

Neutral Yttrium Tris(amide) and Ate Complexes Coordinated by an (*R*)-*N,N'*-Diisopropyl-1,1'-binaphthyl-2,2'-diamido Ligand as Enantioselective Catalysts for Intramolecular Hydroamination

David Riegert,^[a] Jacqueline Collin,^{*[a]} Jean-Claude Daran,^[b] Tauqir Fillebeen,^[a] Emmanuelle Schulz,^[a] Dmitrii Lyubov,^[c] Georgy Fukin,^[c] and Alexander Trifonov^{*[c]}

Keywords: Asymmetric catalysis / N ligands / Yttrium / Hydroamination / Nitrogen heterocycles

A bis(amido)yttrium chloride coordinated by (*R*)-*N,N'*-diisopropyl-1,1'-binaphthyl-2,2'-diamide [Y{(R)-C₂₀H₁₂(NiPr)₂}-Cl(thf)₂] has been prepared and characterized by X-ray analysis along with the corresponding yttrium ate complex [Li(thf)₄][Y{(R)-C₂₀H₁₂(NiPr)₂]₂]. The reaction of [(*R*)-*N,N'*-diisopropyl-1,1'-binaphthyl-2,2'-diamido]yttrium chloride with lithium diisopropylamine leads to the formation of a neutral tris(amido)yttrium complex which was characterized by

NMR spectroscopy. The new complexes [Y{(R)-C₂₀H₁₂(NiPr)₂}-[NiPr₂]] and [Li(thf)₄][Y{(R)-C₂₀H₁₂(NiPr)₂]₂], which contain the same enantiopure binaphthyldiamido ligand, are compared for the catalysis of several intramolecular hydroamination reactions. Both complexes provide pyrrolidines and piperidines with moderate to high enantioselectivities. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The intramolecular hydroamination of alkenes is an atom-economic process that leads to the formation of nitrogen heterocycles that are found in numerous biologically active compounds.^[1] The pioneering work of Marks and co-workers has shown the ability of lanthanocenes to perform hydroamination/cyclization reactions.^[2] More recently non-cyclopentadienido rare-earth complexes^[3] as well as transition metal complexes and others^[4] have been reported to catalyze the intramolecular hydroamination of alkenes. However, enantioselective hydroamination reactions have been less studied and only a few chiral asymmetric catalysts have been reported to date.^[5]

Chiral catalysts that are efficient for the asymmetric cyclization of aminoalkenes are almost all prepared from lanthanides with different types of ligands and are either isolated or used in situ. The first enantioselective catalysts reported for hydroamination/cyclization were the *ansa*-lanthanocene complexes substituted by a menthyl or neomen-

thyl group synthesized by Marks et al. that possess two stereogenic centers (backbone and lanthanide chirality, see **A** in Figure 1).^[6] Diastereomeric mixtures and diastereomerically pure precatalysts yielded the formation of pyrrolidines with identical enantiomeric excesses of up to 74% *ee*. Similar rare-earth metal complexes with an octahydrofluorenyl group instead of a tetramethylcyclopentadienyl group (structure **B** in Figure 1) have been isolated and have been found to be more efficient for the preparation of piperidines (up to 67% *ee*).^[7] Both series of complexes were prepared in a two-step synthesis that includes the formation of a metal chloride followed by its transformation into the amido or alkyl complex. Chiral lanthanide bis(aryloxide)s and bis(naphthoxide)s have been prepared by a different route and studied for the catalysis of aminoalkene cyclization. Scott et al. have thus synthesized chiral rare-earth metal bis(aryloxide) complexes by the reaction of the ligand [a bis(phenol) with a bis(arylamine) providing the chirality, structure **C**] with the tris(amide) precursors [Ln{N(SiHMe₂)₂}₃(thf)₂].^[8] The lanthanum complex was found to cyclize an aminopentene, albeit with low activity (reaction performed at 70 °C), with 61% *ee*. A similar chiral cationic zirconium complex has also been characterized and tested for the hydroamination/cyclization of secondary amines; it affords 82% *ee* for a piperidine.^[9] Hultsch et al. have synthesized various lanthanide bis(phenolate)s and bis(naphtholate)s.^[10] They isolated dimeric alkyl lanthanum bis(phenolate) complexes from the reaction of 3,3'-substituted bis(phenol) with [La{CH(SiMe₃)₂}₃] which exhibited only low enantioselectivity for hydroamination reactions.^[10a] The amidoyttrium biphenolate and binaphtholate

[a] Equipe de Catalyse Moléculaire, ICMO, UMR 8182, Université Paris-Sud, 91405 Orsay, France
Fax: +33-1-69154680
E-mail: jacollin@icmo.u-psud.fr

[b] Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse, France

[c] G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603600 Nizhny Novgorod GSP-445, Russia
Fax: +7-8312-127497
E-mail: trif@imoc.sinn.ru

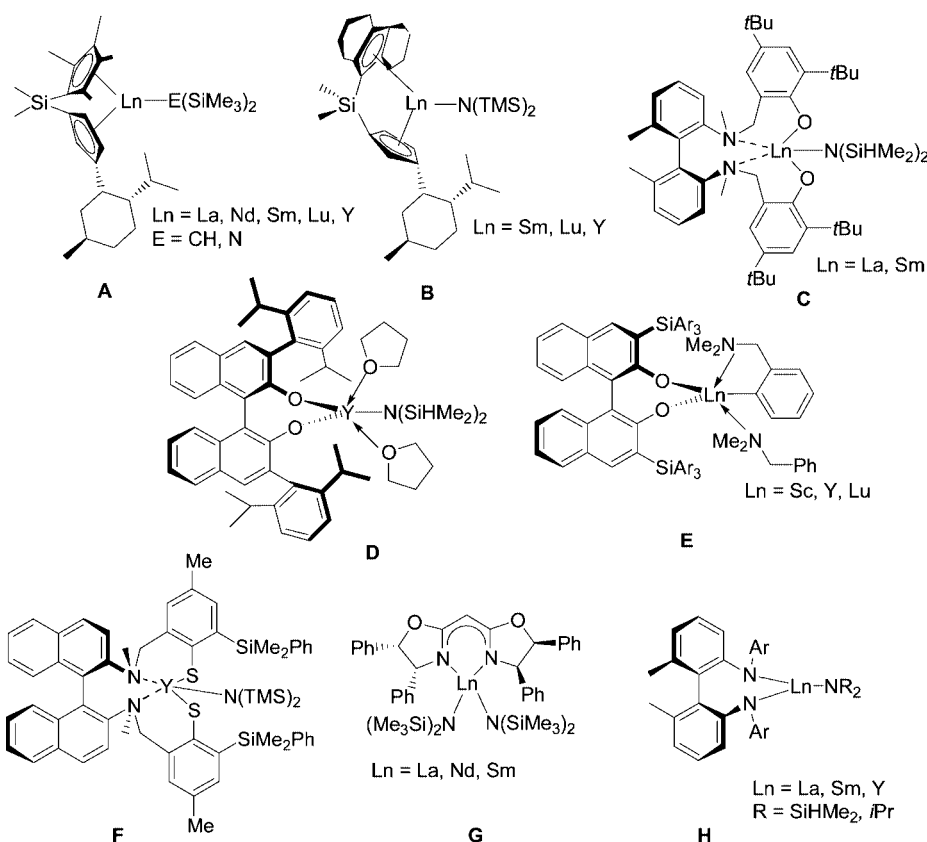


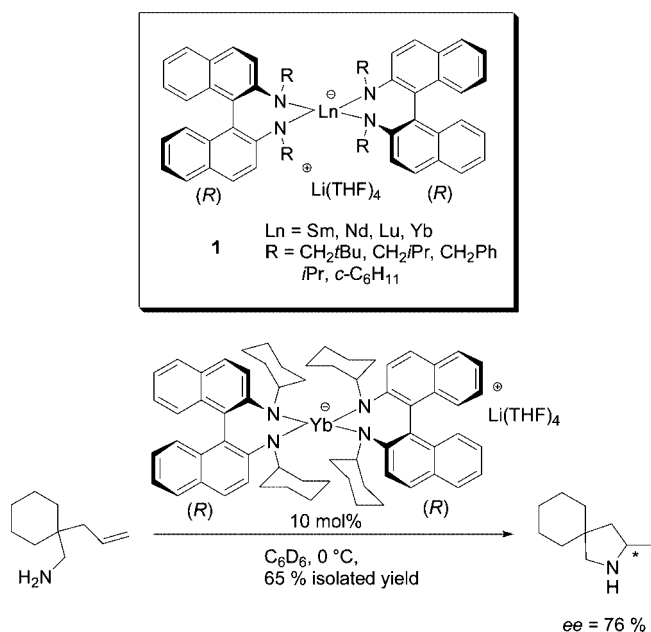
Figure 1. Complexes for intramolecular hydroamination reactions.

