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Synthesis, Structure, and Reactivity of Peralkylcyclopentadienyl *ansa*-Metallocenes of Samarium: Effect of Steric Crowding on the Reactivity of Tris(peralkylcyclopentadienyl)samarium Complexes

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Tris(peralkylcyclopentadienyl)samarium complexes containing two rings connected by a Me_2Si group were synthesized for comparison with $(C_5Me_5)_3Sm$. SmI_3 reacts with $Me_2Si(C_5Me_4K)_2$ in THF to make $Me_2Si(C_5Me_4)_2SmI(THF)$ (**1**) in >90% yield. **1** reacts with KC_5Me_5 in toluene to make $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (**2a**) and in THF to make $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (**2b**). **1** reacts with KC_5Me_4Et, $KC_5Me_4{}^nPr$, and $KC_5Me_4{}^iPr$ in toluene to make $Me_2Si(C_5Me_4)_2Sm(C_5Me_4Et)$ (**3**), $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (**4**), and $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^iPr)$ (**5**), respectively. In contrast to the reactivity of $(C_5Me_5)_3Sm$, complexes **2a** and **3**−**5** do not ring-open THF, do not reduce 1,3,5,7-C_8H_8 or $Ph_3P{=}Se$, and do not polymerize ethylene at 50 psi. Structural data were obtained on **1**, **2a**, **2b**, and **4**. The (ring centroid)−metal−(ring centroid) angles of the $Me_2Si(C_5Me_4)_2$ units in each structure range from 115.2° (**2b**) to 123.3° (**1**) and have average Sm−C(ring) distances of 2.70(6) Å (**1**), 2.82(10) Å (**2a**), 2.92(14) Å (**2b**), and 2.83(10) Å (**4**). The average Sm−C(C_5Me_4R) distance is 2.77(3) Å in **2a**, 2.82(4) Å in **2b**, and 2.78(3) Å in **4**. The β-carbon of the propyl substituent in **4** is oriented toward samarium at a distance of 3.36 Å.

Introduction

For many years, tris(pentamethylcyclopentadienyl)metal compounds were thought to be too sterically crowded to exist. Hence, the isolation and crystallographic characterization of $(C_5Me_5)_3Sm$ were unexpected.[1] It was further surprising that this sterically crowded molecule could have such diverse reaction chemistry, which included CO insertion,[2] olefin polymerization,[3] THF ring opening,[4] and reductive reactivity.[4] Since the enhanced reactivity of the normally inert C_5Me_5 rings could be rationalized on the basis of the extreme steric crowding in this molecule, it was of interest to make closely related samarium complexes with slightly less sterically hindered ligand environments to compare their reactivity. *ansa*-Metallocene cyclopentadienides, $Me_2Si(C_5Me_4)_2Sm(C_5Me_4R)$, would meet this requirement, since the (ring centroid)−metal−(ring centroid) angles of *ansa*-metallocenes are typically smaller compared to those of unconnected bis(cyclopentadienyl)metal systems.[5,6] The smaller angle provides more space for the remaining ligands. Examples of this class of compounds have been previously reported for $[Me_2Si(C_5H_3{}^tBu)(C_5Me_4)]Ln(C_5Me_4H)(THF)$,[6] where Ln = La and Nd. For the purpose of comparison with $(C_5Me_5)_3Sm$, complexes with the same metal and ligands of more similar size were desired.

Accordingly, we report here a direct, general synthesis of dimethylsilylene-bridged bis(tetramethylcyclopentadienyl)lanthanide peralkylcyclopentadienide compounds, $Me_2Si(C_5Me_4)_2Sm(C_5Me_4R)$ (R = Me, Et, ^{n}Pr, ^{i}Pr), and a comparison of their structures and reactivity to those of $(C_5Me_5)_3Sm$. We also describe further evidence for long-distance interactions between lanthanide centers and the ethyl and propyl groups attached to cyclopentadienyl rings.[1b,7]

Experimental Section

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were purified and dried over sodium or potassium benzophenone ketyl or

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over sodium/potassium alloy. $\mathrm{SmI_3}$ was prepared from samarium powder and 1.5 equiv of diiodoethane in THF. $\mathrm{Me_2Si(C_5Me_4K)_2}$ was synthesized from $\mathrm{Me_2Si(C_5Me_4H)_2}$[8] and potassium hydride. $\mathrm{K(C_5Me_4R)}$ (R = Me, Et, $^{\mathrm{n}}$Pr, $^{\mathrm{i}}$Pr) was prepared from $\mathrm{C_5Me_4RH}$ and potassium hydride. ^{1}H, ^{13}C, and HMQC NMR spectra were obtained on a Bruker DRX 400 spectrometer. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrometer. Complexometric titrations were conducted as previously described.[9]

$\mathrm{Me_2Si(C_5Me_4)_2SmI(THF)}$ (1). In the glovebox, 40 mL of THF was added to $\mathrm{SmI_3(THF)_2}$ (1.621 g, 2.40 mmol) and $\mathrm{Me_2Si(C_5Me_4K)_2}$ (0.909 g, 2.42 mmol) in a 100 mL round-bottom flask, and the reaction mixture was stirred. Within minutes a turbid amber mixture formed. After 20 h, the mixture was filtered through a glass frit to separate an amber solution from a white solid, which was discarded. Rotary evaporation of the solvent yielded **1** (1.433 g, 92%) as an amber powder. Anal. Calcd for $\mathrm{C_{24}H_{38}IOSiSm}$: Sm, 23.2. Found: Sm, 23.0. ^{1}H NMR (THF-d_8): δ 3.63 (m, 4H, THF), 3.13 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), 1.78 (m, 4H, THF), 0.94 (s, 6H, $\mathit{Me}_2\mathrm{Si}$), −1.80 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$). ^{13}C NMR (THF-$d_8$): δ 127.7, 126.8, 115.5 ($\mathit{C}_5\mathrm{Me_4}$), 66.2 (THF), 24.0 (THF), 21.6, 17.3 ($\mathrm{C_5}\mathit{Me}_4$), 6.6 ($\mathit{Me}_2\mathrm{Si}$). IR (Nujol): 2856 s, 2726 w, 2360 w, 1612 w, 1464 s, 1377 s, 1306 w, 1262 w, 1154 w, 1075 w, 1012 w, 952 w, 835 w, 812 w, 744 m, 722 m cm^{-1}. Crystals of $\mathrm{Me_2Si(C_5Me_4)_2SmI(THF)}$ (**1**) suitable for X-ray diffraction were grown in THF at −40 °C as orange prisms.

