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Stereochemical Variability in Samarium(II) Reagents Using Carbazole as an Alternative to Iodide: Synthesis and Structure of *cis*-$(C_{12}H_8N)_2Sm(THF)_4$ and *trans*-$(C_{12}H_8N)_2Sm(N\text{-MeIm})_4$

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$SmI_2(THF)_2$ reacts with potassium carbazole ($KC_{12}H_8N$, KCbz) in a 1:2 ratio at room temperature in THF to form $(C_{12}H_8N)_2Sm(THF)_4$, **1**. **1** reacts with *N*-methylimidazole (*N*-MeIm) in a 1:4 ratio at room temperature in THF to form $(C_{12}H_8N)_2Sm(N\text{-MeIm})_4$, **2**. X-ray crystallographic studies on **1** and **2** show that both have distorted octahedral structures but that $(Cbz)_2Sm(THF)_4$ crystallizes as the *cis* isomer (N–Sm–N: 109.8(1)°) and $(Cbz)_2Sm(N\text{-MeIm})_4$ crystallizes as the *trans* isomer (N(Cbz)–Sm–N(Cbz)): 151.7(3) and 159.2(5)°). **1** crystallizes from hot THF in space group $P\bar{1}$ [C_i^1; No. 2] with unit cell parameters at 173 K of $a = 9.8862(9)$ Å, $b = 10.3285(7)$ Å, $c = 18.3670(16)$ Å, $\alpha = 100.368(6)°$, $\beta = 98.522(7)°$, $\gamma = 102.898(6)°$, $V = 1763.2(3)$ Å^3, and $Z = 2$ with $D_{calcd} = 1.45$ g cm^{-3}. Least-squares refinement of the model based on 7577 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 3.0\%$. **2** crystallized from THF/benzene in space group $P\bar{3}$ with unit cell parameters at 163 K of $a = 26.759(2)$ Å, $c = 27.796(4)$ Å, $V = 17\,236(3)$ Å^3, and $Z = 18$ with $D_{calcd} = 1.443$ g cm^{-3}. Least-squares refinement of the model based on 5505 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 6.5\%$. The average Sm–N(Cbz) distances in **1** and **2** are 2.565(13) and 2.591(3) Å, respectively. The average Sm–O(THF) distance in **1** is 2.582(7) Å; the average Sm–N(*N*-MeIm) distance in **2** is 2.685(14) Å.

Introduction

In recent years, Sm(II) has become a commonly used one electron reducing agent in organic synthesis.[1–3] Although Sm(II) has been used in a wide variety of applications, the reagent employed is almost exclusively the diiodide, $SmI_2(THF)_2$,[1] which is easily prepared from the metal and 1,2-diiodoethane. Since a solvated metal halide such as $SmI_2(THF)_2$ has one of the more primitive ligand sets in metal complex chemistry, it is likely that more sophisticated synthetic organic Sm(II) chemistry could be achieved with Sm(II) reagents containing ligands which could exert more regio- and stereochemical control than is possible with iodides. To be widely utilized, such new Sm(II) reagents must be inexpensive and easily prepared.

As part of an effort to expand the diversity of readily available Sm(II) reagents, we have examined the utility of the anion derived by deprotonation of carbazole, $C_{12}H_8N^-$, as a ligand for Sm(II). This "Cbz" anion is an interesting ligand since it can attach to a metal by mono-, tri-, or pentahapto coordination modes.[4–6] Indeed, the ligand recently has been shown to adopt both η^1 and η^3 coordination to cesium in a single complex.[5] We report here the synthesis of two new Sm(II) reagents involving the carbazole anion which can be obtained in one step in high yield from $SmI_2(THF)_2$. Two different stereoisomers are observed in the solid state depending on the coordinating solvent present.

