Synthesis and Characterization of Alkyllanthanum Biphenolate Complexes as Catalysts for Hydroamination/Cyclization and Hydrosilylation

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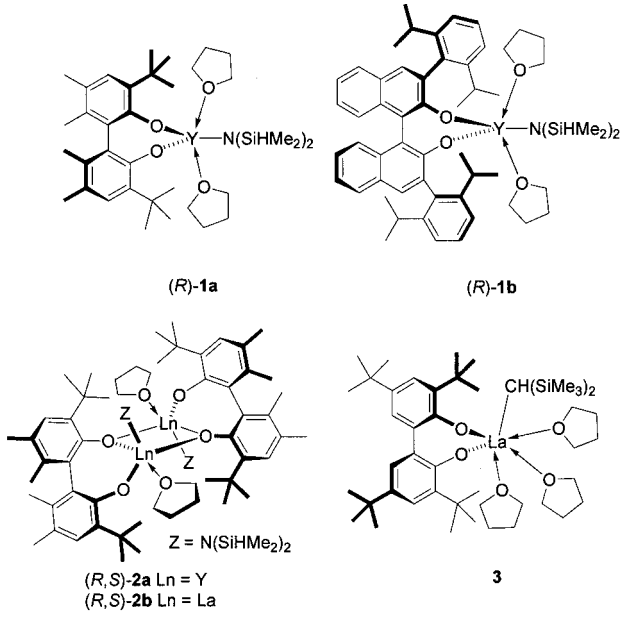
The homochiral, dimeric biphenolate alkyllanthanum complex [La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$}]$_2$ can be prepared by facile alkane elimination starting from [La{CH(SiMe$_3$)$_2$}$_3$] and enantiopure (*R*)-3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol [H$_2${(*R*)-Biphen}]. Single-crystal X-ray diffraction revealed that the two La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$} 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. The biphenolate alkyl complex shows high catalytic activity for hydroamination/cyclization of aminoalkenes, similar to previously known lanthanocene catalysts, but only low enantioselectivity. Addition of THF to [La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$}]$_2$ leads to a monomeric tris-THF adduct [La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$}(THF)$_3$] with higher catalytic activity than the THF-free homochiral dimer in the cyclization of 2,2-dimethylpent-4-enylamine, suggesting that the dimeric structure of the catalyst system prevails under catalytic conditions in the absence of THF. Addition of HN(SiHMe$_2$)$_2$ to [La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$}(THF)$_3$] results in the formation of [La{(*R*)-Biphen}{N(SiHMe$_2$)$_2$}(THF)$_3$] which is in equilibrium with its homochiral dimer [La{(*R*)-Biphen}{N(SiHMe$_2$)$_2$}(THF)]$_2$ at elevated temperatures. The biphenolate alkyl complexes exhibit good catalytic activity and diastereoselectivity in the hydrosilylation of styrene. Hydrosilylation of 1-hexene and norbornene also proceeds with high diastereoselectivity but rather low activity.

Introduction

The chemistry of organometallic rare-earth-metal compounds has advanced significantly over the last two decades and many catalytic applications of these species in polymer chemistry[1,2] and organic synthesis,[3] notably hydroamination,[4−25] hydrophosphination,[26,27] hydrosilylation,[28−47] and hydroboration,[48,49,50] have been investigated. Most catalytic studies have relied on catalyst systems based on organometallic rare-earth-metal complexes containing at least one cyclopentadienyl-type ligand.[51] The chemistry of non-metallocene complexes[52−54] is much less developed and only a limited number of catalytic investigations have been reported.[45,55−69] One significant disadvantage of cyclopentadienyl-based chiral rare-earth-metal catalysts is their facile epimerisation in the presence of donor molecules, such as ethers and amines.[15,70−73] Cyclopentadienyl-free catalyst systems could solve this problem by providing a configurationally stable catalytic site and we[60,65] and others[59,62−64] have reported significant progress over the last year.



(*R*)-**1a** (*R*)-**1b**

(*R*,*S*)-**2a** Ln = Y
(*R*,*S*)-**2b** Ln = La

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Recently we reported the synthesis of monomeric biphenolate and binaphtholate rare-earth-metal amido complexes of the type [Ln{diolate}{N(SiHMe$_2$)$_2$}(THF)$_2$] (**1**) as well as their application in enantioselective hydroamination/cyclization reactions.[60] Based on the high thermal stability of the complexes and the small decrease of enantioselectiv-

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ity with increasing temperature, these complexes are assumed to be configurationally stable under catalytic conditions, even at temperatures as high as 100 °C. Although these catalysts can be prepared quite conveniently by a simple amine-elimination reaction, they require relatively high reaction temperatures (≥ 50 °C) in order to achieve reasonable turnover frequencies.[74] Additionally, we found that complexes derived from the sterically less-hindered racemic 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol [H_2(Biphen)][75][76] readily dimerize to give a phenolate-bridged heterochiral dimer. A presumably homochiral dimeric amidolanthanum species could be observed in situ upon heating heterochiral (*R*,*S*)-[La(Biphen){N(SiHMe$_2$)$_2$}(THF)]$_2$ [(*R*,*S*)-**2b**],[60] but all attempts to obtain the former in pure form starting from enantiopure Biphen ligand have failed to date.

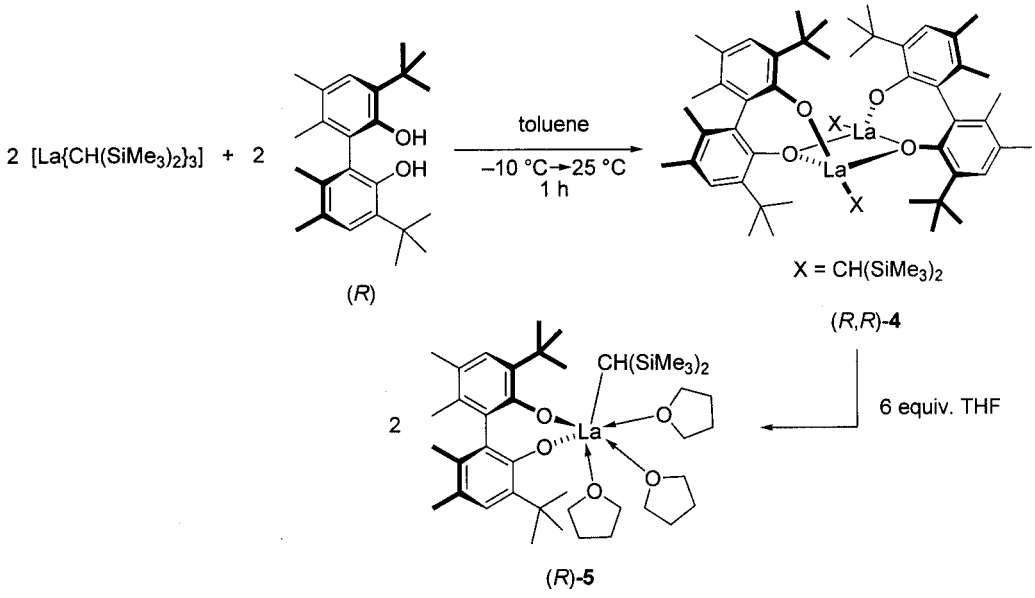
We therefore became interested in understanding the source of the low catalytic activity of complexes [Ln{diolate}{N(SiHMe$_2$)$_2$}(THF)$_2$] (**1**). Possible reasons could be inhibition by THF coordination, sluggish initiation caused by the low basicity of the bis(dimethylsilyl)-amido ligand or the electronic properties of our chiral chelating diolate ligand system.

