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Enantioselective Intramolecular Hydroamination Catalyzed by Lanthanide Ate Complexes Coordinated by *N*-Substituted (*R*)-1,1′-Binaphthyl-2,2′-diamido Ligands†

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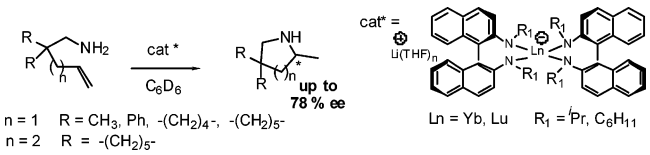
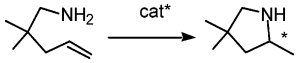


Ytterbium and lutetium ionic complexes derived from enantiopure substituted (*R*)-binaphthylamine ligands, of the general formula $[Li(THF)_n][Ln[(R)\text{-}C_{20}H_{12}(NR)_2]_2]$, have been investigated for the hydroamination/cyclization of several aminopentenes and an aminohexene. Complexes with isopropyl or cyclohexyl substituents on nitrogen atoms were found to be efficient catalysts under mild conditions for the formation of *N*-containing heterocycles with enantiomeric excesses up to 78%.

Intramolecular hydroamination of alkenes is an atom economic process leading to the formation of nitrogen heterocycles that are found in numerous biologically active compounds.[1] Since the pioneering work of Marks and co-workers on the activity of lanthanocene for intramolecular hydroaminations,[2] the interest for these reactions has increased, and some recent reviews have been published.[3] Molander and Pack have furthermore explored this efficient process toward the rapid synthesis of pharmaceutically active molecules.[4]

SCHEME 1. Intramolecular Hydroamination Test Reaction



The first enantioselective intramolecular hydroamination of alkenes, catalyzed by *ansa* lanthanocene complexes substituted by a menthyl or neomenthyl group, has been reported by Marks et al.[5] These catalysts afforded the pyrrolidine depicted in Scheme 1 with up to 74% ee. This transformation is now considered as the test hydroamination/cyclization to evaluate the efficiency of new catalysts.[3b]

Enantioenriched piperidines (up to 67% ee) were obtained with similar lanthanide complexes, including an octahydrofluorenyl instead of a tetramethylcyclopentadienyl group.[6] Livinghouse and co-workers described in 2001 the activity of lanthanide tris-silylamides, $Ln[N(TMS)_2]_3$, for the cyclization of aminopentenes into racemic pyrrolidines.[7] This work opened the way to the synthesis of nonmetallocene lanthanide complexes as catalysts for the intramolecular hydroamination of olefins. Scott et al. thus prepared chiral bisaryloxide lanthanide complexes from salicylaldimine-type ligands that catalyzed the test reaction at 70 °C with enantiomeric excesses as high as 60%.[8] A new chiral zirconium alkyl cation coordinated by a similar aminobiphenoxide ligand proved to be an enantioselective catalyst for the hydroamination/cyclization of secondary amines (up to 82% ee).[9] By the reaction of lanthanide amides with C_2-symmetric bisoxazolines, Marks et al. prepared enantioselective catalysts active at room temperature for the test cyclization (67% ee).[10] Hultzsch et al. synthesized various sterically hindered lanthanum and yttrium biphenolate and binaphtholate complexes.[11] 3,3′-Trisalkylsilylbinaphtholate complexes with a

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† Dedicated to Professor H. B. Kagan on the occasion of his 75th birthday.

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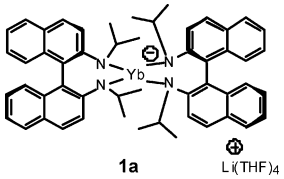

FIGURE 1. Structure of catalyst **1a**, $[Li(THF)_4][Yb[(R)\text{-}C_{20}H_{12}N_2\text{-}(C_6H_{14})]_2]$.

coordinating alkyl ligand revealed indeed highly active catalysts for intramolecular hydroamination[11b] and catalyzed the cyclization of the aminopentene depicted in Scheme 1 with up to 53% ee. To the best of our knowledge, the highest asymmetric induction for intramolecular hydroamination to date (87% ee for the test reaction) was obtained by the group of Livinghouse with yttrium bisthiophenolate catalysts prepared in situ.[12] They showed, however, moderate activities because reactions were performed at 60 °C.

