Di- and Trivalent Dinuclear Samarium Complexes Supported by Pyrrole-Based Tetradentate Schiff Bases

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The reactions of $[N(SiMe_3)_2]_2Sm(THF)_2$ with three similar tetradentate pyrrole-based Schiff base ligands yielded three very different complexes. In two cases, an increase in the oxidation state was obtained via either ligand reductive coupling or disproportionation. The presence of a methyl substituent at the imine carbon atom instead prevented metal oxidation and afforded the first divalent samarium imine complex.

Over the last 20 years, the chemistry of low-valent f-block metal has steadily grown in importance with the realization that many of these metals display unique chemical properties.[1] The use of cyclopentadienyl-based ligand systems has played a pivotal role in the growth of the field, because of their well-known versatility in meeting the electronic and steric requirements necessary to stabilize a wide variety of complexes.[2] Over the past few years, headway has been made in using auxiliary ligands that, while preserving the salient characteristics of the Cp systems, offer distinctive reactivity patterns. One class of them, the polypyrrolide polyanions, has heightened expectations for increasing even further the reactivity of divalent lanthanides.[3–7] In particular, the divalent Sm cluster derivatives were sufficiently reactive to attack the ligand system itself[4] or the solvent[5] or extensively reduce dinitrogen.[3c,d,5a,6,7] Pyrrole rings offer a reasonable mimic of the cyclopentadienyl functions because of their π-ligation ability. On the other hand, they also offer the possibility of forming σ-bonds through the ring nitrogen donor atom, providing the variety of bonding modes necessary to accommodate diversified structures. The recurrently observed formation of large cluster structures and the ability to retain alkali-metal cations is a direct consequence of this unique characteristic. Both features are rather desirable since (1) by favoring polynuclear aggregation, polypyrrolide ligands make possible multielectron redox processes via cooperative attack of several metals on the same substrate[3,5–7] and (2) by retaining the alkali-metal cation via direct coordination to the pyrrolyl rings (both σ and π) it is possible to adjust the metal redox potential.[8]

The salen-type Schiff bases constitute another class of ligands that has lately been shown able to form

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interesting complexes with lanthanides. Recent results have indicated that this type of ligand, when coordinating yttrium, may promote catalytic asymmetric aldol-Tishchenko reactions.[9] Given the well-known versatility of both divalent samarium species in metal-promoted organic synthesis and of tetradentate Schiff base dianions in catalysis, a divalent Schiff base complex may be regarded as especially promising. However, attempts to use imine to stabilize the divalent state of Sm have so far been disappointing, having afforded instead ligand reduction and attack at the solvent.[10]

We thus became interested in combining the characteristics of both pyrrole-based ligands with those of the tetradentate schiff bases for stabilizing divalent Sm complexes. Herein, we describe the results of a preliminary study.

Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of Al_2O_3 under an inert atmosphere prior to use, degassed in vacuo, and transferred and stored under an inert atmosphere. A literature procedure was followed for the preparation of $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$,[11] while the three ligands were synthesized via minor variations of literature procedures.[12,13] NMR spectra were recorded on Varian Gemini 200 and Bruker AMX-500 spectrometers. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside a drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey) and corrected for underlying diamagnetism. Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Preparation of 1,2-Benzenediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)methylene. A 250 mL flask fitted with a magnetic stirrer was charged with phenylenediamine (3.9 g, 36 mmol) and 2-pyrrolecarboxaldehyde (6.9 g, 73 mmol) in ethanol (70 mL). After the suspension was gently heated to solubilize both reactants, a catalytic amount of acetic acid was added (0.5 mL). The solution was allowed to react over a 12 h period, during which time a fine white powder precipitated. The solid was filtered and recrystallized from a minimum amount of boiling methanol, giving analytically pure colorless crystals of the product (6.9 g, 26 mmol, 72% yield). MS-EI (+): *m/e* 262. ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 11.88 (br s, 2H, N−H), 7.70 (s, 2H, C−H imine), 7.24 (mult, 2H, C−H phenyl), 7.05 (mult, 2H, C−H phenyl), 6.40 (q, 2H, C−H pyrrole), 6.25 (q, 2H, C−H pyrrole), 6.02 (q, 2H, C−H pyrrole). Anal. Calcd (found) for C$_{16}$H$_{14}$N$_4$: C, 73.26 (73.15); H, 5.38 (5.31); N, 21.36 (21.33).

