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Reactivity of $(C_5Me_5)_2Sm$ with Cyclopentadiene and Cyclopentadienide: Isolation of the Mixed-Valent Complex $(C_5Me_5)_2Sm^{III}(\mu\text{-}C_5H_5)Sm^{II}(C_5Me_5)_2$[1]

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Abstract: Both $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ react with excess C_5H_6 to form $(C_5Me_5)_2Sm(C_5H_5)$ (**1**). Complex **1** crystallizes from hexane in space group $P2_1/n$ with $a = 9.355$ (3) Å, $b = 14.178$ (9) Å, $c = 17.424$ (6) Å, $\beta = 102.19$ (3)°, and $Z = 4$ for $D_{calcd} = 1.429$ g cm^{-3}. Least-squares refinement on the basis of 3679 observed reflections led to a final R value of 0.052. In the structure, the $(C_5Me_5)_2Sm$ unit is symmetrically bound to an η^5-C_5H_5 ring. With a deficiency of C_5H_6, $(C_5Me_5)_2Sm$ forms the mixed-valence complex $(C_5Me_5)_2Sm^{III}(\mu\text{-}C_5H_5)Sm^{II}(C_5Me_5)_2$ (**2**). Complex **2** can also be obtained from the stoichiometric reaction of **1** and $(C_5Me_5)_2Sm$. Complex **2** crystallizes from hexane in space group $P\bar{1}$ with $a = 10.385$ (4) Å, $b = 16.965$ (4) Å, $c = 12.863$ (3) Å, $\alpha = 104.80$ (2)°, $\beta = 86.61$ (2)°, $\gamma = 105.32$ (2)°, and $Z = 2$ for $D_{calcd} = 1.425$ g cm^{-3}. Least-squares refinement on the basis of 5077 observed reflections led to a final R value of 0.042. The complex crystallizes with a $(C_5Me_5)_2Sm^{II}$ unit coordinating via 2.98–3.18 Å Sm–C distances to two carbon atoms of the C_5H_5 ring in the trivalent $(C_5Me_5)_2Sm^{III}$ (C_5H_5) part of the molecule.

We recently reported the synthesis and structure of a remarkable metallocene complex, $(C_5Me_5)_2Sm$, i.e., decamethylsamarocene.[2,3] Although steric effects, molecular orbital calculations,[4] and simple electrostatic considerations predict a structure involving parallel C_5Me_5 rings, $(C_5Me_5)_2Sm$ has a bent metallocene structure. The ring centroid–Sm–ring centroid angle of 140.1° in $(C_5Me_5)_2Sm$ is nearly the same as that in its disolvated precursor[5,6] $(C_5Me_5)_2Sm(THF)_2$, 136.5°.

As part of our continuing interest in the reactivity of low-valent 4f element systems with unsaturated hydrocarbons,[7-9] we have been examining the reactivity of $(C_5Me_5)_2Sm$ with alkenes and dienes. The system which has provided the most well-defined products to date involves the reducible diene, cyclopentadiene. In this report, we describe the reactions of $(C_5Me_5)_2Sm$ with C_5H_6 to form a trivalent and a mixed-valent product. In the latter case, we have been able to trap the $(C_5Me_5)_2Sm$ unit in its initial approach to an unsaturated hydrocarbon system.

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 as previously described.[6] $(C_5Me_5)_2Sm(THF)_2$[6] and $(C_5Me_5)_2Sm$[3] were made according to the literature. $(C_5Me_5)_2Sm$ must be handled in an ether-free glovebox. Physical measurements were obtained as previously described.[10] Variable-temperature NMR data were obtained on a GE-300 MHz spectrometer over the temperature range −7 to 23 °C.

$(C_5Me_5)_2Sm(C_5H_5)$ (1) from $(C_5Me_5)_2Sm$. In the glovebox, $(C_5Me_5)_2Sm$ (0.162 g, 0.385 mmol) was added to 15 mL of hexane to give a dark green suspension which was placed in a 100-mL Schlenk flask with a Teflon stir bar. The side arm of the reaction vessel was equipped with a septum. The apparatus was removed from the glovebox and cooled to −78 °C. Freshly cracked cyclopentadiene (25 μL, 0.405 mmol) was added via syringe to the stirring solution. The reaction was removed from the −78 °C bath and allowed to warm to room temperature. Upon warming, the solution turned orange-red and was returned to the glovebox. After ca. 1 h, a yellow precipitate developed. The solution was filtered through a fine frit, and the yellow solid was discarded. The solvent of the orange-red supernatant was removed by rotary evaporation leaving an orange-red microcrystalline powder (0.175 g, 94%). ^{1}H NMR (benzene-d_6): δ 15.52 (br s, C_5H_5, 5 H), −1.05 (s, $C_5(CH_3)_5$, 30 H). ^{13}C NMR (benzene-d_6) δ 113.0 (s, $C_5(CH_3)_5$), 108.0 (d, $J = 161$ Hz, C_5H_5), 27.3 (q, $J = 124$ Hz, $C_5(CH_3)_5$). Magnetic susceptibility: $\chi_M{}^{295K} = 1450 \times 10^{-6}$ (cgs); $\mu_{eff}{}^{295K} = 1.86$ μ_B. IR (KBr): 2980 s, sh, 2920 s, 2840 s, 1440 w, 1380 w, 1020 m, 775 s cm^{-1}. Anal. Calcd for $SmC_{25}H_{35}$: Sm, 30.9. Found: Sm, 30.5.

$(C_5Me_5)_2Sm(C_5H_5)$ from $(C_5Me_5)_2Sm(THF)_2$. In the glovebox, $(C_5Me_5)_2Sm(THF)_2$ (0.197 g, 0.349 mmol) was suspended in 15 mL of hexane and placed in a 100 mL Schlenk flask with a Teflon stir bar. The side arm of the reaction vessel was equipped with a septum. The apparatus was removed from the glovebox. Freshly cracked cyclopentadiene (32 μL, 0.518 mmol) was added via syringe to the vigorously stirring solution. The reaction was stirred for ca. 5 min and returned to the glovebox for further stirring. After ca. 2.5 h the reaction mixture was centrifuged, yielding an organge-red solution and a dark plum solid which was discarded. The orange-red solution was concentrated to ca. 7 mL and cooled to −23 °C. The resulting yellow and dark colored solids were removed by filtration and discarded. The solvent of the orange-red supernatant was removed by rotary evaporation leaving an orange-red microcrystalline powder (0.166 g, 98%), which was found to be pure $(C_5Me_5)_2Sm(C_5H_5)$ by ^{1}H NMR spectroscopy.

X-ray Data Collection, Structure Determination and Refinement for $(C_5Me_5)_2Sm(C_5H_5)$. General procedures for data collection and reduction have been described previously.[11] A red crystal measuring 0.56 × 0.25 × 0.14 mm was sealed under N_2 in a glass capillary and mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were obtained from the settings of 15 computer-centered reflections. Monoclinic symmetry was indicated by the interaxial angles and confirmed by axial rotation photography. Data were collected by the θ–2θ scan technique in bisecting geometry. The p factor in the expression[12] for the standard deviations of the observed intensities was given a value of 0.05. Relevant crystal and data collection parameters are given in Table I. All computations were carried out with a local version of the UCLA Crystallographic Computing Package.[13] The space group was determined as $P2_1/n$ (alternate setting of $P2_1/c$, No. 14) from the systematic absences, $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$.

