

# Reaction Chemistry of Sterically Crowded Tris(pentamethylcyclopentadienyl)samarium<sup>1</sup>

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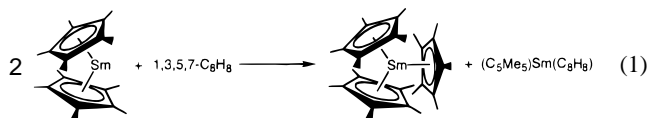
Received March 23, 1998

**Abstract:** Although  $(C_5Me_5)_3Sm$  is an extremely sterically crowded molecule, it displays high reactivity with a variety of substrates including CO, THF, ethylene, hydrogen, nitriles, isonitriles, isocyanates, 1,3,5,7-cyclooctatetraene, azobenzene, and  $Ph_3P=E$  ( $E = O, S, Se$ ). The reactions include polymerization, insertion, ring-opening, and reduction. Depending on the substrate,  $(C_5Me_5)_3Sm$  can react (1) as if it were a bulky alkyl complex of formula  $(C_5Me_5)_2SmR$  in which R is an  $\eta^1-C_5Me_5$  group or (2) as if it were the zwitterion  $[(C_5Me_5)_2Sm]^+[C_5Me_5]^-$  in which the  $[C_5Me_5]^-$  component is a one-electron reductant. In the former mode, this compound (a) reacts with CO to form  $(C_5Me_5)_2Sm(O_2C_7Me_5)$ , which has a ligand containing a nonclassical carbocationic center, (b) undergoes hydrogenolysis with  $H_2$  to form  $[(C_5Me_5)_2Sm(\mu-H)]_2$ , (c) ring-opens THF to form  $(C_5Me_5)_2Sm[O(CH_2)_4(C_5Me_5)](THF)$ , (d) inserts PhCN to form  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NCPh)$ ,

2, and (e) reacts with PhNCO to form  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , **3**, a product which can be rationalized by a C–N coupling between a coordinated PhNCO and a PhNCO unit inserted into a  $Sm(\eta^1-C_5Me_5)$  bond. On the other hand,  $(C_5Me_5)_3Sm$  reduces (a)  $Ph_3P=O$  to form  $PPh_3$ ,  $(C_5Me_5)_2$ , and  $[(C_5Me_5)_2Sm]_2(\mu-O)$ , (b)  $Ph_3P=E$  ( $E = S, Se$ ) to form  $PPh_3$ ,  $(C_5Me_5)_2$ , and a complex which adds THF to form  $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$ , (c) cyclooctatetraene to form  $(C_5Me_5)_2Sm(C_8H_8)$  and  $(C_5Me_5)_2$ , (d) azobenzene to form  $(C_5Me_5)_2Sm(N_2Ph_2)$  and  $(C_5Me_5)_2$ , and (e)  $Me_3CNC$  to form  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3$ , **4**.  $(C_5Me_5)_3Sm$  also initiates the polymerization of ethylene. This reaction chemistry is described here as well as structural data on **2–4**, each of which has a formal eight-coordinate bent metallocene geometry around samarium.

## Introduction

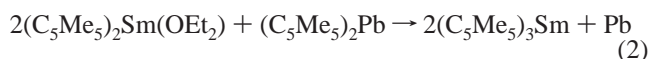
For many years it was assumed that tris(pentamethylcyclopentadienyl) metal complexes,  $(C_5Me_5)_3M$ , were too sterically crowded to exist for any metal in the periodic table. Indeed, when the first example,  $(C_5Me_5)_3Sm$ , **1**,<sup>2</sup> was synthesized, as



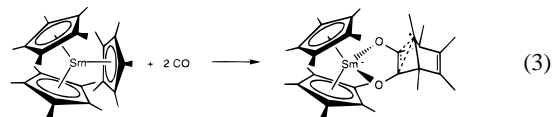
shown in eq 1, and crystallographically characterized, its metrical parameters were found to be extreme. It had a smaller ring-centroid–metal–ring-centroid angle than in any previously characterized  $C_5Me_5$ -containing samarium complex and the longest Sm–C bonds of any trivalent  $C_5Me_5/Sm$  system.<sup>3</sup>

The extreme steric saturation could have limited the reactivity of **1**, since substrates would not be able to approach the metal center. On the other hand, the long Sm–C( $C_5Me_5$ ) distances could provide a basis for reactivity. Neither the  $C_5Me_5$  rings nor the samarium receive the normal electrostatic stabilization from each other at this distance. This could make the  $C_5Me_5$  rings prone to removal and the metal center quite electrophilic. Moreover, space-filling models suggested that there was an open channel down the three-fold axis of the molecule which could

allow small, cylindrical substrates to access the metal center. These possibilities could not be fully evaluated until a more efficient, higher yield synthesis of  $Sm(C_5Me_5)_3$  was developed. This was accomplished as shown in eq 2.<sup>4</sup>



Subsequently, the reaction of  $(C_5Me_5)_3Sm$  with the cylindrical



substrate carbon monoxide was examined and the nonclassical carbocation complex,  $(C_5Me_5)_2Sm(O_2C_7Me_5)$ , shown in eq 3 was isolated.<sup>5</sup>

This reaction was remarkable in several respects. Not only was the product an unusual example of an alkane-soluble, thermally stable carbocation, but the reaction of a  $C_5Me_5$  ligand with CO was also unprecedented. In the scores of previously reported reactions involving CO and  $C_5Me_5$  complexes, the  $C_5Me_5$  group had always been an inert spectator ligand. This result showed that **1** had access to an unusual reaction pathway which allowed coupling of CO with  $C_5Me_5$  rings.

(1) Reported in part at the Fifth Chemical Congress of North America, November 11–15, 1997, Cancún Mexico.

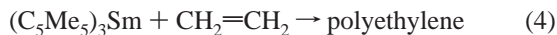
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(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm was also unusual in that it could initiate the polymerization of ethylene, eq 4.<sup>6</sup>



This was unexpected since (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm is a sterically saturated molecule and the approach of the olefin to the metal center appeared to be hindered. Furthermore, lanthanide-based olefin polymerization generally requires alkyl or hydride functionalities or a reactive divalent complex such as (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm.<sup>7,8</sup>

The CO insertion and ethylene polymerization reactions both could be rationalized if an intermediate containing a Sm–C single bond was present, for example in an η<sup>1</sup>-C<sub>5</sub>Me<sub>5</sub> complex such as (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(η<sup>1</sup>-C<sub>5</sub>Me<sub>5</sub>). No spectroscopic evidence for an η<sup>1</sup>-C<sub>5</sub>Me<sub>5</sub> ring was observed by NMR spectroscopy, even at –80 °C, to support such an intermediate, but (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm reacted with hydrogen in a manner analogous to that of σ-bound alkyl complexes to form the expected hydrogenolysis products,



[(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(μ-H)]<sub>2</sub><sup>9</sup> and C<sub>5</sub>Me<sub>5</sub>H, eq 5.<sup>6</sup>

As a consequence of the unusual reactivity observed for (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm, we have expanded the investigation of its reactivity. We report here chemical evidence that an η<sup>1</sup>-intermediate is accessible in the (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm system, but we also describe an extensive one electron-reduction chemistry for this trivalent complex. This is unexpected since a Sm(III)/Sm(IV) redox couple has never been observed.<sup>10</sup> Since the reductive reactivity does not require an η<sup>1</sup>-intermediate, the reactivity of (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>-Sm appears to be variable depending on the nature of the substrate available.

## 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 dried over sodium/benzophenone ketyl and distilled prior to use. (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm was prepared according to the literature procedure.<sup>4</sup> PhCN, PhNCO, and Me<sub>3</sub>CNC were dried over molecular sieves and degassed prior to use. Ph<sub>3</sub>P=E (E = O, S, Se) and azobenzene were used as received (Aldrich). 1,3,5,7-Cyclooctatetraene was purified by drying over CaH<sub>2</sub>, followed by vacuum distillation. 2,5-Dimethyltetrahydrofuran was dried over sodium/benzophenone ketyl and distilled prior to use. ε-Caprolactone was dried over molecular sieves and vacuum transferred prior to use. Pyridine was dried over CaH<sub>2</sub> and vacuum transferred prior to use. Complexometric analyses and physical measurements were obtained as previously described.<sup>11</sup> Elemental analysis was provided

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by Desert Analytics, Tucson, AZ. (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm/pyridine NMR experiments were run with 0.03 M solutions of (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm in toluene-*d*<sub>8</sub>.

