Solution Synthesis and Crystallographic Characterization of the Divalent Organosamarium Complexes $(C_5Me_5)_2Sm(THF)_2$ and $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$

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Abstract: The reaction of SmI_2 in THF solution with a slight excess of 2 equiv of KC_5Me_5 yields $(C_5Me_5)_2Sm(THF)_2$ (I) in high yield and purity. Reaction of I with an equimolar quantity of SmI_2 forms $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (II), which can also be prepared from the 1:1 stoichiometric reaction of SmI_2 and KC_5Me_5. Both I and II have been characterized by spectral, chemical, and X-ray crystallographic methods. I crystallizes from THF in the triclinic space group $P\bar{1}$ with a = 15.155 (6) Å, b = 16.141 (6) Å, c = 16.179 (6) Å, α = 55.92 (3)°, β = 65.13 (3)°, γ = 62.18 (3)°, and D_c = 1.33 g cm^{-3} for Z = 4. Least-squares refinement on the basis of 3949 observed reflections led to a final R value of 0.061. The molecule has a bent metallocene structure in which the two cyclopentadienyl ring centroids and the two THF oxygen atoms roughly describe a tetrahedral coordination geometry. The average Sm–C(ring) distance is 2.86 (3) Å. The average Sm–O distance is 2.64 Å. II crystallizes from THF under hexane diffusion in the monoclinic space group $P2_1/n$ with a = 12.708 (6) Å, b = 13.454 (6) Å, c = 14.859 (6) Å, β = 112.37 (4)°, and D_c = 1.57 g cm^{-3} for Z = 2 (dimers). Least-squares refinement on the basis of 1577 observed reflections led to a final R value of 0.053. The two $(C_5Me_5)(THF)_2Sm$ moieties in the molecule are bridged by iodine ligands via a planar $Sm_2(\mu\text{-}I)_2$ unit with the cyclopentadienyl ring on one side of the plane and the THF molecules on the other side. The two distinct Sm–(μ-I) distances are 3.356 (2) and 3.459 (2) Å, the average Sm–C(ring) distance is 2.81 (2) Å, and the Sm–O distances average 2.64 Å.

In recent years, the organometallic chemistry of the lanthanide metals in low oxidation states has been actively investigated and a variety of new complexes and reactivity patterns have been discovered.[2-10] These low-valent studies have involved the zerovalent metals in the elemental state, using metal-vapor techniques, as well as the complexes of the three lanthanide metals that have divalent states readily accessible under "normal" solution reaction conditions, i.e., Eu, Yb, and Sm. Although Sm(II) is the most reactive of these divalent lanthanides [Sm(III) + e → Sm(II): −1.5 V],[11] its chemistry in organometallic systems had not been previously investigated because the only known divalent organosamarium complexes, $[(C_5H_5)_2Sm(THF)_x]_y$[12,13] and $[(CH_3C_4H_4)_2Sm(THF)_x]_y$,[14] are insoluble.

Recently, however, we reported the synthesis of the first soluble organosamarium(II) complex, $(C_5Me_5)_2Sm(THF)_2$ (I), starting from zerovalent samarium vapor (eq 1).[3] As anticipated, this

$$\text{Sm (vapor)} + C_5Me_5H\ (-120\ °C) \rightarrow \xrightarrow{\text{THF}} \underset{\text{I}}{(C_5Me_5)_2Sm(THF)_2} \quad (1)$$

complex reacts rapidly with a variety of substrates and has provided access to a wealth of new organosamarium complexes.[3-5,15] These include $[(C_5Me_5)_2Sm]_2(C_6H_5)_2C_2$,[4] $[(C_5Me_5)_2SmH]_2$,[4] and $(C_5Me_5)_2Sm$,[5] complexes that are active in homogeneous hydrogenation catalysis[4,16] and in CO activation.[17]

Although the original synthesis of I was achieved on a preparative scale,[3] a rotary metal vaporization reactor was required. We now report the synthesis of I by solution methods, a result that should make soluble divalent organosamarium complexes more generally available for investigation. Considering recent interest in the use of divalent lanthanides in organic synthesis,[10,18] this may be particularly important.

In the course of developing a solution synthesis for I, we have discovered a new, soluble, divalent, organosamarium complex,

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$[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (II) which is potentially important in several respects. Complex II is the first Sm(II) organometallic compound that has a reactive site, the halide ligand, suitable for further modification of the Sm(II) coordination environment.[19] For example, reaction of II with lithium alkyl reagents may provide divalent samarium alkyl complexes that may be hydrogenolyzable[22,23] to form divalent samarium hydride species. The new complexes would combine a reactive lanthanide alkyl or hydride moiety[22] with the strong one-electron reducing capacity of the Sm(II) center. Complex II also completes the series $(C_5Me_5)_2Sm(THF)_2$, $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$, and $SmI_2(THF)_x$, a set of complexes that should allow precise variation of divalent samarium reactivity by varying the steric bulk of the ligands surrounding the metal center.[24]

We report here the synthesis of I and II as well as full details of the X-ray crystal structure determinations of these compounds, which are the first crystallographically characterized organosamarium(II) complexes.[3]

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.

Materials. Pentane and hexane were washed with sulfuric acid, dried over $MgSO_4$, and distilled from potassium benzophenone ketyl solubilized with tetraglyme. Toluene and THF were distilled from potassium benzophenone ketyl. THF-d_8 and benzene-d_6 were vacuum transferred from potassium benzophenone ketyl. C_5Me_5H was prepared by published procedures[25] and converted to KC_5Me_5 with KH in THF.[26] Solutions of $SmI_2(THF)_x$ were prepared from excess Sm metal (Research Chemicals, Phoenix, AZ) and 1,2-$C_2H_4I_2$ in THF solution.[13] (This reaction is quantitative in 1,2-$C_2H_4I_2$.[13]) Evaporation of the solutions of SmI_2 resulting from this preparation yields a free-flowing blue-black powder formulated as $SmI_2(THF)_2$ on the basis of its weight and the moles of 1,2-$C_2H_4I_2$ used.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker WM-250 spectrometer. Chemical shifts were assigned relative to C_6D_5H, 7.15 ppm, for spectra in benzene-d_6, or relative to proteo-THF, 1.72 ppm, for spectra in THF-d_8. Magnetic susceptibility measurements were obtained on the Bruker 250-MHz NMR spectrometer by the Evans method.[27] Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, Germany.

