

Synthesis of $[(C_5Me_5)Sm(CH(SiMe_3)_2)(C_5Me_5)K(THF)_2]_n$ (1). In a glove box, to a purple THF solution (10 mL) of $(C_5Me_5)_2Sm(THF)_2$ (0.565 g, 1 mmol) in a 100 ml-flask was added a THF solution (5 mL) of $KCH(SiMe_3)_2$ (0.198 g, 1 mmol). The resultant solution was stirred at room temperature for 1 h and then transferred to another flask through a glass filter. After the solution was concentrated under reduced pressure, hexane was layered to give green plate crystals of **1** suitable for X-ray analysis. Leaving **1** under vacuum (1 mmHg) at room temperature for 1 h gave **1'** (1-THF) (0.636 g, 0.91 mmol, 91% yield), as confirmed by elemental analysis. 1H NMR (THF- d_8 , 22 °C): δ 10.20 (br s, 30 H, C_5Me_5), -0.02 (s, 18H, SiMe₃). The methine proton in $CH(SiMe_3)_2$ could not be located owing the influence of the paramagnetic Sm(II) ion. Anal. Calcd for $C_{31}H_{57}KOSi_2Sm$ (1-THF): C, 53.85; H, 8.31. Found: C, 53.73; H, 8.26.

Synthesis of $[(C_5Me_5)Sm(\mu-H)_2]_6[(\mu-H)K(THF)_2]_3$ (2). In a glove box, addition of H_3SiPh (0.541 g, 5 mmol) to a THF solution (5 mL) of **1'** (0.692 g, 1 mmol) generated a dark red solution, which after being stirred at room temperature for 10 h, turned to orange-red. After the solvent was removed under reduced pressure, the residue was washed with hexane and toluene. $(Me_3Si)_2CHSiH_2Ph$ was quantitatively obtained from the hexane soluble part. The insoluble residue was recrystallized from THF/hexane, which gave **2** as orange-red crystals. Leaving **2** under vacuum (1 mmHg) at room temperature for 1 h gave **2'** (2-3THF) (0.145 g, 0.07 mmol, 42% based on Sm). 1H NMR (THF- d_8 , 22 °C): δ 1.92 (s, C_5Me_5). The metal-H could not be located. IR (Nujol): 2960 (m), 2920 (s), 2852 (s), 1440 (m), 1424 (m), 1378 (w), 1259 (m, br), 1150 (m, br), 1053 (s, br), 900 (m, br), 797 (s, br) cm^{-1} . Anal. Calcd for $C_{72}H_{129}K_3O_3Sm_6$ (2-3THF): C, 41.93; H, 6.30. Found: C, 42.10, H, 6.03.

A Typical Procedure for Hydrosilylation Reactions. In a glove box, a benzene solution (2 ml) of an olefin (1.0 mmol) and H_3SiPh (1.1 mmol) was added to **1** (0.02 mmol). The mixture was stirred at room temperature for a given time (see Table 1). After filtration through a plug of Florisil, the solvent was removed and the residue was chromatographed on silica with hexane as an eluant. The products were identified by comparison with NMR spectra reported in the literature. The 1H NMR spectra in C_6D_6 at 22 °C are given below.

1-(Phenylsilyl)decane. δ 0.85–0.92 (m, 5 H), 1.22–1.48 (m, 16 H), 4.49 (t, J = 3.6 Hz, 2 H), 7.30–7.60 (m, 5 H).

1-(Diphenylsilyl)-2-methylbut-2-ene.²⁻⁴ δ 1.35 (d, $J = 6.8$, 3 H), 1.61 (t, $J = 1.4$ Hz, 3 H), 2.08 (d, $J = 3.7$ Hz, 2 H), 4.89 (t, $J = 3.7$, 1 H), 5.10 (q, $J = 6.8$, 1 H), 7.30–7.45 (m, 6 H), 7.50–7.60 (m, 4 H).

2-Methyl-4-(diphenylsilyl)but-2-ene.²⁻⁴ δ 1.45 (s, 3 H), 1.65 (s, 3 H), 2.00 (m, 2 H), 4.82 (t, $J = 3.9$, 1 H), 5.20 (t, $J = 8.0$, 1 H), 7.30–7.45 (m, 6 H), 7.50–7.60 (m, 4 H).

4-[2-(Phenylsilyl)ethyl]cyclohex-1-ene.¹ δ 0.73–0.79 (m, 2 H), 1.01–1.10 (m, 1 H), 1.25–1.59 (m, 5 H), 1.87–1.91 (m, 3 H), 4.44 (t, $J = 3.6$ Hz, 2 H), 5.56–5.65 (m, 2 H), 7.0–7.50 (m, 5 H).

1-Phenyl-1-(phenylsilyl)ethane.⁵ δ 1.33 (d, $J = 7.5$ Hz, 3 H), 2.31–2.50 (m, 1 H), 4.44–4.59 (m, 2 H), 6.80–7.40 (m, 10 H).

1-Phenyl-2-(phenylsilyl)ethane.⁵ δ 1.01–1.11 (m, 2 H), 2.50–2.62 (m, 2 H), 4.38 (t, $J = 3.5$ Hz, 2 H), 6.95–7.90 (m, 10 H).

X-Ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glove box under a microscope mounted on the glove box window, and were sealed in thin-walled glass capillaries. Data collections were performed at 173 K for **1** and 295 K for **2** on a Bruker SMART APEX CCD diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å). The SMART program package⁶ was used to determine the unit cell parameters and for data collection. The raw frame data was processed using SAINT⁷ and SADABS⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁹ program. Structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors¹⁰ for neutral atoms were used throughout the analysis. The hydride atoms in **2** were found by the difference Fourier syntheses and their coordinates and isotropic parameters were refined. Other hydrogen atoms were placed at the calculated positions and not refined. Non-hydrogen atoms were refined anisotropically. The residual electron densities were of no chemical significance.

References

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STable 1. Summary of Crystal data for 1.

