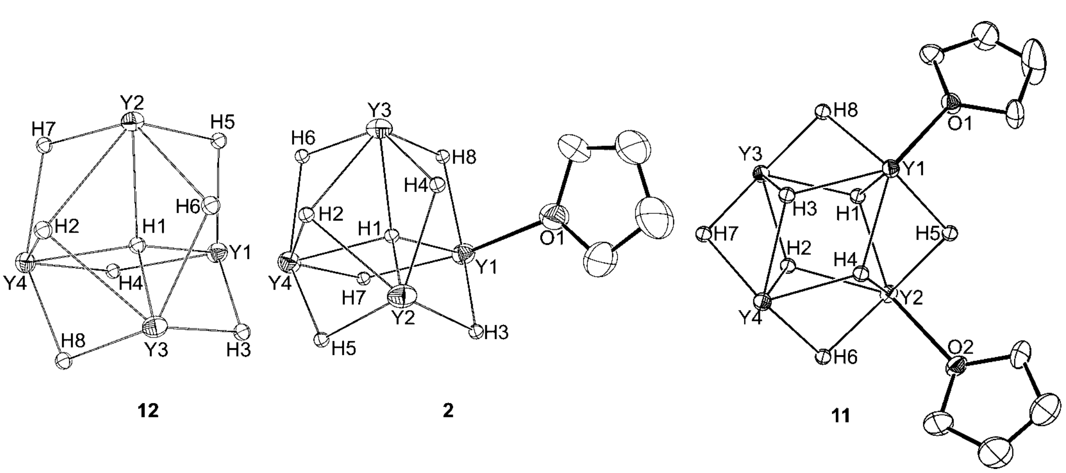
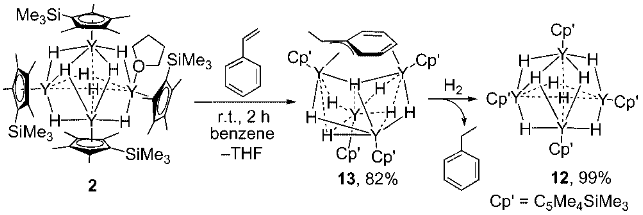


Figure 1. ORTEP drawings of the Y_4H_8 core structures of **12** (left, THF-free), **2** (middle, with one THF ligand), and **11** (right, with two THF ligands).

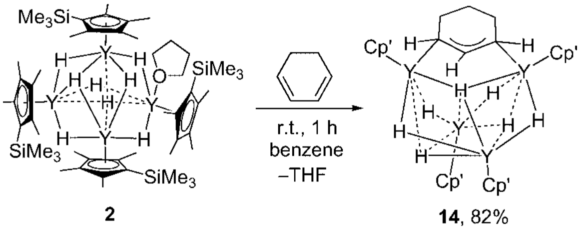
complex was not observed under the same conditions for the smaller Sc and Lu complexes **1**, **9**, and **10**. The bis(THF)-coordinated yttrium polyhydride **11** also adopts a tetrahedral metal skeleton, but it has four μ_3-H and four μ_2-H ligands whereas the mono(THF) analogue **2** possesses one μ_4-H, one μ_3-H, and six μ_2-H ligands (Figure 1). Recrystallization of the bis(THF) complex **11** from hexane regenerates the mono(THF) complex **2**, while treatment of the mono(THF) yttrium complex **2** with styrene followed by hydrogenolysis of the resultant product in benzene yields the corresponding THF-free octahydride complex **12** (Schemes 4 and 5).[8,14] ORTEP drawings of the Y_4H_8 core structures of **2**, **11**, and **12** are shown in Figure 1.