During the data collection, the intensities of three standard reflections measured every 100 reflections showed linear decay of 2%. Data were corrected for Lorentz, polarization, and absorption effects and for decay of standards. Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms which were refined with anisotropic thermal parameters by use of full-matrix least-squares methods. Al-

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(1) Presented in part at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, September, 1986; Paper INOR 222.

(2) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272.

(3) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285–1291.

(4) Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 2095–2104.

(5) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

(6) 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.

(7) Evans, W. J. *Polyhedron* **1987**, *6*, 803–835.

(8) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217–226 and references therein.

(9) Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1722–1723.

(10) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

(11) Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153–156.

(12) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

(13) Strouse, C. E., personal communication to R. J. Doedens.

0002-7863/87/1509-4292$01.50/0

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $(C_5Me_5)_2Sm(C_5H_5)$ (**1**) and $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**2**)

	1	**2**
compd	$SmC_{25}H_{35}$	$Sm_2C_{45}H_{65}$
mol wt	485.905	906.715
space group	$P2_1/n$	$P\bar{1}$
cell consts		
a, Å	9.355 (3)	10.385 (4)
b, Å	14.178 (9)	16.965 (4)
c, Å	17.424 (6)	12.863 (3)
α, deg		104.80 (2)
β, deg	102.19 (3)	86.61 (2)
γ, deg		105.32 (2)
cell vol, $Å^3$	2259	2113
molecules/unit cell	4	2
D(calcd), g cm^{-3}	1.429	1.425
temp, K	295	295
μ(calcd), cm^{-1}	26.2	27.9
radiatn	Mo Kα, λ = 0.71073 Å	Mo Kα, λ = 0.71073 Å
tranmsn factor range	0.62–0.76	0.90–0.94
max cryst dimens, mm	0.56 × 0.25 × 0.14	0.51 × 0.15 × 0.10
scan width	−1.2° in 2θ from Kα_1 to +1.2° from Kα_2	−1.2° in 2θ from Kα_1 to +1.2° from Kα_2
scan rate, deg min^{-1}	variable, 4.0–12.0	variable, 4.0–16.0
bkgd counting	estimated from 96–step peak profile	estimated from 96-step peak profile
std reflctns	−3, 0, 1; 2, 1, −6; −4, −1, 0	1, 0, −2; 1, 5, −1; 2, 0, −4
decay of stds	2%	1%
2θ range, deg	4–55	4–50
total unique data	5536	7497
unique data with $I \geq 3\sigma(I)$	3679	5077
no. of parameters varied	235	424
GOF	1.99	1.48
R	0.052	0.042
R_w	0.066	0.054
max Δ/σ in final cycle	0.03	0.04

though hydrogen atoms were evident in the final difference map, no hydrogen atoms were included in the structure refinement. Atomic scattering factors were taken from ref 14. A final difference map contained no recognizable features; its two largest peaks were of height 3.97 and 3.65 e $Å^{-3}$ at a distance of 0.88 and 1.06 Å from the samarium. Final fractional coordinates are given in Table II.

$(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (2). In the glovebox, $(C_5Me_5)_2Sm$ (0.199 g, 0.473 mmol) was added to 15 mL of hexane to give a dark green suspension which was placed in a 100-mL Schlenk flask equipped with a Teflon stir bar and a septum-capped side arm. The apparatus was removed from the glovebox. Freshly cracked cyclopentadiene (14 μL, 0.227 mmol) was added via syringe to the vigorously stirring solution at room temperature to instantly give a dark brown solution. The solution was allowed to stir for ca. $^1/_2$ h and then returned to the glovebox. The hexane was removed by rotary evaporation to yield a mixture of red and green solids. The red/green powder was dissolved in 10 mL of toluene to yield a dark brown solution. The toluene was removed by rotary evaporation to yield a free-flowing dark brown powder (essentially quantitative yield).

Alternatively, in the glovebox $(C_5Me_5)_2Sm$ (0.055 g, 0.130 mmol) was dissolved in 5 mL of toluene and placed in a 50-mL flask with a Teflon stir bar. Recrystallized $(C_5Me_5)_2Sm(C_5H_5)$ (0.063 g, 0.130 mmol) was dissolved in 3 mL of toluene and pipetted into the stirring $(C_5Me_5)_2Sm$ solution to instantly yield a dark brown solution. The solution was rotary evaporated to yield **2** in quantitative yield. ^1H NMR (benzene-d_6, 13 mM) δ 15.07 (br s, C_5H_5, 5 H, $\Delta\nu_{1/2}$ = 49 Hz), 0.12 (br s, $C_5(CH_3)_5$, 60 H, $\Delta\nu_{1/2}$ = 37 Hz). ^{13}C NMR (benzene-d_6): δ 19.7 (br s, $C_5(CH_3)_5$), 58.1 (q, J = 112 Hz, $C_5(CH_3)_5$), 88.0 (d, J = 168 Hz, C_5H_5). Magnetic susceptibility: $\chi_M^{295K} = 3460 \times 10^{-6}$ (cgs); $\mu_{eff}^{295K} = 2.87\ \mu_B$. IR (KBr): 2920 s sh, 2900 s, 2860 s, 1445 m, 1380 m, 1015 m, 975 w, 790 m, 770 s cm^{-1}. Anal. Calcd for $Sm_2C_{45}H_{65}$: Sm, 33.2. Found: Sm, 32.6.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$. A dark brown crystal measuring 0.51 × 0.15 × 0.10 mm was handled as described above. Lattice parameters for a triclinic cell were determined from 15 computer-centered reflections. Relevant crystal and data collection parameters are given in Table I. The space group $P\bar{1}$ was indicated by intensity statistics and was confirmed by the successful solution and refinement of the structure. During the data collection, the intensities of three standard reflections measured every 100 reflections showed linear decay of 1%. Data were corrected for Lorentz, polarization, and absorption effects and for decay of standards. A combination of direct methods (MITHRIL) and difference Fourier techniques provided the locations of all non-hydrogen atoms which were refined with anisotropic thermal parameters by use of full-matrix least-squares methods. Hydrogen atoms were entered in calculated positions and not refined. A final difference map contained no recognizable features; its largest peak was of height 1.33 e $Å^{-3}$ at a distance of 1.02 Å from C(15). Final fractional coordinates are given in Table II.

