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Synthesis and structure of mono-THF solvates of bis(cyclopentadienyl)samarium(II) complexes: $(C_5Me_5)_2Sm(THF)$ and $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$

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Abstract

X-ray crystallographic data have been obtained on the mono-THF solvates of the organosamarium(II) complexes $(C_5Me_5)_2Sm(THF)$ and $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$. $(C_5Me_5)_2Sm(THF)$ crystallizes from toluene in space group $P2_1/n$ with $a = 9.7606(13)$, $b = 16.6557(17)$, $c = 14.0710(16)$ Å, $\beta = 90.446(10)°$, $V = 2287.4(5)$ Å^3 and $D_{calcd} = 1.431$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 2879 reflections converged to a final $R_F = 3.1\%$. $\{[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)\}(C_6H_{12})_{0.5}$ crystallizes from hexane in space group $P\bar{1}$ with $a = 9.3600(17)$, $b = 11.0311(21)$, $c = 20.4697(33)$ Å, $\alpha = 83.290(14)$, $\beta = 80.569(14)$, $\gamma = 88.785(15)°$, $V = 2071.2(6)$ Å^3 and $D_{calcd} = 1.225$ g cm^{-3} for $Z = 2$. Least-squares refinement of the model based on 5988 reflections converged to a final $R_F = 3.1\%$. In these bent metallocenes, the THF oxygen atoms do not adopt the sterically least crowded positions and lie off the plane defined by the two ring centroids and the samarium by 1.54 Å for $(C_5Me_5)_2Sm(THF)$ and by 0.85 Å for $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$.

Recent studies in organolanthanide chemistry have shown that bis(pentamethylcyclopentadienyl) complexes of Sm^{II} provide access to a wide range of unusual reactions [1–4]. The primary reagents used in these studies have been the disolvated purple complex $(C_5Me_5)_2Sm(THF)_2$ (**1**) [5], and the unsolvated green complex $(C_5Me_5)_2Sm$ (**2**) [6], both of which have been fully defined by X-ray crystallography. Complex **1** is converted to **2** by heating to 80°C under vacuum in what is apparently a two-stage process. Evidence for an intermediate monosolvate, $(C_5Me_5)_2Sm(THF)$, has been obtained [7] from elemental analysis of the brownish-green solid obtained by rotary evaporation of toluene solutions of **1**, but X-ray crystallographic confirmation of the monosolvate formulation has been lacking. We report here the X-ray crystal structure of this THF monosolvate as well as the structure of another THF monosolvate recently obtained with trimethylsilyl-substituted cyclopentadienyl ligands.

1. Experimental details

The complexes described below are extremely sensitive to air and moisture. Therefore, syntheses and manipulations were conducted under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Solvents were purified and physical measurements were obtained as previously described [8]. $(C_5Me_5)_2Sm(THF)_2$ [5] and $C_5H_3(SiMe_3)_3$ [9] were prepared according to the literature, and the diene was purified by fractional distillation.

1.1. $(C_5Me_5)_2Sm(THF)$ (3)

In the glovebox, $(C_5Me_5)_2Sm(THF)_2$ (46 mg, 0.08 mmol) was dissolved in 5 ml of toluene. Removal of solvent by rotary evaporation left $(C_5Me_5)_2Sm(THF)$ [7] as a green-brown powder (40 mg, 100%). Anal. Found: 30.3. $C_{24}H_{30}OSm$ calcd.: Sm, 30.51%. ^1H NMR (C_6D_6, concentration dependent, 21 mg/0.5 ml): δ 3.0 (C_5Me_5), 16.43, 2.65 (THF). ^{13}C NMR (C_6D_6) δ 94.5 ($C_5\mathit{Me}_5$), −80.1 (C_5Me_5), 25.5, 14.5 (THF). M.p. 108°C.

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Dark red crystals suitable for X-ray diffraction were grown from toluene at −35°C over a two-day period.

