Lanthanide Complexes Coordinated by N-Substituted (*R*)-1,1'-Binaphthyl-2,2'-diamido Ligands in the Catalysis of Enantioselective Intramolecular Hydroamination

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Abstract: A new family of lanthanide ionic complexes derived from chiral, substituted (*R*)-binaphthylamine ligands, $[\text{Li}(thf)_4][\text{Ln}\{(R)-\text{C}_{20}\text{H}_{12}(\text{NR})_2]_2]$ (Ln=Yb, Sm, Nd, or Lu), has been synthesized and characterized by X-ray crystal structure analyses. All complexes have been tested as new catalysts for the hydroamination/cyclization of 1-(aminomethyl)-1-allylcyclohexane. Ytterbium complexes proved to be

Keywords: amido ligands • enantioselectivity • homogeneous catalysis • hydroamination • lanthanides both the most active and the most enantioselective, and the use of the complex $[\text{Li}(\text{thf})_4][\text{Yb}\{(R)-C_{20}\text{H}_{12}-(\text{NC}_3\text{H}_7)_2]_2]$, bearing isopropyl radicals on the nitrogen atoms, allowed the formation of the corresponding spiropyrrolidine in high yield with up to 70 % *ee*.

Introduction

Efficient synthetic and environmentally friendly methods for the preparation of enantiomerically enriched nitrogen-containing heterocycles are frequently required nowadays because of the potential biological activity of such compounds.^[1] Intramolecular hydroamination of unsaturated amino derivatives appears to be a good example of an atom-economical reaction, which illustrates the concept developed simultaneously by Trost^[2] and Sheldon^[3] in the 1990s. Indeed, the hydroamination reaction proceeds through a formal addition of the N–H unit onto a carbon– carbon unsaturated bond, with all atoms of the reactants being transferred into the reaction product and without the

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E-mail: trif@imoc.sinn.ru formation of any by-product or salts.^[4] Pioneering work on the lanthanide-catalyzed intramolecular hydroamination reaction has been performed by Marks and co-workers and was recently reviewed.^[5] Cyclopentadienyl-based alkyl or amido lanthanides were found to be active catalysts to perform efficiently the hydroamination/cyclization of aminoalkenes,^[6] aminoalkynes,^[7] aminodienes,^[8] and aminoallenes.^[9] The first examples of the enantioselective intramolecular hydroamination of aminoalkenes were also reported by Marks and co-workers, by the use of C_1 -symmetric chiral organolanthanide complexes. In the first generation, ansa lanthanocenes were modified by introduction of a menthyl-type substituent,^[10] and in subsequent studies a more stereodemanding octahydrofluorenyl replaced the achiral cyclopentadienyl group.^[11] To the best of our knowledge, no other lanthanide catalysts for intramolecular hydroamination of alkenes were reported until the work of Kim et al., who showed that such efficient (nonchiral) reactions could be performed with lanthanide trisamides.^[12] As a real breakthrough in this research field, these results opened the way to the development and use of new cyclopentadienyl-free lanthanide complexes as more easily accessible catalysts.^[13] Scott and coworkers recently published the enantioselective hydroamination/cyclization of 2,2'-dimethylaminopent-4-ene (up to 50% ee) with in situ prepared catalysts obtained from chiral nonracemic N-aryl-substituted biphenyl diamines and yttrium silvl amides.^[14] The same group synthesized and characterized several further chiral lanthanide bisaryloxide com-

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plexes arising from the reduction of salicylaldimine ligands and subsequent N-methylation. The lanthanum complex allowed the cyclization of 2,2'-dimethylaminopent-4-ene with 60% ee.^[15] By preparing a new chiral zirconium alkyl cation coordinated with a similar aminobiphenoxide ligand, Scott and co-workers obtained a highly active and enantioselective catalyst for the hydroamination/cyclization of secondary amines (up to 82% ee).^[16] At the same time as this work, Hultzsch and co-workers prepared new yttrium and lanthanum amides, coordinated by ancillary chiral biphenolate or binaphtholate ligands, that led to the cyclization of aminopentenes with up to 57 % ee.[17] An improvement in terms of activity and selectivity was reported by this team in preparing more sterically hindered yttrium complexes in order to favor a monomeric structure.^[18] The 3,3'-bis(tris(aryl)silyl)substituted binaphtholate ligands allow the isolation of an yttrium aryl complex that is active at room temperature and leads to an enantiomeric excess of 83% for the hydroamination of aminopent-4-ene, the best enantiomeric excess obtained to date. At the same time, Marks and co-workers have employed C_2 -symmetric bis(oxazolinato) ligands for in situ preparation of lanthanide catalysts that are also active at room temperature, with enantiomeric excesses up to 67 % for the lanthanum complex.^[19] Enantioselective hydroamination of other substrates has been less frequently described but some results are reported concerning aminodienes with an ansa fluorenyl samarium complex^[20] and aminoallenes with chiral titanium aminoalcohol complexes.^[21]