$(C_5Me_5)_2Sm(THF)_2$ (I). In the glovebox, KC_5Me_5 (5.43 g, 31.2 mmol) was added to a stirring solution of $SmI_2(THF)_2$ (7.78 g, 14.2 mmol) in 75 mL of THF in a 125-mL Erlenmeyer flask. The solution color rapidly changes from blue-green to purple as off-white solids (KI) are formed. After 4 h at ambient temperature, the THF was removed by rotary evaporation, and 100 mL of toluene was added. The resulting solution of I with suspended potassium salts was stirred vigorously for 10 h and then filtered. The solvent was removed from the filtrate by rotary evaporation leaving solid $(C_5Me_5)_2Sm(THF)_n$, where $1 \leq n \leq 2$. The degree of solvation is conveniently monitored by integration of the absorptions in the NMR spectrum in benzene-d_6. Dissolving this solid in THF and then removing the solvent by rotary evaporation yield the disolvate, I (5.95 g, 74%).[28] Recrystallization from THF (solution saturated at 30 °C cooled to −25 °C overnight) gives large purple crystals (5.52 g in two crops, 69%). The monosolvate, $(C_5Me_5)_2Sm(THF)$, can be obtained by repeated evaporation of the original toluene extraction solutions. Anal. Calcd for the monosolvate, $SmC_{24}H_{38}O$: Sm, 30.50; C, 58.48; H, 7.77; I, 0.0; K, 0.0; O, 3.25. Found: Sm, 30.40; C, 58.50; H, 7.59; I, <0.05; K, <0.04; O by difference, 3.50. ^1H NMR of I (THF-d_8, 25 °C) δ 1.58 (s, 30, $C_5(CH_3)_5$), 3.59 (m, 8, THF), 1.72 (m, 8, THF). NMR spectra in THF-d_8 are concentration independent. Spectra in benzene-d_6 are concentration dependent as reported previously.[3,15] Typical solutions of I in benzene-d_6 have the C_5Me_5 signal between 2.3 and 2.9 ppm. As the THF content is lowered the C_5Me_5 resonance moves downfield in benzene-d_6. When THF stoichiometries based on NMR integration are used, the following data are typical: $(C_5Me_5)_2Sm(THF)_{1.30}$, δ 3.29 (s, 30, C_5Me_5), 1.80 (s, 5.2, THF), 15.6 (br s, 5.2, THF); $(C_5Me_5)_2Sm(THF)_{1.17}$, δ 3.50 (s, 30, C_5Me_5), 1.20 (s, 4.7, THF), 16.0 (br s, 4.7, THF). In some samples, the C_5Me_5 signal has been shifted as far downfield as 4.0 ppm and the THF as far upfield as −3.8 ppm. Magnetic susceptibility: $\chi_M^{296 K} = 5490 \times 10^{-6}$ (cgs); $\mu_{eff} = 3.6\ \mu_B$. IR (KBr) 3100–2725 s, 2705 w, 1440 s, 1370 w, 1240 m, 1210 w, 1080 s, 1040 s, 850 w, 895 s, 795 m cm^{-1}. The charge-transfer absorption in the near-infrared visible spectrum has no maxima in the visible region.

$[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (II) from I and $SmI_2(THF)_2$. I (1.10 g, 1.95 mmol) and $SmI_2(THF)_2$ (1.08 g, 1.97 mmol) were dissolved in 100 mL of THF yielding a dark green solution. After 2 h of being stirred, the solution was filtered through a fine frit and the volume of the filtrate was then slowly reduced to 5–10 mL by rotary evaporation. While still cold, this solution was filtered. The resulting solid was rinsed twice with hexane and allowed to dry, yielding II as a dark green microcrystalline powder (1.78 g, 83%). X-ray quality crystals can be grown by layering hexane over a THF solution and allowing diffusion to occur at glovebox temperature (ca. 30 °C). Anal. Calcd for $SmC_{18}H_{31}IO_2$: Sm, 27.01; C, 38.83; H, 5.61; I, 22.79, O, 5.75. Found: Sm, 27.40; C, 38.35; H, 5.42; I, 23.01; O by difference, 5.82. Magnetic susceptibility: $\chi_M^{298 K} = 5400 \times 10^{-6}$ (cgs); $\mu_{eff} = 3.6\ \mu_B$. IR (KBr) 2962 s, 2883 s, 2858 s, 1444 m, 1030 s, 876 m cm^{-1}. ^1H NMR (THF-d_8, 25 °C, dilute solution, ca. one-tenth of saturation) δ 2.44 (s, 5, C_5Me_5), 1.59 (s, 10, C_5Me_5), 3.57 (m, 8, THF), 1.72 (m, 8, THF). The C_5Me_5 resonances in the ^1H NMR spectrum are highly concentration and temperature dependent. In saturated solutions in THF-d_8 at 25 °C, the C_5Me_5 resonance is very broad at 2.1 ppm. Integration suggests an additional C_5Me_5 resonance hidden under the THF-d_7 resonance centered at 1.66 ppm. ^{13}C NMR (THF/15% THF-d_8; saturated solution) δ 101.3 (q, $J \sim 119$ Hz), 93.2 (q, $J \sim 122$ Hz), −58.9, −67.8.

$[(C_5Me_5)SmI(THF)_2]_2$ (II) from $SmI_2(THF)_2$ + KC_5Me_5. KC_5Me_5 (1.09 g, 6.26 mmol) was added to a blue-green solution of $SmI_2(THF)_2$

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $(C_5Me_5)_2Sm(THF)_2$

compound	$SmO_2C_{28}C_{46}$
M_r	565.05
space group	$P\bar{1}$
cell constants	
a, Å	15.155 (6)
b, Å	16.141 (6)
c, Å	16.179 (6)
α, deg	55.92 (3)
β, deg	65.13 (3)
γ, deg	62.18 (3)
cell vol, Å^3	2829.9
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.33
μ(calcd), cm^{-1}	21.3
radiation	Mo Kα
max crystal dimensions, mm	0.20 × 0.25 × 0.30
scan width	0.8 + 0.2(tan θ)
standard reflections	200 020 002
variation of standards	<3%
reflections measured	5804
2θ range, deg	2–46
observed reflections	3949
no. of parameters varied	479
GOF	3.43
R	0.057
R_w	0.055

(19) Complex II is analogous in importance to bis(cyclopentadienyl)lanthanide(halide) complexes in trivalent lanthanide chemistry.[20,21]

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(28) A small additional yield may be obtained by suspending the filtered-off potassium salts in THF and repeating the isolation procedure.