In our ongoing research we focused on the preparation of lanthanide catalysts coordinated by chiral amido ligands for intramolecular hydroamination. We selected binaphthylamine, which had never been used as a chiral ligand for lanthanides, in contrast to binaphthol.[13,14] We have previously reported the preparation of a new family of lanthanide *ate*-complexes $[Li(THF)_4]$ $[Ln[(R)\text{-}C_{20}H_{12}N_2(C_{10}H_{22})]_2]$ (Ln = Yb, Sm, Nd, Lu), **1**, derived from chiral disubstituted (*R*)-binaphthylamido ligands.[15a] In these compounds, coordination of two (*R*)-binaphthylamine ligands to the lanthanide atom resulted in the formation of a complex anion associated to a discrete counterion $(Li(THF)_4)^+$. Their activity and enantioselectivity for intramolecular hydroamination were evaluated on the cyclization of *C*-(1-allyl-cyclohexyl)-methylamine, **2**. The ytterbium complex was found to give the best results with the formation of the spiropyrrolidine, **3**, with 41% ee. We further investigated the variation of the nitrogen substituent and obtained spiropyrrolidine **3** with up to 70% enantiomeric excess with ytterbium complex **1a** containing (*R*)-1,1′-binaphthyl-2,2′-bis(*iso*-propylamido) ligands (see Figure 1).[15b] In view of a better comparison of the efficiency of complex **1a** with reported catalysts, we present here our results concerning the enantioselective hydroamination starting from various aminoolefins using new ytterbium or lutetium catalysts bearing cyclohexyl groups on nitrogen atoms.

We first examined the reaction of 2,2-dimethyl-pent-4-enylamine, **4**, in the presence of catalyst **1a**, which indeed promoted the cyclization at room temperature. The corresponding pyrrolidine, **5**, was obtained with 69% ee, albeit with a low conversion after a one week reaction time (see Table 1, entry 3). The activity of this catalyst could be increased by performing the reaction at 60 °C, yielding the pyrrolidine in 2 days with a full conversion however together with a loss in enantioselectivity (42% ee, Table 1, entry 4). The cyclization of 2,2-diphenyl-pent-4-enylamine, **6**, at room temperature was achieved in only 24 h (Table 1, entry 5). The enantiomeric analysis of the resulting pyrrolidine, **7**, was performed using proton-decoupled carbon-13 NMR in a PBLG/DMF-d_7 liquid crystal.[16] The ee measured on the aromatic carbons (Figure 2) was 50%.

TABLE 1. Intramolecular Hydroamination Reaction with $[Li(THF)_4]$ $[Yb[(R)\text{-}C_{20}H_{12}N_2(C_6H_{14})]_2]$, 1a

entry	substrate	T^a (°C)	cat. ratio (mol %)	t	product	conv (%)	ee[b] (%)
1	 **2**	25	5	48 h	 **3**	67	70
2		25	5	6 d		100	66
3	 **4**	25	10	7 d	 **5**	49	69
4		60	10	46 h		98	42
5	 **6**	25	10	24 h	 **7**	100	50[c]

[a] Reactions were performed in C_6D_6. [b] Enantiomeric excesses were determined by GC analysis of Mosher amides. [c] Enantiomeric excess determined by NMR analysis in chiral liquid crystals.

It is obvious that the structure of the substituents placed on the aminopentene chain has a significant influence on the reaction rate. Thus, the presence of a *gem*-dimethyl group in the backbone is known to facilitate the cyclization by both a combination of Thorpe−Ingold effect (decrease of the angle at the *gem*-dimethyl group) and a reactive rotamer effect (increase in the population of the more reactive syn rotamer).[17] The *gem*-diphenyl and cyclohexyl groups contributions in hydroamination reactions are more important compared to the *gem*-dimethyl effect, because for substrates **2** and **6**, a large increase in the reaction rate is observed.