1.1.1. X-ray data collection, structure determination, and refinement for $(C_5Me_5)_2Sm(THF)$ (3)

A dark red crystal of approximate dimensions 0.18 × 0.22 × 0.30 mm was immersed in Paratone-N (Exxon), mounted on a glass fiber and transferred to a Siemens R3m/V automated four-circle diffractometer equipped with a modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters and orientation matrix of the crystal were carried out by previously described methods similar to those of Churchill *et al.* [10]. Intensity data were collected at 173 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table 1. All 3354 data were corrected for absorption (empirical correction based on φ-scan data) and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ (C_{2h}^5; No. 14) is, therefore, uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package [11] or the SHELXTL-PLUS program set [12]. The analytical scattering factors for neutral atoms were used throughout the analysis [13a]; both the real ($\Delta f'$) and imaginary ($i\,\Delta f''$) components of anomalous dispersion [13b] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and $U_{iso} = 0.05$ Å^2. Refinement of positional and thermal parameters led to convergence with $R_F = 3.1\%$; $R_{wF} = 3.5\%$ and GOF = 1.14 for 236 variables refined against all 2879 data with $|F_o| > 0$, ($R_F = 2.3\%$, $R_{wF} = 3.2\%$ for those 2465 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.46$ eÅ^{-3}.

TABLE 1. Crystal data and summary of intensity data collection and structure refinement for **3** and **4**

	3	**4**
Compound	$C_{24}H_{38}OSm$	$C_{32}H_{72}OSi_5Sm$
Molecular weight	492.9	763.70
Space group	$P2_1/n$ (C_{2h}^5; No. 14)	$P\bar{1}$ (C_i^1; No. 14)
Cell constants, a(Å)	9.7606(13)	9.3600(17)
b (Å)	16.6557(17)	11.0311(21)
c (Å)	14.0710(16)	20.4697(33)
α (°)	90	83.290(14)
β (°)	90.446(10)	80.569(14)
γ (°)	90	88.785(15)
Cell volume (Å^3)	2287.4(5)	2071.2(6)
Molecules/unit cell	4	2
$D_{calc.}$ (g cm^{-3})	1.431	1.225
Temperature (K)	173	173
$\mu_{calc.}$ (cm^{-1})	25.9	15.8
Radiation	Mo Kα ($\bar{\lambda}$ = 0.710730 Å)	Mo Kα ($\bar{\lambda}$ = 0.710730 Å)
Transmission factor range	0.3812–0.4537	0.814–1.000
Max crystal dimens. (mm)	0.18 × 0.22 × 0.30	0.27 × 0.37 × 0.40
Scan width	Sym. $[2\theta(K\alpha_1) - 1.2] \rightarrow [2\theta(K\alpha_2) + 1.2]$	Sym. $[2\theta(K\alpha_1) - 1.2] \rightarrow [2\theta(K\alpha_2) + 1.2]$
Scan rate (° min^{-1})	3.0 (in ω)	3.0 (in ω)
Background counting	Evaluated from 96-step peak profile	Evaluated from 96-step peak profile
Standard reflections	3 standards, measured after each 97 data	3 standards, measured after each 97 data
2θ range (°)	4.0–45.0	4.0–48.0
Total unique data	3354	7003
Unique data	2879 ($I > 0$)	5988 ($I \geq 3\sigma(I)$)
No. of parameters varied	236	352
G.O.F.	1.14	1.20
R (%)	3.1	3.1
R_w (%)	3.5	4.0
Max Δ/σ in final cycle	0.002	0.02

1.2. $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$ (4)

In the glovebox, $K[C_5H_2(SiMe_3)_3]$ was prepared in THF from KH and a sample of $C_5H_3(SiMe_3)_3$ [9] defined as pure by ^1H NMR. THF was added to a mixture of $SmI_2(THF)_2$ (256 mg, 0.467 mmol) and this $K[C_5H_2(SiMe_3)_3]$ (310 mg, 0.97 mmol) and the reaction was stirred overnight. The resulting mixture was centrifuged to remove solids and the solvent was removed by rotary evaporation. The solids were extracted with hexane to give a purplish-black solution. The solvent was removed and a sample was examined by NMR in C_6D_6. A complicated NMR spectrum was observed which contained several Me_3Si resonances. The first crystals isolated from this mixture by crystallization from hexane at −34°C were identified as **4**, which implied the presence of a small amount of $C_5H_4(SiMe_3)_2$ in the $C_5H_3(SiMe_3)_3$ used. Attempts to obtain additional crops of **4** were unsuccessful and attempts to obtain pure **4** directly from reactions of $SmI_2(THF)_2$ with mixtures of the cyclopentadienyl ligands have only led to mixtures of products.

1.2.1. X-ray data collection, structure determination, and refinement for $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]$-Sm(THF) (4)

General procedures were the same as those for **3**. The diffraction pattern showed only triclinic symmetry; successful refinement was carried out in the centrosymmetric space group $P\bar{1}$. Structure refinement included anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were included in fixed, idealized positions with $B_{iso} = 5.0$ Å^2. The *p*-factor in the weighting scheme [14] was taken as 0.05. The largest feature on a final difference-Fourier map was a peak of height 1.8 e Å^{-3} located 0.5 Å from the samarium atom.

