Sequencing of Products: Unlabeled DNA was prepared from rolling circle replication reaction as above but with all four dNTPs at 0.5 mM. After 1.5 h incubation at 37 °C, the mixture was heated to 90 °C for 5 min and partially purified with Micro Bio-Spin 30 columns (Bio-Rad). Sequencing was carried out using a BigDye Terminator Cycle Sequencing Kit (Applied Biosystems) following the recommended procedure. The linear controls **9**–**12** were used as sequencing primers. Unlabeled RNA was prepared from rolling circle transcription reactions as above but with all four rNTPs at 0.5 mM. After 1.5 h incubation at 37 °C, the mixture was heated to 90 °C for 5 min and the repetitive RNA products were partially purified by size exclusion as above. The complementary DNA was obtained by using these conditions: partially purified RNA, 50 pmol linear primer DNA (either **9**, **10**, **11**, or **12**), 50 U AMV Reverse Transcriptase (Pharmacia), 10 mM dATP, dGTP, dCTP and dTTP, 20 U RNAse inhibitor (Promega) in a buffer (pH 8.3) containing 100 mM Tris · HCl, 10 mM $MgCl_2$, 10 mM DTT, and 50 mM KCl, in a total volume of 20 μL. After 1 h incubation at 42 °C, the reaction mixture was heated to 90 °C for 5 min and cleaned up with a Micro Bio-Spin 30 column. The complementary DNA was then sequenced as above, using primers **5**–**8**.

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Tetrametallic Reduction of Dinitrogen: Formation of a Tetranuclear Samarium Dinitrogen Complex[**]

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Examples of dinitrogen complexes are rare in lanthanide chemistry and have been documented for only four cases.[1, 2] In the case of samarium in particular, the two existing complexes display a completely different extent of dinitrogen reduction.[1] Thus, in an attempt to evaluate the role played by the nature of the ligand in promoting dinitrogen reduction, we have now prepared a novel diphenylmethyldipyrrolide dianion and investigated its ability to stabilize Sm^{II} complexes.[3] Herein we describe the first example in which a four-electron dinitrogen reduction is achieved through the cooperative one-electron oxidation of four metal centers. To the best of our knowledge this type of process has been observed only in the nitrogenase enzyme.[4]

The reaction of $[SmI_2(thf)_2]$ with one equivalent of diphenylmethyldipyrrolide dianion (dipyrr; either as disodium or dipotassium salt) at room temperature under N_2 yielded a dark purple-brown solution from which dark brown crystals of **1** (Figure 1) were isolated in an analytically pure form in good yield on a reproducible basis. Unlike $[\{N(CH_2CH_2NSi\mathit{t}BuMe_2)_3U\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$[5] or $[\{(\eta^5\text{-}C_5Me_5)_2Sm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$,[1a] and similar to the case of the calix-tetrapyrrole derivative,[1b] complex **1** showed no sign of reversible coordination of dinitrogen and remained unchanged upon prolonged exposure to heat or vacuum.

$$[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_4(\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}N_2)] \quad \mathbf{1}$$

The presence of a molecule of coordinated dinitrogen in the molecular structure was demonstrated by an X-ray crystal structure analysis. The complex is composed of four $[\{Ph_2C(C_4H_3N)_2\}Sm]$ units; the four metal atoms arrange to form a slightly distorted lozenge, in the center of which is located a dinitrogen molecule that is coordinated *side-on* to two metal atoms and *end-on* to the other two metal atoms. The N–N distance and the fact that degradation with anhydrous HCl did not release N_2 indicates that the Sm atoms are present in the formal trivalent state.[6]

The same reaction carried out under an argon atmosphere afforded dark red crystals of a new ionic compound formulated as **2** (Figure 1). The ionic structure is formed by a

$$[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_5(\mu_5\text{-}I)]^-\text{-}\;[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]_2[Sm(thf)]_3\}(\mu_3\text{-}I)]^+ \quad \mathbf{2}$$

