(Pentamethylcyclopentadienyl)samarium(II) Alkyl Complex with the Neutral “C_5Me_5K” Ligand: A Precursor to the First Dihydrido Lanthanide(III) Complex and a Precatalyst for Hydrosilylation of Olefins

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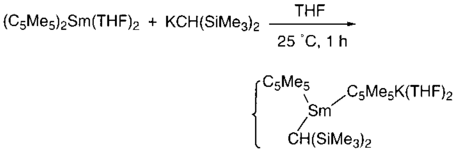
Organolanthanide chemistry has witnessed spectacular growth in the past 20 years. In this development, alkyl and hydrido complexes bearing two substituted or unsubstituted cyclopentadienyl ligands have occupied a specially important place because of their high activity and unique behavior in various catalytic processes.[1] Although mono(cyclopentadienyl or its derivative)-supported lanthanide(II)−alkyl and lanthanide(III)−dihydride complexes are of great interest both structurally and chemically in comparison with the metallocene analogues, isolation and structural characterization of such a species has never been achieved to date owing to ligand redistribution problems. We report here the first example of a structurally characterized (pentamethylcyclopentadienyl)lanthanide(II) alkyl complex **1**,[2] which upon reaction with H_3SiPh afforded the first lanthanide(III) *dihydride* complex **2**.[3,4] Some preliminary results that demonstrate the utility of these new compounds in catalytic processes such as the hydrosilylation of olefins are also described.

During our recent studies on lanthanide(II) complexes bearing mixed pentamethylcyclopentadienyl (C_5Me_5) and a heteroatom-containing monodentate anionic ligand (ER) (ER = OAr, SAr, NRR′, PHAr),[5] we became curious about the analogous lanthanide(II) alkyl or hydride complexes. Since the alkyl or hydride ligand itself could serve as an active site, such a Ln(II) compound was anticipated to show more diverse and higher reactivity than its ER analogues.[5] Analogous to the synthesis of Sm(II) complexes bearing the mixed C_5Me_5/ER ligands,[5c,h] the reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of $KCH(SiMe_3)_2$ afforded the corresponding $C_5Me_5/CH(SiMe_3)_2$-ligated Sm(II) complex $[(C_5Me_5)Sm(CH(SiMe_3)_2)(C_5Me_5)K(THF)_2]_n$ (**1**) in 91% isolated yield as green crystals, in which the “$(C_5Me_5)K(THF)_2$” unit acts as a neutral stabilization ligand (eq 1).[6] The overall structure of **1** is similar to those previously reported for its ER analogues,[5c] and so are the Sm−C_5Me_5 bond distances (av 2.854(5) and 2.906(5) Å in **1**). The Sm−alkyl σ-bond distance (2.652(9) Å) in **1** is somewhat shorter than those found in the only other structurally characterized Sm(II)−alkyl complex $Sm\{C(SiMe)_2(SiMe_2OMe)\}_2(THF)$ (2.787(5) and 2.845(5) Å),[2c] but longer than those found in Sm(III)−alkyl complexes such as $(C_5Me_5)_2SmMe(THF)$ (2.48(1) Å).[7]



1, 91% (1)

When **1** was stirred with 2 or more equiv of H_3SiPh in THF, an orange-red crystalline product, $[(C_5Me_5)Sm(\mu\text{-}H)_2]_6[(\mu\text{-}H)K(THF)_2]_3$ (**2**), was obtained in 42% isolated yield after recrystallization from THF/hexane (eq 2).[8] An X-ray analysis has shown that **2** is a polyhydrido Sm(III)/K cluster complex which consists formally of six “$(C_5Me_5)SmH_2$” and three “$KH(THF)_2$” units (Figure 1).[6] All hydrido ligands in **2** could be located and refined. The six Sm atoms constitute a trigonal prism whose three squares are each capped by one K atom. There are 15 hydrido ligands in this molecule, one being body-centered in a μ_6−H−Sm_6 fashion and others each capping a metal triangle in either μ_3−H−Sm_3 or μ_3−H−Sm_2K form. The whole molecule has crystallographic D_{3h} symmetry. One three-fold axis passes through the Sm_3-μ_3-capped and the Sm_6-μ_6-centered H atoms. Perpendicular to this three-fold axis exist three two-fold axes, each passing through both the μ_6-centered H and one K atoms and bisecting a Sm···Sm prism

$$\mathbf{1} \xrightarrow[\substack{-(Me_3Si)_2CHSiH_2Ph \\ -KC_5Me_5}]{\substack{H_3SiPh\ (5\ equiv) \\ THF,\ 25\ ^\circ C,\ 10\ h}} [(C_5Me_5)Sm(\mu\text{-}H)_2]_6[(\mu\text{-}H)K(THF)_2]_3 \quad (2)$$

