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# Reactivity of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in Ether and Arene Solvents. X-ray Crystal Structures of the Internally Metalated Complex $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$, the Benzyl Complex $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$, and the Siloxide Complex $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$[1]

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In alkanes or benzene, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (**1**) decomposes via an internal metalation reaction to form $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (**2**) and $H_2$. The reaction is reversible and can be inhibited by an atmosphere of hydrogen. **2** crystallizes from benzene in space group $P\bar{1}$ ($C_i^1$; No. 2) with unit cell parameters $a$ = 10.791 (2) Å, $b$ = 10.950 (2) Å, $c$ = 17.166 (4) Å, $\alpha$ = 101.57 (2)°, $\beta$ = 104.35 (2)°, $\gamma$ = 100.11 (2)°, and $V$ = 1870.1 (7) Å$^3$ with $Z$ = 2 for $D_{calcd}$ = 1.50 g cm$^{-3}$. Least-squares refinement of the model based on 4577 observed reflections converged to a final $R_F$ = 4.6%. The four pentamethylcyclopentadienyl rings in **2** approximately describe a tetrahedron. The $\eta^1{:}\eta^5\text{-}CH_2C_5Me_4$ ligand bridges the two samarium atoms, which are separated by 3.842 (1) Å. The hydride ligand was located, and the Sm–($\mu$-H) distances are 2.05 (11) and 2.11 (9) Å. In toluene, the internal metalation reaction that forms **2** is accompanied by metalation of the solvent to form $(C_5Me_5)_2Sm(CH_2C_6H_5)$ (**3**), which was fully characterized as its THF adduct $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (**4**). **4** crystallizes from THF/hexane at -34 °C in space group $P\bar{1}$ with unit cell parameters $a$ = 8.525 (6) Å, $b$ = 9.639 (4) Å, $c$ = 18.687 (7) Å, $\alpha$ = 92.03 (3)°, $\beta$ = 104.09 (4)°, $\gamma$ = 107.01 (4)°, and $V$ = 1414.6 (13) Å$^3$ with $Z$ = 2 for $D_{calcd}$ = 1.37 g cm$^{-3}$. Least-squares refinement of the model based on 3113 observed reflections converged to a final $R_F$ = 3.5%. The four ligands in **4** describe a distorted tetrahedron with an average Sm–C(ring) distance of 2.76 (2) Å and Sm–C(benzyl) and Sm–O(THF) distances of 2.528 (8) and 2.498 (5) Å, respectively. **1** reacts instantaneously with $Et_2O$ to form $(C_5Me_5)_2Sm(OEt)(OEt_2)$ (**5**) and ethane. Tetrahydrofuran forms a marginally stable solvate with **1** of likely composition $(C_5Me_5)_2SmH(THF)$ (**6**), which decomposes to $(C_5Me_5)_2Sm(OBu)(THF)$ (**7**). **7** can be independently synthesized from $(C_5Me_5)_2SmCl(THF)$ and NaOBu. When **1** is dissolved in THF that is distilled from glassware lubricated with Dow Corning high-vacuum grease, $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (**8**) can be obtained in high yield. **8** can be independently synthesized from **1** and hexamethylcyclotrisiloxane. **8** crystallizes from hexane in space group $C2/c$ ($C_{2h}^6$; No. 15) with unit cell parameters $a$ = 32.372 (14) Å, $b$ = 11.317 (1) Å, $c$ = 15.277 (5) Å, $\beta$ = 93.18 (3)°, and $V$ = 5587.9 (31) Å$^3$ with $Z$ = 4 for $D_{calcd}$ = 1.33 g cm$^{-3}$. Least-squares refinement of the model based on 2506 observed reflections converged to a final $R_F$ = 3.7%. **8** contains two $(C_5Me_5)_2Sm(THF)$ units similar to that in **4** which are connected by the bridging siloxide ligand with a Sm–O distance of 2.157 (5) Å and a Sm–O–Si angle of 173.6 (3)°.

During the past several years, an extensive chemistry has been discovered for organometallic complexes containing metal–hydrogen bonds involving yttrium and the lanthanide metals.[2-19] The reactivity of Ln–H linkages (Ln = lanthanide metal or yttrium) has been found to vary greatly, depending on the amount of steric saturation around the metal center and the absence or presence of

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terminal vs bridging hydride ligands.[4,20] For example, a Lu–H moiety in $(C_5Me_5)_2Lu(\mu\text{-}H)LuH(C_5Me_5)_2$,[15,16] which is in equilibrium with the monometallic species $(C_5Me_5)_2LuH$, will metalate benzene and react with ether, whereas the bridging Lu–H unit in $[(C_5H_5)_2Lu(THF)(\mu\text{-}H)]_2$ is stable to arene and ether solvents and will only metalate relatively acidic hydrocarbons such as terminal alkynes.[6,8] The Y–H bonds in $[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)^-$ are even less reactive, and the sterically protected central $\mu_3$-H ligand does not react readily even with $CH_3OH$.[9]

Although these extremes of reactivity for Ln–H bonds have been defined, too few detailed studies of the reactivity of specific Ln–H-containing complexes have been made to allow one to precisely predict the reactivity of a given system. For example, we recently needed detailed information on the reactivity of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (**1**) in connection with a study of the reaction of $(C_5Me_5)_2Sm$ with alkenes.[10] To evaluate possible reaction pathways involving trivalent organosamarium hydride intermediates, we needed to determine not only the reactivity of **1** with alkenes but also the behavior of **1** in common solvents. We report here on the reactivity of this complex with common solvents as well as its internal metalation chemistry and reactivity with dimethylsilicone-containing materials. These results not only extend the known chemistry of lanthanide hydrides[2-19] and present the first X-ray crystal structure of an internally metalated 4f-element metallocene derivative but they also reveal some new avenues for lanthanide-based reactivity.

## Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum-line, and glovebox (Vacuum Atmospheres HE-553 Dri Lab) techniques. Solvents were vacuum-distilled from sodium benzophenone ketyl into collection flasks equipped with Teflon stopcocks. $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$[6] and $(C_5Me_5)_2SmCl(THF)$[21] were made according to the literature. $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ was stored at −34 °C prior to usage. NaOBu was made from sodium and *n*-butanol in THF. $(Me_2SiO)_3$ (Petrarch) was melted over molecular sieves and subsequently sublimed before use. Physical measurements were obtained as previously described.[7,22] $^{13}C$ NMR data were obtained on a GN 500-MHz spectrometer, and all NMR data were obtained at ambient temperature.

**$(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2) from $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (1). NMR Studies.** In the glovebox, an NMR sample of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in $C_6D_6$ was prepared. Over a period of a few weeks, the orange **1** converts to dark brown **2**, which was identified by X-ray crystallography (see below). **2** was the only organosamarium product observed in this reaction except for small amounts of $[(C_5Me_5)_2Sm]_2O$. The ratio **1**:**2** as a function of time was followed by NMR spectroscopy: 1 day (3.5:1), 2 days (1.6:1), 3 days (1:1.1), 7 days (1:3.3), 10 days (1:5.7), 13 days (1:9.1), 16 days (1:13). $^1H$ NMR (benzene-$d_6$): $\delta$ −0.90 (s, $CH_2C_5\mathit{Me}_4$, 6 H), −1.11 (s, $(C_5\mathit{Me}_5)Sm$, 15 H), −1.27 (s, $(C_5\mathit{Me}_5)_2Sm$, 30 H), −2.15 (br s, $C\mathit{H}_2C_5Me_4$, 2 H), −7.46 (s, $CH_2C_5\mathit{Me}_4$, 6 H). $^{13}C$ NMR (benzene-$d_6$): $\delta$ 173.1 (br s, $\mathit{C}H_2C_5Me_4$), 116.4 (s, $CH_2\mathit{C}_5Me_4$), 115.7 (s, $(\mathit{C}_5Me_5)Sm$), 115.3 (s, $(\mathit{C}_5Me_5)_2Sm$), 95.1 (s, $CH_2\mathit{C}_5Me_4$), 30.1 (q, $J_{CH}$ = 124.8 Hz, $CH_2C_5\mathit{Me}_4$), 26.2 (q, $J_{CH}$ = 125.3 Hz, $(C_5\mathit{Me}_5)Sm$), 26.0 (q, $J_{CH}$ = 126.4 Hz, $CH_2C_5\mathit{Me}_4$), 13.1 (q, $J_{CH}$ = 124.8 Hz, $(C_5\mathit{Me}_5)_2Sm$). Magnetic susceptibility: $\chi_M^{295\,K} = 1040 \times 10^{-6}$ cgsu; $\mu_{eff}^{295\,K} = 1.57\ \mu_B$. IR (KBr): 2920–2860 s, 1435 m, 1380 m, 1160 m br, 1140–1090 m, 1020 m, 895 w, 800 w cm$^{-1}$. Anal. Calcd for $Sm_2C_{40}H_{60}$: Sm, 35.73; C, 57.09; H, 7.19. Found: Sm, 35.90; C, 56.69; H, 7.25.

