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Cobalt Alkyl Complexes of a New Family of Chiral 1,3-Bis(2-pyridylimino)isoindolates and Their Application in Asymmetric Hydrosilylation

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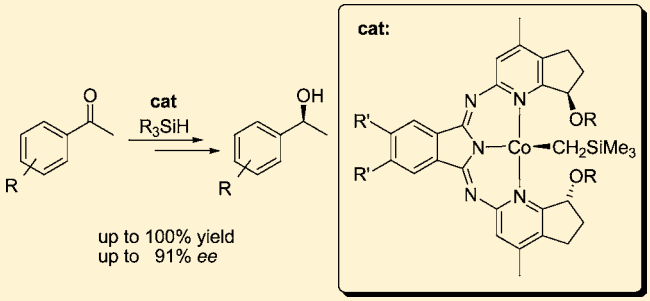
Supporting Information

ABSTRACT: The synthesis of a new family of chiral tridentate monoanionic NNN-pincer ligands based on the 1,3-bis(2-pyridylimino)isoindoline (BPI) framework is reported. Ligands with substituents of varying steric demand were prepared starting from achiral and low priced materials. A kinetic enzymatic resolution was used as a key step for the preparation of enantiomerically pure ligands. In this way, both enantiomers of a given ligand could be produced enantioselectively (>99.5% *ee*). The corresponding cobalt alkyl complexes were obtained using a pyridine alkyl cobalt precursor complex and were applied in asymmetric hydrosilylation of several prochiral alkylaryl ketones with high yields (up to 100%) and enantioselectivity (up to 91% *ee*) to give the chiral alcohols after hydrolysis.



INTRODUCTION

Asymmetric hydrosilylation is one possible method for the preparation of chiral alcohols which are important building blocks in the synthesis of pharmaceutical and agrochemical products as well as advanced materials.[1] Despite its disadvantages compared to direct hydrogenations[2] or transfer hydrogenations,[3] such as the need for a silane as reducing agent and the consecutive hydrolysis, hydrosilylation has emerged as a useful tool in organic synthesis. This is due to the mild reaction conditions, the development of environmentally friendly catalysts and reducing agents as well as a manifold of substrates which can be applied in this reaction.[4]

The asymmetric reduction of prochiral ketones with silanes was first investigated using precious metal catalysts, such as rhodium,[5] iridium,[6] and ruthenium[7] complexes with different N-, P-, or mixed N,P-ligand systems.[8] During the last few years an increasing demand for the substitution of those expensive and rare metals has arisen, and the reaction has been tested using more economical and environmentally benign first row transition metals as catalysts.[9] In this context, highly active and selective titanium and copper complexes as well as organocatalysts have been developed for the reduction of aldehydes and ketones.[8,10]

Moreover, an increasing interest in the use of iron has emerged and different catalytic systems especially concerning $Fe(OAc)_2$ in combination with different ligands and typically tertiary silanes such as $(EtO)_3SiH$, $(EtO)_2MeSiH$, or PMHS (polymethylhydrosiloxane) as reducing agents have been tested.[11−14] Additionally, iron dialkyl complexes have been employed in asymmetric hydrosilylation reactions by Chirik et al. in 2009.[15] Complexes with pyridine bis(oxazoline) (pybox) and bis(oxazoline) (BOX) ligands have been prepared and evaluated in the catalytic hydrosilylation of various ketones. Although displaying good catalytic activity at room temperature with $PhSiH_3$ as reducing agent they showed only low to modest enantioselectivity.

In comparison, Co catalyzed asymmetric hydrosilylations have not been investigated in much detail so far. In 1991 Brunner and Amberger reported the first stereoselective version with 56% *ee* for the reduction of acetophenone as benchmark substrate using 0.5 mol % of a cobalt complex with a chiral monooxazolinylpyridine ligand and Ph_2SiH_2 as reducing agent.[16] Higher enantioselectivity was achieved by Nishiyama et al. in 2010 when they investigated the reduction of various ketones with cobalt acetate and a bis(oxazolinylphenyl)amine ligand. With 5 mol % of the catalyst and $(EtO)_2MeSiH$ as reagent they were able to isolate the chiral alcohols with enantioselectivities of up to 96%.[17] Finally, in 2011 Chan et al. reported the asymmetric hydrosilylation using cobalt(II) acetate and dipyridylphosphine ligands in air. $PhSiH_3$ was employed as reducing agent and the reaction took place at elevated temperatures using 10 mol % catalyst. The chiral alcohols could be obtained in yields from 5 to 99% with up to 96% *ee*.[18]

During the past decade pincer ligands have been investigated thoroughly, especially with regard to their catalytic abilities.[19] 1,3-Bis(2-pyridylimino)isoindolines (BPI) belong to the class of tridentate monoanionic NNN-pincer ligands,[20] and chiral BPI-iron and -cobalt complexes with appropriately substituted ligand backbones proved to be efficient catalysts for asymmetric transformations.[14] The stereodirecting ligands used in these

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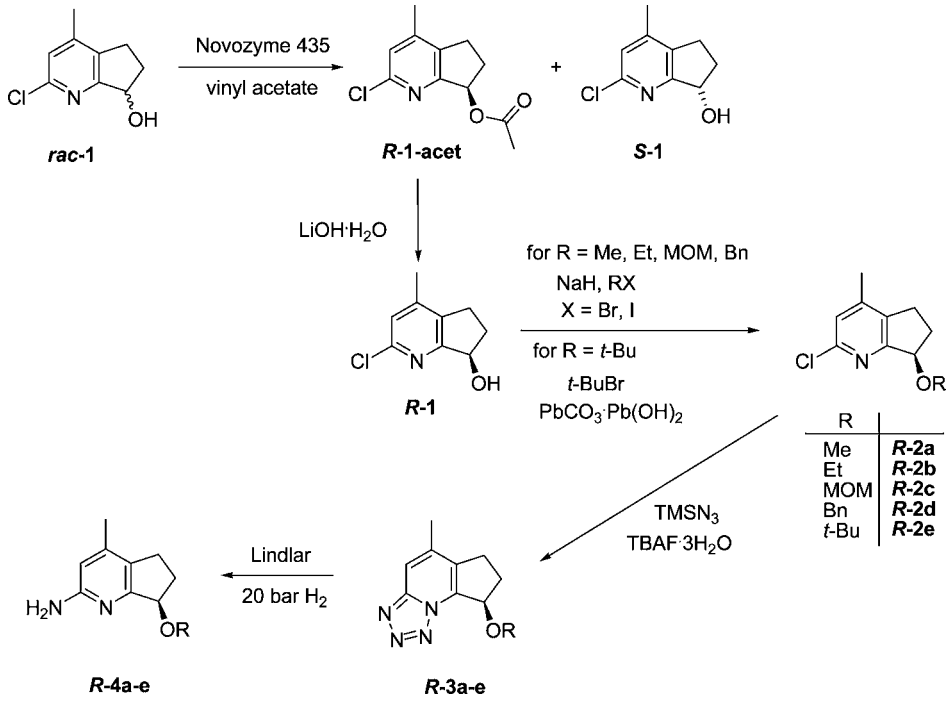
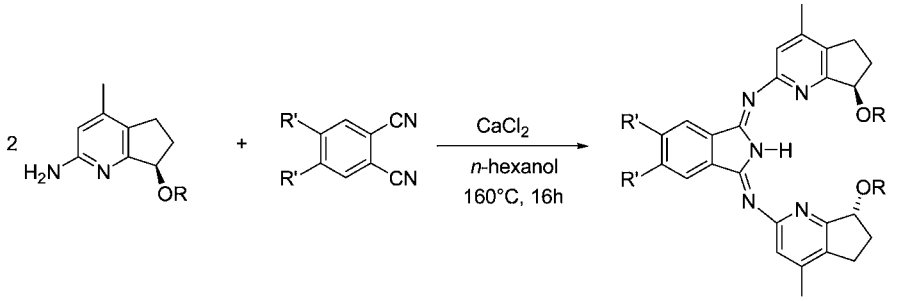
Scheme 1. Preparation of Chiral Pyridyl Amines *R*- and *S*-4a-e for the Synthesis of the New Family of Chiral BPI Ligands[a]



[a]For clarity only the (*R*) enantiomer is shown.

