similar results were obtained when toluene or cyclohexane was employed as a reaction solvent in these reactions either under argon or in vacuo.

b. Photochemical Reaction. Isopropyl methacrylate (8.0 mL, 55 mmol) was added to $MoH_4(dppe)_2$ (0.0932 g, 0.103 mmol) in a Pyrex Schlenk flask in vacuo, and the mixture was irradiated with stirring at 20 °C for 7.5 h to give a deep red solution. Polymerization of methacrylate was observed only in the vapor phase to give polymer films on the flask wall, and considerable reduction of contamination by the polymer in the solution was achieved by employing the photochemical reaction. The workup procedure was much easier than that in the thermal reaction. The resulting red solution was worked up as above to give product **2a** (0.0610 g, 57.5%). Similar results, but with lower yield, were obtained when the reaction was carried out under an argon atmosphere or in vacuo in benzene solution.

Reaction of $MoH_4(dppe)_2$ (1) with Ethyl Methacrylate. Complex 1 (0.475 g, 0.419 mmol) and ethyl methacrylate (3.0 mL, 24.7 mmol) in toluene (20 mL) were heated in vacuo at 80 °C for 30 h to give a deep red solution. Formation of H_2 and ethyl isobutyrate (each ca. 1 mol/mol of **1**) was observed by GLC analyses of the resulting system. The mixture was dried in vacuo to leave a deep red solid, which was dissolved in 15 mL of toluene. A brown precipitate that was formed on addition of 55 mL of hexane to the solution was filtered, and a red powder (0.25 g) was obtained by evaporating the solvent from the filtrate. The powder was recrystallized from toluene–hexane to give deep red, powdery crystals which were spectroscopically analyzed as $\overline{MoH[CH{=}C(CH_3)C(O)OC_2H_5](dppe)_2}$ (**2b**) (0.157 g, 15.6%).

Reaction of $MoH_4(dppe)_2$ (1) with *n*-Butyl Methacrylate. Complex 1 (0.313 g, 0.349 mmol) and 5.0 mL (31.3 mmol) of *n*-butyl methacrylate in toluene (20 mL) were heated at 80 °C in vacuo for 45 h to give a deep red solution. The formation of about 1 mol/mol of 1 of *n*-butyl isobutyrate was confirmed by GLC analysis. The system was worked up as above to yield 0.174 g of a red solid, which was recrystallized from pentane to give deep red, powdery microcrystals of $\overline{MoH[CH{=}C(CH_3)C(O)O\text{-}n\text{-}C_4H_9](dppe)_2}$ (yield 30.1%). Anal. Calcd for $C_{60}H_{62}O_2P_4Mo$: C, 69.63; H, 6.04. Found: C, 67.35; H, 6.04.

Reaction of $MoH_4(dppe)_2$ (1) with Cyclohexyl Methacrylate. To the flask containing 1 (0.273 g, 0.303 mmol) was added 5 mL (28.7 mmol) of cyclohexyl methacrylate by a trap-to-trap method. The mixture was heated at 100 °C in vacuo for 8 h to yield a red solution. The reaction was found to be accompanied by the formation of H_2 and cyclohexyl isobutyrate (0.43 and 1.28 mol/mol of **1**, respectively). From a red solid which was obtained by drying up the reaction mixture, a brick red solid (0.26 g, 81%) was extracted by hexane and was recrystallized from diethyl ether to give red powder of $\overline{MoH[CH{=}C(CH_3)C(O)O\text{-}c\text{-}C_6H_{11}](dppe)_2}$ (**2d**) (0.15 g, 14%). Anal. Calcd for $C_{62}H_{64}O_2P_4Mo$: C, 70.19; H, 6.08. Found: 70.42; H, 6.09.

Reaction of $\overline{MoH[CH{=}C(CH_3)C(O)OCH(CH_3)_2](dppe)_2}$ (2a) with Dry HCl. Red complex **2a** (0.0826 g, 0.089 mmol) dissolved in 4 mL of hexane was allowed to react in vacuo at room temperature for a day with 1.43 mmol of HCl gas, which was generated from NaCl and concentrated H_2SO_4, to give a pink precipitate. The precipitate was filtered off, washed with toluene, and dried to afford 0.0340 g of pink powder which was analyzed as $MoCl_2(dppe)_2$ (43.6%). From the filtrate, isopropyl isobutyrate (76.4% on the basis of **2a**) was detected by GLC analysis.

