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Mixed donor ligands based on sp^2-hybridized nitrogen donors: asymmetric hydrosilylation catalyzed by rhodium complexes that contain the 2-(2-oxazolin-2-ylmethyl)pyridine system

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Abstract

The synthesis and coordination chemistry of a mixed pyridine–oxazoline bidentate ligand, 2-(2-oxazolin-2-ylmethyl)pyridine, are described. Crystal structure data along with variable temperature NMR studies establish the structures of achiral and chiral versions of this ligand system. In addition, the catalytic asymmetric hydrosilylation of acetophenone has been examined.

1. Introduction

Chiral chelating ligands that incorporate the oxazoline heterocycle have been of great interest in the past decade.[1–3] This is because their synthesis involves the use of readily available chiral aminoalcohols and, more importantly, spectacular results in asymmetric synthesis have been obtained using these oxazoline-containing systems.[4] For example, the C_2-symmetric tridentate ligands of the type 2,6-bis(2-oxazoline-2-yl)pyridine (Pybox), **1**, have shown remarkable activity and enantioselectivity in the Rh-catalyzed hydrosilylation of ketones and the Ru-catalyzed cyclopropanation of olefins with diazoacetates.[5–7] Also important are the reports[5,8,9] of bidentate systems similar to **1** in which only one oxazolinyl unit is utilized such as shown in **2**.

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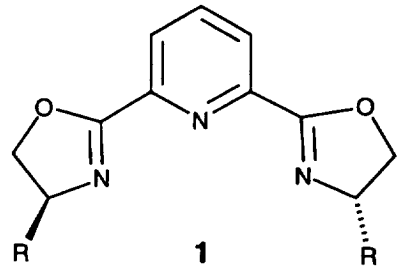

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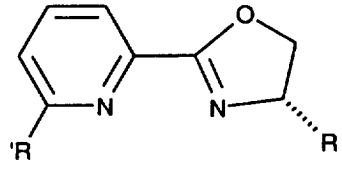
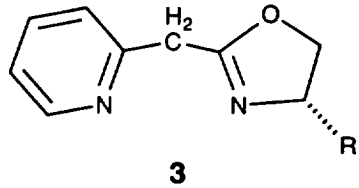


2

R = *i*-Pr, *s*-Bu, *t*-Bu

In both **1** and **2**, the different donors are separated in identical ways such that five-membered chelate rings are generated upon coordination. Our efforts in this area were spurred by the fact that chelate ring size is an important parameter in the optimization of chiral ligands for asymmetric catalysis.[10] In an effort to probe this particular point with these kinds of systems, we investigated the synthesis, coordination chemistry and enantioselectivity of chiral bidentate ligands that contain the oxazolinyl unit and the pyridine separated by a methylene unit, shown here as **3**; such a system should show different behavior to **2** simply because, upon coordination, a six-membered chelate ring would be formed. In this paper we report the synthesis of achiral and chiral versions of this new bidentate mixed donor system, their coordination chemistry to Rh(I) and some preliminary results with regard to asymmetric hydrosilylation of acetophenone.



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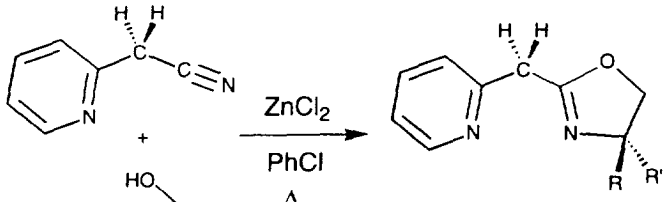
R = *i*-Pr, *s*-Bu

2. Results and discussion

2.1. Synthetic considerations

The synthesis of substituted 2-(2-oxazolin-2-ylmethyl)pyridines relies on the condensation of the appropriate aminoalcohol with 2-cyanomethylpyridine according to standard protocol (Eq. 1).[11] Thus, refluxing a mixture of 2-cyanomethylpyridine and the aminoalcohol in chlorobenzene in the presence of a catalytic amount of zinc chloride produces the desired ligand. Chirality is introduced at the carbon center next to the nitrogen donor on the oxazoline ring by using chiral aminoalcohols such as valinol and leucinol. Phenylglycinol did not react with 2-cyanomethylpyridine even after refluxing the reaction