2. Results and discussion

2.1. Reaction chemistry

$(C_5Me_5)_2Sm(THF)$ (**3**) was prepared by removing solvent from a purple toluene solution of $(C_5Me_5)_2Sm(THF)_2$. This procedure generates a dark green-brown powder which, on the basis of spectroscopic and analytical data, was formulated as the monosolvate, $(C_5Me_5)_2Sm(THF)$ (**3**) [7]. However, since the unsolvated metallocene, $(C_5Me_5)_2Sm$, is green, and since the very intense Sm^{II} colors sometimes obscure the primary species in a mixture, it was desirable to fully confirm the existence of the monosolvate **3** by an X-ray crystallographic study. Suitable single crystals were obtained and the structure is described below.

The procedure by which **3** is formed provides an experimentally convenient way to use the reagent $(C_5Me_5)_2Sm(THF)_2$. Since removal of THF from **3** is much more difficult than removal of THF from **1**, complex **3** is more easily prepared as a solid in a well-defined form of solvation than is **1**. Hence, accurate stoichiometries for Sm^{II} reactions can be readily accessed *via* solid **3**.

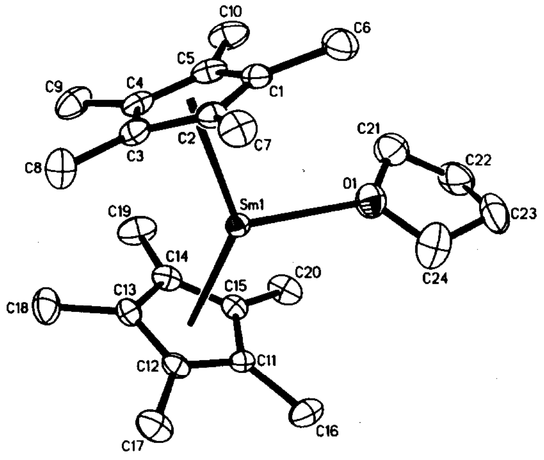

Fig. 1. ORTEP diagram of $(C_5Me_5)_2Sm(THF)$ (3) with the probability ellipsoids drawn at the 50% level.

A second THF monosolvate of a Sm^{II} metallocene has also been obtained and is included here for comparison with **3**. Bis(trimethylsilyl)-substituted cyclopentadienyl ligands have been shown to be useful alternatives to C_5Me_5 in 4f-element chemistry [15]. In the course of studying the utility of more highly substituted trimethylsilyl cyclopentadienyl ligands in Sm^{II} chemistry [15], we have obtained single crystals of $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$ (**4**). This complex preferentially crystallized from a reaction containing an apparent mixture of bis- and tris(trimethylsilyl)-substituted cyclopentadienyl ligands. The preference for this particular species to crystallize out may have interesting implications for the future use of these ligands with Sm^{II}.

2.2. Crystallographic studies

The structure of **3** is shown in Fig. 1. The structural parameters of **3** (Table 2) are very similar to those for the mono(tetrahydropyran) solvate, $(C_5Me_5)_2Sm(OC_5H_{10})$ (**5**) [7]. The ranges of Sm–C(ring) values in the two complexes are nearly the same, 2.787(5)–2.853(4) Å in **3** and 2.770(9)–2.858(6) Å in **5**, and the Sm–C(ring) averages coincide at 2.816(4) Å. The main difference between the two structures in bond distances is the Sm–O lengths. A 2.569(3) Å Sm–O bond is found in **3** compared to a 2.630(6) Å distance in **5**. This is consistent with the larger size of the pyran ring.

The angular parameters in the two complexes are also similar. The ring centroid–Sm–ring centroid an-