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Registry No. 1, 32109-09-4; **2a**, 100351-38-0; **2b**, 100351-39-1; **2c**, 100351-40-4; **2d**, 100351-41-5; isopropyl methacrylate, 4655-34-9; ethyl methacrylate, 97-63-2; *n*-butyl methacrylate, 97-88-1; cyclohexyl methacrylate, 101-43-9.

Asymmetric Catalysis. 29.[1] Optically Active Primary Amines by Enantioselective Catalytic Hydrosilylation of Ketoximes

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Alkyl aryl ketoximes $R^1R^2C{=}NOH$ were shown to undergo a novel catalytic hydrosilylation with diphenylsilane in homogeneous solution. Three moles of H_2SiPh_2 were consumed, giving the products $Ph_2HSiOSiHPh_2$ and the silylamines $R^1R^2HCNHSiHPh_2$ which on hydrolysis yielded the primary amines $R^1R^2HCNH_2$. In situ catalysts consisting of $[Rh(cod)Cl]_2$ and optically active phosphines of the type (–)-diop and (–)-Norphos were used to control the enantioselectivity. Fourteen prochiral ketoximes were studied; optical inductions up to 36% ee (ee = enantiomeric excess) were obtained. Five ketimines, $R^1R^2C{=}NH$, were included in the study to demonstrate that ketimines are intermediates in the oxime hydrosilylation.

Introduction

Enantioselective catalysis with optically active transition-metal compounds is a method of increasing importance for the preparation of optically active compounds.[2] The types of reactions which can be catalyzed enantioselectively have been continuously expanded through the last years. Besides the classical enantioselective hydrogenation, reactions such as hydroformylation, isomerization, hydrovinylation, cross-coupling, allylation, cyclopropanation, hydrocyanation, epoxidation, and hydrosilylation were studied intensively.[3]

Enantioselective hydrosilylation with optically active transition-metal catalysts was used hitherto for the re-

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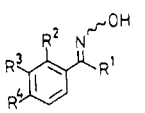
Table I. Hydrosilylation of Ketoximes 1–4 with Diphenylsilane [Solvent = 5 mL of Benzene (Method A) and 2 mL of Benzene (Method B)]

no.	substrate	Rh/substr	Rh/ligand	substr/ silane	reactn time, h	T, °C	yield, %	ee, %	no. of runs	reproduc, ±% ee	method
					Catalyst $[Rh(cod)Cl]_2$/(−)-diop						
1	1	1:100	1:1.2	1:3.2	24	−10→20	47	4.3 (*R*)	3	1.0	A
2	2	1:200	1:1.5	1:3.2	192	−10→20	29	5.8 (*R*)	1		A
3	2	1:200	1:1.5	1:3.0	24	50	39	7.6 (*R*)	3	0.8	A
4	3	1:200	1:1.0	1:3.0	144	−10→20	20	18.9 (*R*)	2	0.2	A
5	3	1:200	1:1.0	1:3.0	44	50	30	12.7 (*R*)	3	0.8	A
6	4	1:100	1:1.0	1:3.3	120	0→20	100	29.7 (*S*)	5	7.5	B
7	4	1:100	1:1.2	1:3.3	120	0→20	100	36.0 (*S*)	4	8.4	B
8[a]	1	1:200	1:1.2	1:3.3	96	−10→20	49	9.4 (*R*)	2	0.9	B
9[b]	1	1:200	1:1.2	1:3.3	96	−10→20	47	14.8 (*R*)	2	1.7	B
10[c]	1	1:200	1:1.2	1:3.3	96	−10→20	22	14.7 (*R*)	3	1.0	B
11[d]	1	1:200	1:1.2	1:3.3	96	−10→20	38	19.4 (*R*)	2	0.4	B
12[d]	4	1:200	1:1.2	1:3.3	120	−10→20	55	11.9 (*R*)	3	1.6	B
13[f]	4	1:200	1:1.2	1:3.3	120	−10→20	60	6.6 (*R*)	3	3.9	B
14[e]	1	1:200	1:1.2	1:3.3	96	−10→20	66	8.1 (*R*)	5	1.6	B
					Catalyst $[Rh(cod)Cl]_2$/(−)-Norphos						
15	4	1:100	1:1.2	1:3.3	96	0→20	68	16.5 (*S*)	3	0.8	B
16[d]	4	1:200	1:1.2	1:3.3	120	−10→20	35	15.0 (*R*)	3	4.0	B
					Catalyst $[Rh(cod)Cl]_2$/(−)-PPM						
17	1	1:200	1:1.2	1:3.3	68	0→20	30	0.8 (*R*)	4	0.8	B

