Catalytic Enantioselective Hydrosilylation of Ketones with Rhodium-Phosphite Complexes Containing a TADDOLate and a Dihydrooxazole Unit

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New types of chiral phosphorus/nitrogen ligands, capable of forming six-membered-ring metal chelates have been prepared from $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,2-dioxolane-4,5-dimethanols (TADDOLs), PCl_3, and dihydrooxazole alcohols (from amino acids) (**7** in *Scheme 1*). The X-ray crystal structure of a Rh complex of one of these ligands, **8b**, has been determined (*Scheme 2* and *Fig.*). Enantioselective hydrosilylations of dialkyl and aryl alkyl ketones with $Ph_2SiH_2/0.01$ equiv. $Rh^I \cdot$ **7** have been studied and found to provide secondary alcohols in enantiomer ratios of up to 97 : 3 (*Scheme 3* and *Table*). The ligand prepared from (R,R)-TADDOL and the (R)-valine-derived (R)-α,α-dimethyl-4-isopropyl-4,5-dihydrooxazole-2-methanol gives better results than the (R,R,S)-isomer (**7d** *vs.* **7c** in *Scheme 3*), and an i-Pr group on the 4,5-dihydrooxazole ring gives rise to a slightly better selectivity than a Ph group. With the (R,R,R)-ligands the hydrogen transfer occurs from the *Re* face of the oxo groups (*Scheme 4*).

1. Introduction. – Since we first described the use [1] and preparation [2] of a $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,2-dioxolane-4,5-dimethanol (TADDOL) **1**, there have been numerous applications of such ligands in stoichiometric, catalytic, and *Lewis*-acid-mediated enantioselective reactions [3]. In the beginning, we focused mainly on the use of the alkoxide oxygens for complexing polar metals such as alkali, alkaline-earth, and early-transition metals, especially titanium. More recently, a considerable effort has been undertaken to replace the OH groups of TADDOLs with other heteroatoms, such as nitrogen and sulfur [4] [5], in order to effect coordination to late-transition metals like copper. Thus, nitrogen- and sulfur-containing ligands have been successfully applied in the copper-catalyzed addition of *Grignard* reagents to cyclic enones [6].

The preparation of cyclic monodentate phosphonites and phosphites, derived from TADDOL, appeared to be a promising approach for creating chiral coordination spheres for late-transition metals such as Rh or Pd. The preparation of the first examples of this class of compounds **2** (R′ = aryl, aryloxy) and their application to Rh^I-catalyzed enantioselective reactions have been described previously [7]. Also, the combination with chiral alcohols and amines (R′ in **2**) led to ligands which were used in conjugate additions of Et_2Zn to α,β-unsaturated carbonyl compounds [8]. However, it is well-known that enantioselective catalysis is generally more efficient with bidentate than with monodentate ligands (for reviews, see [9]). Unfortunately, the C_2-symmetric bis(diphenylphosphinite) **3** of TADDOL was found to be unstable and could only be characterized as the borane adduct or the $PdCl_2$ complex [10]. The latter, on the other

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hand, gave quite good enantioselectivities in 1,3-diphenylallylations of nucleophiles [10]. Replacement of one or both of the TADDOL OH groups by PR_2, to give a TADDOL-based analog of 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthalene (BINAP) has so far not been achieved [11][2]).

Following an approach chosen by *Pfaltz* and co-workers, who have developed a new class of bidentate ligands **4** derived from 1,1′-binaphthalene-2,2′-diol (BINOL) and chiral dihydrooxazole alcohols for Pd-catalyzed allylic substitutions and for conjugate additions [13], we have now prepared analogous chelating P,N ligands from the much cheaper TADDOL. In this paper, we describe, in full detail, the preparation and the first successful application of this new type of ligands.
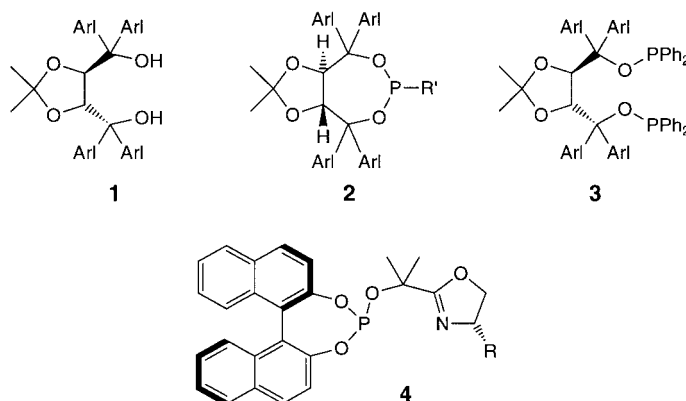

2. Synthesis of the Ligands derived from TADDOL and Chiral Dihydrooxazoles. – By the strategy described for the BINOL-derived ligands **4** [13], a number of enantiomerically pure dihydrooxazole alcohols **6** were easily obtained *via* thermally induced condensation of a chiral amino alcohol with 2-hydroxy-2-methylpropanoic acid, followed by azeotropic removal of H_2O formed [14]. The ligands **7** were then prepared in a one-pot procedure, in which the first step involved addition of TADDOL **1** to a solution of PCl_3 ($-30°$, 2 equiv. Et_3N, CH_2Cl_2) to form the chloro phosphonite **5** (^{31}P-NMR shift δ 148 ppm), which, in turn, was combined *in situ* with the corresponding dihydrooxazole alcohol **6** (in the presence of a fivefold excess of Et_3N). The phosphites **7** were obtained as colorless powders after aqueous workup and purification by chromatography on silica gel. The pure samples are stable towards air and moisture and can be stored in an O_2-containing atmosphere. The preparation of **7** with Ph- and i-Pr-substituted dihydrooxazoles is summarized in *Scheme 1*.

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[2])   Attempts included: *1*) tosylation of **1** with or without added $AgNO_3$, followed by treatment with $HPEt_2$ or $LiPR_2$; *2*) replacement of the OH group in **1** with halogens (F, Cl, Br), followed by treatment with $LiPR_2$ (R = H, Et); *3*) reaction of the dichloro compound with PH_3 in an autoclave at various temperatures and pressures (up to 200 bar), and in the presence of tertiary amines or *Lewis* acids; *4*) reaction of dihalo derivatives with *Rieke* magnesium and XPR_2; and *5*) treatment of the sulfite derivative of TADDOL with an oxidizing agent ($RuCl_3/NaIO_4$, or *m*-chloroperbenzoic acid (*m*CPBA)) did not afford the expected sulfate, which would have been expected to react with phosphines and BuLi to give the target structure (*cf.* the preparation of the DUPHOS ligands [12]).

Scheme 1
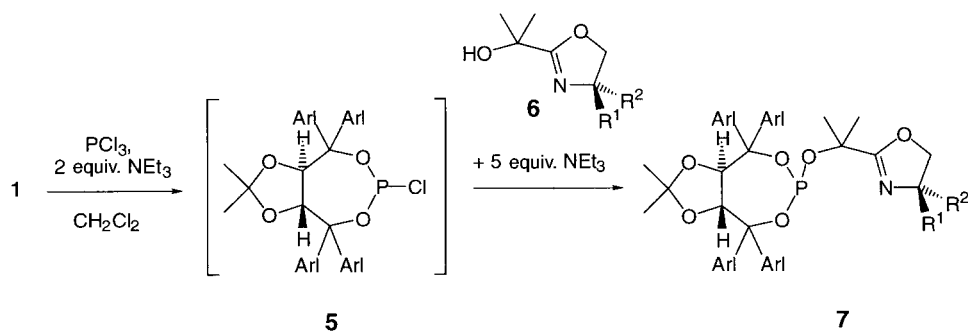
Entry	Product	Arl	R^1	R^2	Yield [%]
1	**7a**	Ph	H	Ph	29^a)
2	**7b**	Ph	Ph	H	66
3	**7c**	Ph	H	i-Pr	63
4	**7d**	Ph	i-Pr	H	68
5	**7e**	β-Np^b)	i-Pr	H	48

^{a}) Reaction carried out with only 1 equiv. of NEt$_3$ in the second step. ^{b}) β-Np = Naphthalen-2-yl.

3. Structural Investigations. – The knowledge of the exact structure of a coordinating ligand, particularly when bound to the metal, is a valuable hint for its further structural evolution. As none of the phosphites **7** showed any tendency to crystallize from any of the solvents tested, we prepared two representative cationic Rh^I complexes by adding a solution of [Rh(cod)Cl]$_2$ (cod = cycloocta-1,5-diene) in CH$_2$Cl$_2$ to the corresponding ligand. Exchange of Cl$^-$ for PF$_6^-$ gave the yellow complexes **8** in *ca.* 90% yield (*Scheme 2*). The complexation was evident from the ^{31}P-NMR spectra of **8**: the P-atom of the ligand couples with ^{103}Rh, giving rise to a *doublet* (^1J(P,Rh) = 255 and 265 Hz, resp.) at a lower chemical shift ($\delta = 103$ and 108 *vs. ca.* 135 ppm).

