

# Serendipitous Isolation of the First Example of a Mixed-Valence Samarium Tripyrrole Complex

Christian D. Bérubé,<sup>†</sup> Mohammad Yazdanbakhsh,<sup>‡</sup> Sandro Gambarotta,<sup>\*,†</sup> and Glenn P. A. Yap<sup>†</sup>

Departments of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, and Fardowsi University of Mashad, Mashad, Iran

Received March 4, 2003

The transamination reaction of  $\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$  with two dipyrrole ligands of formula  $\text{RR}'\text{C}(\alpha\text{-C}_4\text{H}_3\text{NH})_2$  ( $\text{R} = \text{R}' = \text{Et}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ) has been examined. The reactions in THF and under  $\text{N}_2$  gave two similar tetranuclear dinitrogen complexes,  $\{[\text{Et}_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2\text{-Sm}\}_4(\text{THF})_2(\mu\text{-N}_2)\cdot 2\text{THF}$  and  $\{[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\text{DME})_2(\mu\text{-N}_2)$ , where the dinitrogen unit has undergone a four-electron reduction via cooperative attack of four divalent samarium atoms and remained coordinated both side-on and end-on between the four coplanar metal centers. The same reaction carried out with diethyldipyrrolylmethane under an argon atmosphere afforded the divalent samarium macrocyclic cluster  $\{[\text{Et}_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2\text{-Sm}\}_8(\text{THF})_4\cdot 4\text{THF}$ . In the case of the reaction with the methylphenyldipyrrolylmethane ligand under  $\text{N}_2$ , the unprecedented hexanuclear mixed-valence  $\text{Sm}^{\text{II}}/\text{Sm}^{\text{III}}$  cluster  $\{[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2][(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})(\beta\text{-C}_4\text{H}_3\text{N})][[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}]_2(\alpha\text{-C}_4\text{H}_3\text{N})_2(\alpha,\alpha'\text{-C}_4\text{H}_2\text{N})\text{-Sm}_3(\text{THF})_3\}_2$ , containing tripyrrolide, “N-confused”, and regular dipyrrolide ligands was serendipitously formed by reaction with the impurities contained in the nonpurified ligand.

## Introduction

Exciting recent work has substantially expanded the frontiers of low-valent lanthanides by making available new, highly reactive divalent salts.<sup>1,2</sup> However, divalent samarium still offers, for molecular activation purposes, the best combination of high reactivity and availability of well-characterized systems. The wealth of transformations displayed by the samarocenes<sup>3</sup> provides a uniquely various and rich chemistry with a large series of diversified substrates.<sup>4,5</sup> Among the most exciting reactions, the reversible dinitrogen fixation performed by  $\text{Cp}^*_2\text{Sm}$  featured not only an attractive side-on bonding mode but also a puzzling minimal extent of N–N triple-bond reduction.<sup>5</sup> In contrast, the use of ancillary ligands such as calix-tetrapyrrole has afforded four-electron reduction of  $\text{N}_2$ , the mechanism of which has been fully elucidated.<sup>6,7</sup> Alkali-metal cations, unavoidably present in the structures of calix-tetrapyrroles, play a substantial role in determining the occurrence of  $\text{N}_2$  fixation. Their undesirable presence was eliminated by using dipyrroles, affording tetranuclear dinitrogen complexes that conclusively demonstrated the occurrence of a simultaneous cooperative interaction of four metal centers on the same dinitrogen molecule.<sup>9</sup> The dipyrrole ligands have also been successfully used to characterize the  $\text{Sm}(\text{II})$  precursors to dinitrogen activation that appeared to be large polynuclear clusters

where the nuclearity (either hexa- or octanuclear) seems to be controlled by the dipyrrole ligand substituents.<sup>10</sup>

Thus, in an attempt to identify the factors that promote the ability of these systems to interact with  $\text{N}_2$ ,

- (3) (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 140. (c) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007. (d) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *Fundamentals of Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum Press: New York, 1979. (e) Evans, W. J.; Ansari, M. A.; Ziller, J. W.; Khan, S. I. *Organometallics* **1995**, *14*, 3. (f) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219. (g) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270. (h) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285. (i) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389. (j) Evans, W. J.; Keyer, R. A.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837. (k) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928. (l) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1989**, *111*, 3329. (m) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. *Organometallics* **1993**, *12*, 4664. (n) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671. (o) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292. (p) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (q) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772. (r) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797. (s) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983. (t) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1986**, *108*, 7440. (u) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314. (v) Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828. (w) Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811.

- (4) Pikramenou, Z. *Coord. Chem. Rev.* **1990**, *99*, 172.  
(5) Evans, W. J.; Ulibarri, T. A.; Ziller, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6877.

- (6) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *117*, 4477.  
(7) (a) Guan, J.; Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 4820. (b) Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 817.  
(8) Dube, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 1182.

<sup>†</sup> University of Ottawa.

<sup>‡</sup> Fardowsi University of Mashad.

(1) Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3176.

(2) Bochkarev, M. N.; Fagin, A. A. *Chem. Eur. J.* **1999**, *10*, 5.

we are now extending this study to other dipyrrolyl dianions bearing different substituents. The aim is 2-fold: (1) we wish to understand how different substituents could modify the metal redox potential and hopefully to enable complete N–N cleavage and (2) we wish to gather further information about the ability of ligand substituents to control the nuclearity of large clusters. Herein we describe our findings.