$\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_5)}$ (2a). In the glovebox, 10 mL of toluene was added to **1** (202.4 mg, 0.31 mmol) and $\mathrm{KC_5Me_5}$ (59.8 mg, 0.34 mmol). Within several minutes the solution darkened to a reddish orange hue. After it was stirred overnight, the mixture was centrifuged and a red solution was separated from orange solids. Toluene was removed by rotary evaporation from the red solution, and the resulting solids were extracted with hexanes. The hexanes extract was centrifuged to remove any remaining solids, and the solution was dried to afford red-brown **2a** (120 mg, 66%). Anal. Calcd for $\mathrm{C_{30}H_{45}SiSm}$: Sm, 25.7. Found: Sm, 25.4. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.72 (s, 6H, $\mathit{Me}_2\mathrm{Si}$), −0.28 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −1.34 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), −5.49 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$). ^{13}C NMR: δ 121.2 ($\mathit{C}_5\mathrm{Me_4}$), 114.8 ($\mathit{C}_5\mathrm{Me_4}$), 111.7 ($\mathit{C}_5\mathrm{Me_4}$), 28.1 ($\mathrm{C_5}\mathit{Me}_5$), 27.8 ($\mathrm{C_5}\mathit{Me}_4$), 22.1 ($\mathrm{C_5}\mathit{Me}_4$), 11.5 ($\mathit{Me}_2\mathrm{Si}$). IR (neat): 2911 s, 2855 s, 2358 s, 2340 m, 1435 m, 1374 m, 1323 w, 1245 m, 1084 s, 809 s cm^{-1}. Crystals of $\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_5)}$ (**2a**) suitable for X-ray diffraction were grown in hot hexanes as red prisms.

$\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)}$ (2b). In the glovebox, 10 mL of THF was added to **1** (223.2 mg, 0.34 mmol) and $\mathrm{KC_5Me_5}$ (66.0 mg, 0.38 mmol). Within several minutes the mixture darkened slightly. After it was stirred overnight, the mixture was centrifuged to separate white solids from an orange solution. THF was removed by rotary evaporation from the solution, and the resulting solids were extracted with toluene. This red solution was centrifuged to remove residual white solids, and the toluene was removed. The resulting solids were extracted with hexanes, and the mixture was centrifuged to yield a red solution and orange solids, which proved to be unreacted **1**. The red hexanes solution was dried to afford **2b** (103.8 mg, 52%). Anal. Calcd for $\mathrm{C_{34}H_{53}OSiSm}$: Sm, 22.9. Found: Sm, 23.4. ^{1}H NMR (THF-d_8): δ 3.54 (br s, 8H, THF), 2.28 (s, 6H, $\mathit{Me}_2\mathrm{Si}$), 1.70 (br s, 8H, THF), 0.03 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), −0.31 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −1.76 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$). IR (neat): 2951 s, 2912 s, 2853 s, 2038 s, 1798 s, 1483 w, 1462 m, 1436 m, 1377 w, 1096 w, 872 m, 832 s, 745 m, 708 w, 691 m, 616 w, 557 m, 524 m cm^{-1}. Crystals of $\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)}$ (**2b**) suitable for X-ray diffraction were grown in THF at −40 °C as red prisms.

$\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_4Et)}$ (3). In the glovebox, 10 mL of toluene was added to **1** (234 mg, 0.36 mmol) and $\mathrm{KC_5Me_4Et}$ (68.9 mg, 0.37 mmol). Within a few minutes the mixture turned red-orange. After it was stirred overnight, the mixture was centrifuged and a red solution was separated from white solids. Toluene was removed by rotary evaporation from the red solution, and the remaining solids were extracted with hexanes. The red hexanes extract was centrifuged to remove any remaining solids, and the solution was dried to afford a brown powder, **3** (164 mg, 76%). Anal. Calcd for $\mathrm{C_{31}H_{47}SiSm}$: Sm, 25.1. Found: Sm, 25.4. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.69 (s, 6H, $\mathit{Me}_2\mathrm{Si}$), 2.10 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), −0.32 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −0.44 (br s, 2H, $\mathrm{C_5Me_4C}\mathit{H}_2\mathrm{CH_3}$), −2.58 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), −4.97 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −20.96 (br s, 3H, $\mathrm{C_5Me_4CH_2C}\mathit{H}_3$). ^{13}C NMR: δ 125.1 ($\mathit{C}_5\mathrm{Me_4Et}$), 121.3 ($\mathit{C}_5\mathrm{Me_4}$), 114.8 ($\mathit{C}_5\mathrm{Me_4}$), 113.5 ($\mathit{C}_5\mathrm{Me_4Et}$), 111.7 ($\mathit{C}_5\mathrm{Me_4Et}$), 111.1 ($\mathit{C}_5\mathrm{Me_4}$), 33.7 ($\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 27.3 ($\mathrm{C_5}\mathit{Me}_4$), 27.0 ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2CH_3}$), 25.0 ($\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 22.0 ($\mathrm{C_5}\mathit{Me}_4$), 20.9 ($\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_3}$), 11.4 ($\mathit{Me}_2\mathrm{Si}$). IR (neat): 2912 s, 1444 m, 1322 w, 1244 m, 823 s, 811 m cm^{-1}.

$\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)}$ (4). In the glovebox, 10 mL of toluene was added to **1** (135.5 mg, 0.209 mmol) and $\mathrm{KC_5Me_4{}^nPr}$ (44.7 mg, 0.221 mmol). Within a few minutes the mixture turned red-orange. After it was stirred overnight, the mixture was centrifuged and a red solution was separated from white solids. Toluene was removed by rotary evaporation from the red solution, and the solids were extracted with hexanes. The red hexanes extract was centrifuged to remove any remaining solids, and the solution was dried to afford a brown powder, **4** (108.9 mg, 85%). Anal. Calcd for $\mathrm{C_{32}H_{49}SiSm}$: Sm, 24.6. Found: Sm, 24.2. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.68 (s, 6H, $\mathit{Me}_2\mathrm{Si}$), 2.32 (s, 6H, $\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{n}}\mathrm{Pr}$), −0.31 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −0.43 (s, 2H, $\mathrm{C_5Me_4C}\mathit{H}_2\mathrm{CH_2CH_3}$), −2.65 (s, 6H, $\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{n}}\mathrm{Pr}$), −4.82 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −8.58 (s, 3H, $\mathrm{C_5Me_4CH_2CH_2C}\mathit{H}_3$), −26.32 (br s, 2H, $\mathrm{C_5Me_4CH_2C}\mathit{H}_2\mathrm{CH_3}$). ^{13}C NMR: δ 121.3 ($\mathit{C}_5\mathrm{Me_4}$), 114.5 ($\mathit{C}_5\mathrm{Me_4}$), 114.2 ($\mathit{C}_5\mathrm{Me_4{}^nPr}$), 111.1 ($\mathit{C}_5\mathrm{Me_4{}^nPr}$), 111.0 ($\mathit{C}_5\mathrm{Me_4}$), 36.4 ($\mathrm{C_5Me_4\ }\mathit{C}\mathrm{H_2CH_2CH_3}$), 34.4 ($\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_2CH_3}$), 33.9 ($\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{n}}\mathrm{Pr}$), 27.1 ($\mathrm{C_5}\mathit{Me}_4$), 24.7 ($\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{n}}\mathrm{Pr}$), 22.0 ($\mathrm{C_5}\mathit{Me}_4$), 11.3 ($\mathit{Me}_2\mathrm{Si}$), 5.3 ($\mathrm{C_5Me_4\ CH_2CH_2}\mathit{C}\mathrm{H_3}$). IR (neat): 2911 s, 1442 m, 1324 w, 1246 m, 823 s, 811 m cm^{-1}. Crystals suitable for X-ray diffraction were grown in hexanes at −40 °C as red plates.