Scheme 2

8a R^1 = H, R^2 = i-Pr

8b R^1 = i-Pr, R^2 = H
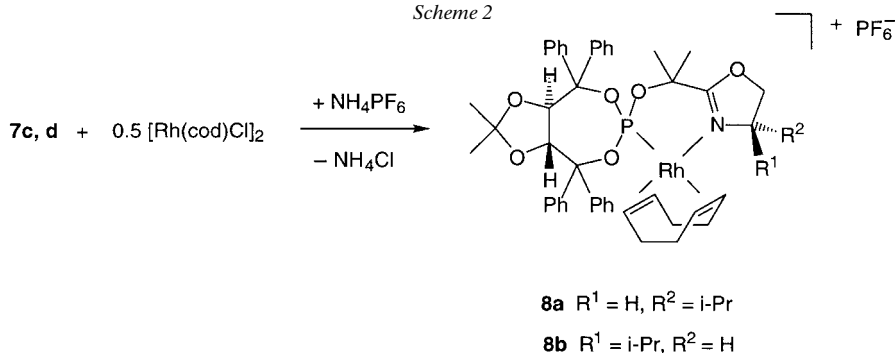
Slow evaporation of a CHCl$_3$ solution of **8b** yielded yellow needles suitable for X-ray crystal-structure determination. The crystals contained **8b** and CHCl$_3$ (not included in the *Fig.*) in a 1:1 ratio.
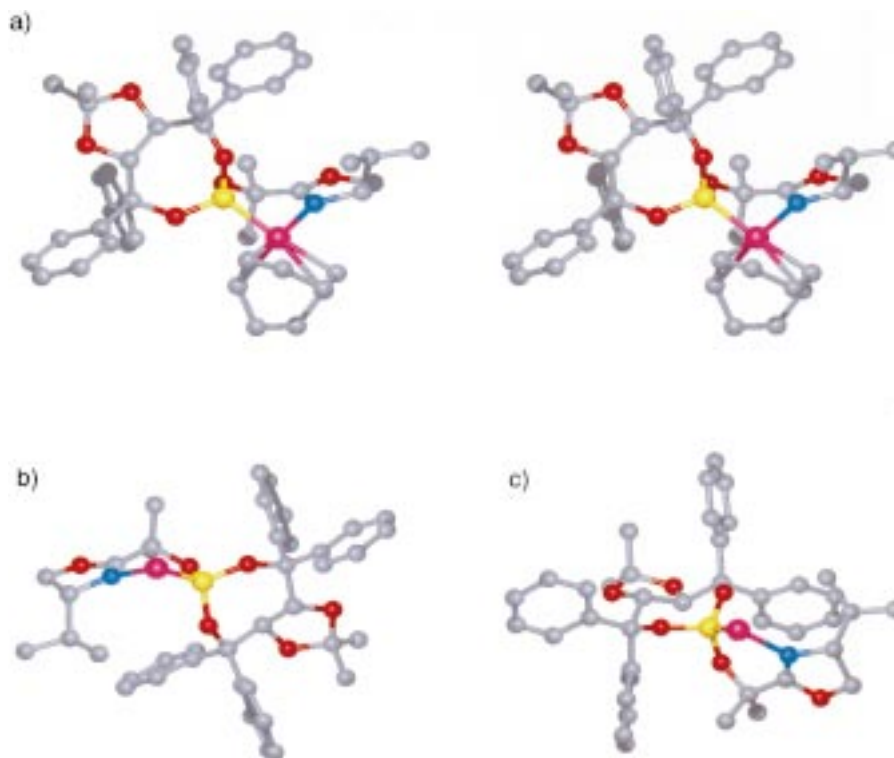
Figure. *X-Ray structure of the Rh^I complex* **8b** · *CHCl₃.* H-Atoms, the hexafluorophospate counterion, and CHCl₃ have been omitted for clarity; C-atoms in grey, N-atoms in blue, O-atoms in red, P-atoms in yellow, and Rh-atoms in pink. The structure was determined by PD Dr. *V. Gramlich*. The presentations were generated with the MolMol program [15] and ray-traced by POV-Ray. The adjacent *quasi*-equatorial Ph substituent forces the i-Pr group to present itself towards the Rh-center like a *t*-Bu group. *a*) Stereo representation of **8b**. *b*) The chelating part of the ligand and the Rh-center form a six-membered ring, in which the atoms Rh, P, O, C, C, N adopt a boat conformation. *c*) This view reveals the envelope conformation (O-atom out of plane) of the dioxolane ring and a chair-type conformation of the seven-membered ring formed by four C- and two O-atoms of the tetraphenylerythritol moiety and the P-atom; the *quasi*-equatorial and *quasi*-axial disposition of the Ph groups on this seven-membered ring is prototypal for TADDOLs and their metal complexes [16].

The TADDOL part adopts the typical conformation with the dioxolane ring as an envelope (the O-atom out of plane) and the Ph substituents in *quasi*-equatorial and *quasi*-axial positions on the seven-membered ring formed by the C−C bonds of the acetal ring and the two diphenylmethylene groups connected *via* the O−P−O bridge. Interestingly, the two Me groups of the i-Pr moiety on the dihydrooxazole ring point in the same direction as one of the Ph rings of the adjacent diphenylmethylene group, thus shielding the Rh-atom in this half-space; the metal center is more readily accessible from the other half-space. This might be the reason for the better performance of the ligand **7d** with (*R*)-configuration on the dihydrooxazole ring, as compared to its 'mismatched' diastereoisomer, in the enantioselective hydrosilylations described in *Chapt. 4*. Unfortunately, we did not succeed in obtaining crystals of complex **8a** suitable for X-ray analysis, thus a direct comparison of the two diastereoisomeric structures is not possible.

4. Catalytic Enantioselective Hydrosilylation of Ketones. – We first turned our attention to the enantioselectively catalyzed reductions of ketones by hydrosilylations. This is a typical reaction for the exploration of the potential of a chiral ligand in late-transition-metal-catalyzed reactions, and it has been studied previously by several groups[3]). The asymmetric reduction of simple ketones can also be achieved with impressive levels of enantioselectivity *via* other catalytic[4]) or stoichiometric[5]) transformations. Thus, only highly effective catalytic processes can possibly compete with known techniques.

With our test substrate for Rh[I]-catalyzed hydrosilylations, acetophenone (**9**), and 0.1 mol-% of the complex prepared *in situ* from [Rh(cod)Cl]$_2$ and the ligand **7d**, the product of reduction, 1-phenylethanol (**10**), was obtained in an enantiomer ratio of 94:6.

Our optimization experiments with the acetophenone (**9**) reduction revealed the following. *i*) A Rh/ligand ratio of 1:1.2 is sufficient for obtaining the highest enantioselectivity[6]). *ii*) At 0°, a reaction time of *ca.* 24 h is sufficient for complete conversion with 1 mol-% catalyst (sampling and ^{1}H-NMR analysis). *iii*) The stereogenic centers of (*R,R*)-TADDOL, and (*R*)- or (*S*)-dihydrooxazole give rise to two diastereoisomeric ligands **7**, the configuration of the product **10**, however, is mainly determined by the configuration of the dihydrooxazole moiety (*cf. Entries 1* with *2*, and *3* with *4* in *Scheme 3*). Still, the TADDOL part exhibits a significant effect (83 *vs.* 93% enantioselectivity; see *Entries 3* and *4*). Thus, the (*R,R*)-TADDOL/(*R*)-dihydrooxazole combination represents what is often dubbed the 'matched case'. The ligand **7d** with an i-Pr substituent on the dihydrooxazole ring (*Entry 4*) gave a slightly better enantioselectivity of 93% than did **7b**, which bears a Ph substituent (91%, *Entry 2*). *iv*) In contrast to the results obtained with monodentate phosphites derived from TADDOL [7], replacement of the Ph by naphthalen-2-yl groups in the diarylmethoxy positions (ligand **7e**) led to a decrease of selectivity (*Entry 5*)[7]). *v*) The temperature-dependence is rather small: at lower temperature a slightly better enantioselectivity was observed[8]), while, at ambient temperature, the enantioselectivity was poorest, and, furthermore, 5% of silylenol ether was formed as a by-product (detected by ^{1}H-NMR spectroscopy)[9]). *vi*) Using toluene as solvent gave slightly higher enantiomer ratios, as

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[3]) For reviews, see [17].

[4]) *Cf.* the borane reduction catalyzed by chiral oxaborolidines (*Corey-Itsuno* method [18a]; for reviews, see [18b]), which usually requires 10 mol-% of an amino-acid-derived amino alcohol.

[5]) Stoichiometric chiral reducing reagents have also been used successfully, in particular BINAL-H by *Noyori et al.* [19] and LiAlH(OEt)-TADDOLate by our group [20a] (for a comparison of TADDOLates and BINOLates, see [20b]). However, these methods require at least a two-fold excess of the chiral reducing agent.

[6]) Using a five-fold amount of ligand, as it is common with nitrogen-only ligands [17], gave neither better selectivities nor improved yields under the standard conditions. Obviously, the P-center improves coordination to the metal.

[7]) A similar effect has been observed for the enantioselective LiAlH(OEt)-TADDOLate reduction of acetophenone (**9**) [20].

[8]) Of course at the expense of reduced rate: (*S*)-1-phenylethanol was formed in ≥90% yield with the following selectivities/specified temperatures/reaction times: 86%/+20°/<1 d, 93%/0°/1 d, 94%/−20°/7 d.

[9]) This competing reaction is often a serious problem with nitrogen-only ligands [21].

compared to THF[10]). However, it was necessary to use THF to solubilize ketones bearing additional polar functional groups, such as 2,3-dihydro-4,4-dimethylfuran-2,3-dione, which was not sufficiently soluble in toluene, since chlorinated solvents such as CH_2Cl_2 or especially CCl_4, which is the solvent of choice for nitrogen-only ligands [21], inhibit the catalytic activity. *vii*) Almost identical enantioselectivities were obtained for catalyst amounts ranging from 2 to 0.1 mol-%[11]). *viii*) In the presence of $[Ir(cod)Cl]_2$ as a metal source in place of $[Rh(cod)Cl]_2$, hydrosilylation of acetophenone (**9**) with ligand **7d** afforded 1-phenylethanol having the same configuration with low enantio-selectivity[12]).

