APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 437–447 (1995)

The Reactivity of Samarium(II) in a Bis(indenyl) Coordination Environment

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The reactivity of the organosamarium(II) indenyl complex $(C_9H_7)_2Sm(THF)_x$, 1, has been compared with that of $(C_5Me_5)_2Sm(THF)_2$, 2, and $(C_5Me_5)_2Sm$, 3, by examination of characteristic organosamarium(II) reactions which form trivalent oxide, iodide, cyclo-octatetraenyl and azobenzene complexes. Complex 1 reacts with excess N_2O to form $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, 4, and $(C_9H_7)_3Sm(THF)$, 5, as the major products. Two equivalents of 1 react with one equivalent of 1,2-di-iodoethane in THF to give $(C_9H_7)SmI_2(THF)_2$, 6, as well as 5. Complex 1 reacts with 1,3,5,7-cyclo-octatetraene in a 2:1 ratio in THF to form 5 and $(C_9H_7)Sm(C_8H_8)(THF)_x$, 7, which has been fully characterized as the 2,2′-bipyridine adduct $(C_9H_7)Sm(C_8H_8)(C_{10}H_8N_2)$, 7a. The reaction of 1 with azobenzene in a 2:1 ratio forms $[(C_9H_7)Sm(N_2Ph_2)(THF)]_x$, 8, and 5. Complexes 4–6 and 7a have been definitively identified by X-ray crystallography.

Complex 4 crystallizes from THF in space group $P\bar{1}$ [C_i^1; No. 2] with unit cell parameters at 163 K of $a=8.072(2)$ Å, $b=9.502(2)$ Å, $c=12.250(3)$ Å, $\alpha=101.42(2)°$, $\beta=90.71(2)°$, $\gamma=102.50(2)°$, $V=897.7(4)$ Å^3 and $Z=1$ for $D_{calcd}=1.704$ Mg m^{-3}. Least-squares refinement of the model based on 3924 reflections ($|F_0|>3.0\,\sigma\,(|F_0|)$) converged to a final $R_F=2.4\%$. The geometry around each Sm atom is a distorted tetrahedron and the Sm–O–Sm angle is 180°.

Complex 5 crystallizes from THF/hexanes at −35 °C in space group $P6_3$ [C_6^6; No. 173] with unit cell parameters at 163 K of $a=11.7370(14)$ Å, $c=10.1994(12)$ Å, $V=1216.8(3)$ Å^3 and $Z=2$ for $D_{calcd}=1.550$ Mg m^{-3}. Least-squares refinement of the model based on 976 reflections ($|F_0|>3.0\sigma\,(|F_o|)$ converged to a final $R_F=2.3\%$. The three ring centroids and the THF oxygen atom define a distorted tetrahedron around samarium with a (ring centroid)–Sm–(ring centroid) angle of 116.0°.

Complex 6 crystallizes from THF/hexanes as the trisolvate $(C_9H_7)SmI_2(THF)_3$, 6a, in space group $P2_1/n$ [C_{2h}^5; No. 14] with unit cell parameters at 163 K of $a=8.3969(12)$ Å, $b=17.165(5)$ Å, $c=33.592(7)$ Å, $\beta=96.468(15)°$, $V=4811(2)$ Å^3 and $Z=8$ for $D_{calcd}=2.031$ Mg m^{-3}. Least-squares refinement of the model based on 5664 reflections ($|F_0|>2.0\,\sigma\,(|F_0|)$) converged to a final $R_F=3.3\%$. The six ligands around Sm in 6a describe a distorted octahedron. The iodide ligands are *trans* to each other with a 153.8(1)° I–Sm–I angle.

Adduct 7a crystallizes from hot THF/toluene in space group $P\bar{1}$ [C_i^1; No. 2] with a unit cell parameters at 163 K of $a=7.886(7)$ Å, $b=16.72(2)$ Å, $c=17.48(2)$ Å, $\alpha=62.96(7)°$, $\beta=85.17(7)°$, $\gamma=85.23(9)°$, $V=2042(3)$ Å^3 and $Z=4$. The cyclo-octateraenyl and indenyl ligands generate a bent metallocene structure for 7a which contains a chelating bipyridyl group in the plane bisecting the two rings.

Keywords: samarium; indenyl; organometallic reactivity; metallocene

INTRODUCTION

In recent years, the potential of lanthanide metal complexes as reagents in organic synthesis has been explored.[1,2] The special properties of samarium (II)[3] [Sm(II)] have been found to be useful in accomplishing a variety of synthetic organic transformations and $SmI_2(THF)_2$ is now used extensively for this purpose.[1,2] Although other soluble Sm(II) complexes such as the pentamethylcyclopentadienyl complexes, $(C_5Me_5)_2Sm(THF)_2$, 2,[4] and $(C_5Me_5)_2Sm$, 3,[5] have also been shown to generate unusual organometallic chemistry,[3,6,7] they have been employed less frequently in organic synthesis, perhaps due to the expense of the C_5Me_5 ligand.

In efforts to expand the number of readily available soluble organosamarium(II) reagents which could be useful in organic reactions, we have recently described the synthesis of the bis(indenyl)samarium(II) complex, $(C_9H_7)_2Sm(THF)_x$, 1,[8] ($x=1$–3 depending on isolation conditions). This soluble complex can be made in high yield

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CCC 0268-2605/95/050437-11

Received 8 July 1994
Accepted 30 July 1994

from $SmI_2(THF)_2$ and inexpensive KC_9H_7. The indenyl moiety provides a ligand environment for Sm(II) alternative to that found in either $SmI_2(THF)_2$ or the $(C_5Me_5)_2Sm(THF)_x$ complexes ($x = 0–2$). For example, since single crystals of $(C_9H_7)_2Sm(THF)_x$ were isolated in which $x = 3$,[8] it appears that the two indenyl ligands could provide a more open coordination environment than the $(C_5Me_5)_2Sm$ unit which commonly adds just two additional ligands.[3,5,9] The coordination environment in **1** is also very different from that found in SmI_2 derivatives.[10]

Since steric factors are so important in organolanthanide chemistry,[3,11,12] the reactivity of Sm(II) in different coordination environments is of interest. In this report, we examine the reactivity of $(C_9H_7)_2Sm(THF)_x$ with a variety of substrates which have been shown to give well-defined products with bis(pentamethylcyclopentadienyl) organosamarium(II) complexes. This allows direct comparison of these soluble organometallic Sm(II) reagents.

EXPERIMENTAL

The reactions described below were conducted under nitrogen with rigorous exclusion of air and water using standard Schlenk, high-vacuum or glovebox techniques.