$\mathrm{Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^iPr)}$ (5). In the glovebox, 10 mL of toluene was added to **1** (138.0 mg, 0.213 mmol) and $\mathrm{KC_5Me_4{}^iPr}$ (43.7 mg, 0.216 mmol). Within a few minutes the mixture turned red-orange. After it was stirred overnight, the mixture was centrifuged and a red solution was separated from orange-white solids. Toluene was removed by rotary evaporation from the red solution, and the resulting solids were extracted with hexanes. The red hexanes extract was centrifuged to remove any remaining solids, and the solution was dried to afford a brown powder, **5** (35 mg, 27%). Anal. Calcd for $\mathrm{C_{32}H_{49}SiSm}$: Sm, 24.6. Found: Sm, 24.2. ^{1}H NMR ($\mathrm{C_6D_6}$, 70 °C): δ 2.58 (s, 6H, $\mathit{Me}_2\mathrm{Si}$), 2.45 (s, 6H, $\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{i}}\mathrm{Pr}$), −0.42 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −2.45 (s, 6H, $\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{i}}\mathrm{Pr}$), −4.51 (s, 12H, $\mathrm{C_5}\mathit{Me}_4$), −9.60 (s, 6H, $\mathrm{C_5Me_4CH(}\mathit{Me}\mathrm{)_2}$). ^{13}C NMR (70 °C): δ 125.0 ($\mathit{C}_5\mathrm{Me_4{}^iPr}$), 120.6 ($\mathit{C}_5\mathrm{Me_4}$), 114.8 ($\mathit{C}_5\mathrm{Me_4}$), 113.0 ($\mathit{C}_5\mathrm{Me_4{}^iPr}$), 111.3 ($\mathit{C}_5\mathrm{Me_4{}^iPr}$), 110.7 ($\mathit{C}_5\mathrm{Me_4}$), 34.3 ($\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{i}}\mathrm{Pr}$), 26.3 ($\mathrm{C_5}\mathit{Me}_4$), 23.9 ($\mathrm{C_5}\mathit{Me}_4{}^{\mathrm{i}}\mathrm{Pr}$), 21.9 ($\mathrm{C_5}\mathit{Me}_4$), 11.0 ($\mathit{Me}_2\mathrm{Si}$), 10.6 ($\mathrm{C_5Me_4CH(}\mathit{C}\mathrm{H_3)_2}$). IR (neat): 2911 s, 1443 m, 1326 w, 1247 m, 823 s, 814 m cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $\mathrm{Me_2Si(C_5Me_4)_2SmI(THF)}$ (1). An orange crystal of approximate dimensions 0.13 × 0.14 × 0.27 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The determination of the Laue symmetry, the crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.[10] Intensity data were collected at 158 K using a $2\theta/\omega$ scan technique with Mo Kα radiation. The raw data were processed with a local version of CARESS,[11] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out using the SHELXTL program.[12] All 7760 data were corrected for absorp-

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Table 1. Experimental Data for the X-ray Diffraction Studies of $Me_2Si(C_5Me_4)_2SmI(THF)$ (1), $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a), and $Me_2Si(C_5Me_3)_2Sm(C_5Me_4{}^nPr)$ (4)

	1	**2a**	**4**
formula	$C_{24}H_{38}IOSiSm$	$C_{30}H_{45}SiSm$	$C_{32}H_{49}SiSm \cdot {}^1/_2C_6H_{14}$
fw	647.88	584.10	655.24
temp (K)	158	157	163
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.7380(9)	9.5710(5)	9.6021(9)
b (Å)	9.980(2)	9.8478(5)	10.066(2)
c (Å)	16.542(2)	15.7165(8)	18.85798(13)
α (deg)	75.254(12)	84.8790(10)	75.467(8)
β (deg)	76.317(8)	82.0630(10)	79.541(7)
γ (deg)	66.057 (9)	70.8850(10)	67.675(11)
V (Å^3)	1260.4(3)	1384.71(12)	1624.5(3)
Z	2	2	2
D(calcd) (g/cm^3)	1.707	1.401	1.340
diffractometer[a]	Siemens P4	Siemens CCD	Siemens P4
μ (mm^{-1})	3.613	2.179	1.865
R1 ($I > 2\sigma(I)$)[b]	0.0263	0.0240	0.0277

[a] Radiation: Mo Kα ($\mu = 0.710\ 73$ Å). Monochromator: graphite. [b] $R1 = [\sum||F_o| - |F_c||/\sum|F_o|]$.

tion and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences, nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.[13] Hydrogen atoms were included in a riding model. At convergence, wR2 = 0.0567 and GOF = 1.083 for 254 variables refined against all 7315 unique data (as a comparison for refinement of F, R1 = 0.0219 for those 6649 data with $F > 4.0\sigma(F)$). Crystal data and selected experimental information are listed in Table 1.

X-ray Data Collection, Structure Determination, and Refinement for $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a). An orange-red crystal of approximate dimensions 0.25 × 0.40 × 0.45 mm was mounted on a glass fiber in oil and transferred to a Siemens CCD platform diffractometer. The determination of crystal class and unit cell parameters was carried out by standard procedures.[14] Intensity data were collected at 157 K with Mo Kα radiation in 20 s frames. The raw frame data were processed using SAINT[15] and SADABS[16] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program.[12] There were no systematic absences, nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was determined to be correct by solution and subsequent refinement of the structure.

The structure was solved, and analytical scattering factors for neutral atoms were used as described for **1**. Hydrogen atoms were included using a riding model. All non-hydrogen atoms were refined anisotropically. At convergence, wR2 = 0.0669 and GOF = 1.095 for 289 variables refined against 6469 unique data (as a comparison for refinement on F, R1 = 0.0240 for those 6159 data with $F > 4\sigma(F)$). Crystal data and selected experimental information are listed in Table 1.

X-ray Data Collection, Structure Determination, and Refinement for $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (2b). A red crystal was handled as described above for **1**. The diffraction symmetry was *mmm*, and the systematic absences were consistent with either the noncentrosymmetric space group $Pna2_1$ or the centrosymmetric space group $Pnma$. It was later determined that space group $Pna2_1$ was correct.

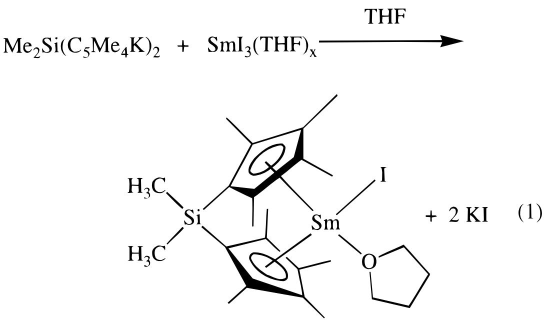
The structure was solved, and analytical scattering factors for neutral atoms were used as described for **1**. Hydrogen atoms were included in a riding model. Isotropic refinement of the light atoms was necessary due to the low data-to-parameter ratio. Anisotropic refinement was attempted, but this led to several atoms becoming nonpositive-definite. At convergence, wR2 = 0.0903 and GOF = 1.096 for 160 variables refined against all 2107 unique data (as a comparison for refinement of F, R1 = 0.0356 for those 1582 data with $F > 4.0\sigma(F)$). The absolute structure was assigned by refinement of the Flack parameter.[17]

X-ray Data Collection, Structure Determination, and Refinement for $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (4). A red crystal of approximate dimensions 0.10 × 0.33 × 0.37 mm was handled as described above for **1**. There were no systematic absences, nor any diffraction symmetry other than the Friedel condition. The noncentrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved, and analytical scattering factors for neutral atoms were used as described for **1**. Hydrogen atoms were included using a riding model. There are two independent molecules in the unit cell as well as a molecule of hexane (a half-molecule of hexane per formula unit), which is disordered. Carbon atoms C(68) and C(69) were included with two components which were assigned site-occupancy factors of 0.65 for the A components and 0.35 for the B components. Hydrogen atoms associated with the hexane were not included in the refinement. Although there was no apparent crystallographic problem with the data, anisotropic refinement led to several atoms becoming nonpositive-definite. Therefore, isotropic refinement for the light atoms was necessary. At convergence, wR2 = 0.0744 and GOF = 1.056 for 327 variables refined against all 5178 unique data (as a comparison for refinement on F, R1 = 0.0277 for those 4686 data with $F > 4.0\sigma(F)$). The absolute structure was assigned by refinement of the Flack parameter.[17] Crystal data and selected experimental information are listed in Table 1.