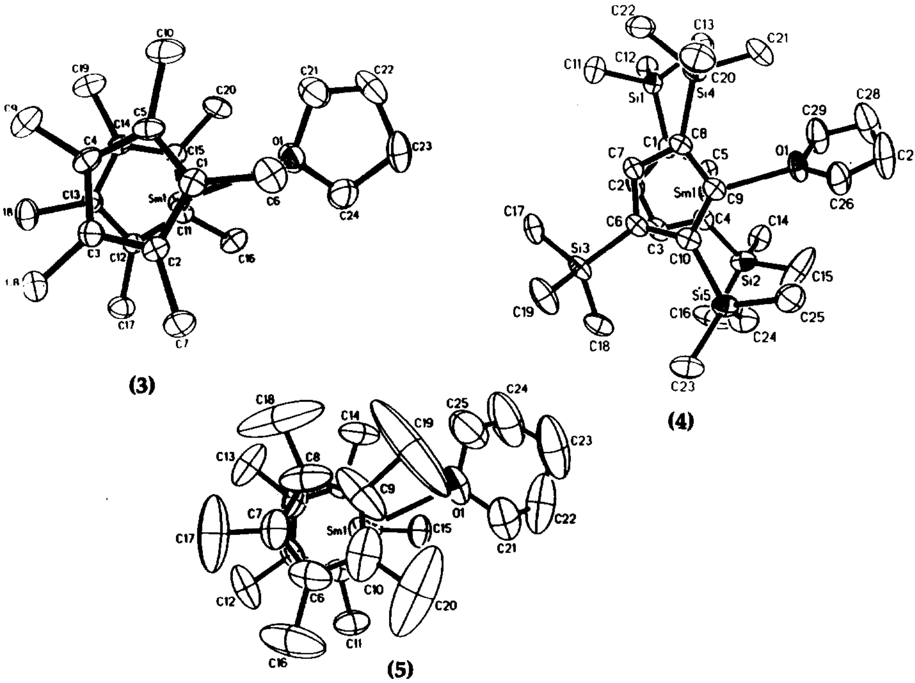

Fig. 2. Top views of $(C_5Me_5)_2Sm(THF)$ (3), $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$ (4), and $(C_5Me_5)_2Sm(OC_5H_{10})$ (5), oriented such that the widest part of the bent metallocene wedge is horizontal in the diagram.

gles in **3** and **5**, are 138.5° and 140.0°. The ring centroid–Sm–O angles of 106.0° and 107.0° in **3** and 107.0° and 107.4° in **5** show that the oxygen is located midway between the two cyclopentadienyl rings. However, in the plane perpendicular to these ring centroid–Sm–O planes, the solvating ether oxygen atom is *not* located symmetrically with respect to the open part of the $(C_5Me_5)_2Sm$ bent metallocene unit. A symmetric position for the oxygen atom would mean that the two ring centroids and the oxygen atom would be rigorously trigonal planar around the samarium and the samarium atom would lie in the trigonal plane. In **3**, the samarium atom lies 0.42 Å out of the plane defined by the two ring centroids and the oxygen donor atom. In **5**, Sm is 0.34 Å out of the analogous plane. Alternatively, this asymmetry can be described by how far the oxygen atom lies out of the plane defined by samarium and the two ring centroids. In **3**, the oxygen is 1.54 Å out of the plane; in **5**, it is 1.33 Å out of the plane. Figure 2 contains top views of **3** and **5** which show this asymmetry.

The trimethylsilyl-substituted complex, **4** (Fig. 3), also has structural parameters (Table 2) similar to those of **3** and **5**, despite the large differences in ring substitution. The tris-substituted ring has a wider range of Sm–C(ring) distances, 2.791(4)–2.872(4) Å, than the di-substituted ring, 2.810(4)–2.849(4) Å, but the Sm–C(ring) averages are the same, 2.825(29) and 2.830(13) Å. The Sm–O distance in **4**, 2.547(3) Å is similar to that in **3** and the (ring centroid)–Sm–(ring centroid) angle, 137.0°, is not unusual.

The Me_3Si groups in **4** are arranged such that the greatest amount of steric bulk is between the THF and the back of the bent metallocene wedge. This leads to near eclipsing of the pairs Si(1) and Si(4) and Si(2) and Si(5) as shown in Fig. 2. As in **3** and **5**, the THF is located midway between the rings with 109.6° and 110.8° ring centroid–Sm–O angles. However, in the plane perpendicular to the centroid–Sm–O planes, the oxygen atom in **4** is not positioned as asymmetrically as

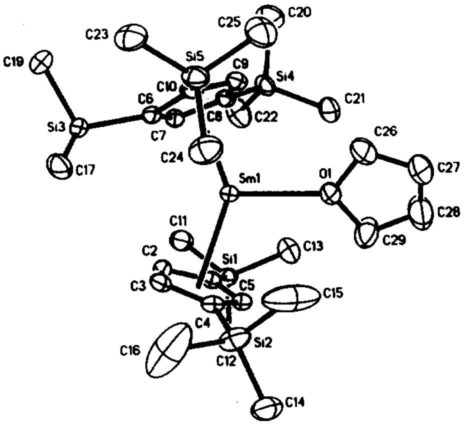

Fig. 3. ORTEP diagram of $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$ (4), with the probability ellipsoids drawn at the 50% level.

