Organometallics 1990, 9, 2124–2130

Synthesis and Reactivity of the Cationic Organosamarium(III) Complex $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$, Including the Synthesis and Structure of a Metallocene with an Alkoxy-Tethered C_5Me_5 Ring, $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$[1]

William J. Evans,* Tamara A. Ulibarri, L. R. Chamberlain, Joseph W. Ziller, and Daniel Alvarez, Jr.

Departments of Chemistry, University of California, Irvine, Irvine, California 92717, and Indiana University, Bloomington, Indiana 47405

Received March 6, 1990

$(C_5Me_5)_2Sm(THF)_2$ (**1**) reacts with $AgBPh_4$ in THF to form Ag and $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (**2**) in high yield. **2** crystallizes from THF in space group $P2/c$ (C^4_{2h}; No. 13) with unit cell parameters $a = 10.594$ (2) Å, $b = 14.254$ (3) Å, $c = 16.199$ (3) Å, $\beta = 107.32$ (1)°, $V = 2335.3$ (8) Å^3, and $Z = 2$ for $D_{calcd} = 1.260$ g cm^{-3}. Least-squares refinement of the model based on 2342 observed reflections converged to $R_F = 6.7\%$. The C_5Me_5 ring centroids (Cn) and the THF oxygen atoms in $(C_5Me_5)_2Sm(THF)_2^+$ form a distorted tetrahedron with a Cn–Sm–Cn angle of 134.2°, a 2.46 (1) Å Sm–O distance, and a 2.69 (2) Å Sm–C(C_5Me_5) average distance. Complex **2** reacts with $KC{\equiv}CR$ to form $KBPh_4$ and $(C_5Me_5)_2Sm(C{\equiv}CR)(THF)$ (R = Ph (**3**), CMe_3 (**4**)). **3** crystallizes from hexane at –34 °C in space group $P2_1/n$ with $a = 14.257$ (5) Å, $b = 16.983$ (4) Å, $c = 25.221$ (8) Å, $\beta = 104.61$ (3)°, $V = 5909$ (3) Å^3, and $Z = 8$ for $D_{calcd} = 1.335$ g cm^{-3}. Least-squares refinement of the model based on 5345 reflections converged to a final $R_F = 8.1\%$. The two ring centroids, the THF oxygen atom, and the terminal carbon of the alkynide ligand form a distorted tetrahedron with an average 137.7° Cn–Sm–Cn angle, a 2.71 (3) Å Sm–C(C_5Me_5) average distance, and 2.47 (2) Å Sm–O and 2.49 (2) Å Sm–C distances. The average alkynide C≡C bond distance in the two molecules in the unit cell is 1.12 (2) Å. Complex **2** reacts with KC_5H_5, LiPh, and LiMe to form $(C_5Me_5)_2Sm(C_5H_5)$, $(C_5Me_5)_2SmPh(THF)$, and $(C_5Me_5)_2SmMe(THF)$, respectively. The reaction of **2** with KC_5Me_5 generates $(C_5Me_5)_2Sm(OCH_2CH_2CH_2CH_2C_5Me_5)(THF)$ (**5**). **5** crystallizes from hexane in space group $C2/c$ (No. 15; C^6_{2h}) with unit cell parameters $a = 30.009$ (6) Å, $b = 13.996$ (2) Å, $c = 17.460$ (3) Å, $\beta = 90.25$ (2)°, $V = 7333$ (2) Å^3, and $Z = 8$ for $D_{calcd} = 1.268$ g cm^{-3}. Least-squares refinement of the model based on 3925 observed reflections converged to $R_F = 7.3\%$. The structure of **5** is similar to that of **3** except that it contains the alkoxide ligand $O(CH_2)_4(C_5Me_5)$ instead of an alkynide group. The Sm–O(alkoxide) distance is 2.081 (8) Å, and the Sm–O–C angle is 165.2 (7)°.

Introduction

As part of our investigation of $(C_5Me_5)_2Sm(THF)_2$,[2,3] $(C_5Me_5)_2Sm$,[4] and their related Sm(III) reaction products,[5,6] we were interested in synthesizing a cationic Sm(III) analogue of $(C_5Me_5)_2Sm(THF)_2$, namely $(C_5Me_5)_2Sm(THF)_2^+$. This complex was of interest (a) for structural comparison with the neutral divalent samarium metallocenes, (b) as a halide-free precursor to trivalent $(C_5Me_5)_2Sm$ complexes, and (c) as a potential participant in cyclic, externally driven reductions involving $(C_5Me_5)_2Sm(THF)_2$. The recent synthesis of $[(C_5H_5)_2ZrMe(THF)][BPh_4]$[7,8] from $(C_5H_5)_2ZrMe_2$ suggested that $AgBPh_4$ could be a suitable reagent for this purpose. In contrast to this zirconium system and the synthesis of the related cationic actinide complex $[(C_5Me_5)_2ThMe(THF)][BPh_4]$,[9] both of which use tetravalent precursors to make tetravalent products, we find it more convenient to use a divalent samarium precursor to make the desired trivalent cation. Hence, $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ can be conveniently made by reduction of $AgBPh_4$ with $(C_5Me_5)_2Sm(THF)_2$. We report here the synthesis and structure of this complex as well as its reactivity in regard to points a–c above, including the synthesis of an unusual pentamethylcyclopentadiene–substituted alkoxide ligand.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum-line, and glovebox (Vacuum Atmospheres HE-553 Dri-Lab) techniques. Solvents were purified and physical measurements were obtained as previously described.[10] $(C_5Me_5)_2Sm(THF)_2$ (**1**) was synthesized according to the literature.[2] $AgBPh_4$ was prepared from $NaBPh_4$ and $AgNO_3$ according to the literature.[11] Precipitates were separated with a Clay Adams 0131 centrifuge operating at 3400 rpm for 1–5 min. ^{11}B NMR spectra were obtained on a Nicolet NT-360 spectrometer at 115 MHz using $BF_3{\cdot}OEt_2$ as an external reference.

Synthesis of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (2). A slight excess of $AgBPh_4$ (0.800 g, 1.87 mmol) was added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (1.000 g, 1.77 mmol) in 15 mL of THF. The suspension was stirred for ~12 h, during which time it turned

---

* To whom correspondence should be addressed at the University of California, Irvine.

[1] Reported in part at the 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; INOR 155.

[2] Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

[3] Evans, W. J. *Polyhedron* **1987**, *6*, 803–835 and references therein.

[4] Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272. Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285–1291.

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

[6] Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994 and references therein.

[7] Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718–1719.