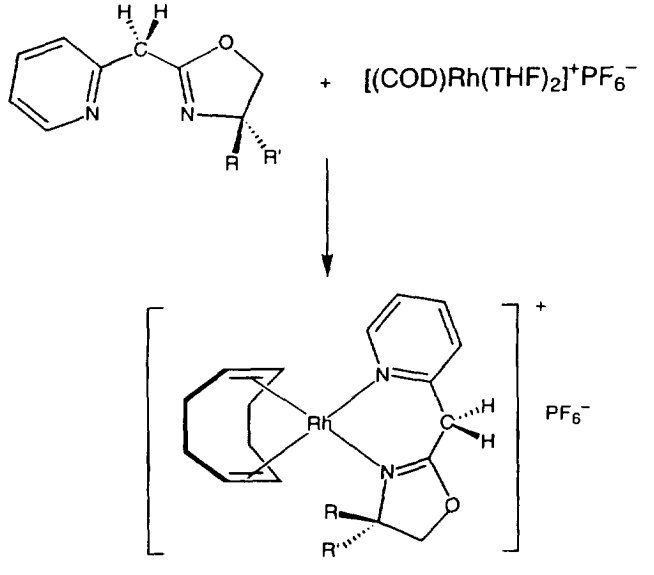
mixture for one week; starting materials were recovered. The new ligands **3a–c** were characterized by NMR spectroscopy and elemental analysis.



(1)

R = R' = Me **3a**
R = H, R' = *i*-Pr **3b**
R = H, R' = *s*-Bu **3c**

Ligands **3a–c** react with $[Rh(COD)(THF)_2]PF_6$ to form the complexes $[Rh(COD)(\mathbf{3a})]PF_6$, $[Rh(COD)(\mathbf{3b})]PF_6$, and $[Rh(COD)(\mathbf{3c})]PF_6$, **4a–c**, respectively, as yellow microcrystalline solids in good yields (Eq. 2).



(2)

R = R' = Me **4a**
R = H, R' = *i*-Pr **4b**
R = H, R' = *s*-Bu **4c**

Yellow needle shaped crystals of **4a** and **4b**, suitable for X-ray analysis, were grown from CH_2Cl_2 or THF solutions layered with hexanes. The X-ray structure determinations for these two complexes have been undertaken and their molecular structures are shown in Figs 1 and 2; Table 1 contains the crystallographic data and Table 2 has a selection of bond distances and bond angles of interest. Comparison of the two structures reveals that they both have a slightly distorted square planar geometry at Rh.

Of particular interest are the conformations of the pyridyl–methyloxazoline ligand system as found in the solid state. Upon coordination, a tricyclic ring system is generated that consists of the six-membered

