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Synthesis and X-ray Crystal Structure of Bis(pentamethylcyclopentadienyl) Complexes of Samarium and Europium: $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$

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$(C_5Me_5)_2Sm(THF)_2$ can be desolvated at 75 °C under high vacuum to form the green complex $(C_5Me_5)_2Sm$, which sublimes at 85 °C and 10^{-5} torr. Single crystals grown by sublimation crystallize in the space group $P2_1/n$ with $a = 9.815$ (3) Å, $b = 13.436$ (9) Å, $c = 14.163$ (8) Å, $\beta = 94.98$ (4)°, $V = 1861$ (2) Å^3, and $D_{calcd} = 1.500$ g cm^{-3} for $Z = 4$. Least-squares refinement on the basis of 2636 unique observed reflections ($I > 3\sigma(I)$) converged to a final $R = 0.035$. The molecule exhibits a bent structure with a (ring centroid)–Sm–(ring centroid) angle of 140.1° and an average Sm–cyclopentadienyl carbon distance of 2.79 (1) Å. Repeated sublimation of $(C_5Me_5)_2Eu(THF)$ at 70 °C under high vacuum yields the deep red unsolvated complex $(C_5Me_5)_2Eu$. X-ray quality crystals grown by resublimation form in the space group $P2_1/n$ with $a = 9.838$ (4) Å, $b = 13.443$ (4) Å, $c = 14.174$ (3) Å, $\beta = 95.03$ (2)°, $V = 1867$ (2) Å^3, and $D_{calcd} = 1.503$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement on the basis of 2543 unique reflections ($I \geq 3\sigma(I)$) converged to $R = 0.055$. $(C_5Me_5)_2Eu$ is isomorphous and isostructural with $(C_5Me_5)_2Sm$. It possesses a bent metallocene structure with a (ring centroid)–Eu–(ring centroid) angle of 140.3° and an average Eu–C(η^5) distance of 2.79 (1) Å.

Introduction

During the past several years we have investigated the low-valent organometallic chemistry of the lanthanide elements by both metal vapor and solution synthesis methods.[2-8] These efforts have led to the discovery of a new family of soluble (pentamethylcyclopentadienyl)samarium(II) complexes which includes the monomeric $(C_5Me_5)_2Sm(THF)_n$ species (n = 0,[6] 1,[7] or 2[8]) and the halide-bridged dimer $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$.[7] These molecules have permitted the first detailed studies on highly reactive divalent organosamarium systems[9] and have opened an area of organolanthanide chemistry which had been inaccessible because of the insolubility of the previously reported organometallic Sm(II) complexes.[10-12]

X-ray crystal studies of $(C_5Me_5)_2Sm(THF)_2$[8] and $[(C_5Me_5)Sm\ (\mu\text{-}I)(THF)_2]_2$[7] provided basic structural information on this new class and revealed structures consistent with established structural patterns.[13] We recently determined the X-ray crystal structure of the solvent-free complex decamethylsamarocene, $(C_5Me_5)_2Sm$,[6] which proved to possess an unusual bent metallocene geometry (Figure 1a). Traditionally, the bonding in organolanthanide complexes has been thought to be predominantly ionic due to the limited radial extension of the 4f valence orbitals,[14] and organolanthanide structures are thought to be controlled to a large degree by electrostatic factors.[13] For an ionic complex of two $C_5Me_5^-$ anions and

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[10] Both $[(C_5H_5)_2Sm(THF)_x]_y$[11] and $[(CH_3C_5H_4)_2Sm(THF)_x]_y$[12] are insoluble in all solvents with which they do not react.

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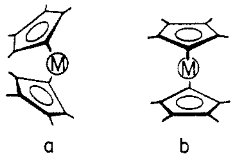

Figure 1. Geometries for bis(pentamethylcyclopentadienyl) metal complexes: (a) nonparallel rings (bent metallocene); (b) parallel rings.

a Sm^{2+} cation, simple electrostatic considerations would suggest a structure with parallel C_5Me_5 rings (Figure 1b). Steric factors, also important in organolanthanide chemistry,[15] would also favor a structure with parallel rings (Figure 1b) rather than a bent metallocene structure with nonparallel rings (Figure 1a). Both the radial extension of the 4f orbitals and the possibility of involvement of the 5d or 6s energy levels are greater for the divalent lanthanide ions than for the more common trivalent systems,[16] but whether any incipient covalent interactions would be manifested structurally is not known. A recent molecular orbital study of bis(cyclopentadienyl) lanthanide hydrides included an analysis of the $(C_5H_5)_2Sm$ unit. A parallel ring structure (Figure 1b) was found to be more stable than a bent structure (Figure 1a), although distortions from the parallel ring arrangement were not energetically costly.[17] Relatively few divalent bis(cyclopentadienyl)organolanthanide complexes have been crystallographically characterized,[18-23] and all of these have contained coligands which sterically force a bent metallocene structure.[24]

The structure of $(C_5Me_5)_2Sm$ was of interest not only because it differed from that expected on the basis of traditional principles but also because it was the first structurally characterized organolanthanide complex containing only two cyclopentadienyl rings, i.e., the first structurally characterized organolanthanide formally analogous to ferrocene. Given the importance of the structure of ferrocene to organo-transition-metal chemistry, we felt it appropriate to document more fully the existence of bent metallocene complexes of this type. Accordingly, we have prepared and characterized the closely related analogue of the organosamarium complex: $(C_5Me_5)_2Eu$. Europium(II) has an ionic radius, 1.10 Å, close to that of Sm(II), 1.11 Å,[25] and possesses a spherically symmetric $4f^7$ valence electronic configuration. Thus $(C_5Me_5)_2Eu$ should be sterically similar to $(C_5Me_5)_2Sm$ but should not be subjected to any directive effects arising from the partly filled $4f^6$ configuration of Sm(II). We present here the full details of the unusual structure of $(C_5Me_5)_2Sm$ and the X-ray crystal structure of the europium analogue $(C_5Me_5)_2Eu$.

