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Bent vs Linear Metallocenes Involving C_5Me_5 vs C_8H_8 Ligands: Synthesis, Structure, and Reactivity of the Triple-Decked $(C_5Me_5)(THF)_xSm(C_8H_8)Sm(THF)_x(C_5Me_5)$ ($x = 0, 1$) Complexes Including a Formal Two-Electron Oxidative Addition to a Single Lanthanide Metal Center[1]

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Abstract: A new series of bimetallic triple-decked organometallic sandwich complexes involving Sm(II) can be prepared by reacting $[(C_5Me_4R)Sm(\mu\text{-}I)(THF)_2]_2$ with 1 equiv of $K_2C_8H_8$ in toluene to form $[(C_5Me_4R)Sm(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, **1**; R = Et, **2**). The diglyme ($[MeOCH_2CH_2]_2O$) adduct of **1**, $\{[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)\}(THF)_2$ (**3**) crystallizes from THF with a bridging $(C_8H_8)^{2-}$ dianion sandwiched between two $[(C_5Me_5)Sm(diglyme)]^+$ cations with a 137.6° (C_5Me_5 ring centroid)−Sm−(C_8H_8 ring centroid) angle. This bent triple-decked metallocene has 2.91(2) Å Sm−C(C_5Me_5) and 2.96(5) Å Sm−C(C_8H_8) average distances. **1** and **2** can be desolvated at 30−50 °C under high vacuum over several hours to yield $[(C_5Me_4R)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, **4**; R = Et, **5**). It was of interest to determine if **4** and **5** had triple-decked metallocene structures with three parallel rings since previously characterized bis(cyclooctatetraenyl) lanthanide and actinide complexes such as uranocene, $(C_8H_8)_2U$, and $[(C_8H_8)_2Ce]^-$ have parallel rings whereas $(C_5Me_5)_2Sm$ is bent. Complex **4** is found to crystallize from toluene with a structure that retains the bent geometry of **3** with 149.3° and 148.9° (C_5Me_5 ring centroid)−Sm−(C_8H_8 ring centroid) angles. **5** crystallizes from toluene with a similar bent triple-decked metallocene structure with 157.6° (C_5Me_5 ring centroid)−Sm−(C_8H_8 ring centroid) angles. The ethyl groups in **5** are oriented toward the metal center with 3.40 Å Sm···C(CH_2CH_3) distances. Complexes **1** and **2** each do two-electron reductions of 1,3,5,7-C_8H_8 to form $(C_5Me_4R)Sm(C_8H_8)(THF)$; **4** and **5** react similarly with 1,3,5,7-C_8H_8 to form $(C_5Me_4R)Sm(C_8H_8)$. A two-electron reduction of C_5Me_5Cl by **1** generates $(C_5Me_5)Sm(C_8H_8)(THF)$ and $(C_5Me_5)_2SmCl(THF)$, a product in which C_5Me_5Cl has been added to a single $(C_5Me_5)Sm(THF)$ unit in **1**.

Introduction

Although the organometallic samarium(II) complexes $(C_5Me_5)_2Sm(THF)_2$[2] and $(C_5Me_5)_2Sm$[3] have provided a wealth of interesting reactivity with organic, inorganic, and organometallic substrates,[4] relatively few other types of organosamarium(II) compounds have been developed. Most divalent samarium organometallic complexes are variations of the bis(cyclopentadienyl) formula $Cp'_2Sm(L)_x$[2,3,5] (Cp′ = cyclopentadienide or substituted cyclopentadienide and L = coordinating solvent or other donor ligands). Alternative organometallic ligand sets for Sm(II) have received much less attention,[6,7] despite the fact that the special properties of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$, namely a strong one-electron Sm(III)/Sm(II) reduction potential[8] coupled with an electrophilic metal center in an arene soluble complex, should be accessible in other systems.

Furthermore, no additional examples of molecular desolvated (polyhapto organic ligand)$_2$Sm(II) complexes related to $(C_5Me_5)_2Sm$ have been structurally characterized. $(C_5Me_5)_2Sm$ is unusual in that, instead of having the sterically least crowded structure in which the two large anionic $(C_5Me_5)^-$ anions are parallel to each other in a linear ML_2 geometry, the complex is unexpectedly bent. Subsequently, other $(C_5Me_5)_2M$ complexes in which M = Eu, Yb, Ba, Ca, and Sr have been found to also have bent structures and the (ring centroid)−M−(ring centroid) angle has been found to vary with the size of the metal.[3,9] The bent structures have proven to be theoretically challenging, and several rationalizations for the bending have been advanced.[10] These include van der Waals interactions between the methyl groups of the rings[10c,d] and ionic polarization effects[3a] analogous to those proposed to account for the bent structures encountered

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in heavy alkaline earth dihalides.[11] However, no other examples of Sm(II) sandwiched between two delocalized anionic organic rings have been discovered to allow evaluation of the theoretical models used to explain the bending in $(C_5Me_5)_2Sm$.

In efforts to increase the variety of soluble organosamarium(II) complexes and to allow the investigation of the effects of new ligand environments on reactivity and structure, we have studied the synthesis of Sm(II) complexes involving cyclooctatetraenide dianions and peralkylcyclopentadienide anions. Although the cyclooctatetraenide ligand was used to synthesize some of the first divalent organometallic compounds of the lanthanides[12] and some other divalent cyclooctatetraenyl derivatives subsequently have been synthesized, this ligand has seen little use in the development of divalent lanthanide reaction chemistry.[6a,13,14]

The main reason that $(C_8H_8)^{2-}$ rings have not been used in divalent lanthanide chemistry is that the dianion fills both valencies of the divalent ion in a single ligand which can occupy only one-half of the coordination sphere of the metal. This does not provide the solubility necessary for reactivity and neutral Ln(II) cyclooctatetraenide complexes were found to be insoluble oligomers or polymers.[15] We report here that this problem can be overcome by sharing the $(C_8H_8)^{2-}$ ring between two Sm(II) centers, each capped with a peralkylcyclopentadienide ligand.

Described here is a convenient route to the alkane soluble $(C_5Me_4R)(THF)Sm(C_8H_8)Sm(THF)(C_5Me_4R)$ (R = Me, **1**; R = Et, **2**) complexes as well as their desolvation to form $(C_5Me_4R)Sm(C_8H_8)Sm(C_5Me_4R)$. The desolvated compounds provide the first opportunity to structurally characterize a desolvated (polyhapto organic anion)$_2$Sm(II) system since $(C_5Me_5)_2Sm$ was reported in 1984.[3a] The unsolvated complexes raise interesting points in the question of linear versus bent structures for ML_2 systems, particularly since bis(cyclooctatetraenyl)actinide and bis(cyclooctatetraenyl)lanthanide complexes, like uranocene, $(C_8H_8)_2U$,[16] $[(C_8H_8)_2U]^-$,[17] $(C_8H_8)_2Ce$,[17] $[(C_8H_8)_2Ce]^-$,[18] and $[(C_8H_8)_2Yb]^{-2}$,[19] have parallel rings, while the bis(pentamethylcyclopentadienyl) complexes such as $(C_5Me_5)_2Sm$ are bent. In addition, since the new Sm(II) organometallic species are bimetallic, they extend the redox chemistry of Sm(II) to include formal two-electron reductions from a single molecule. Preliminary studies of this reduction reactivity are also reported.