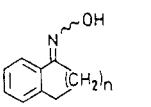
[a] In 2 mL of benzene/CH_2Cl_2 (1:1). [b] In 2 mL of CH_2Cl_2. [c] $Rh:NH_4PF_6$ = 1:1, in 2 mL of benzene. [d] $Rh:NH_4PF_6$ = 1:1, in 2 mL of CH_2Cl_2. [e] $Rh:NEt_3$ = 1:1. [f] $Rh:NH_4PF_6$ = 1:2, in 2 mL of CH_2Cl_2.

duction of prochiral olefines, ketones, and imines to give optically active alkylsilanes,[4,5] secondary alcohols,[6-13] and secondary amines.[14,15] In the literature there is only one paper on the asymmetric hydrogenation of oximes with a $H_4Ru_4(CO)_8$(diop) catalyst.[16] Recently we reported in a short communication on the enantioselective hydrosilylation of ketoximes for the preparation of optically active primary amines.[17] The corresponding hydrosilylation of D-camphor oxime was accompanied by a hydrogenolytic cleavage of a C–C bond, the products being the bornylamines and the optically pure primary amine (+)-(1*R*,3*S*)-1-(2-aminoethyl)-2,2,3-trimethylcyclopentane.[18] For synthesis the reaction seems very promising due to the ready accessibility of oximes by reaction of ketones with hydroxylamine. In this paper we report on our results of the enantioselective hydrosilylation of prochiral oximes 1–14 (Chart I).[19,20] The prochiral imines

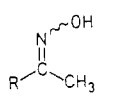
Chart I



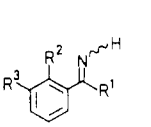
	1	2	3	4	5	6	7	8	9
R^1	CH_3	C_2H_5	$CH(CH_3)_2$	$C(CH_3)_3$	$CH(CH_3)_2$	CH_3	CH_3	CH_3	CH_3
R^2	H	H	H	H	CH_3	H	H	OCH_3	H
R^3	H	H	H	H	H	H	H	H	OCH_3
R^4	H	H	H	H	H	CH_3	OCH_3	H	OCH_3



	10	11
n	1	2



	12	13	14
R	1-$C_{10}H_7$	2-$C_{10}H_7$	$C_6H_5CH_2$



	15	16	17	18	19
R^1	$CH(CH_3)_2$	$CH(CH_3)_2$	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$
R^2	CH_3	H	CH_3	H	H
R^3	H	CH_3	H	CH_3	H

Scheme I

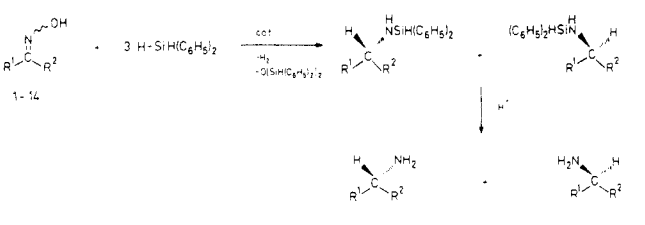


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Table II. Hydrosilylation of Ketoximes 5–9 with Diphenylsilane [Solvent = 5 mL of Toluene (Method A) and 2 mL of Toluene (Method B)]