Results and Discussion

Synthesis and Characterization of $(C_5Me_5)_2Sm(C_5H_5)$. Previous studies of the reactivity of $(C_5Me_5)_2Sm(THF)_2$ with substrates such as CO,[15] $C_6H_5C{\equiv}CC_6H_5$,[16] ROH,[17] and $C_6H_5N{=}NC_6H_5$[18] have shown that organosamarium(II) complexes are strong reducing agents. In the CO, $C_6H_5C{\equiv}CC_6H_5$ and ROH reactions in particular there are parallels with alkali-metal chemistry. Therefore, it is reasonable that $(C_5Me_5)_2Sm(THF)_2$ should reduce C_6H_6, as do alkali metals, to form the $C_5H_5^-$ ion (eq 1).

$$(C_5Me_5)_2Sm(THF)_2 + C_5H_6 \rightarrow (C_5Me_5)_2SmC_5H_5 + {}^1/_2H_2 + 2THF \quad (1)$$

The reactivity of the unsolvated sterically unsaturated $(C_5Me_5)_2Sm$ might be expected to parallel or even exceed the reactivity of $(C_5Me_5)_2Sm(THF)_2$. Consistent with this $(C_5Me_5)_2Sm$ also reduces C_5H_6 to form $(C_5Me_5)_2Sm(C_5H_5)$ as shown in eq 1. Visually, the $(C_5Me_5)_2Sm$ reaction proceeds faster than the $(C_5Me_5)_2Sm(THF)_2$ reaction and gives an immediate color change upon C_5H_6 addition. Alternative synthetic routes to complex **1** such as the reaction of $(C_5Me_5)_2SmCl(THF)$[19] with NaC_5H_5 or the combination of 2 equiv of KC_5Me_5 with NaC_5H_5 and $SmCl_3$ were briefly examined and did not give **1** in good yield.

$(C_5Me_5)_2Sm(C_5H_5)$ (**1**) was characterized by complexometric metal analysis, NMR and IR spectroscopy, and X-ray crystallography. Powdered samples of **1** have an orange red color (cf. yellow $(C_5H_5)_3Sm(THF)$[20]) and crystalline **1** is almost ruby red. The C_5H_5 and C_5Me_5 resonances in the ^1H NMR spectrum are widely spaced due to the paramagnetism of the Sm(III) center: $\mu = 1.86\ \mu_B$. The broad resonance at 15.5 ppm ($\Delta\nu_{1/2}$ = 7.7 Hz) is assigned to the C_5H_5 protons (cf. 12.72 ppm in the ^1H NMR spectrum of $(C_5H_5)_3Sm(THF)$). The C_5Me_5 protons in **1** resonate at −1.05 ppm compared to a range of 0.06–1.44 ppm for $(C_5Me_5)_2Sm(X)(Y)$ and $(C_5Me_5)_2SmZ$ complexes where X = Cl,[19] I,[19] C_6H_5,[21] $CH_2C_6H_5$,[22] and OC_6H_5,[23] Y = THF, and Z = $OSm(C_5Me_5)_2$[24] and OC_6Me_4H.[17]

Structure of $(C_5Me_5)_2Sm(C_5H_5)$. The structurally characterized trivalent bis(pentamethylcyclopentadienyl)samarium complexes currently in the literature fall into two categories: $(C_5Me_5)_2SmZ$ and $(C_5Me_5)_2Sm(X)(Y)$. In all cases, X, Y, and Z are monohapto ligands. The structure of $(C_5Me_5)_2Sm(C_5H_5)$, shown in Figure 1, is the first example of a $(C_5Me_5)_2SmZ$ complex in which Z

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(14) *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

(15) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728–3730.

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

(17) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191–195.

(18) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389–2391.

(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) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42–44.

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

(22) Evans, W. J.; Ulibarri, T. A., unpublished results.

(23) Evans, W. J.; Podejko, K. G., unpublished results.

(24) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–409.

Table II. Atomic Positional Parameters and Equivalent Isotropic Temperature Factors for $(C_5Me_5)_2Sm(C_5H_5)$ (**1**) and $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me)_2$ (**2**)

atom	x	y	z	$10^4\ u$,[a] Å^2	atom	x	y	z	$10^4\ u$,[a] Å^2
Complex **1**									
Sm(1)	0.91443 (3)	0.20110 (3)	0.17298 (2)	452 (2)	C(13)	0.7871 (14)	0.0865 (7)	−0.0267 (6)	977 (87)
C(1)	0.6775 (9)	0.2928 (6)	0.0825 (5)	604 (51)	C(14)	0.9764 (14)	0.2702 (12)	−0.0305 (7)	1241 (114)
C(2)	0.6585 (8)	0.2018 (6)	0.0559 (4)	570 (47)	C(15)	0.8370 (15)	0.4362 (8)	0.0627 (7)	1167 (106)
C(3)	0.7724 (9)	0.1775 (6)	0.0181 (4)	584 (51)	C(16)	0.5832 (12)	0.1257 (9)	0.2568 (8)	1210 (113)
C(4)	0.8600 (10)	0.2606 (8)	0.0184 (5)	748 (62)	C(17)	0.6975 (15)	−0.0330 (7)	0.1493 (6)	1102 (95)
C(5)	0.7974 (11)	0.3315 (6)	0.0581 (5)	662 (57)	C(18)	1.0360 (15)	−0.0472 (9)	0.2027 (8)	1204 (115)
C(6)	0.7413 (6)	0.1021 (5)	0.2554 (5)	574 (49)	C(19)	1.1314 (14)	0.0666 (11)	0.3605 (9)	1429 (122)
C(7)	0.7888 (9)	0.0348 (5)	0.2073 (4)	548 (47)	C(20)	0.8551 (23)	0.1933 (8)	0.3829 (7)	1330 (133)
C(8)	0.9423 (9)	0.0239 (6)	0.2361 (5)	641 (57)	C(21)	1.1288 (13)	0.3293 (10)	0.1562 (9)	1039 (101)
C(9)	0.9828 (10)	0.0779 (6)	0.3018 (5)	719 (60)	C(22)	1.0871 (13)	0.3537 (9)	0.2263 (8)	1015 (95)
C(10)	0.8591 (11)	0.1291 (6)	0.3121 (4)	647 (58)	C(23)	1.1426 (15)	0.2745 (13)	0.2802 (8)	1131 (111)
C(11)	0.5694 (13)	0.3477 (9)	0.1214 (7)	998 (91)	C(24)	1.2053 (11)	0.2109 (13)	0.2386 (11)	1295 (127)
C(12)	0.5155 (10)	0.1459 (8)	0.0493 (6)	908 (76)	C(25)	1.1952 (12)	1.2403 (16)	0.1628 (10)	1379 (136)
Complex **2**									
Sm(1)	0.10849 (4)	0.23903 (3)	0.33041 (3)	399 (3)	C(23)	0.5233 (11)	0.3137 (9)	−0.2096 (9)	789 (116)
Sm(2)	0.48585 (5)	0.29289 (4)	0.00232 (4)	617 (5)	C(24)	0.4322 (13)	0.2315 (9)	−0.2207 (8)	845 (124)
C(1)	0.2133 (8)	0.4046 (5)	0.4401 (6)	456 (5)	C(25)	0.3118 (10)	0.2420 (6)	−0.1726 (7)	630 (87)
C(2)	0.2026 (8)	0.3571 (5)	0.5177 (6)	487 (68)	C(26)	0.6904 (10)	0.3397 (7)	0.1584 (10)	744 (105)
C(3)	0.0628 (8)	0.3261 (5)	0.5377 (6)	485 (68)	C(27)	0.6218 (10)	0.2569 (8)	0.1628 (11)	812 (118)
C(4)	−0.0097 (8)	0.3516 (5)	0.4683 (6)	473 (66)	C(28)	0.6432 (12)	0.2020 (7)	0.0646 (14)	989 (138)
C(5)	0.0818 (9)	0.4005 (5)	0.4087 (6)	492 (69)	C(29)	0.7300 (10)	0.2504 (8)	0.0007 (12)	903 (126)
C(6)	−0.0601 (10)	0.0801 (5)	0.2761 (8)	585 (78)	C(30)	0.7571 (9)	0.3339 (7)	0.0585 (10)	731 (104)
C(7)	0.0650 (10)	0.0638 (5)	0.2499 (8)	606 (83)	C(31)	0.2105 (10)	0.3693 (6)	−0.0881 (7)	657 (90)
C(8)	0.1378 (10)	0.0857 (6)	0.3507 (9)	664 (91)	C(32)	0.5048 (13)	0.4677 (8)	−0.1413 (9)	982 (123)
C(9)	0.0549 (10)	0.1093 (6)	0.4354 (7)	597 (82)	C(33)	0.6588 (15)	0.3326 (12)	−0.2639 (13)	1442 (215)
C(10)	−0.0690 (9)	0.1081 (5)	0.3911 (7)	559 (76)	C(34)	0.4604 (19)	0.1467 (10)	−0.2810 (13)	1418 (199)
C(11)	0.3425 (9)	0.4614 (6)	0.4134 (8)	630 (81)	C(35)	0.1870 (12)	0.1713 (7)	−0.1693 (8)	804 (99)
C(12)	0.3183 (10)	0.3498 (7)	0.5790 (8)	702 (94)	C(36)	0.6958 (12)	0.4191 (8)	0.2497 (11)	938 (130)
C(13)	0.0091 (11)	0.2969 (7)	0.6398 (7)	777 (99)	C(37)	0.5526 (13)	0.2318 (11)	0.2618 (13)	1326 (182)
C(14)	−0.1607 (9)	0.3394 (7)	0.4672 (9)	710 (94)	C(38)	0.5829 (15)	0.1044 (8)	0.0310 (16)	1411 (182)
C(15)	0.0401 (10)	0.4536 (6)	0.3420 (8)	666 (90)	C(39)	0.7915 (13)	0.2143 (10)	−0.1089 (14)	1277 (173)
C(16)	−0.1717 (11)	0.0656 (7)	0.1972 (9)	805 (104)	C(40)	0.8537 (12)	0.4086 (8)	0.0265 (13)	1042 (139)
C(17)	0.1038 (12)	0.0125 (7)	0.1431 (9)	831 (107)	C(41)	0.2984 (10)	0.2985 (6)	0.1871 (7)	645 (86)
C(18)	0.2758 (11)	0.0691 (8)	0.3598 (11)	942 (132)	C(42)	0.2489 (11)	0.2091 (6)	0.1392 (7)	661 (89)
C(19)	0.0832 (13)	0.1160 (7)	0.5527 (8)	875 (114)	C(43)	0.1138 (11)	0.1967 (6)	0.1067 (7)	634 (88)
C(20)	−0.1968 (11)	0.1136 (7)	0.4511 (10)	839 (110)	C(44)	0.0830 (11)	0.2757 (6)	0.1335 (7)	649 (90)
C(21)	0.3248 (9)	0.3294 (6)	−0.1359 (6)	520 (75)	C(45)	0.1981 (11)	0.3388 (6)	0.1804 (7)	618 (89)
C(22)	0.4550 (10)	0.3738 (7)	−0.1572 (7)	632 (88)					