We aimed at preparing asymmetric lanthanide catalysts

coordinated by chiral amine ligands for intramolecular hydroamination. In contrast to binaphthol, which has been largely employed as a ligand in lanthanide catalysis,^[22-24] no binaphthylamine complex has been reported yet, as far as we know. Different families of complexes, with mono- or bicoordinated binaphthol, have

been described, and Shibasaki and co-workers focused on lanthanide heterobimetallic complexes of general formula $[M_3Ln(binol)_3]$ (M=alkali metal, Ln=lanthanide, binol=binaphthol) as highly active and enantioselective catalysts for a wide range of reactions.^[22,25] Many complexes have been prepared, and X-ray crystal structures indicated that the three binaphthol ligands were coordinated to both the lanthanide and alkali metals with a Λ or Δ configuration. The influence of the nature of the alkali metal on the activity and selectivity of these catalysts has been demonstrated.

We have previously reported the preparation of a new family of lanthanide *ate* complexes derived from chiral, substituted (*R*)-binaphthylamine ligands, $[\text{Li}(thf)_4][\text{Ln}\{(R)-C_{20}\text{H}_{12}\text{N}_2(C_{10}\text{H}_{22})\}_2]$ (Ln = Yb (1a), Sm (1b); see Scheme 1). In compounds 1a and 1b, coordination of two (*R*)-binaphthylamine ligands to the lanthanide atom resulted in the formation of a complex anion with a discrete $[\text{Li}(thf)_4]^+$ as

counterion.^[26] The ytterbium complex containing (R)-1,1'-binaphthyl-2,2'-bis(neopentylamine) (**1a**) is an efficient catalyst for the hydroamination of 1-(aminomethyl)-1-allylcyclohexane at room temperature and afforded the corresponding spiropyrrolidine in 41% *ee*.

In order to gain insight into the effect of the nature of the central metal atom and the bulkiness of the chiral ligands on the efficiency and enantioselectivity of the above reaction, we have now extended this study to the synthesis and characterization of new complexes containing various lanthanides and radicals on nitrogen atoms.

Results and Discussion

Preparation of new complexes of type $[Li(thf)_4][Ln\{(R)\}$ - $C_{20}H_{12}(NR)_{2}$: The new family of ionic lanthanide amides that we have described arose at first from the (R)-1,1'-binaphthyl-2,2'-bis(neopentylamine) ligand.[27] The ytterbium complexes $[\text{Li}(\text{thf})_4][\text{Ln}\{(R)-\text{C}_{20}\text{H}_{12}\text{N}_2-\text{C}_{$ and samarium $(C_{10}H_{22})_{2}$ (Ln = Yb (1a), Sm (1b)) have been recently synthesized by metathetic reactions of anhydrous $LnCl_3$ (Ln = Sm, Yb) with two equivalents of $Li_2[(R)-C_{20}H_{12}N_2 (C_{10}H_{22})$ ^[27] in tetrahydrofuran at ambient temperature. By following the same procedure, we have prepared further related derivatives with neodymium and lutetium, [Li(thf)₄]- $[Ln\{(R)-C_{20}H_{12}N_2(C_{10}H_{22})\}_2]$ (Ln = Nd (1c), Lu (1d); Scheme 1). Complexes 1c and 1d were purified by extraction of the solid residue with toluene, after evaporation of



Scheme 1. Preparation of $[Li(thf)_4][Ln\{(R)-C_{20}H_{12}N_2(C_{10}H_{22})\}_2]$: Ln = Yb (1a), Sm (1b), Nd (1c), or Lu (1d).

THF, and subsequent recrystallization from THF/hexane mixtures. Complexes 1c and 1d were isolated as air- and moisture-sensitive brownish-orange and yellow crystals in reasonable yields (74 and 61%, respectively). Both compounds are soluble in THF and aromatic solvents but insoluble in hexane.

Complex **1d** is diamagnetic; its ¹H NMR spectrum has no particular features and presents the expected set of signals. Complex **1c** is paramagnetic with the value of the magnetic moment being 3.3 μ B (293 K), a value that is characteristic for derivatives of trivalent neodymium.^[28]

To modify the steric environment of the lanthanide atom and to tune the complex properties for the catalytic reaction requirements, we have prepared the chiral, substituted (*R*)binaphthylamine ligands bearing various hydrocarbon radicals on the nitrogen atoms, that is, (*R*)-C₂₀H₁₂(NHR)₂ ($\mathbf{R} = i\mathbf{Bu}$ (**2a**), benzyl (Bn; **2b**), *i*Pr (**2c**)).^[29] The ytterbium derivatives were chosen as a model system because they have demonstrated the highest activity and enantioselectivity (see ref. [26] and the results detailed below), and the series of novel complexes [Li(thf)₄][Yb{(R)-C₂₀H₁₂(NR)₂]₂] (R=*i*Bu (**3a**), Bn (**3b**), *i*Pr (**3c**)) have been synthesized. The reactions of anhydrous YbCl₃ with two equivalents of Li₂[(R)-C₂₀H₁₂(NR)₂] were carried out in THF at ambient temperature (Scheme 2). The lithium derivatives Li₂[(R)-C₂₀H₁₂(NR)₂] were prepared by following the general method described by Lappert and co-workers.^[27]