Experimental Section

All procedures were performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried, and pentamethylcyclopentadiene was handled as previously described.[7] $(C_5Me_5)_2Sm(THF)_2$[7] and $(C_5Me_5)_2Eu(THF)$[21] were prepared according to the literature procedures.

Preparation of $(C_5Me_5)_2Sm$. A sublimation device similar to that described for the preparation of $[(C_5Me_5)_2YCl]_2$[26] was charged with $(C_5Me_5)_2Sm(THF)_2$ (0.40 g, 0.71 mmol) and evacuated to 5×10^{-5} torr. As the temperature was raised, a pressure surge to 10^{-3} torr occurred at 70–75 °C. The temperature was held at this level until the pressure diminished.[27] Upon increased heating a dark green sublimate began to appear at 85 °C. The temperature was maintained at 125 °C overnight, after which time a large band of $(C_5Me_5)_2Sm$ had sublimed around the upper part of the tube. The final tube pressure was 2×10^{-5} torr. The apparatus was taken into a THF-free glovebox, and the green $(C_5Me_5)_2Sm$ was scraped from the tube walls. A small additional yield could be obtained by resubliming the residue overnight at 125 °C. The total yield (0.22 g, 0.52 mmol) was 74% based on $(C_5Me_5)_2Sm(THF)_2$. A light beige unsublimed residue (42 mg) was found to contain $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ by its ^1H NMR spectrum.[28] Crystals of $(C_5Me_5)_2Sm$ suitable for X-ray diffraction were obtained by resubliming a small sample (ca. 100 mg) of $(C_5Me_5)_2Sm$ in a sealed glass tube evacuated to 4×10^{-5} torr and maintained at 100 °C. Single crystals gradually formed on the walls of the tube. ^1H NMR ($C_6D_5CD_3$, 250 MHz, 8 mM): δ 1.32 (s, br, $\Delta_{1/2}$ = 9 Hz); (in C_6D_6) δ 1.53, (s, br, $\Delta_{1/2}$ = 20 Hz). ^{13}C NMR ($C_6D_5CD_3$, 63 MHz, ca. 0.05 M) δ 99.04 (q, J = 130 Hz, $C_5(CH_3)_5$), −98.18 (s, $C_5(CH_3)_5$). Magnetic susceptibility: $\chi_M^{297K} = 5700 \times 10^{-6}$ (cgs); $\mu_{eff} = 3.7\ \mu_B$. IR (KBr): 2980–2860 vs, 1450 s, 1390 m, 1260 w, 1150 w, 1090 m, 1060 w, 1020 m, 790 w cm^{-1}. UV–vis ($C_6D_5CD_3$): the only maximum observed was a broad absorbance at 600 nm (ϵ 250).

Preparation of $(C_5Me_5)_2Eu$. In a manner directly analogous to that used for the synthesis of $(C_5Me_5)_2Sm$, $(C_5Me_5)_2Eu(THF)$[21] (0.558 g, 1.13 mmol) was placed in a sublimation apparatus and heated to 75 °C at 3×10^{-5} torr. During the next 7 h, a brick-red crystalline sublimate slowly appeared (0.158 g), which still contained coordinated THF by IR spectroscopy. The sublimate was returned to the bottom of the sublimer and resublimed two additional times before the dimunition of the 1025 cm^{-1} stretch in the IR spectra suggested the absence of THF. Material from the third sublimate was sealed into a tube evacuated to 3×10^{-5} torr. After 5 d at 90 °C deep red crystals suitable for X-ray diffraction had formed. IR (KBr): 2950–2800 vs, 1450 s, 1390 m, 1260 w, 1160 w, 1090 w, 1060 w, 1025 m, 790 w cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm$. General procedures for data collection and reduction have been described previously.[29] A deep green crystal measuring 0.24 × 0.28 × 0.66 mm was sealed under N_2 in a glass capillary and mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were determined at 24 °C from the angular settings of 15 computer-centered reflections with $9° \leq 2\theta \leq 24°$. Relevant crystal and data collection parameters for the present study are given in Table I. The space group was determined as $P2_1/n$ (alternate setting of $P2_1/c$, No. 14) from systematic absences ($0k0$, k odd; $h0l$, $h + l$ odd).

During the data collection, the intensities of three standard reflections measured every 100 reflections decreased by 8.5%. Correction for decay was applied later. An analytical absorption was applied to the observed intensities. A combination of Pat-

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Table I. Crystal Data for $(C_5Me_5)_2Ln$ (Ln = Sm, Eu)

	Ln = Sm	Ln = Eu
formula	$C_{20}H_{30}Sm$	$C_{20}H_{30}Eu$
fw	420.35	422.42
space group	$P2_1/n$	$P2_1/n$
a, Å	9.815 (3)	9.838 (4)
b, Å	13.436 (9)	13.443 (4)
c, Å	14.163 (8)	14.174 (3)
β, deg	94.98 (4)	95.03 (2)
V, Å^3	1861 (2)	1867 (2)
Z	4	4
D_{calcd}, g cm^{-3}	1.500	1.503
temp, °C	24	24
λ(Mo Kα), Å	0.710 73; graphite monochromator	0.710 73; graphite monochromator
μ, cm^{-1}	31.70	33.58
transmission factors (min–max)	0.6402–0.7105	0.463–0.781
type of scan	θ–2θ	θ–2θ
scan width, deg	−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 speed, deg/min	6–12, variable	2–12, variable
bkgd counting	evaluated from 96–step peak profile	evaluated from 96-step peak profile
data collectn range	$0° \leq 2\theta \leq 50°$	$0° \leq 2\theta \leq 50°$
total unique data	3493	3309
unique data with $I \geq 3\sigma(I)$	2636	2543
no. of parameters refined	190	190
$R(F)$	0.035	0.055
$R_w(F)$	0.049	0.066
GOF	1.503	1.993
max Δ/σ in final cycle	0.10	0.02