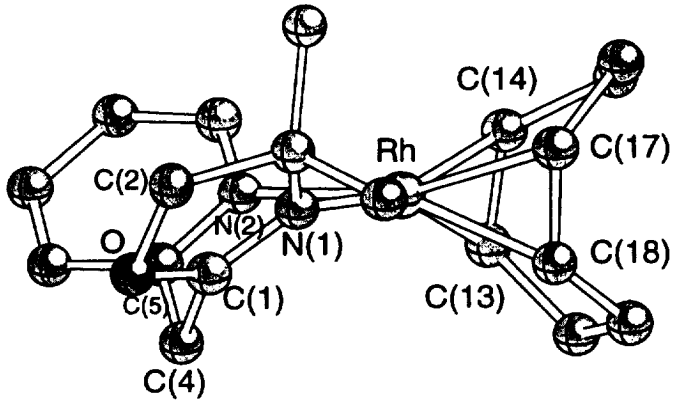


Fig. 1. Ball and stick representation of the cationic portion of **4a**

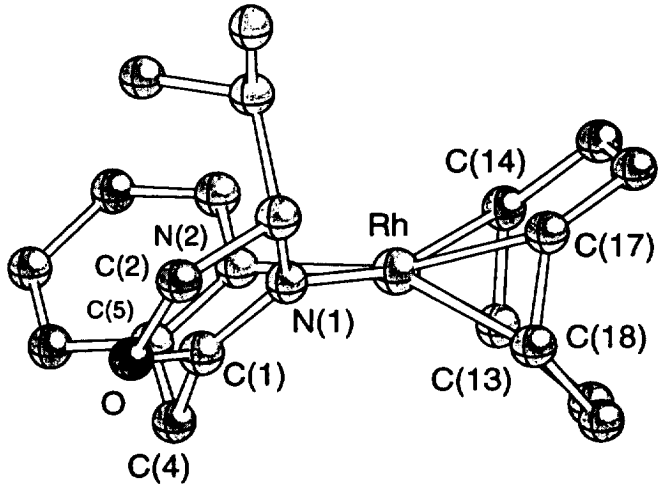


Fig. 2. Ball and stick representation of the cationic portion of **4b**

chelate ring flanked by the two heterocyclic rings containing the sp^2-nitrogen donor atoms. The chelate ring itself adopts a boat conformation with both of the oxazoline and pyridine rings folded towards the 'bottom' of the 'boat'. In the solid state, the oxazoline ring of **4a** is twisted slightly as evidenced by the torsion angle of N1–C1–O1–C2 of 6.4(6)°; in chiral **4b**, this ring is flatter with the same torsion angle now being −2.4(6)°. A key feature in these molecular structures is the orientation of the oxazoline substituents; in achiral **4a**, the geminal methyl groups are disposed such that one is perpendicular to the square planar rhodium center and the other is almost parallel to this plane. For chiral **4b**, the isopropyl group is oriented perpendicular to the square planar rhodium center. As a result, the Rh–N1 distance in **4a** (2.110(3) Å) is longer than in **4b** (2.033(4) Å), possibly a result of the larger steric effect of the two geminal methyl groups as compared to the single isopropyl substituent. Other bond lengths and angles compare favorably with similar rhodium systems that incorporate related nitrogen ligands.[12–14]

In solution, **4a** and **4b** show very different NMR spectral characteristics. The ^{1}H NMR spectrum of **4a** contains very broad resonances that suggest that the molecule is undergoing some fluxional process, while the proton NMR spectrum of **4b** consists of sharp resonances at all temperatures. Cooling a solution of **4a** and monitoring the resulting NMR spectra reveals that a process can be slowed sufficiently on the NMR time scale to generate sharp resonances. Thus, at room temperature, the two methyl groups of the oxazoline unit appear as a singlet at 1.3 ppm, while the protons of the backbone methylene (C4),

Table 1
Crystallographic data

Compound	**4a**[a]	**4b**[b]
Formula	$C_{19}H_{26}F_6N_2OPRh$	$C_{20}H_{28}F_6N_2OPRh$
fw	546.30	560.32
Color, habit	yellow, needle	yellow, plate
Crystal size, mm	0.25 × 0.30 × 0.50	0.10 × 0.35 × 0.45
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
a, Å	14.318(2)	10.5025(5)
b, Å	9.178(3)	14.4247(3)
c, Å	17.739(2)	29.9174(5)
β, deg	105.848(9)	90
V, Å^3	2242.8(8)	4532.3(2)
Z	4	8
T, °C	21(1)	-93(1)
ρ_{calc}, g/cm^3	1.618	1.642
$F(000)$	1104	2272
μ(Mo K$_\alpha$), cm^{-1}	8.79	8.86
Transmission factors	0.96-1.00	0.84-1.00
$2\theta_{max}$, deg	60	60.1
Crystal decay, %	7.5	negligible
Total reflections	7170	39792
Unique reflections	6923	11200[c]
R_{merge}	0.030	0.057
Reflns with $I \geq 3\sigma(I)$	2939	6231
No. of variables	308	568
R (F, $I \geq 3\sigma(I)$)	0.034	0.036
R_w (F^2, all data)	—	0.059
R_w (F, $I \geq 3\sigma(I)$)	0.031	—
gof	1.57	1.37
Max Δ/σ (last cycle)	0.007	0.01
Residual density, e/Å^3	-0.35, +0.44	-3.11, +1.80 (near Ru)

[a] Rigaku AFC6S diffractometer, Mo-K_α radiation (λ = 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and gof = $[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

[b] Rigaku/ADSC CCD diffractometer, Mo-K_α radiation (λ = 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 94 × 94 mm at a distance of 39.21(2) mm from the crystal, oscillation width 0.5°, $\sigma^2(F^2) = 1.5*[(C + B)/Lp^2]$ (C = scan count, B = background count), function minimized $\Sigma w(|F_o^2-F_c^2|)^2$ where $w = 1/\sigma^2(F_o^2)$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o^2-F_c^2|)^2/\Sigma w|F_o^2|^2)^{1/2}$, and gof = $[\Sigma w(|F_o^2|-|F_c^2|)^2/(m-n)]^{1/2}$.