Scheme 3
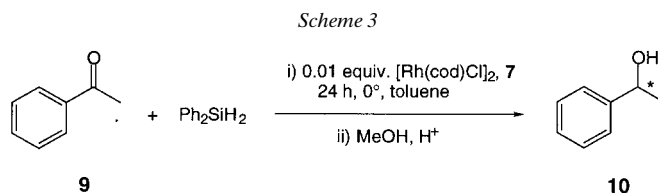
Entry	1	2	3	4	5
Ligand **7**	**a**	**b**	**c**	**d**	**e**
Yield of **10** [%]	97	86	92	89	89
$(R)/(S)$ in **10**	85:15	9:91	83:17	7:93	15:85

To test the scope of the new catalyst system, we examined a number of related aromatic ketones as substrates in the enantioselective hydrosilylation (see the *Table*). The enantioselectivities were determined by NMR or GC analysis, and the absolute configurations assigned by optical comparison or by analogy (see *Exper. Part*). For aromatic residues larger than Ph, such as naphthyl, the reduction provided alcohols **11** and **12** with (*S*)-configuration in similar selectivities. On the other hand, alkyl groups bulkier than Me led to decreased reactivity and selectivity (products **13–15**). Particularly, the hydrosilylation of isobutyrophenone and pivalophenone did not proceed at 0° within an acceptable period of time. Thus, we reduced these ketones at ambient temperature, with the result that the enantioselectivity decreased to nearly zero[13]). On the other hand, phenacyl chloride was reduced smoothly, providing the corresponding (*R*)-2-chloro-1-phenylethanol (**16**) with 91.5% enantioselectivity[14]).

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[10]) (*S*)-1-Phenylethanol was formed in > 98% yield with enantioselectivities of 92% in toluene, 90% in THF, and 88% neat (0.5 mol-% catalyst).

[11]) Of course at the expense of reduced rate: (*S*)-1-phenylethanol was formed in ≥ 90% yield with the following selectivities/amounts of catalyst/reaction times: 93%/2 mol-%/< 1 d, 93%/1 mol-%/1 d, 92%/0.5 mol-%/2 d, 93%/0.25 mol-%/4 d, 94%/0.1 mol-%/10 d.

[12]) (*S*)-1-Phenylethanol was formed in 83% yield with an enantioselectivity of only 65%.

[13]) In fact, the lowest selectivity obtained was for isobutyrophenone. The bulkier *t*-Bu group in pivalophenone led to reversal of selectivity from (*S*)- to (*R*)-configuration, but with no practically useful degree of selectivity.

[14]) The switch from (*S*)- to (*R*)-configuration with the chloro alcohol **16**, as compared with the other products of reduction, is an 'artefact' of the priority rules of the *CIP*-convention.

Reduction of fused alkyl aryl ketones such as α-tetralone and chroman-4-one gave the corresponding alcohols **17** and **18** (both (*S*)-configuration) with enantioselectivities of 90 and 93%, respectively[15]).

Besides aromatic ketones, aliphatic ketones can also be reduced by silanes in the presence of Rh^I complexes. However, the enantioselectivities reported in the literature are significantly lower than those obtained with aromatic ketones [17]. Surprisingly, our ligand **7d** acted effectively, not only with aryl ketones, but also with alkyl methyl ketones (see products **19–23** in the *Table*). Thus, our catalyst system is able to differentiate reasonably well even between the enantiotopic faces of alkyl methyl ketones[16]), with selectivities increasing from Et to i-Pr to *t*-Bu[17]). To the best of our knowledge, the value obtained for **21** is the best ever reported for an enantioselective hydrosilylation of pinacolone[18]). Surprisingly, octan-2-ol (**22**) was obtained with lower selectivity than was butan-2-ol (**19**, 78%), and, likewise, 1-cyclohexylethanol (**23**) was formed less selectively than 3-methylbutan-1-ol (**20**). Ketones bearing additional functional groups could also be selectively reduced: thus, (+)-(*S*)-pantolactone (**24**), (−)-(*S*)-γ-valerolactone (**25**), and ethyl (+)-(*S*)-4-hydroxypentanoate (**26**) were obtained from the corresponding oxo derivatives with selectivities of *ca.* 90%[19]).

5. Conclusion. – The catalyst prepared *in situ* from $[Rh(cod)Cl]_2$ and the P,N ligand **7d** directs silyl hydride addition from Ph_2SiH_2 to the *Re* faces of ketones with good-to-excellent selectivities (*Scheme 4*). The contribution of the TADDOL moiety to this enantioselectivity is minor, as compared to that of the dihydrooxazole unit. Still, it is interesting to point out that *Si* topicity of addition is observed in hydrosilylations with Rh and the monodentate TADDOL phosphite **2** [7], and *Re* topicity with a TADDOLate from LiAlH$_4$ [20]. The *Re* topicity of ketone hydrosilylation is also observed with the bidentate nitrogen-only (*R*)-dihydrooxazole ligands 'Pymox', while the analogous tridentate ligands containing two (*R*)-dihydrooxazole and a central pyridine moiety give rise to opposite topicity! [17]. Further work with the goal to elaborate the potential of the new ligands **7** in other transition-metal-catalyzed reactions is currently in progress.

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[15])   Hydrosilylation of 2,4-dimethoxyacetophenone did not yield the expected *sec*-alcohol, but the corresponding racemic methyl ether. We assume that the silyl ether primarily formed undergoes S_N1 substitution during workup (MeOH/H$^+$). The formation of the methyl ether has also been observed in the NaBH$_4$ reduction of the same substrate [22].

[16])   No by-products were detected with >99% conversion (sampling and ^{1}H-NMR analysis).

[17])   An enantiomer ratio of 96.5:3.5 was observed for **21** under the standard conditions (0°, 24 h), while at −20° the selectivity was 97.5:2.5.

[18])   With a chiral (dihydrooxazolyl)ferrocene-phosphine hybrid ligand (*S,S,S*)-DIPOF, 93.5% (*R*)-selectivity was observed in the hydrosilylation of *tert*-butyl methyl ketone [23].

[19])   Compounds **24** and **25** can be obtained from the same starting material, ethyl laevulinate, depending on the workup. Desilylation of silylated ethyl laevulinate with acidic MeOH provides the lactone, whereas the hydroxy ester is obtained with pure MeOH.

Table. *Asymmetric Hydrosilylation of Various Ketones by Rh^I-**7d** Complexes.* The reactions were carried out in the presence of [Rh(cod)Cl]$_2$ (0.5 mol-%) and **7d** (1.2 mol-%) with Ph$_2$SiH$_2$ (2.2 mmol) and ketones (2.0 mmol) in toluene at the temperature and with the reaction times indicated. Yields refer to purified products. The enantiomer ratios were determined by GC (**10 – 25**) or *via* the MTPA ester (**26**); for details and for configurational assignments, see the *Exper. Part*.
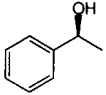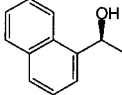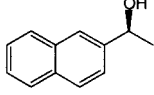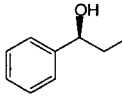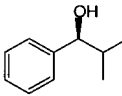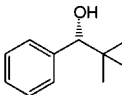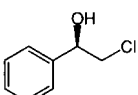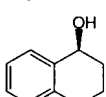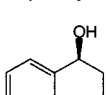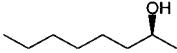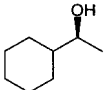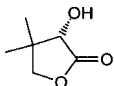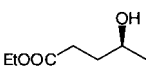
Product	No.	Yield [%]	Reaction time [h]	Temp. [°]	Enantiomer ratio [%]	Abs. configu- ration
	10	89 91	24 168	0 − 20	93 : 7 94 : 6	(*S*) (*S*)
	11	81	24	0	94.5 : 5.5	(*S*)
	12	87	24	0	90 : 10	(*S*)
	13	81	240	0	82 : 18	(*S*)
	14	87	24	20	51.5 : 48.5	(*S*)
	15	69	24	20	53 : 47	(*R*)
	16	89	24	0	91.5 : 8.5	(*R*)
	17	70	42	0	90 : 10	(*S*)
	18	86	24	0	93.5 : 6.5	(*S*)
	19	n.d.^{a})	24	0	78 : 22	(*S*)
	20	n.d.^{a})	24	0	88 : 12	(*S*)

Table. (cont.)

Product	No.	Yield [%]	Reaction Time [h]	Temp. [°]	Enantio-selectivity [%]	Abs. Configu-ration
	21	n.d.[a])	96	− 20	97.5 : 2.5	(S)
			24	0	96.5 : 3.5	
	22	89	40	0	71 : 29	(S)
	23	82	42	0	84 : 16	(S)
	24	76	120[b])	0	92 : 8	(S)
	25	71	24[b])	0	87 : 13	(S)
	26	86	24	0	90 : 10	(S)

[a]) No by-products detectable, $> 99\%$ conversion determined by ^{1}H-NMR analysis. [b]) THF used as solvent.

Scheme 4
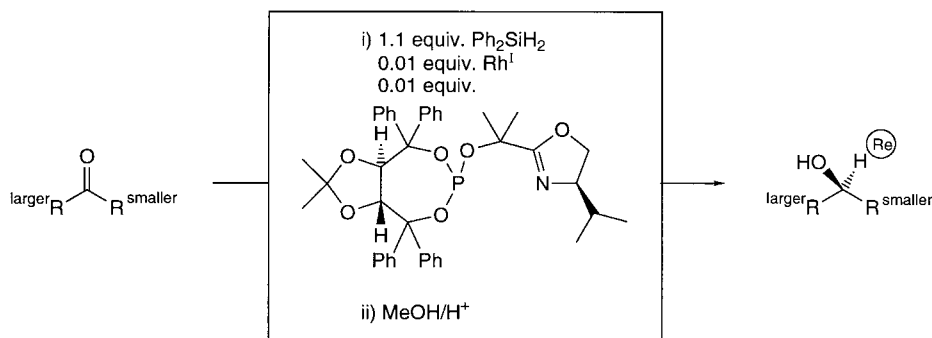
(hydrogen transfer with ligand **7d** from *Re* face, *CIP* priority $O > R^l > R^s$)

