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Preparation and Reactivity of a Compartmental Schiff-Base Samarium Dinuclear Complex

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$SmI_2(THF)_5$ acted as a reducing agent in the reaction with phenylenebis(3,5-$Bu^t{}_4$-salicylidene)iminatosodium, (3,5-$Bu^t{}_4$salophen)$Na_2(THF)_2$, to yield a dimeric compound [Sm_2(SB−SB)$(THF)_3$]·2toluene (**2**) [SB−SB = C−C bonded 3,5-$Bu^t{}_4$salophen dimer] arising from the reductive C−C coupling of two imine functional groups of two 3,5-$Bu^t{}_4$salophenSm units. Complex **2** reacts with MeLi, resulting in a novel oxo-bridged dimer, $\{[(Me_2{-}SB)Sm(\mu\text{-}CH_3)Li(THF)][(Me_2{-}SB)Sm(\mu\text{-}CH_3)Li(THF)_2Li(THF)_2]\}(\mu\text{-}O)(\mu\text{-}Li)_3$ (**3**) [Me_2SB = phenylenebis(3,5-$Bu^t{}_4$salycyl)dimethyldiamidato], featuring alkylation of both Sm atoms and arising from cleavage of the C−C bond connecting the two units, as well as complete reduction of the imine groups of the two salophen ligands and THF deoxygenation. Similar cleavage of the connecting C−C bond of complex **2** was also observed during the reaction with dry O_2 to form a distorted cuboid cluster in which four Sm atoms are bridged by four hydroxyl groups, [(3,5-$Bu^t{}_4$salophen)Sm(OH)]$_4$·4toluene (**4**). The structures of complexes **2**, **3**, and **4** were elucidated by X-ray crystallography.

Introduction

Throughout the last two decades, the chemistry of lanthanides has developed from a minor field into an important area of organometallic chemistry.[1] This activity is a result of the growing awareness of the unique and interesting chemical properties specific to these elements. In view of the radial extension and ionic character of the lanthanides, cyclopentadienyl ligands have been particularly versatile for the stabilization of organolanthanide derivatives because they meet the electronic and steric requirements necessary to form thermally stable, isolable complexes. For Sm(II), the most powerful reductant of the three lanthanides which exist in the +2 oxidation state,[2] the C_5Me_5 ligand has been especially efficient in providing soluble complexes. To date, permethylated cyclopentadienyl anions have allowed for the isolation of some of the most highly reactive organolanthanide derivatives providing new classes of complexes[3] exhibiting remarkable structures[4] and unique reactivities.[5] Given the caliber of the transformations and the number of structurally characterizable, metal-containing products afforded by the $(C_5Me_5)_2Sm(THF)_2$ system with a variety of substrates, the scope of Sm(II) chemistry has widened in order to accommodate other ligands. Nonetheless, examples of well-defined, non-Cp-containing Sm(II) systems remain relatively few, except for a handful of examples of divalent samarium complexes with phosphorus,[6] nitrogen,[7] and oxygen-based[8] ligand systems.

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Recently, a low-valent, macrocyclic Sm complex based on the tetraanionic calix-tetrapyrrole ligand was shown to either reduce dinitrogen[9] or form a divalent, dinuclear Sm complex with an intriguingly short Sm–Sm contact[10] depending upon the reaction conditions.

In the view of expanding the chemistry of low-valent samarium with polydentate ligands, we have now used tetradentate Schiff bases (salen-type) for which lanthanide complexes prepared in nonaqueous media comprise relatively few.[11] Since these ligands are known to display a limited resistance to strongly reducing agents,[12] possible involvement of the ligand in the reactivity of the metal center was anticipated.

Herein we describe the results of our attempts to prepare a Sm(II) tetradentate Schiff-base complex and the unusual reactivity displayed by this derivative.

Experimental Part

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schenk-type glassware in combination with a nitrogen vacuum line. $SmCl_3(THF)_3$,[13] $SmI_2(THF)_5$,[14] phenylenebis(3,5-Bu^t_4salicylideneimine) [3,5-Bu^t_4salophen-H_2], and (3,5-Bu^t_4salophen)$Na_2(THF)_2$[15] were prepared according to literature procedures. C_6D_6 and toluene-d_8 were dried over Na/K alloy, vacuum-transferred into ampules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum-sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods,[16] and corrections for underlying diamagnetism were applied to the data.[17] Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer. Melting and decomposition temperatures were measured on samples sealed in a glass capillary under nitrogen.

Sm(3,5-Bu^t_4salophen)(Cl)(Et_2O) (1). A stirred suspension of $SmCl_3(THF)_3$ (2.6 g, 5.5 mmol) in 100 mL of THF was treated with (3,5-Bu^t_4salophen)$Na_2(THF)_2$ (4.0 g, 5.5 mmol). The resulting clear orange solution was allowed to stir at room temperature for 16 h. The solvent was removed in vacuo, and the residual solid was dissolved in diethyl ether (120 mL). Filtration of NaCl, followed by concentration to 75 mL and subsequent standing at room temperature for 2 days, yielded light orange microcrystals of **1** (1.0 g, 1.2 mmol, 44%). El. Anal. Calcd (Found) for $C_{40}H_{56}N_2O_3SmCl$: C 60.15 (61.52), H 7.07 (7.37), N 3.51 (3.43). IR (Nujol mull, cm^{-1}): 1605 (vs, C=N stretch)), 1578 (vs, C=N stretch), 1531 (vs, aromatic), 1319 (m), 1254 (s), 1198 (m), 1167 (s), 1026 (w), 931 (w), 873 (w), 832 (m), 750 (vs). ^1H NMR (C_6D_6, 500 MHz, 23 °C): δ 8.12 (d, 2H, phenyl), 8.02 (d, 2H, phenyl), 6.50 (m, 2H, phenylene), 6.30 (m, 2H, phenylene), 4.34 (s, 2H, C–H imine), 3.25 (q, 4H, diethyl ether), 1.75 (s, 18H, Bu^t), 1.15 (s, 18H, Bu^t), 1.01 (t, 6H, diethyl ether). ^{13}C NMR (C_6D_6, 125.72 MHz, 23 °C): δ 170.84, 170.00 145.69, 137.99, 137.09 (quaternary aromatic), 131.27, 129.28, 127.81, 116.41 (C–H aromatic), 71.70 (C–H imine), 65.86, 15.48 (diethyl ether), 36.22, 34.89 (quaternary Bu^t), 31.99, 29.79 (Bu^t). $\mu_{eff} = 1.60\,\mu_B$. Mp = 290 °C.

