

Rh(I)-Catalysed Asymmetric Hydrosilylation using New Oxazoline Ligands with Potential Charge-transfer Properties[☆]

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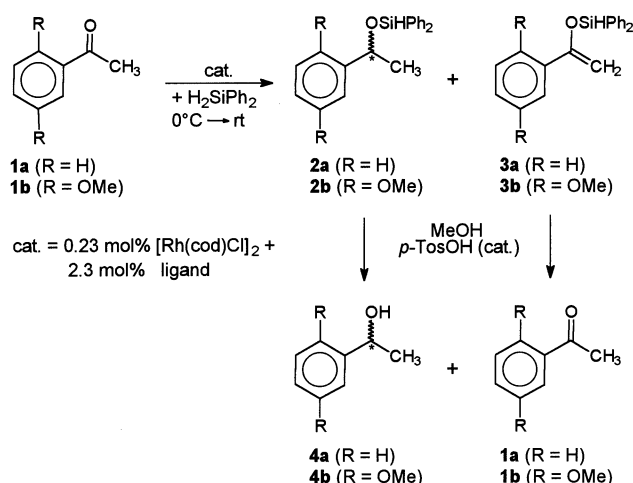
Novel *N*'-methylated 2-(oxazolin-2-yl)-4,4'-bipyridinium salts, bearing a chiral oxazoline moiety, were tested in the Rh(I)-catalysed enantioselective hydrosilylation. After coordination to rhodium these electron-attracting ligands are supposed to exhibit charge-transfer effects with electron-donating substrates. Therefore, a new catalytic hydrosilylation

reaction with 2,5-dimethoxyacetophenone as an electron-rich substrate was developed. The results were compared with those of the non-methylated 2-(oxazolin-2-yl)-4,4'-bipyridine and related ligands. In addition, the new ligands and Rh(I)-complexes were tested in the hydrosilylation of acetophenone.

Introduction

In the Rh(I)-catalysed enantioselective hydrosilylation of prochiral ketones, the substrate (e.g. acetophenone **1a**) reacts with diphenylsilane to yield the chiral silylalkyl ether **2a** (Scheme 1)^{[1][2][3]}. After hydrolysis the chiral 1-phenyl-ethanol **4a** is obtained. Asymmetric induction is brought about by in situ Rh(I)-catalysts consisting of [Rh(cod)Cl]₂ and preferably nitrogen ligands, e.g. chiral oxazolines^{[4][5][6][7]}.

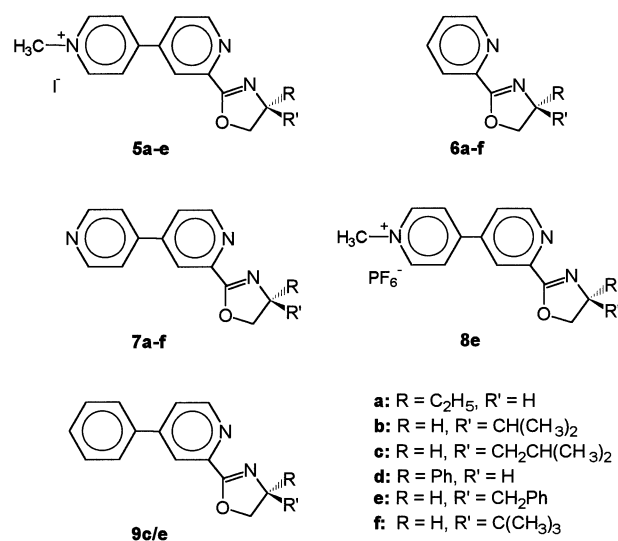
Scheme 1



In the preceding paper, we proposed charge-transfer interactions for a possible pre-orientation of the substrate to be hydrosilylated with respect to the catalytic centre. We

tried to find evidence for charge-transfer effects in the Rh(I)-catalysed hydrosilylation using the electron-rich 2,5-dimethoxyacetophenone as the substrate. As acceptor with electron-accepting properties we resorted to the Rh(I)-coordinated 2-(oxazolin-2-yl)-4,4'-bipyridinium salts **5**, described in the preceding publication. The adduct catalyst/substrate should resemble the charge-transfer complex paraquat/hydroquinone (both formulas are shown in the preceding paper, see Introduction). In the ligands of type **5** chirality is easily introduced into the oxazoline ring. Ligands **5** contain the same 2-(pyridin-2-yl)oxazoline chelating unit as the ligands of type **6** (Scheme 2), which were

Scheme 2



^[◇] Part 117: H. Brunner, R. Störiko, F. Rominger, *Eur. J. Inorg. Chem.* **1998**, 771–781, preceding paper.

among the first successful chiral nitrogen ligands in enantioselective catalysis^{[4][8]}.