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(C_5Me_5)_2Sm$

atom	x	y	z	10^4U_{eq},[a] Å^2
Sm	0.84704 (3)	0.96415 (2)	0.80109 (2)	388 (2)
C(1)	1.1210 (5)	0.9773 (5)	0.8742 (4)	408 (34)
C(2)	1.0997 (6)	1.0609 (4)	0.8165 (4)	410 (34)
C(3)	1.0815 (6)	1.0270 (5)	0.7215 (4)	446 (36)
C(4)	1.0913 (6)	0.9241 (5)	0.7215 (4)	453 (36)
C(5)	1.1156 (6)	0.8920 (5)	0.8168 (4)	434 (34)
C(6)	0.6145 (7)	0.8549 (6)	0.8421 (5)	594 (45)
C(7)	0.7069 (7)	0.7850 (5)	0.8182 (5)	560 (43)
C(8)	0.7238 (7)	0.7936 (5)	0.7230 (5)	572 (44)
C(9)	0.6414 (7)	0.8714 (6)	0.6847 (5)	590 (45)
C(10)	0.5722 (7)	0.9115 (5)	0.7613 (7)	664 (51)
C(11)	1.1622 (7)	0.9772 (6)	0.9795 (5)	576 (44)
C(12)	1.1022 (8)	1.1679 (6)	0.8477 (6)	650 (49)
C(13)	1.0677 (8)	1.0906 (7)	0.6336 (5)	746 (55)
C(14)	1.0962 (9)	0.8614 (7)	0.6332 (6)	728 (54)
C(15)	1.1472 (8)	0.7861 (6)	0.8477 (7)	747 (56)
C(16)	0.5552 (10)	0.8628 (8)	0.9382 (7)	1049 (78)
C(17)	0.7716 (10)	0.7038 (8)	0.8819 (8)	991 (77)
C(18)	0.7977 (10)	0.7186 (7)	0.6655 (8)	1012 (78)
C(19)	0.6248 (13)	0.9016 (10)	0.5831 (7)	1234 (94)
C(20)	0.4657 (9)	0.9910 (8)	0.7582 (11)	1221 (94)

[a] $U_{eq} = {}^1/_3$(trace of orthogonalized $\mathbf{U}_{ij}$ matrix).

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(C_5Me_5)_2Eu$

atom	x	y	z	10^4U_{eq},[a] Å^2
Eu	0.84701 (4)	0.96368 (3)	0.80171 (3)	389 (3)
C(1)	1.1205 (8)	0.9767 (7)	0.8748 (6)	392 (51)
C(2)	1.0995 (9)	1.0614 (7)	0.8151 (6)	432 (54)
C(3)	1.0804 (9)	1.0280 (7)	0.7222 (6)	442 (54)
C(4)	1.0903 (9)	0.9246 (8)	0.7219 (6)	432 (52)
C(5)	1.1135 (9)	0.8913 (8)	0.8156 (6)	442 (52)
C(6)	0.6135 (10)	0.8553 (9)	0.8424 (8)	576 (67)
C(7)	0.7058 (10)	0.7846 (8)	0.8185 (8)	555 (65)
C(8)	0.7244 (11)	0.7944 (8)	0.7230 (7)	556 (66)
C(9)	0.6421 (11)	0.8700 (9)	0.6860 (7)	624 (71)
C(10)	0.5716 (10)	0.9118 (9)	0.7622 (10)	673 (77)
C(11)	1.1606 (9)	0.9803 (9)	0.9799 (7)	531 (62)
C(12)	1.1018 (12)	1.1677 (8)	0.8467 (8)	626 (72)
C(13)	1.0672 (12)	1.0898 (11)	0.6344 (8)	737 (82)
C(14)	1.0951 (13)	0.8602 (11)	0.6338 (8)	785 (88)
C(15)	1.1465 (12)	0.7874 (9)	0.8506 (9)	724 (82)
C(16)	0.5548 (14)	0.8630 (12)	0.9383 (10)	1035 (118)
C(17)	0.7708 (14)	0.7036 (12)	0.8815 (12)	1056 (119)
C(18)	0.7971 (16)	0.7196 (12)	0.6659 (12)	1094 (126)
C(19)	0.6206 (19)	0.9051 (16)	0.5835 (10)	1258 (141)
C(20)	0.4641 (13)	0.9939 (12)	0.7559 (16)	1146 (132)

[a] $U_{eq} = {}^1/_3$(trace of orthogonalized $\mathbf{U}_{ij}$ matrix).

terson and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic thermal parameters using full-matrix least-squares methods. A total of 13 hydrogen atoms were located from difference maps, and the rest were placed in calculated positions (C–H = 0.95 Å); none were refined. A final difference map contained no recognizable features; its largest peak was of height 2.60 e Å^{-3} at a distance of 0.88 Å from the samarium. Final fractional coordinates are given in Table II.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Eu$. A thin hexagonal crystal with maximum dimensions 0.65 × 0.40 × 0.15 mm was handled as described above. Lattice parameters were determined at 24 °C from the angular settings of 15 computer-centered reflections with $5° \leq 2\theta \leq 20°$. Crystal and data collection parameters are listed in Table I. The space group was identified as the monoclinic $P2_1/n$ (alternate setting of $P2_1/c$, No. 14) from systematic absences. The intensities of three standard reflections measured every 100 reflections during the data collection decreased by 6%. Corrections for decay and absorption (Gaussian integration) were applied. Since it was apparent that the crystals of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ were isomorphous, the final fractional coordinates of the former were used as initial values for the europium complex. Full-matrix least-squares refinement using anisotropic thermal parameters for the non-hydrogen atoms converged rapidly. Twelve hydrogen atoms were located from difference maps, and the rest were included in calculated positions (C–H = 0.95 Å); none were refined. The two largest peaks of a final difference map were of height 6.39 and 5.88 e Å^{-3} at 0.99 and 1.05 Å, respectively, from the europium. Due to the elongated shape of the crystal and the difficulty in indexing its faces, these relatively large peaks may reflect imperfections in the absorption correction or partially uncompensated motion of the metal. No other features were recognizable. Final fractional coordinates are given in Table III.