[Sm_2(SB–SB)$(THF)_3$]·2toluene (2) [SB–SB = C–C Bonded 3,5-Bu^t_4salophen Dimer]. Method A. The addition of (3,5-Bu^t_4salophen)$Na_2(THF)_2$ (2.5 g, 3.4 mmol) to a stirred solution of $SmI_2(THF)_5$ (1.9 g, 3.5 mmol) in THF (100 mL) rapidly formed a deep red solution. Stirring was continued for 1.5 h, followed by removal of the solvent in vacuo. The dark red solid residue was redissolved in toluene (100 mL), and NaI was removed by filtration. Red needles of **2** (2.1 g, 1.2 mmol, 70%) separated upon allowing the filtrate to stand at room temperature for 2 days. Crystals suitable for X-ray analysis were obtained by subsequent recrystallizations from toluene. El. Anal. Calcd (Found) for $C_{98}H_{132}N_4O_7Sm_2$: C 66.18 (66.98), H 7.48 (7.05), N 3.15 (3.32). IR (Nujol mull, cm^{-1}): 1605 (s, C=N stretch), 1588 (s, C=N stretch), 1544 (m, aromatic), 1441 (s), 1335 (s), 1315 (m), 1292 (s), 1264 (s), 1167 (s), 1148 (m), 1106 (m), 1033 (w), 905 (m), 750 (vs). ^1H NMR (C_6D_6, 500 MHz, 23 °C): δ 11.42 (s, 1H, C–H imine), 8.65 (s, 1H, C–H phenylene ring), 8.30 (s, 1H, C–H phenylene ring), 8.11 (s, 1H, Ph), 7.73 (pseudo-d, 1H, C–H amidate), 7.03 (two multiplets, 4H, toluene), 5.75 (s, 1H, Ph), 5.71 (pseudo-t, 1H, Ph), 5.35 (pseudo-t, 1H, Ph), 4.69 (pseudo-d, 1H, C–H amidate), 3.25 (s, 6H, THF), 2.45 (s, 9H, Bu^t), 2.21 (s, 9H, Bu^t), 2.09 (s, 6H, THF), 2.03 (s, 3H, Me toluene), 0.47 (broad s, 9H, Bu^t), 0.27 (s, 9H, Bu^t). ^{13}C NMR (C_6D_6, 125.72 MHz, 23 °C): δ 174.1 (imine), 169.78, 163.23, 157.15, 138.18, 137.90, 137.04, 136.33, 133.80, 131.59, 131.31 (quaternary aromatic), 129.28, 128.30, 126.35 (C–H toluene), 128.51, 128.20, 128.11, 128.00, 127.92, 127.81, 125.64, 123.03 (C–H aromatic), 112.90, 112.36, 112.04 (C–H aromatic), 97.98 (quaternary reduced imine), 68.48 (C–H reduced imine), 33.36, 33.18, 32.55, 31.79 (Bu^t), 20.04 (toluene). $\mu_{eff} = 2.41\mu_B$ per formula unit. Mp = 272 °C.

Method B. A stirred solution of **1** (1.0 g, 1.2 mmol) in THF (75 mL) was treated at room temperature with metallic lithium (50 mg, 7.2 mmol). Within 1 h the color changed from light orange to dark red. Stirring was continued for about 16 h, during which no further color changes were noted. The solvent was evaporated to dryness in vacuo and the residual solid was redissolved in toluene. Removal of LiCl by filtration followed by standing at room temperature yielded microcrystals of **2** (0.22 g, 0.13 mmol, 11%) over a period of 4 days.

{[(Me_2-SB)Sm(μ-CH_3)Li(THF)][(Me_2–SB)Sm(μ-CH_3)Li-$(THF)_2$Li$(THF)_2$]}(μ-O)(μ-Li)$_3$ (3) [Me_2–SB = Phenylenebis(3,5-Bu^t_4salycyl)dimethyldiamidato]. The dropwise addition of 1.4 M MeLi in diethyl ether (2.9 mL, 4.1 mmol) at room temperature to a stirred solution of **2** (1.0 g, 0.58 mmol)