Scheme 2. The Protio-Ligands Were Prepared Using a Modular Synthesis via Condensation of the Chiral Amines with Various Phthalonitriles[a]



R	R'	
Me	H	*R,R*- and *S,S*-5
Me	Me	*R,R*- and *S,S*-6
Me	Hex	*R,R*-7
Me	Ph	*R,R*- and *S,S*-8
Et	H	*R,R*- and *S,S*-9
Et	Me	*R,R*- and *S,S*-10
MOM	H	*R,R*- and *S,S*-11
Bn	H	*R,R*- and *S,S*-12
Bn	Ph	*R,R*-13
t-Bu	H	*R,R*- and *S,S*-14

[a]Only preparation of the (*R,R*) enantiomer is shown.

cases were available by a synthesis starting from chiral natural products. Therefore only one enantiomer of the ligand was readily accessible. A more general approach for the synthesis of chiral BPI ligands in both enantiomeric forms involves their preparation employing achiral starting materials which are functionalized enantioselectively.

RESULTS AND DISCUSSION

Ligand Synthesis via Kinetic Enzymatic Resolution. The starting material of the ligand synthesis is the alcohol **1** (Scheme 1), which can be easily prepared in its racemic form ***rac*-1** on a multigram scale using a well-established protocol[21] and is also commercially available. Conversion of the racemic alcohol into its enantiomerically pure form was achieved by a kinetic enzymatic resolution. Novozyme 435 was applied for this synthesis which consists of *Candida antarctica* lipase B (CAL-B) immobilized on polyacrylamide and shows a very high and general specificity for the (*R*) enantiomer in the acylation of chiral secondary alcohols.[22] In this way, the (*S*) enantiomer ***S*-1** could be recovered unreacted from the reaction mixture, while

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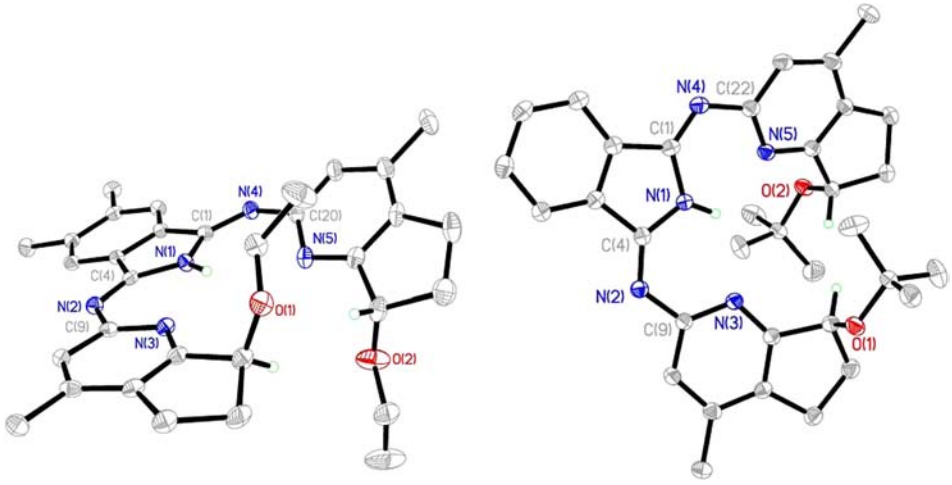
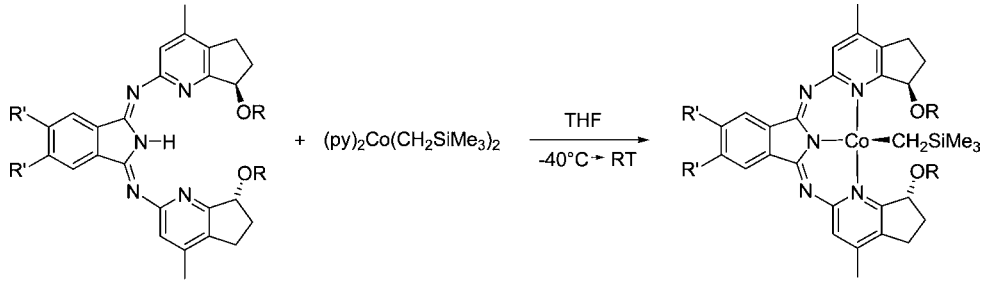


Figure 1. Molecular structures of the protio-ligands ***S,S*-10** (left, only one of the two independent molecules is shown) and ***S,S*-14** (right). Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for ***S,S*-10**: N(1)−C(1)/C(4) = 1.397(3)/1.391(3), N(2)/N(4)−C(4)/C(1) = 1.291(3)/1.282(3), N(2)/N(4)−C(9)/C(20) = 1.398(3)/1.404(3), C(4)/C(1)−N(2)/N(4)−C(9)/C(20) = 122.2(2)/123.5(2), N(2)/N(4)−C(4)/C(1)−N(1) = 139.5(2)/130.3(2), N(3)/N(5)−C(9)/C(20)−N(2)/N(4) = 121.1(2)/ 121.4(2); the geometry of the second molecule is very similar. Selected bond lengths (Å) and angles (°) for ***S,S*-14**: N(1)−C(4) = 1.387(1), N(2)−C(4) = 1.288(1), N(2)−C(9) = 1.403(1), N(2)−C(4)−N(1) = 130.7(1), N(3)−C(9)−N(2) = 121.9(1), C(4)−N(2)−C(9) = 122.2(1).

Scheme 3. Synthesis of the Alkyl Precursor Complex According to Budzelaar et al.[25]

$$(py)_4CoCl_2 + LiCH_2SiMe_3 \xrightarrow[\text{pentane, hexane}]{\text{-78°C} \rightarrow \text{rt}} (py)_2Co(CH_2SiMe_3)_2$$

Scheme 4. General Method for the Synthesis of Cobalt Alkyl Complexes 15−22 by Ligand Displacement[a]



R	R'	
Me	H	***S,S*-5**
Me	Me	***S,S*-6**
Et	H	***R,R*-9**
Et	Me	***S,S*-10**
MOM	H	***S,S*-11**
Bn	H	***S,S*-12**
Bn	Ph	***R,R*-13**
t-Bu	H	***S,S*-14**

R	R'	
Me	H	***S,S*-15**
Me	Me	***S,S*-16**
Et	H	***R,R*-17**
Et	Me	***S,S*-18**
MOM	H	***S,S*-19**
Bn	H	***S,S*-20**
Bn	Ph	***R,R*-21**
t-Bu	H	***S,S*-22**

[a]Only the (*R,R*) enantiomer is shown.

the (*R*) enantiomer was isolated as acetate ***R*-1-acet** which can be easily saponified to the corresponding alcohol ***R*-1**. The alcohols were obtained as colorless crystalline solids in 48% yield and >99.5% *ee*. Subsequently, they were transformed into various primary ethers ***R*-** and ***S*-2a-d** after deprotonation with sodium hydride and reaction with the corresponding alkyl halides. The *tert*-butyl ether derivatives ***R*-** and ***S*-2e** could not be prepared in a similar way but were obtained by reaction of *tert*-butyl bromide with the alcohol using basic lead carbonate as catalyst.[23] The final step of the ligand synthesis involves conversion to a chiral pyridine amine. A Buchwald-Hartwig amination only led to racemization at the stereogenic center probably due to deprotonation by the auxiliary base and reprotonation at the acidic, quasi-benzylic position. An alternative route involved the synthesis of the corresponding tetrazoles ***R*-** and ***S*-3a-e** (for a crystallographic characterization see Supporting Information), which were readily hydrogenated using Lindlar's catalyst to the enantiomerically pure amines ***R*-** and ***S*-4a-e**.

