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Reaction Pathway for the Formation of Binuclear Samarocene Hydride from Monomeric Alkyl Samarocene Derivative and the Effective Catalysis of Samarocene Hydride for the Block Copolymerization of Ethylene with Polar Monomers

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*Summary: The X-ray analysis of $Me_2Si(C_5H_3$-3-$Me_3Si)_2SmCH(Me_3Si)_2(THF)$ (**1**) revealed a monomeric structure, while the hydrogenated complex, $[Me_2Si(C_5H_3$-3-$Me_3Si)_2SmH(THF)]_2$ (**2**), exhibits binuclear μ-H structure to indicate that $Me_2SiCp'_2M \rightarrow M(\mu\text{-}Me_2SiCp'_2)_2M$ rearrangement of the $\eta^5-\eta^5$ ligation occurs during the hydrogenation. The resulting samarocene hydride **2** exhibits high activity as an initiator for the block copolymerization of ethylene with polar monomers such as methyl methacrylate and ϵ-caprolactone.*

The stoichiometric and catalytic properties of organo-f-element hydrides are profoundly influenced by the nature of π-ancillary ligands. Structurally, the ligational transposition $Cp'_2MH_2 \rightarrow Me_2SiCp'_2MH_2$ ($Cp' = \eta^5$-C_5R_4R', η^5-$C_5R_3R''_2$) results in a considerable opening of the metal coordination sphere in the vincity of the σ-ligand equatorial girdle[1,2]/frontier orbitals.[3] For the bridged lanthanocene hydrides, two types of structures have been proposed. One is the binuclear μ-H complex where the metal is coordinated by two cyclopentadiene ligands bridged by a R_2Si group to form the type (a) complex,[4,5] and the other is the binuclear complex where the metal is coordinated with two nonbridged cyclopentadienyl groups of the type (b) (Scheme 1).[6] Isolation of lanthanide hydride complexes is generally very difficult due to their thermal instability, and only one X-ray analysis is reported for $[Et_2Si(C_5H_4)(C_5H_2$-3,4-$Me_2)_2$-$LuH]_2$, which is type (b),[6] while the type (a) structures of $[Me_2Si(C_5Me_4)_2MH]_2$ (M = Nd, Sm, Lu)[4] and $[Me_2Si$-$(C_5H_2$-2-Me_3Si-4-$tBu)_2YH]_2$ [5] have been proposed on the

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[1] Jeske, G.; Shock, L. E.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

[2] (a) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. (b) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J. Day, V. W. *Organometallics* **1984**, *3*, 819.

[3] (a) Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 3195. (b) Tatsumi, K.; Nakamura, A.; Hoffman, P.; Hoffman, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467.

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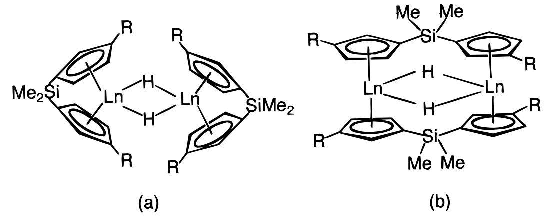
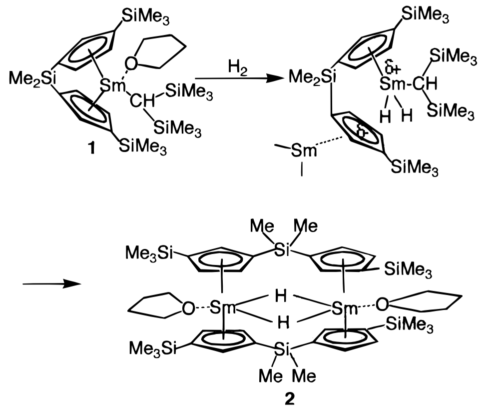
Scheme 1



Scheme 2



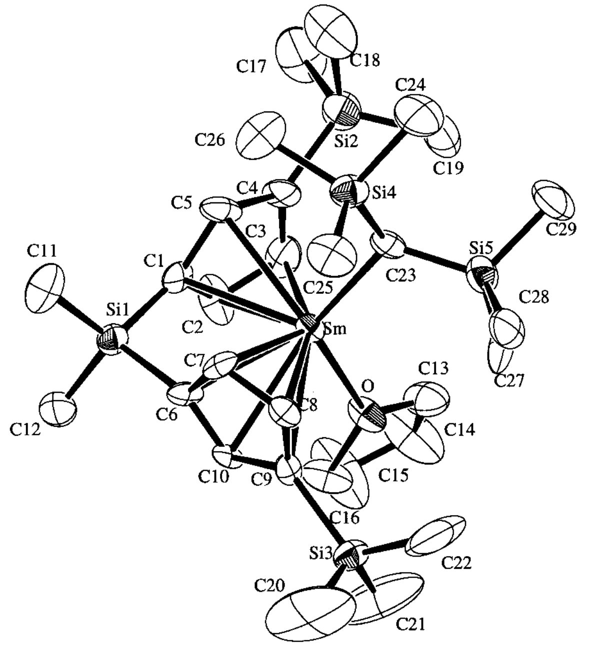


Figure 1. ORTEP drawing of **1** with atom-numbering scheme. Hydrogen atoms are omitted for clarity.