[8] Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410–7411.

[9] Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127–4129.

[10] Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

[11] Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383–386.

0276-7333/90/2309-2124$02.50/0

Table I. Crystallographic Data for $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (2), $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (3), and $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ (5)

	2	3	5
formula	$SmC_{52}H_{66}O_2B$	$SmC_{32}H_{43}O$	$SmC_{38}H_{61}O_2$
mol wt	884.3	594.0	700.2
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2/c$ (C_{2h}^4; No. 13)	$P2_1/n$	$C2/c$ (C_{2h}^6; No. 15)
cell constants			
a, Å	10.594 (2)	14.257 (5)	30.009 (6)
b, Å	14.254 (3)	16.983 (4)	13.996 (2)
c, Å	16.199 (3)	25.221 (8)	17.460 (3)
β, deg	107.32 (1)	104.61 (3)	90.25 (2)
V, Å^3	2335.3 (8)	5909 (3)	7333 (2)
Z	2	8	8
D_{calcd}, Mg/m^3	1.260	1.335	1.268
diffractometer	Nicolet P3	Syntex P2$_1$	Syntex P2$_1$
radiation: Mo Kα, Å	$\bar{\lambda}$ = 0.710730	$\bar{\lambda}$ = 0.710730	$\bar{\lambda}$ = 0.710730
monochromator	highly oriented graphite	highly oriented graphite	highly oriented graphite
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
scan type	$\theta-2\theta$	ω	$\theta-2\theta$
scan width, deg	1.2 plus Kα separation	1.0	1.2 plus Kα separation
scan speed (in ω), deg min^{-1}	2.0	2.0	3.0
$2\theta_{max}$, deg	45.0	45.0	45.0
μ(Mo Kα), mm^{-1}	1.30	2.01	1.63
abs cor	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)	none
no. of rflns collected	3432	8089	4919
no. of rflns with $\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$	2342	5345	3925
no. of variables	254	613	371
R_F, R_{wF}, %	6.7, 7.1	8.1, 7.2	7.3, 11.0
goodness of fit	1.21	1.47	3.14

black. Filtration of the reaction mixture gave a blackish silver deposit and an orange solution. Removal of solvent by rotary evaporation left a red-orange solid, which was washed with 20 mL of hexane to yield the product as an orange powder (1.481 g, 94%). Red-orange crystals of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ can be obtained by redissolving the powder in THF and cooling to −34 °C. ^{1}H NMR (THF-d_8, 20 °C, δ): 0.81 (C_5Me_5); 1.8, 3.7 (OC_4H_8); 6.74 (t, J = 7.14 Hz, p Ph); 6.65 (t, J = 7.4 Hz, m Ph); 7.19 (broad, o Ph). ^{13}C NMR (THF-d_8, 20 °C, δ): 20.55 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5); 26.7, 68.9 (OC_4H_8); 120.3 (C_5Me_5); 123.25 (d, $^1J_{CH}$ = 156 Hz, Ph); 127.1 (d, $^1J_{CH}$ = 152 Hz, Ph); 136.4 (d, $^1J_{CH}$ = 154 Hz, Ph). ^{11}B NMR (THF, δ): −6.59 (s, line width 116 Hz). Anal. Calcd for $SmC_{52}H_{66}O_2B$: Sm, 17.01; C, 70.63; H, 7.52; B, 1.22. Found: Sm, 17.15; C, 68.55; H, 7.31; B, 1.10. IR (KBr): 2880 s, 1580 w, 1430 m, 1382 w, 1250 w, 1150 w, 1000 m, 834 s, 700 s cm^{-1}. Magnetic susceptibility: $\chi_M = 1480 \times 10^{-6}$ cgsu, μ_{eff} = 1.86 μ_B.

X-ray Data Collection, Structure Determination, and Refinement for 2. A bright red-orange crystal of approximate dimensions 0.13 × 0.25 × 0.27 mm was mounted in a thin-walled glass capillary under nitrogen and aligned on a Nicolet P3 automated four-circle diffractometer. Laue symmetry determination, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[12] Room-temperature (22 °C) intensity data were collected by use of the $\theta-2\theta$ scan technique with Mo Kα radiation under the conditions given in Table I. All 3432 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. A careful survey of a preliminary data set revealed the systematic extinction $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The crystal therefore belongs to the monoclinic system. Possible space groups are the noncentrosymmetric Pc (C_s^2; No. 7) or the centrosymmetric $P2/c$ (C_{2h}^4; No. 13). Intensity statistics strongly favored the noncentrosymmetric space group. However, it was later shown that the centrosymmetric space group was correct.

All crystallographic calculations were carried out with use of either our locally modified version of the UCLA Crystallographic Computing Package[13] or the SHELXTL PLUS program set.[14] The analytical scattering factors for neutral atoms were used throughout the analysis;[15a] both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[15b] were included. The function minimized during least-squares refinement was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where $w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0015(\lvert F_o\rvert)^2$.

The structure was solved by direct methods (SHELXTL) with an automatic Patterson routine; both the samarium and boron atoms are located on 2-fold rotation axes (Sm(1), 0, y, $^1/_4$; B(1), $^1/_2$, y, $^1/_4$). Difference-Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. Full-matrix least-squares refinement of positional and anisotropic thermal parameters led to convergence with R_F = 6.7%, R_{wF} = 7.1%, and GOF = 1.21 for 254 variables refined against those 2342 data with $\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$. Hydrogen atoms were included in calculated positions by use of a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. A final difference-Fourier synthesis showed no significant features.

Reaction of 2 with Sodium. Na (2.6 mg, 0.113 mmol) was added to a solution of 2 (100 mg, 0.113 mmol) in 20 mL of THF. The mixture was stirred for 3 h and changed from orange to purple. The mixture was centrifuged to remove a white precipitate, and solvent was removed from the purple decanted solution to give a purple solid identified as $(C_5Me_5)_2Sm(THF)_2$ (52 mg, 80%) by ^{1}H NMR spectroscopy.[2]

Reaction of 2 with KC≡CPh and KC≡CCMe$_3$. THF (20 mL) was added to a flask containing 2 (100 mg, 0.113 mmol) and KC≡CPh (16 mg, 0.113 mmol), and the solution was stirred for 1.5 h. Filtration gave a white precipitate and an orange solution. Removal of THF from the solution left $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (3) as an orange powder (55 mg, 86%). ^{1}H NMR (C_6D_6, δ): 8.14 (d, J = 7.5 Hz, o Ph), 7.29 (t, J = 7.5 Hz, m Ph), 7.08 (t, J = 7.5 Hz, p Ph), 1.59 (s, C_5Me_5), −1.79 (br s, THF), −2.87 (br s, THF). ^{13}C NMR (C_6D_6, δ): 133.48, 128.93, 127.27, 126.42 (Ph); 117.57 (SmC≡C), 116.53 (C_5Me_5); 63.25 (THF); 21.27 (THF); 17.34 (C_5Me_5). IR (KBr): 2850–2950 s, 1595 m, 1565 w, 1485 s, 1460 w, 1445 s, 1380 m, 1260 m, 1200 s, 1175 w, 1110 w, 1095 m, 1090 m, 1065 m, 1020 s, 910 w, 870 br m, 800 m, 775 m, 760 s, 690 m cm^{-1}. Anal. Calcd for $SmC_{32}H_{43}O$: Sm, 25.32; C, 64.69; H, 7.30. Found: Sm, 25.31; C, 64.59; H, 7.22.

