Synthesis and Characterization of New Biphenolate and Binaphtholate Rare-Earth-Metal Amido Complexes: Catalysts for Asymmetric Olefin Hydroamination/Cyclization

Denis V. Gribkov, Kai C. Hultzsch,* and Frank Hampel[a]

Abstract: Monomeric diolate amido yttrium complexes [Y{diolate}{N(SiHMe$_2$)$_2$}(thf)$_2$] can be prepared in good yield by treating [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] with either 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol (H$_2$(Biphen)), 3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (H$_2$(Trip$_2$BINO)) or 3,3′-bis(2,6-diisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (H$_2$(Dip$_2$BINO)) in racemic and enantiopure form. The racemic complex [Y(biphen){N(SiHMe$_2$)$_2$}(thf)$_2$] dimerizes upon heating to give the heterochiral complex (*R*,*S*)-[Y(biphen){N(SiHMe$_2$)$_2$}(thf)]$_2$. The corresponding dimeric heterochiral lanthanum complex was the sole product in the reaction of H$_2$(Biphen) with [La{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$]. Single-crystal X-ray diffraction of both dimeric complexes revealed that the two Ln(biphen){N(SiHMe$_2$)$_2$}(thf) fragments are connected through bridging phenolate groups of the biphenolate ligands. The two different phenolate groups undergo an intramolecular exchange process in solution leading to their equivalence on the NMR timescale. All complexes were active catalysts for the hydroamination/cyclization of aminoalkynes and aminoalkenes at elevated temperature, with [Y((*R*)-dip$_2$bino)-{N(SiHMe$_2$)$_2$}(thf)$_2$] being the most active one giving enantioselectivities of up to 57 % *ee*. Kinetic resolution of 2-aminohex-5-ene proceeded with this catalyst with 6.4:1 *trans* selectivity to give 2,5-dimethylpyrrolidine with a k_{rel} of 2.6.

Keywords: asymmetric catalysis · hydroamination · lanthanum · O ligands · rare earth compounds · yttrium

Introduction

The catalyzed addition of amines to alkenes and alkynes, the so-called hydroamination, has attracted significant attention in recent years, as it has the potential to yield basic and fine chemicals, pharmaceuticals and other industrially relevant building blocks in a highly atom-efficient manner starting from simple and inexpensive materials.[1]

Although many attempts have been made and a wide variety of catalysts, ranging from early[2, 3] to late[4] transition metals, have been developed, many of those are restricted to activated substrates (e.g. anilines with alkynes, styrene, norbornene or cyclohexadiene derivatives). Catalysts based on rare-earth metals are usually more efficient and are more generally applicable to hydroamination reactions.[1b, 5–7] These systems have relied so far solely on the cyclopentadienyl ligand and reports of cyclopentadienyl-free catalyst systems are rare.[6]

Even though the development of an asymmetric variant of the hydroamination would constitute an important goal in current research, only a few reports have emerged over the past decade.[4d–g, 5b–e] Unfortunately, catalyst systems based on rare-earth metals revealed a configurational instability of planar chiral cyclopentadienyl complexes in the presence of donor molecules (e.g. ethers, amines) resulting in fast epimerization under the catalytic conditions employed.[5c,d, 8] Therefore, a more successful strategy to develop asymmetric rare-earth-metal catalysts would utilize non-cyclopentadienyl ligands, which are not prone to catalyst epimerization. Promising ligands include biphenolate or binaphtholate ligands, which have been used widely in asymmetric catalysis. Heterobimetallic rare-earth-metal BINOL (1,1′-bi-2-naphthol) complexes for Lewis acid-catalyzed reactions developed by Shibasaki and co-workers[7g] are some of the most prominent examples in recent years. Unsubstituted BINOL is a sterically undemanding ligand that results in the formation of oligomeric aggregates or coordination of multiple BINOL ligands to the same rare-earth-metal centre. Therefore, biphenolate and binaphtholate ligands containing bulky substituents in the 3 and 3′ position are commonly employed to prevent these problems. Schaverien reported the synthesis of monomeric biphenolate and binaphtholate lanthanum alkyl complexes in 1992,[9] but little is known about their reactivity or catalytic activity. We chose 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol (H$_2$(Biphen)) and

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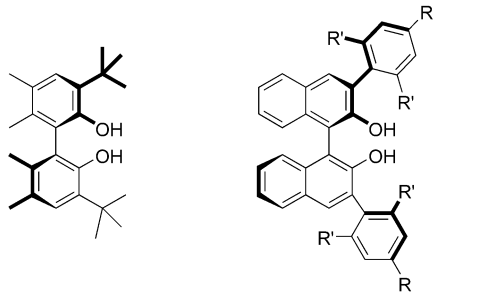
3,3′-arylated binaphthols H_2(Trip$_2$BINO), H_2(Dip$_2$BINO), as well as H_2(Mes$_2$BINO) (Trip = 2,4,6-triisopropylphenyl, Dip = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl) as good candidates, as they have been successfully applied in asymmetric ring-closing-metathesis catalysts[10] and are readily available.[11]



H_2(Biphen)

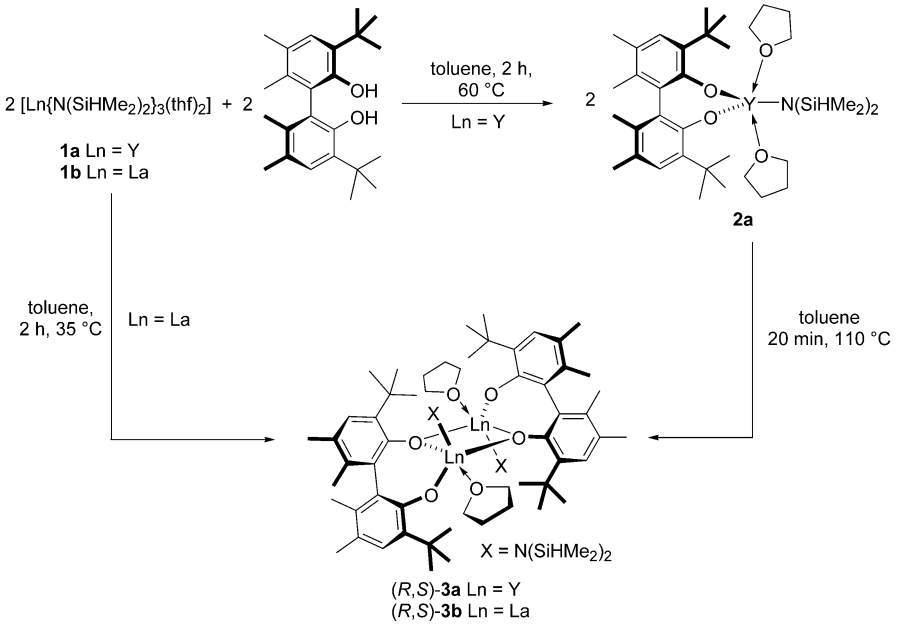
H_2(Trip$_2$BINO) R = R' = *i*Pr
H_2(Dip$_2$BINO) R = H, R'= *i*Pr
H_2(Mes$_2$BINO) R = R'= Me

In this paper we report the synthesis and characterization of several new biphenolate and binaphtholate rare-earth-metal amido complexes and their application as catalysts for hydroamination/cyclization reactions.

Results

Synthesis and characterization of complexes: Initial experiments conducted with the racemic biphenol ligand H_2(Biphen) and with the well-known trisamido complex [Ln{N(SiMe$_3$)$_2$}$_3$] (Ln = Y (**1a**), La (**1b**))[12] led to the formation of complex product mixtures.[13] Reaction of racemic H_2(Biphen)[14] with the trisamido complex [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (**1a**)[15] at room temperature in toluene, on the other hand, showed by NMR spectroscopy relatively clean formation of a major product **2a**, concomitant with the formation of small amounts of a sparingly soluble side-product, which did not contain any amido ligands and which we therefore assumed to be of oligomeric nature with more than one biphenolate ligand per metal centre. The formation of the side-product could be minimized by increasing the reaction temperature to 60 °C, while lower temperatures led to an increase of side product. NMR spectroscopic analysis of the major product revealed the presence of two molecules of coordinated THF as well as one biphenolate and one amido ligand; this suggested a monomeric structure for **2a** (Scheme 1). Both phenol rings of the biphenolate ligand are equivalent on the NMR timescale. The two diastereotopic silicon methyl groups give rise to two doublets at 0.32 and 0.38 ppm ($^3J_{H,H}$ = 3.0 Hz) in the ^{1}H NMR spectrum and two signals at 2.9 and 3.1 ppm in the ^{13}C NMR spectrum. The enantiopure complex (*R*)-**2a** was obtained similarly from H_2((*R*)-Biphen) and **1a** in toluene at 70 °C. The NMR spectra of racemic and enantiopure **2a** are essentially identical except for the two broad multiplets for the diastereotopic THF α-protons at 3.43 and 3.74 ppm in the ^{1}H NMR spectrum of (*R*)-**2a**.[16] Both complexes, racemic and enantiopure **2a**, showed good solubility in aliphatic and aromatic solvents, but only racemic **2a** could be crystallized as a colourless powder from pentane at −30 °C. (*R*)-**2a** could not be crystallized from pentane even at −78 °C.

The reaction of H_2(Biphen) with [La{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (**1b**)[15] in toluene at 35 °C took a slightly different turn. The NMR spectroscopic features of the resulting species are similar to those of **2a**, namely only one set of signals for the biphenolate ligand was observed with both phenol rings being equivalent at room temperature on the NMR timescale. Interestingly, both methyl groups on silicon are equivalent in **3b**; this gives rise to a single doublet at 0.15 ppm ($^3J_{H,H}$ = 3.0 Hz) in the ^{1}H NMR spectrum. However, the low solubility of this lanthanum complex, which crystallizes from the toluene reaction mixture, as well as the presence of only one molecule of coordinated THF led us to believe that complex **3b** is a dimer (Scheme 1). NMR scale experiments confirmed the quantitative formation of a single product. X-ray crystallographic analysis later revealed that **3b** is a phenolate-bridged heterochiral dimer (vide infra). An additional indicator for the formation of a heterochiral dimer was our inability to synthesize an enantiopure biphenolate lanthanum complex. Reaction of H_2((*R*)-Biphen) with **1b** under various conditions gave only product mixtures (vide infra).



Scheme 1.

This suggests that the monomeric biphenolate lanthanum complex cannot form a homochiral dimer as readily as the heterochiral dimer. Due to the larger atomic radius of La, 1.032 Å versus 0.900 Å for Y,[17] the monomeric complex is sterically unshielded and reacts in an uncontrolled fashion with further equivalents of the diol.

The racemic, monomeric yttrium complex **2a** could be transformed into the dimeric species (*R*,*S*)-**3a** by heating a solution of **2a** in toluene to 110 °C. ^{1}H NMR spectroscopic investigations show a monomer-to-dimer ratio of 5:1 at 60 °C, which decreases to 2:1 at 80 °C and a final ratio of 1:0.8 at 100 °C (Figure 1). (*R*,*S*)-**3a** could be separated from monomeric **2a** by crystallization from the toluene reaction mixture. The physical and NMR spectroscopic properties of (*R*,*S*)-**3a** are very similar to those of (*R*,*S*)-**3b** and X-ray crystallographic analysis confirmed it to be isostructural to (*R*,*S*)-**3b** (vide infra).

Heating (*R*,*S*)-**3b** results in the slow formation of a second species at higher temperatures, as can be verified by variable-temperature NMR (Figure 2). Two new overlapping doublets at 0.26 ppm ($^3J_{HH} = 2.9$ Hz) and a new SiH septet at 4.85 are observed at 70 °C in the ^{1}H NMR spectrum, as well as a signal

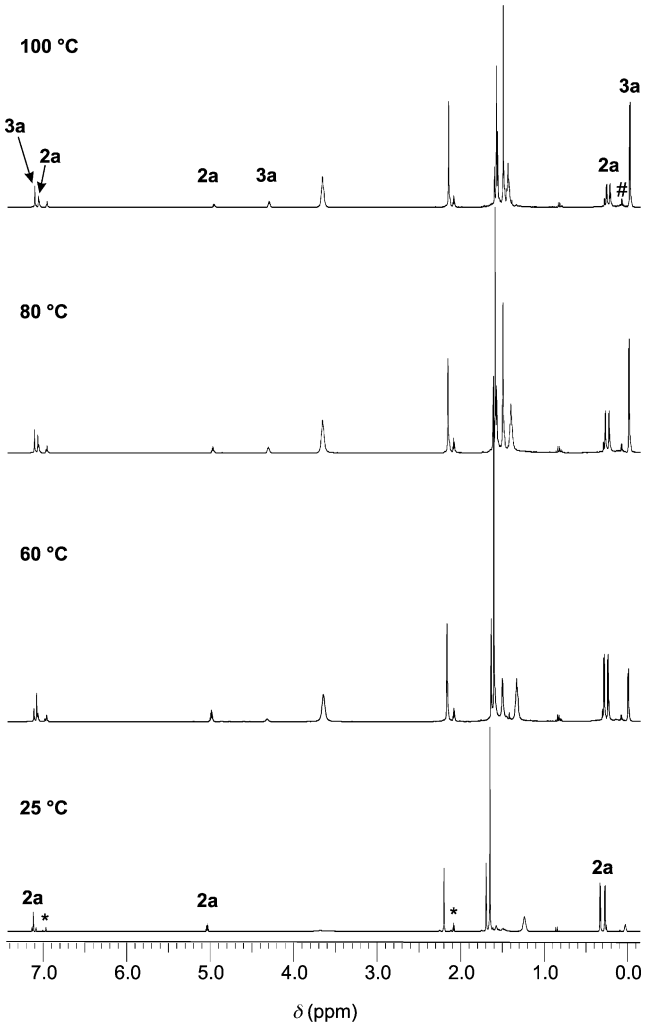


Figure 1. Formation of the dimer (*R*,*S*)-**3a** from **2a** upon heating, as observed in the ^{1}H NMR spectra in [D$_8$]toluene (*). (# = HN(SiHMe$_2$).