basis of ^1H NMR spectra. In relating to the above-mentioned lutetium hydride, the X-ray analysis of the precursor complex $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}Me_2)_2LuCH(Me_3Si)_2$ has not yet been made (only the X-ray analysis of related $Et_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}Me_2)_2LuCH(Me_3Si)_2$ is reported). The best way to analyze the reaction pathway for the formation of binuclear μ-H lanthanocene hydride is to determine the structures of both the precursor complex $Me_2Si(C_5H_3\text{-}3\text{-}R)_2SmCH(Me_3Si)_2$ and the hydrogenated complex, $[Me_2Si(C_5H_3\text{-}3\text{-}R)_2SmH]_2$, by X-ray analyses. On the basis of this idea, we have synthesized $Me_2Si(C_5H_3\text{-}3\text{-}Me_3Si)_2SmCH(Me_3Si)_2(THF)$ (**1**) as a precursor and the hydrogenated complex $[Me_2Si(C_5H_3\text{-}3\text{-}Me_3Si)_2SmH]_2$ (**2**) (Scheme 2). This paper also deals with the high catalytic activity of the resulting binuclear μ-H complex for the block copolymerization of ethylene with polar monomers.

Figure 1 shows the ORTEP drawing of $Me_2Si(C_5H_3\text{-}3\text{-}Me_3Si)_2SmCH(Me_3Si)_2(THF)$ (**1**).[7] The complex **1** is coordinated with a THF molecule in this case, while other related complexes such as $(C_5Me_5)_2NdCH(Me_3Si)_2$ [4] and $Me_2Si[2,3\text{-}(Me_3Si)_2\text{-}C_5H_2][2,4\text{-}(Me_3Si)_2\text{-}C_5H_2]SmCH(Me_3Si)_2$[8] generally bear no THF molecule and exhibit an agostic interaction between the metal and the Me group of the $(Me_3Si)_2CH$ ligand. A remarkable contraction of the Cp ring centroid−Sm−Cp ring centroid angle was observed for **1**. The value of the resulting $SiMe_2$-bridged complex (118.5°) is much smaller than those of trivalent samarocene complexes, 134.5−138.5°, observed for $(C_5Me_5)_2SmCl(THF)$[9] and $(C_5Me_5)_2Sm(C_6H_5)(THF)$[10] and those of divalent samarocene complexes (133−137°) such as $(C_5Me_5)_2Sm(THF)$,[11] $(C_5Me_5)_2Sm$,[12] and $(C_5Me_5)_{10}Sm_5Cl_5$(tetraglyme),[13] and the observed value is also smaller than those of Me_2Ge-bridged metallocene derivatives (124.5° and 127.9°), $Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$[14] and $Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$.[14] The averaged Cp ring centroid−Sm distance of **1** (2.45 and 2.51 Å) is close to those (2.45−2.46 Å) of $(C_5Me_5)_2SmCl(THF)$, $[(C_5Me_5)_2SmCl]_3$,[13] $(C_5Me_5)_2Sm(THF)$, and $(C_5Me_5)_2Sm$.

The complex **1** was hydrogenated by bubbling excess H_2 in toluene/THF for 30 min, and the samarocene hydride **2** was obtained in quantitative yield. The resulting samarocene hydride was recrystallized from toluene/hexane, and its ORTEP drawing is given in Figure 2.[15] The complex assumes the structure (b), despite the use of a wedge-type metallocene as a precursor. This means that the attack of hydrogen resulted in the cleavage of one of the Cp ring−Sm bonds and the samarocene hydride rearranges to a binuclear

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[7] A crystal having approximate dimensions of 0.45 × 0.40 × 0.30 mm was sealed in a thin-walled glass capillary and mounted on a glass fiber. All measurements were carried out on a Rigaku RAXIS-RAPID image plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Of the 34 592 reflections that were collected, 6976 were unique. The number of reflections used for the unit cell determination was 20 408 for $3.1° < \theta < 54.9°$. The structure was solved by direct methods and expanded using Fourier techniques, $R_w = 0.105$. Crystal data for **1**: $SmSi_5C_{29}H_{57}O$, red crystals, $M_r = 712.60$, monoclinic, space group $P2_1/c$ (#14), $a = 15.154(2)$ Å, $b = 13.216(2)$ Å, $c = 21.438(3)$ Å, $\beta = 98.945(4)°$, $V = 4241.5(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.16$ g/cm^3, μ(Mo Kα) = 15.45 cm^{-1}.