Empirical formula	C35 H65 K O2 Si2 Sm	
Formula weight	763.50	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 34.204(6) Å	$\alpha = 90^\circ$.
	b = 10.1887(17) Å	$\beta = 102.016(4)^\circ$.
	c = 11.678(2) Å	$\gamma = 90^\circ$.
Volume	3980.5(12) Å ³	
Z	4	
Density (calculated)	1.274 Mg/m ³	
Absorption coefficient	1.666 mm ⁻¹	
F(000)	1600	
Crystal size	0.6 x 0.4 x 0.2 mm ³	
Theta range for data collection	1.22 to 30.60°.	
Index ranges	-48 ≤ h ≤ 44, -14 ≤ k ≤ 13, -15 ≤ l ≤ 14	
Reflections collected	15301	
Independent reflections	9883 [R(int) = 0.0481]	
Completeness to theta = 30.60°	91.3 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9883 / 1 / 341	
Goodness-of-fit on F ²	0.899	
Final R indices [I > 2σ(I)]	R1 = 0.0571, wR2 = 0.1277	
R indices (all data)	R1 = 0.0986, wR2 = 0.1413	
Absolute structure parameter	0.42(3)	
Largest diff. peak and hole	2.662 and -0.726 e.Å ⁻³	

STable 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Sm(1)	8702(1)	734(2)	42(1)	33(1)
K(1)	8714(1)	-4275(5)	-1659(1)	37(1)
Si(1)	8351(1)	721(8)	2748(2)	52(1)
Si(2)	9292(1)	719(13)	3399(2)	73(1)
O(1)	9369(2)	-4259(18)	-2605(6)	79(2)
O(2)	8229(2)	-4180(20)	-3889(6)	73(2)
C(1)	8428(4)	-1986(11)	-340(12)	48(3)
C(2)	8829(5)	-2099(13)	291(9)	93(7)
C(3)	9085(3)	-1709(13)	-461(13)	98(8)
C(4)	8842(4)	-1353(11)	-1558(9)	51(4)
C(5)	8436(3)	-1525(10)	-1483(10)	44(3)
C(6)	8059(2)	-2299(5)	121(4)	77(4)
C(7)	8960(2)	-2554(7)	1539(5)	61(3)
C(8)	9534(2)	-1677(7)	-151(5)	65(3)
C(9)	8989(2)	-879(7)	-2614(5)	84(4)
C(10)	8077(2)	-1263(7)	-2446(5)	77(4)
C(11)	8544(4)	-6490(8)	-66(8)	50(4)
C(12)	8957(3)	-6622(10)	-78(10)	69(5)
C(13)	8989(3)	-7191(10)	-1164(12)	69(6)
C(14)	8596(4)	-7410(9)	-1825(8)	52(3)
C(15)	8322(2)	-6977(9)	-1146(9)	35(3)
C(16)	8373(2)	-5932(5)	918(4)	84(4)
C(17)	9300(2)	-6229(7)	893(5)	86(4)
C(18)	9372(2)	-7506(7)	-1549(5)	75(4)
C(19)	8490(2)	-7998(7)	-3033(5)	63(3)
C(20)	7873(2)	-7025(7)	-1508(5)	61(3)
C(21)	8815(3)	1029(8)	2343(8)	48(3)
C(22)	7938(3)	780(30)	1382(9)	87(4)
C(23)	8216(6)	2120(20)	3780(18)	101(8)
C(24)	8282(5)	-760(20)	3406(15)	72(5)
C(25)	9366(5)	-720(30)	4487(17)	99(7)
C(26)	9732(3)	750(30)	2678(8)	79(3)
C(27)	9346(8)	2150(40)	4260(20)	189(16)
C(28)	9770(4)	-4160(40)	-2296(12)	136(8)
C(29)	9944(4)	-3990(30)	-3242(13)	116(8)
C(30)	9664(6)	-3700(30)	-4108(16)	214(19)
C(31)	9281(5)	-4080(110)	-3766(16)	440(30)
C(32)	7824(4)	-4390(50)	-3998(11)	201(13)
C(33)	7655(4)	-3779(17)	-5222(12)	112(7)
C(34)	7907(5)	-4060(20)	-5840(12)	115(8)
C(35)	8300(4)	-3980(20)	-4980(11)	111(8)
H(6A)	7932	-3065	-268	115
H(6B)	7877	-1571	-24	115
H(6C)	8132	-2461	948	115
H(7A)	9014	-1806	2046	91
H(7B)	9197	-3079	1612	91
H(7C)	8751	-3069	1753	91
H(8A)	9637	-2529	-276	97
H(8B)	9621	-1435	656	97
H(8C)	9631	-1045	-636	97
H(9A)	9057	-1619	-3043	126
H(9B)	9221	-338	-2366	126
H(9C)	8783	-376	-3107	126
H(10A)	7936	-2070	-2664	116

H(10B)	8163	-903	-3112	116
H(10C)	7903	-650	-2175	116
H(16A)	8582	-5848	1605	125
H(16B)	8169	-6507	1079	125
H(16C)	8260	-5084	696	125
H(17A)	9390	-5368	738	129
H(17B)	9515	-6845	935	129
H(17C)	9213	-6224	1623	129
H(18A)	9312	-7841	-2334	112
H(18B)	9519	-8154	-1035	112
H(18C)	9530	-6724	-1522	112
H(19A)	8731	-8204	-3298	95
H(19B)	8335	-7380	-3560	95
H(19C)	8338	-8785	-3010	95
H(20A)	7757	-6646	-903	91
H(20B)	7788	-7921	-1632	91
H(20C)	7788	-6539	-2221	91
H(21)	8810(30)	1990(100)	2380(80)	57
H(22A)	7990	139	830	130
H(22B)	7929	1639	1038	130
H(22C)	7686	593	1587	130
H(23A)	7999	1829	4125	151
H(23B)	8138	2897	3328	151
H(23C)	8445	2304	4387	151
H(24A)	8383	-1464	3000	108
H(24B)	8002	-899	3374	108
H(24C)	8423	-751	4208	108
H(25A)	9609	-593	5060	148
H(25B)	9383	-1525	4073	148
H(25C)	9144	-760	4871	148
H(26A)	9781	1635	2465	118
H(26B)	9677	211	1989	118
H(26C)	9963	418	3211	118
H(27A)	9188	2845	3833	284
H(27B)	9622	2413	4437	284
H(27C)	9257	1988	4972	284
H(28A)	9877	-4949	-1881	164
H(28B)	9839	-3423	-1766	164
H(29A)	10139	-3283	-3094	139
H(29B)	10078	-4785	-3401	139
H(30A)	9696	-4179	-4801	257
H(30B)	9665	-2767	-4275	257
H(31A)	9083	-3391	-3973	527
H(31B)	9175	-4882	-4161	527
H(32A)	7722	-3944	-3387	242
H(32B)	7763	-5318	-3983	242
H(33A)	7395	-4150	-5561	134
H(33B)	7627	-2835	-5163	134
H(34A)	7896	-3437	-6472	139
H(34B)	7861	-4938	-6167	139
H(35A)	8482	-4649	-5157	133
H(35B)	8421	-3129	-5026	133