Experimental Part

1. *General*. All reactions were carried out under Ar in flame-dried glassware. Toluene, xylene (isomers mixture), and THF were distilled from Na/K; CH$_2$Cl$_2$ p.A. (*Baker*) was stored over activated molecular sieves (4 Å) for at least 48 h and filtered through basic Al$_2$O$_3$ (activity I) directly prior to use. Solvents for flash chromatography (FC) and workup: Et$_2$O was distilled from KOH/FeSO$_4$, AcOEt from *Sikkon* (*Fluka*). Pentane and hexane were used as received. TADDOLs **1a** (Arl = Ph), **1b** (Arl = naphthalen-2-yl) [2] and D-

valinol [24] were prepared according to literature procedures. Liquid ketones were degassed by three freeze-thaw cycles. All other reagents were used as received from *Fluka* or *Aldrich*. TLC: *Macherey-Nagel Alugram SIL G/UV_254* plates; detection by UV or common detecting agents (alcaline $KMnO_4$ soln., anisaldehyde/H_2SO_4 soln., $Ce(SO_4)_2$/phosphomolybdic acid soln.), followed by heating. FC: *Fluka* silica gel *60* (0.040 – 0.063 mm), pressure 0.4 bar. GC: *Carlo Erba GC8000 TOP* with *ChromCard* Software and *Supelco β-Dex 120* capillary column (30 m × 0.25 mm i.d., 0.25 μm film) for enantiomer separations. M.p.: *Büchi-510* apparatus, uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter (10 cm, 1 ml cell) at r.t.. IR Spectra: Perkin-Elmer-1600-FT-IR spectrometer. NMR Spectra: *Varian-Gemini 200* (^{1}H: 200 MHz, ^{13}C: 50 MHz) or *Varian-Gemini 300* (^{1}H: 300 MHz, ^{13}C: 75 MHz, and ^{31}P: 122 MHz); chemical shifts (δ) are reported in ppm downfield to TMS ($\delta = 0.0$ ppm) as internal standard, *J* values are given in Hz. MS: *VG Tribrid* (EI) or *FG ZAB-2 SEQ* (FAB; in a 3-nitrobenzyl-alcohol matrix) spectrometer; in *m/z* (% of basic peak). Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich.

2. *Preparation of Dihydrooxazole Alcohols* **6** [14]. *General Procedure 1* (*GP 1*). 2-Hydroxy-2-methylpropanoic acid (1 equiv.) and the corresponding amino alcohol (1 equiv.) were dissolved in xylene (complete dissolution occurred during heating) and heated to reflux in a *Dean-Stark* apparatus (oil-bath temp. 180°). After 30 h, no more H_2O was formed. The mixture was allowed to cool, and the solvent was removed under reduced pressure. Purification was carried out as described for each individual compound.

3. *Preparation of the Ligands* **7**. *General Procedure 2* (*GP 2*). PCl_3 (1 equiv.) in CH_2Cl_2 (2 ml/mmol) was cooled to – 30° prior to the addition of NEt_3 (2 equiv.). The soln. was stirred for 5 min. TADDOL (1 equiv.) dissolved in CH_2Cl_2 (4 ml/mmol) was added dropwise over 15 min. The mixture (which contained a colorless precipitate) was slowly warmed to – 10° (*ca.* 1 h). Then the bath was removed and the reaction mixture allowed to reach r.t. NEt_3 (2 – 5 equiv.) was then added, and the mixture was stirred at ambient temp. for further 5 min, before the corresponding dihydrooxazole alcohol **6** (1 equiv., dissolved in CH_2Cl_2 (2 ml/mmol)) was added dropwise. The mixture was stirred at r.t., until no further product formation was detectable by sampling and ^{1}H-NMR and ^{31}P-NMR-analysis (3 – 5 days). The mixture was extracted with H_2O (Ar-saturated, 10 ml/mmol), and the aq. phase was then extracted with CH_2Cl_2 (2 × 10 ml/mmol). The combined org. extracts were washed with brine (10 ml/mmol) and dried (Na_2SO_4). Most of the solvent was removed in a rotary evaporator to afford a pale-yellow oil, which was loaded directly on a silica gel column (12 g/mmol, pentane/Et_2O 85:15). FC provided the ligands **7** as colorless solid foams after complete removal of the solvent.

4. *Preparation of the Rh^I Complexes* **8**. *General Procedure 3* (*GP 3*). To a stirred soln. of the ligand **7** (1 equiv.) in CH_2Cl_2 (5 ml/mmol) was added [Rh(cod)Cl]$_2$ (1 equiv. with respect to Rh) in CH_2Cl_2 (2.5 ml/mmol). The yellow soln. was stirred for 2 h, then excess NH_4PF_6 (1.4 equiv.) was added. After stirring overnight at ambient temp., the inorg. salts were filtered by suction (*G4*) and rinsed with CH_2Cl_2 (10 ml/mmol). Pentane (25 ml/mmol) was added to the filtrate to precipitate the complexes **8** as yellow powders.

5. *Hydrosilylation of Ketones*. *General Procedure 4* (*GP 4*). [Rh(cod)Cl]$_2$ (0.005 equiv.) and the ligand **7** (0.01 equiv.) were dissolved in toluene or THF (0.5 ml/mmol substrate). The resulting yellow soln. was stirred at r.t. for 60 min. Then, the ketone (1.0 equiv.) was added. After 3 min, the mixture was cooled to the specified reaction temp. (0° for most cases). Precooled diphenylsilane (1.1 equiv.) was added dropwise over 2 min. The progress of the reaction was monitored by sampling and ^{1}H-NMR. To determine the end of the reaction, the characteristic resonances of the residual ketone were compared with those of the silylated alcohol formed. In the cases where substrates did not exhibit characteristic resonances, the disappearance of the Si–*H* resonance of the silane at 4.9 ppm was used. The silyl ether was cleaved by addition of MeOH (0.7 ml, containing 1% of 4-toluenesulfonic acid, except **26**: pure MeOH). Stirring was continued until gas evolution ceased (3 – 12 h). The mixture was loaded directly on a silica gel column (8 g/mmol) and chromatographed (pentane/Et_2O ratios between 80:20 and 90:10, depending on the relative polarity of the compounds). Yields refer to isolated pure compounds (> 95% by ^{1}H-NMR and GC). The spectra of the products of reduction are as expected. The conversion for low-boiling and volatile compounds (**19 – 21**) was calculated from the ^{1}H-NMR spectra of the silylated products.

(*S*)-*4,5-Dihydro-α,α-dimethyl-4-phenyloxazole-2-ethanol* (**6a**): (+)-(*S*)-2-Amino-2-phenylethanol (2.65 g, 19.3 mmol) was treated with 2-hydroxy-2-methylpropanoic acid (1.99 g, 19.1 mmol) in xylene (50 ml) according to *GP 1*. The resulting yellow oil was purified by FC (60 g; CH_2Cl_2/EtOAc 70:30) to afford **5a** (784 mg, 20%). Colorless crystals. R_f (hexane/AcOEt 50:50) 0.30. M.p. 73 – 74°. $[\alpha]_D^{r.t.} = -76.4$ (*c* = 1.00, $CHCl_3$). IR (neat): 3500*w*, 3066*w*, 2984*s*, 2903*w*, 1662*s*, 1494*w*, 1454*w*, 1338*s*, 1177*s*, 1134*s*, 960*s*, 922*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.52 (d, *J* = 5.8, Me$_2$C); 3.22 (br. *s*, OH); 4.20 – 4.26 (*m*, 1 H); 4.71 – 4.78 (*m*, 1 H); 5.19 – 5.25 (*m*, 1 H); 7.21 – 7.39 (*m*, arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 27.7; 28.1; 68.9; 69.0; 76.3; 126.4; 127.7; 128.8; 141.9; 173.7. Anal. calc. for $C_{12}H_{15}NO_2$ (205.3): C 70.22, H 7.37, N 6.82; found: C 70.13, H 7.36, N 6.75.

(*R*)-*4,5-Dihydro-α,α-dimethyl-4-phenyloxazole-2-ethanol* (**6b**): (−)-(*R*)-2-Amino-2-phenylethanol (2.06 g, 15.0 mmol) was treated with 2-hydroxy-2-methylpropanoic acid (1.56 g, 15.0 mmol) in xylene (45 ml) according to *GP 1*. The resulting yellow oil was purified by FC (60 g; CH₂Cl₂/AcOEt 65 : 35) to afford **5b** (837 mg, 27%). Colorless crystals. An anal. pure sample was prepared by recrystallization from hexane. M.p. 73°. $[α]_D^{r.t.} = +75.8$ ($c = 1.00$, CHCl₃). Spectroscopic and chromatographic data match those of the enantiomer **6a**. EI-MS: 205 (24, M^+), 117 (100), 90 (17), 59 (16). Anal. calc. for C₁₂H₁₅NO₂ (205.3): C 70.22, H 7.37, N 6.82; found: C 70.17, H 7.25, N 6.70.

(*S*)-*4,5-Dihydro-α,α-dimethyl-4-isopropyloxazole-2-ethanol* (**6c**). (*S*)-(+)-2-Amino-3-methylbutan-1-ol (2.15 g, 20.8 mmol) was treated with 2-hydroxy-2-methylpropanoic acid (2.13 g, 20.5 mmol) in xylene (60 ml) according to *GP 1*. The resulting pale-yellow oil was distilled (b.p. 66 – 70°/0.3 Torr). The colorless liquid (1.62 g) thus obtained was subjected to FC (50 g; hexane/AcOEt 85 : 15 → 65 : 35). The product **5c** solidified upon cooling in an ice bath (1.30 g, 31%). R_f (hexane/AcOEt 50 : 50) 0.32. M.p. 33 – 34°. $[α]_D^{r.t.} = -78.5$ ($c = 1.07$, CHCl₃). IR (neat): 3284*s*, 2959*s*, 1665*s*, 1466*m*, 1358*m*, 1250*m*, 1181*s*, 1127*s*, 1042*w*, 964*m*, 935*w*, 850*w*. ¹H-NMR (300 MHz, CDCl₃): 0.88 (*d*, *J* = 6.9, MeCH); 0.95 (d, *J* = 6.9, MeCH); 1.44 (*s*, Me₂COH); 1.73 – 1.80 (*m*, Me₂C*H*); 3.27 (br. *s*, OH); 3.90 – 3.98 (*m*, 1 H); 4.07 – 4.12 (*m*, 1 H); 4.32 – 4.38 (*m*, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 17.8; 18.5; 27.7; 27.9; 32.4; 68.8; 71.4; 71.7; 172.3. EI-MS: 171 (1, M^+), 156 (12), 128 (47), 112 (14), 98 (100), 59 (24). Anal. calc. for C₉H₁₇NO₂ (171.2): C 63.13, H 10.01, N 8.18; found: C 62.97, H 10.29, N 8.13.

