A Study on Chiral Organocalcium Complexes: Attempts in Enantioselective Catalytic Hydrosilylation and Intramolecular Hydroamination of Alkenes

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Z. Naturforsch. **2008**, *63b,* 169 – 177; received August 29, 2007

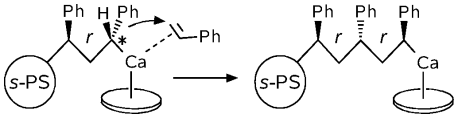
The chiral β-diketimine ligand [(*S*)-Ph(Me)CH-N=C(Me)]$CH_2$was prepared by condensation of acetylacetone with the commercially available chiral building block (*S*)-Ph(Me)CH-NH_2. Reaction of *bis*(*o*-Me_2N-α-Me_3Si-benzyl)calcium with this β-diketimine led to double deprotonation. Reaction of *bis*(*o*-Me_2N-α-Me_3Si-benzyl)calcium with the commercially available chiral *bis*-oxazoline (*S*)-Ph-BOX gave diastereopure [(*S*)-Ph-BOX](*o*-Me_2N-α-Me_3Si-benzyl)calcium which in solution slowly decomposed with formation of *o*-Me_2N-α-Me_3Si-toluene. The corresponding amide complex [(*S*)-Ph-BOX]CaN$(SiMe_3)_2\cdot(THF)_2$ is stable and the crystal structure has been determined. In solution, this heteroleptic amide is in Schlenk equilibrium with the homoleptic species [(*S*)-Ph-BOX]$_2$Ca and Ca[N$(SiMe_3)_2]_2\cdot(THF)_2$. This Schlenk equilibrium can be steered to the heteroleptic side. Use of the enantiopure calcium amide catalyst for the hydrosilylation of styrene with $PhSiH_3$ or in the intramolecular hydroamination of aminoalkenes gave good product yields, but only small *ee*-values were observed (5 – 10 %). From stoichiometric reactions of the catalyst with the substrates it is concluded that the "true" catalytically active species is mainly present as a homoleptic calcium complex, which explains the poor enantioselectivities.

Key words: Alkaline Earth Metals, Calcium, Hydrosilylation, Hydroamination

Introduction

Although use of the main group metal calcium in homogeneous catalysis is relatively rare, reports on well-defined organocalcium catalysts are on the increase [1 – 5]. The unique feature of such catalysts is the combination of the relatively high Lewis acidity of the Ca^{2+} center with the considerable nucleophilicity of the ligands. Consequently, these catalysts have been exploited in living syndioselective styrene polymerization [1], dilactide polymerization [2], hydroamination and hydrophosphination [3], the Tischenko reaction [4] and in alkene hydrosilylation [5].

In calcium-mediated styrene polymerization a syndioselectivity of up to 93 % in *r*-diades was obtained. This corresponds to a considerable stereoselectivity in the chain-end controlled insertion step of *ca.* 87 % *ee* (Eq. 1). Likewise, mixtures of calcium alkoxides with chiral bidentate diol or *bis*-oxazoline ligands have been used for the asymmetric aldol reaction, the Michael addition or the epoxidation of α,β-unsaturated enones [6]. Although in some cases *ee*-values of over 90 % could be obtained, the latter *in situ* prepared Ca catalysts have not been isolated or characterized, and the chemical composition of the catalysts is unclear.



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In the light of these results, we embarked on a search for well-defined chiral enantiopure calcium catalysts. We describe the difficulties encountered in the syntheses of these complexes and in the first attempts to introduce chiral Ca-catalysts for enantioselective hydrosilylation and intramolecular hydroamination of alkenes. The rather low *ee*-values obtained in these particular catalytic conversions are explained by the results of an in-depth study of structure and stability of the heteroleptic chiral calcium catalysts.

Results and Discussion

Synthesis and characterization of chiral enantiopure calcium reagents

In this work, we focussed on two strongly coordinating monoanionic bidentate ligands with C_2-chirality.

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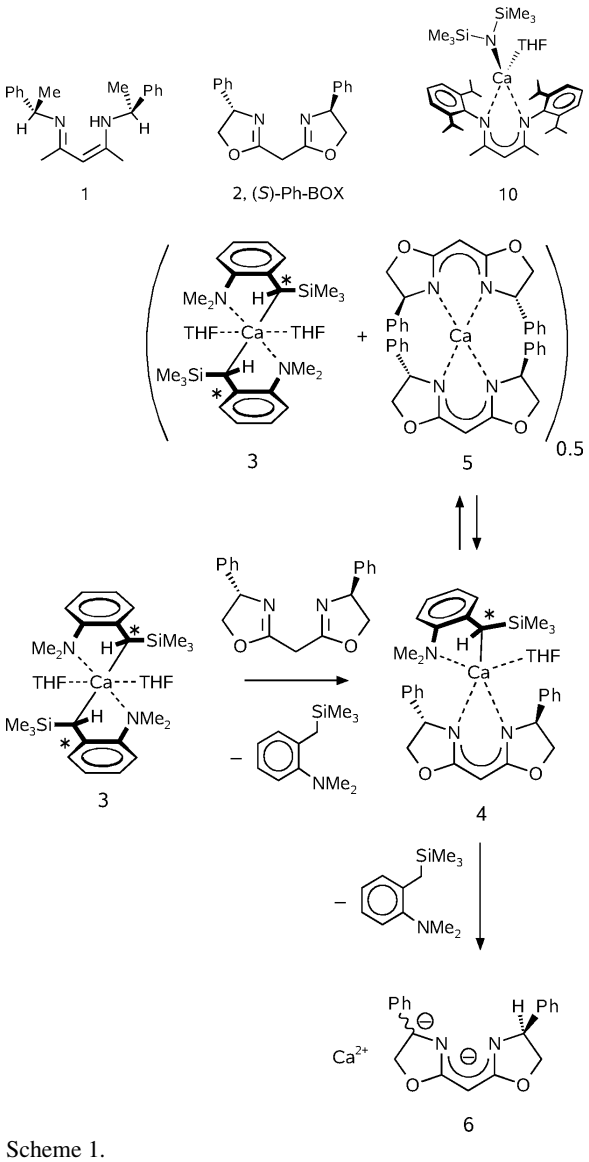


