

Solvent influence on the formation of anhydrous mononuclear or multinuclear lanthanide complexes containing tetradentate Schiff-base ligands

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The syntheses, characterization, and crystal structures of six-coordinate mononuclear [bis-5,5'-(1,3-propanediyl-diimino)-2,2-dimethyl-4-hexene-3-onato]lanthanum [bis(trimethylsilyl)amido][tetrahydrofuran], [bis-5,5'-(1,3-propanediyl-diimino)-2,2-dimethyl-4-hexene-3-onato]neodymium [bis(trimethylsilyl)amido][tetrahydrofuran] and the dinuclear species tris[bis-5,5'-(1,3-propanediyl-diimino)-2,2-dimethyl-4-hexene-3-onato]lanthanum are presented. The complexes are prepared from the reaction of homoleptic tris[(bistrimethylsilyl)amido]-lanthanum or -neodymium with the diprotic tetradentate Schiff base bis-5,5'-(1,3-propanediyl-diimino)-2,2-dimethyl-4-hexene-3-one and final product nuclearity is controlled through solvent choice: heptane affords only the dinuclear species, despite varied reaction stoichiometries and starting material concentrations, whereas coordinating tetrahydrofuran yields the desired mononuclear complexes. All products are reproducibly isolated in high yields and analytical purity.

Introduction

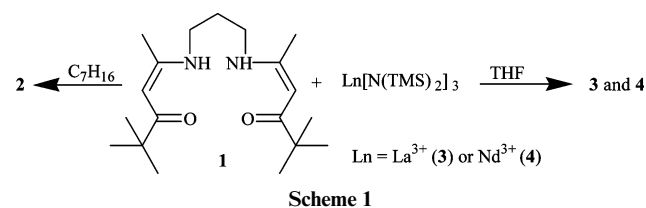
A contemporary theme in modern f-element chemistry is the identification of alternative ligand frameworks (*i.e.*, non-cyclopentadienyl) capable of supporting lanthanide (Ln^{3+}) ions exhibiting low coordination numbers and catalytic activity.^{1–3} Recent research has focused on heteroleptic guanidates,⁴ calix-4-arenes,⁵ phosphoraneiminato,⁶ and Schiff-base lanthanide complexes.^{2,7–10} Of these potential ligators, the advantages of acyclic Schiff bases include ease-of-synthesis, low cost, stereochemical rigidity, facile substitution at both achiral and prochiral positions, and high-binding constants. However, until quite recently, reports of anhydrous, low (*i.e.*, 5 or 6) coordination number (CN) f-element complexes bearing such ligands were sparse. This is presumably due to the fact that these small charge-to-radius ratio ions often prefer to utilize higher coordination numbers (>6) by forming dinuclear species – of the formula $\text{Ln}_2(\text{SB})_3$ (SB = Schiff base) – which contain bridging Schiff base donor atoms.^{2,8,11} With the ionic radius and trivalent nature of yttrium making it an accepted surrogate for trivalent lanthanide ions, recent work from the groups of Evans,¹² Anwender,¹³ and Rajanbabu¹⁴ with six-coordinate mononuclear Salen complexes suggests rich structural and catalytic chemistries are accessible for larger trivalent lanthanide ions bearing tetradentate SB ligands.

Considering the propensity of anhydrous, f-element ions to yield dinuclear,^{8,11} or polymeric,¹³ species upon Schiff base ligation, the ability to control nuclearity (*e.g.*, mononuclear *vs.* dinuclear) is the crux of isolating low CN complexes. We have previously demonstrated that CN = 5 can be achieved for Sm^{3+} and Er^{3+} (and presumably all Ln^{3+} ions in between) complexes of the general formula $\text{XLn}^{3+}(\text{SB})$ (X = NR_2 and OR) where SB is a dianionic, tetradentate, ketoiminato Schiff base ligand possessing a wide variety of substituents and X is a bulky, monoanionic amido or aryl alkoxide.^{7,8,15} Many of these complexes exhibit high catalytic activities for the controlled ring opening polymerization of polar monomers (*e.g.*, lactides, lactones, epoxides) with polymer tacticity directly correlated to the structure of the mononuclear lanthanide complex. Two

features of these SB ligands appear to be critical to the formation of desired mononuclear complexes. First, 1,3-propanediamine spacers are used to increase the N...N separation between the ketoiminato halves and promote complexation with larger Ln^{3+} ions. Second, a “saturated” Schiff base, devoid of backbone aromatic groups, is employed to prevent higher homologue formation through suspected ligand-based π -stacking interactions.⁹