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[15] The final cycle of full-matrix least-squares refinement was based on 4200 observed reflections ($I > 3.00\sigma(I)$). Crystal data for **2**: $Sm_2Si_6C_{44}H_{82}O_2$, yellow prism, monoclinic, space group $C2/c$ (#15), $a = 17.86(1)$ Å, $b = 13.809(5)$ Å, $c = 22.495(7)$ Å, $\beta = 103.62(4)°$, $V = 5391(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.370$ g/cm^3, μ(Mo Kα) = 23.26 cm^{-1}. The structures were solved using the heavy-atom method and refined to $R_w = 0.49$.

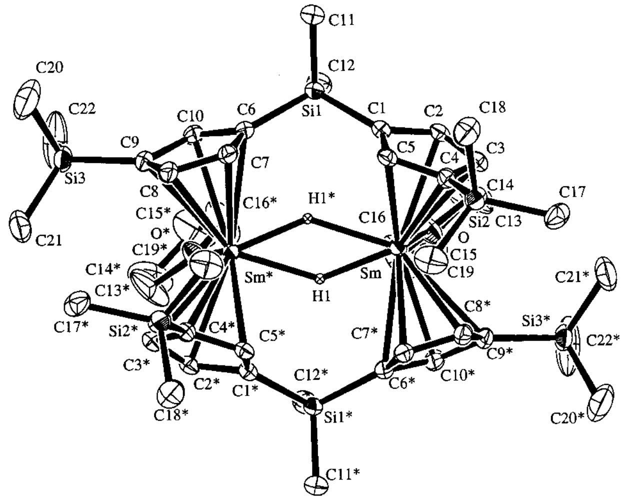
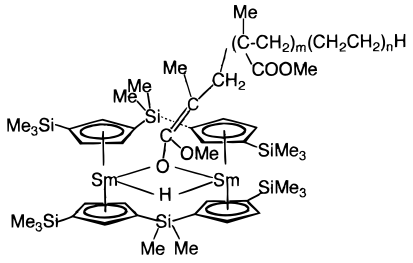


Figure 2. ORTEP drawing of **2** with atom-numbering scheme. Hydrogen atoms are omitted for clarity.

μ-H complex after the removal of $Me_3SiCH_2SiMe_3$ group. Thus, the transformation of **1** to **2** involves $2Me_2SiCp'_2M \rightarrow M(\mu{-}Me_2SiCp'_2)_2M$ rearrangement of the η^5-η^5 ligation. The Sm−Sm bond distance of 3.762(1) Å is shorter than the Sm−Sm distance of 3.905(3) Å for a wedge-type samarocene hydride, $[(C_5Me_5)_2SmH]_2$,[16] while longer than that of the Lu−Lu bond of 3.390(1) Å for $[Et_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}Me_2)_2LuH]_2$.[6] The resulting Sm−Sm distance is slightly longer than that (3.58 Å) estimated from twice the single bond radius of the Sm atom. The Cp centroid−Sm−Cp centroid angle of **2** (132.4°) exceeds that of **1**, and the dihedral angle between the two Cp rings bridged by the Me_2Si group is only 31.2°. The H−Sm−H angle (39.3°) is much smaller than the H−Lu−H angle (75°), and the Sm−H−Sm angle (140.7°) is larger than the Lu−H−Lu angle (105°). The Sm(1)−H(1) length is 1.91 Å, while the Sm(2)−H(1) length is 2.15 Å. The averaged Cp−Sm bond distances (2.46, 2.48 Å) agreed with those of the complex **1**.

The complex **1** is completely ineffective as an initiator for the polymerizations of ethylene and propylene at temperatures of 0−40 °C, while complex **2** exhibits high catalytic activity (2.7×10^4 g PE/mol·Sm·h) for the polymerization of ethylene to lead to high molecular weight polyethylene ($M_n = (3-5) \times 10^4$) with a rather narrow molecular weight distribution ($M_w/M_n = 1.63-1.68$). Further, complex **2** is useful to obtain the block copolymer of ethylene with polar monomers such as methyl methacrylate (MMA) [poly(MMA)/polyethylene = 19/81 mol/mol, $M_n = (6-7) \times 10^4$, $M_w/M_n = 1.67-1.69$] and ϵ-caprolactone (CL) [poly(CL)/polyethylene = 8/92 mol/mol, $M_n = 7 \times 10^4$, $M_w/M_n = 1.65$], when ethylene was polymerized first followed by the addition of polar monomers. Reversed addition, the addition of polar monomers followed by the addition of ethylene, induces no block copolymerization. In these cases, we can obtain only homopolymers of polar monomers. We can readily dye the resulting block copolymer with conventional dispersive dyes, while the dyeing of traditional polyethylene is very hard. Here we can propose the following intermediate for the formation of the block copolymer, since the reaction of $[Et_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}Me_2)_2LuH]_2$ with ethylene is known to produce $[Et_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}Me_2)_2Lu](\mu\text{-}H)(\mu\text{-}C_2H_5)$ exclusively.[6]

Scheme 3



Supporting Information Available: Crystal data, intensity measurement, structure solution and refinement, tables of positional and thermal parameters, bond distances and angles, least-squares planes, and preparation methods for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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