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Synthesis and Structure of New Soluble Organosamarium(II) Reagents: (indenyl)$_2$Sm(THF) and (fluorenyl)$_2$Sm(THF)$_2$

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Samarium diiodide reacts with potassium indenide and potassium fluorenide to form new THF-soluble samarium(II) reagents, the bis(indenyl) complex $(C_9H_7)_2Sm(THF)$ (1) and the bis(fluorenyl) complex $(C_{13}H_9)_2Sm(THF)_2$ (2). Crystallographic data for 2 and the trisolvated derivative of 1, namely $(C_9H_7)_2Sm(THF)_3$ (1a), show that they have monometallic bent-metallocene structures analogous to the pentamethylcyclopentadienyl derivative $(C_5Me_5)_2Sm(THF)_2$ (3). 1a crystallizes from THF in space group $C2/c$ with $a = 15.013(7)$ Å, $b = 10.677(4)$ Å, $c = 19.132(17)$ Å, $\beta = 93.87(6)°$, $V = 3059(3)$ Å^3, and $Z = 4$ for $D_{calcd} = 1.34$ Mg/m^3. 2 crystallizes from toluene/THF in space group $P2_1/n$ (C^5_{2h}; No. 14) with $a = 11.810(2)$ Å, $b = 14.153(3)$ Å, $c = 16.001(4)$ Å, $\beta = 97.60(2)°$, $V = 2651.1(9)$ Å^3, and $Z = 4$ for $D_{calcd} = 1.566$ Mg/m^3. Least-squares refinement of the model based on 2953 reflections ($|F_o| > 2.0\sigma(|F_o|)$) converged to a final $R_F = 4.8\%$. The structural data indicate that the bis(indenyl) and bis(fluorenyl) ligand sets provide a more open Sm(II) reaction environment than in 3.

Introduction

The chemistry of samarium(II) is being employed with increasing frequency to effect useful transformations in synthetic organic chemistry,[1-3] and $SmI_2(THF)_2$[4] is currently the most common reagent. Given the demonstrated importance of steric factors in lanthanide chemistry,[5] it is likely that the utility of Sm(II) in organic synthesis could be significantly enhanced by varying the coordination environment around samarium. Hence, utilization of Sm(II) reagents with ligand sets other than "$I_2(THF)_2$" should provide new opportunities for obtaining better selectivity.

Indeed, using pentamethylcyclopentadienyl ligands, arene-soluble Sm(II) complexes such as $(C_5Me_5)_2Sm(THF)_2$[6] and $(C_5Me_5)_2Sm$[7] have been discovered, which can effect unique organic transformations.[5] For example, $(C_5Me_5)_2Sm(THF)_2$ allows the insertion of two CO molecules into the double bond of an olefin to make a bis(enolate)[8] and the formation of a tetracyclic indenoindenediolate moiety from a simple alkyne and CO[9] can also be accomplished with this complex. Neither of these reactions occur with $SmI_2(THF)_2$. However, in contrast to $SmI_2(THF)_2$, the C_5Me_5 Sm(II) complexes are not being broadly examined in organic synthesis.

To provide a wider variety of readily available soluble organometallic Sm(II) reagents, we have investigated the synthesis of indenyl and fluorenyl derivatives of divalent samarium.[10] Indene and fluorene are less expensive than pentamethylcyclopentadiene, but they can still provide a structured organometallic environment in which unique, sterically controlled Sm(II) reactivity could occur. It was uncertain, however, if indenyl and fluorenyl Sm(II) reagents would be soluble enough to be of practical utility. Simple cyclopentadienyl Sm(II) complexes such as $[(C_5H_5)_2Sm(THF)]_n$[11] and $[(C_5H_4Me)_2Sm]_n$[5] are insoluble and hence less useful as reagents.[12]

We report here that soluble organometallic Sm(II) complexes can be obtained with both indenyl and fluorenyl ligands. Moreover, the crystallographically determined structures of these complexes suggest that these compounds could possess distinctive chemistry compared to their C_5Me_5 analogs.