STable 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm(1)	41(1)	21(1)	39(1)	-1(1)	10(1)	3(1)
K(1)	41(1)	25(1)	45(1)	-11(2)	9(1)	7(2)
Si(1)	54(1)	45(1)	54(1)	8(4)	9(1)	-10(4)
Si(2)	51(1)	121(2)	43(1)	6(6)	5(1)	-5(6)
O(1)	63(4)	85(5)	97(5)	-18(11)	34(4)	30(10)
O(2)	71(4)	68(6)	68(4)	-4(9)	-13(3)	-9(9)
C(1)	58(7)	37(7)	57(8)	-3(6)	27(6)	-4(5)
C(2)	138(16)	50(10)	72(10)	-42(8)	-21(11)	24(11)
C(3)	70(10)	86(13)	146(17)	-99(13)	39(12)	-24(9)
C(4)	88(11)	27(6)	49(7)	-7(5)	39(8)	-32(6)
C(5)	33(6)	24(6)	58(7)	0(5)	-27(6)	0(5)
C(6)	73(8)	49(7)	112(10)	-1(7)	27(8)	-3(6)
C(7)	79(8)	39(6)	63(7)	1(5)	13(6)	2(6)
C(8)	50(6)	55(7)	88(8)	-26(6)	10(6)	6(5)
C(9)	137(12)	66(8)	57(7)	-6(6)	40(8)	31(8)
C(10)	90(9)	46(6)	76(8)	-13(6)	-26(7)	3(6)
C(11)	116(12)	3(4)	42(6)	5(4)	40(8)	4(6)
C(12)	77(9)	25(6)	69(8)	21(6)	-68(8)	-56(6)
C(13)	54(9)	30(6)	139(17)	44(9)	58(11)	7(6)
C(14)	83(10)	16(5)	57(7)	11(5)	10(7)	-1(6)
C(15)	56(7)	11(4)	46(6)	0(4)	30(5)	5(4)
C(16)	128(12)	35(6)	103(10)	-16(6)	61(9)	5(7)
C(17)	94(10)	57(7)	86(9)	-1(7)	-31(8)	-36(7)
C(18)	75(8)	48(6)	116(10)	4(7)	54(8)	-5(6)
C(19)	89(9)	49(6)	52(6)	-2(5)	13(6)	10(6)
C(20)	50(6)	53(6)	73(7)	20(6)	-1(5)	-3(5)
C(21)	70(6)	27(7)	45(5)	0(4)	12(4)	-2(4)
C(22)	63(6)	87(8)	97(7)	3(18)	-12(5)	27(14)
C(23)	76(11)	117(15)	120(17)	-63(13)	47(10)	5(10)
C(24)	57(9)	88(11)	72(10)	30(8)	15(7)	-14(8)
C(25)	61(11)	160(20)	64(11)	53(11)	-6(8)	-16(11)
C(26)	65(6)	98(8)	76(6)	-32(15)	21(5)	-18(16)
C(27)	150(20)	340(40)	59(12)	-84(19)	-20(13)	60(30)
C(28)	70(8)	240(20)	111(10)	-80(20)	45(8)	-62(19)
C(29)	89(10)	140(20)	130(11)	6(14)	43(9)	-50(14)
C(30)	200(20)	340(50)	143(15)	150(20)	116(15)	170(30)
C(31)	56(10)	1160(110)	104(13)	-10(80)	14(9)	30(70)
C(32)	58(8)	460(40)	84(9)	100(30)	1(7)	40(30)
C(33)	89(10)	139(19)	88(10)	-6(10)	-25(8)	40(10)
C(34)	166(14)	84(19)	79(8)	19(11)	-15(9)	-55(16)
C(35)	83(8)	130(20)	107(9)	78(13)	-17(7)	-3(10)

STable 4. Bond lengths [Å] and angles [°] for 1.