Evaporation of THF, extraction of the solid residue with toluene, and subsequent recrystallization from THF/hexane mixtures resulted in the isolation of complexes **3a–c** in 54, 52, and 68% yields, respectively. Complexes **3a** and **3c** are red crystalline solids and **3b** is a brownish-green crystalline solid. Complexes **3a–c** are paramagnetic, with magnetic moments corresponding to the trivalent state of ytterbium.^[28] All the compounds are readily soluble in THF and toluene but insoluble in hexane.



Figure 1. Molecular structure of complex **1c**. The hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Nd–N1 2.366(3), Nd–N2 2.350(3), Nd–N3 2.391(3), Nd–N4 2.397(3), Nd–C111 2.819(3), Nd–C211 2.813(3), Nd–C311 2.770(4), Nd–C312 2.830(3), Nd–C411 2.842(3), N1-Nd-N2 115.98(9), N1-Nd-N3 100.73(9), N2-Nd-N3 106.54(10), N1-Nd-N4 115.01(10), N2-Nd-N4 101.88(9), N3-Nd-N4 117.05(10).



rivative of tetracoordinated neodymium [Li(thf)][Nd(N-*i*Pr₂)₄] (2.283(17), 2.291(16), 2.393(15), 2.406(16) Å),^[31] but they are substantially shorter than the analogous lengths in the *meso*octaethylporphyrinogen complex [{[$(\eta^5:\eta^1:\eta^5:\eta^1-Et_8N_4)$ Nd-

to those in the related ionic de-

Scheme 2. Preparation of $[\text{Li}(\text{thf})_4]$ [Yb{(R)-C₂₀H₁₂(NR)₂]₂]: R = CH₂-*i*Pr (**a**), CH₂Ph (**b**), or *i*Pr (**c**).

X-ray crystal structure analyses of complexes 1 c, d and 3 a, c: Single-crystal samples of complexes 1c,d and 3a,c suitable for X-ray diffraction study were obtained by slow condensation of hexane in the THF/complex solutions at room temperature. Complex 3a was isolated as a THF solvate [Li- $(thf)_4][Yb{(R)-C_{20}H_{12}(NCH_2CHMe_2)_2}_2] \cdot 0.5 THF.$ The molecular structures of complexes 1c, d and 3a, c are shown in Figures 1-4, respectively. Details of the crystal data collections and the structure refinements are listed in Table 3 in the Experimental Section. The X-ray crystal structure analysis revealed that compounds 1c,d and 3a,c are isostructural ionic complexes containing a discrete [Li(thf)₄]⁺ ion and a discrete $[Ln{(R)-C_{20}H_{12}(NR)_2}_2]^-$ complex anion resulting from coordination of two diamido ligands to the trivalent lanthanide atom. The structures are very similar to those formerly reported for complexes 1a, b.

The coordination environment of the central metal atom in complexes **1a**,**b**, made up of four nitrogen atoms of two chelating diamido ligands, may be classified as a distorted tetrahedron. Vicinal bulky hydrocarbyl radicals on the nitrogen atoms adopt a *trans* orientation. The average Ln–N bond lengths in **1c** (2.376(3) Å) and **1d** (2.250(3) Å) are very similar despite the difference in the ionic radii of trivalent neodymium and lutetium.^[30] The Nd–N bond lengths in **1c** (2.350(3), 2.366(3), 2.391(3), 2.397(3) Å) are comparable (dme)]- η^3 -Na}(dioxane)_{1.5}] (dme = 1,2-dimethoxyethane; 2.461(4), 2.527(4) Å) in which the coordination sphere of ne-



Figure 2. Molecular structure of complex **1d**. The hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Lu–N1 2.257(3), Lu–N2 2.275(3), Lu–N3 2.218(3), Lu–N4 2.250(3), Lu–C111 2.719(4), Lu–C211 2.666(4), Lu–C212 2.711(4), Lu–C311 2.733(4), Lu–C411 2.710(4), N1-Lu-N2 122.26(12), N1-Lu-N3 99.50(12), N2-Lu-N3 103.79(12), N1-Lu-N4 111.61(12), N2-Lu-N4 100.71(11), N3-Lu-N4 120.12(11).

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Figure 3. Molecular structure of complex **3a**. The hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): Yb–N1 2.243(5), Yb–N2 2.260(4), Yb–N3 2.255(4), Yb–N4 2.252(5), Yb–C111 2.695(6), Yb–C112 2.804(5), Yb–C211 2.682(6), Yb–C212 2.739(5), Yb–C311 2.690(5), Yb–C312 2.776(6), Yb–C411 2.675(6), Yb–C412 2.748(5), N1-Yb-N2 121.43(17), N1-Yb-N3 101.83(17), N2-Yb-N3 103.79(16), N1-Yb-N4 106.01(17), N2-Yb-N4 102.96(18), N3-Yb-N4 122.31(16).