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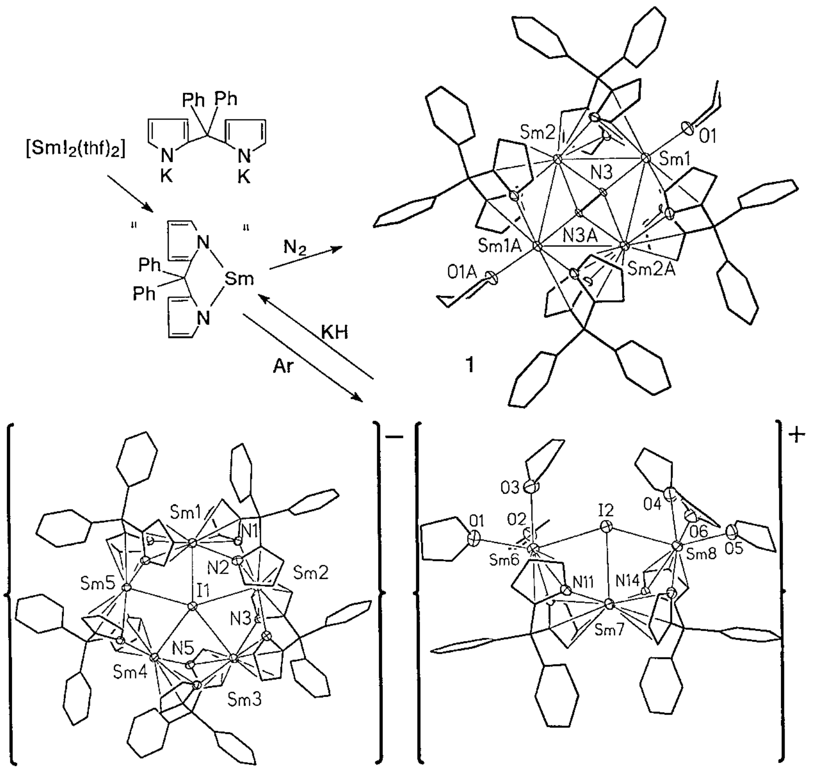

2

Figure 1. Synthesis and structures of **1** and **2**. Bond lengths [Å] and angles [°]: for complex **1**: N3–N3A 1.412(17), Sm1–N3 2.177(8), Sm2–N3 2.327(3), Sm2–N3A 2.327(3), Sm1 ··· Sm2 3.602(9), Sm2 ··· Sm2A 4.434(9), Sm1 ··· Sm1A 5.678(9), Sm1–N1 2.701(8), Sm1–N2 2.736(8), Sm2–N1 2.574(8), Sm2–N2 2.697(7); Sm1-N3-N3A 156.6(11), O1-Sm1-N3 150.5(4); for complex **2**: Sm1–I1 3.434(1), Sm2–I1 3.480(1), Sm3–I1 3.634(1), Sm4–I1 3.455(1), Sm5–I1 3.520(1), Sm1 –N1 2.810(7), Sm1–N2 2.670(7), Sm1–N9 2.664(7), Sm1–N10 2.768(7), Sm6–I2 3.3168(8), Sm7–I2 3.369(1), Sm8–I2 3.3047(9), Sm1 ··· Sm2 4.123(1), Sm1 ··· Sm5 4.101(1), Sm7 ··· Sm6 4.028(1), Sm7 ··· Sm8 4.038(1); Sm1-I1-Sm2 73.211(18), Sm1-I1-Sm5 72.260(16), Sm7-I2-Sm6 74.090(18), Sm7-I2-Sm8 74.468(18), Sm6-I2-Sm8 148.35(2).

trinuclear cation and a pentanuclear anion. The cation consists of three samarium atoms bridged by one nearly coplanar iodine atom which adopts a distorted "T-shape" geometry. The three samarium atoms are also bridged by two diphenylmethyldipyrrolide dianions, which adopt the same bonding mode observed in complex **1**. The counteranion is a pentanuclear samarium complex with five samarium atoms pentagonally arranged around a central, and coplanar iodine atom. The five diphenylmethyldipyrrolide dianions adopt the usual π- and σ-bonding modes with each ligand bridging two samarium centers.