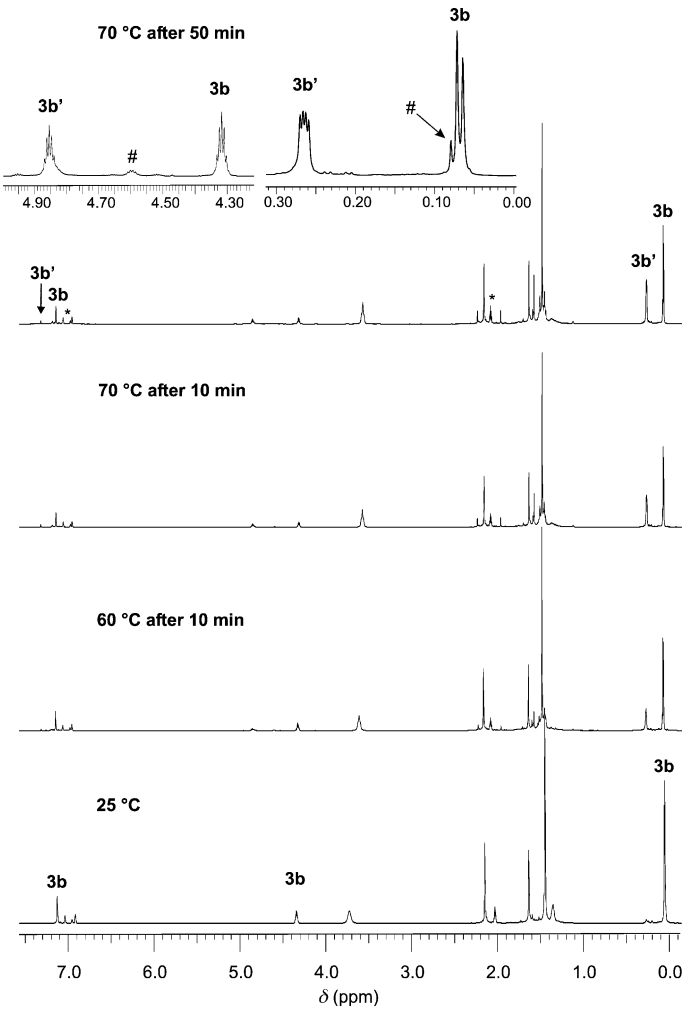


Figure 2. ^{1}H NMR spectra of the equilibration of (*R*,*S*)-**3b** and **3b**′ upon heating a solution of (*R*,*S*)-**3b** in [D$_8$]toluene (*). # = HN(SiHMe$_2$).

set for a biphenolate ligand with two equivalent phenol rings. The ratio between this new species **3b**′ and (*R*,*S*)-**3b** rises from 1:2.5 at 60 °C after 10 min to 0.9:1 at 70 °C after 50 min. Cooling of the sample to room temperature does not regenerate (*R*,*S*)-**3b**, and the ratio of (*R*,*S*)-**3b** to **3b**′ remained unchanged for 11 days at room temperature. We therefore conclude that **3b**′ is not a monomeric complex but rather the homochiral dimer,[18a] and that dissociation of (*R*,*S*)-**3b** or **3b**′ to monomeric species is very slow at room temperature in noncoordinating solvents. Variable temperature NMR spectra of either (*R*,*S*)-**3a** or (*R*)-**2a** did not show any species similar to **3b**′; this suggests that a homochiral dimer cannot form due to higher steric restraints in the case of the smaller yttrium atom.[18b] **3b**′ was also the major (ca. 50 %) of at least three products in the reaction of **1b** with H$_2$((*R*)-Biphen) in toluene at 100 °C, however separation attempts have failed so far.

The ^{1}H and ^{13}C NMR spectra of (*R*,*S*)-**3b** show only one set of signals for *both* phenolate rings at 25 °C; this suggests a chemical equivalence of the terminal and bridging phenolate rings on the NMR timescale at this temperature (Figure 3). Upon lowering the temperature, decoalescence of the signals of the *tert*-butyl and methyl groups is observed at −30 °C and

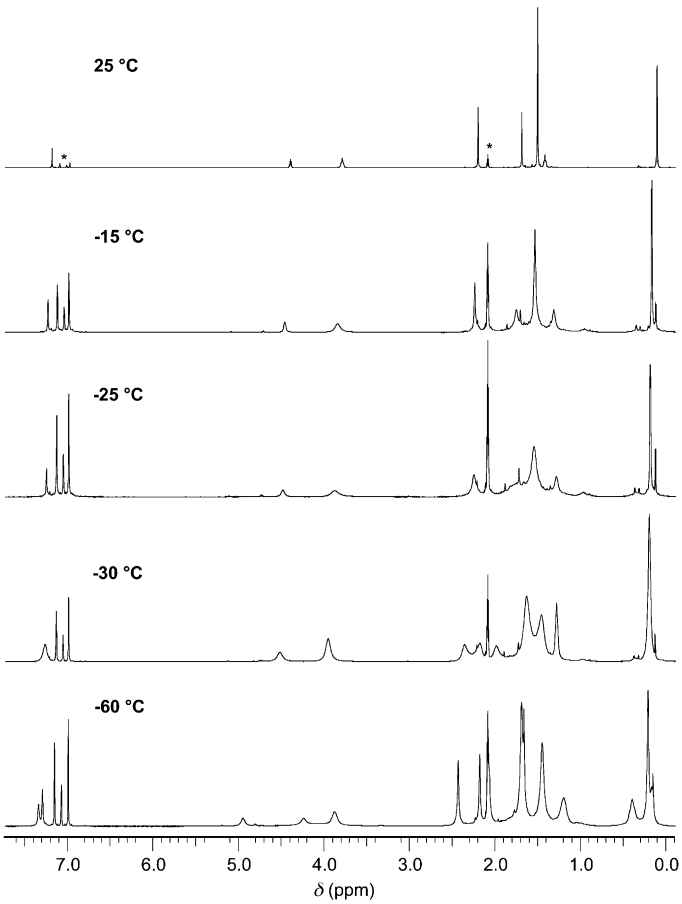


Figure 3. Temperature dependence of the ^{1}H NMR spectrum of (*R*,*S*)-**3b** in [D_8]toluene (*) at low temperatures.

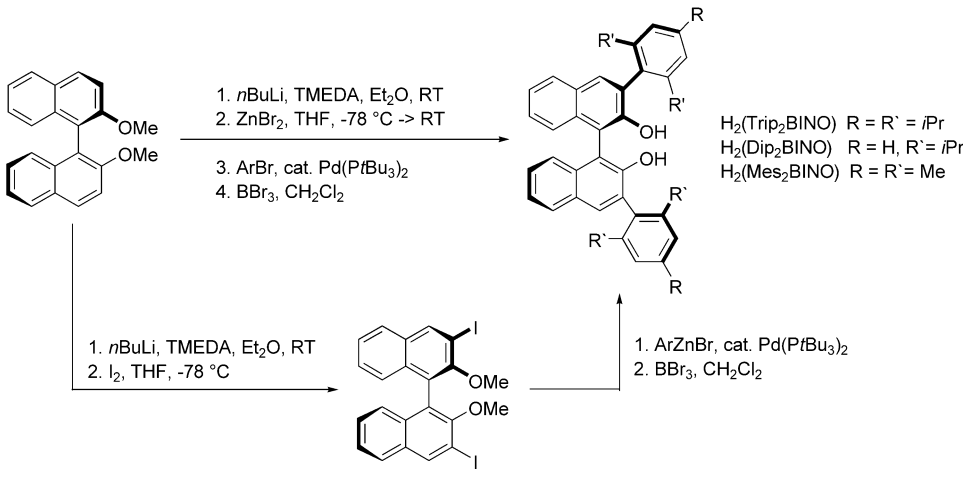
those of the amido ligands at $-60\,^{\circ}C$. The geometry of the complex at the last temperature is highly asymmetric and gives rise to two broad singlets for the SiH protons at 4.24 and 5.00 ppm, as well as three signals for the silicon methyl groups at 0.15, 0.22 and 0.42 ppm in a 3:6:3 ratio. The dynamic-exchange process of bridging and terminal phenolate groups is significantly slower in the yttrium complex (*R*,*S*)-**3a**. The signals of the *tert*-butyl and methyl groups decoalesce at $30\,^{\circ}C$, those of the amido ligand at $-20\,^{\circ}C$.

We then shifted our attention to ligands with larger substituents in *ortho* position, such as H_2(Trip$_2$BINO)[10c] with a 2,4,6-triisopropylphenyl group, because the *tert*-butyl group in H_2(Biphen) could not prevent facile dimerization. Binaphtholate ligands with aryl groups in the 3,3′-position are usually synthesized by nickel-catalyzed coupling[10d,e, 19] or Suzuki coupling.[20] However, these syntheses are usually lengthy multistep procedures that require high catalyst loadings (up to 10 mol% for nickel catalysts) and often give only moderate yields (60–70%). Therefore, we sought a shorter route to the desired arylated binaphthol ligands. We found that attachment of the 3,3′-aryl substituents can be performed in a three-step one-pot procedure starting from 2,2′-dimethoxy-1,1′-dinaphthyl by a Negishi coupling of 3,3′ $\frac{1}{N}$ dimetallated binaphthol with the corresponding aryl bromide (Scheme 2). While the reaction proceeds cleanly for the mesityl-substituted ligand with 74% yield, significantly lower yields in the range of 40–50% were obtained in case of 2,6-isopropyl-substituted aryl bromides. Additionally, the latter products were often contaminated with monoarylated product and starting material. This, however, can be avoided by performing the coupling with 3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthyl and the corresponding aryl zinc bromide to give the desired ligands in 79–91% overall yield after deprotection with boron tribromide (Scheme 2).

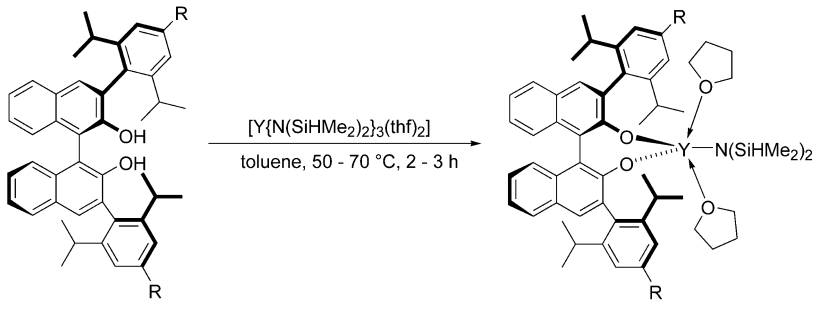
Reaction of racemic H_2(Trip$_2$BINO) with **1a** in toluene at $50\,^{\circ}C$ led to a quantitative formation of the monomeric complex **4a** (Scheme 3). However, due to its high solubility in aliphatic solvents even at $-78\,^{\circ}C$, all crystallization attempts have failed so far. Therefore we decided to use the 2,6-diisopropylphenyl-substituted binaphthol ligand, H_2(Dip$_2$BINO), instead, which should have more advantageous solubility properties. H_2(Dip$_2$BINO) reacts cleanly with **1a** under similar conditions to those used for H_2(Trip$_2$BINO) to give the monomeric complex **5a** (Scheme 3), which was crystallized from hexanes at $-30\,^{\circ}C$ in 67% yield. The enantiopure complex (*R*)-**5a** was synthesized similarly from **1a** and H_2((*R*)-Trip$_2$BINO), but could only be isolated as an oily precipitate from hexanes. We also tried to prepare complexes of the sterically less-hindered mesityl-substituted ligand H_2(Mes$_2$BINO), but its reaction with **1a**,**b** or [Y{N(SiMe$_3$)$_2$}$_3$] under various solvent and temperature conditions gave only complex product mixtures.