**Reaction with PhCN.** In the glovebox, addition of a solution of PhCN (37 mg, 0.36 mmol) in toluene (5 mL) to a brown solution of (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (100 mg, 0.18 mmol) in toluene (5 mL) caused an immediate color change to yellow-orange. After 5 min, the solvent was removed in vacuo leaving (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm[NC(Ph)(C<sub>5</sub>Me<sub>5</sub>)](NCPh), **4a**, (130 mg, 95%) as a yellow solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 6.16 (t, *J*<sub>HH</sub> = 7.1 Hz, C<sub>6</sub>H<sub>5</sub>, 1H) 5.92 (t, *J*<sub>HH</sub> = 7.5 Hz, C<sub>6</sub>H<sub>5</sub>, 2H) 5.19 (d, *J*<sub>HH</sub> = 7.5 Hz, C<sub>6</sub>H<sub>5</sub>, 2H) 2.88 (s, CH<sub>3</sub>, 6H), 2.22 (s, CH<sub>3</sub>, 3H), 2.18 (s, CH<sub>3</sub>, 6H), 1.65 (s, C<sub>5</sub>Me<sub>5</sub>, 30H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 170.4, 144.4, 135.6, 133.6, 131.5, 128.5, 126.7, 112.4, 104.4, 60.8, 25.0, 15.7, 13.0, 12.0. IR (KBr) 2908 s, 2250 m, 1630 s, 1448 m, 1376 w, 1023 w, 758 m, 694 w cm<sup>-1</sup>. Anal. Calcd for C<sub>44</sub>H<sub>55</sub>N<sub>2</sub>Sm: Sm, 19.8. Found: Sm 20.8.

**Reaction with PhNCO.** In the glovebox, PhNCO (12.8 mg, 0.108 mmol) dissolved in toluene (5 mL) was added to (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (30 mg, 0.054 mmol) in toluene. The solution turned yellow immediately upon addition of PhNCO. The solvent was removed in vacuo, leaving (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>SmOC(C<sub>5</sub>Me<sub>5</sub>)N(Ph)C(NPh)O, **6**, (42 mg, 98%) as a yellow solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 9.13 (d, C<sub>6</sub>H<sub>5</sub>, 2H), 7.61 (t, C<sub>6</sub>H<sub>5</sub>, 2H), 7.40 (t, C<sub>6</sub>H<sub>5</sub>, 1H), 2.14 (s, CH<sub>3</sub>, 6H), 1.30 (s, CH<sub>3</sub>, 6H), 0.97 (s, C<sub>5</sub>Me<sub>5</sub>, 30H), –3.61 (s, CH<sub>3</sub>, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 140.2, 138.5, 138.0, 132.1, 128.9, 126.7, 126.1, 125.6, 122.5, 120.1, 118.0, 117.6, 64.2, 31.9, 23.0, 17.6, 14.3, 13.5, 12.2, 10.9. IR (KBr) 2910 m, 1686 w, 1636 s, 1589 m, 1554 m, 1438 m, 1289 w, 764 w, 694 w cm<sup>-1</sup>. Anal. Calcd for C<sub>44</sub>H<sub>55</sub>N<sub>2</sub>O<sub>2</sub>Sm: Sm, 18.93; C, 66.53; H, 6.98; N, 3.53. Found: Sm, 20.6; C, 66.11; H, 7.25; N, 3.09.

**Reaction with THF.** In the glovebox, THF (2.91 mL, 0.36 mmol) was added to (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (100 mg, 0.18 mmol) in toluene (5 mL), and the solution turned yellow immediately. Removal of the solvent by rotary evaporation yielded the previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>-Sm[O(CH<sub>2</sub>)<sub>4</sub>(C<sub>5</sub>Me<sub>5</sub>)](THF)<sup>12</sup> (120 mg, 95%) identified by <sup>1</sup>H NMR spectroscopy (C<sub>6</sub>D<sub>6</sub>).

**Reaction with ε-Caprolactone.** In a glovebox, ε-caprolactone (628 mg, 5.5 mmol) was added dropwise to (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (31 mg, 0.055 mmol) in toluene (10 mL). A yellow color change was observed immediately. The reaction was allowed to proceed at room temperature for 18 h during which time an increase in viscosity was observed. The solution was removed from the glovebox, diluted with toluene (15 mL), and washed with 5% HCl. The toluene solution was then added to hexane (100 mL), and a white solid precipitated. This material was collected by filtration and dried for 20 h on a vacuum line (500 mg, 80% conversion). The white solid was identified as polycaprolactone by <sup>13</sup>C NMR spectroscopy. No evidence for C<sub>5</sub>Me<sub>5</sub> groups was observed by <sup>13</sup>C NMR spectroscopy.

**Reaction with Se=PPh<sub>3</sub>.** In the glovebox, Se=PPh<sub>3</sub> (15 mg, 0.043 mmol) in toluene (5 mL) was added to (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (48 mg, 0.086 mmol) in toluene (5 mL). After 15 min, the color of the toluene solution had turned to orange, and a white precipitate had formed. This precipitate was removed by centrifugation and identified as PPh<sub>3</sub> (10 mg, 90%) by <sup>1</sup>H NMR spectroscopy (C<sub>6</sub>D<sub>6</sub>). The reaction solvent was removed in vacuo to give a tacky orange solid which was washed with hexane to give an orange powder (36 mg, 90%). This orange powder was recrystallized from THF and identified as the previously characterized [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)]<sub>2</sub>(μ-Se)<sup>13</sup> by <sup>1</sup>H NMR spectroscopy (C<sub>6</sub>D<sub>6</sub>). Rotary evaporation of solvent from the hexane wash yielded a tacky material which was identified by <sup>1</sup>H NMR spectroscopy (C<sub>6</sub>D<sub>6</sub>) as the known, oxidatively coupled dimer, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> (12 mg, 97%).<sup>14</sup>

**Reaction with S=PPh<sub>3</sub>.** In the glovebox, S=PPh<sub>3</sub> (13 mg, 0.045 mmol) was reacted with (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (50 mg, 0.091 mmol) as described above. After 3 days, the color had turned to yellow-orange, and a white precipitate was observed. The reaction workup was performed in the

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manner described above to isolate a yellow-orange powder (37 mg, 93%). This yellow-orange powder was recrystallized from THF and identified as the previously characterized  $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)^{13}$  by  $^1H$  NMR spectroscopy ( $C_6D_6$ ).  $(C_5Me_5)_2$  (12 mg, 97%) and  $PPh_3$  (11 mg, 93%) were identified as described above.

**Reaction with  $O=PPh_3$ .** In the glovebox,  $O=PPh_3$  (11 mg, 0.045 mmol) was reacted with  $(C_5Me_5)_3Sm$  (50 mg, 0.091 mmol) as described above. After 30 min, the color had turned to yellow, and a white precipitate was observed. The reaction workup was performed in the manner described above to isolate a yellow powder (35 mg, 94%). This yellow powder was recrystallized from THF and identified as the previously characterized  $[(C_5Me_5)_2Sm]_2(\mu-O)^{15}$  by  $^1H$  NMR spectroscopy ( $C_6D_6$ ).  $(C_5Me_5)_2$  (11 mg, 95%) and  $PPh_3$  (10 mg, 89%) were identified as described above.

**Reaction with  $PhN=NPh$ .** In the glovebox, azobenzene (17 mg, 0.092 mmol) was added to  $(C_5Me_5)_3Sm$  (50 mg, 0.091 mmol) in toluene (5 mL). After 15 min, the mixture had turned dark green. Toluene was removed in vacuo to afford a tacky, dark-green material which was washed with hexane to give a dark-green powder (53 mg, 93%).  $^1H$  NMR spectroscopy identified the green solid as the previously characterized  $(C_5Me_5)_2Sm(N_2Ph_2)^{16}$ .  $(C_5Me_5)_2$  (11 mg, 89%) was identified as described above. Two equivalents of  $(C_5Me_5)_3Sm$  were also reacted with azobenzene in an NMR tube experiment. No evidence for the organosamarium compound containing the dianionic azobenzene moiety,  $[(C_5Me_5)_2Sm]_2(\mu-N_2Ph_2)^{16,17}$  was observed.

**Reaction with  $1,3,5,7-C_8H_8$ .** In an argon-filled glovebox, cyclooctatetraene (1.5  $\mu$ L, 0.013 mmol) was added to  $(C_5Me_5)_3Sm$  (15 mg, 0.027 mmol) in  $C_6D_6$  (1 mL). No color change was observed upon addition. After the solution was allowed to stir at room temperature for 18 h, it was transferred to an NMR tube, and the  $^1H$  NMR spectrum was obtained.  $(C_8H_8)Sm(C_5Me_5)_2$ ,  $(C_5Me_5)_2$ , and  $(C_5Me_5)_3Sm$  were identified by  $^1H$  NMR spectroscopy.

**Reaction with  $Me_3CNC$ .** In the glovebox, addition of  $Me_3CNC$  (30 mg, 0.36 mmol) in toluene (5 mL) to  $(C_5Me_5)_3Sm$  (100 mg, 0.18 mmol) in toluene (5 mL) caused an immediate color change to red. The red toluene solution was transferred to a flask fitted with a high vacuum greaseless stopcock. The flask was removed from the glovebox, attached to a vacuum line, and the system was evacuated to the vapor pressure of the solvent. The flask was heated to 80 °C for 1 h, during which time the solution began to turn yellow with concomitant formation of a yellow precipitate. The yellow, toluene-insoluble material was isolated by filtration (83 mg). Rotary evaporation of the toluene filtrate yielded a tacky material which exhibited an extremely complex  $^1H$  NMR spectrum in  $C_6D_6$  containing several peaks between 1.0 and 3.0 ppm. The toluene-insoluble material was recrystallized from hot THF (51 mg, 54%) over several days and identified as the previously reported  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3$ , **4**,<sup>18</sup> by IR spectroscopy and X-ray crystallography.

