facilitates the formation of a peroxide species with molecular oxygen. The hydride transfer from the aluminum alkoxide of hydrotalcite is effected by the neighboring peroxide on the nickel atom. Hydrotalcites are homogeneous mixtures of heterobimetallic composition having a periodic composition of M^{II} and M^{III} ions. The cationic order of cat. **A** as revealed by IR studies suggests that the presence of one aluminum atom for every two nickel atoms substituted alternately in the hydrotalcite provides the optimum use of nickel in cat. **A**, better than is possible with the other compositions, and is thus responsible for the display of higher activity.

In conclusion, Ni-Al hydrotalcite efficiently oxidizes a wide range of alcohols, such as allylic and benzylic, and α-ketols to the corresponding carbonyl compounds under mild reaction conditions by employing molecular oxygen as the stoichiometric oxidant. This process is not only economically viable but also applicable to large-scale reactions. Moreover, the high yields of oxidized products can be obtained in heterogeneous catalysis using hydrotalcites as catalysts.

Experimental Section

Various catalysts with varied composition of Ni-Al hydrotalcites (Ni:Al = 2:1 (cat. **A**), 2.5:1, 3:1) were prepared by coprecipitation employing NaOH/Na_2CO_3 as described in the literature.[12a] Catalyst **A** was rehydrated according to our previous report[11b] and calcined at 450 °C in a flow of air. Ni-Al hydrotalcite (Ni:Al 2:1, cat. **B**) was prepared by coprecipitation using ammonia solution.[12b] The samples of nickel impregnated on γ-alumina (2, 5, and 10 %) were prepared by adding the required amounts of $Ni(NO_3)_2 \cdot 6H_2O$ in water to γ-alumina and stirring occasionally while heating on a water bath till complete evaporation of water had occurred. The residue was dried in an oven at 110 °C for 16 h.

Typical oxidation procedure: Oxygen was bubbled at atmospheric pressure through a reaction mixture containing *p*-nitrobenzyl alcohol (2 mmol) and catalyst (0.5 g) in toluene (10 mL) at 90 °C under stirring. The reaction was monitored by thin-layer chromatography and purified by column chromatography (hexane:ethyl acetate, 95:5, v:v) to afford the *p*-nitrobenzaldehyde as a pale yellow solid: 0.296 g (98 %), m.p. 105 °C, ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.1$ (d, $^3J(H,H) = 8.3$ Hz, 2H, aryl-H), 8.4 (d, $^3J(H,H) = 8.3$ Hz, 2H, aryl-H), 10.2 (s, 1H, CHO); IR (KBr pellets) $\tilde{\nu} = 1700$ cm^{-1} (sh, C=O); MS (70 eV) m/z (%): 151 (64) [M^+], 150 (61) [$M^+ - H$], 105 (20) [$C_7H_5O^+$], 77 (93) [$C_6H_5^+$], 51 (100) [$C_4H_3^+$].

TPR profiles were recorded on Micromeritics (Auto Chem 2910) using 0.05 g of the uncalcined sample. The sample was dried at 120 °C in an argon flow and then helium was replaced by a flow of a mixture of 5 % hydrogen in helium at room temperature.

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Highly Reactive Sm^{II} Macrocyclic Clusters: Precursors to N_2 Reduction**

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Divalent samarium complexes have been prepared with a wide variety of ligand systems,[1] but the extreme level of reactivity and the uniqueness of transformations displayed by the samarocene derivatives[2] was never reproduced. To date, the Sm^{II} polypyrrolide derivatives[3] are the only systems which share with decamethylsamarocene[4] the ability to react with an exceedingly inert molecule such as dinitrogen. Unlike samarocene, however, these species may perform *four-electron* reduction of dinitrogen, thus indicating that their reducing power is particularly strong. Particularly versatile with this respect are divalent samarium complexes of dipyrrolide dianions,[5] which are reminiscent of the ansa-metallocene ligand systems. So far these species have led to three novel dinitrogen complexes.[6, 7] However, attempts to isolate the presumably highly reactive divalent precursors