Scheme 1.

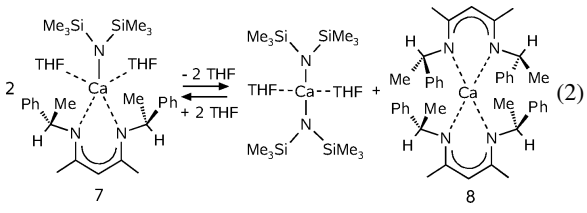
We synthesized a chiral enantiopure β-diketimine (**1**) by condensation of acetylacetone with the readily available building block (*S*)-α-Me-benzylamine. In addition, the commercially available *bis*-oxazoline (*S*)-Ph-BOX (**2**) is addressed. The BOX system is an important class of C_2-symmetric chiral ligands generally used in the neutral form [7]. Although it has been used as an anionic ligand in alkaline-earth metal chemistry [6e, 8], hitherto no complexes have been isolated or structurally characterized.

Attempts to prepare stable well-defined heteroleptic benzylcalcium complexes based on the chiral ligands **1** and **2** failed. Reaction of the ligand **1** with (Me_2N-α-Me_3Si-benzyl)$_2$Ca·(THF)$_2$ (**3**) in a 1/1 ratio gave immediate deprotonation of the ligand already at r. t. The ^{1}H NMR spectra of the reaction mixtures showed several products that could not be identified unambiguously. The immediate appearance of a red color, which intensified over time, and the complete conversion of the benzylcalcium functionality into 2-Me_2N-α-Me_3Si-toluene indicated a second deprotonation of the ligand in the benzylic position.

Deprotonation of (*S*)-Ph-BOX (**2**) with (Me_2N-α-Me_3Si-benzyl)$_2$Ca·(THF)$_2$ (**3**) was more selective and gave clean conversion to **4** (Scheme 1). Whereas the dibenzylcalcium precursor **3** consists of a pair of interconverting diastereomers in benzene solution (T_{coal} = 60 °C, $\Delta G^{\ddagger}$ = 16.8 kcal mol^{-1}), only one diastereomer was observed for **4**. This underlines efficient communication between the chiral (*S*)-Ph-BOX ligand and the chiral benzylic carbon center.

Although **4** can be prepared *in situ*, isolation turned out to be impossible for two reasons. First of all, in solution **4** is in a Schlenk equilibrium with the homoleptic species **3** and **5** (Scheme 1; the ratio of heteroleptic to both homoleptic species is approximately 4/1/1, *i.e.* K $\approx$ 0.06). Similar Schlenk equilibria have also been observed for *in situ* prepared heteroleptic BOX-Mg-*i*Pr complexes [8b]. More importantly, a yellow benzene solution of **4** slowly decomposed completely over a two day period at r. t. to give an intensely red solution (at 50 °C decomposition is complete within 2 h). Although the decomposition product is as yet unidentified (due to very broad signals in the NMR spectrum), complete conversion of the benzylic anion into 2-Me_2N-α-Me_3Si-toluene indicates a second (slower) deprotonation of the Ph-BOX ligand. The intense red color of the decomposition product strongly suggests a species in which one chiral benzylic carbon has been deprotonated (**6**, Scheme 1).

Decomposition reactions of heteroleptic benzylcalcium complexes have been observed earlier [9] and are due to the high reactivity of the benzyl-Ca functionality. Therefore, we directed our investigations to the less reactive calcium amide complexes. Deprotonation of **1** with [(Me_3Si)$_2$N]$_2$Ca·(THF)$_2$ in benzene needed more forcing conditions, but was essentially complete after 16 h at 50 °C. No second deprotonation of the β-diketimine ligand could be observed. The heteroleptic product **7** is in Schlenk equilibrium with the homoleptic species [(Me_3Si)$_2$N]$_2$Ca·(THF)$_2$ and **8** in an approximate ratio of 4/1/1 (Eq. 2).