**X-ray Data Collection, Structure Determination, and Refinement for  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NPh)O$ , **2**.** The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard procedures.<sup>19</sup> Intensity data were collected using a  $2\theta/\omega$  scan technique. Details are given in Table 1. The raw data were processed with a local version of CARESS<sup>20</sup> which employs a modified version of the Lehman-Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out using the SHELXTL<sup>21</sup> program. All 5438 data were corrected for

**Table 1.** Experimental Data for the X-ray Diffraction Studies of  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NPh)O$ , **2**,  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , **3**, and  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3(THF)_2 \cdot 4 \cdot 2THF^a$

compd	<b>2</b>	<b>3</b>	<b>4</b> ·2THF
formula	$C_{44}H_{55}N_2Sm$	$C_{44}H_{55}N_2O_2Sm$	$C_{86}H_{133}N_6O_2Sm_3$
fw	762.25	794.25	1734.03
crystal dimen (mm)	$0.20 \times 0.23 \times 0.30$	$0.17 \times 0.20 \times 0.20$	$0.27 \times 0.30 \times 0.36$
crystal color	yellow	yellow	yellow
Temp (K)	163	158	163
crystal system	triclinic	triclinic	triclinic
space group	$P1$	$P1$	$P1$
$a$ (Å)	10.416(2) Å	11.2894(11)	14.290(2)
$b$ (Å)	10.506(2)	11.442(2)	16.540(2)
$c$ (Å)	18.565(3)	17.509(2)	18.288(2)
$\alpha$ (deg)	77.06(2)	100.280(9)	78.823(8)
$\beta$ (deg)	82.60(2)	97.755(8)	84.929(7)
$\gamma$ (deg)	85.31(2)	115.222(9)	86.441(7)
$V$ (Å <sup>3</sup> )	1960.7(7)	1955.9(4)	4219.5(7)
$Z$	2	2	2
$D_{\text{calc}}$ (mg/m <sup>3</sup> )	1.291	1.349	1.365
diffractometer	Siemens P4	Siemens P4 rotating anode	Siemens P4
$\mu$ (mm <sup>-1</sup> )	1.528	1.538	2.107
refinement, $wR2^b$	0.1557	0.0921	0.0770
refinement, R1	0.0718	0.0390	0.0430
goodness of fit	1.052	1.195	1.046

<sup>a</sup> Radiation: Mo  $K\alpha$  ( $\mu = 0.710$  730 Å). Monochromator: highly oriented graphite. <sup>b</sup>  $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ .

absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P1$  was assigned and later determined to be correct.

The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.<sup>22</sup> Hydrogen atoms were included, using a riding model. The cyclopentadienyl ring defined by atoms C(11)–C(15) is disordered. Two complete rings, each with site-occupancy-factors = 0.50, were included to account for the observed rotational disorder.

#### X-ray Data Collection, Structure Determination, and Refinement

**for  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , **3**.** Intensity data were collected as described above. All 5360 data were corrected for decay (5.0%), absorption, and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P1$  was assigned and later determined to be correct. The structure was solved as described above.

**X-ray Data Collection, Structure Determination, and Refinement for  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3$ , **4**.** Intensity data were collected as described above. All 13 819 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P1$  was assigned and later determined to be correct.

The structure was solved as described above for **2**. There are two THF molecules present per formula unit. The bridging CN ligands appear to be disordered. It was not possible to distinguish between the carbon and nitrogen positions on the basis of either thermal parameters or interatomic distances. Refinement of the ligands as discrete nitrogen and carbon atoms led to lower than expected thermal parameters for the atoms designated as carbon and higher than expected thermal parameters for the atoms designated as nitrogen. The same trend was observed upon reassignment of the carbon atoms as nitrogen and of the nitrogen atoms as carbon. The conclusion is that the nitrogen

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and carbon atoms are equally disordered over the two sites. Refinement of the ligands assuming an equal electron distribution over the two sites resulted in nearly equal thermal parameters for each atom.

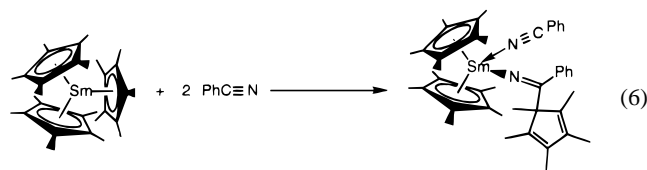
## Results

**Reactions with Lewis Bases.** The initially studied reactions of  $(C_5Me_5)_3Sm$  with  $CO$ ,<sup>5</sup>  $CH_2=CH_2$ ,<sup>6</sup> and  $H_2$ ,<sup>6</sup> eqs 3–5, were consistent with the existence of an intermediate of the type  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$ . Since no evidence was obtained by low-temperature NMR spectroscopy for such a structure, reactions with Lewis bases were examined in efforts to trap an adduct such as  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)L$  ( $L$  = Lewis base). THF was not useful in this regard since it is ring-opened as described below. Likewise,  $Ph_3P=O$  and its sulfur and selenium congeners were not useful because they were reduced as described below. Pyridine proved to be the most informative.

Addition of 1 equiv of pyridine to  $(C_5Me_5)_3Sm$  in toluene-*d*<sub>8</sub> results in a color change from brown to red. Two peaks were observed in the <sup>1</sup>H NMR spectrum in the  $C_5Me_5$  region, one at  $-1.24$  ppm, characteristic for  $(C_5Me_5)_3Sm$ , and one at  $1.20$  ppm. Addition of 3 equiv of pyridine to a toluene solution of  $(C_5Me_5)_3Sm$  gives a red solution with only the  $1.20$  ppm resonance in the  $C_5Me_5$  region plus three very broad signals between  $2.0$  and  $5.5$  ppm. Low-temperature NMR experiments were performed to determine if the peak located at  $1.20$  ppm would split into a pattern indicative of  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)(py)$ . At  $-20$  °C, the <sup>1</sup>H NMR spectrum contained peaks at  $5.39$ ,  $3.06$ ,  $2.41$ , and  $1.66$  ppm of relative intensity 3:6:6:30 consistent with the presence of a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)(pyridine)$  structure. However, the peaks due to coordinated pyridine could not be definitively located in this paramagnetic system. The spectrum provided no additional information at lower temperatures, and attempts to crystallize a pyridine adduct have been unsuccessful.

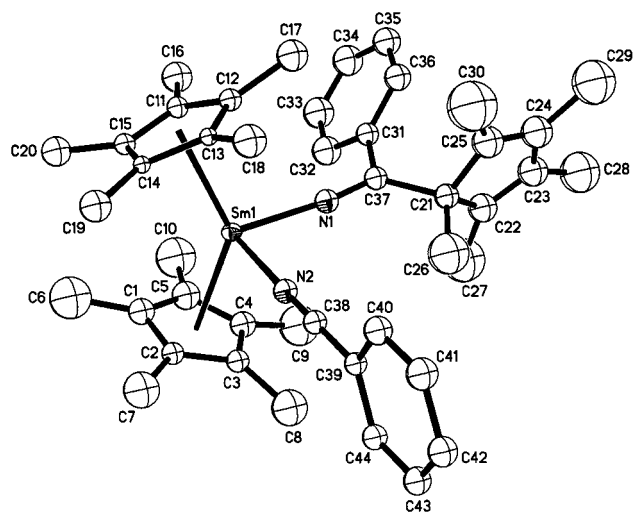
**Insertion Chemistry. Reactions with Nitriles.** In contrast to the pyridine reactions, brown toluene solutions of  $(C_5Me_5)_3Sm$  react with nitriles to form yellow-orange solutions. The yellow product, **2**, obtained from  $(C_5Me_5)_3Sm$  and  $PhC\equiv N$  had a <sup>1</sup>H NMR spectrum containing a singlet at  $1.65$  ppm in the region where resonances for  $C_5Me_5$  groups attached to Sm(III) are found, as well as three other peaks at  $2.88$ ,  $2.12$ , and  $1.47$  ppm. The 2:2:1 integration ratio of these latter three peaks was consistent with the presence of a  $\sigma$ -bound  $C_5Me_5$  moiety. The infrared spectrum of **2** contained an absorption at  $1630$   $cm^{-1}$  in the region characteristic of  $C=N$  stretches and a band at  $2250$   $cm^{-1}$  (cf.  $2232$   $cm^{-1}$  for free  $PhC\equiv N$ ) which could be attributed to  $PhC\equiv N$  coordinated to samarium.<sup>23,24</sup>

X-ray crystallography definitively confirmed the implications of the spectroscopic data and showed that **2** was  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NCPh)$ , Figure 1, in which one benzonitrile unit had been inserted into a  $Sm-C_5Me_5$  linkage while another coordinated to samarium. This reaction, eq 6, presented strong



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**Figure 1.** Thermal ellipsoid plot of  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NCPh)$ , **2**, with ellipsoids drawn at the 50% probability level.

structural evidence for the availability of an intermediate with  $\eta^1-C_5Me_5$ -like reactivity in the  $(C_5Me_5)_3Sm$  system. For example,  $(C_5Me_5)(C_2B_9H_{11})TiMe$  reacts analogously with  $MeCN$  to form  $(C_5Me_5)(C_2B_9H_{11})Ti(NCMe_2)(MeCN)$ , which has similar spectroscopic and structural features.<sup>25a</sup> The spectroscopic properties of  $(C_5Me_5)_2Y\{NC(CMe_3)[CH(SiMe_3)_2]\}(NCCMe_3)$  generated from  $(C_5Me_5)_2Y[CH(SiMe_3)_2]$  and  $Me_3CCN$  are also similar.<sup>25b</sup>