### 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.<sup>11</sup> Solvents were dried by passing through a column of activated Al<sub>2</sub>O<sub>3</sub> under inert atmosphere prior to use, degassed in vacuo, and transferred and stored under an inert atmosphere. DME was dried by distillation over LiAlH<sub>4</sub>. Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> was prepared according to literature procedures.<sup>12</sup> NMR spectra were recorded on a Bruker AMX-500 spectrometer. 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.<sup>13</sup> Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

**Preparation of Diethyldipyrrolylmethane.** A catalytic amount of methanesulfonic acid (0.5 mL) was added under nitrogen flow to a stirred mixture of 2-pentanone (7.6 mL, 70 mmol) and pyrrole (20 mL, 300 mmol). After the mixture was stirred for 30 min, it changed from clear yellow to dark green. The removal of excess pyrrole in vacuo afforded a green paste, which was dissolved in a small volume of ethanol (25 mL). A small quantity of water was added to the solution until it became cloudy. The heterogeneous mixture was placed at 4 °C for 24 h, upon which colorless crystalline needles of diethyldipyrrolylmethane were obtained (3.6 g, 17.8 mmol, 25%). MS-EI (positive ion): *m/e* 202. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 6.84 (br, 2H, N–H pyrrole), 6.22 (m, 4H, C–H pyrrole), 6.12 (q, 2H, C–H pyrrole), 1.75 (q, 4H, CH<sub>2</sub> ethyl), 0.615 (t, 6H, CH<sub>3</sub> ethyl). <sup>13</sup>C NMR (125.72 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 136.9 (quaternary C pyrrole), 116.9 (CH pyrrole), 107.0 (CH pyrrole), 106.1 (CH pyrrole), 43.6 (quaternary C), 29.3 (CH<sub>2</sub> ethyl), 8.01 (CH<sub>3</sub> ethyl). Anal. Calcd (found) for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>: C, 77.18 (76.91); H, 8.97 (8.85); N, 13.84 (13.54). Mp: 193 °C.

**Preparation of Methylphenyldipyrrolylmethane.** Neat pyrrole (25 mL, 360 mmol) was placed in a 250 mL flask under a nitrogen atmosphere, fitted with a magnetic stirrer and a dropping funnel, and cooled with an ice bath. While the mixture was stirred, a solution of acetophenone (8.4 mL, 70 mmol) in ethanol (30 mL) containing a catalytic amount of methanesulfonic acid (0.5 mL) was added over a period of 20 min. The solution was allowed to react overnight, after which the solvent and the excess pyrrole were removed in vacuo. The crude residual solid was solubilized in methylene chloride (20 mL) and filtered over a short column of silica to remove polypyrrole contaminants. Methylene chloride was removed

in vacuo to give a white solid which was further purified by sublimation (110 °C, 50 mmHg) to yield analytically pure product as a colorless crystalline solid (5.2 g, 22.0 mmol, 30%). MS-EI (positive ion): *m/e* 236. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.05 (m, 5H, C–H phenyl), 6.25 (q, 4H, C–H pyr), 6.02 (q, 2H, C–H pyrrole), 3.44 (very br, 2H, N–H pyrrole), 1.79 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125.72 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 148.1 (quaternary C phenyl), 137.4 (quaternary C pyrrole), 128.4 (CH phenyl), 128.0 (CH phenyl), 126.7 (CH phenyl), 117.2 (CH pyrrole), 108.4 (CH pyrrole), 106.9 (CH pyrrole), 45.0 (quaternary C), 29.0 (CH<sub>3</sub> methyl). Anal. Calcd (found) for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>: C, 81.32 (80.99); H, 6.82 (6.85); N, 11.85 (11.74). Mp: 221 °C.

**Synthesis of {[Et<sub>2</sub>C(α-C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>]Sm<sub>8</sub>(THF)<sub>4</sub>·4THF (1).** A solution of Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> (2.0 g, 3.3 mmol) in anhydrous THF (300 mL) was treated with diethyldipyrrolylmethane (0.7 g, 3.3 mmol) at room temperature and under an argon atmosphere. After 5 days at room temperature very air-sensitive red needles of **1** were formed (1.1 g, 0.32 mmol, 79%). Once crystallized, the complex is nearly insoluble in THF. IR (Nujol mull, cm<sup>-1</sup>): ν 3082 (m), 3064 (m), 2722 (w), 2503 (w), 2394 (w), 1685 (w), 1639 (w), 1594 (w), 1543 (m), 1459 (s), 1423 (s), 1377 (s), 1341 (m), 1325 (m), 1284 (m), 1260 (s), 1172 (s), 1132 (s), 1086 (s), 1038 (s), 951 (s), 925 (m), 883 (s), 831 (s), 799 (s), 751 (s), 665 (w), 632 (m). Anal. Calcd (found) for C<sub>136</sub>H<sub>192</sub>N<sub>16</sub>O<sub>8</sub>Sm<sub>8</sub>: C, 48.29 (48.14); H, 5.72 (5.69); N, 6.63 (6.58). μ<sub>eff</sub> = 10.6 μ<sub>B</sub>. Mp: 69 °C (loss of solvent), 245 °C dec.

**Synthesis of {[Et<sub>2</sub>C(α-C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>]Sm<sub>4</sub>(THF)<sub>2</sub>}(μ-N<sub>2</sub>)·2THF (2). Method A.** A solution of Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> (1.1 g, 1.8 mmol) in anhydrous THF (75 mL) was treated with diethyldipyrrolylmethane (0.4 g, 1.9 mmol) at room temperature and under a nitrogen atmosphere. After 3 days at room temperature, dark red, large, air-sensitive crystals of **2** separated (0.72 g, 0.42 mmol, 93%). Once crystallized, the complex is nearly insoluble in THF. IR (Nujol mull, cm<sup>-1</sup>): ν 3092 (w), 2729 (w), 2207 (w), 2057 (w), 1698 (w), 1627 (w), 1562 (w), 1460 (s), 1428 (s), 1406 (m), 1376 (s), 1338 (m), 1326 (m), 1306 (m), 1272 (s), 1254 (s), 1172 (s), 1133 (s), 1069 (s), 1035 (s), 961 (s), 927 (s), 877 (s), 835 (s), 756 (s), 726 (s), 670 (w), 632 (s), 568 (s). Anal. Calcd (found) for C<sub>68</sub>H<sub>96</sub>N<sub>10</sub>O<sub>4</sub>Sm<sub>4</sub>: C, 47.51 (47.44); H, 5.63 (5.59); N, 8.15 (8.08). μ<sub>eff</sub> = 3.6 μ<sub>B</sub>. Mp: 71 °C (loss of solvent), 237 °C dec.