[a] $U_{eq} = (^1/_6\pi^2)\sum\sum\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

is a polyhapto ligand. It was therefore of interest to examine the steric effects of the η^5-C_5H_5 ligand on the $(C_5Me_5)_2Sm$ unit. Note that it is predicted that three C_5Me_5 rings are too large to fit around a metal.[25]

The three cyclopentadienyl rings describe a distorted trigonal-planar geometry around the samarium atom as shown in Figure 2a. The samarium atom lies only 0.015 Å out of the plane defined by the three ring centroids. The two (C_5Me_5 centroid)–Sm–(C_5H_5 centroid) angles are nearly equal, 116.9° and 116.2°, and are smaller than the (C_5Me_5 centroid)–Sm–(C_5Me_5 centroid) angle of 127.0°. The latter angle is the smallest observed for any $(C_5Me_5)_2Sm(X)(Y)$ or $(C_5Me_5)_2SmZ$ system (normal range 130–138°) and is consistent with considerable steric crowding. The C_5Me_5 rings are arranged so that the methyl groups are nearly perfectly staggered as shown in Figure 2b. The position of the C_5H_5 ring with respect to the $(C_5Me_5)_2Sm$ moiety is such that all C_5H_5 carbon atoms are inequivalent.

Bond lengths also show the effects of steric crowding in **1**. The 2.770 (3) Å average Sm–C(C_5Me_5) bond length is on the long end of the range of values observed for $(C_5Me_5)_2Sm(X)(Y)$ and $(C_5Me_5)_2SmZ$ complexes: 2.68–2.77 Å. Only the two isomers of $[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-OCHCHO})$[10] have Sm–C(ring) averages as long: 2.76 and 2.77 Å. Relatively few Sm–C(C_5H_5) distances are available for comparison with the average Sm–C(C_5H_5) distance of 2.738 (4) Å. The analogous average of 2.72 (4) Å found in $[(MeC_5H_4)_2Sm(\mu\text{-}C{\equiv}CCMe_3)]_2$,[26] is slightly shorter and the 2.75-Å average in Sm(indenyl)$_3$[27] is larger.

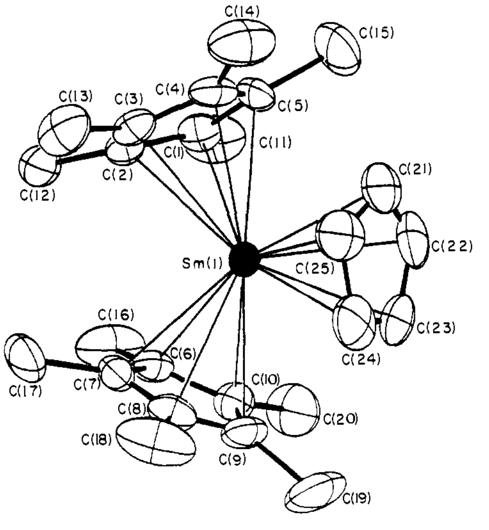

Figure 1. ORTEP diagram of the molecular structure of $(C_5Me_5)_2Sm(C_5H_5)$ (**1**).

Synthesis and Characterization of $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$. When $(C_5Me_5)_2Sm$ reacts with a less than stoichiometric amount of C_5H_6, $(C_5Me_5)_2Sm(C_5H_5)$ and $(C_5Me_5)_2Sm$

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

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

(27) Atwood, J. L.; Burns, J. H.; Laubereau, P. G. *J. Am. Chem. Soc.* **1973**, *95*, 1830–1833.