We then turned our efforts toward the preparation of a more active catalyst. As ytterbium led in our previous attempts to the most enantioselective complex,[15b] we decided to prepare by the same route a new complex **1b** bearing cyclohexyl substituents on the nitrogen atoms (see Scheme 2). To gain insight into the effect of the electronic factor on the catalysts efficiency and enantioselectivity, we simultaneously prepared the analogous lutetium complex **1c** with an ionic radius nearly identical to that of ytterbium [Yb(III) 1.008 Å, Lu(III) 1.001 Å] and possessing one additional electron.[18]

The cyclohexyl-substituted binaphthyldiamine ligand was prepared in 73% yield according to a known procedure.[19] Ytterbium and lutetium complexes **1b** and **1c** were synthesized by the previously described method.[15] After reacting 2 equivalents of the dilithium salt of the ligand with $YbCl_3$ or $LuCl_3$ in THF at room temperature (Scheme 2), solvent was removed. The complexes were used either without further purification or after removal of the LiCl salt by extraction with toluene. Complexes **1b** and **1c** were isolated in 81 and 94% yield, respectively.

The hydroamination/cyclization of *C*-(1-allyl-cyclohexyl)-methylamine **2** catalyzed by complex **1b** and **1c** was first investigated, and the results are summarized in Table 2. With **1b**, the pyrrolidine **3** was obtained with nearly quantitative

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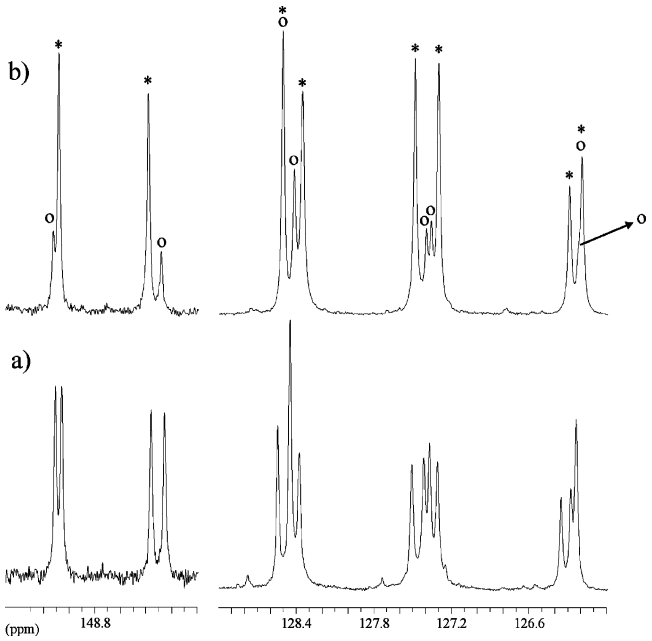
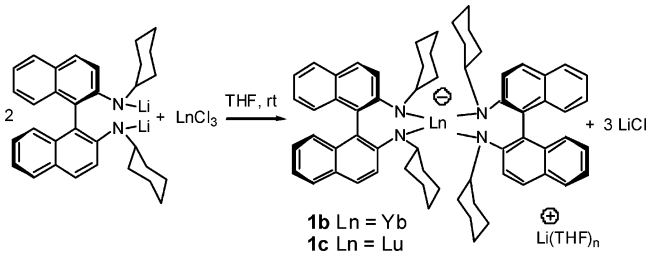


FIGURE 2. Aromatic region of ^{13}C-{^{1}H} NMR spectrum of (a) a racemic mixture of pyrrolidine **7** and (b) pyrrolidine **7** obtained using catalyst **1a** in PBLG/DMF-d_7 liquid crystal at $T = 310$ K. Peaks marked with an asterisk (∗) belong to the major enantiomer, and peaks marked with (o) belong to the minor enantiomer.