2, 42%

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[6] Crystal data for **1**: monoclinic *C*2 (no. 5), $a = 34.204(6)$ Å, $b = 10.189(2)$ Å, $c = 11.678(2)$ Å, $\beta = 102.016(4)°$, $V = 3981(1)$ Å^3, $Z = 4$, $D_c = 1.274$ g cm^{-3}. $R_1(F^2) = 0.0986$, $wR(F^2) = 0.1413$ for all independent data (9883) and 341 parameters. For **2**: rhombohedral $R\bar{3}c$ (no. 167), $a = b = 24.601(1)$ Å, $c = 27.958(2)$ Å, $V = 14654(2)$ Å^3, $Z = 6$, $D_c = 1.549$ g cm^{-3}. $R_1(F^2) = 0.1004$, $wR(F^2) = 0.1067$ for all independent data (4746) and 166 parameters. The largest residual electron densities for **1** (2.662 e Å^{-3}) and **2** (1.930 e Å^{-3}) were 0.89 and 0.93 Å far from the central Sm atom, respectively.

[7] Evans, W. J.; Chamberlian, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.

[8] The formation of **2** from **1** and H_3SiPh might probably proceed through σ-bond metathesis of the Sm(II)−$CH(SiMe_3)_2$ bond with a Si−H bond,[8a] followed by oxidation of the Sm(II) center by H_3SiPh[8b] and ligand rearrangement/exchange between the resulting products such as “$(C_5Me_5)SmH_2(C_5Me_5)K(THF)_2$” and “$(C_5Me_5)Sm(H)(SiH_2Ph)(C_5Me_5)K(THF)_2$”. $(Me_3Si)_2CHSiH_2Ph$ and KC_5Me_5 were also isolated from this reaction, while another expected byproduct, “$(C_5Me_5)_2SmSiH_2Ph$”, was not identified, possibly owing to its instability.[8c] Hydrogenolysis of **1** with H_2 yielded an unidentified product. (a) Voskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz’mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041. (b) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543. (c) Castillo, I.; Tilley, T. D. *Organometallics* **2000**, *19*, 4733.

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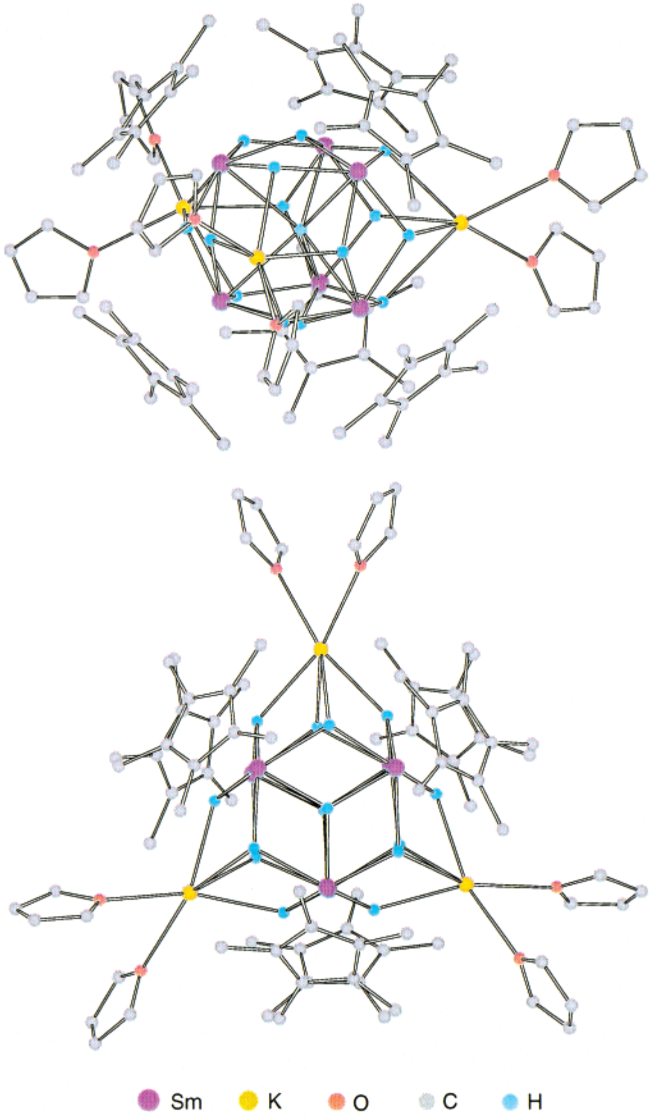
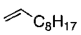
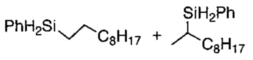
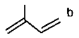
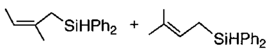
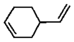
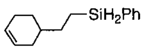
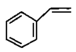
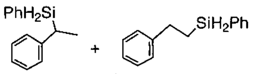