[c] Includes Friedel pairs, 6265 are unique.

the oxazoline methylene (C2) and the olefinic protons of COD appear as two broad singlets at 4.2 and 4.7 ppm, overlapping an extremely broad third resonance. Upon lowering the temperature to 0°C, the very broad resonance decoalesces into two broad peaks that eventually split into two doublets at 4.3 and 5.2 ppm ($^2J_{HH}$=27 Hz) at −30°C; these are caused by the backbone methylene protons. The methylene

Table 2
Selected bond lengths (Å) and angles (deg) for **4a** and **4b**

Bond lengths (Å) and angles (deg)	**4a**	**4b**
Rh-N(1)	2.110(3)	2.073(4)
Rh-N(2)	2.132(3)	2.142(4)
Rh-C(14)	2.151(4)	2.169(7)
Rh-C(13)	2.131(4)	2.157(5)
Rh-C(17)	2.149(4)	2.152(6)
Rh-C(18)	2.145(4)	2.124(6)
N(1)-Rh-N(2)	84.9	83.7
C(1)-C(4)-C(5)	108.3	108.9

protons of the oxazoline ring (C2) decoalesce at −75°C, and at −90°C appear as two broad singlets, at 4.8 and 5.0 ppm.

It is proposed that the fluxional process being exhibited by achiral **4a** is caused by the conformational flipping or inversion of the six-membered chelate ring as shown in Fig. 3. This process of conformational flipping exchanges the backbone methylene protons in the fast exchange limit as well as the methylene protons of the oxazoline ring and the methyl substituents (R=R′=Me). Using line shape analysis of the spectral data from bridging methylenic protons, one can obtain activation parameters from the Arrhenius and Eyring equations of E_a=3.0 kcal mol^{-1}, $\Delta G^{\ddagger}$ (298 K)=5.4 kcal mol^{-1}, $\Delta H^{\ddagger}$=2.5 kcal mol^{-1} and $\Delta S^{\ddagger}$=−10.5 cal K mol^{-1}.

In contrast, no fluxional process was observed for chiral **4b** at any temperature. All the resonances can be assigned in the room temperature ^{1}H NMR spectrum of **4b** by NMR spectroscopy (COSY and NOE experiments). For achiral **4a**, the conformational isomers shown in Fig. 3 with R=R′=Me are enantiomeric; however, for chiral **4b**, these conformers **A** and **B** are diastereomeric, and should in principle have different energies. Therefore, the fact that no fluxional process occurs for this system suggests that the solid state structure observed, in which the isopropyl substituent is pointed perpendicular to the square plane of the complex, is maintained in solution; in other words, only species **A** in Fig. 3 is found since conformer **B** has the R=Pr^i pointed parallel to the square plane.

2.2. *Hydrosilylation of acetophenone with diphenylsilane*

The in situ catalysts were prepared from the rhodium(I) precursors $[Rh(COD)Cl]_2$ or $[Rh(COE)_2Cl]_2$ with the chiral ligands **3b** or **3c**, in neat acetophenone. The standard hydrosilylation was initiated by addition of diphenylsilane to this mixture of substrate and catalyst at 0°C. The reaction mixture was allowed to slowly warm up to room temperature and was stirred for the periods indicated in Table 3. The enantiomeric excesses were determined by GC.[15] Addition of CCl_4 to the reaction mixture showed

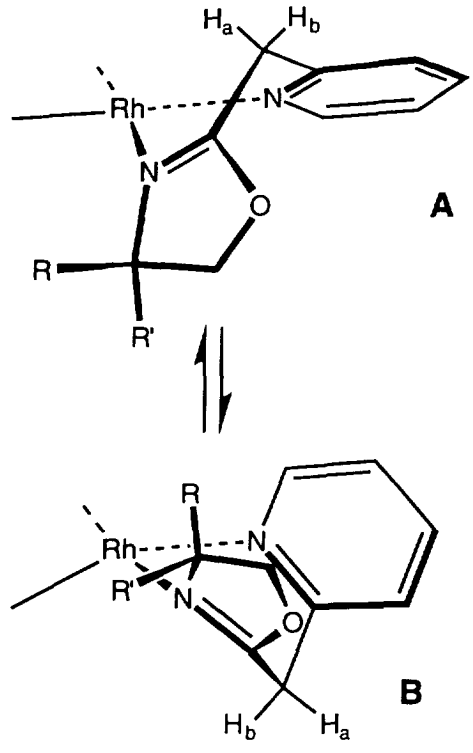
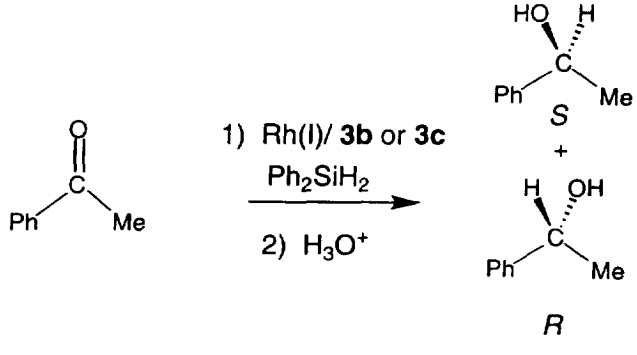