Sm(1)-C(1)	2.930(12)	Sm(1)-C(2)	2.924(13)
Sm(1)-C(3)	2.927(11)	Sm(1)-C(4)	2.934(10)
Sm(1)-C(5)	2.936(10)	Sm(1)-C(11)#1	2.878(10)
Sm(1)-C(12)#1	2.84(5)	Sm(1)-C(13)#1	2.83(5)
Sm(1)-C(14)#1	2.85(5)	Sm(1)-C(15)#1	2.88(5)
Sm(1)-C(21)	2.652(9)	K(1)-O(1)	2.698(6)
K(1)-O(2)	2.783(6)	K(1)-C(1)	3.065(13)
K(1)-C(2)	3.143(12)	K(1)-C(3)	3.109(11)
K(1)-C(4)	3.008(11)	K(1)-C(5)	2.980(11)
K(1)-C(11)	3.055(11)	K(1)-C(12)	3.030(11)
K(1)-C(13)	3.133(11)	K(1)-C(14)	3.220(10)
K(1)-C(15)	3.173(10)	C(13)-C(18)	1.506(10)
Si(1)-C(21)	1.776(10)	Si(1)-C(22)	1.899(9)
Si(1)-C(23)	1.980(19)	Si(1)-C(24)	1.735(18)
Si(2)-C(25)	1.92(2)	Si(2)-C(26)	1.871(9)
Si(2)-C(27)	1.76(3)	Si(2)-C(21)	1.857(10)
O(1)-C(31)	1.34(2)	O(1)-C(28)	1.348(12)
O(2)-C(35)	1.359(14)	O(2)-C(32)	1.382(16)
C(1)-C(2)	1.420(8)	C(3)-C(4)	1.420(8)
C(4)-C(5)	1.420(8)	C(2)-C(3)	1.420(8)
C(1)-C(5)	1.420(8)	C(1)-C(6)	1.506(11)
C(2)-C(7)	1.506(11)	C(3)-C(8)	1.506(11)
C(4)-C(9)	1.506(10)	C(5)-C(10)	1.506(9)
C(11)-C(12)	1.420(7)	C(11)-C(15)	1.420(7)
C(11)-C(16)	1.506(10)	C(12)-C(13)	1.420(7)
C(12)-C(17)	1.506(9)	C(13)-C(14)	1.420(7)
C(14)-C(15)	1.420(7)	C(14)-C(19)	1.506(10)
C(15)-C(20)	1.506(9)	C(28)-C(29)	1.371(17)
C(29)-C(30)	1.27(2)	C(30)-C(31)	1.50(4)
C(32)-C(33)	1.56(2)	C(33)-C(34)	1.267(19)
C(34)-C(35)	1.504(17)		
C(21)-Sm(1)-C(13)#1	115.3(13)	C(21)-Sm(1)-C(12)#1	87.8(14)
C(13)#1-Sm(1)-C(12)#1	29.0(4)	C(21)-Sm(1)-C(14)#1	131.9(12)
C(13)#1-Sm(1)-C(14)#1	29.0(5)	C(12)#1-Sm(1)-C(14)#1	47.6(7)
C(21)-Sm(1)-C(11)#1	85.4(2)	C(13)#1-Sm(1)-C(11)#1	47.5(12)
C(12)#1-Sm(1)-C(11)#1	28.7(13)	C(14)#1-Sm(1)-C(11)#1	47.3(11)
C(21)-Sm(1)-C(15)#1	110.6(13)	C(13)#1-Sm(1)-C(15)#1	47.4(7)
C(12)#1-Sm(1)-C(15)#1	47.3(6)	C(14)#1-Sm(1)-C(15)#1	28.7(4)
C(11)#1-Sm(1)-C(15)#1	28.5(12)	C(21)-Sm(1)-C(2)	91.4(3)
C(13)#1-Sm(1)-C(2)	136.8(13)	C(12)#1-Sm(1)-C(2)	154.1(16)
C(14)#1-Sm(1)-C(2)	136.3(11)	C(11)#1-Sm(1)-C(2)	175.7(3)
C(15)#1-Sm(1)-C(2)	152.8(13)	C(21)-Sm(1)-C(3)	108.9(3)
C(13)#1-Sm(1)-C(3)	108.7(13)	C(12)#1-Sm(1)-C(3)	129.9(15)
C(14)#1-Sm(1)-C(3)	113.7(12)	C(11)#1-Sm(1)-C(3)	156.2(4)
C(15)#1-Sm(1)-C(3)	140.1(13)	C(2)-Sm(1)-C(3)	28.09(16)
C(21)-Sm(1)-C(1)	103.6(3)	C(13)#1-Sm(1)-C(1)	139.9(12)
C(12)#1-Sm(1)-C(1)	168.6(14)	C(14)#1-Sm(1)-C(1)	121.7(13)
C(11)#1-Sm(1)-C(1)	150.6(4)	C(15)#1-Sm(1)-C(1)	126.4(14)
C(2)-Sm(1)-C(1)	28.07(17)	C(3)-Sm(1)-C(1)	46.2(2)
C(21)-Sm(1)-C(4)	136.0(3)	C(13)#1-Sm(1)-C(4)	96.1(13)
C(12)#1-Sm(1)-C(4)	124.3(14)	C(14)#1-Sm(1)-C(4)	90.3(12)
C(11)#1-Sm(1)-C(4)	137.6(3)	C(15)#1-Sm(1)-C(4)	113.4(13)
C(2)-Sm(1)-C(4)	46.2(2)	C(1)-Sm(1)-C(4)	46.1(2)
C(3)-Sm(1)-C(4)	28.04(15)	C(21)-Sm(1)-C(5)	131.7(3)
C(13)#1-Sm(1)-C(5)	112.4(13)	C(12)#1-Sm(1)-C(5)	140.6(14)
C(14)#1-Sm(1)-C(5)	94.7(13)	C(11)#1-Sm(1)-C(5)	135.4(3)