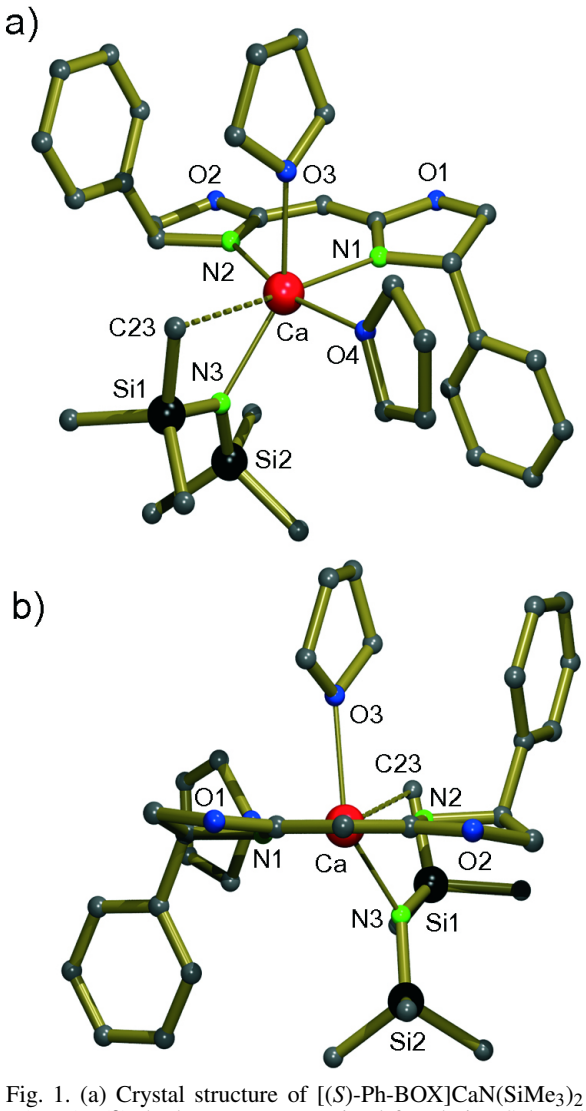


Fig. 1. (a) Crystal structure of [(*S*)-Ph-BOX]CaN(SiMe$_3$)$_2$ · (THF)$_2$ (**9**); hydrogen atoms omitted for clarity. Selected bond lengths and angles are given in Table 1. (b) View along the approximate C_2 axis of the BOX ligand.

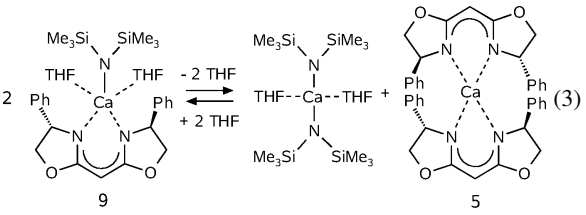
Deprotonation of the (*S*)-Ph-BOX ligand **2** with one equivalent of [(Me$_3$Si)$_2$N]$_2$Ca·(THF)$_2$ was complete after 30 min at r. t. Concentration and cooling of the mother liquor gave crystals of a well-defined product with composition [(*S*)-Ph-BOX]CaN(SiMe$_3$)$_2$·(THF)$_2$ (**9**).

Table 1. Selected bond lengths (Å) and angles (degrees) for [(*S*)-Ph-BOX]CaN(SiMe$_3$)$_2$·(THF)$_2$ (**9**).

Ca-N1	2.404(2)	Ca-O3	2.410(2)
Ca-N2	2.381(2)	Ca-O4	2.417(2)
Ca-N3	2.348(2)	Ca···C23	3.191(4)
N1-Ca-N2	78.84(7)	N2-Ca-O4	88.15(7)
N1-Ca-N3	131.00(7)	N3-Ca-O3	88.70(7)
N2-Ca-N3	96.97(7)	N3-Ca-O4	88.96(7)
N1-Ca-O3	88.15(7)	C23···Ca-N1	163.73(9)
N1-Ca-O4	88.70(7)	C23···Ca-N2	113.42(9)
N2-Ca-O3	88.96(7)	C23···Ca-O3	81.65(8)
C23···Ca-O4	77.94(8)		

The crystal structure of **9** is shown in Fig. 1 and geometrical data are summarized in Table 1. The BOX ligand chelates the calcium metal *via* both nitrogen atoms and retains approximate C_2-symmetry (Fig. 1b). The oxazoline rings are slightly tilted with respect to each other: the dihedral angle between the least-squares planes through both rings is 13.4(2)°. The Ca-N(SiMe$_3$)$_2$ bond of 2.348(2) Å is considerably longer than the terminal Ca-N(SiMe$_3$)$_2$ bond of 2.275(7) Å in [((Me$_3$Si)$_2$N)$_2$Ca]$_2$ [10]. In addition, an agostic Si-Me···Ca^{2+} interaction is evident from a short Ca···C23 distance of 3.191(4) Å (sum of the van-der-Waals radii of Ca and C is 3.49 Å) and corresponding H···Ca distances of 3.03(4) and 3.06(4) Å. This agostic Me···Ca interaction causes tilting of the amide ligand with respect to the Ca-N3 axis: the Ca-N3-Si1 angle of 112.4(1)° is significantly smaller than the Ca-N3-Si2 angle of 121.3(1)°. Likewise, the N3-Si1-C23 angle of 108.4(1) is squeezed somewhat with respect to an ideal tetrahedral angle. Consequently, other N-Si2-C angles in the complex are widened (111.9(2)° – 115.1(1)°). The coordination sphere for Ca is completed by two THF ligands.

