Dimeric samarium(III) alkoxides bearing N_2O_2 tetradentate Schiff bases and their utility for the catalytic epoxidation of *trans*-chalcone

Steven A. Schuetz, Elizabeth A. Bowman, Carter M. Silvernail,
Victor W. Day, John A. Belot [*]

Department of Chemistry, University of Nebraska-Lincoln, 621 Hamilton Hall, Lincoln, NE 68588-0304, USA

Abstract

Two anhydrous, dimeric samarium(III) complexes bearing a bulky μ-alkoxide (diphenylmethoxide) ligand and different "saturated" tetradentate Schiff bases {bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexene-3-onato and bis-5,5′-(2,2-dimethyl-1,3-propanediyldiimino)-2,2-dimethyl-4-hexene-3-onato} were synthesized and fully characterized. The complexes differ only in alkyl substitution at the three-carbon amino linker between the ketoiminato halves, with one having a CH_2 group and the other a $C(CH_3)_2$ substituent along the free-ligand idealized mirror plane. Both metal-containing molecules were isolated in high-yields from direct alcoholysis of the corresponding 5-coordinate, mononuclear complexes and their catalytic activity for the epoxidation of 1,3-diphenyl propenone (*trans*-chalcone), an α,β-unsaturated ketone, investigated.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Rare-earth; Alkoxide; Epoxidation; Catalyst; Schiff-base

1. Introduction

An area of considerable interest in contemporary lanthanide (Ln) chemistry is the identification of robust ligand frameworks which stabilize low metal coordination numbers and support catalytic activity. Toward this goal, we previously synthesized heteroleptic Ln^{3+} complexes which coordinate a "saturated" tetradentate Schiff base (SB) at the four "basal" sites of a square pyramid and a monodentate amido at the apical position [1a–1c]. These complexes offer several potential advantages over cyclopentadienyl systems; most notably, the stability associated with the Schiff-base Ln–O and Ln–N bonds. They also offer inherent attributes of low-cost, rapid synthesis, and straightforward modification at prochiral sites. Furthermore, the labile apical ligand in these 5-coordinate complexes undergoes facile stoichiometric replacement without N_2O_2 ligand degradation or displacement. More specifically, this apical ligand has been converted to both alkoxides and phenoxides [1a], as part of a detailed study designed to assess the effects of steric factors on final product nuclearity and/or reactivity.

Previously, rare-earth alkoxides have been used for the preparation of oxide materials [2] and as active catalysts for small molecule transformations, including the ring-opening polymerization of lactides [3] and lactones [4] and the epoxidation of α,β-unsaturated ketones [5]. They therefore represent potentially useful materials for solving waste management problems through renewable resources (e.g., biobased feedstocks) and for alternative catalytic preparations of epoxides which are of

---

[*] Corresponding author. Tel.: +402 472 5666; fax: +402 472 9402.
E-mail address: jbelot2@unl.edu (J.A. Belot).

interest for the synthesis of pharmaceutical and natural product intermediates.