**Gas Analysis.** In the glovebox, **1** (0.105 g, 0.12 mmol) was dissolved in 20 mL of benzene and placed in a 100-mL Kontes flask equipped with a Teflon stirbar. The flask was evacuated by five freeze–pump–thaw cycles on a high-vacuum line, and the reaction mixture was stirred for 4 weeks. The gases were collected by Toepler pump and determined to be $H_2$ by mass spectrometry (0.076 mmol, 61%).

**Solvent and Hydrogen Dependence.** In the glovebox, three samples of **1** (0.029 g, 0.034 mmol; 0.023 g, 0.027 mmol; 0.021 g, 0.025 mmol) were placed in three 100-mL Kontes flasks equipped with Teflon stirbars. Benzene (3 mL) was added to each of the first two flasks, and cyclohexane (3 mL) was added to the third. The first flask was attached to a high-vacuum line ($2 \times 10^{-5}$ Torr), the system was degassed, 1 atm of hydrogen was admitted, and the reaction flask was sealed. All three of the reaction mixtures were stirred at room temperature for 48 h and then returned to the glovebox. The solvent was removed from each reaction mixture by rotary evaporation, and each residue was analyzed by $^1H$ NMR spectroscopy. The reaction mixtures contained 90%, 60%, and 80% of **1**, respectively. The reaction containing 60% of **1** was then treated with 1 atm of hydrogen for 24 h and subsequently found to contain 90% of **1**.

**$(C_5Me_5)_2Sm(CH_2C_6H_5)$ (3) and $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (4). NMR Studies.** The reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ and toluene was monitored by $^1H$ NMR spectroscopy in a manner analogous to that described above. A toluene-$d_8$ NMR sample of $[(C_5Me_5)_2SmH]_2$ converts to a mixture of **2** and $(C_5Me_5)_2Sm(CH_2C_6H_5)$ (**3**) in approximately a 1.4:1 molar ratio within 1 week. $^1H$ NMR of **3** (benzene-$d_6$): $\delta$ 15.57 (v br s, $C\mathit{H}_2C_6H_5$, 2 H), 5.12 (br t, $CH_2C_6\mathit{H}_5$, 1 H), 3.00 (br s, $CH_2C_6\mathit{H}_5$, 2 H), 2.48 (br s, $CH_2C_6\mathit{H}_5$, 2 H), 0.90 (s, $C_5Me_5$, 30 H).

**Bulk Synthesis.** In the glovebox, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (0.049 g, 0.058 mmol) was dissolved in 10 mL of toluene. As cyclohexene (0.2 mL) was slowly added to the stirred orange solution, it turned orange-red. The solution was stirred for 10 min, the solvent was removed by rotary evaporation, and the red-orange oily solid was extracted with 10 mL of hexane to yield a red-orange solution. THF (1 mL) was added, and the solvent was removed by rotary evaporation, leaving **4** as a red-orange microcrystalline solid (0.061 g, 90%), which was identified by X-ray crystallography (see below). $^1H$ NMR (benzene-$d_6$): $\delta$ 10.32 (br s, $C\mathit{H}_2C_6H_5$, 2 H), 7.73 (d, $J_{HH}$ = 6.7 Hz, $CH_2C_6\mathit{H}_5$, 2 H), 6.80 (t, $J_{HH}$ = 7.1 Hz, $CH_2C_6\mathit{H}_5$, 1 H), 6.33 (t, $J_{HH}$ = 6.9 Hz, $CH_2C_6\mathit{H}_5$, 2 H), 1.31 (s, $C_5Me_5$, 30 H), −1.40 (s, THF, 4 H), −2.30 (s, THF, 4 H). $^{13}C$ NMR (benzene-$d_6$): $\delta$ 163.1 (br s, $\mathit{C}H_2C_6H_5$), 129.95 (d, $J_{CH}$ = 154 Hz, $CH_2\mathit{C}_6H_5$), 129.89 (d, $J_{CH}$ = 154 Hz, $CH_2\mathit{C}_6H_5$), 117.4 (d, $J_{CH}$ = 148 Hz, $CH_2\mathit{C}_6H_5$), 112.2 (d, $J_{CH}$ = 159 Hz, $CH_2\mathit{C}_6H_5$), 114.4 (s, $\mathit{C}_5Me_5$), 61.5 (t, $J_{CH}$ = 146 Hz, THF), 20.3 (t, $J_{CH}$ = 135 Hz, THF), 15.6 (q, $J_{CH}$ = 125 Hz, $C_5\mathit{Me}_5$). Magnetic susceptibility: $\chi_M^{299\,K} = 1466 \times 10^{-6}$ cgsu; $\mu_{eff}^{299\,K} = 1.88\ \mu_B$. IR (KBr): 2940–2860 s, 1590 s, 1485 m, 1470 m, 1445 m, 1380 w, 1300 w, 1250 w, 1220 s, 1180 w, 1100 w, 1015 s, 880 s, 865 m, 845 s, 840 m, 800 s, 740 s, 700 s cm$^{-1}$. Anal. Calcd for $SmC_{31}H_{45}O$: Sm, 25.74. Found: Sm, 25.8.

**$(C_5Me_5)_2Sm(OEt)(OEt_2)$ (5).** Addition of orange $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (0.055 g, 0.065 mmol) to 5 mL of diethyl ether in the glovebox immediately generated a bright yellow solution. The solvent was removed by rotary evaporation, and the resulting bright yellow solid was extracted with 5 mL of hexane. Removal of hexane left **5** as a yellow microcrystalline powder (0.060 g, 84%). $^1H$ NMR (benzene-$d_6$): $\delta$ 5.68 (q, $J_{HH}$ = 6.3 Hz, $OC\mathit{H}_2CH_3$, 2 H), 3.34 (t, $J_{HH}$ = 5.1 Hz, $OCH_2C\mathit{H}_3$, 3 H), 1.39 (s, $C_5Me_5$, 30 H), −2.26 (br s, $O(CH_2C\mathit{H}_3)_2$, 6 H), −3.40 (br s, $O(C\mathit{H}_2CH_3)_2$, 4 H). $^{13}C$ NMR (benzene-$d_6$): $\delta$ 114.64 (s, $\mathit{C}_5Me_5$), 70.23 (t, $J_{CH}$ = 134 Hz, $OCH_2CH_3$), 55.46 (t, $J_{CH}$ = 143 Hz, $O(\mathit{C}H_2CH_3)_2$), 20.14 (q, $J_{CH}$ = 124 Hz, $OCH_2\mathit{C}H_3$), 17.99 (q, $J_{CH}$ = 125 Hz, $C_5\mathit{Me}_5$), 8.39 (q, $J_{CH}$ = 126 Hz, $O(CH_2\mathit{C}H_3)_2$). Magnetic susceptibility: $\chi_M^{294\,K} = 1373 \times 10^{-6}$ cgsu; $\mu_{eff}^{294\,K} = 1.80\ \mu_B$. IR (KBr): 2980–2870 s, 2720 w, 1450 m, 1380 m, 1195 w, 1135 s, 1095 m, 1070 s, 1025 m, 1010 w, 950 w, 910 m, 835 w, 800 w, 780 m cm$^{-1}$. Anal. Calcd for $SmC_{26}H_{45}O_2$: Sm, 27.84. Found: Sm, 28.1.

**Gas Analysis.** In the glovebox, **1** (0.027 g, 0.032 mmol) and a Teflon stirbar were placed in a 100-mL tube fitted with a high-vacuum Teflon stopcock. The flask was evacuated on a high-vacuum line ($2 \times 10^{-5}$ Torr). A mixture of 5 mL of hexane

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and 2 mL of diethyl ether was degassed by five freeze–pump–thaw cycles and was vacuum-transferred with use of a liquid-nitrogen bath to the flask containing 1. The reaction flask was warmed to room temperature, and the gases from the reaction were collected by Toepler pump and determined to be ethane by mass spectrometry (0.046 mmol, 72% (cf. 84% yield of 5)).

**Synthesis and Deuterolysis of $(C_5Me_5)_2SmH(THF)$ (6).** In the glovebox, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (0.035 g, 0.04 mmol) was dissolved in THF in a 100-mL two-neck round-bottom flask equipped with a Teflon stirbar to yield a bright yellow solution. The solvent was removed by rotary evaporation to yield a bright yellow solid. A high-vacuum stopcock adapter and a 10-mL delivery tube that was equipped with a greaseless high-vacuum stopcock and that contained 2 mL of degassed $D_2O$ were attached to the flask, and the apparatus was removed from the glovebox. After the flask was evacuated on a high-vacuum line, $D_2O$ was admitted at room temperature, and gas evolution was observed. The gases were collected by Toepler pump (0.034 mmol, 42%) and determined to be HD by mass spectrometry. The fact that the yield of HD is not closer to the 70–80% usually observed for lanthanide hydride hydrolyses[6,7] is probably due to the continual decomposition of 6 to 7, which happens even in the solid state. The instability of complex 6 in $C_6D_6$ was monitored by $^1H$ NMR spectroscopy. The $\delta$ 1.68 ppm signal in the $^1H$ NMR spectrum of 6 diminishes with time as the resonances for 7 (next section) grow in. The ratio 6:7 changes as follows: 1 h (5:1), 7.5 h (3.3:1), 24 h (1:1), 30 h (1:1.6), 44 h (only 7 present) (time reported is from time of mixing 1 and THF).