$(C_5Me_5)_2Sm(C{\equiv}CCMe_3)(THF)$ (4) was prepared similarly in 87% yield from 2 and KC≡CCMe$_3$. ^{1}H NMR (C_6D_6, δ): 1.85 (s, CMe$_3$); 1.61 (s, C_5Me_5); −1.70 (br s, THF); −2.80 (br s, THF). IR

---

(12) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

(13) UCLA Crystallographic Computing Package; University of California: Los Angeles, 1981. Strouse, C. Personal communication.

(14) Nicolet Instrument Corp., Madison, WI, 1987.

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

(Nujol): 2072 w, 1265 s, 1223 w, 1205 w, 1176 w, 889 s, 789 s, 765 s, 737 s cm^{-1}. Anal. Calcd for $SmC_{30}H_{47}O$: Sm, 26.20. Found: Sm, 25.3.

Synthesis of $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ from 1. Upon addition of $PhC{\equiv}CH$ (29 μL, 0.265 mmol) to **1** (150 mg, 0.265 mmol) in hexane, the purple solution turned yellow and gas was evolved. After 30 min, the solvent was removed, leaving $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (141 mg, 90%) as an orange-yellow solid that was identified by ^{1}H NMR spectroscopy.

X-ray Data Collection, Structure Determination, and Refinement for 3. A bright yellow crystal of approximate dimensions 0.22 × 0.30 × 0.50 mm was handled as described above for **2**. Details are given in Table I. All 8089 data were corrected as described above. A careful survey of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $h0l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (C_{2h}^5; No. 14), is thus uniquely defined. Crystallographic calculations were carried out as described above for **2**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0006(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included by use of a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 8.1%, R_{wF} = 7.2%, and GOF = 1.47 for 613 variables refined against those 5345 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map was "clean" with $\rho(\max)$ = 1.2 e Å^{-3} at a distance of 0.14 Å from Sm(2).

Reaction of 2 with KC_5H_5 and LiC_6H_5. KC_5H_5 (12 mg, 0.113 mmol) was added to **2** (100 mg, 0.113 mmol) in toluene and stirred for 13 h. The mixture was centrifuged, the orange solution was decanted, and the solvent was removed to give an oily orange residue. The oil was dissolved in hexane, and the solvent was removed by rotary evaporation. After this was repeated several times, an orange solid was obtained, which contained primarily $(C_5Me_5)_2Sm(C_5H_5)$ by ^{1}H NMR spectroscopy.[5] LiC_6H_5 reacts similarly with **2** in hexane to form $(C_5Me_5)_2Sm(C_6H_5)(THF)$[16] in 70% yield in 3 h. C_5Me_5-containing byproducts were observed in both reactions.

MeLi Reactions. Addition of MeLi (0.10 mL of 1.135 M THF solution, 0.113 mmol) to **2** (100 mg, 0.113 mmol) in 20 mL of THF caused immediate formation of a precipitate. The reaction mixture was stirred for 30 min, and the THF was removed by rotary evaporation to give an orange-yellow solid. Extraction with toluene and removal of solvent yielded $(C_5Me_5)_2SmMe(THF)$ (52 mg, 90%) as an orange solid identified by ^{1}H NMR spectroscopy.[10]

$(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ (5). Toluene (10 mL) was added to a flask containing **2** (250 mg, 0.283 mmol) and KC_5Me_5 (50 mg, 0.283 mmol), and the mixture was stirred for 36 h. Centrifugation of the solution separated an orange solution from a precipitate containing a large amount of white material (presumably $KBPh_4$) and a small amount of orange material (presumably unreacted **2**). Removal of toluene from the solution by rotary evaporation yielded an oily orange solid. Addition and removal (in vacuo) of 4 × 10 mL portions of hexane left **5** as an orange powder (111 mg, 56%). Anal. Calcd for $SmC_{38}H_{61}O_2$: Sm, 21.48. Found: Sm, 21.5. ^{1}H NMR (C_6D_6, δ): 5.55 (2 H, $(CH_2)_4$), 3.85 (2 H, $(CH_2)_4$), 2.12 (2 H, $(CH_2)_4$), 1.83 (6 H, $(CH_2)_4C_5\mathit{Me}_5$), 1.74 (6 H, $(CH_2)_4C_5\mathit{Me}_5$), 1.37 (30 H, η^5-C_5Me_5), 1.12 (3 H, $(CH_2)_4C_5\mathit{Me}_5$), –2.58 (4 H, THF), –4.10 (4 H, THF). ^{13}C NMR (C_6D_6, δ): 141.16 ($(CH_2)_4\mathit{C}_5Me_5$), 134.37 ($(CH_2)_4\mathit{C}_5Me_5$), 113.96 (η^5-C_5Me_5), 75.58 ($(CH_2)_4$), 61.09 (THF), 57.12 ($(CH_2)_4\mathit{C}_5Me_5$, ipso), 37.58 ($(CH_2)_4$), 37.39 ($(CH_2)_4$), 23.37 ($(CH_2)_4C_5\mathit{Me}_5$), 23.16 ($(CH_2)_4$), 19.75 (THF), 18.36 (η^5-$C_5\mathit{Me}_5$), 11.70 ($(CH_2)_4C_5\mathit{Me}_5$), 10.61 ($(CH_2)_4C_5\mathit{Me}_5$).

X-ray Data Collection, Structure Determination, and Refinement for 5. A bright yellow crystal of approximate dimensions 0.17 × 0.57 × 0.63 mm was immersed in Paratone-N (lube oil additive), mounted on a glass fiber, and transferred to the Syntex P2$_1$ diffractometer, which is equipped with a modified LT-1 apparatus. Subsequent setup operations and collection of low-temperature (203 K) intensity data were carried out as described above.