The catalytic asymmetric epoxidation of conjugated enones (α,β-unsaturated) is well established for metal catalysts such as Ti(O^{i}Pr)$_4$ [6] and Mn(salen) complexes (Jacobsen's catalyst) [7] and poly(amino acids) [8]. It is also successfully accomplished with rare-earth isoprop-oxides with the addition of a bidentate chiral auxiliary ligand such as BINOL and its derivatives [9] yielding product distributions with >90% ee purity. Further-more, rare-earth BINOL systems offer many advantages including mild reaction conditions that avoid the use of halogenated solvents, reduced temperatures, and avoid-ance of complex multi-step syntheses. However, the impetus behind developing new epoxidation pathways for conjugated enones that proceed with enantiospecific conversion in good yields and minimized quantities of catalyst offer inherent advantages, especially when con-sidering large scale preparations. Thus, we sought to combine the success of Jacobsen's Salen systems with the rare-earth alkoxides and build lanthanide complexes of known nuclearity and conformational rigidity for the epoxidation of conjugated enones, as a logical extension of our prior work [1].
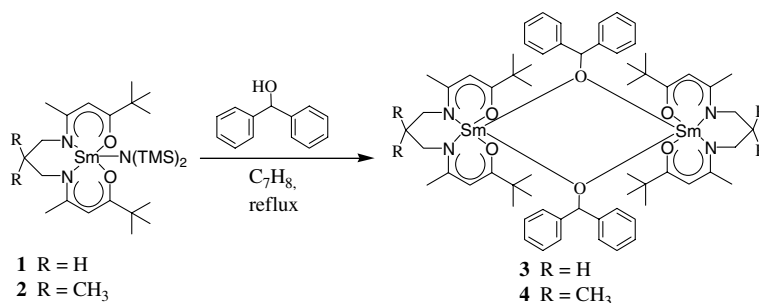
Although we have reported the synthesis and charac-terization of numerous mononuclear and rigorously dinuclear and dimeric Ln^{3+} complexes bearing "satu-rated" Schiff bases [1,10], the subtle structural differ-ences within these molecules and the significant amido lability prompted evaluation of the replacement of the apical, bulky bis(trimethylsilyl)amido group with 2,6-bis(tert-butyl)-4-methylphenol [1a]. Unfortunately these alkoxide species proved to be kinetically inert, thus we sough to reduce alkoxide bulk to afford a more open me-tal center for substrate approach. Herein, we present the results of the stoichiometric alcoholysis results of the Schiff-base complexes, [bis-5,5′-(1,3-propanediyldi-imino)-2,2-dimethyl-4-hexene-3-onato]samarium[bis(tri-methylsilyl)amido], **1**, and [bis-5,5′-(2,2-dimethyl-1,3-propanediyldiimino)-2,2-dimethyl-4-hexene-3-onato]-samarium[bis(trimethylsilyl)amido], **2**, with benzhydrol (diphenylmethanol) (Scheme 1), a ligand previously em-ployed by Tolman and Hillmyer [11] in the polymeriza-

tion of polar lactide monomers. Our reactions yielded rigorously dimeric Sm^{3+}complexes **3** and **4** that have remarkably similar molecular structures even though they contain propyl linkages with quite different steric requirements, crystallize with totally different solid-state packing arrangements and contain sterically different solvent molecules of crystallization. The only molecular difference for Sm^{3+} dimers **3** and **4** involves the substit-uents on the central carbon of the propylene bridge be-tween the two ketoiminato "halves" of the Schiff base. This carbon atom [C(6) or C(26)] has two hydrogen substitutents in **3** and has two methyl substitutents in **4**. The final products were fully characterized and as-sessed as active catalysts for the epoxidation of trans-chalcone.

2. Results and discussion

Although our current interest in **3** and **4** focuses on their reactivity and potential as active catalysts for the epoxidation of conjugated enones, we are interested in understanding any structural basis for such behavior as well as the apical ligand steric influence on nuclearity [1a,10]. Differences in the reactivity or catalytic behavior of **3** and **4** can presumably be attributed to the presence of gem-dimethyl substituents on the propyl bridges in **4**. These compounds also represent additional examples of the ease with which alkoxide or phenoxide species can be straightforwardly prepared from Ln(SB)(amido) com-plexes without Schiff-base degradation or replacement [1a].

The intimate solid-state structures of **3** and **4** are sim-ilar. They both consist of discrete dimeric molecules (Fig. 1(a) and (b)), each of which contains two Sm(SB) moieties bridged by the oxygen anions of the diphenyl-methoxide ligands. Each Sm^{3+} ion is therefore formally 6-coordinate and bonded to the two oxygens and two nitrogens of a single dianionic SB ligand as well as the μ-oxygens of the two diphenylmethoxide anions. For Sm(1) in both structures, the tetradentate Schiff base occupies one square face of a trigonal prism and the oxygens of the two bridging diphenylmethoxide ligands