Complex **2** does not show any appreciable sign of reaction with nitrogen gas even after long periods and upon heating. Thus questions arise about the striking diversity of behavior resulting in the formations of **1** and **2**. Complex **2** exclusively contains divalent samarium atoms. The unit formula formally consists of seven $[\{Ph_2C(C_4H_3N)_2\}Sm]$ units and one SmI_2 organized in stable cluster structures around the two halogen atoms. The presence of the two iodine atoms is likely to be the factor responsible for the lack of reactivity with dinitrogen. Attempts to avoid their presence, by carrying out the preparation of **2** with excess ligand, did not modify the result. The elimination of the formal SmI_2 unit was achieved by reaction of **2** with KH and resulted in an immediate color change and concomitant release of H_2 according to the Equation (1).

$$2[\{(\text{dipyrr})Sm\}_7SmI_2] + 4KH + 3.5N_2 \longrightarrow 2Sm^0 + 2H_2 + 4KI + 3.5[\{(\text{dipyrr})Sm\}_4(N_2)] \quad (1)$$

The fact that this reaction afforded **1** in good yield suggests that halogen elimination from **2** dissociates the cluster structures leading to the release of "$[\{Ph_2C(C_4H_3N)_2\}Sm]$" fragments which are then free to react with dinitrogen.

In an effort to further clarify the role of the halogen atom, attempts were made to generate the "$[\{Ph_2C(C_4H_3N)_2\}Sm]$"unit by reduction of a "$[\{[Ph_2C(C_4H_3N)_2]Sm\}Cl]$" precursor with potassium under nitrogen and in THF (Figure 2). The reaction yielded a new Sm^{II} compound formulated as **3**. Similar to the case of **2, 3** showed no signs of reactivity towards dinitrogen despite the striking structural similarity of its tetrametallic core with that of **1**. A chlorine atom is present instead of N_2 in the center of the square plane defined by the four samarium atoms, while one potassium is π-bonded to one of the pyrrole rings already engaged in σ- and π-bridging interactions with two samarium centers. This result confirms that the halogen has indeed an inhibitory effect on the ability of the samarium diphenylmethyldipyrrolide system to interact with dinitrogen. Notably, in spite of the oxophilicity of samarium, the presence of THF does not prevent dinitrogen fixation.

$[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_4(\mu_4\text{-}Cl)\{K(thf)_2\}]$ **3**