Experimental Section

The reactions described below were conducted under nitrogen using standard Schlenk double-manifold, high-vacuum, or glovebox techniques.

Materials. Tetrahydrofuran (THF) and toluene were distilled from solutions of sodium benzophenone ketyl. THF-d_8 was dried over potassium and vacuum-distilled. Indene (Aldrich) was dried over 3A molecular sieves and degassed before use. Fluorene (Aldrich) was dried under vacuum overnight. Potassium indenide and potassium fluorenide were prepared from KH and indene and fluorene, respectively, in THF. Samarium diiodide was prepared as previously described.[6]

Physical Measurements. ^1H and ^{13}C NMR spectra were obtained on either GN 500-MHz or QE 300-MHz NMR spectrometers. HMQC (heteronuclear multi-quantum correlation) experiments[13] were obtained on an Ω 500-MHz NMR spectrom-

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[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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eter. Chemical shifts were assigned relative to residual protons in THF-d_8. Infrared spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. Magnetic moments were obtained on a QE 300-MHz spectrometer using the Evans method.[14] Complete elemental analyses were obtained from Analytische Laboratorien, Gummersbach, Germany. Complexometric metal analyses were conducted as previously described.[15]

$(C_9H_7)_2Sm(THF)$ (1). Under nitrogen, $SmI_2(THF)_2$ (4.81 g, 8.8 mmol) and KC_9H_7 (2.72 g, 17.6 mmol) were placed in a 250-mL round-bottom flask and stirred in 100 mL of THF. The original purple solution immediately turned cloudy brown. After it was stirred overnight, the solution was centrifuged to yield a white precipitate and a brown solution. The brown solution was decanted from the precipitate and dried by rotary evaporation, yielding black 1 in quantitative yield. ^1H NMR (THF-d_8; saturated, concentration ca. 0.1 M): δ 20.61 ($\nu_{1/2}$ = 200 Hz, 2H, η^5-C_9H_7), 18.9 ($\nu_{1/2}$ = 500 Hz, 1H, η^5-C_9H_7), 9.23 ($\nu_{1/2}$ = 10 Hz, 2H, arene C_9H_7), 8.27 ($\nu_{1/2}$ = 15 Hz, 2H, arene C_9H_7).[16] ^{13}C NMR (THF-d_8): δ 172.1 (arene C_9H_7 by HMQC), 133.4 (arene C_9H_7 by HMQC). Magnetic susceptibility: $\chi_M^{292\ K} = 4.58 \times 10^{-3}$ cgsu, $\mu_{eff}^{292\ K} = 3.3\ \mu_B$. IR (KBr): 3063 w, 2976 m, 2878 m, 1452 m, 1393 w, 1327 s, 1251 m, 1213 m, 1033 s, 919 w, 870 s, 755 vs cm^{-1}. Anal. Calcd for $SmC_{22}H_{22}O$: Sm, 33.21; C, 58.36; H, 4.90. Found: Sm, 33.50; C, 58.08; H, 4.75. Complexometric analysis: found for Sm, 33.4.

X-ray-quality crystals were grown from THF at −35 °C. Although the crystallographic analysis identified the overall structure of the molecule to be that of the trisolvate $(C_9H_7)_2Sm(THF)_3$ (**1a**), detailed bond distance and angle information could not be obtained due to decomposition of the crystal during the X-ray diffraction experiment. Details are given in the supplementary material.[17]