**$(C_5Me_5)_2Sm(OCH_2CH_2CH_2CH_3)(THF)$ (7).** In the glovebox, 3 drops of tetrahydrofuran were added to the stirred suspension of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (0.030 g, 0.035 mmol) in 3 mL of hexane. The solution instantly turned a bright yellow. After 3 days, the solvent was removed by rotary evaporation to yield a tacky yellow solid, which was extracted with 5 mL of hexane, yielding a bright yellow solution and a bright yellow solid. The yellow solid was determined by $^1H$ NMR spectroscopy to be $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$.[23] The solvent was removed from the resulting bright yellow hexane solution by rotary evaporation, leaving pure $(C_5Me_5)_2Sm(OCH_2CH_2CH_2CH_3)(THF)$ (0.021 g, 53%) as a yellow oil. $^1H$ NMR (benzene-$d_6$): $\delta$ 5.55 (br s, $OCH_2CH_2CH_2CH_3$, 2 H), 3.98 (br s, $OCH_2CH_2CH_2CH_3$, 2 H), 2.46 (m, $OCH_2CH_2CH_2CH_3$, 2 H), 1.60 (t, $J_{HH}$ = 7.2 Hz, $OCH_2CH_2CH_2CH_3$, 3 H), 1.38 (s, $C_5Me_5$, 30 H), −2.57 (br s, THF, 4 H), −4.09 (br s, THF, 4 H). $^{13}C$ NMR (benzene-$d_6$): $\delta$ 112.44 (s, $C_5Me_5$), 73.26 (t, $J_{CH}$ = 134 Hz, $O(CH_2)_3CH_3$), 59.60 (t, $J_{CH}$ = 148 Hz, THF), 37.54 (t, $J_{CH}$ = 124 Hz, $O(CH_2)_3CH_3$), 19.88 (t, $J_{CH}$ = 124 Hz, $O(CH_2)_3CH_3$), 18.22 (t, $J_{CH}$ = 134 Hz, THF), 16.86 (q, $J_{CH}$ = 124 Hz, $C_5Me_5$), 14.33 (q, $J_{CH}$ = 124 Hz, $O(CH_2)_3CH_3$). Magnetic susceptibility: $\chi_M^{296\,K} = 1412 \times 10^{-6}$ cgsu; $\mu_{eff}^{296\,K} = 1.84\ \mu_B$. IR (KBr): 2960–2840 s, 1440 m, 1380 m, 1125 s, 1100 s, 1030 m, 875 w, 810 w $cm^{-1}$. Anal. Calcd for $SmC_{28}H_{47}O_2$: Sm, 26.56. Found: Sm, 26.4.

**Synthesis of 7 from $(C_5Me_5)_2SmCl(THF)$.** In the glovebox, a mixture of $(C_5Me_5)_2SmCl(THF)$ (0.127 g, 0.24 mmol) and $NaOCH_2CH_2CH_2CH_3$ (0.023 g, 0.24 mmol) was suspended/dissolved in 6 mL of a 5:1 hexane–THF solvent mixture and stirred. After 16 h, the solvent was removed by rotary evaporation and the slightly tacky yellow solid was extracted with 10 mL of hexane. The solvent was removed from the yellow hexane extract to yield a yellow oil (0.127 g, 94%), which was found to be pure $(C_5Me_5)_2Sm(OCH_2CH_2CH_2CH_3)(THF)$ by $^1H$ NMR spectroscopy.

**$[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8).** When $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ was dissolved in THF that had been distilled with use of Dow Corning high-vacuum grease on the ground-glass joints of the solvent still, it quantitatively converted to the bright yellow $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8). Complex 8 was identified by X-ray crystallography (see below). $^1H$ NMR (benzene-$d_6$): $\delta$ 1.89 (s, $OSiMe_2OSiMe_2O$, 12 H), 1.63 (s, $C_5Me_5$, 60 H), −1.89 (br s, THF, 8 H), −2.99 (br s, THF, 8 H). $^{13}C$ NMR (benzene-$d_6$): $\delta$ 114.14 (s, $C_5Me_5$), 60.74 (t, $J_{CH}$ = 148 Hz, THF), 19.02 (t, $J_{CH}$ = 133 Hz, THF), 16.79 (q, $J_{CH}$ = 124 Hz, $C_5Me_5$), 5.38 (q, $J_{CH}$ = 115.6 Hz, $OSiMe_2OSiMe_2O$). Magnetic susceptibility: $\chi_M^{297\,K} = 1395 \times 10^{-6}$ cgsu; $\mu_{eff}^{297\,K} = 1.83\ \mu_B$. IR (KBr): 2970 s, 2920 s, 2870 s, 1450 w, 1385 w, 1250 m, 1000 s, 966 s, 862 m, 842 w, 790 w, 765 m $cm^{-1}$. Anal. Calcd for $Sm_2C_{52}H_{88}O_5Si_2$: Sm, 26.14. Found: Sm, 26.8.

8 can also be made directly from $(Me_2SiO)_3$. In the glovebox, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (0.070 g, 0.083 mmol) and hexamethylcyclotrisiloxane (0.019 g, 0.086 mmol) were dissolved in 10 mL of THF to give a yellow solution. The solution was stirred for 5 min, the solvent was removed by rotary evaporation, and the resulting yellow solid was extracted with 20 mL of hexane to yield a yellow solution. Removal of hexane by rotary evaporation left 8 as a yellow microcrystalline solid (0.082 g, 88%).

**X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2).** A dark brown crystal of approximate dimensions 0.20 × 0.20 × 0.50 mm was mounted in a thin-walled glass capillary under nitrogen and accurately aligned on a Nicolet P3 automated four-circle diffractometer. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of room-temperature (23 °C) intensity data were carried out with use of standard techniques similar to those of Churchill.[24] Final cell parameters are based on a least-squares analysis of 30 reflections in well-separated regions of reciprocal space, all having $24° < 2\theta < 30°$. Details are given in Table I.

A careful survey of a preliminary data set revealed no extinctions nor any diffraction symmetry other than the Friedel condition. The crystal therefore belongs to the triclinic system. Possible space groups are the noncentrosymmetric $P1$ ($C_1^1$; No. 1) or the centrosymmetric $P\bar{1}$ ($C_i^1$; No. 2). With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[25] and was later confirmed as the correct choice by successful solution of the structure.

All 6765 data were corrected for the effects of absorption ($\mu$ = 31.5 $cm^{-1}$) and for Lorentz and polarization factors and reduced to unscaled $|F_o|$ values. A Wilson plot was used to place the data on an approximate absolute scale. Those 4577 data having $|F_o| > 2.0\sigma(|F_o|)$ were considered observed.

All crystallographic calculations were performed by using either our locally modified version of the UCLA Crystallographic Computing Package[26] or the SHELXTL PLUS program set.[27] The structure was solved by direct methods (SHELXTL PLUS); the positions of the two samarium atoms were located from an "$E$ map". The positions of all carbon atoms and the bridging hydride were determined from a series of difference-Fourier syntheses. The positional parameters of the bridging hydride were refined; however, the isotropic thermal parameter was fixed at 0.08 Å$^2$. The quantity minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2|F_o| + 0.0007(|F_o|)^2$. The remaining hydrogen atoms were included by using a riding model with $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. The model converged with $R_F$ = 4.6%, $R_{wF}$ = 5.8%, and GOF = 1.56 for 382 variables refined against 4577 data with $|F_o| > 2.0\sigma(|F_o|)$ ($R_F$ = 3.9%, $R_{wF}$ = 5.3% for those 4029 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier map was devoid of significant features with $\rho$(max) = 1.17 e Å$^{-3}$. Final fractional coordinates for all structures are given in the supplementary material. The analytical scattering factors[28a] for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[28b] were included.

**X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2SmCH_2C_6H_5(THF)$ (4).** The red crystal measuring 0.44 × 0.35 × 0.051 mm was sealed under nitrogen in a glass capillary and mounted on a Syntex $P2_1$ diffractometer. Lattice parameters for a triclinic cell were determined from 15 computer-centered reflections. Relevant crystal and data collection parameters are given in Table I. The space group $P\bar{1}$ was indicated by intensity statistics and was confirmed by the successful solution and refinement of the structure. During data collection, the intensities of three standard reflections measured

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[27] Nicolet Instrument Corp., Madison, WI, 1988.