Table III. Interatomic Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(C_5H_5)$

Bond Distances			
Sm(1)–C(24)	2.724 (10)	C(4)–C(5)	1.415 (14)
Sm(1)–C(25)	2.727 (10)	C(4)–C(14)	1.524 (13)
Sm(1)–C(23)	2.729 (11)	C(5)–C(15)	1.528 (12)
Sm(1)–C(8)	2.733 (8)	C(6)–C(10)	1.370 (12)
Sm(1)–C(22)	2.742 (10)	C(6)–C(7)	1.403 (11)
Sm(1)–C(7)	2.756 (7)	C(6)–C(16)	1.522 (11)
Sm(1)–C(1)	2.759 (8)	C(7)–C(8)	1.426 (11)
Sm(1)–C(6)	2.763 (7)	C(7)–C(17)	1.520 (11)
Sm(1)–C(3)	2.765 (8)	C(8)–C(9)	1.363 (12)
Sm(1)–C(4)	2.765 (8)	C(8)–C(18)	1.529 (12)
Sm(1)–C(21)	2.768 (9)	C(9)–C(10)	1.409 (12)
Sm(1)–C(5)	2.775 (8)	C(9)–C(19)	1.550 (13)
Sm(1)–C(10)	2.777 (8)	C(10)–C(20)	1.540 (12)
Sm(1)–C(2)	2.798 (7)	C(21)–C(25)	1.400 (22)
Sm(1)–C(9)	2.809 (8)	C(21)–C(22)	1.402 (18)
C(1)–C(2)	1.370 (11)	C(22)–C(23)	1.485 (19)
C(1)–C(5)	1.393 (13)	C(23)–C(24)	1.365 (21)
C(1)–C(11)	1.542 (13)	C(24)–C(25)	1.369 (20)
C(2)–C(3)	1.409 (11)	Sm(1)–Cn(1)	2.502
C(2)–C(12)	1.538 (12)	Sm(1)–Cn(2)	2.501
C(3)–C(4)	1.435 (12)	Sm(1)–Cn(3)	2.464
C(3)–C(13)	1.529 (12)		

Bond Angles			
C(2)–C(1)–C(5)	108.8 (8)	C(6)–C(7)–C(17)	128.5 (9)
C(2)–C(1)–C(11)	125.0 (9)	C(8)–C(7)–C(17)	123.2 (8)
C(5)–C(1)–C(11)	125.5 (9)	C(9)–C(8)–C(7)	108.4 (7)
C(1)–C(2)–C(3)	109.4 (7)	C(9)–C(8)–C(18)	127.6 (9)
C(1)–C(2)–C(12)	124.0 (8)	C(7)–C(8)–C(18)	123.6 (9)
C(3)–C(2)–C(12)	124.8 (8)	C(8)–C(9)–C(10)	107.8 (7)
C(2)–C(3)–C(4)	106.6 (7)	C(8)–C(9)–C(19)	123.2 (11)
C(2)–C(3)–C(13)	127.1 (8)	C(10)–C(9)–C(19)	128.0 (10)
C(4)–C(3)–C(13)	125.6 (8)	C(6)–C(10)–C(9)	108.7 (7)
C(5)–C(4)–C(3)	106.9 (7)	C(6)–C(10)–C(20)	126.2 (11)
C(5)–C(4)–C(14)	128.9 (11)	C(9)–C(10)–C(20)	124.5 (11)
C(3)–C(4)–C(14)	123.1 (11)	C(25)–C(21)–C(22)	110.6 (13)
C(1)–C(5)–C(4)	108.2 (7)	C(21)–C(22)–C(23)	103.9 (13)
C(1)–C(5)–C(15)	124.6 (10)	C(24)–C(23)–C(22)	107.2 (13)
C(4)–C(5)–C(15)	126.5 (10)	C(23)–C(24)–C(25)	111.2 (16)
C(10)–C(6)–C(7)	108.2 (7)	C(24)–C(25)–C(21)	107.0 (17)
C(10)–C(6)–C(16)	124.3 (9)	Cn(1)–Sm(1)–Cn(2)	127.0
C(7)–C(6)–C(16)	126.2 (9)	Cn(1)–Sm(1)–Cn(3)	116.9
C(6)–C(7)–C(8)	106.6 (7)	Cn(2)–Sm(1)–Cn(3)	116.2

[a] Cn = ring centroid.

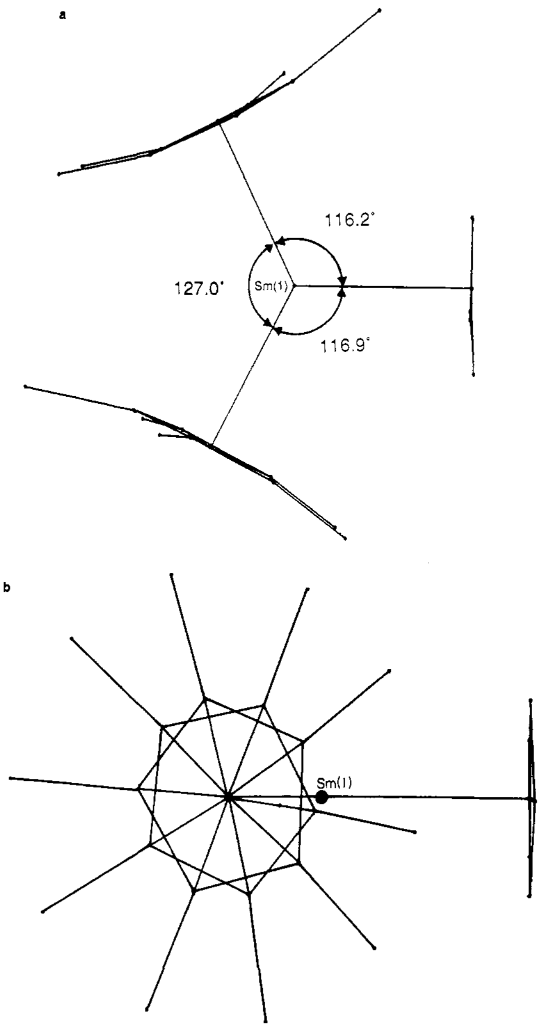

Figure 2. (a) View of **1** looking perpendicular to the plane defined by Sm and the three cyclopentadienyl ring centroids. All unlabeled dots are carbon atoms. (b) View of **1** looking down the (C_5Me_5 ring centroid)–(C_5Me_5 ring centroid) vector.

are present together in solution. By this route or by independently assembling a solution of $(C_5Me_5)_2Sm(C_5H_5)$ and $(C_5Me_5)_2Sm$, a mixture is obtained from which a new complex, $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**2**), can be isolated. Success in isolating **2** depends on subtle variations in concentration and in crystallization procedures. A mixture of orange-red $(C_5Me_5)_2Sm(C_5H_5)$ and green $(C_5Me_5)_2Sm$ in hexane gives a brown solution. Removal of solvent by rotary evaporation in some cases gives back the individual complexes as red and green bands of solids in the flask. With use of toluene as the solvent, only brown solids are obtained. In one case orange-red crystals of **1** and green crystals of $(C_5Me_5)_2Sm$ were obtained from a rapid crystallization of the brown **1**/$(C_5Me_5)_2Sm$ mixture in hexane at −10 °C. Redissolving these crystals in hexane and recrystallization by slow concentration at 30 °C gave brown crystals of **2**. Formation of **2** by combination of **1** and $(C_5Me_5)_2Sm$ is not possible in THF because $(C_5Me_5)_2Sm$ is immediately converted to $(C_5Me_5)_2Sm(THF)_2$. THF also immediately dissociates **2** into $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm(C_5H_5)$.