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

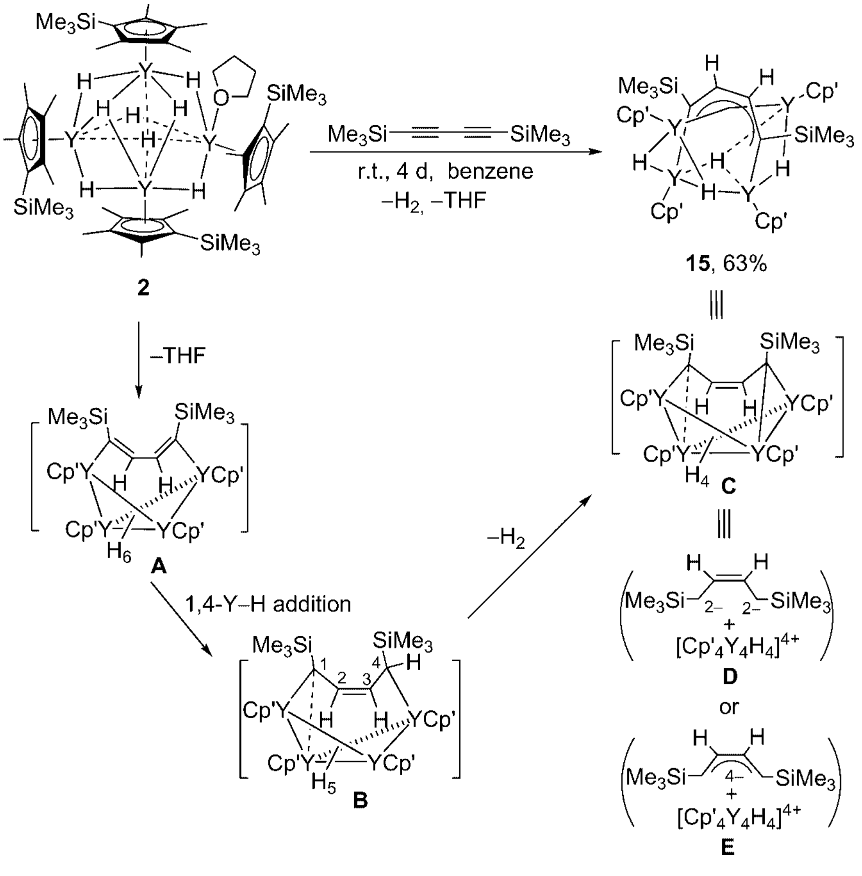
Reaction of the mono(THF)-coordinated tetranuclear yttrium octahydride complex **2** with styrene yields a product formed by insertion of a single molecule of styrene – the benzylic allyl heptahydride complex **13** – in which the allyl part is bonded to one Y atom in an η^3-fashion and the phenyl part is bonded to another Y atom in an η^2-form (Scheme 5).[8] No further reaction was observed even when an excess of styrene was present. Hydrogenolysis of the benzylic allyl complex **13** with H_2 (1 atm) in benzene affords ethylbenzene and the THF-free yttrium octahydride complex $[\{(C_5Me_4SiMe_3)Y(\mu\text{-}H)_2\}_4]$ (**12**).[14] Under 1 atm of H_2, styrene can be catalytically hydrogenated into ethylbenzene by **2** or **12**.



Scheme 5. Formation of a tetranuclear yttrium benzylic allyl heptahydride complex and its reaction with H_2.



Scheme 6. Reaction of an yttrium polyhydride complex with 1,3-cyclohexadiene. Cp′ = $C_5Me_4SiMe_3$.



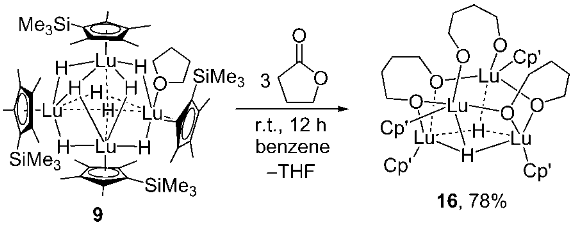
Scheme 7. Reaction of an yttrium polyhydride complex with 1,4-bis(trimethylsilyl)-1,3-butadiyne. Cp′ = $C_5Me_4SiMe_3$.

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-butadien-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. alo **D** and **E**).