Physical measurements

^1H and ^{13}C NMR spectra were obtained on either GN 500 MHz, Ω 500 MHz or QE 300 MHz NMR spectrometers. DEPT (Distortionless Enhancement by Polarization Transfer) experiments[13] were obtained on a GN 500 MHz spectrometer. Chemical shifts were assigned relative to residual protons in THF-d_8 and C_6D_6. Infrared spectra were recorded on a Perkin–Elmer 283 Fourier transform infrared spectrometer. Complete elemental analyses were obtained from Analytische Laboratorien, Gummersbach, Germany. Complexometric metal analyses were conducted as previously described.[14]

Materials

Tetrahydrofuran (THF), toluene and hexane were distilled from solutions of sodium benzophenone ketyl. THF-d_8 and C_6D_6 were dried over potassium, and sodium benzophenone ketyl, respectively, and vacuum-distilled prior to use. $SmCl_3$ (Rhône Poulenc) was dried as previously described.[15] $(C_9H_7)_2Sm(THF)_x$ and KC_9H_7 were prepared as previously described.[8] $SmI_3(THF)_x$ was prepared by reacting two equivalents of $SmI_2(THF)_2$ with one equivalent of 1,2-di-iodoethane. 1,2-Di-iodethane (Aldrich) was purified by extraction with a 0.1 M aqueous solution of sodium thiosulfate. Nitrous oxide (Aldrich) was used as received. 2,2′-Bipyridine (Aldrich) and azobenzene (Aldrich) were dried under high vacuum prior to use. 1,3,5,7-Cyclo-octatetraene (Aldrich) was dried over molecular sieves and vacuum-distilled prior to use.

Note: The degree of solvation of the bulk samples of $(C_9H_7)_2Sm(THF)_x$ and $SmI_3(THF)_x$ depends on the duration of drying on the rotary evaporator. The molecular weight is determined by complexometric titration of the bulk sample.

Reaction of 1 with N_2O

Under nitrogen, $(C_9H_7)_2Sm(THF)_x$ (148 mg, 0.30 mmol) was dissolved in 10 ml of THF in a 30 ml tube equipped with a greaseless stopcock. The system was degassed and stirred under 1 atm of N_2O. After 10 min the reaction mixture turned orange and evolved gas. When gas evolution had ceased, the solvent was removed under reduced pressure. The resulting orange solid was extracted with toluene to give a red solution and a yellow solid. Removal of the toluene by rotary evaporation gave a red solid in which the major component was identified as $(C_9H_7)_3Sm(THF)$, **5**, by comparison of its ^1H NMR spectrum with an independently prepared sample (see below). The yellow solid (67 mg, 50% yield) was recrystallized and identified by X-ray crystallography as $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, **4**. ^1H NMR (THF-d_8): δ 10.03 (s, 2H, η^5-C_9H_7), 8.03 (d, $J = 4$ Hz, 2H, arene C_9H_7), 7.77 (s, 1H, η^5-C_9H_7), 6.81 (d, $J = 5$ Hz, 2H, arene C_9H_7). ^{13}C NMR (THF-d_8): δ 129.72, 126.02, 121.09, 119.61, 90.20. IR (KBr) (cm^{-1}): 3063 w, 3030 w, 2976 w, 2889 w, 1453 w, 1327 m, 1218 w, 1017 m, 864 m, 761 vs, 641 s. Analysis: calcd for $Sm_2C_{44}H_{44}O_3$: Sm, 32.63. Found: Sm 33.4%. X-ray quality crystals of **4** were grown from THF at −35 °C.

Reaction of 1 with 1,2-di-iodoethane

In a glovebox, ICH_2CH_2I (130 mg, 0.461 mmol) in 5 ml of THF was added to $(C_9H_7)_2Sm(THF)_x$ (408 mg, 0.828 mmol) in 5 ml of THF. The mixture immediately turned red and a gas evolved. After 15 min, the solvent was removed by rotary evaporation yielding a red solid that contained three products by ^1H NMR spectroscopy. Two of the products were identified as $(C_9H_7)_3Sm(THF)$, **5**, and $(C_9H_7)SmI_2(THF)_2$, **6**, by comparison with ^1H NMR spectra of the independently prepared samples (see below). Three of the resonances of the third product could be identified. ^1H NMR (THF-d_8) (third product): δ 12.91 (s, 2H, C_9H_7), 10.40 (s, 1H, η^5-C_9H_7), 6.04 (s, 2H, C_9H_7). Recrystallization of the mixture of products by diffusing hexanes into THF at −35 °C over a period of one week gave X-ray quality crystals of the trisolvated species $(C_9H_7)SmI_2(THF)_3$, **6a**.

Preparation of $(C_9H_7)_3Sm(THF)$,[16] 5

In a glovebox, $SmCl_3$ (150 mg, 0.584 mmol) and KC_9H_7 (271 mg, 1.76 mmol) were placed in a vial and 10 ml of THF was added. The reaction mixture immediately turned cloudy red. After the reaction was stirred overnight, a green insoluble material was removed by centrifugation and a red solution remained. The solvent was removed by rotary evaporation to yield a red solid identified as $(C_9H_7)_3Sm(THF)$ (284 mg, 86% yield). ^1H NMR (THF-d_8): δ 10.85 ($\Delta\nu_{1/2}=50$ Hz, 2H, η^5-C_9H_7), 9.5 ($\Delta\nu_{1/2}=45$ Hz, 1H, η^5-C_9H_7) 7.57 (s, 2H, arene C_9H_7), 7.21 (s, 2H, arene C_9H_7). ^{13}C NMR (THF-d_8): δ 132.72, 127.01, 124.03, 119.40, 81.98. IR (KBr) (cm^{-1}): 3030 m, 2976 m, 2878 w, 1447 w, 1327 s, 1218 m, 1033 m, 1006 m, 859 m, 761 vs. Analysis: calcd for $SmOC_{31}H_{29}$: Sm, 26.48; C, 65.56; H, 5.15. Found: Sm, 26.25; C, 65.31; H, 5.10%. Complexometric analysis: found: Sm, 25.8%. X-ray quality crystals were grown by dissolving $(C_9H_7)_3Sm(THF)$ and diffusing in hexanes at −35 °C.

$(C_9H_7)_3Sm(THF)$ has previously been prepared by a similar method; however, the ^1H NMR data reported were for that of the protonated ligand C_9H_8.

Preparation of $(C_9H_7)SmI_2(THF)_2$, 6

In a glovebox, $SmI_3(THF)_x$ (149 mg, 0.191 mmol) and KC_9H_7 (30 mg, 0.194 mmol) were placed in a vial with 10 ml of THF. The reaction mixture immediately turned pink. After stirring overnight, the cloudy pink solution was centrifuged to yield a white solid and a pink solution. The solution was decanted and the solvent was removed by rotary evaporation yielding **6** as a pink solid (125 mg, 98% yield). ^1H NMR (THF-d_8): δ 13.64 (s, 2H, C_9H_7), 11.38 (s, 1H, η^5-C_9H_7), 7.04 (d, $J=4$ Hz, 2H, arene C_9H_7), 5.72 (d, $J=5$ Hz, 2H, C_9H_7). ^{13}C NMR (THF-d_8): δ 128.53, 126.43 (quaternary carbons by DEPT), 125.14, 118.15, 95.16. IR (KBr) (cm^{-1}) 2970 s, 2892 s, 1449 m, 1336 m, 1252 w, 1213 w, 1178 w, 1006 vs, 917 w, 852 vs, 774 vs. Analysis: calcd for $SmO_2C_{17}H_{23}I_2$: Sm, 22.66; C, 30.77; H, 3.49; I, 38.25. Found: Sm, 22.40; C, 30.90; H, 3.68; I, 38.02%.