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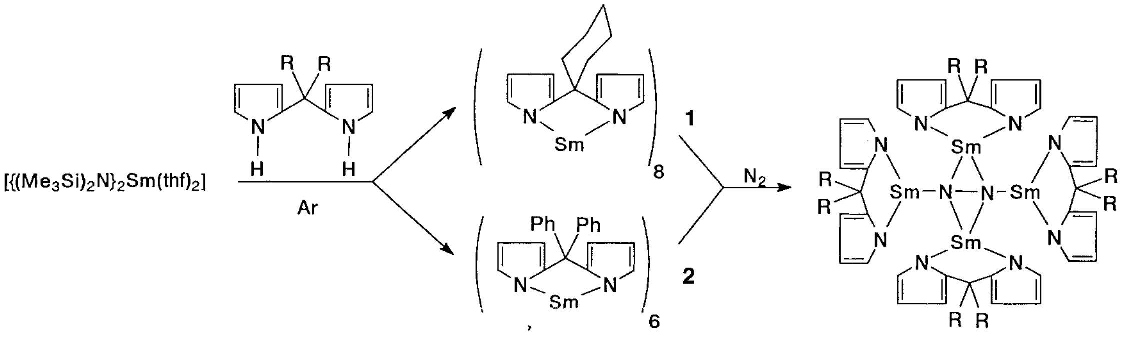

Scheme 1. Synthesis of **1** and **2** and subsequent reaction with N_2.

analogous to the samarocenes instead yielded rather stable tetra-, penta-, or octanuclear mixed-valence complexes,[6–8] containing a variety of fragments. This adds further support to the idea that the divalent precursors may be highly reactive. Herein we describe a different synthetic approach that has allowed us to isolate two halogen- and alkali-free Sm^{II} macrocyclic complexes which are rare examples of lanthanide cyclic clusters[8, 9] and the first of this type exclusively containing highly reactive divalent samarium.

Reaction of $[Sm\{N(SiMe_3)_2\}_2(thf)_2]$[1d] with one equivalent of 1,1-di-(α-pyrrolyl)cyclohexane in THF under an argon atmosphere afforded dark red crystals of the octameric divalent cluster $[\{[1,1\text{-}(\alpha\text{-}C_4H_3N)_2C_6H_{10}]Sm\}_8(thf)_4]\cdot$hexane (**1**) in very good yield (Scheme 1).

The crystal structure of compound **1** shows that the molecule is composed of eight Sm atoms bridged by eight ligands arranged to form a neutral macrocyclic Sm^{II} complex in which the samarium atoms adopt a flattened boatlike conformation (Figure 1). The coordination of four molecules of THF to four of the eight Sm centers results in two sets of samarium atoms. Each samarium atom without coordinated THF is bridged to the next (with coordinated THF) by one dipyrrolide dianion; the pyrrole rings in turn are π-bonded to one samarium atom and σ-bonded to a second. As a result, the coordination geometry around each samarium atom is strongly reminiscent of that of a bent samarocene with one pyrrolyl ring from each ligand being π-bonded and the two others σ-coordinated. The four Sm atoms bearing one THF molecule display a trigonal-bipyramidal geometry. The centroids of two π-bonded pyrrolyl rings and the oxygen atom of the coordinated THF define the equatorial plane, while the nitrogen atoms of two σ-bonded pyrrolyl rings are at the axial positions.

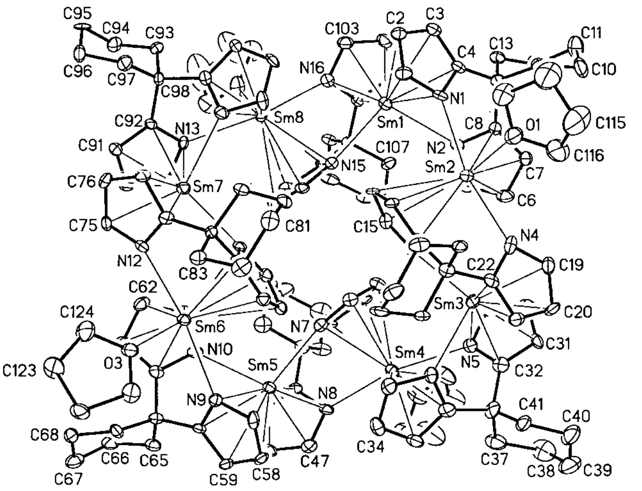

Figure 1. Structure of **1**. Bond lengths [Å] and angles [°]: Sm2-N1 2.588(7), Sm2-O1 2.595(7), Sm2-N4 2.604(8), Sm2-N2 2.812(7), Sm2-N3 2.810(7); N1-Sm2-O1 77.2(2), N1-Sm2-N4 159.9(2), O1-Sm2-N4 82.7(2), N1-Sm2-N2 65.4(2), O1-Sm2-N2 124.7(2), N4-Sm2-N2 128.5(2), N1-Sm2-N3 127.4(2), O1-Sm2-N3 129.8(2), N4-Sm2-N3 66.9(2), N2-Sm2-N3 105.4(2).