To establish charge-transfer effects in the Rh(I)-catalysed enantioselective hydrosilylation, the catalytic results of the ligands of type **5** were compared with those of similar but less electron-accepting ligands. Obvious differences in the optical yield might originate from a charge-transfer mediated pre-orientation.

Hydrosilylation of 2,5-Dimethoxyacetophenone

2,5-Dimethoxyacetophenone (**1b**) has already been tested in the asymmetric hydrosilylation^[9] and in two recent papers it has been reduced with chiral auxiliaries^{[10][11]}. A standard procedure for the hydrosilylation of 2,5-dimethoxyacetophenone with diphenylsilane was set up^[12], similar to the acetophenone/diphenylsilane system. Since the racemic alcohol **4b** was not well characterised in the literature^[13], it was synthesised by reduction of **1b** with KBH_4 in methanol and spectroscopically characterised. The catalytic intermediates **2b** and **3b** were analysed in situ by ^1H NMR spectroscopy. The silylenol ether **3b** originates from the enol tautomer of **1b** and on hydrolysis reverts to the ketone **1b** (Scheme 1). Hence, it reduces the chemical yield of the chiral alcohol **4b**.

For quantification of the catalytic results three parameters were calculated from the ^1H NMR spectra (80 MHz, CDCl_3), which were recorded for each catalysis (reproducibility about $\pm 5\%$): (i) the amount of silylenol ether **3** in the hydrosilylation product: $3/(2+3)$; (ii) the total degree of hydrosilylation (conversion): $(2+3)/(1+2+3)$ and (iii) the chemical yield of the silylalkyl ether **2**, which on hydrolysis is converted to the chiral product **4**: $(2)/(1+2+3)$. The enantiomeric excess of the alcohol **4** was determined by GC with a Chirasil-DEX CB column (reproducibility $\pm 0.5\%$). The values in the tables were averaged over usually two independent runs, differing in most cases less than 5% (conversion and chemical yield) and 1% (ee), respectively.

To compare the *N'*-methylated ligands **5a–e** with the non-methylated ligands **7a–e** (Scheme 2) each pair was doubly tested in parallel runs. No CCl_4 (see later) was added due to the limited solubility of the ionic compounds **5a–e** in chlorinated solvents. For reaction conditions and results see Table 1.

All the *N'*-methylated ligands **5a–e** induced much higher optical inductions than their non-methylated counterparts **7a–e** (Figure 1). The pair **5c/7c** exhibited the largest difference with an average Δee of about 40%. The degree of hydrosilylation was generally high ($>79\%$), in some cases even quantitative. The amount of silylenol ether scattered around 14–58%.

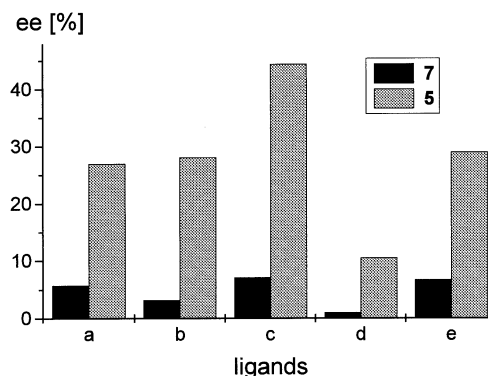
The non-methylated bipyridines **7a** and **7e** performed much better if CCl_4 was added. No silylenol ether was formed and the optical yield increased remarkably (Table 1). This significant increase in asymmetric induction on conducting the hydrosilylation in CCl_4 is known as the CCl_4 effect^{[4][14][15]} and will be referred to later.