[28] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; pp 99–101. (b) *Ibid.*, pp 149–150.

**Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2), $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (4), and $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8)**

| | 2 | 4 | 8 |
|---|---|---|---|
| formula | $Sm_2C_{40}H_{60}$ | $SmC_{31}H_{45}O$ | $Sm_2C_{52}H_{88}O_5Si_2$ |
| fw | 841.6 | 584.05 | 1150.28 |
| temp, K | 296 | 298 | 296 |
| cryst syst | triclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ ($C_i^1$; No. 2) | $P\bar{1}$ ($C_i^1$; No. 2) | $C2/c$ ($C_{2h}^6$; No. 15) |
| $a$, Å | 10.791 (2) | 8.525 (6) | 32.372 (14) |
| $b$, Å | 10.950 (2) | 9.639 (4) | 11.317 (1) |
| $c$, Å | 17.166 (4) | 18.687 (7) | 15.277 (5) |
| $\alpha$, deg | 101.57 (2) | 92.03 (3) | |
| $\beta$, deg | 104.35 (2) | 104.09 (4) | 93.18 (3) |
| $\gamma$, deg | 100.11 (2) | 107.01 (4) | |
| $V$, Å$^3$ | 1870.1 (7) | 1414.6 (13) | 5587.9 (31) |
| $Z$ | 2 | 2 | 4 |
| $D_{calcd}$, g/cm$^3$ | 1.50 | 1.37 | 1.37 |
| radiation ($\lambda$ = 0.710730 Å) | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ |
| monochromator | highly oriented graphite | highly oriented graphite | highly oriented graphite |
| data collected | $+h,\pm k,\pm l$ | $+h,\pm k,\pm l$ | $+h,+k,\pm l$ |
| scan type | coupled $\theta$(cryst)–$2\theta$(counter) | coupled $\theta$(cryst)–$2\theta$(counter) | coupled $\theta$(cryst)–$2\theta$(counter) |
| scan width, deg | symmetrical $[2\theta(K\alpha_1) - 1.2]$–$[2\theta(K\alpha_2) + 1.2]$ | symmetrical $[2\theta(K\alpha_1) - 1.2]$–$[2\theta(K\alpha_2) + 1.2]$ | symmetrical $[2\theta(K\alpha_1) - 1.2]$–$[2\theta(K\alpha_2) + 1.2]$ |
| scan speed (in $2\theta$), deg/min | 4.0, fixed | 4.0–16.0, variable | 4.0, fixed |
| $2\theta_{max}$, deg | 45.0 | 45.0 | 45.0 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 31.5 | 21.0 | 21.7 |
| abs cor | semiempirical ($\psi$-scan method) | Gaussian integration | semiempirical ($\psi$-scan method) |
| transmissn factor (max/min) | 0.408/0.334 | 0.95/0.73 | 0.234/0.181 |
| no. of rflns collected | 6765 | 3724 | 3673 |
| no. of obsd rflns | 4577 with $\|F_o\| > 2.0\sigma(\|F_o\|)$ | 3113 with $\|F_o\| > 6.0\sigma(\|F_o\|)$ | 2506 with $\|F_o\| > 3.0\sigma(\|F_o\|)$ |
| no. of variables | 382 | 298 | 276 |
| $R_F$, $R_{wF}$, % | 4.6, 5.8 | 3.5, 4.7 | 3.7, 4.2 |
| goodness of fit | 1.56 | 1.43 | 1.26 |

every 100 reflections showed no decay. Data were corrected for the effects of absorption and for Lorentz and polarization factors. A combination of direct methods (MITHRIL)[29] and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic thermal parameters by use of full-matrix least-squares methods. A final difference map contained no recognizable features; its largest peak was of height 1.14 e Å$^{-3}$ at a distance of 1.07 Å from C(31).

**X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8).** A bright yellow crystal with approximate dimensions 0.13 × 0.31 × 0.33 mm was handled as described above for 2. Final cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space, all having 23° < $2\theta$ < 28°. Details are given in Table I.

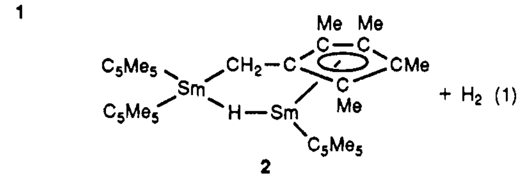
A careful survey of a preliminary data set revealed the systematic extinctions $hkl$ for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The crystal belongs to the monoclinic system; possible space groups are the noncentrosymmetric $Cc$ ($C_s^4$; No. 9) or the centrosymmetric $C2/c$ ($C_{2h}^6$; No. 15). The centrosymmetric space group was later determined to be the correct choice by successful solution of the structure.

All 3673 unique data were corrected for the effects of absorption ($\mu$ = 21.7 cm$^{-1}$) and for Lorentz and polarization factors and reduced to unscaled $|F_o|$ values. The data were placed on an approximate absolute scale by means of a Wilson plot. Those 2506 data having $|F_o| > 3.0\sigma(|F_o|)$ were considered observed and used in subsequent calculations.

The structure was solved by direct methods with the program MITHRIL;[29] the position of the samarium atom was located from an $E$ map. The positions of all remaining independent non-hydrogen atoms were determined from a series of difference-Fourier syntheses. All crystallographic calculations were performed by using either our locally modified version of the UCLA Crystallographic Computing Package[26] or the SHELXTL PLUS program set.[27]. The structure was refined with use of full-matrix least-squares methods (anisotropic thermal parameters were included for all non-hydrogen atoms). The weighting scheme with $p$ = 0.05 has been previously described.[30] Hydrogen atoms were placed in calculated idealized positions with $d$(C–H) = 0.95 Å.[31] At convergence, the discrepancy indices were $R_F$ = 3.7%, $R_{wF}$ = 4.2%, and GOF = 1.26 for 276 variables refined against 2506 data. A final difference-Fourier map showed no significant features. The analytical scattering factors of Cromer and Waber[28a] for the neutral atoms (C, H, O, Si, Sm) were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[28b] were included.

## Results

**Chemistry of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (1) in Alkanes and Benzene. Synthesis and Characterization of $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2).** When $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is dissolved in benzene or alkanes, it converts over a several-day period to a dark brown product identified as $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2) by complete elemental analysis, NMR spectroscopy, and X-ray crystallography (eq 1). 2 is soluble in arenes,



but it is only marginally soluble in alkanes. Hence, saturated solutions of 1 in alkane solvent will deposit 2 as dark brown crystals over time. Toepler pump collection of the gases produced during the conversion of 1 to 2 showed that the amount of $H_2$ produced per $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ dimer was closer to 1 mol than 2 mol which is consistent with the

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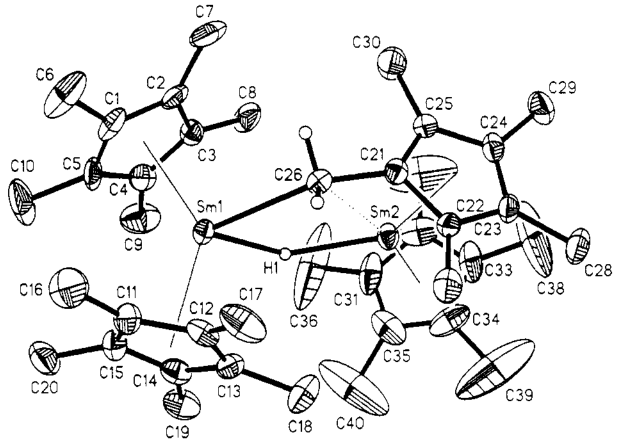

**Figure 1.** ORTEP diagram of $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (**2**) with the probability ellipsoids drawn at the 30% level.

presence of one hydride ligand per molecule of **2**. The IR spectrum of **2** contains an absorption at 1160 cm$^{-1}$, which is in agreement with the assignment of Ln–H absorptions at 1140, 1120, 1135, and 1120 cm$^{-1}$ in the complexes $[(C_5Me_5)_2LnH]_2$, where Ln = Sm,[7] Ce,[14] Nd,[17] and La,[17] respectively. $^{13}C$ NMR data[32] and magnetic susceptibility measurements indicated that the complex was a Sm(III)–Sm(III) complex, which is also consistent with the presence of a hydride ligand. The bridging hydride ligand was also located by X-ray crystallography (see below).