SCHEME 2. Synthesis of Complexes 1b and 1c, [Li(THF)$_n$][Ln[(*R*)-$C_{20}H_{12}N_2(C_{12}H_{22})]_2$], Ln = Yb and Lu



conversion (57% isolated yield) and 65% ee after 18 h reaction time (Table 2, entry 1). This catalyst thus seemed more active than the analogous complex **1a** with isopropyl substituents, whereas no important variation in enantioselectivity was observed. By using an isolated complex, similar enantioselectivity was obtained (68% ee) but with a decrease in activity (Table 2, entry 2).[20] The in situ prepared catalyst was active enough to allow the reaction to be run at 0 °C. Under those conditions, the spiropyrrolidine **3** was isolated after 4 days in 65% yield (88% conversion) and with an enantiomeric excess of 76% (Table 2, entry 3). The lutetium catalyst **1c** afforded similar results with this substrate at room temperature but did not lead to a significant increase of enantioselectivity when the reaction was carried out at 0 °C (Table 2, entries 4 and 5). Complex **1b** led interestingly to a higher conversion than **1a** for the transformation of 2,2-dimethyl-pent-4-enylamine **4** (77% in one week at room temperature) and to a slight increase in the enantiomeric excess (73%; Table 2, entries 6 and 7). Complex **1c** proved to be more active than **1b** but less enantioselective (Table 2, entry 8). To check the versatility of those new catalysts, we tested the hydroamination of two other aminopentenes, namely, the corresponding *gem*-diphenyl compound **6** and the new *C*-(1-allyl-cyclopentyl)-methylamine derivative, **8**. As observed with catalyst **1a**, cyclization of the *gem*-diphenyl substrate was very fast in comparison with that of other substrates: total conversion was observed within 21 h with both catalyst **1b** and catalyst **1c** using low catalytic ratios (3% for **1b**, 2% for **1c**; Table 2, entries 9 and 11). Similar enantiomeric excesses (about 60%) were obtained. The reaction performed at 0 °C allowed the isolation (77% yield) of pyrrolidine **7** with an enantiomeric excess of 66% (Table 2, entry 10). To the best of our knowledge, this value is the highest reported to date for this substrate. The replacement of isopropyl substituents by cyclohexyl radicals in the ligand structure thus yielded significant improvements in both rate and asymmetric induction.

In the case of substrate **8**, 4 days were necessary to perform the cyclization with high conversion (83%) and yield (57% isolated product; Table 2, entry 12). To our delight, the reaction performed at low temperature (0 °C, 6 days, 36% conversion) led to the expected product, **9**, with the highest enantiomeric excess obtained to date with these new ate-complexes. The novel spiropyrrolidine **9** was obtained with 78% ee under those conditions (Table 2, entry 13). Furthermore, the ytterbium catalyst **1b** showed a very high stability, because for this reaction, the conversion reached 74% after two weeks with a similar high enantioselectivity (Table 2, entry 14). The use of lutetium catalyst **1c** led to analogous conversion than did **1b** at room temperature but to small amounts of pyrrolidine when the reaction was performed at 0 °C.

The hydroamination/cyclization reactions of aminohexenes into piperidines are challenging transformations. They indeed often require higher reaction temperatures, and they afford the expected products with lower enantiomeric excesses than the analogous five-membered rings.[3] We selected the aminohexene, **10**, as a test substrate for the synthesis of the corresponding spiropiperidine, **11**. By using the ytterbium ate complex **1b** at room temperature, no reaction was observed. Cyclization occurred, however, with total conversion after a 66 h reaction time at 60 °C (Scheme 3). The new spiropiperidine was isolated in high yield with a promising enantiomeric excess of 45%.