Table II. Final Fractional Coordinates for $(C_5Me_5)_2Sm(THF)_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Sm(1)	0.59583 (6)	0.10847 (5)	0.64137 (5)
Me(1)	0.332 (1)	0.265 (1)	0.554 (1)
Me(2)	0.332 (1)	0.055 (1)	0.764 (1)
Me(3)	0.427 (2)	0.056 (2)	0.908 (1)
Me(4)	0.481 (1)	0.274 (2)	0.785 (2)
Me(5)	0.422 (2)	0.403 (1)	0.564 (1)
Me(6)	0.880 (1)	−0.037 (1)	0.580 (2)
Me(7)	0.742 (2)	−0.019 (2)	0.459 (1)
Me(8)	0.550 (2)	−0.101 (1)	0.628 (2)
Me(9)	0.574 (1)	−0.171 (1)	0.848 (1)
Me(10)	0.771 (2)	−0.131 (2)	0.822 (1)
O(1)	0.6443 (9)	0.2264 (8)	0.4443 (7)
O(2)	0.7118 (9)	0.185 (1)	0.6477 (9)
Sm(2)	0.85870 (6)	0.34547 (5)	0.90437 (5)
Me(11)	0.921 (2)	0.421 (1)	0.619 (1)
Me(12)	1.037 (1)	0.184 (2)	0.758 (2)
Me(13)	0.873 (2)	0.078 (1)	0.948 (1)
Me(14)	0.651 (1)	0.251 (2)	0.924 (1)
Me(15)	0.680 (1)	0.464 (1)	0.725 (1)
Me(16)	0.594 (1)	0.392 (2)	1.070 (2)
Me(17)	0.715 (2)	0.539 (1)	1.022 (1)
Me(18)	0.938 (2)	0.388 (2)	1.076 (1)
Me(19)	0.945 (1)	0.150 (1)	1.169 (1)
Me(20)	0.736 (2)	0.154 (1)	1.165 (1)
O(3)	1.0558 (8)	0.3153 (9)	0.8553 (9)
O(4)	0.853 (1)	0.5457 (8)	0.7850 (8)
Cp(1)	0.383 (1)	0.229 (1)	0.639 (1)
Cp(2)	0.382 (1)	0.136 (1)	0.733 (1)
Cp(3)	0.424 (1)	0.139 (1)	0.795 (1)
Cp(4)	0.446 (1)	0.234 (1)	0.740 (1)
Cp(5)	0.421 (1)	0.290 (1)	0.643 (1)
Cp(6)	0.779 (1)	−0.059 (1)	0.628 (1)
Cp(7)	0.715 (1)	−0.050 (1)	0.577 (1)
Cp(8)	0.632 (1)	−0.085 (1)	0.647 (1)
Cp(9)	0.641 (1)	−0.117 (1)	0.746 (1)
Cp(10)	0.730 (1)	−0.099 (1)	0.734 (1)
C(1)	0.740 (2)	0.244 (2)	0.386 (2)
C(2)	0.710 (2)	0.364 (1)	0.318 (1)
C(3)	0.609 (2)	0.396 (2)	0.305 (2)
C(4)	0.573 (2)	0.295 (2)	0.372 (2)
C(5)	0.797 (2)	0.129 (2)	0.707 (2)
C(6)	0.871 (2)	0.189 (2)	0.617 (2)
C(7)	0.822 (2)	0.285 (2)	0.559 (2)
C(8)	0.706 (2)	0.299 (2)	0.586 (2)
Cp(11)	0.871 (1)	0.347 (1)	0.723 (1)
Cp(12)	0.925 (1)	0.242 (1)	0.784 (1)
Cp(13)	0.852 (1)	0.196 (1)	0.867 (1)
Cp(14)	0.755 (1)	0.269 (1)	0.859 (1)
Cp(15)	0.767 (1)	0.364 (1)	0.767 (1)
Cp(16)	0.704 (1)	0.355 (1)	1.078 (1)
Cp(17)	0.759 (1)	0.420 (1)	1.053 (1)
Cp(18)	0.856 (1)	0.356 (1)	1.079 (1)
Cp(19)	0.862 (1)	0.250 (1)	1.119 (1)
Cp(20)	0.767 (1)	0.251 (1)	1.118 (1)
C(9)	1.130 (2)	0.242 (2)	0.921 (2)
C(10)	1.190 (2)	0.308 (2)	0.894 (2)
C(11)	1.185 (2)	0.394 (2)	0.785 (2)
C(12)	1.117 (2)	0.371 (2)	0.757 (2)
C(13)	0.913 (2)	0.588 (2)	0.797 (2)
C(14)	0.947 (2)	0.664 (2)	0.681 (2)
C(15)	0.881 (2)	0.681 (2)	0.628 (2)
C(16)	0.794 (2)	0.630 (2)	0.706 (2)

(3.43 g, 6.26 mmol) in 100 mL of THF. The stirring solution rapidly turned dark green as off-white solids (KI) formed. After 2 h the solution was filtered through a fine frit. The filtrate volume was slowly reduced by rotary evaporation to 10 to 15 mL and filtered while still cold. The resulting solid was rinsed twice with hexane and allowed to dry, yielding II as a dark green microcrystalline powder (2.12 g, 61%). Additional product can be obtained from the filtrate by solvent reduction and filtration. The ^1H NMR and IR spectra of this material were identical with those of II prepared from I and SmI_2. Anal. (For possible potassium contaminant). Calcd for $SmC_{18}H_{31}IO_2$: K, 0.00. Found: K, <0.20.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(THF)_2$ (I). Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ-2θ scan technique by methods previously described.[29] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[30] Calculations were carried out with the SHELX system of computer programs.[31] Neutral atom scattering factors for Sm, O, and C were taken from Cromer and Waber,[32] and the scattering for the non-hydrogen atoms was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[33] Scattering factors for hydrogen were from ref 34.

The space group was shown to be $P\bar{1}$ by the successful solution and refinement of the structure. The positions of the two independent samarium atoms were revealed by the inspection of a Patterson map. A difference Fourier map phased on the metal atoms revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.095$.