complexes synthesized according to a similar procedure (complex **D** in Figure 1) afforded moderate activities in these transformations, with enantiomeric excesses of up to 57%.^[10b] To the best of our knowledge, the highest enantioselectivities obtained for intramolecular hydroamination are provided by chiral lanthanide 3,3'-tris(arylsilyl)binaphtholates prepared by arene, alkane or amine elimination and used in situ. The yttrium,^[10c] lutetium, and scandium binaphtholates prepared from $[\text{Ln}\{o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2\}_3]$ and 3,3'-bis(triarylsilyl)binaphthol (structure **E**) allow the cyclization of aminopentenes to be performed at room temperature with high turnovers and with enantiomeric excesses of up to 95%.^[10d] Other enantioselective catalysts have also been prepared by the same procedure and used in situ. The amidoyttrium compounds synthesized by Livinghouse et al. from $[\text{Y}\{\text{N}(\text{TMS})_2\}_3]$ and chiral bis(thiolate) ligands (complex **F**) catalyze the cyclization of aminoalkenes at 60 °C and with enantiomeric excesses above 80% for several substrates.^[11] Similarly, by the reaction of lanthanide amides with commercially available C_2 -symmetric bis(oxazoline)s, Marks et al. have prepared enantioselective catalysts (structure **G** in Figure 1) that are active at room temperature (up to 67% *ee*).^[12] A chiral, bridged aminotroponimate complex of lutetium was very recently synthesized by Roesky^[13] that shows moderate enantioselectivities for intramolecular hydroamination.

Since the pioneering work of Livinghouse et al. that showed that lanthanide tris(amide)s are active hydroamin-

ation catalysts and that the stereoselectivity and the rate of the reaction can be tuned by varying the diamine ligands,^[3b,3d] the preparation of chiral lanthanide tris(amide)s for the enantioselective catalysis of hydroamination reactions has been a challenge. Interesting results have been reported by the group of Scott, who prepared precatalysts by the reaction of bis(arylamine)s possessing axial chirality with lanthanide tris(amide)s. These complexes (structure **H** in Figure 1) catalyze the cyclization of 2,2-dimethylpent-4-enylamine at 60 °C, albeit with only moderate asymmetric inductions.^[14]

We have previously reported the preparation of lanthanide catalysts coordinated by chiral amido ligands for intramolecular hydroamination.^[15] A new family of lanthanide ate complexes $[\text{Li}(\text{thf})_4][\text{Ln}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NR})_2\}_2]$ ($\text{Ln} = \text{Yb, Sm, Nd, Lu}$; **1** in Scheme 1) derived from chiral, disubstituted (*R*)-binaphthylamido ligands was studied. These compounds consist of a complex anion resulting from coordination of two (*R*)-binaphthylamine ligands to the lanthanide atom and a discrete $[\text{Li}(\text{thf})_4]^+$ counterion. Both the influence of the lanthanide and of the alkyl substituent on the nitrogen groups was examined in a hydroamination test reaction. The activity and enantioselectivity of these catalysts were evaluated for the cyclization of *C*-(1-allylcyclohexyl)-methylamine. The ytterbium and lutetium complexes with bulky substituents (isopropyl, cyclohexyl) on the nitrogen atom led to the highest enantioselectivities (up to 76% *ee* for the spiropyrrolidine).



Scheme 1. Intramolecular hydroamination catalyzed by chiral lanthanide ate complexes.

In order to gain insight into the nature of the active catalytic species for the hydroamination reaction mediated by the ionic compounds $[\text{Li}(\text{thf})_4][\text{Ln}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NR})_2\}_2]$, we considered the synthesis of both neutral and ate complexes of the same metal coordinated with the same chiral ligand and compared their catalytic properties.

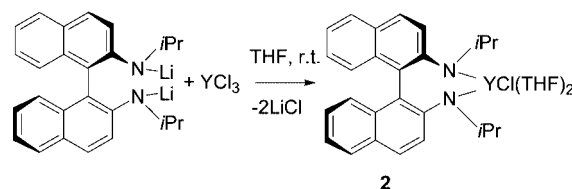
Results and Discussion

Preparation and Characterization of Complexes

With the aim of preparing neutral tris(amido)lanthanide complexes $[\text{Ln}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NR})_2\}_2\{\text{NR}'_2\}]$ with binaphthylamino ligands, we focused on the synthesis of yttrium derivatives since yttrium tris(amide)s have been already synthesized and characterized by X-ray analysis. Several lanthanide tris(amide)s have been prepared by metathesis reactions,^[16] and yttrium complexes coordinated by a chiral bis(arylamido) ligand have been used as enantioselective hydrosilylation catalysts.^[17]

Initially, we attempted to use the amine elimination reaction as a synthetic approach to the neutral complexes $[\text{Ln}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NR})_2\}_2\{\text{NR}'_2\}]$ ($\text{Ln} = \text{Y}, \text{La}, \text{Sm}$; $\text{R} = \text{CH}_2\text{CMe}_3$, $i\text{Pr}$; $\text{R}' = \text{SiMe}_3$). Thus, reactions of $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ ($\text{Ln} = \text{Y}, \text{La}, \text{Sm}$) with chiral diamines $(R)\text{-C}_{20}\text{H}_{12}(\text{NHR})_2$ ($\text{R} = \text{CH}_2\text{CMe}_3$, $i\text{Pr}$) in a 1:1 molar ratio were carried out in toluene at 70 °C. However, these reactions were found to occur with complete substitution of the $\text{N}(\text{SiMe}_3)_2$ groups in the parent tris(amido) complexes since the ^1H NMR spectra of the solid products indicated the absence of the corresponding signals. The salt metathesis reaction of anhydrous YCl_3 with 1 equiv. of $\text{Li}_2\{(R)\text{-C}_{20}\text{H}_{12}(\text{NiPr})_2\}$ in thf at ambient temperature allowed

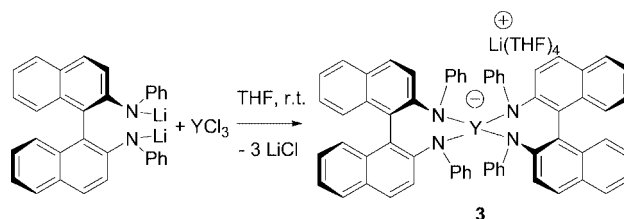
the isolation of the chiral diamido yttrium chloride complex **2** in 81% yield (Scheme 2).



Scheme 2. Synthesis of the neutral yttrium complex $[\text{Y}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NiPr})_2\}\text{Cl}(\text{thf})_2]$ (**2**).

Complex **2** was purified by extraction of the solid residue with toluene after evaporation of thf and subsequent recrystallization from thf/hexane mixtures. The ^1H and ^{13}C NMR spectra of complex **2** in C_6D_6 at 20 °C show the expected sets of resonances due to the $(R)\text{-N,N'}$ -diisopropyl-1,1'-binaphthyl-2,2'-diamido ligand and the coordinated thf molecules.