Ytterbium and lutetium ate complexes **1b** and **1c**, coordinated by *N*-substituted cyclohexyl binaphthylamine, displayed higher activities and selectivities than ytterbium complexes coordinated by *N*-substituted isopropyl ligands. The comparison of ytterbium and lutetium catalysts **1b** and **1c** indicated that lutetium was a more active catalyst, affording, however, slightly lower levels of enantioselectivity. It should be emphasized that the lutetium catalyst **1c** was always used without purification, because it proved to be poorly stable after crystallization. For all aminopentenes, the cyclization proceeded with high conversions at room temperature, and enantiomeric excesses of the pyrrolidines exceeded 60% in all cases. A temperature effect was observed by obtaining an increased enantioselectivity when the reactions were performed at 0 °C. We have successfully been able to isolate new *N*-containing heterocycles, and we assume our catalysts compete favorably with other previously described systems, because they are readily prepared from commercially available precursors. They proved to be active under mild conditions, and up to 78% ee was furthermore obtained in the preparation of spiropyrrolidines. We are currently directing our efforts toward further optimization of our catalysts for intra-

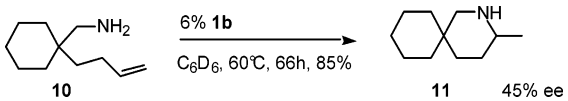
(20) This catalyst was used again after several days storage and was both less active and less enantioselective (49% conversion, 57% ee).

TABLE 2. Intramolecular Hydroamination Reaction with $[Li(THF)_n][Ln[(R)\text{-}C_{20}H_{12}N_2(C_{12}H_{22})]_2]$, Ln = Yb, 1b, Ln = Lu, 1c

entry	substrate	T^a (°C)	cat. (ratio, mol %)	t	product	% conv (isolated yield, %)	ee[b] (%)
1		25	**1b** (6)	18 h		94 (57)	65
2	 **2**	25	**1b** (10)[c]	20 h	 **3**	58	68
3		0	**1b** (10)	4 d		88 (65)	76
4		25	**1c** (8)	44 h		100	66
5		0	**1c** (10)	88 h		75	68
6	 **4**	25	**1b** (10)	48 h	 **5**	34	75
7		25	**1b** (10)	7 d		77	73
8		25	**1c** (10)	5 d		91	66
9	 **6**	25	**1b** (3)	21 h	 **7**	100	62[d]
10		0	**1b** (10)	6 d		100 (77)	66[d]
11		25	**1c** (2)	21 h		100 (34)	60[d]
12		25	**1b** (10)	4 d		83 (57)	69
13	 **8**	0	**1b** (10)	6 d	 **9**	36	78
14		0	**1b** (10)	16 d		74	77
15		25	**1c** (10)	2 d		80 (56)	68
16		0	**1c** (10)	4 d		10	75

[a] Reactions at 25 °C were performed in C_6D_6, and reactions at 0 °C were performed in toluene. [b] Enantiomeric excesses were determined by GC analysis of Mosher amides unless otherwise indicated. [c] Isolated catalyst. [d] Enantiomeric excess determined by NMR analyses in chiral liquid crystals.

SCHEME 3. Synthesis of Piperidine 11 Catalyzed by the Ytterbium Ate Complex 1b



molecular hydroamination reactions and broadening the scope of the substrates.

Experimental Section

Representative Procedure for Pyrrolidine Formation. Preparation of 3. Preparation of Complex 1b, $[Li(THF)_n]$ $[Yb[(R)\text{-}C_{20}H_{12}N_2(C_{12}H_{22})]_2]$. In an argon-filled glovebox, (*R*)-(+)-2,2′-bis(cyclohexylamino)-1,1′-binaphthyl (0.20 g, 0.44 mmol) was dissolved in hexane (10 mL) in a Schlenk flask equipped with a magnetic stirring bar. *n*-BuLi (1.6 M in hexanes, 0.56 mL, 0.89 mmol) was introduced via microsyringe, and the reaction mixture was stirred for 10 min. The solvent was removed in vacuo from the subsequent yellow suspension to afford the corresponding lithium amide salt as a yellow solid. $YbCl_3$ (0.031 g, 0.111 mmol) was added to a solution of the bislithium salt of (*R*)-(+)-2,2′-bis-(cyclohexylamino)-1,1′-binaphthyl (0.102 g, 0.222 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred until the disappearance of $YbCl_3$ (15 min), and the THF was evaporated in vacuo. The resulting solid was extracted with toluene (10 mL). The reaction mixture was centrifuged, and the filtrate was concentrated in vacuo. The product was obtained as a brown powder with 81% yield. IR (KBr, Nujol) 1609, 1589, 1495, 1460, 1420, 1377, 1338, 1285, 1246, 1149, 1027, 810, 743, 728. The solid residue was dissolved in THF (2 mL), and a slow diffusion of hexane in THF solution at 25 °C resulted in the isolation of complex **1b** as brown crystals. The crystals were washed with cold hexane and dried in vacuo at room temperature for 45 min. Anal. Calcd for $C_{72}H_{84}LiN_4O_2Yb$: C, 71.07; H, 6.90. Found: C, 69.73; H, 6.59.