Reaction of 1 with 1,3,5,7-cyclo-octatetraene

In a glovebox, 1,3,5,7-cyclo-octatetraene (33 mg, 0.31 mmol) in 2 ml of THF was added to a stirred solution of $(C_9H_7)_2Sm(THF)_x$ (289 mg, 0.60 mmol) dissolved in 5 ml of THF. The black solution immediately turned dark red. After stirring for 5 min, the solvent was removed by rotary evaporation to give a sticky, dark red solid. After recrystallization by diffusing hexanes into a concentrated solution in THF, two products were observed by ^1H NMR spectroscopy, the previously identified $(C_9H_7)_3Sm(THF)$, **5**, and $(C_9H_7)Sm(C_8H_8)(THF)_x$, **7**. ^1H NMR of **7** (THF-d_8): δ 11.21 (s, 8H, C_8H_8), 8.70 (s, 2H, η^5-C_9H_7), 8.32 (d, $J=6$ Hz, 2H, arene C_9H_7), 7.38 (d, $J=4$ Hz, 2H, arene C_9H_7), 2.7 (s, 1H, η^5-C_9H_7).

Complex **7** was separated from **5** by warming the mixture in toluene and adding 2,2′-bipyridine, followed by THF until all solids were in solution. Upon slow cooling to ambient temperature followed by slow evaporation, X-ray quality crystals of $(C_9H_7)Sm(C_8H_8)(N_2C_{10}H_8)$, **7a**, were formed. ^1H NMR (THF-d_8): δ 12.58 (s, 1H, η^5-C_9H_7), 11.96 (s, 8H, C_8H_8), 11.88 (s, 2H, C_9H_7), 9.44 (d, $J=8$ Hz, 2H, $C_{10}H_8N_2$), 8.52 (t, $J=8$ Hz, 2H, $C_{10}H_8N_2$), 7.47 (t, $J=5$ Hz, 2H, $C_{10}H_8N_2$), 7.01 (s, 2H, C_9H_7), 5.01 (s, 2H, $C_{10}H_8N_2$), 4.92 (s, 2H, C_9H_7). ^{13}C NMR (THF-d_8): δ 167, 163.0, 142.7, 125.3, 122.0, 119.7, 116, 115.3, 80, 74.7, 40. Analysis: calcd for $SmC_{27}H_{23}N_2$: Sm, 28.59. Found: Sm, 29.3%.

Reaction of 1 with azobenzene

In a glovebox, azobenzene (91 mg, 0.499 mmol) in 10 ml of THF was added to $(C_9H_7)_2Sm(THF)_x$ (494 mg, 1.00 mmol) in 35 ml of THF while stirring. The reaction mixture immediately turned red. After stirring for 30 min, the mixture was

Table 1 Crystallographic data for **4–6a**

	Complex		
	4	**5**	**6a**
Formula	$C_{44}H_{44}O_3Sm_2$	$C_{31}H_{29}OSm$	$C_{21}H_{31}O_3I_2Sm$
Mol. wt	921.5	567.9	735.6
Crystal system	Triclinic	Hexagonal	Monoclinic
Space group	$P\bar{1}$; [C_i^1; No. 2]	$P6_3$; [C_6^6; No. 173]	$P2_1/n$; [C_{2h}^5; No. 14]
Cell constants			
a (Å)	8.072(2)	11.7370(14)	8.3969(12)
b (Å)	9.502(2)		17.165(5)
c (Å)	12.250(3)	10.1994(12)	33.592(7)
α (°)	101.42(2)		
β (°)	90.71(2)		96.468(15)
γ (°)	102.50(2)		
Cell volume (Å^3)	897.7(4)	1216.8(3)	4811(2)
Z	1	2	8
D_{calcd} (Mg m^{-3})	1.704	1.550	2.031
Temp (K)	163	163	163
μ_{calcd} (mm^{-1})	3.289	2.441	5.007
R_F (%)	2.4	2.3	3.3
R_{wF} (%)	2.6	3.1	3.7
GOF	1.41	1.23	1.10

Radiation was Mo Kα; $\lambda = 0.710730$ Å.

centrifuged to give a red solution and an orange solid (169 mg, 30% yield) which had an elemental composition consistent with the formula $[(C_9H_7)Sm(N_2(C_6H_5)_2)(THF)]_x$, **8**. The solution was decanted and the solvent was removed by rotary evaporation yielding a red solid (390 mg, 68% yield) which was identified as $(C_9H_7)_3Sm(THF)$, **5**, by comparison of its ^1H NMR spectrum with an independently prepared sample (see above). Analysis: calcd for $SmC_{25}H_{25}N_2O$: C, 57.76; H 4.85; N, 5.39; Sm, 28.92. Found: C, 57.44; H, 4.70; N, 5.46; Sm, 28.95%. Complexometric analysis: found: Sm, 28.9%. IR (KBr) (cm^{-1}) 3050 w, 2970 w, 2880 w, 1581 s, 1474 vs, 1330 w, 1288 m, 1245 vs, 1160 m, 1074 w, 1016 w, 989 w, 872 m, 802 w, 754 s, 696 m.

X-ray data collection, structure determination, and refinement for 4–6a

Crystals were oil-mounted onto a glass fiber: this was done as follows. Each 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 was attached to an elongated brass mounting-pin. Further details appear in Ref. 17.

The mounted crystals were transferred to the nitrogen stream of either a Syntex $P2_1$ or Siemens P3 diffractometer (R3m/V System) equipped with a modified LT-1 or LT-2 low-temperature system respectively. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (163 K) intensity data were carried out using standard techniques similar to those of Churchill *et al.*[18] Details appear in Table 1.

The crystallographic calculations were carried out using either a locally modified version of the *UCLA Crystallographic Computing Package*[19] or the SHELXTL PLUS program set.[20] The analytical scattering factors for neutral atoms were used throughout the analysis;[21] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The structures were refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C\text{–}H) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2.

$[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, 4

A yellow crystal of approximate dimensions 0.10 mm × 0.23 mm × 0.30 mm was manipulated as described above. All 4452 data were corrected for absorption using the absorption correction program XEMP,[22] and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_0| = 0$. 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 $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice. The quantity minimized during least-squares analysis was $\Sigma w(|F_0| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_0|) + 0.0001(|F_0|)^2$.