no.	substr	Rh/substr	Rh/ligand	substr/ silane	reactn time, h	T, °C	yield, %	ee, %	no. of runs	reproduc, ±% ee	method
					Catalyst $[Rh(cod)Cl]_2$/(−)-diop						
1	**5**	1:200	1:1.2	1:3.3	120	0→20	33	13.9 (*R*)	4	0.5	A
2	**6**	1:200	1:1.0	1:3.3	44	−10→20	27	8.2 (*R*)	4	2.2	B
3	**7**	1:200	1:1.0	1:3.3	47	−10→20	39	4.5 (*R*)	6	1.9	B
4	**8**	1:200	1:1.0	1:3.3	94	−10→20	21	14.5 (*R*)	2	0.2	A
5[a]	**8**	1:200	1:1.2	1:3.3	94	−10→20	24	15.3 (*R*)	3	5.8	B
6[b]	**8**	1:200	1:1.2	1:3.3	94	−10→20	28	16.5 (*R*)	2	2.3	B
7	**9**	1:100	1:1.0	1:3.3	48	−10→20		6.5 (*R*)	3	1.6	B
					Catalyst $[Rh(cod)Cl]_2$/(−)-Norphos						
8	**5**	1:200	1:1.0	1:3.3	44	−10→20	28	5.0 (*R*)	6	1.0	B
9	**7**	1:200	1:1.0	1:3.3	93	−10→20	20	1.4 (*R*)	6	1.0	B

[a] $Rh:NH_4PF_6$ = 1:1. [b] $Rh:NH_4PF_6$ = 1:1, in 2 mL of CH_2Cl_2.

Table III. Hydrosilylation of Ketoximes 10–14 with Diphenylsilane Using the $[Rh(cod)Cl]_2$/(−)-diop Catalyst (Solvent = 5 mL of Benzene)

no.	substr	Rh/substr	Rh/ligand	substr/ Ph_2SiH_2	reactn time, h	T, °C	yield, %	ee, %	no. of runs	reproduc, ±% ee
1	**10**	1:200	1:1.0	1:3.3	184	50	32	12.9 (*R*)	2	0.1
2	**10**	1:200	1:1.3	1:3.3	184	50	41	8.4 (*R*)	6	0.8
3	**11**	1:200	1:1.3	1:3.3	120	−10→20	59	9.1 (*R*)	13	1.3
4	**11**	1:200	1:1.2	1:3.3	288	0	50	13.0 (*R*)	2	1.5
5[a]	**11**	1:200	1:1.2	1:3.3	408	−5	26	18.7 (*R*)	2	1.4
6	**12**	1:200	1:1.0	1:3.3	144	−10→20	49	15.0 (*R*)	2	0.5
7	**12**	1:200	1:1.2	1:3.3	144	−10→20	47	16.2 (*R*)	6	2.2
8	**13**	1:200	1:1.0	1:3.3	144	−10→20	49	6.3 (*R*)	2	0.3
9	**13**	1:200	1:1.2	1:3.3	144	−10→20	47	8.3 (*R*)	6	1.1
10[b]	**14**	1:200	1:1.1	1:3.3	264	−10→20	23	4.0 (*S*)	2	0.1
11	**14**	1:200	1:1.4	1:3.3	432	−10→20	30	7.1 (*S*)	2	0.1

[a] In 5 mL of toluene. [b] After 96 h heated to 50 °C.

15–19, containing a NH group, were included in this study to demonstrate common intermediates.

Results

Hydrosilylation of Oximes. The prochiral ketoximes **1–14** prepared from the corresponding ketones,[21] can exist as *E* and *Z* isomers. As the ^1H NMR signals of *E*/*Z* isomers of oximes frequently coalesce,[22,23] especially in $CDCl_3$ solution, the present study used the *E*/*Z* mixtures as formed in the syntheses.[19,20] The catalysts for the hydrosilylation of oximes **1–14** were prepared in situ from the procatalyst $[Rh(cod)Cl]_2$ and the optically active chelate phosphines (−)-diop,[24,25] (−)-Norphos,[26,27] and (−)-PPM.[28,29]

For the catalytic oxime hydrosilylations according to Scheme I the oxime and the catalyst were dissolved in benzene or toluene. The reaction was started by addition of diphenylsilane at 0 or −10 °C. Then the reaction mixture was slowly warmed up to room temperature and stirred for the reaction time indicated in Tables I–III. The progression of the reaction could be monitored by ^1H NMR spectroscopy (disappearance of the SiH signal of H_2SiPh_2 (δ ~5.0) and appearance of the SiH signals of tetraphenyldisiloxane (δ ~5.9) and the silylamine (δ ~5.5)). Chemical and optical yields of the catalytic hydrosilylations were determined by two different methods designated A and B.