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in 100 mL of THF resulted in a color change from dark red to light brown. Stirring was continued for 24 h. The solvent was removed in vacuo and the residual deep yellow solid was dissolved in 75 mL of hexane. Filtration followed by concentration to 30 mL and subsequent standing at room temperature for 7 days yielded yellow needles of **3** (0.30 g, 0.15 mmol, 26%). IR (Nujol mull, cm^{-1}): ν 1550 (m, C=N stretch), 1533 (m, aromatic), 1364 (w), 1250 (s), 1126 (m), 1042 (s), 879 (m), 833 (m), 790 (w), 739 (m). ^1H NMR (THF-d_8, 500 MHz, 23 °C): δ 7.09 (s, 1H, phenyl), 6.92 (mult, 1H, phenylene), 6.90 (s, 1H, phenyl), 6.77 (s, 1H, phenylene), 5.43 (pseudo-q, 1H, C−H amidate), 4.42 (pseudo-q, 1H, C−H amidate), 3.62 (s, 4H, THF), 1.72 (s, 4H, THF), 1.49 (s, 18H, Bu^t), 1.40 (pseudo-dd, 3H, CH_3 amidate). ^{13}C NMR (THF-d_8, 125.72 MHz, 23 °C): δ 164.23, 141.13, 137.73, 133.71, 131.54 (quaternary aromatic), 123.76, 122.62, 122.19, 120.46 (C−H aromatic), 67.74, 31.16 (THF), 59.92 (amidate), 35.83, 34.45, 32.82, 32.46, 32.24, 31.16 (Bu^t), 20.68, 15.66 (CH_3 amidate). $\mu_{eff} = 2.30\mu_B$. Mp = 153 °C (dec).

[(3,5-Bu^t_4salophen)Sm(OH)]$_4$·4toluene (4). Exposure of a stirred toluene solution (50 mL) of **2** (1.0 g, 0.58 mmol) at room temperature to excess dry O_2 resulted in a brown solution after 24 h. Yellow crystals of **4** (0.30 g, 0.095 mmol, 33%) separated upon standing at room temperature for 5 days. El. Anal. Calcd (Found) for $C_{172}H_{220}N_8O_{12}Sm_4$: C 64.69 (64.78), H 6.94 (6.91), N 3.51 (3.57). ^1H NMR (C_6D_6, 500 MHz, 23 °C): δ 13.99 (s, 1H, OH), 8.13 (s, 2H, C−H aromatic), 7.62 (pseudo-d, 2H, aromatic), 7.31 (s, 2H, aromatic), 7.01 (m, 5H, toluene), 6.75 (m, 2H, aromatic), 2.10 (s, 3H, toluene), 1.85 (s, 2H, C−H imine), 1.64 (s, 18H, Bu^t), 1.33 (s, 18H, Bu^t). ^{13}C NMR (C_6D_6, 125.72 MHz, 23 °C): δ 203.78, 159.34, 143.09, 140.40, 137.82, 137.66 (quaternary aromatic and toluene), 165.11, 130.35, 127.45, 127.34, 125.62, 120.08, 119.08 (C−H aromatic and toluene), 35.48 (toluene), 34.25 (C−H imine), 31.63, 29.96 (methyl Bu^t), 32.27, 32.01 (quaternary Bu^t). IR (KBr, Nujol mull, cm^{-1}): ν 3583 (s, stretch O−H), 2960 (vs), 2905 (s), 2866 (m), 1609 (vs, stretch C=N), 1579 (vs, stretch C=N), 1529 (vs, aromatic), 1408 (s), 1258 (s), 1166 (vs), 876 (m), 835 (w), 760 (s), 637 (w), 503 (m). $\mu_{eff} = 4.25\mu_B$ per formula unit. Mp = 301 °C (dec).

Structural Considerations

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AG SMART 1k CCD diffractometer using a proprietary hemisphere scan routine. Cell constants were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. No absorption corrections were applied. The reflection data for **3** were consistent for $P2_1/m$ and $P2_1$; however, solution in the centric option yielded chemically reasonable and computationally stable results of refinement. The data for **2** and **4** were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with subsequent Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. The compound molecule **3** was located on a mirror plane. A lithium atom and a molecule of coordinated THF were located disordered by the mirror plane symmetry. The compound molecule **4** is located at a 4-fold rotoinversion axis. Two half molecules of cocrystallized toluene solvent were each located disordered at inversion centers. Two molecules of toluene solvent were also located in the asymmetric unit of **2**. The carbon and nitrogen atoms of **2** were refined isotropically to conserve a reasonable data/parameter ratio. For **3** and **4** all non-hydrogen atoms, excluding the atoms of the interstitial molecules of solvent, were refined with anisotropic displacement coefficients. Phenyl groups of the cocrystallized solvent in **4** and all the phenyl groups in **2** were treated as idealized, flat, rigid hexagons. Hydrogen atoms were assigned with idealized geometry and constrained with an isotropic, riding model. Crystallographic details are presented in Table 1. Selected bond distances and angles are given in Table 2. Additional information is given as Supporting Information. All scattering factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1994, WI).

Table 1. Crystal Data and Structure Analysis Results

	2	**3**	**4**
formula	$C_{98}H_{132}N_4O_7Sm_2$	$C_{98}H_{148}N_4O_{10}Li_6Sm_2$	$C_{172}H_{220}N_8O_{12}Sm_4$
formula weight	1778.78	1884.54	3192.96
space group	*P*2(1)/*n*	*P*2(1)/*m*	*I*4(1)/*a*
a (Å)	18.0333(2)	18.0906(6)	31.4914(5)
b (Å)	17.2026(2)	17.1075(6)	31.4914(5)
c (Å)	29.3537(2)	19.5591(6)	16.203(3)
β (deg)	100.529(1)	114.073(1)	
V ($Å^3$)	8952.77(6)	5526.8(3)	16068(3)
Z	4	2	4
radiation (Kα, Å)	0.710 73	0.710 73	0.710 73
T (°C)	−100	−100	−100
D_{calcd} (g cm^{-3})	1.320	1.132	1.320
μ_{calcd} (cm^{-1})	1.354	1.101	1.500
R,[a] R_w^2,[b] GOF	0.0654, 0.156, 1.013	0.0555, 0.162, 1.074	0.0501, 0.104, 1.016

[a] $R = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = [(\sum(F_o - F_c)^2/\sum wF_o^2)]^{1/2}$.

