

Synthesis of Sm–SiH₃ Complexes via σ -Bond Metathesis of the Si–C Bond of Phenylsilane

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Reaction of PhSiH₃ with the samarium complexes Cp^{*}₂SmCH(SiMe₃)₂ (**1**) and [Cp^{*}₂Sm(μ -H)]₂ (**8**) (Cp^{*} = C₅Me₅) leads to redistribution at silicon, yielding benzene, silane, Ph₂SiH₂, Ph₃SiH, and dehydrocoupling products. Cleavage of the Si–C bond of PhSiH₃ is accompanied by formation of the lanthanide hydrosilyl complex [Cp^{*}₂SmSiH₃]₃ (**2**). Complex **2** activates the S–O bond of dimethyl sulfoxide (DMSO) to form the bridged species Cp^{*}₂Sm(DMSO)OSiH₂OSm(DMSO)Cp^{*}₂ (**3**). The hard Lewis bases Ph₃PO and HMPA (HMPA = (Me₂N)₃PO) react with **2** to produce the base adducts Cp^{*}₂SmSiH₃(OPPh₃) (**4**) and Cp^{*}₂SmSiH₃(HMPA) (**5**), respectively. Complex **5** thermally decomposes, although not cleanly, to produce Cp^{*}₂Sm[OP(NMe₂)₂](HMPA) (**6**) in low yield. Compound **4** thermally decomposes via liberation of silane to produce Cp^{*}₂SmC₆H₅P(O)Ph₂ (**7**). In toluene solution, **4** acts as a source of SiH₃[–] in reactions with MeI and benzophenone, producing Cp^{*}₂SmI(OPPh₃) (**9**) and Cp^{*}₂SmOCPh₂(SiH₃) (**10**), respectively. The high reactivity of **8** toward a stable Si–C bond is discussed in terms of possible mechanisms for this σ -bond metathesis.

Introduction

Organometallic f-element chemistry is associated with reactive metal–carbon and metal–hydrogen bonds, which are particularly active in σ -bond metathesis.^{1,2} Given our interest in reactive d⁰ metal–silicon bonds, we have been examining the chemistry of lanthanide–silicon bonds in (for example) the dehydrocoupling of hydrosilanes to polysilanes.³ In a previous report, we described the reaction of Cp^{*}₂SmCH(SiMe₃)₂ (**1**) (Cp^{*} = C₅Me₅) with PhSiH₃ in benzene, which resulted in both dehydrocoupling of the silane and redistribution at silicon to produce Ph₂SiH₂, Ph₃SiH, and a mixture of trisamarium clusters [Cp^{*}₂SmSiH_x]₃.^{3a} These results are consistent with our previous suggestion that the low activity of Cp^{*}₂LnR lanthanide complexes as catalysts for phenylsilane dehydrocoupling may be attributed to competing redistribution at silicon.^{3a,b,e}

Despite being ineffective at catalyzing dehydrocoupling, **1** appears to be remarkably active in σ -bond metathesis reactions, since it mediates the formation and cleavage of relatively strong Si–C bonds in the redistribution process. To learn more about the latter reactivity, we have examined the interaction of **1** with PhSiH₃ in more detail. Here we report the isolation of a well-defined samarium-containing product from this reaction, [Cp^{*}₂SmSiH₃]₃ (**2**). This compound is a rare example of a lanthanide silyl complex and represents the first example of an f-element–SiH₃ derivative. For comparison, the known early metal–SiH₃ complexes consist of the spectroscopically characterized CpCp*Hf(SiH₃)Cl⁴ (d⁰) and the structurally characterized [Cp₂Ti(μ -HSiH₂)₂]₂⁵ (d¹).

Experimental Section

General Considerations. Unless otherwise specified, all manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk techniques or an inert atmosphere drybox. Dry, oxygen-free solvents were employed throughout. Olefin-free pentane was obtained by treatment with concentrated H₂SO₄, then 0.5 N KMnO₄ in 3 M H₂SO₄, followed by NaHCO₃, and finally MgSO₄. Thiophene-free benzene and toluene were obtained by pretreating the solvents with concentrated H₂SO₄, followed by Na₂CO₃ and CaCl₂. Pentane, benzene, and toluene were distilled from sodium/benzophenone and stored under nitrogen prior to use, whereas benzene-*d*₆ and toluene-*d*₈ were vacuum distilled from Na/K alloy. Pyridine was distilled from Na and stored under nitrogen. Ph₃PO was purchased from Aldrich Chemical Co. and recrystallized from toluene. (Me₂N)₃PO (HMPA) and dimethyl

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sulfoxide (DMSO) were distilled from CaH_2 . $\text{Cp}^*_2\text{SmCH}(\text{SiMe}_3)_2$ and $[\text{Cp}^*_2\text{Sm}(\mu\text{-H})_2]$ were prepared by literature methods.⁶ NMR spectra were recorded on Bruker AMX-300, AMX-400, or DRX-500 spectrometers at ambient temperature unless otherwise noted. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. Infrared spectra were recorded on a Mattson Infinity 60 FT IR instrument. Samples were prepared as KBr pellets, and data are reported in units of cm^{-1} .