Hydrogen atoms were not included in the refinement, and all ring carbon atoms were treated with isotropic thermal parameters. The thermal motion of all other atoms was dealt with anisotropically. The final agreement factors are $R = 0.061$ and $R_w = 0.066$. A final difference Fourier showed no feature greater than 0.8 e^-/A^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[(C_5Me_5)Sm(THF)_2(\mu\text{-}I)]_2$

compound	$Sm_2I_2O_4C_{36}H_{62}$
M_r	
space group	$P2_1/n$
cell constants	
a, Å	12.708 (5)
b, Å	13.454 (6)
c, Å	14.859 (6)
β, deg	112.37 (4)
cell vol, Å^3	2337.2
molecules/unit cell	2 dimers
ρ(calcd), g cm^{-3}	1.57
μ(calcd), cm^{-1}	38.8
radiation	Mo Kα
max crystal dimensions, mm	0.15 × 0.15 × 0.20
scan width	0.8 + 0.2(tan θ)
standard reflections	400 060 004
decay of standards	<3%
reflections measured	2975
2θ range, deg	2–40
observed reflections	1577
no. of parameters varied	159
GOF	1.13
R	0.053
R_w	0.059

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (II). Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table III. Data were collected and handled as described above.

The space group was shown to be $P2_1/n$ by systematic absences. The positions of the samarium atom and the iodine atoms were revealed by the direct methods program MULTAN.[35] A difference Fourier map phased on these atoms revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.090$.

The carbon atoms of the THF rings were treated with isotropic thermal parameters. The oxygen atoms of the THF rings and all other

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(34) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.
(35) Main, P.; et al., MULTAN 80, a system of computer program for the automatic solution of crystal structures from x-ray diffraction data, 1980.

Table IV. Final Fractional Coordinates for $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$

atom	x/a	y/b	z/c	U, equiv
Sm	0.45970 (9)	0.00857 (9)	0.65678 (8)	0.060
I	0.6240 (1)	−0.1223 (1)	0.5685 (1)	0.089
O(1)	0.657 (1)	0.030 (1)	0.808 (1)	0.102
O(2)	0.454 (2)	0.184 (1)	0.732 (2)	0.136
C(9)	0.253 (3)	−0.095 (3)	0.598 (2)	0.117
C(10)	0.254 (3)	−0.032 (2)	0.673 (3)	0.118
C(11)	0.343 (4)	−0.073 (4)	0.769 (3)	0.170
C(12)	0.385 (2)	−0.157 (3)	0.734 (4)	0.109
C(13)	0.333 (3)	−0.168 (3)	0.632 (4)	0.134
C(14)	0.164 (3)	−0.081 (4)	0.480 (3)	0.233
C(15)	0.179 (3)	0.057 (3)	0.668 (5)	0.333
C(16)	0.370 (5)	−0.045 (5)	0.879 (3)	0.415
C(17)	0.467 (3)	−0.229 (4)	0.796 (6)	0.418
C(18)	0.329 (4)	−0.241 (4)	0.546 (4)	0.353
C(1)	0.717 (3)	−0.055 (2)	0.883 (1)	0.126
C(2)	0.841 (4)	−0.011 (3)	0.923 (3)	0.196
C(3)	0.849 (4)	0.060 (3)	0.849 (3)	0.181
C(4)	0.737 (3)	0.101 (3)	0.788 (3)	0.164
C(5)	0.480 (4)	0.208 (3)	0.845 (3)	0.184
C(6)	0.600 (4)	0.309 (4)	0.847 (3)	0.198
C(7)	0.487 (4)	0.352 (3)	0.753 (3)	0.198
C(8)	0.406 (4)	0.277 (3)	0.686 (3)	0.182

non-hydrogen atoms were dealt with anisotropically. The final agreement factors are $R = 0.053$ and $R_w = 0.059$. A final difference Fourier showed no feature greater than 0.9 e^-/A^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.

Results and Discussion

Synthesis of I. Purple $(C_5Me_5)_2Sm(THF)_2$ (I) is readily prepared in 5- to 10-g quantities by the metathetical reaction of SmI_2 with KC_5Me_5 in THF solution (eq 2). Such metathetical

$$SmI_2 + 2KC_5Me_5 \xrightarrow{THF} (C_5Me_5)_2Sm(THF)_2 + 2KI \quad (2)$$

reactions are common in organolanthanide chemistry[20] and previously have been employed successfully in divalent organolanthanide synthesis of the insoluble $(C_5H_5)_2Sm(THF)_2$ from SmI_2 and NaC_5H_5[13] and in the synthesis of $(C_5Me_5)_2Yb(THF)_2$ from KC_5Me_5 and $YbBr_2$.[7a,36] Hence, extension of this method to I would appear straightforward. However, the reaction of a divalent lanthanide halide with the $C_5Me_5^-$ anion as exemplified by eq 2 is not necessarily generally applicable. The combinations $YbCl_2/LiC_5Me_5/THF$, $YbCl_2/NaC_5Me_5/Et_2O$, and $EuCl_2/NaC_5Me_5/Et_2O$ all fail to yield isolable $(C_5Me_5)_2Ln(ether)_n$ complexes.[7a] Since complexes of the larger lanthanides are generally less stable and experimentally more difficult than those of the smaller metals, the success of this metathesis with the large samarium system was not necessarily assured.

I is routinely recrystallized from THF and is thus isolated as a disolvate. It remains a disolvate after weeks of storage at 30 °C under N_2 or after 18 h at 22 °C under vacuum. When I is recrystallized from cold toluene, it is recovered as a disolvate. However, rotary evaporation of solutions of I in toluene ultimately yield the monosolvate, $(C_5Me_5)_2Sm(THF)$, indicating that the disolvate and monosolvate are in equilibrium in arene solution (eq 3). This equilibrium is also supported by the observed concen-

$$(C_5Me_5)_2Sm(THF)_2 \rightleftharpoons (C_5Me_5)_2Sm(THF) + THF \quad (3)$$

tration dependence of the ^1H NMR spectra of I in benzene-d_6 and the concentration independence in THF-d_8. By comparison, both $(C_5Me_5)_2Eu(THF)$ and $(C_5Me_5)_2Eu(THF)(Et_2O)$ are known, as well as $(C_5Me_5)_2Yb(THF)_n$, where $n = 1$ or 2.[6,7a] In the latter case, the disolvate can be converted to the monosolvate by heating at 90 °C under vacuum.[6] I can also be converted to the fully desolvated $(C_5Me_5)_2Sm$ at 85 °C under high vacuum.[5]