Schaverien reported the synthesis of biphenolate and binaphtholate alkyllanthanum complexes in 1992,[77] but little is known about their reactivity or catalytic activity. Although the structure of the monomeric tris-THF adduct [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}(THF)$_3$] (**3**) was elucidated by single-crystal X-ray diffraction analysis, the structure of its base-free precursor, formulated as the monomeric species [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}], remained unknown.

Herein we report the synthesis, characterization and catalytic activity of related biphenolate alkyllanthanum complexes derived from (*R*)-Biphen. As it turned out, the initial base-free lanthanum complex of this chiral biphenolate ligand exists as a homochiral dimer.[78]

Results and Discussion

Reaction of (*R*)-H_2(Biphen)[76] with the trialkyllanthanum complex [La{CH(SiMe$_3$)$_2$}$_3$][79] at −10 °C in toluene solution resulted in the smooth formation of a single species **4** of the general formula "La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$}" (Scheme 1). Although the reaction seems to proceed relatively cleanly according to NMR spectroscopy, we could only obtain 35% of the product in isolated yield due to its high solubility in pentane. The ^{1}H NMR spectrum at room temperature exhibits only one broad set of signals for the biphenolate ligand, suggesting that both phenolate rings are equivalent at this temperature, as well as two signals for the diastereotopic trimethylsilyl groups (Figure 1). The lanthanum-bound methyne carbon atom resonates in the ^{13}C NMR spectrum at δ = 55.0 ppm ($^1J_{C,H}$ = 101 Hz). The signals of the biphenolate ligand decoalesce into two separate sets of signals for the two phenolate rings upon cooling to 0 °C. Similar temperature-dependent spectroscopic features of the biphenolate ligand have been observed in the heterochiral dimer (*R*,*S*)-[La(Biphen){N(SiHMe$_2$)$_2$}(THF)]$_2$ [(*R*,*S*)-**2b**].[60] The equivalence of both phenolate rings in (*R*,*S*)-**2b** on the NMR timescale at 25 °C is caused by an intramolecular exchange process of terminal and bridging phenolate groups. An analogous intramolecular exchange process of terminal and bridging phenolate groups seems to be operational for (*R*,*R*)-**4** (Scheme 2). The homochiral dimeric structure of (*R*,*R*)-**4** was also confirmed by X-ray crystallographic analysis (vide infra). It seems likely that the related complex [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}] pre-



Scheme 1

pared by Schaverien[77] from [La{CH(SiMe$_3$)$_2$}$_3$] and 3,3′,5,5′-tetra-*tert*-butylbiphenyl-2,2′-diol is also dimeric. The signal of the lanthanum-bound methyne proton of this species appears at $\delta = -1.46$ ppm in the ^{1}H NMR spectrum and the lanthanum-bound carbon atom is found at $\delta =$ 59.4 ppm ($^1J_{C,H} = 95$ Hz).[77] Based on the differences in the NMR spectra of [La{1,1′-(2-OC$_6$H$_2$*t*Bu$_2$-3,5)$_2$}{CH(SiMe$_3$)$_2$}] and (*R*,*R*)-**4** one can rule out a homochiral dimeric structure. A heterochiral[78] dimeric structure is more likely and should be thermodynamically more stable due to the absence of unfavorable steric interactions.

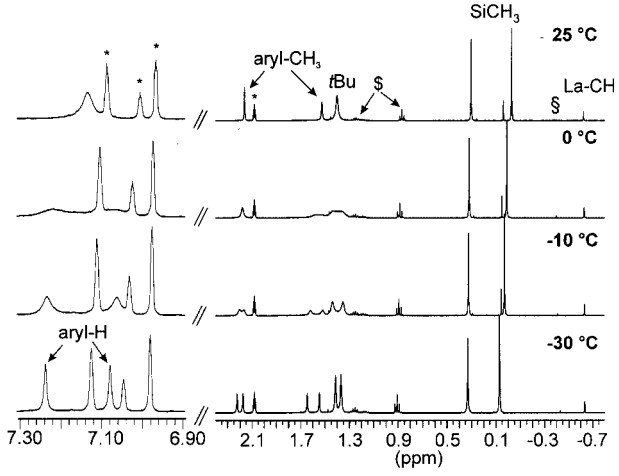


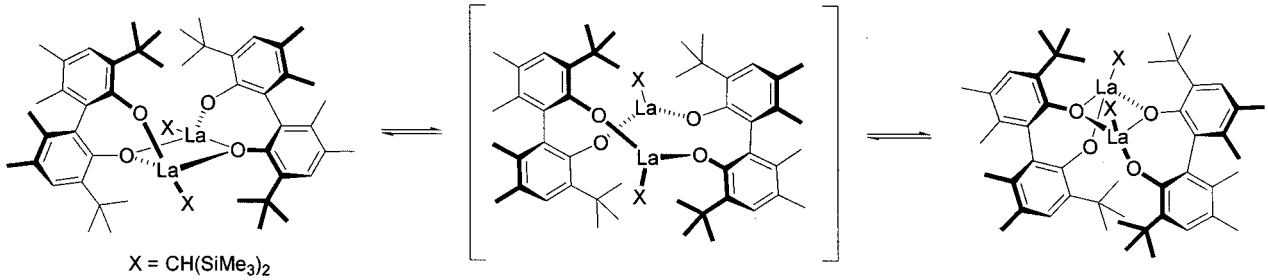
Figure 1. Variable temperature ^{1}H NMR spectra of (*R*,*R*)-**4** in [D$_8$]toluene (*) showing the aliphatic (right) and aromatic region (left, threefold expanded) [$ = *n*-pentane, § = CH$_2$(SiCH$_3$)$_2$]

Addition of six equivalents of THF to (*R*,*R*)-**4** led to the formation of a monomeric species (*R*)-**5** (Scheme 1), which is analogous to the crystallographically characterized biphenolate lanthanum complex **3**.[77] Formation of (*R*)-**5** from (*R*,*R*)-**4** does not proceed instantaneously, but within 30 min. The signal of the lanthanum-bound methyne proton is shifted to higher field at $\delta = -1.64$ ppm in the ^{1}H NMR spectrum and the methyne carbon atom resonates in the ^{13}C NMR spectrum at $\delta = 51.5$ ppm with a $^1J_{C,H}$ value of 97.6 Hz. Addition of three equivalents of THF yields a mixture of (*R*,*R*)-**4**, (*R*)-**5** and a new species at $\delta = -1.12$ ppm, which we believe to be a dimeric mono-THF adduct [La{(*R*)-Biphen}{CH(SiMe$_3$)$_2$}(THF)]$_2$ in a 1:1.2:1.2 ratio (based on the integration of the lanthanum-bound methyne proton signals in the ^{1}H NMR spectrum). Unfortunately, isolation of (*R*)-**5** on a preparative scale was hampered by its high solubility in pentane at −78 °C as well as partial loss of THF under reduced pressure, giving a mixture of the tris-THF adduct (*R*)-**5**, the mono-THF adduct and the THF-free starting material (*R*,*R*)-**4**. Furthermore, (*R*)-**5** could only be obtained when THF was added to complex (*R*,*R*)-**4**, whereas reaction of [La{CH(SiMe$_3$)$_2$}$_3$] with (*R*)-H$_2$(Biphen) in the presence of THF (5 equiv.) in [D$_6$]benzene solution resulted in the slow formation of several products. Complex (*R*)-**5** accounted for only 15% of this mixture after 70% consumption of [La{CH(SiMe$_3$)$_2$}$_3$]. Reactions of (*R*)-H$_2$(Biphen) with [Y{CH(SiMe$_3$)$_2$}$_3$] performed in the presence or absence of THF were unsuccessful as well, producing a mixture of products which did not contain an yttrium−carbon bond.