**Method B.** A suspension of **1** (0.35 g, 0.1 mmol) in THF (15 mL) was exposed to a N<sub>2</sub> atmosphere and stirred overnight. Analytically pure **2** was isolated as a microcrystalline solid in nearly quantitative yield (0.31 g, 0.18 mmol, 90%).

**Synthesis of [((C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)C(α-C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>]Sm<sub>4</sub>(DME)<sub>2</sub>}(μ-N<sub>2</sub>) (3).** A solution of Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> (1.2 g, 2.0 mmol) in anhydrous DME (175 mL) was treated with methylphenyldipyrrolylmethane (0.5 g, 2.0 mmol) at room temperature and under a nitrogen atmosphere. Small air-sensitive red crystals of **3** separated after standing for 2 days at room temperature (0.58 g, 0.33 mmol, 66 %). Once crystallized, the complex is nearly insoluble in both THF and DME. IR (Nujol mull, cm<sup>-1</sup>): ν 3090 (w), 3058 (w), 1599 (m), 1491 (s), 1464 (s), 1426 (m), 1411 (m), 1378 (m), 1363 (m), 1315 (w), 1280 (w), 1260 (m), 1230 (w), 1192 (w), 1180 (m), 1145 (m), 1104 (s), 1079 (s), 1062 (s), 1032 (s), 971 (w), 946 (m), 936 (w), 916 (w), 866 (s), 838 (m), 795 (s), 773 (s), 730 (m), 725 (m), 705 (m), 700 (m), 640 (m), 635 (m), 622 (w), 569 (s), 554 (s), 529 (s). Anal. Calcd (found) for C<sub>72</sub>H<sub>76</sub>N<sub>10</sub>O<sub>4</sub>Sm<sub>4</sub>: C, 49.50 (49.47); H, 4.38 (4.33); N, 8.02 (7.97). μ<sub>eff</sub> = 3.4 μ<sub>B</sub>. Mp: 98 °C (loss of solvent), 256 °C dec.

**Isolation of [((C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)C(α-C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>]((C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)C(α-C<sub>4</sub>H<sub>3</sub>N)(β-C<sub>4</sub>H<sub>3</sub>N))][((C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)C(α-C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>)(α,α'-C<sub>4</sub>H<sub>2</sub>-N)]Sm<sub>3</sub>(THF)<sub>3</sub> (4).** A solution of [Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub>] (1.0 g, 1.6 mmol) in anhydrous THF (50 mL) was treated with nonsublimed methylphenyldipyrrolylmethane (0.39 g, 1.7 mmol) at room temperature and under a nitrogen atmosphere. After it stood 4 days at room temperature, the solution was evaporated to a small volume and diluted with DME (25 mL).

(9) (a) Dube, T.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1432. (b) Guan, J.; Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 4820. (c) Dube, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716.

(10) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 766.

(11) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie Academic & Professional: London, 1997.

(12) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575.

(13) (a) Mabbs, M. B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973. (b) Foese, G.; Gorter, C. J.; Smits, L. J.; *Constantes Selectionnes, Diamagnetisme, Paramagnetisme, Relaxation Paramagnetique*; Masson; Paris, 1957.

**Table 1. Crystal Data and Structure Analysis Results**

	1	2	3	4
formula	C <sub>136</sub> H <sub>192</sub> N <sub>16</sub> O <sub>8</sub> Sm <sub>8</sub>	C <sub>68</sub> H <sub>96</sub> N <sub>10</sub> O <sub>4</sub> Sm <sub>4</sub>	C <sub>72</sub> H <sub>76</sub> N <sub>10</sub> O <sub>4</sub> Sm <sub>4</sub>	C <sub>74</sub> H <sub>80</sub> N <sub>7</sub> O <sub>3.5</sub> Sm <sub>3</sub>
fw	3381.86	1718.95	1746.83	1574.50
space group	orthorhombic	triclinic	monoclinic	monoclinic
<i>a</i> (Å)	32.986(2)	11.1020(10)	9.0634(11)	12.6987(10)
<i>b</i> (Å)	28.819(2)	12.4004(11)	13.5294(17)	31.230(2)
<i>c</i> (Å)	33.030(2)	13.5795(12)	26.030(3)	18.8470(15)
$\alpha$ (deg)	90	101.4330(10)	90	90
$\beta$ (deg)	90	91.272(2)	99.334(2)	90.700(2)
$\gamma$ (deg)	90	113.313(2)	90	90
<i>V</i> (Å <sup>3</sup> )	31400(4)	1672.2(3)	3149.6(7)	7327.1(10)
<i>Z</i>	8	1	2	4
radiation (Mo K $\alpha$ ) (Å)	0.710 73	0.710 73	0.710 73	0.710 73
<i>T</i> (K)	293(2)	203(2)	293(2)	203(2)
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.431	1.707	1.842	1.427
$\mu$ <sub>calcd</sub> (mm <sup>-1</sup> )	2.993	3.514	3.734	2.421
<i>F</i> <sub>000</sub>	13440	854	1716	3148
R1, wR2, <sup>a</sup> GOF	0.0598, 0.1602, 1.056	0.0340, 0.0571, 1.038	0.0589, 0.1273, 1.033	0.0563, 0.1375, 1.018

$$^a R1 = \sum F_o - F_c / \sum F_o; wR2 = [(\sum (F_o - F_c)^2 / \sum wF_o^2)]^{1/2}.$$

After further filtration, the solution was layered with anhydrous hexane (20 mL). Once the layering was complete, the solid mass separated was isolated and examined with a polarized optical microscope and found to consist of two different crystalline products. Red crystals of **3** were the major component of the mixture, and their identity was elucidated by comparison of the IR spectrum of a solid crystalline sample, from which large crystals of **4** were manually removed, with that of an analytically pure sample. Complex **4** was the minor compound, and it was isolated as dark red hexagonal prisms. While the crystals were suitable for X-ray analysis, the physical separation from **3** for other analytical determinations proved to be unfeasible.