$[\text{Cp}^*_2\text{SmSiH}_3]_3$ (2). A Schlenk tube equipped with a magnetic stirbar was charged with $\text{Cp}^*_2\text{SmCH}(\text{SiMe}_3)_2$ (**1**) (0.30 g, 0.52 mmol) and 10 mL of pentane. Another Schlenk tube was charged with PhSiH_3 (0.56 g, 5.20 mmol). The orange-red solution of **1** was stirred while PhSiH_3 was added via cannula. After a variable induction period of 5–30 min, an orange solid started to deposit. Evolution of H_2 (confirmed by ^1H NMR spectroscopy for reaction in benzene- d_6) was evident, and the color of the solution changed from orange-red to deep red. The deep red solution was removed by filtration, and the orange solid **2** was washed with ca. 5 mL of pentane and dried under vacuum. Yields varied between 35 and 56% (0.08–0.14 g, 0.18–0.29 mmol). Mp > 260 °C (210 °C dec). IR: 2964 (s), 2908 (s), 2855 (s), 2144 (w, br), 1992 (m, br, ν_{SiH}), 1884 (m, br, ν_{SiH}), 1437 (s), 1377 (m, sh), 985 (s), 895 (s). ^1H NMR (300 MHz): δ 1.01 (s, 30 H, Cp*). Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{SiSm}$: C, 53.15; H, 7.36. Found: C, 53.30; H, 7.35.

$\text{Cp}^*_2\text{Sm}(\text{DMSO})\text{OSiH}_2\text{OSm}(\text{DMSO})\text{Cp}^*_2$ (3). To a stirred toluene suspension of **2** (0.13 g, 0.30 mmol) in a Schlenk tube was added DMSO (43 μL , 0.60 mmol) via syringe at room temperature. Solid **2** immediately dissolved and afforded a yellow solution, which after further stirring for 2 h was filtered, concentrated to ca. 5 mL, and cooled to –35 °C. Crystalline **3** was obtained in this manner in 53% yield (0.08 g, 0.08 mmol). Mp > 260 °C (224 °C dec). IR: 2963 (s), 2909 (s), 2855 (s), 2080 (m, br, ν_{SiH}), 1658 (w), 1435 (s), 1314 (m, sh), 1261 (m), 1115 (m), 1018 (m), 960 (s), 905 (s), 869 (m, sh), 803 (w), 738 (w). ^1H NMR (300 MHz): δ 0.93 (s, 12 H, DMSO), 1.48 (s, 60 H, Cp*), 2.47 (s, 2 H, SiH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ 17.22 (C_5Me_5), 39.30 (DMSO), 125.87 (C_5Me_5). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz): δ –45.83. Anal. Calcd for $\text{C}_{44}\text{H}_{74}\text{O}_2\text{S}_2\text{SiSm}_2$: C, 49.85; H, 7.04. Found: C, 49.52; H, 7.02.

$\text{Cp}^*_2\text{SmSiH}_3(\text{OPPh}_3)$ (4). A Schlenk tube equipped with magnetic stirbar was charged with **2** (0.08 g, 0.14 mmol) and 5 mL of toluene. Another Schlenk tube was charged with Ph_3PO (0.04 g, 0.15 mmol) and 5 mL of toluene, and both solutions were cooled to –80 °C. The solution of Ph_3PO was then added with a cannula to the stirred suspension of **2** to produce a yellow solution upon warming to room temperature. After further stirring for 2 h the solution was filtered and concentrated to a volume of 5 mL. Yellow microcrystals of **4** were isolated in 81% yield (0.10 g, 0.11 mmol) after cooling to –35 °C. Mp > 260 °C (185 °C dec). IR: 3056 (w, sh), 2965 (m), 2899 (s), 2853 (s), 2072 (m, sh, ν_{SiH}), 1994 (m, sh, ν_{SiH}), 1977 (s, sh, ν_{SiH}), 1438 (s, sh), 1150 (s), 1120 (s), 1087 (s), 992 (s, br), 956 (m), 868 (m), 725 (s), 693 (m, sh), 539 (s). ^1H NMR (300 MHz): δ 1.57 (s, 30 H, Cp*), 6.37 (m, 6 H, *o*-Ph), 6.82 (t, 6 H, *m*-Ph), 6.96 (t, 3 H, *p*-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ 16.49 (C_5Me_5), 114.42 (C_5Me_5), 128.24 (d, J_{PC} = 11.3 Hz, –Ph), 131.79 (d, J_{PC} = 10.8 Hz, –Ph), 132.73 (s, –Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz): δ 26.96. Anal. Calcd for $\text{C}_{38}\text{H}_{48}\text{OPSiSm}$: C, 62.50; H, 6.62. Found: C, 63.01; H, 6.94.

$\text{Cp}^*_2\text{SmSiH}_3(\text{HMPA})$ (5). To a vigorously stirred and cold (–80 °C) suspension of **2** (0.13 g, 0.30 mmol) in 5 mL of toluene was added HMPA (0.05 mL, 0.30 mmol) via syringe. The mixture was stirred for 2 h while warming to room temperature. The resulting yellow solution was then filtered and concentrated to approximately 5 mL. Cooling to –35 °C yielded

69% of yellow, microcrystalline **5** (0.13 g, 0.21 mmol). Mp > 260 °C (171–174 °C dec). IR: 2902 (s), 2858 (s), 2819 (m), 2723 (w), 2003 (m, sh, ν_{SiH}), 1986 (m, sh, ν_{SiH}), 1487 (m), 1450 (m), 1376 (w), 1304 (s), 1193 (s), 1134 (s), 1114 (s), 1071 (w, sh), 993 (s), 955 (m), 873 (m), 798 (w), 760 (m, sh), 740 (m), 466 (m, sh). ^1H NMR (500 MHz): δ 1.41 (d, J_{PH} = 13.5 Hz, 18 H, NMe_2), 1.68 (s, 30 H, Cp*). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ 17.12 (C_5Me_5), 36.84 (NMe_2), 114.77 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz): δ 13.18. Anal. Calcd for $\text{C}_{26}\text{H}_{51}\text{N}_3\text{OPSiSm}$: C, 49.48; H, 8.14; N, 6.66; P, 4.91. Found: C, 49.33; H, 8.34; N, 7.32; P, 4.75.