Results

Synthesis of $(C_5Me_5)_2Sm$. The metal vapor reaction of samarium with C_5Me_5H (eq 1) provided the unsolvated

$$Sm + C_5Me_5H \rightarrow [C_5Me_5SmH] \rightarrow (C_5Me_5)_2Sm \quad (1)$$

complex $(C_5Me_5)_2Sm$ for the first time, but a high yield was not obtained.[8] Following the development of a convenient high-yield solution synthesis of the solvated derivative $(C_5Me_5)_2Sm(THF)_2$,[7] it was advantageous to use that complex as a precursor to $(C_5Me_5)_2Sm$ and desolvation was the obvious route (eq 2). Although desolvation of

$$(C_5Me_5)_2Sm(THF)_2 \rightarrow (C_5Me_5)_2Sm + 2THF \quad (2)$$

THF from sterically crowded trivalent organolanthanide complexes is often facile,[15,30] the success of the desolvation reaction in eq 2 was not necessarily assured. $[(C_5H_5)_2Sm(THF)]_n$ was reported to decompose upon desolvation,[11] and the ytterbium analogue $(C_5Me_5)_2Yb(THF)_2$ was reported to release only one molecule of THF at 90 °C.[31] Since samarium is larger than ytterbium, desolvation of $(C_5Me_5)_2Sm(THF)_2$ would generate a sterically less saturated product than in the ytterbium case. Since steric saturation and stability are often correlated in organolanthanide chemistry,[15,28] it was less likely that complete desolvation of the samarium complex would occur and that the product would be stable.

In contrast to the results reported for $[(C_5H_5)_2Sm(THF)]_n$ and $(C_5Me_5)_2Yb(THF)_2$, $(C_5Me_5)_2Sm(THF)_2$ desolvates cleanly at 75 °C and at 85 °C $(C_5Me_5)_2Sm$ sublimes as a dark green solid. The desolvation/sublimation was also successful at slightly higher temperatures; the highest yield, 74%, was obtained at 125 °C. The major nonvolatile byproduct isolated after the sublimation was the oxide complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$.[28]

The sublimate was identified as $(C_5Me_5)_2Sm$ by spectroscopic methods and by its reaction chemistry. The ^1H NMR spectrum of $(C_5Me_5)_2Sm$ is concentration dependent like that of $(C_5Me_5)_2Sm(THF)_2$[7] due to the paramagnetism of the samarium center ($\mu = 3.7\ \mu_B$, comparable to that of $(C_5Me_5)_2Sm(THF)_2$, 3.6 μ_B) and has a single resonance in the usual C_5Me_5 region. Addition of one drop of THF-d_8 to a dark green C_6D_6 solution of $(C_5Me_5)_2Sm$ instantly turns the color to the purple color of $(C_5Me_5)_2Sm(THF)_2$, and a clean ^1H NMR spectrum of the disolvate is observed. The ^{13}C NMR spectrum of $(C_5Me_5)_2Sm$ is similar to those of the divalent $(C_5Me_5)_2Sm(THF)_2$ and $[(C_5Me_5)SmI(THF)_2]_2$[7] and is different from those of trivalent $(C_5Me_5)_2Sm(X)(Y)$ complexes in that the methyl carbon signals are at low field, 99 ppm, and the ring carbon resonances are at high field, −98 ppm. $(C_5Me_5)_2Sm$ reacts with D_2O to form D_2 and no HD. It reacts with $C_6H_5C{\equiv}CC_6H_5$ like $(C_5Me_5)_2Sm(THF)_2$ to form the black $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$[8] but differs from the disolvate in its reactivity with CO.[32] $(C_5Me_5)_2Sm$ is so reactive with traces of THF that it must be handled in a glovebox free of ethereal solvents.

Synthesis of $(C_5Me_5)_2Eu$. The europium complex $(C_5Me_5)_2Eu(THF)$[21] does not desolvate as readily as $(C_5Me_5)_2Sm(THF)_2$. Sublimation occurs at 75 °C, but the sublimate contains coordinated THF by IR spectroscopy. Some THF is lost during the sublimation, however, and after three repeated sublimations of $(C_5Me_5)_2Eu(THF)$ under high vacuum, no observable coordinated THF remains and solvent-free $(C_5Me_5)_2Eu$ is obtained. The difficulty with which the THF ligand is removed from $(C_5Me_5)_2Eu(THF)$ is somewhat surprising given that unsolvated $(C_5Me_5)_2Sm$ is readily prepared under identical conditions in a single sublimation from the disolvated $(C_5Me_5)_2Sm(THF)_2$. The ionic radii of Sm^{2+} and Eu^{2+} differ only by 0.01 Å,[25] so the electrostatic attraction of both ions for THF should be nearly identical. The IR spectra of $(C_5Me_5)_2Eu$ and $(C_5Me_5)_2Sm$ are essentially superimposable on each other, suggesting that their solid-state structures should be similar. As described below, an X-ray crystal structure determination of $(C_5Me_5)_2Eu$ was completed which allows structural comparisons to be made with the organosamarium complex.

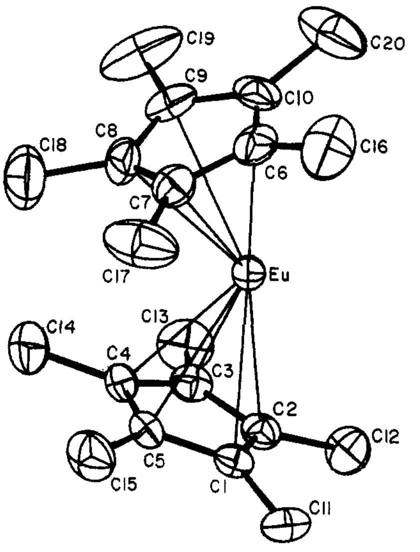

Figure 2. ORTEP drawing of $(C_5Me_5)_2Eu$, giving the numbering scheme used in the tables for both $(C_5Me_5)_2Eu$ and $(C_5Me_5)_2Sm$. Thermal ellipsoids are drawn at the 40% probability level.