Complex **2** has an eight-coordinate geometry around samarium which is typical of trivalent  $(C_5Me_5)_2Sm$ -containing complexes<sup>3</sup> and the metrical parameters for the trivalent decamethylsamarocene component are in the normal range,<sup>3</sup> Table 2. The  $2.225(8)$  Å  $Sm-N(1)$  distance in **2** is considerably shorter than the  $2.533(8)$  Å  $Sm-N(2)$  bond length, Table 3. This is consistent with  $N(1)$  being part of a formally anionic, imine ligand,  $[N=C(Ph)(C_5Me_5)]^-$ , while  $N(2)$  is part of a neutral nitrile ligand.<sup>26</sup> The  $C(37)-N(1)$  distance of  $1.261(12)$  Å is longer than the  $C(38)-N(2)$  distance of  $1.137(11)$  Å, which is consistent with the  $C=N$  double bond character of the imine ligand versus the  $C\equiv N$  triple bond of the coordinated nitrile.<sup>25,27</sup> Hence, the structural data match the IR data presented above. The pentamethylcyclopentadienyl substituent attached to  $C(37)$  has a single bond between  $C(37)$  and  $C(21)$  [ $1.57(1)$  Å], localized  $C=C$  double bonds between  $C(22)$  and  $C(23)$  [ $1.33(2)$  Å] and  $C(24)$  and  $C(25)$  [ $1.29(2)$  Å], and single bonds between  $C(21)$  and  $C(25)$  [ $1.51(2)$  Å] and  $C(21)$  and  $C(22)$  [ $1.49(2)$  Å].<sup>27</sup> The  $1.40(2)$  Å  $C(23)-C(24)$  bond distance is intermediate. Both the coordinated nitrile and the imine ligand are bound in a very nearly linear fashion to Sm; the  $Sm-N(2)-C(38)$  angle is  $174.3(7)^\circ$  while the  $Sm-N(1)-C(37)$  angle is  $173.7(7)^\circ$ .

**Reaction with PhNCO.**  $PhNCO$  also reacts immediately with a toluene solution of  $(C_5Me_5)_3Sm$  to form a yellow product, **3**. The <sup>1</sup>H NMR spectrum of **3** contained resonances attributable to a trivalent decamethylsamarocene unit and an  $\sigma$ -bound  $C_5Me_5$  unit; however, as usual for paramagnetic Sm(III) complexes, it was not structurally definitive. X-ray crystallography

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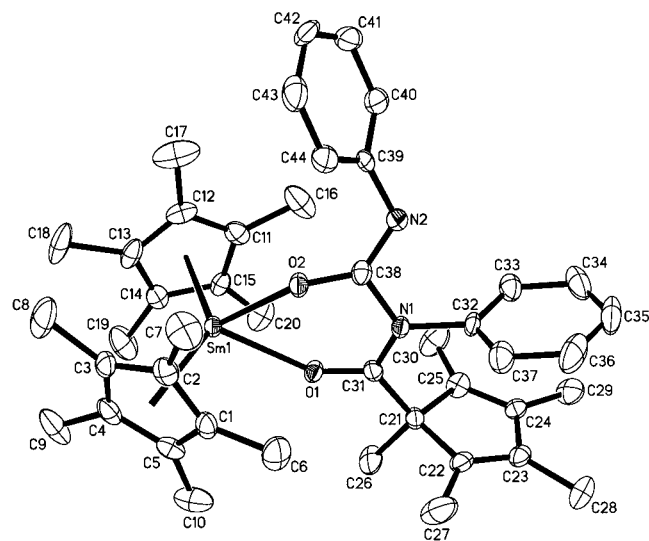
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**Table 2.** Bond Distances (Å) and Angles (°) in Metallocene Components of  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NCPh)$ , **2**,  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , **3**, and  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3$ , **4**

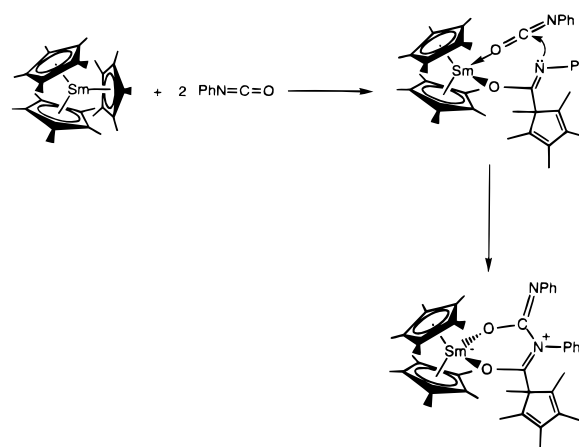
	<b>2</b>	<b>3</b>	<b>4</b>
Sm–C( $C_5Me_5$ ), range	2.69(2)–2.77(2)	2.666(5)–2.747(5)	2.697(5)–2.806(5)
Sm–C( $C_5Me_5$ ), average	2.73(3)	2.71(3)	2.75(3)
(ring centroid)–Sm–(ring centroid) angle	137.6	136.5	132.5

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for  $(C_5Me_5)_2Sm[NC(Ph)(C_5Me_5)](NCPh)$ , **2**,  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , **3**, and  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3$ , **4**

<b>2</b>		<b>3</b>		<b>4</b>	
Sm(1)–N(1)	2.225(8)	Sm(1)–O(1)	2.386(3)	Sm(1)–N(1)	2.561(4)
Sm(1)–N(2)	2.533(8)	Sm(1)–O(2)	2.259(3)	Sm(1)–C(63)	2.604(5)
N(1)–C(37)	1.261(12)	O(1)–C(31)	1.252(6)	Sm(1)–C(64)	2.651(5)
N(2)–C(38)	1.137(2)	N(1)–C(31)	1.354(7)	Sm(2)–N(2)	2.589(4)
C(31)–C(37)	1.509(14)	N(1)–C(32)	1.456(7)	Sm(2)–C(61)	2.606(5)
C(38)–C(39)	1.430(13)	N(1)–C(38)	1.483(7)	Sm(2)–C(69)	2.645(5)
C(21)–C(37)	1.570(14)	N(2)–C(38)	1.278(7)	Sm(3)–N(3)	2.576(5)
C(21)–C(22)	1.49(2)	O(2)–C(38)	1.278(6)	Sm(3)–C(62)	2.612(5)
C(22)–C(23)	1.33(2)	N(2)–C(39)	1.409(7)	Sm(3)–C(74)	2.634(5)
C(23)–C(24)	1.40(2)	C(31)–C(21)	1.541(8)		
C(24)–C(25)	1.29(2)	C(21)–C(22)	1.523(8)	N(1)–Sm(1)–C(63)	72.91(13)
C(21)–C(25)	1.51(2)	C(22)–C(23)	1.342(8)	N(2)–Sm(2)–C(61)	71.33(13)
		C(23)–C(24)	1.447(8)	N(3)–Sm(3)–C(62)	74.27(13)
		C(24)–C(25)	1.344(8)	Sm(1)–N(1)–C(61)	175.1(4)
		C(21)–C(25)	1.526(8)	Sm(2)–N(2)–C(62)	168.5(4)
				Sm(3)–N(3)–C(63)	171.4(4)
N(1)–Sm(1)–N(2)	95.3(3)	O(1)–Sm(1)–O(2)	69.53(12)	Sm(1)–C(63)–N(3)	171.1(4)
Sm(1)–N(1)–C(37)	173.7(7)	Sm(1)–O(1)–C(31)	139.6(3)	Sm(2)–C(61)–N(1)	175.6(4)
Sm(1)–N(2)–C(38)	174.3(7)	Sm(1)–O(2)–C(38)	137.3(3)	Sm(3)–C(62)–N(2)	176.7(4)
N(1)–C(37)–C(31)	119.8(9)	O(1)–C(31)–N(1)	121.3(5)		
N(1)–C(37)–C(21)	123.4(9)	O(1)–C(31)–C(21)	117.6(5)		
C(31)–C(37)–C(21)	116.7(8)	C(21)–C(31)–N(1)	121.1(5)		
N(2)–C(38)–C(39)	178.9(10)	C(31)–N(1)–C(32)	122.5(5)		
		C(31)–N(1)–C(38)	123.4(4)		
		C(32)–N(1)–C(38)	113.9(5)		
		N(1)–C(38)–N(2)	112.8(5)		
		N(1)–C(38)–O(2)	116.6(5)		
		O(2)–C(38)–N(2)	130.5(5)		
		C(38)–N(2)–C(39)	118.7(5)		

**Figure 2.** Thermal ellipsoid plot of  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , **3**, with thermal ellipsoids drawn at the 50% probability level.

