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Ligand Excess and Intermediates in the Rhodium-Catalyzed Enantioselective Hydrosilylation of Acetophenone with Pyridineoxazoline Ligands

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Abstract: The enantioselective hydrosilylation of acetophenone and diphenylsilane with $[Rh(COD)Cl]_2$ and the cocatalysts L1 - L4 was investigated. The substitution of hydrogen in the 6-position of the pyridine ring dramatically reduces the dependence of the optical induction on ligand excess, solvent, and concentration of diphenylsilane, acetophenone, and catalyst. The 6-substituents on the pyridine ring are assumed to block one of the coordination sites of rhodium, preventing further interaction with additional ligands, solvents, substrates, and additives.

Introduction

Optically active pyridineoxazolines are good cocatalysts in the Rh-catalyzed enantioselective hydrosilylation of acetophenone with diphenylsilane to give the silylether $PhCH(Me)(OSiHPh_2)$ and after subsequent hydrolysis 1-phenylethanol.[2-7] As a by-product, the silylenol ether $PhC(OSiHPh_2)=CH_2$ is formed, which on hydrolysis regenerates acetophenone.[2,8,9] Normally, the hydrosilylation with rhodium catalysts derived from optically active pyridineoxazolines requires a ligand excess to achieve the highest optical yield. This has also been observed for other nitrogen ligands.[10-15] Previously we have reported, that no ligand excess is necessary for picolineoxazolines as cocatalysts.[5] In this paper, we propose a mechanism which explains this result and we present further experiments supporting this rationalisation.[16]

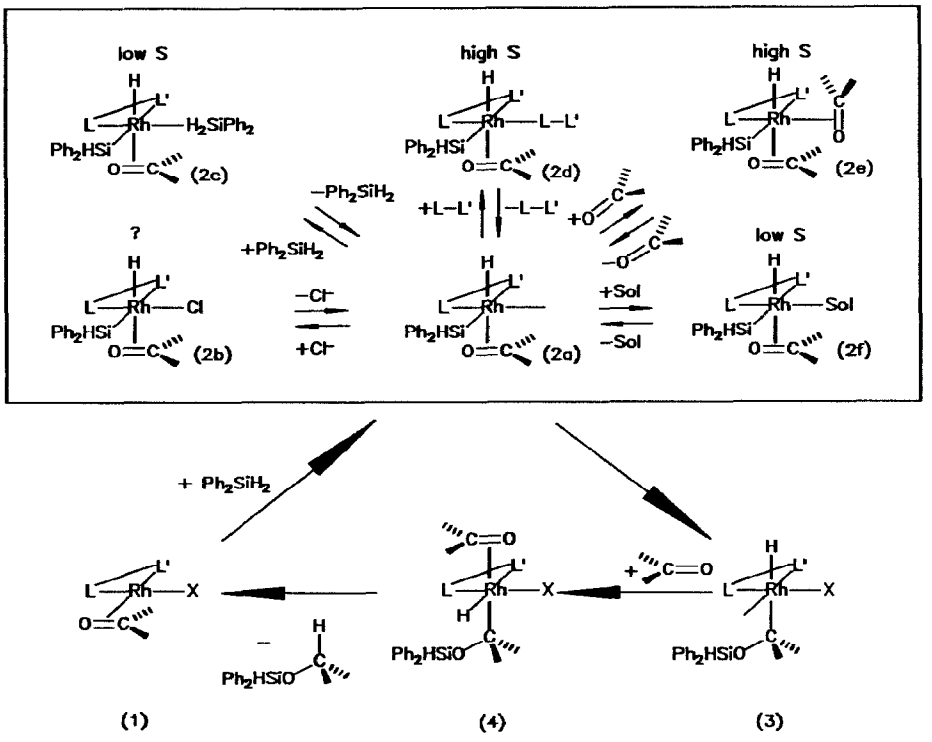
Mechanism

Transferring the mechanism of the hydrosilylation of ketones and diphenylsilane with Rh-catalysts containing phosphine ligands[9] to pyridineoxazoline ligands, the intermediates are as shown in Scheme 1.

In the square planar species 1, we assume bidentate coordination of the pyridineoxazoline L-L', coordination of the ketone and of X, which can be chloride, solvent, ligand L-L', one of the substrates ketone or diphenylsilane, or an additive. After oxidative addition of diphenylsilane, six different species **2a-2f** result, all containing the activated substrates. Insertion of the ketone into the Rh-Si bond of **2a-2f** gives the α-siloxyalkylrhodium hydride intermediates **3**. Addition of another ketone yields **4** and reductive elimination of the silylether produces the starting compound **1**.

