Synthesis, Structure, and Catalytic Reactions of 1,2-Bis(indenyl)ethane-Derived Lanthanocenes

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The synthesis and structure of *meso*-[ethylenebis(η^5-indenyl)]ytterbium(III) bis(trimethylsilyl)amide (**6**) and the syntheses of *rac*- and *meso*-[[ethylenebis(η^5-indenyl)]ytterbium(III) chloride][$LiCl(Et_2O)_2$] (**4**, **5**) and *rac*- and *meso*-[ethylenebis(η^5-indenyl)lutetium(III) chloride][$LiCl(Et_2O)_2$] (**7**, **8**) are reported. The complexes are synthesized by the metathesis of dilithiated 1,2-bis(indenyl)ethane with either $YbCl_3$ or $LuCl_3$ in THF followed by solvent exchange with diethyl ether to give [[ethylenebis(η^5-indenyl)]Ln^{III} chloride][$LiCl(Et_2O)_2$] (Ln = Yb, Lu) in yields of 43% and 30%, respectively. In the Yb case, the major diastereomer formed is *meso*, while in the lutetium reaction, the *rac* diastereomer predominated. Complex **6** is synthesized by reaction of *meso*-[[ethylenebis(η^5-indenyl)]ytterbium(III) chloride][$LiCl(Et_2O)_2$] with $NaN(TMS)_2$; this material was characterized by X-ray diffraction. Complex **6** catalyzes the cyclic hydroamination of primary amino olefins in excellent yields.

Introduction

Organolanthanide complexes have demonstrated catalytic ability for many organic reactions; much of the ground-breaking chemistry demonstrating the wide utility of these complexes is found in the work of Marks and Molander. These groups and others showed that a wide variety of lanthanocene complexes catalyze many organic transformations, including cyclic hydroamination of both alkynes and alkenes,[1−3] hydrogenation,[4,5] and polymerizations,[6] among others.[7−10] Several of the transformations reported demonstrate high degrees of stereoselectivity using a wide variety of asymmetric catalysts.[11,12] Group 4 organometallic complexes have also shown the ability to promote a variety of organic transformations similar to those mentioned above.[13] These reactions include hydrogenation,[14] carbon−carbon bond formation,[15−17] and polymerization.[18] Several of the most selective catalysts reported recently use tethered indenyl-derived ligands oriented in a C_2-symmetric fashion at the metal.[13,19,20] We report herein the synthesis and structure of ethylenebis(η^5-indenyl) complexes of ytterbium(III) and show that an [ethylenebis(η^5-indenyl)]ytterbium amido complex is an effective catalyst for intramolecular hydroamination.

Results and Discussion

The syntheses of ethylenebis(η^5-indenyl) (EBI) complexes were achieved through reaction of $YbCl_3$ with the lithium dianion of 1,2-bis(indenyl)ethane (**1**).[8,21] For the synthesis of these complexes, anhydrous, finely powdered $YbCl_3$ suspended in THF was reacted with **1**, providing a purple solution of (EBI)YbCl[$LiCl(THF)_2$] (**2**, **3**; Scheme 1). The reaction's progress was easily monitored by the disappearance of solid $YbCl_3$, providing the soluble EBI complexes. A mixture of the two diastereomeric products was isolated as a blue solid, after removing the solvent, in 54% yield. Since these complexes were resistant to crystallization, the THF was ex-

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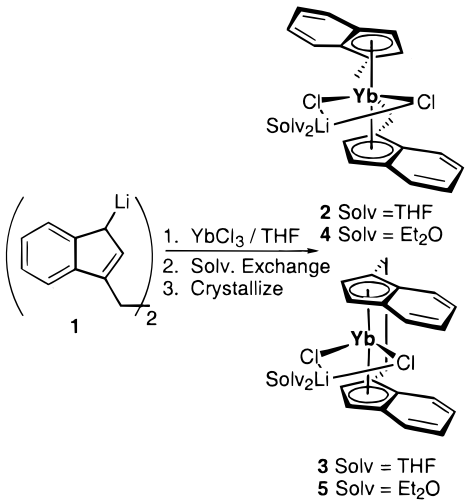
Scheme 1



changed for diethyl ether by repeated trituration of the solid with excess ether followed by removal of the excess solvent under vacuum. The ether exchange provided a mixture of **4** and **5** as a purple solid. Alternatively, the complexes could be synthesized by reaction of **1** with $YbCl_3$ in Et_2O with a small amount of THF added to solubilize **1**. The ether exchange was still necessary under these conditions to remove coordinated THF. Crystallization of the mixture of **4** and **5** by slow cooling of a saturated hexane/ether solution to −30 °C provided crystals with two different morphologies—a bluish, major product and a red, minor isomer, which were physically separated by hand, in an approximately 5.5:1 ratio. Since these complexes are paramagnetic, we were unable to determine which morphology corresponds to **4** and which corresponds to **5** by NMR. Furthermore, even though the ether exchange yielded crystalline material, none of the material proved appropriate for X-ray diffraction.

We chose to convert the blue, major isomer to (EBI)-$YbN(TMS)_2$, since the $N(TMS)_2$ ligand is known to solubilize lanthanide complexes in comparison to their halide counterparts[22] and lanthanocene amido complexes are viable precatalysts for many of the transformations mentioned above.[3] Reaction of the blue diastereomer of [(EBI)YbCl][$LiCl(OEt_2)_2$] with $NaN(TMS)_2$ in diethyl ether at room temperature, followed by crystallization of the solid product from hexane, yielded dark blue (EBI)$YbN(TMS)_2$ (**6**) in 40% yield based on **5**. Compound **6** is quite soluble in nonpolar solvents such as pentane, whereas **4** and **5** are soluble only in THF and methylene chloride and are sparingly soluble in ether.

X-ray structure determination on the dark blue material shows it to correspond to complex **6**, shown in Figure 1. There are two unique molecules in the unit cell, with one of them showing disorder of a $Si(CH_3)_3$ group, which was modeled with approximate populations of 50, 25, and 25% of the rotamers. While there is no crystallographic mirror plane, it is clear that the molecule is best described as *meso*. The complex is quite strained, as is evidenced by several features shown in the structure. The first of these is seen by the 122.0(4)°