The analogous reaction carried out with $Ph_2C(\alpha\text{-}C_4H_3N)_2H_2$ afforded the hexameric paramagnetic cluster $[\{[Ph_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_6(thf)_3]\cdot(THF)_{6.5}$ (**2**) in 56% yield. In this particular case the six samarium atoms form a regular, flat hexagon with Sm–Sm distances ranging from 4.359 to 4.225 Å (Figure 2). The ligand adopts the characteristic bonding mode bridging each pair of metals by crossing σ and π interactions. Again, two sets of samarium atoms are observed: those without coordinated THF, which display the usual bent samarocene-type structures, and those coordinated to THF in which the metal adopts a trigonal-bipyramidal geometry.

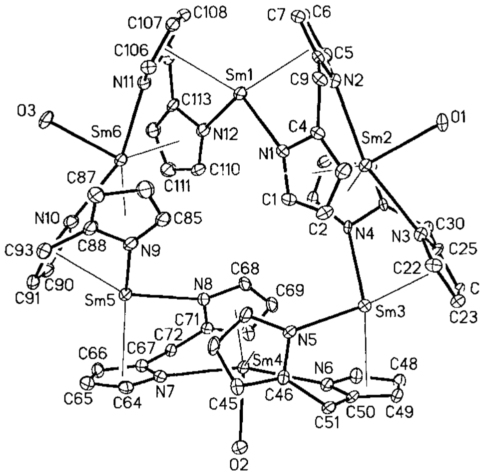

Figure 2. Structure of **2**. Bond lengths [Å] and angles [°]: Sm1-N12 2.656(11), Sm1-N1 2.677(10), Sm1-N2 2.775(10), Sm1-C8 2.780(12), Sm1-N11 2.839(10), Sm2-O1 2.546(8); N12-Sm1-N1 116.6(3), N12-Sm1-N2 124.6(3), N1-Sm1-N2 64.3(3), N12-Sm1-N11 64.5(3), N1-Sm1-N11 124.3(3), N2-Sm1-N11 165.3(3), O1-Sm2-N3 81.1(3), O1-Sm2-N2 80.3(3), N3-Sm2-N2 161.3(3), O1-Sm2-N4 125.5(3), N3-Sm2-N4 63.3(3), N2-Sm2-N4 128.1(3), O1-Sm2-N1 125.0(3), N3-Sm2-N1 129.8(3), N2-Sm2-N1 64.2(3), N4-Sm2-N1 109.5(3).

Upon exposure to N_2, solutions of **1** and **2** in THF (Scheme 1) rapidly formed the corresponding previously reported tetranuclear dinitrogen complexes $[\{[R_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_4 \cdot (THF)_2](\mu\text{-}N_2)$[6, 7] in good yield (71 and 75%, respectively). Complex **2** reacts considerably slower than **1** (2 weeks) presumably due to its very poor solubility. Conversely, when the reactions leading to the formation of **1** and **2** were carried out under an N_2 atmosphere, the corresponding dinitrogen complexes were rapidly obtained in good yield (70 and 77%, respectively). The four-electron reduction of dinitrogen and the irreversibility of the fixation sharply contrast with the labile coordination observed with decamethylsamarocene[4] and calix[4]tetrapyrrole derivatives,[3b] indicating that compounds **1** and **2** probably are stronger reductants.

The formation of the dinitrogen complex from octameric **1** is a relatively straightforward process in which two molecules of dinitrogen cleave the octameric structure into two tetrameric dinitrogen complexes. Conversely, in the case of **2** the formation of the dinitrogen complex $[\{[Ph_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(thf)_2](\mu\text{-}N_2)$ implies dissociation of a dimeric $[\{[Ph_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_2(thf)]$ unit and its possible recombination into a second tetrameric unit.