In method A hydrolysis of the Si–N bonds in the hydrosilylation products was carried out with methanol/HCl. The amine fraction was transferred into an acidic water phase and extracted from it with ether under basic conditions. The chemical yield was determined by weighing the distilled amine fraction. For determination of the optical yield by gas chromatography, part of the amine fraction was trifluoracetylated with trifluoracetic acid anhydride. In all the cases **1–14** there was base-line separation of the enantiomers of the trifluoracetamides on the optically active polysiloxane phase Chirasil-L-Val[30] except for **14a**, the enantiomeric excess of which was determined polarimetrically (Table VI). The optical yield was calculated from the peak areas of the *R* and *S* isomers. The assignment of configuration was made on the basis of the fact that the retention times for the *S* isomers are longer than those for *R* isomers.[31]

In method B 2,6-dimethylnaphthalene was added as an internal standard. Without preceding hydrolysis and acid/base workup of the amine fraction the silylamines were directly converted to the trifluoracetamides. Besides the *N*-trifluoracetamides and the internal standard to be analyzed by gas chromatography the organic phase contained as byproducts the catalyst system, polysiloxanes, and siloxanes, unsuitable for gas chromatography analysis

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because of their low volatility. Therefore, the back-flush technique described in the Experimental Section was used.

In Tables I–III the reaction conditions (columns 2–7), chemical yields and enantiomeric excess (columns 8 and 9), number of runs, reproducibility of enantiomeric excess, and workup methods (columns 10–12) for the catalytic hydrosilylation of ketoximes **1–14** with diphenylsilane are given. Tables I–III contain the results of 132 runs for 37 different systems. The results of further experiments, subsequently used to establish trends in the following paragraphs, are listed in ref 19.

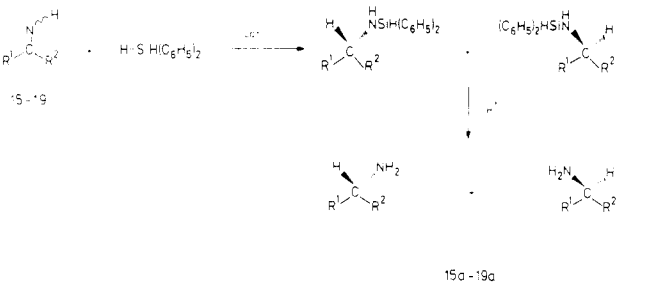
Runs 1–7 (Table I). With the $[Rh(cod)Cl]_2$/(−)-diop catalyst the alkyl phenyl ketoximes 1–4 gave increasing optical yields with increasing size of the alkyl group from 4.3% ee for the Me, 5.8% for the Et, and 18.9% ee for the *i*-Pr to 36.0% ee for the *t*-Bu derivatives (runs 1, 2, 4, and 7). Whereas the *R* configuration in the product was preferred for the oximes **1–3**, the enantioselectivity is reversed for *tert*-butyl phenyl ketoxime **4** (runs 6 and 7), an effect also observed in the hydrosilylation of the corresponding ketones.[32–35] Chemical yields of amines were between 20 and 50%, except for **4** where the yields were quantitative. For sterically hindered ketoximes longer reaction times or higher temperatures were necessary to obtain chemical yields around 30%. Optical yields of oxime **4** were poorly reproducible (runs 6 and 7).

Runs 8–14 (Table I). In the hydrosilylation of **1** optical induction increased from 4.3% ee to 14.8% ee as the solvent was changed from benzene to dichlormethane (runs 1, 8, and 9). A similar increase was observed in both solvents if 1 molar equiv of NH_4PF_6 with respect to Rh was added (runs 10, 11). A comparable admixture of NH_4PF_6 in the hydrosilylation of **4**, however, inverted the direction of enantioselectivity (runs 12, 13, 6, and 7). Addition of corresponding amounts of NBu_4F/18-crown-6 prevented catalysis.[19] Admixture of NEt_3 in the hydrosilylation of **1** in benzene doubled the optical induction, but reaction times were longer (runs 1 and 14).