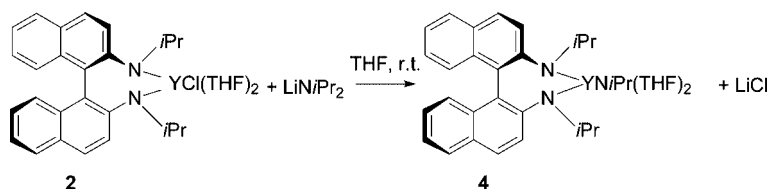
This salt metathesis reaction turned out to be highly sensitive to the substituent on the nitrogen atom of the starting $(R)\text{-1,1'}$ -binaphthyl-2,2'-diamine. Thus, the reaction of equimolar amounts of YCl_3 and the dilithium derivative of $(R)\text{-N,N'}$ -diphenyl-1,1'-binaphthyl-2,2'-diamine under analogous conditions afforded the ate complex $[\text{Li}(\text{thf})_4][\text{Y}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NPh})_2\}_2]$ (**3**) in 42% yield instead of the expected complex $[\text{Y}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NPh})_2\}_2\text{Cl}(\text{thf})_n]$ (Scheme 3).



Scheme 3. Synthesis of the yttrium ate complex $[\text{Li}(\text{thf})_4][\text{Y}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NPh})_2\}_2]$ (**3**).

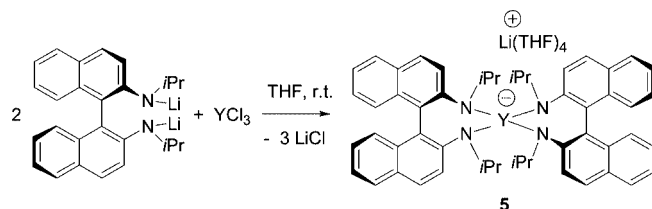
Complex **3** was purified by extraction of the solid residue obtained after evaporation of thf with hot toluene. Slow cooling of hot solutions of **3** in toluene afforded crystalline samples. The ^1H and ^{13}C NMR spectra of complex **3** in C_6D_6 at 20 °C show the expected sets of signals corresponding to the aromatic protons of the diamido ligand and the coordinated thf molecules.

In order to synthesize the amidoyttrium complex containing a chiral ancillary ligand, we carried out the reaction of complex **2** with LiNiPr_2 in thf at room temperature (Scheme 4). After evaporation of thf, the crude complex $[\text{Y}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NiPr})_2\}_2\{\text{NiPr}_2\}\{\text{LiCl}(\text{thf})_2\}]$ (**4**) was characterized by ^1H and ^{13}C NMR spectroscopy. According to the ^1H NMR spectrum, complex **4** contains two molecules of thf. Unfortunately, the experimental data did not allow us to conclude with certainty whether these thf molecules are coordinated to Y or Li. Extraction of the complex with toluene and recrystallization from thf/hexane resulted in the products of ligand-redistribution reactions. All attempts to isolate individual compounds to obtain samples suitable for

Scheme 4. Synthesis of $[Y\{(R)\text{-C}_{20}\text{H}_{12}(\text{N}i\text{Pr})_2\}\{\text{NiPr}_2\}\{\text{LiCl}(\text{thf})_2\}]$ (**4**).

X-ray analysis failed. We also tried to prepare alkylttrium derivatives containing the (*R*)-*N,N'*-diisopropyl-1,1'-binaphthyl-2,2'-diamido ligand. However, reactions of **2** with the alkylttrium reagents $\text{LiCH}_2\text{SiMe}_3$ (toluene 0 °C) and MeLi (Et_2O , 0 °C, in the presence of a twofold molar excess of TMEDA) did not afford any tractable organoyttrium compounds.

The ate complex $[\text{Li}(\text{thf})_4][Y\{(R)\text{-C}_{20}\text{H}_{12}(\text{N}i\text{Pr})_2\}_2]$ (**5**) was synthesized by the metathesis reaction of anhydrous YCl_3 with 2 equiv. of $\text{Li}_2\{(R)\text{-C}_{20}\text{H}_{12}(\text{N}i\text{Pr})_2\}$ in thf at ambient temperature (Scheme 5).

Scheme 5. Synthesis of the ate complex $[\text{Li}(\text{thf})_4][Y\{(R)\text{-C}_{20}\text{H}_{12}(\text{N}i\text{Pr})_2\}_2]$ (**5**).

Complex **5** was purified by extraction of the solid residue remaining after evaporation of thf with toluene and subsequent recrystallization from thf/hexane mixtures; it was isolated in 71 % yield. Complexes **2–5** were obtained as yellow, highly air- and moisture-sensitive crystalline solids. Complexes **2**, **4**, and **5** are soluble in thf and toluene and insoluble in hexane. Complex **3** is soluble in thf and hot toluene. Clear single-crystalline samples of complex **2** suitable for X-ray investigation were obtained by slow condensation of hexane into the concentrated thf solution at room temperature. Complex **2** crystallizes in the monoclinic space group $P2_1$ with four molecules in the unit cell. The molecular structure of **2** is depicted in Figure 2, and the crystal and structural refinement data are listed in the Experimental Section. The X-ray single-crystal structure analysis showed that complex **2** adopts a monomeric structure, thus indicating a considerable steric demand of the diamido ligand.

The coordination sphere of the yttrium atom in **2** contains the two nitrogen atoms of the (*R*)-*N,N'*-diisopropyl-1,1'-binaphthyl-2,2'-diamido ligand, one chlorido ligand, and two oxygen atoms of two thf molecules. The formal coordination number of the metal atom is five, which is rather low for yttrium. The presence in complex **2** of short contacts between the metal atom and the carbon atoms in the *ipso* and *ortho* positions to the amido groups [$\text{Y}(1)\text{--C}(211)$ 2.708(4), $\text{Y}(1)\text{--C}(111)$ 2.719(5), $\text{Y}(1)\text{--C}(112)$

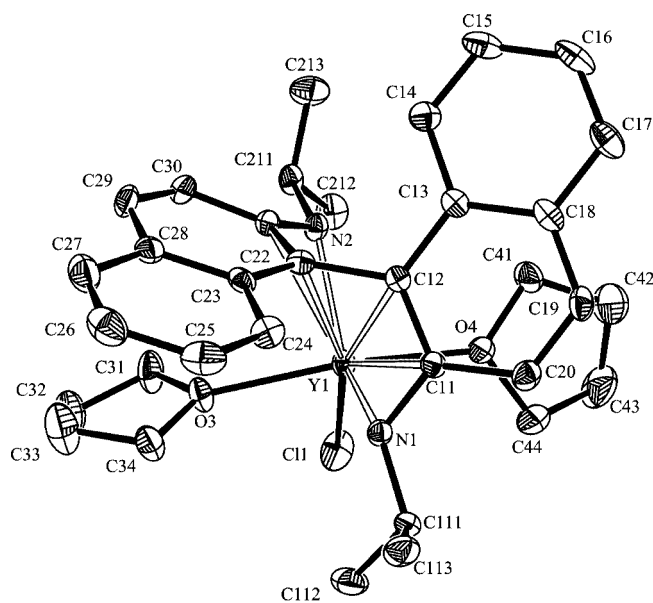


Figure 2. ORTEP drawing of complex **2** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1--N1 2.254(3), Y1--N2 2.257(4), Y1--Cl1 2.5835(14), Y1--C11 2.700(4), Y1--C12 2.756(4), Y1--C21 2.717(4), Y1--C22 2.746(4); N1--Y1--N2 123.36(15), N1--Y1--Cl1 115.78(12), N2--Y1--Cl1 120.86(10).