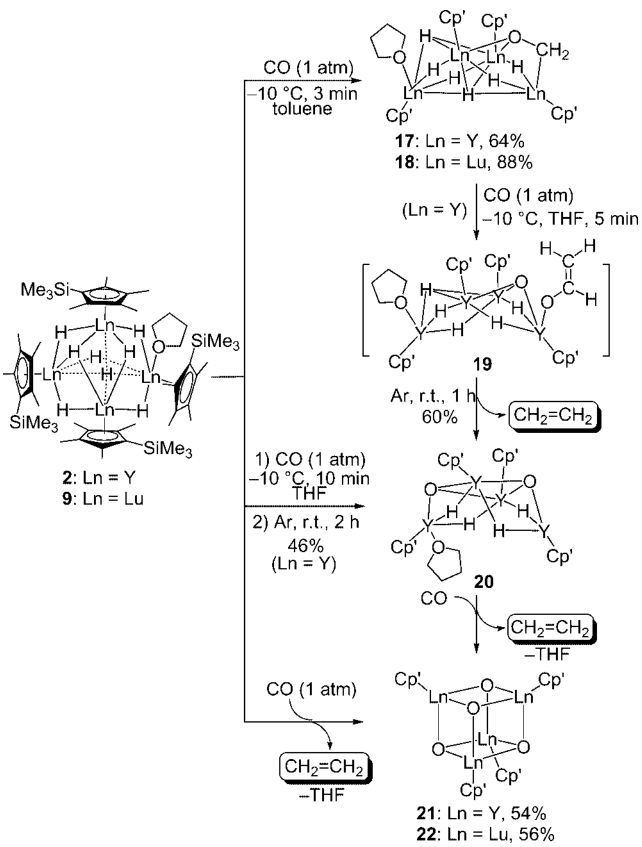
4. Reaction of Rare Earth Metal Polyhydrides with Unsaturated C–O Bonds

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(CH$_2$)$_4$O-”, 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′ = C$_5$Me$_4$SiMe$_3$.

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/tetrahydrido complex $[(C_5Me_4SiMe_3Y)_4(\mu_3\text{-}O)_2(\mu\text{-}H)_4(THF)]$ (**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**. ^{1}H NMR monitoring of the reaction of **17** with CO in [D$_8$]THF at low temperatures revealed the formation of an enolate intermediate such as $[(C_5Me_4SiMe_3Y)_4(OCH{=}CH_2)(\mu\text{-}O)(\mu\text{-}H)_5(THF)]$ (**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′ = C$_5$Me$_4$SiMe$_3$.

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 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-

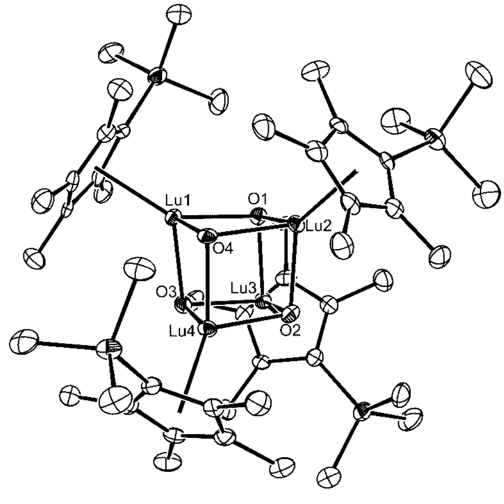
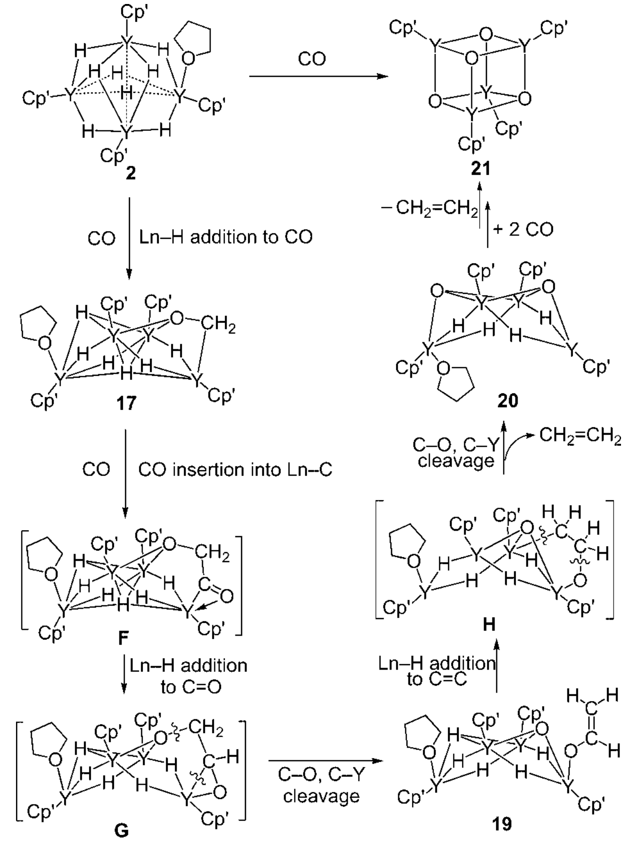