(36) $(C_5Me_5)_2Yb(THF)$ has also been prepared from $YbCl_2$ and NaC_5Me_5 in THF.[26]

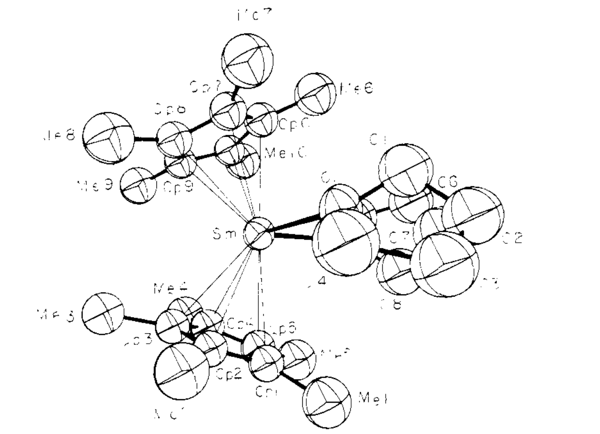

Figure 1. ORTEP plot of the molecular structure and numbering scheme for one of the two independent molecules of $(C_5Me_5)_2Sm(THF)_2$ (I).

Synthesis of II. Dark green $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (II) is formed when the stoichiometry of eq 2 is changed from 1:2 to 1:1 or when I is reacted with an equimolar amount of SmI_2 in THF (eq 4 and 5). The alkali metal free route in eq 5 gives the

$$SmI_2 + KC_5Me_5 \xrightarrow{THF} [(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2 + KI \quad (4)$$

$$(C_5Me_5)_2Sm(THF)_2 + SmI_2 \xrightarrow{THF} [(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2 \quad (5)$$

higher yield (83%) but requires the prior preparation of I. For most purposes, the method in eq 4 is the preferred synthesis of II. II is soluble in THF but insoluble in toluene and alkanes. It is readily isolated as a microcrystalline solid of analytical purity by reducing the volume of the THF solution in which it is prepared and filtering.

The X-ray crystal structure (see below) reveals that II is dimeric in the solid state. In solution, however, one or more equilibria may exist, since the highly temperature- and concentration-dependent ^1H NMR spectra reveal at least two types of C_5Me_5 resonances. The ^{13}C NMR spectrum is consistent with the presence of more than one species in solution. The spectrum contains two resonances split into quartets, presumably due to two $C_5(CH_3)_5$ environments, and two singlets, presumably due to two $C_5(CH_3)_5$ environments. Like the divalent $(C_5Me_5)_2Sm(THF)_2$[3] and in contrast to trivalent samarium organometallics,[15,37] the methyl carbon signals of II are at low field, 101.3 and 93.2 ppm, and the ring carbon resonances are at high field, −58.9 and −67.8 ppm.

Structural Features. General Structure. As shown in Figure 1, $(C_5Me_5)_2Sm(THF)_2$ has a structure typical of the bent metallocene complexes found with transition metals.[38] The cyclopentadienyl rings are canted rather than parallel, and the oxygen atoms of the THF solvate molecules lie approximately in the plane that bisects the ring centroid–metal–ring centroid angle and is normal to the plane defined by the ring centroids and the metal. The plane containing O(1), Sm, and O(2) has a dihedral angle of 92.9° with respect to the plane containing ring centroid(1), Sm, and ring centroid(2) and is tipped only 0.6° from a perfectly equatorial position between the two planes defined by the C_5Me_5 ring carbon atoms. The methyl groups of the two C_5Me_5 rings are staggered with respect to each other as evidenced by the following torsional angles: Me(3)–ring centroid(1)–ring centroid(2)–Me(9), 31°; Me(2)–ring centroid(1)–ring centroid(2)–Me(9), −43°.

The average ring centroid(1)–Sm–ring centroid(2) angle of 137° is similar to those found in other crystallographically characterized bis(C_5Me_5) lanthanide complexes that contain other ligands in the coordination sphere of the metal. Two divalent

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Table V. Bond Lengths (Å) and Angles (deg) for $(C_5Me_5)_2Sm(THF)_2$