2.745(4), $\text{Y}(1)\text{--C}(212)$ 2.758(4) Å] comparable to those reported for the yttrium π -complexes $[(\text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh})\text{Y}_2\{\eta^6\text{-}\eta^6\text{-(C}_6\text{H}_5)_2\}]$ [2.699(1)–2.738(4) Å]^[19] and $[\text{Y}(o\text{-}2,6\text{-Ph}_2\text{C}_6\text{H}_3)_3]$ [2.84(1)–3.38(1) Å]^[20] probably reflects an η^2 -interaction of the yttrium atom with the aromatic rings of the binaphthyl ligand, which leads to a saturation of the coordination sphere of the yttrium atom. The Y–N bond lengths in **2** [2.254(3) and 2.257(4) Å] are very close to the length of the covalent bond reported for the amidoyttrium complexes $[\{[6,6'\text{-Me}_2\text{-(C}_6\text{H}_3)_2](2,2'\text{-NSiMe}_2t\text{Bu})_2\}\text{YCl}(\text{thf})_2]$ [2.247(7) and 2.252(7) Å]^[21] and $[\text{Cp}^*\text{Y}\{\text{N}(\text{SiMe}_3)_2\}]$ [2.274(1) and 2.253(1) Å].^[22] The Y–Cl bond length in **2** [2.5835(14) Å] is comparable to those in $[\{[6,6'\text{-Me}_2\text{-(C}_6\text{H}_3)_2](2,2'\text{-NSiMe}_2t\text{Bu})_2\}\text{YCl}(\text{thf})_2]$ [2.574(2) Å]^[21] and $[\text{Cp}^*\text{YCl}(\text{thf})]$ (2.579 and 2.577 Å).^[23]

Clear single-crystal samples of complex **3** suitable for X-ray investigation were obtained by slow cooling of its hot toluene solution from 70 °C to room temperature. Complex **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. Complex **3** was isolated as a solvate containing three molecules of toluene per molecule

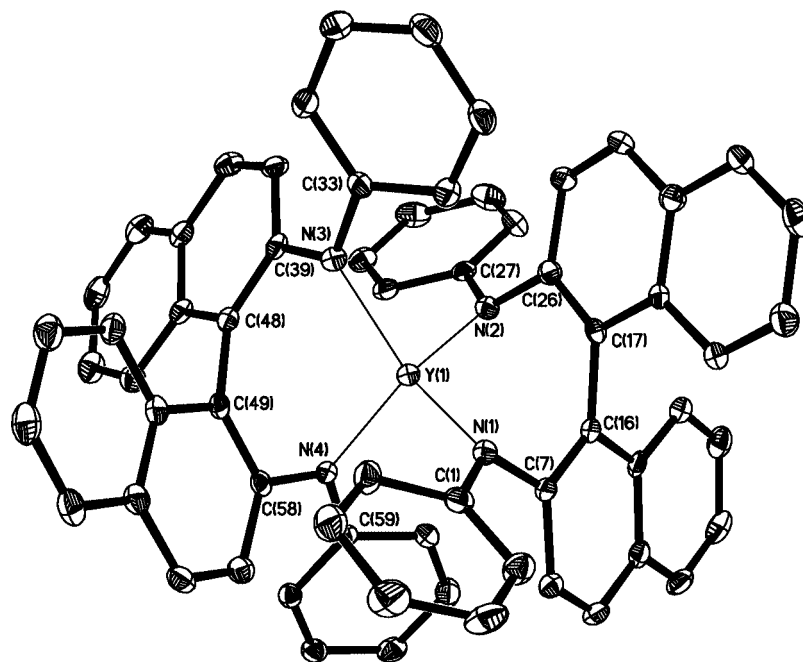


Figure 3. ORTEP drawing of complex **3** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. The $\text{Li}(\text{thf})_4^+$ cation and the hydrogen atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Y1–N1 2.275(2), Y1–N2 2.267(2), Y1–N3 2.270(2), Y1–N4 2.288(2), Y1–C26 2.747(2), Y1–C16 2.849(3), Y1–C7 2.727(3), Y1–C39 2.743(3), Y1–C58 2.746(3); N1–Y1–N2 118.47(8), N1–Y1–N3 103.74(8), N2–Y1–N3 104.69(9), N1–Y1–N4 108.65(8), N2–Y1–N4 103.84(8), N3–Y1–N4 118.15(8).

of complex, i.e., $[\{\text{Li}(\text{thf})_4\}(\text{Y}\{(\text{R})\text{-C}_{20}\text{H}_{12}(\text{NPh})_2\}_2)(\text{C}_7\text{H}_8)_3]$. The molecular structure of **3** is depicted in Figure 3 and the crystal and structural refinement data are listed in the Experimental Section.

The X-ray single-crystal structure analysis revealed that compound **3** is an ionic complex containing a discrete $\text{Li}(\text{thf})_4^+$ cation and a discrete $[\text{Y}\{(\text{R})\text{-C}_{20}\text{H}_{12}(\text{NPh})_2\}_2]^-$ complex anion resulting from the coordination of two diamido ligands to the trivalent yttrium atom. The Y–N bonds within the complex anion of **3** [2.267(2), 2.270(2), 2.275(2), and 2.288(2) $\text{\AA}$] are slightly longer than the same

distances in neutral complex **2** and are comparable to those in ionic $[\text{Li}(\text{thf})_4][\text{Y}(\text{NPh}_2)_4]$ [2.244(2)–2.271(2) $\text{\AA}$].^[24] Short contacts between the yttrium atom and the carbon atoms in the *ipso* and *ortho* positions [Y(1)–C(39) 2.743(3), Y(1)–C(58) 2.746(3), Y(1)–C(26) 2.747(2), Y(1)–C(16) 2.849(3) $\text{\AA}$] to the amido groups are also observed in complex **3**.

Crystals of **5** suitable for X-ray diffraction studies were obtained by slow condensation of hexane into concentrated thf solutions at room temperature. Complex **5** crystallizes as a thf solvate containing one molecule of thf per molecule

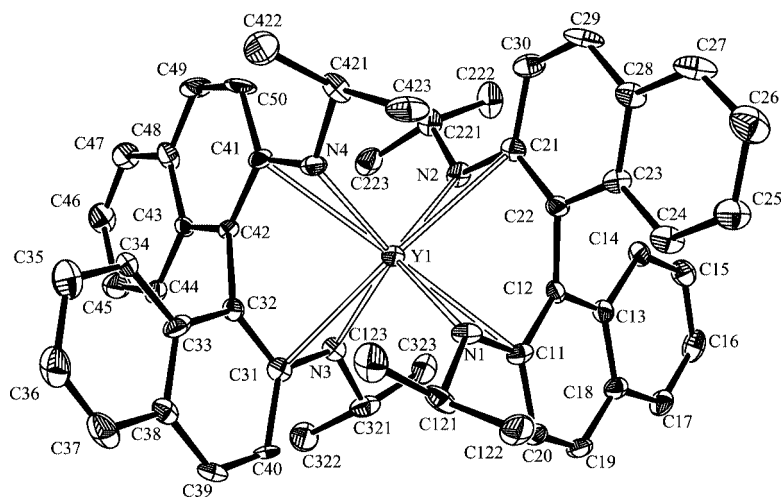


Figure 4. ORTEP drawing of complex **5** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. The $\text{Li}(\text{thf})_4^+$ cation and the hydrogen atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Y1–N1 2.297(5), Y1–N2 2.284(5), Y1–N3 2.290(5), Y1–N4 2.265(6), Y1–C11 2.712(6), Y1–C21 2.767(6), Y1–C31 2.733(7), Y1–C41 2.753(7); N1–Y1–N2 118.50(2), N1–Y1–N3 102.07(18), N2–Y1–N3 109.1(2), N1–Y1–N4 108.7(2), N2–Y1–N4 100.8(2), N3–Y1–N4 118.5(2).

of complex, i.e., $[\text{Li}(\text{thf})_4][\text{Y}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NiPr})_2\}_2](\text{C}_4\text{H}_8\text{O})$. The molecular structure of **5** is shown in Figure 4, and the structure refinement data are listed in the Experimental Section. Complex **5** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The X-ray diffraction study shows that complex **5**, similarly to **3**, is an ionic complex consisting of a discrete $\text{Li}(\text{thf})_4^+$ cation and a complex $\{\text{Y}[(R)\text{-C}_{20}\text{H}_{12}(\text{NiPr})_2]_2\}^-$ anion. The yttrium is coordinated by the four nitrogen atoms of the two (*R*)-1,1'-binaphthyl-2,2'-diamido ligands. The Y–N bond lengths in **5** are 2.297(5), 2.284(5), 2.290(5), and 2.265(6) Å. The average value of the Y–N bond lengths in **5** [2.284(5) Å] is very similar to that found for complex **3** [2.275(2) Å].