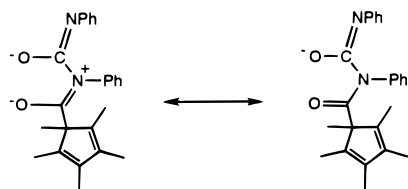
was used to identify the product as  $(C_5Me_5)_2SmOC(C_5Me_5)N(Ph)C(NPh)O$ , Figure 2. This complex is analogous to **2** in that it is composed of one  $(C_5Me_5)_2Sm$  unit, two molecules of substrate, and pentamethylcyclopentadiene. However, it differs in that neither of the substrate molecules are simply coordinated to samarium. Instead, the two substrate molecules are joined

**Scheme 1**

by a C–N bond and form the metallacyclic structure shown in Scheme 1. If the reaction proceeds as observed for the PhCN reaction, an intermediate of the type  $(C_5Me_5)_2Sm[OC(C_5Me_5)N(Ph)](OCNPh)$  could initially form. Since this contains a nucleophilic nitrogen adjacent to the carbon atom of the isocyanate, a position which is generally electrophilic,<sup>28</sup> it is reasonable to expect that a samarium-mediated coupling occurred to form the observed product.

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## Scheme 2



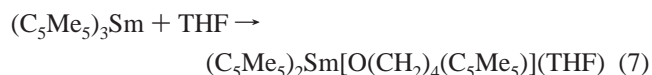
The coordination environment around samarium in complex **3** is typical of trivalent  $(C_5Me_5)_2Sm$ -containing complexes, and the complex has no unusual distances or angles in the metallocene unit,<sup>3</sup> Table 2. The  $69.52(12)^\circ$  O(1)–Sm–O(2) angle in **3** is less than typical donor-atom–metal–donor-atom angles in compounds of this type due to the fact that the two donor atoms are part of a chelating ligand system.

The  $\sigma$ -bound  $C_5Me_5$  portion of the molecule is much like that in **2**, i.e., it has the characteristics of a localized diene substituent, Table 3. This  $C_5Me_5$  ring is attached by a 1.541(8) Å C(21)–C(31) single bond, and localized double bonds are present for C(25)–C(24), 1.344(8) Å, and C(22)–C(23), 1.342(8) Å. The 1.523(8) Å C(21)–C(22) and 1.526(8) Å C(21)–C(25) bonds have typical single bond lengths and the 1.447(8) Å C(23)–C(24) bond distance is between the single and double bond distance ranges as in **2**.

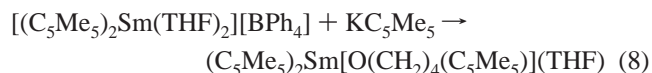
The bond distances in the rest of the chelating ligand indicate considerable delocalization. The bond angles around C(31), C(38), and N(1) are consistent with  $sp^2$  hybridization, although Sm(1), O(1), O(2), C(31), C(38), and N(1) are not rigorously coplanar. O(2) is out of the plane of these atoms by 0.17 Å, and N(2) is out of the plane by 0.12 Å in the other direction. The ipso phenyl carbon atoms C(32) and C(39) and the  $C_5Me_5$  C(21) are out of from this plane by 0.04, 0.06, and 0.17 Å, respectively. The C(32)–C(37) phenyl ring plane is almost perpendicular to this plane with a  $93.6^\circ$  dihedral angle. The C(39)–C(44) phenyl ring plane is tilted at a  $44.6^\circ$  angle to the  $SmO_2C_2N$  plane. Within this extended ligand, there are four short bonds, C(31)–O(1), C(38)–O(2), C(31)–N(1), and C(38)–N(2). The 1.278(6) Å C(38)–O(2) and 1.252(6) Å C(31)–O(1) distances are equivalent within their error limits and are between the 1.192–1.256 Å range of  $C(sp^2)=O$  and the 1.293–1.407 Å range of  $C(sp^2)-O$  distances in the literature.<sup>27</sup> The 1.278(7) Å C(38)–N(2) bond is near the low end of the 1.279–1.329 Å range of reported  $C(sp^2)=N$  distances.<sup>27</sup> The 1.354(7) Å C(31)–N(1) bond is close to the 1.279–1.329 Å range of  $C(sp^2)=N$  distances in the literature but is in the middle of the 1.321–1.416 Å range of  $C(sp^2)-N$  distances which overlaps with the other range. The 1.483(7) Å C(38)–N(1) bond is clearly longer than this typical single bond range. The N–C(iso) bonds, 1.456(7) Å N(1)–C(32) and 1.409(7) Å N(2)–C(39), also have lengths indicative of single bonds. The 2.386(3) Å Sm–O(1) and 2.259(3) Å Sm–O(2) distances are within the 2.08(1) Å to 2.39(1) Å range observed for  $(C_5Me_5)_2Sm-OR$  bonds involving anionic oxygen donor ligands such as alkoxides and are shorter than the 2.44(2) Å to 2.72(2) Å range of  $(C_5Me_5)_2ZSm-(OR)_2$  bonds ( $Z =$  monoanionic ligand) for neutral oxygen donor ligands.<sup>3,12,15</sup> Two resonance structures which correlate with these crystallographic data are shown in Scheme 2. Both reflect the important reaction chemistry, namely that the isocyanate has inserted into a  $Sm-C_5Me_5$  moiety and a second isocyanate has coupled to this unit.

**Ring-Opening Reactions.** Like benzonitrile, THF reacts immediately with  $(C_5Me_5)_3Sm$  to form yellow solutions. It was discovered during a study on the development of new synthetic routes to  $(C_5Me_5)_3Sm^4$  that the product of this reaction,  $(C_5-$

$Me_5)_2Sm[O(CH_2)_4(C_5Me_5)](THF)$ , eq 7, was that previously

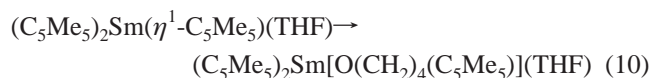


identified from the reaction of  $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$  with  $KC_5Me_5$ , eq 8.<sup>12</sup> In fact, this THF ring-opening reactivity is a



major obstacle in the isolation of  $(C_5R_5)_3M$  complexes, and reaction products of this type have been found for a variety of lanthanides including La, Nd, Tm, and Lu.<sup>29</sup>

Reaction 8 was understandable since THF is activated to nucleophilic ring opening by Lewis acids,<sup>30</sup> and coordination of THF to the cationic electrophilic samarium center should activate it with respect to ring opening by  $(C_5Me_5)^-$ . The reaction of  $(C_5Me_5)_3Sm$  with THF was more difficult to rationalize since the nucleophile rather than THF was attached to the metal. However, this reactivity can be explained if an  $\eta^1-C_5Me_5$  intermediate is accessible as shown in eqs 9 and 10.



If THF could coordinate to make a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)(THF)$  intermediate, this species would have an activated THF adjacent to a nucleophile. Analogous chemistry has been observed for  $(C_5Me_5)_2Sm(PPh_2)(THF)$  and  $(C_5Me_5)_2Sm(AsPh_2)(THF)$ , which can be isolated but subsequently form ring-opened products analogous to  $(C_5Me_5)_2Sm[O(CH_2)_4(C_5Me_5)](THF)$ , i.e.,  $(C_5Me_5)_2Sm[O(CH_2)_4PPh_2](THF)$  and  $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$ .<sup>31</sup>

The fact that increasing the steric bulk of the furan interferes with this reactivity is consistent with this scenario. Hence, 2,5-dimethyltetrahydrofuran does not react with  $(C_5Me_5)_3Sm$ , even at  $75^\circ C$ . This sterically more bulky furan would not be able to coordinate as easily to the sterically crowded  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  unit.

$\epsilon$ -Caprolactone is polymerized by  $(C_5Me_5)_3Sm$ , eq 11, a



reaction which again can be rationalized with the intermediacy of a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)L$  unit since  $\epsilon$ -caprolactone is known to coordinate lanthanides<sup>32</sup> and is readily polymerized by alkyl lanthanide complexes.<sup>33</sup>

**Reduction Chemistry.  $Ph_3P=E$  Reactions.** Triphenylphosphine oxide and its congeners,  $Ph_3P=E$  ( $E = S, Se$ ), were initially examined as possible trapping agents for a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  intermediate.  $(C_5Me_5)_3Sm$  reacts with these

(29) Schumann, H.; Glanz, M.; Hemling, H.; Görlitz, F. H. *J. Organomet. Chem.* **1993**, 462, 155.

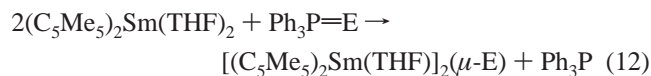
(30) Dreyfuss, P.; Dreyfuss, M. P. In *Ring Opening Polymerization*; Frisch, K. C.; Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Chap 2. Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, 37, 1. Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, 104, 5586.

(31) Evans, W. J.; Leman, J. T.; Ziller, J. W. *Inorg. Chem.* **1996**, 35, 4238.

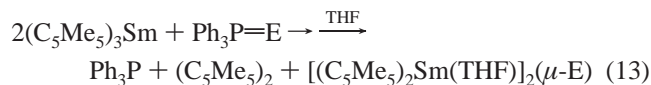
(32) Evans, W. J.; Shreeve, J. L.; Doedens, R. J. *Inorg. Chem.* **1993**, 32, 245. Evans, W. J.; Shreeve, J. L.; Boyle, T. J.; Ziller, J. W. *J. Coord. Chem.* **1995**, 34, 229.