Results and discussion

Initially we attempted to prepare five-coordinate $(\text{TMS})_2\text{N}-\text{La}^{3+}(\text{SB})$ complexes by the synthetic routine previously reported⁸ for the corresponding Sm^{3+} and Er^{3+} complexes (Scheme 1). However, this procedure afforded only a dinuclear $\text{La}_2(\text{SB})_3$ complex, **2**, similar to the $\text{Nd}_2(\text{SB})_3$ species (presumably due to the larger radii).⁸ In each attempted reaction, non-coordinating heptane was the solvent. Compound **2** forms in the same yield and purity regardless of whether the $\text{La}[\text{N}(\text{TMS})_2]_3 : \mathbf{1}$ stoichiometry is varied from 1 : 1 to 2 : 3, or across a continuous lanthanum concentration range from 0.005 to 0.05 M.



The solid-state structure of **2** consists of discrete dinuclear $\text{La}_2(\text{SB})_3$ complexes devoid of crystallographically-imposed symmetry (Fig. 1). Although **2** has the same empirical formula as the previously reported $\text{Nd}_2(\text{SB})_3$ analogue,⁸ the structures are neither isomorphous nor isostructural and the metal connectivities and CN differ. All ketoiminato nitrogen and oxygen atoms in **2** are coordinated to at least one metal ion. The first SB ligand is bound only to La(1), while the other two SB ligands are bound to La(2) and utilize one μ -N and two μ -O bridges to La(1). Thus, La(1) is seven-coordinate and La(2) is

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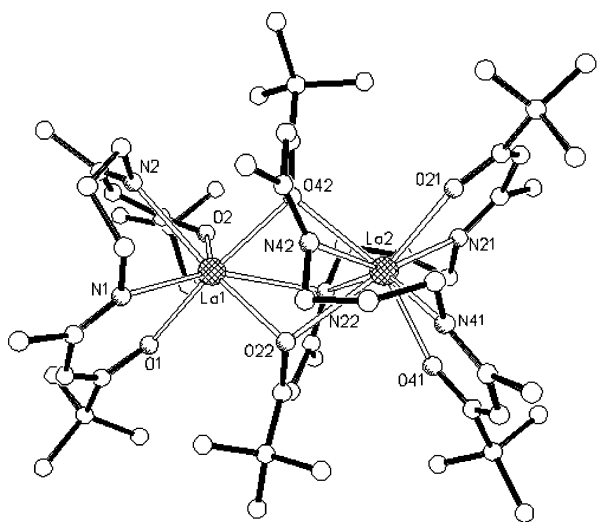


Fig. 1 Molecular structure of dinuclear **2**.

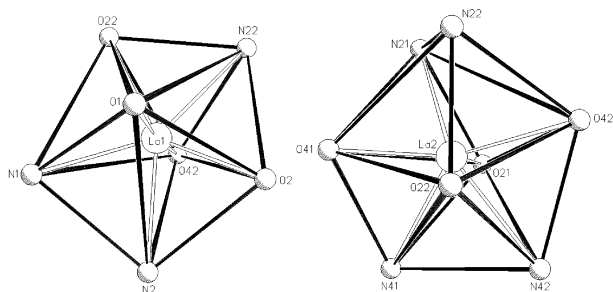


Fig. 2 Coordination polyhedra of the unique La^{3+} ions in **2**; relevant bond lengths discussed in text.