These amines were then reacted with different phthalonitriles according to the well-established procedure[20] to give the protio-ligands **5−14** as yellow to red solids in good to moderate yields (Scheme 2); these were characterized by NMR spectroscopy, mass spectrometry as well as elemental analysis.

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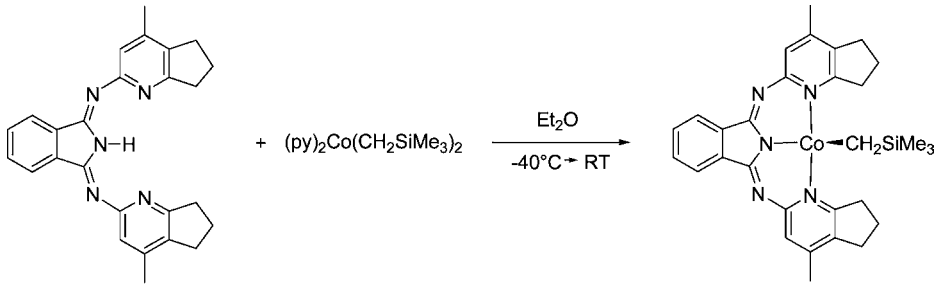
Scheme 5. Synthesis of Achiral Cobalt Alkyl Model Complex 23



The structural details of the ligand molecules in the solid state were established by X-ray diffraction of several derivatives. Invariably, the molecules display approximate or crystallographic C_2 molecular symmetry in the solid state just as in solution, with the rotational axis passing through the N(1)−H bond. Two typical examples are presented in Figure 1.

As expected, the isoindoline backbones of the tridentate ligand systems are almost planar while their pyridyl side groups are rotated out of the plane to avoid steric congestion caused by the substituents at the stereogenic center. The pyridine groups are linked to the central isoindoline unit via imine bonds as is evident from the alternating bond lengths between nitrogen and carbon atoms (typically N(2)−C(4) = 1.30 Å, N(2)−C(9) = 1.40 Å). The ligands show an effective preorganization with bifurcated hydrogen bonding between the central isoindoline proton and the pyridine nitrogen atoms. This preorganization is further enhanced by the delocalized π-system which favors a coplanar arrangement of the isoindoline and pyridyl rings. The sterically crowded nature of the metal binding site is the reason why no octahedral "homoleptic" metal complexes are formed with these BPI ligands.[24]

Preparation of Chiral Cobalt Alkyl Complexes. The chiral alkyl complexes of the general formula (BPI)Co-(CH_2SiMe_3) could not be obtained by reacting a corresponding chloro complex with an alkyllithium or Grignard reagent. Instead they had to be prepared using a route developed by Budzelaar et al. in 2010 by pyridine displacement from the metal dialkyl precursor $(py)_2Co(CH_2SiMe_3)_2$.[25]

In this way a series of paramagnetic monoalkyl Co^{II} complexes were synthesized via protolytic ligand exchange. The most stable cobalt complexes were observed in the case of the sterically less crowded ligands ***S,S*-5**, ***S,S*-6**, ***S,S*-12** and ***R,R*-13**. All alkyl complexes were obtained as dark red extremely air and moisture sensitive solids which are thermally labile and decompose at room temperature over periods of several days.

For all complexes paramagnetic ^1H as well as ^{13}C NMR spectra were recorded at variable temperatures. The complexes gave rise to well resolved paramagnetic NMR spectra in THF-d_8, due to rapid electron relaxation of the high-spin d^7 systems. At 295 K line widths in the ^1H NMR in the range of 30−160 Hz were observed in a signal range of −100 to 140 ppm. Signal patterns were consistent with the presence of the expected C_1 symmetric species. The use of cryogenically cooled ^{13}C NMR detection probe and optimized repetition times allowed recording of paramagnetic ^{13}C NMR spectra within a few minutes. At 295 K not all signals could be detected but those observed were recorded within the range of 0−900 ppm. The carbon resonances were partially assigned via the measurement of proton coupled spectra.

In the ^1H as well as ^{13}C NMR spectra all of these metal complexes display Curie behavior in solution over the studied temperature range of 280−340 K, i.e., the expected linear correlation between chemical shifts and inverse temperature (see Supporting Information). No dynamic behavior in the ^1H NMR spectra was observed.[24] Finally, measuring the paramagnetic susceptibility of the complexes in solution by the Evans' method[26] gave values between μ_{eff} = 3.9−4.5 μ_B, which are comparable to those of previously reported high-spin Co^{II} BPI complexes.[27]

Synthesis and Structural Characterization of an Achiral Co^{II} Model Complex. It proved difficult to obtain single crystals of the chiral Co^{II} complexes **15**−**22** and thus to establish the details of the molecular structures of the new alkyl complexes. To this end, a model compound for the chiral complexes, a cobalt complex bearing the achiral pentBPIH ligand, was prepared (see Supporting Information). It was obtained via the same synthetic route already used for the synthesis of the chiral derivatives and showed the same catalytic activity in hydrosilylations (in this case non-enantioselective). The compound was isolated as a dark green solid, highly sensitive toward oxygen and moisture. The different color in comparison to the chiral complexes may be explained by a weak coordination of the oxygen atoms of the ether moieties of the chiral ligands as was also observed in the case of the copper complexes of these chiral ligands.[28]

At 295 K, 11 signals with chemical shifts in the range of −80 to 45 ppm with a line width of 40−600 Hz were detected in the ^1H NMR. The resonances for the methylene protons at the alkyl ligand were not observed probably due to their close proximity to the paramagnetic metal center. The methylene protons at the cyclopentenyl rings are inequivalent as they point either toward the alkyl ligand or the free coordination site thus leading to two different signals. By measuring NMR spectra at variable temperatures no coalescence of the signals and thus no dynamic behavior was observable which is consistent with a C_s symmetric and thus nonplanar complex on the time scale of the NMR experiment in solution. In the ^{13}C NMR spectrum 14 resonances in the range of 0−850 ppm were assigned based on proton-coupled as well as two-dimensional $^1H-^{13}C$ coupled spectra.

Again, temperature-dependent measurements of all ^1H and ^{13}C shifts showed a linear dependency from the inverse temperature as expected for the paramagnetic complex. Paramagnetic susceptibility in solution was measured using the Evans method[26] giving a value of μ_{eff} = 4.16 μ_B which is somewhat higher than the spin only value (3.87 μ_B) and in accordance with previously reported values for Co^{II} (d^7) high spin complexes.[27]

In order to establish the structural details for this type of BPI cobalt complexes, which are the focus of this work, a single crystal X-ray structure analysis of complex **23** was carried out. Its

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molecular structure is depicted in Figure 2 along with selected bond lengths and angles.