Figure 4. Molecular structure of complex **3c**. The hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Yb–N1 2.263(4), Yb–N2 2.249(4), Yb–N3 2.239(4), Yb–N4 2.236(4), Yb–C311 2.718(5), Yb–C312 2.857(5), Yb–C411 2.774(5), Yb–C412 2.893(6), N1-Yb-N2 120.08(16), N1-Yb-N3 101.24(16), N2-Yb-N3 108.34(19), N1-Yb-N4 109.03(18), N2-Yb-N4 99.67(17), N3-Yb-N4 119.66(17).

odymium also contains four nitrogen atoms.^[32] In the lutetium analogue (1d) the values of the Lu-N bond lengths (2.218(3), 2.257(3), 2.275(3), 2.250(4) Å) are close to those reported for octaethylporphyrinato [{(Et₂C₄NCH₂)₄}LuCH- $(SiMe_3)_2$] (2.356(7), 2.263(6), 2.296(7), 2.256(6) Å)^[33] and pyrazolato $[{(Me_3C)_2C_3N_2}_3Lu(NC_5CMe_3)]$ (2.294(4),2.299(4), 2.300(4), 2.371(4) Å) complexes.^[34] The lanthanide atom in both 1c and 1d has a formal coordination number of four, which is very low for these elements. The presence in complexes 1c,d of the short contacts between the metal atoms and the carbon atoms in the ipso and ortho positions to the amido groups (1c: 2.770(4)-2.842(3) Å; 1d: 2.666(4)-2.733(4) Å), which are comparable to the Ln-C distances reported for the lanthanide π complexes [Nd(η^6 -C₆H₅CH₃)-

(AICl₄)₃] (2.799(1)–2.902(1) Å)^[35] and [[2,6-(C₆H₅)₂C₆H₃O]₃Lu] (2.787(8)–3.087(12) Å),^[36] probably reflects a η^1, η^2 interaction of the Ln^{III} atoms with the aromatic rings of the binaphthyl ligands. The average Yb–N distances in complexes **3a** and **3c** are 2.246(4) and 2.252(4) Å, respectively, and do not differ drastically from those observed in **1a**; evidently, the lanthanide–nitrogen bond lengths in this class of compounds are not dramatically influenced by the steric bulk of the hydrocarbyl radicals bound to the nitrogen atoms.

Catalytic tests: These new ionic lanthanide amides have been evaluated as catalysts for the hydroamination/cyclization of 1-(aminomethyl)-1-allylcyclohexane (4, Scheme 3).



Scheme 3. Hydroamination/cyclization of 1-(aminomethyl)-1-allylcyclohexane (4). Cat* = 1 a-d and 3a-c.

All the reactions were performed in C_6D_6 at room temperature. The complexes obtained by metathetic reactions of anhydrous LnCl₃ with two equivalents of Li₂[(*R*)-C₂₀H₁₂N₂-(C₁₀H₂₂)] were first tested and compared in terms of activity and enantioselectivity for the formation of the corresponding spiropyrrolidine **5**. The results obtained by varying the lanthanide atom are reported in Table 1.

Table 1. The effect of the metal center on the activity and enantioselectivity of the catalyst in the intramolecular hydroamination reaction.

Entry	Catalyst	Ln	Catalyst ratio [%]	Reaction time [h]	Conversion [%]	ee [%]
1	1a	Yb	3.5	1.5	87	41
2	1b	Sm	5	2	78	24
3	1c	Nd	7	3	84	1
4	1 d	Lu	17	3	91	16

Catalysts prepared from neodynium and lutetium allowed the transformation of the unsaturated amine with high conversion in a reaction time of 3 h by using higher catalyst ratios than with the corresponding ytterbium derivative (see entries 3,4 relative to entry 1). Neodynium afforded racemic spiropyrrolidine, whereas the lutetium amide complex led to the expected product with 16% *ee* (entry 4).

As using ytterbium led to the best results, further variations were performed on the complex's amide ligands by introducing different substituents on the nitrogen atom. Ligands with sterically more and less hindered radicals relative to neopentyl were synthesized, and the corresponding ytterbium catalysts were tested in the same intramolecular hydroamination reaction. The results are reported in Table 2.

Table 2.	The	effect	of 1	the	N-substitue	nt on	the	ligand	on	activity	and
enantios	electi	ivity of	the	int	ramolecular	hydro	amiı	nation r	eact	tion.	