To determine the effect of hydrogen on the conversion of **1** to **2**, a sample of **1** in benzene under nitrogen was compared by NMR spectroscopy to a sample in benzene under hydrogen. After 48 h, 40% conversion of **1** to **2** occurred under nitrogen compared to a 10% conversion under hydrogen. The sample under nitrogen was subsequently placed under 1 atm of $H_2$. After 24 h, the sample contained 90% **1** and 10% **2**; i.e., **2** can be hydrogenated back to **1**. It was also found that the conversion of **1** to **2** proceeds faster in benzene than in cyclohexane, which is consistent with the fact that hydrogen is more soluble in cyclohexane than in benzene.[33]

**Structure of $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2).** The structure of **2**[34] is shown in Figure 1, and selected bond distances and angles are given in Table II. The overall structure of **2** is similar to that of other organosamarium complexes containing two $(C_5Me_5)_2Sm$ units in that the four $C_5Me_5$ ring centroids approximately define a tetrahedron.[7,23,36] The angle between the planes defined by the (C(1)–C(5) ring centroid), Sm(1), and the (C(11)–C(15) ring centroid) and by the (C(21)–C(25) ring centroid), Sm(2), and the (C(31)–C(35) ring centroid) is 90.3°, compared to the 90.0° expected for a purely tetrahedral arrangement. The 90.3° value can also be compared with the analogous angles of 90.0, 93.3, and 92.1° found in the tetrakis(pentamethylcyclopentadienyl) complexes $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$,[23] $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[7] and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$,[36] respectively. On each metal center in **2**, the methyl groups on the pentamethylcyclopentadienyl rings are arranged in a staggered orientation.

**Table II. Selected Interatomic Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2)[a]**

| | | | |
|---|---|---|---|
| Sm(1)···Sm(2) | 3.842 (1) | Sm(1)–H(1) | 2.05 (11) |
| Sm(2)–H(1) | 2.11 (9) | Sm(1)–C(26) | 2.628 (7) |
| Sm(2)···C(26) | 2.855 (10) | Sm(1)–C(1) | 2.744 (12) |
| Sm(1)–C(2) | 2.784 (10) | Sm(1)–C(3) | 2.733 (10) |
| Sm(1)–C(4) | 2.712 (9) | Sm(1)–C(5) | 2.745 (10) |
| Sm(1)–C(11) | 2.755 (11) | Sm(1)–C(12) | 2.732 (10) |
| Sm(1)–C(13) | 2.724 (10) | Sm(1)–C(14) | 2.744 (9) |
| Sm(1)–C(15) | 2.771 (10) | Sm(2)–C(21) | 2.484 (8) |
| Sm(2)–C(22) | 2.655 (8) | Sm(2)–C(23) | 2.877 (7) |
| Sm(2)–C(24) | 2.847 (7) | Sm(2)–C(25) | 2.577 (8) |
| Sm(2)–C(31) | 2.717 (13) | Sm(2)–C(32) | 2.696 (15) |
| Sm(2)–C(33) | 2.737 (14) | Sm(2)–C(34) | 2.694 (16) |
| Sm(2)–C(35) | 2.732 (12) | | |
| Cent(1)–Sm(1)–C(26) | 110.7 | Cent(1)–Sm(1)–H(1) | 106.7 |
| Cent(2)–Sm(1)–C(26) | 109.3 | Cent(2)–Sm(1)–H(1) | 104.6 |
| Cent(1)–Sm(1)–Cent(2) | 135.4 | Cent(3)–Sm(2)···C(26) | 59.9 |
| Cent(3)–Sm(2)–H(1) | 125.0 | Cent(4)–Sm(2)···C(26) | 169.1 |
| Cent(4)–Sm(2)–H(1) | 104.0 | Cent(3)–Sm(2)–Cent(4) | 131.0 |
| C(26)–Sm(1)–H(1) | 70.6 (20) | C(26)···Sm(2)–H(1) | 65.2 (25) |
| Sm(1)–H(1)–Sm(2) | 135.3 (41) | Sm(2)–C(21)–C(26) | 88.5 (5) |
| Sm(1)–C(26)···Sm(2) | 88.9 (2) | Sm(1)–C(26)–C(21) | 149.3 (6) |

[a] Abbreviations: Cent(1) is the centroid of the C(1)–C(5) ring; Cent(2) is the centroid of the C(11)–C(15) ring; Cent(3) is the centroid of the C(21)–C(25) ring; Cent(4) is the centroid of the C(31)–C(35) ring.

The Sm–Sm distance of 3.842 (1) Å in **2** is somewhat shorter than the analogous 3.905 (3) Å Sm–Sm distance in **1**.[7]

The local coordination environments around the samarium atoms are much as expected for trivalent $(C_5Me_5)_2Sm(X)(Y)$ complexes. Both the (ring centroid)–metal–(ring centroid) angles of 135.4° (Sm(1)) and 131.0° (Sm(2)) and the average Sm–C($C_5Me_5$) distances of 2.744 (21) Å (Sm(1)) and 2.715 (20) Å (for C(31)–C(35), Sm(2)) are within the 130–138° and 2.68–2.77 Å ranges found in previous structural determinations of $(C_5Me_5)_2Sm(X)(Y)$ complexes.[32] However, the Sm(2)–C(ring) distances involving the $\eta^1{:}\eta^5\text{-}CH_2C_5Me_4$ ligand vary widely. The Sm(2)–C(21) distance is 2.484 (8) Å, whereas Sm(2)–C(23) and Sm(2)–C(24) are 2.877 (7) and 2.847 (7) Å, respectively. This unsymmetrical coordination to Sm(2) is the only unusual point concerning this ring. The bond distances around the ring are statistically equivalent and are as expected for a $C_5Me_5$ ring.

The Sm(1)–C(26) distance of 2.628 (7) Å is somewhat longer than the Sm–C distances found in $(C_5Me_5)_2SmR(THF)$ complexes: R = methyl,[22] 2.484 (14) Å; R = benzyl, 2.498 (5) Å (see below); R = phenyl,[37] 2.511 (8) Å. Presumably, this slight lengthening is due to the bridging nature of the $CH_2C_5Me_4$ ligand. It is also possible that a weak interaction exists between C(26) and Sm(2). The C(26)–Sm(2) distance of 2.855 (10) Å is clearly longer than previously observed Sm(III)–C(alkyl) distances (including the long 2.77 (2) Å distance in $\{[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^2\text{-}O_2CCCO)(THF)\}_2$),[38] and it is 0.14 Å longer than the Sm(2)–C($C_5Me_5$) average distance of 2.715 (20) Å in **2**. However, ligands have been observed to attach to $(C_5Me_5)_2Ln$ units with lanthanide–C distances that are 0.1–0.2 Å longer than the lanthanide–C($C_5Me_5$) distances within the molecule,[39] e.g., in the attachment of the MeC≡CMe, $(H_2C{=}CH_2)Pt(PPh_3)_2$, and $(C_5H_5)Sm(C_5Me_5)_2$ ligands to the $(C_5Me_5)_2Ln$ units in $(C_5Me_5)_2Yb(MeC{\equiv}CMe)$,[40] $(C_5Me_5)_2Yb(H_2C{=}CH_2)Pt(PPh_3)_2$,[41] and

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[32] Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292–4297.

[33] Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1–9.

[34] We have recently been informed that the X-ray crystal structure of the yttrium analogue of **2** has been determined.[35]

[35] Teuben, J. H. Personal communication. Booij, M. Ph.D. Dissertation, University of Groningen.

[36] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877–6879.

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**Table III. Selected Interatomic Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (4)**

| | | | |
|---|---|---|---|
| Sm(1)-O(1) | 2.498 (5) | Sm(1)-C(10) | 2.754 (7) |
| Sm(1)-C(25) | 2.528 (8) | Sm(1)-C(3) | 2.755 (7) |
| Sm(1)-C(2) | 2.728 (7) | Sm(1)-C(6) | 2.760 (7) |
| Sm(1)-C(7) | 2.730 (7) | Sm(1)-C(4) | 2.768 (7) |
| Sm(1)-C(1) | 2.738 (7) | Sm(1)-C(8) | 2.775 (7) |
| Sm(1)-C(5) | 2.749 (7) | Sm(1)-C(9) | 2.793 (7) |

| | | | |
|---|---|---|---|
| O(1)-Sm(1)-C(25) | 102.4 (2) | Cent(1)-Sm(1)-C(25) | 104.1 |
| Sm(1)-C(25)-C(26) | 111.2 (5) | Cent(2)-Sm(1)-O(1) | 106.5 |
| Cent(1)-Sm(1)-Cent(2) | 133.8 | Cent(2)-Sm(1)-C(25) | 103.0 |
| Cent(1)-Sm(1)-O(1) | 103.2 | | |

$(C_5Me_5)_2Sm^{II}(\mu\text{-}C_5H_5)Sm^{III}(C_5Me_5)_2$,[32] respectively. Moreover, the Sm(2)-C(26) distance is equivalent to two of the Sm(2)-C(ring) distances (C(23) and C(24)).