An intriguing question arises about the factors that prevent the complete cleavage of the N≡N bond in these two clusters, which are capable of performing both fixation and four-electron reduction of dinitrogen. Both **1** and **2** have available the six-electron pool necessary for the cleavage of the N≡N bond. Complex **1** in particular seems to be a perfect candidate for the task. A six-electron reduction of N_2, hypothetically performed by **1**, would result in the formation of a mixed-valence octameric compound containing two nitrides in the middle of the polymetallic cycle. This type of structure is perfectly stable and was previously observed with the halide-containing mixed-valence octameric complexes.[8] The fact that the reduction stops at the hydrazido tetraanion stage is even more surprising considering that the cleavage of a N–N single bond requires far less energy ($159\,kJ\,mol^{-1}$) than the four-electron reduction of N_2 ($787\,kJ\,mol^{-1}$). This behavior can be explained by assuming that the encapsulation of N_2 into a small tetranuclear cluster is the factor preventing further dinitrogen reduction. In support of this claim, our recent attempts to cleave the residual N–N bond in $[\{[1,1'\text{-}(\alpha\text{-}C_4H_3N)_2C_6H_{10}]Sm\}_4 \cdot (THF)_2](\mu\text{-}N_2)$ by using a strong reducing agent such as Na, reduced two of the four Sm centers in the process has led to a shortening rather than a lengthening of the N–N distance.[7]

In conclusion, two unique macrocyclic clusters containing highly reactive divalent samarium atoms were prepared. The bent-metallocene type of structure is probably responsible for the very high reactivity. We are currently investigating the use of these macrocyclic compounds for multiple redox processes aimed at molecular activation.

Experimental Section

1: A solution of $[Sm\{N(SiMe_3)_2\}_2(thf)_2]$ (1.1 g, 1.9 mmol) in anhydrous THF (40 mL) was treated with 1,1-di-(α-pyrrolyl)cylohexane (0.4 g, 1.9 mmol) at room temperature under an argon atmosphere. The solution was allowed to stand for 12 h and then concentrated to a small volume (20 mL). The addition of hexane to this solution (10 mL) yielded dark red crystals of **1** (0.7 g, 0.2 mmol, 94% based on Sm) after the mixture had been left to stand for two days at room temperature. Elemental analysis (%) calcd for $C_{134}H_{174}N_{16}O_4Sm_8$: C 49.13, H 5.35, N 6.84; found: C 48.80, H 5.18, N 6.63; IR (Nujol mull): $\tilde{\nu}$: 3090 (m), 3058 (m), 1422 (s), 1346 (w), 1296 (m), 1272 (m), 1262 (m), 1245 (w), 1233 (w), 1192 (m), 1176 (w), 1155 (s), 1135 (w), 1127 (m), 1092 (m), 1030 (vs), 956 (m), 931 (w), 903 (m), 893 (m), 872 (m), 849 (w), 829 (w), 747 (vs), 631 (s), 575 (m) cm^{-1}; $\mu_{eff} = 8.79\,\mu_B$ per unit formula.

2: A solution of $[Sm\{N(SiMe_3)_2\}_2(thf)_2]$ (2.2 g, 3.5 mmol) in THF (40 mL) was treated at room temperature under an argon atmosphere with diphenyl dipyrromethane (1.0 g, 3.5 mmol). The addition of hexane (10 mL) gave dark red crystals of **2** (1.1 g, 0.33 mmol, 56%) after the mixture had been allowed to stand at room temperature for seven days. Elemental analysis (%) calcd for $C_{164}H_{172}N_{12}O_{9.5}Sm_6$: C 58.53, H 5.15, N 4.99; found: C 58.37, H 5.03, N 4.91; IR (Nujol mull): $\tilde{\nu}$: 1371 (w), 1320 (w), 1261 (vs), 1231 (s), 1183 (s), 1150 (vs), 1081 (vs), 1040 (vs), 978 (w), 963 (w), 924 (s), 881 (s), 848 (s), 801 (s), 761 (vs), 742 (vs), 704 (vs), 657 (s), 636 (s), 622 (w), 613 (w) cm^{-1}; $\mu_{eff} = 6.81\,\mu_B$ per unit formula.

Crystal structure analysis data for **1**: $C_{134}H_{174}N_{16}O_4Sm_8$, $M_r = 3275.69$, triclinic, $P\bar{1}$, $a = 16.703(2)$, $b = 18.150(2)$, $c = 24.750(3)$ Å, $\alpha = 102.839(2)$, $\beta = 100.971(2)$, $\gamma = 99.943(2)^\circ$, $V = 6998.5(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.554\,Mg\,m^{-3}$; $\mu = 3.352\,mm^{-1}$, $F(000) = 3236$, 54903 reflections collected, 27927 independent reflections, GOF = 1.018, $R = 0.0436$, $wR_2 = 0.1038$. Crystal structure analysis data for **2**: $C_{164}H_{172}N_{12}O_{9.5}Sm_6$, $M_r = 3365.24$, triclinic, $P\bar{1}$, $a = 16.549(1)$, $b = 18.918(1)$, $c = 26.187(2)$ Å, $\alpha = 102.973(2)$, $\beta = 103.397(2)$, $\gamma = 109.175(1)^\circ$, $V = 7118.7(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.570\,Mg\,m^{-3}$; $\mu = 2.499\,mm^{-1}$, $F(000) = 3376$, 55952 reflections collected, 14841 independent reflections, GOF = 1.072, $R = 0.0550$, $wR_2 = 0.1143$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151133 (**1**) and CCDC-151134 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Enantioselective Desymmetrization of *meso*-Decalin Diallylic Alcohols by a New Zr-Based Sharpless AE Process: A Novel Approach to the Asymmetric Synthesis of Polyhydroxylated *Celastraceae* Sesquiterpene Cores[**]