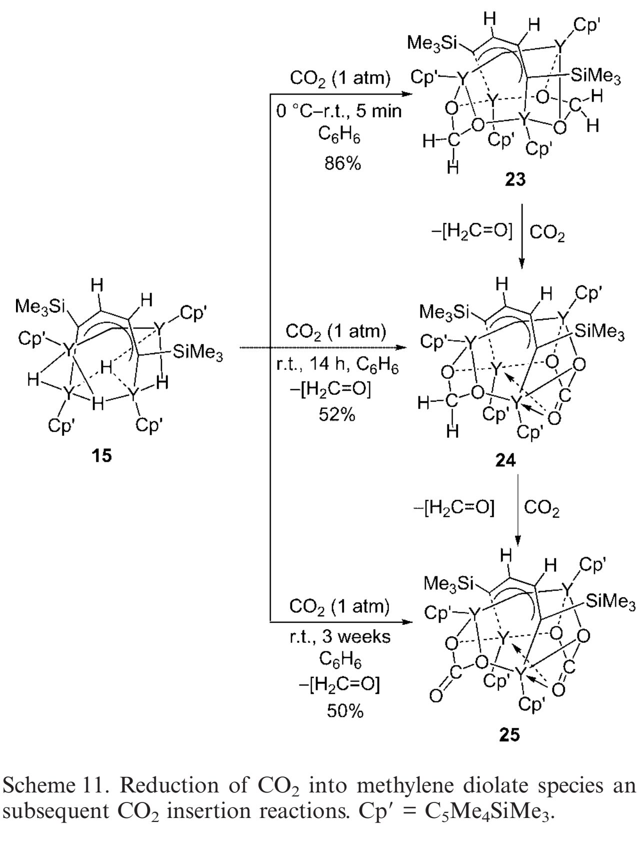
Figure 2. ORTEP drawing of **22**.

tion of another molecule of CO into the Y–CH_2 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 CO_2 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 CO_2, (Scheme 11).[17] In this reaction, the two C–O double bonds of CO_2 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 CO_2 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 $[\{(C_5H_5)Ti(\mu\text{-}H)\}_2(C_{10}H_8)]$,[19] $[(C_5H_5)_2Zr(H)(\mu\text{-}H)(\mu\text{-}NtBu)Ir(C_5Me_5)]$,[20] $[H_2Ru(dmpe)_2]$,[21] and $[H_4Mo(dmpe)_2]$,[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 CO_2. Further insertion of CO_2 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).

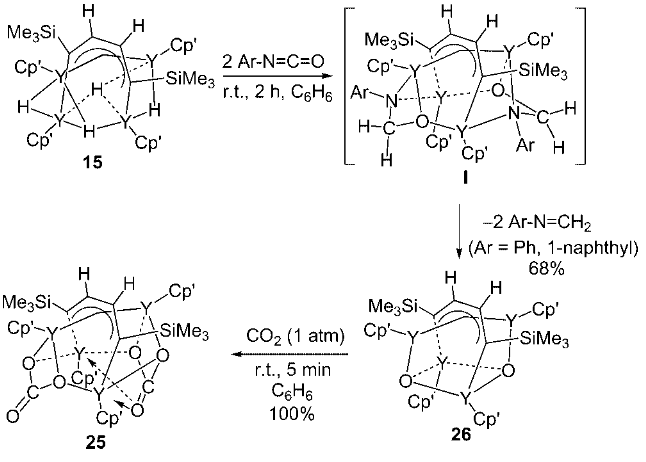


Scheme 10. A possible mechanism for the reaction of an yttrium polyhydride complex with carbon monoxide. Cp′ = $C_5Me_4SiMe_3$.