Interestingly, attempts to synthesize the racemic analogue of (*R*,*R*)-**4** from [La{CH(SiMe$_3$)$_2$}$_3$] and racemic H$_2$(Biphen) yielded only a mixture of complexes. This contrasts our previous observation in the preparation of biphenolate amido complexes using the tris(amido) complex [La{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] as starting material, which gave isolable products only when racemic H$_2$(Biphen) was used.[60] Attempts to synthesize an enantiopure biphenolate lanthanum amido complex resulted in the formation of a mixture of at least three products. In the present study the reactivity seems to be opposite. Using the trialkyllanthanum complex [La{CH(SiMe$_3$)$_2$}$_3$] we were able to prepare the homochiral dimer (*R*,*R*)-**4**, while the synthesis of a racemic complex failed. The formation of biphenolate rare-earth-metal complexes by amine or alkane elimination is very sensitive to the reactivity and steric hindrance of the rare-earth-metal precursor. The desired biphenolate rare-earth-metal alkyl or amido complexes are obtained as kinetic products.

The X-ray diffraction analysis of (*R*,*R*)-**4** (orthorhombic, space group $P2_12_12$) reveals a C_2-symmetric homochiral dimeric structure (Figure 2). It shows a similar binding motif for the biphenolate ligand as was observed in the heterochiral dimer (*R*,*S*)-**2b** and 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)]$_2$.[80] Selected bond lengths and angles of (*R*,*R*)-**4** and (*R*,*S*)-**2b** are summarized in Table 1 for a better comparison.

The two biphenolate metal moieties are connected by two bridging phenolate units and the tetrahedral geometry



Scheme 2

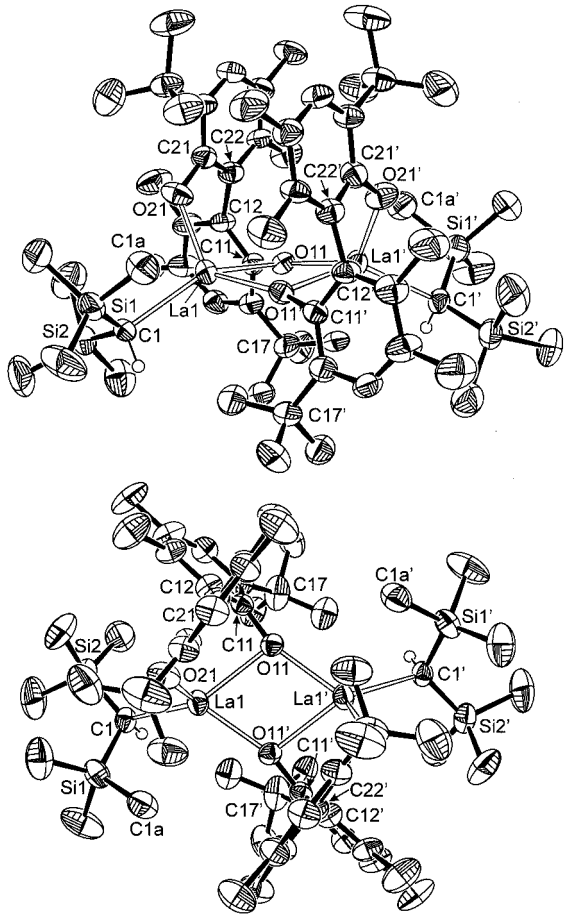


Figure 2. ORTEP diagram of the molecular structure of (*R*,*R*)-**4** (top) and alternative view from the top (bottom); thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms, except for those on C1 and C1′, as well as one position of the disordered *tert*-butyl group on C17 have been omitted for the sake of clarity

around lanthanum is significantly distorted. Both terminal phenolate groups have a *syn* relationship relative to the La_2O_2 core, with their aromatic rings being stacked parallel to each other in order to avoid destabilizing steric interactions of the *tert*-butyl groups.

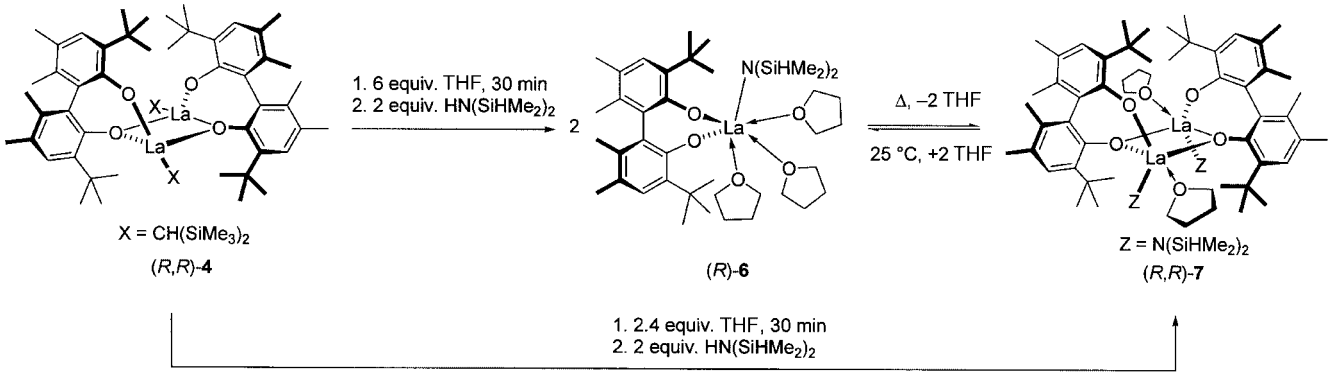
The La_2O_2 core displays an even more distorted geometry than was observed in (*R*,*S*)-**2b**[60] (Table 1). The lanthanum−oxygen bond to the bridging phenolate oxygen atom of the same biphenolate metal moiety (La1−O11) is 0.14 Å longer than the corresponding bond to the bridging phenolate oxygen atom of the other biphenolate metal moiety (La1−O11′). The terminal lanthanum−oxygen bond La1−O21 is 0.34 Å (for La1−O11) and 0.20 Å (for La1−O11′) shorter than the bond to the bridging phenolates [typical range La−OAr(term.) = 2.17−2.32 Å; La−OAr(bridg.) = 2.32−2.43 Å].[60] The dihedral angle between the two phenol rings [−97.0(7)° for (*R*,*R*)-**4**] is about 9° larger than in (*R*,*S*)-**2b** [87.8(4)°][60] and 24° larger than in [La{1,1′-(2-$OC_6H_2tBu_2$-3,5)$_2$}{$CH(SiMe_3)_2$}$(THF)_3$] (**3**) [72.9(1.9)°],[77] due to its lower coordination number. The O11−La1−O21 bite angle of the biphenolate ligand for (*R*,*R*)-**4** [95.86(12)°] is larger than the values of 88.83(7)° for (*R*,*S*)-**2b**[60] and 88.1(3)° for [La{1,1′-(2-$OC_6H_2tBu_2$-3,5)$_2$}{$CH(SiMe_3)_2$}$(THF)_3$].[77] The La···La separation [3.8750(5) Å] is the shortest observed for complexes with an La_2O_2 core (usual range for La: 3.96−4.02 Å),[60][81−84] in accordance with the observations mentioned earlier.