$\text{Cp}^*_2\text{Sm}[\text{OP}(\text{NMe}_2)_2](\text{HMPA})$ (6). A toluene solution of **5** (0.12 g, 0.19 mmol) and HMPA (33 μL , 0.19 mmol) was stirred at ambient temperature for a period of 2 weeks. Removal of volatile materials under vacuum was followed by extraction with ca. 15 mL of pentane. The yellow pentane solution was cannula filtered, concentrated to 5 mL, and cooled to –35 °C. Low yields of isolated yellow microcrystals were always obtained, ranging from 7 to 16% (10–23 mg, 0.01–0.03 mmol). ^1H NMR (300 MHz): δ 0.76 (s, 18 H, HMPA), 1.57 (s, 30 H, Cp*), 3.10 (d, J_{PH} = 7.92 Hz, 12 H, NMe_2).

$\text{Cp}^*_2\text{SmC}_6\text{H}_4(\text{O})\text{Ph}_2$ (7). A Schlenk tube was charged with $[\text{Cp}^*_2\text{Sm}(\mu\text{-H})_2]$ (**8**) (0.15 g, 0.35 mmol), Ph_3PO (0.10 g, 0.35 mmol), and 10 mL of toluene. A burgundy solution was obtained after stirring overnight at room temperature. The solution was cannula filtered and concentrated. Compound **7** was isolated by crystallization from ca. 5 mL of toluene at –35 °C, but the burgundy crystals contained toluene and other unidentified impurities. Analytically pure compound was obtained by washing the crystals with ca. 5 mL of pentane. In this manner, yellow, microcrystalline **7** was obtained in 58% yield (0.14 g, 0.20 mmol). Mp: 204–208 °C. IR: 3055 (w), 2960 (m), 2906 (s), 2854 (s), 2721 (w), 1591 (w, sh), 1485 (w, sh), 1437 (s), 1378 (w), 1189 (m), 1154 (m), 1119 (s), 1081 (m), 1058 (m), 1026 (w, sh), 999 (w, sh), 749 (m), 721 (s), 695 (s), 540 (s), 445 (w, sh). For the following NMR data, the positions of the protons in the metalated phenyl ring are labeled *a* through *d* starting from samarium. ^1H NMR (300 MHz): δ –4.41 (s, 1 H, *a*- C_6H_4), 1.25 (s, 30 H, Cp*), 5.67 (m, 1 H, *b*- C_6H_4), 7.21 (m, 4 H, *m*-Ph), 7.30 (m, 2 H, *p*-Ph), 7.56 (m, 1 H, *c*- C_6H_4), 7.95 (m, 4 H, *o*-Ph), 9.01 (t, 1 H, *d*- C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ 16.96 (C_5Me_5), 116.49 (C_5Me_5), 122.36 (C_6H_4), 126.76 (d, J_{PC} = 13.9 Hz, *ipso*-Ph), 129.21 (d, J_{PC} = 11.3 Hz, *o*-Ph), 132.77 (*p*-Ph), 133.47 (d, J_{PC} = 8.8 Hz, *m*-Ph), 135.55 (C_6H_4), 136.33 (C_6H_4), 139.01 (d, J_{PC} = 22.7 Hz, *ipso*- C_6H_4), 151.06 (C_6H_4), 152.01 (C_6H_4). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz): δ 52.08. Anal. Calcd for $\text{C}_{38}\text{H}_{44}\text{OPSm}$: C, 65.38; H, 6.35. Found: C, 65.36; H, 6.10.

$\text{Cp}^*_2\text{SmI}(\text{OPPh}_3)$ (9). A Schlenk tube was charged with **4** (0.15 g, 0.14 mmol), 5 mL of toluene, and a magnetic stirbar. To the stirred yellow solution was added MeI (14 μL , 0.14 mmol) via syringe at room temperature. After further stirring for 2 h, the volatile materials were evaporated under vacuum. The resulting yellow-orange oil was triturated with 10 mL of pentane. The yellow-orange microcrystals were then washed further with 5 mL of pentane and dried in vacuo. The isolated yield of **9** was 71% (0.13 g, 0.10 mmol). Mp > 260 °C. IR: 3058 (w), 2963 (m), 2900 (s), 2854 (s), 2722 (w), 2107 (w, br), 1438 (s), 1262 (w, sh), 1143 (s), 1120 (s), 1085 (s), 1025 (m), 998 (m), 803 (m), 751 (m, sh), 725 (s, sh), 694 (s, sh), 540 (s). ^1H NMR (500 MHz): δ 1.35 (s, 30 H, Cp*), 6.91 (m, 12 H, *o*, *m*-Ph), 7.04 (t, 3 H, *p*-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ 19.08 (C_5Me_5), 116.27 (C_5Me_5), 128.90 (broad, *ipso*-Ph), 129.08 (d, J_{PC} = 11.3 Hz, *o*-Ph), 133.46 (d, J_{PC} = 8.8 Hz, *m*-Ph), 133.60 (*p*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz): δ 25.85. Anal. Calcd for $\text{C}_{38}\text{H}_{45}\text{IOPSm}$: C, 55.25; H, 5.49. Found: C, 55.07; H, 5.75.