Catalytic Tests

We have previously reported the efficiency of an yttrium ate complex $[\text{Li}(\text{thf})_4][\text{Yb}\{(R)\text{-C}_{20}\text{H}_{12}(\text{NiPr})_2\}_2]$ for the cyclization of various aminopentene derivatives to the corresponding pyrrolidines with high enantioselectivities (up to 70% *ee*).^[15b] This complex requires several days of reaction at room temperature, however, to reach complete conversion. The new amidoyttrium complexes **3**, **4**, and **5** have been tested for their ability to perform enantioselective intramolecular hydroamination reactions. Complex **3** is not active for the cyclization of *C*-(1-allylcyclohexyl)methylamine (**6**), whereas **4** and **5** are efficient catalysts for several intramolecular hydroaminations (see Table 1).

The hydroamination/cyclization of **6** was initially investigated with both complexes at room temperature; the expected spiropyrrolidine (**7**) was obtained with a similar enantioselectivity (68% *ee*). It should be noted that catalyst **4** is much more active since it cyclized substrate **6** in 4 h, whereas a reaction time of 20 h was necessary for catalyst **5** to achieve the same transformation (Entries 1 and 2, Table 1). Similarly, in the cyclization of *C*-(1-allylcyclopentyl)methylamine (**8**) both catalysts afforded the spiropyrrolidine **9** with the same enantiomeric excess (Entries 3 and 4). With other substrates, however, the enantioselectivity depended on the catalyst employed. For the cyclization of 2,2-

dimethylpent-4-enylamine (**10**) and 2,2-diphenylpent-4-enylamine (**12**), for example, complex **4** proved to be both more active and enantioselective than **5** – catalysts **4** and **5** afforded the pyrrolidine **11** with 68% *ee* and 40% *ee*, respectively (Entries 5 and 6), and the pyrrolidine **13** with 65% *ee* and 50% *ee* (Entries 7 and 8).

The cyclization of aminohexene derivatives into piperidines is a more difficult process, and substrate **14** could only be partially transformed into the corresponding spiropiperidine **15** within 12 d in the presence of catalyst **4** (Entry 9). This transformation was greatly accelerated at 60 °C, however, and the piperidine was obtained after only 8 h with 18% *ee* (Entry 10). Under the same reaction conditions, the aminohexene was cyclized in 17 h in the presence of complex **5**. Surprisingly, and only for this substrate, catalyst **5** gave a better enantioselectivity and product **15** was isolated with 29% *ee* (Entry 11).

The yttrium complex **4** is more stable than the ate lanthanide complexes that we prepared earlier as we performed catalytic hydroamination reactions with samples of **4** prepared two months previously with no loss of enantioselectivity. We thus investigated the possibility of reusing catalyst **4** in successive reactions. The results are given in Table 2.

Table 2. Reuse of catalyst **4** for the cyclization of aminopentene **6**.

Reuse	Cat. ratio (mol-%)	<i>t</i> (h)	Conv. (%)	<i>ee</i> (%)
0	8	4	100	69
1	4	17	100	67
2	3	14	100	65
3	2	14	79	65
4	1.5	23	59 ^[a]	62

[a] New substrate was added in the fourth reuse before complete consumption of the substrate in the preceding run.

The experiments were performed in an NMR tube. After the first reaction, an aliquot of the reaction mixture was separated to determine the enantiomeric excess and additional substrate in solution in C_6D_6 was added to the NMR tube. This procedure was repeated three times without loss of enantioselectivity. For the fourth reuse, a slight

Table 1. Intramolecular hydroamination reactions with **4** and **5**.

Entry	Substrate	<i>T</i> (°C)	Cat. (ratio, mol-%)	<i>t</i> (h)	Product	Conv. (%)	<i>ee</i> (%)
1		25	4 (4)	4		100	68
2	6	25	5 (7)	20	7	100	67
3		25	4 (10)	72		> 95	50
4	8	25	5 (8)	20	9	49	51
5		25	4 (11)	23		77	68
6	10	25	5 (10)	44	11	73	40
7		25	4 (6)	12		100	65
8	12	25	5 (5)	43	13	100	50
9		25	4 (10)	288		50	19
10	14	60	4 (14)	8	15	100	18
11	14	60	5 (10)	17	15	> 90	29

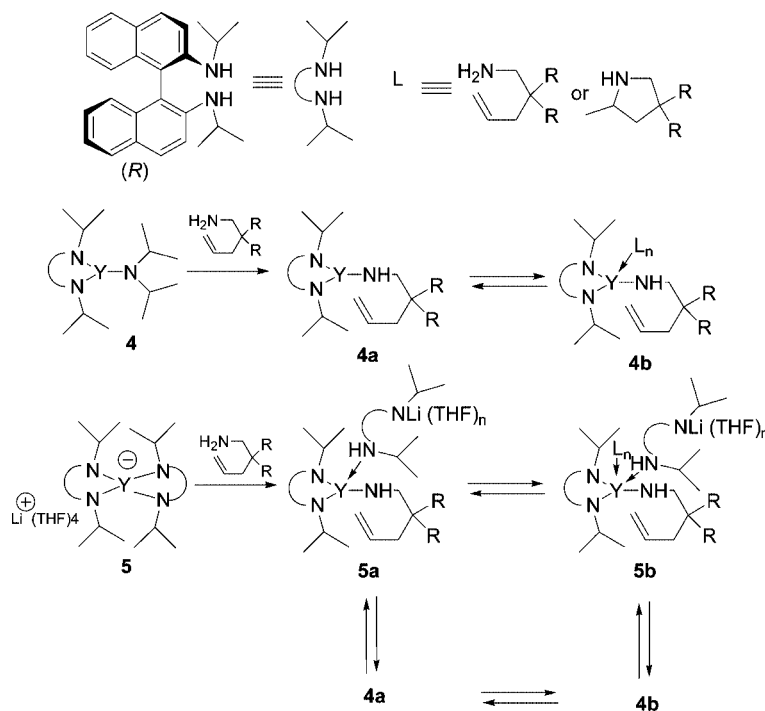
decrease of enantioselectivity was observed together with a lower rate of reaction due to the decrease in the catalytic ratio or inhibition by the reaction product.^[10d,25] Nevertheless, these results indicate that this neutral, chiral yttrium complex is highly stable and active for performing enantioselective hydroamination reactions. While this work was going on, Marks et al. reported a new procedure for the reuse of nonchiral organolanthanide hydroamination catalysts.^[26] Their homogeneous lanthanocene precatalyst was recycled three times in the presence of amino-derived polystyrene resins.

The reactions catalyzed by the neutral yttrium complex **4** and the yttrium ate complex **5** coordinated with the same binaphthylamine ligand do not afford the same rates and/or enantiomeric excesses for the various hydroamination reactions studied. Shibasaki has demonstrated that for enantioselective carbon–carbon bond formation promoted by heterodimetallic catalysts both lanthanide and alkali metals are involved in the reaction mechanism.^[27] Hence, these results suggest that the catalytically active species are not the same in the reactions involving precatalysts **4** and **5**. A mechanism for hydroamination reactions catalyzed by lanthanocenes has been proposed by Marks.^[2] In the first step, the lanthanide–carbon or lanthanide–nitrogen bond of the precatalyst is cleaved by the amino olefin to form an amidolanthanide intermediate. This proton transfer is then followed by the insertion of the double bond in the lanthanide–nitrogen bond, which is the rate-determining step. Release of the cyclized product is favored by reaction of another amino olefin. For hydroamination reactions catalyzed

by *ansa*-lanthanocenes^[2] or lanthanide binaphtholates,^[10d] several species with different coordination numbers that are in equilibrium have been proposed to be formed after the reaction of the amino olefin with the precatalyst.