Table 1. Comparison of selected bond lengths (Å), atomic distances (Å) and angles (°) for (*R*,*R*)-**4** (E = C1) and (*R*,*S*)-**2b**[60] (E = N1)

	(*R*,*R*)-**4** E = C1	(*R*,*S*)-**2b**[60] E = N1
La1−O21	2.169(4)	2.234(2)
La1−O11	2.506(3)	2.503(2)
La1−O11′	2.364(3)	2.407(2)
La1−E	2.543(5)	2.416(3)
La1··· La1′	3.8750(5)	3.9954(3)
La1···C11	2.899(5)	2.911(3)
La1···C1A	3.088(7)	−
La1···Si1	3.3685(16)	3.5240(11)
La1···Si2	3.8643(18)	3.3703(10)
O11−La1−O21	95.86(12)	88.83(7)
O11−La1−O11′	73.24(11)	71.10(8)
O21−La1−O11′	124.07(13)	108.79(8)
E−La1−O11	137.47(16)	123.41(9)
E−La1−O11′	119.42(15)	142.14(9)
E−La1−O21	105.51(17)	106.41(9)
La1−O11−La1′	105.39(11)	108.90(8)
La1−O11−C11	91.9(3)	92.81(16)
La1−O21−C21	125.0(4)	132.5(2)
La1−E−Si1	99.2(2)	116.17(14)
La1−E−Si2	124.0(3)	109.56(14)
Si1−E−Si2	118.4(3)	133.94(17)
C11−C12−C22−C21	−97.0(7)	87.8(4)

The lanthanum−carbon bond [2.543(5) Å] in (*R*,*R*)-**4** is similar in length to that in [La(Cp*){$CH(SiMe_3)_2$}$_2$] [2.537(5) and 2.588(4) Å],[85] but significantly shorter than in [La{1,1′-(2-$OC_6H_2tBu_2$-3,5)$_2$}{$CH(SiMe_3)_2$}$(THF)_3$] (**3**) [2.676(13) Å][77] and [La(Cp*){$CH(SiMe_3)_2$}$_2$(THF)] [2.651(8) and 2.627(10) Å].[85] The alkyl ligand avoids unfavorable steric interactions with the bridging phenolate groups by increasing C1−La1−O11 [137.47(16)°] and C1−La1−O11′ [119.42(15)°], while C1−La1−O21 [105.51(17)°] is slightly decreased from an ideal tetrahedral geometry around lanthanum. The geometry of the alkyl ligand displays a β-SiC monoagostic interaction [La−C−Si = 99.2(2)°, 124.0(3)°; La···C = 3.088(7) Å] resembling those found in previously characterized coordinatively unsaturated bis(trimethylsilyl)methyl rare-earth-metal complexes[86][87] such as [La(Cp*){$CH(SiMe_3)_2$}$_2$] [La−C−Si = 99.6(3)°, 126.4(4)° and 98.8(3)°, 129.6(3)°; La···C = 2.978(6), 2.988(6) Å],[85] [La(Cp*)-{$CH(SiMe_3)_2$}$_2$(THF)] [La−C−Si = 102.9(4)°, 134.8(6)° and 103.6(4)°, 131.1(5)°; La···C = 3.241(19), 3.265(14) Å].[85] One silicon−carbon bond is distorted towards the metal center with La1···Si1 [3.3685(16) Å] and La1···C1A [3.088(7) Å] being within the sum of the van der Waals radii. Note that the coordinatively saturated monomeric biphenolate complex **3** [La−C−Si = 116.5(7)° and 118.7(6)°][77] does not display such an agostic interaction.

Reaction of (*R*,*R*)-**4** with tetramethyldisilazane in the presence of six equivalents of THF results in the formation



Scheme 3

of [La{(*R*)-Biphen}{N(SiHMe$_2$)$_2$}(THF)$_3$] [(*R*)-**6**] as the major product (Scheme 3), which is not available from the reaction of (*R*)-H$_2$(Biphen) with [La{N(SiHMe$_2$)$_2$}$_3$-(THF)$_2$]. The ^{1}H NMR spectrum of (*R*)-**6** has similar features to the previously characterized (*R*)-**1a**,[60] showing two doublets for the methyl groups on silicon at δ = 0.24 and 0.28 ppm ($^3J_{H,H}$ = 2.9, 3.0 Hz) and a septet for SiH at δ = 5.00 ppm in (*R*)-**6** compared to δ = 0.32 and 0.38 ppm ($^3J_{H,H}$ = 3.0 Hz) and δ = 5.12 ppm in (*R*)-**1a**. In addition to the signals of (*R*)-**6**, small quantities of a second species can be observed to appear over the course of 2 h in the ^{1}H NMR spectrum. The equilibrium is shifted towards this second species upon heating, which we believe to be the homochiral dimer [La{(*R*)-Biphen}{N(SiHMe$_2$)$_2$}(THF)]$_2$ [(*R*,*R*)-**7**]. The equilibrium between (*R*)-**6** and (*R*,*R*)-**7** is shifted from 3:1 at 25 °C to 1:1.5 at 60 °C and 1:3.2 at 80 °C (Figure 3). Formation of (*R*,*R*)-**7** is reversible and the initial 3:1 ratio of (*R*)-**6** to (*R*,*R*)-**7** is regenerated upon cooling back to 25 °C (however, equilibration generally requires 1−2 h at room temperature). (*R*,*R*)-**7** has identical spectroscopic data to the species that is formed upon heating (*R*,*S*)-**2b** in [D$_8$]toluene.[60] Reaction of (*R*,*R*)-**4** with tetramethyldisilazane in the presence of only 2.4 equivalents of THF gives (*R*,*R*)-**7** as the major product.

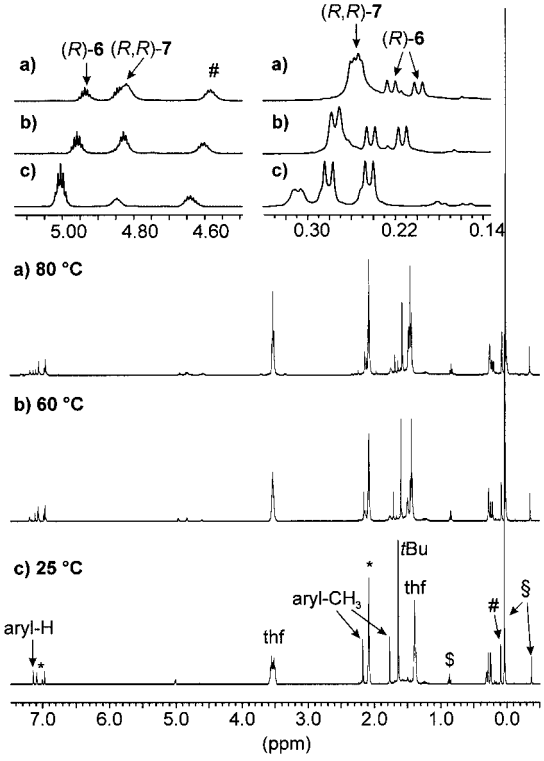


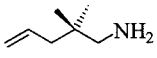
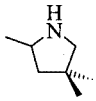
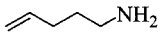
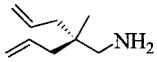
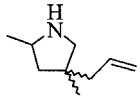
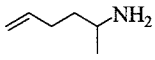
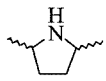
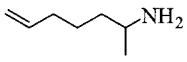
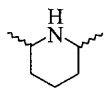
Figure 3. ^{1}H NMR spectrum of the equilibrium between (*R*)-**6** and (*R*,*R*)-**7** in [D$_8$]toluene at: a) 80 °C, b) 60 °C and c) 25 °C [# = HN(SiHMe$_2$)$_2$, § = CH$_2$(SiMe$_3$)$_2$, $ = pentane]