(*R*)-*α,α-4,5-Dihydro-dimethyl-4-isopropyloxazole-2-ethanol* (**6d**): (−)-(*R*)-2-Amino-2-phenylethanol (5.15 g, 50.0 mmol) was treated with 2-hydroxy-2-methyl-propanoic acid (5.20 g, 50.0 mmol) in xylene (80 ml) according to *GP 1*. The resulting pale-yellow oil was distilled (b.p. 66 – 70°/0.3 Torr). The colorless liquid obtained (3.08 g) was subjected to FC (50 g; CH₂Cl₂/AcOEt 65 : 35). The product solidified upon cooling in an ice bath (2.66 g, 31%). M.p. 34°. $[α]_D^{r.t.} = +78.1$ ($c = 0.85$, CHCl₃). Spectroscopic and chromatographic data match those of the enantiomer **6c**. Anal. calc. for C₉H₁₇NO₂ (171.2): C 63.13, H 10.01, N 8.18; found: C 63.27, H 10.02, N 7.98.

*(3a*R,8a*R)-6-{1-[(4*S*)-4,5-Dihydro-4-phenyloxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetra-phenyl-1,3,5,7-tetraoxa-6-phosphazulene* (**7a**): According to *GP 2*, PCl₃ (0.22 ml, 2.51 mmol) was treated with NEt₃ (*1*) 0.73 ml, 5.22 mmol; *2*) 0.36 ml, 2.60 mmol), (*R,R*)-TADDOL **1a** (1.17 g, 2.50 mmol), and **6a** (515 mg, 2.51 mmol) to yield **7a** (515 mg, 29%). R_f (hexane/AcOEt 80 : 20) 0.29. M.p. 86 – 88°. $[α]_D^{r.t.} = -240.5$ ($c = 0.84$, CHCl₃). IR (CHCl₃): 3062*w*, 3007*m*, 2937*w*, 1656*m*, 1600*w*, 1494*m*, 1447*m*, 1383*m*, 1164*m*, 976*s*, 887*s*. ¹H-NMR (300 MHz, CDCl₃): 0.70 (*s*, 2 Me); 1.26 (*s*, Me); 1.37 (*s*, Me); 3.98 – 4.03 (*m*, 1 H); 4.53 – 4.59 (*m*, 1 H); 5.05 – 5.13 (*m*, 2 H); 5.51 (*d*, *J* = 8.0, 1 H); 7.12 – 7.33 and 7.45 – 7.58 (*m*, 25 arom. H). ¹³C-NMR (75 MHz, CDCl₃): 26.4; 26.5; 27.4; 27.5; 69.6; 74.7; 74.8; 75.2; 80.1; 82.1; 84.1; 85.5; 112.9; 126.8; 127.0; 127.1; 127.2; 127.3; 127.3; 127.5; 127.6; 127.6; 127.7; 128.0; 128.7; 129.2; 129.2; 141.8; 142.1; 142.1; 146.4; 146.6; 170.3. ³¹P-NMR (122 MHz, CDCl₃): 134.8. FAB-MS: 700 (43, $[M + H]^+$), 431 (100), 345 (34), 268 (95), 237 (37), 207 (23), 195 (30), 188 (70), 179 (91), 167 (55), 105 (25). Anal. calc. for C₄₃H₄₂NO₆P (699.79): C 73.80, H 6.05, N 2.00; found: C 73.84, H 6.25, N 2.12.

*(3a*R,8a*R)-6-{1-[(4*R*)-4,5-Dihydro-4-phenyloxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetra-phenyl-1,3,5,7-tetraoxa-6-phosphazulene* (**7b**). According to *GP 2*, PCl₃ (0.22 ml, 2.51 mmol) was treated with NEt₃ (*1*) 0.73 ml, 5.22 mmol; *2*) 0.73 ml, 5.22 mmol), (*R,R*)-TADDOL **1a** (1.17 g, 2.50 mmol) and **6b** (515 mg, 2.51 mmol) to yield **7a** (1.15 g, 66%). R_f (hexane/AcOEt 80 : 20) 0.31. M.p. 84 – 85°. $[α]_D^{r.t.} = -123.9$ ($c = 0.82$, CHCl₃). IR (CHCl₃): 3060*w*, 2992*m*, 2936*w*, 1659*m*, 1601*w*, 1494*m*, 1448*m*, 1383*m*, 1164*m*, 1088*w*, 1052*w*, 978*s*, 887*s*. ¹H-NMR (300 MHz, CDCl₃): 0.69 (*s*, Me); 0.70 (*s*, Me); 1.31 (*s*, Me); 1.34 (*s*, Me); 4.00 – 4.06 (*m*, 1 H); 4.49 – 4.58 (*m*, 1 H); 5.04 – 5.10 (*m*, 2 H); 5.52 (*d*, *J* = 8.4, 1 H); 7.11 – 7.35 and 7.45 – 7.58 (*m*, 25 arom. H). ¹³C-NMR (75 MHz, CDCl₃): 26.5; 26.6; 27.4; 27.8; 69.6; 74.7; 74.9; 75.2; 80.2; 82.2; 83.8; 85.4; 112.8; 126.7; 126.9; 127.0; 127.1; 127.1; 127.2; 127.4; 127.4; 127.5; 127.6; 127.9; 128.1; 128.6; 129.0; 129.1; 141.8; 142.1; 146.2; 146.4; 146.4; 170.1. ³¹P-NMR (122 MHz, CDCl₃): 135.0. FAB-MS: 716 (16), 699 (51, M^+), 431 (77), 345 (26), 268 (42), 237 (16), 178 (100), 167 (40), 165 (45), 152 (20). Anal. calc. for C₄₃H₄₂NO₆P (699.79): C 73.80, H 6.05, N 2.00; found: C 73.75, H 6.23, N 2.00.

*(3a*R,8a*R)-6-{1-[(4*S*)-4,5-Dihydro-4-isopropyloxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetraphenyl-1,3,5,7-tetraoxa-6-phosphazulene* (**7c**). According to *GP 2*, PCl₃ (0.27 ml, 3.09 mmol) was treated with NEt₃ (*1*) 0.87 ml, 6.24 mmol; *2*) 1.75 ml, 12.5 mmol), (*R,R*)-TADDOL **1a** (1.40 g, 3.00 mmol), and **6c** (513 mg, 3.00 mmol) to yield **7c** (1.25 g, 63%). R_f (hexane/AcOEt 75 : 25) 0.42. M.p. 75 – 77°. $[α]_D^{r.t.} = -210.8$ ($c = 0.74$, CHCl₃). IR (CHCl₃): 3063*w*, 3007*m*, 2964*m*, 1660*m*, 1600*w*, 1494*m*, 1447*m*, 1383*m*, 1164*m*, 1088*w*, 1052*w*, 957*s*, 887*s*. ¹H-NMR (300 MHz, CDCl₃): 0.71 (*s*, Me); 0.72 (*s*, Me); 0.79 (*d*, *J* = 6.9, 3 H, *Me*₂CH); 0.89 (*d*, *J* = 6.9, 3 H, *Me*₂CH); 1.20 (*s*, Me); 1.30 (*s*, Me); 3.84 – 3.95 (*m*, 2 H); 4.13 – 4.20 (*m*, 1 H); 5.05 (*d*, *J* = 7.5, 1 H); 5.49 (*d*, *J* = 7.5, 1 H); 7.18 – 7.38 and 7.45 – 7.61 (*m*, 20, arom. H). ¹³C-NMR (75 MHz, CDCl₃): 17.7; 18.8; 26.6;

27.5; 27.6; 32.3; 70.1; 71.9; 74.8; 80.1; 82.1; 84.0; 85.3; 112.8; 126.9; 127.0; 127.1; 127.3; 127.4; 127.6; 127.6; 127.9; 129.1; 129.2; 141.8; 142.1; 146.4; 146.6; 168.6. ^{31}P-NMR (122 MHz, CDCl$_3$): 134.4. FAB-MS: 682(7), 665(24, M^+), 431(83), 345(30), 234(100), 179(75), 167(38), 154(30). Anal. calc. for C$_{40}$H$_{44}$NO$_6$P (665.77): C 72.16, H 6.66, N 2.10; found: C 72.16, H 6.63, N 2.14.