It is to the different intermediates **2a-2f** (Scheme 1) that we ascribe different enantioselectivities. In the following paragraphs, it is shown how each set of experimental conditions results in a specific set of species **2a-2f**, giving rise to the observed enantioselectivity.

Scheme 1: Mechanism of the hydrosilylation with pyridineoxazolines as cocatalysts

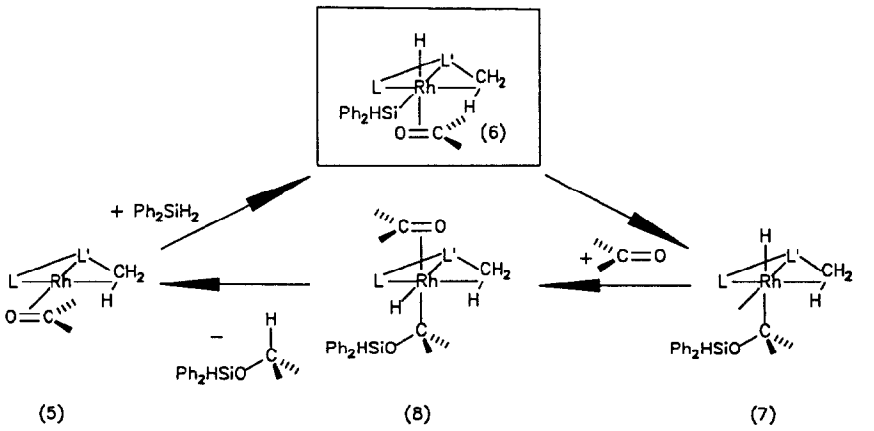


X = chloride, diphenylsilane, ligand L–L', acetophenone, solvent

It is well known, that the enantiomeric excess in the hydrosilylation with Rh/pyridineoxazoline catalysts is enlarged by ligand excess.[2-7] In the equilibria between species **2a-2f**, ligand excess favors species **2d** which has a second ligand L-L' in the coordination sphere, presumably bonded in a monodentate fashion. Obviously, the ligand excess species **2d** has a much higher S selectivity than other intermediates of type **2**. The intermediates with coordinated toluene **2f** or diphenylsilane **2c** must have lower enantioselectivities, because addition of toluene or high silane concentrations diminish the enantiomeric excess.[2] Species **2e** induces high ee's in favour of the S-enantiomer, because a high acetophenone concentration relative to silane increases the optical yields.[2] As the concentration of chloride has not been varied, the enantioselectivity of **2b** at present is unclear.

Using picolineoxazolines as cocatalysts, the 6-methyl group blocks the coordination site, occupied by X in the pyridineoxazoline catalysts, by an agostic or steric interaction (Scheme 2). Therefore, no coordination of X = solvent, ketone, diphenylsilane, chloride or further ligand L-L' is possible. After oxidative addition of the silane to the square planar species **5**, there is only one precursor **6** before the insertion step. Interestingly, species **6** has a high R selectivity in contrast to most of the species **2**, which induce the S configuration in the product. It is obvious, that the optical induction in the picolineoxazoline catalyzed

Scheme 2: Mechanism of the hydrosilylation with picolineoxazolines as cocatalysts



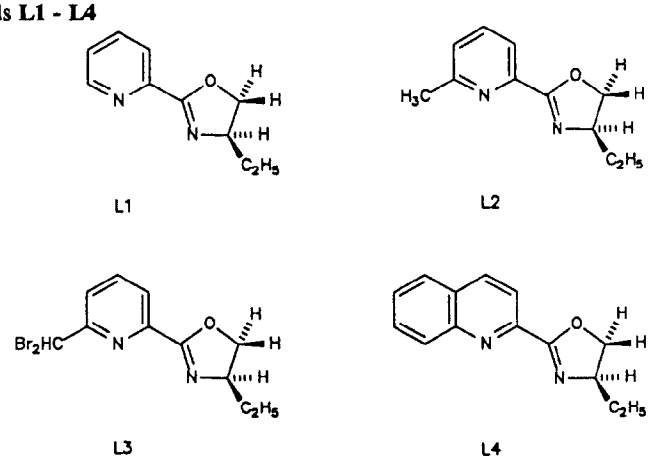
reaction should be hardly affected by ligand excess, change in solvent, silane or acetophenone concentration.

