CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: A Tethered Ru-S Complex with an Axial Chiral Thiolate Ligand for Cooperative Si-H Bond Activation: Application to Enantioselective Imine Reduction

Authors: Simon Wübbolt, Modhu Sudan Maji, Elisabeth Irran, and Martin Oestreich

To be cited as: *Chem. Eur. J.* 10.1002/chem.201700304

Link to VoR: http://dx.doi.org/10.1002/chem.201700304

Supported by
ACES

WILEY-VCH

10.1002/chem.201700304

WILEY-VCH

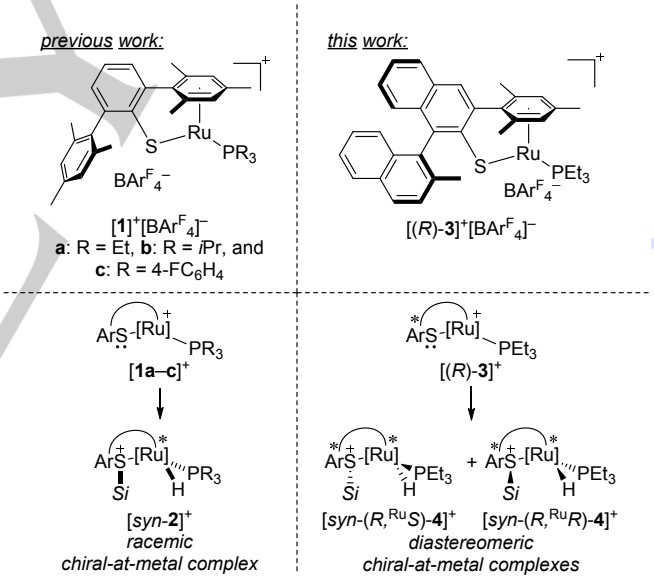
A Tethered Ru–S Complex with an Axial Chiral Thiolate Ligand for Cooperative Si–H Bond Activation: Application to Enantioselective Imine Reduction

Simon Wübbolt, Modhu Sudan Maji, Elisabeth Irran, and Martin Oestreich*[a]

Abstract: An axial chiral version of the 2,6-dimesitylphenyl group attached to sulfur is reported. Its multistep preparation starts from (*S*)-binol, and the thiol group is established by a racemization-free thermal Newman–Kwart rearrangement. The new chiral thiolate ligand decorated with one mesityl group is used in the synthesis of a tethered ruthenium chloride complex. Its spectroscopic characterization revealed solvent-dependent epimerization at the ruthenium center. The major diastereomer is crystallographically characterized. Chloride abstraction with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$) yields the corresponding coordinatively unsaturated ruthenium complex with the Ru–S bond exposed. Si–H bond activation at this Ru–S bond proceeds in *syn* fashion but with moderate facial selectivity (d.r. = 70:30), generating diastereomeric chiral-at-ruthenium hydrosilane adducts. Their application to catalytic imine hydrosilylation led to promising enantioinduction (40% *ee*), thereby providing proof of concept for asymmetric catalysis involving cooperative Si–H bond activation.

Introduction

Heterolytic splitting of Si–H bonds at the Ru–S bond of Ohki–Tatsumi complexes[1] $[\mathbf{1}]^+[BAr^F_4]^-$ has become a useful synthetic tool for the catalytic generation of silicon electrophiles. The mechanism of the Si–H bond activation step is fully understood and proceeds in *syn* fashion on either of the enantiotopic faces of the C_S-symmetric, trigonal planar ruthenium site ($[\mathbf{1}]^+ \rightarrow [\textit{syn}\text{-}\mathbf{2}]^+$, Scheme 1, left).[2] Chiral-at-metal[3] adduct $[\textit{syn}\text{-}\mathbf{2}]^+$ is formed reversibly in racemic form. While the stereogenicity at the metal is irrelevant in the various dehydrogenative coupling reactions promoted by $[\mathbf{1}]^+[BAr^F_4]^-$,[4] it will be vital in asymmetric reduction processes[2,5] where the hydride transfer from the asymmetrically substituted ruthenium center is the enantioselectivity-determining step.[8] We therefore set out to prepare an axial chiral congener of $[\mathbf{1}]^+[BAr^F_4]^-$, namely tethered complex $[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$ (Scheme 1, right). Chiral $[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$ was designed to promote enantioselective C=N hydrosilylation reactions[9] involving cooperative Si–H bond activation. It is interesting to note that such catalysts are unprecedented whereas tethered ruthenium complexes for Noyori-type enantioselective hydrogenation[10] were intensively investigated by Wills and co-workers.[11] Asymmetric catalysis with $[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$ is predictably difficult as the chiral backbone in $[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$ renders the *syn* Si–H bond activation[2] diastereoselective ($[(R)\text{-}\mathbf{3}]^+ \rightarrow [\textit{syn}\text{-}(R,^{Ru}S)\text{-}\mathbf{4}]^+$ and/or $[\textit{syn}\text{-}(R,^{Ru}R)\text{-}\mathbf{4}]^+$, Scheme 1, right), hence adding another stereoselectivity-controlling factor to the asymmetric C=N reduction with hydrosilanes. We describe here the synthesis of the chiral Ru–S complex $[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$, its behaveior in the Si–H bond activation, and application to the enantioselective hydrosilylation of imines.



Scheme 1. Tethered Ru–S complexes with an achiral ($[\mathbf{1a–c}]^+[BAr^F_4]^-$, left) or a chiral ($[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$, right) thiolate ligand applied to Si–H bond activation. Ar^F = 3,5-bis(trifluoromethyl)phenyl; *Si* = triorganosilyl.