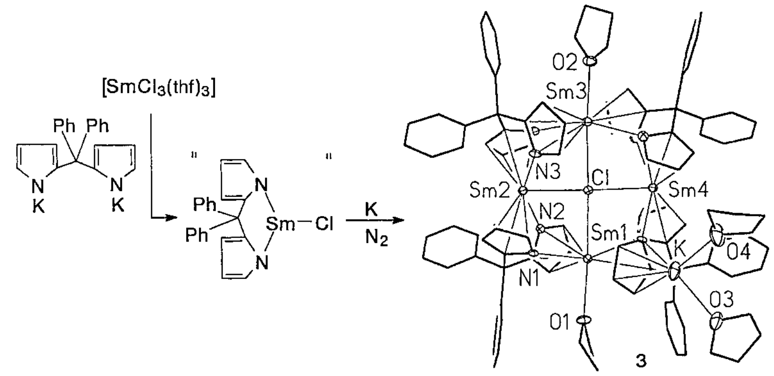

Figure 2. Synthesis and structure of **3**. Bond lengths [Å] and angles [°]: Sm1–Cl 3.045(2), Sm2–Cl 2.847(2), Sm3–Cl 3.042(2), Sm4–Cl 2.845(2), Sm1–N1 2.726(6), Sm1–N2 2.849(6), Sm1–N7 3.040(8), Sm1–N8 2.712(7), Sm1 ··· Sm2 4.136(2), Sm1 ··· Sm4 4.240(2), Sm1 ··· Sm3 6.087(2), Sm2 ··· Sm4 5.689(2); Sm1-Cl-Sm2 89.10(6), Sm1-Cl-Sm3 178.30(8), Sm1-Cl-Sm4 92.03(6), Sm2-Cl-Sm4 176.69(9), O1-Sm1-Cl 168.53(13).

Experimental Section

1: Method A: A solution of potassium diphenylmethyldipyrrolide (1.3 g, 3.4 mmol) in THF (100 mL) was treated under N_2 with $[SmI_2(thf)_2]$ (1.8 g, 3.4 mmol). The color immediately changed to dark purple-brown. Stirring was continued for 12 h after which the solution was filtered to eliminate a small amount of insoluble material. The filtrate was concentrated to 50 mL and layered with toluene (50 mL). After the mixture had been left to stand at room temperature for 24 h, large, red-brown crystals of **1** (1.3 g, 0.66 mmol, 78 %) were obtained. Elemental analysis (%) calcd for $Sm_4C_{92}H_{80}O_2N_{10}$: C 56.40, H 4.12, N 7.15; found: C 56.35, H 4.08, N 7.09; IR (Nujol mull): $\tilde{\nu}$ = 3048 w, 1597 w, 1491 m, 1464 s, 1417 w, 1377 s, 1261 w, 1182 w, 1147 m, 1078 w, 1043 s, 985 w, 874 w, 798 m, 785 m, 756 s, 740 s, 696 s, 658 w, 640 m cm^{-1}. $\mu_{eff} = 6.55\,\mu_B$ per formula unit.

Method B: A solution of **2** (0.7 g, 0.25 mmol) in THF (50 mL) under N_2 was treated with KH (0.050 g, 1.2 mmol). A vigorous reaction with effervescence and a color change to purple-brown was immediately observed. The solution was allowed to stir for 30 min, followed by filtration to remove a small amount of insoluble material. After the mixture had been layered with toluene and left to stand at room temperature for three days, crystals of **1** were obtained (Yield 76 %).

2: A solution of diphenylmethyldipyrrolide (1.0 g, 3.4 mmol) in THF (100 mL) was stirred with KH (0.3 g, 6.7 mmol) for 30 min at room temperature under argon. Subsequent addition of $[SmI_2(thf)_2]$ (1.8 g, 3.4 mmol) resulted in an immediate color change to dark brown. After stirring overnight the solution was filtered to eliminate a small amount of dark insoluble material, concentrated to 50 mL, and layered with toluene (25 mL). The mixture was allowed to stand for 24 h at room temperature, which resulted in the precipitation of large, dark red crystals of **2** (1.0 g, 0.22 mmol, 53 % calculated relative to Sm). Elemental analysis (%) calcd for $Sm_8N_{14}O_7C_{206.5}H_{205.5}$: C 59.07, H 4.93, N 4.67; found: C 58.88, H 4.81, N 4.59; IR (Nujol mull): $\tilde{\nu}$ = 3049 w, 1595 w, 1489 m, 1464 s, 1419 w, 1377 s, 1263 w, 1234 w, 1184 w, 1151 m, 1076 m, 1038 s, 980 w, 964 w, 926 w, 891 m, 848 m, 789 m, 748 s, 704 s, 658 w, 634 m cm^{-1}. $\mu_{eff} = 9.14\,\mu_B$ per formula unit.