Entry	Catalyst	Substituent	Catalyst ratio [%]	Reaction time [h]	Conversion [%]	ee [%]
1	1 a ^[a]	CH ₂ - <i>t</i> Bu	3.5	1.5	87	41
2	3 a ^[a]	CH ₂ - <i>i</i> Pr	3	1.5	98	9
3	3 b ^[a]	CH ₂ -Ph	7	0.5	100	12
4	3 c ^[a]	<i>i</i> Pr	5	18	14	49
5	3 c ^[b]	iPr	5	48	67	70
6	3 c ^[b,c]	<i>i</i> Pr	5	144	100	66

[a] Recrystallized complex. [b] Complex used without any purification. [c] Reaction performed on a preparative scale (see the Experimental Section).

Sterically less hindered substituents such as the iBu or Bn functionalities led to very active but less enantioselective catalysts than 1a (see entries 2,3 relative to entry 1). The best results in terms of enantioselectivity were obtained with the introduction of *i*Pr groups on the nitrogen atoms, as an ee value of 49% was measured for the spiropyrrolidine 5, although this catalyst gave a poor conversion (14%) after 18 h reaction time (entry 4). These first experiments (entries 1-4) were run with catalysts in pure form, that is, after recrystallization. As complex 3c led to nonreproducible results in terms of activity in the catalytic reaction after a few days storage, it was also used directly in catalytic tests without any purification. To our delight, under similar conditions (5 mol% nonisolated catalyst, estimated on the basis of NMR signal integration), spiropyrrolidine 5 was obtained with 70% ee (entry 5). Total conversion was obtained after a reaction time of 6 days (entry 6); in this case, the product was isolated and its enantiopurity was measured by GC analysis of amides prepared with Mosher's chloride [37] and by optical rotation. Comparison of entries 5 and 6 showed that there was no measurable variation of enantiomeric excess during the reaction course.

Conclusion

A new family of ionic lanthanide amides based on (R)-1,1'binaphthyl-2,2'-bis(alkylamine) ligands with various lanthanide and N-alkyl substituents has been synthesized and characterized. All the complexes have similar structures containing a complex anion with a discrete $[Li(thf)_4]^+$ as counterion. Although X-ray crystal structure studies indicated that the cation is not coordinated to the ligand, we will further study the possible influence of its nature on the activity and enantioselectivity of the corresponding catalyst, as its behavior in solution could be different. These lanthanide amides are coordinated by 1,1'-binaphthyl-2,2'-bis(alkylamine), a family of asymmetric ligands that are easily prepared and that allow the bulkiness and electronic properties to be tuned. The present studies have allowed the enantiomeric excess for the cyclization of 1-(aminomethyl)-1-allylcyclohexane (4) into spiropyrrolidine 5 to be increased up to 70%, a result showing that these catalysts are highly promising for enantioselective intramolecular hydroamination. We are continuing our efforts to optimize the asymmetric inductions and to widen the scope of substrates for hydroamination reactions.

Experimental Section

General remarks: All procedures were performed under vacuum by using standard Schlenk and glove-box techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl prior to use. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or CaH2. Deuterated benzene was dried with sodium benzophenone ketyl and vacuum-transferred. Anhydrous LnCl₃ was purchased from Aldrich. All other commercially available chemicals were used after the appropriate purification. Bruker AM 250 and Bruker DRX 400 NMR spectrometers (operating at 250 and 400 MHz, respectively) were used for recording the NMR spectra. Chemical shifts for ¹H and ¹³C spectra were referenced internally according to the residual solvent resonances and are reported relative to tetramethylsilane. IR spectra were recorded on a Specord M80 instrument as Nujol mulls. Lanthanide metal analyses were carried out by complexometric titration. Elemental analyses were performed by the Microanalytical Laboratory of the Institute of Organometallic Chemistry of the Russian Academy of Sciences. Optical rotations were measured with a Perkin-Elmer 341 polarimeter.

Synthesis of [Li(thf)₄][Nd{(R)-C₂₀H₁₂N₂(C₁₀H₂₂)]₂] (1c): NdCl₃ (0.044 g, 0.175 mmol) was slowly added to a solution of Li₂[(R)-C₂₀H₁₂N₂(C₁₀H₂₂)] (0.153 g, 0.350 mmol) in THF (5 mL) at 20 °C under vigorous stirring. The reaction mixture was stirred for 3 h, THF was evaporated in vacuo, and the resulting solid was extracted with toluene (15 mL). The extracts were filtered, toluene was evaporated, and the solid residue was dissolved in THF (1 mL). Slow condensation of hexane in the THF/complex solution at 20 °C resulted in brownish-orange crystals of 1c (0.166 g, 74%). IR (KBr, Nujol): \tilde{v}=3030 (w), 1610 (s), 1600 (s), 1500 (s), 1340 (s), 1315 (s), 1280 (s), 1250 (m), 1200 (m), 1150 (m), 1025 (w), 810 (s), 745 (s), 725 cm⁻¹ (s); elemental analysis calcd (%) for C₇₆H₁₀₀Lin₄MdO₄ (1284.8): C 71.04, H 7.78, Nd 11.22; found: C 70.62, H 8.32, Nd 11.64.