Experimental Section

All manipulations described below employing $[(C_5Me_4R)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, Et) and workup of subsequent reaction products were carried out under argon in an inert-atmosphere glovebox free from coordinating solvents. All other chemistry was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Physical measurements were obtained, and solvents were purified as previously described.[20,21] $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$[2b] and $[(C_5Me_4Et)Sm(\mu\text{-}I)(THF)_2]_2$ were prepared from $SmI_2(THF)_2$[22] and $(C_5Me_5)_2Sm(THF)_2$[2] and $(C_5Me_4Et)_2Sm(THF)_2$,[5j] respectively, following literature procedures.[21] 1,3,5,7-Cyclooctatetraene (Aldrich) was dried over activated 4 Å molecular sieves and was vacuum distilled before use. $K_2C_8H_8$ was prepared from potassium and 1,3,5,7-cyclooctatetraene according to literature procedures.[23] ^1H and ^{13}C NMR spectra were obtained using Bruker AC-300 MHz, Omega 500 MHz, and Bruker DRX-400 MHz NMR spectrometers at 25 °C. IR spectra were obtained using a Perkin-Elmer series 1600 FTIR spectrophotometer, and UV−vis spectra were obtained

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Synthesis of $[(C_5Me_5)Sm(THF)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (1). In the glovebox, $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (3.533 g, 3.173 mmol) and $K_2C_8H_8$ (0.581 g, 3.19 mmol) were weighed into a 250-mL round-bottom flask equipped with a stir bar. Toluene (175 mL) was added and stirring was begun. A dark green solution immediately began to form along with a white precipitate. After 4 days, the dark green solution was filtered and the solvent was removed under vacuum. The product was transferred with a minimum amount of THF to a tared vial and dried under vacuum for several hours to yield olive green **1** (2.153 g, 83%). ^{1}H NMR (C_6D_6, 500 MHz): δ −31.86 (s, 8H, THF), 2.71 (s, 30H, C_5Me_5), 3.47 (s, 8H, THF), 65.8 (s, 8H, C_8H_8). ^{13}C NMR (C_6D_6, 75 MHz): δ −86.7 (C_5Me$_5$), 27.7 (THF), 103.2 (C$_5$*Me*$_5$). UV−vis (hexane): λ_{max} 570, 395 nm. FTIR (KBr): 2955 s, 2905 s, 2848 s, 1445 m, 1258 w, 1072 m, 1037 s, 886 m cm^{-1}. Anal. Calcd for $Sm_2O_2C_{36}H_{54}$: Sm, 36.70; C, 52.76; H, 6.64. Found: Sm, 36.85; C, 52.59; H, 6.53. Crystals of the diglyme ($[MeOCH_2CH_2]_2O$ = diglyme) adduct of **1,** $[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)\cdot 2THF$ (**3**) suitable for X-ray structural analysis were obtained by treatment of **1** with diglyme followed by recrystallization at −35 to −40 °C from THF.

Synthesis of $[(C_5Me_4Et)Sm(THF)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (2). **2** was prepared according to the synthesis of **1** using $[(C_5Me_4Et)Sm(\mu\text{-}I)(THF)_2]_2$ (1.046 g, 1.016 mmol) and $K_2C_8H_8$ (0.196 g, 1.07 mmol) to yield olive green **2** (0.530 g, 62%). ^{1}H NMR (C_6D_6, 300 MHz): δ −3.08 (br m, THF), −0.17 (s, 12H, C$_5$*Me*$_4$Et), 0.84 (br m, 4H, C$_5$Me$_4$C*H*$_2$CH$_3$), 2.63 (br m, THF), 3.73 (s, 12H, C$_5$*Me*$_4$Et), 10.57 (br m, 6H, C$_5$Me$_4$CH$_2$C*H*$_3$), 65.8 (s, 8H, C_8H_8). ^{13}C NMR (C_6D_6, 100 MHz): δ −90.3 (*C*$_5$Me$_4$Et), −86.3 (*C*$_5$Me$_4$Et), −64.1 (*C*$_5$Me$_4$Et), 27.8 (THF), 92.5 (C$_5$*Me*$_4$Et), 102.5 (C$_5$Me$_4$CH$_2$C*H*$_3$), 106.0 (C$_5$*Me*$_4$Et), 117.6 (C$_5$Me$_4$C*H*$_2$CH$_3$)**.** UV−vis (hexane): λ_{max} 595, 445 nm. FTIR (KBr) 2955 s, 2919 s, 2855 s, 1459 s, 1480 w, 1258 w, 1087 m, 1037 s, 886 m cm^{-1}. Anal. Calcd for $Sm_2O_2C_{38}H_{58}$: Sm, 35.48; C, 53.84; H, 6.90. Found: Sm, 35.60; C, 51.27; H, 6.80.

Synthesis of $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (4). **1** (1.126 g, 1.374 mmol) was weighed into a thick-walled tube equipped with a vacuum adapter. The tube was attached to a high vacuum line and evacuated to ∼10^{-7} Torr overnight. The tube was slowly (∼10 °C/h) heated to 50 °C. When the tube was heated between 35 and 40 °C the pressure rose to ∼10^{-3} Torr. The temperature was slowly raised to and maintained at 50 °C overnight. After heating overnight the pressure had returned to ∼10^{-7} Torr and the solid had become a darker blue-green. In an argon-filled glovebox, the solid was extracted with a minimum amount of toluene, the solvent was removed, and the resulting solids were dried under vacuum to yield dark blue-green **4** (0.795 g, 86%). ^{1}H NMR (C_6D_6, 300 MHz): δ 3.14 (s, 30H, C$_5$*Me*$_5$), 75.4 (s, 8H, C_8H_8). ^{13}C NMR (C_6D_6, 125 MHz): δ −101.9 (*C*$_5$Me$_5$), 107.9 (C$_5$*Me*$_5$). UV−vis (hexane): λ_{max} 595, 440 nm. FTIR (KBr): 2906 s, 2848 s, 1438 m, 1373 w, 1080 w, 1030 m, 887 m, 708 s cm^{-1}. Anal. Calcd for $Sm_2C_{28}H_{38}$: Sm, 44.54; C, 49.79; H, 5.67. Found: Sm, 44.30; C, 49.56; H, 5.83. Crystals of **4** suitable for X-ray structural analysis were obtained by recrystallization at −35 to −40 °C from toluene (Table 1).

Synthesis of $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (5). **5** was prepared according to the synthesis of **4** using **2** (0.286 g, 0.337 mmol) to yield **5** (0.198 g, 83%) as a dark blue-green powder. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.05 (br m, 4H, C$_5$Me$_4$C*H*$_2$CH$_3$), 2.31 (s, 12H, C$_5$*Me*$_4$Et), 3.72 (s, 12H, C$_5$*Me*$_4$Et), 7.96 (br m, 6H, C$_5$Me$_4$CH$_2$C*H*$_3$), 72.8 (s, 8H, C_8H_8).^{13}C NMR (C_6D_6, 100 MHz): δ −102.5 (*C*$_5$Me$_4$Et), −96.9 (*C*$_5$Me$_4$Et), −71.3 (*C*$_5$Me$_4$Et), 102.1 (C$_5$Me$_4$C*H*$_2$CH$_3$), 102.7 (C$_5$*Me*$_4$Et), 106.8 (C$_5$*Me*$_4$Et), 117.2 (C$_5$Me$_4$CH$_2$C*H*$_3$)**.** UV−vis (hexane): λ_{max} 570, 410 nm. FTIR (KBr): 2955 s, 2912 s, 2855 s, 2032 w, 1445 m, 1373 s, 1087 w, 1023 w, 887 w, 822 m, 708 m cm^{-1}. Anal. Calcd for $Sm_2C_{30}H_{42}$: Sm, 42.74; C, 51.22; H, 6.02. Found: Sm, 42.45; C, 50.99; H, 5.96. Crystals of **5** suitable for X-ray structural analysis were obtained by recrystallization at −35 to −40 °C from toluene.

