Organometallics **1996,** *15,* 527−531

New Synthetic Routes to Tris(pentaalkylcyclopentadienyl)lanthanide Complexes Including the X-ray Crystal Structure of $(C_5Me_4Et)_3Sm$[1]

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Received October 2, 1995[⊗]

The synthetic chemistry leading to tris(pentamethylcyclopentadienyl)samarium complexes has been examined to determine why some routes fail and to develop routes superior to the first synthesis from $(C_5Me_5)_2Sm$ and 1,3,5,7-cyclooctatetraene (COT). $(C_5Me_5)_2Sm(THF)$ fails as a reagent since $(C_5Me_5)_3Sm$ reacts with any THF present to form the ring-opened product $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$. However, $(C_5Me_5)_2Sm(OEt_2)$ reacts cleanly with COT to form $(C_5Me_5)_3Sm$ and $(C_5Me_5)Sm(C_8H_8)$. A more efficient synthesis involves the reaction of $(C_5Me_5)_2Sm(OEt_2)$ with $(C_5Me_5)_2Pb$ which generates $(C_5Me_5)_3Sm$ in >90% yield. This route has been used to synthesize the more sterically crowded tris(pentaalkylcyclopentadienyl) complex $(C_5Me_4Et)_3Sm$, which shows that the limit of steric crowding in this class has not yet been realized. X-ray crystallographic study of $(C_5Me_4Et)_3Sm$ revealed a trigonal planar arrangement of ring centroids around samarium with an average Sm−C(C_5Me_5) distance of 2.834 Å. Two ethyl groups point toward samarium with a minimum Sm−C distance of 3.620(13) Å.

Introduction

In the past it was assumed that tris(pentamethylcyclopentadienyl)metal complexes were too sterically crowded to exist.[2] This belief was supported by the fact that despite years of extensive work with the C_5Me_5 ligand by many research groups, no example of a $(C_5Me_5)_3M$ complex had ever been reported. However, exploration of the reaction chemistry of the unusual bent metallocene $(C_5Me_5)_2Sm$[3] revealed that a $(C_5Me_5)_3M$ compound could be made simply upon mixing $(C_5Me_5)_2Sm$ and 1,3,5,7-cyclooctatetraene (COT)[4] according to eq 1. This result showed that the limits of

$$2(C_5Me_5)_2Sm + COT \rightarrow (C_5Me_5)_3Sm + (C_5Me_5)Sm(C_8H_8) \quad (1)$$

steric saturation in tris(pentaalkylcyclopentadienyl) systems had not yet been reached. Subsequent studies aimed to make tris(multiply-alkylated cyclopentadienyl) complexes have shown that $(C_5Me_4H)_3Ln$,[5] $(C_5Me_4H)_3UCl$,[6] and the phosphorus-substituted species $(C_4Me_4P)_3UZ$ (Z = H, Me, O^{i}Pr)[7] can be made. However, since these tetramethyl ligands are smaller than C_5Me_5, these types of compounds were not unexpected once the existence of $(C_5Me_5)_3Sm$ was known.

Although the synthesis of $(C_5Me_5)_3Sm$ by eq 1 is facile, it is not efficient in terms of either samarium or C_5Me_5. As a result, we have examined other routes to this compound and related species. We report here improved syntheses of $(C_5Me_5)_3Sm$ and the use of the best route to make an even more sterically crowded, crystallographically-characterizable, tris(pentaalkylcyclopentadienyl)metal complex, $(C_5Me_4Et)_3Sm$. We also show why some alternative routes to $(C_5Me_5)_3Sm$ are unlikely to succeed.

Experimental Section

The chemistry described below was performed under nitrogen or argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were purified and physical measurements were obtained as previously described.[8,9] $(C_5Me_5)_2Sm(OEt_2)$[10] was prepared on a Schlenk line and stored in a tightly sealed container in the freezer of a THF-free, argon-filled glovebox. 1,3,5,7-Cyclooctatetraene was purified by drying over CaH_2 followed by vacuum distillation. $PbCl_2$ was dried at 100 °C at 10^{-4} Torr for 24 h. LiC_5Me_5 and LiC_5Me_4Et were prepared by reaction of the respective cyclopentadienes with 10% excess *n*-BuLi in hexane. Assignment of the ^{13}C NMR resonances in $(C_5Me_4Et)_3Sm$ was facilitated by the use of standard ^1H-coupled and DEPT experiments. Elemental analyses were performed by Analytische Laboratorien (Gummersbach, Germany) or in-house on a Carlo Erba EA 1108 CHN analyzer.