$\text{Cp}^*_2\text{SmOCPh}_2(\text{SiH}_3)$ (10). A Schlenk tube equipped with stirbar was charged with **2** (0.10 g, 0.24 mmol) and ca. 5 mL of toluene. In another Schlenk tube, benzophenone (0.04 g, 0.24 mmol) was dissolved in ca. 5 mL of toluene, and both solutions

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Table 1. Summary of Crystallographic Data

	6	10
formula	C ₃₀ H ₆₀ SmO ₂ P ₂ N ₅	C ₃₃ H ₄₃ SmSiO
MW	735.18	643.19
cryst color, habit	yellow, plate	yellow, rhomboidal
cryst dimens, mm	0.26 × 0.09 × 0.08	0.21 × 0.18 × 0.16
cryst syst	monoclinic	triclinic
cell determination (2θ range)	6636 (4.0–45.0°)	8192 (4.0–45.0°)
lattice params	<i>a</i> = 10.0228(1) Å <i>b</i> = 17.9055(3) Å <i>c</i> = 10.7947(2) Å <i>β</i> = 111.413(1)° <i>V</i> = 1803.54(8) Å ³	<i>a</i> = 12.4727(2) Å <i>b</i> = 14.4791(2) Å <i>c</i> = 17.2790(2) Å <i>α</i> = 80.291(1)° <i>β</i> = 73.983(1)° <i>γ</i> = 79.002(1)° <i>V</i> = 2985.17(8) Å ³
space group	<i>P</i> ₂ ₁ (#4)	<i>P</i> ₁ (#2)
<i>Z</i> value	4	4
<i>D</i> _{calc}	2.707 g/cm ³	1.411 g/cm ³
<i>μ</i> (Mo Kα)	35.04 cm ^{−1}	15.50 cm ^{−1}
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo Kα	Mo Kα
temperature	−119.0 °C	−161.0 °C
scan type	<i>ω</i> (0.3° per frame)	<i>ω</i> (0.3° per frame)
no. of refls measd	8735	14 144
no. of refls obsd	2969 (<i>I</i> > 3.00σ(<i>I</i>))	12460 (<i>I</i> > 3.00σ(<i>I</i>))
solution	direct methods (SIR92)	direct methods (SIR92)
refinement	full-matrix least-squares	full-matrix least-squares
<i>R</i> , <i>R</i> _w	0.025; 0.029	0.041; 0.065
max. peak in diff map	0.45 e [−] /Å ³	1.48 e [−] /Å ³
min. peak in diff map	−0.47 e [−] /Å ³	−2.17 e [−] /Å ³

were cooled to −80 °C. The benzophenone solution was then added to the stirred suspension of **2** via cannula. The reaction mixture was allowed to reach room temperature, and after approximately 2 h, the volatile materials were removed under vacuum. The solid products were extracted into ca. 20 mL of pentane and filtered with a cannula. Concentrating to a volume of 5 mL and cooling to −35 °C yielded 79% of yellow-orange, crystalline **10** (0.12 g, 0.19 mmol). Mp > 260 °C (225–229 °C dec). IR: 3029 (w), 2963 (m), 2910 (s), 2856 (m), 2177 (m, *ν*_{SiH}), 2146 (s, *ν*_{SiH}), 1596 (w), 1491 (m, sh), 1443 (s), 1380 (w), 1184 (w), 1158 (w), 1045 (s), 1025 (s), 942 (s), 904 (s), 765 (m), 747 (m), 700 (s), 661 (w, sh). ¹H NMR (500 MHz): *δ* 0.25 (s, 30 H, Cp*), 4.44 (d, 4 H, *o*-Ph), 6.05 (t, 4 H, *m*-Ph), 6.68 (s, 3 H, SiH), 6.76 (t, 3 H, *p*-Ph). ¹³C{¹H} NMR (126 MHz): *δ* 22.29 (C₅Me₃), 93.59 (CPh₂), 120.21 (C₃Me₃), 126.73 (−Ph), 127.98 (−Ph), 130.42 (*ipso*-Ph), 148.23 (−Ph). ²⁹Si{¹H} NMR (99 MHz): *δ* −59.88 (q, *J*_{SiH} = 196.0 Hz). Anal. Calcd for C₃₃H₄₃OSiSm: C, 62.50; H, 6.83. Found: C, 62.20; H, 7.18.

X-ray Crystal Structure Determination of 6. A yellow, platelike crystal of approximate dimensions 0.26 × 0.09 × 0.08 mm was mounted on a glass capillary using Paratone N hydrocarbon oil and placed under a stream of cold nitrogen on a Siemens SMART diffractometer with a CCD area detector. Preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames. A hemisphere of data was collected at a temperature of −119 ± 1 °C using *ω* scans of 0.30° and a collection time of 20 s per frame. Frame data were integrated using SAINT. An absorption correction was applied using SADABS (*T*_{max} = 0.976, *T*_{min} = 0.886). The 8735 reflections that were integrated were averaged in the point group *P*₂₁ to yield 3311 unique reflections (*R*_{int} = 0.031). No correction for decay was necessary. The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan. The number of variable parameters was 360, giving a data/parameter ratio of 8.25. The maximum and minimum peaks on the final difference Fourier map correspond to 0.45 and −0.48 e[−]/Å³: *R* = 0.025, *R*_w = 0.029, GOF = 1.19. The crystallographic data are summarized in Table 1.

X-ray Crystal Structure Determination of 10. A yellow-orange, rhomboidal crystal with approximate dimensions 0.21 × 0.18 × 0.16 mm was mounted on a glass capillary using Paratone N hydrocarbon oil and placed under a stream of cold nitrogen on the same SMART diffractometer. Preliminary orientation matrix and unit cell parameters were determined as described above. A hemisphere of data was collected at a temperature of −161 ± 1 °C using *ω* scans of 0.30° and a collection time of 20 s per frame. Frame data were integrated using SAINT. An absorption correction was applied using SADABS (*T*_{max} = 0.977, *T*_{min} = 0.787). The 14 144 reflections that were integrated were averaged in point group *P*₁ to yield 9865 unique reflections (*R*_{int} = 0.037). No correction for decay was necessary. The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan. The two independent molecules in the unit cell are virtually identical. All non-hydrogen atoms were refined anisotropically. The six hydrogen atoms on the two silicon centers were found in the difference Fourier map, and all other hydrogen atoms were included at calculated positions, but neither were refined. The number of variable parameters was 649, giving a data/parameter ratio of 19.20. The maximum and minimum peaks on the final difference Fourier map correspond to 1.48 and −2.17 e[−]/Å³: *R* = 0.041, *R*_w = 0.065, GOF = 2.48. The crystallographic data are summarized in Table 1.