Reaction of 1 with Cyclooctatetraene. Cyclooctatetraene (0.052 g, 0.50 mmol) was added to a solution of **1** (0.022 g, 0.027 mmol) in 2 mL of toluene. The solution turned red immediately. After the solution was stirred overnight, it was decanted and the solvent removed under vacuum to yield $(C_5Me_5)Sm(C_8H_8)(THF)$[24] (0.023 g, 81%) identified by NMR spectrometry.

Table 1. Experimental Data for the X-ray Diffraction Studies of $[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)(THF)_2$ (**3**) $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (**4**), and $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (**5**)

	3	**4**	**5**
formula	$C_{48}H_{82}O_8Sm_2$	$C_{28}H_{38}Sm_2$	$C_{30}H_{42}Sm_2$
fw	1087.94	675.28	703.34
temp (K)	163	158	163
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pna2_1$	$P2_1/n$
a (Å)	10.0050(9)	14.5665(9)	7.5884(8)
b (Å)	17.787(2)	13.0377(13)	13.020(2)
c (Å)	13.9217(14)	13.3864(12)	14.198(2)
β (deg)	98.810(6)	90	97.536(12)
V (Å^3)	2448.2(4)	2542.3(4)	1390.7(3)
Z	2	4	2
ρ_{calcd} (mg/m^3)	1.476	1.764	1.680
diffractometer[a]	Siemens P4	Siemens P4	Siemens P4
μ (mm^{-1})	2.423	4.586	4.195
refinement[b]	$R1$, 2.85%	$R1$, 2.03%	$R1$, 4.31%
w$R2$ [$I > 2\sigma(I)$]	w$R2$, 6.04%	w$R2$, 4.76%	w$R2$, 9.89%

[a] Radiation: Mo Kα (λ = 0.710 730 Å). Monochromator: highly oriented graphite. [b] $R = \sum||F_o| - |F_c||/\sum|F_c|$; w$R2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Reaction of 1 with C_5Me_5Cl. C_5Me_5Cl (0.008 g, 0.047 mmol), dissolved in 2 mL of hexane, was added dropwise to a stirred solution of **1** (0.038 g, 0.046 mmol) in 5 mL of hexane. The solution changed from dark green to red-brown as addition was continued. The solvent was removed under vacuum. The NMR spectrum of the resulting product mixture showed only $(C_5Me_5)Sm(C_8H_8)(THF)$ and $(C_5Me_5)_2SmCl(THF)$.[25]

Reaction of 4 with Cyclooctatetraene. Cyclooctatetraene (0.052 g, 0.50 mmol) dissolved in 2 mL of hexane was added dropwise to a stirred solution of **4** (0.013 g, 0.019 mmol) in 5 mL of hexane. The solution immediately turned red. The solution was decanted and solvent removed under vacuum to yield $(C_5Me_5)Sm(C_8H_8)$[26] (0.014 g, 95%) identified by NMR spectrometry.

Reaction of 5 with Cyclooctatetraene. This reaction was run in a manner analogous to that for the reaction of **4** with cyclooctatetraene, above, using **5** (0.015 g, 0.023 mmol) and cyclooctatetraene (0.050 g, 0.48 mmol) to yield $(C_5Me_4Et)Sm(C_8H_8)$ (0.016 g, 87%). ^{1}H NMR (C_6D_6, 300 MHz): δ −1.07 (br, m, 3H, C$_5$Me$_4$CH$_2$C*H*$_3$), 0.30 (s, 6H, C$_5$*Me*$_4$CH2CH3), 0.68 (br, m, 2H, C$_5$Me$_4$C*H*$_2$CH$_3$), 1.69 (s, 6H, C$_5$*Me*$_4$CH$_2$CH$_3$), 9.03 (s, 8H, C_8H_8).

X-ray Data Collection, Structure Determination, and Refinement for 3. A crystal of approximate dimensions 0.13 × 0.17 × 0.50 mm was mounted on a glass fiber under Paratone and transferred to the Siemens P4 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures (Table 1).[27] Intensity data were collected at 163 K using a $2\theta/\omega$ scan technique with Mo Kα radiation. The raw data were processed with a local version of CARESS[28] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 3672 data were corrected for absorption 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 $P2_1/n$ is therefore uniquely defined.

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[24] Schumann, H.; Kohn, R. D.; Reier, F.; Dietrich, A.; Pickardt, J. *Organometallics* **1989**, *8*, 1388.

[25] Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614.

[26] Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

[27] *XSCANS Software Users Guide*, Version 2.1, Siemens Industrial Automation, Inc.: Madison, WI, 1994.

[28] Broach, R. W. Argonne National Laboratory, Illinois, 1978.

All calculations were carried out using the SHELXTL program.[29] The analytical scattering factors for neutral atoms were used throughout the analysis.[30] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. The molecule is located about an inversion center, and there are two molecules of THF solvent present per formula unit. Atom C(23) of the THF molecule is disordered. Two components, each with site occupancy = 0.50, were included to account for the disorder. At convergence, w$R2$ = 0.0667 and GOF = 1.071 for 271 variables refined against all 3198 unique data (as a comparison for refinement on F, $R1$ = 0.0285 for those 2600 data with $F > 4.0\sigma(F)$).

X-ray Data Collection, Structure Determination, and Refinement for 4. A blue-green crystal of approximate dimensions 0.07 × 0.10 × 0.37 mm was mounted on a glass fiber, transferred to a Siemens P4 rotating-anode diffractometer, and handled as described for **3**. Intensity data (3046 total) were collected at 158 K using a $2\theta/\omega$ scan technique with Mo Kα radiation. The systematic absences were consistent with either the centrosymmetric orthorhombic space group *Pnma* or the noncentrosymmetric space group $Pca2_1$. It was later determined that space group $Pca2_1$ was correct.

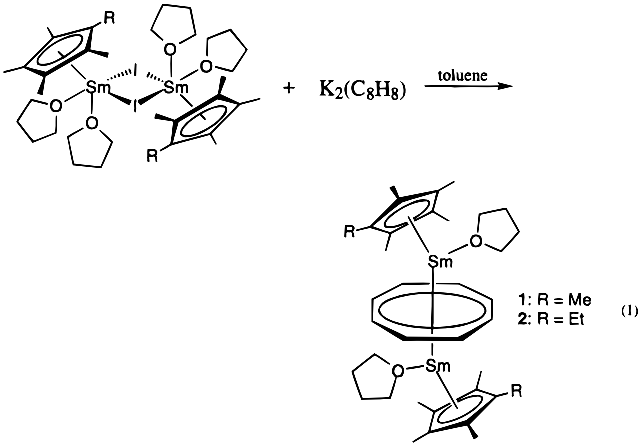
All calculations were carried out as described for **3**. The ring defined by atoms C(21)−C(28) is disordered. Two components (site-occupancy = 0.50) were included for each of the eight carbon atoms to account for this disorder. At convergence, w$R2$ = 0.0502 and GOF = 1.061 for 264 variables refined against all 3046 data (as a comparison for refinement on F, $R1$ = 0.0203 for those 2711 data with $F > 4.0\sigma(F)$). The absolute structure was assigned by refinement of the Flack parameter.[31]

X-ray Data Collection, Structure Determination, and Refinement for 5. A black crystal of approximate dimensions 0.10 × 0.13 × 0.26 mm was handled as described for **3**. 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 $P2_1/n$ is therefore uniquely defined. At convergence, w$R2$ = 0.1190 and GOF = 1.073 for 145 variables refined against all 2741 unique data (as a comparison for refinement on F, $R1$ = 0.0431 for those 1865 data with $F > 4.0\sigma(F)$).