Results

Synthesis of $Me_2Si(C_5Me_4)_2SmI(THF)$ (1). The direct reaction of dipotassium dimethylbis(tetramethylcyclopentadienyl)silane with SmI_3 in THF leads to the ionic metathesis product $Me_2Si(C_5Me_4)_2SmI(THF)$ (**1**) in >90% yield, as shown in eq 1. The above synthesis is



analogous to the synthesis of $Me_2Si(C_5Me_4)_2LnCl_2Li(Et_2O)_2$ (Ln = Nd, Lu) from $LnCl_3$ and $Me_2Si(C_5Me_4Li)_2$.[5i] The ^1H NMR spectrum of **1** (Table 2) contains resonances at 3.13 and −1.80 ppm, which can be assigned to the methyl groups on the cyclopentadienyl rings, and a singlet at 0.94 ppm, which is assigned to the silylene methyl groups. A similar resonance pattern

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(13) *International Tables for X-ray Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

(14) *SMART Software Users Guide*, Version 4.21; Siemens Industrial Automation: Madison, WI, 1996.

(15) *SAINT Software Users Guide*, Version 4.05; Siemens Industrial Automation: Madison, WI, 1996.

(16) Sheldrick, G. M. SADABS; Siemens Industrial Automation, Inc.; Madison, WI, 1996.

(17) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

Table 2. ^{1}H NMR Data of *ansa*-Metallocene Compounds $Me_2Si(C_5Me_4)_2SmI(THF)$ (1), $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a), $Me_2Si(C_5Me_4)_2Sm(C_5Me_4Et)$ (3), $Me_2Si(C_5Me_3)_2Sm(C_5Me_4{}^nPr)$ (4), and $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^iPr)$ (5)

	δ					
assignt	**1**[a]	**2a**[b]	**2b**[a]	**3**[b]	**4**[b]	**5**[c]
Me_2Si	0.94	2.72	2.28	2.69	2.68	2.58
$C_5\mathit{Me}_4$	3.13, −1.80	−0.28, −5.49	−0.31, −1.76	−0.32, −4.97	−0.31, −4.82	−0.42, −4.51
$C_5\mathit{Me}_5$		−1.34	0.03			
$C_5\mathit{Me}_4Et$				2.10, −2.58		
$C_5Me_4C\mathit{H}_2CH_3$				−0.44		
$C_5Me_4CH_2C\mathit{H}_3$				−20.96		
$C_5\mathit{Me}_4{}^nPr$					2.32, −2.65	
$C_5Me_4C\mathit{H}_2CH_2CH_3$					−0.43	
$C_5Me_4CH_2C\mathit{H}_2CH_3$					−26.32	
$C_5Me_4CH_2CH_2C\mathit{H}_3$					−8.58	
$C_5\mathit{Me}_4{}^nPr$						2.45, −2.45
$C_5Me_4CH(C\mathit{H}_3)_2$						−9.60

[a] Taken at 25 °C in THF-d_8, THF resonances omitted. [b] Taken at 25 °C in C_6D_6. [c] Taken at 70 °C in C_6D_6.

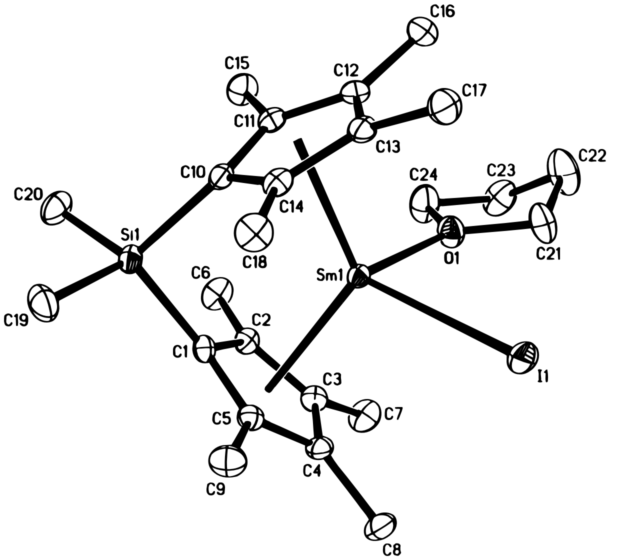


Figure 1. Thermal ellipsoid plot of $Me_2Si(C_5Me_4)_2SmI(THF)$ (**1**) with ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

was observed in the ^{1}H NMR spectrum of $Me_2Si(C_5Me_4)_2NdCl_2Li(ether)_2$.[5i] A samarium analogue of this LiCl adduct was synthesized in situ, but it was never characterized by spectroscopic methods.[5i]

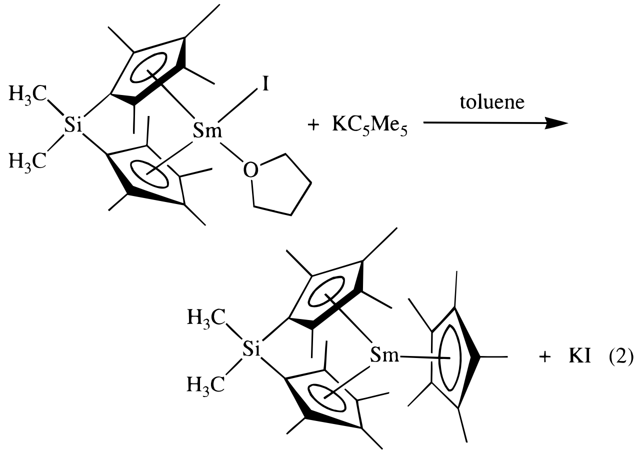
Structure of $Me_2Si(C_5Me_4)_2SmI(THF)$ (1). Complex **1** was characterized by X-ray crystallography (Figure 1) so that direct structural comparison with $(C_5Me_5)_2SmI(THF)$[18] could be made. A comparative summary of the bond lengths and bond angles is given in Table 3. All of the analogous bond lengths listed in Table 3 for the two compounds are equivalent within the error limits. However, the two most important bond angles, the (ring centroid)−metal−(ring centroid) angle and the I−Sm−O angle, differ. The (ring centroid)−metal−(ring centroid) angle in **1** is 13−14° smaller than that in $(C_5Me_5)_2SmI(THF)$. Hence, **1** is more open than $(C_5Me_5)_2SmI(THF)$ and the silylene bridge creates a less sterically hindered metallocene. Related to this, the I−Sm−O angle in **1** is 3−5° larger than in $(C_5Me_5)_2SmI(THF)$. Similar differences in (ring centroid)−metal−(ring centroid) angles have been noted in the pairs $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$[19]/$Me_2Si(C_5Me_4)_2Nd[CH(SiMe_3)_2]$[5i] and $(C_5Me_5)_2Y[CH(SiMe_3)_2]$[20]/$Me_2Si(C_5Me_4)_2Y[CH(SiMe_3)_2]$:[5c] the (ring centroid)−metal−(ring centroid) angle contracts from 134.4 to 121.3° in the neodymium case and from 134.4 to 124.3° in the yttrium case.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Me_2Si(C_5Me_4)_2SmI(THF)$ (1) vs $(C_5Me_5)_2SmI(THF)$