**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°  $\omega$ -scans at 0, 90, and 180° in  $\phi$ . 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.<sup>14</sup> No symmetry higher than triclinic was observed for **2**·2THF, 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**·4THF, **3** and **4**·3THF. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*<sup>2</sup>.

The compound molecules of **2**·2THF, **3**, and **4**·3THF reside on an inversion center. One, eight (half-occupancy), and three (half-occupancy) molecules of tetrahydrofuran solvent were located cocrystallized in the asymmetric units of **2**·2THF, **1**·4THF, and **4**·3THF, respectively. The half-occupied, cocrystallized THF molecules were found to be severely disordered, and the atoms having the smallest isotropic parameter per ring were 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 (G. M. Sheldrick, Bruker AXS, Madison, WI, 1997). Crystal data and relevant bond distances and angles are given in Tables 1 and 2.

### Description of Crystal Structures

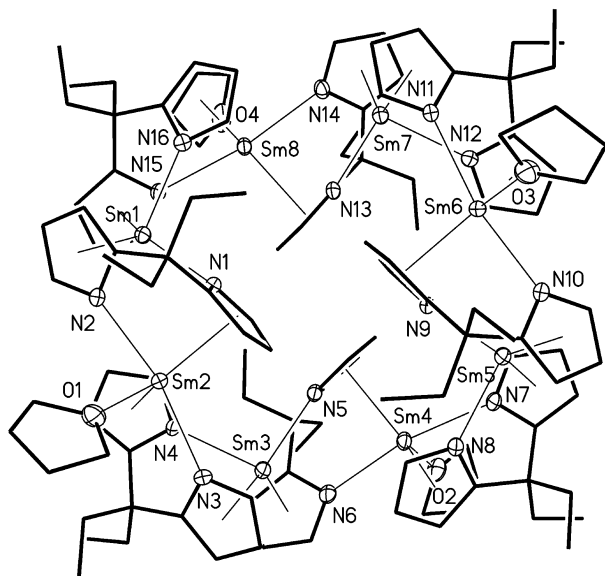
Complex **1** (Figure 1) is formed by eight samarium atoms bridged by eight diethyldipyrrolylmethane ligands,

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

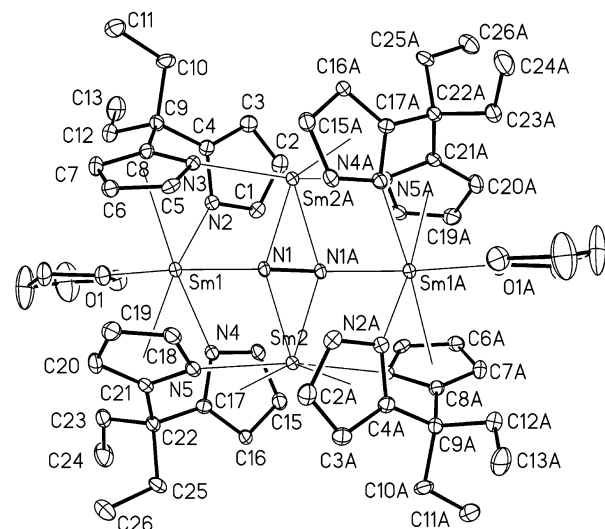
Compound 1			
Sm(1)–N(1)	2.617(10)	Sm(2)–N(2)	2.625(10)
Sm(1)–N(2) <sub>cent</sub>	2.582(10)	Sm(2)–N(3)	2.644(10)
Sm(1)–N(16)	2.600(11)	Sm(2)–O(1)	2.599(10)
N(1)–Sm(1)–N(16)	99.1(3)	N(3)–Sm(2)–O(1)	85.4(3)
N(2)–Sm(2)–O(1)	77.3(3)	N(2)–Sm(2)–N(4) <sub>cent</sub>	101.8(3)
N(2)–Sm(2)–N(3)	162.7(3)	N(2)–Sm(2)–N(1) <sub>cent</sub>	85.1(3)
Compound 2			
N(1)–N(1A)	1.415(6)	Sm(1)–O(1)	2.525(3)
Sm(1)–N(1)	2.145(3)	Sm(1)–N(2)	2.698(4)
Sm(2)–N(1)	2.342(3)	Sm(1)–N(3) <sub>cent</sub>	2.693(4)
Sm(2)–N(1A)	2.342(3)	Sm(2)–N(5)	2.579(4)
N(4)–Sm(1)–N(3) <sub>cent</sub>	170.5(13)	O(1)–Sm(1)–N(1)	145.56(13)
N(2)–Sm(1)–N(5) <sub>cent</sub>	170.3(13)	N(1)–Sm(1)–N(2)	77.16(13)
Sm(1)–N(1)–N(1A)	156.64(13)	N(2)–Sm(1)–N(4)	76.83(13)
Compound 3			
N(1)–N(1A)	1.42(2)	Sm(1)–O(2)	2.629(10)
Sm(1)–N(1)	2.149(11)	Sm(1)–N(2)	2.585(12)
Sm(2)–N(1)	2.316(13)	Sm(2)–N(2)	2.828(12)
Sm(2)–N(1A)	2.316(13)	Sm(1)–N(3)	2.586(12)
Sm(1)–O(1)	2.588(10)	Sm(1)–N(5A)	2.817(14)
Sm(1)–N(1)–N(1A)	167.0(13)	N(1)–Sm(1)–N(3)	80.8(4)
N(2)–Sm(1)–N(3)	66.3(4)		
Compound 4			
Sm(1)–N(1)	2.583(6)	Sm(2)–N(5)	2.544(6)
Sm(1)–N(2) <sub>cent</sub>	2.670(6)	Sm(2)–N(7)	2.495(6)
Sm(1A)–N(1) <sub>cent</sub>	4.042	Sm(3)–N(6)	2.602(6)
Sm(1)–N(3) <sub>cent</sub>	2.708(6)	Sm(3)–N(5) <sub>cent</sub>	2.581(6)
Sm(2)–N(2)	2.771(6)	Sm(3)–O(1)	2.575(6)
Sm(2)–N(3)	2.481(6)	Sm(3)–O(2)	2.574(6)
Sm(2)–N(4)	2.392(6)		
N(2)–Sm(2)–N(4)	84.1(2)	N(4)–Sm(2)–N(5)	159.5(2)
N(2)–Sm(2)–N(7)	78.6(19)	O(1)–Sm(3)–O(2)	77.3(2)
N(3)–Sm(2)–N(7)	155.2(2)	N(6)–Sm(3)–O(2)	77.36(2)
N(3)–Sm(2)–N(4)	74.4(2)		