*(3a*R,8a*R)-6-{1-[(4*R)-4,5-Dihydro-4-isopropyloxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetraphenyl-1,3,5,7-tetraoxa-6-phosphazulene* (**7d**). According to *GP 2*, PCl$_3$ (0.44 ml, 5.00 mmol) was treated with NEt$_3$ (*1*) 1.40 ml, 10.0 mmol; *2*) 3.50 ml, 25.0 mmol), (*R,R*)-TADDOL **1a** (2.33 g, 5.00 mmol), and **6d** (856 mg, 5.00 mmol) to yield **7d** (2.26 g, 68%). R_f (pentane/Et$_2$O 80:20) 0.31. M.p. 73–75°. $[\alpha]_D^{r.t.} = -155.2$ ($c = 0.52$, CHCl$_3$). IR (CHCl$_3$): 3059*w*, 3008*m*, 2964*w*, 1659*m*, 1599*w*, 1494*w*, 1447*m*, 1383*m*, 1164*m*, 1088*m*, 1052*w*, 957*s*, 886*s*, 835*w*. ^{1}H-NMR (300 MHz, CDCl$_3$): 0.69 (*s*, *Me*); 0.70 (*s*, Me); 0.77 (*d*, *J* = 6.7, 3 H, *Me*$_2$CH); 0.88 (*d*, *J* = 6.7, 3 H, *Me*$_2$CH); 1.22 (*s*, Me); 1.26 (*s*, Me); 1.66–1.72 (*m*, Me$_2$C*H*); 3.79–3.87 (*m*, 1 H); 3.90–3.95 (*m*, 1 H); 4.09–4.15 (*m*, 1 H); 5.03 (*d*, *J* = 8.4, 1 H); 5.47 (*d*, *J* = 8.4, 1 H); 7.16–7.35 and 7.45–7.58 (*m*, 20 arom. H). ^{13}C-NMR (75 MHz, CDCl$_3$): 17.7; 18.7; 26.5; 27.4; 27.7; 32.3; 70.1; 71.9; 74.9; 80.2; 82.1; 83.7; 85.2; 112.7; 126.9; 126.9; 127.0; 127.1; 127.2; 127.4; 127.5; 127.6; 127.9; 129.1; 129.1; 141.8; 142.1; 146.2; 146.5; 168.5. ^{31}P-NMR (122 MHz, CDCl$_3$): 134.9. FAB-MS: 665(8, M^+), 431(23), 345(9), 234(100), 179(100), 167(58), 154(67). Anal. calc. for C$_{40}$H$_{44}$NO$_6$P (665.77): C 72.16, H 6.66, N 2.10; found: C 72.30, H 6.81, N 2.11.

*(3a*R,8a*R)-6-{1-[(4*R)-4,5-Dihydro-4-isopropylaoxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetra(naphthalen-2-yl)-1,3,5,7-tetraoxa-6-phosphazulene* (**7e**). According to *GP 2*, PCl$_3$ (0.26 ml, 3.00 mmol) was treated with NEt$_3$ (*1*) 0.84 ml, 6.00 mmol; *2*) 2.10 ml, 15.00 mmol), (*R,R*)-TADDOL **1b** (2.00 g, 3.00 mmol), and **6e** (514 mg, 3.00 mmol) to yield **7e** (1.61 mg, 48%). R_f (pentane/Et$_2$O 50:50) 0.26. M.p. >130° (slow continuous shrinking, no sharp m.p.). $[\alpha]_D^{r.t.} = -176.4$ ($c = 1.25$, CHCl$_3$). IR (CHCl$_3$): 3060*m*, 2981*m*, 2961*m*, 1660*m*, 1600*w*, 1505*m*, 1464*w*, 1382*m*, 1161*s*, 1126*w*, 981*s*, 900*s*, 863*s*, 824*w*. ^{1}H-NMR (300 MHz, CDCl$_3$): 0.67 (*d*, *J* = 6.9, 3 H, *Me*$_2$CH); 0.75 (*s*, Me); 0.78 (*d*, *J* = 6.7, 3 H, *Me*$_2$CH); 1.14 (*s*, Me); 1.28 (*s*, Me); 1.52–1.59 (*m*, Me$_2$C*H*); 3.63–3.68 (*m*, 1 H); 3.77–3.82 (*m*, 1 H); 3.92–3.98 (*m*, 1 H); 5.41 (*d*, *J* = 8.4, 1 H); 5.85 (*d*, *J* = 8.4, 1 H); 7.42–7.91 and 7.45–7.58 (*m*, 24 arom. H). 8.17 (*s*, 2 H); 8.31 (*s*, 1 H); 8.44 (*s*, 1 H). ^{13}C-NMR (75 MHz, CDCl$_3$): 17.7; 18.6; 26.8; 27.4; 27.7; 32.2; 70.2; 71.7; 75.1; 80.5; 82.4; 84.3; 85.5; 113.0; 125.3; 125.4; 125.6; 125.7; 125.8; 125.9; 126.0; 126.1; 126.2; 126.3; 126.8; 127.2; 127.3; 127.5; 127.8; 128.3; 128.4; 128.6; 128.7; 132.5; 132.6; 132.6; 132.8; 132.8; 139.1; 139.4; 143.2; 143.6; 168.3. ^{31}P-NMR (122 MHz, CDCl$_3$): 135.1. FAB-MS: M^+ not detectable, 631(61), 337(31), 307(19), 295(32), 279(100), 267(59), 234(46), 155(45), 127(15). Compound **7e** was much less stable than the phenyl analogue **7d** during workup and purification, thus we were unable to obtain a correct elemental analysis. Anal. calc. for C$_{58}$H$_{52}$NO$_6$P (890.03): C 78.27, H 5.89, N 1.57; found: C 77.74, H 6.42, N 1.49.

*(−)-(η^4-Cycloocta-1,5-diene)((3a*R,8a*R)-6-{1-[(4*S)-4,5-dihydro-4-isopropyloxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetraphenyl-1,3,5,7-tetraoxa-6-phosphazulene-*P,N)rhodium(I)* (**8a**). Compound **7c** (68.0 mg, 0.10 mmol) was treated with [Rh(cod)Cl]$_2$ (25.0 mg, 0.05 mmol) and NH$_4$PF$_6$ (22.1 mg, 0.13 mmol) according to *GP 3* to yield **8a** (95.5 mg, 91%). M.p. >200° (dec.). $[\alpha]_D^{r.t.} = -88.8$ ($c = 0.74$, CHCl$_3$). IR (CHCl$_3$): 3039*w*, 2962*w*, 2887*w*, 1626*m*, 1494*w*, 1448*m*, 1374*m*, 1053*w*, 975*s*, 909*s*, 852*s*. ^{1}H-NMR (300 MHz, CDCl$_3$): 0.41 (*s*, Me); 0.76 (*s*, Me); 0.81 (*d*, *J* = 6.5, 3 H, *Me*$_2$CH); 0.94 (*s*, Me); 1.04 (*d*, *J* = 6.5, 3 H, *Me*$_2$CH); 1.23–1.32 (*m*, 1 H); 1.55 (*s*, Me); 1.89–2.15 (*m*, 5 H); 2.20–2.42 (*m*, 3 H); 2.50–2.65 (*m*, 1 H); 3.82–3.90 (*m*, 1 H); 3.95–4.02 (*m*, 1 H); 4.35–4.45 (*m*, 2 H); 4.77 (*m*, 1 H); 5.03 (*d*, *J* = 7.8, 1 H); 5.20–5.31 (*m*, 1 H); 5.64 (*d*, *J* = 7.8, 1 H); 5.78–5.90 (*m*, 1 H); 6.97–7.05 (*m*, 2 H); 7.26–7.32 (*m*, 8 arom. H); 7.40–7.61 (*m*, 10 arom. H). ^{31}P-NMR (122 MHz, CDCl$_3$): 107.6 (*d*, *J*(P, Rh) = 254.9); −143.5 (*sept.*, *J*(P,F) = 712, PF$_6^-$). FAB-MS: 876.2(100, M^+). Anal. calc. for C$_{48}$H$_{56}$NF$_6$O$_6$P$_2$Rh (1021.82): C 56.42, H 5.52, N 1.37; found: C 56.46, H 5.63, N 1.41.

*(−)-(η^4-Cycloocta-1,5-diene)((3a*R,8a*R)-6-{1-[(4*R)-4,5-dihydro-4-isopropyloxazol-2-yl]-1-methylethoxy}-3a,4,8,8a-tetrahydro-4,4,8,8-tetraphenyl-1,3,5,7-tetraoxa-6-phosphazulene-*P,N)rhodium(I)* (**8b**). Compound **7d** (133 mg, 0.20 mmol) was treated with [Rh(cod)Cl]$_2$ (49.3 mg, 0.10 mmol) and NH$_4$PF$_6$ (44.8 mg, 0.27 mmol) according to *GP 3* to yield **8a** (158 mg, 90%). M.p. 214-215° (dec.). $[\alpha]_D^{r.t.} = -85.8$ ($c = 0.62$, CHCl$_3$). IR (CHCl$_3$): 3039*w*, 2950*w*, 1624*m*, 1495*w*, 1448*m*, 1374*w*, 1010*m*, 968*s*, 850*s*. ^{1}H-NMR (300 MHz, CDCl$_3$): 0.32 (*s*, Me); 0.64 (*s*, Me); 0.87 (*d*, *J* = 6.5, 3 H, *Me*$_2$CH); 1.07 (*s*, Me); 1.39 (*d*, *J* = 6.5, 3 H, *Me*$_2$CH); 1.50–1.65 (*m*, 1 H); 1.97 (*s*, Me); 1.80–2.22 (*m*, 4 H); 2.45–2.78 (*m*, 4 H); 3.55–3.65 (*m*, 1 H); 3.82–3.92 (*m*, 1 H); 4.21–4.28 (*m*, 2 H); 4.70–4.80 (*m*, 1 H); 4.93 (*d*, *J* = 7.9, 1 H); 5.19–5.31 (*m*, 1 H); 5.66 (d, *J* = 7.9, 1 H); 5.80–5.92 (*m*, 1 H); 7.20–7.49 (*m*, 20 arom. H). ^{31}P-NMR (122 MHz, CDCl$_3$): 103.4 (*d*, *J*(P, Rh) = 264.9); −143.86 (*sept*, *J*(P, F) = 713, PF$_6^-$). FAB-MS: 876.3(100, M^+). Inclusion of varying amounts of solvent precluded correct elemental analysis. See also the stoichiometric inclusion of CHCl$_3$ in the crystal used for the X-ray structure determination.