C(15)#1-Sm(1)-C(5)	106.9(14)	C(2)-Sm(1)-C(5)	46.2(2)
C(3)-Sm(1)-C(5)	46.1(2)	C(1)-Sm(1)-C(5)	28.02(16)
C(4)-Sm(1)-C(5)	28.00(15)	O(1)-K(1)-O(2)	90.0(2)
O(1)-K(1)-C(5)	109.1(5)	O(2)-K(1)-C(5)	84.0(5)
O(1)-K(1)-C(4)	83.3(5)	O(2)-K(1)-C(4)	93.1(5)
C(5)-K(1)-C(4)	27.43(16)	O(1)-K(1)-C(12)	96.2(4)
O(2)-K(1)-C(12)	129.3(5)	C(5)-K(1)-C(12)	138.7(3)
C(4)-K(1)-C(12)	137.6(3)	O(1)-K(1)-C(11)	122.2(4)
O(2)-K(1)-C(11)	116.4(5)	C(5)-K(1)-C(11)	123.3(3)
C(4)-K(1)-C(11)	138.7(2)	C(12)-K(1)-C(11)	26.99(13)
O(1)-K(1)-C(1)	125.5(5)	O(2)-K(1)-C(1)	104.7(5)
C(5)-K(1)-C(1)	27.12(16)	C(4)-K(1)-C(1)	44.4(2)
C(12)-K(1)-C(1)	111.7(3)	C(11)-K(1)-C(1)	97.8(2)
O(1)-K(1)-C(3)	83.3(4)	O(2)-K(1)-C(3)	119.9(6)
C(5)-K(1)-C(3)	44.3(2)	C(4)-K(1)-C(3)	26.78(15)
C(12)-K(1)-C(3)	110.8(3)	C(11)-K(1)-C(3)	117.3(3)
C(1)-K(1)-C(3)	43.7(2)	O(1)-K(1)-C(13)	80.7(4)
O(2)-K(1)-C(13)	107.7(6)	C(5)-K(1)-C(13)	165.2(2)
C(4)-K(1)-C(13)	153.6(4)	C(12)-K(1)-C(13)	26.57(13)
C(11)-K(1)-C(13)	43.6(2)	C(1)-K(1)-C(13)	138.1(3)
C(3)-K(1)-C(13)	129.5(4)	O(1)-K(1)-C(2)	107.6(4)
O(2)-K(1)-C(2)	127.8(5)	C(5)-K(1)-C(2)	44.0(2)
C(4)-K(1)-C(2)	43.8(2)	C(12)-K(1)-C(2)	98.0(3)
C(11)-K(1)-C(2)	95.2(2)	C(1)-K(1)-C(2)	26.40(15)
C(3)-K(1)-C(2)	26.25(15)	C(13)-K(1)-C(2)	123.2(3)
O(1)-K(1)-C(15)	120.2(5)	O(2)-K(1)-C(15)	90.9(5)
C(5)-K(1)-C(15)	130.5(3)	C(4)-K(1)-C(15)	156.2(3)
C(12)-K(1)-C(15)	43.4(2)	C(11)-K(1)-C(15)	26.27(13)
C(1)-K(1)-C(15)	112.0(3)	C(3)-K(1)-C(15)	142.6(3)
C(13)-K(1)-C(15)	42.7(2)	C(2)-K(1)-C(15)	118.0(3)
O(1)-K(1)-C(14)	94.9(5)	O(2)-K(1)-C(14)	86.4(5)
C(5)-K(1)-C(14)	154.1(4)	C(4)-K(1)-C(14)	178.1(3)
C(12)-K(1)-C(14)	43.0(2)	C(11)-K(1)-C(14)	42.9(2)
C(1)-K(1)-C(14)	137.4(3)	C(3)-K(1)-C(14)	153.6(4)
C(13)-K(1)-C(14)	25.79(13)	C(15)-K(1)-C(14)	25.66(13)
C(2)-K(1)-C(14)	137.6(3)	C(24)-Si(1)-C(21)	118.9(8)
C(24)-Si(1)-C(22)	104.7(11)	C(21)-Si(1)-C(22)	108.7(5)
C(24)-Si(1)-C(23)	106.7(7)	C(21)-Si(1)-C(23)	111.7(8)
C(22)-Si(1)-C(23)	105.2(10)	C(27)-Si(2)-C(21)	102.1(11)
C(27)-Si(2)-C(26)	104.1(14)	C(27)-Si(2)-C(25)	105.9(8)
C(21)-Si(2)-C(26)	112.1(5)	C(21)-Si(2)-C(25)	123.0(8)
C(26)-Si(2)-C(25)	107.6(11)	C(31)-O(1)-C(28)	105.3(13)
C(31)-O(1)-K(1)	112.5(8)	C(28)-O(1)-K(1)	141.0(6)
C(35)-O(2)-C(32)	107.9(8)	C(32)-O(2)-K(1)	118.1(7)
C(35)-O(2)-K(1)	134.0(7)	C(5)-C(1)-C(2)	108.0
C(5)-C(1)-C(6)	126.0(12)	C(2)-C(1)-C(6)	126.0(12)
C(5)-C(1)-Sm(1)	76.2(4)	C(2)-C(1)-Sm(1)	75.7(4)
C(6)-C(1)-Sm(1)	114.3(6)	C(5)-C(1)-K(1)	73.1(4)
C(2)-C(1)-K(1)	79.9(4)	C(6)-C(1)-K(1)	113.4(6)
Sm(1)-C(1)-K(1)	132.1(3)	C(3)-C(2)-C(1)	108.0
C(3)-C(2)-C(7)	126.0(12)	C(1)-C(2)-C(7)	126.0(12)
C(3)-C(2)-Sm(1)	76.1(4)	C(1)-C(2)-Sm(1)	76.2(4)
C(7)-C(2)-Sm(1)	114.1(7)	C(3)-C(2)-K(1)	75.5(4)
C(1)-C(2)-K(1)	73.7(4)	C(7)-C(2)-K(1)	116.8(7)
Sm(1)-C(2)-K(1)	129.1(4)	C(2)-C(3)-C(4)	108.0
C(2)-C(3)-C(8)	126.0(12)	C(4)-C(3)-C(8)	126.0(12)
C(2)-C(3)-Sm(1)	75.9(5)	C(4)-C(3)-Sm(1)	76.3(4)
C(8)-C(3)-Sm(1)	114.2(6)	C(2)-C(3)-K(1)	78.2(4)
C(4)-C(3)-K(1)	72.6(4)	C(8)-C(3)-K(1)	115.3(6)