Fig. 3. Proposed conformational change of the six-membered chelate ring; for R=R′=Me, the process is fast on the NMR time scale; for R=H and R′=Pr^i, no exchange is observed and only structure **A** is observed both in solution and in the solid state

mixed results with respect to enantioselectivity. While it increased the enantioselectivity by a factor of 30 when $[Rh(COD)Cl]_2$ was used, the enantioselectivity plummeted to zero with $[Rh(COE)_2Cl]_2$. The so-called 'CCl_4 effect' was observed in the asymmetric hydrosilylation of ketones when ligand **2** was used; although the effect is not understood, the use of CCl_4 has been found to lead to increases in enantioselectivity.[3–5]



(3)

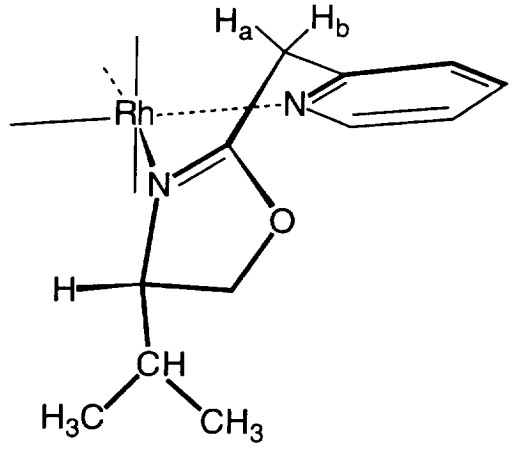
The best result was obtained when the catalyst system was $[Rh(COD)Cl]_2$, **3b**, and CCl_4 (entry 4, Table 3). The enantioselectivities for the catalyst precursor $[Rh(COE)_2Cl]_2$ were very low (entries 1–3, 7, Table 3). Ligand **3b** results in a higher enantioselectivity than **3c** (entries 5, 8, Table 3) probably because the chiral isobutyl substituent in **3c** is further away from the reaction center as a result of the presence of the extra methylene group. Our best result, 42% *ee*, is considerably lower than that observed for similar catalyst systems using the related ligands **1** and **2**. Two explanations can be put forward to rationalize

Table 3
Catalytic asymmetric hydrosilylation of acetophenone with diphenylsilane

run	ligand	precursor	ligand/Rh	reaction time, h	% alcohol	% ee
1	**3b**	$[Rh(COE)_2Cl]_2$	8/1	48	67	15 (R)
2	**3b**	$[Rh(COE)_2Cl]_2$	8/1	72	70	15 (R)
3*	**3b**	$[Rh(COE)_2Cl]_2$	8/1	48	60	0
4*	**3b**	$[Rh(COD)Cl]_2$	10/1	48	70	42 (R)
5*	**3b**	$[Rh(COD)Cl]_2$	10/1	72	70	40 (R)
6	**3b**	$[Rh(COD)Cl]_2$	10/1	48	65	7 (R)
7	**3c**	$[Rh(COE)_2Cl]_2$	8/1	48	33	5 (R)
8*	**3c**	$[Rh(COD)Cl]_2$	10/1	48	70	19 (R)
9	**3c**	$[Rh(COD)Cl]_2$	10/1	48	25	0

In all runs 5mol% of ligand, 1 gr. acetophenone and 2.45 gr. diphenylsilane were used. * With 5 mL CCl_4

our modest results: in the chiral ligands **3b,c**, the presence of only one chiral center on a bidentate ligand could result in lower enantioselectivities given that the catalytic cycle involves octahedral Rh(III) type species;[10] however, a more serious effect is the conformation of the six-membered ring which orients the chiral substituent away from the rhodium center towards the bottom of the boat. This is shown here for a generic octahedral Rh(III) complex.



3. Conclusions

The incorporation of a methylene unit into the backbone of mixed pyridine–oxazoline systems, such as **2a–c**, generates a six-membered ring upon coordination. Solid state structural studies on two square planar rhodium complexes show the presence of a folded boat conformation; for the chiral system **4b**, the isopropyl substituent on the oxazoline ring is oriented towards the bottom of the boat. The use of these ligand systems in the homogeneous asymmetric hydrosilyation of acetophenone results in rather low enantiomeric excesses (42% *ee*), presumably because the six-membered ring orients the chiral substituent away from the incoming substrate.