Variable-temperature ^{1}H NMR spectra of neither racemic nor enantiopure **5a** showed the presence of dimeric species.

Treatment of H_2(Trip$_2$BINO) with **1b** gave **4b** in a relatively clean reaction (ca. 80% purity according to NMR spectroscopy for the racemic ligand and 60–70% for the (*R*) ligand), but crystallization could not improve purity. Treatment of H_2(Dip$_2$BINO) with **1b** on the other hand gave a product



Scheme 2.



Scheme 3.

mixture containing only about 50% of the desired product. We attribute this discrepancy to the significantly lower solubility of H_2(Dip$_2$BINO) compared with H_2(Trip$_2$BINO) in the reaction mixture, which results in a different ratio of kinetic products (see Discussion).

Molecular structure of (*R*,*S*)-[Ln(Biphen){N(SiHMe$_2$)$_2$}-(thf)]$_2$ (Ln = Y, La): Clear, colourless crystals of (*R*,*S*)-**3a** and (*R*,*S*)-**3b** suitable for X-ray diffraction analysis were obtained by cooling a warm, concentrated benzene or toluene solution to room temperature. An ORTEP diagram of the structure of (*R*,*S*)-**3b** is shown in Figure 4. Crystallographic data are compiled in the Experimental Section, selected bond lengths and angles are summarized in Table 1.

In the centrosymmetric, heterochiral dimers (*R*,*S*)-**3a** and (*R*,*S*)-**3b**, the two biphenolate metal moieties are connected by bridging of two phenolate units. A similar bridging motif of a biphenolate ligand was observed in the thiobinaphtholate complex [Sm{1,1′-S(2-OC$_{10}$H$_4$*t*Bu$_2$-3,6}(OC$_6$H$_3$*t*Bu$_2$-2,6)]$_2$.[21] The metals are coordinated in a distorted trigonal bipyramidal fashion, with one of the bridging phenolate ligands (O11) and the THF ligand occupying axial positions and the amido ligand, the terminal phenolate and the second bridging phenolate group in equatorial positions. The increased stability of the heterochiral dimer in (*R*,*S*)-**3a** and (*R*,*S*)-**3b** is in contrast to the majority of previously reported crystal structures of binaphtholate- or biphenolate-bridged M_2O_2 complexes in which the homochiral dimer is the more stable form,[22] while heterochiral dimers are scarce.[21, 23]

As commonly observed,[24] the bridging metal–phenolate bond lengths are a minimum of 0.17 Å longer than the terminal phenolate group (typical range Y–OAr (term.) = 2.00–2.15 Å, Y–OAr (bridge) = 2.18–2.36 Å, La–OAr (term.) = 2.17–2.32 Å, La–OAr (bridge) = 2.32–2.43 Å).[9, 25] The bridging mode of the phenolate ligands is slightly asymmetrical in the case of the lanthanum complex (*R*,*S*)-**3b**, in which the axial phenolate bond (La1–O11) is about 0.1 Å longer than the equatorial phenolate bond (La1–O11′). The Y_2O_2 ring in (*R*,*S*)-**3a**, on the other hand, displays a symmetric bridging mode, with almost identical yttrium-to-bridging-phenolate bond lengths. The Ln···Ln separations are on the upper end of the scale of known complexes with a Ln_2O_2 core (Y: 3.42–3.75 Å, La: 3.96–4.02 Å).[24, 25b, 26] The La–O bond to the terminal phenolate group (2.234(2) Å) in (*R*,*S*)-**3b** is in the same range as that found in [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}(thf)$_3$] (2.271(9) and 2.216(7) Å).[9] While the bite angle O-La-O of the Biphen ligand (88.83(7)°) in (*R*,*S*)-**3b** compares well with the 88.1(3)° found in [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}(thf)$_3$],[9] the dihedral angle between the two phenol rings (87.8(4)° for (*R*,*S*)-**3b** is significantly larger than the 72.9(1.9)° found in hexacoordinate [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}(thf)$_3$],[9] which is caused by steric restrains enforced on the Biphen ligand to adopt the bridging-ligating mode. The distance between lanthanum and the *ipso*-carbon of the bridging phenolate La···C11 (2.911(3) Å) in (*R*,*S*)-**3b** and the decreased La-O11-C11 angle of only 92.81(16)° indicate a

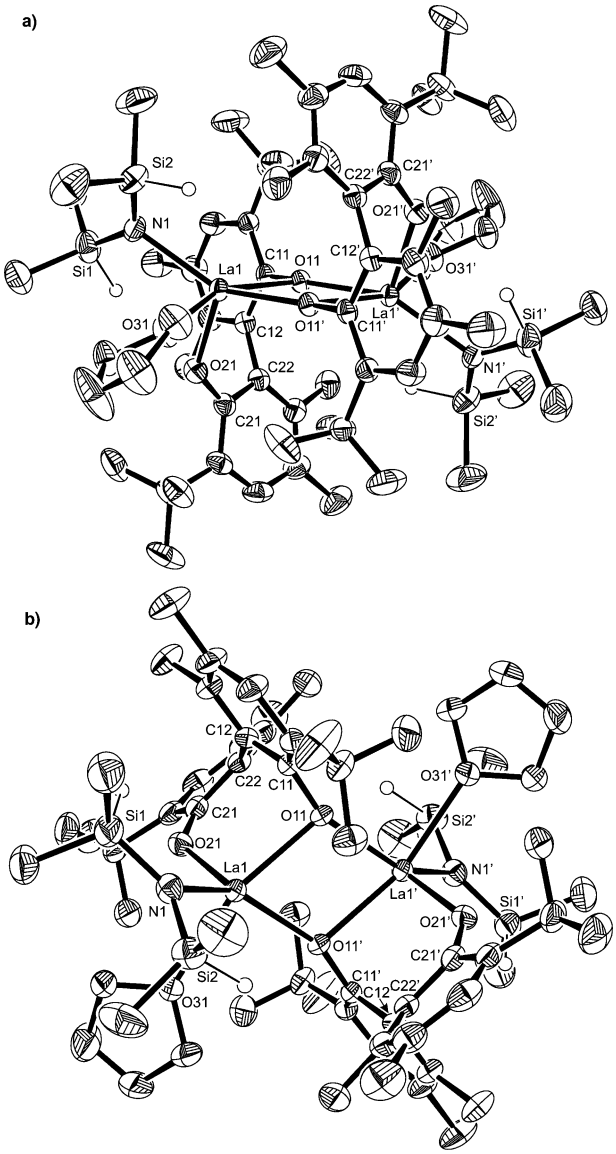


Figure 4. ORTEP diagram of the molecular structure of (*R*,*S*)-**3b**: a) side view, b) top view. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for those on silicon, are omitted for the sake of clarity.

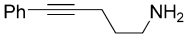
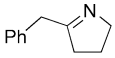
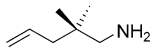
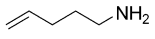
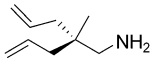
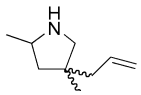
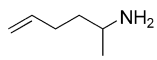
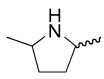
Table 1. Selected bond lengths [Å], atomic separations [Å] and angles [°] for (*R*,*S*)-**3a** and (*R*,*S*)-**3b**.

	(*R*,*S*)-**3a**	(*R*,*S*)-**3b**
M–O21	2.099(2)	2.234(2)
M–O11	2.280(2)	2.503(2)
M–O11′	2.270(2)	2.407(2)
M–O31	2.389(2)	2.575(2)
M–N1	2.260(2)	2.416(3)
M···M	3.7006(8)	3.9954(3)
M···C11	3.010(2)	2.911(3)
M···Si1	3.1344(9)	3.5240(11)
M···Si2	3.6088(10)	3.3703(10)
O11-M-O21	88.79(6)	88.83(7)
O11-M-O11′	71.15(6)	71.10(8)
M-O11-M′	108.85(6)	108.90(8)
O11-M-O31	157.18(6)	153.24(7)
O21-M-O31	91.40(6)	86.71(8)
O11′-M-O31	89.17(6)	85.43(7)
M-O11-C11	107.88(13)	92.81(16)
M-O21-C21	133.52(14)	132.5(2)
N1-M-O11	113.08(6)	123.41(9)
N1-M-O11′	136.11(7)	142.14(9)
N1-M-O31	89.02(7)	83.07(9)
O21-M-N1	103.82(7)	106.41(9)
O21-M-O11′	120.06(6)	108.79(8)
M-N1-Si1	103.81(10)	116.17(14)
M-N1-Si2	130.02(11)	109.56(14)
Si1-N-Si2	123.29(13)	133.94(17)
C11-C12-C22-C21	76.7(3)	87.8(4)

stronger bonding interaction between lanthanum and C11 than that observed in $[La\{1,1'\text{-}(2\text{-}OC_6H_2tBu_2\text{-}3,5)_2\}\{CH(SiMe_3)_2\}(thf)_3]$ (La···C_{ipso} = 3.096(13) Å, La-O-C_{ipso} = 113.6(7)°).[9] This interaction is also significantly less pronounced in (*R*,*S*)-**3a**, to the point that the corresponding Y···C_{ipso} distance (3.010(2) Å) is *longer* and the Y-O-C_{ipso} angle (107.88(13)°) *larger* than those found in (*R*,*S*)-**3b**, although the atomic radius of yttrium is 0.132 Å *smaller* than that of lanthanum.[17] The metal–nitrogen bond lengths (2.260(2) Å in (*R*,*S*)-**3a**, 2.416(3) Å in (*R*,*S*)-**3b**) are in the centre of the typical range found in other amido complexes (Y: 2.18–2.32 Å,[27] La: 2.30–2.49 Å[28]) and they are close to those found in their starting materials **1a**[29] and **1b**.[28f] The geometry of the amido ligand is asymmetric and can best be compared to the geometry found in $[(C_5HPh_4)_2La\{N(SiHMe_2)_2\}]$.[28k] One of the silicon atoms is getting closer to the metal centre (La···Si = 3.3703(10) vs. 3.5240(11) Å for (*R*,*S*)-**3b**, 3.261(2) vs. 3.472(2) Å for one of the two independent molecules of $[(C_5HPh_4)_2La\{N(SiHMe_2)_2\}]$[28k]) concomitant with a decrease in the La-N-Si angle (109.56(14) vs. 116.17(14)° for (*R*,*S*)-**3b**, 107.7(2) vs. 117.2(2)° for one of the two independent molecules of $[(C_5HPh_4)_2La\{N(SiHMe_2)_2\}]$[28k]). This is indicative of a weak β-SiH monoagostic interaction as has been discussed for other dimethylsilylamido rare-earth-metal complexes.[15, 28h,k, 30] The monoagostic interaction is significantly more pronounced in the smaller yttrium complex (*R*,*S*)-**3a** (Y···Si = 3.1344(9) vs. 3.6088(10) Å, Y-N-Si = 103.81(10) vs. 130.02(11)°). The Si-N-Si angle is slightly widened in (*R*,*S*)-**3b** (133.94(17)°) as a result of the agostic interaction, while it remains normal in (*R*,*S*)-**3a** (123.29(13)°).

Catalytic hydroamination/cyclization: Complexes **2**–**5** were investigated for their catalytic activity in the hydroamination/cyclization of an aminoalkyne and aminoalkenes (Table 2). The binaphtholate complex (*R*)-**5a** shows the highest activity.

Table 2. Catalytic hydroamination/cyclization reactions.

Substrate	Product	Entry	Cat.[a]	*T* [°C]	Reaction time [h]	Conv. [%]	TOF[b] [h^{-1}]	*ee* product;[c] diastereomeric ratio	*ee* reactant;[c] k_{rel}
		1	(*rac*)-**2a**	60	19	>99	3		
		2	(*R*,*S*)-**3a**	60	28.5	46	0.6		
6	**7**	3	(*R*,*S*)-**3b**	60	19	79	5		
		4	(*R*)-**5a**	60	9	>99	11		
		5	(*R*)-**2a**	70	22	77	2.5	36	
		6	(*R*,*S*)-**3b**	70	11	82	4		
8		7	(*R*)-**5a**	50	40	75	–[d]	29.2	
	9	8	(*R*)-**5a**	60	7	92	13.5	28.3	
		9	(*R*)-**5a**	100	0.75	>99	–[d]	28.0	
		10	(*R*)-**2a**	80	23	13	–[d]	–[d]	
		11	(*R*)-**5a**	70	43	91	–[d]	57	
10		12	(*R*)-**5a**	100	16	>99	–[d]	52	
	11								
		13	(*R*)-**5a**[e]	70	72	49	0.07	33/33; 54:46	
		14	(*R*)-**5a**[e]	90	6.5	>99	1.5	32/34; 53:47	
12	**13**								
		15	(*R*)-**5a**[f]	90	1.5	61	–[d]	35 (*trans* isomer); 6.4:1 (*trans*/*cis*)	43; 2.6
14	**15**								

[a] Reaction conditions: 4 mol% cat., C_6D_6, Ar atm. [b] Turnover frequency. [c] Determined by ^{19}F NMR of the Mosher amides. [d] Not determined. [e] 10 mol% cat. [f] 5 mol% cat.