The molar magnetic susceptibility of **2**, determined in C_6H_6 by the Evans method,[28] 3460×10^{-6} (cgs), is close to the average of the susceptibilities of its components, $(C_5Me_5)_2Sm(C_5H_5)$, 1450×10^{-6}, and $(C_5Me_5)_2Sm$, 5700×10^{-6}. These data plus an X-ray crystal structure of **2** (see later section) indicate that this is a class I mixed-valence system by using the classification scheme of Robin and Day.[29]

The NMR spectra of **2** also show averaged signals. The ^1H NMR spectrum of **2** in C_6D_6 shows a single C_5Me_5 resonance at 0.12 ppm, indicating that in solution these rings experience the same magnetic environment on the NMR time scale. The position of this signal is intermediate between the −1.05 ppm value for the C_5Me_5 rings in trivalent **1** and the 1.3 ppm shift typical for divalent $(C_5Me_5)_2Sm$.[3] Variable-temperature studies down to 196 K in toluene-d_8 did not freeze out two C_5Me_5 resonances. The addition of $(C_5Me_5)_2Sm$ to NMR samples of **2** also gave only a single averaged C_5Me_5 resonance. Added $(C_5Me_5)_2Sm$ moves the C_5H_5 signal upfield and the C_5Me_5 signal downfield. The ^{13}C NMR signals of the C_5Me_5 carbon atoms are particularly interesting since Sm(II) and Sm(III) complexes give very different ranges for these resonances. For trivalent **1**, the ring carbons resonate at 113.0 ppm and the methyl carbons at 27.3 ppm. For divalent $(C_5Me_5)_2Sm$,[3] the order is reversed: shifts of −98.2 ppm for the ring carbon atoms and 99 ppm for the methyl carbon atoms are found. In **2**, the resonances are intermediate: 19.7 ppm for the ring carbon atoms and 58 ppm for the methyl carbon atoms. The ^1H NMR and ^{13}C NMR resonances of the C_5H_5 ligand in **2** are close to those for C_5H_5 in **1**. Hence, it appears that the C_5H_5 ring is always near a Sm(III) center, but the $(C_5Me_5)_2Sm$ units are rapidly switching between Sm(II) and Sm(III) oxidation states. ^1H NMR line-broadening methods were used to study this ex-

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(28) Evans, D. F. *J. Chem. Soc.* 1959, 2003–2005. Becconsall, J. K. *Mol. Phys.* **1968**, *15*, 129–139.

(29) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422.

Table IV. Interatomic Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$

Bond Distances

Sm(1)-C(10)	2.738 (8)	C(7)-C(8)	1.456 (13)	Sm(2)-C(22)	2.815 (9)	C(27)-C(28)	1.408 (18)
Sm(1)-C(6)	2.739 (8)	C(7)-C(17)	1.522 (13)	Sm(2)-C(26)	2.818 (10)	C(27)-C(37)	1.524 (17)
Sm(1)-C(4)	2.752 (8)	C(8)-C(9)	1.384 (13)	Sm(2)-C(24)	2.826 (11)	C(28)-C(29)	1.422 (17)
Sm(1)-C(5)	2.755 (8)	C(8)-C(18)	1.551 (14)	Sm(2)-C(23)	2.830 (10)	C(28)-C(38)	1.568 (16)
Sm(1)-C(2)	2.756 (8)	C(9)-C(10)	1.431 (13)	Sm(2)-C(27)	2.847 (9)	C(29)-C(30)	1.388 (15)
Sm(1)-C(1)	2.765 (7)	C(9)-C(19)	1.531 (13)	Sm(2)-C(41)	2.986 (8)	C(29)-C(39)	1.560 (19)
Sm(1)-C(43)	2.774 (8)	C(10)-C(20)	1.511 (13)	Sm(2)-C(42)	3.180 (9)	C(30)-C(40)	1.531 (14)
Sm(1)-C(8)	2.775 (9)	C(21)-C(25)	1.402 (12)	C(1)-C(5)	1.420 (11)	C(41)-C(45)	1.401 (13)
Sm(1)-C(3)	2.785 (8)	C(21)-C(22)	1.413 (12)	C(1)-C(2)	1.429 (11)	C(41)-C(42)	1.455 (14)
Sm(1)-C(42)	2.787 (9)	C(21)-C(31)	1.539 (12)	C(1)-C(11)	1.510 (11)	C(42)-C(43)	1.432 (14)
Sm(1)-C(41)	2.789 (8)	C(22)-C(23)	1.403 (14)	C(2)-C(3)	1.441 (11)	C(43)-C(44)	1.413 (13)
Sm(1)-C(9)	2.790 (9)	C(22)-C(32)	1.504 (15)	C(2)-C(12)	1.513 (12)	C(44)-C(45)	1.419 (14)
Sm(1)-C(44)	2.803 (8)	C(23)-C(24)	1.451 (16)	C(3)-C(4)	1.428 (12)	Sm(1)-Cn(1)	2.478
Sm(1)-C(7)	2.805 (9)	C(23)-C(33)	1.529 (15)	C(3)-C(13)	1.541 (11)	Sm(1)-Cn(2)	2.491
Sm(1)-C(45)	2.845 (8)	C(24)-C(25)	1.394 (14)	C(4)-C(5)	1.413 (11)	Sm(1)-Cn(5)	2.524
Sm(2)-C(25)	2.782 (10)	C(24)-C(34)	1.530 (17)	C(4)-C(14)	1.525 (12)	Sm(2)-Cn(3)	2.540
Sm(2)-C(21)	2.786 (8)	C(25)-C(35)	1.528 (14)	C(5)-C(15)	1.546 (12)	Sm(2)-Cn(4)	2.548
Sm(2)-C(28)	2.797 (10)	C(26)-C(27)	1.415 (14)	C(6)-C(7)	1.400 (13)	Sm(2)-Cn(5)	3.513
Sm(2)-C(30)	2.806 (9)	C(26)-C(30)	1.419 (15)	C(6)-C(10)	1.439 (12)	Sm(1)-Sm(2)	5.668
Sm(2)-C(29)	2.814 (9)	C(26)-C(36)	1.535 (16)	C(6)-C(16)	1.521 (13)		