Scheme 1. Synthesis of dimeric lanthanide alkoxide dimers, **3** and **4**. HN(TMS)$_2$ by products omitted for clarify.
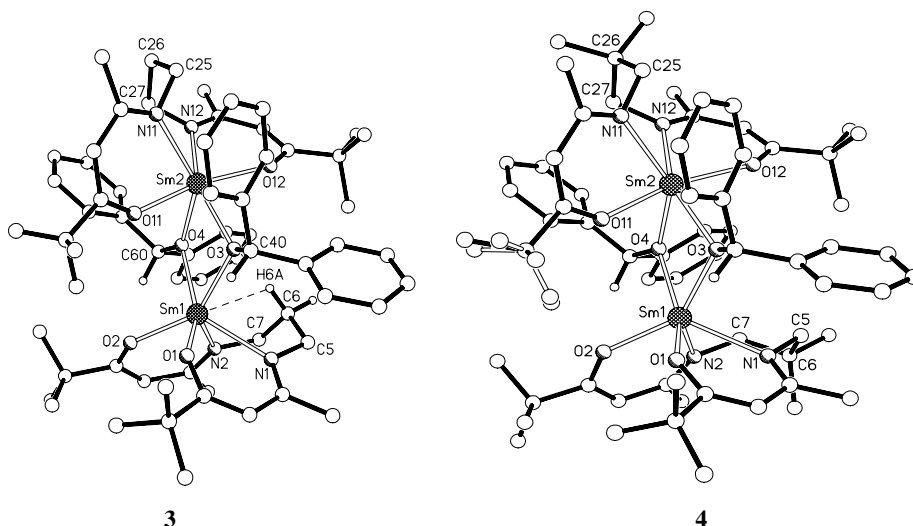
Fig. 1. X-ray crystal structure of compounds **3** and **4**. Solvent molecules of crystallization omitted for clarity. Relevant bond lengths (Å) with esds for **3**: Sm1–O1 2.227(5); Sm1–O2 2.224(5); Sm1–O3 2.338(5); Sm1–O4 2.417(4); Sm1–N1 2.477(6); Sm1–N2 2.457(6); Sm2–O3 2.321(5); Sm2–O4 2.275(5); Sm2–O11 2.318(5); Sm2–O12 2.319(6); Sm2–N11 2.481(7); Sm2–N12 2.495(7); **4**: Sm1–O1 2.256(4); Sm1–O2 2.246(5); Sm1–O3 2.369(4); Sm1–O4 2.405(4); Sm1–N1 2.469(6); Sm1–N2 2.469(7); Sm2–O3 2.348(4); Sm2–O4 2.305(4); Sm2–O11 2.318(5); Sm2–O12 2.312(5); Sm2–N11 2.510(6); Sm2– N(12) 2.513(5).
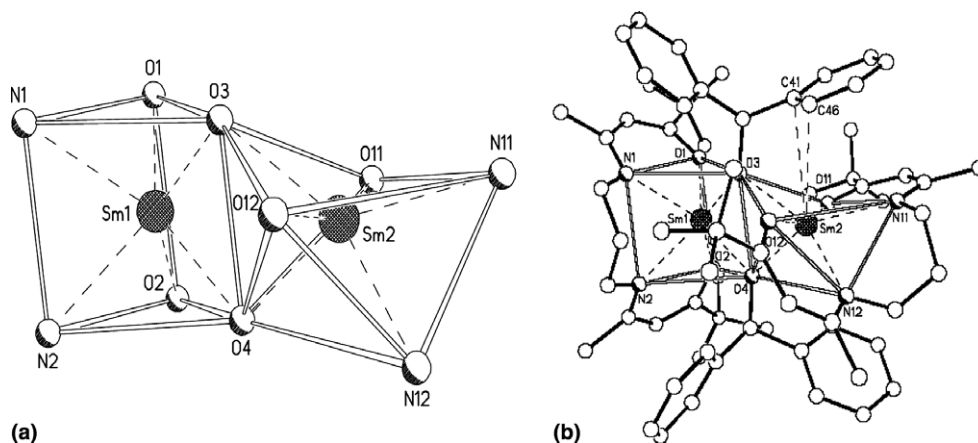

Fig. 2. Identically oriented Sm^{3+} coordination polyhedra (a) and molecular structures without hydrogens (b) for compounds **3** and **4**. The weak $Sm^{3+} \cdots$phenyl interaction is indicated by dashed lines.

complete the trigonal prismatic coordination polyhedron (Fig. 2(a)). The 6-coordinate polyhedron for Sm(2) in both structures is *highly* distorted and resembles neither idealized octahedral nor trigonal prismatic geometry. It almost appears to be a monocapped trigonal prism with one vertex missing. Both Sm(2) ions have a large vacant region on one side of their coordination sphere and one of the alkoxide phenyl rings is folded into the space above this void. The Sm(2)···C(41) and Sm(2)···C(46) interactions (Fig. 2(b)) in **3** and **4** are 3.12–3.30 Å and are in good agreement with previously observed Ln ··· arene π interactions [12].