4. Experimental section

4.1. General procedures and reagent syntheses

All reactions were carried out under an atmosphere of nitrogen unless otherwise stated. Tetrahydrofuran and hexanes were predried over CaH_2 and distilled from sodium benzophenone ketyl under argon prior to use. Dichloromethane was dried and distilled from CaH_2 under argon. 2-pyridylacetonitrile, diphenylsilane, acetophenone, and carbon tetrachloride were purchased from Aldrich and used without further purification. $[Rh(COD)Cl]_2$ and $[Rh(COE)_2Cl]_2$ were prepared by the published methods. Chiral amino acids were purchased from Acros. $CDCl_3$ was purchased from CIL and dried and distilled over CaH_2. d_8-THF was purchased from CIL and dried and vacuum transferred over potassium. It was then degassed by three 'freeze–pump–thaw' cycles. The chiral amino alcohols were prepared from chiral amino acids by the literature procedure.[16]

^1H NMR spectra were recorded on Varian XL-300, Bruker WP-200, Bruker WH-400, or Bruker AM-500 spectrometers with $CDCl_3$ and d_8-THF as solvents; the spectra were referenced to $CHCl_3$ at 7.24 ppm and C_4D_7HO at 3.58 ppm.

Elemental analyses were carried out by P. Borda of this department.

4.2. General procedure for the synthesis of the ligands 2-(2-(4,-R,4-R′)oxazolin-2-ylmethyl)pyridine (R=R′=Me; R=i-Pr, R′=H; R=sec-Butyl R′=H), 3a–c

In a 250 ml flask, $ZnCl_2$ (0.3 g, 2.12 mmol) was melted under vacuum and cooled under nitrogen, then 2-pyridyl acetonitrile (5 g, 42 mmol), the appropriate amino alcohol (84 mmol), and chlorobenzene (60 ml) were added to the flask. The mixture was refluxed under nitrogen for one day and then was allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the resulting orange brown slurry was dissolved in CH_2Cl_2 (60 ml), and was washed with water (3×30 ml). The aqueous phase was then extracted with CH_2Cl_2 (2×25 ml). The organic phases were combined, dried over Na_2SO_4 and the volatiles were removed under reduced pressure. The brown residue was distilled under vacuum (at 0.1 mmHg 76°C **3a**; 80°C **3b**; 90°C **3c**).

For **3a**: ^1H NMR ($CDCl_3$): δ 7.7 (d, 1H, J=10.0 Hz, pyridine), 6.8 (t, 1H, J=8.0 Hz, pyridine), 6.5 (d, 1H, J=10.0 Hz, pyridine), 6.1 (t, 1H, J=8.0 Hz, pyridine), 3.1 (s, 2H, CH_2 oxazoline), 2.95 (s, 2H, CH_2 aliphatic); 0.4 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 162 (*C*-ipso), 155 (quat, oxazoline), 149 (*o-C*), 137 (*m-C*), 124 (*p-C*), 121 (*m-C*), 78 (CH_2, oxazoline), 66 (CMe_2), 37 (CH_2, aliphatic), 28 (CH_3). Anal. calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.22; H, 6.99; N, 15.01.

For **3b**: ^{1}H NMR ($CDCl_3$): δ 8.1 (d, 1H, *J*=7.0 Hz, pyridine), 7.2 (t, 1H, *J*=8.0 Hz, pyridine), 6.9 (d, 1H, *J*=10.0 Hz, pyridine), 6.7 (t, 1H, *J*=8.0 Hz, pyridine), 3.8 (m, 1H, C*H*, oxazoline), 3.6 (m, 2H, CH_2, oxazoline), 3.4 (s, 2H, CH_2, aliphatic), 1.3 (m, 1H, $CHMe_2$), 0.6 (d, 3H, *J*=12.0 Hz, CH_3), 0.5 (d, 3H, *J*=12.0 Hz, CH_3). ^{13}C{^{1}H} NMR: δ 164 (*C*-ipso), 155 (quat, oxazoline), 148 (*o*-*C*), 137 (*m*-*C*), 123 (*p*-*C*), 121 (*m*-*C*), 76 (CH_2, oxazoline), 56 ($CHMe_2$), 37 (CH_2, aliphatic), 19 ($CHMe_2$), 18 (CH_3), 17 (CH_3). Anal. calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.89; N, 13.71. Found: C, 70.58; H, 7.85; N, 13.95