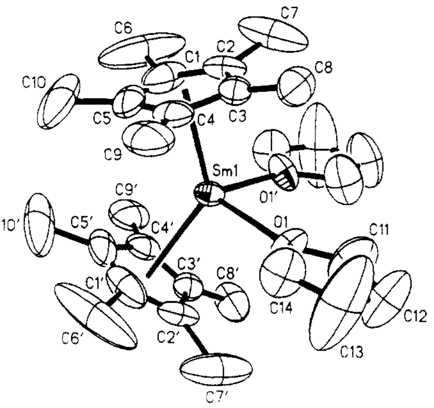

Figure 1. ORTEP diagram of the cation in $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (**2**) with the probability ellipsoids drawn at the 30% level.

All 4919 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. Due to an interruption in the nitrogen flow on the low-temperature unit, the crystal decomposed before absorption correction reflections (ψ scans) could be collected. An absorption correction was not applied. A careful examination of a preliminary data set revealed the systematic extinctions hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. Possible space groups are the noncentrosymmetric monoclinic Cc (C_s^4; No. 9) and the centrosymmetric $C2/c$ (C_{2h}^6; No. 15). The latter was chosen and later proved to be correct by successful solution and refinement of the structure. Crystallographic calculations were carried out as described above for **2**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0008(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included by use of a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å. Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 7.3%, R_{wF} = 11.0%, and GOF = 3.14 for 371 variables refined against those 3925 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features with $\rho(\max)$ = 2.3 e Å^{-3} at a distance of 0.88 Å from Sm(1).

Results and Discussion

Synthesis. The strongly reducing $(C_5Me_5)_2Sm(THF)_2$ (**1**) reacts readily with $AgBPh_4$ to form Ag and $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (**2**) in high yield (eq 1). The

$$\underset{\mathbf{1}}{(C_5Me_5)_2Sm(THF)_2} + AgBPh_4 \rightarrow \underset{\mathbf{2}}{[(C_5Me_5)_2Sm(THF)_2][BPh_4]} + Ag \quad (1)$$

reduction of a Ag(I) salt by **1** was expected on the basis of reduction potentials and the fact that the weaker reductant $(C_5Me_5)_2Yb$ reduces AgF.[17] **2** was characterized by complexometric analysis, ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, IR spectroscopy, and an X-ray crystal structure (Figure 1) as described later. **2** is readily soluble in THF, but it is insoluble in arene solvents. Replacement of $AgBPh_4$ in reaction 1 by $AgPF_6$ was examined and found to be inferior: the reaction of **1** with $AgPF_6$ gave a mixture of products (by ^{1}H NMR spectroscopy), none of which corresponded to **2**.

Alternative syntheses of **2** from trivalent $(C_5Me_5)_2SmZ(THF)$ precursors (Z = halide,[18,19] alkyl,[10]

---

(16) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112–119.

(17) Burns, C. J.; Berg, D. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 272–273.

(18) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928–3936.

aryl,[16] or hydride[20]) in reactions analogous to those used in the syntheses of $[(C_5H_5)_2ZrMe(THF)][BPh_4]$[7,8] and $[(C_5Me_5)_2ThMe(THF)][BPh_4]$[9] are less desirable in this case because each of these trivalent precursors is generally best made from 1. Hence, the synthesis would take an extra step. The reaction of $(C_5Me_5)_2SmCl(THF)$ with $AgBPh_4$ was examined briefly but did not form 2 cleanly. Recently, the successful synthesis of cations such as 2 from trivalent early-lanthanide iodide precursors has been reported.[21] Hence, the complexes $[(Me_3Si)_2C_5H_3]_2Ln(DME)(MeCN)][BPh_4]$ (Ln = La, Ce) have been prepared from $[(Me_3Si)_2C_5H_3]_2LnI(MeCN)_2$ and $AgBPh_4$. For these metals, a divalent precursor analogous to 1 is not available and a trivalent precursor must be used.

Reactivity. Complex 2 can be reduced to 1 in high yield (eq 2). Attempts to remove the THF ligands from 2 under

$$[(C_5Me_5)_2Sm(THF)_2][BPh_4] + Na \rightarrow (C_5Me_5)_2Sm(THF)_2 + NaBPh_4 \quad (2)$$

vacuum with heating (100 °C, 10^{-5} Torr, 14 h) were unsuccessful. This heated material was dissolved in pyridine and dried in vacuo. The ^1H NMR spectrum of this solid in THF-d_8 showed pure 2 with no evidence of free or coordinated pyridine in the sample. The protio THF peaks of the heated sample were unchanged in intensity compared to those of the original. Hence, the $(C_5Me_5)_2Sm(THF)_2^+$ ion binds its THF much more tightly than $(C_5Me_5)_2Sm(THF)_2$.[2,22] Such a trend might be expected for a cation. For example, cationic samarium(III) diiodide binds THF to the extent that it can be crystallized as the pentasolvate $SmI_2(THF)_5^+$.[23] However, this tight binding is unusual compared to transition-metal systems including $(C_5H_5)_2ZrMe(THF)^+$, which is thought to lose THF as a first step in its reactions.[24]

The THF ligands on 2 do exchange, however, in the presence of a catalytic amount of $(C_5Me_5)_2Sm(THF)_2$. Hence, when a 10:1 mixture of 2 and 1 in THF-d_8 was examined by ^1H NMR spectroscopy no protio THF bound to 2 was observed, which indicated that complete exchange had occurred.

The reactivity of 2 with neutral substrates is in accord with the tight binding of THF observed for 2. No reactivity was observed between 2 and CO, azobenzene, ethylene, phenylacetylene, epoxybutane, and pyridine. This, again, is in contrast to the chemistry observed with the cationic organozirconium complexes.[7,8,24]

To probe the limits of the stability of 2, reactions with anionic reagents were examined to see if Coulombic attraction could help induce reactivity. Anionic reagents do react with 2, as shown in eqs 3–6.

$$2 + KC_5H_5 \rightarrow (C_5Me_5)_2Sm(C_5H_5) + KBPh_4 \quad (3)$$

$$2 + LiPh \rightarrow (C_5Me_5)_2SmPh(THF) + LiBPh_4 \quad (4)$$

$$2 + MeLi \rightarrow (C_5Me_5)_2SmMe(THF) + LiBPh_4 \quad (5)$$

$$2 + KC{\equiv}CR \rightarrow (C_5Me_5)_2Sm(C{\equiv}CR)(THF) + KBPh_4 \quad R = Ph\ (3),\ CMe_3\ (4) \quad (6)$$

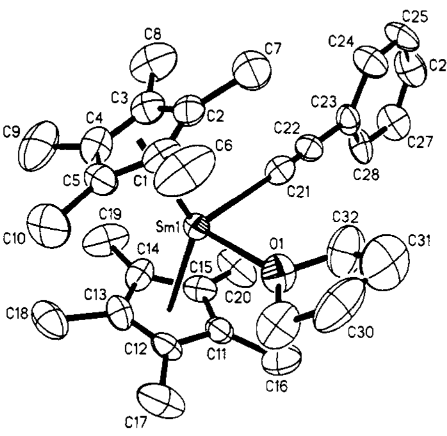

Figure 2. ORTEP diagram of $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (3) with the probability ellipsoids drawn at the 30% level.