$(C_{13}H_9)_2Sm(THF)_2$ (2). Under nitrogen, $SmI_2(THF)_2$ (5.06 g, 9.2 mmol) and $KC_{13}H_9$ (3.77 g, 18.4 mmol) were placed in a 250-mL round-bottom flask and stirred in 100 mL of THF overnight. The cloudy brown solution was centrifuged to obtain a white precipitate and a brown solution. The brown solution was decanted from the precipitate, and the solvent was removed by rotary evaporation, yielding **2** as a brown powder in quantitative yield. ^1H NMR (THF-d_8; saturated, concentration ca. 0.1 M): δ 13.3 ($\nu_{1/2}$ = 300 Hz, 1H, η^5-$C_{13}H_9$), 9.21 ($\nu_{1/2}$ = 60 Hz, 2H, arene $C_{13}H_9$), 8.54 ($\nu_{1/2}$ = 40 Hz, 2H, arene $C_{13}H_9$), 7.93 ($\nu_{1/2}$ = 30 Hz, 2H, arene $C_{13}H_9$), 7.52 ($\nu_{1/2}$ = 30 Hz, 2H, arene $C_{13}H_9$).[18] ^{13}C NMR (THF-d_8): 127.3, 125.6, 111.3. The HMQC experiment was unsuccessful due to the inherent short relaxation time. Magnetic susceptibility: $\chi_M^{292\ K} = 4.05 \times 10^{-3}$ cgsu, $\mu_{eff}^{292\ K} = 3.1\ \mu_B$. IR (KBr): 3030 m, 2976 m, 2878 m, 1578 m, 1442 s, 1322 s, 1218 m, 1197 m, 1028 s, 870 m, 750 vs, 690 w, 570 w cm^{-1}. Anal. Calcd for $C_{34}H_{34}O_2Sm$: Sm, 24.06; C, 65.34; H, 5.48. Found: Sm, 24.35; C, 65.06; H, 5.29. Complexometric analysis: found for Sm, 23.9. X-ray-quality crystals of **2** were grown by slow evaporation from a toluene/THF solution at ambient temperature in the glovebox.

X-ray Data Collection, Structure Determination, and Refinement for $(C_{13}H_9)_2Sm(THF)_2$ (2). Under nitrogen, a brown crystal of approximate dimensions 0.10 × 0.20 × 0.20 mm was oil-mounted[19] onto a glass fiber and transferred to the nitrogen stream of a Siemens P3 diffractometer (R3m/V system) equipped with a modified LT-2 low-temperature system. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (173 K) intensity data were carried out using standard techniques similar to those of Churchill.[20] Details appear in Table 1.

Table 1. Crystallographic Data for $(C_{13}H_9)_2Sm(THF)_2$ (2)[a]

formula	$C_{34}H_{34}O_2Sm$
mol wt	625.0
cryst syst	monoclinic
space group	$P2_1/n$ (C^5_{2h}; No. 14)
cell constants	
a, Å	11.810(2)
b, Å	14.153(3)
c, Å	16.001(4)
β, deg	97.60(2)
cell vol, Å^3	2651.1(9)
Z	4
D_{calcd}, Mg m^{-3}	1.566
temp, K	158
μ_{calcd}, mm^{-1}	2.250
transmissn coeff, min/max	0.5556/0.6536
R_F, %	4.8
R_{wF}, %	4.9
GOF	1.25

[a] Mo Kα radiation; λ = 0.710 730 Å.

All 3857 data were corrected for absorption and for Lorentz and polarization effects, merged to yield a unique data set, and placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences for $0k0$ (where $k = 2n + 1$) and $h0l$ (for $h + l = 2n + 1$). The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (C^5_{2h}; No. 14), is therefore uniquely defined. The Z value is 4, and D_{calc} = 1.566 g/cm^3.

The crystallographic calculations were carried out using either a locally modified version of the UCLA Crystallographic Computing Package[21] or the SHELXTL PLUS program set.[22] The analytical scattering factors for neutral atoms were used throughout the analysis;[23] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0006(|F_o|)^2$.