Table 1. Hydrosilylation of 2,5-dimethoxyacetophenone with **5a–e**, **7a–e**, **8e**, **9c** and **9e**; reaction time: 90 h (no solvent) or 18 h (in CCl_4); catalyst: 0.23 mol% $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.46 mol% Rh) and 2.3 mol% ligand; substrate/Rh: 214:1

ligand	no of runs	silylenol ether [%]	conversion [%]	chemical yield [%]	ee (config.) [%]
7a	2	26	95 ^[a]	71	5.8 (S)
	2 (+ CCl_4)	0	77	77	38.5 (S)
5a	2	22	86 ^[a]	68	27.0 (S)
7b	2	23	99 ^[a]	77	3.2 (R)
5b	2	34	90 ^[a]	60	28.1 (R)
7c	2	26	100	75	7.1 (R)
5c	2	19	86	70	44.4 (R)
9c	2 (18 h)	11	97 ^[a]	88	46.3 (R)
7d	2	25	100	76	1.0 (S)
5d	2	50	93 ^[a]	47	10.5 (S)
7e	4	21	96 ^[a]	76	6.7 (R)
	2 (+ CCl_4)	0	96 ^[a]	96	52.1 (R)
5e	4	26	91 ^[a]	68	29.0 (R)
8e	2	30	78	55	9.4 (R)
9e	2 (18 h)	12	99 ^[a]	87	44.8 (R)

^[a] No more diphenylsilane detectable by ^1H NMR spectroscopy (80 MHz, CDCl_3).

Figure 1. Comparison of the enantioselectivities of the hydrosilylation of 2,5-dimethoxyacetophenone with the ligands **7a–e** and **5a–e**



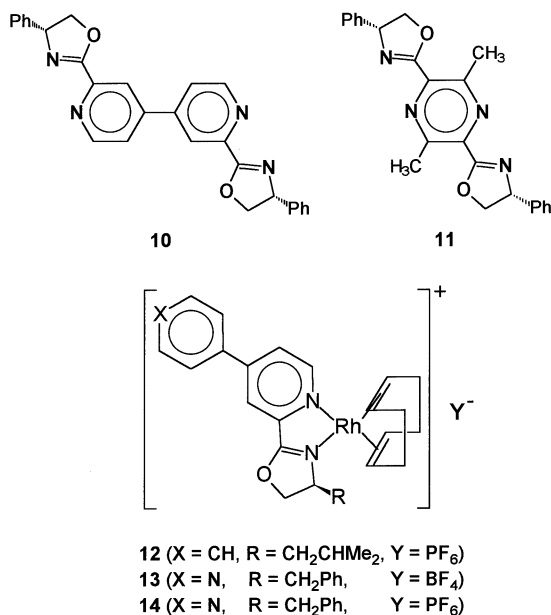
Unexpectedly, the anion exchanged **8e** (hexafluorophosphate instead of iodine in **5e**, Scheme 2) led to a much lower enantioselectivity than **5e** (Table 1), a result which does not fit into the picture of charge-transfer interactions between coordinated ligand and substrate.

The 2-(4-phenylpyridin-2-yl)oxazoline ligands **9c** and **9e** (Scheme 2) are sterically almost identical to **7c** and **7e**, respectively. As they are definitely less electron-attracting than **5c** and **5e**, no charge-transfer effects were expected in the hydrosilylation of 2,5-dimethoxyacetophenone. Surprisingly, both ligands yielded relatively high enantioselectivities (**9c**: 46.3% ee, **9e**: 44.8% ee, Table 1), which are slightly better than the *N'*-methylated ligands **5c** and **5e** and differ markedly from their sterically equivalent 4,4'-bipyridine counterparts **7c** and **7e**. An explanation of these findings might be the free *N'*-position in the ligands **7**. It is known that for the Rh(I)-catalysed hydrosilylation with nitrogen ligands, a ligand excess is beneficial. This points to equilibria involving catalytically active species containing at least two ligand molecules, one of which could be even monodentate^[15]. Only the non-methylated ligands **7** can bind via

their free pyridine' nitrogen and this might result in the low optical yields. Due to the methylation of this nitrogen in **5** and due to the phenyl substituent in **9** the formation of such species is impossible for these ligands.

Also, the bisoxazolines **10** and **11** (Scheme 3) were tested due to their potential charge-transfer properties if coordinated to two Rh-centres. A Rh/ligand ratio of 2:1 was used and CCl₄ was added (no precipitation as with ligands **5a–e** was observed). However, no asymmetric induction was observed with **10** and **11**^[12].