Preparation of 3,4-Dimethyl-1,2-benzenediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)methylene. A 250 mL flask fitted with a magnetic stirrer was charged under a nitrogen atmosphere with 3,4-dimethyl-1,2-phenyldiamine (5.6 g, 41 mmol) and 2-pyrrolecarboxaldehyde (7.8 g, 82 mmol) in ethanol (70 mL). A catalytic amount of acetic acid (0.5 mL) was added to the mixture, and the solution was allowed to react over a 12 h period, during which time a bright yellow fine powder pre-

cipitated. The solid was filtered and washed with small portions of chilled ethanol (−38 °C), affording analytically pure product (6.2 g, 21 mmol, 52% yield). MS-EI (+): *m/e* 290. ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 11.28 (br s, 2H, N−H), 7.75 (s, 2H, C−H imine), 6.85 (s, 2H, C−H phenyl), 6.36 (q, 2H, C−H pyrrole), 6.27 (q, 2H, C−H pyrrole), 6.00 (q, 2H, C−H pyrrole), 2.25 (s, 6H, CH$_3$). Anal. Calcd (found) for C$_{18}$H$_{18}$N$_4$: C, 74.46 (74.41); H, 6.25 (6.22); N, 19.30 (19.26).

Preparation of 1,2-Ethanediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)ethylidene. Ethylenediamine (1.4 g, 22 mmol) was added with stirring to a solution of acetylpyrrole (4.9 g, 45 mmol) in ethanol (40 mL). A catalytic amount of acetic acid (0.5 mL) was added to the mixture, which was subsequently refluxed for 48 h. The resulting orange solution was evaporated to dryness, yielding a slightly oily orange solid. The crude product was recrystallized from a minimum amount of hot methanol. The resulting off-white crystalline product was rinsed with three portions of ethanol (10 mL) to remove possible traces of unreacted acetylpyrrole, affording analytically pure product (2.6 g, 11 mmol, 48% yield). MS-EI (+): *m/e* 242. ^{1}H NMR (200 MHz, CDCl$_3$, 298 K): δ 10.28 (br s, 2H, N−H), 6.75 (q, 2H, C−H pyr), 6.43 (q, 2H, C−H pyr), 6.12 (q, 2H, C−H pyr), 6.58 (s, 4H, CH$_2$ ethylene), 1.79 (s, 6H, CH$_3$). Anal. Calcd (found) for C$_{14}$H$_{18}$N$_4$: C, 69.39 (69.21); H, 7.49 (7.52); N, 23.17 (23.13).

Synthesis of [(SB-SB)Sm$_2$(THF)$_4$]·THF (1; SB-SB = C−C-Bonded 1,2-Benzenediamine-*N*,*N*-bis(pyrrol-2-yl)-methylene Dimer). A solution of [N(SiMe$_3$)$_2$]$_2$Sm(THF)$_2$ (1.1 g, 1.7 mmol) in anhydrous THF (30 mL) was treated with 1,2-benzenediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)methylene (0.5 g, 1.7 mmol) at room temperature and under an argon atmosphere. The mixture turned instantly red, and the resulting solution was allowed to stand for 3 days at room temperature, yielding red crystalline plates of **1** (0.65 g, 1.1 mmol, 64% yield). Anal. Calcd (found) for C$_{52}$H$_{64}$N$_8$O$_5$Sm$_2$: C, 52.84 (52.78); H, 5.46 (5.37); N, 9.48 (9.45). IR (Nujol mull, cm^{-1}): ν 3083 (w), 3051 (w), 1646 (w), 1576 (s), 1542 (m), 1505 (m), 1465 (s), 1435 (s), 1389 (s), 1329 (s), 1301 (m), 1261 (m), 1261 (s), 1220 (w), 1183 (m), 1169 (m), 1155 (m), 1097 (m), 1088 (m), 1062 (s), 1027 (s), 969 (m), 991 (w), 867 (m), 803 (m), 779 (m), 733 (s), 701 (w), 687 (w), 670 (w), 629 (w), 608 (w), 571 (w), 562 (w). μ_{eff} = 2.45 μ_B/mol (room temperature).