Complex **2** is dimeric and is formed by two similar (3,5-Bu^t_4salophen)Sm moieties. The linkage between the two units is realized via a C−C bond that connects the two reduced imine carbon atoms of the two ligands. The C−C bond joining the two salophen units [C(15)−C(51) = 1.549(16) Å] is only slightly longer than a regular C−C bond and compares well with those of the Bu^t groups. The C−N bond distances of the reduced imino functions [N(1)−C(15) = 1.485(14) Å] are as expected for a C−N single bond, while the C−N bonds of the intact imine functions are somewhat shorter and are consistent with the presence of some extent of C−N double-bond character [N(2)−C(22) = 1.303(13) Å]. As a result of the sp^3 hybridization of the carbon atoms, the ligands are no longer planar, as would be expected on the basis of the structural parameters featured in transition metal-based complexes of the same type.[18] The reduction of one of the two imino functions of each ligand also imparts a tetrahedral sp^3 geometry to the nitrogen atoms that bridge the two metal centers. The Sm−N bond distances are rather short in comparison to those of other complexes of nitrogen-donor-based macrocyclic ligands[19] [Sm(1)−N(1) = 2.418(8) Å, Sm(1)−N(3) = 2.465(8) Å, Sm(2)−N(1) = 2.453(8) Å, Sm(2)−N(3) = 2.368(8) Å]. Despite the fairly similar organization of the two tetradentate moieties around the dimetallic unit, the two metal centers display two different coordination geometries. One of them is six-coordinated and is bound to two oxygen atoms [Sm(2)−O(3) = 2.180(7) Å, Sm(2)−O(4) = 2.219(8) Å], one imine nitrogen [Sm(2)−N(4) = 2.503(9) Å], and two reduced

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[18] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 756, and references therein.

[19] See for comparison: Abid, K. K.; Fenton, D.; Casellato, U.; Vigato, A.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1984**, 351.

Table 2. Selected Bond Distances (Å) and Angles (deg)

1		2		3	
Sm(1)−O(1)	2.217(7)	Sm(1)−O(1)	2.293(6)	Sm−O(1)	2.260(5)
Sm(1)−O(2)	2.240(7)	Sm(1)−O(2)	2.318(5)	Sm−O(2)	2.205(5)
Sm(1)−N(1)	2.418(8)	Sm(1)−N(1)	2.435(6)	Sm−O(3)	2.573(5)
Sm(1)−N(2)	2.546(8)	Sm(1)−C(39)	2.606(10)	Sm−O(3B)	2.433(5)
Sm(1)−N(3)	2.465(8)	Sm(2)−C(40)	2.570(11)	Sm−O(3C)	2.470(5)
Sm(1)−O(5)	2.453(7)	Sm(2)−O(1)	2.314(6)	Sm−N(1)	2.542(6)
Sm(1)−O(6)	2.522(7)	Sm(2)−O(3)	2.385(5)	Sm−N(2)	2.566(6)
C(15)−C(51)	1.549(16)	Sm(2)−N(2)	2.405(6)	N(1)−C(15)	1.310(10)
Sm(2)−O(3)	2.180(7)	N(1)−C(15)	1.446(10)	N(2)−C(22)	1.303(10)
Sm(2)−O(4)	2.219(8)	C(15)−C(16)	1.542(10)		
Sm(2)−O(7)	2.478(7)	N(2)−C(34)	1.463(10)		
Sm(2)−N(3)	2.368(8)	C(34)−C(35)	1.539(10)		
Sm(2)−N(4)	2.503(9)				
C(22)−N(2)	1.303(13)				
C(15)−N(1)	1.485(14)				
O(1)−Sm(1)-O(2)	161.5(3)	O(1)−Sm(1)-O(2)	79.35(14)	Sm−O(3)−Sm(A)	102.43(18)
O(1)−Sm(1)-O(5)	85.7(3)	O(1)−Sm(1)-N(1)	146.00(15)	Sm−O(3)−Sm(C)	112.15(19)
O(1)−Sm(1)-O(6)	80.0(3)	O(2)−Sm(1)-N(1)	77.05(18)	Sm(A)-O(3)−Sm(C)	105.49(18)
O(1)−Sm(1)-N(1)	77.6(3)	O(1)−Sm(1)-C(39)	85.1(3)	O(3)−Sm-O(3C)	66.94(19)
O(1)−Sm(1)-N(2)	125.6(3)	O(1)−Sm(2)-C(40)	177.5(3)	O(3)−Sm-O(3B)	70.37(19)
O(2)−Sm(1)-O(5)	89.9(3)	Sm(1)−O(1)-Sm(2)	168.2(3)	O(1)−Sm-O(2)	89.7(2)
O(2)−Sm(1)-O(6)	81.6(3)	O(1)−Sm(2)-O(3)	76.59(12)		
O(2)−Sm(1)-N(1)	120.9(3)	O(1)−Sm(2)-N(2)	87.50(19)	N(1)−Sm-N(2)	62.4(2)
O(2)−Sm(1)-N(2)	70.1(3)	Li(1)−O(1)-Li(2)	113.4(4)	O(1)−Sm-N(1)	70.8(2)
O(5)−Sm(1)-O(6)	82.2(3)	Li(1)−O(1)-Li(1A)	133.1(8)	O(2)−Sm-N(2)	71.5(2)
N(1)−Sm(1)-N(2)	61.2(3)	Sm(1)−O(1)-Li(1)	92.0(4)	O(1)−Sm-N(2)	108.48(19)
		Sm(1)−O(1)-Li(2)	89.1(5)		
		Sm(1)−O(1)-Li(1A)	92.0(4)		