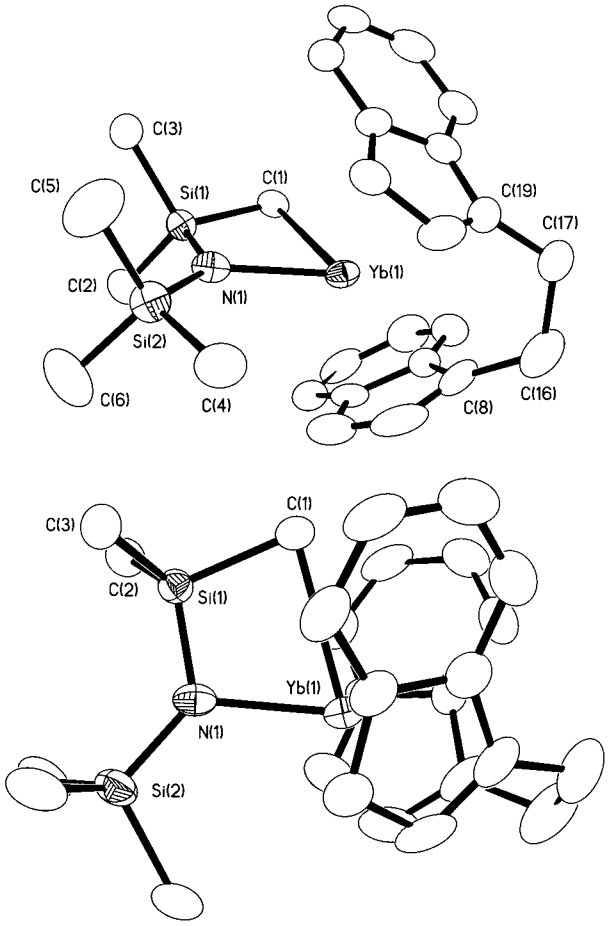


Figure 1. ORTEP[27,28] drawing and numbering scheme for the first molecular unit of complex **6**, with thermal ellipsoids drawn at the 50% probability level. Relevant distances (Å) and angles (deg): Yb(1)−C(1), 2.732; Si(1)−C(1), 1.906; Si(1)−C(2), 1.865; Si(1)−C(3), 1.865; C(19)−C(17)−C(16), 115.1; C(8)−C(16)−C(17), 111.9; Yb(1)−N(1)−Si(1), 104.34; Yb(1)−N(1)−Si(2), 126.6. See the Supporting Information for full details.

angle made between the "Cp-centroid" (Cg) of each indenyl with the Yb atom, compared to an angle of 126.2(1)° for Cg−Zr−Cg in *meso*-$EBIZrCl_2$,[23] the 125.4° angle seen in the $(CH_3)_2$Si-bridged CpCp*LuCH[Si-$(CH_3)_3]_2$ complex,[24] or the 131.4, 132.3, and 132.6° angles (Nd, Gd, and Ho, respectively) in the five-atom-bridged bis(indenyl)lanthanocenes reported by Qian.[25] Additionally, quite large angles are seen at the two bridging carbons. The angle for C(8)−C(16)−C(17) is 111.9°, and the angle for C(19)−C(17)−C(16) is 115.1°, which are both larger than the 109° preferred for sp^3 carbon atoms and on average larger than the 112.2° angle seen in the similar *meso*-(EBI)$ZrCl_2$ structure.[23] The small Cg−Yb−Cg angle in **6** and the expanded angle in the bridging carbons both suggest that the ethyl bridge constrains the two indenyl ligands from adopting their most stable coordination geometry with this large ionic radius metal. A corollary to this is that larger lanthanide metals would form even more strained

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Scheme 2

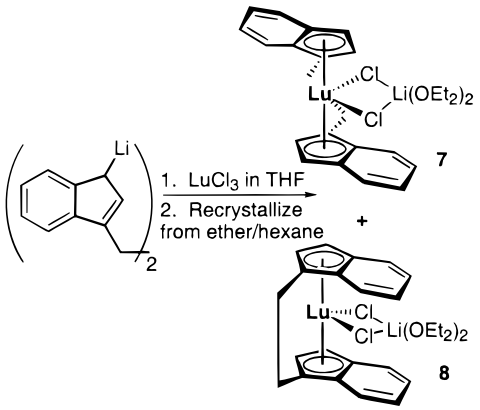
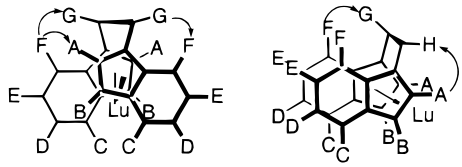


Chart 1



Show nOe for:
A and G;
F and G;
AND
A and F

Should Show nOe for:
A and H;
F and G

% nOe enhancement for Major Isomer:

A to F 2.7% F to G 2.2%
A to G 3.8% G to A 10%
F to G 3.1% G to F 2.2%

complexes with this ligand, which is consistent with our observation that $LaCl_3$ and $NdCl_3$ form intractable materials when treated under the reaction conditions which provided **4** and **5**.

Interestingly, one N−Si bond is not free to rotate and one of the methyl groups lies between the two benzene rings of the EBI ligand. The methyl group closest to the metal is 2.732(5) Å from the Yb (Yb(1)−C(1); Yb(2)−C(27) is 2.738(5) Å) and is consistent with a small interaction of the Yb with this methyl group.[24,26] An interaction between the ytterbium and the methyl is also shown by the smaller angle formed between the interacting $Si(CH_3)_3$ group and the metal; the angle for Yb(1)−N(1)−Si(1) is 104.34(19)°, while the angle for the freely rotating TMS group (Yb(1)−N(1)-Si(2)) is 126.6-(2)°. An interaction is also indicated by the increased length of the Si(1)−C(1) bond (1.906(5) Å) compared to Si(1)−C(2) or Si(1)−C(3) (1.865(5) Å) bond lengths. A similar interaction was seen by Marks in the crystal structure of $Cp^*_2NdCH[Si(CH_3)_3]_2$, where the interaction was described as that of the electron-deficient metal interacting with the carbon, rather than an agostic C−H to Nd interaction.[26]

The structural assignment of **6** suggests that the major isomer isolated after ether exchange is **5** and, by extension, the initially formed material is predominately **3**. It is possible, however, that the two complexes are in equilibrium under the reaction conditions. Since the materials are paramagnetic, we were not able to test this by NMR experiments such as magnetization transfer. Diamagnetic lutetium, however, is closely related to paramagnetic ytterbium in size, and its complexes often show reactivity similar to that of their ytterbium analogues.[10] We therefore chose to synthesize the Lu analogues of **4** and **5**. The synthetic path leading to the lutetium complexes was similar to that used for Yb complexes. Reaction of **1** with $LuCl_3$ in THF followed by exchange of the THF for diethyl ether provided a mixture of **7** and **8** (Scheme 2). Crystallization of the crude product from an ether/hexane mixed solvent by slow evaporation yielded a mixture of **7** and **8** as a pink microcrystalline solid in 30% overall yield based on $LuCl_3$. Attempts to separate the isomers have been unsuccessful. The products of the reactions are diamagnetic compounds, and the ^{1}H NMR of the mixture was consistent with their formulation as **7** and **8**. Assignment of individual resonances was accomplished by standard NMR experiments as well as by analogy to the spectrum of **1**. The spectrum of the mixture showed two distinct sets of peaks in a 2.5:1 ratio by integration. Each resonance of the predominant isomer had a minor isomer resonance which was shifted between ±0.3 ppm. To determine whether the major isomer was **7** or **8**, we undertook an nOe study on the mixture in THF-d_8.