The rationalisations given in Schemes 1 and 2 are in accord with all the published experimental results[2-6]. They are also in agreement with the following experimental facts.

Ligands L1 - L4

All the ligands L1 - L4 contain the same Et-substituted oxazoline ring of (R)-configuration. The pyridine ring is modified in **L2** by a methyl group in 6-position, in **L3** by a dibromomethyl group in 6-position and in **L4** by a quinoline ring.

Scheme 3: Ligands **L1 - L4**



Tables 1-6

In the following experiments, the influence of ligand excess, solvent, and the concentration of silane, acetophenone and catalyst in the $[Rh(COD)Cl]_2$-catalyzed hydrosilylation of acetophenone with

diphenylsilane using pyridineoxazoline L1 and the modified ligands L2, L3, and L4 as cocatalysts is tested.[16] In Tables 1-6 hydros. [%] means hydrosilylation yield defined as 100(silylether + silylenol ether)/(silylether + silylenol ether + acetophenone). Chem. yield [%] is defined as 100(silylether)/(silylether + silylenol ether + acetophenone). Both are determined by ^{1}H-NMR spectroscopy as described previously.[2,16]

Ligand excess

The ratio Rh/ligand is varied from 1/0.8 to 1/5 at a constant Rh/substrate ratio of 1/200 (Table 1).

Table 1
temperature: 0→20 °C **Rh/PhCOMe: 1/200**
reaction time: 18h **PhCOMe/Ph_2SiH_2: 1/1**

entry	lig.	Rh/lig.	hydros. [%]	chem. yield [%]	induction ee [%]	config.	number of runs
1	L1	1/0.8	86 - 88	66	17.7 - 19.7	S	2
2	L1	1/0.9	88 - 91	63 - 67	17.3 - 19.6	S	3
3	L1	1/1.0	86 - 88	66 - 70	19.0 - 21.2	S	2
4	L1	1/1.1	84 - 86	65 - 68	21.0 - 22.0	S	2
5	L1	1/1.2	87 - 91	68 - 70	20.0 - 21.8	S	2
6	L1	1/2.0	88 - 92	68 - 73	30.9 - 33.1	S	3
7	L1	1/5.0	88 - 91	68 - 71	38.8 - 39.8	S	3
8	L2	1/0.8	91 - 95	61 - 64	30.3 - 32.7	R	2
9	L2	1/0.9	92 - 95	66 - 69	34.1 - 36.4	R	3
10	L2	1/1.0	81 - 84	67 - 71	40.9 - 42.5	R	3
11	L2	1/1.1	87 - 93	73 - 76	44.0 - 45.2	R	2
12	L2	1/1.2	88 - 91	80 - 82	45.1 - 47.3	R	3
13	L2	1/2.0	90 - 95	80 - 84	46.2 - 48.0	R	3
14	L2	1/5.0	90 - 93	80 - 84	46.9 - 48.1	R	3
15	L3	1/0.8	88 - 92	83 - 87	23.1 - 25.1	R	3
16	L3	1/1.0	90 - 94	88 - 90	28.7 - 31.1	R	3
17	L3	1/1.2	94 - 98	91 - 93	29.8 - 32.0	R	2
18	L3	1/2.0	92 - 96	90 - 95	28.9 - 29.5	R	3
19	L3	1/5.0	94 - 96	92 - 95	29.7 - 31.3	R	3
20	L4	1/0.8	86 - 90	48 - 51	3.1 - 5.3	R	2
21	L4	1/1.0	86 - 88	47 - 51	4.0 - 5.0	R	2
22	L4	1/1.2	90 - 94	53 - 59	4.8 - 5.4	R	2
23	L4	1/2.0	88 - 93	47 - 52	7.2 - 9.2	R	2
24	L4	1/5.0	74 - 79	45 - 50	10.4 - 12.4	R	3