The structure was solved via an automatic Patterson routine (SHELXTL PLUS). The molecule is a dimer with O(1) located on an inversion center. Refinement of the model led to convergence with $R_F = 2.4\%$; $R_{wF} = 2.6\%$ and GOF = 1.41 for 311 variables refined against those 3924 data with $|F_0| > 3.0\sigma(|F_0|)$. A final difference-Fourier map yielded $\rho(\max) = 1.31$ e Å^{-3}.

$(C_9H_7)_3Sm(THF)$, 5

An orange/red crystal of approximate dimensions 0.23 mm × 0.24 mm × 0.27 ppm was manipulated as described above. All 3128 data were corrected for absorption (XEMP program)[22] and for Lorentz and polarization effects, merged to yield a unique data set ($R_{\text{int}} = 1.4\%$) and placed on an approximately absolute scale. The diffraction symmetry indicated a hexagonal crystal system with systematic absences for $00l$ where $l = 2n + 1$. The three possible hexagonal space groups are $P6_3$, $P6_3/m$ and $P6_322$. The Z value is 2 and the molecule may have molecular three-fold symmetry if the THF ligand is disordered. The noncentrosymmetric space group $P6_3$ [C_6^6; No. 173] is consistent with $Z = 2$ for the given molecular symmetry and was later determined to be correct by successful solution and refinement of the structure. The quantity minimized during least-squares analysis was $\Sigma w(|F_0| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_0|) + 0.0005(|F_0|)^2$.

The structure was solved by direct methods (SHELXTL). The molecule is located on a site of three-fold symmetry. The THF molecule is disordered and was modeled with site-occupancy factors of 0.40333 for C(10A), 0.26333 for C(10B) and 0.66667 for C(11). Hydrogen atoms associated with the THF ligand were not included. Refinement of positional and thermal parameters led to convergence with $R_F = 2.3\%$; $R_{wF} = 3.1\%$ and GOF = 1.23 for 101 variables refined against those 976 data with $|F_0| > 3.0\sigma(|F_0|)$. A final difference-Fourier map yielded $\rho(\max) = 0.86$ e Å^{-3}. The absolute structure was determined by refinement of the Rogers' η-parameter.[22]

$(C_9H_7)SmI_2(THF)_3$, 6a

A dark red crystal of approximate dimensions 0.40 mm × 0.40 mm × 0.45 mm was manipulated as described above. All 7115 data were corrected for absorption (XEMP program)[22] and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences for $0k0$ where $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ [C_{2h}^5; No. 14], is therefore uniquely defined. The quantity minimized during least-squares analysis was $\Sigma w(|F_0| - F_c|)^2$ where $w^{-1} = \sigma^2(|F_0|) + 0.0001(|F_0|)^2$.

The structure was solved by direct methods (SHELXTL). There are two independent molecules present in the asymmetric unit. Refinement of the positional and thermal parameters led to convergence with $R_F = 3.3\%$; $R_{wF} = 3.7\%$ and GOF = 1.10 for 487 variables refined against those 5664 data with $|F_0| > 2.0\sigma(|F_0|)$. A final difference-Fourier map yielded $\rho(\max) = 0.88$ e Å^{-3}.

RESULTS

Reactivity

Synthesis of $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, 4

One of the more characteristic reactions of $(C_5Me_5)_2Sm(THF)_2$, **2**, is the formation of the oxide, $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$, according to reaction [1]. The oxide can be formed from a variety of sources, such as N_2O and 1,2-epoxybutane; however, 1,2-epoxybutane gives the highest yield.[23] Recently, it has been found that a by-product of these reactions is often the THF solvate $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$, which readily loses THF to form the more commonly observed $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$.[24]

$$\underset{\mathbf{2}}{(C_5Me_5)_2Sm(THF)_2} + N_2O \rightarrow [(C_5Me_5)_2Sm]_2(\mu\text{-}O) \quad [1]$$

The reactivity of $(C_9H_7)_2Sm(THF)_x$, **1**, with N_2O has similarities to that of **2** in that an oxide product is formed. However, in the indenyl case

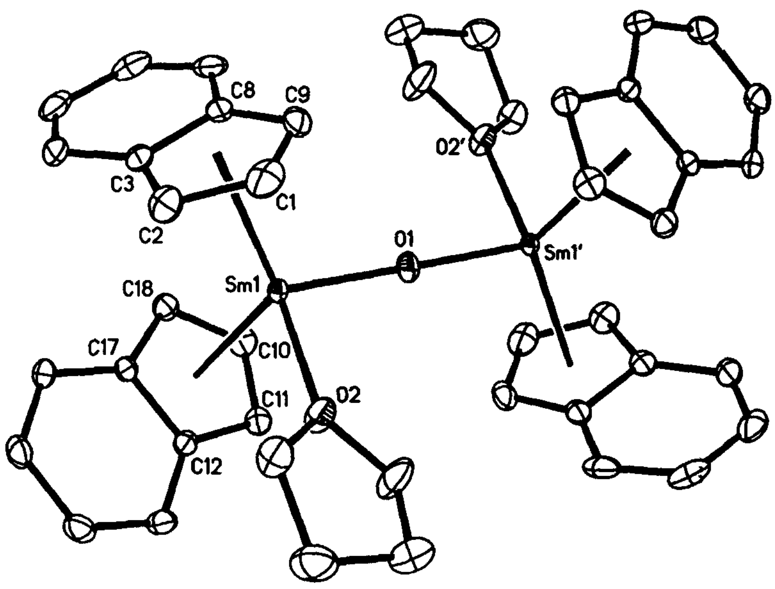

Figure 1 Thermal ellipsoid plot of $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, **4**, with ellipsoids drawn at the 50% probability level.

the primary product is a *solvated* species $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, **4**, and a major by-product is the tris(indenyl) complex $(C_9H_7)_3Sm(THF)$, **5**, reaction [2]. The toluene-soluble **5** was readily separated from the THF-soluble **4** by extraction. Complex **4** was characterized by NMR and IR spectroscopy, and was definitively identified by an X-ray crystallographic study (Fig. 1). Complex **5** was identified by comparing its ^1H NMR spectrum with that of a crystallographically characterized sample (Fig. 2 ; see below).