Results

Synthesis of $[(C_5Me_4R)Sm(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, 1; R = Et, 2). The desired Sm(II) complex could not be prepared in the same manner as $[(C_5Me_5)Eu(THF)_2]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$,[14] since the europium complex is formed by reduction of europium(III) chloride using KC_5Me_5 and $K_2C_8H_8$ and samarium(III) is not reduced under these conditions. Instead, the divalent precursor, $[(C_5Me_5)Sm(\mu\text{-I})(THF)_2]_2$,[26] was used and found to react with $K_2C_8H_8$ in toluene over several days to form $[(C_5Me_5)Sm(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**1**) in over 80% yield according to eq 1. The tetramethylethyl analogue, $[(C_5Me_4Et)Sm(\mu\text{-I})(THF)_2]_2$, can be used to prepare $[(C_5Me_4Et)Sm(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**2**) by an analogous reaction. Both **1** and **2** are olive green complexes which are soluble in arenes and slightly soluble in hexane. The ^{1}H NMR spectra of **1** and **2** indicate that the complexes form with variable amounts of solvated THF: 1−2 THF per samarium. Extensive drying under vacuum at room temperature generally gives complexes with one THF per samarium.

The ^{1}H NMR spectra of **1** and **2** are consistent with complexes containing $(C_5Me_4R)^-$ and $(C_8H_8)^{2-}$ ligands in a 2:1 ratio. The resonances for the $(C_5\mathit{Me}_4R)^-$ ligands are in the normal −1 to 4 ppm region for (C_5Me_5)/Sm(II) complexes and the $(C_8H_8)^{2-}$ resonances due to **1** and **2** are shifted downfield to 65.8 and 65.8 ppm, respectively. For comparison, the ^{1}H NMR spectra of the trivalent samarium cyclooctatetraenides, $(C_5Me_5)Sm(C_8H_8)$, $(C_5Me_5)Sm(C_8H_8)(THF)$, $(C_5Me_4Et)Sm(C_8H_8)$, and $(C_5Me_4Et)Sm(C_8H_8)(THF)$, have $(C_8H_8)^{2-}$ signals in the δ 8−11 ppm range. No NMR data are available on divalent $[Sm(C_8H_8)]_n$, which is insoluble, and reexamination of the ^{1}H NMR spectrum of $K_2Sm(C_8H_8)_2$[6a] reveals a peak at 31.3 ppm.[32] Apparently, a large downfield shift is indicative of samarium(II) bound to cyclooctatetraenide.



(1)

The resonances due to the ethyl groups in **2** are found at 0.84 and 10.57 ppm for the methylene and methyl protons, respectively. On the basis of previously observed shifts, the downfield shift of these methyl protons suggests an interaction of the methyl group with samarium in solution. For example, in the ^{1}H NMR spectrum of $(C_5Me_4{}^iPr)_2Sm(THF)$, the chemical shift of the isopropyl methyl groups is 27.6 ppm and X-ray crystallography shows the methyl groups oriented toward the metal at a distance of 3.22 Å.[33] Spectroscopic and structural correlations described below for **5** also support this assignment for **2**.

The ^{13}C NMR spectra of **1** and **2** contain shifts due to the ring and methyl carbons of $(C_5Me_5)^-$ and $(C_5Me_4Et)^-$ in the unusual regions characteristic of the presence of samarium(II).[2,3,5j] The ^{13}C NMR resonances of the $(C_8H_8)^{2-}$ ligands could not be located.

Synthesis and Structure of $\{[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)\}(THF)_2$ (3). To definitively establish the composition of these complexes, characterization by X-ray crystallography was attempted. Crystals of **1** suitable for X-ray crystallography could not be obtained, but addition of diglyme produced a derivative that could be fully characterized. X-ray crystallography revealed that $\{[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)\}(THF)_2$ (**3**), has a solvated triple-decked metallocene structure (Figure 1) with an inversion center at the centroid of the $(C_8H_8)^{2-}$ ring. The 137.6° (C_5Me_5 ring centroid)−Sm−(C_8H_8 ring centroid) angle in **3** (Table 2) is only slightly larger than the 136.7° (C_5Me_5 ring centroid)−Sm−(C_5Me_5 ring centroid) angle found in $(C_5Me_5)_2Sm(THF)_2$.[3b]

Comparison of bond distances with $(C_5Me_5)_2Sm(THF)_2$ is also appropriate. Larger distances would be expected in **3** since it has a higher formal coordination number, 11 (counting each electron pair around the metal as a coordination position), than that of formally 8-coordinate $(C_5Me_5)_2Sm(THF)_2$. The Sm−C(C_5Me_5) ring distances in **3** range from 2.889(5) to 2.931(5) Å and average 2.91(2) Å compared to a range of 2.81(1)−2.91-

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[29] Sheldrick, G. M. *SHELXTL*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

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

[31] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

[32] No resonance is observed at 5.78 ppm as reported,[6b] and this peak is likely to have occurred as a result of foldover.

[33] Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *Polyhedron*, in press.

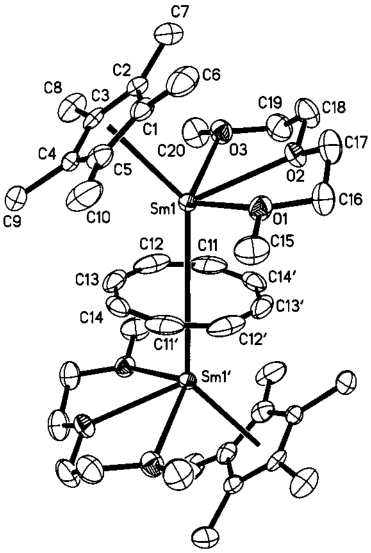


Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)(THF)_2$ (**3**) with ellipsoids drawn at the 50% level. Hydrogen atoms and the THF in the lattice are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)(THF)_2$ (**3**)

Sm(1)−Cnt(1)[a]	2.653	Sm(1)−Cnt(2)[b]	2.344
Sm(1)−O(1)	2.761(4)	Sm(1)−O(2)	2.715(4)
Sm(1)−O(3)	2.880(4)	Cnt(1)[a]−Sm(1)−Cnt(2)[b]	137.6
Sm(1)−C(1)	2.931(5)	Sm(1)−C(2)	2.917(5)
Sm(1)−C(3)	2.889(5)	Sm(1)−C(4)	2.893(5)
Sm(1)−C(5)	2.918(5)		
Sm(1)−C(11)	2.998(6)	Sm(1)−C(11′)	2.931(6)
Sm(1)−C(12)	2.924(6)	Sm(1)−C(12′)	3.009(6)
Sm(1)−C(13)	2.896(6)	Sm(1)−C(13′)	3.028(6)
Sm(1)−C(14)	2.905(6)	Sm(1)−C(14′)	3.018(6)

[a] Cnt(1) is the centroid of the C(1)−C(5) ring. [b] Cnt(2) is the centroid of the C(11)−C(14)′ ring.