forming a planar Sm<sup>II</sup> macrocyclic complex. Each samarium atom is both  $\sigma$ -bonded and  $\pi$ -bonded to two pyrrolyl rings of the same ligand (Sm(1)–N(1) = 2.617(10) Å, Sm(1)–N(2)<sub>cent</sub> = 2.582(10) Å) that in turn are also  $\sigma$ - and  $\pi$ -bonded to the next Sm center. The presence of four THF molecules coordinated to every second metal atom (Sm(2)–O(1) = 2.599(10) Å) gives rise to two sets of samarium atoms. The samarium atoms that bear the THF molecule adopt a distorted-trigonal-bipyramidal conformation with the solvent's donor atom and two  $\pi$ -bonded pyrrolyl centroids occupy-

(14) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.



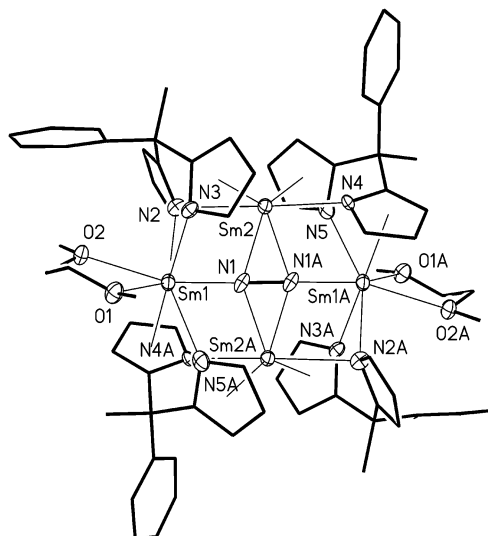
**Figure 1.** Partial thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 30% probability level.



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

ing the equatorial positions and the two N atoms of the  $\sigma$ -bonded rings occupying the axial positions ( $N(2)-Sm(2)-N(3) = 62.7(3)^\circ$ ,  $O(1)-Sm(2)-N(2) = 77.3(3)^\circ$ ,  $N(4)_{cent}-Sm(2)-N(2) = 101.8(3)^\circ$ ,  $N(1)_{cent}-Sm(2)-N(2) = 85.1(3)^\circ$ ). The other samarium atoms, which are not coordinated to solvent molecules, adopt a severely distorted-pseudo-tetrahedral geometry defined by the  $\sigma$ -bonded N atoms and the centroids of the  $\pi$ -bonded rings [ $N(2)_{cent}-Sm(1)-N(1) = 84.9(3)^\circ$ ,  $N(2)_{cent}-Sm(1)-N(16) = 111.9(3)^\circ$ ,  $N(2)_{cent}-Sm(1)-N(15)_{cent} = 126.8(3)^\circ$ ].

Complex **2** is comprised of four samarium atoms, bridged by four diethyldipyrrolylmethane ligands, that are coplanar with a dinitrogen molecule ( $N(1)-N(1A) = 1.415(4) \text{ \AA}$ ) (Figure 2). Each samarium is both  $\sigma$ -bonded and  $\pi$ -bonded to the pyrrolyl rings of two adjacent dipyrrole ligands. Each ligand acts as a tetradentate dianion, with each pyrrole ring being both  $\sigma$ -bonded to one samarium ( $Sm(1)-N(2) = 2.698(4) \text{ \AA}$ ) and  $\pi$ -bonded to another adjacent metal ( $Sm(1)-N(3)_{cent} = 2.693(4) \text{ \AA}$ ). Two of the samarium atoms are end-on bonded to the dinitrogen molecule ( $Sm(1)-N(1) = 2.145(3) \text{ \AA}$ ), each



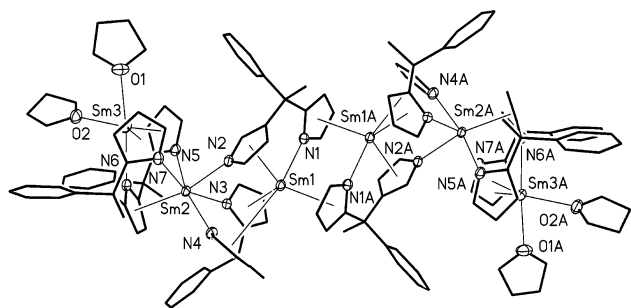
**Figure 3.** Partial thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 30% probability level.