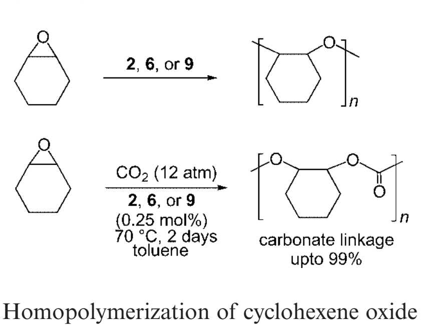
Scheme 11. Reduction of CO_2 into methylene diolate species and subsequent CO_2 insertion reactions. Cp′ = $C_5Me_4SiMe_3$.

To see how complex **15** would behave toward an isocyanate, which is a commonly accepted model for CO_2 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(methylene olate/amido) intermediate **I** (Scheme 12). Exposure of the di-μ_3-oxo complex **26** to an atmosphere of CO_2 at room temperature led to immediate formation of the dicarbonate complex **25** (Scheme 12). Although formation of metal oxo complexes, such as $[\{Cp_2ZrCl\}_2(\mu\text{-}O)]$,[24] $[\{Cp_2Zr(\mu\text{-}O)\}_3]$,[25] and $[\{(C_5H_4SiMe_3)_3U\}_2(\mu\text{-}O)]$,[26] has been observed in various CO_2 reduction reactions, the insertion of CO_2 into such a metal oxo species has not been reported previously. The present reaction of **26** with CO_2 may provide, at a molecular level, a nice piece of evidence for interactions of CO_2 with metal oxides.[27]



Scheme 12. Formation of a μ_3-oxo yttrium complex and its reaction with CO_2. Cp′ = $C_5Me_4SiMe_3$.

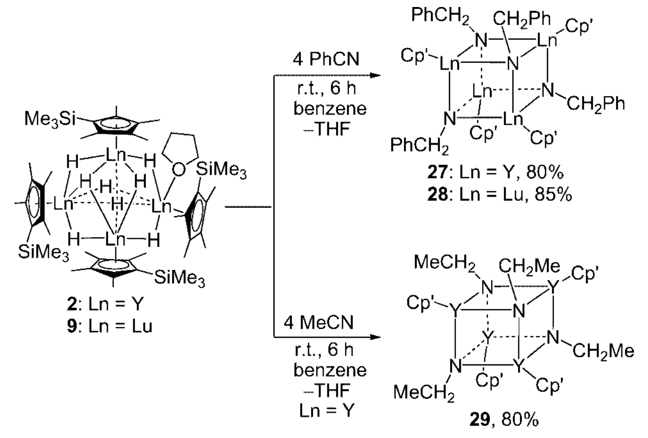
Polyhydride complexes such as **2**, **6**, and **9** can also act as single-component catalysts for the ring-opening homopolymerization of cyclohexene oxide (CHO) and the alternating copolymerization of CHO and CO_2. The homopolymerization of CHO in bulk takes place much more rapidly than in solution and affords the corresponding polyethers [$M_n = (60–80) \times 10^3$ and $M_w/M_n \approx 2$] in high yields in most cases. The copolymerization of CHO and CO_2 at 70–110 °C under 12 atm of CO_2 yields the corresponding polycarbonates [$M_n = (20–40) \times 10^3$, $M_w/M_n = 4–5$; carbonate linkages = 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 CO_2 into two Ln–H bonds.



Scheme 13. Homopolymerization of cyclohexene oxide (CHO) and copolymerization of CHO with CO_2.

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 $[\{(C_5Me_4SiMe_3)Ln(\mu_3\text{-}NCH_2Ph)\}_4]$ (Ln = Y (**27**), Lu (**28**)] or $[\{(C_5Me_4SiMe_3)Y(\mu_3\text{-}NCH_2Ph)\}_4]$ (**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 $[\{(C_5H_5)_2Y(\mu\text{-}N{=}CHtBu)\}_2]$ or $[(C_5Me_5)_2Zr(H)(N{=}CHR)]$ (R = C_6H_4Me-*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′ = $C_5Me_4SiMe_3$.