As is shown in Chart 1, an important difference between the two isomers will result from irradiation of H_A or H_F. The *rac* complex **7** should exhibit an nOe enhancement between H_A and H_F, while the *meso* complex **8** should not produce any change at H_F upon irradiation of H_A. In the experiment, irradiation of the resonance at δ 7.6 ppm, (assigned as H_F of the major isomer), produced enhancements at 6.7 ppm (H_E) and 6.1 ppm (H_A), as well as at 3.6 ppm (H_G). Importantly, irradiation of either H_A or H_G resulted in enhancements at H_F. These data are consistent with formulation of the major isomer as the *rac* diastereomer. Further ^{1}H NMR experiments on the Lu complexes show that the ratio of isomers does not change with heating or upon UV irradiation. While we still cannot rule out a dynamic process, any interconversion must be slower than the intramolecular nOe process.[26] It is interesting to note that the two closely related metals favor formation of the opposite diastereomer; Lu forms a majority of the *rac* diastereomer, but Yb favors the *meso* form.

The reason for the different formations of major diastereomers in these two cases may result from the decreased ionic radius of Lu. Similar changes in the *rac*/*meso* ratio have been observed for group IV EBI complexes, where small decreases in the ionic radius of the metal correlate with increased diastereomeric ratios. The *rac*/*meso* ratio was found to be 2/1 in the formation of (EBI)$ZrCl_2$ from $ZrCl_4$ and the dipotassium salt of EBI (Zr ionic radius 0.79 Å[29]), while reaction of $HfCl_4$ with the same salt led to the isolation of only the *rac* isomer of (EBI)$HfCl_2$ (Hf ionic radius 0.78 Å[29]).[21] This is analogous to the lanthanide result here, where switching from Yb with an ionic radius of 0.86 Å[29] to the smaller Lu (0.85 Å[29]) also provides an increased *rac*/

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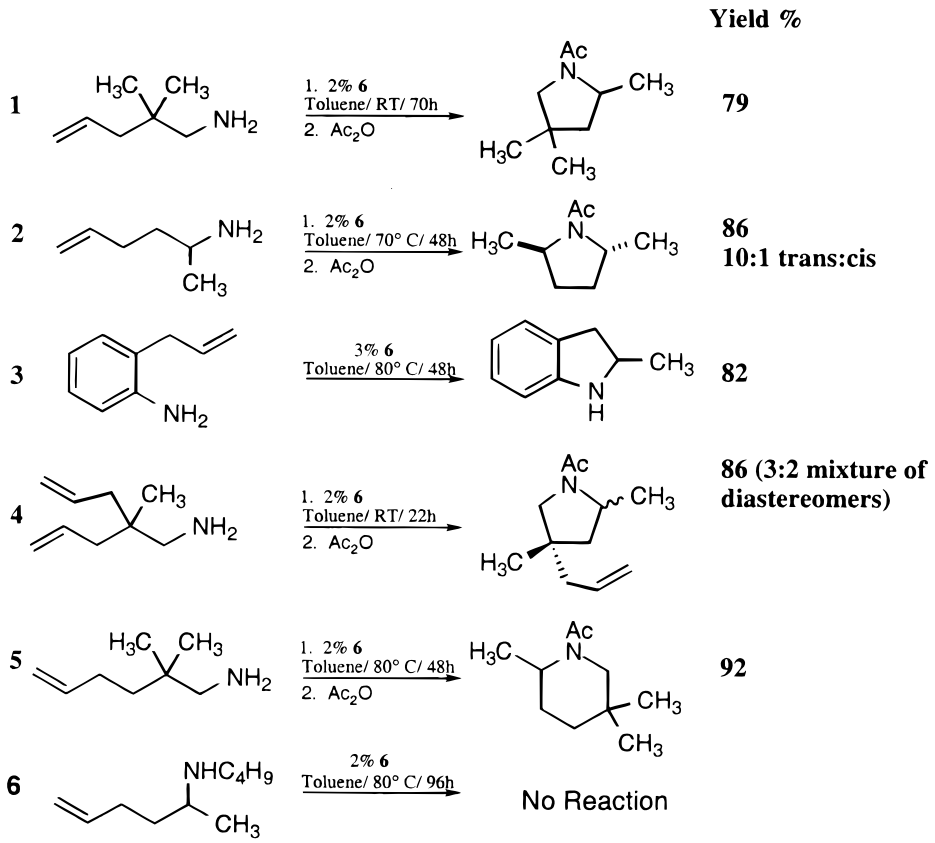
Table 1. Cyclization of Aminoolefins



meso ratio. Switching from the ethyl bridge to a longer tether provides the same, more favorable, *rac* coordination geometry, as does decreasing the size of the metal. Qian synthesized several lanthanocenes using indenyl rings tethered with a 3-oxapentane bridge.[25] In all of the complexes reported, this longer tether yielded the *rac* diastereomer as the major isomer, with as much as a 6:1 excess of *rac* to *meso*. This suggests that, when conformationally possible, the more stable coordination geometry is to have the indenyl rings staggered, which would minimize nonbonded interactions between the rings in the transition state[30] and/or product[31] and yield the racemic diastereomer.

To demonstrate the activity of these complexes as catalysts for organic transformations, we tested compound **6** for its ability to promote the cyclization of a series of aminoolefins (Table 1).[32] The reactions were performed with ~2 mol % catalyst in toluene, at either room temperature or 70−80 °C, depending on the substrate. These conditions provided excellent yields of the desired cyclized secondary amine products, which were generally isolated after acylation with acetic anhydride. The reaction proceeded faster in toluene than hexane by a factor of ca. 3. The rate of cyclization to provide five-membered rings generally proceeds at lower temperatures than does the formation of six-membered rings (entry 1 vs entry 5). Primary amine substitution is tolerated on both primary and secondary carbons as well as on aromatic rings. The reaction also provides a high degree of diastereoselectivity, with a 10:1 *trans* to *cis* ratio of the 2,5-dimethylpyrrolidine diastereomers produced upon cyclization of 2-amino-5-hexene (entry 2). The assignment of the major isomer as *trans* is based on spectroscopic and chromatographic comparison to a commercial sample. When the existing chiral center is further from the amine, the selectivity is reduced (approximately 3:2; entry 4). No evidence was seen for further cyclization of the secondary amine product of entry 4 into the remaining alkene; this is consistent with our observation that 2-(butylamino)-5-pentene (entry 6) also failed to react, although the strained bicyclic product may present an enthalpic barrier to further reaction. As a comparison, the rate of the reaction with **6** as catalyst is close to that seen by Marks[3] for similar cyclic hydroaminations catalyzed by a lutetium complex.

In summary, we successfully synthesized the bis(indenyl)ethane derivatives of late lanthanide metals and structurally characterized one of them. (EBI)YbCl(LiCl(OEt_2)$_2$] is formed in a 6:1 ratio of *meso* to *rac* diastereomer, while the related Lu complex (EBI)LuCl[LiCl(OEt_2)$_2$] is formed in a 3:1 ratio of the *rac* to *meso* diastereomers. The (EBI)YbN($TMS)_2$ complex is an active catalyst for the intramolecular hydroamination of amino alkenes, and yields secondary amines in excellent isolated yields and moderate diastereoselectivity. We are currently working to develop methods suitable for the production of greater ratios of *rac* to *meso* catalysts, especially bis(indenyl) ligands with longer tethers, as well as studying the possible interconversion of the diastereomers.