bearing one coordinated molecule of THF ( $Sm(1)-O(1) = 2.525(3) \text{ \AA}$ ). These metals display a distorted-pseudo-octahedral geometry ( $O(1)-Sm(1)-N(1) = 145.56(13)^\circ$ ,  $N(4)-Sm(1)-N(3)_{cent} = 170.5(14)^\circ$ ,  $N(2)-Sm(1)-N(5)_{cent} = 170.3(14)^\circ$ ) defined by one of the two nitrogen atoms of the  $N_2$  unit, the O atom of THF, the two N atoms of two  $\sigma$ -bonded pyrrolyl rings, and the two centroids of the two  $\pi$ -bonded rings. The second pair of samarium atoms are bound in a side-on fashion to the dinitrogen molecule and have slightly longer Sm-N bond lengths ( $Sm(2)-N(1) = 2.328(3) \text{ \AA}$ ).

Complex **3** is similar to complex **1** (Figure 3), the main difference being the different substituents of the dipyrrolyl dianion and the presence of coordinated DME replacing the two THF molecules. Again, the nitrogen-nitrogen distance ( $N(1)-N(1A) = 1.42(2) \text{ \AA}$ ) indicates four-electron reduction of the dinitrogen molecule. The major differentiation with **1** resides in the different bonding mode adopted by the ligand system. Two of the methylphenyldipyrrolylmethane ligands bear a pyrrole ring that does not form the expected  $\sigma$  and  $\pi$  bonds but has a nitrogen atom that bridges two contiguous samarium centers. These nitrogen atoms do not interact equally between both metal atoms ( $Sm(1)-N(2) = 2.585(12) \text{ \AA}$ ,  $Sm(2)-N(2) = 2.828(12) \text{ \AA}$ ) and form a shorter  $\sigma$ -bond with one of the two metal centers.

The unit cell of complex **4** consists of two crystallographically independent but chemically equivalent units (Figure 4). Each molecule is composed by six samarium atoms forming a symmetry-generated sinusoidal type of array. The three independent samarium atoms are bridged by three different pyrrole-based ligands. The first ligand is an "N-confused"<sup>15</sup> methylphenyldipyrrolylmethane, where one of the pyrrole rings is attached to the central carbon by using the  $\beta$  position instead of the  $\alpha$  position. This ligand acts as a tetradentate

(15) (a) Depraetere, S.; Smet, M.; Dehaen, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3359 and references therein. (b) Gale, P. A.; Sessler, J. L. *Chem. Commun.* **1998**, 1 and references therein. (c) Sessler, J. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1348. (d) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (e) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779. (f) Liu, B. Y.; Bruckner, C.; Dolphin, D. *J. J. Chem. Soc., Chem. Commun.* **1996**, 2141.