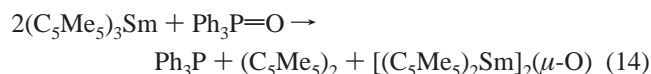
reagents but not in the manner originally expected. Addition of THF to the  $\text{Ph}_3\text{P}=\text{S}$  and  $\text{Ph}_3\text{P}=\text{Se}$  reaction products gives the previously characterized trivalent organosamarium compounds  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2](\mu\text{-E})$ .<sup>13</sup> The conversion of  $\text{Ph}_3\text{P}=\text{E}$  to  $(\text{E})^{2-}$  is a two-electron reduction equivalent to that previously observed with  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$  according to eq 12.<sup>13</sup> In the case of reaction 12, however, the reduction is done



with 2 equiv of the strongly reducing divalent  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ , whereas the reaction starting with  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  involves 2 equiv of a trivalent samarium complex. Since a Sm(III) to Sm(IV) conversion is not thermodynamically reasonable,<sup>10</sup> the reduction in this  $(\text{C}_5\text{Me}_5)_3\text{Sm}$ -based reaction must be arising from a  $\text{C}_5\text{Me}_5$  ligand. Indeed, isolated as a byproduct along with triphenylphosphine was  $(\text{C}_5\text{Me}_5)-(\text{C}_5\text{Me}_5)$ , the product known to form by oxidative coupling of  $(\text{C}_5\text{Me}_5)^-$ .<sup>14</sup> The overall reaction is shown in eq 13.  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  also reduces

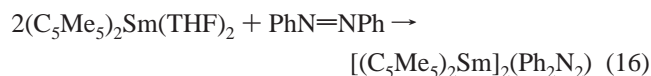
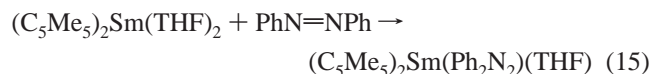


$\text{Ph}_3\text{P}=\text{O}$  to make the previously characterized oxide complex,  $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-O})$ ,<sup>15</sup> as shown in eq 14.

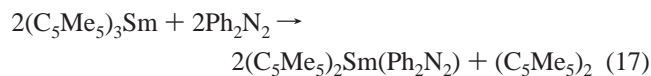


**Azobenzene, Cyclooctatetraene, and Pyrene Reactions.** To determine if the reductive reactivity of  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  observed in the  $\text{Ph}_3\text{P}=\text{E}$  reactions was general and to estimate the effective reduction potential of  $(\text{C}_5\text{Me}_5)_3\text{Sm}$ , reactions with other reducible substrates with known reduction potentials were examined. Substrates which had been previously reduced with divalent  $(\text{C}_5\text{Me}_5)_2\text{Sm}$  were preferred because their organosamarium reduction products had already been fully characterized.

Azobenzene, which has a first reduction potential of  $-1.35$  to  $-1.41\text{V}$  and a second reduction potential of  $-1.75$  to  $-2.03\text{V}$  (vs SCE),<sup>34</sup> can be reduced by 1 and 2 equiv of  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$  as shown in eqs 15 and 16.<sup>16</sup>  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  reacts with



azobenzene to form only the one-electron reduction product,  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{Ph}_2\text{N}_2)$ , as shown in eq 17. This reaction estab-

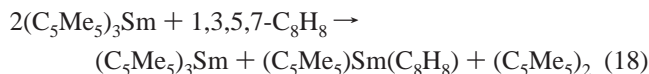


lished that  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  is a reducing agent weaker than  $(\text{C}_5\text{Me}_5)_2\text{Sm}$ .

(33) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330. Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 4011. McLain, S. J.; Ford, T. M.; Drysdale, N. E. *Polym. Prepr.*, (Am. Chem. Soc., Div. Polym. Chem.) **1992**, *33*, 463.

(34) Thomas, F. G.; Boto, K. G. In *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; Chapter 12.

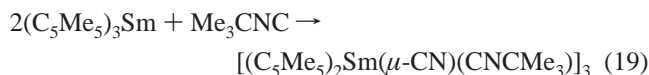
1,3,5,7-Cyclooctatetraene is reduced at  $-1.83\text{V}$  (vs SCE)<sup>35</sup> and is converted by  $(\text{C}_5\text{Me}_5)_2\text{Sm}$  to  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  and  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}_8\text{H}_8)$  according to eq 1.<sup>2</sup>  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  also reduces 1,3,5,7- $\text{C}_8\text{H}_8$ , as shown in eq 18, in a reaction which is parallel



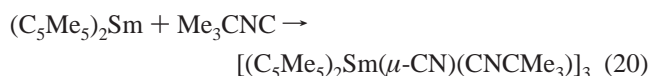
to eq 1.

In contrast to  $(\text{C}_5\text{Me}_5)_2\text{Sm}$ ,  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  is not a strong enough reducing agent to reduce anthracene ( $-1.98\text{V}$  vs SCE<sup>35</sup>) or pyrene ( $-2.10\text{V}$  vs SCE<sup>35</sup>).  $(\text{C}_5\text{Me}_5)_2\text{Sm}$  reduces these substrates to form the crystallographically characterized trivalent complexes,  $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-C}_{14}\text{H}_{10})$  and  $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-C}_{16}\text{H}_{10})$ .<sup>36</sup>

**$\text{Me}_3\text{CNC}$  Reactions.** The reactivity of  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  with isocyanides was examined since  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  readily reacts with  $\text{CO}$ ,<sup>5</sup> and isocyanides often have chemistry similar to that of  $\text{CO}$ .  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  reacts instantly with  $\text{Me}_3\text{CNC}$  in a 1:1 molar ratio in toluene at room temperature, but in contrast to the  $\text{CO}$  reaction which gives a yellow product, an intensely colored red solution is obtained. Removal of the solvent yields a red powder that exhibits two singlets in the  $^1\text{H}$  NMR spectrum at 0.37 ppm and  $-0.10$  ppm which integrate in a 5:1 ratio, respectively, consistent with formation of a  $(\text{C}_5\text{Me}_5)_3\text{Sm}(\text{CNCMe}_3)$  adduct. The signal at 0.37 ppm, which corresponds to three  $\text{C}_5\text{Me}_5$  ligands, is shifted 1.61 ppm downfield from the  $-1.24$  ppm resonance of  $(\text{C}_5\text{Me}_5)_3\text{Sm}$ , while the resonance corresponding to the  $\text{Me}_3\text{C}$  group is shifted 1.90 ppm upfield from that of free  $\text{Me}_3\text{CNC}$ . Infrared spectroscopy reveals a strong band at  $2155\text{cm}^{-1}$  in the  $\text{C}\equiv\text{N}$  bond stretching region which is  $20\text{cm}^{-1}$  higher than that of free  $\text{Me}_3\text{CNC}$ .<sup>37</sup> Hence, the spectroscopic data imply that an isocyanide adduct had formed without causing an  $\eta^5$  to  $\eta^1$ - $(\text{C}_5\text{Me}_5)$  shift and that no insertion had taken place. Crystals suitable for structural characterization were not isolated from this product, but crystallographic data were obtainable from this system when the  $\text{Me}_3\text{CNC}/(\text{C}_5\text{Me}_5)_3\text{Sm}$  reaction was heated to  $80^\circ\text{C}$  in toluene for 1 h. The solution turned pale yellow, and a yellow precipitate was isolated in 87% yield. Yellow crystals were obtained from a concentrated THF solution and identified by IR spectroscopy and X-ray crystallography as  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-CN})(\text{CNCMe}_3)]_3$ , **4** (Figure 3), reaction 19. This



product was previously obtained by reduction of  $\text{Me}_3\text{CNC}$  with  $(\text{C}_5\text{Me}_5)_2\text{Sm}$ ,<sup>18</sup> reaction 20.

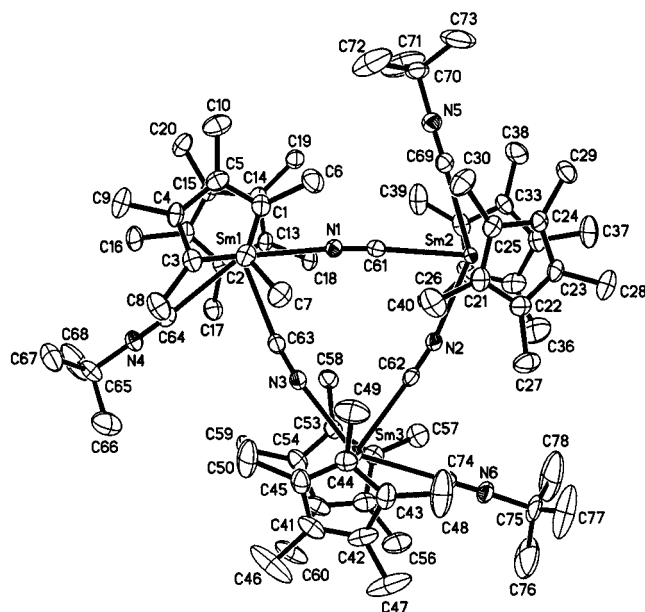


Since only a low quality crystal structure was obtainable on **4** previously, the full structural details are included here. The structure of **4** is very similar to that of  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-CN})(\text{CNC}_6\text{H}_{11})]_3$ , **5**, obtained from  $(\text{C}_5\text{Me}_5)_2\text{Sm}$  and  $\text{CNC}_6\text{H}_{11}$ ,<sup>18</sup> i.e., three isocyanide-solvated decamethylsamarocene units are located at the corners of a triangle connected by bridging cyanide ligands along the edges. As is common for X-ray analyses of

(35) de Boer, E. *Adv. Organomet. Chem.* **1964**, *2*, 115.