atoms	distance	atoms	distance	atoms	angle	atoms	angle
Sm(1)-Cp(1)	2.89 (1)	Sm(1)-Cp(2)	2.87 (1)	O(1)-Sm(1)-O(2)	82.7 (4)	O(3)-Sm(2)-O(4)	82.4 (4)
Sm(1)-Cp(3)	2.81 (2)	Sm(1)-Cp(4)	2.84 (2)	Cp(2)-Cp(1)-Cp(5)	109 (1)	Cp(2)-Cp(1)-Me(1)	124 (1)
Sm(1)-Cp(5)	2.89 (1)	Sm(1)-Cp(6)	2.86 (2)	Cp(5)-Cp(1)-Me(1)	126 (1)	Cp(1)-Cp(2)-Cp(3)	107 (1)
Sm(1)-Cp(7)	2.82 (1)	Sm(1)-Cp(8)	2.86 (1)	Cp(1)-Cp(2)-Me(2)	125 (1)	Cp(3)-Cp(2)-Me(2)	128 (1)
Sm(1)-Cp(9)	2.88 (1)	Sm(1)-Cp(10)	2.86 (1)	Cp(2)-Cp(3)-Cp(4)	108 (1)	Cp(2)-Cp(3)-Me(3)	123 (2)
Sm(1)-O(1)	2.620 (9)	Sm(1)-O(2)	2.64 (1)	Cp(4)-Cp(3)-Me(3)	129 (2)	Cp(3)-Cp(4)-Cp(5)	109 (1)
Sm(2)-Cp(11)	2.85 (1)	Sm(2)-Cp(12)	2.84 (1)	Cp(3)-Cp(4)-Me(4)	124 (2)	Cp(5)-Cp(4)-Me(4)	126 (2)
Sm(2)-Cp(13)	2.85 (1)	Sm(2)-Cp(14)	2.89 (2)	Cp(1)-Cp(5)-Cp(4)	107 (1)	Cp(1)-Cp(5)-Me(5)	126 (1)
Sm(2)-Cp(15)	2.90 (1)	Sm(2)-Cp(16)	2.84 (1)	Cp(4)-Cp(5)-Me(5)	126 (1)	Cp(7)-Cp(6)-Cp(10)	105 (1)
Sm(2)-Cp(17)	2.83 (1)	Sm(2)-Cp(18)	2.90 (1)	Cp(7)-Cp(6)-Me(6)	127 (1)	Cp(10)-Cp(6)-Me(6)	128 (2)
Sm(2)-Cp(19)	2.91 (1)	Sm(2)-Cp(20)	2.88 (1)	Cp(6)-Cp(7)-Cp(8)	111 (1)	Cp(6)-Cp(7)-Me(7)	125 (1)
Sm(2)-O(3)	2.62 (1)	Sm(2)-O(4)	2.66 (1)	Cp(8)-Cp(7)-Me(7)	124 (1)	Cp(7)-Cp(8)-Cp(9)	107 (1)
Cp(1)-Cp(2)	1.42 (2)	Cp(1)-Cp(5)	1.39 (2)	Cp(7)-Cp(8)-Me(8)	128 (1)	Cp(9)-Cp(8)-Me(8)	124 (1)
Cp(1)-Me(1)	1.56 (2)	Cp(2)-Cp(3)	1.42 (2)	Cp(8)-Cp(9)-Cp(10)	108 (1)	Cp(8)-Cp(9)-Me(9)	126 (1)
Cp(2)-Me(2)	1.54 (2)	Cp(3)-Cp(4)	1.39 (2)	Cp(10)-Cp(9)-Me(9)	126 (1)	Cp(6)-Cp(10)-Cp(9)	109 (1)
Cp(3)-Me(3)	1.55 (2)	Cp(4)-Cp(5)	1.42 (2)	Cp(6)-Cp(10)-Me(10)	126 (2)	Cp(9)-Cp(10)-Me(10)	124 (1)
Cp(4)-Me(4)	1.54 (2)	Cp(5)-Me(5)	1.53 (2)	Cp(12)-Cp(11)-Cp(15)	109 (1)	Cp(12)-Cp(11)-Me(11)	124 (1)
Cp(6)-Cp(7)	1.44 (2)	Cp(6)-Cp(10)	1.42 (2)	Cp(15)-Cp(11)-Me(11)	127 (1)	Cp(11)-Cp(12)-Cp(13)	107 (1)
Cp(6)-Me(6)	1.49 (2)	Cp(7)-Cp(8)	1.39 (2)	Cp(11)-Cp(12)-Me(12)	127 (2)	Cp(13)-Cp(12)-Me(12)	126 (1)
Cp(7)-Me(7)	1.58 (2)	Cp(8)-Cp(9)	1.43 (2)	Cp(12)-Cp(13)-Cp(14)	110 (1)	Cp(12)-Cp(13)-Me(13)	126 (1)
Cp(8)-Me(8)	1.56 (2)	Cp(9)-Cp(10)	1.42 (2)	Cp(14)-Cp(13)-Me(13)	125 (1)	Cp(13)-Cp(14)-Cp(15)	107 (1)
Cp(9)-Me(9)	1.52 (2)	Cp(10)-Me(10)	1.53 (2)	Cp(13)-Cp(14)-Me(14)	128 (2)	Cp(15)-Cp(14)-Me(14)	124 (2)
Cp(11)-Cp(12)	1.42 (2)	Cp(11)-Cp(15)	1.40 (2)	Cp(11)-Cp(15)-Cp(14)	108 (1)	Cp(11)-Cp(15)-Me(15)	127 (1)
Cp(11)-Me(11)	1.53 (2)	Cp(12)-Cp(13)	1.41 (2)	Cp(14)-Cp(15)-Me(15)	125 (1)	Cp(17)-Cp(16)-Cp(20)	107 (1)
Cp(12)-Me(12)	1.52 (2)	Cp(13)-Cp(14)	1.39 (2)	Cp(17)-Cp(16)-Me(16)	126 (2)	Cp(20)-Cp(16)-Me(16)	127 (2)
Cp(13)-Me(13)	1.56 (2)	Cp(14)-Cp(15)	1.44 (2)	Cp(16)-Cp(17)-Cp(18)	109 (1)	Cp(16)-Cp(17)-Me(17)	126 (2)
Cp(14)-Me(14)	1.54 (2)	Cp(15)-Me(15)	1.53 (2)	Cp(18)-Cp(17)-Me(17)	124 (2)	Cp(17)-Cp(18)-Cp(19)	107 (1)
Cp(16)-Cp(17)	1.42 (2)	Cp(16)-Cp(20)	1.40 (2)	Cp(17)-Cp(18)-Me(18)	129 (1)	Cp(19)-Cp(18)-Me(18)	123 (1)
Cp(16)-Me(16)	1.52 (2)	Cp(17)-Cp(18)	1.42 (2)	Cp(18)-Cp(19)-Cp(20)	107 (1)	Cp(18)-Cp(19)-Me(19)	129 (1)
Cp(17)-Me(17)	1.54 (2)	Cp(18)-Cp(19)	1.41 (2)	Cp(20)-Cp(19)-Me(19)	123 (1)	Cp(16)-Cp(20)-Cp(19)	108 (1)
Cp(18)-Me(18)	1.53 (2)	Cp(19)-Cp(20)	1.44 (2)	Cp(16)-Cp(20)-Me(20)	126 (1)	Cp(19)-Cp(20)-Me(20)	125 (1)
Cp(19)-Me(19)	1.53 (2)	Cp(20)-Me(20)	1.51 (2)	C(1)-O(1)-C(4)	106 (1)	C(5)-O(2)-C(8)	107 (1)
O(1)-C(1)	1.42 (2)	O(1)-C(4)	1.51 (2)	C(9)-O(3)-C(12)	104 (1)	C(13)-O(4)-C(16)	110 (1)
O(2)-C(5)	1.54 (2)	O(2)-C(8)	1.50 (2)	O(1)-C(1)-C(2)	103 (1)	C(1)-C(2)-C(3)	107 (2)
O(3)-C(9)	1.46 (2)	O(3)-C(12)	1.46 (2)	C(2)-C(3)-C(4)	107 (2)	O(1)-C(4)-C(3)	100 (2)
O(4)-C(13)	1.48 (2)	O(4)-C(16)	1.47 (2)	O(2)-C(5)-C(6)	95 (2)	C(5)-C(6)-C(7)	112 (2)
C(1)-C(2)	1.55 (2)	C(2)-C(3)	1.43 (2)	C(6)-C(7)-C(8)	110 (2)	O(2)-C(8)-C(7)	98 (2)
C(3)-C(4)	1.57 (3)	C(5)-C(6)	1.54 (3)	O(3)-C(9)-C(10)	103 (2)	C(9)-C(10)-C(11)	107 (2)
C(6)-C(7)	1.31 (3)	C(7)-C(8)	1.56 (3)	C(10)-C(11)-C(12)	103 (2)	O(3)-C(12)-C(11)	104 (2)
C(9)-C(10)	1.49 (3)	C(10)-C(11)	1.52 (2)	O(4)-C(13)-C(14)	99 (2)	C(13)-C(14)-C(15)	107 (2)
C(11)-C(12)	1.52 (3)	C(13)-C(14)	1.58 (3)	C(14)-C(15)-C(16)	110 (2)	O(4)-C(16)-C(15)	97 (2)
C(14)-C(15)	1.40 (3)	C(15)-C(16)	1.57 (3)				

