

Tetranuclear Rare Earth Metal Polyhydrido Complexes Composed of “(C₅Me₄SiMe₃)LnH₂” Units. Unique Reactivities toward Unsaturated C–C, C–N, and C–O Bonds

Dongmei Cui, Olivier Tardif, and Zhaomin Hou*

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan, and PRESTO, Japan Science and Technology Agency (JST), Japan

Received October 30, 2003; E-mail: houz@riken.jp

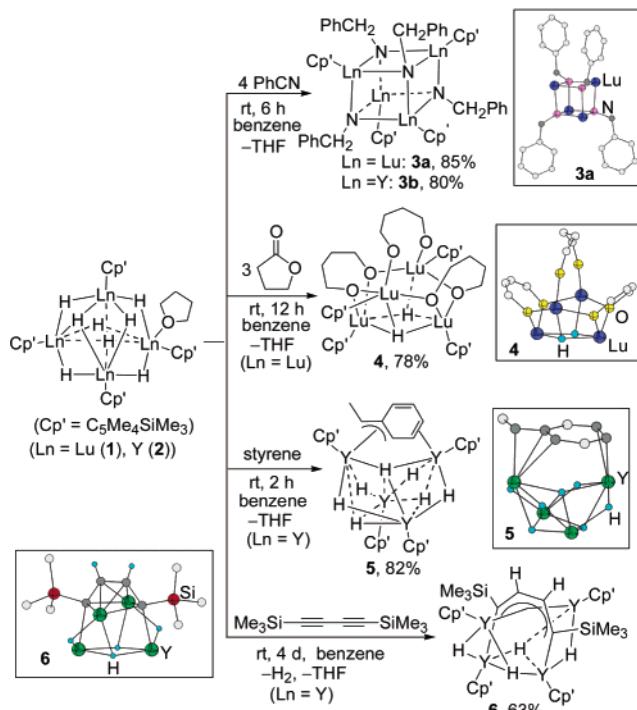
Metal hydrido complexes are among the most important metal compounds because of their critical importance in a variety of stoichiometric and catalytic reactions. For the rare earth metals, a large number of mono(hydrido) complexes of general type “L₂MH” or “(L)(L’)MH” have been synthesized and have had their reactivity studied¹ since the discovery of the first metallocene hydrido complex in the early 1980s.² Although dihydrido or polyhydrido rare earth metal complexes are of great interest both structurally and chemically in comparison with analogous mono(hydrido) complexes and d-transition metal polyhydrides,³ such complexes have hardly been investigated.⁴ Thus far, the reaction chemistry of polyhydrido rare earth metal complexes has remained an almost unexplored field.

We recently described the synthesis and structural characterization of the tetranuclear lutetium and yttrium polyhydrido complexes [(C₅Me₄SiMe₃)Ln(μ-H)₂]₄(THF)_n (Ln = Lu, Y; n = 0–2),^{4b} which represent the first examples of well-defined salt-free rare earth metal polyhydrido complexes.⁴ In this Communication, we wish to report the reactions of [(C₅Me₄SiMe₃)Ln(μ-H)₂]₄(THF) (Ln = Lu, Y) with styrene, 1,4-bis(trimethylsilyl)-1,3-butadiene, benzonitrile, and γ-butyrolactone, to probe the fundamental reactivity of this new class of polyhydrido complexes toward unsaturated C–C, C–N, and C–O bonds. Some of these reactions were found unique to the polyhydrido rare earth metal complexes.

The reaction of [(C₅Me₄SiMe₃)Lu(μ-H)₂]₄(THF) (**1**) with 4 equiv of benzonitrile in benzene at room temperature afforded the tetranuclear benzylimido complex [(C₅Me₄SiMe₃)Lu(μ₃-NCH₂Ph)]₄ (**3a**) in 85% isolated yield as colorless blocks (Scheme 1).⁵ An analogous reaction of [(C₅Me₄SiMe₃)Y(μ-H)₂]₄(THF) (**2**) with benzonitrile gave the yttrium analogue **3b** in 80% isolated yield. The formation of the CH₂ group was evident in the ¹H and ¹³C NMR (DEPT) spectra. An X-ray analysis established that **3a** adopts a novel Lu₄N₄ cubane core structure via μ₃-imido bridges (Lu–N = 2.192(4)–2.322(4) Å; C–N = 1.480(6)–1.483(6) Å). A crystallographic two-fold axis exists in this molecule. Obviously, the C–N triple bond of benzonitrile was completely reduced into the C–N single bond via double Lu–H addition. This is in sharp contrast to the previously reported reactions of rare earth metallocene hydrido complexes^{6a} or zirconocene dihydrido complexes,^{6b} which yielded only the monoinsertion products, such as [(C₅H₅)₂Y(μ-N=CH^tBu)]₂ or (C₅Me₃)₂Zr(H)(N=CHR) (R = C₆H₄Me-*p*). The formation of an imido species from a nitrile is, as far as we are aware, unprecedented. This reaction may offer a convenient route to rare earth metal imido complexes, a class of compounds that is of considerable current interest but still remains very limited.⁷