For pyridineoxazoline cocatalysts, the optical induction in the Rh-catalyzed hydrosilylation can be increased by an excess of ligand [2-6]. This is confirmed in the present study. Variation of the Rh/L1 ratio in small steps from 1/0.8 to 1/1.2 causes a change in the optical induction from 17.3 to 22.0% ee (entries 1-5). The use of a twofold excess increases the ee to 33.1% ee and a fivefold excess to more than 38% ee (entries 6, 7). However, for ligand L2 or L3 the optical induction cannot be enlarged by a ligand excess in accord with the mechanism shown in Scheme 2. With a Rh/L2 or Rh/L3 ratio of 1/0.8, enantioselectivities of 30.3 - 32.7% ee and 23.1 - 25.1% ee are obtained (entries 8, 15). In these cases and also in runs 1, 2, and 9 the hydrosilylation reaction probably is partially catalyzed by an achiral species. Increasing the concentration of the ligand in small steps to a Rh/L2 or Rh/L3 ratio of 1/1.2, the optical induction rises to 45.1 - 47.3% ee and 29.8 - 32.0% ee (entries 12, 17). Rh/ligand ratios of 1/2 or 1/5 do not give higher ee's (entries 13, 14, 18, 19). For the quinolineoxazoline L4 as a cocatalyst, the enantiomeric excess increases from 4.0 - 5.0% ee for a stoichiometric Rh/ligand ratio to 10.4 - 12.4% ee for a fivefold ligand excess.

Solvent

In Table 2 the influence of the solvents toluene and CCl_4 on the chemical yield and enantiomeric excess is investigated.

Table 2
temperature: 0→20 °C Rh/PhCOMe: 1/200 Rh/ligand: 1/5
reaction time: 18h PhCOMe/Ph_2SiH_2: 1/1

entry	lig.	solvent	hydros. [%]	chem. yield [%]	induction ee [%]	config.	number of runs
1	L1	-	88 - 91	68 - 71	37.8 - 39.8	S	3
2	L1	toluene	87 - 89	64 - 67	31.1 - 32.5	S	3
3	L1	CCl_4	97 - 98	88 - 94	56.0 - 58.2	S	2
4	L2	-	90 - 93	80 - 84	46.9 - 48.1	R	3
5	L2	toluene	90 - 92	71 - 74	45.0 - 46.8	R	3
6	L2	CCl_4	92 - 94	80 - 83	55.0 - 56.8	R	3
7	L3	-	94 -96	92 - 95	29.7 - 31.3	R	3
8	L3	toluene	94	91 - 93	32.0 - 32.8	R	2
9	L3	CCl_4	100	100	27.0 - 28.6	R	3

With ligand L1 as a cocatalyst, the highest optical induction of 56.0 - 58.2% is achieved with CCl_4 as the solvent (entry 3). The ee is 31.1 - 32.5% for toluene (entry 2) and 37.8 - 38.8% without solvent (entry 1). It should be recalled, that the "CCl_4-effect" already operates with CCl_4 quantities stoichiometric with respect to rhodium. Thus, another type **2** species has to be assumed to explain the "CCl_4-effect".[7]

The cocatalysts L2 and L3 give the same optical yields in toluene solution and without solvent (entries 4, 5, 7, 8), because solvent species of the **2f** type are of no importance in the catalysis with 6-substituted

pyridineoxazoline cocatalysts. Using CCl_4 as the solvent, the ee is somewhat increased with ligand L2 and slightly decreased with ligand L3 (entries 6, 9).

Diphenylsilane concentration

Normally, in hydrosilylation reactions a diphenylsilane/acetophenone ratio of 1/1 is used. Previously we have reported that for pyridineoxazoline ligands the optical induction increases markedly, if the diphenylsilane/acetophenone ratio is low.[2] This is confirmed by the following results (Table 3).

Table 3
temperature: 0→20 °C Rh/PhCOMe: 1/200 Rh/ligand: 1/5
reaction time: 18h no solvent *) 2 ml toluene

entry	lig.	Ph_2SiH_2/ PhCOMe	hydros. [%]	chem. yield [%]	induction ee [%]	config.	number of runs
1	L1	1	88 - 91	68 - 71	37.8 - 38.8	S	3
2	L1	0.5	93 - 97	93 - 97	51.7 - 52.9	S	3
3	L1	0.25	100	100	51.4 - 52.4	S	2
4*)	L1	1	86 - 90	63 - 69	31.2 - 33.2	S	2
5*)	L1	0.5	100	81 - 84	46.7 - 47.7	S	2
6*)	L1	0.25	100	94 - 97	54.4 - 56.4	S	3
7	L2	1	90 - 93	80 - 84	46.9 - 48.1	R	3
8	L2	0.5	95	95	46.6 - 49.0	R	4
9	L2	0.25	93 - 95	93 - 95	48.8 - 50.8	R	2
10	L3	1	94 - 96	91 - 93	29.7 - 31.3	R	3
11	L3	0.5	100	100	30.1 - 32.1	R	3

For ligand L1, the enantiomeric excess increases from 37.8 - 38.8% ee to 51.4 - 52.4% ee, if only 25 mol% diphenylsilane is added (entries 1-3). With toluene as the solvent, we observe an increase from 31.2 - 33.2% ee to 54.4 - 56.4% ee (entries 4-6). Both results can be rationalized on the basis of Scheme 1, in which species **2e** is favored and species **2c** is disfavoured. With the cocatalysts L2 and L3, the optical induction is nearly independent from the diphenylsilane/acetophenone ratio (entries 7-11), because species of the type **2c** and **2e** do not play a role.