Ring-closing of aminoalkyne **6** proceeds with a turnover frequency of 11 h^{-1} at 60 °C. The dimeric lanthanum complex (*R*,*S*)-**3b** and the monomeric yttrium complex **2a** have similar activity (5 and 3 h^{-1} respectively), while the dimeric yttrium complex (*R*,*S*)-**3a** shows the lowest activity (0.6 h^{-1}). This indicates that (*R*,*S*)-**3a** remains dimeric under the catalytic conditions employed. Similar observations were made for the hydroamination of aminoalkene **8** (Figure 5). (*R*)-**5a** was

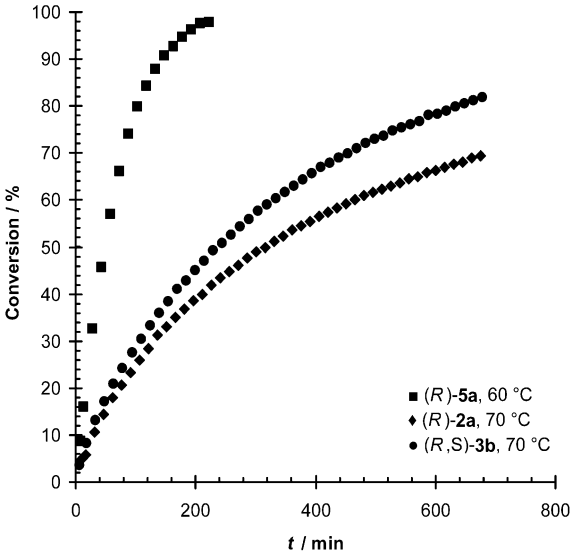


Figure 5. Hydroamination/cyclization of **8** with (*R*)-**5a**, (*R*,*S*)-**3b** and (*R*)-**2a** in C_6D_6.

significantly more active (13.5 h^{-1} at 60 °C) than (*R*,*S*)-**3b** (4 h^{-1} at 70 °C) or (*R*)-**2a** (2.5 h^{-1} at 70 °C). One important feature is that all biphenolate and binaphtholate complexes show significant deviation from commonly observed zeroth-order rate dependence in the substrate.[5] Deviation from zeroth-order kinetics has been attributed previously to a competitive coordination of the product heterocycles and thereby inhibition of the catalysts when sterically more accessible *ansa*-lanthanocenes were employed.[5c] Preliminary kinetic data suggest first-order rate dependence on substrate concentration for complex (*R*,*S*)-**3b** and (*R*)-**5a** and second-order for complex (*R*)-**2a** (Figures 6 and 7).

Hydroamination of **8** by using the enantiopure complexes (*R*)-**2a** and (*R*)-**5a** gave the pyrrolidine **9** in 36 or 29 % *ee*, respectively (Table 2, entries 5 and 7–9). Interestingly, the ring-closing of **10** proceeded with a higher enantioselectivity of 57 % *ee*. The enantiomeric excess is nearly independent of the reaction temperature over the range 50–100 °C (Table 2, entries 7–9, 11 and 12); this is a significant advantage, because most of the catalytic reaction had to be performed at elevated temperatures to achieve economical turnover frequencies. Reaction of the amino diolefin derivative **12** proceeded essentially without diastereoselectivity when using (*R*)-**5a** (54:46) and with essentially the same enantioselectivity as for the amino olefin **8**. In order to achieve appreciable turnover numbers, significantly higher reaction temperatures and higher catalyst loadings are required for substrate **12**.

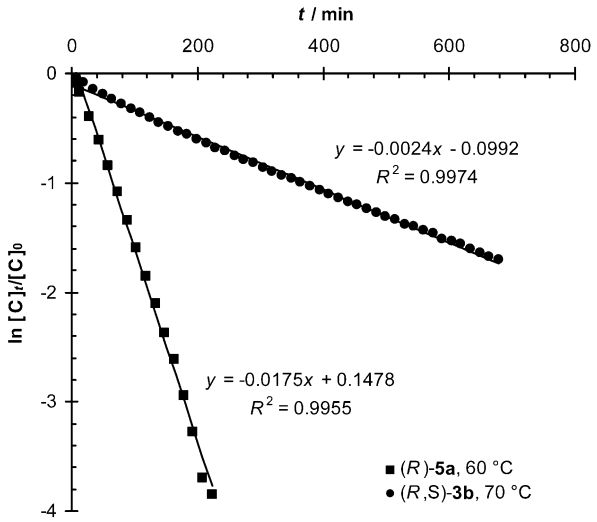


Figure 6. First-order plot for the hydroamination/cyclization of **8** with (*R*)-**5a** and (*R*,*S*)-**3b** in C_6D_6.

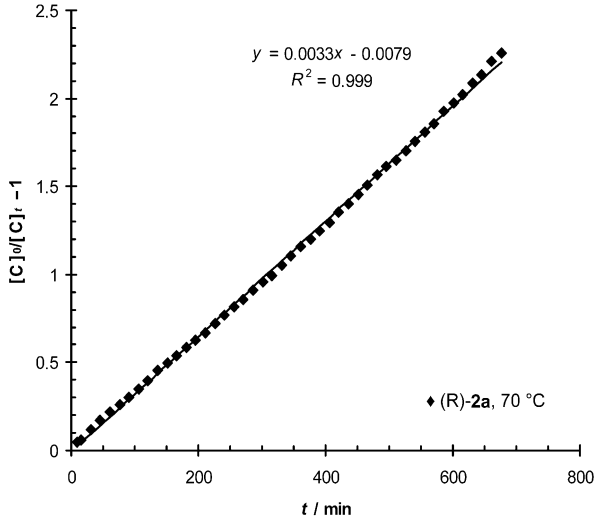
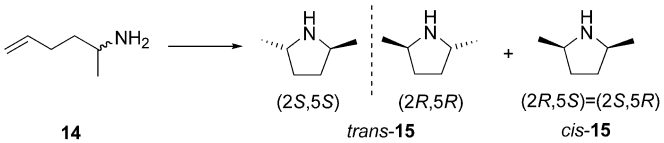


Figure 7. Second-order plot for the hydroamination/cyclization of **8** with (*R*)-**2a** in C_6D_6.

Ring-closing of racemic 2-aminohex-5-ene (**14**) produced two enantiomeric *trans*-2,5-dimethylpyrrolidines as well as *meso cis*-2,5-dimethylpyrrolidine (Scheme 4). Kinetic resolution of **14** to enantiomerically enriched *trans*-**15** and **14** should become feasible if a chiral catalyst is employed and exchange between coordinated and free substrate is fast. Indeed, 5 mol % (*R*)-**5a** gave 2,5-dimethylpyrrolidine in 61 % conversion with good *trans*-selectivity (6.4:1) and 35 % *ee* for the



Scheme 4.

trans product. The remaining starting material **14** was obtained in 43% *ee*. Therefore the relative rate constant for the two enantiomers of **14** was determined to be 2.6.[31]

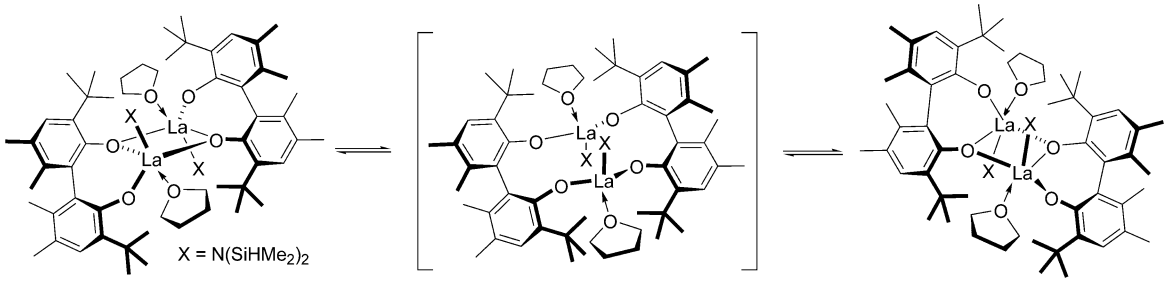
Discussion

The success of an organometallic complex synthesis depends often on the right choice of starting materials, reaction conditions and solvents. This is especially important in the synthesis of rare-earth-metal complexes. Various methods have been designed in recent years to circumvent common problems, such as alkali-metal salt incorporation. The most successful strategies involve amine[28h, k, 29, 32f, 33] or alkane[9, 27, 32] elimination starting from well-defined, alkali-metal-salt-free rare-earth-metal tris(alkyl) or tris(amido) complexes. Whereas rare-earth-metal tris(alkyl) complexes generally react under milder conditions, tris(amido) complexes are usually easier to prepare and thermally robust; this is often more desirable for catalytic applications in organic synthesis. One problem frequently observed in the synthesis of complexes containing bi- or multidentate ligands is the formation of product mixtures,[33d,e, 34] rooted in the desire of rare-earth metals to achieve high coordination numbers and their tendency to form aggregated structures. Due to the multistep nature of complex formation and the different reactivity of the various species involved, the desired disubstituted complexes [(diolate)Ln(amido)(thf)$_n$] have to be regarded as kinetic products. The failure to obtain any viable product from the reaction of [Ln{N(SiMe$_3$)$_2$}$_3$] can be ascribed to a higher reactivity of the sterically more open species formed upon substitution of the first bulky bis(trimethylsilylamido) ligand in the starting tris(amido) complex. The dimethylsilylamido ligand has been applied successfully over recent years by Herrmann and Anwander.[15, 28h,k, 29, 33d–f] It reacts differently because the smaller amido ligand can modulate the reactivity of different species by allowing THF coordination or stabilizing β-SiH agostic interactions. An important factor contributing to the clean reaction of racemic H$_2$(Biphen) with [La{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (**1b**) is the facile dimerization of La(Biphen){N(SiHMe$_2$)$_2$}(thf)$_x$ forming the heterochiral dimer (*R*,*S*)-**3b**. The corresponding monomeric enantiopure species derived from H$_2$((*R*)-Biphen) and **1b** does not dimerize readily; this results in uncontrolled side reactions with free-ligand or other lanthanum species. Similar side reactions were observed in the case of the yttrium complexes at ambient temperatures, although to a significantly lower extent due to the smaller atomic radius of yttrium. Higher temperatures diminish such side reactions, as intermolecular reactions are entropically disfavoured.

The majority of structurally characterized biphenolate- or binaphtholate-bridged complexes are composed of homochiral C_2-symmetric dimers.[22] The preference for the formation of homochiral dimers has been attributed to the absence of unfavourable interligand contacts combined with favourable solvation properties by a parallel stacking of the *syn* terminal phenolate ligands.[22b] While most of these complexes have only small substituents in the 3 and 3′ positions (H, Me), only one example with a bulky substituent has been reported.[22i] The formation of homochiral [Fe{1,1′-(2-OC$_6$H$_3$-3-SiPh$_3$)$_2$}]$_2$ can be rationalized by the π-coordination of one of the silicon phenyl groups of the bridging phenolate to an iron centre, which would be impossible in a heterochiral dimer. In fact, the higher stability of the heterochiral dimers (*R*,*S*)-**3** can be explained by unfavourable 1,3-*trans*-annular interactions of the bulky *tert*-butyl groups in a potential homochiral dimer, similar to (*R*,*S*)-[(daib)ZnR]$_2$ (daib = 3-*exo*-(dimethylamino)-isoborneol).[35] This difference in stability of homo- and heterochiral dimers is the explanation for many nonlinear effects in asymmetric synthesis.[36]

The exchange of bridging and terminal phenolate groups in (*R*,*S*)-**3b** on the NMR timescale can be postulated to involve a nonchelating bridging biphenolate ligand (Scheme 5).[22a, 37] An intermolecular mechanism involving dissociation of the heterochiral dimer into two monomeric species can be ruled out on the basis of i) the heterochiral dimer (*R*,*S*)-**3a** showing significantly lower catalytic activity than the monomeric complex (*R*)-**2a** (Table 2, entries 1 and 2) and ii) the stability of a supposedly homochiral species **3b**′, formed upon heating (*R*,*S*)-**3b** for several weeks at room temperature. Additionally, this exchange of terminal and bridging phenolate groups was not observed in the dimeric thiobinaphtholate complex [Sm{1,1′-S(2-OC$_{10}$H$_4$*t*Bu$_2$-3,6}(OC$_6$H$_3$*t*Bu$_2$-2,6)]$_2$.[21] While a dissociative process should be as facile as in the case of (*R*,*S*)-**3b**, an intramolecular process is highly disfavoured due to the restricted flexibility of the ligand enforced by the thioether coordination.