The reaction of **1** with γ-butyrolactone gave the tetranuclear mixed alkoxo/hydrido complex **4** in 78% isolated yield (Scheme 1).⁵ γ-Butyrolactone is known as a stable, nonpolymerizable cyclic ester.⁸ In this reaction, three molecules of γ-butyrolactone were

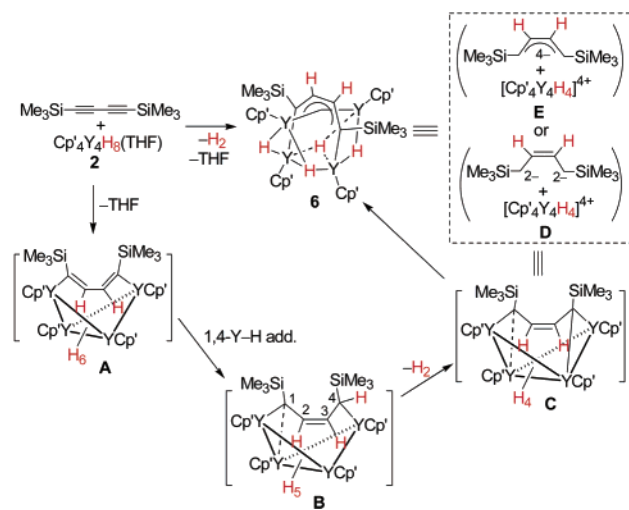
Scheme 1. Reactions of Rare Earth Metal Polyhydrido Complexes with Unsaturated Organic Substrates (The C₅Me₄SiMe₃ Ligands in the X-ray Structures Are Omitted for Clarity)



completely ring-opening reduced by one molecule of **1** to give the linear diolate species “-O(CH₂)₄O-”, which again demonstrates the unusually high reactivity of the rare earth metal polyhydrido complex. Complex **4** adopts a novel basket-like core structure, in which one of the three diolate units forms the “handle” (Lu–(μ₁-O) = 2.051(5) Å) and the other two constitute the “brims” (Lu–(μ₂-O) = 2.145(4)–2.226(4) Å), while the Lu(μ-H)₂Lu unit acts as the “bottom” that is protected also by the C₅Me₄SiMe₃ ligands. A crystallographic two-fold axis exists in this molecule. No further reaction between **4** and γ-butyrolactone was observed, even when an excess of γ-butyrolactone was present. Both **4** and **1**, however, showed high activity for the ring-opening polymerization of ε-caprolactone.

The reaction of the yttrium hydrido complex [(C₅Me₄SiMe₃)Y(μ-H)₂]₄(THF) (**2**) with styrene gave the tetranuclear benzylidene allyl complex **5** in 82% yield as red crystals, in which the allyl part is bonded to one Y atom in a η³-fashion (Y–C = 2.572(14)–2.872(9) Å), while the phenyl part is bonded to another Y atom in a η²-form (Y–C = 2.698(4), 2.780(10) Å) (Scheme 1).⁹ Only one of the eight hydrides in **2** was able to add to styrene; no further reaction

Scheme 2. A Possible Scenario for Formation of 6



was observed even when an excess of styrene was present. The overall structure of the Y_4H_7 core in **5** did not change much from that of **2**. Its four Y atoms are combined by one μ_4 -H ($Y-H = 2.27(3)-2.42(3)$ Å), two μ_3 -H ($Y-H = 2.16(2)-2.53(2)$ Å), and four μ_2 -H ($Y-H = 2.04(2)-2.14(3)$ Å) ligands to form a distorted tetrahedron. Complex **5** was fluxional in C_6D_6 . In THF, it decomposed into a complex mixture. Addition of ca. 10 equiv of THF to a C_6D_6 solution of **5**, however, resulted in clean formation of $[(C_5Me_4SiMe_3)Y(\mu-H)_4](THF)_2$ and styrene. Hydrogenolysis of **5** with H_2 (1 atm) in C_6D_6 afforded ethylbenzene and the THF-free yttrium polyhydrido complex $[(C_5Me_4SiMe_3)Y(\mu-H)_2]$ (**2'**). Under 1 atm of H_2 , styrene could be catalytically hydrogenated into ethylbenzene by **2** or **2'**.¹⁰

The reaction of **2** with 1,4-bis(trimethylsilyl)-1,3-butadiyne afforded **6** in 63% yield as dark blue blocks (Scheme 1).⁵ Complex **6** consists formally of a $[(C_5Me_4SiMe_3)YH]_4^{4+}$ unit and a butadiene-derived species. A crystallographic two-fold axis exists in this molecule. The butadiene-derived unit can be best described as a delocalized 2-buten-1,1',4,4'-tetrayl or butene-tetraanion species, which is bonded to two Y atoms in a π : η^4 -“inverse-sandwich” fashion ($Y-C = 2.506(2)-2.550(2)$ Å; $C-C = 1.404(4), 1.454(3)$ Å) and to the other two Y atoms in a σ_1 : μ_1 -terminal form at the two terminal carbon atoms ($Y-C = 2.492(2)$ Å).¹¹ Two of the four hydrides are bonded to three Y atoms in a μ_3 -H form ($Y-H = 2.23(2)-2.43(2)$ Å), while the other two hydrides bonded to two Y atoms in a μ_2 -H form ($Y-H = 2.06(3), 2.09(2)$ Å). The location of the olefin hydrogen atoms in the butene-tetraanion unit was confirmed by both X-ray and $^1H-^{29}Si$ HMBC NMR analyses.