Synthesis of {[3,4-dimethyl-1,2-benzenediamine-*N*,*N*-bis-(pyrrol-2-yl)methylene]Sm (THF)$_4$}{[3,4-dimethyl-1,2-benzene-diamine-*N*,*N*-bis(pyrrol-2-yl)methylene]$_2$Sm}·2.5THF (2). A solution of [N(SiMe$_3$)$_2$]$_2$Sm(THF)$_2$ (1.0 g, 1.6 mmol) in anhydrous THF (30 mL) was treated with 3,4-dimethyl-1,2-benzenediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)methylene (0.5 g, 1.6 mmol) at room temperature and under an argon atmosphere. After the mixture stood for 2 days at room temperature, yellow rectangular prisms of 2 separated (0.27 g, 0.3 mmol, 38% yield). Anal. Calcd (found) for C$_{80}$H$_{100}$N$_{12}$O$_{6.5}$Sm$_2$: C, 58.79 (58.73); H, 6.17 (6.11); N, 10.28 (10.22). IR (Nujol mull, cm^{-1}): ν 3090 (w), 3072 (w), 1725 (w), 1696 (w), 1591 (s), 1554 (s), 1516 (s), 1493 (s), 1459 (s), 1459 (s), 1436 (s), 1393 (s), 1384 (s), 1340 (s), 1295 (s), 1259 (s), 1227 (m), 1188 (m), 1174 (s), 1093 (s), 1063 (s), 1029 (s), 975 (s), 954 (m), 899 (s), 888 (s), 872 (s), 865 (s), 811 (s), 795 (s), 749(s), 713 (s), 688 (m), 674 (w), 665 (w), 645 (w), 615 (s). μ_{eff} = 2.16 μ_B/mol (room temperature).

Synthesis of {[1,2-ethylenediamine-*N*,*N*-bis(1-pyrrol-2-yl)ethylidene]Sm(THF)$_2$}$_2$·2THF (3). A solution of [N(SiMe$_3$)$_2$]$_2$Sm(THF)$_2$ (2.2 g, 3.6 mmol) in anhydrous THF (50 mL) was treated with 1,2-ethylenediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)ethylidene (0.9 g, 3.6 mmol) at room temperature and under a nitrogen atmosphere. After 15 min a light-colored precipitate separated while the color of the solution changed from deep red to greenish-brown. The reaction mixture was allowed to stand for 12 h at room temperature, after which time a small amount of unreacted ligand was removed by centrifugation. The brown supernatant was reduced to a small volume (15 mL) and allowed to stand at room temperature for 1 day.

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Table 1. Crystal Data and Structure Analysis Results

	1	2	3
formula	$C_{52}H_{64}N_8O_5Sm_2$	$C_{80}H_{100}N_{12}O_{6.5}Sm_2$	$C_{52}H_{80}N_8O_6Sm_2$
fw	1191.94	1634.42	1213.94
space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	orthorhombic, $P2_12_12_1$
a (Å)	17.9715(16)	12.7933(9)	11.1931(10)
b (Å)	16.2171(14)	16.9239(12)	17.9546(17)
c (Å)	18.1897(16)	18.9680(14)	26.580(2)
α (deg)		80.7450(10)	
β (deg)	110.655(2)	72.2360(10)	
γ (deg)		88.9190(10)	
V (Å³)	4932.9(8)	3858.1(5)	5341.6(8)
Z	4	2	4
radiation (Mo Kα)	0.710 73	0.710 73	0.710 73
T (K)	203(2)	203(2)	203(2)
D_{calcd} (g cm⁻³)	1.591	1.407	1.510
μ_{calcd} (mm⁻¹)	2.413	1.567	2.232
$F(000)$	2384	1680	2480
R1, wR2, GOF[a]	0.0506, 0.0951, 1.002	0.0431, 0.1373, 1.010	0.0517, 0.1066, 1.040

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$; $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/N_{observns} - N_{params})]^{1/2}$.

Bright yellow crystals of **3** separated (1.1 g, 1.8 mmol, 48% yield). Anal. Calcd (found) for $C_{52}H_{80}N_8O_6Sm_2$: C, 51.44 (51.33); H, 6.64 (6.61); N, 9.23 (9.21). IR (Nujol mull, cm⁻¹): ν 3084 (w), 2727 (w), 2659 (w), 1574 (s), 1504 (s), 1462 (s), 1378 (s), 1340 (s), 1313 (m), 1291 (m), 1260 (s), 1210 (m), 118 0(m), 1147 (s), 1093 (s), 1039 (s), 939 (s), 891 (m), 873 (m), 840 (m), 818 (s), 803 (s), 772 (s), 734 (s), 695 (w), 684 (w), 668 (w), 617 (w). $\mu_{eff} = 3.62$ μ_B/unit formula (room temperature).