Results and Discussion

The reaction of **1** with 10 equiv of PhSiH₃ in pentane results in rapid formation of the insoluble orange powder **2** after a variable induction period (5–30 min). This product was spectroscopically identified as the intermediate previously observed in the transformation of **1** to the mixture of trisamarium clusters [Cp*₂-SmSiH₃]₃.^{3a} It exhibits only one peak in the ¹H NMR spectrum (at *δ* 1.01 in benzene-*d*₆), and *ν*(SiH) stretching frequencies at 1992 and 1884 cm^{−1} indicate the presence of the hydrosilyl ligand. Apparently, the Si–H hydrogens are not observed in the ¹H NMR spectrum due to their close proximity to the paramagnetic Sm center. In addition, the relatively low value for the stretching frequencies is consistent with binding of the −SiH₃ group to an electropositive element.^{3a,e,7} The combustion analysis of **2** is consistent with the formula Cp*₂SmSiH₃. On the basis of this formulation, the isolated yield of **2** was 35–56%. Further characterization of **2** has been precluded by its low solubility in solvents that do not promote decomposition.

Slow diffusion of PhSiH₃ into a pentane solution of **1** produced microcrystalline **2**, and further attempts to obtain X-ray quality crystals have proven unsuccessful. We have also been unable to observe a parent ion by EI mass spectroscopy due to the negligible volatility of **2**. In addition, the FAB method has been unavailable due to the low solubility of **2** in suitable solvents, and this property has also precluded the determination of a solution molecular weight. However, on the basis of the fact that a trimeric form of **2** has been characterized in the solid state as a part of a solid solution with other samarium–silicon clusters,^{3a} we assume that **2** exists predominantly as the trimer.

Compound **2** is unstable in benzene-*d*₆ and decomposes within 1 h to the above-mentioned trinuclear samarium clusters (by ¹H NMR spectroscopy). In ethereal and chlorinated solvents, decomposition to intrac-

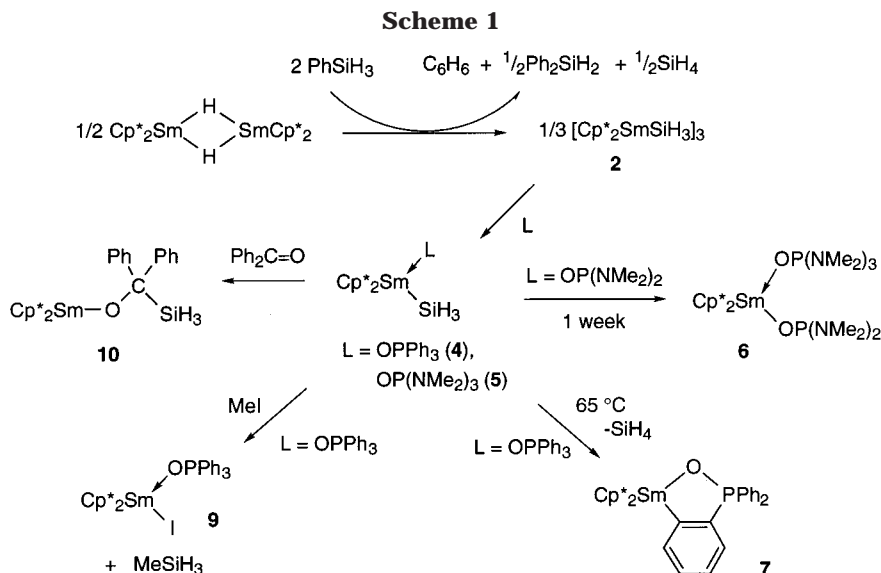
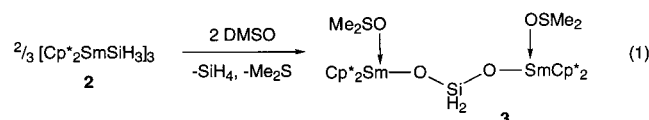


table samarium-containing products occurs within minutes. In contrast, **2** does not undergo significant decomposition over one week in aliphatic solvents such as pentane and cyclohexane.

In the absence of structural data for pure **2**, we sought to prepare soluble base adducts which might be more amenable to structural and chemical investigations. Addition of PMe_3 or pyridine to suspensions of **2** in pentane or toluene resulted in production of complex reaction mixtures. An attempt to prepare a dimethyl sulfoxide (DMSO) adduct instead led to reaction of the $\text{Sm}-\text{Si}$ bond. Addition of 2 equiv of DMSO to a toluene suspension of **2** gave sparingly soluble, yellow $\text{Cp}^*_2\text{Sm}(\text{DMSO})\text{OSiH}_2\text{OSm}(\text{DMSO})\text{Cp}^*_2$ (**3**, eq 1). Monitoring



the reaction by ^1H NMR spectroscopy (benzene- d_6 solution) revealed the production of Me_2S (1 equiv) and SiH_4 as the only byproducts. The ^1H NMR spectrum of **3** consists of a singlet at δ 1.48 (for the Cp^* ligands) and a broad resonance centered at δ 0.93 (for the DMSO ligands). In the IR spectrum the $\nu(\text{SiH})$ stretch was observed at 2080 cm^{-1} . X-ray quality crystals of **3** were obtained by cooling a concentrated toluene solution to -35°C . Although the structure and connectivity of **3** were confirmed by X-ray crystallography, including the bridging nature of the $-\text{OSiH}_2\text{O}-$ unit, the refinement of accurate metric parameters was not possible due to severe disorder of two toluene molecules of crystallization present in the unit cell.