Experimental Section

Solvents were purified and measurements were made as previously described.[7] UV–vis spectra were recorded on a Shimadzu UV 160U instrument. Carbazole (Aldrich) was dried under high vacuum and treated with KH in THF to form $KC_{12}H_8N$.[8] $SmI_2(THF)_2$ was prepared as previously described.[9] Redistilled *N*-methylimidazole was obtained from Aldrich.

$(C_{12}H_8N)_2Sm(THF)_4$, 1. $KC_{12}H_8N$ (374 mg, 1.82 mmol) was added to a dark blue solution of $SmI_2(THF)_2$ (500 mg, 0.91 mmol) in 50 mL of THF under nitrogen and immediately gave a black suspension. After 4 h, the reaction mixture was centrifuged and the supernatant was discarded. **1** was separated from the less soluble KI by repeated extraction of the precipitate with hot THF. Removal of THF from the extracts gave **1** as a dark blue powder (561 mg, 80%). ^1H NMR (THF-d_8, 300 MHz, 60 °C): δ 11.34 (br, $\Delta\nu_{1/2}$ = 150 Hz, 4H), 7.85 (s, 4H), 6.15 (s, 4H), 4.79 (br, $\Delta\nu_{1/2}$ = 120 Hz, 4H). Anal. Calcd for $C_{40}H_{48}N_2O_4Sm$: C, 62.30; H, 6.27; N, 3.63; Sm, 19.50. Found: C, 62.03; H, 6.07; N, 3.64; Sm, 19.75. IR (Nujol): 3043 (w), 1581 (w), 1439 (m), 1342 (w), 1327 (m), 1288 (m), 1269 (m), 1227 (s), 1146 (m), 1119 (w), 1030 (s), 995 (w), 918 (w), 879 (m), 849 (m), 760 (m), 725 (s) cm^{-1}. Crystals were obtained by slowly cooling a saturated solution of **1** in THF at 60–25 °C.

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(1) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.

(2) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Vol. 6, Chapter 50. Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573–6614.

(3) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29–88.

(4) Hacker, R.; Kaufmann, E.; Schleyer, P. v. R.; Mahdi, W.; Dietrich, H. *Chem. Ber.* **1987**, *120*, 1533–1538.

(5) Gregory, K.; Bremer, M.; Schleyer, P. v. R.; Klusener, P. A. A.; Brandsma, L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224–1226.

(6) Mösges, G.; Hampel, F.; Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 10880–10889.

(7) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

(8) Pi, R.; Friedl, T.; Schleyer, P. v. R. *J. Org. Chem.* **1987**, *52*, 4299–4303.

(9) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

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Table 1. Experimental X-ray Data for $(Cbz)_2Sm(THF)_4$, 1, and $(Cbz)_2Sm(N\text{-}MeIm)_4$, 2

	1	**2**
formula	$C_{40}H_{48}N_2O_4Sm$	$C_{40}H_{40}N_6Sm\cdot{}^1/_3(C_4H_8O)$
fw	771.2	832.2
temp (K)	173	163
space group	$P\bar{1}$	$P\bar{3}$
a (Å)	9.8862(9)	26.759(2)
b (Å)	10.3285(7)	
c (Å)	18.3670(16)	27.796(4)
α (deg)	100.368(6)	
β (deg)	98.522(7)	
γ (deg)	102.898(6)	
V (Å^3)	1763.2(3)	17 236(3)
Z	2	18
ρ_{calc} (g/cm^3)	1.45	1.443
λ(Mo Kα)	0.710 730	0.710 730
μ (mm^{-1})	1.711	1.58
R_F (%)	3.0	6.4
R_{wF} (%)	3.8	7.6