Sm(1)-C(3)-K(1)	130.4(3)	C(5)-C(4)-C(3)	108.0
C(5)-C(4)-C(9)	126.0(12)	C(3)-C(4)-C(9)	126.0(12)
C(5)-C(4)-Sm(1)	76.1(4)	C(3)-C(4)-Sm(1)	75.7(4)
C(9)-C(4)-Sm(1)	114.5(6)	C(5)-C(4)-K(1)	75.2(4)
C(3)-C(4)-K(1)	80.6(4)	C(9)-C(4)-K(1)	110.9(6)
Sm(1)-C(4)-K(1)	134.5(3)	C(4)-C(5)-C(1)	108.0
C(4)-C(5)-C(10)	126.0(11)	C(1)-C(5)-C(10)	126.0(11)
C(4)-C(5)-Sm(1)	75.9(4)	C(1)-C(5)-Sm(1)	75.8(5)
C(10)-C(5)-Sm(1)	114.6(6)	C(4)-C(5)-K(1)	77.4(4)
C(1)-C(5)-K(1)	79.8(4)	C(10)-C(5)-K(1)	109.7(6)
Sm(1)-C(5)-K(1)	135.7(3)	C(12)-C(11)-C(15)	108.0
C(12)-C(11)-C(16)	126.0(10)	C(15)-C(11)-C(16)	126.0(10)
C(12)-C(11)-K(1)	75.5(4)	C(15)-C(11)-K(1)	81.5(4)
C(16)-C(11)-K(1)	109.8(5)	C(13)-C(12)-C(11)	108.0
C(13)-C(12)-C(17)	126.0(11)	C(11)-C(12)-C(17)	126.0(11)
C(13)-C(12)-K(1)	80.8(4)	C(11)-C(12)-K(1)	77.5(4)
C(17)-C(12)-K(1)	108.7(5)	C(12)-C(13)-C(14)	108.0
C(12)-C(13)-C(18)	126.0(11)	C(14)-C(13)-C(18)	126.0(11)
C(12)-C(13)-K(1)	72.6(4)	C(14)-C(13)-K(1)	80.5(4)
C(18)-C(13)-K(1)	113.2(5)	C(15)-C(14)-C(13)	108.0
C(15)-C(14)-C(19)	126.0(10)	C(13)-C(14)-C(19)	126.0(10)
C(15)-C(14)-K(1)	75.3(4)	C(13)-C(14)-K(1)	73.7(3)
C(19)-C(14)-K(1)	117.0(5)	C(14)-C(15)-C(11)	108.0
C(14)-C(15)-C(20)	126.0(9)	C(11)-C(15)-C(20)	126.0(9)
C(14)-C(15)-K(1)	79.0(4)	C(11)-C(15)-K(1)	72.2(3)
C(20)-C(15)-K(1)	114.9(5)	Si(1)-C(21)-Si(2)	120.3(5)
Si(1)-C(21)-Sm(1)	107.5(4)	Si(2)-C(21)-Sm(1)	125.1(5)
O(1)-C(28)-C(29)	112.5(12)	C(30)-C(29)-C(28)	106.7(15)
C(29)-C(30)-C(31)	107(2)	O(1)-C(31)-C(30)	106.2(17)
O(1)-C(31)-K(1)	46.4(6)	C(30)-C(31)-K(1)	149(3)
O(2)-C(32)-C(33)	101.4(15)	C(34)-C(33)-C(32)	105.3(15)
C(33)-C(34)-C(35)	103.2(13)	O(2)-C(35)-C(34)	108.0(11)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x,y-1,z

STable 5. Summary of crystal data for 2.

Empirical formula	C84 H153 K3 O6 Sm6	
Formula weight	2278.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R-3c	
Unit cell dimensions	a = 24.6009(12) Å	$\alpha = 90^\circ$.
	b = 24.6009(12) Å	$\beta = 90^\circ$.
	c = 27.958(2) Å	$\gamma = 120^\circ$.
Volume	14653.5(15) Å ³	
Z	6	
Density (calculated)	1.549 Mg/m ³	
Absorption coefficient	3.718 mm ⁻¹	
F(000)	6803	
Crystal size	0.3 x 0.2 x 0.2 mm ³	
Theta range for data collection	1.66 to 30.47°	
Index ranges	-34 ≤ h ≤ 33, -16 ≤ k ≤ 34, -39 ≤ l ≤ 39	
Reflections collected	36993	
Independent reflections	4746 [R(int) = 0.0573]	
Completeness to theta = 30.47°	95.5 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4746 / 0 / 166	
Goodness-of-fit on F ²	0.826	
Final R indices [I > 2σ(I)]	R1 = 0.0374, wR2 = 0.0856	
R indices (all data)	R1 = 0.1004, wR2 = 0.1067	
Largest diff. peak and hole	1.930 and -0.391 e.Å ⁻³	

STable 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^i tensor.

	x	y	z	$U(\text{eq})$
Sm(1)	5809(1)	3360(1)	188(1)	44(1)
K(1)	6667	5081(1)	833	70(1)
O(1)	7186(3)	6235(3)	355(2)	113(2)
C(1)	4959(3)	3718(3)	-83(2)	61(2)
C(2)	5472(3)	4044(3)	-391(2)	60(2)
C(3)	4657(3)	3071(3)	-187(2)	60(2)
C(4)	4988(3)	2996(3)	-568(2)	58(2)
C(5)	5498(3)	3601(3)	-689(2)	57(2)
C(6)	4726(4)	4012(4)	278(3)	94(3)
C(7)	4046(3)	2551(4)	24(3)	89(2)
C(8)	4786(3)	2398(3)	-834(3)	85(2)
C(9)	5951(3)	3748(4)	-1101(2)	85(2)
C(10)	5873(4)	4737(3)	-4303	88(2)
C(11)	7102(6)	6417(5)	-100(4)	136(4)
C(12)	7403(6)	7075(5)	-130(4)	152(5)
C(13)	7650(8)	7300(5)	318(5)	232(8)
C(14)	7574(5)	6780(5)	607(4)	135(4)
H(1)	6667	3333	-50(30)	90(20)
H(2)	5260(20)	2760(20)	809(15)	43(13)
H(3)	6730(30)	4270(30)	110(30)	70(30)
H(4)	6667	3333	833	140(80)
H(6A)	4927	4048	580	141
H(6B)	4280	3752	314	141
H(6C)	4824	4421	169	141
H(7A)	3719	2413	-211	133
H(7B)	3935	2708	299	133
H(7C)	4100	2205	116	133
H(8A)	4689	2066	-611	127
H(8B)	5119	2448	-1041	127
H(8C)	4421	2297	-1022	127
H(9A)	6014	4120	-1265	128
H(9B)	5779	3402	-1324	128
H(9C)	6345	3814	-984	128
H(10A)	5667	4900	-623	132
H(10B)	6269	4839	-570	132
H(10C)	5943	4918	-114	132
H(11A)	7273	6259	-340	163
H(11B)	6657	6239	-163	163
H(12A)	7734	7230	-368	183
H(12B)	7106	7208	-218	183
H(13A)	7433	7496	465	279
H(13B)	8092	7613	291	279
H(14A)	7978	6813	665	162
H(14B)	7386	6779	912	162