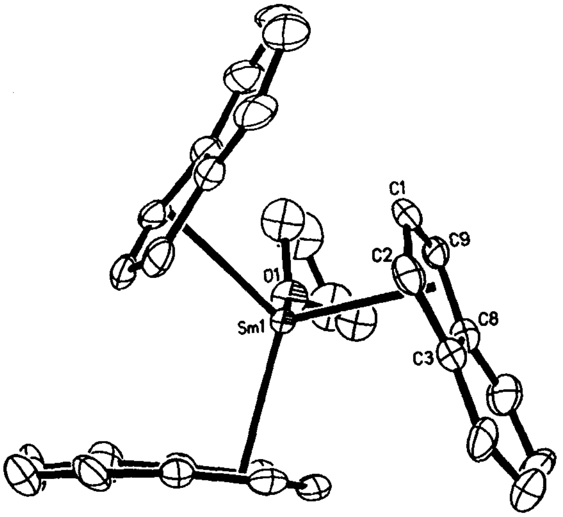

Figure 2 Thermal ellipsoid plot of $(C_9H_7)_3Sm(THF)$, **5**, with ellipsoids drawn at the 50% probability level.

$$\underset{\mathbf{1}}{(C_9H_7)_2Sm(THF)_x} + N_2O \xrightarrow{THF,\ 15\ min} \qquad [2]$$

$$\underset{\mathbf{4}}{[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)} + \underset{\mathbf{5}}{(C_9H_7)_3Sm(THF)}$$

In contrast to the N_2O reaction, when 1,2-epoxybutane is reacted with **1** in attempts to make **4** in higher yield, an unidentifiable mixture of products is obtained. Further differences compared with the C_5Me_5 system were observed in terms of desolvation. Whereas $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$ readily desolvates in arene solution at room temperature and can only be obtained as the oxide is being formed (i.e. $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ does not readily resolvate), **4** does not desolvate under mild conditions.

Reaction of 1 with 1,2-di-iodoethane

$(C_5Me_5)_2Sm(THF)_2$, **2**, reacts with a variety of halide sources to make complexes of general formula $(C_5Me_5)_2SmZ(THF)$ (Z = halide) as exemplified in reaction [3].[25] The reaction of **1** with ICH_2CH_2I forms an iodide product, but in this case a mono-ring diiodide, $(C_9H_7)SmI_2(THF)_2$, **6**, is formed as well as substantial amounts of $(C_9H_7)_3Sm(THF)$, **5**, reaction [4]. A third minor product is consistently formed in this reaction, which may be $(C_9H_7)_2SmI(THF)_x$; however it has not been definitively identified. Reaction [4] is not as straightforward as reaction [3], which forms

$(C_5Me_5)_2SmI(THF)$ in greater than 90% yield. The products of reaction [4] are not readily separated and were identified by comparing their ^1H NMR spectra with samples independently synthesized and crystallographically characterized (see below). Attempts to make $(C_9H_7)_2SmI(THF)_x$ by various routes repeatedly gave mixtures of **5**, **6** and the minor product of reaction [4].

$$\underset{\mathbf{2}}{2(C_5Me_5)_2Sm(THF)_2} + ICH_2CH_2I \xrightarrow{THF,\ 5\ min} 2(C_5Me_5)_2SmI(THF) \quad [3]$$

$$\underset{\mathbf{2}}{2(C_9H_7)_2Sm(THF)_x} + ICH_2CH_2I \xrightarrow{THF,\ 10\ min} \underset{\mathbf{5}}{(C_9H_7)_3Sm(THF)} + \underset{\mathbf{6}}{(C_9H_7)SmI_2(THF)_2} \quad [4]$$

Synthesis of $(C_9H_7)Sm(C_8H_8)(THF)_x$, 7

Since $(C_5Me_5)_2Sm$, **3**, forms disproportionation products involving mono- and tris(cyclopentadienyl) products in its reaction with 1,3,5,7-cyclooctatetraene (reaction [5]),[26] the reaction of **1** with 1,3,5,7-cyclooctatetraene was studied for comparison. As shown in reaction [6], analogous chemistry occurs. Complex **5** was identified by ^1H NMR spectroscopy and $(C_9H_7)Sm(C_8H_8)(THF)_x$, **7**, was separated and identified by making the 2,2′-bipyridine derivative $(C_9H_7)Sm(C_8H_8)(N_2C_{10}H_8)$, **7a**, which was characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography (Fig. 3).

$$\underset{\mathbf{3}}{2(C_5Me_5)_2Sm} + C_8H_8 \xrightarrow{toluene,\ 5\ min} (C_5Me_5)Sm(C_8H_8) + (C_5Me_5)_3Sm \quad [5]$$

$$\underset{\mathbf{1}}{2(C_9H_7)_2Sm(THF)_x} + C_8H_8 \xrightarrow{THF,\ 15\ min} \underset{\mathbf{7}}{(C_9H_7)Sm(C_8H_8)(THF)_x} + \underset{\mathbf{5}}{(C_9H_7)_3Sm(THF)} \quad [6]$$

Reaction of 1 with azobenzene

The reaction of **1** with azobenzene was also investigated since **2** has a rich chemistry with this substrate,[27–29] which has also been used to evaluate other Sm(II) complexes.[30] Complex **2** reacts with azobenzene according to reaction [7] to form

$$\underset{\mathbf{2}}{2(C_5Me_5)_2Sm(THF)_2} + PhN{=}NPh \xrightarrow{toluene,\ 6\ h} [(C_5Me_5)_2Sm]_2(N_2Ph_2) \quad [7]$$

a 2 : 1 samarium–azobenzene product.[28] However, when two equivalents of **1** react with one equivalent of azobenzene, the analogous product is not formed. As shown in reaction [8], the isolated products are the tris(indenyl) compound **5** and the mono(indenyl) compound **8**. The THF-insoluble **8** is easily separated from **5**, which was identified by ^1H NMR spectroscopy. Elemental analysis of **8** is consistent with the formula $[(C_9H_7)Sm(N_2Ph_2)(THF)]_x$ and an absorption at 1581 cm^{-1} in the IR spectrum is in the range in which azobenzene N–N stretching absorptions are found. In symmetrical azobenzenes, the N–N stretching absorption at 1580 cm^{-1} is Raman-, not IR-active.[31] These data plus the mass balance of the indenyl groups in the products suggest that **8** is an indenyl analog of the mono(ring) C_5Me_5 complex, $[(C_5Me_5)Sm(THF)]_2[\mu\text{-}\eta^2:\eta^2\text{-}N_2Ph_2]_2$, which has

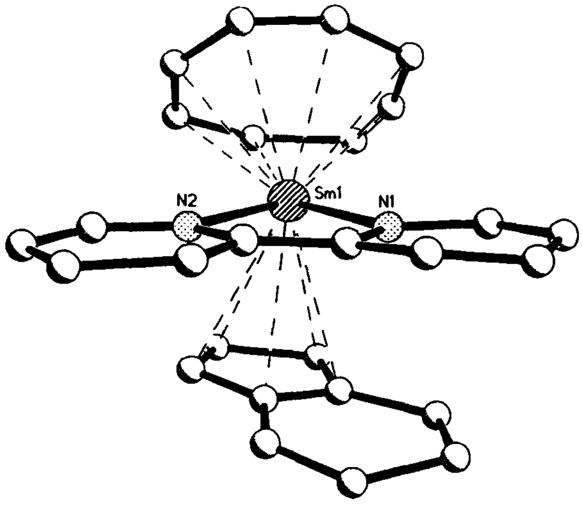

Figure 3 Ball and stick plot of $(C_9H_7)Sm(C_8H_8)(N_2C_{10}H_8)$, **7a**.