Results and Discussion

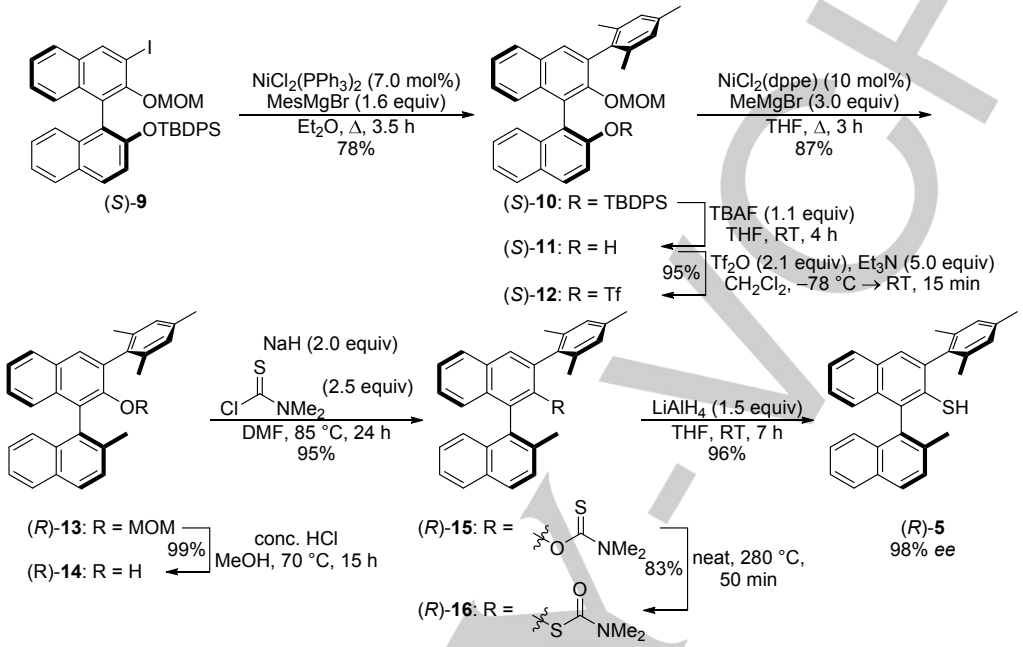
Thiol (*R*)-**5** was prepared from (*S*)-binol [(*S*)-**6**] in eleven steps (Scheme 2). Orthogonally protected (*S*)-**9** was accessed by following a reported three-step sequence by Maruoka and co-workers [(*S*)-**6**→(*S*)-**9**, see the Supporting Information].[12] The mesityl group that will later become the arene ligand was installed by Kumada coupling [(*S*)-**9**→(*S*)-**10**]. Fluoride-mediated cleavage of the silyl ether [(*S*)-**10**→(*S*)-**11**] and direct triflation of the free hydroxy group [(*S*)-**11**→(*S*)-**12**] set the stage for nickel-catalyzed methylation in this position [(*S*)-**12**→(*R*)-**13**]. Acid-

[a] S. Wübbolt, Dr. M. S. Maji, Dr. E. Irran, Prof. Dr. M. Oestreich
Institut für Chemie, Technische Universität Berlin
Straße des 17. Juni 115, 10623 Berlin (Germany)
E-mail: martin.oestreich@tu-berlin.de
Homepage: http://www.organometallics.tu-berlin.de

Supporting information for this article is given via a link at the end of the document.

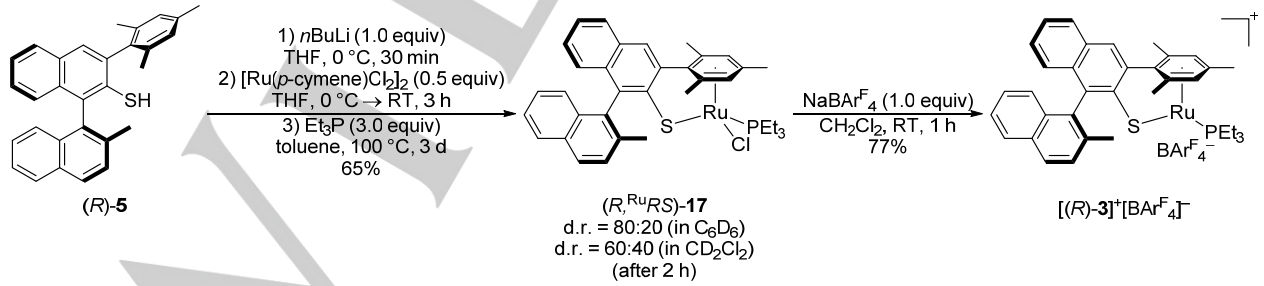
10.1002/chem.201700304

mediated cleavage of the MOM group [(*R*)-**13**→(*R*)-**14**] liberated the other phenol that was reacted with dimethylthiocarbamoyl chloride [(*R*)-**14**→(*R*)-**15**]. The thus-obtained *O*-thiocarbamate (*R*)-**15** was converted into the corresponding *S*-thiocarbamate (*R*)-**16** by thermal Newman–Kwart rearrangement [(*R*)-**15**→(*R*)-**16**]. Hydride reduction [(*R*)-**16**→(*R*)-**5**] afforded the desired thiol (*R*)-**5** in excellent 31% overall yield. The enantiomeric purity of 98% *ee* was determined by comparison with a racemic sample.



Scheme 2. Preparation of chiral thiolate ligand (*R*)-**5**.

We next applied the procedure, previously reported by Ohki and Tatsumi for complexes [**1**]$^+$[BAr$^F_4$]$^-$,[1] to thiol (*R*)-**5** to obtain the ruthenium chloride (*R,*^{Ru}*RS*)-**17** precursor. Thiol (*R*)-**5** was deprotonated with *n*-BuLi and then combined with [Ru(*p*-cymene)Cl$_2$]$_2$ in THF. After solvent change to toluene and filtration, Et$_3$P was added to furnish (*R,*^{Ru}*RS*)-**17** [(*R*)-**5**→(*R,*^{Ru}*RS*)-**17**]. As expected, the ^{1}H NMR spectroscopic analysis of this compound showed the formation of two diastereomers whose ratio was found to be dependent on the solvent. Measurements in C_6D_6 and CD_2Cl_2 led to diastereomeric ratios of 80:20 and 60:40, respectively (reached after 2 h in the indicated solvent). The major diastereomer in C_6D_6 was (*R,*^{Ru}*S*)-**17** as verified by 2D-NOESY experiments. This diastereomer also gave suitable single crystals for X-ray diffraction, allowing us to secure the molecular structure of (*R,*^{Ru}*S*)-**17** (Figure 1). Chloride abstraction with NaBAr$^F_4$ then afforded the coordinatively unsaturated 16-electron complex [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$ {(*R,*^{Ru}*RS*)-**17**→[(*R*)-**3**]$^+$[BAr$^F_4$]$^-$}.



Scheme 3. Preparation of the chiral, coordinatively unsaturated Ru–S complex [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$.