Runs 15–17 (Table I). With the $[Rh(cod)Cl]_2$/(−)-Norphos catalyst an induction of 16.5% ee (*S*) in the hydrosilylation of **4** was obtained which was inverted to 15.0% ee (*R*) by NH_4PF_6 addition (runs 15 and 16). The cocatalyst (−)-PPM did not lead to appreciable enantiomeric enrichment (run 17).

Runs 1–9 (Table II): In the hydrosilylation of ring-substituted alkyl phenyl ketoximes **5–9** chemical yields were lower than for the unsubstituted acetophenone oxime **1**. *m*- and *p*-nitroacetophenone oxime could not be hydrosilylated, even at temperatures of 50 °C.[19] Enantioselectivity for the *o*-CH_3-substituted isopropyl phenyl ketoxime **5** with 13.9% (*R*) was comparable to the unsubstituted derivative **3** (run 1; cf. runs 3 and 4 of Table I). Optical inductions for the ring-substituted acetophenone oximes **6–9** were in the range 4.5–14.5% (*R*) for the $[Rh(cod)Cl]_2$/(−)-diop catalyzed reaction (runs 2–4 and 7) and thus higher than for unsubstituted **1** (cf. run 1 of Table I). Compared to the *p*-OCH_3 derivative **7**, the *o*-OCH_3 derivative **8** gave a threefold increase in enantioselectivity, whereas the turnover number decreased (runs 3 and 4). Addition of NH_4PF_6 in the hydrosilylation of **8** in toluene and CH_2Cl_2 caused a slight increase in induction (runs 5 and 6) without reversing the product configuration as observed in runs 12 and 13 of Table I. Similar to the results in Table I the $[Rh(cod)Cl]_2$/(−)-Norphos system was less enantioselective than the $[Rh(cod)Cl]_2$/(−)-diop system (runs 8 and 9).

Scheme II



Runs 1–5 (Table III). Hydrosilylation of 1-indanone oxime **10** and 1-tetralone oxime **11** required long reaction times. 1-Indanone oxime could only be hydrosilylated in acceptable reaction times at higher temperatures. The optical induction in the hydrosilylation was dependent on the Rh/(−)-diop ratio for **10**, but not for **11** (runs 1–3).[19,20] However, optical induction for **11** could be improved to 13.0 and 18.7% ee when the reaction was carried out at 0 °C in benzene or at −5 °C in toluene, although reaction times became very long (runs 4 and 5).

Runs 6–11 (Table III). A dependence of optical induction on the position of the oxime function in the naphthalene system was found in the hydrosilylation of **12** and **13**. In the $[Rh(cod)Cl]_2$/(−)-diop catalyzed reaction the optical yield for the 1-naphthalene isomer was about two to three times as high as for the 2-naphthalene isomer. Also, a slight increase of ee values with increasing Rh/(−)-diop ratio was observed (runs 6–9).[19,20]

Dialkyl ketoximes, like methyl ethyl ketoxime and methyl isopropyl ketoxime, could not be catalytically hydrosilylated.[19] With methyl benzyl ketoxime, however, amphetamine was formed after long reaction periods in up to 7.1% ee (runs 10 and 11).

Attempts to hydrosilylate *O*-substituted oximes were not successful. *O*-Trimethylsilyl-, *O*-dimethylsilyl-, *O*-acetyl-, *O*-methyl-, and *O*-tosyl-substituted acetophenone oximes could not be reduced to amines with several hydrosilanes and catalysts.[19]

Diphenylsilane was used for all the hydrosilylations described above. In an additional screening it was investigated whether H_2SiPh_2 could be replaced by other hydrosilanes. A series of experiments using Me_2SiHCl, $MeSiHCl_2$, Et_3SiH, and $(EtO)_3SiH$ together with Rh, Pt, and Pd catalysts in benzene solution was monitored by ^1H NMR spectroscopy.[19] Only the systems with Me_2SiHCl and $MeSiHCl_2$ and Zeise's salt as the catalyst showed catalytic activity, although conversion was only <60%.