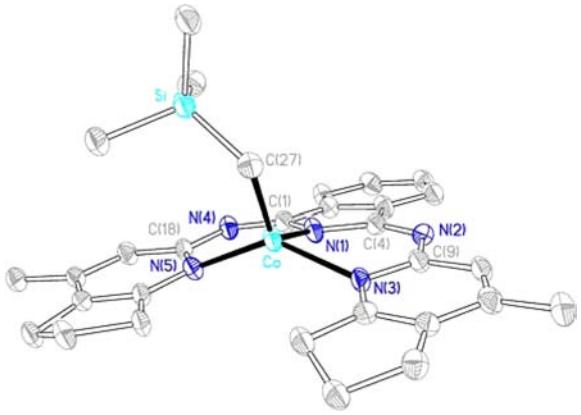


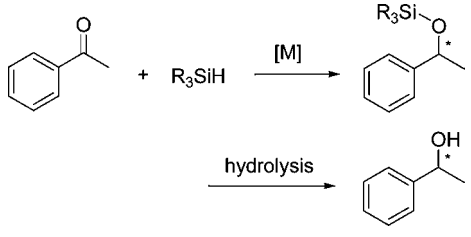
Figure 2. Molecular structure of the cobalt BPI complex **23**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co−N(1) = 1.949(5), Co−C(27) = 2.022(6), Co−N(3)/N(5) = 2.076(4)/2.078(4), Si−C(27) = 1.845(6), N(1)−C(1)/C(4) = 1.355(7)/1.376(7), N(2)/N(4)−C(4)/C(1) = 1.284(7)/1.304(7), N(2)/N(4)−C(9)/C(18) = 1.391(7)/1.404(7), N(1)−Co−C(27) = 128.1(2), N(1)−Co-N(3)/N(5) = 88.2(2)/87.6(2), C(27)−Co−N(3)/N(5) = 103.4(2)/111.4(2), N(3)−Co−N(5) = 138.6(2), N(1)−C(4)/C(1)−N(2)/N(4) = 128.8(5)/128.8(5), C(4)/C(1)−N(2)/N(4)−C(9)/C(18) = 124.5(5)/123.3(5).

The approximately C_s symmetric complex adopts a distorted tetrahedral coordination geometry around the cobalt center. While three coordination sites are occupied by the rigid BPI ligand the alkyl ligand is bound as the fourth ligand. The N(1)−Co−N(3) and N(1)−Co−N(5) angles (88.2(2)° and 87.6(2)°) are mostly influenced by the connectivity of the ligand backbone, whereas the N(3)−Co−N(5) angle (138.6(2)°), which deviates significantly from the ideal value expected for either tetrahedral or square planar coordination, reflects a distorted coordination geometry.

The Co−N bond lengths (Co−N(1) shorter than Co−N(3)/N(5)) are characteristic of monoanionic BPI ligands, and the Co−C(27) bond length is in accordance with previously published data for alkyl cobalt(II) species.[29]

Asymmetric Hydrosilylation of Ketones. The chiral cobalt alkyl complexes were first tested as catalysts for the enantioselective hydrosilylation of acetophenone as reference substrate, and diethoxymethylsilane as reducing agent according to the simple reduction protocol previously reported for iron catalysts[14] (Scheme 6). As frequently observed in hydrosilylation catalysis studies of ketones in our group an excess of the silane was required for high turnovers while no other additive was necessary. After basic hydrolysis and column chromatography the corresponding *sec*-phenethyl alcohol could be obtained in high yield (90−100%) as well as enantioselectivity (up to 91% *ee*).

Scheme 6. Catalytic Hydrosilylation of Aromatic Ketones



Optimization of the reaction conditions showed that high catalyst activities were observed using THF as solvent allowing for catalyst loadings of 2.5 mol %. At reaction temperatures of 15 °C reaction times of less than 8 h were needed for complete conversion. Other hydrosilanes such as the secondary diphenylsilane proved to be less reactive in this transformation.

Analysis of the *sec*-phenethyl alcohol produced from the reduction with the (*S*,*S*) enantiomer of the cobalt complex established preference for formation of the (*R*) enantiomer of the product (Table 2, entry 1). Likewise, performing the catalytic hydrosilylation with the (*R*,*R*) cobalt compound yielded the (*S*) enantiomer as major stereoisomer of the alcohol (Table 2, entry 3).

Variation of the substitution patterns in the stereodirecting ligand showed no dependence of the activity and selectivity of the reaction on the type of substitution of the ligand backbone. Complexes ***S*,*S*-15** and ***S*,*S*-16** gave similar results with regard to conversion and enantiomeric excess (Table 2, entry 1 and 2), as was the case for complex ***R*,*R*-21** with diphenyl substitution in the backbone (Table 2, entry 8). This implies that the stereodiscriminating step of the catalysis does not involve an approach of the substrate from the backside of the ligand.

The substitution pattern at the ether moiety of the ligand proved to be more significant. The chiral induction decreased for complexes ***R*,*R*-17** and ***S*,*S*-18** and dramatically for complexes ***S*,*S*-19** and ***S*,*S*-22** which displayed the lowest enantioselectivity (Table 2, entries 3, 4, 5, 6). Complexes ***S*,*S*-15**, ***S*,*S*-16**, ***S*,*S*-20** and ***R*,*R*-21** gave similar results yielding high enantiomeric excess between 85 and 90% *ee*. Longer alkyl chains (ethyl and methoxymethyl) and bulkier chiral moieties (*tert*-butyl) appeared to hinder the stereoselective reaction and favor catalyst decomposition pathways.

Other aromatic ketones were examined to establish the substrate scope under the optimized reaction conditions. Different arylmethylketones and naphthylketones were successfully employed as substrates for the catalytic reaction. Introduction of electron rich or electron poor groups in 3,4- or 5-position had no effect on the productivity and selectivity of the catalytic hydrosilylation. Unfortunately, substitution at the aromatic ring in 2-position to the keto group led to a significant decrease in activity and selectivity of the reaction, while 2,6-disubstituted acetophenones underwent no catalytic reduction at all.

■ CONCLUSIONS

A new family of chiral C_2 symmetric BPI ligands has been prepared, and the corresponding tetracoordinated cobalt alkyl complexes were synthesized establishing a reliable and convenient synthetic route. These complexes proved to be efficient and stereoselective catalysts for the asymmetric hydrosilylation of a variety of arylalkyl ketones with a tertiary silane. Whereas backbone substitution in the ligand had no significant effect on the catalytic performance, substitution at the chiral center in the "wingtips" of the pincers seemed to influence catalyst stability and performance. Further investigations aimed at elucidation of the reaction mechanism are currently under way.

■ EXPERIMENTAL SECTION

General Methods. All manipulations of air- and moisture-sensitive materials were carried out under an inert atmosphere of dry argon using

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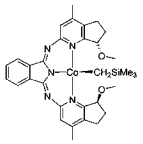
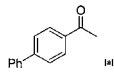
Table 1. Optimization of the Reaction Conditions for the Asymmetric Hydrosilylation of Acetophenone Using Co BPI Complex *S,S*-15[a,b]

#		t [h]	T [°C]	solvent	silane	conversion [%][a]	*ee* [%][b]
1	5.0 mol%	6	25	THF	$(EtO)_2MeSiH$	>99	85
2	2.5 mol%	6	30	THF	$(EtO)_2MeSiH$	>99	85
3	2.5 mol%	7	15	THF	$(EtO)_2MeSiH$	>99	90
4	2.5 mol%	8	0	THF	$(EtO)_2MeSiH$	>99	91
5	2.5 mol%	144	25	toluene	$(EtO)_2MeSiH$	>99	68
6	2.5 mol%	120	25	THF	Ph_2SiH_2	>99	60

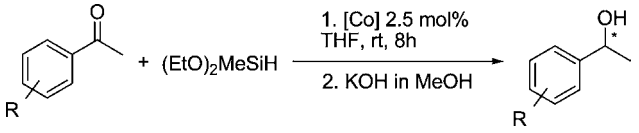
[a]Determined via NMR. [b]Determined via HPLC.