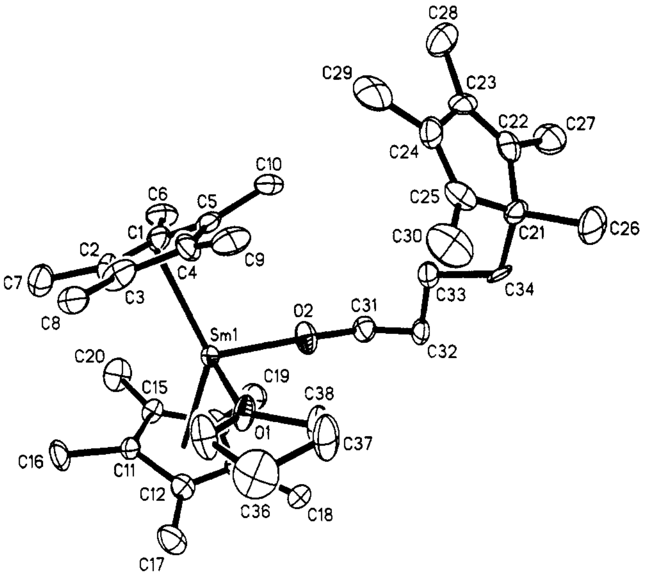

Figure 3. ORTEP diagram of $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ (5) with the probability ellipsoids drawn at the 30% level.

The products of reactions 3–5 previously had been fully characterized by NMR spectroscopy and X-ray crystallography[5,10,16] and were identified in these reactions by their NMR spectra. Complexes 3 and 4 (eq 6) were identified by analytical and spectroscopic methods and as described later, 3 was independently synthesized from alternative precursors and fully defined by X-ray crystallography (Figure 2).

The fact that cationic 2 is more reactive with anionic reagents (eq 3–6) than with neutral substrates is reasonable on the basis of electrostatic considerations. Given the reluctance of 2 to dissociate THF, reactions 3–6 may occur through an associative pathway in which the anionic reagent displaces one THF molecule. The coordination number of samarium has been observed to be variable in trivalent samarium complexes containing the $(C_5Me_5)_2Sm$ unit.[25] For example, the $(C_5Me_5)_2SmI$ unit can crystallize as an eight-coordinate complex, $(C_5Me_5)_2SmI(THF)$, or as a nine-coordinate species, $(C_5Me_5)_2SmI(\eta^2\text{-}N_4C_6H_{10})$.[25] Other nine-coordinate complexes incorporating the trivalent $(C_5Me_5)_2Sm$ moiety are known,[5] and even a 10-coordinate complex has been crystallographically identified.[26]

---

(19) 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.

(20) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

(21) Bruno, J. W.; Hazin, P. N. 44th Northwest Regional Meeting of the American Chemical Society, Reno-Sparks, NV, June 1989; Abstract No. 25. Hazin, P. N.; Bruno, J. W.; Schulte, G. K. *Organometallics* **1990**, *9*, 416–423.

(22) Evans, W. J.; Ulibarri, T. A. *Polyhedron* **1989**, *8*, 1007–1014.

(23) Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620–4623.

(24) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778–779.

(25) Evans, W. J.; Drummond, D. K.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Polyhedron* **1988**, *7*, 1693–1703.

(26) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219–223.

Hence, it is conceivable that the electrostatic interaction between the cation and the anionic reagent is strong enough to generate a transient nine-coordinate intermediate, e.g., "$(C_5Me_5)_2SmR(THF)_2$".[27] Extrusion of THF from this neutral species to form the favored eight-coordinate products observed in these reactions would be facile. Reactions 3–6 demonstrate that 2 can be used as a halide-free precursor to trivalent $(C_5Me_5)_2$Sm–hydrocarbyl complexes if conventional syntheses are inadequate.

The reaction of 2 with KC_5Me_5 was of interest in that the product analogous to that in eq 3, namely $(C_5Me_5)_3Sm$, was predicted to be too sterically crowded to exist.[28] Although $(C_5Me_5)_3Sm$ does not form, a remarkable reaction occurs nonetheless (eq 7). The trivalent alkoxide complex

$$2 + KC_5Me_5 \rightarrow (C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF) + KBPh_4 \quad (7)$$

$(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ (5), identified by X-ray crystallography (Figure 3), is formed in 55% yield. The trivalent alkoxide ligand is composed of an *n*-butoxide ligand terminally substituted with pentamethylcyclopentadiene. Hence, the product is formally derived from a ring-opening attack of $C_5Me_5^-$ on THF.

Ring-opening reactions involving THF have been known for many years.[29-34] Schemes involving Lewis acid initiated formation of an oxonium ion (eq 8) that is opened by nucleophilic attack by THF (eq 9) have been cited.[30,32]


(8)


(9)

The formation of 5 could occur analogously. In this case, the Sm^{3+} center in 2 functions as the Lewis acid and $C_5Me_5^-$ is the attacking nucleophile. The large size of $C_5Me_5^-$ may cause it to react differently from the other anionic reagents. Although attracted toward the cation in 2, $C_5Me_5^-$ may be too large to get close enough to the samarium center to form a strong interaction. The proximity of the coordinated THF may enhance the ring-opening attack, which leads to the observed formation of this alkoxy-tethered pentamethylcyclopentadiene group.