$(C_5Me_5)_2Pb$.[11] In the glovebox in a flask shielded from light with aluminum foil, $PbCl_2$ (1.28 g, 4.60 mmol) was added in portions to a stirred suspension of LiC_5Me_5 (1.32 g, 9.29 mmol) in THF (50 mL). A pale yellow color developed immediately, which progressively changed to orange and finally deep red.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

[1] Reported in part at the 209th American Chemical Society National Meeting, Anaheim, CA, April 1995, INOR 105.

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0276-7333/96/2315-0527$12.00/0

The reaction was stirred for 12 h with no further change in appearance. The solvent was removed under vacuum, and the dark red solid was repeatedly extracted with hexane and separated from precipitated LiCl by centrifugation until no further red coloration was evident in the supernatant. Removal of the solvent from the extracts under vacuum gave crystalline $(C_5Me_5)_2Pb$ (1.60 g, 76%). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 2.18 [s, with ^{205}Pb satellites, $J(^{205}Pb-^1H) = 11$ Hz, $C_5\mathit{Me}_5$]. ^{13}C NMR (C_6D_6, 25 °C): δ 117.1 (C_5Me_5), 10.4 ($C_5\mathit{Me}_5$).

$(C_5Me_4Et)_2Pb$. Following the above procedure, $PbCl_2$ (0.364 g, 1.31 mmol) and LiC_5Me_4Et (0.404 g, 2.59 mmol) were combined in 50 mL of THF. A deep red color developed in the solution, and after 12 h $(C_5Me_4Et)_2Pb$ (0.57 g, 87%) was isolated as described above as a red oil. Anal. Calcd for $C_{22}H_{34}Pb$: C, 52.25; H, 6.78; Pb, 40.97. Found: C, 52.06; H, 6.69; Pb, 40.70. ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 2.56 (q, 2H, $C_5Me_4C\mathit{H}_2CH_3$), 2.19 (s with ^{205}Pb satellites, $J(^{205}Pb-^1H)$ = 17 Hz, 6H, $C_5\mathit{Me}_4CH_2CH_3$), 2.17 (s, with ^{205}Pb satellites, $J(^{205}Pb-^1H) = 17$ Hz, 6H, $C_5\mathit{Me}_4CH_2CH_3$), 1.05 (t, 3H, $C_5Me_4CH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 127.0, 117.3, 117.0 ($\mathit{C}_5Me_4CH_2CH_3$); 19.5 ($C_5Me_4CH_2\mathit{C}H_3$), 18.4 ($C_5Me_4\mathit{C}H_2CH_3$); 10.0, 9.9 ($C_5\mathit{Me}_4Et$).

$(C_5Me_5)_3Sm$ from COT. In a THF-free glovebox, $(C_5Me_5)_2Sm(OEt_2)$ (1.30 g, 2.29 mmol) was placed in a Schlenk flask, dissolved in toluene (5 mL), and removed to a Schlenk manifold. A yellow solution of 1,3,5,7-cyclooctatetraene (0.118 g, 1.14 mmol) in toluene (5 mL) was added by cannula to the dark green $(C_5Me_5)_2Sm(OEt_2)$ solution causing an immediate color change to a dark red-brown. After 15 min, the solvent was removed under vacuum and the Schlenk flask containing the red-brown residue was transferred to a THF-free glovebox. The residue was washed with cold (−36 °C) hexane and then vacuum dried to afford pure brown $(C_5Me_5)_3Sm$ (0.400 g, 50%). Further $(C_5Me_5)_3Sm$ can be recovered from the hexane extract by removal of solvent followed by sublimation, which yields $(C_5Me_5)Sm(C_8H_8)$[12] as an orange sublimate and $(C_5Me_5)_3Sm$ as a brown residue.