X-Ray Crystal-Structure Analysis of **8b**: C$_{48}$H$_{56}$NF$_6$O$_6$P$_2$Rh · CHCl$_3$. Suitable crystals were obtained by slow evaporation of a CHCl$_3$ soln. A *Picker-Stoe* 4-circle diffractometer equipped with a graphite monochromator (CuK_a, $\lambda = 1.5418$ Å) was used. Crystal temp. 293 K, crystal size $0.2 \times 0.1 \times 0.1$ mm, orthorhombic crystal

system, space group $P2_12_12_1$, cell: $a = 10.334(10)$, $b = 13.861(14)$, $c = 36.46(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 5222(10)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.435$ g cm^{-3}, $\mu = 5.217$ mm^{-1}, $F(000) = 2316$. Number of reflections measured 3073 (ω scan $2.42 < 2\theta < 50.09°$); 3073 independent reflections, of which 2369 with $I > 2\sigma(I)$ were used for the determination. The structure was solved by direct methods with SHELXS-86 and refined by full-matrix least-squares analysis on F^2 with SHELXL-93. Goodness of fit on $F^2 = 1.024$; Final agreement factors (observed refl.): $R = 0.0685$ ($wR^2 = 0.1620$); $\Delta\rho$ (max, min) $= 1.527$, -1.140 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-118729. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ UK (fax: + 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

(S)-1-Phenylethanol (**10**). Acetophenone (234 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **10** (218 mg, 89%). $[\alpha]_D^{r.t.} = -39.8$ ($c = 0.93$, MeOH), ([25]: $[\alpha]_D^{r.t.} = -45.5$ ($c = 1.0$, MeOH)). E.r. $(S)/(R)$ 93 : 7. t_R (R) 6.85, t_R (S) 7.10 min. T 110 → 122° with 1.5°/min, 130 kPa.

(S)-1-(Naphthalen-1-yl)ethanol (**11**): 1-(Naphthalen-1-yl)ethanone (305 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **11** (280 mg, 81%). $[\alpha]_D^{r.t.} = -68.5$ ($c = 1.07$, MeOH) ([26]: $[\alpha]_D^{r.t.} = -77$ ($c = 2.8$, MeOH)). E.r. $(S)/(R)$ 94.5 : 5.5, t_R $(R) = 19.77$, t_R $(S) = 19.20$ min. $T = 150 → 172°$ with 1°/min, 130 kPa.

(S)-1-(Naphthalen-2-yl)ethanol (**12**): 1-(Naphthalen-2-yl)ethanone (340 mg, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **12** (301 mg, 87%). $[\alpha]_D^{r.t.} = -30.5$ ($c = 1.00$, MeOH) ([27]: $[\alpha]_D^{r.t.} = -41.1$ ($c = 6.01$, EtOH)). E.r. $(S)/(R)$ 90 : 10. t_R $(R) = 18.60$, t_R (S) 18.92 min. T 150 → 170° with 1°/min, 130 kPa.

(S)-1-Phenylpropan-1-ol (**13**). Propiophenone (266 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **13** (221 mg, 81%). $[\alpha]_D^{r.t.} = -27.3$ ($c = 1.21$, CHCl$_3$) ([28]: $[\alpha]_D^{r.t.} = -46.3$ ($c = 1.12$, CHCl$_3$)). E.r. $(S)/(R)$ 82 : 18. t_R (R) 9.95, t_R $(S) = 10.20$ min. T 110 → 128° with 1.5°/min, 130 kPa.

(S)-1-Phenyl-2-methylpropan-1-ol (**14**). Isobutyrophenone (305 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at r.t. to yield **14** (258 mg, 87%). $[\alpha]_D^{r.t.} = -1.1$ ($c = 3.40$, Et$_2$O) ([29]: $[\alpha]_D^{r.t.} = -35$ ($c = 1.0$, MeCN)). E.r. $(S)/(R)$ 51.5 : 48.5. t_R (R) 19.49, t_R (S) 20.00 min. $T = 100 → 122°$ with 1°/min, 130 kPa.

(R)-1-Phenyl-2,2-dimethylpropan-1-ol (**15**). Pivalophenone (336 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at r.t. to yield **15** (224 mg, 69%). $[\alpha]_D^{r.t.} = +2.2$ ($c = 2.00$, Et$_2$O) ([30]: $[\alpha]_D^{r.t.} = +39.2$ ($c = 0.12$, Et$_2$O, (R)-isomer)). E.r. $(R)/(S)$ 53 : 47. t_R (S) 32.53, t_R (R) 32.97 min. T 90 → 125° with 1°/min, 130 kPa.

(R)-2-Chloro-1-phenylethanol (**16**): Phenacyl chloride (309 mg, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **16** (279 mg, 89%). $[\alpha]_D^{r.t.} = -38.4$ ($c = 2.15$, C$_6$H$_{12}$) ([31]: $[\alpha]_D^{r.t.} = -49.9$ ($c = 2.00$, C$_6$H$_{12}$, (R)-isomer)). E.r. $(R)/(S)$ 91.5 : 8.5. t_R (R) 29.17, t_R (S) 29.95 min. $T = 100 → 132°$ with 1°/min, 130 kPa.

(+)-(S)-1,2,3,4-Tetrahydronaphthalen-1-ol (**17**). 1,2,3,4-Tetrahydronaphthalen-1-one (267 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **17** (206 mg, 70%). $[\alpha]_D^{r.t.} = +28.5$ ($c = 0.70$, CHCl$_3$) ([32]: $[\alpha]_D^{r.t.} = +34.4$ ($c = 1.01$, CHCl$_3$)). E.r. $(S)/(R)$ 90 : 10. t_R (R) 33.13 min, t_R (S) 32.53 min. $T = 100 → 135°$ with 1°/min, 130 kPa.

(−)-(S)-3,4-Dihydro-2H-1-benzopyran-4-ol (**18**). 3,4-Dihydro-2H-1-benzopyran-4-one (296 mg, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **18** (258 mg, 86%). $[\alpha]_D^{r.t.} = -59.7$ ($c = 1.48$, CHCl$_3$) ([33]: $[\alpha]_D^{r.t.} = -69.1$ ($c = 1.1$, CHCl$_3$)). E.r. $(S)/(R)$ 93.5 : 6.5. t_R (R) 44.12, t_R (S) 44.46 min. $T = 90 → 140°$ with 1°/min, 130 kPa.

(S)-Butan-2-ol (**19**). Butan-2-one (180 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **19** (> 99% conversion by ^{1}H-NMR). The (S)-configuration was determined by comparison of the t_R values with an enantiomerically pure sample of the commercially available (S)-isomer. E.r. $(S)/(R)$ 78 : 22. t_R (R) 12.06, t_R $(S) = 12.40$ min. $T = 35 → 45°$ with 0.5°/min, 40 kPa.

(S)-3-Methylbutan-2-ol (**20**): 3-Methylbutan-2-one (214 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **20** (> 99% conversion by ^{1}H-NMR). The (S)-configuration was assigned by analogy to **19**, **22**, and **23**. E.r. $(S)/(R)$ 88 : 12. t_R 12.73, 13.08 min. $T = 40 → 55°$ with 1°/min, 60 kPa.

(S)-3,3-Dimethylbutan-2-ol (**21**). 3,3-Dimethylbutan-2-one (247 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **21** (> 99% conversion by ^{1}H-NMR). The (S)-configuration was assigned by analogy to **19**, **22**, and **23**. E.r. $(S)/(R)$ 96.5 : 3.5. t_R 15.74, 16.57 min. $T = 50°$, 80 kPa.

(+)-(S)-Octan-2-ol (**22**). Octan-2-one (315 µl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 µl, 2.20 mmol) according to *GP 4* at 0° to yield **22** (238 mg, 91%). $[\alpha]_D^{r.t.} = +4.0$ ($c = 1.00$, EtOH) ([34]: $[\alpha]_D^{r.t.} = +10.5$ ($c = 0.2$,

EtOH)). E.r. $(S)/(R)$ 71:29. t_R (R) 36.83, t_R (S) 35.99 min (trifluoroacetyl (TFA) derivative). $T = 50 \rightarrow 60°$ with 0.25°/min, 40 kPa.

(S)-1-Cyclohexylethanol (**23**). 1-Cyclohexylethanone (275 μl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 μl, 2.20 mmol) according to *GP 4* at 0° to yield **23** (216 mg, 84%). $[\alpha]_D^{\text{r.t.}} = +5.0$ ($c = 2.00$, Et$_2$O) ([35]: $[\alpha]_D^{\text{r.t.}} = -8.1$ ($c = 0.48$, Et$_2$O, (R)-isomer)). E.r. $(S)/(R)$ 84:16. t_R (R) 24.84, t_R (S) 24.23 min (TFA derivative). T 60 → 75°, 60 kPa.

(−)-(S)-2,3,4,5-Tetrahydro-3-hydroxy-4,4-dimethylfuran-2-one (*(−)-D-Pantolactone*) (**24**). 2,3,4,5-Tetrahydro-4,4-dimethylfuran-2,3-dione (256 mg, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 μl, 2.20 mmol) according to *GP 4* (THF was used as solvent) at 0° to yield **24** (198 mg, 76%). $[\alpha]_D^{\text{r.t.}} = +40.0$ ($c = 1.20$, CHCl$_3$) ([36]: $[\alpha]_D^{\text{r.t.}} = +49.9$ ($c = 1.00$, CHCl$_3$)). E.r. $(S)/(R)$ 92:8. t_R (S) 10.64, t_R (R) 11.82 min. T = 110°, 130 kPa.

(−)-(S)-2,3,4,5-Tetrahydro-5-methylfuran-2-one (**25**). Ethyl 4-oxopentanoate (285 μl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 μl, 2.20 mmol) according to *GP 4* (THF was used as solvent) at 0° to yield **25** (142 mg, 71%) after desilylation with acidic MeOH. $[\alpha]_D^{\text{r.t.}} = -22.0$ ($c = 0.98$, CHCl$_3$). ([37]: $[\alpha]_D^{\text{r.t.}} = -29$ ($c = 2.25$, CHCl$_3$)). E.r. $(S)/(R)$ 87:13. t_R (R) 18.40, t_R (S) 18.71 min. $T = 60 \rightarrow 80°$ with 1°/min, 130 kPa.