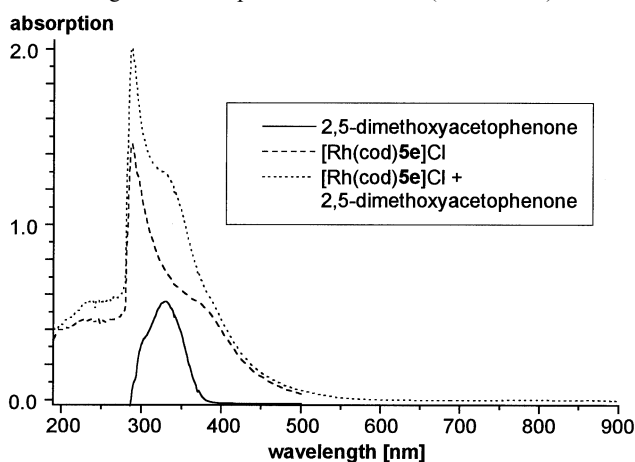
Scheme 3



So far the hydrosilylation results did not provide definitive proof for charge-transfer interactions between coordinated ligand and substrate. Hence, we investigated the absorption behaviour of some presumed catalytic intermediates looking for charge-transfer transitions^[16]. The UV spectra of equally concentrated methanol solutions of 2,5-dimethoxyacetophenone, [Rh(cod)**5e**]Cl (prepared in situ), and [Rh(cod)**5e**]Cl + 2,5-dimethoxyacetophenone (1:1) were recorded. 2,5-Dimethoxyacetophenone showed an absorption maximum at 330 nm in accord with the literature^[17]. [Rh(cod)**5e**]Cl exhibited a maximum at 287 nm and a shoulder at ca. 380 nm. The spectrum of the 1:1 catalyst/substrate mixture was only a superposition of the compounds' single spectra. No charge-transfer transitions were found up to 900 nm (Figure 2).

By substituting the electron-rich 2,5-dimethoxyacetophenone for the much less electron-donating acetophenone (to be described next), charge-transfer interactions should be strongly reduced. However, **5e** used as a cocatalyst in the hydrosilylation of acetophenone gave a higher optical induction than the non-methylated **7e** (17.8% compared to 9.6% ee, similar amounts of silylenol ether and chemical yields under identical conditions)^[12].

All these experiments showed that the desired charge-transfer interactions, if existent at all, had only little influ-

Figure 2. UV-Spectra in methanol (ca. 10^{−5} M)

ence on the catalytic results compared to other effects resulting from the nature of the ligands.

Hydrosilylation of Acetophenone

The new ligands were tested in the hydrosilylation of acetophenone with diphenylsilane in CCl₄. The results of the oxazolines **7a–f** and the bisoxazoline **10** are shown in Table 2. In general good chemical (up to 95%) and optical yields (up to 74% ee) were obtained. In most cases no silylenol ether was formed.

Table 2. Hydrosilylation of acetophenone with **7a–f** and **10**; reaction time: 18 h; catalyst: 0.24 mol% [Rh(cod)Cl]₂ (0.48 mol% Rh) and 2.35 mol% ligand; substrate/Rh: 210:1

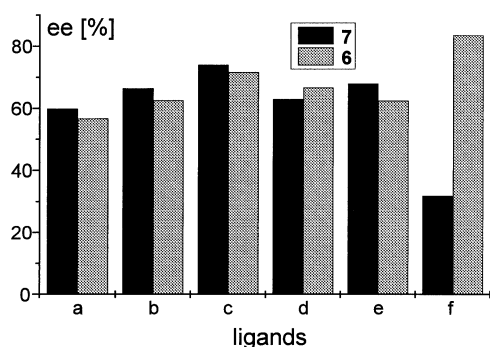
ligand	no of runs (solvent)	silylenol ether [%]	conversion [%]	chemical yield [%]	ee (config.) [%]
7a	2 (CCl ₄)	0	92 ^[a]	92	59.8 (S)
7b	2 (CCl ₄)	0	91 ^[a]	91	66.5 (R)
7c	2 (CCl ₄)	0	94 ^[a]	94	73.9 (R)
7d	2 (CCl ₄)	7	78 ^[a]	70	62.9 (S)
10 ^[b]	2 (CCl ₄)	50	85 ^[a]	42	29.8 (S)
7e	2 (CCl ₄)	0	94 ^[a]	94	67.9 (R)
7e ^[c]	2 (none)	34	98 ^[a]	65	9.6 (R)
7e	1 (C ₆ F ₆)	46	99 ^[a]	53	4.3 (R)
7e	1 (C ₆ HF ₅)	11	96 ^[a]	85	37.1 (R)
7e	1 (Cl ₂ -C=CCl ₂)	49	96 ^[a]	49	racemate
7e	2 (CCl ₃ Br)	—	0	0	—
7f	2 (CCl ₄)	14	81 ^[a]	70	31.8 (R)