$Me_2Si(C_5Me_4)_2SmI(THF)$		$(C_5Me_5)_2SmI(THF)$[a]	
Sm(1)−I(1)	3.0485(4)	Sm(1)−I(1)	3.043(2), 3.053(2)
Sm(1)−O(1)	2.427(2)	Sm(1)−O(1)	2.45(1), 2.45(1)
Sm(1)−Cnt(1)	2.412	Sm(1)−Cnt(1)	2.47(2), 2.46(2)
Sm(1)−Cnt(2)	2.415	Sm(1)−Cnt(2)	2.44(2), 2.45(2)
Cnt−Sm−Cnt	123.3	Cnt−Sm−Cnt	136(1), 137(1)
Cnt−Sm−I	109.7, 110.7	Cnt−Sm−I	106.2(2), 106.1(2) 104.7(2), 106.4(2)
Cnt−Sm−O	108.4, 107.2	Cnt−Sm−O	105.7(4), 104.2(4) 104.4(4), 104.6(4)
I−Sm−O	93.24(5)	I−Sm−O	88.8(3), 90.5(3)

[a] Two molecules in the unit cell.

Synthesis of $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a) and $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (2b). The reaction of KC_5Me_5 with **1** in toluene gives the (pentamethylcyclopentadienyl)samarium *ansa*-metallocene $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (**2a**) in 66% yield according to eq 2. **2a** was characterized by elemental analysis and IR and NMR spectroscopy and by a single-crystal X-ray diffraction study (Figure 2). The resonances in the ^{1}H NMR



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[18] Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614−3619.

[19] (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. (b) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200−202.

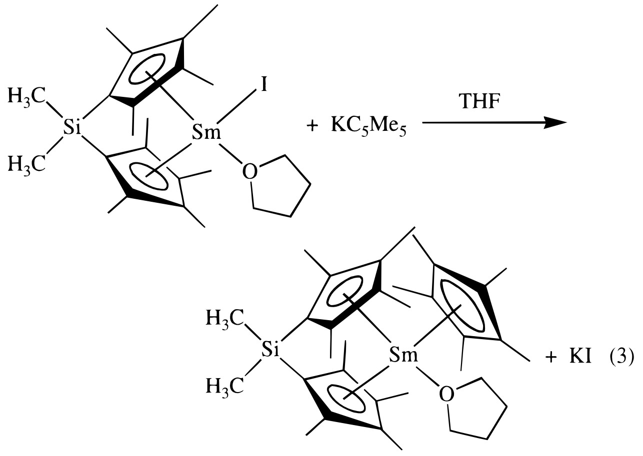
Table 4. ^{13}C NMR Data of *ansa*-Metallocene Compounds $Me_2Si(C_5Me_4)_2SmI(THF)$ (1), $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a), $Me_2Si(C_5Me_4)_2Sm(C_5Me_4Et)$ (3), $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (4), and $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^iPr)$ (5)

	δ				
assignt	**1**[a]	**2a**[b]	**3**[b]	**4**[b]	**5**[c]
$\mathit{Me}_2\mathrm{Si}$	6.6	11.5	11.4	11.3	11.0
$\mathit{C}_5\mathrm{Me}_4$	127.7, 126.8, 115.5	121.1, 116.0, 111.7	121.3, 114.8, 111.1	121.3, 114.5, 111.1	120.6, 114.8, 110.7
$\mathrm{C}_5\mathit{Me}_4$	21.6, 17.3	27.8, 22.1	27.3, 22.0	27.1, 22.0	26.3, 21.9
$\mathit{C}_5\mathrm{Me}_5$		114.8			
$\mathrm{C}_5\mathit{Me}_5$		28.1			
$\mathit{C}_5\mathrm{Me}_4\mathrm{Et}$		125.1, 113.5, 111.7			
$\mathrm{C}_5\mathit{Me}_4\mathrm{Et}$			33.7, 25.0		
$\mathrm{C}_5\mathrm{Me}_4\mathit{C}\mathrm{H}_2\mathrm{CH}_3$			27.0		
$\mathrm{C}_5\mathrm{Me}_4\mathrm{CH}_2\mathit{C}\mathrm{H}_3$			20.9		
$\mathrm{C}_5\mathrm{Me}_4\mathrm{CH}_2\mathrm{CH}_2\mathrm{C}\mathit{H}_3$				−125.1, 114.2, 111.0	
$\mathrm{C}_5\mathit{Me}_4{}^n\mathrm{Pr}$				33.9, 24.7	
$\mathrm{C}_5\mathrm{Me}_4\mathit{C}\mathrm{H}_2\mathrm{CH}_2\mathrm{CH}_3$				36.4	
$\mathrm{C}_5\mathrm{Me}_4\mathrm{CH}_2\mathit{C}\mathrm{H}_2\mathrm{CH}_3$				34.4	
$\mathrm{C}_5\mathrm{Me}_4\mathrm{CH}_2\mathrm{CH}_2\mathrm{C}\mathit{H}_3$				5.3	
$\mathit{C}_5\mathrm{Me}_4{}^i\mathrm{Pr}$					125.3, 113.0, 111.5
$\mathrm{C}_5\mathit{Me}_4{}^i\mathrm{Pr}$					34.3, 23.9
$\mathrm{C}_5\mathrm{Me}_4\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$					10.6

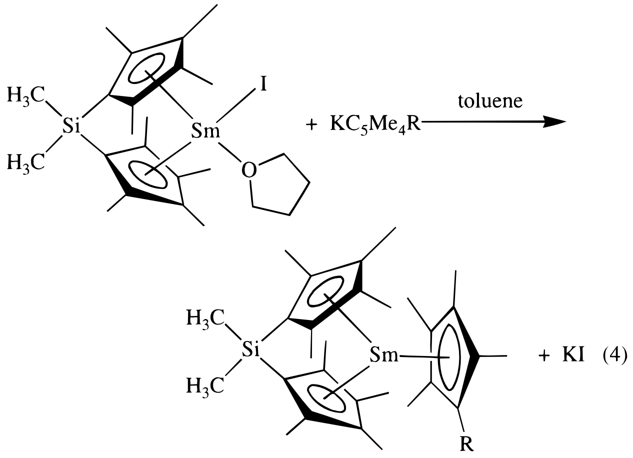
[a] Taken at 25 °C in THF-d_8, THF resonances omitted. [b] Taken at 25 °C in C_6D_6. [c] Taken at 70 °C in C_6D_6.

spectrum of **2a** shift from those of **1,** as shown in Table 2. The ^{13}C NMR (Table 4) spectrum was assigned via an HMQC experiment.