$(C_{12}H_8N)_2Sm(N\text{-}MeIm)_4$, 2. Addition of N-MeIm (0.21 mL, 2.60 mmol) to a dark blue slurry of 1 (500 mg, 0.65 mmol) in 50 mL of THF under nitrogen immediately gave a dark green solution. After 20 min, the solvent was removed. The residue was washed with toluene and dried under vacuum to give 2 as a dark green powder (442 mg, 90%). ^1H NMR (THF-d_8, 300 MHz, 25 °C): δ 13.55 (br, $\Delta\nu_{1/2}$ = 60 Hz, 4H), 8.15 (s, 4H), 7.46 (s, 4H), 6.15 (s, 4H), 5.69 (s, 4H), 3.96 (s, 4H), 3.81 (s, 4H), 3.58 (s, 12H, CH_3). ^{13}C NMR (THF-d_8, 300 MHz, 25 °C): δ 174.8, 162.8, 159.5, 131.5, 114.2, 111.9, 111.4, 30.9 (CH_3). Anal. Calcd for $C_{40}H_{40}N_6Sm$: C, 59.22; H, 4.97; N, 17.27; Sm, 18.54. Found: C, 59.05; H, 5.11; N, 17.17; Sm, 18.40. IR (Nujol): 3363 (m), 3113 (w), 1613 (m), 1602 (m), 1579 (w), 1527 (m), 1511 (w), 1327 (m), 1290 (m), 1275 (m), 1232 (s), 1143 (w), 1106 (m), 1082 (m), 994 (w), 921 (s), 887 (m), 850 (w), 827 (m), 763 (s), 755 (m), 731 (s), 661 (s), 617 (m) cm^{-1}. UV–vis (THF, λ_{max}, nm (ϵ)): 324 (6500), 293 (30 000), 236 (44 000). Crystals were obtained by diffusion of benzene into a THF solution of 2.

X-ray Data Collection, Structure Determination, and Refinement for $(C_{12}H_8N)_2Sm(THF)_4$, 1. Under nitrogen, a dark purple crystal of approximate dimensions 0.20 × 0.33 × 0.43 mm was immersed in Paratone-D oil.[10] The oil-coated crystal was then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Siemens $P2_1$ diffractometer which is equipped with a modified LT-2 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques simlar to those of Churchill.[11] Low-temperature (173 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation under the conditions given in Table 1.

All 8632 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P\bar{1}$ [C_1^1; No. 2] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[12] or the SHELXTL PLUS program set.[13] The analytical scattering factors for neutral atoms were used throughout the analysis;[14a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[14b] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0002(|F_o|)^2$.

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) = 0.08 Å^2. Refinement of the model led to convergence with R_F = 3.0%, R_{wF} = 3.8%, and GOF = 1.78 for 424 variables refined against those 7577 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 1.10 e Å^{-3}.

X-ray Data Collection, Structure Determination, and Refinement for $(C_{12}H_8N)_2Sm(N\text{-}MeIm)_4$, 2. Under nitrogen, a green crystal of approximate dimensions 0.32 × 0.43 × 0.43 mm was handled as described for 1. Intensity data were collected at 163 K. Details appear in Table 1.

All 10 668 data were corrected for absorption and for Lorentz and polarization effects, merged to yield a unique data set (R_{int} = 2.1%), and placed on an approximately absolute scale. Diffraction symmetry indicated a rhombohedral crystal system with systematic absences for hkl where $-h + k + l = 3n+1$. The two possible space groups are the noncentrosymmetric $R3$ or the centrosymmetric $P\bar{3}$. The latter was chosen and determined to be correct by successful solution and refinement of the structure.

All crystallographic calculations were carried out as described for 1. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0008(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. There are two disordered ligands and one disordered solvent molecule present. The disordered ligands (Cbz and N-MeIm) each have two orientations in approximately a 60:40 ratio. Site occupancy factors were fixed at 0.60 for the "A" orientations and 0.40 for the "B" orientations. The THF solvent molecule is located about a 3-fold rotation axis ($^1/_3$, $^2/_3$, z). Three atoms were included to model the disorder with site occupancy factors of $^1/_3$ for O(1) and $^2/_3$ for C(41) and C(42). Hydrogen atoms (except those associated with disordered 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 = 6.4%, R_{wF} = 7.6%, and GOF = 2.11 for 298 variables refined against those 5505 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 1.30 e Å^{-3}.