Table 2. Catalytic Ketone Hydrosilylation with (BPI)Co(CH_2SiMe_3) Compounds[a]

#	catalyst				
		isolated yield	enantiomeric excess	isolated yield	enantiomeric excess
1	***S,S*-15**	89 %	88 %*ee* (*R*)	100 %	87 %*ee*
2	***S,S*-16**	100 %	90 %*ee* (*R*)	100 %	88 %*ee*
3	***R,R*-17**	73 %	83 %*ee* (*S*)	100 %	87 %*ee*
4	***S,S*-18**	100 %	82 %*ee* (*R*)	98 %	81 %*ee*
5	***S,S*-19**	100 %	23 %*ee* (*R*)	100 %	21 %*ee*
6	***S,S*-22**	78 %	13 %*ee* (*R*)	90 %	23 %*ee*
7	***S,S*-20**	90 %	87 %*ee* (*R*)	100 %	85 %*ee*
8	***R,R*-21**	90 %	87 %*ee* (*S*)	100 %	86 %*ee*

[a]Enantiomeric excess determined by HPLC.

Scheme 7. Optimized Reaction Conditions for the Asymmetric Hydrosilylation



standard Schlenk techniques. All substrates were obtained commercially and used as received if not otherwise stated. Solvents were purified and dried by standard methods before use. The racemic alcohol was prepared according to a literature procedure.[21] The pyridine Co alkyl precursor was also prepared using the method described in the literature.[25] ^1H and ^{13}C spectra were recorded on Bruker Avance II 400 and Bruker Avance III 600 NMR spectrometers and were referenced using the residual protio solvent (^1H) or solvent (^{13}C) resonances. The paramagnetic ^{13}C NMR spectra were measured with a Bruker QNP Cryo Probe. Mass spectrometry and elemental analysis were obtained by the analytical service of the Heidelberg Chemistry Department. IR spectra were recorded on an Excalibur 3100 FT-IR spectrometer by Varian as potassium bromide pellets. UV−vis spectra were measured using a Varian Cary 5000 instrument. HPLC was performed on an Agilent 1200 series HPLC. The analyses were performed using Chiralcel AS-H, AD-H, OD-H or OJ-H columns.

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are listed in Tables 4−7. Single crystals of the protio-ligands were obtained by slow diffusion of pentane in concentrated solutions in dichloromethane. Complex **23** was crystallized from toluene. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, sealed tube, graphite monochromator) or an Agilent Technologies Supernova-E CCD diffractometer (Cu-K_α radiation, microfocus tube, multilayer mirror optics). Data were corrected for air and detector absorption, Lorentz and polarization effects;[30,31] absorption by the crystal was treated numerically (Gaussian grid)[31] (complex **23**) or with a semiempirical multiscan method (all others).[31−33] The structures were solved by the charge flip procedure[34] and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[35] Hydrogen atoms were generally placed at calculated positions and refined with a riding model. When justified by the quality of the data the positions of some hydrogen atoms (except those of the methyl groups) were taken from difference Fourier syntheses and refined.

During reduction of the data sets collected with Mo X-radiation from the compounds without heavy elements, Friedel opposites were merged and $\delta f''$ were set to zero. In addition, separate refinements of both enantiomorphs were carried out with complex atomic *f* and Friedel pairs unmerged. In all these cases, likelihood[36] and Parsons' quotient (based on $[I_+-I_-]/[I_++I_-]$) methods[37] indicated that the absolute structure had been correctly assigned (better, but not always highly significant indicators were calculated for the expected enantiomorph).

CCDC 901898−901907 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.

Synthesis of Chiral Alcohols *S*-1 and *R*-1-acet. The racemate of the alcohol (6.00 g, 32.67 mmol) was dissolved in vinyl acetate (60 mL)

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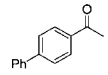
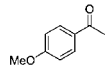
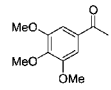
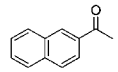
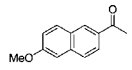
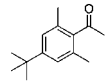
Table 3. Catalytic Ketone Hydrosilylation with (BPI)Co(CH_2SiMe_3) *S,S*-20[a]

#	substrate	isolated yield [%]	*ee* [%][a]
1		100	87
2		100	85
3		96	80
4		90	90
5		91	89
6		88	90
7		65	40
8		58	25
9		0	0

[a]Determined by HPLC.

and novozyme 435 (6.00 g) was added. The resulting suspension was vigourously stirred at r. t. for 4 h. Afterward, the enzyme was separated via filtration and washed with dichloromethane. The solvent was then removed under reduced pressure and the resulting mixture separated via column chromatography (SiO_2, pentane:ethyl acetate 1:1). The (*S*) alcohol ***S*-1** was obtained as a white crystalline solid (2.71 g, 45.2%) and the (*R*) acetate ***R*-1-acet** was isolated as yellow oil (3.63 g, 49.3%). The analytical data are in accordance to the literature data found for the racemic compound.[21]

General Method for the Etherification. To a suspension of sodium hydride (1.8 equiv) in THF a solution of the enantiomerically pure alcohol **1** (1.0 equiv) in THF was added at 0 °C. After stirring at 0 °C for 1 h the alkyl halide (2.0 equiv) was added and the resulting suspension was stirred for an additional hour at 0 °C. The reaction mixture was warmed to r. t. overnight. After careful addition of water to the mixture the product was extracted with diethyl ether, dried over magnesium sulfate and the solvent was removed. The crude product was purified via column chromatography on silica gel. As an example the analytical data for ***R*-** and ***S*-2a** is given here, whereas the analytical data for all other derivatives is available in the Supporting Information.

***R*- *and S*-2a.** 1.43 g (7.26 mmol = 94.8%). ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.04 (s, 1H, H^3), 4.69 (m, 1H, H^7), 3.52 (s, 3H, OCH_3), 2.95 (m, 1H, H^5), 2.71 (m, 1H, H^5), 2.37 (m, 1H, H^6), 2.26 (s, 3H, H^8), 2.14 (m, 1H, H^6). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ [ppm] = 162.48 (C^{7a}), 150.07 (C^2), 146.96 (C^4), 135.50 (C^{4a}), 123.98 (C^3), 83.17 (C^7), 57.15 (OCH_3), 29.87 (C^6), 26.03 (C^5), 18.55 (C^8). MS (EI$^+$) *m*/*z* (%) = 196.1 (4.2) $[M]^{+\bullet}$, 166.0 (100.0) $[M-OCH_3]^+$. HR-MS (HR-EI$^+$): calcd. for $C_9H_9NO^{35}Cl$ 166.0423, found 166.0422 [100.0]. Anal. Calcd. for $C_{10}H_{12}NOCl$: C 60.76, H 6.12, N 7.09; found C 60.78, H 6.17, N 7.00. IR $\tilde{\nu}$ 3067 (w), 2927 (m), 2852 (w), 2820 (w), 1720 (s), 1589 (m), 1440 (m), 1285 (w), 1202 (m), 1112 (s), 893 (m), 870 (m). HPLC Chiralcel AD-H, hexane:*i*-propanol 90:10, 0.5 mL/min, detection at 254 nm, $t_{(S)}$ = 9.5 min, $t_{(R)}$ = 11.0 min, >99.5% *ee*.