Alternative Synthesis of $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$. The reaction of 1 with PhC≡CH (eq 10) was examined as an alternative route to 3. The reaction, which

$$\underset{1}{(C_5Me_5)_2Sm(THF)_2} + PhC{\equiv}CH \rightarrow \underset{3}{(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)} + {}^1\!/_2H_2 \quad (10)$$

is formally analogous to the reduction of cyclopentadiene by 1 to form $(C_5Me_5)_2Sm(C_5H_5)$,[5] produces 3 in high yield. Reaction 10 differs from the reactions of $(C_5Me_5)_2Yb(OEt_2)$ and $(C_5Me_5)_2Eu(OEt_2)$ with PhC≡CH, which form $[(C_5Me_5)_2Yb^{III}]_2(\mu\text{-}C{\equiv}CPh)_4Yb^{II}$ and $[(C_5Me_5)Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]_2$, respectively.[35] The differences in the reactions of these divalent lanthanide metallocenes can be explained on the basis of reduction potentials. For the weakest reducing agent, $(C_5Me_5)_2Eu(OEt_2)$, no reduction occurs and the product is a divalent species resulting from proton transfer from HC≡CPh to $C_5Me_5^-$.[36] For the strongest reducing agent, $(C_5Me_5)_2Sm(THF)_2$, reductive metalation of HC≡CPh is the exclusive reaction with no loss of C_5Me_5. For the reductant of intermediate strength, $(C_5Me_5)_2Yb(OEt_2)$, a combination of these reactions occurs to give a mixed-valence species that has lost some $C_5Me_5^-$ ligands.

Table II. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (2)

Sm(1)–O(1)	2.46 (1)	Sm(1)–C(1)	2.66 (3)
Sm(1)–C(2)	2.70 (2)	Sm(1)–C(3)	2.70 (1)
Sm(1)–C(4)	2.67 (1)	Sm(1)–C(5)	2.71 (2)
O(1)–Sm(1)–O(1′)	92.9 (4)	O(1)–Sm(1)–Cent[a]	105.8
Cent–Sm(1)–Cent′	134.2	Sm(1)–O(1)–C(14)	128.0 (9)
Sm(1)–O(1)–C(11)	130.7 (8)		

[a] Cent is the centroid of the C(1)–C(5) ring.

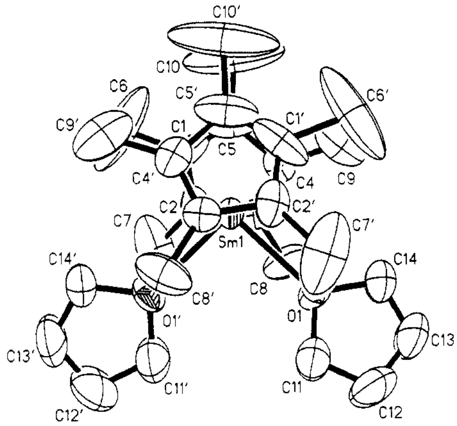

Figure 4. Top view of $[(C_5Me_5)_2Sm(THF)_2]^+$.

Structure. $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ (2). The structure of 2 is shown in Figure 1, and selected bond distances and angles are given in Table II. The BPh_4^- anion has normal distances and angles and is well separated from the cation. $(C_5Me_5)_2Sm(THF)_2^+$ has an overall structure similar to that of $(C_5Me_5)_2Sm(THF)_2$.[2] The two ring centroids and the two oxygen atoms in 2 define a distorted tetrahedron. The 92.9 (4)° O(1)–Sm–O(1′) angle in 2 is larger than the analogous 82.6 (4)° angle in 1, and the 134.2° Cn–Sm–Cn angle (Cn = C_5Me_5 ring centroid) is smaller than the 137° angle in 1. The 2.69 (2) Å average Sm–C(ring) distance in 2 is 0.17 Å less than the analogous 2.86-Å average in 1. This difference can be compared to the 0.19-Å difference between eight-coordinate Sm^{2+} and Sm^{3+} in halide and chalcogenide structures.[37] The Sm–O distance in 2, 2.46 (1) Å, is 0.18 Å less than the analogous 2.64 (2) Å average in 1.

The most unusual feature about $(C_5Me_5)_2Sm(THF)_2^+$ is that the C_5Me_5 rings are nearly eclipsed (Figure 4). The five torsional angles of the type C(6)–Cn(1)–Cn(2)–C(9′) average 9.9°, compared to 0° for a perfectly eclipsed system

---

(27) This is supported by the isolation of the nine-coordinate early-lanthanide complexes $[[(Me_3Si)_2C_5H_3]_2Ln(DME)(MeCN)][BPh_4]$.[21]

(28) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267–3270.

(29) Kern, R. J. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1105–1109.

(30) Dreyfuss, P.; Dreyfuss, M. P. In *Comprehensive Chemical Kinetics*; Banford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol. 15, pp 259–330, and references therein. Dreyfuss, P.; Dreyfuss, M. P. In *Ring Opening Polymerization*; Frisch, K. C.; Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Chapter 2.

(31) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1–144.

(32) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5586–5594 and references therein.

(33) Tsuji, Y.; Kobayashi, M.; Okuda, F.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1253–1254.

(34) DeShong, D.; Sidler, D. R. *J. Org. Chem.* **1988**, *53*, 4892–4894.

(35) Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710–712.

(36) This has been observed before in trivalent systems: Fischer, R. D.; Bielang, G. *J. Organomet. Chem.* **1980**, *191*, 61–72.

(37) Shannon, R. D. *Acta Crystallogr., Sect. A.: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

Table III. Selected Bond Distances (Å) and Angles (deg) for One of the Crystallographically Independent Molecules in the Unit Cell of $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (3)

Sm(1)–O(1)	2.49 (1)	Sm(1)–C(1)	2.73 (2)
Sm(1)–C(2)	2.71 (2)	Sm(1)–C(3)	2.68 (2)
Sm(1)–C(4)	2.71 (2)	Sm(1)–C(5)	2.72 (2)
Sm(1)–C(11)	2.66 (2)	Sm(1)–C(12)	2.68 (2)
Sm(1)–C(13)	2.72 (2)	Sm(1)–C(14)	2.78 (2)
Sm(1)–C(15)	2.70 (2)	Sm(1)–C(21)	2.50 (2)
C(22)–C(23)	1.49 (2)	C(21)–C(22)	1.11 (2)
O(1)–Sm(1)–C(21)	91.1 (5)	O(1)–Sm(1)–Cent(1)	104.9
O(1)–Sm(1)–Cent(2)	106.3	C(21)–Sm(1)–Cent(1)	103.8
C(21)–Sm(1)–Cent(2)	104.7	Cent(1)–Sm(1)–Cent(2)	136.9
Sm(1)–C(21)–C(22)	170 (1)	C(21)–C(22)–C(23)	178 (2)

Table IV. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(OC_4H_8C_5Me_5)(THF)$ (5)