Results and Discussion

Synthesis. $SmI_2(THF)_2$ reacts in THF with 2 equiv of $KC_{12}H_8N$ to form the new samarium(II) complex $(C_{12}H_8N)_2Sm(THF)_4$, 1, in high yield, eq 1. The successful

$$SmI_2(THF)_2 + 2KC_{12}H_8N \rightarrow \underset{1}{(C_{12}H_8N)_2Sm(THF)_4} + 2KI \quad (1)$$

synthesis was similar to the reaction of $SmI_2(THF)_2$ with $NaN(SiMe_3)_2$ which forms $[(Me_3Si)_2N]_2Sm(THF)_2$,[15] and the composition of 1 mimics (2-phenylindol-1-yl)$_2$Sm(THF)$_4$[16] and $(Cbz)_2Yb(THF)_4$ and $(Cbz)_2Eu(THF)_4$, which were obtained from the metal bis(pentafluorophenyl) complexes.[17,18]

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[10] Paratone-D oil is an Exxon lube oil additive.

[11] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16* 265–271.

[12] *UCLA Crystallographic Computing Package*; University of California, Los Angeles, 1981. C. Strouse, personal communication.

[13] Sheldrick, G. M. Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

[14] *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

[15] Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575–579.

[16] Deacon, G. B.; Forsyth, C. M. *Inorg. Chim. Acta* **1988**, *154*, 121–122.

[17] Deacon, G. B.; Forsyth, C. M.; Newham, R. H. *Polyhedron* **1987**, *6* 1143–1145.

[18] Deacon, G. B.; Forsyth, C. M.; Gatehouse, B. M.; White, P. A. *Aust. J. Chem.* **1990**, *43*, 795–806.

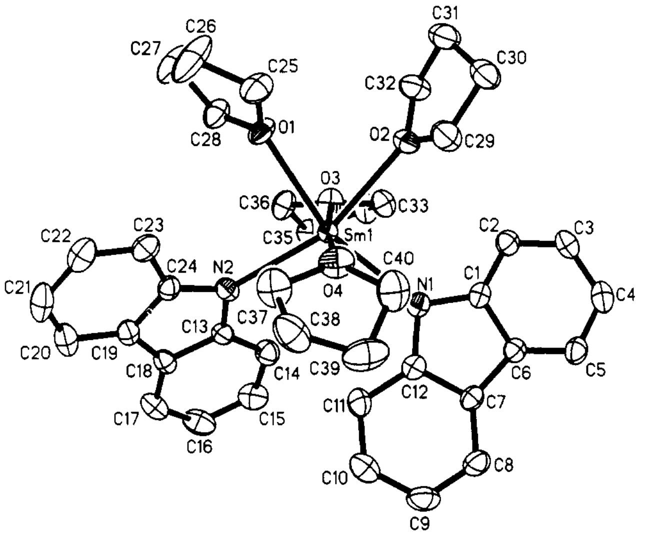

Figure 1. Thermal ellipsoid plot of $(C_{12}H_8N)_2Sm(THF)_4$, **1**, drawn at the 50% probability level.

The intense dark blue color of $(Cbz)_2Sm(THF)_4$ is similar to that of $SmI_2(THF)_2$. The complex was characterized by complete elemental analysis and an X-ray crystallographic study (Figure 1) as described below. **1** is not as soluble in THF as $SmI_2(THF)_2$ and can be readily separated from the potassium iodide byproduct by extraction using hot THF. The lower solubility of **1** compared to $SmI_2(THF)_2$ provides an opportunity to control Sm(II) reductions by controlling the rate of dissolution of $(Cbz)_2Sm(THF)_4$ using variable reaction temperatures. Kagan has shown that the insoluble Sm(II) compounds $(C_5H_5)_2Sm$[19] and $SmBr_2$[20] can be useful in special applications.