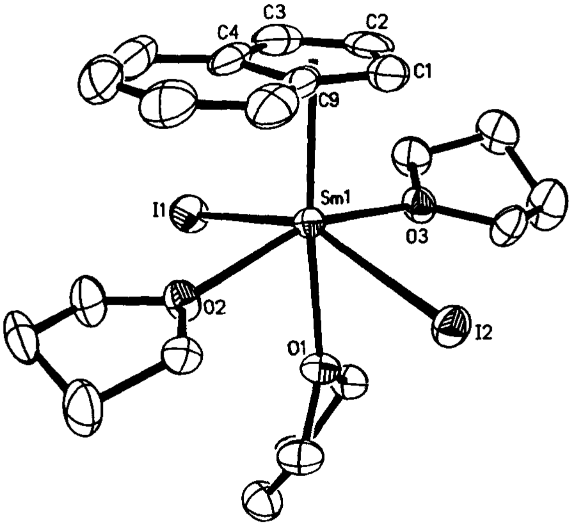

Figure 4 Thermal ellipsoid plot of $(C_9H_7)SmI_2(THF)_3$, **6a**, with ellipsoids drawn at the 50% probability level.

been crystallographically characterized and exhibits an IR stretching frequency at $1580\ cm^{-1}$.[29]

$$\underset{\mathbf{1}}{2(C_9H_7)_2Sm(THF)_x + PhN{=}NPh} \xrightarrow{THF,\ 1\ h} \underset{\mathbf{5}}{(C_9H_7)_3Sm(THF)} + \underset{\mathbf{8}}{[(C_9H_7)Sm(N_2Ph_2)(THF)]_x} \quad [8]$$

Synthesis of $(C_9H_7)_3Sm(THF)$, 5, and $(C_9H_7)SmI_2(THF)_2$, 6

To definitively identify products of the above reactions, the independent syntheses of the tris(indenyl) and mono(indenyl) complexes **5** and **6** were carried out according to reactions [9] and [10]. Both compounds were characterized by NMR and IR spectroscopy and by X-ray crystallography, (Figs 2 and 4). Bulk samples of $(C_9H_7)SmI_2(THF)_2$, **6**, are isolated as the disolvate, but crystallization by hexane diffusion into THF generates single crystals of the trisolvate, $(C_9H_7)SmI_2(THF)_3$, **6a**.

$$SmCl_3 + 3KC_9H_7 \xrightarrow[86\%]{THF,\ 12\ h} \underset{\mathbf{5}}{(C_9H_7)_3Sm(THF)} \quad [9]$$

$$SmI_3(THF)_x + KC_9H_7 \xrightarrow[98\%]{THF,\ 12\ h} \underset{\mathbf{6}}{(C_9H_7)SmI_2(THF)_2} \quad [10]$$

Structural studies

$[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, 4

The structure of **4** (Fig. 1) contains a coordination environment similar to that commonly found in eight-coordinate trivalent $(C_5Me_5)_2Sm$ systems.[9] Selected bond distances and angles are given in Table 2. The 2.79(6) Å average Sm–C distance in **4** is not significantly different from the 2.80(12) Å average in ten-coordinate **5** and the 2.80(1) Å average in eight-coordinate $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$. ($[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$ crystallizes with two independent molecules in the unit cell and the values discussed are the averages of the two molecules.[32]) The average Sm–C distance is slightly longer than the 2.73(1) Å average in seven-coordinate $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$.[23] The 2.078(1) Å Sm–(μ-O) distance in **4** is slightly shorter than the analogous distances of 2.094(1) Å in $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ and 2.109(8) Å in $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$. The latter distances were already some of the shortest Sm–O distances known.

The Sm–O–Sm angle in **4** is rigorously linear as it is in unsolvated $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$. In comparison, the Sm–O–Sm angle in $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$ is 174.3(4)°. The centroid–Sm–centroid angle of 127.6° in **4** is considerably smaller than the 137.2° centroid–Sm–centroid angle in $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ and the 132.7° in $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$. This is consistent with the smaller steric constraints of the indenyl ligand.

$(C_9H_7)_3Sm(THF)$, 5

The structure of **5** (Fig. 2) is similar to that of other tris(cyclopentadienyl)lanthanide THF complexes[12a, 33] in that the three indenyl rings and the oxygen of the THF define a distorted tetrahedron around samarium. Selected bond distances and angles are given in Table 3. Complex **5** is isostructural with previously characterized

Table 2 Selected bond distances (Å) and angles (°) for $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, **4**

Sm–C(1)	2.743(4)	Sm–C(10)	2.735(3)
Sm–C(2)	2.824(4)	Sm–C(11)	2.804(3)
Sm–C(3)	2.878(3)	Sm–C(12)	2.872(3)
Sm–C(8)	2.785(3)	Sm–C(17)	2.813(3)
Sm–C(9)	2.713(3)	Sm–C(18)	2.702(3)
Sm–C(ave. 1)	2.79(6)	Sm–C(ave. 2)	2.79(6)
Sm–C (cent. 1)	2.515	Sm–C(cent. 2)	2.509
Sm–O(1)	2.078(1)	Sm–O(2)	2.410(2)
cent. (1)–Sm–cent. (2)	127.6	Sm(1)–O(1)–Sm(1′)	180.0(1)

$(C_9H_7)_3Ln(THF)$ (Ln = Nd, Gd).[34] The 2.80(12) Å average Sm–C distance in **5** can be directly compared with the analogous Sm–C distances in unsolvated $(C_9H_7)_3Sm$:[35] 2.73(2), 2.74(3) and 2.77(6) Å. The average Sm–C distance in **5** is larger as expected since it has a higher coordination number. Comparison can also be made with sterically crowded $(C_5Me_5)_3Sm$,[26] which has the longest Sm–C(C_5Me_5) average in the literature: 2.82(5) Å. The 2.662(7)–2.954(7) Å range of the Sm–C distances in **5** is large and the arrangement of the disparate lengths is in the direction of slippage to an η^3 coordination mode typical for indenyl complexes[36] with C(1), C(2) and C(9) located closest to the metal. Analysis of the data on $(C_9H_7)_3Ln(THF)$ (Ln = Nd, Gd) shows that distortions toward a slipped η^3 coordination are present in these complexes as well.