The structure was solved by direct methods 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) = 0.08 Å^2. Refinement of positional and thermal parameters led to convergence with R_F = 4.8%, R_{wF} = 4.9%, and GOF = 1.25 for 334 variables refined against those 2953 data with $|F_o| > 2.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features; ρ(max) = 0.76 e Å^{-3}.

Results and Discussion

Synthesis. Indenyl and fluorenyl derivatives of Sm(II) can be readily made from $SmI_2(THF)_2$ and the potassium salts of indene and fluorene according to eqs 1 and 2, which parallel the synthesis of $(C_5Me_5)_2Sm(THF)_2$.[24] $(C_9H_7)_2Sm(THF)$ (**1**) was first prepared by metal vapor methods (eq 3) to ensure the formation of an iodide-

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[16] For lower concentrations, the peak furthest downfield has been observed as low as δ 21.3 ppm.

[17] $(C_9H_7)_2Sm(THF)_3$ (**1a**) crystallizes from THF in space group $C2/c$ with a = 15.013(7) Å, b = 10.677(4) Å, c = 19.132(17) Å, β = 93.87(6)°, V = 3059(3) Å^3, and Z = 4 for D_{calcd} = 1.34 Mg/m^3. See supplementary material for details.

[18] For lower concentrations, the peak furthest downfield can be found anywhere between δ 13.0 and 17.0 ppm.

[19] The crystal was immersed in a lube-oil additive which allows for manipulation on the bench top and prevents decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting pin. Further details appear in: Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; ACS Symposium Series 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987.

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$$SmI_2(THF)_2 + 2KC_9H_7 \rightarrow \underset{\textbf{1}}{(C_9H_7)_2Sm(THF)} + 2KI \quad (1)$$

$$SmI_2(THF)_2 + 2KC_{13}H_9 \rightarrow \underset{\textbf{2}}{(C_{13}H_9)_2Sm(THF)_2} + 2KI \quad (2)$$

free product.[25] It was subsequently shown that iodide-

$$Sm + 2C_9H_8 \xrightarrow{THF} \rightarrow (C_9H_7)_2Sm(THF) \quad (3)$$

free products can be readily obtained by solution methods and the solution syntheses in eqs 1 and 2 are the most convenient routes to these Sm(II) reagents.

Hence, **1** and **2** can be prepared in one step from commercially available $SmI_2(THF)_2$.[27] Solutions of **1** and **2** can be readily handled using a nitrogen double manifold and do not require a glovebox for either preparation or utilization. Both $(C_9H_7)_2Sm(THF)$ (**1**) and $(C_{13}H_9)_2Sm(THF)_2$ (**2**) are soluble in THF, and **2** is slightly soluble in toluene.

Structural Studies. Attempts to obtain crystallographic data for **1** were frustrated by the fact that its crystals readily redissolved upon warming to room temperature. When crystallographic data were finally obtained, a trisolvated structure, $(C_9H_7)_2Sm(THF)_3$ (**1a**), was found (Figure 1). In contrast, analytically pure, bulk samples are typically isolated as the monosolvated $(C_9H_7)_2Sm(THF)$[28] (**1**), which has a direct analog in $(C_5Me_5)_2Sm(THF)$.[29] Although the quality of the structural determination on **1a** was sufficient to unequivocally define the overall connectivity of the atoms, the data were not good enough to allow a detailed discussion of bond distances and angles.[17]

Since $(C_5Me_5)_2Sm(THF)_2$ readily crystallizes as a disolvate rather than a trisolvate, the two indenyl ligands in **1a** apparently can provide a more open Sm(II) coordination environment than two C_5Me_5 ligands. Previous studies have shown that the $(C_5Me_5)_2Sm$ unit is sterically flexible enough to form structurally characterizable complexes with coordination numbers from 6 to 10.[30,31] For example, divalent $(C_5Me_5)_2Sm$ crystallizes as unsolvated $(C_5Me_5)_2Sm$,[7] monosolvated $(C_5Me_5)_2Sm(THF)$,[29] *and* disolvated $(C_5Me_5)_2Sm(THF)_2$.[6] However, the preference for the $(C_5Me_5)_2Sm$ unit is coordination number 8.[31] Nine-coordination appears to be more accessible with the divalent bis(indenyl) ligand system.