X-ray Crystallography. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied (Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33–38).

No symmetry higher than triclinic was observed for **2·** 2.5THF, and refinement in the centrosymmetric space group option yielded computationally stable and chemically reasonable results of refinement. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space groups for **1**·THF and **3**·2THF. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2.

One, three (one at half-occupancy), and two molecules of tetrahydrofuran solvent were located cocrystallized in the asymmetric units **1**·THF, **2**·2.5THF, and **3**·2THF, respectively. The cocrystallized THF molecules in **2**·2.5THF and **3**·2THF were found to be severely disordered and were treated as rigid, flat pentagons with the atoms having the smallest isotropic parameter per ring assigned oxygen atom identities. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHEXTL 5.10 program library (Sheldrick, G. M. Bruker AXS, Madison, WI, 1997). Crystal data and selected bond distances and angles are given in Tables 1 and 2, respectively.

Results

The reaction of 1,2-benzenediamine-*N*,*N*-bis(1*H*-pyrrol-2-yl)methylene with [N(SiMe₃)₂]₂Sm(THF)₂ in THF afforded a bright red solution from which bright red air-sensitive crystals precipitated (Scheme 1). The formulation as [(SB-SB)Sm₂(THF)₄]·THF (**1**; SB-SB = C–C-bonded 1,2-benzenediamine-*N*,*N*-bis(pyrrol-2-yl-methylene) dimer) was provided by the X-ray crystal structure. Combustion analysis data consistent with the

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

Compound 1			
Sm(1)–N(1)	2.502(5)	Sm(1)–O(1)	2.491(5)
Sm(1)–N(2)	2.516(5)	Sm(1)–N(5)$_{cent}$	2.424(5)
Sm(1)–N(3)	2.373(5)	C(5)–N(2)	1.288(8)
Sm(1)–N(4)	2.561(5)	C(12)–N(3)	1.460(8)
O(1)–Sm(1)–O(2)	78.31(15)	N(1)–Sm(1)–N(4)	154.49(17)
N(1)–Sm(1)–O(2)	79.57(17)	N(3)–C(12)–C(13)	110.3(5)
N(1)–Sm(1)–N(2)	60.30(18)	N(2)–C(5)–N(4)	120.6(6)
N(3)–Sm(1)–N(4)	68.42(17)	O(1)–Sm(1)–N(5)$_{cent}$	174.5(17)
Compound 2			
Sm(1)–N(1)	2.491(4)	Sm(1)–N(8)	2.504(4)
Sm(1)–N(2)	2.545(4)	Sm(2)–N(9)	2.478(4)
Sm(1)–N(3)	2.536(4)	Sm(2)–N(10)	2.519(4)
Sm(1)–N(4)	2.478(4)	Sm(2)–N(11)	2.529(4)
Sm(1)–N(5)	2.504(4)	Sm(2)–N(12)	2.507(4)
Sm(1)–N(6)	2.561(4)	Sm(2)–O(1)	2.479(4)
Sm(1)–N(7)	2.526(4)	Sm(2)=O(3)	2.517(4)
N(11)–Sm(2)–N(12)	66.88(13)	N(1)–Sm(1)–N(4)	161.72(15)
N(9)–Sm(2)–N(12)	161.80(15)	N(5)–Sm(1)–N(8)	162.51(14)
O(2)–Sm(2)–O(3)	74.55(15)	N(1)–Sm(1)–N(2)	67.36(13)
O(3)–Sm(2)–O(4)	70.86(14)	N(1)–Sm(1)–N(8)	85.71(13)
Compound 3			
Sm(1)–N(1)	2.474(8)	N(3)–C(9)	1.364(12)
Sm(1)–N(2)	2.477(8)	Sm(1)–O(1)	2.534(6)
Sm(1)–N(3)	2.391(9)	Sm(1)–O(2)	2.547(6)
Sm(1)–N(4)	2.502(8)	Sm(1)–N(8)$_{cent}$	2.578(6)
N(2)–C(5)	1.302(12)		
Sm(1)–N(4)–Sm(2)	105.2(3)	N(4)–Sm(1)–O(2)	75.0(2)
N(4)–Sm(1)–N(8)	74.4(2)	O(1)–Sm(1)–O(2)	76.8(2)
N(1)–Sm(1)–N(4)	150.8(3)	O(1)–Sm(1)–N(8)$_{cent}$	174.6(3)