Preparation of *C*-(1-allyl-cyclohexyl)-methylamine, 2. A solution of cyclohexane carbonitrile (11 mL, 99 mmol) in THF (100 mL) was slowly added to a solution of freshly prepared lithium diisopropylamine (118.6 mmol) in 150 mL of THF/hexane (50/50) at 0 °C. The reaction mixture was subsequently stirred for an additional hour, and a solution of allylbromide (9.9 mL, 113.6 mmol) in THF (20 mL) was added dropwise in 30 min. The mixture was allowed to warm to room temperature overnight. After hydrolysis and extraction with ether, the organic layers were concentrated in vacuo. The crude product was used in the following step without any purification. To a suspension of $LiAlH_4$ (3.75 g, 98.8 mmol) in ether (100 mL) at 0 °C was added dropwise a solution of *C*-(1-allyl-cyclohexyl)-nitrile in ether (20 mL) in 10 min. The reaction mixture was allowed to warm to room temperature overnight and was then hydrolyzed with water until the formation of white hydroxide aluminum salts occurred. The solid was separated from the mixture by filtration. The organic layer was dried and concentrated in vacuo, and the residue was distilled (bp = 100 °C, 3 mBar) to afford compound **2** (11.3 g, 74 mmol, 75%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (br s, 2H), 1.15−1.47 (m, 10H), 2.07 (d, J = 7.5, 2H), 2.54 (s, 2H), 4.94−5.10 (m, 2H), 5.82 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.4, 26.4, 33.2, 37.0, 39.8, 48.8, 116.7, 135.0. IR ($CHCl_3$) 1156, 1272, 1422, 1552, 1637, 2306, 2411, 2686, 2855, 2929, 2987, 3055. HRMS (EI) calcd for $C_{10}H_{19}N$, 153.1512; found, 153.1514.

Preparative-Scale Hydroamination Cyclization of 2. In an argon-filled glovebox, **2** (0.616 mmol) was dissolved in C_6D_6 (0.5 mL) and dried on 4 Å molecular sieves for 2 h. The complex **1b** (6 mol %) was introduced into a vial and dissolved in C_6D_6 (1 mL), and the aminoalkene solution was then added at 25 °C. After 18 h, the reaction mixture was quenched with CH_2Cl_2. After the evaporation of the solvents, the crude oil was distilled in vacuo (bp = 100 °C, 0.15 mBar) to afford **3** as a colorless oil (57% yield). $[\alpha]_D$ +26.9 (*c* 0.43, $CHCl_3$) for 65% ee. The enantiomeric excess was determined by a reaction with Mosher chloride. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.93 (dd, J = 12.5, 9.2 Hz, 1H), 1.13 (d, J = 6.5 Hz, 3H), 1.32−1.44 (m, 10H), 1.69 (dd, J = 12.5, 6.5 Hz, 1H), 1.89 (br s, 1H), 2.56 (d, J = 11.0 Hz, 1H), 2.75 (d, J = 11.0 Hz, 1H), 3.13 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.5, 23.7, 23.9, 26.1, 37.3, 38.6, 44.0, 47.6, 54.0, 59.2. IR (NaCl, CCl_4) ν 1376, 1450, 2856, 2928 cm^{-1}. MS (ESI): 154.2 ($M - H^+$), 100%.

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Supporting Information Available: Complete experimental procedures, full characterization, and enantiomeric excess determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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