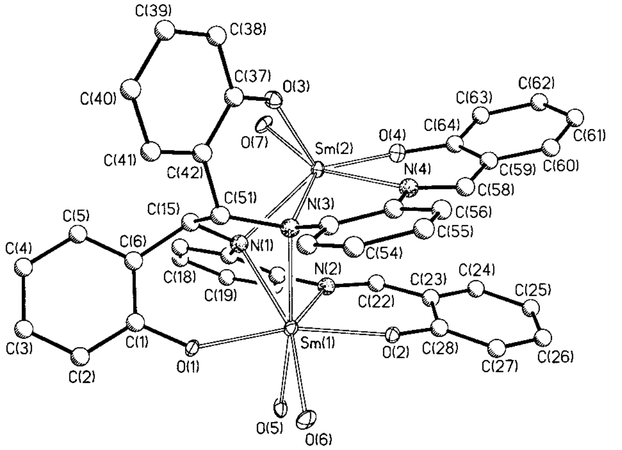

Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. The four Bu^t groups have been deleted for clarity.

imine nitrogens as well as to one molecule of THF [Sm(2)−O(7) = 2.478(7) Å] (Figure 1). The second Sm atom is seven-coordinate with basically the same coordination geometry except for one additional molecule of THF.

Complex **3** is also dimeric with two nonequivalent Sm atoms bridged by a single oxygen atom [Sm(1)−O(1) = 2.293(6) Å, Sm(2)−O(1) = 2.314(6) Å]. The slightly bent Sm−O−Sm array [Sm(1)−O(1)−Sm(2) = 168.2(3)°] lies on a crystallographic mirror plane. Each samarium is surrounded by a tetradentate and tetraanionic diaryloxo/diamido ligand (Me$_2$SB) arising from the methylation of each carbon atom [C(34)−C(35) = 1.539(10) Å, C(15)−C(16) = 1.542(10) Å] of both imino functions of the original 3,5-Bu$^t{}_4$salophen ligand [Sm(1)−O(2) = 2.318(5) Å, Sm(1)−N(1) = 2.435(6) Å, Sm(2)−O(3) = 2.385(5) Å, Sm(2)−N(2) = 2.405(6) Å]. As a result of the alkylation of the imino functions and consequent change of the hybridization of the C and N atoms [N(1)−C(15)−C(16) = 112.5(6)°, N(1)−C(15)−C(5) = 111.3(6)°], the carbon atoms display a regular tetrahedral geometry. The two amidato nitrogen atoms of each ligand are engaged in bridging interactions with three lithium atoms [N(1)−Li(3) = 2.111(15) Å, N(2)−Li(4) = 2.18(3) Å, N(2A)−Li(2) = 2.245(14) Å]. Both samarium atoms possess a distorted coordination geometry [N(1)−Sm(1)-N(1A) = 64.5(3)°, O(2)−Sm(1)−O(2A) = 118.1(2)°, N(1)−Sm(1)−O(1) = 146.00(15)°, C(39)−Sm(1)−N(1) = 84.5(2)°]. Each samarium atom also bears a methyl group [Sm(1)−C(39) = 2.606(10) Å, Sm(2)−C(40) = 2.570(11) Å]. The first has the methyl pointing away from the molecular core and placed in trans position with respect to the bridging oxo atom [O(1)−Sm(2)−C(40) = 177.5(3)°]. This methyl is also bonded to a Li(THF) moiety [C(40)−Li(4) = 2.21(3) Å], which in turn is attached to one nitrogen atom of the tetradentate amidato ligand, thus forming a planar Sm−CH$_3$−Li−N unit [torsion angle Sm(2)−C(40)−Li(4)−N(2) = 0(1)°]. The second samarium atom has the methyl group placed in cis position with respect to the bridging oxygen [O(1)−Sm(1)−C(39) = 85.1(3)°]. The lithium atom connected to the two nitrogen atoms of the second samarium amidate moiety bears two THF molecules rather than one [O(4)−Li(3)−O(5) = 102.2(9)°]. The molecular core is formed by the Sm−O−Sm array and three lithium atoms. The Li$_3$O plane [Li(1)−O(1)−Li(2) = 113.4(4)°, Li(1)−O(1)−Li(1A) = 133.1(8)°] is perpendicular to the Sm−O−Sm vector and is arranged in such a manner that the central lithium atom is also coplanar with the Sm−O−Sm array [Li(1)−O(1)−Sm(1) = 92.0(4)°, Li(1)−O(1)−Sm(2) = 92.7(4)°], thus lying on the crystallographic mirror plane. As a result, the central oxygen atom is pentacoordinated and adopts a distorted trigonal bipyramidal geometry defined by two axial samarium atoms and three equatorial lithiums [L1(2)−O(1)−Li(1) = 113.4(4)°]. Two of the equatorial

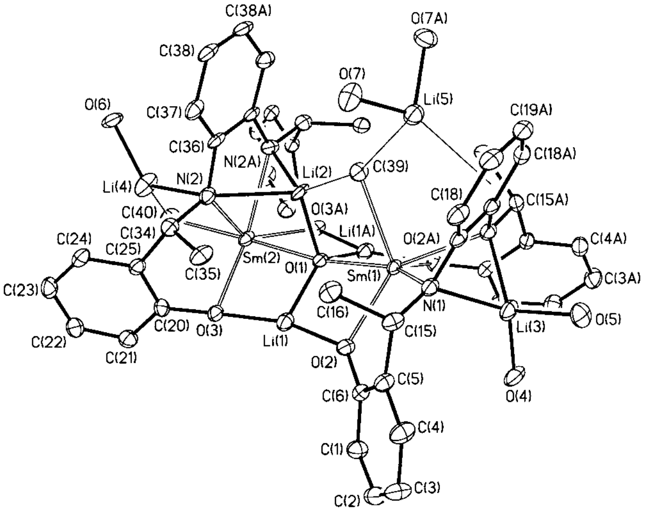

Figure 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level. The four Bu^t groups have been deleted for clarity.