In both complexes, the Sm–O bond lengths about Sm(2) generally tend to be slightly longer than the corresponding Sm–O bond lengths for Sm(1) and those for **4** tend to be slightly longer than the corresponding

bonds in **3**. Both trends can be explained by Sm(2) having a highly distorted coordination polyhedron and by **4** containing a bulkier Schiff base ligand. The $Sm(1)–O_{SB}$ bond lengths average [13] 2.235(5,9) and 2.251(5,5) Å in **3** and **4**, respectively; the $Sm(2)–O_{SB}$ bond lengths average 2.319(6,1) and 2.315(5,3) Å, respectively. The $Sm(1)–N_{SB}$ bond lengths average 2.467(6,10) and 2.469(6,0) Å in **3** and **4**, respectively; the $Sm(2)–N_{SB}$ bond lengths average 2.488(7,7) and 2.512(6,1) Å, respectively. The Sm–O(3) bond lengths to the first bridging diphenylmethoxide ligand average 2.330(5,9) and 2.359(4,11) Å in **3** and **4**, respectively. The Sm–O(4) bond lengths to the second bridging ligand average 2.346(5,71) and 2.355(4,50) Å in **3** and **4**, respectively; Sm(1)–O(4) bond is significantly longer (>0.10 Å) than the Sm(2)–O(4) bond in both complexes. The remaining
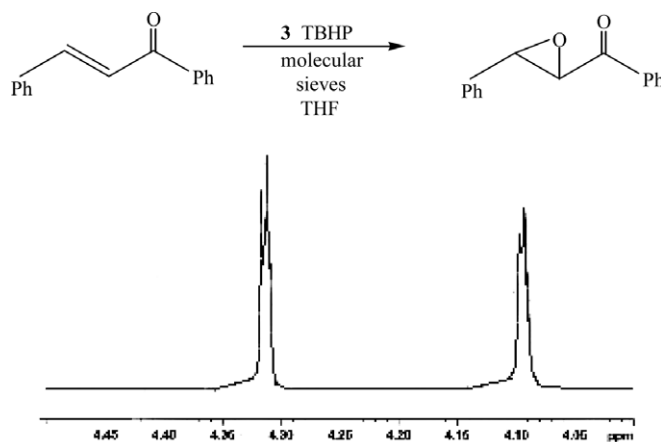
Scheme 2. Epoxidation reaction (above) and ^{1}H NMR of epoxidation product using **3** (below) at t = 24 h.

bond lengths and angles in both compounds are unexceptional.

The only noticeable difference between the solid-state structures of **3** and **4** involves the 6-membered –Sm(1)–N(1)–C(5)–C(6)–C(7)–N(2)– diamine chelate ring which adopts a flattened boat conformation in **3** and a flattened chair conformation in **4**. The boat conformation in **3** permits a 2.63 Å agostic Sm···H interaction that is not possible in **4** where the methylene hydrogens on the central carbon of the propyl bridge have been replaced by methyl groups. This same behavior has been previously observed for diamine chelate rings in a variety of mononuclear Ln(SB)(L) complexes [1a]. The second diamine chelate ring in both molecules is twisted into a conformation midway between the boat and chair. This twisted chelate ring conformation produces two ~3.09 Å Sm(2)···H contacts in each molecule; they involve one hydrogen on each of the terminal methylene groups [C(25) and C(27)] of the propyl bridge.

The close similarity of the structures for **3** and **4** is indicated by the fact that the two metals, six oxygens and four nitrogens of each dimer superimpose with a rms deviation of 0.10 Å When carbon atom C(6) and *tert*-butyl methyl carbons are excluded, the remaining 63 non-hydrogen atoms common to both dimers superimpose with a rms deviation of 0.23 Å. This close similarity was unanticipated since it did not appear that the methylene hydrogens on the central carbons of the propyl bridges in **3** could be replaced by methyl groups without substantially distorting the structure. The molecule easily accommodated one *gem*-dimethyl substituent by changing the conformation of one diamine chelate ring. It accommodated the second *gem*-dimethyl substituent through small displacements of nearby groups toward the exterior of the molecule as previously observed in dinuclear Ln$_2$(SB)$_3$ species [1d].