Reaction of neutral complex **4** with an amino olefin may indeed form the tris(amido) species **4a** with selective replacement of the diisopropylamido group by the unsaturated substrate as the amido ligand. One or two amino ligands arising from the substrate or the cyclized product may then coordinate to the lanthanide center to give species **4b**. As for the yttrium ate complex **5**, at least two different structures can be considered for the active species formed by reaction with the amino olefin: after the proton transfer, a binaphthylamine ligand is transformed into the corresponding monolithium salt, which can coordinate (**5a**), or not (**4a**), to the yttrium atom.^[28] In the case of the complete decooordination of one binaphthylamine ligand, the structures of the active species for the catalysis by neutral complex **4** or ate complex **5** should be identical (**4a** and **4b**, Scheme 6). Furthermore, additional amino ligands from the substrate or the product may coordinate to the yttrium atom to form species **5b**.

For reactions involving substrates **6** or **8** the same catalytic species could be involved during catalysis by complexes **4** or **5**. This is probably not the case for hydroamination reactions involving the other substrates, although further studies are required to gain insight into the mechanism of hydroamination catalyzed by lanthanide ate complexes for more precise explanations concerning the role of the second chiral ligand.



Scheme 6. Proposed structures for the intermediate catalytic species.

Conclusion

We have prepared new asymmetric yttrium ate complexes and an asymmetric yttrium tris(amide) coordinated by *N*-substituted binaphthylamine ligands. An ate and a neutral complex coordinated with the same ligand are active catalysts for intramolecular hydroamination reactions. Comparison of the hydroamination reactions with different substrates catalyzed by both complexes has shown differences in activity and/or enantioselectivity, thus indicating that different active species are involved. Higher reaction rates and/or higher asymmetric inductions are generally observed for the formation of several pyrrolidines with the neutral yttrium tris(amide).

Experimental Section

General: All procedures were performed under argon using standard Schlenk and glove-box techniques. Tetrahydrofuran (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. The *N,N'*-diisopropylbinaphthylidiamine ligand and its lithium salt were prepared according to ref.^[15b] The *N,N'*-diphenylbinaphthylidiamine ligand was prepared according to ref.^[29] The substrates for the hydroamination/cyclization reactions were prepared as reported in ref.^[15c] 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 to record the NMR spectra. Chemical shifts for ¹H and ¹³C NMR spectra were referenced internally with respect to the residual solvent resonances. IR spectra were recorded with a Perkin–Elmer FT-IR spectrometer as Nujol mulls. Elemental analyses were performed by the Microanalytical laboratory of the Institute of Organometallic Chemistry of RAS.

Synthesis of [Y{(R)-C₂₀H₁₂(NiPr)₂}Cl(thf)₂] (2): Li₂{(R)-C₂₀H₁₂(NiPr)₂} (0.303 g, 0.799 mmol) was slowly added to a suspension of YCl₃ (0.156 g, 0.799 mmol) in thf (25 mL) at 20 °C with vigorous stirring. The reaction mixture was stirred for 3 h, then the thf was evaporated in vacuo and the resulting solid extracted with toluene (15 mL). The extracts were filtered, the toluene was evaporated off, and the solid residue was dissolved in thf (5 mL). Slow condensation of hexane into the thf solution at 20 °C resulted in yellow crystals of **1** (0.410 g, 81%). C₃₄H₄₂ClN₂O₂Y (634.77): calcd. C 64.33, H 6.61, Y 14.00; found C 63.81, H 6.20, Y 14.11. ¹H NMR (C₆D₆): δ = 1.07 (br. s, 8 H, β-CH₂, thf), 1.35 (d, ³J_{H,H} = 5.8 Hz, 6 H, CHCH₃), 1.62 (d, ³J_{H,H} = 5.8 Hz, 6 H, CHCH₃), 3.28, 3.40 (2 br. s, 8 H, α-CH₂, thf), 4.04 (br. m, 4 H, CHCH₃), 7.07–7.34 (m, 8 H, Ar), 7.64–7.74 (m, 4 H, Ar) ppm. ¹³C NMR (C₆D₆): δ = 24.7 (β-CH₂, thf), 25.4, 25.2 (CHCH₃), 46.6 (CHCH₃), 70.7 (α-CH₂, thf), 112.7, 116.4, 121.2, 124.7, 126.7, 127.6, 128.1, 131.6, 136.4, 150.2 (Ar) ppm. IR (Nujol, KBr): ν̄ = 3048 (w), 1610 (s), 1591 (s), 1541 (s), 1364 (s), 1301 (s), 1286 (s), 1249 (s), 1209 (s), 1146 (m), 1118 (w), 1036 (m), 1016 (m), 976 (w), 940 (w), 918 (m), 870 (m), 836 (w), 808 (w), 745 (s) cm⁻¹.

Synthesis of [Li(thf)₄][Y{(R)-C₂₀H₁₂(NPh)₂}₂] (3): Li₂{(R)-C₂₀H₁₂(NPh)₂} (0.338 g, 0.756 mmol) was slowly added to a suspension of YCl₃ (0.147 g, 0.756 mmol) in thf (25 mL) at 20 °C with vigorous stirring. The reaction mixture was stirred for 5 h, then the

thf was evaporated in vacuo and the resulting solid extracted with hot toluene (15 mL). Slow cooling of the toluene extract from 70 to 20 °C resulted in yellow crystals of **3** (0.480 g, 42%). C₁₀₁H₁₀₀LiN₄O₄Y (1529.7): calcd. C 79.30, H 6.53, Y 5.81; found C 78.86, H 6.17, Y 6.00. ¹H NMR (C₆D₆): δ = 1.08 (br. s, 16 H, β-CH₂, thf), 2.09 (s, 9 H, CH₃C₆H₅), 3.10 (br. s, 16 H, α-CH₂, thf), 6.58–7.99 (m, 59 H, Ar) ppm. ¹³C NMR (C₆D₆): δ = 21.1 (CH₃), 24.8 (β-CH₂, thf), 67.9 (α-CH₂, thf), 117.0, 117.5, 118.3, 120.0, 122.1, 123.1, 123.7, 124.7, 125.2, 125.4, 125.6, 126.6, 127.6, 128.0, 129.0, 129.2, 129.5, 129.7, 129.9, 130.2, 130.5, 134.4, 136.1, 137.6, 140.8, 142.7, 154.7 (Ar) ppm. IR (Nujol, KBr): ν̄ = 3050 (w), 1587 (m), 1348 (s), 1297 (s), 1173 (m), 1148 (m), 1079 (m), 1015 (m), 965 (m), 859 (m), 726 (s), 696 (s) cm⁻¹.

Synthesis of [Y{(R)-C₂₀H₁₂(NiPr)₂}₂][NiPr₂][LiCl(thf)₂] (4): [Y{(R)-C₂₀H₁₂(NiPr)₂}Cl(thf)₂] (0.039 g, 0.061 mmol) was slowly added to a solution of LiNiPr₂ (0.007 g, 0.061 mmol) in thf (1.5 mL) at 20 °C with vigorous stirring. The reaction mixture was then stirred for 20 h and the thf evaporated in vacuo. The complex was used without further purification as a crude yellow powder. ¹H NMR (C₆D₆): δ = 1.06–1.14 (m, 12 H, CHCH₃), 1.20–1.27 (m, 6 H, CHCH₃), 1.28 (br. s, 8 H, β-CH₂, thf), 1.48–1.62 (m, 6 H, CHCH₃), 3.02–3.15 (m, 2 H, CHCH₃), 3.35 (br. s, 8 H, α-CH₂, thf), 3.88–4.13 (m, 2 H, CHCH₃), 6.62–7.84 (m, 12 H, Ar) ppm. ¹³C NMR (C₆D₆): δ = 25.1, 25.3, 25.4, 25.52, 25.60, 25.64, 25.7, 26.0 (CH₃), 25.2 (β-CH₂, thf), 47.1, 48.3, 48.5, 67.9 (α-CH₂, thf), 116.0, 116.4, 117.2, 118.0, 118.8, 120.8, 121.0, 121.1, 122.7, 124.7, 126.6, 126.7, 128.9, 131.5, 131.9, 132.5, 133.2, 135.4, 150.5, 154.9 (Ar) ppm. IR (Nujol, KBr): ν̄ = 3047 (m), 1610 (s), 1593 (s), 1540 (m), 1496 (s), 1421 (s), 1377 (s), 1310 (s), 1246 (s), 1171 (s), 1038 (s), 916 (m), 810 (s), 746 (s) cm⁻¹.