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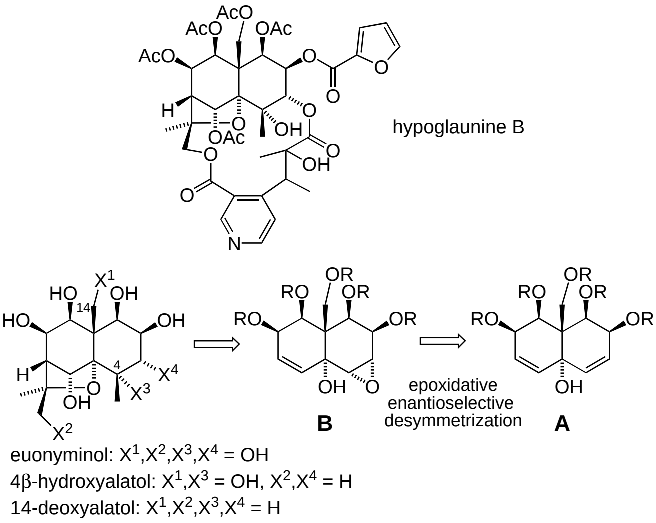
Crude plant extracts of the *Celastraceae* have been valued since antiquity for their stimulant, appetite suppressive, antiarthritic, antibacterial, insect repellent, and memory-restorative properties.[1] Pervasive among the secondary metabolites isolated from this class of plants is a large family of polyhydroxylated sesquiterpene esters having a dihydro-β-agarofuran skeleton.[2] Many members of this family, particularly esters of three polyhydroxylated agarofurans: euonyminol, 4β-hydroxyalatol, and 14-deoxyalatol, exhibit significant biological activity. These include: triptogelins A-1/A-6[3a] and celhin A[3b] (antitumor), wilfortrine[4] (immunosuppressive), wilforine[5] (insecticidal), and celangulin[6a] and cathedulins E-3/E-4/E-5[6b] (insect antifeedant). Additionally, hypoglaunine B and related macrocyclic lactone derivatives of euonyminol have recently been shown to display significant anti-HIV activity[7] (Scheme 1).



Scheme 1. Desymmetrization strategy. R = protecting group, Ac = acetyl.

One striking feature of the three core structures common to these natural products is a symmetric array of hydroxyl groups on the top face of their "northern" periphery. We were intrigued by the possibility of exploiting this symmetry to facilitate their synthesis. In particular, we identified epoxide **B** as a pivotal intermediate for the preparation of all the core structures and we envisaged that a two-directional synthesis of *meso*-diallylic alcohol **A** followed by epoxidative enantioselective desymmetrization[8] would provide an efficient route to this intermediate (Scheme 1). Here we describe how the successful implementation of this plan required the development of a Zr-based Sharpless asymmetric epoxidation (AE) process for tertiary diallylic alcohols.

At the outset of our work, only one *trans*-decalinic diallylic alcohol had been reported.[9] In view of this limited precedent, and the potentially labile nature of the structure, we opted to evaluate the feasibility of our strategy on simple model system **5** (Scheme 2). Epoxide **1** was prepared from naphthalene by Birch reduction (Na/NH_3; 74% yield) then epoxidation (CH_3CO_3H; 87% yield).[10] Ring opening with Et_2AlCN,[11] followed by completely diastereoselective epoxidation and *trans*-diaxial ring opening with Me_3Al gave triol **4**. Selective mesylation then *anti* elimination in neat DBU furnished the requisite diallylic alcohol **5**. This alcohol was prone to partial [1,3]-allylic rearrangement to give the corresponding conjugated dienyl alcohol on silica, but could be obtained pure after chromatography on grade 1 basic alumina.

Sharpless AE[12] with either catalytic[13] or stoichiometric[13] amounts of Ti(O*i*Pr)$_4$/D-(−)-diisopropyl tartrate (DIPT) pro-

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