An interesting comparison can be made with the heteroleptic achiral calcium amide **10** [11]. The CH{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$ ligand (= DIPP-nacnac) in this complex coordinates in a bidentate fashion with Ca-N bonds of 2.352(1) and 2.370(1) Å, *i.e.* slightly shorter than those in **9**. Also the Ca-N(SiMe$_3$)$_2$ bond of 2.313 Å in **10** is slightly shorter than that in **9**. A similar agostic interaction with comparable features as in **9** is also observed for **10**. The larger spatial requirement of the DIPP-nacnac ligand in **10** allows coordination of only one THF ligand. Therefore, the steric bulk of the DIPP-nacnac ligand equals that of one (*S*)-Ph-BOX ligand and a THF ligand.



In contrast to **4**, complex **9** is stable against a second deprotonation of the bidentate ligand. However, **9** is not stable against ligand exchange: the ^{1}H NMR spectrum of crystals of **9** dissolved in C_6D_6 shows a Schlenk equilibrium with the two homoleptic calcium complexes $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ and **5** (Eq. 3) in a ratio of 4.2/1/1. The α-CH_2 protons of the THF ligands in **9** are diastereotopic and give separate signals in the ^{1}H NMR spectrum, whereas the more distant β-CH_2 protons display a single resonance. This indicates that also in solution the BOX ligand and both THF ligands are bonded to Ca^{2+}.

The Schlenk equilibria observed for enantiopure calcium amides **7** and **9** in solution could seriously hamper the stereoselectivity in catalytic conversions (assuming that $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ is also catalytically active). Both Schlenk equilibria in Eqs. 2 and 3, however, can be steered to the heteroleptic species **7** and **9**, simply by adding the homoleptic species **8** and **5**, respectively, which are not catalytically active in hydrosilylation or hydroamination catalysis. A 1/1 mixture of **7** and **8** in benzene only contains small amounts of $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ ($< 3\,\%$). Similarly, only minor amounts of $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ ($< 2\,\%$) could be detected in a 1/1 mixture of **9** and **5** in benzene.

Catalytic hydrosilylation and hydroamination with chiral calcium amide complexes

We recently introduced the catalytic hydrosilylation of alkenes with early main group metal catalysts [5] for which we proposed a mechanism similar to that for organolanthanide catalysts [12] (Scheme 2, left). Although these catalysts can not compete with the well-established class of highly active transition metal catalysts [13], they exhibit some remarkable features. Complete regiocontrol of the hydrosilylation reaction, which in some cases could be switched by either metal or solvent choice, was observed. Moreover, use of catalysts based on the much cheaper and biocompatible calcium could certainly be of interest for potential applications. Additional control over the stereochemistry is therefore highly desirable.

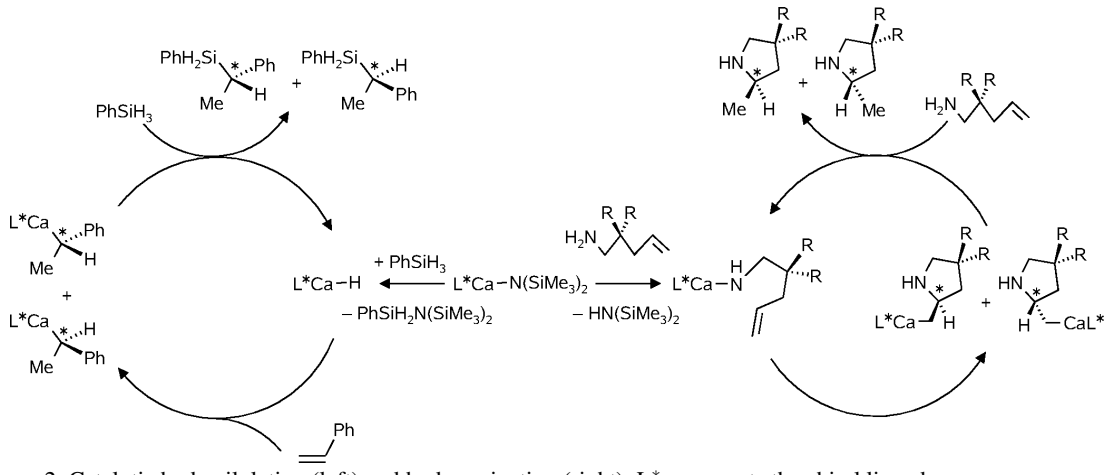
Table 2. Catalytic conversion of styrene and phenylsilane into $PhCH(SiH_2Ph)Me$.

Entry	mol-%	cat.	T(°C)	t(h)	conv.(%)
1 [5]	2.5 %	**3**	20	< 0.1	> 98
2	2.5 %	$[(Me_3Si)_2N]_2Ca\cdot(THF)_2$	50	1	> 98
3	2.5 %	**9**	50	16	> 98 (S(-), 5 % *ee*)
4	5 %	**5/9** (1/1)[a]	50	16	> 98 (S(-), 9 % *ee*)
5	5 %	**7/8** (1/1)[a]	50	16	> 98 (S(-), 9 % *ee*)

[a] mol-% catalyst calculated on the basis of the active Ca-N($SiMe_3$)$_2$ functionality.