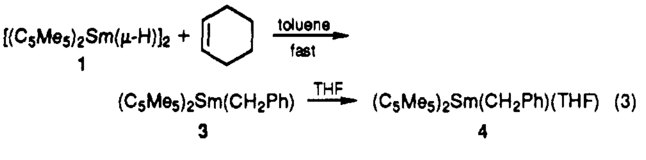
The bridging hydride ligand in **2** was located and is the first hydride bonded to samarium that has been characterized by X-ray crystallography. The Sm(1)-H(1) distance of 2.05 (11) Å is statistically equivalent to the Sm(2)-H(1) distance of 2.11 (9) Å. These distances can be compared to the Y-H(bridge) distances of 2.17 (8) and 2.19 (8) Å in $[(MeC_5H_4)_2Y(\mu\text{-}H)(THF)]_2$[6] and the 2.29 (3) Å Th-H(bridge) distance in $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$,[42] since the ionic radii of nine-coordinate $Y^{3+}$ (1.075 Å), nine-coordinate $Th^{4+}$ (1.09 Å), and eight-coordinate $Sm^{3+}$ (1.079 Å) are all very similar.[43]

**Chemistry of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in Toluene. Synthesis and Characterization of $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (4).** When **1** is dissolved in toluene, it slowly converts to a mixture of complex **2** and $(C_5Me_5)_2Sm(CH_2C_6H_5)$ (**3**) (reaction 2). After 1 week, no

$$\underset{\mathbf{1}}{[(C_5Me_5)_2Sm(\mu\text{-}H)]_2} + C_6H_5CH_3 \rightarrow \mathbf{2} + \underset{\mathbf{3}}{(C_5Me_5)_2Sm(CH_2C_6H_5)} + H_2 \quad (2)$$

more **1** remains and **2** and **3** are present in a 1.4:1 ratio. Complex **3** is an orange-red oil that is extremely soluble in alkane solvents and can readily be separated from the less soluble **2** by alkane extraction. Addition of THF to **3** forms the monosolvate $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (**4**).

Bulk syntheses of complexes **3** and **4** are much better accomplished by reacting **1** with toluene in the presence of alkenes (reaction 3). A rapid reaction occurs in this



(3)

case, and **4** can be obtained in 90% yield in 10 min. This reaction presumably proceeds by formation of an intermediate alkyl complex which is the active reagent that metalates toluene (see below). Complex **3** was characterized by NMR spectroscopy and by its quantitative conversion to **4**.[44] Complex **4** was fully characterized by complexometric metal analysis, NMR and IR spectroscopy, and X-ray crystallography.

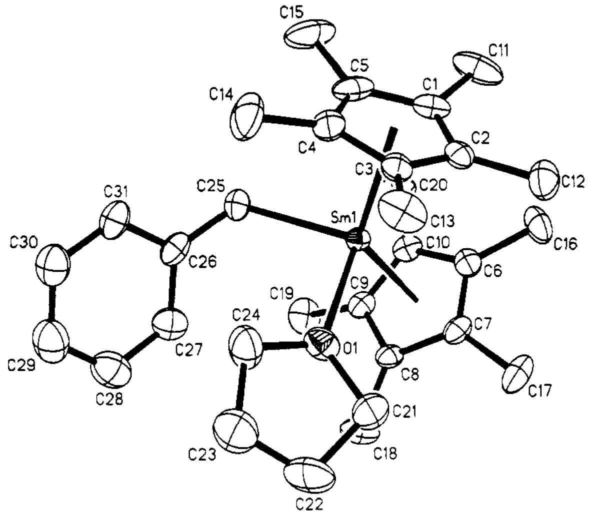


**Figure 2.** ORTEP diagram of $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (**4**) with the probability ellipsoids drawn at the 30% level.

**Structure of $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$ (4).** The structure of **4** is shown in Figure 2, and pertinent bond distances and angles are given in Table III. The overall structure of **4** is typical of $(C_5Me_5)_2Sm(X)(THF)$ complexes (X = Ph,[37] Cl,[21] I,[21] C≡CPh,[46] and Me[22]), with the four ligands describing a distorted tetrahedron about the metal center. Complex **4** has a ($C_5Me_5$ centroid)-Sm-($C_5Me_5$ centroid) angle of 133.8° and an average Sm-C($C_5Me_5$) distance of 2.755 (20) Å, which are in the normal range.[32] The Sm-O(THF) distance of 2.498 (5) Å is also within the 2.44 (2)-2.511 (4) Å range found in the $(C_5Me_5)_2Sm(X)(THF)$ complexes cited above. The Sm(1)-C(25)-C(26) bond angle of 111.2 (5)° is consistent with a simple metal $\eta^1$-benzyl complex and is nearly equal to the 112° value expected from analogy with organic structures.[47] The 70.3° twist of the phenyl ring out of the O(1)-Sm(1)-C(25) plane can be explained through the optimization of steric interactions between the four ligands about the metal center.

**Chemistry of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in Ether Solvents. Synthesis and Characterization of $(C_5Me_5)_2Sm(OEt)(OEt_2)$ (5) Obtained from Diethyl Ether.** When $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is added to diethyl ether, it reacts instantly to form bright yellow, hexane-soluble **5** in 84% yield (eq 4). As **1** is dissolved in the ether, gas evolution

$$\underset{\mathbf{1}}{[(C_5Me_5)_2Sm(\mu\text{-}H)]_2} + 4(CH_3CH_2)_2O \rightarrow 2\underset{\mathbf{5}}{(C_5Me_5)_2Sm(OCH_2CH_3)[O(CH_2CH_3)_2]} + 2CH_3CH_3 \quad (4)$$

is evident. The gas was collected by Toepler pump and found to be ethane by mass spectrometry. The amount of gas recovered was 85% of the ethane expected for an 84% yield of **5** in reaction 4. This reaction appears to be extremely facile, since no evidence for a detectable intermediate such as $(C_5Me_5)_2SmH(OEt_2)$ was observed (see below).

**Synthesis and Characterization of $(C_5Me_5)_2Sm(OCH_2CH_2CH_2CH_3)(THF)$ (7) Obtained from Tetrahydrofuran.** When $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is dissolved in

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(40) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 941-942.

(41) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915-917.

(42) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172-174.

(43) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751-767.

(44) The X-ray crystal structure of the cerium analogue of **3** has recently been determined.[35]

(45) Evans, W. J.; Keyer, R. A.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837-838.

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(47) Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T. *J. Chem. Soc. D* **1971**, 1511-1512 and references therein.

tetrahydrofuran, it instantly forms a bright yellow, hexane-soluble complex, **6**, which exhibits a single $^1H$ NMR resonance in the $C_5Me_5$ region. **6** is not stable in solution, however, and immediately begins to convert to a new product identified as the samarium-*n*-butoxide complex **7** (eq 5).

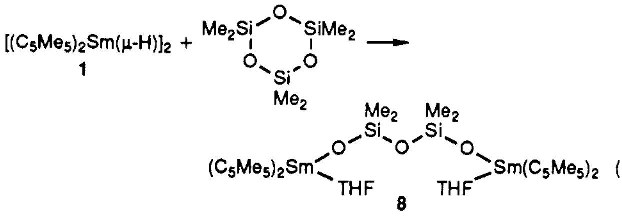
$$\underset{\mathbf{1}}{[(C_5Me_5)_2Sm(\mu\text{-H})]_2} \xrightarrow{THF} \mathbf{6} \xrightarrow{THF} \underset{\mathbf{7}}{2(C_5Me_5)_2Sm(OCH_2CH_2CH_2CH_3)(THF)} \quad (5)$$

The conversion of **6** to **7** is too fast to allow isolation of pure **6**. Deuterolysis of a mixture rich in complex **6** produces HD, which indicates that a hydride ligand is present, and $(C_5Me_5)_2SmH(THF)$ is a likely composition for **6**. The low 42% yield of HD can be attributed to the rapid conversion of **6** to **7**. Samples of **6**, prepared by adding THF to **1** and immediately removing the solvent, convert to pure **7** when left at room temperature for several days. Since the approximately 50% yield of the butoxide **7** formed from THF is lower than the >80% yield of ethoxide **5** formed from diethyl ether (reaction 4), alternative modes of decomposition for **6** must exist. The isolation of significant amounts of the oxide complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[23] from reaction 5 is consistent with the presence of other decomposition routes.