The biphenolate and binaphtholate complexes exhibit only moderate activity for the catalytic hydroamination/cyclization of aminoalkynes and aminoalkenes in comparison with lanthanocene catalysts.[5] The latter systems show especially high activities for aminoalkyne substrates, for example, turnover frequencies of up to 2830 h^{-1} for **6** with [Cp*$_2$Sm{CH(SiMe$_3$)$_2$}] at 60 °C (or 77 h^{-1} at 21 °C).[5h] Activ-



Scheme 5.

ities for aminoalkene substrates are usually one or two orders of magnitude smaller, for example, turnover frequencies for the cyclization of **8** can range from $<1\ h^{-1}$ at 80 °C with $[Cp^*_2Lu\{CH(SiMe_3)_2\}]$ up to $95\ h^{-1}$ at 25 °C with $[Cp^*_2La\{CH(SiMe_3)_2\}]$.[5a] The activities for aminoalkyne **6** and aminoalkene **8**, on the other hand, are of the same order of magnitude when using the binaphtholate complex (*R*)-**5a**, and ring-closing of **8** falls well within the range of activities observed for lanthanocene catalysts. Certainly, significant catalyst deactivation has to be attributed to inhibition by coordination of THF, so that higher reaction temperatures are required to facilitate THF dissociation. While lanthanocene systems are generally not affected by small amounts of THF,[5a] the sterically more open biphenolate and binaphtholate systems are significantly more sensitive in this respect.

Despite being only low to moderate by current general standards, the enantioselectivities in the catalytic hydroamination/cyclization reactions are in a comparable range to those obtained with C_1-symmetric lanthanocene complexes at temperatures at or below room temperature.[5c,d] The increase in enantioselectivity on going from dimethyl-aminopentene **8** to the unsubstituted aminopentene **10** was also noted for the lanthanocene catalysts, although the difference is generally lower than 20 %.[5c,d] The thermal robustness of the catalysts and relatively insensitivity of enantioselectivity to reaction temperature seems to be noteworthy. Rare-earth-metal complexes have a high tendency to ligand redistribution reactions, especially in the presence of donor molecules. Such reactions would have a significant detrimental effect on enantioselectivity, as different diastereomeric or achiral complexes with different catalytic activity and selectivity may be present. The small temperature dependence of the observed enantioselectivities therefore suggests that the biphenolate and binaphtholate catalysts do not undergo such ligand redistributions to a significant extent under these conditions. Another important finding seems to be the kinetic resolution of racemic 2-aminohex-5-ene (**14**) with (*R*)-**5a**, although with a moderate relative rate of 2.6. This should, however, be compared with C_1-symmetric lanthanocene catalysts, which have been reported to give enrichments below 20 % *ee* at 25 °C at various extents of conversion.[5c] For an effective kinetic-resolution reaction to occur, a fast exchange process between coordinated amido (or amino) ligands and free substrate has to be operative prior to ring closing. This process must be easier for the binaphtholate catalyst than the lanthanocene catalysts, either due to the higher reaction temperature applied or due to a sterically more open coordination sphere.

Conclusion

We have presented here the facile synthesis of new chiral $[Y\{diolate\}\{N(SiHMe_2)_2\}(thf)_2]$ complexes, which represent, to the best of our knowledge, the first examples of chiral, cyclopentadienyl-free rare-earth-metal-based catalysts for asymmetric hydroamination/cyclization. The synthesis and solution behaviour of the complexes based on the Biphen ligand are complicated by the formation of stable heterochiral dimers. The 3,3′-arylated binaphtholate gave only isolable complexes in the presence of isopropyl substituents in the 2 and 6 positions of the 3,3′-aryl groups. The resulting complexes are monomeric in solution and show the highest catalytic activity. However, catalytic activity is limited due to the coordination of THF molecules. Although the enantioselectivities obtained with these systems remain unsatisfactory for the moment, the modularity of the binaphtholate ligand set, as well as utilization of rare-earth metals with varying atomic radii should allow catalyst optimization. Current investigations are focused on addressing these problems. Further kinetic and mechanistic investigations will be reported in due course. Finally, we believe that this new class of chiral rare-earth-metal catalyst will find applications in other areas of organic and polymer synthesis.[7c–j]

Experimental Section

General considerations: All operations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk-line or glovebox techniques. After being dried over KOH, THF was distilled from sodium benzophenone ketyl. Hexanes, pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous YCl_3 (Aldrich) and (*R*)-BINOL (>99 % *ee*)[11] were used as received. $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Y (**1a**), La (**1b**)),[15] (*rac*)- and (*R*)-2,2′-dimethoxy-1,1′-dinaphthyl,[19a] and substrates **6**,[5h] **8**,[38] **10**[5a] and **14**[39] were synthesized as described in the literature. The substrates were dried by distillation over CaH_2, followed by a second distillation over trioctyl aluminium (2 mol % added). H_2(Biphen) was conveniently prepared by oxidative coupling of 2-*tert*-butyl-4,5-dimethylphenol by using $K_3Fe(CN)_6$/KOH,[40] thus avoiding the use of $K_2Cr_2O_7/H_2SO_4$. H_2(Biphen) was then resolved by use of the diastereomeric phosphates prepared with (−)-menthyldichlorophosphite[41] as previously described.[10c] 2,6-Diisopropylphenyl bromide was prepared by Sandmeyer reaction from 2,6-diisopropylanilin.[42] The 2,6-diisopropylphenol, which is formed as a side product, can be removed by stirring a solution with solid KOH in hexanes, followed by filtration through a short column of silica gel. 2,2′-Dimethoxy-3,3′-diiodo-1,1′-binaphthyl[10e] was prepared by *ortho*-lithiation of 2,2′-dimethoxy-1,1′-binaphthyl followed by treatment with elemental iodine. The preparation of the *ortho*-lithiated species via lithiation of 2,2′-dimethoxy-3,3′-dibromo-1,1′-binaphthyl as reported earlier[10e] was not found to be necessary. (*R*)-(+)-α-Methoxy-α-trifluoromethylphenylacetic acid (RCA) was transformed to its acid chloride by using oxalyl chloride/DMF in hexanes.[43] All other chemicals were commercially available and used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or Avance 400 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department. Although metal complexes were combusted with V_2O_5 as burning aid, analyses often gave low carbon content repeatedly, presumably due to carbide formation.

3,3′-Bis(2,4,6-triisopropylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl: *n*BuLi (5.0 mL, 2.27 M in hexane, 11.4 mmol) was added to a solution of TMEDA (*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine, 1.5 mL, 10 mmol) in diethyl ether (25 mL). Finely powdered 2,2′-dimethoxy-1,1′-dinaphthyl (1.57 g, 5.0 mmol) was added to the mixture in one portion. The mixture was stirred overnight at room temperature, then the solvent was removed in vacuo. The dilithium salt was dried in vacuo for 2 h (0.1 Torr). The flask was placed in a dry ice/acetone bath, and a solution of $ZnCl_2$ (11.5 mL, 1M in THF, 11.5 mmol) was added. The resulting mixture was stirred at room temperature until the dilithium salt completely dissolved, then 2,4,6-triisopropylphenylbromide (3.00 g, 10.6 mmol) and $Pd(PtBu_3)_2$ (50 mg, 0.1 mmol) were added. The mixture was transferred into a 25 mL round-bottom flask with teflon valve through a cannula and heated to 105 °C overnight. After being cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was dissolved in CH_2Cl_2 (40 mL). The solution was washed with dilute HCl, dried over Na_2SO_4 and passed through a short column of silica. After removal of the solvent, the residue was dissolved in hexanes (15 mL), and the solution was cooled to 0 °C. After 24 h, the

resulting powder was filtered off, washed with cold hexanes and dried in air; yield 1.78 g (49%), contaminated with 10% of mono adduct. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.83$ (d, $^3J_{H,H} = 8.0$ Hz, 2H; aryl), 7.72 (s, 2H; aryl), 7.27–7.42 (m, 8H; aryl), 7.07 (d, 4H; aryl), 3.06 (s, 6H; OCH_3), 2.94 (sept, $^3J_{H,H} = 6.8$ Hz, 2H; $CH(CH_3)_2$), 2.80 (m, 4H; $CH(CH_3)_2$), 1.30 (d, $^3J_{H,H} = 6.9$ Hz, 12H; $CH(CH_3)_2$), 1.04–1.19 (m, 24H; $CH(CH_3)_2$). Deprotection of 3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl by using boron tribromide in CH_2Cl_2 was facilitated as described in the literature.[10d]

(*R*)-3,3′-Bis(2,4,6-triisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (H_2((*R*)-Trip$_2$BINO)): *n*BuLi (3.1 mL, 2.5 M in hexane, 7.75 mmol) was added to a solution of 2,4,6-triisopropylphenylbromide (2.19 g, 7.73 mmol) in THF (5 mL) at −70 °C. The reaction mixture was stirred at this temperature for 20 min, and a solution of $ZnBr_2$ (9 mL, 1 M in THF, 9 mmol) was added. The reaction mixture was allowed to warm to room temperature, and the solvent was removed in vacuo. The colourless oily residue was dried in vacuo for 2 h (0.1 Torr) in order to remove *n*BuBr. THF (15 mL), (*R*)-3,3′-diiodo-2,2′-dimethoxy-1,1′-dinaphthyl (1.90 g, 3.36 mmol) and Pd(P*t*Bu$_3$)$_2$ (17 mg, 34 μmol) were added, and the resulting mixture was heated to 60 °C overnight. After the mixture had been cooled to room temperature, dilute HCl (10 mL, 2–3%) and ether (20 mL) were added. The organic layer was separated, washed with brine, dried over Na_2SO_4 and passed through a short column of silica with Et_2O as eluent. After removal of the solvent, the residue was dried in vacuo for 4 h. The crude material was dissolved in dry CH_2Cl_2 (15 mL), cooled to −5 °C, and a solution of boron tribromide (13 mL, 1 M in CH_2Cl_2, 13 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature, then cooled to 0 °C, and water (10 mL) was added slowly. Stirring was continued for 30 min. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the remaining brown oil was separated by chromatography on a silica-gel column with hexanes/CH_2Cl_2 (5:1; $R_f = 0.2$) to give 2.04 g (88%) of a white crystalline powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (d, $^3J_{H,H} = 7.8$ Hz, 2H; aryl), 7.77 (s, 2H; aryl), 7.27–7.38 (m, 6H; aryl), 7.14 (d, $^3J_{H,H} = 7.4$ Hz, 4H; aryl), 4.92 (s, 2H; OH), 2.96 (sept, $^3J_{H,H} = 6.9$ Hz, 2H; $CH(CH_3)_2$), 2.86 (sept, $^3J_{H,H} = 6.8$ Hz, 2H; $CH(CH_3)_2$), 2.67 (sept, $^3J_{H,H} = 6.8$ Hz, 2H; $CH(CH_3)_2$), 1.32 (d, $^3J_{H,H} = 6.9$ Hz 12H; $CH(CH_3)_2$), 1.20 (d, $^3J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$), 1.12 (d, $^3J_{H,H} = 7.0$ Hz, 6H; $CH(CH_3)_2$), 1.09 (d, $^3J_{H,H} = 7.0$ Hz, 6H; $CH(CH_3)_2$), 1.04 (d, $^3J_{H,H} = 6.9$ Hz, 6H; $CH(CH_3)_2$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 150.6$, 149.1, 147.8, 147.7, 133.4, 130.6, 130.4 129.1, 129.0, 128.2, 126.6, 124.5, 123.7, 121.22, 121.16, 113.1 (aryl), 34.3, 30.9, 30.8 ($CH(CH_3)_2$), 24.29, 24.27, 24.05, 23.99, 23.91, 23.7 ($CH(CH_3)_2$).

3,3′-Bis(2,6-diisopropylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl

Method A: *n*BuLi (13 mL, 2.6 M in hexane, 33.8 mmol) was added to a solution of TMEDA (4.5 mL, 30 mmol) in diethyl ether (75 mL). Finely powdered 2,2′-dimethoxy-1,1′-dinaphthyl (4.71 g, 15 mmol) was added to the mixture in one portion. The mixture was stirred overnight at room temperature, then the solvent was removed in vacuo. The dilithium salt was dried in vacuo for 2 h (0.1 Torr), and THF (20 mL) was added. The flask was placed in a dry ice/acetone bath and a solution of $ZnBr_2$ (34 mL, 1 M in THF, 34 mmol) was added. The resulting mixture was stirred at room temperature until the dilithium salt completely dissolved (1 h), 2,6-diisopropylphenylbromide (7.23 g, 30 mmol) and Pd(P*t*Bu$_3$)$_2$ (0.1 g, 0.2 mmol) were then added. The mixture was transferred into a 100 mL round-bottom flask with a teflon valve by a needle and heated to 105 °C for 24 h. During the reaction time, the product precipitated from homogeneous solution. After the reaction mixture had been cooled to room temperature, the solvent was removed by rotary evaporation and CH_2Cl_2 (40 mL) and water (30 mL) were added to the residue. The mixture was shaken vigorously for several minutes, and a white powder was filtered off, washed with dilute HCl, water, CH_2Cl_2 and dried in air. Yield: 4.32 g (45%).