Structure of $(C_5Me_5)_2Sm$. The crystallographically determined structure of $(C_5Me_5)_2Sm$ consists of discrete, monomeric units possessing a bent metallocene geometry.[24] The ORTEP plot of $(C_5Me_5)_2Eu$ (Figure 2) shows the general structure for the $(C_5Me_5)_2Ln$ complexes (Ln = Sm, Eu) and also gives the numbering scheme used in the Tables for $(C_5Me_5)_2Ln$. Selected interatomic bond lengths and angles are listed in Table IV.

The average Sm–C(ring) distance in $(C_5Me_5)_2Sm$, 2.79 (1) Å, is shorter than that found in other C_5Me_5 samarium(II) complexes, $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$, 2.81 (2) Å, and $(C_5Me_5)_2Sm(THF)_2$, 2.86 (3) Å,[7,33] and is consistent with the diminished steric crowding around the metal center. Similarly, the (ring centroid)–Sm–(ring centroid) angle of 136.7° in $(C_5Me_5)_2Sm(THF)_2$ opens up in the less crowded $(C_5Me_5)_2Sm$ to 140.1°. Such trends are also found in the divalent $(C_5Me_5)_2YbL_x$ complexes. The (ring centroid)–metal–(ring centroid) angle of 136.3 (3)° in $(C_5Me_5)_2Yb(py)_2$[22] increases to 144° in the less crowded monosolvated $(C_5Me_5)_2Yb(THF)(toluene)_{0.5}$ complex.[21] $(C_5Me_5)_2Yb(py)_2$ has an average Yb–C(η^5) distance of 2.74 Å compared to 2.66 Å in $(C_5Me_5)_2Yb(THF)\ (toluene)_{0.5}$.

The interesting question, of course, is why the (ring centroid)–Sm–(ring centroid) angle is not larger than 140.1°. A detailed examination of the rings shows them to be normal. The individual cyclopentadienyl rings in $(C_5Me_5)_2Sm$ are planar to within 0.007 Å, and as is typical in permethylated cyclopentadienyl ring systems, the methyl groups lie out of the five-carbon least-squares planes and away from the metal. In ring 1 (C(1)–C(10)),

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(30) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2015.

(31) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652–653.

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

(33) Although the structure of $(C_5Me_5)_2Sm(THF)_2$ was initially reported in the triclinic space group $P\bar{1}$,[7] it was subsequently found under the advice of Professor F. A. Cotton at Texas A&M University to belong to the higher symmetry space group $C2/c$. Refinement in this space group led to a lower $R = 0.044$ but no significant changes in bond lengths or angles. Cell constant data follows. The space group is $C2/c$ with $a = 21.94$ (1) Å, $b = 20.91$ (1) Å, $c = 16.41$ (1) Å, $\beta = 130.15$ (4)°, $V = 4566.0$ Å^3, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 8$.

Table IV. Selected Bond Distances and Angles in $(C_5Me_5)_2Ln$ (Ln = Sm, Eu)

	Ln = Sm	Ln = Eu
	Bond Distances (Å)	
Ln–C(1)	2.802 (5)	2.803 (8)
Ln–C(2)	2.790 (6)	2.802 (9)
Ln–C(3)	2.780 (6)	2.783 (9)
Ln–C(4)	2.789 (6)	2.786 (8)
Ln–C(5)	2.800 (6)	2.787 (8)
Ln–C(6)	2.815 (6)	2.822 (9)
Ln–C(7)	2.792 (7)	2.800 (10)
Ln–C(8)	2.775 (6)	2.765 (10)
Ln–C(9)	2.786 (6)	2.786 (9)
Ln–C(10)	2.798 (6)	2.806 (9)
C(1)–C(2)	1.395 (9)	1.423 (13)
C(2)–C(3)	1.418 (9)	1.388 (13)
C(3)–C(4)	1.386 (9)	1.393 (14)
C(4)–C(5)	1.417 (9)	1.401 (12)
C(5)–C(1)	1.403 (9)	1.420 (13)
C(6)–C(7)	1.370 (10)	1.377 (15)
C(7)–C(8)	1.378 (10)	1.388 (14)
C(8)–C(9)	1.403 (10)	1.374 (15)
C(9)–C(19)	1.434 (11)	1.447 (16)
C(10)–C(6)	1.406 (11)	1.399 (16)
C(1)–C(11)	1.510 (9)	1.508 (12)
C(2)–C(12)	1.503 (9)	1.497 (14)
C(3)–C(13)	1.505 (9)	1.492 (14)
C(4)–C(14)	1.513 (9)	1.524 (14)
C(5)–C(15)	1.513 (10)	1.508 (15)
C(6)–C(16)	1.529 (11)	1.526 (15)
C(7)–C(17)	1.520 (11)	1.514 (17)
C(8)–C(18)	1.520 (11)	1.510 (16)
C(9)–C(19)	1.490 (12)	1.525 (16)
C(10)–C(20)	1.494 (12)	1.526 (19)
	Bond Angles (deg)	
C(1)–Ln–C(2)	28.9 (2)	29.4 (3)
C(2)–Ln–C(3)	29.5 (2)	28.8 (3)
C(3)–Ln–C(4)	28.8 (2)	29.0 (3)
C(4)–Ln–C(5)	29.4 (2)	29.1 (3)
C(5)–Ln–C(1)	29.0 (2)	29.4 (3)
C(6)–Ln–C(7)	28.3 (2)	28.4 (3)
C(7)–Ln–C(8)	28.7 (2)	28.9 (3)
C(8)–Ln–C(9)	29.2 (2)	28.7 (3)
C(9)–Ln–C(10)	29.8 (2)	30.0 (3)
C(10)–Ln–C(6)	29.0 (2)	28.8 (3)
C(2)–C(1)–C(5)	108.8 (5)	107.4 (8)
C(2)–C(1)–C(11)	126.3 (6)	125.0 (9)
C(5)–C(1)–C(11)	124.4 (6)	127.2 (9)
C(1)–C(2)–C(3)	107.3 (5)	107.8 (8)
C(1)–C(2)–C(12)	126.9 (6)	126.0 (9)
C(3)–C(2)–C(12)	125.7 (6)	126.1 (9)
C(4)–C(3)–C(2)	108.5 (5)	108.8 (8)
C(4–)–C(3)–C(3)	124.7 (6)	123.6 (9)
C(2)–C(3)–C(14)	126.7 (6)	127 (1)
C(3)–C(4)–C(5)	108.1 (6)	108.7 (8)
C(3)–C(4)–C(14)	124.3 (6)	125.2 (9)
C(5)–C(4)–C(14)	127.1 (6)	126 (1)
C(1)–C(5)–C(4)	107.4 (6)	107.3 (8)
C(1)–C(5)–C(15)	127.1 (6)	123.8 (9)
C(4)–C(5)–C(15)	125.1 (6)	128.3 (9)
C(7)–C(6)–C(10)	109.0 (7)	109 (1)
C(7)–C(6)–C(16)	125.4 (9)	125 (1)
C(10)–C(6)–C(16)	125.3 (8)	125 (1)
C(6)–C(7)–C(8)	108.9 (7)	109 (1)
C(6)–C(7)–C(17)	126.7 (8)	127 (1)
C(8)–C(7)–C(17)	124.2 (8)	124 (1)
C(7)–C(8)–C(9)	109.1 (6)	108.6 (9)
C(7)–C(8)–C(18)	124.9 (8)	125 (1)
C(9)–C(8)–C(18)	125.1 (8)	125 (1)
C(8)–C(9)–C(10)	106.5 (6)	108 (1)
C(8)–C(9)–C(19)	125.9 (9)	128 (1)
C(10)–C(9)–C(19)	127.5 (9)	124 (1)
C(6)–C(10)–C(9)	106.7 (6)	106 (1)
C(6)–C(10)–C(20)	124.0 (1)	126 (1)
C(9)–C(10)–C(20)	129.0 (1)	128 (1)