Although the identity of complex **7** was established by complexometric metal analysis and NMR and IR spectroscopy, the independent synthesis of **7** from $(C_5Me_5)_2SmCl(THF)$[21] and NaOBu was carried out to further verify its composition (eq 6). In all cases, **7** is isolated as an oily product.

$$(C_5Me_5)_2SmCl(THF) + NaOBu \rightarrow \underset{\mathbf{7}}{(C_5Me_5)_2Sm(OBu)(THF)} + NaCl \quad (6)$$

**Synthesis and Characterization of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8).** Initial studies of the reactivity of **1** with THF resulted in the exclusive formation of a bright yellow hexane-soluble compound, **8**. The production of **8** was traced to impurities in the THF, which had been distilled from an apparatus in which dimethylsilicone grease was used on the ground-glass joints. Indeed, gas chromatographic–mass spectral analysis of the THF revealed the presence of dimethylsilicones, such as octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane. Attempts to synthesize **8** with use of dimethylsilicone grease as a reagent were unsuccessful. Complex **1** reacts with a variety of dimethylsilicone reagents, including decamethylcyclopentasiloxane, decamethyltetrasiloxane, and octamethylcyclotetrasiloxane in both alkane and THF solvents, but none of these reactions generate **8**. However, **8** can be generated by the reaction of **1** with hexamethylcyclotrisiloxane in THF (eq 7). Complex **8** has been identified by NMR and IR spectroscopy and by X-ray crystallography.



(7)

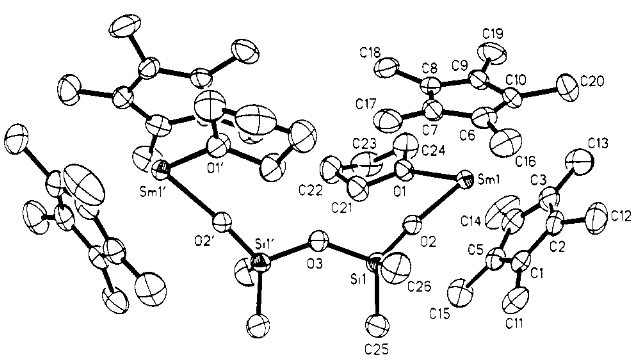


**Figure 3.** ORTEP diagram of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8) with the probability ellipsoids drawn at the 30% level. The halves of the molecule are related by the $C_2$ rotation axis that passes through O(3).

**Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8)[a]**

| | | | |
|---|---|---|---|
| Sm(1)–C(1) | 2.725 (7) | Sm(1)–C(9) | 2.785 (8) |
| Sm(1)–C(2) | 2.755 (7) | Sm(1)–C(10) | 2.765 (7) |
| Sm(1)–C(3) | 2.795 (8) | Sm(1)–O(1) | 2.465 (5) |
| Sm(1)–C(4) | 2.775 (8) | Sm(1)–O(2) | 2.157 (5) |
| Sm(1)–C(5) | 2.727 (7) | Si(1)–C(25) | 1.868 (9) |
| Sm(1)–C(6) | 2.697 (7) | Si(1)–C(26) | 1.852 (9) |
| Sm(1)–C(7) | 2.730 (8) | Si(1)–O(2) | 1.601 (5) |
| Sm(1)–C(8) | 2.785 (8) | Si(1)–O(3) | 1.646 (3) |
| O(1)–Sm(1)–O(2) | 85.9 (2) | O(2)–Si(1)–C(26) | 110.5 (4) |
| O(1)–Sm(1)–Cent(1) | 107.1 | O(3)–Si(1)–C(25) | 108.2 (4) |
| O(1)–Sm(1)–Cent(2) | 104.3 | O(3)–Si(1)–C(26) | 106.7 (3) |
| O(2)–Sm(1)–Cent(1) | 108.4 | C(25)–Si(1)–C(26) | 110.1 (5) |
| O(2)–Sm(1)–Cent(2) | 107.2 | Sm(1)–C(21)–O(1) | 119.7 (4) |
| Cent(1)–Sm(1)–Cent(2) | 133.5 | Sm(1)–C(24)–O(1) | 131.2 (5) |
| O(2)–Si(1)–O(3) | 110.5 (3) | Sm(1)–O(2)–Si(1) | 173.6 (3) |
| O(2)–Si(1)–C(25) | 110.9 (4) | Si(1)–O(3)–Si(1′) | 139.4 (5) |

[a] Abbreviations: Cent(1) is the centroid of the C(1)–C(5) ring; Cent(2) is the centroid of the C(6)–C(10) ring.

**Structure of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (8).** The structure of **8** is shown in Figure 3, and important bond distance and angle data are given in Table IV. **8** contains two $(C_5Me_5)_2Sm(THF)$ moieties bridged by a $-OSiMe_2OSiMe_2O-$ fragment. The two sides of the molecule are related by a crystallographic 2-fold axis, which goes through O(3). As with complex **4**, the four ligands around the samarium atoms describe a distorted tetrahedron. The (ring centroid)–Sm–(ring centroid) angle of 133.5°, the Sm–O(1)(THF) distance of 2.465 (5) Å, and the average Sm–C($C_5Me_5$) distance of 2.754 (32) Å are all normal. The Sm–O(2) distance of 2.157 (5) Å is equivalent to the Sm–O distances in $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$[48] (2.13 (1) Å) and *cis*-$[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$[7b] (2.147 (10) and 2.179 (10) Å). The 173.6 (3)° Sm–O(2)–Si(1) angle is equivalent to the 172.3 (13)° Sm–O–C(phenoxide) angle in $(C_5Me_5)_2Sm(OC_6HMe_4)$.[48] The coordination environment about the silicon atoms has the normal tetrahedral arrangement.

## Discussion

The reactivity of $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$ (**1**) will be discussed in comparison with that of other bis(pentamethylcyclopentadienyl)metal hydride and alkyl complexes of trivalent lanthanides and early transition metals. Similarities in reactivity were expected, and indeed, σ-bond metathesis reaction pathways,[49] which are commonly found for this class, can be used to explain much of the reactivity of **1**. It was of primary interest in this study to identify

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the specific differences in the reactivity of 1 and to examine possible correlations of these differences with factors such as the degree of steric saturation and the availability of terminal or bridging ligands. Accordingly, this section begins with a discussion of the structure of 1.

Although the bimetallic structure of 1 was established by X-ray crystallography, the positions of the hydrogen atoms were not located.[7a] Steric considerations and a subsequent structural determination[36] suggest reasonable bridging positions for these atoms as follows. The tetrahedral arrangement of the four $C_5Me_5$ ring centroids in 1 required that, if the hydrogen atoms were in either of the two perpendicular planes which bisect the (ring centroid)–Sm–(ring centroid) angles of each $(C_5Me_5)_2Sm$ unit (as is common for transition-metal bent metallocene complexes[18]), they would point directly at the $C_5Me_5$ rings of the other $(C_5Me_5)_2Sm$ unit. Such unfavorable steric interaction could be avoided if the hydrogen atoms were located in a plane between the above two planes. This arrangement was found by neutron diffraction for the bridging hydrogen atoms in $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$,[42] which also has a tetrahedral arrangement of $C_5Me_5$ rings and which also contains a metal of similar radius (see above). $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ is another molecule similar to 1 in that it has a tetrahedral disposition of $C_5Me_5$ groups and two atoms bridging the $(C_5Me_5)_2Sm$ units.[36] In this case, the bridging atoms were located and the $Sm_2N_2$ plane was found to lie between the two (centroid)–Sm–(centroid) planes. It is likely that the $Sm_2H_2$ plane in 1 is similarly located between the two (centroid)–Sm–(centroid) planes; i.e., a simple bridged structure is sterically reasonable for 1.

**Alkane and Benzene Reactivity.** Complex 1 shows no appreciable net reactivity with alkanes and benzene, and in this regard, it is more stable than many other complexes in this class. For example, $[(C_5Me_5)_2ScH]_n$[49] (9) decomposes in alkanes to unidentified products and it metalates benzene. The methyl complexes $(C_5Me_5)_2Ln(\mu\text{-}Me)LnMe(C_5Me_5)_2$[15,16,50] (10; Ln = Lu, Y), $(C_5Me_5)_2SmMe(THF)$[22] (11), and $(C_5Me_5)_2ScMe$[49] (12) readily metalate both alkanes and benzene. $(C_5Me_5)_2Lu(\mu\text{-}H)LuH(C_5Me_5)_2$[15,16] (13) metalates benzene to form the phenyl derivative $(C_5Me_5)_2LuPh$, but this metalation is reversible and the hydride complex is said to be thermodynamically favored compared to the metalation products. The solvent metalation chemistry of 9 is also reversible, and this complex does not give metalation products under 4 atm of hydrogen even at 150 °C in benzene.[49] Exchange of hydrogen for deuterium between $D_2$ or $C_6D_6$ and $Si(CH_3)_4$, $H_2C(SiMe_3)_2$, or the $C_5Me_5$ rings is common for the $[(C_5Me_5)_2LnH]_2$ hydrides and has been reported for Ln = La,[17] Ce,[14,17] Nd,[17] Y,[12,13] and Lu,[15-17] as well as for 1.[7a,17] The lower reactivity of 1 in the formation of alkyl and phenyl complexes from alkanes and benzene compared to that of 10–13 is consistent with the fact that 10–13 have terminal ligands and the hydride ligands in 1 are bridging.