Catalytic Evaluation

Complexes (*R*,*R*)-**4** and (*R*)-**5** were evaluated for their catalytic activity in hydroamination/cyclization and hydrosilylation reactions (Table 2 and 3 respectively). The most notable feature of alkyl complexes (*R*,*R*)-**4** and (*R*)-**5** in comparison to bis(dimethylsilylamido) complexes **1** and **2** is their significantly higher catalytic activity for the hydroamination/cyclization of aminoalkenes. Especially noteworthy seems to be the almost twofold increase in catalytic activity of complex (*R*)-**5** compared to the dimer (*R*,*R*)-**4** in the cyclization of 2,2-dimethylpent-4-enylamine (**8**; Table 2, entries 1 and 2). This strongly suggests that (*R*,*R*)-**4** remains dimeric under the catalytic conditions, which is in accordance with our earlier finding that (*R*,*S*)-**2a** has a lower catalytic activity than **1a**. However, (*R*,*R*)-**4** and (*R*)-**5** show similar rates in the cyclization of the sterically less bulky pent-4-enylamine **10** (Table 2, entry 3 and 4).

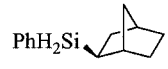
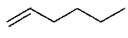
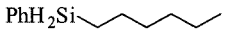
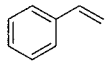
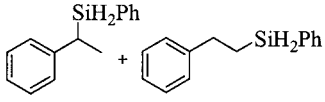
The turnover frequency of 61 h^{-1} for complex (*R*)-**5** in the cyclization of substrate **8** is of the same magnitude as that of other highly active lanthanocene catalysts, such as [Cp*$_2$LaCH(SiMe$_3$)$_2$] (95 h^{-1} at 25 °C),[13] and twice as active as the lanthanum bisoxazoline complex [{(4*R*,5*S*)-Ph$_2$Box}La{N(SiMe$_3$)$_2$}$_2$] (25 h^{-1} at 23 °C).[25] Unfortunately, both lanthanum catalysts (*R*,*R*)-**4** and (*R*)-**5** achieve significantly lower enantioselectivities than the yttrium biphenolate complex (*R*)-**1a**[60] — pyrrolidines **9** and **11** are produced in essentially racemic form. The larger atomic radius (0.900 Å for Y vs. 1.032 Å for La)[88] concomitant with the low steric hindrance presented by the *tert*-butyl substituents of the biphenolate ligand results in a low level of stereodifferentiation.

Table 2. Catalytic hydroamination/cyclization reactions

Entry	Substrate	Product	Cat.[a]	*T* [°C]	Time[b] [h]	Conv. [%]	TOF [h^{-1}]	*ee* Product;[c] dr
1			(*R*,*R*)-**4**	25	1.5	95	35	8
2	**8**	**9**	(*R*)-**5**	25	1	98	61	8
3			(*R*,*R*)-**4**	60	19	> 99	5	2
4	**10**	**11**	(*R*)-**5**	60	25	98	5.3	0
5			(*R*,*R*)-**4**	29	0.4	> 99	≥ 120	5 / 18; 1.15:1
6	**12**	**13**	(*R*)-**5**	25	0.15	> 99	≥ 330	1 / 28 ; 1.4:1
7			(*R*,*R*)-**4**	25	49	93	1.7[d]	nd; 9:1 (*trans*:*cis*)
8	**14**	**15**	(*R*)-**5**	60	5	95	23[d]	nd; 5.3:1 (*trans*:*cis*)
9			(*R*,*R*)-**4**	80	38	> 96	3.5[d]	nd; 1:3.7 (*trans*:*cis*)
10	**16**	**17**	(*R*)-**5**	80	42	87	3.8[d]	nd; 1:4 (*trans*:*cis*)

[a] Reaction conditions: 2 mol % cat., C_6D_6, Ar atm. [b] Reaction time. [c] Determined by ^{19}F NMR spectroscopy of the Mosher amides. [d] The reactions are not zero order in substrate concentration. TOF is based on the initial rate. nd = not determined.

Table 3. Catalytic hydrosilylation of olefins with $PhSiH_3$ [93]

Entry	Substrate	Product	Cat.[a]	Time[b] [h]	Conv. [%]	dr[c]
1			(*R*,*R*)-**4**[d]	22	79	> 30:1
	18	**19**				
2			(*R*,*R*)-**4**[d]	22	87	38:1
3	**20**	**21**	(*R*)-**5**	66.5	81	52:1
4			(*R*,*R*)-**4**	2	95	17:1
5	**22**	**23a** + **23b**	(*R*)-**5**	6.7	82	18:1

[a] Reaction conditions: 2 mol % cat., C_6D_6, 1 equiv. $PhSiH_3$, 60 °C, Ar atm. [b] Reaction time. [c] Determined by ^1H NMR spectroscopy. [d] 4 mol % cat.

The amino diolefin **12** cyclizes very rapidly to diastereomeric 4-allyl-2,4-dimethylpyrrolidine (**13**) with a similarly low diastereoselectivity [1.15:1 for (*R*,*R*)-**4** and 1.4:1 for (*R*)-**5**] as observed for (*R*)-**1b**.[60] Interestingly, whereas (*R*)-**1b** gave both diastereomers in almost identical enantiomeric ratios,[60] (*R*,*R*)-**4** and (*R*)-**5** deliver the minor diastereomer with higher enantioselectivity than the almost racemic major diastereomer.

Cyclization of 1-methylpent-4-enylamine (**14**) in the presence of (*R*,*R*)-**4** at 25 °C gives 2,5-dimethylpyrrolidine (**15**) with a good diastereoselectivity of 9:1 (*trans*:*cis*). The monomeric catalyst (*R*)-**5** produces **15** with a somewhat lower diastereoselectivity of 5.3:1, albeit at 60 °C. Cyclization of 1-methylhex-5-enylamine (**16**), on the other hand, yields preferentially *cis*-2,5-dimethylpiperidine (*cis*-**17**) in a roughly 1:4 ratio (*trans:cis*) using either (*R*,*R*)-**4** or (*R*)-**5**, which is similar to the diastereoselectivity observed with a catalyst system prepared from [Y{N(SiMe$_3$)$_2$}$_3$] and *N*,*N*′-diarylethane-1,2-diamines.[58] Formation of the six-membered ring requires heating to 80 °C for both biphenolate lanthanum catalysts. Preferred formation of *trans*-2,5-dimethylpyrrolidine can be rationalized by a minimization of the 1,3-diaxial interaction in the seven-membered cyclization transition state.[23] Similar considerations explain the preferred formation of *cis*-2,5-dimethylpiperidine via an eight-membered transition state.[22]

Cyclization of 2,2-dimethylpent-4-enylamine (**8**) using (*R*,*R*)-**4** or (*R*)-**5** as catalysts proceeds with a zero-order rate dependence on substrate concentration (Figure 4). This result is in accordance with the generally accepted mechanism of lanthanocene-catalyzed hydroamination reactions, in which olefin insertion into the rare-earth-metal amido bond is the rate-determining step.[13] However, this result contrasts our previous finding that ring-closing of **8** using bis(dimethylsilyl)amido complexes **1** and **2** proceeds with a first- [(*R*)-**1b** and **2**] or second-order rate dependence [(*R*)-**1a**] on substrate concentration.[60]