formulation were also obtained. Both the light color and the value of the magnetic moment suggested that the samarium atoms are present in the trivalent state. Complex **1** is a dimer composed by two nearly identical units connected by a C–C bond (C(12)–C(21) = 1.598-(9) Å) between the two reductively coupled C atoms of two former imine functions (Figure 1). Each metal center is σ-bonded to the four nitrogen atoms of the dianionic ligand and to two THF molecules (Sm(1)–O(1) = 2.491(5) Å; Sm(1)–O(2) = 2.554(4) Å; Sm(2)–O(3) = 2.473(5) Å; Sm(2)–O(4) = 2.618(5) Å). One of the two pyrrolyl rings, σ-bonded to the first samarium, is in turn π-bonded to the Sm center of the second moiety and vice versa with the ring centroid placed in the second axial position trans to the THF molecule of the distorted pentagonal bipyramid centered on samarium (Sm(1)–

Scheme 1
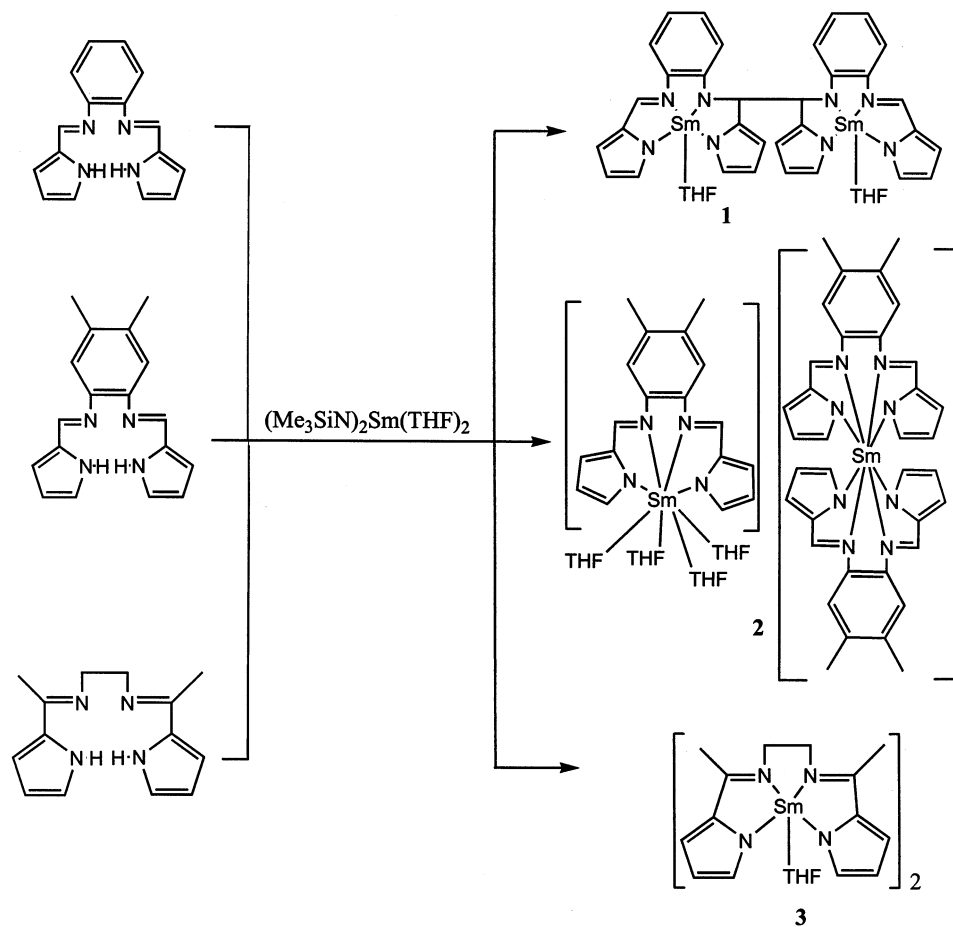
N(5)$_{cent}$ = 2.524(5) Å; Sm(2)−N(4)$_{cent}$ = 2.563(5) Å). The lengths of the carbon−nitrogen bonds of the reduced imino functions are as expected for a C−N single bond (C(21)−N(6) = 1.446(8) Å; C(12)−N(3) = 1.460(8) Å) and are considerably shorter than those of the intact imine groups, displaying significantly shorter C−N bond distances (C(5)−N(2) = 1.288(8) Å; C(28)−N(7) = 1.283-(8) Å). Accordingly, the N atoms of the reduced imine groups form with Sm rather shorter bond distances (Sm(1)−N(3) = 2.373(5) Å; Sm(2)−N(6) = 2.365(5) Å).