Method B: *n*BuLi (7.9 mL, 2.6 M in hexane, 20.5 mmol) was added to a solution of 2,6-diisopropylphenylbromide (4.94 g, 20.5 mmol) in THF (25 mL) at −70 °C. The reaction mixture was stirred at the same temperature for 20 min, and a solution of $ZnBr_2$ (21.5 mL, 1 M in THF, 21.5 mL) was added. The reaction mixture was allowed to warm to room temperature, and the solvent was removed in vacuo. The colourless oily residue was dried in vacuo for 2 h (0.1 Torr). THF (30 mL), 3,3′-diiodo-2,2′-dimethoxy-1,1′-dinaphthyl (5.09 g, 9 mmol) and Pd(P*t*Bu$_3$)$_2$ (53 mg, 0.1 mmol) were added. The mixture was heated to 60 °C overnight. After the mixture had been cooled to room temperature, the solvent was removed by rotary evaporation, and CH_2Cl_2 (30 mL) and water (20 mL) were added to the residue. The mixture was shaken vigorously for 1 min, and a white powder was filtered off, washed with dilute HCl, water and diethyl ether and dried in air to yield 4.84 g (85%) of a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.85$ (d, $^3J_{H,H} = 8.1$ Hz, 2H; aryl), 7.71 (s, 2H; aryl), 7.21–7.42 (m, 12H; aryl), 3.05 (s, 6H; OCH_3), 2.85 (sept, $^3J_{H,H} = 6.8$ Hz, 2H; $CH(CH_3)_2$), 2.77 (sept, $^3J_{H,H} = 6.8$ Hz, 2H; $CH(CH_3)_2$), 1.18 (d, $^3J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$), 1.15 (d, $^3J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$), 1.11 (d, $^3J_{H,H} = 6.9$ Hz, 6H; $CH(CH_3)_2$), 1.05 (d, $^3J_{H,H} = 6.9$ Hz, 6H; $CH(CH_3)_2$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 154.9$, 147.5, 147.1, 135.8, 133.9, 130.6, 130.2, 128.0, 127.9, 126.0, 125.7, 124.6, 122.62, 122.60 (aryl), 59.8 (OCH_3), 31.0, 30.8 ($CH(CH_3)_2$), 25.4, 25.1, 23.3, 23.2 ($CH(CH_3)_2$).

3,3′-Bis(2,6-diisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (H_2(Dip$_2$BINO)): A solution of boron tribromide (45 mL, 1 M in CH_2Cl_2, 45 mmol) was added dropwise to a suspension of 3,3′-bis(2,6-diisopropylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl (4.72 g, 7.44 mmol) in dry CH_2Cl_2 (40 mL) at −10 °C. The reaction mixture was stirred overnight at room temperature, then cooled to 0 °C. Water (20 mL) was added slowly, and stirring was continued for another 30 min. The mixture was diluted with CH_2Cl_2 (250 mL) to dissolve the solid material, and the organic layer was separated, dried over Na_2SO_4 and passed through a short column of silica. The solvent was removed in vacuo. Hexanes/ether (1:1, 40 mL) were added to the residue, and the mixture was stirred vigorously for 1 h. The resulting white powder was filtered, washed with hexanes and dried in air; yield: 4.21 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.91$ (d, $^3J_{H,H} = 8.0$ Hz, 2H; aryl), 7.79 (s, 2H; aryl), 7.23–7.45 (m, 12H; aryl), 4.92 (s, 2H; OH), 2.88 (sept, $^3J_{H,H} = 6.8$ Hz, 2H; $CH(CH_3)_2$), 2.71 (sept, $^3J_{H,H} = 6.9$ Hz, 2H; $CH(CH_3)_2$), 1.22 (d, $^3J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$), 1.14 (d, $^3J_{H,H} = 6.9$ Hz, 6H; $CH(CH_3)_2$), 1.11 (d, $^3J_{H,H} = 6.9$ Hz, 6H; $CH(CH_3)_2$), 1.05 (d, $^3J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 150.6$, 148.0, 147.9, 133.4, 133.1, 130.6, 129.0, 128.9, 128.3, 126.8, 124.4, 123.9, 123.10, 123.05, 112.9 (aryl), 30.9, 30.8 ($CH(CH_3)_2$), 24.3, 24.2, 23.8, 23.6 ($CH(CH_3)_2$); elemental analysis calcd (%) for $C_{44}H_{46}O_2$: C 87.09, H 7.64; found: C 85.98, H 7.54.

(*R*)-3,3′-Bis(2,6-diisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (H_2((*R*)-Dip$_2$BINO))

Method A: *n*BuLi (12.6 mL, 2.68 M in hexane, 33.8 mmol) was added to a solution of TMEDA (4.5 mL, 30 mmol) in diethyl ether (75 mL). Finely powdered (*R*)-2,2′-dimethoxy-1,1′-dinaphthyl (4.71 g, 15.0 mmol) was added to the mixture in one portion. The mixture was stirred overnight at room temperature, then the solvent was removed in vacuo. The dilithium salt was dried in vacuo for 2 h (0.1 Torr), and THF (20 mL) was added. The flask was placed in a dry ice/acetone bath and a solution of $ZnBr_2$ (34 mL, 1 M in THF, 34 mmol) was added. The resulting mixture was stirred at room temperature until the dilithium salt completely dissolved (1 h), then 2,6-diisopropylphenyl bromide (7.23 g, 30 mmol) and Pd(P*t*Bu$_3$)$_2$ (77 mg, 0.15 mmol) was added. The mixture was transferred into a 100 mL round-bottom flask with teflon valve by a cannula and heated to 105 °C for 24 h to give a homogeneous solution. After the mixture had been cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was dissolved in CH_2Cl_2 (100 mL). The solution was washed with dilute HCl, dried over Na_2SO_4 and passed through a short column of silica. Removal of the solvent gave brown oil, which contained 60% of product (by ^{1}H NMR spectroscopy). The crude material (9.17 g) was dissolved in dry CH_2Cl_2 (50 mL) and cooled to −10 °C, then a solution of boron tribromide (45 mL, 1 M in CH_2Cl_2, 45 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature and cooled to 0 °C, then water (20 mL) was added slowly. Stirring was continued for another half hour. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the remaining brown oil was chromatographed on a silica gel column with hexanes/CH_2Cl_2, (7:3, $R_f = 0.2$) to give a white powder in 3.2 g yield (35%).

Method B: *n*BuLi (1.8 mL, 2.5 M in hexane, 4.5 mmol) was added to a solution of 2,6-diisopropylphenylbromide (1.08 g, 4.47 mmol) in THF (5 mL) at −70 °C. The reaction mixture was stirred at this temperature for 20 min, and a solution of $ZnBr_2$ (5 mL, 1 M in THF, 5 mmol) was then added. The reaction mixture was allowed to warm to room temperature, and the solvent was removed in vacuo. The colourless oily residue was dried in vacuo for 2 h (0.1 Torr) in order to remove *n*BuBr. THF (10 mL), (*R*)-

3,3′-diiodo-2,2′-dimethoxy-1,1′-dinaphthyl (1.10 g, 1.94 mmol) and $Pd(PtBu_3)_2$ (0.01 g, 0.02 mmol) were added, and the mixture was heated to 60 °C overnight. After the mixture had been cooled to room temperature, dilute HCl (10 mL, 2–3 %) and diethyl ether (20 mL) were added. The organic layer was separated, washed with brine, dried over Na_2SO_4 and passed through a short column of silica with Et_2O as eluent. The solvent was removed, and the residue was dried in vacuo for 4 h. The crude material was dissolved in dry CH_2Cl_2 (10 mL) and cooled to −5 °C, and a solution of boron tribromide (8 mL, 1M in CH_2Cl_2, 8 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature, then cooled to 0 °C, and water (10 mL) was added slowly. Stirring was continued for 30 min, after which the organic layer was separated and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the remaining brown oil was chromatographed on silica with hexanes/CH_2Cl_2 (7:3, R_f 0.2) to give 1.07 g (91 %) of a white crystalline powder. The ^1H and ^{13}C NMR spectra are identical to those of the racemic ligand. Elemental analysis calcd (%) for $C_{44}H_{46}O_2$: C 87.09, H 7.64; found: C 86.30, H 7.76.

3,3′-Bis(mesityl)-2,2′-dimethoxy-1,1′-dinaphthyl: *n*BuLi (30 mL, 2.27 M in hexane, 68.1 mmol) was added to a solution of TMEDA (9.0 mL, 60 mmol) in diethyl ether (150 mL). Finely powdered 2,2′-dimethoxy-1,1′-dinaphthyl (9.42 g, 30.0 mmol) was added to the mixture in one portion. The mixture was stirred overnight at room temperature, then the solvent was removed in vacuo. The dilithium salt was dried in vacuo for 2 h (0.1 Torr). The flask was placed in a dry ice/acetone bath and a solution of $ZnCl_2$ (70 mL, 1M in THF, 70 mmol) was added. The resulting mixture was stirred at room temperature until the dilithium salt completely dissolved, then mesitylbromide (9.2 mL, 60 mmol) and $Pd(PtBu_3)_2$ (0.15 g, 0.3 mmol) were added. The mixture was transferred into a 100 mL round-bottom flask with teflon valve by a cannula and heated to 100 °C overnight. After the mixture had been cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was dissolved in CH_2Cl_2 (150 mL). The solution was washed with dilute HCl, dried over Na_2SO_4 and passed through a short column of silica. The solvent was removed, and hexanes/ether (1:1, 50 mL) were added to the remaining residue. The flask was placed in an ultrasound bath for 10 min and cooled to 0 °C, then the resulting powder was filtered off, washed with hexanes and dried in air to yield 12.3 g (74 %) of an off-white powder. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$ (d, $^3J_{H,H} = 8.2$ Hz, 2H; aryl), 7.68 (s, 2H; aryl), 7.38 (m, 2H; aryl), 7.25 (m, 4H; aryl), 6.96 (s, 4H; aryl), 3.09 (s, 6H; OCH_3), 2.33 (s, 6H; aryl-CH_3), 2.17 (s, 6H; aryl-CH_3), 2.12 (s, 6H; aryl-CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 154.5$, 136.8, 136.7, 136.3, 135.5, 134.3, 133.7, 130.7, 130.5, 128.08, 128.05, 127.8, 126.0, 125.7, 125.4, 124.6 (aryl), 59.9 (OCH_3), 21.1, 20.8, 20.7 (aryl-CH_3).

3,3′-Bis(mesityl)-2,2′-dihydroxy-1,1′-dinaphthyl (H_2(Mes$_2$BINO)):[10e] A solution of boron tribromide (24 mL, 1M in CH_2Cl_2, 24 mmol) was added dropwise to a solution of 3,3′-bis(mesityl)-2,2′-dimethoxy-1,1′-dinaphthyl (3.32 g, 6.04 mmol) in dry CH_2Cl_2 (30 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature, then cooled to 0 °C, and water (20 mL) was added slowly. Stirring was continued for another 30 min. The organic layer was separated, dried over Na_2SO_4 and passed through a short column of silica (CH_2Cl_2). After removal of the solvent, Et_2O (10 mL) was added to the residue, and the mixture was stirred vigorously for 1 h then cooled to 0 °C. A white powder was filtered off, washed with Et_2O then hexanes and dried in air to yield 2.90 g (92 %) of a white powder. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (d, $^3J_{H,H} = 8.0$ Hz, 2H; aryl), 7.77 (s, 2H; aryl), 7.27–7.40 (m, 6H; aryl), 7.03 (s, 4H; aryl), 5.03 (s, 2H; OH), 2.37 (s, 6H; aryl-CH_3), 2.18 (s, 6H; aryl-CH_3), 2.10 (s, 6H; aryl-CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 150.0$, 137.7, 137.13, 137.06, 133.4, 132.9, 130.6, 129.4, 128.5, 128.4, 128.2, 126.8, 124.5, 123.8, 112.9 (aryl), 21.1, 20.5, 20.4 (aryl-CH_3).