Further reactions of the rare earth metal imido complexes with nitriles can also take place. The reaction of the benzylimidolutetium complex $[\{(C_5Me_4SiMe_3)Lu(\mu_3\text{-}NCH_2Ph)\}_4]$ (**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

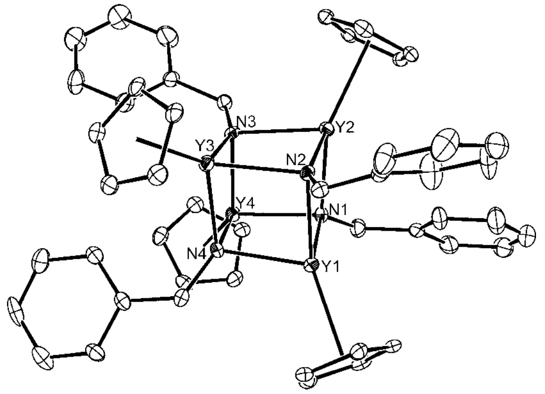
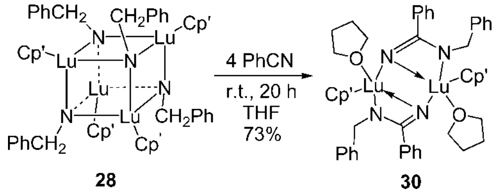


Figure 3. ORTEP drawing of **27**. The Me_3Si and Me groups in $C_5Me_4SiMe_3$ have been omitted for clarity.

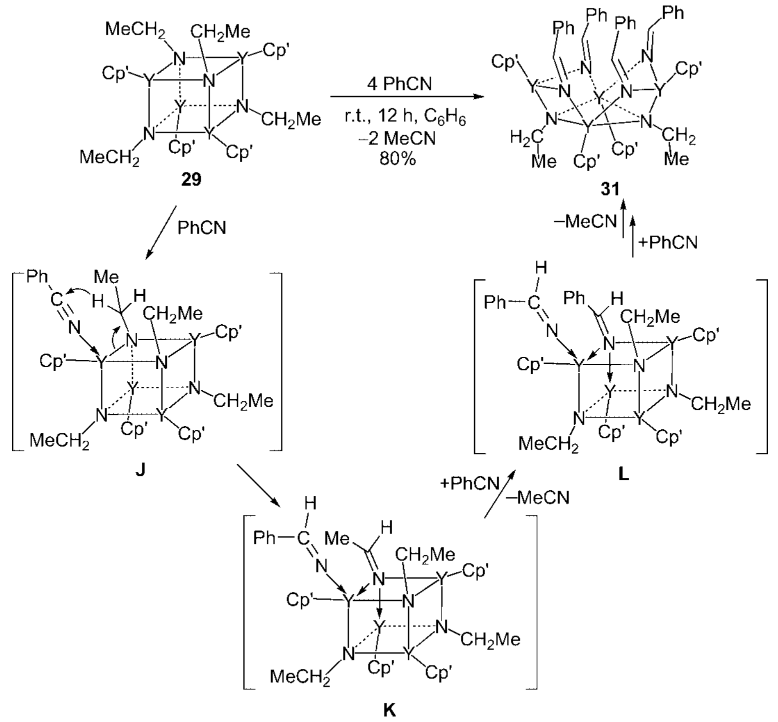
contrasts with what was observed previously for transition metal imido bridging bonds, which are usually robust and unreactive.[33]



Scheme 15. Nucleophilic addition of an imido complex to benzonitrile. Cp′ = $C_5Me_4SiMe_3$.