Although 1 does not readily form alkyl or phenyl complexes from alkanes and benzene, it does undergo an internal metalation reaction in these solvents to form the complex $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ (2) (eq 1). This complex contains a bridging $\eta^1{:}\eta^5\text{-}C_5Me_4CH_2$ ligand of the type found in the titanium complex $(C_5Me_5)_2Ti(\mu\text{-}O)_2(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ti(C_5Me_5)$[51a] and in the iridium complex $[(C_5Me_5)(CO)Ir(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ir(CO)_2]^+$.[51b] An yttrium analogue of 2, i.e., the complex $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$ (14), has been reported to form from $[(C_5Me_5)_2YH]_2$ (15) at 100 °C in octane or benzene.[34,52]

Internal metalation of $C_5Me_5$ rings in early-transition-metal complexes of general formula $(C_5Me_5)_2MZ_{1,2}$ (Z = H, R) has been discussed for many years, and schemes involving σ-bond metathesis reaction pathways have been described.[49,50,53-58] In most of these cases, a "tucked-in" monometallic complex $(C_5Me_5)\overline{M(C_5Me_4C}H_2)$ was considered. A similar monometallic tuck-in structure was postulated in $(C_5Me_5)_2LuZ$ (Z = alkyl, hydride) chemistry.[16,50,57] The demonstrated accessibility of the bimetallic "tuck-over" complexes 2 and 14 suggests that this bimetallic form may be generally available across the lanthanide series when internal metalation occurs.

The relatively low reactivity of 1 with alkanes and benzene, coupled with the fact that the formation of 2 is rather slow, means that 1 can be used for most reactions in alkane or benzene solvents without the occurrence of complicating side reactions.

**Toluene.** In toluene, metalation of the solvent is observed as well as self-metalation of 1 (eq 2) and, hence, mixtures of 2 and the benzyl complex $(C_5Me_5)_2Sm(CH_2C_6H_5)$ are formed in this solvent. The higher metalation reactivity of toluene compared to that of benzene was also observed for 11. In contrast, 9 and 12 show higher reactivity with benzene than with the methyl group of toluene.[59]

The rapid formation of $(C_5Me_5)_2Sm(CH_2Ph)$ from toluene and 1 in the presence of an alkene is consistent with the sequence in reaction 8. The first part of this sequence,

$$\tfrac{1}{2}[(C_5Me_5)_2SmH]_2 + RCH{=}CHR \rightarrow \\ (C_5Me_5)_2Sm(CHRCH_2R) \xrightarrow{C_6H_5CH_3} \\ (C_5Me_5)_2Sm(CH_2C_6H_5) + RCH_2CH_2R \quad (8)$$

the addition of Ln–H bond to alkenes, is well-established.[5e,f,17] Since $(C_5Me_5)_2SmMe(THF)$ metalates toluene, the unsolvated alkyl complex $(C_5Me_5)_2Sm(CHRCH_2R)$ would be expected to do the same even more rapidly. Obviously, toluene is a less desirable arene reaction solvent for 1 than benzene. However, toluene has been reported as one of the solvents used for catalytic hydrogenations of alkenes with the $[(C_5Me_5)_2LnH]_2$ complexes (Ln = La, Nd, Sm, Lu).[17c] In these cases, the hydrogen in the system may convert the benzyl complexes present in solution back to the hydride complex.

**Ether Solvents.** The reaction of 1 with $Et_2O$ to form $(C_5Me_5)_2Sm(OEt)(OEt_2)$ has precedence in the reaction of 13 with $Et_2O$ to form $(C_5Me_5)_2Lu(OEt)$ and ethane.[15,60] In the lutetium case, an ether adduct was cited to exist below

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(50) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493.

(51) (a) Bottomley, F.; Egharevba, G. O.; Lin, I. J. B.; White, P. S. *Organometallics* **1985**, *4*, 550–553. (b) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1424–1426.

(52) den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682–683.

(53) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238.

(54) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095.

(55) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136–148.

(56) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

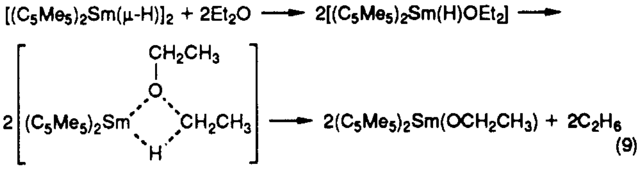
(57) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–6473.

(58) Pattiasina, J. W.; Hissink, C. E.; de Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7758–7759.

(59) Cf. the bulky alkyl complexes $(C_5Me_5)_2LnCH(SiMe_3)_2$ react with toluene to form benzyl products exclusively for Ln = La and Ce,[35] whereas for Ln = Y, a mixture of the benzyl product and ortho-, meta-, and para-metalated $C_6H_4CH_3$ products is formed.[12c]

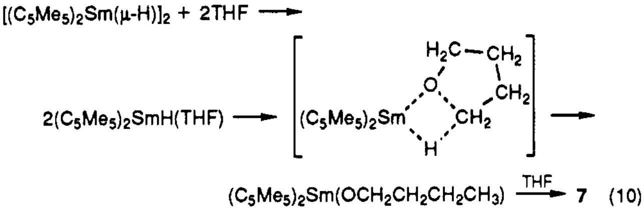
(60) For a review of alkali-metal ether cleavage reactions, see: Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972–989.

−30 °C and deuterium labeling studies were consistent with a $\sigma$-bond metathesis sequence. A similar sequence is likely in the case of 1 (eq 9).



(9)

Complex 1 also reacts with THF, but in this case, an intermediate with properties consistent with the formula $(C_5Me_5)_2SmH(THF)$ can be observed. A $\sigma$-bond metathesis scheme[49] can also be used to explain the formation of $(C_5Me_5)_2Sm(OBu)(THF)$ (7) (eq 10).



(10)

The instability of the THF adduct is not unexpected. $(C_5Me_5)_2ScH(THF)$ is unstable at room temperature over several days, and $(C_5Me_5)_2ScD(THF)$ incorporates deuterium into the $\alpha$-positions of THF.[49] $(C_5Me_5)_2YH(THF)$ has been isolated from $[(C_5Me_5)_2YH]_2$, but only in 28% yield.[12c] The ring-opening reaction observed in eq 10 is probably a common mode of decomposition for molecules of this type in THF, although, to our knowledge, this is the first time the products have been fully defined.[61] This type of reactivity may explain why the rate of $\{[C_5Me_4(SiMe_2)C_5Me_4]NdH\}_2$-catalyzed cyclohexene hydrogenation was "immeasurably slow" in THF.[17c]

**Siloxane Reactions.** The reaction of 1 with siloxanes to form 8 has no precedent in the reported chemistry of bis(cyclopentadienyl) lanthanide and early-transition-metal alkyl and hydride complexes to our knowledge. Recently, TlOEt has been used to convert poly(dimethylsiloxane) to the thallium ladder polymer complex $\{[Tl_2(OSiMe_2)_2O]_2\}_n$,[62] which contains the $\mu$-$OSiMe_2OSiMe_2O$ unit found in 8. Nucleophilic attack by $OEt^-$ at silicon was offered as a possible route for this reaction.[63] Similar pathways can be envisaged for 1 and would be aided by formation of strong Sm–O bonds. The high reactivity of 1 with THF solutions containing dimethylsiloxane compounds is noteworthy. Obviously, grease- and silicone-free reaction systems are always most desirable, but for reactions involving 1 and complexes of similar reactivity and oxophilicity, these are essential.

## Conclusion

$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ has an extensive reactivity with common solvents, which provides new pathways to organosamarium(III) complexes. Although 1 exhibits high reactivity parallel to that found with scandium, yttrium, cerium, and lutetium alkyl and hydride complexes, the somewhat lower rate of reactivity with alkanes and benzene allows it to be used for reactions with other substrates in these solvents. The numerous subtle differences in the reactivity of 1 compared to that of other similar lanthanide and early-transition-metal hydrides emphasizes the importance of the *specific* metal–ligand combination in determining the reactivity of a Ln–H bond.

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**Registry No.** 1, 84751-30-4; 2, 130013-51-3; 3, 130013-52-4; 4, 115731-51-6; 5, 130013-53-5; 6, 130013-54-6; 7, 130013-55-7; 8, 130013-56-8; $(Me_2SiO)_3$, 541-05-9.

**Supplementary Material Available:** Tables of crystal data, final fractional coordinates, hydrogen atom coordinates, bond distances and angles, and thermal parameters for 2, 4, and 8 (21 pages); tables of observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

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[61] $[(C_5Me_5)_2CeH]_2$ reacts with THF to form $[(C_5Me_5)_2Ce(THF)]_2(\mu\text{-}O)$ as one of the products.[35]

[62] Harvey, S.; Lappert, M. F.; Raston, C. L.; Skelton, B. W.; Srivastava, G.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1216–1217.

[63] For a review, see: Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1981.