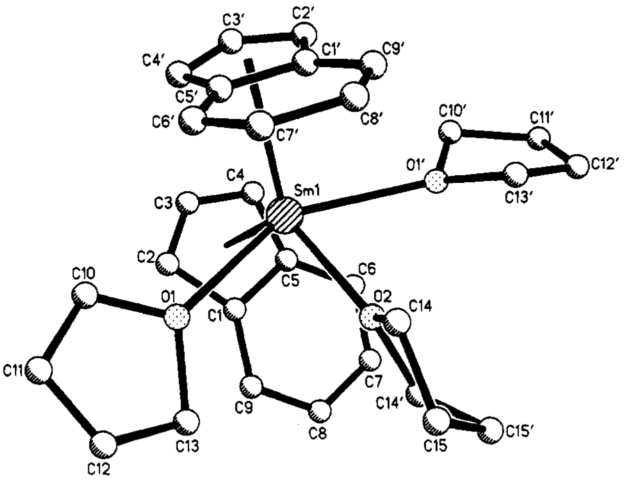

Figure 1. Ball and stick plot of crystallographically characterized $(C_9H_7)_2Sm(THF)_3$ (**1a**).

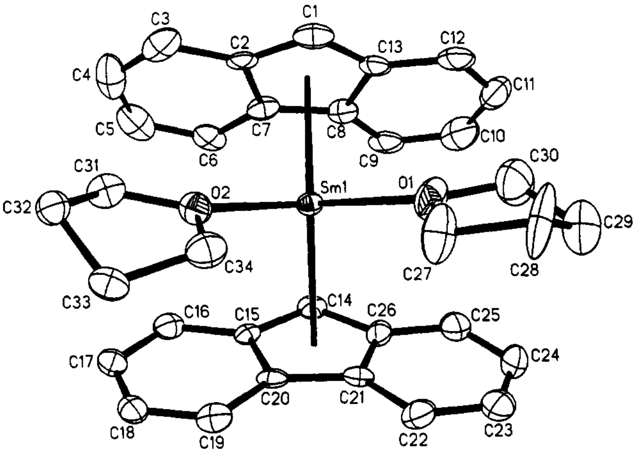

Figure 2. Thermal ellipsoid plot of $(C_{13}H_9)_2Sm(THF)_2$ (**2**), shown at the 50% probability level.

The fluorenyl complex $(C_{13}H_9)_2Sm(THF)_2$ (**2**) crystallizes as an eight-coordinate disolvated complex (Figure 2) analogous to $(C_5Me_5)_2Sm(THF)_2$ (**3**). Good metrical data are available on **2** (Table 2) for comparison with **3**.[6] Although the 2.90(7) Å average Sm–C(ring) distance in **2** is not very different from the 2.86(3) Å average in **3**, the 2.759(7)–3.004(7) Å range of Sm–C(ring) distances is substantially larger than the typical range for C_5Me_5 complexes. For example, the range for **3** is only 2.83(1)–2.899(9) Å. Interestingly, the extremes of the range for **2** are found in a single ring: C(14) is closest to samarium and C(21) is farthest away. Although the analogous carbon atoms in the other ring have neither the longest nor the shortest Sm–C bond distance, the averages of each ring are the same.