Table 4. Details of the Crystal Structure Determinations of *S*-3a, *R,R*-7, and *S,S*-8

	***S*-3a**	***R,R*-7**	***S,S*-8**
formula	$C_{10}H_{12}N_4O$	$C_{40}H_{53}N_5O_2$	$C_{40}H_{37}N_5O_2$
M_r	204.24	635.87	619.75
crystal system	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$	$P1$	$P2_1$
a /Å	6.799(4)	8.265(4)	15.171(7)
b /Å	8.888(4)	12.523(7)	7.052(3)
c /Å	15.767(8)	18.640(9)	16.168(7)
α /°	90	95.869(9)	90
β /°	90	99.529(8)	113.144(7)
γ /°	90	107.30(1)	90
V /Å^3	952.7(8)	1792.9(15)	1590.6(12)
Z	4	2	2
F_{000}	432	688	656
d_c /Mg·m^{-3}	1.424	1.178	1.294
X-radiation, λ /Å	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Mo-K_α, 0.71073
μ /mm^{-1}	0.098	0.073	0.081
max, min transmission factors	0.8623, 0.7671	0.8623, 0.7953	0.8623, 0.8106
data collect. temp /K	100(2)	100(2)	100(2)
θ range /°	2.6 to 32.2	2.2 to 32.3	2.4 to 32.3
index ranges *h,k,l*	−10 ... 10, −13 ... 13, −22 ... 22	−12 ... 12, −18 ... 18, −27 ... 27	−22 ... 20, −10 ... 10, −23 ... 24
reflections measured	20140	45236	40254
unique [R_{int}]	1862 [0.0334]	11787 [0.0409]	5802 [0.0329]
observed [$I \geq 2\sigma(I)$]	1735	10190	5463
parameters refined	158	865	507
GOF on F^2	1.099	1.027	1.058
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0384, 0.1045	0.0462, 0.1129	0.0422, 0.1091
R indices (all data) $R(F)$, $wR(F^2)$	0.0418, 0.1072	0.0569, 0.1208	0.0453, 0.1128
absolute structure parameter			
largest residual peaks/e·Å^{-3}	0.536, −0.212	0.479, −0.261	0.579, −0.261

Synthesis of *tert*-Butylether *R*- and *S*-2e. A mixture of the enantiomerically pure alcohol **1** (1.00 g, 5.45 mmol) and basic lead carbonate (2.11 g, 2.72 mmol) was cooled to 0 °C and *tert*-butylbromide (1.23 mL, 10.90 mmol) was added slowly. The mixture was then suspended in chloroform (10 mL) and stirred under reflux for 7 days. After cooling to r. t. the suspension was diluted with water and ethyl acetate and stirred for 30 min at r. t. Afterward the insoluble parts were separated via filtration and the aqueous layer extracted with ethyl acetate. The combined organic phases were dried over magnesium sulfate, the solvent removed and purified via column chromatography on silica gel (pentane:ethyl acetate 1:1) to give the product as a yellow oil 0.80 g, (3.35 mmol, 61.5%). ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 6.97 (s, 1H, H^3), 4.96 (m, 1H, H^7), 2.92 (m, 1H, H^5), 2.63 (m, 1H, H^5), 2.41 (m, 1H, H^6), 2.22 (s, 3H, H^8), 2.02 (m, 1H, H^6), 1.32 (s, 9H, $OC(CH_3)_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ [ppm] = 163.9 (C^{7a}), 150.4 (C^2), 146.3 (C^4), 134.8 (C^{4a}), 123.3 (C^3), 74.8 (C^7), 74.4 ($OC(CH_3)_3$), 33.2 (C^6), 28.8 ($OC(CH_3)_3$), 25.7 (C^5), 18.4 (C^8). MS (FAB$^+$) *m*/*z* (%) = 240.11 (51.1) [M + H]$^+$, 166.04 (100.0) [M-O*t*-Bu]$^+$. HR-MS (HR-FAB$^+$): calcd. for $C_{13}H_{19}NO^{37}Cl$ 242.1126, found: 242.1124 [17.7]; calcd. for $C_{13}H_{19}NO^{35}Cl$ 240.1155, found: 240.1139 [51.1]. Anal. Calcd. for $C_{13}H_{19}NOCl$: C 65.13; H 7.57; N 5.84; found C 64.75; H 7.55; N 5.67. IR $\tilde{\nu}$ 3065 (w), 2965 (m), 2927 (w), 2903 (w), 1653 (m), 1559 (m), 1262 (s), 1100 (s), 1050 (s), 1040 (s), 1019 (s),

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Table 5. Details of the Crystal Structure Determinations of *R,R*-9, *S,S*-10·CH_2Cl_2, and *S,S*-11

	R,R-9	*S,S*-10.CH_2Cl_2	*S,S*-11
formula	$C_{30}H_{33}N_5O_2$	$C_{33}H_{39}Cl_2N_5O_2$	$C_{30}H_{33}N_5O_4$
M_r	495.61	608.59	527.61
crystal system	monoclinic	triclinic	monoclinic
space group	*I*2	*P*1	*C*2
a /Å	13.362(6)	8.0452(2)	21.095(12)
b /Å	12.353(6)	13.3300(3)	12.889(6)
c /Å	15.330(8)	15.0284(3)	19.284(10)
α /°	90	89.484(2)	90
β /°	93.210(12)	74.921(2)	95.88(1)
γ /°	90	88.934(2)	90
V /Å^3	2526(2)	1555.91(6)	5216(5)
Z	4	2	8
F_{000}	1056	644	2240
d_c /Mg·m^{-3}	1.303	1.299	1.344
X-radiation, λ /Å	Mo-K_α, 0.71073	Cu-K_α, 1.54184	Mo-K_α, 0.71073
μ /mm^{-1}	0.084	2.178	0.091
max, min transmission factors	0.8623, 0.8037	1.00000, 0.88175	0.8623, 0.8113
data collect. temp /K	100(2)	120(1)	100(2)
θ range /°	2.1 to 32.2	4.5 to 71.9	1.9 to 32.2
index ranges *h,k,l*	−19 ... 19, −18 ... 18, −22 ... 22	−9 ... 9, −16 ... 16, −17 ... 18	−31 ... 31, −19 ... 19, −28 ... 28
reflections measured	31824	46907	65021
unique [R_{int}]	4422 [0.042]	10781 [0.0427]	9136 [0.0451]
observed [$I \geq 2\sigma(I)$]	3953	10752	7390
parameters refined	341	776	838
GOF on F^2	1.033	1.013	1.026
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0444, 0.1117	0.0475, 0.1198	0.0660, 0.1715
R indices (all data) $R(F)$, $wR(F^2)$	0.0518, 0.1183	0.0476, 0.1198	0.0838, 0.1899
absolute structure parameter		0.04(1)	
largest residual peaks/e·Å^{-3}	0.669, −0.290	0.543, −0.501	0.810, −0.305

Table 6. Details of the Crystal Structure Determinations of *R,R*-12, *S,S*-12, and *S,S*-14