Since Ca-mediated hydrosilylation of alkenes is limited to activated alkenes, *e. g.* conjugated alkenes, styrene was chosen as an appropriate prochiral substrate. Hydrosilylation of styrene with phenylsilane using the benzylcalcium catalyst **3** was shown to be fast and completely regioselective (Table 2, entry 1) [5]. Use of chiral calcium amides as catalysts requires the catalytic activity of the calcium amide functionality. We found that $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ is also an efficient, but somewhat less active, catalyst for this reaction giving exclusively one regio-isomer (Table 2, entry 2). Catalysis with the chiral amide catalyst **9** gave overnight essentially full conversion of the substrates (Table 2, entry 3). Oxidation of the chiral product according to Tamao-Fleming, which is known to proceed with retention of configuration at the chiral benzylic carbon atom [14], gave the corresponding 1-Phethanol, however, a very low enantiomeric excess of *ca.* 5 % *ee* was observed. As $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ is an effective catalyst for this reaction, this could originate from insufficient control of the Schlenk equilibrium. Runs with a 1/1 mixture of **9** and **5**, which is largely free of homoleptic $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$, gave only slightly improved results. Likewise, hydrosilylation of styrene with a 1/1 mixture of **7** and **8** gave a similarly low *ee* of 9 % (Table 2, entry 4).

These remarkably low *ee* values indicate that the "true" catalytically active species might be achiral. The proposed chiral catalyst (L^*CaH in Scheme 2) is a heteroleptic calcium hydride for which recently an example has been isolated [15]. Although Schlenk equilibria for the catalyst precursors ($L^*CaN(SiMe_3)_2$ in Scheme 2) can be directed quite well to the heteroleptic side, Schlenk equilibria for L^*CaH could mainly be shifted to the homoleptic side. In this case catalytic conversion of styrene into $PhCH(SiH_2Ph)Me$ would largely proceed *via in situ* generated CaH_2. This presumption is enforced by the observation that stoichio-



Scheme 2. Catalytic hydrosilylation (left) and hydroamination (right); L* represents the chiral ligand.

Table 3. Catalytic intramolecular hydroamination of $HNCH_2C(R)_2CH_2CH{=}CH_2$.

Entry	mol-%	cat.	substrate	T(°C)	t(h)	conv.(%)
1 [3]	10 %	**10**	R = H	25	21	> 98
2	10 %	**9**	R = H	20	84	4
3	10 %	**9**	R = Ph	20	1	> 98 (R(+), 5 % *ee*)
4	10 %	**5/9** (1/1)[a]	R = Ph	20	2	> 98 (R(+), 6 % *ee*)
5	10 %	**7/8** (1/1)[a]	R = Ph	20	1	> 98 (R(+), 10 % *ee*)

[a] mol-% catalyst calculated on the basis of the active Ca-$N(SiMe_3)_2$ functionality.

metric addition of $PhSiH_3$ to **9** gave exclusive formation of homoleptic **5** and CaH_2.

Alternatively, we tested the chiral calcium amide catalysts presented here for intramolecular hydroamination, a reaction for which a variety of transition and lanthanide metal catalysts have been introduced [16]. The calcium-mediated intramolecular hydroamination was recently demonstrated by Hill, and the catalytic cycle in Scheme 2 (right) has been proposed [3]. In a first step the Ca-$N(SiMe_3)_2$ functionality is protonated by the amino-alkene substrate. After ring closure and subsequent protolysis the cyclic amine is eliminated.

It has been reported that the heteroleptic calcium amide **10** is a catalyst for the ring closure of 1-amino-pent-4-ene, whereas the homoleptic $[(Me_3Si)_2N]_2Ca{\cdot}(THF)_2$ catalyst gave no conversion [3]. The inactivity of the homoleptic calcium amide makes control over the Schlenk equilibrium of a chiral heteroleptic calcium amide less relevant for the stereocontrol in enantioselective reactions. Heteroleptic chiral calcium amide **9**, however, gave even at elevated temperatures essentially no ring closure of the 1-amino-pent-4-ene (Table 3, entry 2).

Since substituents in 2-positions of the aminoalkene largely influence these ring closure reactions by the Thorpe-Ingold effect [3, 16], a substrate with phenyl substituents was investigated. It was found that the chiral catalyst **9** gave clean and full conversion of 1-amino-2,2-diphenyl-pent-4-ene to 2-methyl-4,4-diphenylpyrollidine under mild reaction conditions. However, a rather low *ee* of 5 % was observed (Table 3, entry 3). Mixtures of **5** and **9** or **7** and **8** gave full conversions but no significant increase in the *ee* values (Table 3, entries 4 – 5).

In sharp contrast to the conversion of the unsubstitued aminoalkene, we found that homoleptic $[(Me_3Si)_2N]_2Ca{\cdot}(THF)_2$ is an efficient catalyst for ring closure of the diphenyl-substituted aminoalkene (5 mol-%, 20 °C, 1h, full conversion). Therefore, poor control over the Schlenk equilibria of the catalytically active species could in this particular case also be an issue in the enantioselective hydroamination. This was verified by stoichiometric reactions between catalyst and substrates.

Addition of one equivalent of 1-amino-pent-4-ene to **9** gave $HN(SiMe_3)_2$ and homoleptic **5** (and presumably $Ca[HNCH_2C(R)_2CH_2CH{=}CH_2]$ for which broad signals appeared in the ^{1}H NMR spectrum). No ring closure products could be observed. The inactivity of catalyst **9** in ring closure of 1-amino-pent-4-ene (entry 2) can be explained by full conversion to homoleptic calcium species, which are known to be inactive for this substrate [3].