eight-coordinate (Fig. 2). Not surprisingly, the smaller Nd^{3+} centers in $\text{Nd}_2(\text{SB})_3$ are both seven coordinate.⁸

The seven-coordinate La(1) and eight-coordinate La(2) in **2** best approximate pentagonal bipyramidal and triangular dodecahedral geometries, respectively.^{16,17} The average coordination bond lengths in **2** are: La(1)–O(non-bridged), 2.338 (2, 18, 18, 2) Å; La(1)–N(non-bridged), 2.572 (2, 34, 34, 2) Å; La(1)–μ-O(bridge), 2.566 (2, 15, 15, 2) Å; La(1)–μ-N(bridge), 2.794 (2) Å; La(2)–O(non-bridged), 2.346 (2, 4, 4, 2) Å; La(2)–N(non-bridged), 2.694 (2, 18, 26, 3) Å; La(2)–μ-O(bridge), 2.565 (2, 2, 2, 2) Å; La(2)–μ-N(bridge), 2.884 (2) Å.¹⁸ As anticipated, the average La–SB bonds are 0.06 Å shorter for the seven-coordinate La(1) than the eight-coordinate La(2).¹⁹ Interestingly, nearly all of this difference appears in the La–N bonds – bridging as well as non-bridging. Furthermore, the longer La(2)–N and shorter La(2)–O bonds occupy A-type and B-type sites of an idealized triangular dodecahedron, respectively (Fig. 2).¹⁷ The similarities in bridging bond lengths clearly indicate a strong symmetrical complexation of the two metal ions in this dinuclear complex. As such, no disassociation of **2** is observed (*via* NMR spectroscopy) in the presence of excess coordinating monodentate (*e.g.*, THF) and bidentate (*e.g.*, DME) ethers.

Since anhydrous five-coordinate mononuclear complexes containing lanthanide ions larger than Sm^{3+} remained elusive, we attempted, and achieved, the synthesis of six-coordinate mononuclear complexes for the larger lanthanides. Toward this goal, our previous work,^{7,8,15} and that of others^{12–14} served as a guide. Rationalizing that the larger Ln^{3+} ($\text{Ln}^{3+} = \text{La}^{3+}$ and Nd^{3+}) ions might compensate for a third methyl group on each silyl group of the coordinated amide, we undertook our standard $(\text{TMS})_2\text{Ln}^{3+}(\text{SB})$ synthesis in THF solvent (Scheme 1) which could bind to the metal ion and preclude homologation. As expected this reaction yielded the unsaturated, trigonal prismatic, six-coordinate $(\text{TMS})_2\text{Ln}^{3+}(\text{SB})(\text{THF})$ complexes (Fig. 3) with essentially the same gross