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Experimental Section

General Considerations. All procedures unless otherwise noted were carried out using standard techniques for air-sensitive reactions, either in a Vacuum Atmospheres Model MO-40M glovebox under nitrogen or using Schlenk line techniques with nitrogen or argon as the inert gas. All solvents were commercially obtained and then dried and distilled from Na/benzophenone under an atmosphere of nitrogen, except for methylene chloride, which was dried over CaH_2. All solvents were degassed prior to use by freeze−pump−thaw cycling. Deuterated solvents for NMR were obtained from Cambridge Scientific: benzene-d_6, toluene-d_8, and THF-d_8 were dried and distilled from sodium/benzophenone and then degassed as above. $CDCl_3$ was used as received. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-300 Fourier transform spectrometer at 300 MHz for hydrogen and 75 MHz for carbon. Spectra were referenced to either TMS or the residual protio-solvent peak. Infrared (IR) spectra were recorded on either a Perkin-Elmer 1600 Series Fourier transform spectrometer or a Nicolet FT-IR. Gas chromatography was carried out on a Hewlett-Packard 5890 GC with a flame ionization detector on a 25 m × 0.25 μm DB-5 capillary column (J&W Scientific) using a HP 3396 Series III Integrator. Elemental analysis was performed by Desert Analytics, Tucson, AZ. X-ray crystallographic determination was carried out by Dr. Thomas Emge at Rutgers University. HRMS experiments were performed in the Department of Chemistry, University of British Columbia. Preparative flash chromatography was performed on silica (E. M. Science Kieselgel 60, 230−400 mesh) or basic alumina (ICN Alumina N, activity I). All reagents, unless otherwise stated, are commercially available and were used as received. All yields for organic materials are for compounds greater than 95% pure by both GC and ^{1}H NMR.

Synthesis of Lanthanocene Precatalysts. *rac*- and *meso*-[[Ethylenebis(η^5-indenyl)]ytterbium chloride][LiCl(THF)$_2$] (2, 3). To a solution of 1,2-bis(3-indenyl)ethane (2.00 g, 7.74 mmol) in THF (36 mL) cooled to −78 °C was added dropwise 11.3 mL of *n*-BuLi (Aldrich, 1.40 M in hexanes, 15.87 mmol), resulting in a yellow suspension which upon warming to room temperature became a clear orange solution. To a separate sealable Schlenk flask was added $YbCl_3$ (Aesar, 2.16 g, 7.74 mmol) and 36 mL of THF, yielding a cloudy suspension. The contents of the previous lithiation reaction were transferred via cannula dropwise (5 min total addition time), resulting in a disappearance of $YbCl_3$; the solution which became dark purple by the end of the addition. The reaction mixture was heated overnight at 80 °C, after which time solvent was reduced in vacuo to leave a dark purple solid. This was extracted with toluene (2 × 15 mL) and filtered, resulting in a dark purple solution: the solvent volume was reduced by about half and the vessel placed in a −10 °C freezer to crystallize, yielding purple needles (410 mg, 8.1% yield). The remaining solvent was removed, yielding 2.75 g (54% combined yield) of a purple solid. Anal. Calcd for $C_{28}H_{32}Cl_2LiO_2Yb$: C, 51.62; H, 4.95; Found: C, 51.59; H, 5.11. IR (Nujol mull, cm^{-1}): 1900 (w), 1872 (w), 1777 (w), 1750 (w), 1661 (w), 1605 (w), 1344 (s), 1322 (s), 1222 (w), 1183 (w), 1033 (vs), 1011 (s) 917 (w), 883 (s), 828 (w), 755 (s), 739 (vs), 667 (s), 433 (w). ^{1}H NMR (300 MHz, THF-d_8, δ; the two isomers were assigned by relative integration, although the broadness of the paramagnetic spectrum precludes absolute identification): isomer A, 65.95 (b, 2H), 58.09 (b, 2H), 48.80 (b, 2H), 6.32 (b, 4H), −37.33 (b, 2H), −41.83 (b, 2H), −46.85 (b, 2H); isomer B, 40.80 (b, 2H), 37.99 (b, 2H), 36.22 (b, 2H), 12.16 (b, 4H), −31.43 (b, 2H), −33.49 (b, 2H), −43.27 (b, 2H).

***rac*- and *meso*-[[Ethylenebis(η^5-indenyl)]ytterbium chloride][LiCl(Et$_2$O)$_2$] (4, 5)**. To a solution of 1,2-bis(3-indenyl)ethane (1.50 g, 5.80 mmol) in Et_2O (50 mL) and THF (4.5 mL) cooled to −78 °C was added dropwise *n*-BuLi (Aldrich, 4.6 mL, 2.6 M in hexanes, 11.90 mmol), yielding a dark brown suspension. The reaction mixture was warmed to room temperature with no change in the suspension. Additional THF (2 × 4 mL) was added to dissolve the suspension. To a separate sealable Schlenk flask was added $YbCl_3$ (Aesar, 1.62 g, 5.80 mmol) and 30 mL of Et_2O, yielding a cloudy suspension. The contents of the previous lithiation reaction were transferred quickly via cannula, resulting in the disappearance of the $YbCl_3$ and the resultant appearance of a dark blue solution which became dark blue-green after several minutes. The reaction mixture was stirred for 18 h at ambient temperature. The solvent was removed in vacuo to leave a blue-green foamy solid which was dried under vacuum for 30 min. To this was added Et_2O (30 mL), yielding a blue-green solution, which was stirred for 15 min; the solvent was then removed in vacuo and the residue dried for 1 h under vacuum. A second portion of Et_2O (30 mL) was added, the mixture was stirred for 15 min, the solvent was removed in vacuo, and the solid was dried for 1 h. A third portion of Et_2O was added, and the solution was stirred overnight. The resulting blue-green solution was filtered and the filter cake washed with Et_2O (2 × 10 mL) and then with Et_2O (4 × 5 mL) until the Et_2O ran colorless through the filter cake, leaving a grayish green solid. The air-sensitive blue-green solution was reduced in volume by half under vacuum and left at room temperature. Solid material crystallized as large dark red prisms (assigned as **4**) among dark green precipitated solid (assigned as **5**, 1.70 g, 43% total yield): the red prisms were physically separated (0.315 g, 8%). Anal. Calcd for $C_{28}H_{36}Cl_2LiO_2Yb$ (green solid): C, 51.31; H, 5.54; Found: C, 51.59; H, 5.21. IR (Nujol mull, cm^{-1}); 1335 (s), 1225 (w), 1151 (w), 1120 (w), 1089 (w), 1055 (w), 1037 (w), 1021 (w), 896 (m), 770 (s), 735 (s). ^{1}H NMR (300 MHz, THF-d_8, δ): 66.5 (2H), 58.7 (2H), 49.4 (2H), 6.3 (4H), 3.3 (4H), 1.1 (6H), −36.8 (2H), −41,3 (2H), −46.3 (2H).