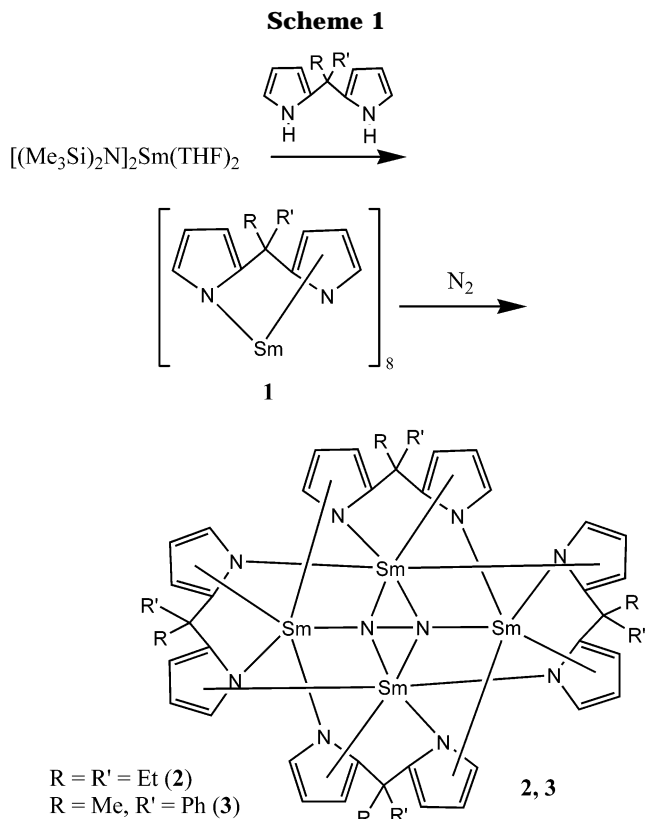


**Figure 4.** Partial thermal ellipsoid plot of **4**. Thermal ellipsoids are drawn at the 30% probability level.

dianion, being  $\sigma$ -bonded to two different samarium atoms ( $\text{Sm}(1)-\text{N}(1) = 2.583(6) \text{ \AA}$ ,  $\text{Sm}(2)-\text{N}(2) = 2.464(6) \text{ \AA}$ ),  $\pi$ -bonded to one of these two metal atoms ( $\text{Sm}(1)-\text{N}(2)_{\text{cent}} = 2.670(6) \text{ \AA}$ ), and also  $\pi$ -bonded to another samarium from the symmetry-generated unit ( $\text{Sm}(1\text{A})-\text{N}(1)_{\text{cent}} = 4.042 \text{ \AA}$ ). The second ligand is a normal methylphenyldipyrrolylmethane, and it is similar to the previous ligand in its bonding mode, with both pyrrole rings  $\sigma$ -bonded to the same samarium ( $\text{Sm}(2)-\text{N}(3) = 2.481(6) \text{ \AA}$ ,  $\text{Sm}(2)-\text{N}(4) = 2.392(6) \text{ \AA}$ ) and forming  $\pi$ -bonds to the next samarium atom ( $\text{Sm}(1)-\text{N}(3)_{\text{cent}} = 2.708(6) \text{ \AA}$ ). The third ligand is an unprecedented trianionic bis(phenylmethyl)tripyrrolide acting as a hexadentate ligand. The two terminal pyrrolyl rings are  $\sigma$ -bonded to the same samarium ( $\text{Sm}(2)-\text{N}(5) = 2.544(6) \text{ \AA}$ ,  $\text{Sm}(2)-\text{N}(7) = 2.495(6) \text{ \AA}$ ) and also form  $\pi$ -bonds to the  $\text{Sm}(3)$  atom ( $\text{Sm}(3)-\text{N}(5)_{\text{cent}} = 2.581(6) \text{ \AA}$ ). The central pyrrole ring forms a  $\sigma$ -bond to the third samarium atom ( $\text{Sm}(3)-\text{N}(6) = 2.602(6) \text{ \AA}$ ) while  $\pi$ -bonding to the  $\text{Sm}(2)$  atom ( $\text{Sm}(2)-\text{N}(6)_{\text{cent}} = 2.514(6) \text{ \AA}$ ). The  $\text{Sm}(1)$  atom is thus  $\pi$ -bonded to four pyrrole rings and  $\sigma$ -bonded to a fifth. The metal adopts a highly distorted trigonal bipyramidal geometry where the nitrogen atom of the  $\sigma$ -bonded rings of the N-confused ligand occupies one of the two axial positions. The second axial position is occupied by the centroid of another bridging pyrrolide ring. The three equatorial positions are defined by the centroids of the three  $\pi$ -bonded rings from the three ligands surrounding the metal ( $\text{N}(1)-\text{Sm}(1)-\text{N}(4)_{\text{cent}} = 167.0(2)^\circ$ ,  $\text{N}(1)-\text{Sm}(1)-\text{N}(1\text{A})_{\text{cent}} = 94.8(2)^\circ$ ,  $\text{N}(1)-\text{Sm}(1)-\text{N}(2)_{\text{cent}} = 83.4(2)^\circ$ ,  $\text{N}(1)-\text{Sm}(1)-\text{N}(3)_{\text{cent}} = 103.9(2)^\circ$ ). The  $\text{Sm}(2)$  atom is distorted octahedral, being  $\sigma$ -bonded to one axial and four equatorial pyrrolyl rings. The centroid of a sixth  $\pi$ -bonded pyrrole ring occupies the second axial position ( $\text{N}(2)-\text{Sm}(2)-\text{N}(6)_{\text{cent}} = 164.1(2)^\circ$ ,  $\text{N}(4)-\text{Sm}(2)-\text{N}(5) = 159.5(2)^\circ$ ,  $\text{N}(3)-\text{Sm}(2)-\text{N}(7) = 155.2(2)^\circ$ ). Finally, the  $\text{Sm}(3)$  atom is  $\sigma$ -bonded to a single pyrrolyl nitrogen,  $\pi$ -bonded to two pyrrole rings, and coordinatively bound by two THF molecules ( $\text{Sm}(3)-\text{O}(1) = 2.575(6) \text{ \AA}$ ,  $\text{Sm}(3)-\text{O}(2) = 2.574(5) \text{ \AA}$ ), which confers a distorted-trigonal-bipyramidal geometry to the metal center ( $\text{N}(6)-\text{Sm}(1)-\text{O}(1)_{\text{cent}} = 174.2(2)^\circ$ ,  $\text{N}(6)-\text{Sm}(1)-\text{O}(2)_{\text{cent}} = 99.9(2)^\circ$ ,  $\text{N}(6)-\text{Sm}(3)-\text{N}(5)_{\text{cent}} = 83.4(2)^\circ$ ,  $\text{N}(6)-\text{Sm}(3)-\text{N}(7)_{\text{cent}} = 81.1(2)^\circ$ ).

## Results and Discussion

The trans-amination reaction of alkali-metal- and halogen-free  $\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$  with diethyldipyrrolylmethane was performed in a small volume of THF

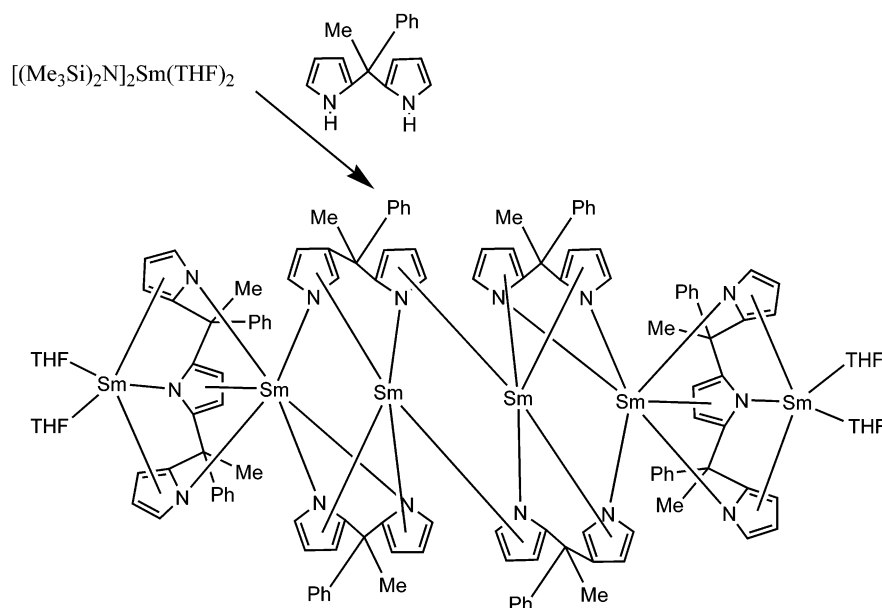


at room temperature and under Ar, affording rapid precipitation of divalent **1** as a dark red microcrystalline powder (Scheme 1). Suitable crystals for X-ray analysis were grown upon carrying out reactions in dilute solutions and allowing the reaction flask to rest in a vibration-free environment for 5 days. Compound **1** is an octameric macrocycle (Figure 1) formed by eight divalent samarium dipyrrolide units. The magnetic moment is nearly as expected for eight divalent samarium centers, thus indicating that there is minimal magnetic exchange within the ring.