3: A solution of diphenylmethyldipyrrolide (1.1 g, 3.7 mmol) in THF (100 mL) was treated with KH (0.3 g, 7.5 mmol). Stirring was continued at room temperature for 30 min until all of the KH had been consumed. Subsequent addition of $[SmCl_3(thf)_3]$ (1.7 g, 3.7 mmol) resulted in the formation of a yellow suspension which was stirred for 1 h. Potassium metal (0.15 g, 3.8 mmol) was then added to the reaction mixture together with a catalytic amount of naphthalene (0.01 g, 78 μmol). Within minutes the color began to deepen to reddish-brown. After 4 h all the potassium had been consumed. The solution was filtered to remove a small amount of insoluble material. The dark brown filtrate was concentrated to 50 mL and layered with toluene (30 mL). After the mixture had been left to stand at room temperature for two days, large, dark brown crystals of **3** were obtained (1.2 g, 0.5 mmol, 58 %). Elemental analysis (%) calcd for $C_{104}H_{104}N_8O_5KClSm_4$: C 56.21, H 4.72, N 5.04; found: C 56.11, H 4.66, N 4.97; IR (Nujol mull): $\tilde{\nu}$ = 3050 w, 1597 w, 1493 m, 1464 s, 1415 w, 1377 s, 1261 m, 1236 w, 1182 w, 1151 m, 1091 m, 1078 m, 1039 s, 980 w, 924 w, 879 w, 849 m, 795 m, 760 s, 700 s, 660 m, 636 m cm^{-1}. $\mu_{eff} = 7.02\,\mu_B$ per tetramer.

Crystal data for **1**: $Sm_4C_{92}H_{80}O_2N_{10}$, $M_r = 1059.32$, monoclinic, $C2/m$, $a = 21.542(6)$, $b = 19.232(6)$, $c = 12.437(3)$ Å, $\beta = 116.96(3)^\circ$, $V = 4593(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.405$ Mg m^{-3}; absorption coefficient 2.567 mm^{-1}, $F(000) = 1900$, reflections collected 17557, independent reflections 5668, GOF = 1.007, $R = 0.0546$, $wR^2 = 0.1696$.

Crystal data for **2**: $Sm_8N_{14}O_7C_{206.5}H_{205.5}$, $M_r = 4451.95$, monoclinic, $P2(1)/c$, $a = 18.186(2)$, $b = 23.349(2)$, $c = 43.492(4)$ Å, $\beta = 90.169(2)^\circ$, $V = 18467(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.601$ Mg m^{-3}; absorption coefficient 2.895 mm^{-1}, $F(000) = 8802$, reflections collected 145877, independent reflections 44562, GOF = 1.018, $R = 0.0553$, $wR^2 = 0.1086$.

Crystal data for **3**: $C_{104}H_{104}N_8O_5KClSm_4$, $M_r = 2221.90$, triclinic, $P\bar{1}$, $a = 13.462(1)$, $b = 17.534(2)$, $c = 20.970(2)$ Å, $\alpha = 110.006(1)$, $\beta = 100.343(2)$, $\gamma = 90.421(1)^\circ$, $V = 4562.8(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.617$ Mg m^{-3}; absorption coefficient 2.670 mm^{-1}, $F(000) = 2216$, reflections collected 35786, independent reflections 11862, GOF = 1.047, $R = 0.0385$, $wR^2 = 0.1010$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117425 (**1**), CCDC-117426 (**2**), CCDC-117427 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Paramagnetic Diniobium Complex with a Very Short Nb–Nb Distance: Evidence for a Pseudo Nb–Nb Triple Bond?[**]

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Low-valent second- and third-row transition metals typically form significant and robust M–M bonds.[1, 2] Divalent Group 5 metals provide a puzzling exception. In principle, the d^3 electronic configuration makes them good candidates for the formation of triple bonds. Exceedingly short V≡V triple bonds were indeed observed in a few dinuclear V^{II} complexes,[3] although these bonds seem to display the same paradoxical weakness[4] that was previously observed for quadruply bonded dichromium compounds.[5] Conversely, for the heavier Nb and Ta homologues no such information is

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