10.1002/chem.201700304

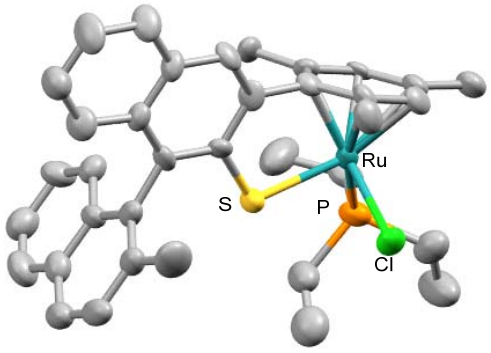
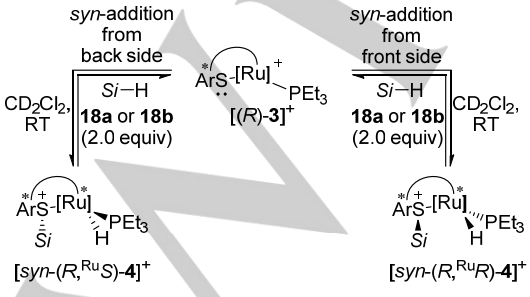


Figure 1. Molecular structure of ($R,^{Ru}S$)-**17**. Thermal ellipsoids are shown at a 50% possibility level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru–S, 2.382(2), Ru–Cl, 2.410(2), Ru–P, 2.355(2). For comparison, the distances of the chloride precursor of [**1a**]$^+$ are as follows (Å): Ru–S, 2.388(2), Ru–Cl, 2.489(2), Ru–P, 2.329(2).[1]

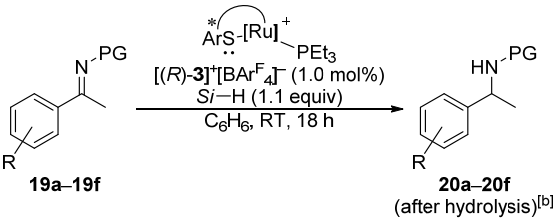
The Si–H bond activation by [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$ was analyzed by ^{1}H NMR spectroscopy to learn about the diastereoselectivity of this *syn* addition.[2] For this, [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$ was mixed with excess of Me_2PhSiH (**18a**) as well as $MePh_2SiH$ (**18b**) at room temperature {[(*R*)-**3**]$^+$→[*syn*-(*R*,^{Ru}*S*)-**4**]$^+$ and [*syn*-(*R*,^{Ru}*R*)-**4**]$^+$, Scheme 4}. The resonance signals of the hydrosilane adducts appeared to be too broad at 300 K but better resolution was observed at 250 K. Adducts [*syn*-(*R*,^{Ru}*S*)-**4**]$^+$ and [*syn*-(*R*,^{Ru}*R*)-**4**]$^+$ formed with diastereomeric ratios of 70:30 for both **18a** and **18b**. This shows that facial selectivity is indeed enforced by the chiral thiolate ligand but ratios are moderate. However, attempts to assign the relative configuration of the major diastereomer were unsuccessful. ^{29}Si NMR resonances of the adducts were in the expected range: δ 29.2 ppm (major) and δ 25.9 ppm (minor) for [*syn*-(*R*,^{Ru}*S*)-**4a**]$^+$/[*syn*-(*R*,^{Ru}*R*)-**4a**]$^+$ and δ 18.7 ppm (major) and δ 10.8 ppm (minor) for [*syn*-(*R*,^{Ru}*S*)-**4b**]$^+$/[*syn*-(*R*,^{Ru}*R*)-**4b**]$^+$. For hydrosilane adducts [*syn*-(*R*,^{Ru}*S*)-**4a**$^+$]/[*syn*-(*R*,^{Ru}*R*)-**4a**]$^+$, the ^{31}P NMR resonances were shifted downfield to δ 40.7 ppm (major) and δ 41.5 ppm (minor) relative to [(*R*)-**3**]$^+$ (δ 23.0 ppm); [*syn*-(*R*,^{Ru}*S*)-**4b**]$^+$/[*syn*-(*R*,^{Ru}*R*)-**4b**]$^+$ showed a single resonance at δ 40.5 ppm. As in previously reported similar experiments, the reaction also yielded the corresponding disiloxanes and Et_3POSi^+ adducts as byproducts.[2]



Scheme 4. ^{1}H NMR spectroscopic analysis of the diastereoselective Si–H bond-activation step.[b,c] [a] Diastereomeric ratios were determined by integration of the ^{1}H NMR resonances of the protons bound to the tethered aryl group. [b] Reactions were performed in sealed NMR tubes on a 10 µmol scale. [c] Full assignment of all resonance signals was difficult due signal overlapping and byproduct formation (selected spectra are given in the Supporting Information).

We tested the new catalyst [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$ in the asymmetric hydrosilylation of N-aryl-substituted, acetophenone-derived imines **19a**–**19f** (Table 1, entries 1–6). All reactions were performed at room temperature overnight, routinely employing Me_2PhSiH (**18a**) as the hydride source. Parent **19a** was converted into amine **20a** in quantitative yield with 41% *ee* (entry 1). This moderate enantiomeric excess did not improve with $MePh_2SiH$ (**18b**), essentially affording the amine with the same level of enantioinduction (entry 2). As before in the reversible hydrosilane adduct formation with [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$ (see Scheme 4), the influence of the substitution pattern at the silicon atom had hardly any influence on the stereochemical outcome. An increase of the steric bulk of the aryl group at the nitrogen atom (phenyl versus xylyl) resulted in lower enantioinduction (**19b**→**20b**, entry 3). Electronic modification of the aryl group with either an OMe (as in **19c**) or a CF_3 group (as in **19d**) shut down the reaction (entries 4 and 5). Conversely, a bromine substituent in the *ortho* position of the aryl group slowed down the reaction without affecting the enantiomeric excess (**19e**→**20e**, entry 6). Replacing the phenyl by the benzyl protection group led to lower yield and poor enantiomeric excess (**19f**→**20f**, entry 7).

Table 1. Asymmetric hydrosilylation of imines catalyzed by [(*R*)-**3**]$^+$[BAr$^F_4$]$^-$ [a]



Entry	Imine	R	PG	Hydrosilane	Yield [%][c]	*ee* [%][d]
1	**19a**	H	Ph	**18a**	99	41
2	**19a**	H	Ph	**18b**	95	40
3	**19b**	H	3,5-Xylyl	**18a**	99	30
4	**19c**	H	4-Anisyl	**18a**	—[e]	—
5	**19d**	H	4-$CF_3C_6H_4$	**18a**	—[f]	—
6	**19e**	2-Br	Ph	**18a**	70	48

7	**19f**	H	Bn	**18a**	56	17

[a] Reactions were performed on a 0.1 mmol scale. [b] Hydrolysis of the N-silylated amine during flash chromatography on silica gel, affording the free amines. [c] Determined after purification by flash chromatography on silica gel. [d] Determined by HPLC analysis using chiral stationary phases. [e] Inseparable mixture. [f] N-silylated enamine as major component.