When reaction 2 is performed in THF, the THF solvate of **2a**, $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (**2b**), is obtained according to eq 3. **2b** was characterized by IR and NMR spectrometry and by X-ray diffraction (Figure 3). **2b** can also be made by adding THF directly to **2a**. The ^{1}H NMR spectrum reveals that when a THF molecule coordinates to the samarium center the effect on the chemical shifts for the methyl protons is quite large, as shown in Table 2. It is interesting to note that although THF-solvated **2b** readily forms in THF, it is not formed in reaction 2 despite the presence of 1 equiv of THF.



Synthesis of $Me_2Si(C_5Me_4)_2Sm(C_5Me_4R)$ (R = Et (3), ^{n}Pr (4), ^{i}Pr (5)). Slightly modified (peralkylcyclopentadienyl)samarium *ansa*-metallocenes similar to **2a** were also prepared from **1** and KC_5Me_4R according to eq 4. The yields for the ethyl and *n*-propyl derivatives, 78% and 85%, respectively, were significantly higher than that for the isopropyl derivative, 27%.



R = Et, **3**; ^{n}Pr, **4**; ^{i}Pr, **5**

The ^{1}H NMR spectra of **3** and **4** are similar to each other, and each has one unusually high field resonance: −20.96 ppm for **3** and −26.32 ppm for **4**. Unusually high field resonances have been observed in the past in complexes such as $(C_5Me_4Et)_3Sm$ (δ −7.30 ppm)[1b] and $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}Ph(CH_2)_2C{=}C{=}C{=}C(CH_2)_2Ph]$ (δ −12.94),[7] which have hydrocarbyl ligand substituents oriented toward samarium in the solid state at distances of approximately 3.6−3.8 Å. These high-field shifts are consistent with long-range Sm···HC interactions. HMQC experiments and integration data led to the assignments of the spectra of **3** and **4** shown in Tables 2 (^{1}H) and 4 (^{13}C). The high-field resonance in the spectrum of **3** arises from the methyl group of the ethyl substituent. In **4**, the β-methylene protons of the *n*-propyl substituent are assigned to the high-field resonance. The structure of **4** suggests that these high-field shifts arise due to long-range interactions of the type described above, since the *n*-propyl group is oriented toward the samarium center with the β-methylene at a distance of 3.36 Å (see below).

The ^{1}H NMR spectrum of **5** differed from those of **2**−**4** in that only five of the expected seven resonances are observed at 25 °C and three of these are broad ($\nu_{1/2}$ = 250 Hz for δ 2.77 ppm, 450 Hz for δ −4.94 ppm, 325 Hz for δ −11.21 ppm). However, when the temperature is raised to 70 °C, the singlet originally at 2.77 ppm changes into singlets at 2.58 and 2.45 ppm and the broad resonances originally at −4.94 and −11.21 ppm

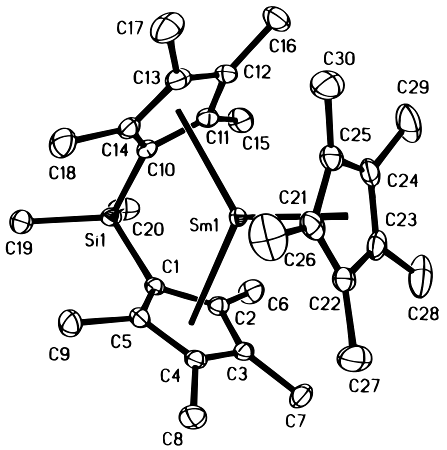


Figure 2. Thermal ellipsoid plot of $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (**2a**) with ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

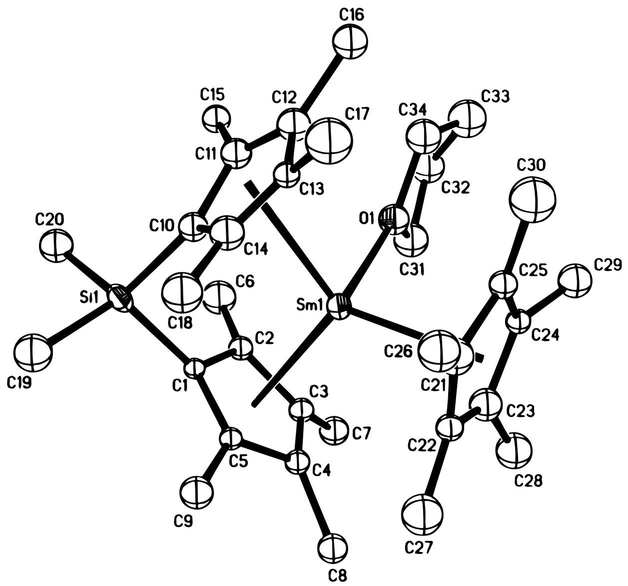


Figure 3. Thermal ellipsoid plot of $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (**2b**) with ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

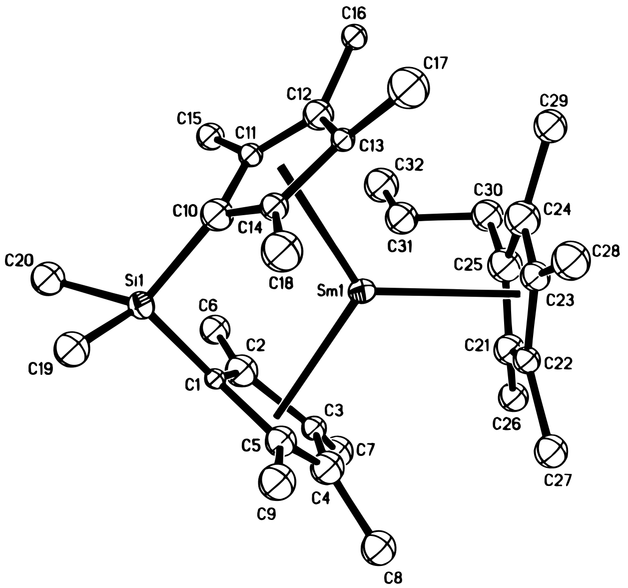


Figure 4. Thermal ellipsoid plot of molecule 1 of $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (**4**), with ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) in $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a)

Sm(1)−C(1)	2.732(3)	Sm(1)−C(10)	2.693(2)
Sm(1)−C(2)	2.742(2)	Sm(1)−C(11)	2.750(2)
Sm(1)−C(3)	2.898(2)	Sm(1)−C(12)	2.957(2)
Sm(1)−C(4)	2.913(2)	Sm(1)−C(13)	2.960(3)
Sm(1)−C(5)	2.794(2)	Sm(1)−C(14)	2.760(2)
Sm(1)−C(21)	2.731(3)	Sm(1)−Cnt(1)	2.544
Sm(1)−C(22)	2.806(3)	Sm(1)−Cnt(2)	2.554
Sm(1)−C(23)	2.784(3)	Sm(1)−Cnt(3)	2.494
Sm(1)−C(24)	2.766(3)		
Sm(1)−C(25)	2.756(3)		
Cnt(1)−Sm(1)−Cnt(2)	116.9	Cnt(2)−Sm(1)−Cnt(3)	121.7
Cnt(1)−Sm(1)−Cnt(3)	121.4		

