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

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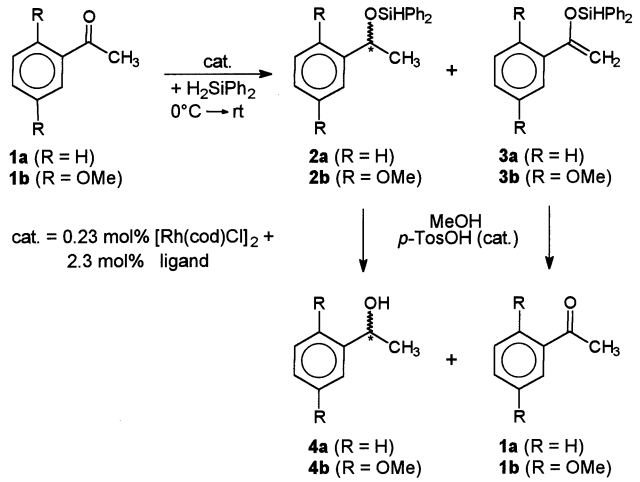
Novel *N*′-methylated 2-(oxazolin-2-yl)-4,4′-bipyridinium salts, bearing a chiral oxazoline moiety, were tested in the Rh(I)-catalysed enantioselective hydrosilylation. After coordination to rhodium these electron-attracting ligands are supposed to exhibit charge-transfer effects with electron-donating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

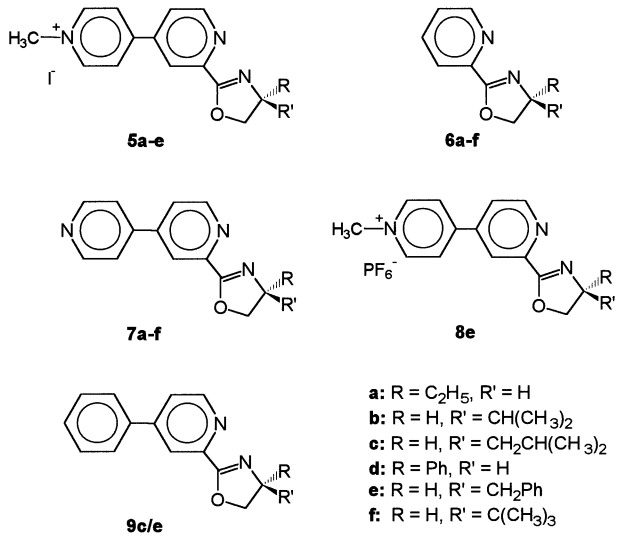
In the Rh(I)-catalysed enantioselective hydrosilylation of prochiral ketones, the substrate (e.g. acetophenone **1a**) reacts with diphenylsilane to yield the chiral silylalkyl ether **2a** (Scheme 1)[1][2][3]. After hydrolysis the chiral 1-phenylethanol **4a** is obtained. Asymmetric induction is brought 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



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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 ±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 ±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%.

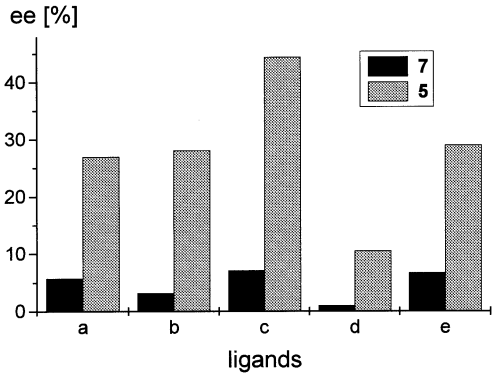
The non-methylated bipyridines **7a** and **7e** performed much better if CCl_4 was added. No silylenol ether was formed and the optical yield increased remarkably (Table 1). This significant increase in asymmetric induction on conducting the hydrosilylation in CCl_4 is known as the CCl_4 effect[4][14][15] 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% $[Rh(cod)Cl]_2$ (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**