The THF of solvation in **1** can be displaced by the strong donor ligand *N*-methylimidazole (*N*-MeIm)[21,22] to form the tetrasolvated adduct $(Cbz)_2Sm(N\text{-MeIm})_4$, **2**, eq 2. **2**

$$\underset{\mathbf{1}}{(C_{12}H_8N)_2Sm(THF)_4} + 4N\text{-MeIm} \rightarrow \underset{\mathbf{2}}{(C_{12}H_8N)_2Sm(N\text{-MeIm})_4} + 4THF \quad (2)$$

was also characterized by elemental analysis and identified by X-ray crystallography, Figure 2. Complex **2**, like **1** and $SmI_2(THF)_2$, is also intensely colored, but in this case it is green. **2** is soluble up to 0.1 M in THF, which is the concentration of the commerically available $SmI_2(THF)_2$ in THF solution. All eight unique types of protons are detected in the ^1H NMR spectrum of **2** despite the presence of paramagnetic Sm(II).[23]

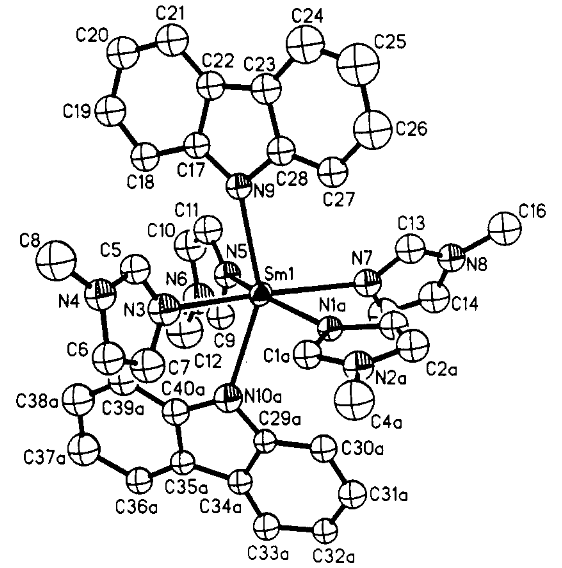

Figure 2. Thermal ellipsoid plot of $(C_{12}H_8N)_2Sm(N\text{-MeIm})_4$, **2**, drawn at the 50% probability level.

Structure. Both **1** and **2** crystallize as distorted octahedra: $(Cbz)_2Sm(THF)_4$, **1**, has the cis configuration shown in Figure 1, whereas $(Cbz)_2Sm(N\text{-MeIm})_4$, **2**, is trans, Figure 2. The existence of cis and trans octahedral Sm(II) isomers is rare due to the dearth of structural data on this class and the fact that this metal frequently adopts nonoctahedral coordination geometries. However, cis and trans isomers have been observed in the *eight*-coordinate diglyme adducts of samarium diiodide, $SmI_2[O(CH_2CH_2OMe)_2]_2$.[24] In that case, the trans isomer was isolated by direct addition of diglyme to SmI_2 in THF[24] and the cis isomer was isolated as a minor byproduct of a SmI_2/$KOCMe_3$ reaction.[25] **1** is isostructural with $(Cbz)_2Eu(THF)_4$ which was structurally characterized by Deacon et al. at 20 °C.[18]

Table 2 shows the most significant metrical parameters for **1** and **2**. The deviation from octahedral geometry is most readily seen by examing the interligand angles. For **1**, the three (ligand)–Sm–(trans ligand) angles are 162.4(1), 161.2(1), and 174.4(1)° and the (ligand)–Sm–(cis ligand) angles range from 73.8(1) to 109.8(1)°. The largest of the latter angles involves the unique N(CBz)–Sm–N(Cbz) angle in **1**. The angle between the average planes of the two carbazole ligands is 55.9°, and this undoubtedly leads to the large interligand angle. Excluding the N(Cbz)–Sm–N(Cbz) angle, the other interligand angles for the cis ligands average to 88(1)°.