To assess the generality of the ability of samarium to reduce imines, we have performed the same reaction

with the same type of ligand carrying a minor modification such as the presence of methyl substituents in a remote part of the backbone. The result of the reaction was surprisingly different, since the dinuclear ({[3,4-dimethyl-1,2-benzenediamine-*N,N*-bis(pyrrol-2-yl)methylene]Sm(THF)$_4$}{[3,4-dimethyl 1,2-benzenediamine-*N,N*-bis(pyrrol-2-yl)methylene]$_2$Sm})·2.5THF (**2**) was formed. Complex **2** is ionic in nature, with both the anion and the cation containing a single Sm(III) atom (Figure 2). In the cationic unit, the metal center is 8-coordinate, being σ-bonded to the planar tetradentate 3,4-dimethyl-1,2-benzenediamine-*N,N*-bis(pyrrol-2-yl)-methylene ligand and coordinatively bound to four molecules of THF (Sm(2)−O(1) = 2.479(4) Å; Sm(2)−O(2) = 2.523(4) Å; Sm(2)−O(3) = 2.517(4) Å; Sm(2)−O(4) = 2.441(3) Å). The ligand maintains a planar arrangement of the three rings and the metal center, with the four nitrogen donor atoms forming comparable Sm−N distances (Sm(2)−N(9) = 2.478(4) Å; Sm(2)−N(10) = 2.519(4) Å; Sm(2)−N(11) = 2.529(4) Å; Sm(2)−N(12) = 2.507(4) Å). The Sm center in the counteranion is also eight-coordinate, but with the coordination environment defined by two tetradentate ligands without retention of solvent molecules. Despite their similarities, the two ligands of the anionic unit are not identically bound to the metal center. The ligand containing the nitrogens labeled 1−4 is planar and very similar to the ligand observed in the cation (Sm(1)−N(1) = 2.491(4) Å; Sm(1)−N(2) = 2.545(4) Å; Sm(1)−N(3) = 2.536(4) Å; Sm(1)−N(4) = 2.487(4) Å), while the second
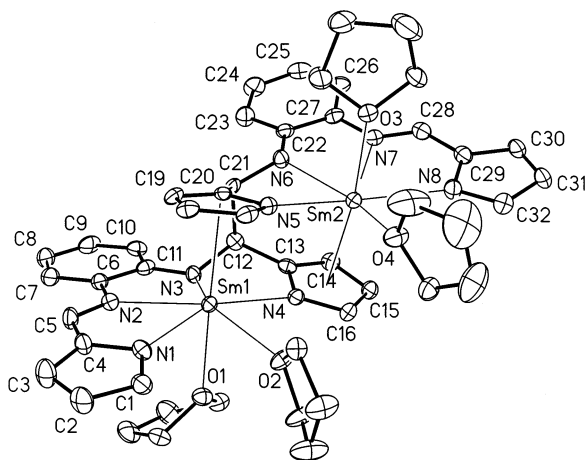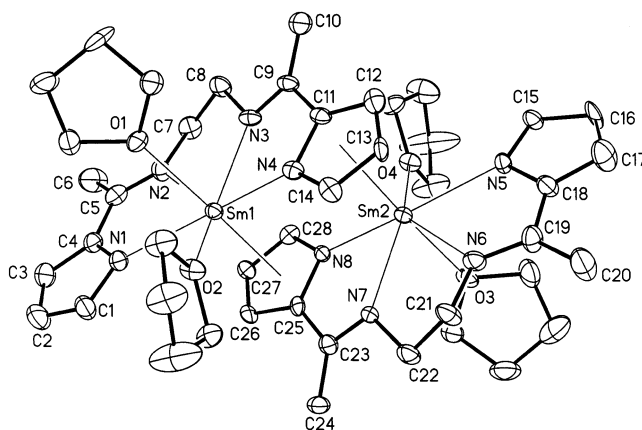