$(C_5Me_5)_3Sm$ from $(C_5Me_5)_2Pb$. In a THF-free glovebox, separate Schlenk flasks were charged with $(C_5Me_5)_2Sm(OEt_2)$ (1.05 g, 1.85 mmol) and $(C_5Me_5)_2Pb$ (0.420 g, 0.880 mmol) each in toluene (5 mL). The flasks were attached to a Schlenk manifold outside the glovebox, and the $(C_5Me_5)_2Pb$ solution was added via cannula to the $(C_5Me_5)_2Sm(OEt_2)$ solution. The reaction flask was immediately wrapped in aluminum foil, and the reaction was stirred for 20 h. The solvent was removed under vacuum, and the brown residue was transferred to a THF-free glovebox. Dissolution of the residue in toluene (10 mL), centrifugation to remove Pb, and removal of the solvent under vacuum gave a dark brown powder which was identified as $(C_5Me_5)_3Sm$ (0.980 g, 96%) by ^1H and ^{13}C NMR spectroscopy. Magnetic susceptibility: $\chi_M^{293K} = 5360 \times 10^{-6}$ (cgs); $\mu_{eff} = 1.13$ μ_B.

$(C_5Me_4Et)_3Sm$ from $(C_5Me_4Et)_2Pb$. Following the above procedure, $(C_5Me_4Et)_2Sm(OEt_2)$ (0.200 g, 0.383 mmol) and $(C_5Me_4Et)_2Pb$ (0.084 g, 0.17 mmol) were combined in toluene (10 mL). After 20 h, $(C_5Me_4Et)_3Sm$ (0.210 g, 92%) was isolated as above as a dark brown powder. Anal. Calcd for $C_{33}H_{51}Sm$: C, 66.27; H, 8.59; Sm, 25.14. Found: C, 65.41; H, 8.46; Sm, 25.40. ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 0.34 (s, 2 H, $C_5Me_4C\mathit{H}_2CH_3$), 0.13 (s, 6 H, $C_5\mathit{Me}_4CH_2CH_3$), −1.37 (s, 6 H, $C_5\mathit{Me}_4CH_2CH_3$), −7.30 (s, 3 H, $C_5Me_4CH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 122.1, 113.2, 112.1 ($\mathit{C}_5Me_4CH_2CH_3$); 31.0 ($C_5\mathit{Me}_4CH_2CH_3$), 29.6 ($C_5Me_4\mathit{C}H_2CH_3$), 26.9 ($C_5\mathit{Me}_4CH_2CH_3$), 1.0 ($C_5Me_4CH_2\mathit{C}H_3$). Magnetic susceptibility: $\chi_M^{293K} = 5190 \times 10^{-6}$ (cgs); $\mu_{eff} = 1.11$ μ_B.

Table 1. Experimental Data for the X-ray Diffraction Study of $(C_5Me_4Et)_3Sm$, 1

formula	$C_{33}H_{51}Sm$
fw	598.13
temp (K)	163
cryst system	triclinic
space group	$P\bar{1}$
a (Å)	9.9610(8)
b (Å)	10.0250(10)
c (Å)	16.239(2)
α (deg)	90.329(7)
β (deg)	90.271(11)
γ (deg)	118.964(8)
V (Å^3)	1418.7(2)
Z	2
D_{calcd} (Mg/m^3)	1.40
diffractometer	Siemens P4
radiation:	Mo Kα ($\lambda = 0.7107$ 30 Å)
monochromator	highly oriented graphite
data collected	$+h,\pm k,\pm l$
scan type	$\theta - 2\theta$
scan range (deg)	1.20 plus Kα separation
scan speed (deg min^{-1}; in ω)	3.0
2θ range (deg)	4.0−45.0
μ(Mo Kα) (mm^{-1})	2.088
abs corr	semiempirical (ψ-scan method)
reflcns collected	4483
reflcns with $\lvert F_o\rvert > 6.0\sigma(\lvert F_o\rvert)$	3614
no. of variables	143
R_F (%)	5.6
R_{wF} (%)	8.5
goodness of fit:	5.48

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_4Et)_3Sm$. An orange crystal of approximate dimensions 0.26 × 0.30 × 0.33 mm was oil-mounted[13] on a glass fiber, and intensity data were collected under the conditions given in Table 1. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard techniques.[14] All 4483 data were corrected for absorption[15] and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $\lvert F_o\rvert = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ (C_1^1; No. 1) or the centrosymmetric $\bar{P}1$ (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[16] or the SHELXTL PLUS program set.[17] The analytical scattering factors[18] for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where $w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0001(\lvert F_o\rvert)^2$. The structure was solved by direct methods (SHELXTL) 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) = 0.06 Å^2. Anisotropic refinement of the carbon atoms resulted in non-positive-definite thermal parameters for atoms C(25)

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[12] The unsolvated $(C_5Me_5)Sm(C_8H_8)$ can be recovered from the hexane extract and is a useful compound with a rich chemistry of its own: Evans, W. J.; Forrestal, K. J. Unpublished results.