Catalyst/Acetophenone Ratio

In Table 4, the catalyst and acetophenone concentration in the catalysis with ligand L1 is varied. Low catalyst concentrations increase the enantiomeric excess compared to high catalyst concentrations (entries 3-6). For high catalyst concentrations the enantioselectivity is independent of the excess of acetophenone (entries 1,2). However, the lower the catalyst concentration the higher is the increase of the enantiomeric excess on addition of further acetophenone (entries 3-6), indicating that the "acetophenone species" **2e** is highly enantioselective.

Table 4
temperature: 0→20 °C Rh/L1: 1/5 configuration: S
reaction time: 18h no solvent

entry	$Rh/Ph_2SiH_2/PhCOMe$	hydros. [%]	chem. yield [%]	induction ee[%]	number of runs
1	1/100/100	96 - 98	83 - 87	48.0 - 49.2	3
2	1/100/200	100	81 - 84	46.7 - 47.7	2
3	1/200/200	87 - 89	64 - 67	31.1 - 32.5	2
4	1/200/400	95	80	41.2 - 43.2	2
5	1/500/500	94	59	9.9 - 10.9	2
6	1/500/1000	89	68	32.4 - 33.0	2

Catalyst/Diphenylsilane Ratio

Table 5 shows the dependence of the chemical yield and enantiomeric excess on the catalyst and silane concentration. Importantly, a change in the concentration of the catalyst also leads to a change in the Rh/diphenylsilane and Rh/acetophenone ratio. Therefore, the results have to be compared with the results in Tables 3 and 4.

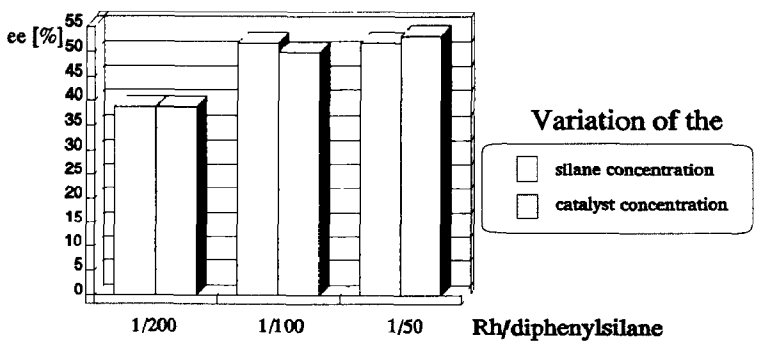
Table 5
temperature: 0→20 °C $PhCOMe/Ph_2SiH_2$: 1/1 Rh/ligand: 1/5
reaction time: 18h no solvent *) 2 ml toluene

entry	lig.	Rh/Ph_2SiH_2	hydros. [%]	chem. yield [%]	induction ee [%]	config.	number of runs
1	L1	1/200	88 - 91	68 - 71	37.8 - 39.8	S	3
2	L1	1/100	93 - 96	91 - 95	49.4 - 50.4	S	3
3	L1	1/50	93 - 96	91 - 95	52.2 - 54.4	S	3
4*)	L1	1/200	86 - 90	63 - 69	31.2 - 33.2	S	3
5*)	L1	1/100	94 - 98	81 - 88	47.5 - 50.1	S	2
6*)	L1	1/50	96 - 100	87 - 91	53.8 - 55.4	S	3
7	L2	1/200	90 - 93	80 - 84	46.9 - 48.1	R	3
8	L2	1/100	93 - 97	87 - 93	51.5 - 54.1	R	2
9	L2	1/50	91 - 95	84 - 90	51.5 - 53.5	R	2