Bond Angles

C(5)-C(1)-C(2)	108.4 (7)	C(21)-C(22)-C(32)	126.6 (10)	C(6)-C(7)-C(8)	106.6 (8)	C(29)-C(28)-C(38)	125.0 (16)
C(5)-C(1)-C(11)	127.7 (8)	C(22)-C(23)-C(24)	107.8 (9)	C(6)-C(7)-C(17)	126.4 (9)	C(30)-C(29)-C(28)	107.2 (12)
C(2)-C(1)-C(11)	123.1 (8)	C(22)-C(23)-C(33)	125.7 (13)	C(8)-C(7)-C(17)	125.4 (9)	C(30)-C(29)-C(39)	126.6 (12)
C(1)-C(2)-C(3)	107.3 (7)	C(24)-C(23)-C(33)	125.7 (12)	C(9)-C(8)-C(7)	108.9 (8)	C(28)-C(29)-C(39)	126.1 (12)
C(1)-C(2)-C(12)	126.1 (8)	C(25)-C(24)-C(23)	107.7 (10)	C(9)-C(8)-C(18)	126.7 (10)	C(29)-C(30)-C(26)	109.3 (10)
C(3)-C(2)-C(12)	126.2 (8)	C(25)-C(24)-C(34)	126.2 (13)	C(7)-C(8)-C(18)	123.5 (10)	C(29)-C(30)-C(40)	126.7 (12)
C(4)-C(3)-C(2)	107.5 (7)	C(23)-C(24)-C(34)	126.0 (12)	C(8)-C(9)-C(10)	108.5 (8)	C(26)-C(30)-C(40)	123.8 (11)
C(4)-C(3)-C(13)	126.1 (8)	C(24)-C(25)-C(21)	107.7 (9)	C(8)-C(9)-C(19)	124.2 (10)	C(45)-C(41)-C(42)	109.1 (9)
C(2)-C(3)-C(13)	123.7 (8)	C(24)-C(25)-C(35)	125.2 (10)	C(10)-C(9)-C(19)	126.2 (10)	C(43)-C(42)-C(41)	105.5 (9)
C(5)-C(4)-C(3)	108.5 (7)	C(21)-C(25)-C(35)	127.0 (9)	C(9)-C(10)-C(6)	106.9 (8)	C(44)-C(43)-C(42)	109.0 (9)
C(5)-C(4)-C(14)	125.2 (8)	C(27)-C(26)-C(30)	107.3 (11)	C(9)-C(10)-C(20)	127.1 (9)	C(43)-C(44)-C(45)	108.4 (9)
C(3)-C(4)-C(14)	125.9 (8)	C(27)-C(26)-C(36)	124.4 (12)	C(6)-C(10)-C(20)	124.5 (9)	C(41)-C(45)-C(44)	108.0 (9)
C(4)-C(5)-C(1)	108.2 (7)	C(30)-C(26)-C(36)	128.1 (10)	C(25)-C(21)-C(22)	109.8 (8)	Cn(1)-Sm(1)-Cn(2)	127.8
C(4)-C(5)-C(15)	122.8 (8)	C(28)-C(27)-C(26)	107.6 (11)	C(25)-C(21)-C(31)	124.7 (8)	Cn(1)-Sm(1)-Cn(5)	115.3
C(1)-C(5)-C(15)	127.9 (8)	C(28)-C(27)-C(37)	126.7 (13)	C(22)-C(21)-C(31)	125.3 (9)	Cn(2)-Sm(1)-Cn(5)	116.8
C(7)-C(6)-C(10)	109.0 (8)	C(26)-C(27)-C(37)	125.4 (14)	C(23)-C(22)-C(21)	107.0 (9)	Cn(3)-Sm(2)-Cn(4)	139.7
C(7)-C(6)-C(16)	126.1 (9)	C(27)-C(28)-C(29)	108.6 (11)	C(23)-C(22)-C(32)	125.9 (10)	Cn(3)-Sm(2)-Cn(5)	103.2
C(10)-C(6)-C(16)	124.8 (9)	C(27)-C(28)-C(38)	126.4 (15)			Cn(4)-Sm(2)-Cn(5)	115.8

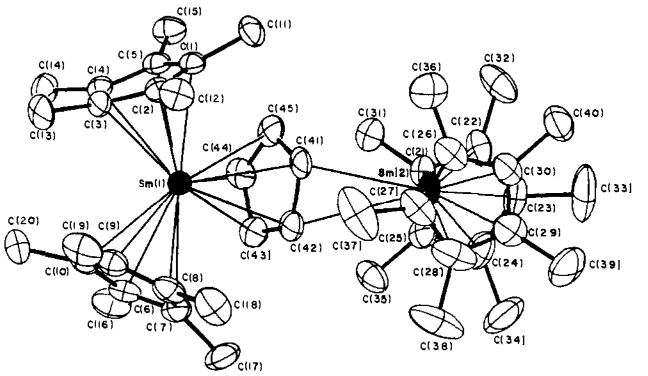

Figure 3. ORTEP diagram of the molecular structure of $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**2**).

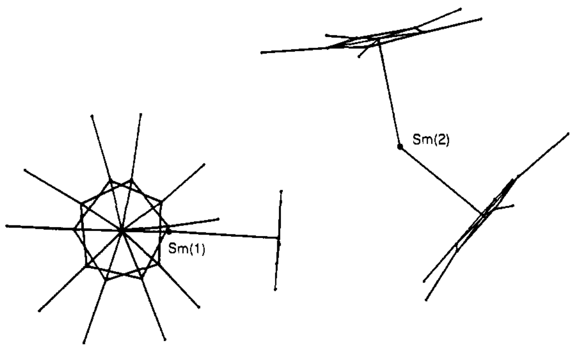

Figure 4. View of **2** looking down the (C_5Me_5 ring centroid)-(C_5Me_5 ring centroid) vector associated with Sm(1) for comparison with Figure 2b.

changing system. Using the Eyring equation,[30] an approximate $\Delta G^{\ddagger}{}_{298K}$ value of 10.1 ± 1.2 kcal/mol was obtained.

Structure of $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (2). The molecular structure of **2** is shown in Figures 3 and 4. The coordination environment around Sm(1) is very similar to that in complex **1** and displays bonding parameters consistent with those of Sm(III). The C_5Me_5-1, C_5Me_5-2, and μ-C_5H_5 rings are arranged in a trigonal-planar geometry around Sm(1) which is only 0.046 Å out of the plane of their centroids. The (C_5Me_5 centroid)-Sm(1)-(C_5Me_5 centroid) angles, 127.8° in **2** and 127.0° in **1**, the (C_5Me_5 centroid)-Sm(1)-(μ-C_5H_5) angles, 115.3° and 116.8° in **2** and 116.2° and 116.9° in **1**, and the Sm(1)-C(C_5Me_5) average distances of 2.766 (3) Å in **2** and 2.770 (3) Å in **1** are all similar. The main difference in the bonding parameters of the Sm(1) atom and the Sm atom in complex **1** is in the Sm-C-(C_5H_5) distances. The Sm(1)-C(C_5H_5) average in **2** is longer, 2.800 (4) vs. 2.738 (4) Å. This is not unusual considering that the C_5H_5 ring is attached to metals on both sides. For example, in $[(MeC_5H_4)(THF)Yb(\mu\text{-}MeC_5H_4)]_n$, the Yb-C($\mu$-$MeC_5H_4$)[31] distances are 0.11-0.15 Å longer than the Yb-C(terminal MeC_5H_4) lengths. Similarly, in the complexes $[(C_5H_5)_2Ln(\mu\text{-}C_5H_5)]_n$ (Ln = La,[32] Pr[33]), the metal-ring centroid distances for

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(30) Sandström, J. *Dynamic NMR Spectroscopy*, Academic Press: New York, 1982.

(31) Zinnen, H. A.; Pluth, J. J.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810-812.

(32) Eggers, S.; Kopf, J.; Fischer, R. D. *Organometallics* **1986**, *5*, 383-385.