[13] 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. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series No. 357; American Chemical Society: Washington, DC, 1987.

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and C(27). No clear reason for this phenomenon could be determined. It was decided to complete the refinement using isotropic thermal parameters for all carbon atoms. A final difference-Fourier map yielded $\rho(\max) = 1.98$ e Å^{-3}, at a distance of 1.02 Å from the samarium atom.

Results and Discussion

Syntheses of $(C_5Me_5)_3Sm$ Involving THF. Since the discovery of the existence of $(C_5Me_5)_3Sm$ according to eq 1,[4] several attempts were made to synthesize related species.[5-7] A major difficulty in the development of new routes to $(C_5Me_5)_3Sm$ and related compounds is that $(C_5Me_5)_3Sm$ reacts with THF to form the ring-opened product, $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$, according to eq 2. This product was originally identified

$$(C_5Me_5)_3Sm + 2THF \xrightarrow{\text{toluene}} (C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF) \quad (2)$$

from the reaction of KC_5Me_5 with the cation $[(C_5Me_5)_2Sm(THF)_2]^+$, eq 3, a reaction which could have formed

$$[(C_5Me_5)_2Sm(THF)_2]BPh_4 + KC_5Me_5 \xrightarrow{\text{THF}} (C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF) + KBPh_4 \quad (3)$$

$(C_5Me_5)_3Sm$. The generality of this ring-opening reaction has been demonstrated by Schumann et al.,[19] who have found that the reaction of $LnCl_3$ with 3 equiv of NaC_5Me_5, another reaction which could have given $(C_5Me_5)_3Ln$, gives only the ring-opened products, eq 4. It

$$LnCl_3 + 3NaC_5Me_5 \xrightarrow{\text{THF}} (C_5Me_5)_2Ln[O(CH_2)_4C_5Me_5](THF) + 3NaCl \quad (4)$$

$$Ln = La, Nd, Tm, Lu$$

was postulated that the intermediate formed in eq 4, $(C_5Me_5)_2LnCl(THF)$, loses chloride to form $[(C_5Me_5)_2Ln(THF)]^+$, which is attacked by the $C_5Me_5^-$ anion as described above in eq 3. If reaction 4 *did* form any $(C_5Me_5)_3Ln$ products, these also could react with THF to form the observed $(C_5Me_5)_2Ln[O(CH_2)_4C_5Me_5](THF)$ according to eq 2 (see above). This route to the observed products would not require the formation of the cationic intermediate in toluene solution.

The reactivity of $(C_5Me_5)_3Sm$ with THF precludes the use of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm(THF)$ as starting materials. Since these compounds are precursors to the original starting material, $(C_5Me_5)_2Sm$, they would be more desirable. Edelmann et al.[20] have examined the reactions of 1 equiv of COT with 1 and 2 equiv of $(C_5Me_5)_2Sm(THF)_2$ over a period of 12 h but obtained only the previously known $(C_5Me_5)Sm(C_8H_8)(THF)$[21] and the oxidatively coupled dimer $(C_5Me_5)_2$.[22] We have examined the reaction of $(C_5Me_5)_2Sm(THF)_2$ with COT at short reaction times (15 min) and find not only $(C_5Me_5)Sm(C_8H_8)(THF)$ and $(C_5Me_5)_2$ but also NMR signals for $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ and $(C_5Me_5)_3Sm$, eq 5. Since the peaks for

$$2(C_5Me_5)_2Sm(THF)_2 + C_8H_8 \xrightarrow{\text{toluene}} (C_5Me_5)Sm(C_8H_8)(THF) + (C_5Me_5)_2 + (C_5Me_5)_3Sm + (C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF) \quad (5)$$

the $[O(CH_2)_4C_5Me_5]$ ligand in $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ overlap with those of $(C_5Me_5)_2$, it is difficult to quantify the results. The observation that $(C_5Me_5)_3Sm$ forms in this reaction in small quantities indicates that $(C_5Me_5)_2Sm(THF)_2$ does react as shown in eq 1. However, in the presence of as little as 2 equiv of THF, further reaction occurs to give $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ as is found in the reaction of $(C_5Me_5)_3Sm$ with bulk THF. It is likely that several reaction pathways are traversed in the $(C_5Me_5)_2Sm(THF)_2$/COT reaction system including the formation of $(C_5Me_5)_3Sm$ and reaction 2. In any case, this is not a useful synthesis of $(C_5Me_5)_3Sm$.