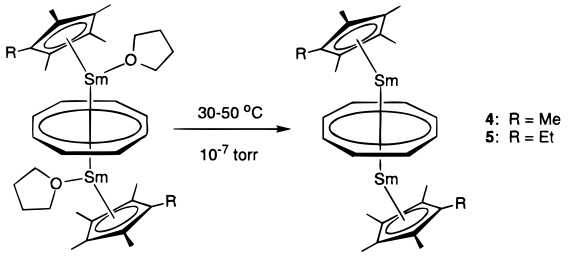
(1) Å and an average of 2.86(3) Å in $(C_5Me_5)_2Sm(THF)_2$. Hence, although **3** has more distances which are longer, the ranges overlap and the averages are equivalent within the error limits. This is somewhat surprising considering the substantial difference in formal coordination number. Shannon radii for Sm(II) show an increase of 0.05 Å for each increase in coordination number.[34]

Comparison of the Sm−O distances in **3** and $(C_5Me_5)_2Sm(THF)_2$ is less straightforward since the three Sm−O(diglyme) values are dissimilar: 2.715(4), 2.761(4), and 2.880(4) Å. The latter Sm(1)−O(3) distance is out of the normal Sm(II)−O bonding range even considering the larger coordination number,[35] but O(3) is clearly oriented toward the metal. This complicates the assignment of formal coordination number. The 2.62(1)−2.66(1) Å Sm−O(THF) distances in $(C_5Me_5)_2Sm(THF)_2$ are significantly shorter than in **3** as expected. Other Sm(II)−O(diglyme) distances are in the range of the two smaller values in **3**: 2.676(4)−2.720(4) Å in *trans*-$SmI_2(diglyme)_2$,[36] 2.653(9)−2.699(11) Å in *cis*-$SmI_2(diglyme)_2$,[37] and 2.654(4)−2.675(4) Å in $[Sm(diglyme)_3][Co(CO)_4]_2$.[38]

The Sm−C(C_8H_8) distances have a broad range, 2.896(6)−3.028(6) Å, and average 2.96(5) Å. 10-Coordinate $[(C_5Me_5)Eu(THF)_2]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$[14] has similar parameters: a range of 2.850(14)−3.024(12) Å and an average of 2.92(5) Å (Sm(II) is 0.02 Å larger than Eu(II)[34]). It is interesting to note that each samarium in **3** approaches three of the cyclooctatetraenyl carbon atoms, C(12−14), with Sm−C distances in the range found for the Sm−C(C_5Me_5) distances and as such this part of the $(C_8H_8)^{2-}$ ligand resembles a typical pentamethylcyclopentadienyl coordination environment (see below).

In general, there is significant overlap between the structural parameters of **3** and $(C_5Me_5)_2Sm(THF)_2$. This suggested that **1** could have somewhat similar chemistry and could be desolvated to yield a triple-decked analogue of $(C_5Me_5)_2Sm$. This was quite desirable because it would provide another unsolvated Sm(II) metallocene for structural comparison with the unusual bent $(C_5Me_5)_2Sm$.

Synthesis of $[(C_5Me_4R)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, 4; R = Et, 5). The desolvation of **1** and **2** under high vacuum (~10^{-7} Torr) proceeds at mild temperatures, 30−50 °C, to yield the desolvated complexes $[(C_5Me_4R)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, **4**; R = Et, **5**), which were characterized by X-ray diffraction (eq 2). This reaction is analogous to the procedure used in the preparation of $(C_5Me_5)_2Sm$ from $(C_5Me_5)_2Sm(THF)_2$,[3b] but in this case, the unsolvated complexes can be isolated by extraction with toluene rather than by sublimation and the yields are somewhat higher. Complexes **4** and **5** are isolated as dark blue-green almost black solids. They are both soluble in arenes and slightly soluble in hexane.



(2)

The NMR spectra of **4** and **5** are similar to those of **1** and **2** but lack the resonances due to coordinated THF. The signals due to $(C_8H_8)^{2-}$ in **4** and **5** are again shifted in these Sm(II) complexes to 75.4 and 72.8 ppm, respectively. Resonances due to the methylene and methyl protons of the ethyl group in **5** are found at −0.05 and 7.96 ppm, respectively, which again is consistent with a long-range interaction between the methyl group and samarium (see below). The ^{13}C NMR spectrum of **4** contains resonances at δ −101.9 and 107.9 due to the ring and methyl carbons of $(C_5Me_5)^-$, respectively, in the ranges expected for $(C_5Me_5)^-$ attached to Sm(II) and similar resonances are found for **5**. As in **1** and **2**, resonances due to $(C_8H_8)^{2-}$ could not be located in the ^{13}C NMR spectra.

Structure of $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (4). The structure of **4** was determined by X-ray crystallography and found to be a triple-decked metallocene. As shown in eq 2 and Figure 2, the complex retains the bent structure of the solvated complex with 149.3° and 148.9° (C_5Me_5 ring centroid)−Sm−(C_8H_8 ring centroid) angles (Table 3). These are larger than the 137.6° angle in **3** just as the 140.1° (C_5Me_5 ring centroid)−Sm−(C_5Me_5 ring centroid) in unsolvated $(C_5Me_5)_2Sm$ is larger than the 136.7° angle in solvated $(C_5Me_5)_2Sm(THF)_2$. The difference is larger in this $(C_8H_8)^{2-}$ system, but this angle does not approach the 180° that might be expected based on simple steric and electrostatic considerations. When viewed along the Sm···Sm vector, the (C_5Me_5 ring centroid)−Sm−Sm−(C_5Me_5 ring centroid) torsional angle is found to be 148.6°, which is

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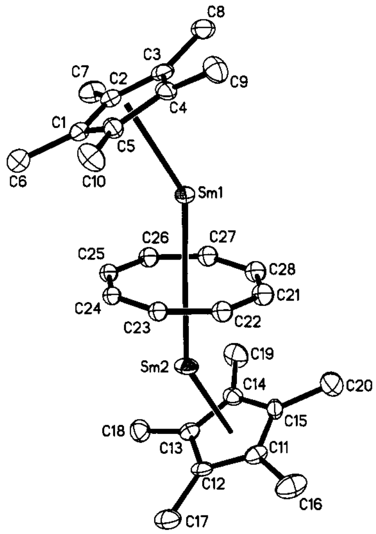

Figure 2. Thermal ellipsoid plot of $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**4**) with ellipsoids drawn at the 50% level. Hydrogen atoms and the disorder in the $(C_8H_8)^{2-}$ ring are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**4**)

Sm(1)−Cnt(1)[a]	2.510	Sm(1)−Cnt(2)[b]	2.151
Sm(2)−Cnt(2)[b]	2.120	Sm(2)−Cnt(3)[c]	2.497
Cnt(1)[a]−Sm(1)−Cnt(2)[b]	149.3	Cnt(2)[b]−Sm(2)−Cnt(3)[c]	148.9
Sm(1)−C(1)	2.783(5)	Sm(2)−C(11)	2.763(6)
Sm(1)−C(2)	2.784(5)	Sm(2)−C(12)	2.768(5)
Sm(1)−C(3)	2.798(5)	Sm(2)−C(13)	2.761(5)
Sm(1)−C(4)	2.784(5)	Sm(2)−C(14)	2.777(5)
Sm(1)−C(5)	2.778(5)	Sm(2)−C(15)	2.790(5)
Sm(1)−C(21)	2.882(11)	Sm(2)−C(21)	2.753(12)
Sm(1)−C(21B)	2.885(12)	Sm(2)−C(21B)	2.789(13)
Sm(1)−C(22)	2.852(11)	Sm(2)−C(22)	2.799(11)
Sm(1)−C(22B)	2.847(12)	Sm(2)−C(22B)	2.838(12)
Sm(1)−C(23)	2.814(11)	Sm(2)−C(23)	2.824(10)
Sm(1)−C(23B)	2.835(13)	Sm(2)−C(23B)	2.842(13)
Sm(1)−C(24)	2.810(10)	Sm(2)−C(24)	2.855(10)
Sm(1)−C(24B)	2.810(20)	Sm(2)−C(24B)	2.838(14)
Sm(1)−C(25)	2.808(10)	Sm(2)−C(25)	2.854(10)
Sm(1)−C(25B)	2.798(14)	Sm(2)−C(25B)	2.827(14)
Sm(1)−C(26)	2.823(11)	Sm(2)−C(26)	2.823(11)
Sm(1)−C(26B)	2.800(20)	Sm(2)−C(26B)	2.814(15)
Sm(1)−C(27)	2.849(11)	Sm(2)−C(27)	2.798(12)
Sm(1)−C(27B)	2.824(12)	Sm(2)−C(27B)	2.794(12)
Sm(1)−C(28)	2.878(11)	Sm(2)−C(28)	2.760(12)
Sm(1)−C(28B)	2.851(10)	Sm(2)−C(28B)	2.780(11)