Figure 1. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 30% probablility level.
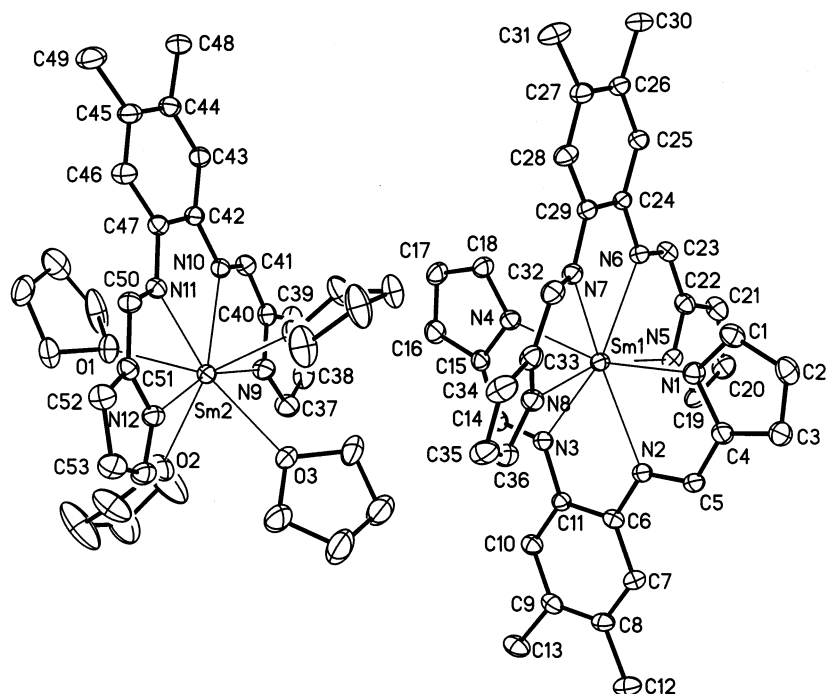
Figure 2. Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at the 30% probablility level.

ligand, which contains the nitrogen atoms labeled 5−8, is not planar but slightly twisted along the N(7)−C(32) and the N(6)−C(23) bonds. Other than this bizarre difference in spatial arrangement, probably determined by crystal-packing forces, the Sm−N distances (Sm(1)−N(5) = 2.504(4) Å; Sm(1)−N(6) = 2.561(4) Å; Sm(1)−N(7) = 2.526(4) Å; Sm(1)−N(8) = 2.504(4) Å) and the imino carbon−nitrogen distances (C(23)−N(6) = 1.302(6) Å; C(32)−N(7) = 1.304(6) Å) are in the same range as those in the planar ligand (C(5)−N(2) = 1.297(6) Å; C(14)−N(3) = 1.310(6) Å).

Since the simple addition of two methyl groups at the very periphery of the ligand system had such a spectacular effect on the structure and stability of intermediate divalent species, the next obvious step was to place alkyl groups directly at the imino function. This was in an attempt to prevent metal oxidation via ligand reductive coupling. Unfortunately, the acetylpyrrole molecule proved unreactive toward the condensation with 1,2-phenylenediamine under a variety of conditions, mainly affording polymeric materials, and thus, we have been forced to use the more reactive 1,2-ethylenediamine. This modification of the ligand backbone was not desirable for comparative purposes, given that the replacement of the phenyl ring by an ethylene bridge removes considerable charge delocalization. On the other hand, it also allows free rotation of the pyrrolyl rings and makes possible to accommodate samarocene-type structures. The reaction of [N(SiMe₃)₂]₂Sm(THF)₂] with 1,2-ethanediamine-*N,N*-bis(1-pyrrol-2-yl)ethylidene was carried out in THF and at room temperature for a few days, affording yellow cuboid crystals of {[1,2-ethylenediamine-*N,N*-bis(1-pyrrol-2-yl)ethylidene]Sm-(THF)₂}₂·2THF (**3**). Complex **3** is dimeric (Figure 3) and is formed by two identical units linked by two Sm−pyrrole π interactions. Each unit is composed of a Sm(II) atom σ-bonded to a tetradentate 1,2-ethylenediamine-*N,N*-bis(1-pyrrol-2-yl)ethylidene ligand, which defines the equatorial plane of the pentagonal bipyra-

Figure 3. Thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 30% probablility level.

mid centered on samarium. The four nitrogen donor atoms are basically coplanar with the metal center. One molecule of THF occupies the fifth position of the equatorial plane (Sm(1)−O(2) = 2.547(6) Å), while the two axial positions are respectively occupied by the second THF molecule (Sm(1)−O(1) = 2.534(6) Å) and the centroid of the π-bonded pyrrolyl ring of the second unit (Sm(1)−N(8)$_{cent}$ = 2.578(6) Å, Sm(2)−N(4)$_{cent}$ = 2.565(6) Å).