Figure 1. Molecular structure of **2**. (Top) A general view. (Bottom) A view along the three-fold axis. The Sm$-$C$_5$Me$_5$ bonds are omitted for clarity.

edge. The Sm$-$H bond distances of the $\mu_3$$-H-Sm_3$ bonds (2.25(2) Å) are almost the same as those of the $\mu_3$$-H-Sm_2$K bonds (2.23(4) and 2.26(6) Å), which are much shorter than those of the interstitial $\mu_6$$-H-$Sm bonds (2.8010(3) Å). These Sm$-$H bond distances could be compared with the 1.80$-$2.75 Å bond distance range reported for the Sm(III)$-$H bonds in samarocene complexes.[9] The Sm$-$C$_5$Me$_5$ bond distances in **2** (av 2.745(6) Å) are typical for Sm(III)$-$C$_5$Me$_5$ bonds, while the Sm$\cdots$Sm separations in **2** (3.6084(6) and 3.7133(5) Å) are significantly shorter than those found in the metallocene type Sm(III) complexes such as [(C$_5$Me$_5$)$_2$Sm(μ-H)]$_2$ (3.905(3) Å).[10] The K$-$H bond distances in **2** (2.58(4) and 2.89(7) Å) can be compared with those found in KOsH$_3$(PMe$_2$Ph)$_3$ (2.52$-$3.02 Å)[11a] and [K(18-crown-6)][WH$_5$(PMe$_3$)$_3$] (2.684(6)-2.750(6) Å).[11b]

Table 1. Hydrosilylation of Olefins by **1**[a]

substrate	time	product (ratio)	yield/%
	3 d	 (95 : 5)	95
	5 h	 (85 : 15)	100
	17 h		97
	10 h	 (93 : 7)	100

[a] Conditions: substrate (1.0 mmol), H$_3$SiPh (1.1 mmol), **1** (0.02 mmol), in toluene, at room temperature, unless otherwise noted. [b] H$_2$SiPh$_2$ (1.1 mmol) was used instead of H$_3$SiPh.

The "self-assembly" of "(C$_5$Me$_5$)SmH$_2$" to form a trigonal prism Sm$_6$ skeleton in **2** is in contrast with what was previously observed in the case of (cyclopentadienyl)lanthanide(III) dichloride species such as "CpYbCl$_2$" and "CpSmCl$_2$", which constituted a Yb$_6$ octahedron in [Cp$_6$Yb$_6$Cl$_{13}$]$^-$ and a Sm$_{12}$ icosahedron in [Cp$_{12}$Sm$_{12}$Cl$_{24}$], respectively.[12,13] As far as we are aware, complex **2** represents the first example of a structurally characterized *dihydrido* lanthanide complex[1a,3] and also the first example of a structurally characterized polyhydrido lanthanide cluster with an interstitial hydrogen atom.[14−17]

In relation to the formation of **2**,[8] **1** showed good activity and selectivity for the hydrosilylation of several types of olefins (Table 1).[18] Some of these results are in contrast with those previously reported for the lanthanide metallocene catalysts.[19] Further studies on the reactivity of **1** and **2** as well as on the synthesis and reactivity of other lanthanide(II) alkyl complexes analogous to **1** are in progress.[20]

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Supporting Information Available: Experimental details, ORTEP drawings, and tables of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) For examples of μ_3-H-bridged trimetallic organolanthanide polyhydride complexes, see: Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439 and references therein.

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(16) For a review on heterometallic organometallic complexes of the lanthanides, see: Soloveichik, G. L. *New. J. Chem.* **1995**, *19*, 597.

(17) For a review on organolanthanide clusters, see: Anwander, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 599.

(18) Complex **2** could also be isolated from a completed hydrosilylation reaction of **1** and also showed an activity, albeit lower, for the hydrosilylation reactions. These results might offer some hints for the reaction mechanism involved by **1**.

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(20) Preliminary polymerization studies demonstrate that **1** was extremely active for the polymerization and block-copolymerization of ethylene and styrene.[5a−f]