Sm(1)–C(1)	2.73 (1)	Sm(1)–C(2)	2.80 (1)
Sm(1)–C(3)	2.78 (1)	Sm(1)–C(4)	2.72 (1)
Sm(1)–C(5)	2.74 (1)	Sm(1)–C(11)	2.79 (1)
Sm(1)–C(12)	2.80 (1)	Sm(1)–C(13)	2.73 (1)
Sm(1)–C(14)	2.72 (1)	Sm(1)–C(15)	2.78 (1)
Sm(1)–O(1)	2.49 (1)	Sm(1)–O(2)	2.08 (1)
C(21)–C(25)	1.55 (2)	C(22)–C(23)	1.30 (2)
C(21)–C(22)	1.53 (2)	C(23)–C(24)	1.47 (2)
C(24)–C(25)	1.33 (2)		
O(1)–Sm(1)–O(2)	89.1 (3)	Cent(1)–Sm(1)–O(1)	106.7
Cent(1)–Sm(1)–O(2)	108.5	Cent(2)–Sm(1)–O(1)	103.5
Cent(1)–Sm(1)–O(2)	104.4	Cent(1)–Sm(1)–Cent(2)	135.1
Sm(1)–O(2)–C(31)	165.2 (7)		

and 30° for a perfectly staggered arrangement. In 1,[2] the analogous torsional angles average 31°, and in the unsolvated complex $(C_5Me_5)_2Sm$,[4] they average 19°. Traditionally, eclipsed C_5Me_5 rings in organolanthanide complexes were thought to occur when forced by steric crowding in other parts of the molecule.[38] However, several complexes with eclipsed rings recently have been found in which the steric crowding is not so obvious.[39-42] The near-eclipsed arrangement in 2 is particularly surprising in comparison to 1, since 2 has shorter Sm–C distances and a smaller Cn–Sm–Cn angle: i.e., the rings are closer together. The shortest intramolecular inter-ring methyl carbon–methyl carbon distance in 2 is 3.04 Å for C(10)–C(10′) compared to 3.74 Å in 1 and 3.56 Å in $(C_5Me_5)_2Sm$. This distance is very short compared to the 4.0-Å sum of van der Waals radii appropriate for two nonbonded methyl groups.[43]

It is possible that the eclipsed arrangement arises from interactions with the THF ligands. The shorter Sm–O distances in 2 compared to those in 1 would bring the two THF molecules closer together if all other parameters were the same. In 2, the larger O–Sm–O angle compared to that for 1 keeps the THF molecules further apart. However, this larger angle also may cause unfavorable THF–C_5Me_5 interactions, which may be minimized by having the C_5Me_5 rings eclipsed with respect to each other. A sterically crowded coordination environment for 2 is consistent with some of the reactions discussed above. For example, the difficulty in substituting the THF ligands in 2 and the attack of $C_5Me_5^-$ on THF molecules to form 5 can be explained in this way. However, the possibility that 2 reacts with other anionic reagents, possibly through a nine-coordinate intermediate, is not consistent with this steric crowding unless there is a change in structure due to charge neutralization by the approaching anion. Obviously, more data are needed to assess the origin and consequences of eclipsed rings in molecules of this type.

$(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (3). One of the two crystallographically independent molecules in the unit cell of 3 is shown in Figure 2, and selected bond distances and angles are given in Table III. Complex 3 has an overall structure typical of other $(C_5Me_5)_2SmZ(THF)$ species (Z = Cl,[19] I,[19] Ph,[16] Me,[10] CH_2Ph[44]), and the average Sm–C(ring) distance of 2.71 (3) Å and the average Sm–O(THF) distance of 2.47 (2) Å are within the range normal for complexes of this type.[5,10] The 138° average Cn–Sm–Cn angle is at the upper end of the 130–138° range found for similar complexes.[5]

The average Sm–C(alkynide) distance of 2.49 (2) Å is very similar to the Sm–C distances of 2.48 (1), 2.498 (5), and 2.511 (8) Å in $(C_5Me_5)_2SmMe(THF)$,[10] $(C_5Me_5)_2Sm(CH_2Ph)(THF)$,[44] and $(C_5Me_5)_2SmPh(THF)$,[16] respectively. This is unusual in that metal–alkynide bonds are generally shorter than comparable metal–alkyl and –aryl bonds by 0.05–0.10 Å as shown by the metal–carbon single bonds in the following sets of compounds (Cp = C_5H_5): $Cp_3U(C{\equiv}CH)$[45] (2.36 Å) and $Cp_3U(C{\equiv}CPh)$[46] (2.33 Å) vs $Cp_3U(n\text{-}Bu)$[47] (2.55 Å) and $Cp_3U[CH_2C(Me){=}CH_2]$[48] (2.46 Å), $[Cp_2Er(\mu\text{-}C{\equiv}CCMe_3)]_2$[49] (2.42 and 2.47 Å) vs $[Cp_2Y(\mu\text{-}Me)]_2$[50] (2.49 and 2.54 Å), and $Cp_2VC{\equiv}CCMe_3$[51] (2.075 (5) Å) vs $[(MeC_5H_4)_2V]_2(C_6H_4)$[52] (2.12 (1) and 2.15 (1) Å).

In contrast to the Sm–C≡C bonds, which are longer than expected, the C≡C bonds are somewhat shorter than commonly found in molecules of this type, although there is more overlap when the error limits are considered. Hence, the C≡C bond lengths of the alkynide ligands in 3, 1.11 (2) and 1.13 (2) Å, can be compared to the following distances (in Å) found in lanthanide, actinide, and early-transition-metal alkynides: $[(MeC_5H_4)_2Sm(\mu\text{-}C{\equiv}CCMe_3)]_2$,[53] 1.20 (2); $[Cp_2Er(\mu\text{-}C{\equiv}CCMe_3)]_2$,[49] 1.26 (3); $[(C_5Me_5)_2Yb]_2(\mu\text{-}C{\equiv}CPh)_4Yb$,[35] 1.22 (1); $[(C_5Me_5)Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]$,[35] 1.188 (8); $Cp_3U(C{\equiv}CPh)$,[46] 1.25 (2); $Cp_3U(C{\equiv}CH)$,[45] 1.25, 1.29 (5); $Cp_2Zr(C{\equiv}CMe)_2$,[54] 1.206 (4); $Cp_2V(C{\equiv}CCMe_3)$,[51] 1.191 (7); $[Cp_2Ti(\mu\text{-}C{\equiv}CSiMe_3]_2$,[55] 1.25 (2). In general, C≡C distances in transition-metal alkynides[56] are longer than those in 3, as are the 1.19–

---

(38) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271–3278.