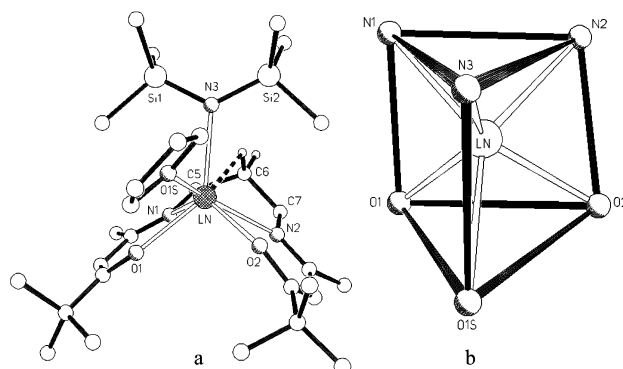


Fig. 3 (a) General molecular structure of $[\text{O}_2\text{N}_2\text{C}_{10}\text{H}_{32}]\text{Ln}[\text{N}(\text{Si}(\text{CH}_3)_3)_2][\text{OC}_4\text{H}_8]$ where $\text{LN} = \text{La}^{3+}$ (**3**) and Nd^{3+} (**4**), and (b) trigonal prismatic metal coordination geometry in **3** and **4**. Bond lengths are discussed in text and selected bond angles ($^\circ$) for **3** are: N(3)–La–O(1s) 80.7(1), O(1)–La–O(2) 94.3(1), N(1)–La–N(2) 74.3(1), O(1)–La–N(3) 132.9(1), O(2)–La–N(3) 120.9(1), O(1)–La–N(1) 70.6(1), O(2)–La–N(2) 70.1(1), N(1)–La–N(3) 100.6(1), N(2)–La–N(3) 108.5(1), O(1)–La–O(1s) 78.0(1), O(2)–La–O(1s) 76.9(1), N(1)–La–O(1s) 137.9(1), N(2)–La–O(1s) 145.8(1).

structural features as the Y^{3+} complex of Anwender and co-workers¹³ that contains a smaller cation and a correspondingly less sterically demanding amido.

Compound **3** and its isomorph **4** exhibit several noteworthy structural features, the first of which is the boat conformation for the six-membered chelate ring comprised of Ln, N(1), C(5), C(6), C(7), and N(2). This chelate ring conformation, without crystallographic disorder on the C(5)–C(7) positions,²⁰ has previously been observed in all mononuclear five-coordinate $\text{XLn}^{3+}(\text{SB})$ complexes bearing unsubstituted propyl spacers^{8,15} and produces a short (~ 2.7 Å) interaction between the metal and a diastereotopic proton on the central (C(6)) methylene carbon (Fig. 3(a)). This “agostic” interaction²¹ is thought to aid in stabilizing the low coordination number and simultaneously function as a pivot point for SB distortions. These distortions are manifested as a ± 0.19 Å, in **3**, or ± 0.20 Å, in **4**, “ S_4 -ruffling” of the “square plane” delineated by the four hard SB donor atoms from which the La^{3+} and Nd^{3+} ions are displaced 1.14 and 1.09 Å, respectively. Unlike Anwender’s Y^{3+} complex which possessed a rigorous or pseudo molecular mirror plane, only the slightly distorted trigonal prismatic metal coordination spheres of **3** and **4** (Fig. 3(b)) contain this pseudo-symmetry element even though the entire molecule could possess a mirror plane. The most obvious deviation from idealized molecular C_s-m for **3** and **4** involves a rotation of the THF ligand about its idealized C_2 axis to give a conformation midway between two different idealized C_s-m species. The La, O(1s), N(3) and C(6) atoms in **3** are coplanar to within 0.01 Å, and their mean plane makes an angle of 90.7° with the O_2N_2 SB mean plane. Additionally, the angle between the two triangular N(1), N(2), N(3) and O(1), O(2), O(1s) faces in the trigonal prismatic coordination polyhedron of **3** is 14.8° . In order to accommodate the dative THF ligand, the bulky $\text{N}(\text{TMS})_2$ monoanion is tilted by 15° off the O_2N_2 mean plane normal, and is directed back toward the propyl bridge by $\sim 13^\circ$ relative to its position in our previously⁸ reported five-coordinate, non-solvated Sm^{3+} analogue (**5**)⁸ of **3** and **4**. The THF is also rotated 42° out of the pseudo-mirror plane in **3** and the two ketoiminato (La–O–C–C–N) six-membered chelate rings are folded about the $\text{O} \cdots \text{N}$ polyhedral edges by 5° and 16° . Being isomorphous with **3**, compound **4** displays nearly identical structural features in the solid-state.

Average coordination bond lengths in **3** are: La–O(SB), 2.307 (4, 16, 16, 2) Å; La–N(SB), 2.625 (4, 1, 1, 2) Å; La–N(amido), 2.443 (3) Å; La–O(THF), 2.662 (4) Å. The average bond lengths in the isomorphous compound **4** are expectedly compressed by 0.06 Å due to the slightly smaller radius of Nd^{3+} . As anti-