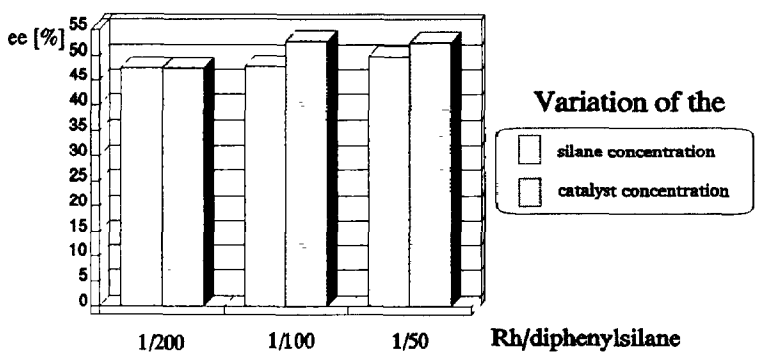
For ligand L1, the optical induction is strongly dependent on the Rh/diphenylsilane ratio. Varying the Rh/Ph_2SiH_2 ratio from 1/200 to 1/50 increases the enantiomeric excess appreciably (entries 1-6). The reason is that at high dipenylsilane concentrations, the reaction is dominated by the silane species **2c**, which has only a low enantioselectivity. The highly enantioselective ligand excess species **2d** and acetophenone species **2e** are suppressed. However, varying the Rh/Ph_2SiH_2 ratio in the same way in the catalysis with ligand L2, the optical induction increases only from 46.9 - 48.1% ee to 51.5 - 53.5% ee (entries 7-9), because the silane species **2c** is of no importance in the Rh/L2 system (Scheme 2).

A change of the Rh/diphenylsilane ratio at a constant acetophenone concentration automatically changes the PhCOMe/Ph_2SiH_2 ratio, which in Table 3 was shown to be an important variable. Therefore, the results in Tables 3 and 5 are compared in the block diagrams of Schemes 4 and 5.

Scheme 4: Catalysis with Rh/L1



Scheme 5: Catalysis with Rh/L2



In the catalytic system Rh/L1, nearly the same the optical inductions for the same Rh/Ph_2SiH_2 ratio under the conditions of Tables 3 and 5 are obtained, demonstrating, the strong dependence of the enantiomeric excess on the Rh/diphenylsilane ratio. In both cases the ee rises with the Rh/Ph_2SiH_2 ratio (Scheme 4). In the system Rh/L2, the Rh/Ph_2SiH_2 ratio has only a small influence on the optical induction. An increase of the concentration of the catalyst or a decrease of the concentration of diphenylsilane causes only a small increase of the enantiomeric excess (Scheme 5).

Enantiomeric Excess During Catalysis

At the time-intervals given in Table 6, samples were taken during the catalysis and hydrosilylation yield, chemical yield, silylenol ether yield, and enantiomeric excess were measured. Hydrosilylation yield, chemical yield, and silylenol ether yield of each sample were obtained by ^{1}H-NMR integration after addition of an excess of KCN at 0°C to stop the hydrosilylation reaction. At the same time a second sample was taken and treated with a large excess of acetone/HCl at 0°C. From this sample the enantiomeric excess was measured by GC as described previously.[2]

Silylenol ether [%] tot. is defined as 100(silylenol ether)/(silylether + silylenol ether+ acetophenone) and silylenol ether [%] rel. is defined as 100(silylenol ether)/(silylether + silylenol ether).

Table 6
temperature: 0 °C Rh/PhCOMe: 1/200 Rh/L1: 1/5
reaction time: 60 h PhCOMe/Ph_2SiH_2: 1/1
Rhodium: 0.24 mmol Rh

time [h]	hydros. [%]	chem. yield [%]	silylenol ether [%] tot.	[%] rel.	induction ee [%]	ee' [%]	config.
						24.5	
1	15	7	8	54	24.5		S
						34.1	
2	21	12	9	43	28.5		S
						37.4	
4	25	17	8	32	31.1		S
						40.4	
6	28	20	8	29	32.5		S
						40.9	
8	33	24	9	27	33.9		S
						43.7	
12	37	28	9	24	35.3		S
						43.3	
24	50	38	12	24	37.4		S
						45.8	
36	59	45	14	24	38.7		S
						34.0	
60	65	47	18	28	38.5		S

The enantiomeric excess %ee' of the 1-phenylethanol, produced in the time interval between t1 and t2, is calculated by the following formula (CA = chemical yield).

$$\%ee' = \frac{\%CA_{t2} * \%ee_{t2} - \%CA_{t1} * \%ee_{t1}}{\%CA_{t2} - \%CA_{t1}}$$

Within the first hour of the reaction, the enantiomeric excess is only 24.5% ee (Table 5). Over the subsequent hours, the enantiomeric excess grows. After 36 h, the enantioselectivity increases to 38.7% ee. The product, formed in the second hour, already has an enantiomeric excess of 34.1% ee. After 4 - 6 h, the new 1-phenylethanol has an optical purity of 40.4% and after 24 - 36 h an ee of 45.8% (Table 6). The relative amount of silylenol ether is also changing during the catalysis (54% at the beginning and 28% at the end).