the displacement is from 0.05 to 0.19 Å, and in ring 2 (C(11)–C(20)), the displacement is from 0.10 to 0.24 Å. The average is 0.13 Å, giving a displacement angle $\bar{\alpha}$ of 5°. This is in the range of displacements of the methyl groups observed in $(C_5Me_5)_2Sm(THF)_2$, 0.09–0.18 Å, $(C_5Me_5)_2Yb(py)_2$, 0.03–0.21 Å, and $(C_5Me_5)_2Yb(THF)(toluene)_{0.5}$, 0.13–0.31 Å.

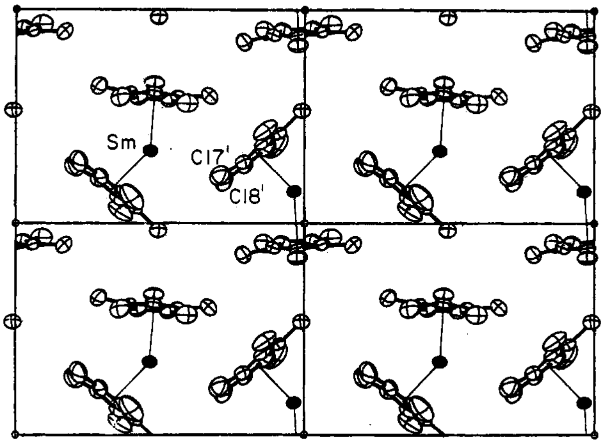

Figure 3. Four unit cells of $(C_5Me_5)_2Sm$ projected down the crystallographic "c" axis, illustrating the "herring-bone weave" pattern formed by the complexes. For clarity, only one layer of $(C_5Me_5)_2Sm$ units is shown. The samarium ellipsoids have been filled in.

The relative orientation of the two C_5Me_5 rings is quite interesting. In $(C_5Me_5)_2Sm(THF)_2$, the rings are almost fully staggered with a twist angle[34] of 31°. The closest intramolecular inter-ring (methyl carbon)–(methyl carbon) distance is 3.74 Å. In $(C_5Me_5)_2Sm$, the rings are less staggered: the twist angle is 19°. This orientation plus the relative tilt of the two rings brings methyl carbons C(14) and C(18) to within 3.56 Å of each other. This is considerably less than the 4.0 Å sum of the appropriate van der Waals radii[35] and represents the closest nonbonding intramolecular inter-ring contact.[36] A larger (ring centroid)–Sm–(ring centroid) angle or a larger twist angle (a more staggered orientation) would reduce these close contacts, but this is not observed.

An examination of crystal packing diagrams for $(C_5Me_5)_2Sm$ reveals that some close intermolecular contacts also exist in this structure. A projection down the "c" axis (Figure 3) shows that one layer of $(C_5Me_5)_2Sm$ molecules is packed in a "herring-bone weave" pattern. The smallest intermolecular methyl–methyl distance involves C(13) and C(17)′ and is 3.65 (1) Å. The smallest intermolecular metal–carbon′ distance is the 3.75-Å Sm–C(18)′ length, a distance which is in the range of intramolecular samarium–(methyl carbon) distances, 3.73 (1)–3.84 (1) Å.

(Methyl carbon)–(methyl carbon) distances *between* these layers are even shorter. The smallest distance, shown in Figure 4, occurs between C(11) and C(11)′ and is only 3.34 (1) Å. The corresponding smallest Sm–carbon interlayer distance involves the samarium center of one molecule and C(11) of another. This Sm–C(11)′ distance is 3.22 (1) Å. With the assumption of an internuclear C–H

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(34) The twist angle is defined as the average of the five smallest dihedral angles formed between the ten planes which consist of a ring carbon atom and the two ring centroids.

(35) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 2650.