Table 1 Crystallographic data for compounds **2–4**^a

	2	3	4
Formula	La ₂ [O ₂ N ₂ C ₁₉ H ₃₂] ₃	[O ₂ N ₂ C ₁₉ H ₃₂]La[N(Si(CH ₃) ₃) ₂]-[OC ₄ H ₈]	[O ₂ N ₂ C ₁₉ H ₃₂]Nd[N(Si(CH ₃) ₃) ₂]-[OC ₄ H ₈]
<i>M_r</i>	1239.22	691.87	697.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group ^b	<i>P</i> 2 ₁ / <i>c</i> (<i>C</i> _{2h} ⁵) (no. 14)	<i>P</i> 2 ₁ / <i>n</i> (no. 14) ^f	<i>P</i> 2 ₁ / <i>n</i> (no. 14) ^f
<i>a</i> /Å	15.888(1)	11.361(2)	11.307(2)
<i>b</i> /Å	18.916(2)	15.812(1)	15.739(2)
<i>c</i> /Å	20.475(2)	20.387(3)	20.156(2)
β /°	92.124(2)	94.909(2)	95.012(1)
<i>V</i> /Å ³	6149(1)	3649(1)	3573(1)
<i>Z</i> , <i>D_c</i> /g cm ⁻³	4, 1.339	4, 1.259	4, 1.296
μ (Mo-K α)/mm ⁻¹	1.42	1.27	1.55
Crystal size/mm	0.80 × 0.50 × 0.30	0.24 × 0.20 × 0.10	0.20 × 0.16 × 0.11
Data completeness (%) (max. θ _{Mo-Kα})	96.5 (28.33)	99.7 (25.34)	90.5 (28.33)
Absorption correction	Empirical	Empirical	Empirical
Max./min. transmission	0.675/0.396	0.453/0.407	0.454/0.405
Largest diff. peak, hole/e ⁻ Å ⁻³	1.21, -0.84	0.83, -0.57	1.28, -0.47
<i>T</i> /K	203(2)	193(2)	193(2)
No. of reflns. (collected/unique)	71093/14797	19926/6646	21937/8046
<i>R</i> ₁ ^c (<i>I</i> > 2 σ (<i>I</i>))	0.030 (13100)	0.049 (3439)	0.040 (5474)
<i>wR</i> ₂ ^d (unique reflections)	0.078 (14797)	0.080 (6646)	0.078 (8046)
Goodness of fit indicator ^e	1.050	0.878	0.857

^a G. M. Sheldrick, SHELXTL v.5.1, Bruker-AXS, Madison, WI, 1999. ^b *International Tables for X-Ray Crystallography*, Symmetry Groups, ed. N. F. M. Henry and K. Lonsdale, Kynoch Press, England, 1969. ^c $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$. ^d $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$. ^e Goodness of fit $[(\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}}))]^{1/2}$. ^f *P*2₁/*n* is an alternate setting for *P*2₁/*c* (*C*_{2h}⁵) (no. 14).

culated, the average La–SB and La–N(3) bonds in the six-coordinate **3** and **4** are 0.14 and 0.08 Å longer, respectively, than the corresponding bonds in the five-coordinate Sm³⁺ complex (**5**) and the individual Ln–O and Ln–N bonds in **3** are 0.054–0.075 Å longer than the corresponding bonds in **4**.

In summary, this paper reports a facile synthetic strategy for the selective formation of anhydrous mononuclear or dinuclear lanthanide Schiff base complexes through judicious solvent choice. Utilizing the non-coordinating solvent heptane affords only the dinuclear lanthanum species, **2**, which does not dissociate upon exposure to excess coordinating monodentate and bidentate ethers. However, employing THF as the reaction solvent successfully presents the desired isomorphous, six-coordinate mononuclear species, **3** and **4** in high yields and analytical purity.

Experimental

General

Bis-5,5'-(1,3-propanediylidimino)-2,2-dimethyl-4-hexene-3-one, **1**, and the homoleptic Ln[N(TMS)₂]₃ (Ln = Nd³⁺, La³⁺) were prepared according to literature procedures.⁸ THF (Fisher) was dried and distilled over the Na/benzophenone ketal. Pentane (Fisher) was dried and distilled over CaH₂. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX Avance 400, 500 or 600 MHz using J. Young NMR tubes. Elemental analyses were performed by Midwest Microlabs (Indianapolis, IN, USA) and the melting points (uncorrected) collected on a modified Mel-Temp II apparatus providing digital thermocouple readouts.