Table 6. Selected Interatomic Distances (Å) and Angles (deg) in $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (4)

Sm(1)−C(1)	2.723(14)	Sm(1)−C(10)	2.71(2)
Sm(1)−C(2)	2.81(2)	Sm(1)−C(11)	2.789(14)
Sm(1)−C(3)	2.984(13)	Sm(1)−C(12)	2.88(2)
Sm(1)−C(4)	2.99(2)	Sm(1)−C(13)	2.907(15)
Sm(1)−C(5)	2.718(2)	Sm(1)−C(14)	2.747(15)
Sm(1)−C(21)	2.769(14)	Sm(1)−C(11)	3.36
Sm(1)−C(22)	2.814(11)		
Sm(1)−C(23)	2.839(15)	Sm(1)−Cnt(1)	2.573
Sm(1)−C(24)	2.80(2)	Sm(1)−Cnt(2)	2.536
Sm(1)−C(25)	2.72(2)	Sm(1)−Cnt(3)	2.511
Cnt(1)−Sm(1)−Cnt(2)	117.1	Cnt(2)−Sm(1)−Cnt(3)	122.3
Cnt(1)−Sm(1)−Cnt(3)	120.3		

sharpen into singlets and shift to −4.51 and −9.60 ppm. This high-temperature spectrum is similar to the spectra of **3** and **4** taken at 25 °C and is consistent with the expected structure, except that the methine proton of the isopropyl group was not located. In **5**, no unusual upfield shift of the protons of the alkyl substituent is observed, in contrast to the spectra of **3** and **4**.

Structures of $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a), $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (2b), and $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (4). Crystallographic data were collected on $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (**2a**), $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)(THF)$ (**2b**), and $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (**4**; Figure 4) to compare their steric crowding with that of $(C_5Me_5)_3Sm$.[1] Crystal decomposition during data collection on **2b** limited the quality of the structure, and only the connectivity of the atoms can be reliably described. The most significant feature is that when the peralkylcyclopentadienyl rings are linked with a Me_2Si unit, there is room for C_5Me_5 and an additional THF ligand.

The crystallographic data on $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (**2a**) and $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (**4**) do allow detailed analysis, and comparisons will be made with $(C_5Me_5)_3Sm$ and $(C_5Me_4Et)_3Sm$, the most closely related compounds in the literature. Selected interatomic distances and bond angles are presented in Table 5 (**2a**) and Table 6 (**4**), and a comparison is presented in Table 7. The (ring centroid)−Sm−(ring centroid) angles in **2a** and **4** differ only slightly from those found in $(C_5Me_5)_3Sm$ (120°) and $(C_5Me_4Et)_3Sm$ (120.1, 120.0, and 119.1°) and sum to 360°, indicating that all of these molecules are trigonal planar. As is typical in bridged (peralkylcyclopentadienyl)lanthanide complexes, there is a wide range of Sm−C(ring) bond distances in the $[Me_2Si(C_5Me_4)_2]^{2-}$ ligands. The carbon atoms attached to silicon have the smallest Sm−C(ring) distances, 2.693(2)−2.732(3) Å, which are on the short end of the range

Table 7. Comparison of Sm−C(ring) Bond Lengths (Å) between $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ (2a), $Me_2Si(C_5Me_4)_2Sm(C_5Me_4{}^nPr)$ (4), $(C_5Me_5)_3Sm$, and $(C_5Me_4Et)_3Sm$

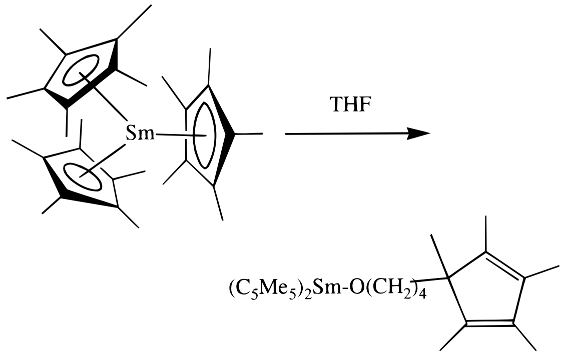
	$(C_5Me_5)_3Sm$	$(C_5Me_4R)_3Sm$	**2a**	**4**
Sm−C(C_5Me_4R)	2.782(2)−2.910(3)	2.787(12)−2.900(14)	2.731(3)−2.806(3)	2.72(2)−2.839(15)
Sm−C(C_5Me_4R)	2.82(5)	2.83(4)	2.77(3)	2.78(3)
Sm−C(C_5Me_4R)	-	-	2.693(2)−2.960(3)	2.71(2)−2.99(2)
Sm−C(C_5Me_4R)	-	-	2.82(10)	2.83(10)

of distances typical for trivalent samarium peralkylcyclopentadienyl complexes.[21] The carbons adjacent to these carbons have the next longest Sm−C(ring) bond lengths, 2.742(2)−2.81(2) Å, which span the range of normal Sm−C(ring) distances in compounds of this type. The carbon atoms most distant from the silicon have a 2.88(2)−2.99(2) Å Sm−C(ring) range, which is very long compared to the distances in typical Sm−C(C_5R_5) complexes. As such, the *ansa* cyclopentadienyl unit is structurally oriented toward being a bis(η^3-allyl) ligand.

Because of these large variations, it is the remaining $C_5Me_4R^-$ ligands in **2a** and **4** that are best compared with the peralkylcyclopentadienyl ligands in $(C_5Me_5)_3Sm$ and $(C_5Me_4Et)_3Sm$. As shown in Table 7, the ranges and averages in **2a** and **4** are similar and are significantly shorter than those in $(C_5Me_5)_3Sm$ and $(C_5Me_4Et)_3Sm$. Hence, although the overall structures of **2a** and **4** are very similar to those of $(C_5Me_5)_3Sm$ and $(C_5Me_4Et)_3Sm$, the steric crowding of the $C_5Me_4R^-$ ligand in **2a** and **4** is much less than that encountered by the $C_5Me_4R^-$ ligands in $(C_5Me_5)_3Sm$ and $(C_5Me_4Et)_3Sm$. This is exactly what was desired in synthesizing **2a** and **4**—to obtain compounds as closely related as possible to $(C_5Me_5)_3Sm$ and $(C_5Me_4Et)_3Sm$ structurally and electronically, but less sterically crowded as far as the $C_5Me_4R^-$ ligand is concerned.