complexes are available for comparison, $(C_5Me_5)_2Yb(THF)(C_7H_8)_{0.5}$ (III),[7a] in which the toluene is in the lattice and is not coordinated to the metal, and $(C_5Me_5)_2Yb(pyridine)_2$ (IV).[7d] The ring centroid–metal–ring centroid angles for III and IV are 143.5 (3)° and 136.3 (3)°, respectively. Comparable angles for trivalent species are similar:[39] $(C_5Me_5)_2Yb(\mu\text{-}I)_2Li(OEt_2)_2$[26] (V), 135.6°; $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (VI),[26] 136.6°; $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2AlCl_2$ (VII),[26] 137.3°; $[(C_5Me_5)_2SmH]_2$,[4] 130.5°; $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$,[40] 137.2°; $(C_5Me_5)_2Sm(C_6H_5)(THF)$,[15] 136.9°; $(C_5Me_5)_2SmCl(THF)$,[41] 134°; $(C_5Me_5)_2SmI(THF)$ (VIII),[41] 136.5°; $(C_5Me_5)_2YCl(THF)$,[41] 136.4°; $[(C_5Me_5)_2YCl]_2$ (IX),[42] 139.3° and 135.8°; *cis*-$\{(C_5Me_5)_2Sm[OP(C_6H_5)_3]\}_2(\mu\text{-}OCHCHO)$,[43] 132.6° and 133.2°; *trans*-$\{[(C_5Me_5)_2Sm[OP(C_6H_5)_3]\}_2(\mu\text{-}OCHCHO)$,[43] 132.6° and 131.4°; $(C_5Me_5)_2YbCl(Me_2PCH_2PMe_2)$,[44] 134.9°. With the exception of the 143.5 (3)° angle for $(C_5Me_5)_2Yb(THF)\cdot(C_7H_8)_{0.5}$, all of these angles fall within the 131–138° range regardless of their coordination numbers or oxidation states. This range is also within the 128–139° span of ring centroid–metal–ring centroid angles observed for bis(pentamethylcyclopentadienyl) actinide complexes that contain other ligands.[45,46]

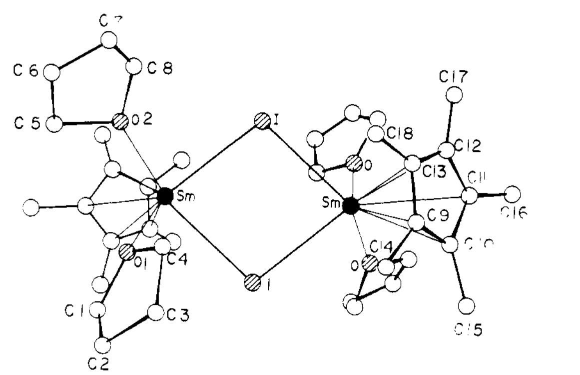

Figure 2. Molecular structure and numbering scheme for $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (II).

The molecular structure of $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ is shown in Figure 2. One can roughly think of this divalent complex as related to trivalent $(C_5Me_5)_2Ln(\mu\text{-}X)_2M(ligand)_2$ species[26,47,48] such as V–VII except that one C_5Me_5 ligand is replaced by two THF molecules. The $Sm(\mu\text{-}I)_2Sm'$ unit is exactly planar as re-

(39) When more than one value is available from the crystal structure an average is given here.
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Table VI. Bond Lengths (Å) and Angles (deg) for $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$

atoms	distance	atoms	distance
Sm–Sm′	5.142 (2)	Sm–I′	3.459 (2)
Sm–I	3.356 (2)	Sm–O(1)	2.66 (1)
Sm–O(2)	2.62 (2)	Sm–C(9)	2.80 (2)
Sm–C(10)	2.77 (2)	Sm–C(11)	2.84 (3)
Sm–C(12)	2.83 (3)	Sm–C(13)	2.81 (3)
Sm–Cnt(1)	2.534	Sm–Ave(1)	2.81 (2)
I–I′	4.474 (2)	O(1)–C(1)	1.57 (3)
O(1)–C(4)	1.51 (4)	O(2)–C(5)	1.61 (4)
O(2)–C(8)	1.44 (4)	C(1)–C(2)	1.57 (5)
C(2)–C(3)	1.48 (5)	C(3)–C(4)	1.47 (5)
C(5)–C(6)	1.39 (5)	C(6)–C(7)	1.46 (5)
C(7)–C(8)	1.51 (5)	C(9)–C(10)	1.40 (4)
C(9)–C(13)	1.37 (4)	C(9)–C(14)	1.69 (4)
C(10)–C(11)	1.54 (5)	C(10)–C(15)	1.51 (4)
C(11)–C(12)	1.44 (5)	C(11)–C(16)	1.58 (4)
C(12)–C(13)	1.41 (4)	C(12)–C(17)	1.47 (4)
C(13)–C(18)	1.59 (5)		