(36) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600.

(37) Dolphin, D.; Wick, A. E. *Tabulation of Infrared Spectral Data*; Wiley: New York, 1977. Malatesta, L.; Bonati, R. *Isocyanide Complexes of Metals*; Wiley: New York, 1969.



**Figure 3.** Thermal ellipsoid plot of  $[(C_5Me_5)_2Sm(\mu-CN)(CNCMe_3)]_3$ , **4**, with ellipsoids drawn at the 50% probability level.

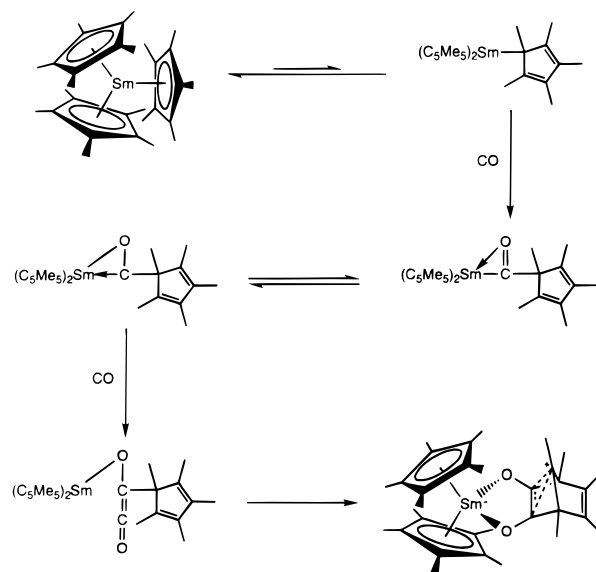
cyanide groups,<sup>38</sup> it was not possible to differentiate between carbon and nitrogen atoms for these ligands. Hence, the three independent values of the Sm-C(isocyanide donor atom) distance are 2.651(5) Å, 2.645(5) Å, and 2.634(5) Å and are equivalent within experimental error to the analogous distances found in **5**. The 1.165(6) Å, 1.162(6) Å, and 1.156(6) Å C–N distances also compare favorably to the cyanide distances in **5** and are consistent with the presence of a triple bond in a cyanide ligand.<sup>27</sup> The Sm–C–N (Sm–N–C) angles in these sides approach linearity, ranging from 171.1(4)° to 176.7(4)°. The Sm–C(ring) distances and ring-centroid–Sm–ring-centroid angles are typical for trivalent decamethylsamarocene units, Table 2.<sup>3</sup>

## Discussion

The reactions of  $(C_5Me_5)_3Sm$  investigated so far appear to fall into two categories, depending on the substrate encountered. One class of reactions can be explained in terms of access to an  $\eta^1$ -pentamethylcyclopentadienyl intermediate such as  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  and the other in terms of one-electron reduction in which one of the  $(C_5Me_5)^-$  ligands is functioning as the reductant. These are unusual reaction pathways for  $C_5Me_5$  ligands attached to metals, but both are reasonable in this sterically crowded  $(C_5Me_5)_3Sm$  complex since they lead to relief of the steric strain. Since the first class of reactions is the easiest to rationalize, this will be discussed first.

**$(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  Reactivity.** Several of the reactions of  $(C_5Me_5)_3Sm$  are typical of metallocene alkyl complexes such as  $(C_5Me_5)_2SmR$ , and in the case of these  $(C_5Me_5)_3Sm$  reactions, R is  $\eta^1-C_5Me_5$ . The general class of  $(C_5Me_5)_2SmR$  complexes is well-documented in the literature with crystallographically characterized examples known for the solvated  $(C_5Me_5)_2SmR$ -(THF) analogues with R = Ph,<sup>39</sup>  $CH_2Ph$ ,<sup>40</sup> and  $Me^{7c}$  and for the closely related  $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$ .<sup>7c</sup> Since hydrogenolysis reactivity is well-known for these  $(C_5Me_5)_2SmR$  complexes,<sup>7c,9,40</sup> the analogous reaction by  $(C_5Me_5)_3Sm$  shown

## Scheme 3



in eq 5 is quite reasonable, assuming a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  intermediate.

The  $(C_5Me_5)_3Sm$  insertion chemistry of CO, eq 3, PhCN, eq 6, and PhCNO, Scheme 1, can also be explained using this  $(C_5Me_5)_2SmR$  model since insertion reactions are also common for this class of complexes. It is well established that CO inserts into lanthanide alkyl bonds to make reactive intermediates which can add 1 equiv of CO.<sup>41</sup> Hence, a sequence of the type shown in Scheme 3 can be envisioned for the reaction of CO with  $(C_5Me_5)_3Sm$ .

The steps in Scheme 2 are strongly supported by the insertion reactions with PhCN and PhNCO. The PhCN reaction, eq 6, models the first insertion of a substrate into a  $Sm(\eta^1-C_5Me_5)$  unit, and the isolation of the coupled ligand in **3** shows that a second equivalent of substrate can be incorporated into the first insertion product (Scheme 1).

Although the reaction patterns and products are consistent with a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  intermediate, there is no spectroscopic or structural evidence for this species in the solid state or in solution at low temperature. However, pyridine appears to form a Lewis base adduct with  $(C_5Me_5)_3Sm$  which has an NMR spectrum consistent with a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$ -(pyridine) structure. This suggests that, in the presence of the appropriate Lewis base,  $(C_5Me_5)_3Sm$  can react as if it were an alkyl complex such as  $(C_5Me_5)_2Sm(R)L$ .

The ring-opening reactivity of  $(C_5Me_5)_3Sm$  with THF is also consistent with a  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)L$  intermediate. A  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$  complex alone would not be expected to ring-open THF, since the THF is not activated for nucleophilic attack. However, in a complex such as  $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)$ -(THF), the THF could be Lewis acid-activated to nucleophilic attack by the adjacent  $C_5Me_5$  group. Such a situation has been demonstrated crystallographically with  $(C_5Me_5)_2Sm(AsPh_2)(THF)$  and  $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$ .<sup>31</sup> Consistent with the scenario that substrate coordination must occur to access the  $\eta^1-C_5Me_5$  intermediate is the fact that the sterically more crowded ether, 2,5-dimethyltetrahydrofuran, is not ring-opened by  $(C_5Me_5)_3Sm$  presumably because it is less likely to coordi-

(38) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: New York, 1976.

(39) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112.

(40) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics*, **1991**, *10*, 134.

(41) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706 and references therein. Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772.

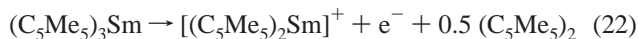
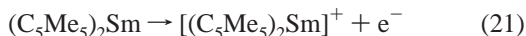


The fact that hydrogen can also react with  $(C_5Me_5)_3Sm$ , eq 5, suggests that the formation of a base adduct may not be necessary to access an  $\eta^1-C_5Me_5$  intermediate. Furthermore, it is interesting to note that the  $^1H$  NMR spectrum of  $(C_5Me_5)_3Sm$  in the presence of  $Me_3CNC$  is consistent with the formation of a Lewis base adduct of the type  $(\eta^5-C_5Me_5)_3SmL$  in which all of the rings retain their  $\eta^5$ -orientation. This is consistent with the channel available down the  $S_3$  axis in  $(C_5Me_5)_3Sm$  and with the cylindrical nature of the donor portion of  $Me_3CNC$ . It is therefore conceivable that other cylindrical molecules such as CO, PhCN, and PhNCO could also form such intermediates. Access to a transient  $\eta^1-C_5Me_5$  intermediate should be favored even more from  $(\eta^5-C_5Me_5)_3SmL$  than from  $(\eta^5-C_5Me_5)_3Sm$  since it is more crowded.

Collectively, we find that a variety of substrates with considerable differences in size and basicity can react with  $(C_5Me_5)_3Sm$  to form products consistent with the intermediacy of an  $(\eta^1-C_5Me_5)$  unit. As such, we can consider  $(C_5Me_5)_3Sm$  as a bulky  $(C_5Me_5)_2SmR$  complex in disguise. It appears that it is a rather special system, however, since it can lead to derivatization of  $C_5Me_5$  ligands which are usually inert and it can readily insert nitriles, a reaction generally found only for very reactive metal carbon bonds.

**Reduction Chemistry.** A second major class of reactions of  $(C_5Me_5)_3Sm$  involves reductions in which trivalent  $(C_5Me_5)_3Sm$  acts as a one-electron reducing agent analogous to divalent  $(C_5Me_5)_2Sm(THF)_x$  ( $x = 0$  or  $2$ ) as shown in eqs 12–18. A variety of substrates can be reduced including  $O=PPh_3$ ,  $S=PPh_3$ ,  $Se=PPh_3$ ,  $PhN=NPh$ , and  $1,3,5,7-C_8H_8$ , and the organosamarium products are the same as those obtained from reductions with  $(C_5Me_5)_2Sm$  or  $(C_5Me_5)_2Sm(THF)_2$ .