lithium atoms are also bonded to two oxygens from the two tetradentate ligands of the two moieties [Li(1)−O(2) = 1.977(13) Å, Li(1)−O(3) = 1.901(12) Å, O(2)−Li(1)−O(3) = 160.3(8)°]. Conversely, the third one, which is coplanar with the bridging oxo and the two samarium atoms, is bonded to the two nitrogen atoms [Li(2)−N(2) = 2.245(15) Å] of one ligand attached to one samarium and the methyl group [Li(2)−C(39) = 2.129(19) Å] attached to the second samarium atom (in cis position with respect to the bridging oxo). A fifth lithium atom is connected to this methyl group [Li(5)−C(39) = 2.56-(2) Å] and to four phenyl carbon atoms [Li(5)−C(18) = 2.702(17) Å, Li(5)−C(19) = 2.487(19) Å] of the salophen ligand of the second Sm unit. The large network of bridging interactions between the two samarium moieties results in rather unusual coordination geometries of the donor atoms. The salophen oxygen atoms possess a distorted T-shape geometry [Li(1)−O(2)−Sm(1) = 89.5(4)°, Li(1)−O(2)−C(6) = 141.1(6)°], while the nitrogen atoms are severely distorted pentacoordinated. The methyl group engaged in the formation of the core has also a distorted T-shape geometry [Li(2)−C(39)−Li(5) = 162.1(8)°, Li(2)−C(39)−Sm(1) = 76.8(5)°, Li(5)−C(39)−Sm(1) = 121.0(6)°]. As in the case of **2**, there is no planar arrangement of the [SmN_2O_2] set of atoms due to complete reduction of both imine functions. Accordingly, the C−N bond distances are slightly longer than in the coordinated salophen ligand and are consistent with the presence of some C−N single-bond character [C(34)−N(2) = 1.463(10) Å, N(1)−C(15) = 1.446(10) Å].

The tetrameric structure of **4** consists of a distorted cuboid core formed by four samarium atoms and four μ^3-OH bridging groups [Sm−O(3) = 2.573(5) Å, Sm−O(3C) = 2.470(5) Å, Sm−O(3B) = 2.433(5) Å] (Figure 3). The Sm−O distances compare well with those observed in the hydroxo-bridged $[Cp_2Sm(OH)]_2$.[20] The distortion arising from the compression alongside each Sm−Sm diagonal is introduced by the small bridging hydroxides [Sm−O(3)−Sm(A) = 102.43(18)°, Sm−O(3)−Sm(C) = 112.15(19)°, Sm(A)−O(3)−Sm(C) = 105.49-(18)°] and originates short Sm···Sm contacts [Sm···Sm(A) = 3.9023(8) Å]. Each of the four identical Sm atoms occupying opposite corners of the distorted cube possesses a distorted seven-coordinate geometry [O(1)−Sm−O(2) = 89.7(2)°, N(1)−Sm−N(2) = 62.4(2)°, N(1)−Sm−O(1) = 70.8(2)°, O(1)−Sm−O(3) = 143.66(17)°]. Three of the seven coordination sites of samarium are engaged by the bridging hydroxyl groups [O(3)−Sm−O(3C) = 66.94(19)°, O(3)−Sm−O(3B) = 70.37(19)°, O(3B)−Sm−O(3C) = 93.11(18)°]. The coordination geometry is completed by two oxygens [Sm−O(1) = 2.260-(5) Å, Sm−O(2) = 2.205(5) Å] and two nitrogens [Sm−N(1) = 2.542(6) Å, Sm−N(2) = 2.566(6) Å] of one 3,5-$Bu^t{}_4$salophen ligand. The ligand adopts a rather normal and slightly distorted geometry [O(2)−Sm−N(1) = 119.0(2)°, O(1)−Sm−N(2) = 108.48(19)°] surrounding the metal on the side opposite that occupied by the three bridging hydroxyl groups. The C=N bond distances are as expected for a coordinated Schiff base and are comparable with those of **2** [N(1)−C(15) = 1.31(1) Å, N(2)−C(22) = 1.30(1) Å].

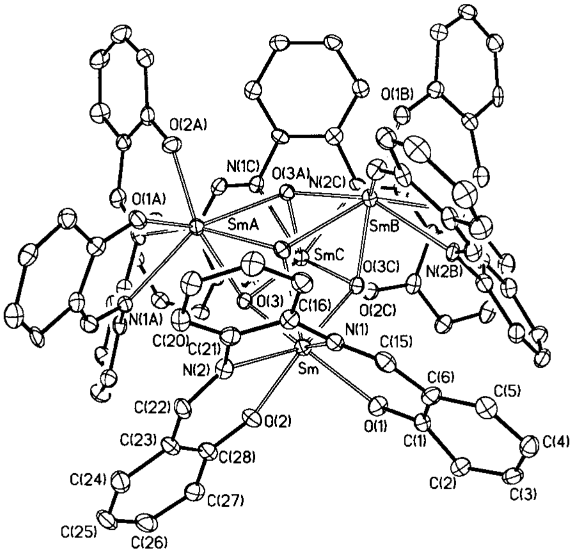

Figure 3. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level. The four Bu^t groups have been deleted for clarity.