Preliminary data indicates that **3** is an active catalyst for the asymmetric epoxidation of α,β-unsaturated ketones in THF using a 185:1 *trans*-chalcone:catalyst ratio.

The ^{1}H NMR (Scheme 2) demonstrates that ~50% conversion of *trans*-chalcone to 2,3-epoxy-1,3-diphenyl propanone occurs at ambient temperature over a 24 h. period. These results are in good agreement with those reported using La(O^{i}Pr)$_3$/(R)- BINOL/Ph$_3$PO as the catalytically active species [14]. Initial attempts at the catalytic epoxidation of *trans*-chalcone under identical conditions without activated molecular sieves failed, perhaps through the formation of tetranuclear clusters [1b]. This can be attributed to the presence of spurious water, most likely from the commercial source of TBHP, which results in inactivity by accelerated oligomerization and/or degradation of the rare-earth catalyst. These results demonstrate the epoxidation of *trans*-chalcone using **3** proceeds under mild conditions without elevated temperatures.

3. Conclusions

Presented in this manuscript are the syntheses and characterization of two dimeric Schiff-base lanthanide complexes whose molecular structures are formed by bridging diphenylmethoxides. The crystallographically observed open coordination sites about the metal centers prompted us to explore their utility as epoxidation catalysts toward the electron-rich, α,β-unsaturated ketone, *trans*-chalcone with TBHP as the oxidant. The epoxidation is successful when molecular sieves are present, but not observed in their absence.

4. Materials and methods

4.1. X-ray crystallographic characterization of compounds 3 and 4

Crystallographic data for the X-ray structural analysis of solvated crystals of **3** and **4** are summarized in

Table 1
Crystallographic data for **3** and **4**[a]

Compound No.	**3**	**4**
Formula	$Sm_2C_{67.5}H_{94}N_4O_6$	$Sm_2C_{37.5}H_{51}N_2O_3$
F_w	1358.17	728.15
Crystal system, Space group[b]	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	12.611(2)	13.027(7)
b (Å)	14.584(2)	13.520(7)
c (Å)	18.441(2)	22.782(1)
α (°)	87.973(3)	96.589(9)
β (°)	82.343(3)	104.536(10)
γ (°)	87.324(4)	109.184(9)
V (Å^3)	3356.4(8)	3582(3)
Z, ρ_{calc} (Mg/m^3)	2, 1.344	4, 1.350
μ (Mo Kα) (mm^{-1})	1.782	1.675
Crystal size (mm^3)	$0.08 \times 0.07 \times 0.04$	$0.56 \times 0.08 \times 0.06$
Data completeness (max $\theta_{Mo\,K\alpha}$)	100% (26.00)	98.6% (25.41)
Absorption correction	Empirical	Empirical
Max/min transmission	0.6014/0.5384	0.8060/0.6668
Largest diff. peak/hole (e/Å^3)	2.312/−1.528	1.681/−1.563
Temperature (K)	173(2)	193(2)
No. of reflns (collected/unique)	40 948/13 195	26 538/13 039
R_1[c] ($I > 2\sigma I$)	0.0730 (9150)	0.0513 (8403)
wR_2[d] (unique reflections)	0.0953 (13 195)	0.1339 (13 039)
Goodness of fit indicator[e]	1.240	0.970

[a] G.M. Sheldrick, SHELXTL v.5.1, Bruker-AXS, Madison, WI, 1999.

[b] N.F.M. Henry, K. Lonsdale (Eds.), International Tables for X-ray Crystallography, Symmetry Groups, vol. 1, Kyntoch Press, England, 1969.

[c] $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$.

[d] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$.