Conclusions

We disclosed here the preparation, characterization, and application of an Ohki–Tatsumi complex[1] with axial chirality in the tethered thiolate backbone. For this, we elaborated, starting from (*S*)-binol, an eleven-step synthesis of the corresponding mesityl-substituted thiol that essentially is an axial chiral version of the previously used terphenyl-type thiol. A thermal Newman–Kwart rearrangement was employed to install the thiol group, and no racemization was seen in that high-temperature step (280 °C) as verified by comparison with an independently prepared racemic sample. The tethered ruthenium chloride complex made from this ligand is chiral at the ruthenium center and showed solvent-dependent epimerization at the ruthenium center. The molecular structure of the major diastereomer was confirmed by X-ray diffraction. This catalyst precursor was transformed into the active catalyst by chloride abstraction with $NaBAr^F_4$. The resulting coordinatively unsaturated ruthenium complex with its Ru–S bond engages in reversible heterolytic splitting of the Si–H bond of moderately hindered hydrosilanes. The addition of the Si–H bond across the Ru–S bond proceeds in *syn* fashion[2] but the facial selectivity is rather low (d.r. = 70:30). The thus-generated diastereomeric chiral-at-ruthenium hydrosilane adducts were applied to catalytic imine hydrosilylation but enantioinduction (40% *ee*) was at best promising. One challenge could be that there is no bonding interaction between the neutral ruthenium hydride and the silyliminium ion in the enantioselectivity-determining hydride transfer.[7] This work is nevertheless proof of concept for asymmetric catalysis involving cooperative Si–H bond activation.

Experimental Section

General Remarks.

All reactions were performed in flame-dried glassware using an *MBraun* glove box or conventional Schlenk techniques under a static pressure of argon or nitrogen. Liquids and solutions were transferred with syringes. Solvents (THF, toluene, C_6H_6, Et_2O, DMF, and CH_2Cl_2) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (*tert*-butyl methyl ether, CH_2Cl_2, cyclohexane, and ethyl acetate) were distilled prior to use. C_6D_6, CD_2Cl_2, and $CDCl_3$ (purchased from *Eurisotop*) were degassed by three freeze–pump–thaw cycles and dried over 4 Å molecular sieves. Imines **19a**–**19f** were synthesized according to reported procedures.[13] Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel LC60A (40–63 µm) by *Grace* using the indicated solvents. ^{1}H, ^{13}C, ^{11}B, ^{31}P, and ^{29}Si NMR spectra were recorded in $CDCl_3$, C_6D_6, or CD_2Cl_2 on *Bruker* AV700, *Bruker* AV500 or *Bruker* AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ 77.16 ppm for ^{13}C NMR, C_6D_5H: δ 7.16 ppm for ^{1}H NMR and C_6D_6: δ 128.06 ppm for ^{13}C NMR, $CDHCl_2$: δ = 5.32 ppm for ^{1}H NMR and CD_2Cl_2: δ = 53.84 ppm for ^{13}C NMR).[14] Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. ^{1}H,^{29}Si HMQC NMR spectra were measured with an optimized coupling constant of 7.0 Hz for the $^3J_{H,Si}$ coupling. The peak intensities in the ^{1}H,^{29}Si HMQC NMR spectra cannot be correlated to the amount of compound. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FTIR spectrophotometer equipped with an ATR unit and are reported as wavenumbers [cm^{-1}] (w = weak, m = medium, s = strong). Melting points (m.p.) were determined with a *Stuart Scientific* SMP20 melting point apparatus and are not corrected. Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) analysis on an *Agilent Technologies* 1200 Infinity instrument with a chiral stationary phase using a *Daicel Chiralcel* OD-H or OJ-H column (*n*-heptane/*i*-PrOH mixtures as solvents). Optical rotations were measured on a Schmidt & Haensch Polatronic H532 polarimeter with $[\alpha]_\lambda$ values reported in 10^{-1} (° cm^2 g^{-1}); concentration *c* is in g/100 mL and λ = 589 nm. Mass spectrometry (MS) was obtained from the Analytical Facility of the Institut für Chemie, Technische Universität Berlin.

General Procedure for Enantioselective Reduction of Imines

In a glove box, a flame-dried GLC vial equipped with a magnetic stir bar was charged with $[(R)\text{-}\mathbf{3}]^+[BAr^F_4]^-$ (1.00 mol%) and the indicated imine (1.00 equiv). C_6H_6 (0.10 mL) was added, and the vial was closed with a rubber septum cap. Either Me_2PhSiH (**18a**) or $MePh_2SiH$ (**18b**) (1.10 equiv) was added dropwise through the cap, and the resulting reaction mixture was maintained at room temperature for the indicated time. The vial was removed from the glove box and the reaction was quenched by the addition of a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (0.5 mL). The resulting solution was filtered through a pad of Celite® coated by a small layer of silica gel with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (3–4 mL). Solvents are removed under reduced pressure, and the residue is purified by flash column chromatography on silica gel using the indicated cyclohexane/ethyl acetate mixtures. The procedure affords the amines as colorless to yellow oils.

(S)-tert-Butyl((3'-(2,4,6-trimethylphenyl)-2'-(methoxymethoxy)-[1,1'-binaphthalen]-2-yl)oxy)diphenylsilane (10)

Aryl iodide (*S*)-**9** (7.65 g, 11.0 mmol, 1.00 equiv) and $NiCl_2(PPh_3)_2$ (544 mg, 0.770 mmol, 0.07 equiv) were dissolved in Et_2O (70 mL). Freshly prepared 2,4,6-trimethylphenylmagnesium bromide (1.00M in Et_2O, 17.6 mL, 17.6 mmol, 1.60 equiv) was added dropwise, and the resulting solution was stirred for 10 min at room temperature followed by heating at reflux for 3.5 h. As TLC analysis indicated complete consumption of the starting material, the reaction mixture was allowed to cool to room temperature and was quenched by addition of saturated aqueous NH_4Cl solution (30 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10:1 to 5:1) afforded (*S*)-**10** (5.9 g, 78%) as a gummy solid. m.p.: 98 °C (*tert*-butyl methyl ether); R_f = 0.62