Results and Discussion

The room-temperature reaction of $SmI_2(THF)_5$ with 1 equiv of (3,5-$Bu^t{}_4$salophen)$Na_2(THF)_2$ in THF formed a deep red, air-sensitive solution from which bright red needles of dimeric $[Sm_2(SB-SB)(THF)_3]\cdot2$toluene (**2**) [SB−SB = C−C bonded salophen dimer] were isolated in good yield upon crystallization from toluene (Scheme 1). The light color suggested that the Sm metal center was oxidized to the trivalent state, while qualitative halogen and flame tests indicated the absence of both iodine and sodium. Combustion analysis data were in agreement with the formulation as elucidated by an X-ray crystal structure (Figure 1). Solution NMR spectra were well resolved and accordingly displayed four distinct resonances for the Bu^t groups. A new resonance attributed to the C−H engaged in the formation of the C−C bond connecting the two monomeric units was observed at 4.69 ppm. Complex **2** was also conveniently prepared via reduction of (3,5-$Bu^t{}_4$salophen)-SmCl·ether **1** with metallic lithium in THF (Scheme 1).

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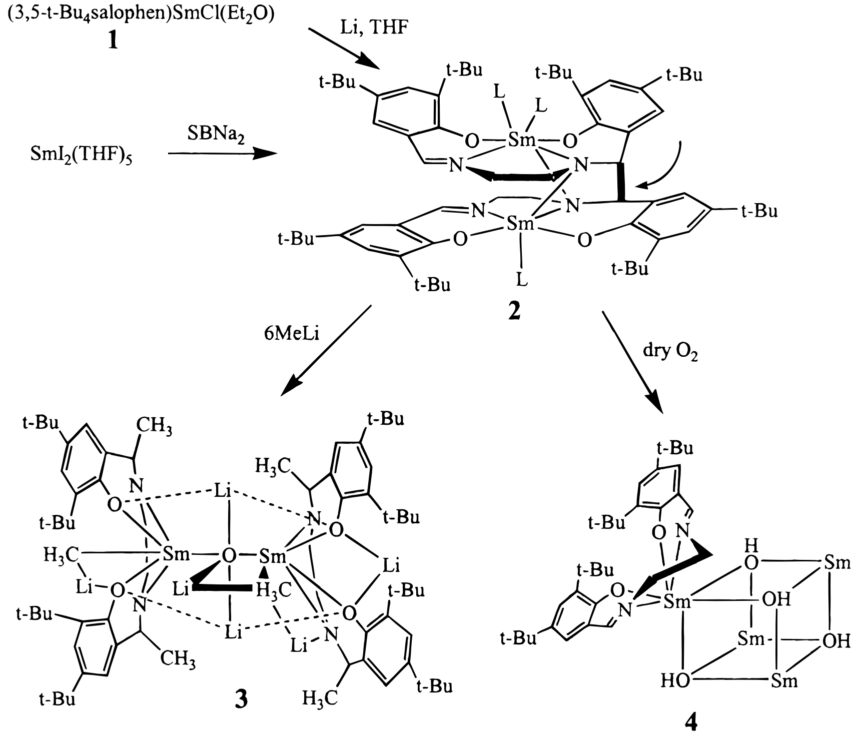
(20) Hitchcock, P. B.; Lappert, M. F.; Prashar, F. *J. Organomet. Chem.* **1991**, *413*, 79.

Scheme 1



(bridging phenylene ring was omitted for clarity)

Complex **2** arises from the reduction of the ligand performed by the low-valent samarium center. In other words, the intermediate Sm(II)(3,5-Bu$^t{}_4$salophen) derivative, presumably originated in the first step of the reaction, reduces one of the ligand imino functions, thus forming a Sm(III) and a mainly carbon-centered radical. Obviously, the extensive π-delocalization of this particular ligand provides a sufficiently long lifetime to allow for coupling with an identical unit and to form the final dimeric structure. The compartmental ligand formed in this process wraps the dimetallic samarium unit with a network of bridging interactions (Figure 1). The metal-promoted reductive coupling of tetradentate Schiff bases has a few precedents in the literature of first-row transition metals.[21] However, these reactions are usually performed by strong reductants (alkali metals) with the role of the transition metal simply being that of a mediator or of a templating agent. Conversely, in the reaction described above the reductive coupling is exclusively originated by the one-electron oxidation of Sm(II). In addition, the C−C bond that results from the dimerization reaction, which is typically rather long and easily cleaved by mild oxidizing agents, is in this case normal [C(15)−C(51) = 1.569 Å] and rather robust.

As expected for a formal Sm(III) derivative, complex **2** proved to be unreactive toward mild oxidizing agents such as MeI or PhCH$_2$Cl. On the other hand, it was surprising that no reaction was also observed with strong reductants such as Mg, Na, and Li upon stirring at room temperature or in refluxing THF. No visible evidence of reaction was observed over prolonged periods, and unreacted starting material was always recovered. However, reaction of **2** with PhCH$_2$MgCl gave a sudden color change from red to light yellow. The IR spectrum of the resulting yellow microcrystalline solid, isolated in modest yield from hexane, indicated the absence of any C═N resonance. Similarly, the NMR spectrum did not show any signal that could possibly be attributed to the C−H amidate of the reduced imino function. Unfortunately, it was not possible to grow crystals of suitable size for X-ray analysis. Therefore, complex **2** was reacted with excess MeLi at room temperature. When MeLi was added to complex **2**, the reaction proceeded to completion in a matter of minutes, and no further color changes were noted even after prolonged periods. Yellow, extremely air-sensitive crystals of a new compound **3** were isolated in reasonable yield after filtration, solvent replacement with hexane, and standing. Even in this case, the absence of C═N resonances in the IR spectrum indicated a complete reduction of the imine functions. The formulation of this new species as {[(Me$_2$−SB)Sm(μ-CH$_3$)Li(THF)][(Me$_2$−SB)Sm(μ-CH$_3$)Li(THF)$_2$Li(THF)$_2$]}(μ-O)(μ-Li)$_3$ (**3**) [Me$_2$-SB = phenylenebis(3,5-Bu$^t{}_4$salycyl)dimethyldiamidato] was elucidated by an X-ray crystal structure (Figure 2). Due to the high sensitivity and pyrophoricity, difficulties were encountered in obtaining meaningful combustion analysis data for complex **3**. The NMR spectra showed a pattern consistent with the solid-state crystal structure. Two C−H amidate signals were observed as multiplets at 5.43 and 4.42 ppm, corresponding to the inequivalent coordination environments about Sm(1) and Sm(2). In addition, solution NMR spectra showed two signals each for THF (3.63, 1.72 ppm) and THF-d_8