[e] Goodness of fit $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 1. Lattice constants and final orientation matrices for solvated single crystals of each compound were determined using peak centers for 4799(**3**) or 922(**4**) reflections. Complete spheres (2474 30-s frames for **3**) or hemispheres (1868 15-s frames for **4**) of diffraction data were collected for both compounds using graphite-monochromator Mo Kα radiation on a Bruker SMART (**4**) or APEX (**3**) CCD diffractometer. X-rays for both studies were provided by a fine-focus (**3**) or normal-focus (**4**) sealed X-ray tube operated at 50 kV and 35 or 40 mA. Frame data were collected using the Bruker SMART software package and final lattice constants were determined with the Bruker SAINT software package. The Bruker SHELXTL-NT software package was used to solve and refine both structures. "Direct methods" techniques were used to solve each structure and the resulting structural parameters were refined with F^2 data to convergence using counter-weighted full-matrix least-squares techniques.

The final structural model for heptane-solvated crystals of **3** incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms of the metal complex. The heptane solvent molecule of crystallization is disordered about the crystallographic inversion center at (1/2, 0,1/2) in the unit cell and each of its carbon atoms was included in the structural model as an isotropic atom with an occupancy factor of 0.50. A continuous chain of only 6 carbon atoms could be located for

this molecule from difference Fouriers and chemically reasonable metrical parameters could not be achieved unless all of the solvent C–C bond lengths and $C_\alpha \cdots C_\gamma$ separations (for the tetrahedral C_α–C_γ–C_γ angles) were restrained to values which were 1.000 and 1.633 times a common distance. This distance was included in the least-squares refinement cycles as a common free variable which refined to a final value of 1.47(2) Å. All methyl groups for metal complex **3** were included in the structural model as rigid rotors (assuming idealized sp^3 hybridization of the carbon atom and a C–H bond length of 0.98 Å) allowed to rotate about their C–C bonds in least squares refinement cycles. All other hydrogens were incorporated in the structural model as fixed idealized (assuming idealized sp^3 hybridization of the carbon atom carbon and C–H bond lengths of 0.95–1.00 Å) atoms "riding" on their respective carbon atoms. The isotropic thermal parameter for each of these idealized hydrogens was fixed at a value that was 1.2 (non-methyl) or 1.5 (methyl) times the equivalent carbon atom isotropic thermal parameter to which it is bonded. Hydrogen atoms were not included for the solvent molecule of crystallization.

The final structural model for toluene-solvated crystals of **4** incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. One of the *t*-butyl groups is disordered with two preferred (30% and 70% occupancy) orientations about the C(21)–C(22) bond.

All methyl groups were included in the structural model as rigid rotors (assuming idealized sp^3 hybridization of the carbon atom and a C–H bond length of 0.98 Å) allowed to rotate about their C–C bonds in least squares refinement cycles. All other hydrogens were incorporated in the structural model as fixed idealized (assuming idealized sp^3 hybridization of the carbon atom and C–H bond lengths of 0.95–1.00 Å) atoms "riding" on their respective carbon atoms. The isotropic thermal parameter for each of these idealized hydrogens was fixed at a value that was 1.2 (non-methyl) or 1.5 (methyl) times the equivalent carbon atom isotropic thermal parameter to which it is bonded.

4.2. Materials and methods

All reactions were carried out under an atmosphere of dry dintrogen using standard Schlenk and glovebox techniques. Compounds **1** and **2** were synthesized by a previous published procedure [1a,1c]. Diphenylmethanol (benzhydrol) (Aldrich) was doubly sublimed on a vacuum line fitted with an oil diffusion pump operating at 10^{-5}–10^{-6} Torr. Heptane (C_7H_{16}) and tetrahydrofuran (THF) were dried and distilled from CaH_2 and Na/benzophenone ketal, respectively. Mallinckrodt, grade 514GT, 4 Å molecular sieves (VWR) and *trans*-chalcone (Lancaster) were predried for 24 h (120 °C, 10^{-4}–10^{-5} Torr and 50 °C, 10^{-4}–10^{-5} Torr, respectively). *Tert*-butyl hydroperoxide (5.0–6.0 M, Aldrich) in decane was used as received. ^{1}H and ^{13}C NMR were recorded on a Bruker DRX Avance 500 MHz (^{1}H frequency) or DRX Avance 400 MHz (^{1}H frequency). Elemental analyses were performed at Midwest Microlabs (Indianapolis, IN). Melting points were collected on a modified Mel-Temp II apparatus providing digital thermocouple readouts and are uncorrected.