	R,R-12	*S,S*-12	*S,S*-14
formula	$C_{40}H_{37}N_5O_2$	$C_{40}H_{37}N_5O_2$	$C_{34}H_{41}N_5O_2$
M_r	619.75	619.75	551.72
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$P2_1$	$P2_12_12_1$
a /Å	18.4159(2)	18.4175(1)	9.7536(1)
b /Å	14.0269(1)	14.0280(1)	17.8086(2)
c /Å	25.7679(2)	25.7702(2)	17.8545(2)
α /°	90	90	90
β /°	102.0747(9)	102.0858(6)	90
γ /°	90	90	90
V /Å^3	6509.1(1)	6510.41(7)	3101.28(5)
Z	8	8	4
F_{000}	2624	2624	1184
d_c /Mg·m^{-3}	1.265	1.265	1.182
X-radiation, λ /Å	Cu-K_α, 1.54184	Cu-K_α, 1.54184	Cu-K_α, 1.54184
μ /mm^{-1}	0.626	0.626	0.588
max, min transmission factors	1.00000, 0.79595	1.00000, 0.76431	1.00000, 0.75282
data collect. temp /K	120(1)	120(1)	115(1)
θ range /°	3.5 to 71.9	3.5 to 71.9	3.5 to 71.8
index ranges (indep. set) *h,k,l*	−22 ... 22, −17 ... 17, −31 ... 31	−22 ... 22, −17 ... 17, −31 ... 31	−11 ... 12, −21 ... 21, −21 ... 22
reflections measured	214499	183894	67023
unique [R_{int}]	25387 [0.0360]	25284 [0.0404]	6048 [0.0349]
observed [$I \geq 2\sigma(I)$]	24973	24575	5878
parameters refined	1754	1754	437
GOF on F^2	1.018	1.007	1.054
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0304, 0.0772	0.0346, 0.0766	0.0253, 0.0647
R indices (all data) $R(F)$, $wR(F^2)$	0.0309, 0.0778	0.0357, 0.0778	0.0262, 0.0652
absolute structure parameter	0.01(7)	0.04(7)	0.01(12)
largest residual peaks/e·Å^{-3}	0.181, −0.201	0.167, −0.173	0.118, −0.163

873 (m), 802 (s). HPLC Chiralcel AD-H, hexane:*i*-propanol 90:10, 0.5 mL/min, detection at 254 nm, $t_{(S)}$ = 7.3 min, $t_{(R)}$ = 7.8 min, >99.5% *ee*.

General Method for the Synthesis of Tetrazoles. The chloropyridine **2** (1.0 equiv) was added to tetrabutylammonium-fluoride-trihydrate (1.0 equiv) under ice cooling and trimethylsilyl azide (4.0 equiv) was carefully added dropwise. After the exothermic reaction was finished the mixture was stirred at 85 °C for 96 h. Then it was cooled to r.t. and water was carefully added. The reaction mixture was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over magnesium sulfate, and the solvent was removed under reduced pressure. The raw product was purified via column chromatography on silica gel. As an example the analytical data for ***R***- and ***S*-3a** is given here, whereas the analytical data for all other derivatives is available in the Supporting Information.

***R*- and *S*-3a.** 2.72 g (13.34 mmol = 60.6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.67 (s, 1H, H^3), 5.40 (m, 1H, H^7), 3.60 (s, 3H, OCH_3), 3.12 (m, 1H, H^5), 2.88 (m, 1H, H^5), 2.56 (m, 1H, H^6), 2.42 (s, 3H, H^8), 2.36 (m, 1H, H^6). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 149.66 (C^2), 141.63 (C^{7a}), 136.01 (C^4), 133.80 (C^{4a}), 113.48 (C^3), 81.10 (C^7), 58.43 (OCH_3), 30.21 (C^6), 27.81 (C^5), 19.41 (C^8). MS (EI$^+$) *m/z* (%) = 204.10 (28.5) $[M]^{+\cdot}$, 174.09 (47.2) $[M-OCH_3]^+$, 146.09 (100.0) $[M-OCH_3N_2]^+$. HR-MS (HR-EI$^+$): calcd. for $C_{10}H_{12}N_4O$ 204.1011, found 204.1020 [28.5]; calcd. for $C_9H_{10}N_4$ 174.0906, found 174.0884 [47.2]; calcd. for 146.0844, found 146.0847 [100.0]. Anal. Calcd. for $C_{10}H_{12}N_4O$: C 58.81, H 5.92, N 27.43; found C 58.79, H 5.84, N 27.13. IR $\tilde{\nu}$ 3059 (w), 2995 (m), 2955 (w), 2829 (w), 1644 (m), 1551 (m), 1492 (m), 1455 (m), 1438 (m), 1392 (m), 1374 (m), 1262 (m), 1188 (m), 1107 (s), 1090 (s), 1060 (s), 1040 (m), 1012 (m), 955 (m), 891 (w), 867 (m), 803 (m).

General Method for the Hydrogenation. The tetrazole **3** (1.0 equiv) was dissolved in ethanol and Lindlar catalyst (0.27 w/w) was added. The reaction mixture was stirred at r.t. at 20 bar H_2 pressure for 72 h. Afterward the catalyst was filtered off and the solvent was removed under reduced pressure. The raw product could be used for the ligand synthesis without further purification. As an example the analytical data for ***R***- and ***S*-4a** is given here, whereas the analytical data for all other derivatives are available in the Supporting Information.

***R*- and *S*-4a:** Quantitative. ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 6.25 (s, 1H, H^3), 4.65 (m, 1H, H^7), 4.32 (br s, 2H, NH_2), 3.50 (s, 3H, OCH_3), 2.84 (m, 1H, H^5), 2.61 (m, 1H, H^5), 2.35 (m, 1H, H^6), 2.15 (s, 3H, H^8), 2.04 (m, 1H, H^6). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 159.72 (C^{7a}), 158.45 (C^2), 145.68 (C^4), 126.48 (C^{4a}), 108.77 (C^3), 84.01 (C^7), 56.79 (OCH_3), 29.43 (C^6), 25.64 (C^5), 18.71 (C^8). MS (FAB$^+$) *m/z* (%) = 178.11 (17.0) $[M]^{+\bullet}$, 147.07 (100.0) $[M-OCH_3]^+$. HR-MS (HR-FAB$^+$): calcd. for $C_{10}H_{14}N_2O$ 178.1106, found 178.1094 [17.0]; calcd. for $C_9H_{11}N_2$ 147.0922; found 147.0908 [100.0]. HPLC Chiralcel AD-H, hexane/*i*-propanol 90:10, 0.5 mL/min, detection at 254 nm, $t_{(S)}$ = 22.5 min, $t_{(R)}$ = 23.8 min, >99.5% *ee*.

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Table 7. Details of the Crystal Structure Determinations of 23

	23
formula	$C_{30}H_{35}CoN_5Si$
M_r	552.65
crystal system	triclinic
space group	$P\bar{1}$
a /Å	10.5259(8)
b /Å	11.787(2)
c /Å	12.058(2)
α /°	87.71(1)
β /°	68.56(1)
γ /°	76.29(1)
V /Å^3	1350.9(3)
Z	2
F_{000}	582
d_c /Mg·m^{-3}	1.359
X-radiation, λ /Å	Cu-K$_\alpha$, 1.54184
μ /mm^{-1}	5.619
max, min transmission factors	0.924, 0.376
data collect. temp /K	110(1)
θ range /°	3.9 to 72.6
index ranges (indep. set) h,k,l	−12 ... 12, −14 ... 14, −12 ... 14
reflections measured	20629
unique [R_{int}]	5195 [0.0915]
observed [$I \geq 2\sigma(I)$]	3972
parameters refined	339
GOF on F^2	1.048
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0895, 0.2138
R indices (all data) $R(F)$, $wR(F^2)$	0.1126, 0.2301
largest residual peaks/e·Å^{-3}	2.190, −0.599

General Method for Synthesis of the Protio-Ligands. The amine **4** (2.3 equiv) and the appropriate phthalodinitrile (1.0 equiv) were suspended together with calcium chloride (0.2 equiv) in *n*-hexanol and stirred at 160 °C for 16 h. After cooling to r.t. the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane. The mixture was filtered through Celite and the raw product was purified using column chromatography on silica gel (dichloromethane/diethylether) after removal of the solvent. As an example the analytical data for ***R,R***- and ***S,S*-5** is given here, whereas the analytical data for all other derivatives are available in the Supporting Information.