Table 7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm(1)	44(1)	47(1)	43(1)	-2(1)	-2(1)	25(1)
K(1)	80(2)	61(1)	76(1)	-2(1)	-4(1)	40(1)
O(1)	135(6)	76(4)	108(5)	7(4)	0(4)	39(4)
C(1)	67(4)	73(5)	64(4)	-10(3)	-15(3)	50(4)
C(2)	63(4)	57(4)	66(4)	3(3)	-12(3)	36(3)
C(3)	49(4)	70(4)	63(4)	2(3)	-8(3)	31(3)
C(4)	64(4)	63(4)	53(3)	-10(3)	-15(3)	37(4)
C(5)	59(4)	66(4)	50(3)	4(3)	-1(3)	36(3)
C(6)	110(6)	135(8)	84(5)	-29(5)	-19(5)	96(6)
C(7)	54(4)	101(6)	94(6)	8(5)	2(4)	27(4)
C(8)	82(5)	82(5)	85(5)	-29(4)	-26(4)	38(4)
C(9)	79(5)	127(7)	57(4)	11(4)	6(4)	58(5)
C(10)	96(6)	61(4)	112(6)	2(4)	-21(5)	43(4)
C(11)	174(12)	77(7)	133(8)	-8(6)	-37(8)	44(8)
C(12)	180(13)	98(8)	127(9)	9(7)	-9(8)	31(8)
C(13)	350(20)	72(7)	164(13)	-21(8)	-109(13)	21(10)
C(14)	163(11)	106(7)	106(7)	-27(6)	-40(7)	46(7)

STable 8. Bond lengths [Å] and angles [°] for 2.

Sm(1)-C(1)	2.750(6)	Sm(1)-C(2)	2.745(6)
Sm(1)-C(3)	2.760(6)	Sm(1)-C(4)	2.746(6)
Sm(1)-C(5)	2.722(6)	Sm(1)-H(1)	2.25(2)
Sm(1)-H(2)	2.23(4)	Sm(1)-H(3)	2.26(6)
Sm(1)-H(4)	2.8010(3)	Sm(1)-Sm(1)#1	3.6084(6)
Sm(1)-Sm(1)#2	3.7133(5)	Sm(1)-K(1)#3	4.1871(17)
Sm(1)-K(1)	4.0864(17)	K(1)-O(1)#4	2.802(6)
K(1)-O(1)	2.802(6)	K(1)-Sm(1)#4	4.0864(16)
K(1)-Sm(1)#2	4.1871(17)	K(1)-Sm(1)#1	4.1871(17)
K(1)-H(3)	2.89(7)	K(1)-H(2)	2.58(4)
O(1)-C(14)	1.388(10)	O(1)-C(11)	1.399(10)
C(1)-C(2)	1.404(9)	C(1)-C(3)	1.409(9)
C(1)-C(6)	1.510(9)	C(2)-C(5)	1.397(8)
C(2)-C(10)	1.486(9)	C(3)-C(4)	1.406(9)
C(3)-C(7)	1.524(9)	C(4)-C(5)	1.427(8)
C(4)-C(8)	1.495(9)	C(5)-C(9)	1.521(8)
C(11)-C(12)	1.406(13)	C(12)-C(13)	1.380(14)
C(13)-C(14)	1.444(14)		
C(5)-Sm(1)-C(1)	48.75(19)	C(5)-Sm(1)-C(4)	30.26(18)
C(1)-Sm(1)-C(4)	48.64(18)	C(5)-Sm(1)-C(2)	29.61(18)
C(1)-Sm(1)-C(2)	29.6(2)	C(4)-Sm(1)-C(2)	49.24(19)
C(5)-Sm(1)-C(3)	49.40(19)	C(1)-Sm(1)-C(3)	29.63(19)
C(4)-Sm(1)-C(3)	29.58(18)	C(2)-Sm(1)-C(3)	49.29(19)
Sm(1)#1-Sm(1)-Sm(1)#2	90.847(4)	Sm(1)#1-Sm(1)-Sm(1)#3	89.070(5)
Sm(1)#2-Sm(1)-Sm(1)#3	60.0	Sm(1)#1-Sm(1)-K(1)	65.590(14)
Sm(1)#2-Sm(1)-K(1)	64.729(14)	Sm(1)#3-Sm(1)-K(1)	118.041(19)
Sm(1)#2-Sm(1)-K(1)#3	115.596(18)	K(1)-Sm(1)-K(1)#3	128.30(2)
Sm(1)-H1-Sm(1)#2	111.4 (4)	Sm(1)-H1-Sm(1)#3	111.4 (4)
Sm(1)-H2-Sm(1)#1	106.0(11)	Sm(1)-H2-K(1)	120.7(11)
Sm(1)#1-H2-K(1)	114.3(11)	Sm(1)-H3-Sm(1)#2	114.6(12)
Sm(1)-H3-K(1)	104.3(6)	Sm(1)#2-H3-K(1)	111.5(6)
Sm(1)-H4-Sm(1)#1	80.2(5)	Sm(1)-H4-Sm(1)#2	83(1)
Sm(1)-H4-Sm(1)#4	137.2(5)	H(1)-Sm(1)-H(2)	118.4(18)
H(1)-Sm(1)-H(3)	61.0(16)	H(2)-Sm(1)-H(3)	134(2)
O(1)#4-K(1)-O(1)	76.5(3)	O(1)#4-K(1)-H(3)	155.6(12)
O(1)-K(1)-H(3)	102.0(14)	C(14)-O(1)-C(11)	106.9(7)
C(14)-O(1)-K(1)	118.9(6)	C(11)-O(1)-K(1)	133.9(6)
C(2)-C(1)-C(3)	109.4(6)	C(2)-C(1)-C(6)	125.9(7)
C(3)-C(1)-C(6)	124.6(7)	C(2)-C(1)-Sm(1)	75.0(3)
C(3)-C(1)-Sm(1)	75.6(3)	C(6)-C(1)-Sm(1)	120.0(4)
C(1)-C(2)-C(5)	107.5(6)	C(1)-C(2)-C(10)	126.1(7)
C(5)-C(2)-C(10)	126.2(7)	C(1)-C(2)-Sm(1)	75.4(3)
C(5)-C(2)-Sm(1)	74.3(3)	C(10)-C(2)-Sm(1)	120.9(4)
C(4)-C(3)-C(1)	107.1(6)	C(4)-C(3)-C(7)	125.1(7)
C(1)-C(3)-C(7)	127.5(7)	C(4)-C(3)-Sm(1)	74.7(3)
C(1)-C(3)-Sm(1)	74.8(3)	C(7)-C(3)-Sm(1)	121.5(5)
C(3)-C(4)-C(5)	107.9(5)	C(3)-C(4)-C(8)	125.3(6)
C(5)-C(4)-C(8)	126.4(6)	C(3)-C(4)-Sm(1)	75.8(3)
C(5)-C(4)-Sm(1)	73.9(3)	C(8)-C(4)-Sm(1)	122.1(4)
C(2)-C(5)-C(4)	108.2(6)	C(2)-C(5)-C(9)	125.6(6)
C(4)-C(5)-C(9)	125.9(6)	C(2)-C(5)-Sm(1)	76.1(3)
C(4)-C(5)-Sm(1)	75.8(3)	C(9)-C(5)-Sm(1)	119.1(4)
C(12)-C(11)-O(1)	110.2(9)	C(13)-C(12)-C(11)	106.3(11)
C(12)-C(13)-C(14)	108.4(10)	O(1)-C(14)-C(13)	107.2(8)