4.3. Bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexene-3- one benzhydrol samarium(III) dimer (3)

In a 100 mL Schlenk flask, 0.336 g (0.532 mmol) of **1** was dissolved in 30 mL C_7H_8. While stirring, 0.0980 g (0.532 mmol) of benzhydrol dissolved in 30 mL C_7H_8 was added in one portion and the reaction heated at reflux overnight. Upon cooling to ambient temperature, the pale yellow solution was concentrated in vacuo and the solids recrystallized from C_7H_{16}. Pale yellow crystals resulted after 1 week at −18 °C. Yield: 85.6% (0.298 g); m.p. 150–151 °C (dec.); ^{1}H NMR (δ, C_6D_6, all peaks paramagnetically broadened): −25.34, −6.35 (b), −4.02 (b), −1.62 (b), 0.87, 1.13 (b), 1.27 (b), 1.78 (b), 3.72(b), 4.66 (b), 6.86 (b), 14.31 (b), 17.22 (b); ^{13}C NMR (δ, C_6D_6): 14.3, 18.8, 23.0, 29.4 (b), 30.0, 32.2, 36.9, 44.5, 101.9 (b), 123.7 (b), 176.1 (b); Anal. Calcd. for $Sm_2N_4O_6C_{64}H_{86}·1/2C_7H_{16}$: C, 59.69; H, 6.98.

Found: C, 59.36; H, 7.02 (the presence of heptane was confirmed by X-ray diffraction).

4.4. Bis-5,5′-(2,2-dimethyl-1,3-propanediyldiimino)-2,2-dimethyl- 4-hexene-3-one benzhydrol samarium(III) dimer (4)

In a 100 mL Schlenk flask, 0.228 g (0.346 mmol) of **2** was dissolved in 30 mL C_7H_8. While stirring, 0.0640 g (0.347 mmol) of benzhydrol dissolved in 30 mL C_7H_8 was added in one portion and the reaction heated at reflux overnight. Upon cooling to ambient temperature, the light yellow solution was concentrated in vacuo (~10 mL) and pale yellow crystals resulted from the mother liquor after 2 weeks at −18 °C. Yield: 90.7% (0.210 g); m.p. 150.5–152 °C (dec.); ^{1}H NMR (δ, C_6D_6, all peaks paramagnetically broadened): −14.0, −6.45(b), −2.85 (b), −1.92 (b), −0.80, 0.725(b), 0.89 (m), 1.049 (b), 1.24 (b), 1.28 (b), 1.91 (b), 2.11 (b), 2.32 (b), 2.68 (m, b), 3.32 (b), 6.89 (b), 9.18 (b); ^{13}C NMR (δ, C_6D_6): 14.7, 17.2 (b), 19.4 (b), 20.4, 20.6, 23.4 (b), 26.6, 27.5, 28.7, 29.0, 29.8, 30.2 (b), 30.6 (b), 30.6, 32.6, 32.7, 36.8, 37.4 (b), 43.8 (b), 52.7 (b), 58.7, 98.7, 102.2, 126.3 (b), 172.8, 176.2, 191.9. Anal. Calcd. for $Sm_2N_4O_6C_{68}H_{94}·1/2C_7H_8$: C, 60.22; H, 7.13. Found C, 60.39; H, 6.85 (the presence of toluene was confirmed by X-ray diffraction).

4.5. Epoxidation of trans-chalcone

In a 100 mL 2-neck round-bottom flask is placed 0.0191 g (0.140 mmol) of **3** and ~1.00 g of predried 4 Å molecular sieves. The flask is fitted with a rubber septum and a Merlic solid addition funnel containing 0.548 g (2.60 mmol) of predried 1,3-diphenyl-2-propenone. The flask is removed from the glovebox, interfaced to an N_2-containing Schlenk line and 10mL of dry THF is introduced via syringe. While stirring, the contents of the Merlic solid addition funnel are added and the reaction allowed to stir for 1 h. at ambient temperature. Following this, 1.00 mL of 5–6 M TBHP in decane was added in one portion via syringe and the reaction stirred for an additional 24 h. TLC analysis followed by flash chromatography of the reaction mixture using 90:10 hexane:ethyl acetate mobile phase confirmed the presence of 2,3-epoxy-1,3-diphenyl propanone, which was subsequently calculated via ^{1}H NMR integration to be >50% conversion.