Similarly, addition of one equivalent of 1-amino-2,2-diphenyl-pent-4-ene to a benzene solution of **9**, which is in Schlenk equilibrum, gave $HN(SiMe_3)$ and

resulted in a sharp increase of signals for homoleptic **5** in the NMR spectrum of the reaction mixture. Apparently, substitution of the bulky amide ligand $(Me_3Si)_2N$ in **9** by less sterically demanding amides substantially affects the Schlenk equilibria in favor of the homoleptic species. A similar observation has been made for the comparable complex **10** [17]. Low *ee* values can therefore tentatively be explained by formation of substantial amounts of homoleptic calcium species in the catalytic process.

Conclusions

Several difficulties have been encountered in the preparation of chiral enantiopure organocalcium reagents. The diastereopure heteroleptic benzylcalcium complex **4** could be prepared *in situ*, but decomposed *via* a route that likely involves a second deprotonation of the BOX ligand by the benzyl functionality (Scheme 1). Less reactive heteroleptic chiral calcium amides **7** and **9** could be prepared and a second deprotonation of the chiral ligands was not observed. Complex **9** crystallized as an enantiopure heteroleptic calcium amide, however, in solution it is in equilibrium with the homoleptic species. A similar observation was made for **7**. The Schlenk equilibria for these enantiopure calcium amide complexes can be directed to the heteroleptic side by addition of one of the homoleptic components.

Hydrosilylation of styrene with phenylsilane was shown to be catalyzed efficiently by $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$. Application of the enantiopure amides **7** and **9** in the hydrosilylation of styrene shows a very low stereoselectivity which can be slighly improved by directing the Schlenk equilibria for the catalyst precursors to the heteroleptic side. Similarly, intramolecular hydroamination of an aminoalkene with chiral calcium amide catalysts gave good conversion but rather poor *ee* values.

Stoichiometric reactions between the chiral amide **9** and the substrates used in catalysis show that Schlenk equilibria for the "true" catalytically active species are largely on the homoleptic side, explaining the low *ee*-values. The dynamic behavior of loosely bound, highly ionic calcium complexes seriously hinders stereocontrol in Ca-mediated catalytic reactions. The results of these first attempts in enantioselective hydrosilylation and hydroamination with organocalcium catalysts suggest that future research should be directed to developing chiral ligands that: (i) are inert to the high reactivity of calcium hydride and amide functionalities and (ii) effectively stabilize the heteroleptic intermediates against ligand exchange reactions.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (argon or nitrogen) by using freshly dried solvents and Schlenk line and glove box techniques. The reactants **3** [1b], $[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ [13], 4-(1-phenyl-ethylamino)-pent-3-en-2-one [18] and the aminoalkenes [19] were prepared according to literature procedures.

*Synthesis of **1***

4-(1-Phenyl-ethylamino)-pent-3-en-2-one (1.30 g, 6.39 mmol) was dissolved in 5.0 mL of dichloromethane. A solution of triethyloxonium tetrafluoroborate (1.34 g, 7.03 mmol) in 3.0 mL of dichloromethane was added slowly. After stirring the slightly yellow solution for 12 h, a solution of (*S*)-α-Me-benzylamine (2.32 g, 19.1 mmol) in 5.0 mL of dichloromethane was added slowly. The mixture was stirred at r. t. for 24 h. The solvents were removed by vacuum evaporation and the remaining yellow slurry was stirred in hexane for 30 min. The colorless precipitate was isolated from the yellow hexane solution and dissolved in 30 mL of water containing 340 mg of KOH. The aqueous phase was extracted 3 times with 30 mL of toluene. The combined organic phases were dried over Na_2SO_4, and all volatiles were removed. Cooling an ethanol solution of the raw product to −20 °C resulted in crystallization of large colorless needles. Yield: (710 mg, 2.32 mmol, 36 %) – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (d, J = 6.7 Hz, 6H, PhCH(CH_3)), 1.92 (s, CH_3 backbone), 4.60 (s, 1H, C*H* backbone), 4.79 (q, J = 6.7 Hz, 2H, PhC*H*(CH_3)), 7.29 – 7.47 (m, 10H, Ar-H), 11.9 (s, 1H, N*H*). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (PhCH*C*H_3), 27.6 (Me backbone), 57.7 (Ph*C*HCH$_3$), 96.9 (*C*H backone), aromatics: 127.9, 128.2, 130.2, 148.7; 161.5 (C=N). – $C_{21}H_{26}N_2$ (306.45): calcd. C 82.31, H 8.55; found C 82.56, H 8.31.

*In situ synthesis of **4***

(*S*)-Ph-BOX (**2**) (23 mg, 0.075 mmol) was added to a solution of $(Me_2N\text{-}\alpha\text{-}Me_3Si\text{-benzyl})_2Ca\cdot(THF)_2$(**3**) (45 mg, 0.075 mmol) in 0.50 mL of C_6D_6. This resulted in clean formation of the heteroleptic complex **4** which was fully characterized by 2D-NMR spectroscopy. Only one set of signals was observed in the ^{1}H NMR spectrum of **4**. The methyl groups of the Me_2N-substituent are diastereotopic at 20 °C, which indicates that the Ca-N bond is stable on the NMR time scale. It is therefore unlikely that the single set of resonances observed for **4** is due to fast exchange of both possible diastereomers (this would involve dissociation of the