Ethyl (+)-(S)-3-Hydroxypentanoate (**26**): Ethyl 4-oxopentanoate (285 μl, 2.00 mmol) was treated with Ph$_2$SiH$_2$ (406 μl, 2.20 mmol) according to *GP 4* at 0° to yield **26** (142 mg, 71%) after desilylation with pure MeOH. $[\alpha]_D^{\text{r.t.}} = +10.7$ ($c = 1.45$, CHCl$_3$) ([38]: $[\alpha]_D^{\text{r.t.}} = +12.8$ ($c = 2.37$, CHCl$_3$)). E.r. $(S)/(R)$ 90:10. Determination of e.r. by ^{1}H- and ^{19}F-NMR of the 3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid (MTPA) ester, δ(MeO) 3.56 for (R)- and 3.54 for (S)-enantiomer; δ(CF$_3$) -71.43 for (R)- and -71.47 for (S)-enantiomer.

Derivatization with Trifluoroacetic Anhydride. The alcohol (0.05 mmol) was dissolved in CH$_2$Cl$_2$ (0.3 ml). Trifluoroacetic anhydride (0.5 mmol) was added and the mixture kept at ambient temp. for 5 h, concentrated in a stream of Ar and dissolved in Et$_2$O (1 ml). The soln. was used directly for the GC determination of the e.r.

Preparation of the Mosher *Ester.* The alcohol (0.03 mmol), 4-(dimethylamino)pyridine (DMAP) (0.3 mmol) and (R)-MTPA-Cl (0.04 mmol) were added to CDCl$_3$ (0.5 ml). The mixture was shaken and kept for 10 min. Et$_2$O (10 ml) was added and the mixture extracted with 1M HCl, H$_2$O and sat. NaHCO$_3$ soln. (10 ml each). The org. phase was concentrated, the residue of which was dissolved in CDCl$_3$ and filtered to be analyzed.

REFERENCES

[1] D. Seebach, A. K. Beck, M. Schiess, L. Widler, A. Wonnacott, *Pure Appl., Chem.* **1983**, *55*, 1807.

[2] A. K. Beck, B. Bastani, D. A. Plattner, W. Petter, D. Seebach, H. Braunschweiger, P. Gysi, L. La Vecchia, *Chimia* **1991**, *45*, 238.

[3] R. Dahinden, A. K. Beck, D. Seebach, in 'Encyclopedia of Reagents for Organic Synthesis', Ed. L. A. Paquette, J. Wiley and Sons, Chichester (GB), 1995, Vol. 3, 2167–2170.

[4] D. Seebach, M. Hayakawa, J.-i. Sakaki, W. B. Schweizer, *Tetrahedron* **1993**, *49*, 1711.

[5] D. Seebach, A. K. Beck, M. Hayakawa, G. Jaeschke, F. N. M. Kühnle, I. Nägeli, A. B. Pinkerton, B. P. Rheiner, R. O. Duthaler, P. M. Rothe, W. Weigand, R. Wünsch, S. Dick, R. Nesper, M. Wörle, V. Gramlich, *Bull. Soc. Chim. Fr.* **1997**, *134*, 315.

[6] D. Seebach, G. Jaeschke, A. Pichota, L. Audergon, *Helv. Chim. Acta* **1997**, *80*, 2515.

[7] J.-i. Sakaki, W. B. Schweizer, D. Seebach, *Helv. Chim. Acta* **1993**, *76*, 2654.

[8] A. Alexakis, J. Vastra, J. Burton, C. Benhaim, P. Mangeney, *Tetrahedron Lett.* **1998**, *39*, 7869.

[9] a) L. S. Hegedus, L. G. Wade, Jr., 'Compendium of Organic Synthetic Methods', Wiley, New York, Chichester, Brisbane, Toronto, 1977, Vol. 3; b) 'Homogeneous Catalysis with Metal Phosphine Complexes', Ed. L. H. Pignolet, Plenum Press, New York, London, 1983; c) H. B. Kagan, in 'Comprehensive Organometallic Chemistry', Ed. S. G. Wilkinson, 1982, Vol. 8, 463–498; d) R. Noyori, M. Kitamura, in 'Modern Synthetic Methods', Ed. R. Scheffold, Springer Verlag, Berlin-Heidelberg, 1989, Vol. 5, p. 115–198; e) H. Brunner, *Topics Stereochem.* **1988**, *18*, 129; f) H.-U. Blaser, *Chem. Rev.* **1992**, *92*, 935; f) W. A. Nugent, T. V. RajanBabu, M. J. Burk, *Science* **1993**, *259*, 479.

[10] D. Seebach, E. Devaquet, A. Ernst, M. Hayakawa, F. N. M. Kühnle, W. B. Schweizer, B. Weber, *Helv. Chim. Acta* **1995**, *78*, 1636.

[11] R. Wünsch, unpublished results, ETH-Zürich, 1997.

[12] M. J. Burk, T. G. P. Harper, C. S. Kalberg, *J. Am. Chem. Soc.* **1995**, *117*, 4423.

[13] A. K. H. Knöbel, I. H. Escher, A. Pfaltz, *Synlett* **1997**, 1429; P. Prètôt, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 337; *Angew. Chem. Int. Ed.* **1998**, 323.

[14] J. V. Allen, J. M. J. Williams, *Tetrahedron: Asymmetry* **1994**, *5*, 277; L. N. Pridgen, G. Miller, *J. Heterocycl. Chem.* **1983**, *20*, 1223.

[15] R. Koradi, M. Billeter, K. Wüthrich, *J. Mol. Graphics* **1996**, *14*, 51.

[16] D. Seebach, R. Dahinden, R. E. Marti, A. K. Beck, D. A. Plattner, F. N. M. Kühnle, *J. Org. Chem.* **1995**, *60*, 1788.

[17] H. Brunner, H. Nishiyama, K. Itoh, in 'Catalytic Asymmetric Synthesis', Ed. I. Ojima, VCH Publishers, New York, Weinheim, 1993, 303–322; H. Brunner, in 'Transition Metals for Organic Synthesis', Eds. M. Beller, C. Bolm, Wiley-VCH, Weinheim, New-York, 1998, Vol. 2, 131–140.

[18] a) S. Itsuno, M. Nakano, K. Miyazaki, H. Masuda, K. Ito, A. Hirao, S. Nakahama, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2039; E. J. Corey, R. K. Bakshi, S. Shibata, *J. Am. Chem. Soc.* **1987**, *109*, 5551; b) L. Deloux, M. Srebnik, *Chem. Rev.* **1993**, *93*, 763; D. J. Mathre, I. Shinkai, in 'Encyclopedia of Reagents for Organic Synthesis', Ed. L. Paquette, J. Wiley & Sons, Chichester, 1995, Vol. 4, 2247–2250; G. J. Quallich, J. F. Blake, T. M. Woodall, in 'Reductions in Organic Synthesis. Recent Advances and Practical Applications', Ed. A. F. Abdel-Magid, ACS Symposium Series 641, American Chemical Society, Washington, DC, 1996, Chapt. 7, 112–126.

[19] R. Noyori, I. Tomino, Y. Tanimoto, M. Nishizawa, *J. Am. Chem. Soc.* **1984**, *106*, 6709; R. Noyori, I. Tomino, M. Yamada, M. Nishizawa, *J. Am. Chem. Soc.* **1984**, *106*, 6717.

[20] a) D. Seebach, A. K. Beck, R. Dahinden, M. Hoffmann, F. N. M. Kühnle, *Croat. Chim. Acta* **1996**, *69*, 459; b) A. K. Beck, R. Dahinden, F. N. M. Kühnle, in 'Reductions in Organic Synthesis. Recent Advances and Practical Applications', Ed. A. F. Abdel-Magid, ACS Symposium Series 641, American Chemical Society, Washington, DC, 1996, Chapt. 3, 52–69.

[21] H. Brunner, U. Obermann, *Chem. Ber.* **1989**, *122*, 499.

[22] P. Teixidor, F. Camps, A. Messeguer, *Heterocycles* **1988**, *27*, 2459.

[23] Y. Nishibayashi, K. Segawa, K. Ohe, S. Uemura, *Organometallics* **1995**, *14*, 5486.

[24] D. A. Dickman, A. I. Meyers, G. A. Smith, R. E. Gawley, *Org. Synth. Coll. Vol. VII*, J. Wiley & Sons, New York, 1990, pp. 530–533.

[25] R. Huisgen, C. Rüchardt, *Justus Liebigs Ann. Chem.* **1956**, *601*, 21.

[26] A. Siewinski, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1969**, *17*, 475.

[27] H. C. Brown, J. Chandrasekharan, P. V. Ramachandran, *J. Amer. Chem. Soc.* **1988**, *110*, 1539.

[28] T. Wirth, K. J. Kulicke, G. Fragale, *Helv. Chim. Acta* **1996**, 79, 1957.

[29] L. E. Craine, L. K. Bicknell, R. C. Mailloux, J. P. Mark, S. A. Mitchell, *J. Org. Chem.* **1993**, 58, 1251.

[30] M. Knollmueller, C. R. Noe, G. Steinbauer, K. Dungler, *Synthesis* **1986**, 501.

[31] M. A. Poelert, L. A. Hulshof, R. M. Kellogg, *Recl. Trav. Chim. Pays-Bas* **1994**, 113, 355.

[32] M. Palmer, T. Walsgrove, M. Wills, *J. Org. Chem.* **1997**, *62*, 5226.

[33] D. R. Boyd, N. D. Sharma, R. Boyle, T. A. Evans, J. F. Malone, *J. Chem. Soc. Perkin Trans. 1* **1996**, 1757.

[34] R. Iriye, K. Takai, M. Noguchi, *Bioorg. Med. Chem. Lett.* **1997**, 7, 199.

[35] K. Nakamura, M. Kawasaki, A. Ohno, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1079.

[36] M. Calmes, J. Daunis, R. Jacquier, F. Natt, *Org. Prep. Proced. Int.* **1995**, *27*, 107.

[37] J. D. White, T. C. Somers, G. N. Reddy, *J. Org. Chem.* **1992**, 57, 4991.

[38] H. Jacobs, K. Berryman, J. Jones, A. Gopalan, *Synth. Commun.* **1990**, *20*, 999.