Isolable base adducts were obtained by use of the hard Lewis bases Ph_3PO and $(\text{Me}_2\text{N})_3\text{PO}$ (HMPA), which react with **2** in toluene at -78°C to produce $\text{Cp}^*_2\text{SmSiH}_3(\text{OPPh}_3)$ (**4**) and $\text{Cp}^*_2\text{SmSiH}_3(\text{HMPA})$ (**5**, Scheme 1), respectively. Both compounds were isolated as yellow, air- and moisture-sensitive microcrystals by cooling concentrated toluene solutions to -35°C . In benzene-

d_6 or toluene solution, **5** slowly decomposes to several samarium-containing products over a period of 7 days. We were able to identify one of these decomposition products as $\text{Cp}^*_2\text{Sm}[\text{OP}(\text{NMe}_2)_2](\text{HMPA})$ (**6**), on the basis of its ^1H NMR spectrum. A low yield of yellow single crystals of **6** suitable for X-ray diffraction was obtained by crystallization from pentane. The solid state structure determination revealed a pseudo-tetrahedral environment about the Sm atom, with two distinct $\text{Sm}-\text{O}$ distances of 2.22 and 2.32 Å associated with the $-\text{OP}(\text{NMe}_2)_2$ and HMPA ligands, respectively. The $\text{Sm}-\text{Cp}^*$ centroid distances of 2.49 and 2.51 Å and the centroid-Sm-centroid angle of 131.2° are characteristic for $\text{Sm}(\text{III})$ metallocenes.⁸ The molecular structure of **6** is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The $-\text{OP}(\text{NMe}_2)_2$ ligand is likely formed via activation of a P-N bond in HMPA by the reactive $\text{Sm}-\text{SiH}_3$ group. To support this hypothesis, the decomposition of **5** was carried out in a sealed NMR tube in the presence of 1 equiv of HMPA. The ^1H NMR spectrum contained two singlets (at δ 2.51 and δ 4.70) in an approximately 3:1 ratio, assigned to Me_2NSiH_3 .

Complex **4** is considerably more stable in solution, but attempts to obtain X-ray quality crystals have so far

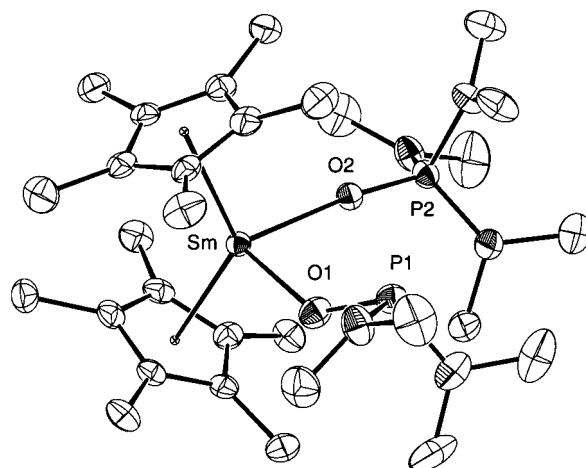


Figure 1. ORTEP diagram of $\text{Cp}^*_2\text{Sm}[\text{OP}(\text{NMe}_2)_2](\text{HMPA})$ (**6**).

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 6

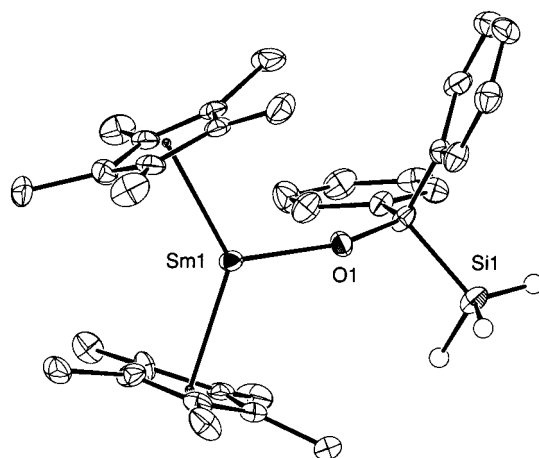
(a) Bond Distances							
Sm(1)	O(1)	2.222(3)	Sm(1)	O(2)	2.324(3)		
Sm(1)	Cp*(1) ^a	2.5089(1)	Sm(1)	Cp*(2)	2.4858(1)		
P(1)	O(1)	1.572(3)	P(2)	O(2)	1.498(3)		
P(1)	N(1)	1.722(5)	P(2)	N(3)	1.623(4)		
P(1)	N(2)	1.703(4)	P(2)	N(4)	1.640(4)		
			P(2)	N(5)	1.639(4)		
(b) Bond Angles							
O(1)	Sm(1)	O(2)	89.0(1)	Cp*(1)	Sm(1)	Cp*(2)	131.166(6)
Sm(1)	O(1)	P(1)	137.4(2)	Sm(1)	O(2)	P(2)	173.2(2)
O(1)	P(1)	N(1)	99.6(2)	O(2)	P(2)	N(3)	110.3(2)
O(1)	P(1)	N(2)	104.2(2)	O(2)	P(2)	N(4)	114.0(2)
N(1)	P(1)	N(2)	106.2(2)	O(2)	P(2)	N(5)	108.6(2)
N(3)	P(2)	N(4)	104.9(2)	N(3)	P(2)	N(5)	111.2(2)
				N(4)	P(2)	N(5)	107.8(2)

^a Cp* denotes the centroids of the rings.

proven unsuccessful. In benzene-*d*₆ solution, **4** decomposes quantitatively at 65 °C over 18 h via the clean elimination of SiH₄ (by ¹H NMR spectroscopy; Scheme 1). The resulting cyclometalated phosphineoxide complex Cp*₂SmC₆H₄P(O)Ph₂ (**7**) was independently synthesized by the reaction of [Cp*₂Sm(*μ*-H)]₂ (**8**) with Ph₃PO. The thermal decomposition of **4** in benzene-*d*₆ is inhibited by an atmosphere of hydrogen, such that it requires 48 h at 65 °C, and in this case the generation of **7** is accompanied by SiH₄, Si₂H₆, and unidentified samarium-containing compounds as byproducts.