Exposure of **1** to nitrogen gas or more simply carrying out the above preparation directly under an  $\text{N}_2$  atmosphere afforded large red crystals of the dinitrogen complex  $\{[(\text{C}_2\text{H}_5)_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N}_2)]\text{Sm}\}_4(\text{THF})_2(\mu\text{-N}_2) \cdot 2\text{THF}$  (**2**) in good yield (Scheme 1). The long N–N distance ( $\text{N}(1)-\text{N}(1\text{A}) = 1.415(4) \text{ \AA}$ ) showed by the X-ray crystal structure (Figure 2) indicated that the dinitrogen molecule has undergone a four-electron reduction. In turn, this implies that each metal center was oxidized to the trivalent state. Accordingly, the coordination of  $\text{N}_2$  was irreversible, with the complex remaining unchanged when exposed to vacuum at high temperature. As a feature common to the other very similar dinitrogen complexes of other dipyrrolides previously reported,<sup>7</sup> complex **2** displays poor solubility in the most common solvents.

Use of the methylphenyldipyrrolylmethane ligand and the usual reaction conditions afforded neither the dinitrogen nor the macrocyclic complex but yielded instead intractable compounds. However, the same reaction in a small volume of anhydrous DME gave the dinitrogen complex **3** as red crystals. This compound is very similar to **2** as far as the  $\text{Sm}_4\text{N}_2$  core (Figure 3) and fits in what turns out to be a trend in the behavior of divalent Sm dipyrrolide compounds.<sup>7</sup> However, there are slight

Scheme 2



variations in the bonding mode of the ligand. Whether these variations are due to change in the solvent denticity (DME versus THF) or to ligand backbone asymmetry is unclear. Attempts to reproduce the divalent octacyclic samarium precursor were unsuccessful with this particular ligand system.

When the reaction affording **3** was carried out with recrystallized (nonsublimed) methylphenyldipyrrrolylmethane, two distinct types of crystals were formed upon reducing the volume of the reaction mixture, diluting with DME, and layering with hexanes. The major component consisted of small reddish brown crystals that, after manual separation under a stereomicroscope, were rapidly identified as compound **3** by the identity of their IR spectrum with that of an analytically pure sample. The minor component consisted of large red hexagonal prisms that were invariably contaminated by **3** but were still of sufficient quality to be analyzed by X-ray crystallography (Figure 4). Complex **4** is very unusual and interesting (Scheme 2). Its hexameric structure with a sinusoidal arrangement of the metals clearly shows the presence of three different ligand systems. In addition to the presence of two normal ligands, the complex contains two "N-confused"<sup>15</sup> dipyrrrole units: i.e., a dipyrrrole where the attachment of one of the two pyrrolyl rings was switched from the  $\alpha$ - to the  $\beta$ -position. The last consists of two attractive tripyrrole moieties, thus making **4** the first metal complex of a tripyrrole ligand. Regrettably, purification or isolation of the crystalline **4** in analytically pure form proved unfeasible, and therefore no other analytical determination could be carried out. This is even more unfortunate, given that the complex is a mixed-valence Sm(II)/Sm(III) species.

Questions arise about the generation of both the tripyrrole and the N-confused ligand. Although the mixed valence of **4** might suggest that some complex redox transformation could be at the origin of their formation, a careful inspection of the 500 MHz <sup>1</sup>H NMR of the ligand used for the reaction revealed the presence of two unexpected ligands in the starting material. Two small peaks between 1.77 and 1.78 ppm were integrated

to approximately 10% of the dipyrrromethane methyl peak at 1.79 ppm. Because of the resemblance of all the methylphenyl-polypyrrolide ligands, this was found to be the only evidence for the presence of unwanted analogues besides TLC separation. Attempts to perform chromatographic separation have been unsuccessful so far. In any event, sublimation of the ligand eliminated the impurities and systematically gave clean formation of **3** without the presence of contaminants. Therefore, the formation of **4** may be attributed only to the ability of divalent samarium to scavenge the impurities produced during the formation of the particular methylphenyldipyrrrolylmethane. This is still puzzling though, given that the presence of **4**, although a minor product, was rather substantial in the crystalline mass. Furthermore, the partial oxidation of the metal center during this reaction remains unexplained.

### Conclusion

Two new dinitrogen complexes from the reactions of divalent samarium and dipyrrrolides have been prepared and characterized, as well as the octameric cyclic cluster precursor of one of them. Complexes **1–3** are in line with the behavior of other dipyrrrole ligands,<sup>8–10</sup> and no evidence was found that this ligand system may support N–N cleavage, despite assembling large octanuclear clusters. However, the serendipitous isolation of **4** indicates that N-confused dipyrrrole and tripyrroles may also be versatile and exciting ligand systems for assembling noncyclic cluster structures. Further work to rationally prepare complexes of these new ligand systems is in progress at the moment.

**Acknowledgment.** This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC).

**Supporting Information Available:** Listings of atomic coordinates, thermal parameters, and bond distances and angles for structures **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM030155Q