The fact that three indenyl rings and a THF can fit samarium is consistent with the smaller steric demands of the indenyl ligand compared with C_5Me_5. When THF is added to $(C_5Me_5)_3Sm$, simple solvate formation does not occur. Instead, a THF ring-opening reaction occurs to form $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$, (W. J. Evans and S. L. Gonzales, unpublished results). The smaller steric demands of the indenyl ligand are also reflected in the smaller (ring centroid)–Sm–(ring centroid) angles of 116.0° in **5** compared with the 120.0° angles in $(C_5Me_5)_3Sm$, which are the smallest (C_5Me_5)–Ln–(C_5Me_5) angles ever observed.[26]

Table 3 Selected bond distances (Å) and angles (°) for $(C_9H_7)_3Sm(THF)$, **5**

Sm–C(1)	2.662(7)	Sm–C(ave.)	2.80(12)
Sm–C(2)	2.715(8)	Sm–C(cent.)	2.530
Sm–C(3)	2.954(7)	Sm–O(1)	2.482(9)
Sm–C(8)	2.953(7)		
Sm–C(9)	2735(7)		
cent.–Sm–cent.	116.0		
cent.–Sm–O	101.7		

$(C_9H_7)SmI_2(THF)_3$, 6a

Complex **6a** (Fig. 4) crystallizes with two molecules in the unit cell and the data reported here are averages of the two molecules (Table 4). The structure of **6a** is analogous to that found in $(C_5H_5)LnCl_2(THF)_3$ (Ln = Nd, Yb, Gd, Er, Y, Ho),[37] $(C_5H_5)YbBr_2(THF)_3$,[38] $(C_5Me_5)CeI_2(THF)_3$,[39] $(C_5H_4CMe_3)SmI_2(THF)_3$, **9**,[40] and $[(C_9H_7)GdCl_2(THF)_3]THF$, **10**.[41] These monocyclopentadienyl dihalide complexes have similar structures regardless of the specific cyclopentadienyl ring or halide present. Each has a distorted octahedral structure with the cyclopentadienyl ring and the halides arranged in a *mer–trans* orientation. In all cases, the *trans* halides bend away from the cyclopentadienyl ring so that the X–Ln–X angles are in the 153–158° range. The composition of **6a** is most closely related to that of **9** and **10**. The structural parameters for **6a** are not unusual and very similar to those of **9**. The 2.75(2) Å average Sm–C distance in **6a** is shorter than the 2.80(12) Å in **5** as expected for a lower-coordinate complex. The narrow 2.723(8)–2.788(7) Å range of Sm–C distances in **6a** does not suggest slippage of the indenyl rings toward η^3

Table 4 Selected bond distances (Å) and angles (°) for $(C_9H_7)SmI_2(THF)_3$, **6a**

Sm–C(1)	2.721(8)	Sm–I(1)	3.130(6)
Sm–C(2)	2.736(8)	Sm–I(2)	3.113(13)
Sm–C(3)	2.730(8)	Sm–O(1)	2.474(13)
Sm–C(4)	2.77(2)	Sm–O(2)	2.447(2)
Sm–C(9)	2.768(8)	Sm–O(3)	2.421(1)
Sm–C(ave.)	2.75(2)		
Sm–C(cent.)	2.465(3)		
cent.–Sm–I(1)	102.9(14)	cent.–Sm–O(1)	175(1)
cent.–Sm–I(2)	101.8(2)	cent.–Sm–O(2)	106(1)
I(1)–Sm–I(2)	155(2)	cent.–Sm–O(3)	99(1)

coordination as was observed in complex **5**. Surprisingly, the indenyl gadolinium dihalide, **10**, has a broad range of Gd–C distances [2.594(20)–2.876(23) Å] which are arranged to give a slipped orientation.

Structure of $(C_9H_7)Sm(C_8H_8)(N_2C_{10}H_8)$, 7a

The crystal quality of **7a** was not good enough to provide detailed metrical information; however, the structure was unequivocally defined as the bent metallocene adduct shown in Fig. 3. The overall structure of **7a** is not much different from that of $(C_9H_7)Pr(C_8H_8)(THF)_2$,[42] $(C_5H_5)Pr(C_8H_8)(THF)_2$[42] and $(C_5H_4PPh_2)Sm(C_8H_8)(THF)_2$,[43] all of which are nine-coordinate mono-(cyclopentadienyl ring) cyclo-octatetraenyl complexes.

DISCUSSION

The reaction of **1** with N_2O to form an oxide product shows that **1** and **2** can have parallel reactivity. The fact that the oxide product of reaction **2** is the solvate $[(C_9H_7)_2Sm(THF)]_2(\mu\text{-}O)$, **4**, rather than a direct analog of $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$, is consistent with the view that the indenyl ligands provide a more open coordination environment for samarium. In fact, the indenyl complex does not readily lose THF to form the unsolvated complex, whereas $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$ loses THF quite easily.

The main difference between reactions [1] and [2] is the formation of substantial amounts of the tris(indenyl) species **5** as a by-product. The tendency to form a tris species is prevalent in all of the reactions investigated in this study. Hence, a main difference between the reactivity of **1** and **2** is the greater accessibility of $(C_9H_7)_3Sm$ compared with $(C_5Me_5)_3Sm$.

The reaction of **1** with 1,2-di-iodoethane, reaction [4], shows further differences between **1** and **2**. Although oxidation occurs and an iodide is formed, there is a clear preference for the formation of a mixture of the mono(ring) complex $(C_9H_7)SmI_2(THF)_2$, **6**, and the tris complex $(C_9H_7)_3Sm(THF)$, **5**, rather than the bis(indenyl) species $(C_9H_7)_2SmI(THF)_x$, which would be analogous to the iodide formed from $(C_5Me_5)_2Sm(THF)_2$. Since eight-coordinate complexes are by far the most common pentamethylcyclopentadienyl samarium systems, the tendency for the indenyl system *not* to form an analog is a significant difference.

The reaction of **1** with azobenzene, reaction [8], also generates the tris(indenyl) complex **5** and a mono(indenyl) complex **8**, rather than any of the bis(cyclopentadienyl) analogs formed by $(C_5Me_5)_2Sm(THF)_2$. Given the tendency of **1** to form the tris(indenyl) species, the reaction of **1** with 1,3,5,7-cyclo-octatetraene was examined. As expected, this directly parallels the reactivity of **3** with 1,3,5,7-cyclo-octatetraene in that the tris species **5** and a mono(indenyl) product, **7**, are obtained. The main difference between reactions [5] and [6] is the solvent. Reaction [6] can be carried out in THF whereas reaction [5] cannot, because the $(C_5Me_5)_3Sm$ ring-opens THF to make $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$.[37]

When reactions [2], [4], [6] and [8] are compared, reaction [2] becomes the exception in that one of the two major products is a *bis*(indenyl)-samarium(III) compound and not a mono(indenyl)samarium(III) complex. Hence, in C_5Me_5/Sm chemistry, bis(cyclopentadienyl) products are predominant and mono(ring) compounds are formed only rarely. In the C_9H_7/Sm system this trend is reversed. In fact, to our knowledge, only one other crystallographically characterized bis(indenyl)lanthanide(III) complex exists besides **4**, namely $[(C_9H_7)_2PrCl(THF)]_2$.[44] It is interesting to note that this complex is also a bridged dimer which contains small bridging atoms. The tendency to form mono(ring) indenyl complexes may be stoichiometrically related to the tendency to form the tris(indenyl)product, **5**.