Both results agree with previous experiments.[2] They can be explained by assuming that the Rh/Ph_2SiH_2 ratio is a very important variable in the system. During the reaction, diphenylsilane is consumed, therefore the optical induction is increasing. The catalysis described in table 6 has been carried out four times. The results of all the experiments agree, although the hydrosilylation yield, the chemical yield, the silylenol ether yield, and the optical induction varies to some extent.[16]

Addition of Diphenysilane in Small Portions

In the experiment of Table 7, diphenylsilane is added in small portions during the reaction. If the stoichiometric quantity of Ph_2SiH_2 is added at the beginning of the reaction, the ee is 38%. However, if the same amount of silane is added in small portions, the ee rises to 55%. After 14 h and 24 h the same optical induction is achieved, because during the reaction there is always a low concentration of diphenylsilane. In addition, only traces of silylenol ether are produced, the reaction being chemoselective.

Table 7

temperature: 0→20°C Rh/PhCOMe: 1/200 Rh/L1: 1/5

reaction time: 24 h PhCOMe/Ph_2SiH_2: 1/1

Rhodium: 0.24 mmol

addition of Ph_2SiH_2: at the beginning: 0.25 mol% Ph_2SiH_2

after 2 h: 0.0625 mol% Ph_2SiH_2 every hour

time [h]	hydros. [%]	chem. yield [%]	silylenol ether [%] rel	induction ee [%] (S)	number of runs
14	73 - 78	73 - 78	0	53.5 - 55.9	3
24	85 - 93	85 - 91	0 - 6	53.5 - 55.1	3

Experimental section

(R)-(+)-4-Ethyl-2-(2-pyridinyl)oxazoline (L1) was synthesized as described previously.[2] (R)-(+)-4-Ethyl-2-(2-picolinyl)oxazoline (L2) and (R)-(+)-ethyl-2-(2-(6-dibromomethyl)pyridinyl)oxazoline were prepared in the same way as L1, starting from 2-cyano-6-methylpyridine[17] and 2-cyano-6-dibromomethylpyridine[18].

(R)-(+)-4-Ethyl-2-(2-picolinyl)oxazoline (L2). 2-Cyano-6-methylpyridine was converted into 2-methylcarboximidate-6-methylpyridine with a 10% excess of CH_3ONa. For purification, L2 was passed with ether through a 30 cm layer of Al_2O_3 of medium activity. Yield 58-64%, colourless oil; $[\alpha]_{589}^{20}$+81.6, $[\alpha]_{578}^{20}$+85.7, $[\alpha]_{546}^{20}$+99.6, $[\alpha]_{436}^{20}$+200.6, $[\alpha]_{365}^{20}$+406.6 (c 1.49 in $CHCl_3$); found: C, 69.09; H, 7.89; N, 14.26. $C_{11}H_{14}N_2O$ requires C, 69.46; H, 7.41, N, 14.72%; δ_H 1.03 [t, J=7.5 Hz, 3H, CH_2CH_3], 1.55-1.88 [m, 2H, CH_2CH_3], 2.64 [s, 3H, py-CH_3], 4.13 [dd, J=8.0 Hz, J=8.0 Hz, 1H], 4.29 [m, 1H], 4.56 [dd, J=8.0 Hz, J=8.0 Hz, 1H], 7.25 [m, 1H, py-H^5], 7.66 [m, 1H, py-H^4], 7.88 [m, 1H, py-H^3]; m/z 190 (M^+, 8), 161 (100), 133 (37), 106 (73), 92 (38), 65 (37).