atoms	angle	atoms	angle
I–Sm–I′	82.04 (5)	I′–Sm–O(1)	127.7 (4)
I–Sm–O(1)	81.9 (4)	I′–Sm–O(2)	88.0 (5)
I–Sm–O(2)	139.5 (6)	O(1)–Sm–O(2)	73.5 (6)
O(1)–Sm–Cnt(1)	116.691	O(2)–Sm–Cnt(1)	109.965
I–Sm–Cnt(1)	109.779	I′–Sm–Cnt(1)	115.624
Sm–I–Sm′	97.96 (5)	Sm–O(1)–C(1)	125 (1)
Sm–O(1)–C(4)	113 (2)	C(1)–O(1)–C(4)	114 (2)
Sm–O(2)–C(5)	126 (2)	Sm–O(2)–C(8)	131 (2)
C(5)–O(2)–C(8)	101 (3)	O(1)–C(1)–C(2)	98 (3)
C(1)–C(2)–C(3)	108 (3)	C(2)–C(3)–C(4)	112 (4)
O(1)–C(4)–C(3)	102 (3)	O(2)–C(5)–C(6)	101 (4)
C(5)–C(6)–C(7)	114 (5)	C(6)–C(7)–C(8)	100 (4)
O(2)–C(8)–C(7)	102 (3)	C(10)–C(9)–C(13)	111 (3)
C(10)–C(9)–C(14)	124 (5)	C(13)–C(9)–C(14)	125 (4)
C(9)–C(10)–C(11)	108 (3)	C(9)–C(10)–C(15)	128 (5)
C(11)–C(10)–C(15)	124 (5)	C(10)–C(11)–C(12)	101 (2)
C(10)–C(11)–C(16)	132 (6)	C(12)–C(11)–C(16)	127 (6)
C(11)–C(12)–C(13)	113 (3)	C(11)–C(12)–C(17)	125 (6)
C(13)–C(12)–C(17)	122 (6)	C(9)–C(13)–C(12)	108 (3)
C(9)–C(13)–C(18)	111 (5)	C(12)–C(13)–C(18)	141 (5)

quired by the crystallographic symmetry of the molecule.[49] The C_5Me_5 ring is on one side of the plane, and the two THF molecules are on the other. The I–Sm–I′ angle of 82.04 (5)° and the Sm–I–Sm′ angle of 97.46 (5)° are roughly comparable to the 86–94° Ln–X–M angles found in V–VIII. Comparison of the structure of II with trivalent complexes such as V–VII indicates that the samarium atom in II is much more coordinatively unsaturated since Sm^{2+} is larger than any trivalent lanthanide and two THF ligands take up fewer coordination positions than a C_5Me_5 ring. Tables V and VI present bond length and angle data on I and II, respectively.

Bond Lengths. The average Sm–C bond length in I, 2.86 (3) Å, is somewhat longer than the average Sm–C bond distance in the sterically less crowded II, 2.81 (2) Å. These distances can be compared to average divalent Yb–C distances of 2.66 (2) Å in the seven-coordinate III[7a] and 2.74 (4) Å in the eight-coordinate IV.[7d] The metal–carbon bond lengths in the seven-coordinate Sm(II) and Yb(II) species differ by 0.15 Å, and the metal–carbon distances in the eight-coordinate Sm(II) and Yb(II) species differ by 0.12 Å. The difference in ionic radii of Sm(II) and Yb(II) is generally cited to be between 0.18[50] and 0.19 Å.[51]

The Sm–O bond lengths in I, 2.62 (1), 2.62 (1), 2.64 (1), and 2.66 (1) Å, are similar to those in II, 2.62 (2) and 2.66 (1), Å. These distances are 0.21 to 0.25 Å larger than the Yb(II)–THF oxygen distance of 2.412 (5) Å in III. Hence, the C_5Me_5 groups in I and II are positioned somewhat closer to the Sm^{2+} centers than expected compared with Yb^{2+} complexes and the THF groups in I and II are bound at slightly longer distances.[52]

The Sm–I bridge bond distances of 3.356 (2) and 3.459 (2) Å can be compared with the terminal Sm–I distances in the two crystallographically independent molecules in the unit cell of the trivalent $(C_5Me_5)_2SmI(THF)$ (VIII),[40] 3.043 (2) and 3.053 (2) Å. Taking account of the fact that Sm^{2+} is 0.141[50]–0.146[51] Å larger than Sm^{3+}, the bridge distances in II are 0.16–0.27 Å longer than the terminal bond lengths. A recent survey of lanthanide chloride distances in 12 organolanthanide complexes shows that bridging chloride distances are larger than terminal chloride distances by 0.04 to 0.22 Å.[42] This comparison indicates that the Sm–I′ distance of 3.459 (2) Å is rather long. The difference in the two bridge iodide distances in II, 0.103 Å, is larger than the difference found in the chloride bridges in $[(C_8H_8)Ce(THF)(\mu\text{-}Cl)]_2$ (X),[53] 0.08 Å, but is less than the difference in the two bridge chloride distances found in $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$, (IX),[42] 0.136 Å. The Ln_2X_2 moieties in X, II, and IX, in that specific order, constitute a structural paradigm for successive stages of a dimer-to-monomer dissociation process for molecules containing Ln_2X_2 subunits.[54]

Conclusion

The development of a solution synthesis for $(C_5Me_5)_2Sm(THF)_2$ and the discovery of $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ make divalent organosamarium chemistry readily accessible for organic as well as inorganic and organometallic applications. These complexes, together with $SmI_2(THF)_n$, allow a choice of highly reactive, one-electron reducing agents. The three different coordination environments of these Sm(II) reagents lead to different solubility properties and should also provide variations in the Sm(II) reactivity patterns. The most sterically crowded $(C_5Me_5)_2Sm(THF)_2$ may provide certain substrate size selectivity and may react only with molecules or functional groups that can fit into a $(C_5Me_5)_2Sm$ coordination sphere. $[(C_5Me_5)Sm(THF)_2(\mu\text{-}I)]_2$ is less sterically congested and may dissociate easily to provide an even more open (yet soluble) Sm(II) species. Complex II may also be important as a precursor to other Sm(II) alkyl and hydride complexes via the derivatizable iodide ligand. Complex I has already proven to be an important precursor to other samarium complexes[3–5,15,43,55] and II may be useful similarly.

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Registry No. I, 79372-14-8; II, 94161-37-2; $(C_5Me_5)_2Sm(THF)$, 94138-27-9; $SmI_2(THF)_2$, 94138-28-0.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

(49) Atoms O(1), O(2), I, and I′ are also approximately planar. The distances of the four atoms from the average plane they define are as follows: O(1), 0.19 Å; O(2), –0.17 Å; I, –0.13 Å; I′, +0.12 Å. The samarium atom is 1.17 Å from this plane and the C_5Me_5 ring centroid is 3.69 Å away. An alternative view of the molecule is that the four atoms O(1), O(2), I, and I′ plus the C_5Me_5 ring centroid approximately describe a square pyramid with the ring centroid at the apical position. This is similar to viewing the two C_5Me_5 ring centroids and the two THF oxygen atoms of I as a distorted tetrahedron.

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