Synthesis of [Li(thf)₄][Y{(R)-C₂₀H₁₂(NiPr)₂}₂] (5): YCl₃ (0.061 g, 0.313 mmol) was slowly added to a solution of Li₂{(R)-C₂₀H₁₂(NiPr)₂} (0.238 g, 0.626 mmol) in thf (15 mL) at 20 °C with vigorous stirring. The reaction mixture was stirred for 3 h, then the thf was evaporated in vacuo and the resulting solid extracted with toluene (20 mL). The extracts were filtered, the toluene was evaporated off, and the solid residue was dissolved in thf (2 mL). Slow condensation of hexane into the thf solution at 20 °C resulted in yellow crystals of **5** (0.276 g, 71%). C₇₂H₉₂LiN₄O₅Y (1189.35): calcd. C 72.75, H 7.73, Y 7.47; found C 72.28, H 7.30, Y 7.81. ¹H NMR (C₆D₆): δ = 1.29–1.35 (m, 20 H, β-CH₂, thf), 1.37 (d, ³J_{H,H} = 6.1 Hz, 12 H, CHCH₃), 1.41 (d, ³J_{H,H} = 6.1 Hz, 12 H, CHCH₃), 3.30–3.50 (m, 20 H, α-CH₂, thf), 3.90–4.10 (m, 4 H, CHCH₃), 6.90–7.85 (m, 24 H, Ar) ppm. ¹³C NMR (C₆D₆): δ = 24.7 (CH₃), 25.1 (β-CH₂, thf), 26.9 (CH₃), 45.9, 67.7 (α-CH₂, thf), 113.5, 115.3, 117.9, 124.9, 125.2, 125.8, 127.1, 129.1, 138.5, 155.0 (Ar) ppm. IR (Nujol, KBr): ν̄ = 3036 (w), 2802 (w), 2578 (w), 1609 (s), 1590 (s), 1540 (m), 1496 (m), 1420 (s), 1364 (s), 1304 (m), 1286 (s), 1247 (m), 1208 (w), 1168 (m), 1145 (m), 1115 (w), 1043 (s), 1015 (w), 916 (m), 886 (m), 851 (w), 835 (w), 808 (s), 745 (s) cm⁻¹.

General Procedure for NMR-Scale Hydroamination/Cyclization of Aminoalkenes: In an argon-filled glove box, the appropriate aminoalkene (0.176 mmol) was dissolved in C₆D₆ (0.1 mL) and dried with molecular sieves (4 Å) for 2 h. Complex **4** or **5** (see Tables 1 and 2 for the corresponding catalytic ratio) was introduced into an NMR tube equipped with a Teflon screw cap, dissolved in C₆D₆ (0.5 mL), and the aminoalkene solution was then introduced. The hydroamination reaction was monitored by ¹H NMR spectroscopy by observing the decrease of the signals of the olefinic protons. After the reaction time mentioned in the tables, the reaction was quenched with CH₂Cl₂. Determination of the enantiomeric excesses of the products was performed as described in ref.^[15c]

Table 3. Crystal data and structure refinement for complexes **2**, **3** and **5**.

	2	3	5
Empirical formula	C ₃₄ H ₄₂ ClN ₂ O ₂ Y	C ₁₀₁ H ₁₀₀ LiN ₄ O ₄ Y	C ₇₂ H ₉₂ LiN ₄ O ₅ Y
Formula mass	635.06	1529.70	1189.35
Temperature [K]	180(2)	180(2)	180(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	9.8722(7)	17.8673(5)	10.5453(10)
<i>b</i> [Å]	10.3133(8)	19.9247(6)	17.7356(16)
<i>c</i> [Å]	15.9820(11)	23.1695(7)	35.465(3)
<i>a</i> [°]	90	90	90
<i>β</i> [°]	99.829(6)°	90	90
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	1603.3(2)	8248.4(4)	6632.9(11)
<i>Z</i>	2	4	4
<i>D</i> _{calcd.} [Mg m ⁻³]	1.315	1.232	1.191
<i>μ</i> [mm ⁻¹]	1.933	0.763	0.930
<i>F</i> (000)	664	3232	2536
Crystal size [mm]	0.43 × 0.37 × 0.15	0.30 × 0.27 × 0.25	0.44 × 0.17 × 0.06
<i>θ</i> range [°]	3.26 to 26.37	1.76 to 24.50	3.00 to 24.97
Reflections collected	11197	63151	45105
Independent reflections [<i>R</i> _{int}]	5691 [0.0489]	13688 [0.0888]	11698 [0.1777]
Absorption correction	multi-scan	sadabs	multi-scan
Refinement method	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
Data/restraints/parameters	5691/1/365	13688/27/1006	11698/144/801
GOF on <i>F</i> ²	0.985	1.000	1.000
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0474, 0.1029	0.0486, 0.0961	0.0915, 0.1210
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0585, 0.1089	0.0743, 0.1035	0.1475, 0.1421
Flack parameter	−0.002(6)	0.022(4)	0.000(8)
Largest diff. peak/hole	0.593/−0.533	0.450/−0.320	0.615/−0.499

X-ray Structure Determination: A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of an Oxford Diffraction XCALIBUR CCD diffractometer for **2**, **3**, and **5**. Data were collected using monochromatic Mo-*K*_α radiation (*λ* = 0.71073). Further details are provided in Table 3. The structures were solved by direct methods (SIR97)^[30] and refined by least-squares procedures on *F*² using SHELXL-97.^[31] All hydrogen atoms attached to carbon atoms were introduced in the calculation in idealized positions and treated as riding models. In compound **5**, there is one thf solvate molecule disordered over two positions. The disordered moieties were refined applying the restraints available within SHELXL-97.^[32] The absolute configuration was determined by refining the Flack parameter^[32] using a large number of Friedel pairs. The drawings of the molecules were produced with ORTEP32.^[33] CCDC-615714, -615715 and -625520 (**2**, **3**, and **5**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The CNRS is acknowledged for giving financial support and a postdoctoral grant to D. R. A. T. thanks the Russian Foundation for Basic Research (grant no. 05-03-32390), the Russian Foundation for Science Support, the Federal Agency for Science and Innovation (contract 02.445.11.7365), and a Grant of the President of the RF for leading scientific schools (grant no. 8017.2006.3).

- [1] For general reviews on hydroamination reactions, see: a) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, 98, 675–704; b) M. Nobis, B. Driessen-Hölscher, *Angew. Chem. Int. Ed.* **2001**, 40, 3983–