[a] Cnt(1) is the centroid of the C(1)−C(5) ring. [b] Cnt(2) is the centroid of the C(21)−C(28B) ring. [c] Cnt(3) is the centroid of the C(11)−C(15) ring.

between the 180° arrangement observed in **3** and **5** and a 0° arrangement in which both $(C_5Me_4R)^-$ rings are on the same side.

The Sm−C(C_5Me_5) distances in **4** range from 2.761(5) to 2.798(5) Å and average 2.79(1) and 2.77(1) Å. These numbers are almost identical to those of $(C_5Me_5)_2Sm$,[4a] which has a 2.775(6)−2.815(6) Å range and a 2.79(1) Å average, even though the two complexes have different formal coordination numbers. Since the $(C_8H_8)^{2-}$ ring in **4** is disordered, less can be said about the Sm−C(C_8H_8) distances which range from 2.753(12) to 2.885(12) Å and average 2.84(3) and 2.81(3) Å. These are much shorter than those in **3**, as is consistent with the difference in coordination number.

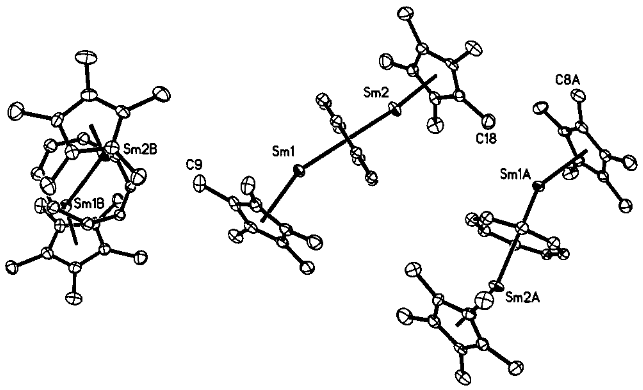

Figure 3. Illustration of the intermolecular contacts of three $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ units. Selected contacts: Sm(1A)···C(18), 3.247 Å; Sm(2B)···C(9), 3.652 Å; C(18)···C(8A), 3.497.

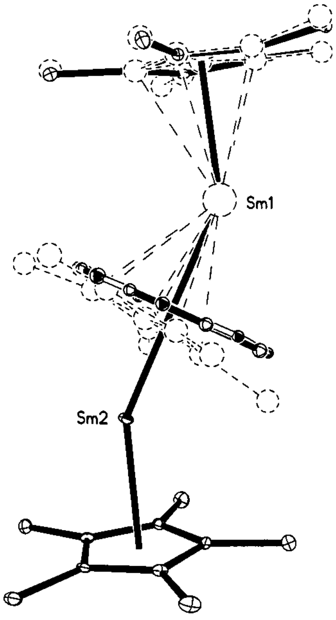

Figure 4. Overlay of $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**4**) and $(C_5Me_5)_2Sm$ (dashed lines).

The intermolecular contacts in **4** (Figure 3) are similar to those found in $(C_5Me_5)_2M$ (M = Ca, Yb, Sm, Eu, Ba) systems.[9a] The closest intermolecular CH_3···CH_3* contact (asterisk-marked components are in another molecule) in **4** is the 3.50 Å C(18)···C(8A) distance, which is in the 3.3−3.5 Å range observed for $(C_5Me_5)_2M$ complexes and is slightly longer than the analogous 3.34 Å distance in $(C_5Me_5)_2Sm$. The closest intermolecular M···CH_3* distance in **4** is 3.25 Å (Sm(1A)···C(18)), which is in the 2.98−3.35 Å range observed in $(C_5Me_5)_2M$ systems and quite similar to the 3.22 Å distance in $(C_5Me_5)_2Sm$. The orientation of the closest M···CH_3* approach in **4** is also of interest although the analogous orientations in $(C_5Me_5)_2M$ complexes are quite variable. The ring containing C(18) approaches Sm(1A) "edge-on" as is observed in $(C_5Me_5)_2M$ for M = Ca, Yb, Eu, and Sm, but not for M = Ba which has a more facial orientation.[9a] However, in contrast to $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$, the C(18) in **4** approaches the widest part of the metallocene wedge. In $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$, the closest CH_3 is oriented to the side of the wedge.[3]

To visually examine the similarities of **4** and $(C_5Me_5)_2Sm$ and to compare the central $(C_8H_8)^{2-}$ ring with a $(C_5Me_5)^-$ ligand, overlays of the crystallographic data on the two structures are given in Figures 4 and 5. In Figure 4, the $(C_5Me_5)^-$ ring carbons of the two complexes are overlaid such that the difference in the second $(C_5Me_5)^-$ ring in $(C_5Me_5)_2Sm$ and the $(C_8H_8)^{2-}$ ring in **4** can be viewed. As discussed above, the Sm−C(C_5Me_5) distances in the two complexes are similar and therefore the top parts of these compounds coincide very closely.

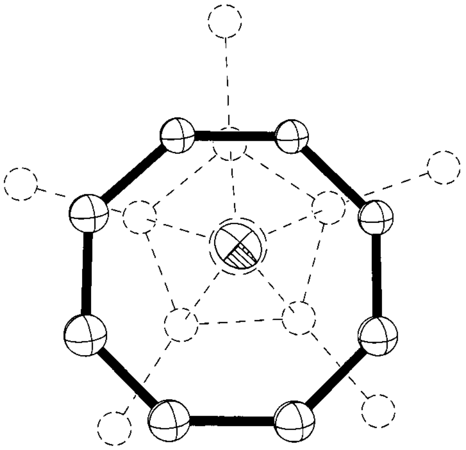

Figure 5. Overlay of $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**4**) and $(C_5Me_5)_2Sm$ showing only the overlap of the middle $(C_8H_8)^{2-}$ and $(C_5Me_5)^-$ ligands in Figure 4. This view has $(C_5Me_5)^-$ in the plane of the paper.

In fact, the overlap of the $(C_5Me_5)Sm$ units from the two compounds is such that none of the carbon atoms of the two different $(C_5Me_5)^-$ rings differ in position by more than 0.08 Å, the ring centroids coincide to within 0.02 Å, and the Sm atoms coincide to within 0.01 Å. This view shows that although the (ring centroid)−Sm−(ring centroid) angle in **4** is larger, i.e., it has a less bent structure than $(C_5Me_5)_2Sm$, the $(C_8H_8)^{2-}$ ring is oriented such that several of the eight ring atoms are close to the positions of the "second" $(C_5Me_5)^-$ ring in $(C_5Me_5)_2Sm$. This comparison also shows that **4** has a slightly less open wedge than $(C_5Me_5)_2Sm$, which may explain the more facile desolvation of **1** when compared to that of $(C_5Me_5)_2Sm(THF)_2$.