TABLE 2. Selected bond distances (Å) and angles (°) of $(C_5Me_5)_2Sm(THF)$ (**3**) and $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$ (**4**)

Complex **3**		Complex **4**	
Cnt(1)–Sm(1)–O(1)	106.0	Cnt(1)–Sm(1)–O(1)	109.6
Cnt(2)–Sm(1)–O(1)	107.0	Cnt(2)–Sm(1)–O(1)	110.8
Cnt(1)–Sm(1)–Cnt(2)	138.5	Cnt(1)–Sm(1)–Cnt(2)	137.0
C(1)–Sm(1)	2.826(5)	C(1)–Sm(1)	2.830(4)
C(2)–Sm(1)	2.853(4)	C(2)–Sm(1)	2.811(4)
C(3)–Sm(1)	2.839(4)	C(3)–Sm(1)	2.826(4)
C(4)–Sm(1)	2.792(5)	C(4)–Sm(1)	2.848(4)
C(5)–Sm(1)	2.787(5)	C(5)–Sm(1)	2.835(4)
C(11)–Sm(1)	2.824(4)	C(6)–Sm(1)	2.790(4)
C(12)–Sm(1)	2.819(4)	C(7)–Sm(1)	2.811(4)
C(13)–Sm(1)	2.804(4)	C(8)–Sm(1)	2.872(4)
C(14)–Sm(1)	2.807(4)	C(9)–Sm(1)	2.842(4)
C(15)–Sm(1)	2.809(4)	C(10)–Sm(1)	2.806(4)
O(1)–Sm(1)	2.569(3)	O(1)–Sm(1)	2.547(3)
Cnt(1)–Sm(1)	2.542	Cnt(1)–Sm(1)	2.559
Cnt(2)–Sm(1)	2.549	Cnt(2)–Sm(1)	2.553

For **3**, Cnt(1) and Cnt(2) are the centroids of the C(1)–C(5) and C(11)–C(15) rings, respectively. For **4** they are the centroids of the C(1)–C(5) and C(6)–C(10) rings.

those in **3** and **5**. The samarium atom lies closer to the plane defined by the two ring centroids and the oxygen (0.23 Å) than in **3** and **5**, *i.e.*, the coordination geometry around the metal is closer to trigonal planar in **4**. The oxygen lies 0.85 Å off the plane defined by samarium and the two ring centroids, which corresponds to an angle of 20° between the Sm–O vector and the samarium centroids plane.

It is interesting to note that calculations by Lauher and Hoffmann [16] on the "mythical d^0 complex Cp_2TiH^+" indicate that an asymmetrical location for the hydrogen ligand would be orbitally optimal. In that study, the energy minimum was found for a structure which had a 65° angle between the Ti–H vector and the plane defined by titanium and the two ring centroids. The only previously reported examples of a d^0 Cp_2ML complex in the literature, $(C_5Me_5)_2ScMe$, has a 0° angle [17].

The analogous angles in complexes **3**, **4** and **5**, which comprise another class of d^0 Cp_2ML complexes, are 37°, 20° and 30°, respectively. It is unusual that the sterically least crowded structure, *i.e.*, the symmetrical structure which has a 0° angle, is not formed. This result, along with the fact that the unsolvated complex $(C_5Me_5)_2Sm$ does not adopt the sterically optimal planar ring structure, may suggest that for divalent lanthanide complexes, steric factors may not be as dominant as they are in trivalent systems [1,18].

3. Conclusion

X-ray crystallographic analysis has fully established the existence of mono-THF solvates of bis(cyclopentadienyl)samarium(II) complexes. The fact that all members of the series $(C_5Me_5)_2Sm(THF)_x$ where $x = 0$, 1, and 2, can be crystallographically characterized demonstrates the flexibility of the $(C_5Me_5)_2Sm$ unit to stabilize Sm^{II} complexes with several sterically different coordination environments. In these complexes and in $(C_5Me_5)_2Sm$(tetrahydropyran), the oxygen donor atom is consistently out of the plane defined by samarium and the two ring centroids although the distance out of the plane is variable. The selective crystallization of $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$ suggests that cyclopentadienyl rings polysubstituted with substituents larger than methyl may be useful in designing specific metallocene complexes of lanthanides containing two cyclopentadienyl rings which have different substituents.

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