The crystal structure of complex **2** has disorder in the carbazole ligand containing N(10) and the *N*-MeIm ligand containing N(1), which leads to the additional bond distance and angle values in Table 2. The range of (ligand)–Sm–(trans ligand) angles in **2**, 151.7(3)–166.4(3)°, is larger than that in **1** and the range of (ligand)–Sm–(cis ligand) angles, 75.9(4)–108.5(2)°, is similar. Again, the angles which differ most from those in a regular octahedron are the ones involving the two Cbz ligands, namely, the 151.7(3) and 159.2(5)° N(Cbz)–Sm–N(Cbz) angles. The angles between the average planes of the two carbazole ligands are 19.8 and 24.7°. The *N*-MeIm ligands

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[19] Collin, J.; Namy, J.-L., Dallemer, F.; Kagan, H. B. *J. Org. Chem.* **1991**, *56*, 3118–3122. Collin, J.; Namy, J.-L.; Bied, C.; Kagan, H. B. *Inorg. Chim. Acta* **1987**, *140*, 29–30. Collin, J.; Namy, J.-L.; Zhang, J.; Kagan, H. B. *J. Organomet. Chem.* **1987**, *328*, 81–86. Kagan, H. B.; Collin, J.; Namy, J.-L.; Bied, C.; Dallemer, F.; Lebrun, A. *J. Alloys Compd.* **1993**, *192*, 191–196.

[20] Lebrun, A.; Namy, J.-L.; Kagan, H. B. *Tetrahedron Lett.* **1993**, *34*, 2311–2314.

[21] Dev, S.; Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6385–6386. Dev, S.; Ramli, E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 2514–2519. Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043–4044. Rauchfuss, T. B.; Dev, S.; Wilson, S. R. *Inorg. Chem.* **1992**, *31*, 154–156. Wozniak, M. E.; Sen, A.; Rheingold, A. L. *Chem. Mater.* **1992**, *4*, 753–755.

[22] Evans, W. J.; Rabe, G. W.; Ziller, J. W. Submitted for publication.

[23] Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299–306.

[24] Chebolu, V.; Whittle, R. R.; Sen, A. *Inorg. Chem.* **1985**, *24*, 3082–3085.

[25] Sen, A.; Chebolu, V.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1821–1823.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

1		2	
Sm(1)-N(1)	2.547(3)	Sm(1)-N(1A)	2.694(14)
Sm(1)-N(2)	2.583(3)	Sm(1)-N(1B)	2.724(22)
Sm(1)-O(1)	2.584(3)	Sm(1)-N(3)	2.631(8)
Sm(1)-O(2)	2.602(3)	Sm(1)-N(5)	2.676(8)
Sm(1)-O(3)	2.560(2)	Sm(1)-N(7)	2.701(7)
Sm(1)-O(4)	2.580(2)	Sm(1)-N(9)	2.587(6)
		Sm(1)-N(10A)	2.597(16)
		Sm(1)-N(10B)	2.588(20)
N(1)-Sm(1)-N(2)	109.8(1)	N(9)-Sm(1)-N(10A)	151.7(3)
N(1)-Sm(1)-O(1)	162.4(1)	N(9)-Sm(1)-N(10B)	159.2(5)
N(1)-Sm(1)-O(2)	89.0(1)	N(3)-Sm(1)-N(5)	108.5(2)
N(1)-Sm(1)-O(3)	93.2(1)	N(3)-Sm(1)-N(7)	164.9(3)
N(1)-Sm(1)-O(4)	83.4(1)	N(5)-Sm(1)-N(7)	86.5(2)
N(2)-Sm(1)-O(1)	87.5(1)	N(3)-Sm(1)-N(9)	79.5(2)
N(2)-Sm(1)-O(2)	161.2(1)	N(5)-Sm(1)-N(9)	91.3(2)
N(2)-Sm(1)-O(3)	88.7(1)	N(7)-Sm(1)-N(9)	100.2(2)
N(2)-Sm(1)-O(4)	96.6(1)	N(3)-Sm(1)-N(1A)	88.3(3)
O(1)-Sm(1)-O(2)	73.8(1)	N(5)-Sm(1)-N(1A)	161.5(3)
O(1)-Sm(1)-O(3)	83.4(1)	N(7)-Sm(1)-N(1A)	76.9(3)
O(1)-Sm(1)-O(4)	98.5(1)	N(9)-Sm(1)-N(1A)	99.5(3)
O(2)-Sm(1)-O(3)	90.1(1)	N(3)-Sm(1)-N(1B)	77.8(4)
O(2)-Sm(1)-O(4)	85.5(1)	N(5)-Sm(1)-N(1B)	166.4(3)
O(3)-Sm(1)-O(4)	174.4(1)	N(7)-Sm(1)-N(1B)	87.6(4)
		N(9)-Sm(1)-N(1B)	101.7(3)
		N(3)-Sm(1)-N(10A)	75.9(4)
		N(5)-Sm(1)-N(10A)	83.5(5)
		N(7)-Sm(1)-N(10A)	107.2(4)
		N(1A)-Sm(1)-N(10A)	93.6(5)
		N(1B)-Sm(1)-N(10A)	86.6(6)
		N(3)-Sm(1)-N(10B)	85.5(6)
		N(5)-Sm(1)-N(10B)	79.7(7)
		N(7)-Sm(1)-N(10B)	98.0(5)
		N(1A)-Sm(1)-N(10B)	94.4(6)
		N(1B)-Sm(1)-N(10B)	89.1(7)