Synthesis of [Li(thf)₄][Lu{(R)-C₂₀H₁₂N₂(C₁₀H₂₂)}₂] (1d): LuCl₃ (0.097 g, 0.344 mmol) was slowly added to a solution of $Li_2[(R)-C_{20}H_{12}N_2(C_{10}H_{22})]$ (0.300 g, 0.688 mmol) in THF (5 mL) at 20°C under vigorous stirring. The reaction mixture was stirred for 3 h, THF was evaporated in vacuo, and the resulting solid was extracted with toluene (20 mL). The extracts were filtered, toluene was evaporated, and the solid residue was dissolved in THF (2 mL). Slow condensation of hexane in the THF/complex solution at 20°C resulted in yellow crystals of 1d (0.276 g, 61%). ¹H NMR (200 MHz, CD_2Cl_2): $\delta = 7.70$ (d, J = 9.1 Hz, 4H), 7.53 (d, J = 7.8 Hz, 4H), 7.32 (d, J=9.2 Hz, 4H), 6.89 (dd, J=7.5 Hz, 4H), 6.73 (brs, 4H), 6.42 (d, J=7.7 Hz, 4H), 3.58 (brs, 24H; THF and CH₂), 1.91 (s, 16H; THF), 0.43 ppm (s, 36 H); IR (KBr, Nujol): v=3030 (w), 1610 (s), 1600 (s), 1545 (m), 1500 (s), 1440 (s), 1340 (s), 1325 (s), 1275 (s), 1250 (m), 1215 (m), 1160 (m), 1040 (m), 930 (w), 880 (w), 815 (s), 745 $\rm cm^{-1}$ (s); elemental analysis calcd (%) for C76H100LiLuN4O4 (1315.6): C 69.38, H 7.60, Lu 13.29; found: C 69.77, H 8.00, Lu 12.99.

Synthesis of [Li(thf)₄][Yb{(*R*)- $C_{20}H_{12}N_2(C_8H_{18})]_2$]-0.5THF (3a): YbCl₃ (0.048 g, 0.171 mmol) was slowly added to a solution of Li₂[(*R*)- $C_{20}H_{12}N_2$ -(C_8H_{18})] (0.140 g, 0.342 mmol) in THF (5 mL) at 20 °C under vigorous stirring. The reaction mixture was stirred for 3 h, THF was evaporated in vacuo, and the resulting solid was extracted with toluene (15 mL). The extracts were filtered, toluene was evaporated, and the solid residue was dissolved in THF (2 mL). Slow condensation of hexane in the THF/complex solution at 20 °C resulted in red crystals of **3a** (0.119 g, 54%). IR (KBr, Nujol): $\tilde{\nu}$ =3030 (w), 1625 (s), 1605 (s), 1575 (s), 1435 (s), 1375 (s), 1345 (s), 1315 (s), 1300 (s), 1250 (s), 1225 (m), 1160 (m), 1100 (w), 1025 (m), 925 (w), 750 cm⁻¹ (s); elemental analysis calcd (%) for $C_{74}H_{96}LiN_4O_{45}Yb$ (1293.6): C 68.71, H 7.42, Yb 13.37; found: C 68.50, H 6.99, Yb 13.59.

Synthesis of [Li(thf)₄][Yb{(*R***)-C₂₀H₁₂N₂(C₁₄H₁₄)₂] (3b): YbCl₃ (0.072 g, 0.257 mmol) was slowly added to a solution of Li₂[(***R***)-C₂₀H₁₂N₂(C₁₄H₁₄)] (0.245 g, 0.515 mmol) in THF (5 mL) at 20 °C under vigorous stirring. The reaction mixture was stirred for 12 h, THF was evaporated in vacuo, and the resulting solid was extracted with toluene (20 mL). The extracts were filtered, toluene was evaporated, and the solid residue was dissolved in THF (5 mL). Slow condensation of hexane in the THF/complex solution at 20 °C resulted in a brownish-green microcrystalline solid 3b** (0.187 g, 52 %). IR (KBr, Nujol): \vec{v} =3030 (w), 1625 (s), 1605 (s), 1580 (s), 1505 (m), 1425 (s), 1345 (s), 1300 (w), 1150 (m), 1305 (s), 1025 (m), 815 (s), 710 (s), 700 cm⁻¹ (m); elemental analysis calcd (%) for C₈₄H₈₄LiN₄O₄Yb (1392.92): C 72.43, H 6.03, Yb 12.41; found: C 72.01, H 6.47, Yb 12.91.