(cyclohexane/*tert*-butyl methyl ether 5:1); IR (ATR): nu(tilde) = 3526 (w), 3050 (w), 2928 (w), 2855 (w), 1590 (m), 1427 (m), 1242 (m), 997 (s), 810 (s) cm^{-1}; HRMS (APCI) calculated for $C_{46}H_{43}O_2Si$ $[M–OMe]^+$: 665.3032; found: 665.3008; ^1H NMR (500 MHz, C_6D_6): δ 0.66 (s, 9H), 2.24 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 2.38 (s, 3H), 4.48 (d, J = 5.7 Hz, 1H), 4.78 (d, J = 5.7 Hz, 1H), 6.95 (d, J = 16.8 Hz, 2H), 7.10–7.13 (m, 3H), 7.17–7.23 (m, 8H), 7.29 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.64 (s, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.81–7.83 (m, 2H), 7.88–7.86 ppm (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 19.2 (s), 21.0 (s), 21.2 (s), 21.5 (s), 26.3 (s, 3C), 55.5 (s), 98.7 (s), 120.5 (s), 122.2 (s), 124.1 (s), 125.3 (s), 126.1 (s), 126.3 (s), 126.7 (s), 126.8 (s), 127.3 (s), 128.2 (s, 2C), 128.2 (s, 3C), 128.3 (s), 128.4 (s), 128.6 (s), 129.3 (s), 129.7 (s), 130.3 (s), 130.3 (s), 130.6 (s), 131.8 (s), 133.0 (s), 133.4 (s), 134.3 (s), 135.0 (s), 135.6 (s), 136.0 (s, 2C), 136.0 (s, 2C), 136.4 (s), 136.8 (s), 136.8 (s), 137.4 (s), 151.3 (s), 151.7 (s) ppm.

(S)-3'-(2,4,6-Trimethylphenyl)-2'-(methoxymethoxy)-[1,1'-binaphthalen]-2-ol (11)

To a stirred solution of (*S*)-**10** (5.8 g, 8.4 mmol, 1.0 equiv) and THF (50 mL), TBAF (2.9 g, 9.3 mmol, 1.1 equiv) was added. The resulting mixture was stirred at room temperature for 4 h and quenched by the addition of H_2O (50 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The title compound (*S*)-**11** was isolated along with TBDPSOH and used without further purification.

(S)-3'-(2,4,6-Trimethylphenyl)-2'-(methoxymethoxy)-[1,1'-binaphthalen]-2-yl Trifluoromethanesulfonate (12)

To a solution of (*S*)-**11** (65 wt%, 5.85 g, 8.43 mmol, 1.00 equiv) in CH_2Cl_2 (60 mL) cooled to –78 °C, Et_3N (6.0 mL, 42 mmol, 5.0 equiv) and subsequently trifluoromethanesulfonic anhydride (3.0 mL, 18 mmol, 2.1 equiv) were added. The cooling bath was removed after 10 min, and the mixture was allowed to warm within 15 min. As TLC analysis indicated complete consumption of the starting material, the reaction was quenched with H_2O (50 mL). After extraction of the aqueous phase, the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (8:1 to 5:1) as eluent afforded (*S*)-**12** (4.7 g, 95% over two steps) as a gummy solid. m.p.: 84 °C (*tert*-butyl methyl ether); R_f = 0.5 (cyclohexane/*tert*-butyl methyl ether 10:1); IR (ATR): nu(tilde) = 3518 (w), 2920 (w), 1592 (w), 1495 (w), 1418 (m), 1205 (s), 1137 (m), 1076 (m), 989 (m), 939 (s), 831 (s), 748 (m), 675 (m) cm^{-1}; HRMS (EI) calculated for $C_{31}H_{24}F_3O_4S$ $[M–OCH_3]^+$: 549.1347; found: 549.1345; $[\alpha]_D^{RT}$: +38.8 (*c* 0.70, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 2.17 (s, 3H), 2.18 (s, 3H), 2.19 (s, 3H), 2.34 (s, 3H), 4.20 (s, 2H), 6.79 (d, J = 5.1 Hz, 2H), 7.15 (d, J = 8.5 Hz, 1H), 7.29 (m_c, 1H), 7.40–7.46 (m, 3H), 7.54–7.57 (m, 1H), 7.61 (d, J = 9.1 Hz, 1H), 7.80 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 8.05 ppm (d, J = 9.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 20.5 (s), 21.13 (s), 21.24 (s), 55.7 (s), 98.1 (s), 118.4 (q, $^1J_{C,F}$ = 320.1 Hz), 119.6 (s), 122.8 (s), 125.4 (s), 126.1 (s), 126.5 (s), 127.1 (s), 127.4 (s), 127.5 (s), 127.7 (s), 128.0 (s), 128.2 (s), 128.3 (s), 128.4 (s), 130.5 (s), 131.0 (s), 132.4 (s), 132.5 (s), 133.1 (s), 134.1 (s), 134.4 (s), 135.1 (s), 136.4 (s), 137.3 (s), 137.8 (s), 145.9 (s), 151.8 (s) ppm.

(R)-3-(2,4,6-Trimethylphenyl)-2-(methoxymethoxy)-2'-methyl-1,1'-binaphthalene (13)

(*S*)-**12** (2.32 g, 4.00 mmol, 1.00 equiv) and $NiCl_2$(dppe) (0.21 g, 0.40 mmol, 0.10 equiv) were dissolved in THF (32 mL). Methylmagnesium bromide (3.0M in Et_2O, 4.0 mL, 12 mmol, 3.0 equiv) was added dropwise, and the resulting solution was stirred for 10 min at room temperature followed by heating at reflux for 3 h. As TLC analysis indicated complete consumption of the starting material, the reaction mixture was allowed to cool to room temperature and was quenched by addition of saturated aqueous NH_4Cl solution (20 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 40 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (50:1 to 25:1) afforded (*R*)-**13** (1.55 g, 87%) as a gummy solid. m.p.: 72 °C (*tert*-butyl methyl ether); R_f = 0.45 (cyclohexane/*tert*-butyl methyl ether 50:1); IR (ATR): nu(tilde) = 3522 (w), 3047 (w), 2915 (w), 2243 (w), 2108 (w), 2083 (w), 1907 (w), 1610 (w), 1434 (m), 1376 (w), 1151 (m), 987 (s), 905 (m), 810 (m), 729 (s) cm^{-1}; HRMS (EI) calculated for $C_{31}H_{27}O$ $[M–OCH_3]^+$: 415.2062; found: 415.2052; $[\alpha]_D^{RT}$: –45.8 (*c* 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 2.22 (s, 6H), 2.25 (s, 3H), 2.34 (s, 3H), 4.16 (d, J = 5.6 Hz, 1H), 4.23 (d, J = 5.6 Hz, 1H), 6.97 (s, 2H), 7.12 (d, J = 8.4 Hz, 1H), 7.22–7.28 (m, 4H), 7.38–7.44 (m, 2H) 7.74 (s, 1H), 7.86–7.89 ppm (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 20.7 (s), 20.9 (s), 21.1 (s), 21.2 (s), 55.7 (s), 97.9 (s), 124.9 (s), 125.2 (s), 125.9 (s), 126.2 (s), 126.3 (s, 2C), 127.8 (s), 128.0 (s), 128.0 (s), 128.2 (s), 128.3 (s), 128.8 (s), 129.0 (s), 130.7 (s), 131.2 (s), 132.2 (s), 132.6 (s), 133.2 (s), 133.7 (s), 134.9 (s), 135.6 (s), 135.6 (s), 136.8 (s), 137.0 (s), 137.0 (s), 151.1 (s) ppm.