Other reactions of **4** characterize this complex as a source of the SiH₃[−] silyl anion. For example, the reaction with MeI in benzene-*d*₆ produces quantitative yields of MeSiH₃ and Cp*₂SmI(OPPh₃) (**9**; Scheme 1). Both **2** and **4** react quantitatively (by ¹H NMR spectroscopy in benzene-*d*₆) with benzophenone to produce the insertion product Cp*₂SmOCPh₂(SiH₃) (**10**). The ²⁹Si NMR spectrum of **10** consists of a quartet centered at δ −59.88 associated with a coupling constant of *J*_{SiH} = 196 Hz. The −SiH₃ group of **10** also gives rise to an infrared stretching band at 2146 cm^{−1}. The X-ray crystal structure of **10** revealed the presence of a simple insertion product, with the alkoxide ligand bound to the samarium center only through the oxygen atom. All three hydrogen atoms bound to silicon were found in the difference Fourier map, but their positions were not refined. Two molecules with virtually identical bond lengths are present in the asymmetric unit. An ORTEP view of one of the molecules is shown in Figure 2, and a list of selected bond distances and angles is shown in Table 3. The Sm–O distance of 2.12 Å is within the range of known samarium–oxygen single bond distances (2.09–2.25 Å), as are the Sm–ring centroid average distance of 2.46 Å and the centroid–Sm–centroid angle of 132.9°. The large Sm–O–C angle of 162.9° probably reflects the high steric demand of the −OCPh₂(SiH₃) ligand and perhaps donation of a lone pair on oxygen to the samarium center.

To gain more insight into the Si–C bond cleavage chemistry responsible for the formation of **2**, we established the stoichiometry of the reaction of PhSiH₃ (8 equiv) with **1** in cyclohexane-*d*₁₂. The reaction mixture turns deep red after an induction period of 5–30 min, at which point quantitative formation of CH₂(SiMe₃)₂ was observed, along with unreacted PhSiH₃ (2.11 equiv), H₂ (0.19 equiv in solution), Ph₂SiH₂ (0.63 equiv), Ph₃SiH (trace), PhSiH₂SiH₂Ph (0.18 equiv), benzene (1.53 equiv), silane oligomers, and a mixture of the previously reported trisamarium clusters.^{3a} The identities and quantities of the silane products were confirmed by GC–mass spectrometry.

**Figure 2.** ORTEP view of Cp*₂SmOCPh₂(SiH₃) (**10**).**Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 10**

(a) Bond Distances							
Sm(1)	O(1)	2.125(5)	Sm(2)	O(2)	2.120(5)		
Sm(1)	Cp*(1) ^a	2.4358(4)	Sm(2)	Cp*(3)	2.4319(4)		
Sm(1)	Cp*(2)	2.5572(4)	Sm(2)	Cp*(4)	2.4262(4)		
O(1)	C(21)	1.415(8)	O(2)	C(54)	1.410(9)		
Si(1)	C(21)	1.922(8)	Si(2)	C(54)	1.913(8)		
(b) Bond Angles							
Sm(1)	O(1)	C(21)	162.9(4)	Cp*(1)	Sm(1)	Cp*(2)	131.01(1)
Sm(2)	O(2)	C(54)	162.9(5)	Cp*(3)	Sm(2)	Cp*(4)	134.73(2)
Si(1)	C(21)	O(1)	105.5(5)	Si(2)	C(54)	O(2)	107.1(5)

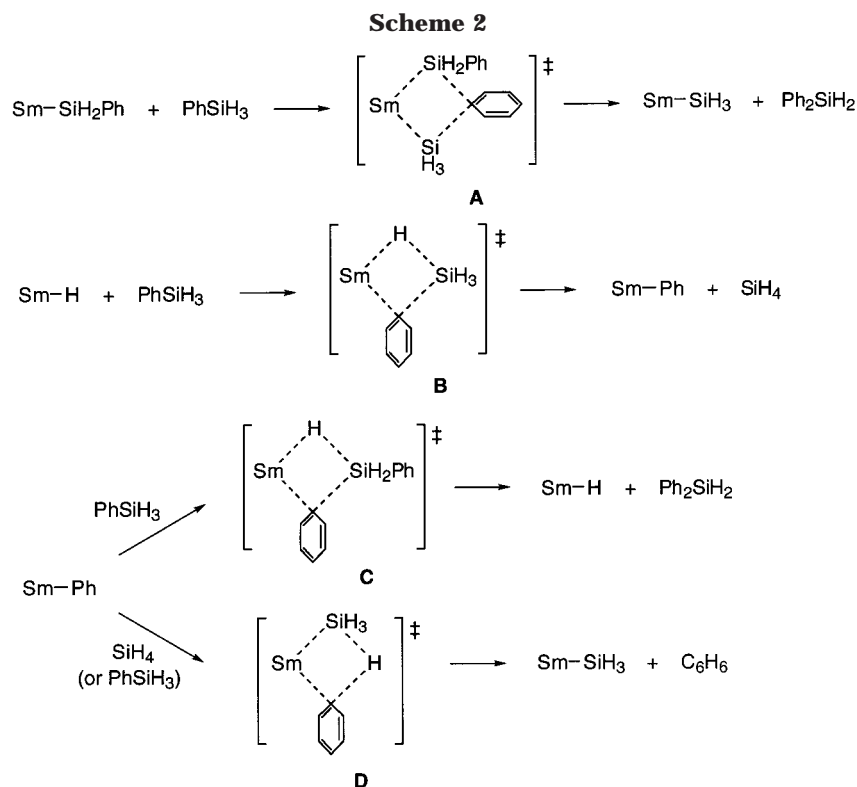
^a Cp* denotes the centroids of the rings.