^[a] No more diphenylsilane detectable by ¹H NMR spectroscopy (80 MHz, CDCl₃). — ^[b] 1.16 mol% ligand. — ^[c] Reaction time: 90 h.

Figure 3 compares the enantioselectivities obtained with the ligands **7a–f** and the reported values (comparable conditions) of the 2-(pyridin-2-yl)oxazolines **6a–f** (Scheme 1)^[4].

The 2-(4,4'-bipyridin-2-yl)oxazolines **7a–c** and **7e** induced a slightly higher optical induction compared to the corresponding 2-(pyridin-2-yl)oxazolines **6**. Only **7d** and **7f** performed worse than their counterparts **6d** and **6f**. The results with the *tert*-butyl substituted **7f** were surprising, because the enantiomeric excess dropped appreciably with re-

Figure 3. Comparison of the enantioselectivities of the hydrosilylation of acetophenone with the ligands **7a–f** and **6a–f** (values of **6a–f** taken from the literature^[4])



gard to **6f**, which still is the best 2-(pyridin-2-yl)oxazoline for asymmetric hydrosilylation^[4].

With the bisoxazoline **10** less than half the optical yield of its mono-oxazoline equivalent **7d** was obtained (Table 2), while the amount of silylenol ether was more than sevenfold. The pyrazine ligand **11** did not yield any optically active product at all (three double experiments with different concentrations of **11**)^[12].

It is well known, that Rh(I)-catalysed hydrosilylations with nitrogen ligands tend to give higher chemical and, in particular, optical yields in the presence of CCl₄ ("CCl₄ effect")^{[4][14][15]}. So far the highest increase in the asymmetric induction by conducting the catalysis in CCl₄ has been 18.3% ee compared to toluene solution or the solvent-free procedure^[15]. As already mentioned, the bipyridine ligands **7a** and **7e** improved the optical yields in the hydrosilylation of 2,5-dimethoxyacetophenone in CCl₄ by striking 32.7 and 45.4% ee, respectively (Table 1).

Using acetophenone as the prochiral substrate and **7e** as the cocatalyst the optical induction in CCl₄ increased by 58.3% compared to the solvent-free reaction (Table 2). Therefore, we studied the hydrosilylation of acetophenone using the ligand **7e** in other polyhalide solvents (Table 2). None of these solvents increased the enantioselectivity compared to CCl₄. Replacing hexafluorobenzene by pentafluorobenzene the content of silylenol ether decreased from 46 to 11%, while the optical yield increased from 4.3 to 37.1%. In perchloroethylene only racemic alcohol was produced, whereas CCl₃Br totally inhibited the hydrosilylation. This inhibition had been reported for similar reactions^[14] and explained by an oxidative addition of CCl₃Br to Rh(I) yielding a catalytically inactive Rh(III)-species.

The activity of in situ catalysts consisting of [Rh(cod)Cl]₂ and the 2-(4-phenylpyridin-2-yl)oxazolines **9c** and **9e** depended on the stage, when the additive CCl₄ came into play (Table 3). If the in situ catalyst (always easily recognised by its red colour) was prepared in the presence of CCl₄, no hydrosilylation activity was observed. If the in situ catalyst was prepared in acetophenone and CCl₄ was added later together with the diphenylsilane, smooth reaction took place as usual.