(36) Note that the average intra-ring distance between methyl carbon atoms is much smaller, 3.17 Å. Inter-ring (methyl carbon)–(methyl carbon) distances as short as 3.23 Å have been observed in bis(pentamethylcyclopentadienyl) lanthanide complexes, e.g., in the sterically crowded $(C_5Me_5)_2YbI_2Li(OEt_2)_2$.[37]

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

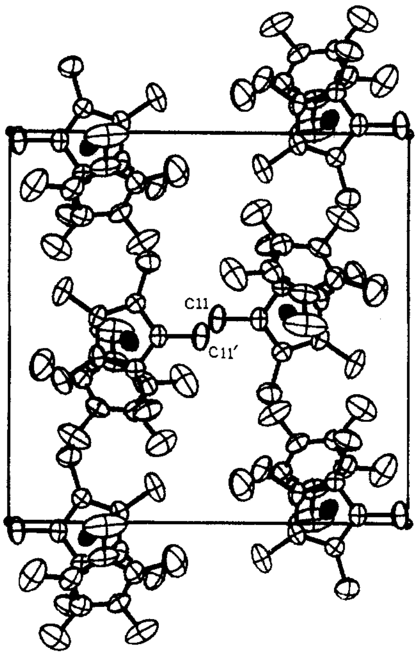

Figure 4. Side-by-side approach of two $(C_5Me_5)_2Sm$ units via C(11) as seen in a packing diagram projected down the "*a*" axis.

Table V. Structural Parameters in $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$

	$(C_5Me_5)_2Sm$	$(C_5Me_5)_2Eu$
M–C(ring)(av)	2.79(1) Å	2.79(1) Å
centroid–M–centroid	140.1°	140.3°
displacement of CH_3 groups from ring plane	0.13 Å (av)	0.13 Å (av)
displacement angle (α)	5° (av)	5° (av)
closest intermolecular M–CH_3 contact	Sm–C(11)′ (3.22 (1) Å)	Eu–C(11)′ (3.19 (1) Å)
closest intermolecular CH_3–CH_3 contact	C(11)–C(11)′ (3.34 (1) Å)	C(11)–C(11)′ (3.30 (2) Å)
closest intramolecular CH_3–CH_3 contact	C(14)–C(18) (3.56 (1) Å)	C(14)–C(18) (3.55 (2) Å)
smallest intermolecular H(CH_3)–M contact (assuming C–H = 1.08 Å)	2.75 Å	2.81 Å

distance of 1.08 Å,[38] the nearest approach of a hydrogen on C(11)′ to the samarium is 2.75 Å.

This samarium–hydrogen distance is the closest intermolecular approach of any atom in another molecule to the samarium coordination sphere and warrants some attention. First of all, it is interesting to note that this short intermolecular distance does not occur through the sterically most accessible open "front" part of the bent metallocene structure but rather from the side. Second, the 2.75-Å distance is considerably longer than the 2.29 Å cited[39] as the longest crystallographically observed agostic hydrogen in a transition-metal complex. The latter was found in $Ti(CH_2CH\text{-}\mu\text{-}H)Cl_3(dmpe)$.[40] Consistent with the long distance, $(C_5Me_5)_2Sm$ exhibits no lower frequency ν(CH) stretches as are often found in agostic hydrogen complexes.[39]

These intermolecular samarium–carbon and –hydrogen distances can also be compared with intermolecular distances in other organolanthanides. Two neodymium structures offer some relevant data. The tetrameric structure of $[(CH_3C_5H_4)_3Nd]_4$ arises from the interaction of a carbon atom on a cyclopentadienyl ring in one $(CH_3C_5H_4)_3Nd$ unit with the metal of an adjacent $(CH_3C_5H_4)_3Nd$ unit at a distance of 2.990 (7) –2.978 (7) Å.[41] In comparison the average Nd–C(ring) distance is 2.79 (5) Å. The Nd–C distances holding $(C_8H_8)_2Nd^-$ to $(C_8H_8)Nd(THF)_2^+$ in a tight ion pair are 2.69 (2), 2.89 (2), and 3.02 (2) Å in comparison to the Nd–C distances in the $(\eta^8\text{-}C_8H_8)Nd$ units of 2.68 (1), 2.79 (1), and 2.68 (1) Å.[42] In both of these cases the intermolecular Nd–C distances are within 0.2 Å of the bonding intramolecular Nd–C distances, and significant interaction is probably present. In $(C_5Me_5)_2Sm$, the shortest intermolecular Sm–C distance, 3.22 (1) Å, is 0.405 Å longer than the longest intramolecular Sm–C bonding distance, 2.815 (6) Å for Sm–C(6).

The intermolecular distances in $(C_5Me_5)_2Sm$ can also be compared with the lanthanide metal–(methyl carbon) distances in the complexes $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$,[43] $NaYb[N(SiMe_3)_2]_3$,[44] and $NaEu[N(SiMe_3)_2]_3$.[44] The shortest metal–carbon distances in each of these three molecules were 3.04, 2.86 (2), and 2.971 (7) Å, respectively. When the differences in metallic radii are considered,[25] (Sm^{2+} is 0.18 Å larger than Yb^{2+} and 0.01 Å larger than Eu^{2+}), $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_3PMe_2]$ has a metal–carbon distance approximately equivalent to the 3.22 (1) Å Sm–C(11)′ length and $NaYb[N(SiMe_3)_2]_3$ and $NaEu[N(SiMe_3)_2]_3$ have shorter metal–carbon distances. For $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$, hydrogen atoms were located and ytterbium–hydrogen distances as short as 2.76 (8) and 2.85 (6) Å were reported. Considering the difference in metallic radii, these are closer metal–hydrogen distances than are found in $(C_5Me_5)_2Sm$. Although the origin of the close contacts in these bis(trimethylsilyl)amido complexes was uncertain, the energy of the interaction was thought to be "undoubtedly small".[44]

It is interesting to note that the average thermal parameters (Table II) for the methyl groups on the C_5Me_5 ring closest to another samarium center (i.e., ring 1) are lower ($(576\text{–}747) \times 10^{-4}$) than those of the other ring ($(991\text{–}1234) \times 10^{-4}$). The methyl carbon atom closest to another samarium, C(11), has the smallest thermal parameters. The same is true for the carbon atoms closest to Yb in $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$ and $NaYb[N(SiMe_3)_2]_3$.[43,44] These lower thermal parameters could arise from intermolecular interactions which limit motion of one of the rings.