Addition of catalytic amounts of hydrogen (<1 atm) to the above reaction mixture results in elimination of the induction period. On this basis and our earlier study of the mechanism of the metathesis reaction of **1** with (Me₃Si)₂SiH₂,^{3b} we propose that the observed induction period is associated with conversion of **1** to a samarium hydride species, which is much more active toward σ-bond metathesis. To further investigate this possibility, we examined the reaction of [Cp*₂Sm(*μ*-H)]₂ (**8**) with PhSiH₃ (8 equiv), which after 10 min (no induction period observed) gave a mixture of products similar to that observed in the reaction with **1**: PhSiH₃ (5.80 equiv), H₂ (0.16 equiv in solution), Ph₂SiH₂ (0.39 equiv), PhSiH₂SiH₂Ph (0.12 equiv), benzene (1.15 equiv), and uncharacterized silane oligomers. Trace amounts of SiH₄ were detected when less than 1 equiv of PhSiH₃ was added to solutions of either **1** or **8** (presumably more SiH₄ existed in the headspace of the NMR tube). Thus, although less PhSiH₃ is consumed in this reaction, it appears that **8** may be the active species which mediates redistribution via Si–C bond cleavage. The stoichiometry of this redistribution chemistry corresponds approximately to that shown in eq 2.

$$\text{Cp}^*_2\text{SmH} + 2\text{PhSiH}_3 \rightarrow$$

$$\text{Cp}^*_2\text{SmSiH}_3 + 0.5\text{SiH}_4 + 0.5\text{Ph}_2\text{SiH}_2 + \text{C}_6\text{H}_6 \quad (2)$$

In the chemistry described above, we have not yet directly observed the elementary processes responsible



for Si-C bond cleavage. However, it is interesting to speculate on the mechanisms of these unusual σ -bond metathesis reactions. Particularly since oxidative addition/reductive elimination processes for Sm are highly unlikely, the observations suggest the presence of a highly active samarium species which can mediate σ -bond metathesis reactions through four-centered transition states for bonds (Si-C) that normally do not participate in such processes. It is important to note that when the reaction between **1** or **8** and PhSiH_3 is carried out in aliphatic solvents (pentane or cyclohexane- d_{12}), the only source of phenyl groups is PhSiH_3 , thus ruling out the possible involvement of benzene as a co-reagent in the redistribution at silicon. We propose that the dehydrocoupling chemistry occurs via $\text{Cp}^*_2\text{SmSiH}_2\text{Ph}$, which reacts with PhSiH_3 to produce **8** and $\text{PhSiH}_2\text{SiH}_2\text{Ph}$. Although one can also imagine interaction of the Sm-Si bond of $\text{Cp}^*_2\text{SmSiH}_2\text{Ph}$ with the Si-C bond of PhSiH_3 to produce Ph_2SiH_2 and $\text{Cp}^*_2\text{SmSiH}_3$, we believe that this is unlikely for two reasons. First, the four-centered transition state required for this transformation (**A**, Scheme 2) would be very crowded.^{3b} Second, four-centered transition states with a carbon atom in the β -position seem to be disfavored.^{2b,9,10} In an attempt to observe the proposed intermediate Sm-silyl species in this system, we examined the reaction of **8** with 1 equiv of PhSiH_3 at -80°C in toluene- d_8 . However, even at this temperature, dehydrocoupling and redistribution products appear rapidly, and no intermediates could be detected. Kinetic studies have so far been prevented by the speed of the reaction, even at low temperatures, and by the formation of insoluble species.

A more likely scenario that could account for the redistribution chemistry is outlined in Scheme 2. An interaction between **8** and the Si-C bond of PhSiH_3 proceeds through transition state **B**, which corresponds to nucleophilic attack at an unhindered silicon center. The resulting samarium phenyl species could arylate PhSiH_3 (transition state **C**) in a hydrocarbyl/hydrogen exchange process that is well known in σ -bond metathesis chemistry.^{1b,c,i,11} Alternatively, the samarium phenyl species could undergo reactions with Si-H or H-H bonds present in the reaction mixture to produce benzene (via transition state **D**).

Conclusions

The samarium complex $[\text{Cp}^*_2\text{SmSiH}_3]_3$ (**2**), which represents the first f-element complex of the simplest silyl ligand (SiH_3), has been prepared. Although **2** is rather insoluble, it forms soluble adducts with Ph_3PO and HMPA, which are in some ways more amenable to reactivity studies. As might be expected for a complex featuring a bond between two rather electropositive elements, **2** has a high affinity for oxygen, as demonstrated by its deoxygenation of DMSO. Also, the $-\text{SiH}_3$ ligand in **2** and **4** is nucleophilically transferred to electrophiles such as MeI and benzophenone. The formation of **2** involves cleavage of a very stable Si-C

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bond and represents a redistribution of phenyl groups at silicon.¹² Such redistributions are known to be catalyzed by late transition metals, but have only been rarely observed for d⁰ transition metal systems.^{3a,13} For the samarium system under study, this process is proposed to occur via σ -bond metathesis steps that pass through four-center transition states in a σ -bond metathesis process. The exact mechanism of the Si–C bond activation and cleavage is open to speculation, but the proposed pathways outlined in Scheme 2 seem reason-

able based on the known reactivity of organolanthanide complexes.^{2,10}

Acknowledgment is made to the National Science Foundation for their generous support of this work.

Supporting Information Available: Tables of crystal, data collection and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for **6** and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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