***R,R*- and *S,S*-5.** 1.04 g (2.22 mmol = 58.8%). ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 12.49 (s, 1H, N*H*), 8.06 (m, 2H, H^{11}), 7.64 (m, 2H, H^{10}), 7.14 (s, 2H, H^3), 4.77 (m, 2H, H^7), 3.26 (s, 6H, OC*H*$_3$), 3.02 (m, 2H, H^5), 2.80 (m, 2H, H^5), 2.41 (m, 2H, H^6), 2.32 (s, 6H, H^6), 2.21 (m, 2H, H^8). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 160.41 (C^{7a}), 159.87 (C^2), 152.53 (C^9), 145.84 (C^4), 135.55 (C^{9a}), 133.30 (C^{4a}), 131.41 (C^{10}), 122.32 (C^{11}), 122.01 (C^3), 83.50 (C^7), 56.28 (OCH$_3$), 30.06 (C^6), 26.33 (C^5), 18.60 (C^8). MS (EI$^+$) m/z (%) = 467.24 (24.6) [M]$^{+\bullet}$, 436.21 (22.1) [M−OCH$_3$]$^+$, 422.20 (100.0) [M−OC$_2$H$_5$)]$^+$. HR-MS (HR-EI$^+$): calcd. for $C_{28}H_{29}N_5O_2$ 467.2321, found 467.2360 [24.6]; calcd. for $C_{27}H_{26}N_5O$ 436.2137, found 436.2099 [8.1]; calcd. for $C_{26}H_{24}N_5O$ 422.1981, found 422.1964 [100.0]. Anal. Calcd. for $C_{28}H_{29}N_5O_2$: C 71.93, H 6.25, N 14.98; found C 71.63, H 6.33, N 15.12. IR $\tilde{\nu}$ 3400 (br), 2960 (w), 2928 (w), 2855 (m), 2817 (m), 1735 (m), 1701 (m), 1684 (m), 1653 (s), 1636 (m), 1559 (s), 1540 (m), 1521 (m), 1506 (m), 1473 (w), 1457 (m), 1435 (w), 1085 (w). UV−vis (CH_2Cl_2, 50.58 μmol^{-1}) λ = 398 nm (shoulder), ε = 9478 M^{-1} cm^{-1}, λ = 379 nm, ε = 11388 M^{-1} cm^{-1}, λ = 356 nm, ε = 10933 M^{-1} cm^{-1}, λ = 339 nm, ε = 10933 M^{-1} cm^{-1}, λ = 307 nm (shoulder), ε = 11720 M^{-1}cm^{-1}, λ = 283 nm, ε = 13839 M^{-1} cm^{-1}. $[\alpha]_D$ = ± 684.9°.

General Method for the Preparation of the Cobalt(II) Alkyl Complexes. The protio-ligand (0.25 mmol) was dissolved in THF (5 mL) and slowly added dropwise to a solution of the alkyl precursor (0.27 mmol) in 4 mL of THF at −40 °C. After 20 min the solution was allowed to warm to r. t. over a period of 3 h and stirred an additional hour at r.t. Afterward, the solution was filtered and the solvent removed under reduced pressure. The crude product was purified by washing with either toluene or diethyl ether. As an example the analytical data for ***S,S*-15** is given here, whereas the analytical data for all other derivatives is available in the Supporting Information.

***S,S*-15.** 135.5 mg (0.22 mmol = 88.4%). ^{1}H NMR (600 MHz, toluene-d_8, paramagnetic) δ [ppm] = 139.37, 55.96, 47.31, 44.95, 42.27, 18.13, 14.78, 14.12, 12.22, 10.81, 9.07, 7.59, 5.27, −0.99, −5.02, −12.27, −14.43, −24.33, −41.86, −94.37. Not all resonances could be detected. ^{13}C NMR (150 MHz, toluene-d_8, paramagnetic) δ [ppm] = 814.0, 805.1, 597.0, 564.9, 514.4, 505.2, 497.3, 458.4, 418.6, 394.1, 341.6, 329.3, 231.5, 227.4, 211.4, 208.8, 197.6, 192.7, 183.7, 165.2, 146.4, 84.7, 68.1, 56.4, 51.9, 45.0, 31.6, 26.4, 0.5. Not all resonances could be detected. Anal. Calcd. for $C_{32}H_{39}N_5O_2CoSi$: C 62.73, H 6.42, N 11.43; found C 62.70, H 6.39, N 11.45.

General Catalytic Procedure for the Asymmetric Hydrosilylation. A catalyst stock solution (0.50 mL, 16.70 mmol^{-1}) was filled in a Schlenk tube in the glovebox and cooled to 15 °C using a cryostat. To start the catalytic reaction the silane (2.0 equiv, 0.67 mmol) and the ketone (1.0 equiv, 0.33 mmol) were added and the reaction was stirred for 8 h. Afterward 2 mL of a solution of potassium carbonate in methanol (1.0 mol^{-1}) were added and the mixture was stirred for 2 h at r.t. until the hydrolysis was completed. Then the mixture was extracted with diethyl ether, dried over magnesium sulfate, and evaporated. The raw product was purified via column chromatography on silica gel (pentane/diethyl ether).

Characterization of Hydrosilylation Products by HPLC. *1-Phenylethanol.* Chiralcel OD-H, hexane/*i*-propanol 98:2, 0.8 mL/min, 20 °C. Enantiomer retention times: 15.51 min (*R*), 19.33 min (*S*).

1-(4-Phenylphenyl)ethanol. Chiralcel AD-H, hexane/*i*-propanol 95:5, 0.8 mL/min, 20 °C. Enantiomer retention times: 15.99 min (*R*), 17.73 min (*S*).

1-(4-Fluorphenyl)ethanol. Chiralcel OD-H, hexane/*i*-propanol 98:2, 0.8 mL/min, 20 °C. Enantiomer retention times: 13.40 min (*S*), 14.30 min (*R*).

1-(4-Methoxyphenyl)ethanol. Chiralcel OD-H, hexane/*i*-propanol 98:2, 1 mL/min, 10 °C. Enantiomer retention times: 25.02 min, 30.00 min.

1-(3,4,5-Trimethoxyphenyl)ethanol. Chiralcel AS-H, hexane/*i*-propanol 95:5, 1 mL/min, 20 °C. Enantiomer retention times: 48.50 min, 65.90 min.

1-Naphthalen-2-ethanol. Chiralcel OJ-H, hexane/*i*-propanol 95:5, 0.8 mL/min, 20 °C. Enantiomer retention times: 37.08 min, 50.58 min.

6-Methoxynaphthalen-2-ethanol. Chiralcel OD-H, hexane/*i*-propanol 95:5, 0.8 mL/min, 20 °C. Enantiomer retention times: 20.59 min, 29.42 min.

1-Naphthalen-1-ethanol. Chiralcel OJ-H, hexane/*i*-propanol 95:5, 0.8 mL/min, 20 °C. Enantiomer retention times: 22.57 min, 40.38 min.

1-(2-Methylphenyl)ethanol. Chiralcel AD-H, hexane/*i*-propanol 98:2, 0.8 mL/min, 20 °C. Enantiomer retention times: 17.63 min, 20.30 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Analytical data for **2**−**22** and experimental procedures for the synthesis of complex **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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