An additional structural point of interest is the orientation of the β-carbon of the propyl group, C(31) in **4**, toward the samarium center. The Sm···C(31) distance is 3.36 Å, which is 0.31 Å shorter than the interatomic distance for the β-carbon of the ethyl groups oriented toward the metal in $(C_5Me_4Et)_3Sm$[1b] and 0.39 Å shorter than the reported agostic interaction in $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}Ph(CH_2)_2C{=}C{=}C{=}C(CH_2)_2Ph]$.[7] The orientation of C(31) toward the metal center is most likely responsible for the upfield shifts observed in the ^{1}H NMR spectrum for **4**. The fact that this carbon is closer to samarium than those in the other cases is consistent with the fact that the shift in the NMR signal is much greater. It is likely that the methyl group of the ethyl substituent on the cyclopentadienyl ring in **3** is similarly oriented. Agostic interactions are common with the electrophilic lanthanides, and many examples are known.[5f,7,19a,20,22] These frequently are associated with unusual bond angles. In **4**, some unusual C−C−C angles are also observed. In particular, the 119.5(14)° C(30)−C(31)−C(32) angle is rather large for an sp^3 carbon. The 114.3(14)° C(24)−C(25)−C(30) angle is rather different than its adjoining angle, C(21)−C(25)−C(30), which is 136.2(15)°. However, each of the pairs of adjoining angles around the ring carbons are disparate: 111.2(12) and 139.5(12)°, 114.0(11) and 134.5(11)°, 123.2(12) and 131.2(14)°, and 111.9(12) and 137.7(15)°. This is not observed for **2a**, which has the following pairs of angles: 123.1(3) and 127.0(3)°, 123.5(3) and 127.2(3)°, 123.6(3) and 127.6(3)°, 124.2(3) and 126.4(3)°, and 125.0(3) and 126.2(3)°.

Reactivity of $Me_2Si(C_5Me_4)_2Sm(C_5Me_4R)$. Three types of reactivities typical of $(C_5Me_5)_3Sm$ were examined with the new tris(cyclopentadienyl) complexes described above: (a) ring-opening reactivity with THF, as shown in eq 5 for $(C_5Me_5)_3Sm$



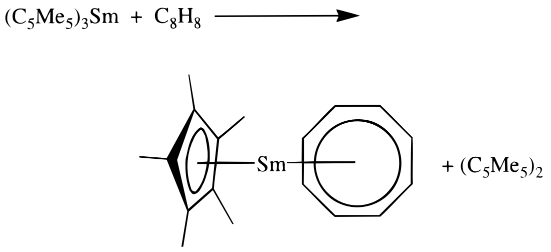
(5)

(b) ethylene polymerization reactivity as shown in eq 6

$$(C_5Me_5)_3Sm \xrightarrow{n CH_2{=}CH_2} \text{polyethylene} \qquad (6)$$

and (c) reductive chemistry with $Ph_3P{=}Se$ and 1,3,5,7-cyclooctatetraene, as shown in eqs 7 and 8, respectively.

$$2(C_5Me_5)_2Sm + Ph_3P{=}Se \xrightarrow{THF} [(C_5Me_5)_2Sm(THF)]_2Se + (C_5Me_5)_2 + Ph_3P \qquad (7)$$



(8)

Since **2a** forms the THF adduct **2b** when exposed to THF and **2b** can be prepared directly from **1** and KC_5Me_5 in THF, no THF ring-opening reactivity is observed with this less crowded molecule. Similarly, **3**−**5** also do not ring-open THF. Clearly the ligand, $[Me_2Si(C_5Me_4)_2]^{2-}$, does not generate the same type of reactivity with THF as the $[(C_5Me_5)^-]_2$ ligand set. **3**−**5** are evidently more crowded than **2a**, as expected, since they show no evidence of THF coordination to make analogues of **2b**.

Exposure of **2a**, **2b**, and **3**−**5** to 1 atm of ethylene yields no evidence of polymerization after 24 h. **2a** and **4** were placed under 50 psi of ethylene for 18 h, and again there was no evidence of ethylene polymerization. The possible reaction of **3** with $Ph_3P{=}Se$ was monitored

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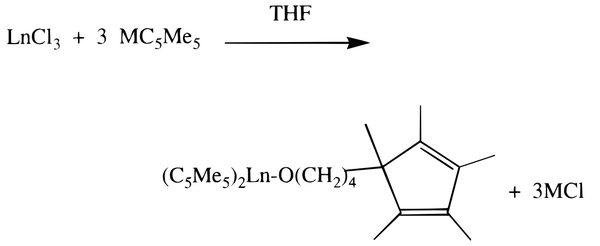
by NMR spectroscopy. No evidence of a reaction was observed even after heating at 120 °C for 6 h. Similarly, no reaction was observed between **3** and 1,3,5,7-C_8H_8 after heating to 120 °C for 6 h.

Discussion

Complexes **2a** and **3**−**5** were chosen for comparison with $(C_5Me_5)_3Sm$, since they are very close electronically and any differences in chemistry should arise from steric factors. Previous studies of *ansa*-metallocenes of the lanthanides suggest that the bridged complexes are less sterically crowded. The results on these specific samarium systems verify that. Structural comparisons of the bis(pentamethylcyclopentadienyl) and *ansa*-metallocene iodides $(C_5Me_5)_2SmI(THF)$ and $Me_2Si(C_5Me_4)_2SmI(THF)$ show that the bridged-cyclopentadienyl ring system provides a less crowded coordination environment for the other ligands on the metal. Structural studies of **2a**, **2b**, and **4** are consistent with this. The C_5Me_4R ligands have smaller average Sm−C(C_5Me_4R) bond distances than are found in $(C_5Me_5)_3Sm$. Hence, the complexes **2a** and **3**−**5** appear to be sterically less congested than $(C_5Me_5)_3Sm$.

Complexes **2a** and **3**−**5** are also much less reactive than $(C_5Me_5)_3Sm$. The most striking example is that **2a** is able to form a THF adduct in THF and no evidence of ring-opening reactivity is observed. Previous attempts to make $(C_5Me_5)_3Ln$ complexes directly in THF have uniformly given THF ring-opened products (eq 9),[23] whereas for years it has been known that less crowded tris(cyclopentadienyl) complexes such as $(C_5H_5)_3Ln$ readily form THF adducts, $(C_5H_5)_3Ln(THF)$.[5j]



(9)

Consistent with the reduced THF ring-opening reactivity, there is no facile polymerization of ethylene or reduction chemistry as observed for $(C_5Me_5)_3Sm$. These results are consistent with the theory that the special reactivity of $(C_5Me_5)_3Sm$ is due to the steric crowding. Since the Sm−C bond distances in $(C_5Me_5)_3Sm$ are extremely long, neither the positively charged metal nor the negatively charged ligands are electrostatically well stabilized, since they cannot get close to each other. The high reactivity of $(C_5Me_5)_3Sm$ can be rationalized by invoking intermediates of the type $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ and $[(C_5Me_5)_2Sm]^+[(C_5Me_5)]^-$ to explain routes by which the steric strain could be relieved. The less crowded **2a** and **3**−**5** would not be expected to form the analogous $Me_2Si(C_5Me_4)_2Sm(\eta^1\text{-}C_5Me_4R)$ and $[Me_2Si(C_5Me_4)_2Sm]^+[(C_5Me_4R)]^-$ types of intermediates, since the rings are not crowded. Consequently, the special reactivity typical of $(C_5Me_5)_3Sm$ is not observed with **2a** and **3**−**5**.

Conclusion

Comparison of electronically similar but sterically less crowded (peralkylcyclopentadienyl)samarium *ansa*-metallocenes, $Me_2Si(C_5Me_4)_2Sm(C_5Me_4R)$, with $(C_5Me_5)_3Sm$ is consistent with the theory that the unusual reactivity of $(C_5Me_5)_3Sm$ arises from the steric crowding. THF ring opening, ethylene polymerization, and reductive reactivity are not observed for the less congested *ansa*-metallocene analogues.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters and additional figures showing the structures for **1**, **2a**, **2b**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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