THF-Free Syntheses of $(C_5Me_5)_3Sm$. One option for a THF-free synthesis of $(C_5Me_5)_3Ln$ complexes involves the deprotonation of C_5Me_5H by precursors of general formula $(C_5Me_5)_2SmZ$ (Z = alkyl, aryl, amide, hydride) as shown in eq 6. Although these precursors

$$(C_5Me_5)_2SmZ + C_5Me_5H \rightarrow (C_5Me_5)_3Sm + HZ \quad (6)$$

$$Z = [CH(SiMe_3)_2], [N(SiMe_3)_2], Ph, H$$

require more steps to prepare than $(C_5Me_5)_2Sm$, they are available across the lanthanide series and could allow synthesis of a wider range of $(C_5Me_5)_3Ln$ species. Unfortunately, $(C_5Me_5)_3Sm$ was not obtained from the reaction of C_5Me_5H with $(C_5Me_5)_2Sm[N(SiMe_3)_2]$ in ether or toluene, with $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ in benzene or toluene, with $(C_5Me_5)_2SmPh$ in benzene, nor with $[(C_5Me_5)_2SmH]_2$ or $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}C_5Me_4CH_2)Sm(C_5Me_5)$[23] in hexane. Since these complexes all contain anionic ligands sufficiently basic[24] to deprotonate C_5Me_5H, these reactions may fail for steric reasons. The third C_5Me_5H ligand may be sterically prevented from getting close enough to the trivalent $(C_5Me_5)_2SmZ$ species for proton transfer to occur.

Given the failure of these trivalent reagents and the larger, more favorable size of Sm(II) vs Sm(III),[25] options with other divalent samarium precursors were examined. The fact that $(C_5Me_5)_2Sm(THF)_2$ reacts with COT to form detectable amounts of $(C_5Me_5)_3Sm$ suggested that $(C_5Me_5)_2SmL_x$ reagents could be used if the subsequent reaction of $(C_5Me_5)_3Sm$ with L were slow or nonexistent. Accordingly, the diethyl ether adduct, $(C_5Me_5)_2Sm(OEt_2)$, was examined. This material is conveniently prepared from THF-free SmI_2 and KC_5Me_5 in Et_2O in 70% yield.[10] The reaction of the Et_2O adduct with COT provides a successful route to $(C_5Me_5)_3Sm$ as

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shown in eq 7.

$$2(C_5Me_5)_2Sm(Et_2O) + COT \xrightarrow{\text{toluene}} (C_5Me_5)_3Sm + (C_5Me_5)Sm(C_8H_8) \quad (7)$$

$(C_5Me_5)_3Sm$ can be isolated in 50% yield after extraction of $(C_5Me_5)Sm(C_8H_8)^{12}$ from the crude reaction mixture with cold hexane. The success of this transformation is critically dependent upon the absence of THF. It is imperative that all manipulations, including the synthesis of the starting material $(C_5Me_5)_2Sm(OEt_2)$, be performed in a THF-free environment. For example, when this reaction was conducted in a glovebox containing THF vapor, only the ring-opened product $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ was obtained.

Although reaction 7 provided an improved route to $(C_5Me_5)_3Sm$, the reaction was still inefficient in that the $(C_5Me_5)_2Sm(C_8H_8)$ byproduct was formed stoichiometrically. A better route to $(C_5Me_5)_3Sm$ was developed by reacting $(C_5Me_5)_2Sm(OEt_2)$ with $(C_5Me_5)_2Pb$ as shown in eq 8. $(C_5Me_5)_2Sm(OEt_2)$ readily reduces $(C_5Me_5)_2Pb$

$$2(C_5Me_5)_2Sm(OEt_2) + (C_5Me_5)_2Pb \xrightarrow{\text{toluene}} 2(C_5Me_5)_3Sm + Pb \quad (8)$$

quantitatively to form elemental lead which is easily removed by centrifugation. $(C_5Me_5)_3Sm$ is obtained in >90% yield by evaporation of the reaction solvent. This constitutes the preferred method to make $(C_5Me_5)_3Sm$.