Since the Rh-complex **12** (Scheme 3), containing **9c** as the ligand, had been synthesised (preceding paper), it was tested in three different catalytic runs (Table 3). **12** proved to be a poor catalyst with respect to the chemical and optical yield. However, by adding a fourfold amount of ligand establishing the Rh/ligand ratio of 1:5, a catalytic system resulted, which formed almost no silylenol ether and which gave 74.8% ee, exceeding the asymmetric induction of the in situ system (70.5% ee) to some extent.

Table 3. Hydrosilylation of acetophenone with the ligands **9c**, **9e** and the complexes **12–14**; reaction time: 18 h (if not otherwise stated); 0.48 mol% Rh; substrate/Rh: 210:1

catalytic system	no of runs (solvent)	silylenol ether [%]	conversion [%]	chemical yield [%]	ee (config.) [%]
[Rh(cod)Cl] ₂ + 2.35 mol% 9e	1 (none)	13	99 ^[a]	86	54.9 (R)
[Rh(cod)Cl] ₂ + 2.35 mol% 9e	3 (CCl ₄ from the beginning)	—	0, 0 ^[b]	0, 0 ^[b]	—
[Rh(cod)Cl] ₂ + 2.35 mol% 9e	1 (CCl ₄ added with H ₂ SiPh ₂)	0	93 ^[a]	93	64.2 (R)
[Rh(cod)Cl] ₂ + 2.35 mol% 9c	2 (none)	22	100	78	45.0 (R)
[Rh(cod)Cl] ₂ + 2.35 mol% 9c	1 (CCl ₄ from the beginning)	—	0	0	—
[Rh(cod)Cl] ₂ + 2.35 mol% 9c	1 (CCl ₄ added with H ₂ SiPh ₂)	5	95 ^[a]	90	70.5 (R)
12 ^[c]	1 (CCl ₄ from the beginning)	62	96 ^[a]	36	2.9 (R)
12 ^[c]	1 (CCl ₄ added with H ₂ SiPh ₂)	76	92 ^[a]	22	2.6 (R)
12 + 1.9 mol% 9c ^[d]	2 (CCl ₄ added with H ₂ SiPh ₂)	2	84	83	74.8 (R)
13	1 (CCl ₄) ^[c]	17	81 ^[a]	68	33.6 (R)
	1 (CCl ₄) ^[d]	29	86 ^[a]	61	34.6 (R)
14	2 (CCl ₄) ^[d]	25	74 ^[a]	57	14.4 (R)
14 + 1.9 mol% 7e	2 (CCl ₄) ^[c]	0	85	85	66.2 (R)

^[a] No more diphenylsilane detectable by ¹H NMR spectroscopy (80 MHz, CDCl₃). — ^[b] After 90 h. — ^[c] Reaction time: 66 h. —

^[d] Reaction time: 42 h.

All these results show that the inhibition of the catalyst by CCl_4 is only possible during its formation. Once the catalyst is formed, CCl_4 cannot inhibit its activity. Instead, it leads to a lower amount of silylenol ether and a higher enantioselectivity compared to the hydrosilylation without CCl_4 (Table 3). The "inertness" of the prepared Rh(I)-complex **12** towards CCl_4 was also proven by recording ^1H NMR spectra of **12** in CDCl_3 before and after adding 25 vol% of CCl_4 . Even 24 h after the addition no changes of the original spectrum were evident.

Two other Rh(I)-complexes **13** and **14** (Scheme 3) were tested in the hydrosilylation of acetophenone (Table 3). Although they only differ in the nature of their anion, the BF_4 -complex **13** gave a much higher optical yield than the PF_6 -complex **14**. The enantioselectivities of these complexes (Rh/ligand ratio: 1:1) are quite low compared to the in situ catalysts (Rh/ligand ratio: 1:5). In line with this, addition of a fourfold excess of **7e** to **14** resulted in similar chemical and optical yields as the in situ catalyst of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and **7e** (Tables 3 and 2).

We thank the *Fonds der Chemischen Industrie* for providing a *Kekulé* scholarship for R.S. and for financial support.

Experimental Section

Chromatography: Merck silica gel 60 (63–200 mesh). – Elemental analysis: Microanalytical Laboratory, University of Regensburg. – ^1H / ^{13}C NMR: Bruker AW-80 (80 MHz, $T = 31^\circ\text{C}$) and AC-250 (250 / 62.9 MHz, $T = 24^\circ\text{C}$), TMS as internal standard. – MS: Finnigan MAT 311 A (EI, 70 eV). – IR: Beckman IR 4240 (film between NaCl plates), only characteristic bands are listed. – UV/Vis: Kontron Instruments Spectrophotometer UVIKON 922. – All liquids were distilled and stored under argon. – η^4 -1,5-Cyclooctadiene = cod.