Discussion

The oxidation of the metal center as observed during the formation of **1** is realized at the expenses of one of the two imine functions with consequent reductive coupling with an identical function of a second molecule. The C−C bond generated in the process holds together the dimetallic structure. This type of reductive coupling promoted by strongly reducing metals, including divalent samarium, has a precedent in the chemistry of the salycilidene diiminate tetradentate Schiff bases (salen

type).[9] The reaction may be envisioned by assuming a substantial transfer of charge from the samarium center toward the imino function. The resulting radical character developed by the carbon atom is the driving force for the formation of the C−C bond and irreversible oxidation of the metal center toward the trivalent state. However, the fact that the ligand contains two pyrrolyde rings, the ability of which to stabilize the divalent samarium center has been exhaustively documented,[3−8] makes this behavior somewhat unexpected. In fact, there is no constraint within the ligand, except the electronic delocalization through the bridging phenylene ring, to prevent the two pyrrolyl rings from both π-ligating the same samarium, forming a bent samarocene type of structure. As mentioned above, this arrangement has been already observed with di- and polypyrrolide[3−8] and even simple pyrrolides[9] and is apparently capable of enhancing the reactivity of the metal center.

A very minor ligand modification such as the presence of two methyl groups in the ligand phenyl ring at the 3,4-positions pointing well away from the metal center was sufficient to drive the reaction toward the formation of the ionic and trivalent **2**. The ionic structure is a complete departure from the ligand dimerization observed in the case of **1**, since the ligand system, by being untouched, was not involved in the oxidation of the metal center. In addition, *three ligand molecules have been consumed* by two metal centers. Therefore, the formation of trivalent samarium is likely to be ascribed to a disproportionation mechanism likely producing colloidal elemental Sm. Attempts to isolate other possible coproducts only yielded smaller crops of impure **2** and no evidence for the formation of other compounds.

In sharp contrast to the light color, the X-ray crystal structure of the dinuclear **3** doubtlessly indicated that the two metal centers are in the divalent state. On the other hand, pale-colored and even colorless divalent samarium complexes, although very rare, have a precedent in the chemistry of polypyrrolide derivatives.[5a] The value of the magnetic moment is lower than expected for mononuclear divalent samarium species but is still significantly higher than in the other two trivalent complexes. The structure of **3** is closely reminiscent of **1** in both the way the ligand binds the samarium center and the dinuclear aggregation realized via the π-interaction of the samarium center with the pyrrolyl ring of the second unit. The only significant difference appears to be that the two units are staggered with respect to each other and, therefore, by preventing the two imino functions from coming to close proximity, the reduction of the imino function with consequent oxidation of the metal to the trivalent state was avoided. It is conceivable that the two pyrrole rings bridging the two metal centers permit a magnetic coupling between the two samarium atoms, thus accounting for the weak paramagnetism. Complex **3** provides the first case of stabilization of a divalent samarium center by a tetradentate Schiff base.

Conclusion

In this paper we have investigated the ability of three similar pyrrole-based tetradentate Schiff bases to stabilize divalent samarium. The long-term goal was to obtain divalent complexes free of alkali-metal cations and hopefully capable of interacting with N_2. Two of the complexes obtained contained trivalent samarium centers, while a divalent samarium species was isolated only in the third case. The introduction of a methyl group attached to the imino carbon atom prevented in this latter case both disproportionation and ligand reductive coupling, which are instead the oxidation pathways of divalent Sm centers in the other two complexes. We found no indication of the ability of the divalent **3** to interact with dinitrogen. This is rather surprising, given the behavior of the dipyrrolides and tetrapyrrolide systems where dinitrogen reduction with and without the assistance of alkali-metal cations is a leitmotif.[3−7] We are puzzled by the fact that a metallocene type of structure was not formed in the case of **3**, despite favorable ligand geometry. The retention of THF in the coordination sphere that prevented the π-ligation of a second ring is probably the result of a decreased steric hindrance with respect to the dipyrrolide ligands. We speculate that this diversity of behavior is perhaps the key to understand the factors determining the occurrence of dinitrogen fixation. However, electronic factors inherent to the metal−imine bond cannot be ruled out at this stage. We are continuing our synthetic work to probe this idea.

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for structures **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.