Synthesis of [Li(thf)₄][Yb{(*R***)-C₂₀H₁₂N₂(C₆H₁₄)₂] (3c): YbCl₃ (0.064 g, 0.228 mmol) was slowly added to a solution of Li₂[(***R***)-C₂₀H₁₂N₂(C₆H₁₄)] (0.174 g, 0.457 mmol) in THF (5 mL) at 20 °C under vigorous stirring. The reaction mixture was stirred for 3 h, THF was evaporated in vacuo, and the resulting solid was extracted with toluene (15 mL). The extracts were filtered, toluene was evaporated, and the solid residue was dissolved in THF (2 mL). Slow condensation of hexane in the THF/complex solution at 20 °C resulted in red crystals of 3c** (0.187 g, 68%). IR (KBr, Nujol): $\bar{\nu}$ = 3030 (w), 1615 (s), 1600 (s), 1500 (s), 1425 (s), 1375 (s), 1350 (s), 1325 (s), 1305 (s), 1280 (s), 1250 (m), 1215 (m), 1175 (m), 1070 (w), 1040 (m), 925 (w), 880 (w), 815 (s), 745 cm⁻¹ (s); elemental analysis calcd (%) for C₆₈H₈₄LiN₄O₄Yb (1201.4): C 67.98, H 6.99, Yb 14.39; found: C 67.42, H 6.94, Yb 14.77.

Catalytic test procedures

NMR-spectroscopy-scale intramolecular hydroaminations of 1-(aminomethyl)-1-allylcyclohexane (4) and determination of enantiomeric excess values were performed with catalysts 1c, 1d (entries 3 and 4, Table 1), and 3a-c as isolated crystals (entries 2–4, Table 2).

Typical procedure: Inside a glove box, a solution of 1-(aminomethyl)-1allyl-cyclohexane (4, 0.02 g, 0.131 mmol) in C_6D_6 (0.5 mL, dried over mo-

lecular sieves) was added to the complex (see Tables 1 and 2 for catalytic ratios) charged in an NMR tube equipped with a teflon stopcock. After disappearance of the olefinic protons as monitored by NMR spectroscopy, CH₂Cl₂ was added and amine 5 was transformed into the corresponding amide by reaction with Mosher's chloride. The reaction mixture was diluted with CH2Cl2 (2 mL) and treated with Et3N (100 µL), 4-dimethylaminopyridine (20 mg), and (R)-(-)- α -methoxy- α -(trifluoromethyl)phenylacetyl chloride (Mosher's chloride, 30 µL). After being stirred for 2 h at room temperature, the mixture was washed with saturated NH₄Cl solution and extracted with CH2Cl2. After drying, the crude product dissolved in diethyl ether was injected onto a GC DB-1 capillary column (80°C, rise of 10°Cmin⁻¹, 200°C for 10 min, rise of 10°Cmin⁻¹, 250°C for 10 min; injector temperature 250 °C, detector temperature 250 °C). The retention times of diastereoisomeric amides formed from the cyclized amine 3-methyl-2-aza-spiro[4,5]decane (5) and of the amide formed from the nonreacted 1-(aminomethyl)-1-allyl-cyclohexane (4) are 21.6, 22.4, and 23.15 min, respectively. Enantiomeric excesses of 3methyl-2-aza-spiro[4,5]decane (5) and GC yields of the cyclized product were determined by integration of these three peaks.

In situ preparation of catalyst **3 c**: YbCl₃ (0.034 g, 0.12 mmol) was slowly added to a solution of $\text{Li}_2[(R)-\text{C}_{20}\text{H}_{12}\text{N}_2(\text{C}_6\text{H}_{14})]$ (0.091 g, 0.24 mmol) in THF (5 mL) at 20 °C under vigorous stirring. The reaction mixture was stirred for 3 h and THF was evaporated in vacuo to yield a greenish-brown solid (**3c**) that was used without further purification.

Preparative enantioselective hydroamination/cyclization of 1-(aminomethyl)-1-allylcyclohexane (4, see Table 2, entry 6): Inside a glove box, a solution of 1-(aminomethyl)-1-allyl-cyclohexane (4, 0.122 g, 0.8 mmol) in C_6D_6 (2 mL, dried over molecular sieves) was added to the complex **3c** (0.048 g, 0.04 mmol). After the reaction mixture was stirred for 6 days at room temperature, the solvent was evaporated and the residue was distillated in a Kugelrohr apparatus (b.p. 175 °C, 0.1 mbar) to afford the spiropyrrolidine **5** (33 % yield). ¹H NMR (CDCl₃): δ =3.08 (m, 1H), 2.71 (d, J=11 Hz, 1H), 2.52 (d, J=11 Hz, 1H), 2.14 (brs, 1H), 1.69 (dd, J=11,