[Y(biphen){N(SiHMe$_2$)$_2$}(thf)$_2$] (2a): A solution of H_2(Biphen) (900 mg, 2.54 mmol) in toluene (5 mL) was added dropwise with a syringe to a solution of **1a** (1.50 g, 2.38 mmol) in toluene (4 mL) at 60 °C. The mixture was stirred at 60 °C for 1 h. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried in vacuo for 30 min. The crude material was dissolved in hexanes (6 mL) and cooled to 0 °C. After 24 h, the solution was decanted from the solid precipitate formed (presumably polymeric side product), concentrated to 4 mL volume and the product was crystallized at −30 °C to give 790 mg (46 %) of **2a** as white microcrystals. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.18$ (s, 2H; biphen), 5.12 (sept, $^3J_{H,H} = 3.0$ Hz, 2H; SiH), 3.61 (brs, 8H; thf), 2.22, (s, 6H; aryl-CH_3), 1.77 (s, 6H; aryl-CH_3), 1.70 (s, 18H; $C(CH_3)_3$), 1.17 (brs, 8H; thf), 0.38, 0.32, (each d, $^3J_{H,H} = 3.0$ Hz, 6H; $SiH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 157.6$, 136,4, 135.2, 130.0, 127.6, 123.7 (aryl), 71.2 (brs, thf), 35.3 ($C(CH_3)_3$), 30.7 ($C(CH_3)_3$), 25.1 (thf), 20.4, 16.5 (aryl-CH_3), 3.1, 2.9 ($SiH(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (79.5 MHz, C_6D_6): $\delta = -24.1$; elemental analysis calcd (%) for $C_{36}H_{62}NO_4Si_2Y$: C 60.22, H 8.70, N 1.95; found: C 60.70, H 8.64, N 1.78.

[Y((*R*)-biphen){N(SiHMe$_2$)$_2$}(thf)$_2$] ((*R*)-2a): A solution of H_2((*R*)-Biphen) (200 mg, 0.56 mmol) in toluene (1.5 mL) was added dropwise with a syringe to a solution of **1a** (315 mg, 0.50 mmol) in toluene (1.5 mL) at 70 °C. The mixture was stirred at 70 °C for 15 min and then at room temperature overnight. The solvent was removed in vacuo, and the residue was dried in vacuo for 2 h. All attempts to crystallize (*R*)-**2a** from pentane at −30 or −78 °C failed, and therefore the crude complex was used for catalytic reactions. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.18$ (s, 2H; biphen), 5.12 (sept, $^3J_{H,H} = 3.0$ Hz, 2H; SiH), 3.74 (brs, 4H; thf), 3.43 (brs, 4H; thf), 2.22, (s, 6H; aryl-CH_3), 1.77 (s, 6H; aryl-CH_3), 1.71 (s, 18H; $C(CH_3)_3$), 1.15 (brs, 8H; thf), 0.38, (d, $^3J_{H,H} = 3.0$ Hz, 6H; $SiH(CH_3)_2$), 0.32, (d, $^3J_{H,H} = 3.0$ Hz, 6H; $SiH(CH_3)_2$); elemental analysis calcd (%) for $C_{36}H_{62}NO_4Si_2Y$: C 60.22, H 8.70, N 1.95; found: C 61.22, H 8.49, N 1.65. The ^{13}C and ^{29}Si NMR spectra are identical to those of racemic **2a**.

(*R*,*S*)-[Y(biphen){N(SiHMe$_2$)$_2$}(thf)]$_2$ ((*R*,*S*)-3a)

*Method A: One pot synthesis starting from **1a***: A solution of H_2(Biphen) (374 mg, 1.06 mmol) in toluene (2.5 mL) was added dropwise with a syringe to a solution of **1a** (630 mg, 1.00 mmol) in toluene (2.5 mL) at 60 °C. The mixture was stirred at 60 °C for 30 min. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried in vacuo for 30 min. The crude material was dissolved in toluene (3 mL), the solution was heated to 110 °C for 3 min and allowed to cool to room temperature followed by cooling to 0 °C overnight. The solution was decanted from the white crystals formed. The crystals were washed with hexanes (1 mL) and dried in vacuo to give 170 mg (26 %) of (*R*,*S*)-**3a**.

*Method B: From isolated racemic **2a***: A solution of racemic **2a** (260 mg, 0.362 mmol) in toluene (1.5 mL) was heated to 110 °C for 20 min. After the mixture had been cooled to room temperature, the solvent was removed in vacuo. Toluene (2.5 mL) was added to the residue, and the solution was heated to 110 °C and allowed to reach room temperature, then cooled to −30 °C overnight. The solution was decanted from the crystals formed. The crystals were washed with toluene (2 × 0.5 mL) and dried in vacuo. Yield: 117 mg (50 %). ^1H NMR (400 MHz, C_6D_6, 60 °C): $\delta = 7.16$ (s, 4H; biphen), 4.39 (brs, 4H; SiH), 3.79 (brs, 8H; thf), 2.19, (s, 12H; aryl-CH_3), 1.63 (s, 12H; aryl-CH_3), 1.54 (s, 36H; $C(CH_3)_3$), 1.42 (brs, 8H; thf), 0.05 (d, $^3J_{H,H} = 2.9$ Hz, 24H; $SiH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 60 °C): $\delta = 157.8$, 136.6, 135.3, 130.1, 128.6, 123.7 (aryl), 70.3 (brs, thf), 34.8 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 25.4 (thf), 20.2, 17.0 (aryl-CH_3), 2.6 ($SiH(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (79.5 MHz, C_6D_6, 60 °C): $\delta = -22.6$; elemental analysis calcd (%) for $C_{64}H_{108}N_2O_6Si_4Y_2$: C 59.51, H 8.43, N 2.17: found: C 58.82, H 8.56, N 2.26.

(*R*,*S*)-[La(biphen){N(SiHMe$_2$)$_2$}(thf)]$_2$ ((*R*,*S*)-3b): A solution of H_2(Biphen) (195 mg, 0.55 mmol) in toluene (2 mL) was added dropwise with a syringe to a solution of **1b** (340 mg, 0.50 mmol) in toluene (2 mL) at 35 °C. The mixture was stirred for 2 h, and then heated until all the precipitate had dissolved. The solution was allowed to cool to room temperature and then cooled to −30 °C overnight. The solution was decanted from the crystals. The white crystals were washed with hexanes (1 mL) and dried in vacuo (0.05 Torr) to give 225 mg (65 %) of (*R*,*S*)-**3b**. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.22$ (s, 4H; biphen), 4.45 (sept, $^3J_{H,H} = 3.0$ Hz, 4H; SiH), 3.77 (brm, 8H; thf), 2.21, (s, 12H; aryl-CH_3), 1.73 (s, 12H; aryl-CH_3), 1.53 (s, 36H; $C(CH_3)_3$), 1.36 (m, 8H; thf), 0.15 (d, $^3J_{H,H} = 3.0$ Hz, 24H; $SiH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 156.1$, 136.1, 135.7, 133.0, 129.0, 124.0 (aryl), 69.6 (thf), 35.0 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 25.2 (thf), 20.5, 17.0 (aryl-CH_3), 2.6 ($SiH(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (79.5 MHz, C_6D_6) $\delta = -25.7$; elemental analysis calcd (%) for $C_{64}H_{108}La_2N_2O_6Si_4$: C 55.23, H 7.82, N 2.01; found: C 53.84, H 7.79, N 2.03.

Equilibration of (*R*,*S*)-3b and 3b′: A screw-cap NMR tube was charged with (*R*,*S*)-**3b** (15 mg, 10.8 μmol) and [D_8]toluene (0.5 mL). The sample was inserted into the NMR probe, and the temperature gradually increased. The transformation was followed by ^1H NMR until a final ratio of 0.9:1 (**3b′**/(*R*,*S*)-**3b**) was reached after 50 min at 70 °C. Spectroscopic data for **3b′** that are not obstructed by (*R*,*S*)-**3b** or solvent: ^1H NMR (400 MHz, [D_8]toluene): $\delta = 7.30$ (s, 4H; biphen), 4.87 (sept, $^3J_{H,H} = 2.9$ Hz,

4H; SiH), 1.94 (s, 12H; aryl-CH_3), 1.59 (s, 36H; $C(CH_3)_3$), 0.295, (d, $^3J_{H,H}$ = 2.8 Hz, 12H; $SiH(CH_3)_2$), 0.290 (d, $^3J_{H,H}$ = 2.8 Hz, 12H; $SiH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_8$]toluene): δ = 169.2, 140,2, 138.8, 130.2, 125.9, 125.4 (aryl), 35.8 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$), 16.8 (aryl-CH_3), 3.2 ($SiH(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (79.5 MHz, [D$_8$]toluene): δ = −25.4.

Crystallography: Clear, colourless crystals of (*R*,*S*)-**3a** and (*R*,*S*)-**3b** suitable for X-ray diffraction analysis were obtained by cooling a concentrated solution of (*R*,*S*)-**3a** in toluene or (*R*,*S*)-**3b** in benzene to room temperature. Data were collected on a Nonius KappaCCD area detector. Crystal data for (*R*,*S*)-**3a**·2C$_7$H$_8$: $C_{64}H_{108}N_2O_6Si_4Y_2 \cdot 2C_7H_8$, M_r = 1475.97, crystal size 0.35 × 0.35 × 0.30 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 13.240(3), b = 18.517(4), c = 16.448(3) Å, β = 98.27(3)°, V = 3990.6(14) Å^3, Z = 2, ρ_{calcd} = 1.228 g cm^{-3}, $F(000)$ = 1576, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), T = 173(2) K, μ = 1.556 mm^{-1}, 17644 reflections measured of which 9136 independent (R_{int} = 0.0390), GOF = 1.052, R ($I > 2\sigma(I)$) = 0.0395, wR^2 (all data) = 0.1055, largest e (max/min) = 0.474, −0.522 e Å^{-3}. Crystal data for (*R*,*S*)-**3b**·C$_6$H$_6$: $C_{64}H_{108}La_2N_2O_6Si_4 \cdot C_6H_6$, M_r = 1469.83, crystal size 0.30 × 0.20 × 0.20 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 12.8480(2), b = 14.1186(2), c = 20.8061(3) Å, β = 94.229(1)°, V = 3763.86(10) Å^3, Z = 2, ρ_{calcd} = 1.297 g cm^{-3}, $F(000)$ = 1532, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), T = 173(2) K, μ = 1.230 mm^{-1}, 12733 reflections measured of which 6616 independent (R_{int} = 0.0153), GOF = 1.130, R ($I > 2\sigma(I)$) = 0.0318, wR^2 (all data) = 0.0916, largest e (max/min) = 1.636, −0.872 e Å^{-3}. Cell parameters for (*R*,*S*)-**3a** and (*R*,*S*)-**3b** were obtained from 10 frames by using a 10° scan and refined with 9377 reflections for (*R*,*S*)-**3a** and 6744 reflections for (*R*,*S*)-**3b**. Lorentz, polarization and empirical absorption corrections were applied.[44a,b] The space group was determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 by using SHELXL-97.[44c] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in idealized positions by using a riding model. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from literature.[44d] Graphical representation were prepared with ORTEP-III for Windows.[44e]

CCDC-205801 ((*R*,*S*)-**3a**·2(C$_7$H$_8$)) and 205800 ((*R*,*S*)-**3b**·(C$_6$H$_6$)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

[Y(trip$_2$bino){N(SiHMe$_2$)$_2$}(thf)$_2$] (4a): A solution of H$_2$(Trip$_2$BINO) (380 mg, 0.55 mmol) in toluene was added dropwise (2 mL) with a syringe to a solution of **1a** (315 mg, 0.5 mmol) in toluene (2 mL) at 55 °C. The mixture was stirred at 55 °C for 3 h. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried in vacuo for 2 h (0.1 Torr) to give a yellow glassy solid. Attempts to crystallize this material from hexanes at −30 °C or −70 °C only resulted in the precipitation of a yellow oily material. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.81 (s, 2H; aryl), 7.64 (m, 2H; aryl), 7.31 (s, 2H; aryl), 7.27 (s, 2H; aryl), 6.97–7.13 (m, 6H; aryl), 4.73 (sept, $^3J_{H,H}$ = 2.8 Hz, 2H; SiH), 3.0–3.8 (v br s, 8H; thf), 3.46, 3.26 (each sept, $^3J_{H,H}$ = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$, partially obscured by thf), 2.94 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 1.49 (d, $^3J_{H,H}$ = 6.7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.35 (m, 24H; CH(C*H*$_3$)$_2$), 1.27 (d, $^3J_{H,H}$ = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.00 (br s, 8H; thf), 0.07, −0.01 (each d, $^3J_{H,H}$ = 3.0 Hz, 6H; SiH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C$_6$D$_6$): δ = 159.0, 148.4, 147.5, 146.1, 137.6, 136.6, 133.9, 130.9, 126.0, 125.6, 121.9, 120.8, 120.7, 118.5 (aryl), 71.8 (thf), 34.9, 31.2, 31.1 (*C*H(CH$_3$)$_2$), 26.7, 25.2, 25.1, 25.0, 24.6, 24.0 (CH(*C*H$_3$)$_2$), 2.2, 2.0 (SiH(CH$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (79.5 MHz, C$_6$D$_6$): δ = −23.5.