Asymmetric Hydrosilylation of 2,5-Dimethoxyacetophenone: 8 mg (0.016 mmol) of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.032 mmol Rh) and ligand (0.16 mmol, if not otherwise stated) were dissolved in 2,5-dimethoxyacetophenone (1.1 ml, 7.0 mmol) under argon. Eventually, 1.7 ml of CCl_4 were added and the solution was stirred at r. t. for 30 min. After cooling to 0°C for at least 30 min diphenylsilane (1.3 ml, 7.0 mmol) was added and stirring in the ice bath, which was warming-up, continued for the period quoted.

To determine the amount of silylenol ether, the degree of hydrosilylation and the chemical yield, a sample was taken and a ^1H NMR spectrum (CDCl_3 , 80 MHz) recorded. The following integrals were used: $\delta = 5.43$ (s, SiH) and 5.36 (q, CH) together (silylalkyl ether I_A), $\delta = 5.10$ and 4.77 (2 d, CH_2) together (silylenol ether I_E), and $\delta = 2.60$ (s, CH_3 , 2,5-dimethoxyacetophenone I_{DMAP}). Calculations: silylenol ether [%] = $[I_E / (I_A + I_E)] \cdot 100$, conversion [%] = $[(3 I_E + 3 I_A) / (3 I_A + 3 I_E + 2 I_{\text{DMAP}})] \cdot 100$, and chemical yield [%] = $[3 I_A / (3 I_A + 3 I_E + 2 I_{\text{DMAP}})] \cdot 100$.

Hydrolysis was performed by adding methanol (8 ml) and a few crystals of *p*-TosOH. After stirring at r. t. for 30 min the solvents were evaporated. Ca. 0.1 ml of the residue were purified by chromatography (4–5 cm SiO_2 in a Pasteur pipette) with CH_2Cl_2 as eluent ($R_f = 0.12$). The first fraction (ca. 3 ml) was discarded, the following 10 ml were collected and evaporated. The enantiomeric excess was determined by injecting 0.4 μl of a solution of the resulting oil (1–2 drops) in 1 ml of CH_2Cl_2 (Merck Uvasol®) into a Fisons 8130 gas chromatograph. Column: Chrompack Chirasil-DEX CB

($l = 25$ m, $\phi = 0.25$ mm), integrator: Varian 4290, retention times (160°C): 8.6–8.8 min [(*R*)-1-(2,5-dimethoxyphenyl)ethanol] and 9.2–9.4 min [(*S*)-1-(2,5-dimethoxyphenyl)ethanol].

1-(2,5-Dimethoxyphenyl)ethyl Diphenylsilyl Ether (2b). – ^1H NMR (250 MHz, CDCl_3): $\delta = 1.45$ (d, $^3J = 6.2$ Hz, 3 H, CH_3), 3.65 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3'), 5.36 (q, $^3J = 6.2$ Hz, 1 H, CHCH_3), 5.43 (s, 1 H, SiH), 6.71 / 6.72 / 7.19 (3 m, 3 H, H-3, H-4, H-6), 7.29–7.45 (m, 6 H, Ph-H), 7.56–7.65 (m, 4 H, Ph-H).

1-(2,5-Dimethoxyphenyl)ethenyl Diphenylsilyl Ether (3b)^[18]. – ^1H NMR (250 MHz, CDCl_3): $\delta = 3.69$ (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3'), 4.77 (d, $^2J = 1.2$ Hz, 1 H, $\text{C}=\text{CHH}'$), 5.10 (d, $^2J = 1.2$ Hz, 1 H, $\text{C}=\text{CHH}'$), 5.64 (s, 1 H, SiH), 6.79–6.81 (m, 2 H, Ar-H), 7.15 (m, 1 H, Ar-H), 7.27–7.49 and 7.52–7.71 (m, 10 H, Ph-H).