(R)-3-(2,4,6-Trimethylphenyl)-2'-methyl-[1,1'-binaphthalen]-2-ol (14)

(*R*)-**13** (3.4 g, 7.6 mmol, 1.0 equiv) was dissolved in a mixture of $CHCl_3$ (45 mL) and methanol (30 mL). Concentrated aqueous HCl solution (8 mL) was added, and the resulting reaction mixture heated at 70 °C for 15 h. After the mixture was allowed to cool to room temperature, the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (40 mL), H_2O (40 mL) was added, the layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by filtration over silica gel using cyclohexane/*tert*-butyl methyl ether (25:1) afforded (*R*)-**14** (3.05 g, 99%) as a white solid. m.p.: 108 °C (cyclohexane); R_f = 0.58 (cyclohexane/*tert*-butyl methyl ether 5:1); IR (ATR): nu(tilde) = 3471 (m), 3048 (w), 2914 (m), 2854 (w), 1614 (w), 1498 (m), 1425 (m), 1376 (m), 1237 (m), 1193 (m), 1140 (m), 1026 (m), 940 (m), 849 (m), 811 (s), 744 (s), 681 (m) cm^{-1}; HRMS (EI) calculated for $C_{30}H_{26}O$ $[M]^+$: 402.1984; found: 402.1977; $[\alpha]_D^{RT}$: –61.6 (*c* 1.25, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 2.13 (s, 3H), 2.16 (s, 3H), 2.21 (s, 3H), 2.36 (s, 3H), 4.75 (br s, 1H), 7.02–7.04 (m, 3H), 7.23–7.26 (m, 1H), 7.30 (d, J = 3.9 Hz, 2H), 7.36 (m_c, 1H), 7.41–7.47 (m, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.93 ppm (t, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 20.3 (s), 20.6 (s), 20.6 (s), 21.3 (s), 118.3 (s), 123.7 (s), 124.8 (s), 125.4 (s), 125.6 (s), 126.5 (s), 126.7 (s), 128.2 (s), 128.3 (s), 128.6 (s 2C), 128.7 (s), 129.0 (s), 129.4 (s), 129.4 (s), 129.8 (s), 130.2 (s), 132.6 (s), 133.3 (s), 133.4 (s), 133.4 (s), 136.5 (s), 137.2 (s), 137.3 (s), 137.7 (s), 148.8 (s) ppm.

(R)-O-(3-(2,4,6-Trimethylphenyl)-2'-methyl-[1,1'-binaphthalen]-2-yl) Dimethylcarbamothioate (15)

To a stirred solution of (*R*)-**14** (1.55, 3.86 mmol, 1.00 equiv) and DMF (16 mL) cooled to 0 °C, sodium hydride (60% dispersion in mineral oil, 306 mg, 7.75 mmol, 2.00 equiv) was added. After stirring at room temperature for 1.5 h, a solution of dimethylthiocarbomyl chloride (1.23 g, 9.65 mmol, 2.50 equiv) and DMF (3 mL) was added dropwise. The resulting reaction mixture was heated at 85 °C for 24 h. After cooling to room temperature, the reaction was quenched with an aqueous KOH solution (2 wt%, 40 mL), and the resulting aqueous phase extracted with

ethyl acetate (3 × 40 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (50:1 to 20:1) afforded (*R*)-**15** (1.79 g, 95%) as a white solid. m.p.: 112 °C (cyclohexane); R_f = 0.23 (cyclohexane/*tert*-butyl methyl ether 50:1); IR (ATR): nu(tilde) = 3044 (w), 2920 (m), 2847 (w), 1522 (m), 1446 (m), 1389 (m), 1284 (m), 1190 (m), 1136 (s), 849 (m), 810 (m), 743 (m) cm^{-1}; HRMS (EI) calculated for $C_{33}H_{32}NOS$ $[M+H]^+$: 490.2199; found: 490.2193. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.04–2.76 (m, 18H), 6.87–6.97 (m, 2H), 7.08–7.62 (m, 7H), 7.78–7.95 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): Two sets of signals are seen for this compound (see the Supporting Information for copies of NMR spectra).

(R)-S-(3-(2,4,6-Trimethylphenyl)-2'-methyl-[1,1'-binaphthalen]-2-yl) Dimethylcarbamothioate (16)

(*R*)-**15** (845 mg, 1.72 mmol, 1.00 equiv) was heated with constant rotation (50 rpm) at 280 °C in a Kugelrohr apparatus. Purification of the crude reaction mixture by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (50:1 to 20:1 respectively) afforded (*R*)-**16** (700 mg, 83%) as a white solid. m.p.: 94 °C (cyclohexane); R_f = 0.21 (cyclohexane/*tert*-butyl methyl ether 10:1); IR (ATR): nu(tilde) = 2917 (m), 2848 (w), 1664 (vs), 1445 (m), 1356 (m), 1257 (m), 1084 (m), 849 (w), 809 (m), 744 (m), 684 (m) cm^{-1}; HRMS (EI) calculated for $C_{33}H_{32}NOS$ $[M+H]^+$: 490.2205; found: 490.2192. $[\alpha]_D^{RT}$: –164.7 (*c* 0.95, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.15–2.16 (m, 6H), 2.21 (s, 3H), 2.24–2.40 (m, 9H), 6.97 (s, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.21–7.31 (m, 3H), 7.36–7.43 (m, 1H), 7.46–7.56 (m, 2H), 7.83 (s, 1H), 7.85–7.95 ppm (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 20.7 (s), 21.0 (s), 21.1 (s), 21.3 (s), 36.9 (br s, 2C), 126.0 (s), 126.0 (s), 126.5 (s), 126.7 (s), 126.9 (s), 127.0 (s), 127.7 (s), 127.7 (s), 128.0 (s), 128.0 (s), 128,1 (s), 128.8 (s), 129.4 (s), 129.9 (s), 132.0 (s), 132.4 (s), 133.1 (s), 134.1 (s), 135.1 (s), 135.5 (s), 136.7 (s), 137.0 (s), 137.1 (s), 138.1 (s), 143.0 (s), 144.4 (s), 165.1 (s) ppm.