are not oriented with respect to the two Cbz ligands in a regular way: only three of the four *N*-MeIm ligands have average planes approximately perpendicular to the plane containing samarium and the four *N*-MeIm nitrogen donor atoms (N1, N3, N5, N7), and only two of these three *N*-MeIm ligands have a methyl group pointing up in Figure 2.

The 2.56(2) and 2.59(4) Å average Sm–N(Cbz) distances for **1** and **2**, respectively, are equivalent within the error limits of the determinations. These distances are significantly larger than the 2.301(3) Å Sm–N trivalent samarium amide distance in $(C_5Me_5)_2Sm[N(SiMe_3)_2]$,[26] as well as the 2.424(9)–2.445(7) Å Sm–N divalent samarium amide distances in $[(Me_3Si)_2N]_2Sm(THF)_2$ and $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$,[15] respectively. Direct comparison of these data in terms of oxidation state and coordination number using Shannon radii[27] is complicated by the fact that some methyl groups are oriented toward the metal in these complexes as well as the nitrogen donor atom of the bis(trimethylsilyl)amide ligands.[15,26,28–31] The 2.545(5) and 2.572(5) Å Eu–N bonds in $(Cbz)_2Eu(THF)_4$[18] are only slightly longer than the 2.530(4) Å Eu–N bonds in $[(Me_3Si)_2N]_2Eu(MeOCH_2CH_2OMe)_2$.[28] In any case, the long Sm–N distances in **1** and **2** are clearly typical of divalent rather than trivalent samarium nitrogen bonds.[32]

The Sm–O(THF) distances in **1** range from 2.560(2) to 2.602(3) Å. The 2.582(7) Å average distance can be compared to the 2.27(1) Å divalent Sm–O(OPPh$_3$) distance in octahedral $SmI_2(OPPh_3)_4$,[33] the 2.614(7) and 2.652(8) Å Sm–O(THF) distances in eight-coordinate $(C_5Me_5)_2Sm(THF)_2$,[9] and the 2.569(3) Å Sm–O(THF) distance in seven-coordinate $(C_5Me_5)_2Sm(THF)$,[34] respectively. As in $(Cbz)_2Eu(THF)_4$, the numbers for the trans Ln–O bond lengths are smaller than those for the cis Ln–O distances, but in **1** the differences are not statistically significant.