	1c	1d	3a	3c
formula	C76H100LiN4NdO4	C76H100LiLuN4O4	C74H96LiN4O4.50Yb	C68H84LiN4O4Yb
$M_{ m r}$	1284.84	1315.57	1293.58	1201.42
<i>T</i> [K]	180	180	180	180
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a [Å]	11.114(5)	25.200(5)	10.480(5)	10.529(5)
<i>b</i> [Å]	25.073(5)	11.074(5)	17.846(5)	17.796(5)
<i>c</i> [Å]	25.236(5)	24.954(5)	37.228(5)	35.282(5)
α [°]	90°	90°	90°	90°
β [°]	90°	90°	90°	90°
γ [°]	90°	90°	90°	90°
$V[Å^3]$	7032(4)	6964(4)	6963(4)	6611(4)
Z	4	4	4	4
$\rho_{\rm calcd} [{\rm mg}{\rm m}^{-3}]$	1.213	1.255	1.234	1.207
$\mu [\mathrm{mm}^{-1}]$	0.788	1.467	1.392	1.461
F(000)	2716	2760	2708	2500
crystal size [mm ³]	$0.60 \times 0.50 \times 0.25$	$0.52 \times 0.48 \times 0.26$	$0.45 \times 0.15 \times 0.10$	$0.60 \times 0.55 \times 0.34$
θ range [°]	1.807-24.186	2.449-26.202	1.999-24.144	2.076-26.078
index ranges	$-12 \le h \le 12$,	$-31 \le h \le 30,$	$-12 \le h \le 12$,	$-12 \le h \le 12,$
-	$-28 \le k \le 28,$	$-13 \le k \le 13$,	$-20 \le k \le 20,$	$-20 \le k \le 21,$
	-28 < l < 29	$-30 \le l \le 30$	$-42 \le l \le 42$	-43 < l < 43
reflections collected	57 599	69315	38353	54819
independent reflections	$11176 (R_{int} = 0.04)$	$13687 (R_{int} = 0.05)$	$10980 \ (R_{\rm int} = 0.06)$	$12544 \ (R_{\rm int} = 0.06)$
max/min transmission	0.821/0.616	0.683/0.478	0.869/0.747	0.609/0.428
data/restraints/parameters	10015/0/672	11 920/0/672	8294/5/656	9737/2/600
goodness-of-fit on F	1.0539	1.0723	1.1229	1.0610
final R indices $(I > 3\sigma(I))$	$R_1 = 0.0317, R_w = 0.0369$	$R_1 = 0.0317, R_w = 0.0368$	$R_1 = 0.0342, R_w = 0.0365$	$R_1 = 0.0443, R_w = 0.0451$
R indices (all data)	$R_1 = 0.0349, R_w = 0.0370$	$R_1 = 0.0380, R_w = 0.0377$	$R_1 = 0.0459, R_w = 0.0387$	$R_1 = 0.0548, R_w = 0.0452$
Flack parameters	0.014(9)	0.016(6)	0.013(9)	0.017(9)
largest diff. peak/hole [e Å ⁻³]	1.37/-0.87	1.50/-1.65	1.34/-0.70	2.04/-3.34

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 $J=7 \text{ Hz}, 1 \text{ H}), 1.32 \text{ (m, 10 H)}, 1.07 \text{ (d, } J=7 \text{ Hz}, 3 \text{ H}), 0.93 \text{ ppm (dd, } J=10, J=9 \text{ Hz}, 1 \text{ H}); {}^{13}\text{C} \text{ NMR (CDCl}_3, 20 °\text{C}): \delta=59.30, 54.42, 47.84, 44.37, 39.00, 37.62, 26.46, 24.24, 24.06, 21.71 \text{ ppm}; \text{ IR (NaCl, CCl}_4): <math>\tilde{\nu}=3854 \text{ (w)}, 3747 \text{ (w)}, 3672 \text{ (w)}, 3650 \text{ (w)}, 3630 \text{ (w)}, 2928 \text{ (s)}, 2856 \text{ (m)}, 1450 \text{ (w)}, 1376 \text{ cm}^{-1} \text{ (w)}; \text{ MS (electrospray): } m/z \text{ (\%): } 154.2 \text{ (100) } [M+\text{H}]^+; [\alpha]_{\text{D}}^{20}=+28 (c=1, \text{ CHCl}_3); 66\% \text{ enantiomeric excess.}$

Crystal structure determinations: Single crystals for the four compounds were mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of the diffractometer. All data were collected on a Stoe IPDS diffractometer operating with monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$).

The structures were solved by direct methods (SIR92)^[38] and refined by full-matrix least-squares procedures on F using the CRYSTALS program.^[39] A semiempirical absorption correction based on equivalent reflections was applied for all four compounds. All H atoms were introduced into the calculation in idealized positions (d(CH) = 1.0 Å) and treated as riding models. The $[{\rm Li}({\rm thf})_4]$ cations and the THF solvent molecule were refined isotropically. The weighting scheme used in the last refinement cycles was $w = w' [1 - [\Delta F/6\sigma(F_0)]^2]^2$, in which $w' = 1/\sum_{1}^{n} A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ in which x is $F_c/F_c(\max)$.^[40] Models reached convergence with $R = \Sigma(||F_0| - |F_c||)/$ $\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o^2)]^{1/2}$. Final refinements allowed the fraction contribution of the inverted enantiomer to vary,[41] with the Flack parameter quoted being the refined value of this contribution. Crystal data and refinement parameters are shown in Table 3. The views of the molecules in Figures 1-4 were produced with ORTEP III for Windows.^[42]

CCDC-256428–CCDC-256431 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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