#1 $x-y+1/3, -y+2/3, -z+1/6$ #2 $-x+y+1, -x+1, z$ #3 $-y+1, x-y, z$ #4 $-x+4/3, -x+y+2/3, -z+1/6$

Figure 1. ORTEP drawing of 1

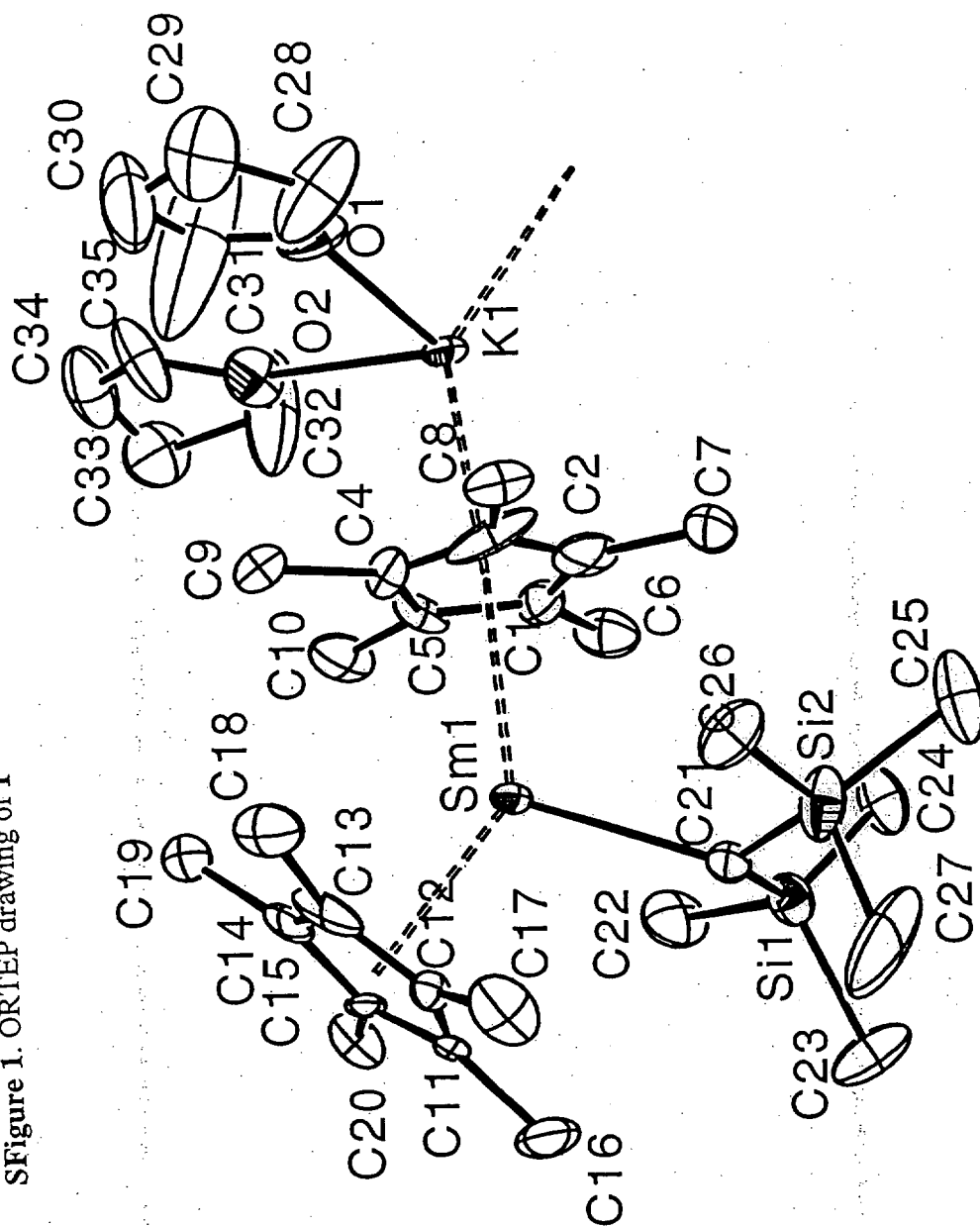


Figure 2. ORTEP drawing of 2