Since Sm(III) rather than Sm(IV) products are isolated in the  $(C_5Me_5)_3Sm$  reductions and since the pentamethylcyclopentadienyl dimer,  $(C_5Me_5)_2$ , is a byproduct, it is the  $(C_5Me_5)^-$  anion and not the metal that is the reducing agent in these reactions. These  $(C_5Me_5)_3Sm$  reductions would be expected to make the same products as  $(C_5Me_5)_2Sm$  reductions since, after electron transfer, the same cation,  $[(C_5Me_5)_2Sm]^+$ , remains with the reduced substrate. This is shown in the half reactions 21 and 22.



One way to view the observed reductions involves a homolytic cleavage of a  $Sm-C_5Me_5$  bond to give a divalent  $[(C_5Me_5)_2Sm^{II}](C_5Me_5^{\bullet})$  intermediate. In this case, one would expect that  $(C_5Me_5)_3Sm$  would have the same reduction potential as  $(C_5Me_5)_2Sm$ . Since  $(C_5Me_5)_3Sm$  does not reduce anthracene or pyrene as  $(C_5Me_5)_2Sm$  does<sup>36</sup> and since  $(C_5Me_5)_3Sm$  reduces azobenzene by only one electron whereas  $(C_5Me_5)_2Sm$  can effect a two-electron reduction,<sup>16</sup> the reduction potentials of  $(C_5Me_5)_3Sm$  and  $(C_5Me_5)_2Sm$  are not the same, and a homolytic explanation seems unlikely. In addition, homolytic cleavage of a  $Sm-C_5Me_5$  bond to give divalent  $(C_5Me_5)_2Sm$  and the  $C_5Me_5^{\bullet}$  radical is equivalent to saying that a  $(C_5Me_5)^-$  anion is capable of reducing Sm(III) to Sm(II). This is not consistent with known  $C_5Me_5$  lanthanide chemistry. Of the four lanthanide metals with the most available divalent oxidation states, Tm, Sm, Eu, and Yb, only Eu(III) is readily reduced to Eu(II) by the  $(C_5Me_5)^-$  anion.<sup>42</sup>

(42) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999. Evans, W. J.; Shreeve, J. L.; Ziller, J. W. *Organometallics* **1994**, *13*, 731.

Alternatively, the reduction chemistry of  $(C_5Me_5)_3Sm$  can be viewed as an electron-transfer involving heterolytic separation of a  $(C_5Me_5)^-$  anion. In this case,  $(C_5Me_5)_3Sm$  can be viewed as having a zwitterionic intermediate,  $[(C_5Me_5)_2Sm]^+(C_5Me_5)^-$ , in which one pentamethylcyclopentadienide ligand is arbitrarily written separately to show it as the reducing agent. If the  $(C_5Me_5)^-$  moiety which is doing the reduction is still interacting with the metal, it could have either an  $\eta^5$ -form or an  $\eta^1$ -form like that discussed above. As in the case of the  $(C_5Me_5)_2Sm-(\eta^1-C_5Me_5)$  intermediates discussed above, there is no physical evidence for this zwitterionic form.

Reactivity consistent with a zwitterionic form may happen as a result of the extreme steric crowding around  $(C_5Me_5)_3Sm$ . The 2.82(5) Å average Sm-C(ring) distance observed for  $(C_5Me_5)_3Sm$  is the longest distance known for a trivalent samarium complex. This means that the  $(C_5Me_5)^-$  anions are not as stabilized by the cationic center as in typical organometallic pentamethylcyclopentadienyl compounds. As such, a  $(C_5Me_5)^-$  ring could act as a separate entity and do reduction chemistry.

This zwitterionic explanation means that  $(C_5Me_5)_3Sm$  can be viewed as providing a reactive, solubilized form of  $(C_5Me_5)^-$ . Simple  $(C_5Me_5)^-$  salts do not exhibit this type of reductive reactivity; neither  $KC_5Me_5$  nor  $ClMg(C_5Me_5)$  nor  $Pb(C_5Me_5)_2$  reduces  $Se=PPh_3$  and  $1,3,5,7-C_8H_8$ .<sup>43</sup> This zwitterionic analysis also means that  $(C_5Me_5)_3Sm$  is providing a soluble form of the unsolvated cation  $[(C_5Me_5)_2Sm]^+$ .

**Implications of the Reduction Chemistry. Reduction Chemistry for Trivalent Lanthanides Which Do Not Have a Divalent State.** The fact that trivalent  $(C_5Me_5)_3Sm$  can do one-electron reduction chemistry suggests that one-electron reduction chemistry can be extended to lanthanides beyond those with accessible divalent states. This would be quite valuable since an extensive amount of chemistry has been developed with the divalent lanthanides that is not readily accessible for the other lanthanides.<sup>44,45</sup>

In the lanthanide metallocene area in general,  $(C_5Me_5)_2Sm$ -containing complexes have been much more extensively investigated than any other type of  $C_5Me_5/Ln$  combination because  $(C_5Me_5)_2Sm$  and  $(C_5Me_5)_2Sm(THF)_2$  provide facile reductive routes unavailable to the other metals. For example, the first  $[(C_5Me_5)_2LnH]_2$  complex was prepared with  $Ln=Sm$  via a Sm(II) route.<sup>9</sup> Direct reduction of substrates by  $(C_5Me_5)_2Sm$  or  $(C_5Me_5)_2Sm(THF)_2$  to complexes of the form  $[(C_5Me_5)_2Ln]_2$ - (substrate) is much easier than attempting an ionic metathesis between a lanthanide metallocene halide adduct such as  $(C_5Me_5)_2LnCl_2M(solvent)_2$  and a substrate which has been previously reduced by an alkali metal. The facile formation of adducts containing alkali metals and anions in the system make these ionic metathesis reactions complicated.<sup>46</sup> For example, there are no routes to trivalent azobenzene complexes of the

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type  $(C_5Me_5)_2Sm(Ph_2N_2)(THF)^{16}$  for the lanthanides which lack a divalent state, and complexes such as  $(C_5Me_5)_2LnMe(THF)^{7e,47}$ ,  $(C_5Me_5)_2Ln(allyl)^{7c,f}$ ,  $[(C_5Me_5)_2Ln(THF)_2][BPh_4]^{12,48}$  and  $[(C_5Me_5)_2LnH]_2^{7c,9}$  can be prepared much more easily for  $Ln=Sm$  via a divalent route than the analogues with  $Ln=$ other metals.

Since trivalent  $(C_5Me_5)_3Sm$  is a one-electron reductant, this suggests that other trivalent  $(C_5Me_5)_3Ln$  complexes could also be one-electron reductants. If the reduction chemistry of  $(C_5Me_5)_3Sm$  arises from severe steric crowding, then the other  $(C_5Me_5)_3Ln$  or related  $(C_5R_5)_3Ln$  complexes must be similarly crowded to have the same reduction chemistry. Since the steric crowding can be adjusted by changing the size of the ligand, this seems quite possible, and extension of the special chemistry of  $Sm(II)$  to all of the lanthanides is conceivable if synthetic routes to the other  $(C_5R_5)_3Ln$  complexes can be developed.<sup>49</sup>

Extension of samarium-like reduction chemistry to the other lanthanides would be quite valuable since one of the powerful aspects of trivalent lanthanide metal chemistry is that one can be highly selective in picking the lanthanide of just the proper size to optimize a specific reaction.<sup>44,50</sup> At present, many lanthanide metallocene-based reactions can only be done conveniently with samarium, and hence, variation of the size of the lanthanide metal is not possible. In addition, the lanthanide series offers a wide variety of specific physical properties, e.g., magnetic or fluorescent properties, which may be desirable for particular applications. Analogues of samarium

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compounds now readily accessible from  $(C_5Me_5)_2Sm(THF)_x$  could become available for other metals in the series via  $(C_5Me_5)_3Sm$  reduction chemistry.

## Conclusion

Despite its extreme steric saturation,  $(C_5Me_5)_3Sm$  has an extensive and chameleon-like reaction chemistry. With some substrates, it can behave as a bulky alkyl complex and participate in polymerization, hydrogenolysis, insertion, and ring-opening chemistry. With other substrates, it displays one-electron reduction chemistry as if it were a zwitterion in which  $(C_5Me_5)^-$  is a reductant. In both of these reaction modes, the  $(C_5Me_5)^-$  ring adopts uncharacteristic reactivity patterns since it is usually an inert spectator ligand. This is likely to be the result of the steric crowding in the molecule and demonstrates a powerful approach to expand both lanthanide and  $C_5Me_5$  chemistry.

The fact that trivalent  $(C_5Me_5)_3Sm$  can do one-electron reduction chemistry suggests that reduction reactions of this type can be extended to the other trivalent lanthanides. Hence, by preparing the proper sterically crowded tris(peralkylcyclopentadienyl) complexes of the other lanthanides, they can be “samaricized” into the one-electron reducing systems which have been so productive for  $Sm(II)$  complexes.

**Acknowledgment.** We thank the National Science Foundation for support of this research, the U. S. Department of Education Graduate Assistantship in Areas of National Needs program for a fellowship (to K.J.F.), and Robert D. Clark and Gregory W. Nyce for experimental assistance.

**Supporting Information Available:** Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles (46 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9809859