University of Nebraska–Lincoln for their crystallographic and paramagnetic NMR assistance, respectively.

Appendix A. Supplementary data

ORTEP plots of compounds **3** and **4** are available and may be obtained using any current masthead page. Crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk) under assigned CCDC numbers of 250074 (**3**) and 250073 (**4**). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.11.011.

References

[1] (a) S.A. Schuetz, C.M. Silvernail, C.D. Incarvito, A.L. Rheingold, J.L. Clark, V.W. Day, J.A. Belot, Inorg. Chem. 43 (2004) 6203;
(b) S.A. Schuetz, V.W. Day, J.L. Clark, J.A. Belot, Inorg. Chem. Commun. 5 (2002) 706;
(c) S.A. Schuetz, V.W. Day, R.D. Sommer, A.L. Rheingold, J.A. Belot, Inorg. Chem. 40 (2001) 5292;
(d) S.A. Schuetz, M.A. Erdmann, V.W. Day, J.L. Clark, J.A. Belot, Inorg. Chim. Acta. 357 (2004) 4045.
[2] L.G. Hubert-Pfalzgrapf, New J. Chem. (1995) 727.
[3] (a) B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, J. Chem. Soc., Dalton Trans. 15 (2001) 2215;
(b) M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, Macromolecules 33 (2000) 3920;
(c) B.M. Chamberlain, Y. Sun, J.R. Hagadorn, E.W. Hemmesch, V.G. Young, M. Pink, M.A. Hillmyer, W.B. Tolman, Macromolecules 32 (1999) 2400.
[4] (a) E. Martin, P. Dubois, R. Jérôme, Macromolecules 36 (2003) 7094;
(b) E. Martin, P. Dubois, R. Jérôme, Macromolecules 33 (2000) 1530;
(c) M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, Macromolecules 29 (1996) 1798.
[5] (a) J. Inanaga, H. Furuno, T. Hayano, Chem. Rev. 102 (2002) 2211;
(b) M. Shibasaki, N. Yoshikawa, Chem. Rev. 102 (2002) 2187.
[6] R.A. Johnson, K.B. Sharpless, in: B.M. Trost, I.Fleming (Eds.),Comprehensive Organic Synthesis, vol. 7, New York, 1991, p. 389.
[7] (a) C.E. Song, S.-G. Lee, Chem. Rev. 102 (2002) 3495;
(b) T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[8] (a) C. Lauret, M. Roberts, Aldrichim. Acta 35 (2002) 47;
(b) M.J. Porter, J. Skidmore, Chem. Commun. (2000) 1215.
[9] (a) R. Chen, C. Qian, J.G. deVries, Tetrahedron 57 (2001) 9837;
(b) T. Nemoto, T. Ohshima, K. Yamaguchi, M. Shibasaki, J. Am. Chem. Soc. 123 (2001) 2725;
K. Daikai, M. Kamaura, J. Inanaga, Tetrahedron Lett. 39 (1998) 7321.
[10] S.A. Schuetz, V.W. Day, A.L. Rheingold, J.A. Belot, J. Chem. Soc., Dalton Trans. (2003) 4303.
[11] B.J. O'Keefe, L.E. Breyfogle, M.A. Hillmyer, W.B. Tolman, J. Am. Chem. Soc. 124 (2002) 4384.
[12] G.B. Deacon, G.M. Forsyth, P.C. Junk, B.W. Skelton, A.H. White, Chem. Eur. J. 5 (1999) 1452.
[13] Throughout this manuscript, a standard formalism of crystallography-derived estimated standard deviations is used to provide a more concise, yet comprehensive, synopsis of metrical parameters. Hence, the first number in parenthesis following an average value of a bond length is the root-mean-squared estimated standard deviation of an individual datum. The second number is the average deviation from the average value, respectively..
[14] K. Daikai, T. Hayano, R. Kino, H. Furuno, T. Kagawa, J. Inanaga, Chirality 15 (2003) 83.