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[21] (a) Gambarotta, S.; Urso, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 3966. (b) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1116.

(3.62, 1.78 ppm), indicating slow exchange of coordinated THF with that of the solvent. Unfortunately, it was not possible to conclusively locate the resonances of the CH_3 groups attached to Sm either due to overlap with ligand signals or due to direct effect of the close vicinity of the paramagnetic center. However, a Toepler pump experiment involving bulk degradation of **3** with anhydrous HCl yielded 77% of the expected amount of CH_4.

Although the origin of the oxygen atom in complex **3** cannot be conclusively explained at this stage, it seems that its likely source is the THF solvent. It may be argued that small amounts of oxygen, adventitiously present in the reaction mixture, should lead to methoxy derivatives rather than alkyls. In addition, given the excess of MeLi employed in the reaction, the tremendous sensitivity to air and moisture of the resulting complex, and the yield in which **3** may be isolated on a reproducible basis, the possibility that the formation of **3** may be the result of trace oxygen present in the reaction mixture may be confidently ruled out. In addition, the gas-chromatogram of the reaction mixture showed the presence of a substantial amount of ethylene, thus confirming a process involving THF deoxygenation. Deoxygenation and fragmentation of THF by early transition metal and lanthanides to generate oxo derivatives or other exotic functions is well documented in the literature.[22] The formation of an oxo-metal derivative and ethylene implies the reduction of THF by two electrons. This requires that upon the attack of MeLi on both the ligand and the metal center of complex **2** the two electrons, used for the formation of the C−C bond connecting the two samarium units, are transferred back to the two metal centers and are used in the THF deoxygenation process. The high oxophilicity of samarium and the consequent stability of the Sm−O−Sm bond may well provide the necessary energy for this reaction to take place. In addition, the overall reaction requires the addition of 6 equiv of MeLi per dimeric unit, four methyl groups to be attached to the four imine carbon atoms and two to the two Sm atoms.

As mentioned above, solutions of complex **2** are sensitive to air and moisture. To further explore the reactivity of this species, its behavior in the presence of dry oxygen was investigated. When a toluene solution of **2** was exposed to an excess of dry O_2, the color turned to brown. After 5 days, yellow cubic crystals appeared in the reaction mixture and were isolated in reasonable yield. This compound, confirmed by a single and sharp IR stretch at 3585 cm^{-1} to be a hydroxide, was observed to be stable in the presence of air and moisture. The resonance of the OH group as a singlet at 13.99 ppm of the ^1H NMR spectrum was clearly identified by HQMC and deuterium labeling experiments (see below).

Questions arise about the genesis in compound **4** of the hydroxyl group. Consistent with our observations, O′Halloran and co-workers[23] recently showed that reaction of the Mn(III)PHAB dimer with O_2 in the absence of external oxidants and under anhydrous conditions results in the catalytic dehydroxylation of THF and formation of a Mn(V) hydroxyl derivative. We speculate that during the reduction of dioxygen operated by the in situ generated (salophen)Sm(II) a superoxide intermediate similar to that isolated and characterized by Takats[24] abstracts a hydrogen atom from the solvent, thus reforming in the process a half equivalent of dioxygen. At this stage it is impossible to distinguish between these two or other reasonable pathways. At least to verify the hypothesis that the solvent (toluene) is the donor of the hydrogen atom, we have carried out the reaction in deuterated toluene. The product had spectral features identical to those of **4** except for the resonance at 13.99 ppm, which was absent in the ^1H NMR spectrum but was clearly visible in the ^2H NMR spectrum.

Concluding Remarks

In view of the reactivity of transition metal systems stabilized by tetradentate Schiff bases, it is surprising that complex **2** did not show a more pronounced reactivity toward electron-accepting molecules. However, such behavior may be understood if **2** is regarded as a pseudo-samarium(II) species which is effectively stabilized by storing two electrons in the C−C bond linking the two 3,5-Bu^t_4salophen units. The C−C bond may be cleaved and the two electrons made available to the metal centers by the attack either of oxidizing agents directly on the metal centers or of nucleophiles on the two carbon atoms.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC) and NATO. We are also grateful to Dr. A. Carty (NRC) for making available a CCD diffractometer and to Dr. C. Bensimon for collecting data and providing preliminary solutions for the structures.

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **2**, **3**, and **4** (41 pages). Ordering information is given on any current masthead page.

OM9803319

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[22] See for example: (a) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2641. (b) Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163. (c) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291.

[23] MacDonnell, F. M.; Fackler, N. L.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431.

[24] Takats, J.; Zhang, X.; Lopnow, G. R.; McDonald, R. *J. Am. Chem. Soc.* **1995**, *117*, 7828.