***meso*-[[Ethylenebis(η^5-indenyl)]ytterbium(III)][N(TMS)$_2$] (6)**. To a stirred suspension of *meso*-[(EBI)YbCl][$LiCl_2$-(OEt_2)$_2$] (390 mg, 0.839 mmol) in ether (10 mL) was added $NaN(TMS)_2$ (151 mg, 0.881 mmol). The suspension became a dark green solution after approximately 1 h. The reaction mixture was stirred for 48 h, and the solvent was removed to yield a brown-green solid. The solid was extracted with hexane (1 × 10 mL, then 6 × 5 mL). The hexane washes were reduced in volume to ∼15 mL and cooled to −25 °C, yielding first 160 mg and then an additional 34 mg of dark green-blue crystalline plates (40% yield). Anal. Calcd for $C_{26}H_{34}NSi_2Yb$ (**6**): C: 52.95; H, 5.81; N, 2.37. Found: C, 53.24; H, 6.02; N, 2.13. ^{1}H NMR (300 MHz, C_6D_6, δ): 49.72 (2, b), 42.10 (9, b), 17.47 (2, b), −3.49 (2, b), −38.1 (4, b), −49.09 (2, b), −63.23 (2, b). IR (Nujol mull, cm^{-1}): 1339 (w) 1244 (w), 1167 (w), 1022 (b), 867 (w), 839 (w), 826 (w), 810 (w), 766 (s), 741 (s), 721 (w), 667 (s), 605 (w), 439 (w).

***rac*- and *meso*-[(EBI)LuCl][LiCl(Et$_2$O)$_2$] (7, 8)**. To a solution of 1,2-bis(3-indenyl)ethane (0.500 g, 1.93 mmol) in THF (9 mL) cooled to −78 °C was added dropwise *n*-BuLi (Aldrich, 1.58 mL, 2.5 M in hexane, 3.96 mmol), resulting in a yellow suspension which, upon warming to room temperature, became a clear orange solution. To a separate, sealable Schlenk flask was added $LuCl_3$ (Aesar, 0.543 g, 1.93 mmol) and THF (9 mL), yielding a cloudy white suspension. The solution of **1** was transferred dropwise via cannula to the $LuCl_3$, resulting in a tan-yellow solution which became darker after addition was complete (5 min). The reaction mixture was heated to reflux for 6 h and became dark brown. The THF was removed in vacuo to yield a red-brown solid. The solid was left to dry under vacuum for 1 h. The solid was extracted with toluene (10 mL) and filtered, yielding a burgundy solution; the solvent was removed under vacuum and the resultant solid washed with diethyl ether (3 × 2 mL), yielding 385 mg of a rose-colored solid. The solid was analyzed by ^{1}H NMR, revealing a 3:1 *rac:meso* mixture of **7** and **8**. Anal. Calcd for $C_{28}H_{36}Cl_2LiO_2Lu$: C, 51.15; H, 5.48. Found: C, 50.83; H,

5.12. ^{1}H NMR (300 MHz, THF-d_8, δ): *rac* isomer, 7.55 (d, J = 8.2 Hz, 2H, H_F), 7.11 (J = 8.2 Hz, 2H, H_C), 6.73 (overlapping dd, 4H, H_D, H_E), 6.01 (d, J = 3.0 Hz, 2H, H_A), 5.83 (d, J = 3.0 Hz, 2H, H_B), 3.20 (s, 4H, H_g); *meso* isomer, 7.39 (d, J = 7.8 Hz, 2H, $H_{F'}$), 7.04 (d, J = 7.8 Hz, 2H, $H_{C'}$), 6.53 (2 × dd, 4H, $H_{D'}$, $H_{E'}$), 6.32 (d, J = 2.8 Hz, 2H, $H_{A'}$), 6.01 (b, 2H, $H_{B'}$), 3.70 (m, 4H, $H_{G'}$). ^{13}C NMR (THF-d_8, δ): 145.3, 145.2, 129.6, 128.9, 128.4, 126.7, 125.3, 124.5, 124.3, 124.1, 121.6, 120.9, 120.8, 120.5, 119.5, 115.1, 100.9, 99.5, 68.2, 66.3, 38.2, 28.7, 27.2, 26.3. IR (Nujol mull, cm^{-1}): 1721 (w), 1606 (w), 1346 (m), 1330 (m), 1222 (w), 1120 (w), 1046 (m), 1012 (m), 933 (w), 859 (s), 837 (w), 769 (s), 740 (s).

Synthesis of Aminoalkenes for Hydroamination. Where appropriate, the materials below were synthesized by literature methods; in those cases the spectroscopic data for each compound were consistent with the literature data. Only those cases where significant modifications were made are reported in detail.

1-Amino-2,2-dimethyl-4-pentene.[33] A solution of isobutyronitrile (Aldrich, 11.4 g, 0.165 mol) in THF (120 mL) was cooled to 0 °C, and to it was added dropwise a solution of lithium dimethylamide (Aldrich, 9.76 g, 190 mmol) in THF (80 mL). The reaction mixture was warmed to room temperature and stirred for 2 h, after which the brown solution was cooled to 0 °C; to it was added allyl bromide (16 mL, 95 mmol, dried over 4 Å mol sieves). The reaction mixture became pale yellow by the end of the addition; it was allowed to react at room temperature for 2 h. To the reaction mixture was then added saturated $NaHCO_3$ solution (20 mL), followed by water (40 mL). The organic phase was separated, and the aqueous phase was washed with ethyl acetate (80 mL). The combined organic portions were extracted with brine (2 × 200 mL) and dried over excess $MgSO_4$. The product solution was reduced by rotary evaporation at room temperature, yielding 9.78 g of a yellow solution. The product was reduced with lithium aluminum hydride (Aldrich, 6.7 g, 170 mmol) in ether (400 mL) at reflux for 2 h. The reduced product was cooled to 0 °C, and to it was added water (6.7 mL), 15% NaOH (6.7 mL), and then water (20 mL), resulting in a vigorous reaction and formation of a white precipitate, which was filtered from the product-containing solution. The organic solvent was separated from the aqueous layer and dried over $MgSO_4$ and the solvent removed by rotary evaporation at room temperature to yield a colorless liquid. The product was dried over NaOH and then distilled under argon at 160 °C from CaH_2 to yield 1-amino-2,2-dimethyl-4-pentene (2.97 g, 30 mmol, 20%). ^{1}H NMR ($CDCl_3$, δ): 5.86 (m, 1H), 5.05 (overlapping doublets, 2H), 2.44 (s, 2H), 1.97 (m, 2H), 0.85 (s, 6H).