The method of reaction 8 was subsequently extended to include a more highly substituted pentaalkylcyclopentadienyl system. Hence, $(C_5Me_4Et)_2Pb$ was prepared and reacted with $(C_5Me_4Et)_2Sm(OEt_2)$ to form $(C_5Me_4Et)_3Sm$ according to eq 9. $(C_5Me_4Et)_3Sm$ was isolable as a dark brown solid.

$$(C_5Me_4Et)_2Sm(OEt_2) + (C_5Me_4Et)_2Pb \rightarrow 2(C_5Me_4Et)_3Sm + Pb \quad (9)$$

Spectroscopic properties for the ethyl derivative are similar to those of $(C_5Me_5)_3Sm$ and other tricyclopentadienyl samarium(III) derivatives in that the ^1H NMR resonances for the ring substituents are shifted to high-field positions. For example, $(C_5Me_5)_3Sm$,[4] $(C_5Me_5)_2Sm(C_5H_5)$,[26] and $[1,3\text{-}C_5H_3(SiMe_3)_2]_3Sm$[27] have ring substituent resonances at $\delta = -1.24$, -1.05, and -1.85 ppm, respectively. These values are atypical compared to most other Sm(III) cyclopentadienyl compounds. $(C_5Me_4Et)_3Sm$ exhibits another unusual feature in that, in addition to resonances at 0.127 and -1.40 ppm for the two sets of ring methyls, it shows an even further upfield resonance at -7.42 ppm for the $-CH_2C\mathit{H}_3$ methyl group. The $CH_2C\mathit{H}_3$ methyl group resonance in the ^{13}C NMR spectrum also occurs at anomalously high field. It is located at 1.0 ppm, approximately 30 ppm more shielded than the resonances for the two pairs of ring methyls in the molecule ($\delta = 31.0$ and 26.9 ppm) or the ring methyls of $(C_5Me_5)_3Sm$ ($\delta = 28.3$ ppm). These unusual resonances are understandable on the basis of the single-crystal X-ray diffraction study described in the next section.

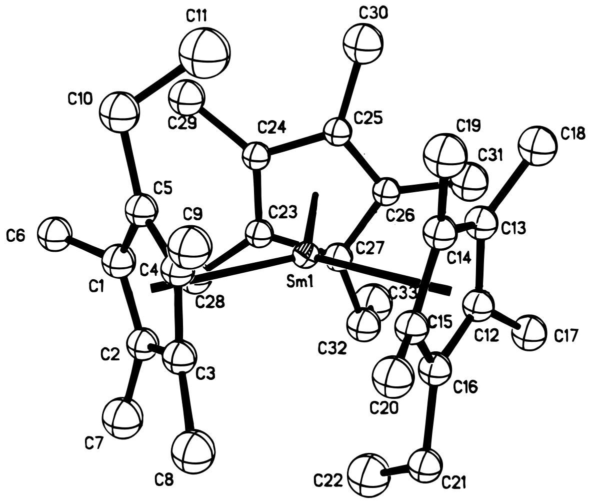

Figure 1. Thermal ellipsoid plot of $(C_5Me_4Et)_3Sm$, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) in $(C_5Me_4Et)_3Sm$

Sm(1)−C(1)	2.900(14)	Sm(1)−C(12)	2.789(14)
Sm(1)−C(2)	2.864(13)	Sm(1)−C(13)	2.843(14)
Sm(1)−C(3)	2.815(12)	Sm(1)−C(14)	2.887(11)
Sm(1)−C(4)	2.787(12)	Sm(1)−C(15)	2.890(10)
Sm(1)−C(5)	2.800(14)	Sm(1)−C(16)	2.792(12)
Sm(1)−C(23)	2.796(9)	Sm(1)···C(11)	3.691(16)
Sm(1)−C(24)	2.812(9)	Sm(1)···C(22)	3.620(13)
Sm(1)−C(25)	2.823(9)	Sm(1)−Cnt(1)	2.568
Sm(1)−C(26)	2.886(10)	Sm(1)−Cnt(2)	2.573
Sm(1)−C(27)	2.829(9)	Sm(1)−Cnt(3)	2.563
Cnt(1)−Sm(1)−Cnt(2)	120.0	Cnt(2)−Sm(1)−Cnt(3)	120.1
Cnt(1)−Sm(1)−Cnt(3)	119.9		