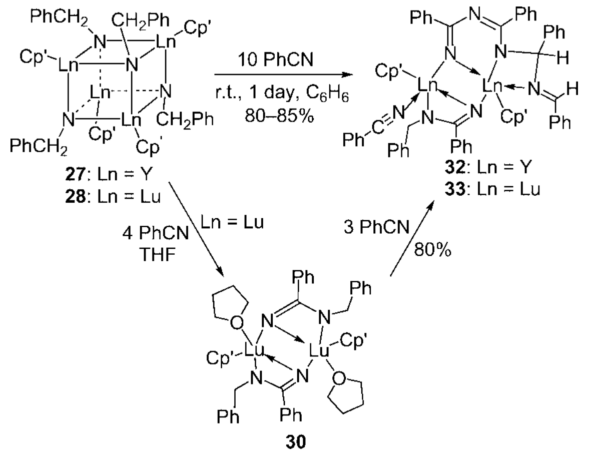
In sharp contrast to the above-mentioned nucleophilic addition reaction of the benzylimido complex **28**, the reaction of the ethylimido complex $[\{(C_5Me_4SiMe_3)Y(\mu_3\text{-}NCH_2CH_3)\}_4]$ (**29**) with benzonitrile gives the mixed benzaldimido/ethylimido complex **31** rather than an insertion 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 ($PhCH{=}N^-$) by abstraction of four methylene hydrogen atoms from two of the four ethylimido units ($CH_3CH_2N^{2-}$) 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

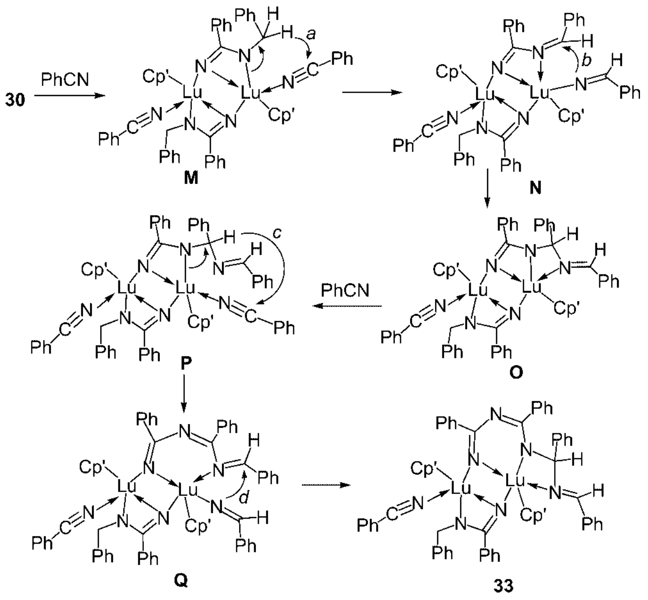


Scheme 16. Unique hydrogen transfer from ethyl imido species to benzonitrile. Cp′ = $C_5Me_4SiMe_3$.

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**.

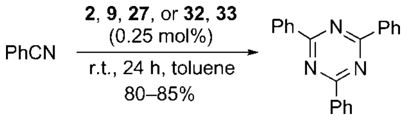


Scheme 17. Tetramerization of benzonitrile. Cp′ = $C_5Me_4SiMe_3$.

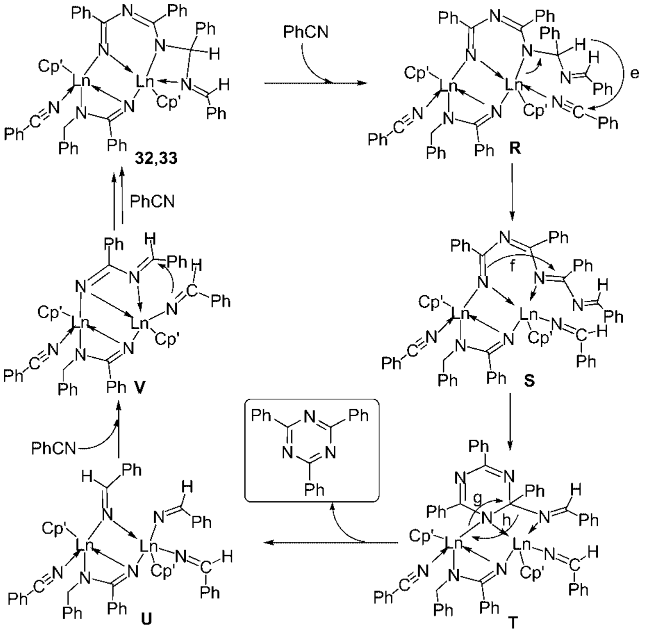


Scheme 18. Possible mechanism for the formation of **33**. Cp′ = $C_5Me_4SiMe_3$.