X-Ray crystallographic studies of **2**, **3** and **4**

Lattice constants, space groups and other relevant data for the crystallographic characterization of single crystals of **2**, **3** and **4** grown from pentane are given in Table 1. Complete hemispheres of diffraction data were collected for each compound with a Bruker SMART APEX (**2** and **4**) or SMART 1000 (**3**) CCD Area Detector using 0.30°-wide ω scans and graphite-monochromated Mo-K α radiation. X-Rays were provided by a fine-focus (**2** and **4**) or normal-focus (**3**) sealed X-ray tube operated at 50 kV and 35 mA (**2** and **4**) or 40 mA (**3**). Frame

data (10 s 0.30-wide omega scans) 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 each structure. “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 and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Final agreement factors are given in Table 1. The highest peaks (1.21–0.63 e⁻ Å⁻³) in the final difference Fourier for the structure of **2** were within 0.81 Å of a La atom; there were no additional peaks above the background level (0.59 e⁻ Å⁻³). The highest peak in the final difference Fourier for **3** was 0.83 e⁻ Å⁻³ and it was not near the metal atom. The highest ten peaks (1.28–0.62 e⁻ Å⁻³) in the final difference Fourier for the structure of **4** were within 1.05 Å of a Nd atom; there were no additional peaks above the background level (0.42 e⁻ Å⁻³). All methyl groups were refined as rigid rotors [using idealized sp³-hybridized geometry and C–H bond lengths of 0.97 Å (**2**) or 0.98 Å (**3** and **4**)] which were allowed to rotate about their C–C bonds in least-squares cycles. The remaining hydrogen atoms were included in each structural model as fixed atoms (using idealized sp²- or sp³-hybridized geometry and C–H bond lengths of 0.94–0.99 Å) “riding” on their respective carbons. The isotropic thermal parameters of all hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

CCDC reference numbers 212787, 212788 and 218982.

See <http://www.rsc.org/suppdata/dt/b3/b310340b/> for crystallographic data in CIF or other electronic format.

Tris[bis-5,5'-(1,3-propanediylidimino)-2,2-dimethyl-4-hexene-3-onato]lanthanum dimer (**2**)

Ligand **1** (780 mg, 2.42 mmol) was dissolved in 30 mL heptane and added to tris[bis(trimethylsilyl)amido]lanthanum (1.50 g, 2.42 mmol) previously dissolved in 20 mL heptane. The reaction was heated at reflux overnight, the volatiles removed *in vacuo*, and the solids redissolved in 30 mL pentane. This linear alkane solution was concentrated to ~10 mL, and pale yellow

crystals were collected, after standing at $-35\text{ }^{\circ}\text{C}$, in 2 weeks. Yield: 79% (1.4 g); mp 166.0–167.5 $^{\circ}\text{C}$. $^1\text{H NMR}$ (δ , C_6D_6): 0.87 (t), 1.19 (br), 1.24 (s), 1.25 (s), 1.30 (br), 1.32 (br), 1.37 (br), 1.40 (br), 1.45 (br), 1.63 (s), 1.69 (br), 1.76 (br), 1.87 (br), 2.60 (q), 3.01 (br), 3.21 (q), 3.44 (br), 3.80 (br), 4.67 (t), 4.97 (s), 4.99 (s), 5.10 (s), 5.13 (s), 5.14 (s), 5.34 (br). $^{13}\text{C NMR}$ (δ , C_7D_8): 18.57, 21.49 (t), 28.01, 28.40, 29.09, 29.41, 29.43, 29.64, 29.74, 38.65, 38.80, 39.10, 45.01, 45.55, 48.69, 51.33, 90.65, 95.31, 95.94, 96.46, 101.03 (br), 167.03, 167.12, 168.57 (d), 183.21, 183.81, 185.53. Anal. Calc. for $\text{La}_2\text{C}_{57}\text{H}_{96}\text{N}_6\text{O}_6 \cdot \frac{1}{2}\text{C}_5\text{H}_{12}$: C, 56.04; H, 8.06. Found: C, 55.77; H, 7.81%.