much stronger Ca-C bond followed by inversion). In benzene solution, complex **4** is in equilibrium with **3** and **5** (ratio $\approx 4/1/1$, respectively). In solution **4** decomposes at r. t. over a two days period. – ^{1}H NMR (500 MHz, C_6D_6): δ = 0.19 (s, 9H, Si(CH_3)$_3$), 0.88 (s, 1H, CHSiMe$_3$), 1.26 (m, 8H, THF), 2.11 (s, 3H, NMe_2), 2.52 (s, 3H, NMe_2), 3.31 (m, 8H, THF), 3.83 (t, J = 7.3 Hz, 2H, CH_2-BOX), 4.03 (t, J = 8.5 Hz, 2H, CH_2-BOX), 4.64 (s, 1H, CH backbone), 4.21 (t, J = 7.3 Hz, 2H, PhCH-BOX), 6.46 (t, 1H, J = 7.2 Hz, Ar-H), 6.85 (d, 1H, J = 7.5 Hz, Ar-H), 6.93 – 7.14 (m, 11H, Ar-H), 7.33 (d, 1H, J = 7.5 Hz, Ar-H). – ^{13}C NMR (125 MHz, C_6D_6): δ = 2.6 (Me$_3$Si), 25.4 (THF), 44.3 (Me$_2$N), 44.8 (Me$_2$N), 44.8 (Me$_3$SiCH), 54.9 (*C*H backbone), 67.2 (Ph*C*H), 68.1 (THF), 72.5 (*C*H$_2$O), aromatics: 112.0, 120.4, 123.5, 126.7, 127.1, 127.7, 128.3, 136.2, 144.9, 147.8; 172.4 (N*C*O).

In situ synthesis of ***5***

Addition of [(Me$_3$Si)$_2$N]$_2$Ca·(THF)$_2$ (38 mg, 0.075 mmol) to a solution of (*S*)-Ph-BOX (46 mg, 0.15 mmol) in 0.50 mL of C_6D_6 gave at r. t. fast and quantitative formation of **5**, which was characterized *via* 2D-NMR spectroscopy. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.43 (m, 8H, THF), 3.53 (m, 8H, THF), 3.63 (dd, J = 7.5, 7.5 Hz, 4H, CH_2), 3.98 (t, J = 8.0 Hz, 4H, CH_2), 4.37 (s, 2H, CH backbone), 4.68 (dd, J = 8.4, 8.4 Hz, 4H, PhCH), 6.89 – 7.20 (m, 20H, Ar-H). – ^{13}C NMR (75 MHz, C_6D_6): δ = 25.8 (THF), 54.7 (*C*H backbone), 67.9 (THF), 68.8 (Ph*C*H), 75.2 (*C*H$_2$O), aromatics: 126.9, 127.0, 128.5, 146.5, 173.3 (N*C*O).

In situ synthesis of ***7***

Chiral ligand **1** (92 mg, 0.30 mmol) was deprotonated by [(Me$_3$Si)$_2$N]$_2$Ca·(THF)$_2$ (152 mg, 0.30 mmol) in 0.50 mL of benzene. The conversion was essentially complete after heating the slightly yellow solution to 50 °C for 16 h. The solvents were removed by vacuum evaporation and the remaining slightly yellow precipitate was dried for 1 h at 50 °C *in vacuo*. In benzene solution, **7** is in equilibrium with the homoleptic species Ca[N(SiMe$_3$)$_2$]$_2$ and **8** (ratio $\approx 4/1/1$, respectively). – ^{1}H NMR (300 MHz, C_6D_6): δ = 0.24 (s, 18H, Si(CH_3)$_3$), 1.28 (m, 8H, THF), 1.55 (d, J = 6.6 Hz, 6H, PhCH(CH_3)), 1.83 (s, 6H, CH_3 backbone), 3.49 (m, 8H, THF), 4.41 (s, 1H, CH backbone), 4.59 (q, J = 6.6 Hz, 2H, PhCH(CH$_3$)), 7.04 (t, J = 7.4 Hz, 2H, *p*-H Ph), 7.22 (t, J = 7.4 Hz, 4H, *m*-H Ph), 7.37 (d, J = 7.4 Hz, 4H, *o*-H Ph). – ^{13}C NMR (75 MHz, C_6D_6): δ = 5.9 (Me$_3$Si), 23.1 (PhCHCH$_3$), 25.1 (THF), 25.8 (Me backbone), 58.9 (PhCHCH$_3$), 69.6 (THF), 92.9 (*C*H backbone), aromatics: 126.8, 127.0, 129.2, 148.2; 164.8 (C=N).

In situ synthesis of ***8***

[(Me$_3$Si)$_2$N]$_2$Ca·(THF)$_2$ (76 mg, 0.15 mmol) was added to a solution of **1** (92 mg, 0.30 mmol) in 0.50 mL of benzene. After heating the slightly yellow solution to 50 °C for 16 h, clean and quantitative conversion to **8** was observed. Analyses by 2D-NMR spectroscopy. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.26 (m, 8H, THF), 1.51 (d, J = 6.7 Hz, 12H, PhCH(CH_3)), 1.72 (s, 12H, CH_3 backbone), 3.47 (m, 8H, THF), 4.28 (s, 2H, CH backbone), 4.47 (q, J = 6.7 Hz, 4H, PhCH(CH$_3$)), 7.01 (t, J = 7.3 Hz, 4H, *p*-H Ph), 7.16 (t, J = 8.3 Hz, 8H, *m*-H Ph), 7.26 (d, J = 7.4 Hz, 8H, *o*-H Ph). – ^{13}C NMR (75 MHz, C_6D_6): δ = 23.2 (PhCHCH$_3$), 25.3 (THF), 26.2 (Me backbone), 58.5 (PhCHCH$_3$), 68.7 (THF), 92.3 (*C*H backbone), aromatics: 126.4, 126.7, 128.9, 148.5; 164.7 (C=N).