For **3c**: ^{1}H NMR ($CDCl_3$): δ 8.4 (d, 1H, *J*=10.0 Hz, pyridine), 7.3 (t, 1H, *J*=8.0 Hz, pyridine), (d, 1H, *J*=10.0 Hz, pyridine), 7.0 (t, 1H, *J*=8.0 Hz, pyridine), 4.3 (m, 2H, CH_2 oxazoline), 4.1 (m, 1H, C*H* oxazoline), 3.7 (m, 2H, CH_2 aliphatic), 1.4 (m, 2H, CH_2CHMe_2), 1.2 (m, 1H, $CHMe_2$), 0.7 (d, 3H, *J*=10.0 Hz, CH_3), 0.6 (d, 3H, *J*=10.0 Hz, CH_3). ^{13}C{^{1}H} NMR: 164 (*C*-ipso), 155 (quat, oxazoline), 149 (*o*-*C*), 137 (*m*-*C*), 123 (*p*-*C*), 122 (*m*-*C*), 77 (CH_2, oxazoline), 64 (CHC_4H_9), 45 (CH_2CHMe_2), 37 (CH_2, aliphatic), 25 ($CHMe_2$), 23 (CH_3). Anal. calcd for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 70.91; H, 7.94; N, 13.47.

4.3. Synthesis of {Rh(COD)[2-(2-(4,-R,4-R′)oxazolin-2-ylmethyl)pyridine]}PF_6, ***4a–c***

$[Rh(COD)Cl]_2$ (200 mg, 0.4 mmol) was dissolved in THF (30 ml) and a solution of $AgPF_6$ (210 mg, 0.8 mmol) in THF (10 ml) was added to it. A yellow precipitate was formed immediately, the flask then was covered with aluminum foil and the reaction mixture was stirred for 1 h. The precipitate (AgCl) was filtered through Celite on a Schlenk frit. The solution of the ligand (160 mg, 0.8 mmol) in THF (10 ml) was degassed and added to the filtrate. The reaction mixture was then allowed to stir overnight. The solvent evaporated under reduced pressure, the yellow powder was washed with hexanes and ether to give yellow semi-crystalline solid which was recrystallized from 1:1.5:1.5 CH_2Cl_2:hexanes:ether (1.8 g, 81%).

For **4a**, room temperature ^{1}H NMR ($CDCl_3$): δ 8.4 (d, 1H, *J*=6.0 Hz, pyridine), 7.9 (t, 1H, *J*=7.5 Hz, pyridine), 7.6 (d, 1H, *J*=9.0 Hz, pyridine), 7.4 (t, 1H, *J*=6.0 Hz, pyridine), 4.7 (br s, 3H, CH_2 oxazoline and aliphatic), 4.2 (broad, 5H, C*H* COD and CH_2 aliphatic), 2.5 (br s, 2H, CH_2 COD), 1.9 (br s, 2H, COD aliphatic), 1.3 (s, 6H, CH_3). ^{1}H NMR (d_8-THF) at −90°C: δ 5.2 (δ, 1H, *J*=15 Hz, CH_2 aliphatic), 4.9 (br s, 1H, CH_2 oxazoline), 4.8 (br s, 1H, CH_2 oxazoline), 4.4 (d, 1H, *J*=9.0 Hz, COD olefinic), 4.3 (d, 1H, *J*=15.0 Hz, CH_2 aliphatic), 4.2 (br s, 1H, COD olefinic), 4.0 (d, 1H, *J*=9.0 Hz, COD olefinic), 3.9 (br s, 1H, COD olefinic), 1.3 (s, 3H, CH_3), 1.2 (s, 3H, CH_3). Anal. calcd for $C_{19}H_{26}N_2OPF_6Rh$: C, 41.77; H, 4.80; N, 5.13. Found: C, 41.74; H, 4.70; N, 4.98.

For **4b**, ^{1}H NMR ($CDCl_3$): δ 8.4 (d, 1H, *J*=6.0 Hz, pyridine), 7.9 (t, 1H, *J*=7.5 Hz, pyridine), 7.6 (d, 1H, *J*=9.0 Hz, pyridine), 7.4 (t, 1H, *J*=6.0 Hz, pyridine), 4.9 (d, 1H, *J*=19.0 Hz, CH_2 aliphatic), 4.6 (t, 1H, *J*=9.0 Hz, CH_2 oxazoline), 4.3 (m, 2H, COD olefinic), 4.2 (br s, 2H, COD olefinic), 4.0 (d, 1H, *J*=19.0 Hz, CH_2 aliphatic), 3.8 (m, 1H, CH_2 oxazoline), 2.7 (m, 2H, COD aliphatic), 2.4 (m, 3H, COD aliphatic), 2.2 (br s, 3H, COD aliphatic), 1.9 (m, 1H, $CHMe_2$), 1.8 (m, 1H, C*H* oxazoline), 0.8 (d, 3H, *J*=10.0 Hz, CH_3), 0.6 (d, 3H, *J*=10.0 Hz, CH_3). Anal. calcd for $C_{20}H_{28}N_2OPF_6Rh$: C, 42.87; H, 5.04; N, 5.00. Found: C, 42.73; H, 5.06; N, 5.13.