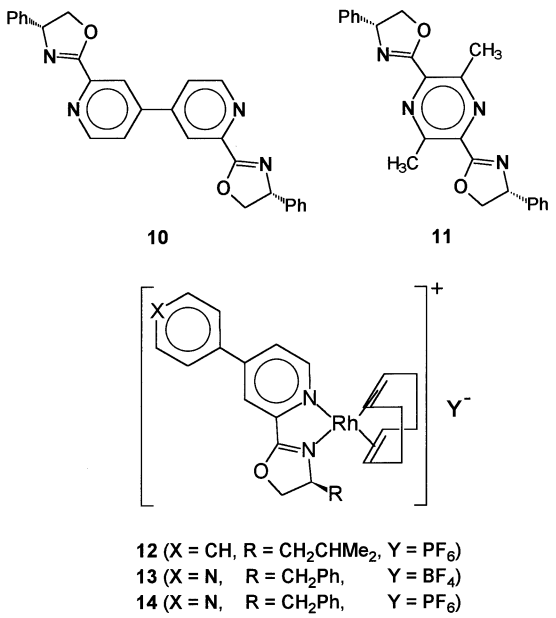
Unexpectedly, the anion exchanged **8e** (hexafluorophosphate instead of iodine in **5e**, Scheme 2) led to a much lower enantioselectivity than **5e** (Table 1), a result which does not fit into the picture of charge-transfer interactions between coordinated ligand and substrate.

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 CCl_4 was added (no precipitation as with ligands **5a−e** was observed). However, no asymmetric induction was observed with **10** and **11**[12].

Scheme 3



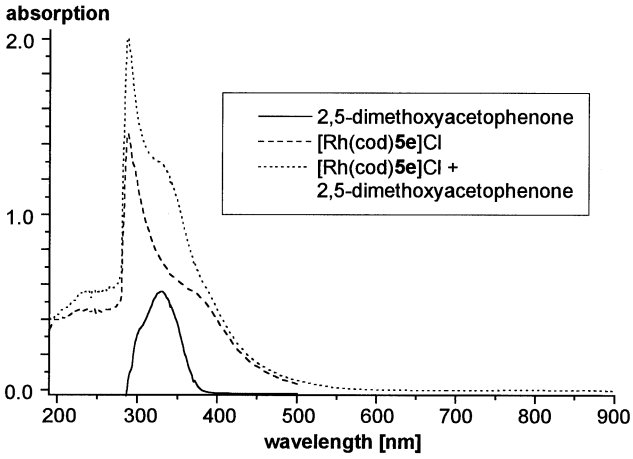
12 (X = CH, R = CH_2CHMe_2, Y = PF_6)
13 (X = N, R = CH_2Ph, Y = BF_4)
14 (X = N, R = CH_2Ph, Y = PF_6)

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

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



Hydrosilylation of Acetophenone

The new ligands were tested in the hydrosilylation of acetophenone with diphenylsilane in CCl_4. 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

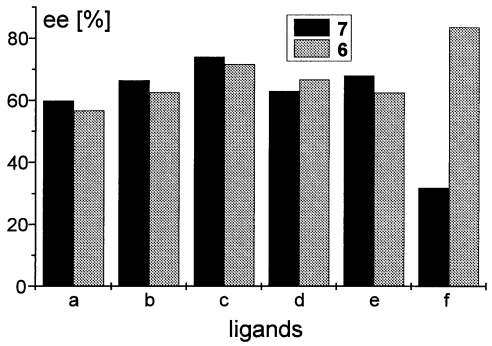
ligand	no of runs (solvent)	silylenol ether [%]	conversion [%]	chemical yield [%]	ee (*config.*) [%]
7a	2 (CCl_4)	0	92[a]	92	59.8 (*S*)
7b	2 (CCl_4)	0	91[a]	91	66.5 (*R*)
7c	2 (CCl_4)	0	94[a]	94	73.9 (*R*)
7d	2 (CCl_4)	7	78[a]	70	62.9 (*S*)
10[b]	2 (CCl_4)	50	85[a]	42	29.8 (*S*)
7e	2 (CCl_4)	0	94[a]	94	67.9 (*R*)
7e[c]	2 (none)	34	98[a]	65	9.6 (*R*)
7e	1 (C_6F_6)	46	99[a]	53	4.3 (*R*)
7e	1 (C_6HF_5)	11	96[a]	85	37.1 (*R*)
7e	1 (Cl_2-C=CCl_2)	49	96[a]	49	*racemate*
7e	2 (CCl_3Br)	–	0	0	–
7f	2 (CCl_4)	14	81[a]	70	31.8 (*R*)