(R)-3-(2,4,6-Trimethylphenyl)-2'-methyl-[1,1'-binaphthalene]-2-thiol (5)

To a stirred solution of (*R*)-**16** (1.20 g, 2.45 mmol, 1.00 equiv) and THF (20 mL) cooled to 0 °C, $LiAlH_4$ (136 mg, 3.68 mmol, 1.50 equiv) was added, and the resulting reaction mixture was maintained at room temperature for 7 h. As TLC analysis indicated complete consumption of the starting material, the reaction was cooled to 0 °C, diluted with Et_2O (10 mL), and carefully quenched with aqueous HCl (2 N, 5 mL). After extraction of the crude reaction mixture with Et_2O (3 × 40 mL), the combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (20:1) afforded (*R*)-**5** (0.98 g, 96%) with 98% *ee* as a white solid. m.p.: 109 °C (cyclohexane); R_f = 0.65 (cyclohexane/*tert*-butyl methyl ether 10:1); IR (ATR): nu(tilde) = 3049 (w), 2944 (w), 2913 (m), 2853 (w), 2555 (w), 1610 (w), 1438 (m), 1389 (m), 1097 (m), 849 (m), 809 (s), 743 (s) cm^{-1}; HRMS (EI) calculated for $C_{30}H_{26}S$ $[M]^+$: 418.1755; found: 418.0803; $[\alpha]_D^{RT}$: –69.8 (*c* 0.95, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): *δ* 2.11 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 2.38 (s, 3H), 3.10 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 7.04 (s, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.21–7.34 (m, 2H), 7.38–7.48 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.93 ppm (m_c, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): *δ* 20.0 (s), 20.4 (s), 20.5 (s), 21.4 (s), 125.2 (s), 125.3 (s, 2C) 125.4 (s), 126.7 (s), 126.7 (s), 128.1 (s), 128.2 (s), 128.3 (s), 128.5 (s), 128.6 (s), 128.6 (s), 129.1 (s), 131.8 (s), 132.4 (s, 2C), 132.6 (s), 132.9 (s), 133.2 (s), 134.6 (s), 135.3 (s), 136.8 (s), 136.8 (s), 137.2 (s), 137.4 (s), 137.8 (s) ppm; HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 99/1, flow rate 0.7 mL/min, λ = 254 nm): t_R = 6.9 min (minor **5**), t_R = 7.6 min (major **5**).

Ruthenium Chloride Complex (R,^{Ru}RS)-17

n-BuLi (1.58M in hexanes, 0.280 mL, 0.400 mmol, 1.00 equiv) was slowly added to a solution of (*R*)-**5** (167 mg, 0.400 mmol, 1.00 equiv) in THF (4 mL) at 0 °C. After 30 min, the orange solution was added dropwise to a suspension of di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (122 mg, 0.200 mmol, 0.500 equiv) in THF (4 mL) at 0 °C. The resulting blue suspension was stirred for 3 h at room temperature. All solvents were removed under reduced pressure, and the residue was dissolved in toluene (15 mL). Salts formed during the reaction were removed by filtration under inert atmosphere, toluene (6 mL) and triethylphosphine (10 wt% solution in *n*-hexane, 708 mg, 0.600 mmol, 1.50 equiv) were added to the filtrate to form a red solution which was maintained at 100 °C for 3 d. The solvent was removed under reduced pressure and the crude material was purified by recrystallization from toluene–*n*-pentane to furnish ruthenium complex (*R,*^{Ru}*RS*)-**17** (174 mg, 65%) as a red powder. HRMS (ESI) calcd for $C_{36}H_{40}PSRu$ $[M–Cl]^+$: 637.1632, Found: 637.1636; NMR spectroscopic data major diastereomer: ^1H NMR (500 MHz, CD_2Cl_2): *δ* 0.83 (dt, *J* = 14.6 Hz, *J* = 7.6 Hz, 9H), 1.56–1.69 (m 3H), 1.72–1.88 (m, 3H), 1.96 (s, 3H), 2.12 (d, *J* = 3.0 Hz, 3H), 2.17 (s, 3H), 2.21 (s, 3H), 5.27 (s, 1H), 5.56 (s, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 7.09–7.17 (m, 3H), 7.34 (m_c, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.63 (s, 1H), 7.88 ppm (m_c, 3H); Selected carbon signals determined by 2D NMR spectra $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): *δ* 7.9 (s), 17.3 (s), 17.8 (s), 18.0 (s), 18.3 (s), 20.2 (s), 86.2 (s), 102.2 (s) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): *δ* 22.9 ppm; Minor diastereomer: ^1H NMR (500 MHz, CD_2Cl_2): *δ* 1.00 (dt, *J* = 14.6 Hz, *J* = 7.6 Hz, 9H), 1.72–1.88 (m, 3H), 1.88–1.97 (m, 3H) 1.90 (s, 3H), 2.01 (s, 3H), 2.16 (d, *J* = 3.1 Hz, 3H), 2.19 (s, 3H), 5.27 (s, 1H), 5.53 (s, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 7.09–7.17 (d, underneath multiplet, 1H), 7.22–7.27 (m, 3H), 7.40 (m_c, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.72–7.83 ppm (m_c, 3H); Selected carbon signals determined by 2D NMR spectra $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): *δ* 8.0 (s), 17.9 (s), 18.1 (s), 18.2 (s), 20.0 (s), 84.8 (s) 102.4 (s) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): *δ* 21.7 ppm; The crystallographic data is available online in the CCDC database under number CCDC 1515411.

Ruthenium Complex [(R)-3]$^+$[BAr$^F_4$]$^-$

Chloride complex (*R,*^{Ru}*RS*)-**17** (67 mg, 0.10 mmol, 1.0 equiv) and $NaBAr^F_4$ (89 mg, 0.10 mmol, 1.0 equiv) were suspended in CH_2Cl_2 (8 mL). After stirring the dark blue reaction mixture for 2 h, the precipitate was filtered off under inert atmosphere, and the solvent was removed under vacuum, yielding the ruthenium thiolate complex [(*R*)-**3**]$^+$[BAr^F_4]$^-$ (115 mg, 77%) as a blue powder. HRMS (ESI) calcd for $C_{36}H_{40}PSRu^+$ [M–BAr_4^F]$^+$: 637.1626, Found: 637.1631; ^1H NMR (500 MHz, CD_2Cl_2): *δ* 0.92 (dt, *J* = 17.3 Hz, *J* = 7.6 Hz, 9H), 1.73–1.86 (m, 6H), 1.93 (s, 3H), 2.01 (s, 3H), 2.09 (s, 3H), 2.39 (s, 3H), 4.97 (s, 2H), 7.07 (d, *J* = 9.0 Hz, 1H), 7.20–7.29 (m, 2H), 7.29–7.45 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.56 (s, 4H), 7.71 (m_c, 10H), 7.90–7.97 (m, 2H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.28 ppm (s, 1H); Selected signals for $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): *δ* 8.4 (s), 18.0 (d, *J* = 27.8 Hz), 19.4 (s), 20.3 (s), 20.4 (s), 73.3 (s), 117.9 (m), 121.7 (s), 123.9 (s), 125.5 (s), 125.6 (s), 126.1 (s), 126.9 (s), 128.6 (s), 129.1 (s), 129.2 (m), 129.3 (m), 135.2 (s), 162.2 (q, *J* = 49.3 Hz) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): *δ* 23.0 ppm; $^{11}B\{^1H\}$ NMR (161 MHz, CD_2Cl_2): *δ* –6.6 ppm.