The "second" $(C_5Me_5)^-$ ring in $(C_5Me_5)_2Sm$ and the $(C_8H_8)^{2-}$ ring in **4** are further compared in Figure 5. This perspective shows an overlay of the $(C_8H_8)^{2-}$ ring onto the "lower" $(C_5Me_5)^-$ ring of $(C_5Me_5)Sm$ in Figure 4 viewed with this $(C_5Me_5)^-$ ring in the plane of the paper. This view along the Sm−(C_5Me_5 ring centroid) vector shows just the middle two rings in Figure 4 and the coincident samarium atoms of each compound. Figure 5 shows visually the relative size of the $(C_8H_8)^{2-}$ and $(C_5Me_5)^-$ rings in comparable structures. Although the methyl carbons of the $(C_5Me_5)^-$ ligand extend beyond the $(C_8H_8)^{2-}$ ring on all sides, several of the carbon atoms of the $(C_8H_8)^{2-}$ ring match the bonding area of the $(C_5Me_5)^-$ ring and show how the $(C_8H_8)^{2-}$ ring can make a metallocene similar to $(C_5Me_5)_2Sm$.

Structure of $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (5). The structure of **5** (Figure 6), was found to be similar to that of **4** in many respects. Complex **5** has an inversion center at the center of the $(C_8H_8)^{2-}$ ring which results in a 180° (ring centroid)−Sm−Sm−(ring centroid) torsional angle. The 2.75(2) Å Sm−C(C_5Me_4Et) and 2.78(2) Å Sm−C(C_8H_8) average distances in **5** (Table 4) are identical within experimental error to those in **4**.

Complexes **4** and **5** differ in that **5** contains two ethyl substituents, and these apparently have a significant effect on the structure. The ethyl groups of the $(C_5Me_4Et)^-$ ligands are bent in toward the samarium atoms as might be expected from the structure of $(C_5Me_4Et)_3Sm$,[39] in which two of the three ethyl groups point in toward the two least crowded areas around the trivalent samarium. The 3.40 Å Sm···C(CH_2CH_3) distance in **5**, however, is significantly shorter than the analogous 3.620(13) Å distance in $(C_5Me_4Et)_3Sm$. Considering that the radius of Sm(II) is 0.1[40]−0.2[34] Å larger than that of Sm(III), this is consistent with a much larger interaction in **5**. Interestingly, the magnitude of the 7.96 ppm shift observed for this group in the ^1H NMR spectrum is not significantly larger than that of the −7.42 ppm shift found in $(C_5Me_4Et)_3Sm$ even though the magnetic moment of Sm(II) is much larger than that of Sm(III). The 3.40 Å distance in **5** is longer than the 3.22 Å Sm···(CHMe*C*H_3) interaction in $(C_5Me_4{}^iPr)_2Sm(THF)$ which generated a 27.6 ppm ^1H NMR resonance.[33]

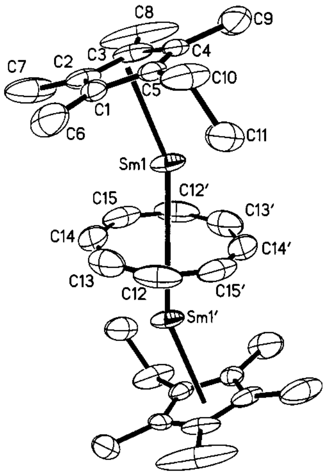

Figure 6. Thermal ellipsoid plot of $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**5**) with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table 4. Selected Bond Distances (Å), Contact Distances (Å), and Angles (deg) for $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**5**)

Sm(1)−Cnt(1)[a]	2.474	Sm(1)−Cnt(2)[b]	2.102
Cnt(1)[a]−Sm(1)−Cnt(2)[b]	157.6	Sm(1)···C(11)	3.395
Sm(1)−C(1)	2.762(7)	Sm(1)−C(2)	2.777(8)
Sm(1)−C(3)	2.742(7)	Sm(1)−C(4)	2.730(8)
Sm(1)−C(5)	2.724(7)		
Sm(1)−C(12)	2.772(8)	Sm(1)−C(12′)	2.786(9)
Sm(1)−C(13)	2.759(10)	Sm(1)−C(13′)	2.793(10)
Sm(1)−C(14)	2.751(10)	Sm(1)−C(14′)	2.786(9)
Sm(1)−C(15)	2.776(10)	Sm(1)−C(15′)	2.789(9)

[a] Cnt(1) is the centroid of the C(1)−C(5) ring. [b] Cnt(2) is the centroid of the C(12)−C(15′) ring

The main difference between the structures of **4** and **5** is that the 157.6° (C_5Me_4Et ring centroid)−Sm−(C_8H_8 ring centroid) angle in **5** is more than 8° larger than that in **4**. Hence, replacement of one methyl group on a $(C_5Me_5)^-$ ligand with a more bulky ethyl group which forms a long-range agostic interaction causes the rings to move toward a more parallel orientation. In effect, the agostic interaction in **5** serves to increase the bonding area of the cyclopentadienide ligand and the larger ligand leads to a more linear structure. A similar situation exists between $(C_5Me_5)_2Sm$ and $[(C_5Me_5)Sm]_2(C_8H_8)$: replacing one $(C_5Me_5)^-$ ligand in $(C_5Me_5)_2Sm$ with a $(C_8H_8)^{2-}$ ligand gives **4**, which has a larger (ring centroid)−Sm−(ring centroid) angle.

Reactivity. Initial reactivity studies on **1** focused on substrates that could be reduced by two electrons to form organosamarium complexes which previously had been fully characterized. The reaction with 1,3,5,7-C_8H_8 met these criteria, and as anticipated, the reaction forms 2 equiv of $(C_8H_8)Sm(C_5Me_5)(THF)$ according to eq 3. The reaction occurs immediately upon mixing and forms the product in high yield without any byproducts detectable by NMR spectroscopy.

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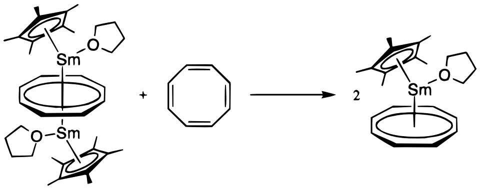
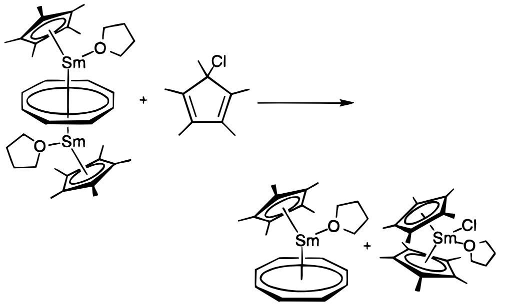
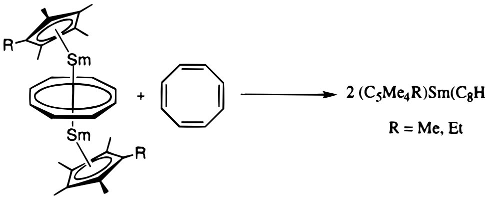


(3)

The reaction of **1** with C_5Me_5Cl is similarly fast and forms $(C_5Me_5)Sm(C_8H_8)(THF)$ and $(C_5Me_5)_2SmCl(THF)$ (eq 4). The reactions of unsolvated **4** and **5** with 1,3,5,7-C_8H_8 were also examined and found to parallel the reaction of **1** except that the product isolated was unsolvated (eq 5).