Synthesis of ***9***

[(Me$_3$Si)$_2$N]$_2$Ca·(THF)$_2$ (412 mg, 0.82 mmol) was added to a solution of **2** (250 mg, 0.82 mmol) in 3.0 mL of benzene. After stirring at r. t. for 30 min, the reaction mixture was concentrated to half of its volume. Cooling to 7 °C overnight resulted in crystallization of the product as slightly yellow crystals. Yield: (330 mg, 0.51 mmol, 62 %). – ^{1}H NMR (300 MHz, C_6D_6): δ = 0.19 (s, 18H, Si(CH_3)$_3$), 1.23 (m, 8H, THF), 3.30 (m, 4H, THF), 3.46 (m, 4H, THF), 3.80 (dd, J = 7.9, 7.9 Hz, 2H, CH_2-BOX), 4.07 (t, J = 8.3 Hz, 2H, CH_2-BOX), 4.79 (s, 1H, CH backbone), 4.90 (dd, J = 8.6, 8.6 Hz, 2H, PhCH), 7.02 – 7.25 (m, 10H, Ph). – ^{13}C NMR (75 MHz, C_6D_6): δ = 1.4 (Me$_3$Si), 25.3 (THF), 55.0 (*C*H backbone), 68.3 (THF), 68.5 (Ph*C*H), 73.4 (*C*H$_2$O), aromatics: 126.6, 127.4, 128.9, 145.8, 173.4 (N*C*O). – $C_{33}H_{51}CaN_3O_4Si_2$ (650.04): C 60.98, H 7.91; found: C 60.63, H 7.75.

Typical procedure for the catalytic hydrosilylation of styrene

The catalysts were used either in crystalline purity ([(Me$_3$Si)$_2$N]$_2$Ca·(THF)$_2$ and **9**) or as a mixture of complexes (**5/9** and **7/8**). The appropriate amount of catalyst was added to neat $PhSiH_3$ and styrene and the resulting solution was heated to 50 °C. Generally, a color change to red was observed at the beginning of the reaction. The conversion was followed by taking samples at regular time intervals which were analyzed by ^{1}H NMR-spectroscopy. After full conversion (> 98 %) 5 mL of pentane was added to the solution. Then the mixture was treated with 1 mL of concentrated HCl and the volatiles were removed to afford (1-phenyl-ethyl)(phenyl)silane as a viscous, high-boiling, colorless oil. The silane was converted to the corresponding alcohol 1-phenyl-ethanol by Tamao-Fleming [14] oxidative cleavage of the carbon-silicon bond according to a literature procedure [12]. Subsequently, the enantiomeric excess was determined by ^{1}H NMR measurement of the alcohol in the presence of the shift reagent *tris*[3–(heptafluoropropylhydroxymethylene)–(+)–camphorate]europium(III) and by measurement of the optical rotation.

Typical procedure for the intramolecular hydroamination of aminoalkenes

The catalysts were used either in crystalline purity ($[(Me_3Si)_2N]_2Ca\cdot(THF)_2$ and **9**) or as a mixture of complexes (**5/9** and **7/8**). To a 0.1 M solution of the catalyst in C_6D_6 was added the appropriate amount of the aminoalkene (Table 3). The conversion was followed by taking samples at regular time intervals which were analyzed by ^{1}H NMR spectroscopy. After full conversion (> 98 %) the solution was diluted with Et_2O, flushed through a short silica pad and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated by vacuum evaporation to give the pyrrolidine product as a colorless oil. The enantiomeric excess was determined by conversion of the product to the diastereomeric Mosher amide and analysis with ^{19}F NMR spectroscopy [19b].

Crystal structure determination

The structure was solved by Direct Methods (SHELXS-97) [20] and refined with SHELXL-97 [21]. All geometry calculations and graphics were performed with PLATON [22]. CCDC 632999 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for [(S)-Ph-BOX]CaN(SiMe$_3$)$_2$·(THF)$_2$

$C_{33}H_{51}CaN_3O_4Si_2$, M_r = 650.03, orthorhombic, space group $P2_12_12_1$, a = 9.0862(2), b = 19.7012(4), c = 20.5119(4) Å, V = 3761.8(1) Å^3, Z = 4, ρ_{calcd} = 1.176 Mg m^{-3}, $F(000)$ = 1400, $\mu(MoK_\alpha)$ = 0.273 mm^{-1}. The data were collected on a Siemens SMART CCD diffractometer at −70 °C. Of the 81299 measured reflections, 4055 were independent (R_{int} = 0.047) and 3871 observed [$I \geq 2\sigma(I)$]. The final refinement converged to $R1$ = 0.026 for $I \geq 2\sigma(I)$, $wR2$ = 0.065 and GOF = 1.04 for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.14/+0.30 e Å^{-3}. The Flack parameter refined to 0.001(32). Part of the hydrogen atoms have been located in the Fourier difference map and were refined isotropically, others have been placed on calculated positions and were refined in a riding mode.

Acknowledgement

Prof. Dr. R. Boese and D. Bläser (Universität Duisburg-Essen) are thanked for collection of the X-ray diffraction data.

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