2-Allyl-1-amino-2-methyl-4-pentene.[34] To a −85 °C suspension of lithium diisopropylamide in cyclohexane (Aldrich, 189 mL, 0.28 mol) was added dry THF (200 mL) and then, dropwise, proprionitrile (Eastman, 20 mL, 0.28 mol, dried over CaH_2), resulting in an orange solution which was stirred for 2.5 h at −85 °C. To the lithiated proprionitrile was added allyl bromide (24 mL, 0.28 mol) dropwise over 5 min, and this mixture was then stirred at −85 °C for 2 h. To the resulting yellow solution was added three alternating portions of deionized water (50 mL) and 2 M HCl (50 mL) until the washings were acidic. The organic mixture was then washed with brine (2 × 50 mL) and separated, and the organic material was dried over Na_2SO_4. The solvent was removed by rotary evaporation and the residue distilled at 125 °C to yield 2-allyl-2-methyl-4-pentenenitrile. The crude nitrile was reduced immediately with LAH by the method described above and purified by vacuum distillation through a 10 cm Vigreux column to yield 2-allyl-1-amino-2-methyl-4-pentene (4.8 g, 0.035 mol, 12.5%). ^{1}H NMR ($CDCl_3$, δ): 5.8 (m, 2H), 5.01 (overlapping doublets, 4H), 2.46 (s, 2H), 1.99 (d, J = 7.5 Hz, 2H), 0.83 (s, 3H). ^{13}C NMR (C_6D_6, δ): 135.6, 117.0, 50.0, 42.0, 37.9, 22.3. IR (neat, cm^{-1}): 3393 (m), 3312 (m), 3074 (s), 3002 (s), 2914 (s), 1830 (m), 1638 (s), 1464 (s), 1438 (s), 1414 (m), 1378 (m), 1323 (w), 1294 (w), 1066 (m), 997 (s), 911 (s), 815 (s), 754 (m).

2-Amino-5-hexene.[3,35] This compound was made by the method of House, as modified by Marks, from 5-hexen-2-one by reduction of the corresponding oxime. 2-Amino-5-hexene (3.5 g, 38% from ketone) was isolated after drying over CaH_2 and distillation. ^{1}H NMR ($CDCl_3$, δ): 5.76 (m, 1H), 4.98 (d, J = 17 Hz, 1H), 4.90 (d, J = 7.8 Hz, 1H), 2.87 (sextet, J = 6.4 Hz, 1H), 2.05 (m, 1H), 1.35 (m, 5H), 1.02 (d, J = 6.4 Hz, 3H).

2-(Butylamino)-5-hexene.[36] 5-Hexen-2-one (4.2 g, 46 mmol) and butylamine (4.25 mL, 43 mmol) were dissolved in CH_2Cl_2 (35 mL) in a round-bottom flask equipped with a reflux condenser. To this solution was added 2.67 g of $MgSO_4$. The mixture was heated at reflux for 24 h, after which time GC showed no remaining starting material. The solid was filtered and the residual volatile material removed under vacuum to yield clear, colorless 2-(butylimino)-5-hexene. This material was immediately reduced. 2-(Butylimino)-5-hexene (3.4 g, 18 mmol) was dissolved in 50 mL of methanol at 0 °C, and to this solution was added $NaBH_4$ (0.67 g, 18 mmol). After 1 h the reaction mixture was partitioned between 1 M HCl and CH_2Cl_2. The acidic layer was then made basic to litmus with KOH(s) and the cloudy mixture extracted into diethyl ether. The resulting organic solution was dried over Na_2SO_4 and rotary-evaporated to yield 2.1 g of yellow oil. This oil was dried over CaH_2 and then was distilled under vacuum from solid NaOH to yield 2-(butylamino)-5-hexene (1.2 g, 6.4 mmol, 14%). ^{1}H NMR ($CDCl_3$, δ): 5.8 (m, 1H), 5.0 (m, 2H), 2.6 (m, 3H), 2.4 (bs, 1H), 1.67 (m, 2H), 1.45 (m, 2H), 1.58 (p, J = 6.3 Hz, 2H), 1.29 (sextet, J = 6.3 Hz, 2H), 1.0 (d, J = 6.7 Hz, 3H), 0.90 (t, J = 6.3 Hz, 3H).

2-Allylaniline.[3] This compound was made from aniline and allyl bromide by Cope rearrangement of *N*-allylaniline by the method described by Marks. 2-Allylaniline (1.5 g, 30% yield from *N*-allylaniline) was isolated after distillation. ^{1}H NMR ($CDCl_3$, δ): 7.05 (m, 2H), 6.7 (m, 2H), 5.96 (m, 1H), 5.09 (m, 2H), 3.63 (bs, 2H), 3.29 (d, J = 6.1 Hz, 2H).

1-Amino-2,2-dimethyl-5-hexene.[37] This compound was synthesized through elimination of 6-bromo-2,2-dimethylhexanenitrile with KOBu^t. In a 500 mL Schlenk flask was added 27.6 g of KOBu^t and 250 mL of THF. To this solution was added, via syringe, 20.0 mL of 6-bromo-2,2-dimethylhexanenitrile (0.113 mol) in a rapid fashion. After the flask was fitted with a condenser, the resulting solution was heated to reflux for 1 day. The resulting suspension was diluted with 60 mL of diethyl ether and filtered. The material was filtered through Celite and the solvent removed under reduced pressure to yield a gold-colored oil. The crude nitrile was reduced with LAH in THF by the same method as above and purified by vacuum distillation through a 10 cm Vigreux column to yield 2,2-dimethyl-4-hexeneamine (9.2 g, 0.072 mol, 64%). ^{1}H NMR ($CDCl_3$, δ): 5.83 (m, 1H), 5.07 (dd, J = 17, 1.7 Hz, 1H), 5.07 (dd, J = 10, 1.7 Hz, 1H), 2.28 (s, 2H), 1.94 (m, 2H), 1.25 (m, 2H), 0.85 (s, 6H), 0.486 (bs, 2H).

General Method for Catalytic Cyclic Hydroamination. All cyclic hydroamination reactions were carried out using 2−6 mol % of **6** in 1−2 mL of toluene. Normally, between 100 and 150 mg of the substrate was used and the reaction monitored by GC until completion. The product was isolated by one of two methods. Method A consisted of making the amine solution acidic with 1 M HCl, extracting the resulting ammonium salt into water, and separating the organic layer, followed by

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making the aqueous layer basic with NaOH. The mixture was then extracted with diethyl ether, dried, and rotary-evaporated at room temperature to yield the corresponding cyclized amine. In method B, excess acetic anhydride was added to the reaction solution, with the acylated product isolated by aqueous workup followed by flash chromatography on silica. Where the products were known, spectroscopic data were consistent with literature values.