rac-1-(2,5-Dimethoxyphenyl)ethanol (4b): 2,5-Dimethoxyacetophenone (1.5 ml, 9.5 mmol) and KBH_4 (800 mg, 14.8 mmol) in dry methanol (10 ml) were stirred for 15 h. After acidifying with 2 N HCl (10 ml) the solution was extracted with ether (3×10 ml). The combined organic layers were washed with water (10 ml) and brine (10 ml), and dried over MgSO_4 . Evaporation of the solvent yielded 1.73 g (100%) of the oily alcohol **4b**. – ^1H NMR (250 MHz, CDCl_3): $\delta = 1.48$ (d, $^3J = 6.4$ Hz, 3 H, CH_3), 2.76 (d, $^3J = 4.8$ Hz, 1 H, OH), 3.76 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3'), 5.05 (dq, $^3J = 6.4$ Hz, $^3J = 4.8$ Hz, 1 H, CH_3CHOH), 6.74 (dd, $^3J = 8.7$ Hz, $^4J = 2.8$ Hz, 1 H, H-4), 6.79 (dd, $^3J = 8.7$ Hz, $^5J = 0.8$ Hz, 1 H, H-3), 6.94 (dd, $^4J = 2.8$ Hz, $^5J = 0.8$ Hz, 1 H, H-6). – ^{13}C NMR (62.9 MHz, CDCl_3): $\delta = 23.1$ (CH_3), 55.8 and 55.9 (OCH_3), 66.4 (CHOH), 111.6 / 112.4 / 112.5 (C-3, C-4, C-6), 134.9 (C-1), 150.7 (C-2), 154.0 (C-5). – MS (EI): m/z (%) = 182 (100) [M^+], 167 (95) [$\text{M}^+ - \text{CH}_3$], 152 (24), 139 (88), 137 (32), 124 (33), 43 (29). – IR (film): $\tilde{\nu}$ (cm^{-1}) = 3400 s (O–H), 2960/2945 s (C–H), 2830 s (OC–H), 1275/1210/1070/1045/1020 s (C–O). – $\text{C}_{10}\text{H}_{14}\text{O}_3$ (182.22): calcd. C 65.91, H 7.74; found C 65.64, H 7.81.

Asymmetric Hydrosilylation of Acetophenone: 10 mg (0.02 mmol) of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.04 mmol Rh) and ligand (0.2 mmol, if not otherwise stated) were dissolved in acetophenone (1.0 ml, 8.5 mmol) under argon. Usually, 2.0 ml of CCl_4 were added and the solution was stirred at r. t. for 30 min. After cooling to 0°C for at least 30 min diphenylsilane (1.6 ml, 8.6 mmol) was added and stirring in the ice bath, which was warming-up, continued for the period quoted.

To determine the amount of silylenol ether, the degree of hydrosilylation and the chemical yield, a sample was taken and a ^1H NMR (CDCl_3 , 80 MHz) recorded. The following integrals were used: $\delta = 5.70$ ppm (s, SiH, silylenol ether I_E), $\delta = 5.40$ (s, SiH, silylalkyl ether I_A), and $\delta = 2.50$ (s, CH_3 , acetophenone I_{AP}). Calculations: silylenol ether [%] = $[I_E / (I_A + I_E)] \cdot 100$, conversion [%] = $[(3 I_E + 3 I_A) / (3 I_A + 3 I_E + I_{\text{AP}})] \cdot 100$, and chemical yield [%] = $[3 I_A / (3 I_A + 3 I_E + I_{\text{AP}})] \cdot 100$.

Hydrolysis was performed by adding methanol (10 ml) and a few crystals of *p*-TosOH. After stirring at r. t. for 30 min the solvents were evaporated and the residue was distilled in a kugelrohr apparatus at 100 – 120°C / ca. 1 Torr. The enantiomeric excess was determined by injecting 0.4 μl of a solution of the distillate (3–4 drops) in 1 ml of CH_2Cl_2 (Merck Uvasol®) into a Fisons 8130 gas chromatograph. Column: Chrompack Chirasil-DEX CB ($l = 25$ m, $\phi = 0.25$ mm), integrator: Varian 4290, retention times (118°C): 7.3–7.7 min [(*R*)-1-phenylethanol] and 8.0–8.3 min [(*S*)-1-phenylethanol].

★ Dedicated to Professor H. Nöth on the occasion of his 70th birthday.

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