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]



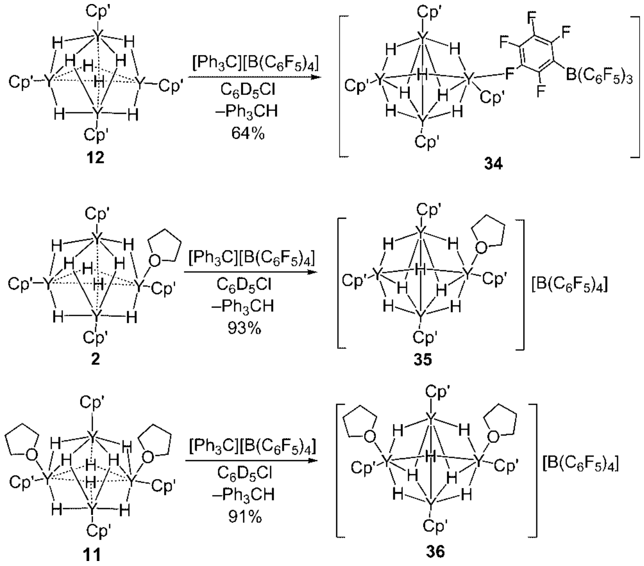
Scheme 19. Catalytic cyclotrimerization of benzonitrile. Cp′ = $C_5Me_4SiMe_3$.



Scheme 20. A possible mechanism for the catalytic cyclotrimerization of benzonitrile. Cp′ = $C_5Me_4SiMe_3$.

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 $[Ph_3C][B(C_6F_5)_4]$ afford the corresponding cationic heptahydride complexes **35**, **36**, and **34**, respectively, in high yields (Scheme 21). An direct bonding interaction between the $[(C_5Me_4SiMe_3)_4Y_4H_7]^+$ cation and the $[B(C_6F_5)_4]^-$ 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. Cp′ = $C_5Me_4SiMe_3$.

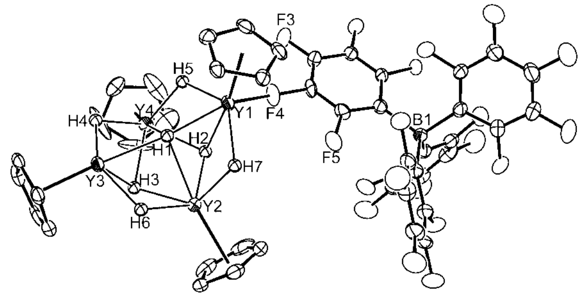


Figure 4. ORTEP drawing of **34**. The Me_3Si and Me groups in $C_5Me_4SiMe_3$ have been omitted for clarity.

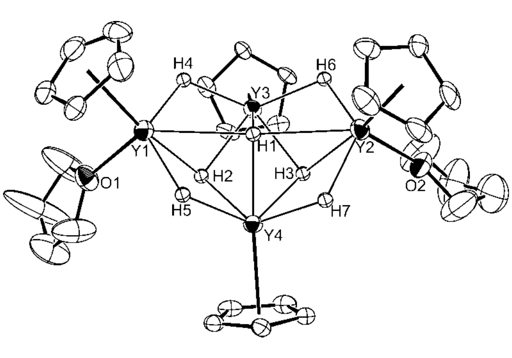
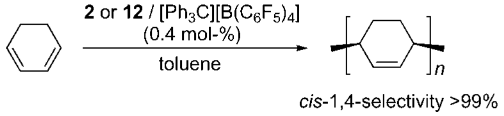


Figure 5. ORTEP drawing of **36**. The Me_3Si and Me groups in $C_5Me_4SiMe_3$ and the $[B(C_6F_5)_4]$ ion have been omitted for clarity.

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 described 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 activity 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 $[(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(THF)]$ 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 $C_5Me_4SiMe_3$ 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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