1-Acyl-2,5,5-trimethyl-1-azacyclohexane. In a sealable Schlenk flask was added **6** (0.018 g, 0.03 mmol), 1-amino-2,2-dimethyl-5-hexene (0.184 g, 1.47 mmol), and toluene (1 mL) in the drybox to give a purple solution. The flask was sealed and moved to a 80 °C oil bath in the fume hood. The reaction was monitored by removing aliquots for GC analysis by syringe. The reaction was complete after 48 h, after which time it was isolated by method B. Acetic anhydride (0.250 mL) was added to the reaction mixture, yielding a yellow solution. The solvent and volatile material were removed under vacuum, and the residue was partitioned between CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$, filtered, and rotary-evaporated to give a yellow oil. The material was purified by flash chromatography (SiO_2, EtOAc in hexane gradient from 10% EtOAc to 100% EtOAc) to yield 1-acyl-2,5,5-trimethyl-1-azacyclohexane (0.237 g, 95% yield) as a pale yellow oil. HRMS: calculated for $C_{10}H_{19}NO$, 169.146 67; found, 169.146 46. NMR analysis showed the presence of two rotamers for the amide, which coalesced upon heating to 335 K. ^{1}H NMR ($CDCl_3$, 335 K, δ): 2.1−5.3 (coalesced broad m, 3H, CH−N), 2.1 (s, 3H, CH_3C═O), 1.9 (m, 1H), 1.5 (dt, J = 3.9, 13.2 Hz, 1H), 1.3 (m, 2H), 1.13 (d, J = 6.8 Hz, 3H), 0.94 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (C_6D_6): 168.4, 50.3, 47.2, 32.9, 31.1, 28.9, 26.5, 23.1, 21.1, 17.8. IR (neat, cm^{-1}): 2939 (s), 2066 (s), 1721 (w), 1633 (s), 1434 (s), 1390 (m), 1365 (m), 1365 (m), 1294 (m), 1227 (m), 1248 (w), 1227 (m), 1189 (m), 1161 (m), 1027 (s), 996 (w), 977 (w), 914 (w), 863 (w).

2-Methylindoline.[33] In a sealable Schlenk flask was added **6** (0.015 g, 0.025 mmol), 2-allylaniline (0.121 g, 0.90 mmol), and 1 mL of toluene in the drybox to give a purple solution. The flask was sealed and moved to a 80 °C oil bath in the fume hood. The reaction was monitored by removing aliquots by syringe for GC analysis. The reaction was complete after 3 days. The reaction mixture was added directly to a SiO_2 (20 mL, EtOAc in hexane, gradient from 5% EtOAc to 50% EtOAc) column for flash chromatography to yield 2-methylindoline (0.100 g, 82% yield) as an oil. ^{1}H NMR ($CDCl_3$, δ): 7.10 (d, J = 7.1 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 7.0 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 4.01 (ddq, J = 7.7, 8.5 Hz, 1H), 3.8 (bs, 1H), 3.15 (dd, J = 8.5, 15.4 Hz, 1H), 2.65 (dd, J = 7.7, 15.4 Hz, 1H), 1.31 (d, J = 6.1 Hz, 3H).

1-Acyl-4-allyl-2,4-dimethylpyrrolidine. In a sealable Schlenk flask was added 2.0 mL of a 0.014 M solution of **6** (0.027 mmol) and 2-allyl-1-amino-2-methyl-4-pentene (0.146 g, 1.17 mmol) in the drybox to give a burgundy solution. The flask was sealed and stirred at room temperature. The reaction was monitored by removing aliquots for GC analysis. The reaction was complete after 22 h, after which time acetic anhydride (0.25 mL) was added; the mixture became yellow. The solvent and volatile material were removed under vacuum, and the residue was partitioned between CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$, filtered, and rotary-evaporated to give a yellow oil. The material was purified by flash chromatography (20 mL of SiO_2, EtOAc in hexane gradient from 0% EtOAc to 100% EtOAc) to yield 1-acyl-4-allyl-2,4-dimethylpyrrolidine (0.169 g, 86% yield) as an oil. NMR analysis showed the presence of two rotamers of two diastereomers for the amide which coalesced upon heating but did not reach the fast-exchange manifold at obtainable temperatures. HRMS: calculated for $C_{11}H_{19}NO$, 181.146 67; found, 181.146 50. NMR data are for room-temperature spectra of the mixture; the material was not in fast exchange at 483 K. ^{1}H NMR ($CDCl_3$, δ, room temperature): 5.73 (m, 1H), 5.0 (m, 2H), 3.8 (m, 1H), 3.1 (m, 2H), 2.0 (m, 6H), 1.3 (m, 1H), 1.25 (d, J = 6.8 Hz, 3H), 1.0 (s, 3H). ^{13}C NMR (C_6D_6, δ, mixture did not coalesce up to 443 K): 169.4, 169.2, 169.0, 168.4, 137.2, 136.8, 134.2, 134.0, 117.9, 117.7, 117.6, 117.5, 58.9, 57.8, 56.1, 55.7, 53.1, 52.7, 52.1, 52.0, 46.8, 46.3, 45.5, 44.1, 44.0, 43.4, 42.7, 42.0, 40.8, 30.5, 39.5, 39.7, 23.9, 23.7, 23.5, 23.3, 23.0, 23.0, 22.3, 22.2, 21.1, 20.8, 20.3, 20.2. IR (neat, cm^{-1}): 3074 (m), 2961 (s), 2928 (s), 2868 (s), 1720 (w), 1640 (s), 1417 (s), 1380 (m), 1351 (m), 1284 (w), 1215 (w), 1197 (w), 1168 (w), 1034 (w), 997 (m), 913 (w), 618 (m).

Isolation Method A. In a sealable Schlenk flask was added **6** (0.035 g, 0.059 mmol), 2-allyl-1-amino-2-methyl-4-pentene (0.137 g, 0.984 mmol), and 1.5 mL of toluene in the drybox to give a burgundy solution. The flask was sealed and stirred at room temperature. The reaction was monitored by removing aliquots for GC analysis by syringe. The reaction was complete after 22 h, after which time the solution was diluted with diethyl ether and extracted with 1 M HCl (2 × 6 mL). The aqueous layer was separated and made basic with LiOH to provide a white solid. The solid was extracted into ether and the resulting solution dried over $MgSO_4$. Removal of the solvent under reduced pressure yielded 2,4-dimethyl-4-allyl-1-pyrrolidine (0.75 mmol, 76%). ^{1}H NMR ($CDCl_3$, δ): 5.79 (m, 1H), 5.05 (m, 2H), 3.29 (m, 1H), 2.73 (m, 2H), 2.12 (m, 3H), 1.72 (m, 2H), 1.23 (s, 3H), 1.07 (d, J = 6.6 Hz, 3H).

2,5-Dimethyl-1-pyrrolidine.[35] In a sealable Schlenk flask was added 3 mL of C_6D_6, **6** (0.022 g, 0.037 mmol), and 2-amino-5-hexene (0.181 g, 1.87 mmol) in the drybox to give a wine red solution. The flask was sealed and stirred at 70 °C. The reaction was monitored by ^{1}H NMR and GC. It was complete after 48 h. After the reaction was complete, the reaction mixture was partitioned between 1 M HCl (3 mL) and diethyl ether (10 mL). The ether layer was extracted with a further 1 mL of HCl, and the combined acidic solutions were made basic to litmus with NaOH pellets. Extraction of the two-layer basic solution with ether, followed by microscale spinning band distillation, yielded 2,5-dimethyl-1-azacyclopentane (0.082 g, 45% yield; the reaction was quantitative by NMR). GC analysis showed the material to coelute with a commercial sample of 2,5-dimethyl-1-azacyclopentane (Aldrich, 2:1 *trans:cis*). The reaction sample was found to be 10:1 enriched in the *trans* diastereomer by integration of the CH_3 doublets at 1.17 and 1.04 in the reaction mixture. ^{1}H NMR ($CDCl_3$, δ): 3.27 (m, 2H,) 1.93 (m, 1H), 1.6 (bs, 1H), 1.23 (m, 1H), 1.17 (d, J = 7.1 Hz, 3H).