(33) Hinrichs, W.; Melzer, D.; Rehwoldt, M.; Jahn, W.; Fischer, R. D. *J. Organomet. Chem.* **1983**, *251*, 299-305.

the bridging rings are 0.07–0.15 Å longer than for the terminal rings.

The Sm(2) part of complex **2** is structurally similar to the divalent complexes $(C_5Me_5)_2Sm(THF)_2$[6] (**3**) and $(C_5Me_5)_2Sm$[3] (**4**). The Sm(2)–C(C_5Me_5) average of 2.812 (4) Å is intermediate between the values of 2.86 (1) Å for eight-coordinate **3** and 2.79 (1) Å for six-coordinate **4** and is closer to the value for the lower coordinate **4**. Note that all of these distances are longer than the longest Sm–C(C_5Me_5) averages in trivalent $(C_5Me_5)_2Sm(X)(Y)$ and $(C_5Me_5)_2SmZ$ systems. Hence, the Sm–C(C_5Me_5) distances are clearly in the range observed for divalent complexes. Another parameter in the structure of complex **2** which is intermediate between those observed in **3** and **4** is the (C_5Me_5 centroid)–Sm–(C_5Me_5 centroid) angle: **2**, 139.7°; **3**, 136.5°; **4**, 140.1°. Once again, the value in **2** is closer to that in lower coordinate **4**.

The interaction of the $(C_5Me_5)_2Sm(2)$ unit with the bridging C_5H_5 ligand is much different from that of the $(C_5Me_5)_2Sm(1)$ unit. Sm(2) is not symmetrically bonded to the five carbon atoms of the μ-C_5H_5 ring. Instead it is closer to two atoms, C(41) and C(46), at distances of 2.986 (8) and 3.180 (9) Å, respectively. Sm(2) is 3.78 Å or more from the other ring carbon atoms. The Sm(2)–C_5H_5 centroid vector makes a 49.6° angle with the ring plane as opposed to the common 90° angle. Calculated positions for hydrogen atoms on C(41) and C(42) are 2.88 and 3.22 Å away from Sm(2).

Since there are no crystallographically characterized Sm(II) alkyl or hydride complexes in the literature, no direct comparison of such bond lengths with the Sm(2) to C(41) and C(42) distances can be made. The closest divalent complex for comparison is $(C_5Me_5)_2Sm$,[3] which has a 3.22 (1) Å distance as the shortest intermolecular Sm–C distance and 2.80 Å as the shortest Sm–H intermolecular interaction. These interactions were considered weak at best. Since the Sm(2)–H distance in **2** is greater than 2.80 Å, it is unlikely to be significantly involved in bonding Sm(2) to the μ-C_5H_5 ring.

The Sm(2)–C(41) distance therefore deserves further examination. Comparisons can be made with trivalent samarium complexes, although the difference in Sm(II) and Sm(III) radii is not well-established. For eight-coordinate oxide and halide complexes, Shannon[34] cites Sm(II) as 0.191 Å larger than Sm(III). In eight-coordinate organosamarium complexes Sm–C(C_5Me_5) average distances range from 2.842 (4) to 2.86 (3) Å for Sm(II) and from 2.72 to 2.77 Å for Sm(III). This gives a Sm(II)–Sm(III) difference in the range 0.07–0.14 depending on which pair of eight-coordinate structures is used for comparison. The three known examples of Sm(III)–carbon bonds in $[(MeC_5H_4)_2Sm(\mu\text{-}C{\equiv}CCMe_3)]_2$,[26] $(C_5Me_5)_2Sm(C_6H_5)(THF)$,[21] and $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$[22] fall in the range 2.48–2.55 Å. Even if a generous 0.20 Å is added to this value for the Sm(II)–Sm(III) difference to give a possible Sm(II)–C distance of 2.75 Å, the observed Sm(2)–C(41) distance of 2.986 (8) Å is quite long compared to a single Sm(III)–C bond. One unusually long Sm(III)–C distance has been observed in the polyhapto ketene carboxylate complex $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$.[15] In this case, a 2.77 (2)-Å Sm-C distance is found as part of a OCC unit coordinated to Sm. Adding 0.20 Å to the 2.77 (2)-Å distance gives a number almost as large as the observed Sm(2)–C(41) distance.

Comparisons can also be made with oligomeric tris(cyclopentadienyl) 4f element structures. The tetrameric structure of $[(MeC_5H_4)_3Nd]_4$ is maintained by interaction of Nd in one $(MeC_5H_4)_3Nd$ unit with a carbon atom of an η^5-ring in another $(MeC_5H_4)_3Nd$ unit.[35] The Nd–C(η^5) average distance is 2.79 (5) Å whereas the intermolecular distances range from 2.990 (7) to 2.978 (7) Å. The difference in these numbers of about 0.2 Å is similar to the difference between the Sm(2)–C(η^5) average distance, 2.812 (4) Å, and the Sm(2)–C(41) bond, 2.986 (8) Å. $(C_5H_5)_3La$ oligomerizes in a $(C_5H_5)_2La(\mu\text{-}\eta^2{:}\eta^5\text{-}C_5H_5)$ structure[32] in which the bridging ring connects via all five carbon atoms on one side (La–C average distance 2.955 Å) and via two carbon atoms on the other with La–C distances of 3.034 (6) and 3.032 (6) Å. The difference between these La–C bond lengths and the La–C (terminal C_5H_5) average distances of 2.77 and 2.79 Å is also near the 0.2 Å value found above for the neodymium structure. In contrast $[(C_5H_5)_2Lu(\mu\text{-}\eta^1{:}\eta^1\text{-}C_5H_5)]_n$[36] has Lu–C($\eta^1$) distances of 2.519 and 2.645 Å, which are close to the Lu–C-(η^5-C_5H_5) average distance of 2.602 Å.

These data show that the Sm(2)–(η-C_5H_5) distance is longer than expected for a normal Sm(II)–C bond but that it is in the range observed for other Ln–C interactions in oligomeric structures. This is consistent with the observed chemistry of **2**, i.e., that it can readily revert to its constituents $(C_5Me_5)_2Sm(C_5H_5)$ and $(C_5Me_5)_2Sm$.

Conclusion

The reaction of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ with C_5H_6 to form $(C_5Me_5)_2Sm(C_5H_5)$ is another example of the chemical parallels between organosamarium(II) complexes and alkali metals. The reaction of $(C_5Me_5)_2Sm$ with $(C_5Me_5)_2Sm(C_5H_5)$ to form $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ demonstrates how $(C_5Me_5)_2Sm$ can participate in chemistry beyond that found for the alkali metals. In addition, this complex gives us the first indication of how this bent metallocene can approach an unsaturated hydrocarbon system. By trapping this metastable mixed-valent system, we have obtained structural data on the initial steps by which $(C_5Me_5)_2Sm$ can interact with a hydrocarbon prior to activation. The implications of these structural features to reactivity will be explored.

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Supplementary Material Available: Tables of thermal parameters (2 pages); listing of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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

(35) Burns, J. H.; Baldwin, W. H.; Fink, F. H. *Inorg. Chem.* **1974**, *13*, 1916–1920.

(36) Eggers, S. H.; Schultze, H.; Kopf, J.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 656–657.