(39) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994.

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

(41) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772–2774.

(42) Rausch, M. D.; Moriarity, K. J.; Atwood, J. L.; Weeks, J. A.; Hunter, W. E.; Brittain, H. G. *Organometallics* **1986**, *5*, 1281–1283.

(43) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(44) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Submitted for publication.

(45) Atwood, J. L.; Tsutsui, M.; Ely, N.; Gebala, A. E. *J. Coord. Chem.* **1976**, *5*, 209–215.

(46) Atwood, J. L.; Hains, C. F., Jr.; Tsutsui, M.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 452–453.

(47) Perego, G.; Cesari, M.; Farina, F.; Lugli, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 3034–3039.

(48) Halstead, G. W.; Baker, E. C.; Raymond, K. N. *J. Am. Chem. Soc.* **1975**, *97*, 3049–3052.

(49) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119.

(50) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61.

(51) Evans, W. J.; Bloom, I.; Doedens, R. J. *J. Organomet. Chem.* **1984**, *265*, 249–255.

(52) Kohler, F. H.; Prossdorf, W.; Schubert, U. *Inorg. Chem.* **1981**, *20*, 4096–4101.

(53) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709–714.

(54) Erker, G.; Fromberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Kruger, C. *Organometallics* **1989**, *8*, 911–920.

(55) Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382–384.

(56) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89–124.

1.21-Å $C\equiv C$ distances in free alkynes.[57] However, the $C\equiv C$ distances in alkali-metal alkynides[58] are more similar to those in **3**: $NaC\equiv CMe$, 1.09 (2) Å; $NaC\equiv CH$, 1.17 (6) Å; $KC\equiv CMe$, 1.19 (6) Å.

The long Sm—C distance is consistent with the short $C\equiv C$ distance in that less Sm—C interaction should lead to a more isolated $C\equiv C$ bond which should be similar in length to that in alkali-metal alkynides. Unfortunately, the $\nu_{C\equiv C}$ stretch in the infrared spectrum of **3** was too weak to assign. However, the $\nu_{C\equiv C}$ stretch in the *tert*-butylalkynide analogue $(C_5Me_5)_2Sm(C\equiv CCMe_3)(THF)$ (**4**) is observed at 2072 cm^{-1}.[59] This absorption is at higher energy than the $\nu_{C\equiv C}$ absorptions in the crystallographically characterized organolanthanide alkynides $[(C_5H_5)_2Er(C\equiv CCMe_3)]_2$[49] (2050 cm^{-1}) and $[(MeC_5H_4)_2Sm(C\equiv CCMe_3)]_2$[53] (2035 cm^{-1}) and is consistent with a shorter $C\equiv C$ distance in **3**.

$(C_5Me_5)_2Sm[O(CH_2)_4(C_5Me_5)](THF)$ (5). The structure of complex **5** is shown in Figure 3, and selected bond distance and angle data are given in Table IV. Complex **5**, like **3**, has an overall geometry like other $(C_5Me_5)_2SmZ(THF)$ complexes,[10,16,19] and its structural details are unexceptional. The 2.49 (1) Å Sm–O(THF) distance and the 135.1° Cn–Sm–Cn angle are normal. The 2.76 (3) Å average Sm–C(C_5Me_5) distance is on the long end of the range observed for $(C_5Me_5)_2Sm(X)(Y)$ complexes.[5] The 2.08 (1) Å Sm–O(2) distance is slightly shorter than any $(C_5Me_5)_2$Sm–O(alkoxide) distance observed to date.[60] The 165.2 (7) Å Sm–O(2)–C(31) angle is typical of many strongly ligated early-transition-metal, lanthanide, and actinide complexes containing terminal alkoxide ligands.[63,64] The distances and angles in the butoxide chain are normal. The pentamethylcyclopentadiene ring attached to the $(CH_2)_4$ chain has two short C–C distances in the ring, C(22)–C(23) (1.30 (2) Å) and C(24)–C(25) (1.33 (2) Å), and the other three C–C lengths are greater than 1.47 (2) Å. This is consistent with a localized diene structure.

Conclusion

The cationic analogue of $(C_5Me_5)_2Sm(THF)_2$, namely $(C_5Me_5)_2Sm(THF)_2^+$, can be readily generated from **1** and $AgBPh_4$. The THF ligands are not readily substituted in the cationic complex, but it does react with alkyl anions to provide a halide-free route to trivalent $(C_5Me_5)_2Sm$ hydrocarbyls. When the large anionic reagent $C_5Me_5^-$ is used, reaction occurs with THF rather than with the metal. The result, ring opening of the THF to form the cyclopentadiene-substituted alkoxide, $O(CH_2)_4C_5Me_5$, may be a prototypical example of the type of ligand reaction chemistry that can be generated by Coulombic attractions in a crowded lanthanide coordination environment. Additional examples of such reactivity are being pursued as well as the synthetic utility of the alkoxy-tethered pentamethylcyclopentadiene moiety.

Acknowledgment. We thank the National Science Foundation for support for this research through Grant CHE-88-22093 (to W.J.E.) and Grant CHE-87-07055 (to K. G. Caulton). We also thank Professor K. G. Caulton for helpful discussion and Samuel E. Foster and Roy A. Keyer for experimental assistance. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: Additional ORTEP drawings of **2** and **3** and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for **2**, **3**, and **5** (33 pages); tables of observed and calculated structure factor amplitudes for **2**, **3**, and **5** (51 pages). Ordering information is given on any current masthead page.

---

[57] Dale, J. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; pp 3–96. *Spec. Publ.—Chem. Soc.* **1965**, *No. 18* (tables).

[58] Weiss, E.; Plaso, H. *Chem. Ber.* **1968**, *101*, 2947–2955.

[59] Similarly, the $\nu_{C\equiv C}$ absorption in $(C_5Me_5)_2Y(C\equiv CPh)(OEt_2)$ is weaker than that in $(C_5Me_5)_2Y(C\equiv CMe)(OEt_2)$: den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053–2060.

[60] Compare the Sm–O distances (Å) in $[(C_5Me_5)_2Sm]_2O$[61] (2.094 (1)), *trans*-$[(C_5Me_5)_2(Ph_3PO)Sm](OCH{=}CHO)$[62] (2.107 (7), 2.122 (8)), and $(C_5Me_5)_2Sm(OC_6HMe_4)$[63] (2.13 (1)).

[61] Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–409.

[62] Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

[63] Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191–195 and references therein.

[64] Evans, W. J.; Sollberger, M. S.; Hanusa, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 1841–1850.