For **4c**, ^{1}H NMR ($CDCl_3$): δ 8.4 (d, 1H, *J*=6.0 Hz, pyridine), 7.9 (t, 1H, *J*=7.5 Hz, pyridine), 7.6 (d, 1H, *J*=9.0 Hz, pyridine), 7.4 (t, 1H, *J*=6.0 Hz, pyridine), 4.8 (m, 1H, CH_2 aliphatic), 4.4 (m, 2H, COD olefinic), 4.2 (d, 1H, *J*=20.0 Hz, CH_2 aliphatic), 3.9 (m, 1H, CH_2 oxazoline), 2.8 (m, 2H, COD aliphatic), 2.5 (m, 3H, COD aliphatic), 2.3 (m, 3H, COD aliphatic), 1.8 (m, 2H, CH_2CHMe_2), 1.4 (m, 2H, C*H* oxazoline and $CHMe_2$), 1.0 (d, 6H, *J*=10.0 Hz, CH_3).

4.4. Hydrosilylation standard procedure

The in situ catalysts were prepared by dissolving the precursor $[Rh(COD)Cl]_2$ or $[Rh(COE)_2Cl]_2$ (0.04 mmol, 0.05 mol%) and the chiral ligand (0.34 mmol) in neat acetophenone (0.73 g, 6 mmol). The hydrosilylation was started by adding diphenylsilane (1.1 ml, 6.6 mmol) at 0°C. When $[Rh(COD)Cl]_2$ was used as the precursor, CCl_4 (5 ml) was also added to the reaction mixture. The deep red mixture was slowly warmed to room temperature and stirred for the periods indicated in Table 3. For workup, the reaction mixture was cooled in an ice bath and hydrolyzed by adding methanol (10 ml) and HCl (1N, 14 ml). After stirring at 0°C for 2 h followed by 30 min at room temperature, the mixture was extracted with ether (2×30 ml). The organic phase was dried over Na_2SO_4, and the solvent was removed using a rotary evaporator. Kugelrohr distillation yielded the product and the ratio of the secondary alcohol/ketone was determined by ^1H NMR spectroscopy.

4.5. Determination of optical purity

To measure the enantiomeric excess, the product (20 mg) was mixed with isopropylisocyanate (0.3 ml) and one drop of triethylamine in a Reacti-vial. It was heated at 60°C for 12 h, cooled to room temperature, and the excess isocyanate was evaporated in a stream of nitrogen. The urethane thus formed was dissolved in ether (2 ml). 0.5 ml of this solution was injected onto a chiral column, Chirasil-Val III. Gas chromatographic analysis was performed isothermally at 130°C with the injector and detector temperature of 220°C. The enantiomeric excess was taken as the average of 3–4 injections.

4.6. X-Ray crystallographic analyses of **4a** and **4b**

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ=19.1–31.2° for **4a** and 30921 reflections with 2θ=4.0–60.1° for **4b**. The data were processed[17] and corrected for Lorentz and polarization effects, decay (**4a**), and absorption (empirical: based on azimuthal scans for three reflections for **4a**; based on a three-dimensional analysis of symmetry-equivalent data for **4b**).

The structures were solved by direct methods. The PF_6 anion of **4a** was modeled as (64:36) two-fold disordered with respect to rotation about the F(1)–P(1)–F(2) axis. There are two independent molecules in the asymmetric unit of **4b**. One isopropyl methyl carbon atom of **4b** (C(25)) was modeled as (54:46) two-fold disordered. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions with C–H=0.98 Å and B_H=1.2 $B_{\text{bonded atom}}$. A correction for secondary extinction (Zachariasen type) was applied for **4a**, the final value of the extinction coefficient being $9.0(2)\times10^{-7}$. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-Ray Crystallography*.[18] The absolute configuration of **4b** (for the particular crystal used for data collection) was determined by parallel refinement of the mirror-image. The R and R_w factor ratios were 1.026 and 1.043, respectively.

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