Acknowledgements

This research was supported by the Deutsche Forschungsgemeinschaft (Oe 249/10-1) and in part by the Cluster of Excellence *Unifying Concepts in Catalysis* (EXC

314/2). M.O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship. We thank Dr. Hendrik F. T. Klare and Susanne Bähr for insightful discussions (both TU Berlin).

Keywords: asymmetric catalysis • homogeneous catalysis • hydrosilylation • Lewis acids • Si–H bond activation

[1] Y. Ohki, Y. Takikawa, H. Sadohara, C. Kesenheimer, B. Engendahl, E. Kapatina, K. Tatsumi, *Chem. Asian J.* **2008**, *3*, 1625–1635.

[2] T. Stahl, P. Hrobárik, C. D. F. Königs, Y. Ohki, K. Tatsumi, S. Kemper, M. Kaupp, H. F. T. Klare, M. Oestreich, *Chem. Sci.* **2015**, *6*, 4324–4334.

[3] For selected reviews of chiral-at-metal complexes related to catalysis, see: a) E. B. Bauer, *Chem. Soc. Rev.* **2012**, *41*, 3153–3167; b) C. Ganter, *Chem. Soc. Rev.* **2003**, *32*, 130–138; c) H. Brunner, *Angew. Chem. Int. Ed.* **1999**, *38*, 1194–1208.

[4] a) H. F. T. Klare, M. Oestreich, J.-i. Ito, H. Nishiyama, Y. Ohki, K. Tatsumi, *J. Am. Chem. Soc.* **2011**, *133*, 3312–3315; b) C. D. F. Königs, H. F. T. Klare, Y. Ohki, K. Tatsumi, M. Oestreich, *Org. Lett.* **2012**, *14*, 2842–2845; c) C. D. F. Königs, M. F. Müller, N. Aiguabella, H. F. T. Klare, M. Oestreich, *Chem. Commun.* **2012**, *49*, 1506–1508; d) J. Hermeke, H. F. T. Klare, M. Oestreich, *Chem. Eur. J.* **2014**, *20*, 9250–9254; e) S. Wübbolt, M. Oestreich, *Angew. Chem. Int. Ed.* **2015**, *54*, 15876–15879.

[5] The 1,4-selective reduction of pyridines[6] has been the only true hydrosilylation promoted by catalysts [**1**]$^+$[BAr$^F{}_4$]$^-$. Enolizable imines[4d] and, likewise, ketones[4b] do undergo dehydrogenative couplings, yielding N-silyl enamines and silyl enol ethers, respectively. At prolonged reaction times, these are hydrogenated in the presence of [**1**]$^+$[BAr$^F{}_4$]$^-$ by the released dihydrogen gas.[7,8]

[6] C. D. F. Königs, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2013**, *52*, 10076–10079.

[7] For a synthetic and mechanistic study of hydrogenation catalyzed by [**1a**]$^+$[BAr$^F{}_4$]$^-$, see: A. Lefranc, Z.-W. Qu, S. Grimme, M. Oestreich, *Chem. Eur. J.* **2016**, *22*, 10009–10016.

[8] For an in-depth investigation of this dehydrogenation–hydrogenation sequence, see: S. Bähr, M. Oestreich, *Organometallics* **2017**, *36*, DOI: 10.1021/acs.organomet.7b00030.

[9] For a summary of imine hydrosilylation, see: O. Riant, in *Modern Reduction Methods*; (Eds.: P. G. Andersson, I. Munslow), Wiley-VCH: Weinheim, Germany, **2008**; pp 321−337.

[10] a) T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393–406; b) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102.

[11] a) A. M. Hayes, D. J. Morris, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2005**, *127*, 7318–7319; b) F. K. K. Cheung, A. M. Hayes, J. Hannedouche, A. S. Y. Yim, M. Wills, *J. Org. Chem.* **2005**, *70*, 3188–3197; c) D. J. Morris, A. M. Hayes, M. Wills, *J. Org. Chem.* **2006**, *71*, 7035–7044; d) R. Soni, K. E. Jolley, G. J. Clarkson, M. Wills, *Org. Lett.* **2013**, *15*, 5110–5113; e) R. Hodgkinson, V. Jurčík, A. Zanotti-Gerosa, H. G. Nedden, A. Blackaby, G. J. Clarkson, M. Wills, *Organometallics* **2014**, *33*, 5517–5524.

[12] E. Tayama, A. Saito, T. Ooi, K. Maruoka, *Tetrahedron* **2002**, *58,* 8307–8312.

[13] F.-M. Gautier, S. Jones, S. J. Martin, *Org. Biomol. Chem.* **2009**, *7*, 229–231.

[14] A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, G. R. Fulmer, *Organometallics* **2010**, *29*, 2176–2179.

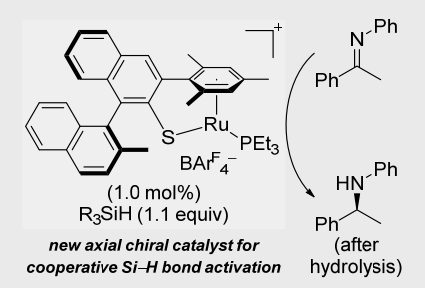
10.1002/chem.201700304

WILEY-VCH

Suggestion for the Entry for the Table of Contents

FULL PAPER

Chiral spine. The preparation of an axial chiral version of the bulky 2,6-dimesitylphenyl group attached to sulfur is reported. This new thiol ligand is used for the formation of a tethered ruthenium complex (see scheme) suitable for stereocontrolled Si–H bond activation. Its application as a chiral catalyst in imine hydrosilylation leads to moderate but promising enantioinduction.



*S. Wübbolt, M. S. Maji, E. Irran, M. Oestreich**

Page No. – Page No.

A Tethered Ru–S Complex with an Axial Chiral Thiolate Ligand for Cooperative Si–H Bond Activation: Application to Enantioselective Imine Reduction