[Bis-5,5'-(1,3-propanediylidimino)-2,2-dimethyl-4-hexene-3-onato]lanthanum bis(trimethylsilyl)amido tetrahydrofuran (3)

Ligand **1** (273 mg, 0.847 mmol) in 30 mL THF was added to tris[bis(trimethylsilyl)amido]lanthanum (525 mg, 0.847 mmol) dissolved in 30 mL THF and the reaction was heated at reflux overnight. The solvent was removed *in vacuo*, 20 mL pentane was added and subsequently concentrated *in vacuo* to approximately 2 mL. Pale yellow crystals were harvested from the mother-liquor, standing at $-40\text{ }^{\circ}\text{C}$, in 1 week. Yield: 72% (0.42 g); mp 149–151 $^{\circ}\text{C}$ (decomp.). $^1\text{H NMR}$ (δ , C_6D_6): 0.084 (s), 0.34 (s), 1.23 (s), 1.56 (br), 2.38 (br), 3.30 (br), 4.17 (t), 5.02 (s). $^{13}\text{C NMR}$ (δ , C_7D_8): 4.33, 22.25, 25.32, 28.25, 28.77, 38.54, 51.74, 69.57, 96.34, 127.67, 170.18, 184.00. Anal. Calc. for $\text{LaSi}_2\text{C}_{29}\text{H}_{58}\text{N}_3\text{O}_3$: C, 50.34; H, 8.45. Found: C, 50.26; H, 8.47%.

[Bis-5,5'-(1,3-propanediylidimino)-2,2-dimethyl-4-hexene-3-onato]neodymium bis(trimethylsilyl)amido tetrahydrofuran (4)

Ligand **1** (0.270 g, 0.838 mmol) in 40 mL THF was added to tris[bis(trimethylsilyl)amido]neodymium (0.524 g, 0.838 mmol) dissolved in 40 mL THF and the reaction stirred overnight at ambient temperature (NOTE: The successful synthesis only involves stirring, not refluxing, the solution overnight. If refluxed, a tetrameric oxo species was repeatedly synthesized, presumably due to THF ring opening). The THF was removed *in vacuo*, 20 mL pentane was added and subsequently concentrated *in vacuo* to approximately 2 mL. Pale blue crystals were harvested from the mother-liquor, standing at $-18\text{ }^{\circ}\text{C}$, in 1 week. Yield: 66% (0.38 g); mp 171–173 $^{\circ}\text{C}$ (decomp.). $^1\text{H NMR}$ (δ , C_6D_6): -64.20 (br, d), -46.45 (s), -44.84 (s), -39.52 (s), -22.65 (s), -12.64 (s), -4.65 (br, s), -3.35 (br), -2.75 (br, d), 0.08 (s), 0.45 (br, s), 0.85 (br, s), 1.23 (br, s), 2.44 (br, s), 2.78 (br, s), 4.94 (br, s), 9.90 (br), 23.16 (br, s). $^{13}\text{C NMR}$ (δ , C_6D_6): 2.80 (br, s), 8.72 (br), 12.59 (br), 14.43, 21.76 (br), 22.88, 27.71, 28.56, 34.70, 37.69, 42.62 (br), 43.10, 44.07, 53.14 (br), 60.64, 70.20, 113.77 (br), 217.27 (br), 270.50 (br). Anal. Calc. for $\text{NdSi}_2\text{C}_{25}\text{H}_{50}\text{N}_3\text{O}_2 \cdot x(\text{OC}_4\text{H}_8)$: C, 49.05; H, 8.23. Found: C, 48.88; H, 7.94%.²²

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