Comparison of the 2.759(7) Å Sm–C(14) distance to the adjacent Sm–C distances in this ring (2.839(7) Å for Sm–C(15) and 2.899(8) Å for Sm–C(26)) and the two nonadjacent Sm–C distances (2.986(7) Å for Sm–C(20) and 3.004(7) Å for Sm–C(21)) suggests that this ring is beginning to move toward an η^3-fluorenyl orientation.[32] Distortions toward η^3 coordination have also been observed

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[25] A freshly polished ingot of samarium metal (3.193 g) was placed on an alumdum-coated tungsten coil basket in a resistively heated metal vapor reactor.[26] The reactor was evacuated for 1–2 h at 10^{-5} Torr. Indene was condensed onto the walls of the reactor at 77 K, and the current in the electrodes was gradually increased until the metal vaporized. Cocondensation of indene and samarium was continued for 30–60 min. The current was turned off, the mixture was warmed to room temperature, and the excess ligand was removed *in vacuo*. The reaction vessel was transferred to a glovebox, where the purple residue was extracted with hexanes, toluene, and THF. The portion of the samarium ingot which did not vaporize was recovered (1.537 g, 52% vaporized). Removal of solvent from the purple THF extract gave $(C_9H_7)_2Sm(THF)$ (**1**; 0.311 g, 6%), identified by NMR and complexometric titration. Anal. Calcd for $SmC_{22}H_{22}O$: Sm, 33.21. Found: Sm, 34.0.

[26] Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112–119.

[27] Samarium(II) iodide is available from Aldrich as a 0.1 M solution in THF.

[28] The degree of solvation of the bulk samples depends on the duration of drying on the rotary evaporator.

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[32] We thank a reviewer for pointing this out.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(C_{13}H_9)_2Sm(THF)_2$ (2)

Sm(1)–O(1)	2.560(6)	Sm(1)–O(2)	2.540(6)
Sm(1)–C(1)	2.855(8)	Sm(1)–C(2)	2.921(8)
Sm(1)–C(7)	2.906(8)	Sm(1)–C(8)	2.914(8)
Sm(1)–C(13)	2.913(8)	Sm(1)–C(14)	2.759(7)
Sm(1)–C(15)	2.839(7)	Sm(1)–C(20)	2.986(7)
Sm(1)–C(21)	3.004(7)	Sm(1)–C(26)	2.899(8)
Sm(1)–Cnt(1)	2.633	Sm(1)–Cnt(2)	2.629
O(1)–Sm(1)–Cnt(1)	110.0	O(1)–Sm(1)–Cnt(2)	105.0
O(2)–Sm(1)–Cnt(1)	113.0	O(2)–Sm(1)–Cnt(2)	104.7
Cnt(1)–Sm(1)–Cnt(2)	126.4	O(1)–Sm(1)–O(2)	92.3(2)
O(1)–Sm(1)–C(1)	91.9(2)	O(2)–Sm(1)–C(1)	97.3(2)
O(1)–Sm(1)–C(2)	119.8(2)	O(2)–Sm(1)–C(2)	89.2(2)
O(1)–Sm(1)–C(7)	134.2(2)	O(2)–Sm(1)–C(7)	110.3(2)
O(1)–Sm(1)–C(8)	111.1(2)	O(2)–Sm(1)–C(8)	136.3(2)
O(1)–Sm(1)–C(13)	87.6(2)	O(2)–Sm(1)–C(13)	125.7(2)
O(1)–Sm(1)–C(14)	120.5(2)	O(2)–Sm(1)–C(14)	121.1(2)
O(1)–Sm(1)–C(15)	128.1(2)	O(2)–Sm(1)–C(15)	91.6(2)
O(1)–Sm(1)–C(20)	101.7(2)	O(2)–Sm(1)–C(20)	80.9(2)
O(1)–Sm(1)–C(21)	81.6(2)	O(2)–Sm(1)–C(21)	100.8(2)
O(1)–Sm(1)–C(26)	91.5(2)	O(2)–Sm(1)–C(26)	126.8(2)

in lithium[33] and barium[34] fluorenyl complexes. However, the difference in the Sm–C distances in 2 is not as great as the difference in $(C_{13}H_9)_2Ba(NH_3)_4$,[34] which has Ba–C distances of 3.05, 3.10, 3.30, 3.44, and 3.57 Å in one of the rings of the two independent molecules in the unit cell of the barium fluorenyl complex. In that crystal structure, three of the four rings are symmetrically bound with Ba–C bonds in the range 3.071–3.295 Å. The barium and lithium structures, fluorenylsodium structures,[35] and the structure of 2 suggest that the η^5-fluorenyl and η^3-fluorenyl orientations are similar in energy in these complexes.