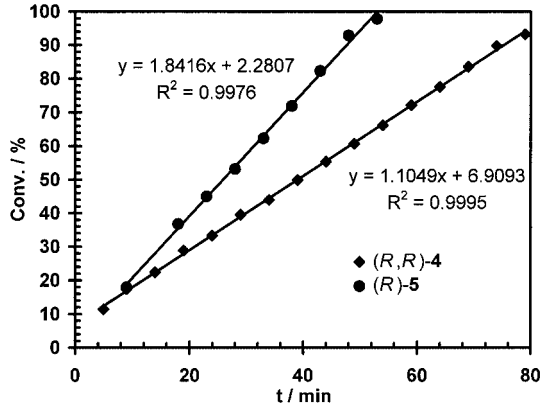


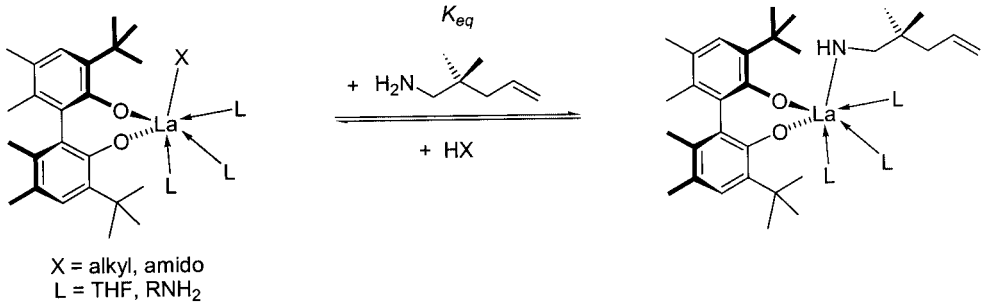
Figure 4. Hydroamination/cyclization of **8** (0.63 M) with 1 mol % (*R*,*R*)-**4** (= 2 mol % La) and 2 mol % (*R*)-**5** at 25 °C in C_6D_6

(*R*,*R*)-[La(Biphen){N(SiHMe$_2$)$_2$}(THF)] [(*R*,*R*)-**7**], prepared in situ by reaction of (*R*,*R*)-**4** with HN(SiHMe$_2$)$_2$ and one equivalent of THF, shows a significantly reduced catalytic activity in the ring-closing of substrate **8**, with an initial rate of 0.36 h^{-1} at 60 °C. Similar to the amidoyttrium biphenolate complex (*R*)-**1a**, ring-closing of **8** with (*R*,*R*)-**7** proceeds with a second-order rate dependence (**1a**) on substrate concentration. The ^{1}H NMR spectra of the catalytic reaction show free tetramethyldisilazane as well as unchanged catalyst, indicating that only 36% of the catalyst is activated. The unchanged catalyst most likely exists as a monomeric species of the general type [La{(*R*)-Biphen}{N(SiHMe$_2$)$_2$}(THF)(L)$_n$] (L = substrate **8** or pyrrolidine **9**; n = 1 or 2) based on the well-separated doublets for the amido silicon methyl groups at δ = 0.30 and 0.35 ppm ($^3J_{H,H}$ = 2.9 Hz) in the ^{1}H NMR spectrum, which is typical for the monomeric biphenolate complexes (*R*)-**1a** and (*R*)-**6**. Therefore, the low catalytic activity of bis(dimethylsilyl)amido complexes **1**, **2** and (*R*)-**6** in comparison to alkyl catalysts (*R*,*R*)-**4** and (*R*)-**5** has to be attributed mainly to the low basicity of the bis(dimethylsilyl)amido ligand resulting in incomplete protonolysis of the amido ligand by the aminoalkene substrate [Scheme 4, X = N(SiHMe$_2$)$_2$, K_{eq} < 1]. Protonolysis of the biphenolate alkyl complexes, on the other hand, is instantaneous and quantitative [Scheme 4, X = CH(SiMe$_3$)$_2$, K_{eq} >> 1]. Complexes with the bis(trimethylsilyl)amido ligand generally give similar catalytic activity to that of alkyl complexes.[13][89] Tetramethyldisilazane (pK_a = 22.8)[90] is more acidic than hexamethyldisilazane (pK_a = 25.8).[91] Obviously, this slight difference in basicity between the two amido ligands renders the bis(dimethylsilyl)amido ligand an unsuitable leaving group for the catalyst precursor.[92] Coordinated THF in the bis(dimethylsilyl)amido complexes cannot contribute significantly to the low catalytic activity, because rare-earth-metal-based hydroamination catalysts generally show only a small decrease in rate in the presence of THF.[13,65,66]

Both complexes (*R*,*R*)-**4** and (*R*)-**5** are also active in the hydrosilylation of various olefinic substrates (Table 3).[93] However, catalytic activity for the monomeric tris-THF adduct (*R*)-**5** is generally lower than for the THF-free dimer (*R*,*R*)-**4**.

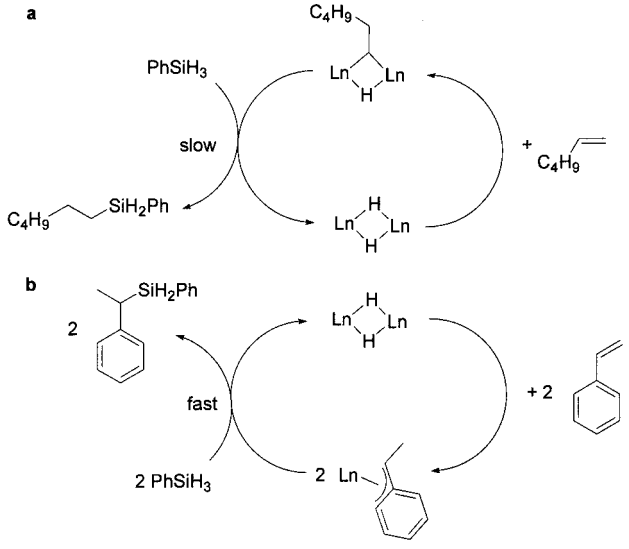
Hydrosilylation of styrene proceeds with good activity to give the Markovnikov product with high selectivity. Plausible reasons for the preferred formation of this isomer can be derived from the electronically preferred secondary insertion of styrene into the metal−hydride bond of the catalytically active rare-earth-metal hydrido species.[33,94] In contrast to previously investigated lanthanocene[33] and diamidobiphenyl[45] catalyst systems, the catalytic activities of complexes (*R*,*R*)-**4** and (*R*)-**5** in the hydrosilylation of 1-hexene or norbornene are significantly lower than for styrene, and higher catalyst loadings are required to complete the reaction. The stereoselectivity substrates is very high for these, giving exclusively 1,2-addition for 1-hexene and the *exo* adduct for norbornene.