The Sm–N(*N*-MeIm) distances in **2** range from 2.631(8) to 2.724(22) Å and average 2.685(14) Å. These distances are not too different from the 2.621(7)–2.641(6) Å Sm–N(*N*-MeIm) bonds in $[SmI(\mu\text{-}I)(N\text{-}MeIm)_3]_2$, **3**, which also contains Sm(II) in an octahedral coordination environment.[22] Comparison can also be made with $(C_5Me_5)_2Sm(N\text{-}MeIm)_2$[35] which has Sm–N distances of 2.618(10) and 2.673(10) Å. It is interesting to note that in the structurally equivalent pair of THF/*N*-MeIm analogs $(C_5Me_5)_2Sm(THF)_2$[9] and $(C_5Me_5)_2Sm(N\text{-}MeIm)_2$,[35] the Sm–O(THF) and Sm–N(*N*-MeIm) distances are almost identical. In contrast in the compositionally equivalent pair **1** and **2**, the Sm–O(THF) distance is significantly shorter than the Sm–N(*N*-MeIm) distance, as would be expected. Since **1** and **2** differ in their cis–trans isomerism, it is possible that some of this difference could be due to the difference in trans ligand arrangements. However, such correlations are not well documented in lanthanide chemistry, which often involves coordination numbers greater than 6.

The cis and trans structures of **1** and **2** are of interest in light of recent structural studies and calculations on carbazole complexes of Ca, Sr, and Ba.[6] In that study $(Cbz)_2Ba(DME)_4$ was found to have a cisoid structure and $(Cbz)_2Ca(pyridine)_4$ and $(Cbz)_2Sr(NH_3)(DME)_2$ were found to be transoid in the arrangement of the two carbazole ligands. Ab initio calculations were consistent with these results but showed that the cis and trans arrangements were very close in energy. This latter assertion is supported by the samarium structures described here, since by simply changing the donor ligand, the preferred geometry in the solid state can change.

Conclusion

The synthesis of **1** and **2** introduces new alternative Sm(II) reagents for organic synthesis. Since the structural studies show that there is a preference for cis or trans depending on the coordinating solvent, it is possible that this carbazole-based system will be more selective than $SmI_2(THF)_2$ in organic reductions in which steric factors are important. The strong preference for *N*-MeIm to displace THF and remain attached to Sm(II) in THF suggests that $(Cbz)_2Sm(N\text{-}MeIm)_4$ may have a Sm(II) coordination environment much more rigidly crowded than that of $SmI_2(THF)_2$. This too may influence the selectivity of the Sm(II) reductions. The lower solubility of (Cbz)$_2$Sm-

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(26) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618–2633.

(27) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(28) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551–554.

(29) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725–3727. Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271–2276. Andersen, R. A.; Boncella, J. M. *Organometallics* **1985**, *4*, 205–206.

(30) Den Haan, K. H.; De Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726–1733.

(31) The closest approach of a hydrogen on the carbazole anion to samarium is 3.245 Å for **1** (H on C(11) on **1**) and 3.162 Å for **2** (H on C(27) on **2**).

(32) Evans, W. J.; Foster, S. E *J. Organomet. Chem.* **1992**, *433*, 79–94.

(33) Sen, A.; Chebolu, V.; Holt, E. M. *Inorg. Chim. Acta* **1986**, *118*, 87–90.

(34) Evans, W. J.; Kociok-Köhn, G.; Foster, S. E.; Ziller, J. W.; Doedens, R. J. *J. Organomet. Chem.* **1993**, *444*, 61–66.

(35) Evans, W. J.; Rabe, G. W.; Ziller, J. W. Submitted for publication.

(THF)$_4$ compared to SmI$_2$(THF)$_2$ may allow the Sm(II) reductions to be more precisely controlled by adjusting the temperature and the rate of dissolution. The utility of these complexes derivable in one step from SmI$_2$(THF)$_2$ remains to be determined by examination of their chemistry in a variety of systems.

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Supplementary Material Available: Thermal ellipsoid plots, textual presentation of crystal data collection details, and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (31 pages). Ordering information is given on any current masthead page.

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