Several bond distances and angles suggest that the effective steric bulk of the fluorenyl ligand in 2 is less than that provided by the C_5Me_5 ligand. The 126.4° (C_5 ring centroid)–Sm–(C_5 ring centroid) angle in 2 is significantly smaller than the 136.8° angle in $(C_5Me_5)_2Sm(THF)_2$ and is more in the range of angles found for lanthanide compounds containing two C_5H_5 rings.[36] Consistent with the smaller steric demands of $C_{13}H_9$ vs C_5Me_5, the 92.3(2)° O–Sm–O angle in 2 is larger than the analogous 82.7(4)° angle in $(C_5Me_5)_2Sm(THF)_2$ and the 2.550(6) Å Sm–O(THF) distance in 2 is shorter than the corresponding 2.63(1) Å distance in $(C_5Me_5)_2Sm(THF)_2$.

The side view of 2 (Figure 3) shows another interesting aspect of this bis(fluorenyl) system: one annulated benzene ring is oriented forward toward the open part of the bent metallocene, but the other ring is pointing in the opposite direction. Hence, if the two unsubstituted ring carbons are placed "trans" to each other, steric interaction can be minimized and a less crowded coordination environment is available. Examination of a side view of **1a** (Figure 4) shows that when the coordinating cyclopentadienide moiety has only one attached benzene ring (i.e. with an indenyl ligand system), both arene substituents of the bent metallocene point toward the open part of the compound. Consequently, an even less crowded environment around the samarium results and three THF molecules can bind to the metal, compared to two in 3.

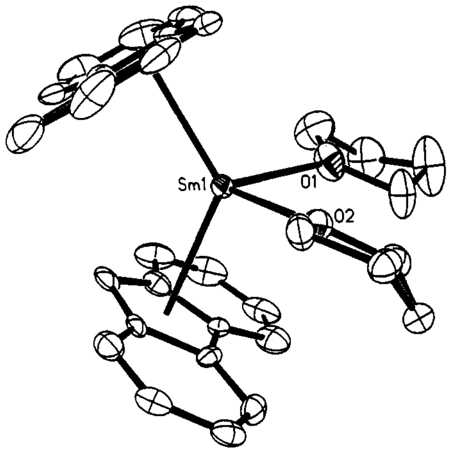

Figure 3. Side view of 2.

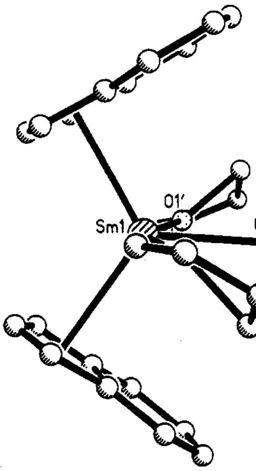

Figure 4. Side view of **1a**.

Conclusion

New soluble organometallic Sm(II) reagents have been prepared in one step from $SmI_2(THF)_2$ using indenyl and fluorenyl ligands. Both $(C_9H_7)_2Sm(THF)$ (1) and $(C_{13}H_9)_2Sm(THF)_2$ (2) have a more sterically defined coordination environment than $SmI_2(THF)_2$. These complexes also appear to have a sterically less crowded environment around the Sm(II) center compared to $(C_5Me_5)_2Sm(THF)_2$. The steric and electronic effects of the ligands on Sm(II) reactivity are under investigation.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for **1a** and **2** (21 pages). Ordering information is given on any current masthead page.

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