[La(trip$_2$bino){N(SiHMe$_2$)$_2$}(thf)$_2$] (4b): A solution of H$_2$(Trip$_2$BINO) (370 mg, 0.54 mmol) was added dropwise with a syringe to a solution of **1b** (340 mg, 0.5 mmol) in toluene (2 mL) at 50 °C. The mixture was stirred at 50 °C for 3 h. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried in vacuo for 2 h (0.05 Torr). The purity of this material was approximately 80–90% based on ^{1}H NMR. The crude material was crystallized from hexanes/toluene (1:1, 2.5 mL) at −30 °C overnight, however the purity did not improve. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.81 (s, 2H; aryl), 7.62 (d, 2H; aryl), 7.30 (s, 2H; aryl), 7.27 (s, 2H; aryl), 7.23–6.99 (m, 6H; aryl), 4.73 (sept, $^3J_{H,H}$ = 3.0 Hz, 2H; SiH), 3.46 (m, 2H; C*H*(CH$_3$)$_2$), 3.30 (br s, 8H; thf), 3.16 (m, 2H; C*H*(CH$_3$)$_2$), 2.92 (m, 2H; C*H*(CH$_3$)$_2$), 1.46–1.28 (m, 36H; CH(C*H*$_3$)$_2$), 1.07 (br s, 8H; thf), 0.12, 0.03 (each d, $^3J_{H,H}$ = 3.0 Hz, 6H; SiH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C$_6$D$_6$): δ = 158.5, 148.5, 147.6, 146.2, 136.4, 135.5, 131.9, 126.0, 125.4, 122.3, 120.9, 120.5, 118.9 (aryl), 69.9 (thf), 34.9, 31.7 (*C*H(CH$_3$)$_2$), 26.4, 25.25, 25.19 (CH(*C*H$_3$)$_2$), 25.11 (thf), 24.5, 24.4, 24.3 (CH(*C*H$_3$)$_2$), 2.5, 2.4 (SiH(CH$_3$)$_2$); ^{29}Si NMR (79.5 MHz, C$_6$D$_6$): δ = −25.9.

[La((*R*)-trip$_2$bino){N(SiHMe$_2$)$_2$}(thf)$_2$] ((*R*)-4b): A solution of H$_2$(Trip$_2$BINO) (386 mg, 0.56 mmol) was added dropwise with a syringe to a solution of **1b** (360 mg, 0.53 mmol) in toluene (2 mL) at 80 °C over 30 min. The mixture was stirred at 80 °C for 1 h. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried for 2.5 h (0.1 Torr). The crude material was dissolved in hexanes (2.5 mL) and cooled to −30 °C, however the whole solution solidified as a colourless gel. The purity of this material was approximately 60–70% based on ^{1}H NMR. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.81 (s, 2H; aryl), 7.62 (m, 2H; aryl), 7.30, 7.27 (each s, 2H; aryl), 7.23–6.99 (m, 6H; aryl), 4.73 (sept, $^3J_{H,H}$ = 2.9 Hz, 2H; SiH), 3.46 (br m, 6H; C*H*(CH$_3$)$_2$ and thf), 3.16 (m, 6H; C*H*(CH$_3$)$_2$ and thf), 2.92 (m, 2H; C*H*(CH$_3$)$_2$), 1.46–1.28 (m, 36H; CH(C*H*$_3$)$_2$), 1.06 (br s, 8H; thf), 0.12, 0.03 (each d, $^3J_{H,H}$ = 2.8 Hz, 6H; SiH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C$_6$D$_6$): δ = 158.5, 148.5, 147.6, 146.2, 136.3, 135.6, 132.0, 126.0, 125.4, 122.3, 121.0, 120.5, 118.9 (aryl), 70.1 (thf), 34.9, 31.3 (*C*H(CH$_3$)$_2$), 26.3, 25.24, 25.16 (CH(*C*H$_3$)$_2$), 25.10 (thf), 24.51, 24.49, 24.43 (CH(*C*H$_3$)$_2$), 2.5, 2.3 (SiH(CH$_3$)$_2$); ^{29}Si NMR (79.5 MHz, C$_6$D$_6$): δ = −26.0.

[Y(dip$_2$bino){N(SiHMe$_2$)$_2$}(thf)$_2$] (5a): A suspension of H$_2$(Dip$_2$BINO) (625 mg, 1,03 mmol) was added dropwise with a syringe to a solution of **1a** (630 mg, 1 mmol) in toluene (2.5 mL) at 50 °C. The mixture was stirred at 50 °C for 2 h and then heated to 100 °C for 30 min. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried in vacuo for 2 h (0.05 Torr). The crude material was crystallized from hexanes (4 mL) at −30 °C overnight. The solution was decanted from the precipitate. The precipitate was washed with hexanes (1 mL) and dried in vacuo to give 650 mg (67%) of **5a** as a white powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.80 (s, 2H; aryl), 7.64 (d, $^3J_{H,H}$ = 8.3 Hz, 2H; aryl), 7.28–7.39 (m, 6H; aryl), 7.07 (d, $^3J_{H,H}$ = 8.3 Hz, 2H; aryl), 6.93–7.01 (m, 4H; aryl), 4.69 (m, 2H; SiH), 3.43 (br m, 10H; C*H*(CH$_3$)$_2$ and thf), 3.25 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 1.44 (d, $^3J_{H,H}$ = 6.7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{H,H}$ = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{H,H}$ = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.01 (br s, 8H; thf), 0.06, -0.02 (each d, $^3J_{H,H}$ = 3.0 Hz, 6H; SiH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C$_6$D$_6$): δ = 158.8, 148.5, 146.3, 139.0, 137.7, 133.7, 130.7, 126.0, 125.7, 122.9, 122.8, 122.0, 118.5 (aryl), 71.9 (thf), 31.1, 31.0 (*C*H(CH$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 25.1 (thf), 25.0, 24.9, 23.8 (CH(*C*H$_3$)$_2$), 2.1, 2.0 (SiH(CH$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (79.5 MHz, C$_6$D$_6$): δ = −23.5; elemental analysis calcd (%) for $C_{56}H_{74}NO_4Si_2Y$: C 69.32, H 7.69, N 1.44; found: C 68.55, H 7.57, N 1.75.

[Y((*R*)-dip$_2$bino){N(SiHMe$_2$)$_2$}(thf)$_2$] ((*R*)-5a): A suspension of H$_2$((*R*)-Dip$_2$BINO) (625 mg, 1,03 mmol) in toluene (2.5 mL) was added dropwise with a syringe to a solution of **1a** (630 mg, 1.00 mmol) in toluene (2.5 mL) at 70 °C. The mixture was stirred at 70 °C for 2.5 h. After the mixture had been cooled to room temperature, the solvent was removed in vacuo, and the residue was dried in vacuo for 2 h (0.05 Torr). The crude material was dissolved in hexanes (3 mL) and cooled to −30 °C to give an oily precipitate after 24 h in quantitative yield. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.80 (s, 2H; aryl), 7.64 (d, $^3J_{H,H}$ = 8.3 Hz, 2H; aryl), 7.28–7.39 (m, 6H; aryl), 7.07 (d, $^3J_{H,H}$ = 8.3 Hz, 2H; aryl), 6.93–7.01 (m, 4H; aryl), 4.69 (m, 2H; SiH), 3.61 (br s, 4H; thf), 3.44 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 3.24 (br m, 6H; C*H*(CH$_3$)$_2$ and thf), 1.44 (d, $^3J_{H,H}$ = 6.7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.31 (d, $^3J_{H,H}$ = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{H,H}$ = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.00 (br m, 8H; thf), 0.06, −0.02 (each d, $^3J_{H,H}$ = 2.9 Hz, 6H; SiH(C*H*$_3$)$_2$); elemental analysis calcd (%) for $C_{56}H_{74}NO_4Si_2Y$: C 69.32, H 7.69, N 1.44; found: C 68.45, H 7.60, N 1.44. The ^{13}C and ^{29}Si NMR spectra are identical to those of racemic **5a**.

2-Allyl-2-methylpent-4-enenitrile: *n*BuLi (100 mmol, 2.5 M solution in hexanes) was added dropwise to a solution of diisopropylamine (10.38 g, 102.6 mmol) in THF (45 mL) at −78 °C. The resulting light yellow solution was stirred for 90 min at 0 °C. 49 mL of this solution of lithium diisopropylamide (LDA) was transferred to a dropping funnel and was added slowly dropwise to a solution of propionitrile (2.89 g, 52.5 mmol) in THF (40 mL) at −78 °C. The solution was stirred for 90 min at this temperature and was then treated with allyl bromide (5.99 g, 49.5 mmol)

dropwise. The solution was stirred for another 30 min at −78 °C and was then allowed to warm to room temperature. After 1 h, the solution was cooled back to −78 °C, and the second part of LDA was added over 30 min. The solution was allowed to warm to 0 °C and was stirred for 30 min. Cooling back to −78 °C and treatment with allyl bromide (7.30 g, 60.3 mmol) resulted in a bright orange solution, which was allowed to warm slowly to room temperature and stirred overnight. The reaction was quenched by addition of water (3 mL), and the solvent was removed in vacuo (40 °C, 300 mbar). The residue was taken up with Et_2O (200 mL), washed with brine (2 × 30 mL) and water (10 mL), dried over $MgSO_4$. Concentration in vacuo (40 °C, 150 mbar) gave 6.91 g (97 %) of a yellow oil, which was shown to be clean by NMR spectroscopy and was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.85$ (m, 2H; =CH), 5.18 (m, 4H; $=CH_2$), 2.27 (m, 4H; $=CHCH_2$), 1.27 (s, 3H; $C(CH_3)$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 131.9$ (=CH), 123.6 (CN), 120.1 ($=CH_2$), 43.0 ($=CHCH_2$), 36.3 ($C(CH_3)$), 23.4 ($C(CH_3)$).

2-Allyl-2-methylpent-4-enylamine (12):[5k] A solution of 2-allyl-2-methylpent-4-enenitrile (6.91 g, 51.1 mmol) in Et_2O (50 mL) was added dropwise to a suspension of $LiAlH_4$ (2.15 g, 56.7 mmol) in Et_2O (50 mL). The suspension was heated at reflux for 2 h and was stirred at room temperature overnight. The suspension was diluted with Et_2O (100 mL) and treated carefully with water (2.2 mL), 15 % NaOH (2.2 mL) and then again with water (7.4 mL). The ether phase was decanted from the white precipitate, and the precipitate was extracted with Et_2O (3 × 60 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo (40 °C, 100 mbar) to give 6.50 g (91 %) of a yellow oil, which was shown to be clean by NMR spectroscopy. The crude product was stirred over calcium hydride for several days and was then distilled in vacuo, followed by a second distillation over Al(octyl)$_3$ (3 mol %). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.74$ (m, 2H; =CH), 4.99 (m, 4H; $=CH_2$), 2.29 (s, 2H; CH_2N), 1.92 (d, $^3J_{H,H} =$ 7.6 Hz, 4H; $=CHCH_2$), 0.72 (s, 3H; $C(CH_3)$), 0.47 (br s, 2H; NH_2); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 135.6 (=CH), 117.0 ($=CH_2$), 50.0 (CH_2N), 42.0 ($=CHCH_2$), 37.9 ($C(CH_3)$), 22.3 ($C(CH_3)$).

General procedure for catalytic hydroamination/cyclization reactions: In a glovebox, a screw-cap NMR tube was charged with the catalyst (15 μmol), C_6D_6 (0.5 mL) and the substrate (0.38 mmol) in that order. The NMR tube was then placed in a pretempered oil bath, and the conversion was followed by NMR. Kinetic experiments were performed by placing the sample in the thermostated probe (±0.5 °C) of a Bruker Avance 400 spectrometer. NMR spectra were taken at appropriate time intervals (e.g. 5 or 30 min) by using the *multizg* script from the Bruker XWinNMR software package.

Preparation of Mosher amides:[45] A solution of the amine (175 μmol) in C_6D_6 (0.5 mL) was treated with Hünig's base (33 mg, 255 μmol) and (*R*)-(+)-α-methoxy-α-trifluoro-methylphenylacetic acid chloride (48 mg, 190 μmol). Enantiomeric excesses were determined in comparison to racemic samples by ^{19}F NMR spectroscopy. Spectra were collected at 60 or 80 °C with a pulse delay of 5 s. The amides were purified by chromatography on silica by using hexanes/EtOAc (10:1) as eluent when necessary. The following ^{19}F NMR data are given for reference.

9: ^{19}F NMR (79.5 MHz, C_6D_6, 60 °C): $\delta = -69.7, -70.6$.

11: ^{19}F NMR (79.5 MHz, C_6D_6, 60 °C): $\delta = -70.1, -70.6$.

13: ^{19}F NMR (79.5 MHz, $CDCl_3$, 80 °C): $\delta = -70.0$ (diast. a), −70.1 (diast. b), −70.8 (diast. a), −71.0 (diast. b).

14: ^{19}F NMR (79.5 MHz, C_6D_6, 70 °C): $\delta = -69.3, -69.4$.

15: ^{19}F NMR (79.5 MHz, C_6D_6, 80 °C): $\delta = -69.1$ (*trans*), −69.5 (*trans*), −69.7 (*cis*).

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