[a] No more diphenylsilane detectable by ^1H NMR spectroscopy (80 MHz, $CDCl_3$). – [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 CCl_4 ("CCl_4 effect")[4][14][15]. So far the highest increase in the asymmetric induction by conducting the catalysis in CCl_4 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 CCl_4 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 CCl_4 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 CCl_4. 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 CCl_3Br totally inhibited the hydrosilylation. This inhibition had been reported for similar reactions[14] and explained by an oxidative addition of CCl_3Br 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 CCl_4 came into play (Table 3). If the in situ catalyst (always easily recognised by its red colour) was prepared in the presence of CCl_4, no hydrosilylation activity was observed. If the in situ catalyst was prepared in acetophenone and CCl_4 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_2SiPh_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**	(CCl_4 from1 the beginning)	−	0	0	−	
$[Rh(cod)Cl]_2$ + 2.35 mol% **9c**	1 (CCl_4 added with H_2SiPh_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_2SiPh_2)	76	92[a]	22	2.6	(*R*)
12 + 1.9 mol% **9c**[d]	2 (CCl_4 added with H_2SiPh_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, $CDCl_3$). − [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 $[Rh(cod)Cl]_2$ 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°C) and AC-250 (250 / 62.9 MHz, T = 24°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 $[Rh(cod)Cl]_2$ (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: δ = 5.43 (s, Si*H*) and 5.36 (q, C*H*) together (silylalkyl ether I_A), δ = 5.10 and 4.77 (2 d, CH_2) together (silylenol ether I_E), and δ = 2.60 (s, CH_3, 2,5-dimethoxyacetophenone I_{DMAP}). Calculations: silylenol ether [%] = $[I_E/(I_A + I_E)]\cdot 100$, conversion [%] = $[(3\ I_E + 3\ I_A)/(3\ I_A + 3\ I_E + 2\ I_{DMAP})]\cdot 100$, and chemical yield [%] = $[3I_A/(3I_A + 3I_E + 2I_{DMAP})]\cdot 100$.

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, ⊘ = 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, $CDCl_3$): δ = 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, Si*H*), 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, $CDCl_3$): δ = 3.69 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3'), 4.77 (d, ^2J = 1.2 Hz, 1 H, C=C*H*H′), 5.10 (d, ^2J = 1.2 Hz, 1 H, C=CH*H*′), 5.64 (s, 1 H, Si*H*), 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, $CDCl_3$): δ = 1.48 (d, ^3J = 6.4 Hz, 3 H, CH_3), 2.76 (d, ^3J = 4.8 Hz, 1 H, O*H*), 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, $CDCl_3$): δ = 23.1 (CH_3), 55.8 and 55.9 (OCH_3), 66.4 (*C*HOH), 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) [$M^+ - CH_3$], 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). − $C_{10}H_{14}O_3$ (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 $[Rh(cod)Cl]_2$ (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: δ = 5.70 ppm (s, Si*H*, silylenol ether I_E), δ = 5.40 (s, Si*H*, silylalkyl ether I_A), and δ = 2.50 (s, CH_3, acetophenone I_{AP}). Calculations: silylenol ether [%] = $[I_E/(I_A + I_E)]\cdot 100$, conversion [%] = $[(3\ I_E + 3\ I_A)/(3\ I_A + 3\ I_E + I_{AP})]\cdot 100$, and chemical yield [%] = $[3\ I_A/(3\ I_A + 3\ I_E + I_{AP})]\cdot 100$.

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, & osol; = 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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