(R)-(+)-Ethyl-2-(2-(6-dibromomethyl)pyridinyl)oxazoline (L3). 2-Cyano-6-dibromomethylpyridine was converted into 2-methylcarboximidate-6-dibromomethylpyridine with 100% excess of CH_3ONa. For purification, L3 was passed with ether through a 30 cm layer of Al_2O_3. Yield 85%, colourless oil; $[\alpha]_{589}^{20}$+45.1, $[\alpha]_{578}^{20}$+47.0, $[\alpha]_{546}^{20}$+54.9, $[\alpha]_{436}^{20}$+110.2, $[\alpha]_{365}^{20}$+223.8 (c 2.88 in $CHCl_3$); found: C, 37.95; H, 3.50; N, 7.73; Br 46.17. $C_{11}H_{12}N_2OBr_2$ requires C, 37.29; H, 3.48, N, 8.05, Br 45.92%; δ_H 1.01 [t, J=7.5 Hz, 3H, CH_2CH_3], 1.58-1.86 [m, 2H, CH_2CH_3], 4.15 [dd, J=8.0 Hz, J=8.0 Hz, 1H], 4.31 [m, 1H], 4.56 [dd, J=8.0 Hz, J=8.0 Hz, 1H], 6.76 [s, 1H, py-$CHBr_2$], 7.90 - 8.07 [m, 3H, py-H^{3-5}]; m/z 348 (M^+, 5), 321 (51), 320 (24), 318 (100), 316 (51), 212 (41), 210 (41), 131 (21), 90 (42).

(R)-(+)-4-Ethyl-2-(2-quinolinyl)oxazoline (L4). Quinolinecarbocyclic acid (1.6 g, 9 mmol) was treated with $SOCl_2$ (20 ml, 37 mmol) at reflux temperature. After removing the excess of $SOCl_2$ the acid chloride was obtained as a red liquid. To a solution of R-(-)-2-amino-1-butanol (1 ml, 10 mmol) and triethylamine (9 ml, 64 mmol), the acid chloride was slowly added in chloroform solution (40 ml) at 0°C. The mixture was stirred for 1 day at room temperature. Then, $SOCl_2$ (20 ml, 37 mmol) in 20 ml benzene was added and the mixture was stirred 12 h at room temperature and 2 h at reflux temperature. The solvent and $SOCl_2$ were removed and a slightly brown solid was obtained. The product was stirred in a mixture of 170 ml of methanol and 80 ml of 2n NaOH for 3 days. After evaporation of the solvent, the resulting oil was dissolved in 200 ml of ether and extracted two times with 30 ml of water. The ether layer was dried with $MgSO_4$. The crude product was purified by chromatography on 35 cm of Al_2O_3 with medium activity. Yield 0.29 g (14%), yellow oil; $[\alpha]_{589}^{20}$+90.1, $[\alpha]_{578}^{20}$+96.3, $[\alpha]_{546}^{20}$+108.7, $[\alpha]_{436}^{20}$+213.1 (c 0.12 in $CHCl_3$); found: C, 74.36; H, 6.19; N, 12.43. $C_{14}H_{14}N_2O$ requires C, 74.29; H, 6.19, N, 12.38%; δ_H 1.05 [t, J=7.5 Hz, 3H, CH_2CH_3], 1.43-1.91 [m, 2H, CH_2CH_3], 4.22 [dd, J=8.0 Hz, J=8.0 Hz, 1H], 4.37 [m, 1H], 4.65 [dd, J=8.0 Hz, J=8.0 Hz, 1H], 7.56 - 8.29 [m, 6H, quin-H^{3-8}]; m/z 226 (M^+, 19), 197 (86), 169 (26), 142 (43), 128 (40), 101 (15).

Catalysis. The enantioselective hydrosilylations were carried out as described in ref. 2 under the reaction conditions specified in Tables 1-7. Under standard conditions 10 mg (0.04 mmol Rh) of $[Rh(COD)Cl]_2$, 0.2 mmol of ligand, and 1 ml (8 mmol) of acetophenone were stirred for 10 min at room temperature. After cooling to 0°C, 1.6 ml (8 mmol) of diphenylsilane were added. The reaction mixture was stirred for 18 h while warming up to room temperature. Before hydrolysis, a sample was taken to measure hydrosilylation yield, chemical yield, and silylenol ether yield by ^{1}H-NMR . The silylenol ether and silylether were hydrolyzed with p-toluenesulfonic acid in methanol according to ref 2.

In Tables 6 and 7, the products were hydrolyzed with 2.5 ml of 10% HCl in 10 ml of acetone at 0°C. The solutions were washed with aqueous Na_2CO_3 and extracted two times with ether. The ether layers were dried with $MgSO_4$ and purified by distillation (120 °C, 1 torr) for GC analysis.

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