CONCLUSION

$(C_9H_7)_2Sm(THF)_x$, **1**, shows parallel reductive reactivity compared with $(C_5Me_5)_2Sm(THF)_2$, **2**, and $(C_5Me_5)_2Sm$, **3**, with many substrates. However, the difference in size of the two ring systems often favors different types of reaction products in the sterically less crowded indenyl systems. The indenyl system also differs from the pentamethylcyclopentadienylsamarium chemistry in that its reactions appear to favor the formation of mono(indenyl) products and $(C_9H_7)_3Sm$ as a by-product. Hence, the indenyl system may be advantageous in reactions in which steric crowding is a problem and formation of mono(ring) systems is desirable.

Note Supplementary crystallographic data are obtainable from the authors.

REFERENCES

1. H. B. Kagan and J. L. Namy, *Tetrahedron* **42**, 6573 (1986).
2. (a) G. A. Molander, *Chem. Rev.* **92**, 29 (1992); (b) J. A. Soderquist, *Aldrichim. Acta* **24**, 15 (1991).
3. W. J. Evans, *Polyhedron* **6**, 803 (1987).
4. W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.* **107**, 941 (1985).
5. W. J. Evans, L. A. Hughes and T. P. Hanusa, *J. Am. Chem. Soc.* **106**, 4270 (1984).
6. W. J. Evans and D. K. Drummond, *J. Am. Chem. Soc.* **108**, 7440 (1986).
7. W. J. Evans, L. A. Hughes, D. K. Drummond, H. Zhang and J. L. Atwood, *J. Am. Chem. Soc.* **108**, 1722 (1986).
8. W. J. Evans, T. S. Gummersheimer, T. J. Boyle and J. W. Ziller, *Organometallics* **13**, 1281 (1994).
9. W. J. Evans and S. E. Foster, *J. Organomet. Chem.* **433**, 79 (1992).
10. (a) A. Sen, V. Chebolu and A. L. Rheingold, *Inorg. Chem.* **26**, 1821 (1987); (b) V. Chebolu, R. R. Whittle and A. Sen, *Inorg. Chem.* **24**, 3082 (1985); (c) W. J. Evans and G. W. Rabe, *Inorg. Chem.* **33**, 3072 (1994).
11. (a) W. J. Evans, R. Dominguez and T. P. Hanusa, *Organometallics* **5**, 263 (1986); (b) D. Alvarez, K. G. Caulton, W. J. Evans and J. W. Ziller, *J. Am. Chem. Soc.* **112**, 5674 (1990).
12. (a) C. J. Schaverien, *Adv. Organomet. Chem.* **36**, 283 (1994); (b) T. J. Marks and R. D. Ernst, in *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A. and Abel, E. W. (eds), Pergamon, Oxford, 1982, Chapter 21; (c) H. Schumann and W. Genthe, in: *Handbook on the Physics and Chemistry of Rare Earths*, Gschneidner, K. A., Jr and Eyring, L. (eds), Elsevier, Amsterdam, 1985, Vol. 7, Chapter 53, and references therein.
13. D. T. Pegg, D. M. Doddrell and M. R. Bendall, *J. Chem. Phys.* **77**, 2745 (1982).
14. J. L. Atwood, W. E. Hunter, A. L. Wayda and W. J. Evans, *Inorg. Chem.* **20**, 4115 (1981).
15. M. D. Carter and C. P. Carter, *J. Inorg. Nucl. Chem.* **24**, 387 (1962).
16. M. Tsutsui and H. J. Gysling, *J. Am. Chem. Soc.* **90**, 6880 (1968).
17. H. Hope, *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*, Wayda, A. L., and Darensbourg, M. Y. (eds), ACS Symposium Series No. 357, 1987.
18. M. R. Churchill, R. A. Lashewycz and F. J. Rotella, *Inorg. Chem.* **16**, 265 (1977).
19. (a) *UCLA Crystallographic Computing Package*, University of California, Los Angeles, 1981. (b) C. Strouse, personal communication.
20. G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical X-ray Instruments, Inc, Madison, WI, 1990.
21. *International Tables for X-ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
22. D. Rogers, *Acta Cryst., Sect. A* **37**, 734 (1981).
23. W. J. Evans, J. W. Grate, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.* **107**, 405 (1985).
24. W. J. Evans and S. L. Gonzales, *J. Organomet. Chem.* **480**, 41 (1994).
25. W. J. Evans, J. W. Grate, K. R. Levan, I. Bloom, T. T. Peterson, R. J. Doedens, H. Zhang and J. L. Atwood, *Inorg. Chem.* **25**, 3614 (1986).
26. W. J. Evans, S. L. Gonzalez and J. W. Ziller, *J. Am. Chem. Soc.* **113**, 7423 (1991).
27. W. J. Evans, D. K. Drummond, S. G. Bott and J. L. Atwood, *Organometallics* **5**, 2389 (1986).
28. W. J. Evans and D. K. Drummond, *J. Am. Chem. Soc.* **108**, 7440 (1986).
29. W. J. Evans, D. K. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang and J. L. Atwood, *J. Am. Chem. Soc.* **110**, 4983 (1988).
30. J. Takats and X. W. Zhang, *Organometallics* **12**, 4286 (1993).
31. L. J. Bellamy, *The Infrared Spectroscopy of Complex Molecules*, Wiley, New York, 1964.
32. W. J. Evans, D. K. Drummond, L. A. Hughes, H. Zhang and J. L. Atwood, *Polyhedron* **7**, 1693 (1988).
33. Z. Wu, Z. Xu, X. You, X. Zhou, X. Huang and J. Chen, *Polyhedron* **13**, 379 (1994).
34. J. Xia, Z. Jin, G. Lin and W. Chen, *J. Organomet. Chem.* **408**, 173 (1991).
35. J. L. Atwood, J. H. Burns and P. G. Laubereau, *J. Am. Chem. Soc.* **95**, 1830 (1973).
36. J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, pp. 255–258.
37. X. Zhou, Z. Wu, H. Ma, *Polyhedron* **13**, 375 (1994), and references therein.
38. G. B. Deacon, G. D. Fallon and D. L. Wilkinson, *J. Organomet. Chem.* **293**, 45 (1985).
39. P. N. Hazin, J. C. Huffman and J. W. Bruno, *Organometallics* **6**, 23 (1987).
40. V. K. Bel'skii, Y. K. Gun'ko, E. B. Lobkovskii, B. M. Bulychev and G. L. Soloveichik, *Organomet. Chem. USSR* **4**, 202 (1991).
41. G. Fuxing, W. Gecheng, J. Zhongsheng and C. Wenqi, *J. Organomet. Chem.* **438**, 289 (1992).
42. K. Wen, Z. Jin and W. Chen, *J. Chem. Soc., Chem. Commun.* 680 (1991).
43. M. Visseaux, A. Dormond, M. M. Kubicki, C. Moïse, D. Baudry and M. Eqhritikhine, *J. Organomet. Chem.* **433**, 95 (1992).
44. M. Qi, Q. Shen and Y. Lin, *Chin. Sci. Bull.* **36**, 1934 (1991).