The reason for the low catalytic activity in the hydrosilylation of 1-hexene and norbornene is not completely clear at present. NMR spectroscopic investigation could not reveal an identifiable species during the catalysis, for example a lanthanum hydride species. Schaverien noted that replacing a six-electron π-donor cyclopentadienyl ligand in a lanthanocene complex by a four-electron donating aryloxide ligand results in reduced activity in the polymerization of α-olefins due to the formation of deactivated μ-hydrido and μ-alkyl species.[95] Insertion of linear terminal olefins proceeded exclusively in a 1,2-fashion and no μ-isoalkyls were observed. Similarly, the highly electrophilic biphenolate lanthanum complexes can be expected to form stable μ-hydrido



Scheme 4

and μ-alkyl species[96] with reduced reactivity towards olefin insertion or phenylsilane σ-bond metathesis (Scheme 5a). Whereas insertion of 1-hexene into a terminal lanthanum hydride species is expected to give an appreciable amount of branched product[33,39] due to the sterically undemanding features of the biphenolate ligand, insertion into a bridging μ-hydrido would explain the high regioselectivity observed in the hydrosilylation of 1-hexene. The secondary insertion product formed in the reaction of the lanthanum hydride species with styrene on the other hand should adopt an η^3-benzylic coordination mode[94] rather than a bridging μ-benzyl arrangement. The terminal η^3-benzyl group should be significantly more reactive towards phenylsilane than a μ-alkyl species.



Scheme 5

Conclusion

We have presented here the facile synthesis of chiral biphenolate alkyllanthanum complexes. These complexes show good catalytic activity for the hydroamination/cyclization of aminoalkenes, which is of comparable magnitude to well established lanthanocene catalysts. The catalytic activity is significantly higher than previously prepared biphenolate bis(dimethylsilyl)amido complexes. This can be attributed to a sluggish catalyst initiation in the case of the amido complexes caused by the low basicity of the bis(dimethylsilyl)amido ligand. Despite their high catalytic activity, practical use of the biphenolate alkyl complexes for asymmetric hydroamination is limited by the low enantiomeric excess in the product heterocycles, because the *tert*-butyl groups of the biphenolate ligand have an insufficient stereodifferentiating effect. However, catalysts with larger substituents should be more enantioselective, as shown by yttrium complexes bearing tris(aryl) substituted binaphtholate ligands,[65] while retaining the high catalytic activity. Although the biphenolate lanthanum complexes show good regioselectivity in the hydrosilylation of olefins, they are less attractive catalysts than lanthanocene complexes due to their lower catalytic activity.

Experimental Section

General Remarks: All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexanes, pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. [Ln{$CH(SiMe_3)_2$}$_3$] (Ln = Y, La),[79] (*R*)-H_2(Biphen)[76] and substrates **8**,[97] **10**,[13] **12**,[60] **14**[98][99] and **16**[58] were synthesized as described in the literature. Olefins for hydrosilylation reactions were distilled from sodium and stored over molecular sieves. The substrates were dried by distillation from CaH_2 and stored over molecular sieves. (*R*)-(+)-α-Methoxy-α-trifluoromethylphenylacetic acid (RCA, Freiburg, Germany) was transformed into its acid chloride by reaction with oxalyl chloride/DMF in hexanes.[100] Mosher amides were prepared and analyzed by ^{19}F NMR spectroscopy as described earlier.[60] All other chemicals were commercially available and used as received. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 300 (300.1, 75.5 and 282.4 MHz for ^1H, ^{13}C, and ^{19}F, respectively) or Avance 400 (400.1 and 100.6 MHz for ^1H and ^{13}C, respectively) spectrometer. Spectra were referenced internally using the residual solvent resonances (^1H, ^{13}C) or referenced externally to $CFCl_3$ (^{19}F; δ = 0 ppm). 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.

(*R*,*R*)-[La(Biphen){$CH(SiMe_3)_2$}]$_2$ [(*R*,*R*)-4]: A solution of (*R*)-H_2(Biphen) (156 mg, 0.44 mmol) in toluene (1 mL) was added to a solution of [La{$CH(SiMe_3)_2$}$_3$] (280 mg, 0.454 mmol) in toluene (1 mL) over 10 min at −10 °C with a syringe. The mixture was stirred at room temperature for 1 h and the solvent was evaporated

in vacuo. The remaining yellow residue was dried in vacuo. Pentane (2 mL) was added to the residue and the mixture was heated to 50 °C and left in a fridge overnight. The solvent was decanted at −30 °C, acetone bath) from a slightly yellow crystalline precipitate, and the precipitate was washed with pentane (0.5 mL) and dried in vacuo. Yield 110 mg (35%). The crystals contain one equiv. of pentane per molecule of the dimer. ^{1}H NMR (400.1 MHz, [D$_8$]toluene, 25 °C): δ = 7.13 (br. s, 4 H, Biphen), 2.16 (br. s, 12 H, aryl-CH$_3$), 1.53 (br. s, 12 H, aryl-CH$_3$), 1.40 (br. s, 36 H, C(CH$_3$)$_3$], 0.30 [s, 18 H, Si(CH$_3$)$_3$], −0.03 [s, 18 H, Si(CH$_3$)$_3$], −0.62 (s, 2 H, LaCH). ^{1}H NMR (400.1 MHz, [D$_8$]toluene, −30 °C): δ = 7.24 (s, 2 H, Biphen), 7.08 (s, 2 H, Biphen), 2.22 (s, 6 H, aryl-CH$_3$), 2.18 (s, 6 H, aryl-CH$_3$), 1.65 (s, 6 H, aryl-CH$_3$), 1.55 (s, 6 H, aryl-CH$_3$), 1.41 [s, 18 H, C(CH$_3$)$_3$], 1.37 [s, 18 H, C(CH$_3$)$_3$], 0.33 [s, 18 H, Si(CH$_3$)$_3$], 0.07 [s, 18 H, Si(CH$_3$)$_3$], −0.63 (s, 2 H, LaCH) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]toluene, −30 °C): δ = 156.1, 150.3, 137.8, 137.3, 137.2, 137.0, 135.0, 133.4, 131.2, 130.1, 128.5, 126.6, (aryl), 55.0 (LaCH), 35.0 [*C*(CH$_3$)$_3$], 32.2, 30.7 [C(*C*H$_3$)$_3$], 20.0, 17.5 (aryl-CH$_3$), 4.8, 4.5 [Si(CH$_3$)$_3$] ppm. C$_{62}$H$_{102}$La$_2$O$_4$Si$_4$·(C$_5$H$_{12}$) (1373.8): calcd. C 58.58, H 8.36; found C 57.73, H 8.10.

(*R*)-[La(Biphen){CH(SiMe$_3$)$_2$}(THF)$_3$] [(*R*)-5]: THF (7.2 μL, 89 μmol, 3 equiv. per lanthanum) was added to a solution of (*R*,*R*)-**4** (20 mg, 14.6 μmol) in [D$_6$]benzene (0.5 mL). Removal of the solvent in vacuo led to partial loss of THF, therefore the catalyst was always prepared in situ directly prior to use. ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 7.17 (s, 2 H, Biphen), 3.55 (br. m, 12 H, THF), 2.15 (s, 6 H, aryl-CH$_3$), 1.74 (s, 6 H, aryl-CH$_3$), 1.63 [s, 18 H, C(CH$_3$)$_3$], 1.30 (br. m, 12 H, THF), 0.35 (s, 9 H, SiMe$_3$), 0.33 (s, 9 H, SiMe$_3$), −1.64 [s, 1 H, *CH*(SiMe$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]benzene): δ = 156.3, 138.3, 136.4, 130.7, 128.9, 124.4 (aryl), 68.9 (THF), 51.5 (LaCH), 35.2 [*C*(CH$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 25.4 (THF), 20.4 (aryl-CH$_3$), 16.2 (aryl-CH$_3$), 5.1 (SiMe$_3$), 5.0 (SiMe$_3$) ppm.