Isolation Method B. In a sealable Schlenk flask was added 2.0 mL of a 0.014 M solution of **6** (0.027 mmol) and 2-amino-5-hexene (0.111 g, 1.05 mmol) in the drybox to give a red solution. The flask was sealed and stirred at 70 °C. The reaction was monitored by removing aliquots for GC analysis by syringe under argon. The reaction was complete after 48 h. After the reaction was complete, acetic anhydride (0.25 mL) was added. The reaction mixture was partitioned between CH_2Cl_2 and water, followed by drying the organic layer over $MgSO_4$, filtering, and removing the solvent under reduced pressure to give an oil. The material was purified by flash chromatography (10 mL of SiO_2, EtOAc in hexane gradient from 0% EtOAc to 100% EtOAc) to yield 1-acyl-2,5-dimethyl-1-pyrrolidine (0.133 g, 86% yield) as a slightly yellow oil. The two rotamers are not yet at fast exchange at 383 K. ^{1}H NMR (Tol-d_8, room temperature, δ): 4.42 (sextet, J = 6.5 Hz, 2H), 3.6 (sextet, J = 6.4 Hz, 2H), 2.08 (s, 6H), 1.96 (m, 2H), 1.41 (d, J = 6.5 Hz, 3H), 1.37 (m, 2H), 1.00 (d, J = 6.4 Hz, 3H).

1-Acyl-2,4,4-trimethylpyrrolidine.[35] In a sealable Schlenk flask was added 2.0 mL of a 0.0136 M solution of (EBI)YbN(TMS)$_2$ (2.7×10^{-5} mol) in 2 mL of toluene; 1-amino-2,2-dimethyl-4-pentene (0.105 g, 0.92 mmol) was added in the drybox to give a burgundy solution. The flask was sealed and stirred at room temperature. The reaction was monitored by removing aliquots for GC analysis by syringe. The reaction was complete after 70 h, at which time acetic anhydride (250

uL) was added; the mixture became yellow. The solvent and volatile material were removed under vacuum, and the residue was partitioned between CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$, filtered, and rotary-evaporated to give a yellow oil. The material was purified by flash chromatography (SiO_2, EtOAc in hexane gradient from 10% EtOAc to 100% EtOAc) to yield 1-acyl-2,5,5-trimethyl-1-azacyclopentane (0.112 g, 79% yield). ^{1}H NMR (C_6D_6, 350 K, δ): 3.18 (m, 1H), 2.63 (d, J = 10.7 Hz, 1H), 2.49 (d, J = 10.6 Hz, 1H), 2.1 (s, 3H), 1.62 (m, 2H), 1.6 (bs, 1H), 1.05 (d, J = 6.2 Hz, 3H), 0.98 (s, 3H), 0.94 (s, 3H).

Cyclization of 1-Amino-2,2-dimethyl-4-pentene in Hexane. In a sealable Schlenk flask was added 1-amino-2,2-dimethyl-4-pentene (0.162 g, 1.43 mmol) and **6** (0.017 g, 0.029 mmol) in hexane in the drybox to give a burgundy solution. The flask was sealed and stirred at room temperature. The reaction was monitored by removing aliquots for GC analysis by syringe. The reaction was complete after 205 h, as evidenced by GC.

Attempted Cyclization of 2-(butylamino)-5-hexene. To a sealable Schlenk flask was added **6** (0.028 g, 0.048 mmol), toluene (1.5 mL), and 2-(butylamino)-5-hexene (0.123 g, 0.792 mmol) in the drybox to give a purple solution. The flask was sealed and stirred at 80 °C. The reaction was monitored by GC analysis; no evidence for reaction was observed after 4 days.

X-ray Crystallographic Experiment on 6. Details of the single-crystal X-ray diffraction experiment (CAD4 data) are given in Table 2. Three standard reflections were examined every 1 h and showed no significant variation in intensity during the course of the experiment. ψ-Scan intensity data indicated that absorption effects were significant (approximately ±12%), and a numerical absorption correction was made (SHELX-76).[38] The structure of **6** was solved by use of SHELXS97[39] and refined by use of SHELXL97.[40] An approximate isotropic extinction correction was applied; however, the extinction effect appeared to be rather anisotropic and the following low-angle extinction-affected transmissions were omitted: 040, 120, 102, −1,0,2, 022, 0,2,−2, and 200.

Only one of the four $Si(CH_3)_3$ groups of the two unique molecules in the asymmetric unit was found to be rotationally disordered, and it was found to be distributed over three sites of approximately 50, 25, and 25% occupancy, respectively. Restraints were only used for this group in the least-squares refinement, and include the following: (A) all atoms in the three-part disordered group were restrained with effective standard deviation 0.02 Å^2 to have the same U_{ij} components (SIMU restraint in SHELXL97); (B) all equivalent bond distances were restrained to be equal with effective standard deviation 0.03 Å (SADI restraint in SHELXL97); (C) the Si−C bond distances were restrained to 1.87 Å, with effective standard deviation 0.01 Å. Further details of the experiment can be found in the Supporting Information.

Table 2. Crystallographic Details for [(EBI)Yb][N(TMS)$_2$] (6)

empirical formula	$C_{52}H_{68}N_2Si_4Yb_2$
M_r	1179.52
temp	153(5) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
no., range for cell data	25, $16.3 < \theta < 17.7°$
a	10.421(3) Å
b	21.224(7) Å
c	22.958(8) Å
α	90.00(3)°
β	92.24(3)°
γ	90.00(3)°
V	5074(3) Å^3
Z	4
calcd density	1.54 Mg/m^3
abs coeff	3.794 mm^{-1}
F(000)	2360
cryst size	0.44 × 0.20 × 0.12 mm
θ range for data collecn	2.02−22.96°
index ranges	$-11 \le h \le 11$, $0 \le k \le 23$, $-19 \le l \le 25$
no. of rflns collected/unique	7484/6883 (R(int) = 0.025)
completeness to 2θ	97.70%
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	6883/255/614
GOF on F^2	1.003
R (5834 data $I > 2\sigma(I)$)	R1= 0.025, wR2= 0.058
R (all 6883 data)	R1= 0.038, wR2= 0.060

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Supporting Information Available: Text giving information regarding the structure determination of **6** and tables of atomic coordinates, interatomic distances, angles, torsion angles, and isotropic displacement parameters for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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