The formation of **6** could be explained by the reaction paths shown in Scheme 2. Addition of two $Y-H$ units to the two $C\equiv C$ units in a “2,1-fashion” would yield the 1,3-butadien-1,4-diyl (or butadiene-dianion)/hexahydride species **A**. The subsequent 1,4- $Y-H$ addition to the 1,3-butadiene unit in **A** could give the 2-buten-1,1',4'-triy/pentahydride species **B**. Deprotonation at the C4 position of the butene species by $Y-H$ in **B** should afford the 2-buten-1,1',4'-tetrayl/tetrahydride species **C**. This species can be regarded as a resonance structure (a localized form) of **6** (cf. also **D** and **E**).

In summary, the tetranuclear Lu and Y polyhydrido complexes such as **1** and **2** can undergo novel multiple hydrogenation reactions with unsaturated organic compounds such as benzonitrile, γ -butyrolactone, and conjugated diyne to afford a new series of structurally characterizable polynuclear complexes that possess novel structures and are otherwise difficult to access. These reactions demonstrate, for the first time, that polyhydrido rare earth

metal complexes can show unique reactivity that differs from those of analogous mono(hydrido) complexes and d-transition polyhydrides.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078224, “Reaction Control of Dynamic Complexes”) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We thank Dr. M. Nishiura and Mr. J. Baldamus for help in X-ray analyses and Dr. H. Koshino for help in NMR analyses. We are also grateful to the Japan Society for the Promotion of Science (JSPS) for Postdoctoral Fellowships for D. Cui and O. Tardif.

Supporting Information Available: Experimental details, ORTEP drawings, and tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for **2**–**6** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Selected reviews: (a) Hou, Z. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2253. (b) Okuda, J. *J. Chem. Soc., Dalton Trans.* **2003**, 2367. (c) Arndt, S.; Okuda, J. *J. Chem. Rev.* **2002**, *102*, 1953. (d) Molander, G. A.; Romero, J. A. C. *J. Chem. Rev.* **2002**, *102*, 2161. (e) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1. (f) Hou, Z.; Wakatsuki, Y. In *Science of Synthesis*; Imamoto, T., Noyori, R., Eds.; Thieme: Stuttgart, 2002; Vol. 2, p 849. (g) Hoskin, A. J.; Stephan, D. W. *Coord. Chem. Rev.* **2002**, *233*–234, 107. (h) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193. (i) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (j) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon: Oxford, 1995; Vol. 4, p 11. (k) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.
- Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008.
- Selected reviews on d-transition metal polyhydrido complexes: (a) Suzuki, H. *Eur. J. Inorg. Chem.* **2002**, 1009. (b) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077. (c) Crabtree, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, J. A., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, p 689. (d) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1.
- It was not until very recently that structurally characterized rare earth metal polyhydrido complexes of “LMH₂” units became known. See: (a) Hou, Z.; Zhang, Y.; Tardif, O.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9216. (b) Tardif, O.; Nishiura, M.; Hou, Z. *Organometallics* **2003**, *22*, 1171. (c) Hultzsich, K. C.; Voth, P.; Spaniol, T. S.; Okuda, J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1272.
- All complexes reported in this paper have been fully characterized. See Supporting Information for experimental details.
- (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.
- For rare earth metal imido complexes, most of which incorporated a main group metal ion via imido-bridges, see: (a) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652. (b) Gordon, J. C.; Giesbrecht, G. R.; Clark, D. L.; Hay, P. J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Watkin, J. G. *Organometallics* **2002**, *21*, 4726. (c) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1578. (d) Trifonov, A. A.; Bochkarev, M. N.; Schumann, H.; Loebel, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1149.
- (a) Johns, D. B.; Lenz, R. W.; Luick, A. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: London, 1984; Vol. 1, Chapter 7, p 461. (b) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798. (c) Nishiura, M.; Hou, Z.; Koizumi, T.; Imamoto, T.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 8245.
- Monomeric rare earth metal η^3 -benzyl allyl complexes are known. For example, see: Hultzsich, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228.
- Catalytic hydrogenation of styrene by rare earth metallocene complexes was reported. For examples, see: (a) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (b) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.
- Formation of a binuclear lutetium butene-tetraanion species via reductive coupling of PhCCPh by a lutetium naphthalenide complex was reported. Bochkarev, M. N.; Protchenko, A. V.; Zakharov, L. N.; Fukin, G. K.; Struchkov, Y. T. *J. Organomet. Chem.* **1995**, *501*, 123.

JA0393240