(*R*)-[La(Biphen){N(SiHMe$_2$)$_2$}(THF)$_3$] [(*R*)-6]: THF (6.3 μL, 78 μmol, 3.5 equiv. per lanthanum) was added to a solution of (*R*,*R*)-**4** (15 mg, 10.9 μmol) in [D$_8$]toluene (0.5 mL). The solution was kept at 25 °C for 30 min and then tetramethyldisilazane (4.0 μL, 23 μmol) was added. Removal of the solvent in vacuo led to partial loss of THF. ^{1}H NMR (400.1 MHz, [D$_8$]toluene, 25 °C): δ = 7.14 (s, 2 H, Biphen), 5.00 (sept, $^3J_{H,H}$ = 3.0 Hz, 2 H, SiH), 3.55 (m, THF), 3.50 (br. m, THF), 2.17 (s, 6 H, aryl-CH$_3$), 1.77 (s, 6 H, aryl-CH$_3$), 1.64 [s, 18 H, C(CH$_3$)$_3$], 1.38 (m, THF), 0.28 [d, $^3J_{H,H}$ = 3.0 Hz, 6 H, SiH(C*H*$_3$)$_2$], 0.24 [d, $^3J_{H,H}$ = 2.9 Hz, 6 H, SiH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]toluene, 25 °C): δ = 156.6, 139.1, 136.3, 131.4, 128.4, 123.9 (aryl), 68.6 (THF), 35.3 [*C*(CH$_3$)$_3$], 30.6 [C(*C*H$_3$)$_3$], 25.6 (THF), 16.2 (aryl-CH$_3$), 3.0 [SiH(CH$_3$)$_2$], 2.9 [SiH(CH$_3$)$_2$] ppm.

(*R*,*R*)-[La(Biphen){N(SiHMe$_2$)$_2$}(THF)]$_2$ [(*R*,*R*)-7]: THF (1.4 μL, 17.3 μmol, 1.2 equiv. per lanthanum) was added to a solution of (*R*,*R*)-**4** (10 mg, 7.3 μmol) in [D$_6$]benzene (0.5 mL). The solution was kept at 25 °C for 30 min and then tetramethyldisilazane (3.1 μL, 17.8 μmol) was added. The ^{1}H and ^{13}C NMR spectra show broad signals for the biphenolate ligand at room temperature. ^{1}H NMR (400.1 MHz, [D$_6$]benzene, 60 °C): δ = 7.23 (s, 2 H, Biphen), 4.90 (br. sept, 2 H, SiH), 3.58 (br. m, THF), 3.50 (br. m, THF), 2.15 (br. s, 6 H, aryl-CH$_3$), 1.80 (br. s, 6 H, aryl-CH$_3$), 1.54 [br. s, 18 H, C(CH$_3$)$_3$], 1.33 (m, THF), 0.32 [m, 12 H, SiH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]benzene, 60 °C): δ = 138.4, 137.3, 136.2, 129.6, 128.6, 124.7 (aryl), 69.3 (THF), 35.3 [*C*(CH$_3$)$_3$], 34.9 [*C*(CH$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 30.5 [C(*C*H$_3$)$_3$], 25.3 (THF), 20.0, 16.3 (aryl-CH$_3$), 3.2 [SiH(CH$_3$)$_2$], 3.1 [SiH(CH$_3$)$_2$] ppm.

X-ray Crystallographic Study: Clear, colourless crystals of (*R*,*R*)-**4** suitable for X-ray diffraction analysis were obtained by cooling a concentrated pentane solution to −30 °C. Data were collected on a Nonius KappaCCD area detector. Crystal data: C$_{62}$H$_{102}$La$_2$O$_4$Si$_4$·C$_5$H$_{12}$, M_r = 1373.78, crystal size 0.10 × 0.10 × 0.10 mm, orthorhombic, space group $P2_12_12$ (No. 18), a = 16.3814(7) Å, b = 17.5277(5) Å, c = 12.9592(6) Å, V = 3721.0(3) Å^3, Z = 2, $\rho_{calcd.}$ = 1.225 g cm^{-3}, F(000) = 1434, Mo-K_α radiation (λ = 0.71073 Å), T = 173(2) K, μ = 1.237 mm^{-1}, 8519 independent reflections measured, GOF = 0.945, R [$I > 2\sigma(I)$] = 0.0473, wR_2 (all data) = 0. 1084, absolute structure parameter = −0.04(2), largest e-max, e-min = 0.555 and −0.767 e·Å^{-3}. Cell parameters for (*R*,*R*)-**4** were obtained from 10 frames using a 10° scan and refined with 4689 reflections. Lorentz, polarization, and empirical absorption corrections were applied.[101,102] 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 using SHELXL-97.[103] Hydrogen atoms were fixed in idealized positions using a riding model. Non-hydrogen atoms were refined anisotropically. The methyl groups attached to C17 are disordered and were refined with two independent orientations (position occupation of 48.52% and 51.48%, respectively). Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[104] Graphical representations were prepared with ORTEP-III for Windows.[105] CCDC-235041 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for NMR-Scale Catalytic Hydroamination/Cyclization Reactions: In a glovebox, a screw-cap NMR tube was charged with 10 μmol of the catalyst, C$_6$D$_6$ (0.5 mL) and the substrate (0.33 mmol) in that order. The NMR tube was then placed in a pre-heated oil bath and conversion followed by ^{1}H NMR spectroscopy (for acquisition parameters see below). Final conversion was determined by ^{1}H NMR spectroscopy (disappearance of olefinic signals) and by GC analysis. Diastereomeric ratios of pyrrolidines **13** and **15** as well as piperidine **17** were determined by vacuum-transfer of all volatiles and subsequent ^{1}H NMR spectroscopic analysis of characteristic signals.

General Procedure for Kinetic Catalytic Hydroamination/Cyclization Reactions: In a glovebox, a screw-cap NMR tube was charged with 10 μmol of the catalyst, C$_6$D$_6$ (0.5 mL) and the substrate (0.33 mmol) in that order. The NMR tube was then placed in the thermostatted probe (± 0.5 °C) of the Bruker Avance 400 spectrometer. The conversion was monitored by ^{1}H NMR spectroscopy by following the disappearance of the olefinic signals of the substrate relative to the internal standard CH$_2$(SiMe$_3$)$_2$. NMR spectra were taken at 5 min time intervals using the *multizg* script from the Bruker XWin NMR software package. In order to ensure accurate integration, a 10 s delay between 30° pulses was utilized (number of scans = 4, acquisition time = 4 s). Substrate and catalyst concentration was verified by comparison of the integrals of characteristic signals [olefinic signals for substrates; Si(CH$_3$) signal of CH$_2$(SiMe$_3$)$_2$]. The linear part of the data (minimum two half-lives) was fit by least-squares analysis and the turnover frequency (TOF) was determined from the slope a. TOF = a × [subst]$_0$/[cat]

General Procedure for NMR-Scale Catalytic Hydrosilylation Reactions: In the glovebox, a screw-cap NMR tube was charged with (*R*,*R*)-**4** (5.0 mg, 3.6 μmol), C$_6$D$_6$ (0.5 mL), the olefin (0.30 mmol) and phenylsilane (33 mg, 0.30 mmol) in that order. The NMR tube

was then placed in a pre-heated oil bath and conversion followed by ^{1}H NMR spectroscopy. Final conversion was determined by ^{1}H NMR spectroscopy (disappearance of olefinic signals). Diastereomeric ratios were determined by ^{1}H NMR spectroscopic analysis of characteristic signals in comparison to literature spectroscopic data.[30,33]

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