- 3985; c) J. J. Brunet, D. Neibecker, in *Catalytic Heterofunctionalization: From Hydroamination to Hydrosilylation* (Eds.: A. Togni, H. Grützmaier), Wiley-VCH, Weinheim, **2001**, pp. 91–141; d) F. Pohlki, S. Doye, *Chem. Soc. Rev.* **2003**, 32, 104–114; e) M. Beller, A. Tillack, J. Seayad, in *Transition Metals for Organic Synthesis*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**, vol. 2, pp. 403–414; f) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, 37, 673–686.
- [2] M. R. Gagné, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, 114, 275–294 and references cited therein.
- [3] a) Y. K. Kim, T. Livinghouse, J. E. Bercaw, *Tetrahedron Lett.* **2001**, 42, 2933–2935; b) Y. K. Kim, T. Livinghouse, *Angew. Chem. Int. Ed.* **2002**, 41, 3645–3647; c) Y. K. Kim, T. Livinghouse, Y. Horino, *J. Am. Chem. Soc.* **2003**, 125, 9560–9561; d) J. Y. Kim, T. Livinghouse, *Org. Lett.* **2005**, 7, 4391–4393; e) K. C. Hultsch, F. Hampel, T. Wagner, *Organometallics* **2004**, 23, 2601–2612; f) A. Zulys, T. K. Panda, M. T. Gamer, P. W. Roesky, *Chem. Commun.* **2004**, 2584–2585; g) T. K. Panda, A. Zulys, M. T. Gamer, P. W. Roesky, *J. Organomet. Chem.* **2005**, 690, 5078–5089; h) M. Rastätter, A. Zulys, P. W. Roesky, *Chem. Commun.* **2006**, 874–876; i) S. Bambirra, H. Tsurugi, D. van Leusen, B. Hessen, *Dalton Trans.* **2006**, 1157–1161; j) F. Lauterwasser, P. G. Hayes, S. Bräse, W. E. Piers, L. L. Schafer, *Organometallics* **2004**, 23, 2234–2237.
- [4] a) A. Ates, C. Quinet, *Eur. J. Org. Chem.* **2003**, 1623–1626; b) P. Horillo Martinez, K. C. Hultsch, F. Hampel, *Chem. Commun.* **2006**, 2221–2223; c) M. R. Crimmin, I. J. Casely, M. S. Hill, *J. Am. Chem. Soc.* **2005**, 127, 2042–2043; d) A. Zulys, M. Dochnahl, D. Hollmann, K. Löhnwitz, J.-S. Herrmann, P. W. Roesky, S. Blechert, *Angew. Chem. Int. Ed.* **2005**, 44, 7794–7798; e) N. Meyer, K. Löhnwitz, A. Zulys, P. W. Roesky, M. Dochnahl, S. Blechert, *Organometallics* **2006**, 25, 3730–3734; f) J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer, *Org. Lett.* **2005**, 7, 1959–1962; g) C. Müller, C. Loos, N. Schulenberg, S. Doye, *Eur. J. Org. Chem.* **2006**, 2499–2503; h) R. K. Thomson, J. A. Bexrud, L. L. Schafer, *Organometallics* **2006**, 25, 4069–4071; i)

- C. F. Bender, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2005**, *127*, 1070–1071; j) A. Takemiya, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 6042–6043.
- [5] For reviews on enantioselective hydroamination reactions, see: a) P. W. Roesky, T. E. Müller, *Angew. Chem. Int. Ed.* **2003**, *42*, 2708–2710; b) K. C. Hultsch, *Adv. Synth. Catal.* **2005**, *347*, 367–391; c) K. C. Hultsch, *Org. Biomol. Chem.* **2005**, *3*, 1819–1824.
- [6] a) M. R. Gagné, L. Brard, V. P. Conticello, M. A. Giardello, C. L. Stern, T. J. Marks, *Organometallics* **1992**, *11*, 2003–2005; b) M. A. Giardello, V. P. Conticello, L. Brard, M. Sabat, A. L. Rheingold, A. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10212–10240; c) M. A. Giardello, V. P. Conticello, L. Brard, M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10241–10254.
- [7] M. R. Douglass, M. Ogasawara, S. Hong, M. V. Metz, T. J. Marks, *Organometallics* **2002**, *21*, 283–292.
- [8] P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie, P. Scott, *Chem. Commun.* **2003**, 1770–1771.
- [9] P. D. Knight, I. Munslow, P. N. O'Shaughnessy, P. Scott, *Chem. Commun.* **2004**, 894–895.
- [10] a) D. V. Gribkov, F. Hampel, K. C. Hultsch, *Eur. J. Inorg. Chem.* **2004**, 4091–4101; b) D. V. Gribkov, K. C. Hultsch, F. Hampel, *Chem. Eur. J.* **2003**, *9*, 4796–4810; c) D. V. Gribkov, K. C. Hultsch, *Chem. Commun.* **2004**, 730–731; d) D. V. Gribkov, K. C. Hultsch, F. Hampel, *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759.
- [11] J. Y. Kim, T. Livinghouse, *Org. Lett.* **2005**, *7*, 1737–1739.
- [12] S. Hong, S. Tian, M. V. Metz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 14768–14783.
- [13] N. Meyer, A. Zulus, P. W. Roesky, *Organometallics* **2006**, *25*, 4179–4182.
- [14] a) P. N. O'Shaughnessy, P. Scott, *Tetrahedron: Asymmetry* **2003**, *14*, 1979–1983; b) P. N. O'Shaughnessy, K. M. Gillespie, P. D. Knight, I. Munslow, P. Scott, *Dalton Trans.* **2004**, 2251–2256.
- [15] a) J. Collin, J. C. Daran, E. Schulz, A. Trifonov, *Chem. Commun.* **2003**, 3048–3049; b) J. Collin, J.-C. Daran, O. Jacquet, E. Schulz, A. Trifonov, *Chem. Eur. J.* **2005**, *11*, 3455–3462; c) D. Riegert, J. Collin, A. Meddour, E. Schulz, A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514–2517.
- [16] a) F. G. N. Cloke, B. R. Elvidge, P. B. Hitchcock, V. M. E. Lamarche, *J. Chem. Soc., Dalton Trans.* **2002**, 2413–2414; b) A. G. Avent, F. G. N. Cloke, B. R. Elvidge, P. B. Hitchcock, *Dalton Trans.* **2004**, 1083–1096.
- [17] T. I. Gountchev, T. D. Tilley, *Organometallics* **1999**, *18*, 5661–5667.
- [18] C. Drost, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1996**, 3595–3601.
- [19] a) M. D. Fryzuk, J. B. Love, S. J. Rettig, *J. Am. Chem. Soc.* **1997**, *119*, 9071–9072; b) M. D. Fryzuk, L. Jafarpour, F. M. Kerton, J. B. Love, B. O. Patrick, S. J. Rettig, *Organometallics* **2001**, *20*, 1387–1396.
- [20] G. B. Deacon, T. Feng, C. M. Forsyth, A. Gitlits, D. Hockless, Q. Slien, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **2000**, 961–966.
- [21] T. I. Gountchev, T. D. Tilley, *Organometallics* **1999**, *18*, 2896–2905.
- [22] K. H. Den Haan, J. L. De Boer, J. H. Teuben, A. L. Speak, B. Kojic-Prodic, G. R. Hays, R. Huis, *Organometallics* **1986**, *5*, 1726–1733.
- [23] W. J. Evans, J. W. Grate, K. R. Levan, I. Bloom, T. T. Petersen, R. J. Doedens, H. Zhang, J. L. Atwood, *Inorg. Chem.* **1986**, *25*, 3614–3619.
- [24] Y. Yao, X. Lu, Q. Shen, K. Yu, *J. Chem. Crystallogr.* **2004**, *34*, 275–279.
- [25] S. Hong, A. M. Kawaoka, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 15878–15892.
- [26] J. Zhao, T. J. Marks, *Organometallics* **2006**, *25*, 4763–4772.
- [27] M. Shibasaki, N. Yoshikawa, *Chem. Rev.* **2002**, *102*, 2187–2209.
- [28] We have checked that the mono- and dilithium salts of the (*R*)-*N,N'*-diisopropyl-1,1'-binaphthyl-2,2'-diamido ligand are not active catalysts for the hydroamination reactions even at higher temperatures (see ref.^[4b]).
- [29] S. Vyskocil, S. Jaracz, M. Smrcina, M. Sticha, V. Hanus, M. Polasek, P. Kocovsky, *J. Org. Chem.* **1998**, *63*, 7727–7737.
- [30] *SIR97, a program for automatic solution of crystal structures by direct methods*: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagn, *J. Appl. Crystallogr.* **1999**, *32*, 115.
- [31] G. M. Sheldrick, *SHELXL97, a program for crystal structure refinement*, University of Göttingen, Germany, **1997**.
- [32] a) H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881; b) G. Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985**, *41*, 500–511.
- [33] *ORTEP3 for Windows*: L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received: September 19, 2006

Published Online: February 9, 2007