Structure of $(C_5Me_4Et)_3Sm$. The structure of $(C_5Me_4Et)_3Sm$, Figure 1, is similar to that of $(C_5Me_5)_3Sm$. In both complexes, the three cyclopentadienyl ring centroids describe a trigonal planar geometry around the samarium. The crystallographically imposed 3-fold symmetry found in $(C_5Me_5)_3Sm$ requires 120° centroid−Sm−centroid angles. $(C_5Me_4Et)_3Sm$ has lower symmetry due to the variation in the positions of the ethyl groups, but the centroid−Sm−centroid angles are still very similar: 120.0, 119.9, and 120.1°. Like $(C_5Me_5)_3Sm$, $(C_5Me_4Et)_3Sm$ has extremely large Sm−C(ring carbon) distances. The 2.834 Å average Sm−C(C_5Me_4Et) distance is the largest observed to date in a $Sm^{III}C_5R_5$ complex, and the 2.900(14) Å Sm−C(1) bond length is equivalent within error limits to the longest Sm−C(ring carbon) distance in $(C_5Me_5)_3Sm$, 2.910(3) Å. In each ring, the two shortest Sm−C distances are adjacent and one of the longest distances involves the carbon atom across the ring from this pair. As with $(C_5Me_5)_3Sm$, maximum use of the flexibility of C_5R_5 rings is made in adopting an arrangement which minimizes steric demands of these bulky ligands. Each ring is tipped away from the Sm such that the Sm-(ring centroid)-(ring carbon) angles (92.6−93.8°) associated with ring carbons farthest from the metal center all exceed the idealized 90° value. Additionally, the ring substituent carbons are each located from 0.076 Å (C(21)) to 0.507 Å (C(6)) out of the plane of the ring carbons and bend back away from the center of the molecule. The methylene carbons C(10) and C(21) are minimally displaced from the ring planes (0.109 and

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(26) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292−4297.

(27) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *J. Organomet. Chem.* **1990**, *394*, 87−97.

0.076 Å, respectively) and are thus distinguished from the ring methyls and from the other methylene C(32) (*vide infra*). No regular pattern exists between the location of the ethyl substituent and the Sm−C distance of the carbon to which it is attached.

The three ethyl groups divide into two types depending on their orientation with respect to the metal. The group comprised of carbon atoms C(32)−C(33) points away from the metal outside the cavity formed by the three cyclopentadienyl rings, whereas the C(10)−C(11) and C(21)−C(22) ethyl groups point inward. The closest Sm−C distance in these ethyl groups involves C(22) at a distance of 3.620(13) Å. The location of two ethyl groups oriented toward the metal is likely to be responsible for the high-field shifts observed in the ^{1}H and ^{13}C NMR spectra. A similar situation was observed in $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}Ph(CH_2)_2C{=}C{=}C{=}C(CH_2)_2Ph]$, which has two methylene groups oriented toward the metal at a distance of 3.748 Å and a ^{1}H NMR resonance at $\delta = -12.94$ ppm.[28] With respect to the ^{1}H NMR spectrum, the nonequivalence of ethyl groups in the solid state is not preserved in solution and the exchange process could not be stopped at −80 °C.

Conclusion

The reaction of $(C_5R_5)_2Sm(OEt_2)$ with lead cyclopentadienyl reagents, $(C_5R_5)_2Pb$, provides the best synthetic route to date to make tris(pentaalkylcyclopentadienyl) metal complexes. This method has allowed the synthesis of a complex more sterically crowded than $(C_5Me_5)_3Sm$ which shows that the limits of steric saturation of tris(pentaalkylcyclopentadienyl) complexes had not yet been reached. The isolation of $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ from the reaction of $(C_5Me_5)_2Sm(THF)_2$ with COT and the fact that $(C_5Me_5)_3Sm$ reacts with THF to make $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ suggests that complexes of general formula $(C_5Me_5)_3M$ may form in other systems, but they have not been isolated due to their high THF ring-opening activity. Since, even in the absence of THF, trivalent samarium precursors have not led to $(C_5Me_5)_3Sm$ and given that all currently known syntheses of $(C_5R_5)_3Sm$ compounds employ *divalent* precursors, a key factor in these syntheses may be the more favorable steric access in the larger divalent precursors.

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 (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM950779Z

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[28] Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics*, **1993**, *12*, 2618−2633.