An attempt was made to determine the gas-phase structure of $(C_5Me_5)_2Sm$ by electron diffraction, but the volatility/thermal stability of the complex was insufficient to obtain adequate data.[45]

Structure of $(C_5Me_5)_2Eu$. Sublimation of $(C_5Me_5)_2Eu$ forms crystals which are isomorphous and isostructural with $(C_5Me_5)_2Sm$. An ORTEP view of the molecule presented in Figure 2 shows that $(C_5Me_5)_2Eu$ was found to have the same bent metallocene geometry as $(C_5Me_5)_2Sm$. Selected interatomic bond distances and angles are given in Table IV. A comparison of the structural parameters of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ is provided in Table V and shows that virtually every structural feature of interest between the two molecules is identical within experimental

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(38) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214. Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986–1992.

(39) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

(40) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802–803.

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

(42) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625–631.

(43) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Chem. Soc.* **1982**, *104*, 3725–3727.

(44) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271–2276.

(45) Haaland, A., private communication.

error. Intermolecular methyl–methyl, methyl–M, and M–H contacts are also very similar in the two complexes.

Discussion

As discussed in the Introduction, neither simple electrostatic considerations, nor molecular orbital calculations,[17] nor steric effects predict the bent structure observed for metallocenes $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$. From all of these viewpoints, a parallel ring structure like that found in $(C_5Me_5)_2Fe$ might be expected.[46] The similarity of the structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ indicates that the bent structure cannot be explained on the basis of the specific $4f^6$ or $4f^7$ electron configuration. The relative 4f electron configurations in these molecules evidently exert no structurally discernible effect. Such a result is consistent with previous observations that the f electron configuration has a minimal effect on the structure of organolanthanide complexes.[13]

It is conceivable that the bent structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ result from intermolecular interactions and crystal packing effects. Certainly, some intermolecular distances exist in the crystal which are shorter than normal. The Ln–C(11)′ distance, the shortest of the intermolecular metal carbon contacts, would be the most likely candidate for an interaction with structural consequences. It is curious that this "interaction", if it exists, occurs from the side of the bent structure rather than from the more sterically accessible front end. It is not clear, why such an "interaction" could not occur in a parallel ring structure in which unfavorable intramolecular methyl–methyl contacts would be diminished. In addition, the length of the Ln–C(11)′ distance is sufficiently long that the energy involved is likely to be very small. Since the bent structure leads to short, possibly unfavorable methyl–methyl distances, the reason for bending must have some energetic advantage. Crystal packing effects are also difficult to rationalize into a simple explanation. For example, neither the (ring centroid)–Ln–(ring centroid) angle nor the twist angle, describing the partial staggering of the rings, are such as to minimize intramolecular methyl–methyl distances. It is unlikely that these interactions are the determining factors in giving the observed structure.

Perhaps the best explanation for the bent metallocene structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ is the polarization argument used to analyze bent vs. linear MX_2 alkaline-earth-metal dihalide complexes.[25,47] In a parallel ring $(C_5Me_5)_2Ln$ structure analogous to a linear MX_2 structure, polarization of the cation by one C_5Me_5 anion could diminish the electrostatic interaction between the cation and the second C_5Me_5 anion directly opposite. A bent structure may optimize the polarization of a large cation by two anions and may give better total electrostatic bonding for the two rings. This argument provides a nice electrostatic rationale for the bent structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ without involving 4f orbital participation and without invoking high-energy 5d and 6s orbitals (via a stereochemically active lone-pair argument).

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Registry No. $(C_5Me_5)_2Sm$, 90866-66-3; $(C_5Me_5)_2Eu$, 101200-04-8; $(C_5Me_5)_2Ca$, 101200-05-9; $(C_5Me_5)_2Sm(THF)_2$, 79372-14-8; $(C_5Me_5)_2Eu(THF)$, 74282-45-4; Ca, 7440-70-2; C_5Me_5H, 41539-64-4.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes for $(C_5Me_5)_2Eu$ and $(C_5Me_5)_2Sm$ (26 pages). Ordering information is given on any current masthead page.

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Organolanthanide and Organoyttrium Enolate Chemistry. Synthesis of $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ Complexes and the Molecular Structure of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$

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The reaction of $LiOCH{=}CH_2$ with $[(C_5H_4R)_2LnCl]_2$ (R = H, CH_3; Ln = Lu, Yb, Y) generates the dimeric complexes $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ in good yield. $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ crystallizes from toluene under hexane diffusion in space group $P2_1/n$ with unit-cell dimensions a = 15.793 (3) Å, b = 9.983 (4) Å, c = 8.257 (1) Å, β = 93.51 (1)°, V = 1300 (2) Å^3, and Z = 2 dimers for D_{calcd} = 1.483 g cm^{-3}. Least-squares refinement on the basis of 1518 observed reflections led to a final R value of 0.034. Each $OCH{=}CH_2$ group bridges the two $(CH_3C_5H_4)_2Y$ units through the oxygen atom with Y–O distances of 2.275 (3) and 2.290 (3) Å. The enolate has a C—O distance of 1.324 (6) Å, a C=C distance of 1.287 (8) Å, and an O—C=C angle of 128.0 (6)°. The $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ complexes can also be formed by thermolysis of $(C_5H_4R)_2Y(CH_2SiMe_3)(THF)$ (R = H, CH_3) and by thermolysis of $[(C_5H_5)_2YbCH_3]_2$ in the presence of LiCl and THF.

Introduction

In recent years a variety of substituted enolate ligands of the general formula O—CR=CR′R″ have been reported in organolanthanide and organoactinide complexes.[2-7] Most of these are derived from CO activation reactions and representative examples are shown in Chart I. Simple

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