(4)



(5)

Discussion

The reactions of $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$[2b] and its ethyl derivative, $[(C_5Me_4Et)Sm(\mu\text{-}I)(THF)_2]_2$, with $K_2C_8H_8$ conveniently provide a new class of organometallic Sm(II) complexes, $[(C_5Me_4R)Sm(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, **1**; R = Et, **2**), which have interesting implications in organolanthanide synthesis, structure, and reactivity. The syntheses are straightforward and occur in high yield to provide products which are soluble in nonpolar hydrocarbons. Moreover, complexes **1** and **2** can be easily desolvated to make the unsolvated analogues $[(C_5Me_4R)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (R = Me, **4**; R = Et, **5**).

The X-ray crystal structure of the diglyme adduct of **1**, $\{[(C_5Me_5)Sm(diglyme)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)\}(THF)_2$ (**3**) as well as those of **4** and **5** show that when a $(C_8H_8)^{2-}$ dianion is shared between two $[(C_5Me_4R)Sm]^+$ units, it structurally mimics a $(C_5Me_5)^-$ monoanion. The $(C_5Me_5)Sm$ portions of **1** and **4** are rather similar to those in their monometallic analogues $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$. Moreover, as shown in Figures 4 and 5, the $(C_8H_8)^{2-}$ ring in **4** compares favorably with a $(C_5Me_5)^-$ ring in $(C_5Me_5)_2Sm$.

Hence, the $(C_8H_8)^{2-}$ dianion, by being shared between two Sm(II) centers, effectively uses only one valency of each metal and a second ligand can be attached to each metal to fill the other part of the coordination sphere and provide solubility. Another way to view these complexes is to consider that in the case of **4** the $[(C_5Me_5)Sm]^+$ unit is complexed to a $[(C_8H_8)Sm(C_5Me_5)]^-$ monoanion just as the $[(C_5Me_5)Sm]^+$ moiety is complexed to a $(C_5Me_5)^-$ monoanion in $(C_5Me_5)_2Sm$.

Since each of the metals in the unsolvated complexes **4** and **5** is an unsolvated Sm(II) center sandwiched between two polyhapto organic anions, they can be structurally compared with $(C_5Me_5)_2Sm$. Since one of the polyhapto organic anions is now a $(C_8H_8)^{2-}$ ring and f element metallocenes containing two cyclooctatetraenyl rings have parallel rings as in uranocene, $U(C_8H_8)_2$,[16] $Th(C_8H_8)_2$,[16] $Ce(C_8H_8)_2$,[17] $[Ce(C_8H_8)_2]^-$,[18] $[U(C_8H_8)_2]^-$,[17] and $[Yb(C_8H_8)_2]^{2-}$,[19] the structures of **4** and **5** represent an opportunity to evaluate the effect of the specific polyhapto organic anion on the structure. The fact that **4** and **5** adopt bent structures such as that of $(C_5Me_5)_2Sm$ shows that the bent structure of $(C_5Me_5)_2Sm$ and the analogues with Eu, Yb, Ba, Ca, and Sr are not anomalies for this particular $(C_5Me_5)_2$ ligand set. This could have been the case. For example, in addition to the parallel plane bis(cyclooctatetraenyl) complexes listed above, the polypyrazolylborate ligands in the Sm(II) complex, $Sm[HB(3,5\text{-}Me_2pz)_3]_2$,[6h] adopt a linear rather than bent orientation with respect to each other and polypyrazolylborates are often considered to be analogues of cyclopentadienyl ligands. In the case of $Sm[HB(3,5\text{-}Me_2pz)_3]_2$, the linear orientation of the ligands is expected considering their steric bulk. However, this is also what is expected for the metallocenes. The same analysis can be made for the parallel plane bis(tri-*tert*-butylbenzene) lanthanide complexes, $[1,3,5\text{-}(Me_3C)_3\text{-}C_6H_3]_2Ln$.[41] The structures of **4** and **5** also show that attractive methyl–methyl interactions[10c,d] are not needed to generate a bent structure.

Since complexes **1**–**5** are bimetallic Sm(II) species, they provide an opportunity for a single molecular organosamarium species to do two-electron reduction chemistry. Two-electron reductions are typical of Sm(II) chemistry since, once the first electron is transferred to a substrate to make a $(Sm^{3+})(substrate^{\cdot -})$ species, this radical is often reduced further by Sm(II) to make $(Sm^{3+})_2(substrate^{2-})$ species. In other cases, the originally formed radicals couple to make $(Sm^{3+})_2(substrate{-}substrate)^{2-}$ species, but again bimetallic samarium products result and the overall reduction involves two electrons.[4,42]

Preliminary studies of the reactions of **1** show that $(C_5Me_5)Sm(C_8H_8)(THF)$ is almost always formed as one of the products. This is a reasonable product to expect from a mixture of Sm(III) with $(C_5Me_5)^-$ and $(C_8H_8)^{2-}$ ligands. When complex **1** participates in a two-electron reduction and forms $(C_5Me_5)Sm(C_8H_8)(THF)$, the remaining portion of the product is $[(C_5Me_5)Sm]^{2+}$. This unit is charge balanced by the dianion or (two monoanions) formed from the two-electron reduction of the substrate. In the 1,3,5,7-C_8H_8 reaction, the reduced substrate is $(C_8H_8)^{2-}$ and with $[(C_5Me_5)Sm]^{2+}$ this makes another equivalent of $(C_5Me_5)Sm(C_8H_8)(THF)$. With C_5Me_5Cl, the reduced products are $(C_5Me_5)^-$ and $(Cl)^-$ and they both combine with $[(C_5Me_5)Sm]^{2+}$ to make the observed $(C_5Me_5)_2SmCl(THF)$. The net result of both of these reactions is that the substrate gets reduced by two electrons and added to a single metal center. This is reminiscent of typical transition metal oxidative additions (eq 6) in which a substrate is reduced by

$$M^{n+} + A{-}B \rightarrow A{-}M^{(n+2)+}{-}B \qquad (6)$$

two electrons and added to a single metal center. However, the reaction with **1** must occur via two Sm(III)/Sm(II) single electron reductions. The net result of these reductions with **1** is to oxidatively add C_8H_8 and C_5Me_5Cl to a $(C_5Me_5)Sm$ unit. Mechanistically, however, the reaction is more complex. These

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reactions raise interesting questions regarding the sequence of electron transfer, the inner or outer sphere nature of the reduction, and lanthanide reduction chemistry in general. These topics are under investigation.

Conclusion

By sandwiching the $(C_8H_8)^{2-}$ dianion between two $[(C_5Me_5)Sm(THF)_x]^+$ units, this ligand can be used to support new soluble organometallic divalent samarium complexes and provide new ligand environments with which to explore organosamarium(II) chemistry. The pair of complexes $[(C_5Me_5)Sm(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ and $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ are analogous in many respects to the $(C_5Me_5)_2Sm(THF)_2$[2] and $(C_5Me_5)_2Sm$[3] pair which has provided so much new organolanthanide chemistry. As bimetallic systems, the new complexes offer additional opportunities to study Sm(II) reduction mechanisms. The substantial change in (ring centroid)−Sm−(ring centroid) angle which occurs in $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ upon changing from $(C_5Me_5)^-$ to $(C_5Me_4Et)^-$ suggests that ligand substitution can be used to change the bent nature of these metallocenes to determine how this angle affects reactivity.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (33 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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