Hydrosilylation of Ketimines. The imines **15–19** were prepared from nitriles and Grignard reagents followed by methanolysis.[36–38] The hydrosilylation reactions were run without solvent with in situ catalysts composed of $[Rh(cod)Cl]_2$ and optically active P and N ligands, respectively, according to Scheme II.[19,20]

Diphenylsilane was added to the mixture of procatalyst, cocatalyst, and imine at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for the time given in Table IV. Reaction could be monitored by ^1H NMR spectroscopy (disappearance of the SiH signal at δ ~5.0 and appearance of the SiH doublet at δ ~5.5 of the silylamines). For workup the reaction mixture was hydrolyzed with methanol/HCl. The amine fraction was

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Table IV. Hydrosilylation of Ketimines 15–19 with Diphenylsilane without Solvent Using the Catalyst $[Rh(cod)Cl]_2$/(-)-diop

no.	substr	Rh/substr	Rh/ligand	substr/Ph_2SiH_2	reactn time, h	T, °C	yield, %	ee, %	no. of runs	reproduc, ±% ee	method
1	15	1:400	1:1.2	1:1.1	46	0→20	77	11.6 (*R*)	23	2.3	A
2	15	1:200	1:1.2	1:1.1	149	0	69	1.2 (*R*)	3	0.6	A/B
3	15	1:200	1:1.2	1:1.1	117	−5	54	0.7 (*R*)	2	0.1	A
4[a]	15	1:200	1:1.2	1:1.1	72	0→20	71	8.0 (*R*)	2	0.2	A
5	16	1:200	1:1.1	1:1.1	24	0→20	60	13.8 (*R*)	7	1.1	A
6	17	1:200	1:1.4	1:1.1	40	75	75	4.4 (*R*)	13	1.3	A
7[a]	17	1:200	1:1.2	1:1.1	96	54	70	6.0 (*S*)	2	0.3	A
8	18	1:200	1:1.1	1:1.1	24	0→20	30	13.2 (*S*)	4	3.3	A
9	19	1:190	1:1.2	1:1.2	24	−10→25	75	23.1 (*S*)	17	13.8	A
10[a]	15	1:200	1:1.1	1:1.1	15	0→20	57	7.9 (*R*)	4	0.4	A
11[b]	16	1:200	1:1.1	1:1.1	72	0→20	50	1.5 (*R*)	2	0.5	A
12[c]	15	1:350	1:1.0	1:1.1	40	0→20	77	0.5 (*R*)	4	0.4	A
13[d]	15	1:350	1:1.3	1:1.1	24	0→20	69	5.6 (*S*)	1		A
14[e]	15	1:200	1:5.1	1:1.1	147	0→20	77	1.0 (*S*)	3	1.0	A
15[f]	15	1:200	1:3.0	1:1.1	15	0→20	65	2.5 (*S*)	7	1.4	A

[a] In 5 mL of benzene. [b] Catalyst $[Rh(cod)Cl]_2$/(-)-Norphos. [c] Catalyst $[Rh(cod)Cl]_2$/(-)-Prophos. [d] Catalyst $[Rh(cod)Cl_2]$/(-)-BPPFA. [e] Catalyst $[Rh(cod)Cl]_2$/(+)-L, (+)-L = pyridine imine derived from 2-pyridine carbaldehyde and (*S*)-(-)-1-phenylethylamine.[10] [f] Catalyst: $[Rh(cod)Cl]_2$/(+)-L′, (+)-L′ = pyridinethiazolidine derived from 2-acetylpyridine and L-(-)-cysteine methyl ester hydrochloride.[13]

isolated, distilled, and analyzed according to methods A and B.

Table IV contains the results for the catalytic hydrosilylation of imines **15–19** with diphenylsilane (94 runs for 15 different systems). To our knowledge, imines, containing a NH group, have not been previously used in the asymmetric hydrosilylation.

Runs 1–11 (Table IV). In the hydrosilylation with the $[Rh(cod)Cl]_2$/(-)-diop catalyst the imine **15** gave an optical induction of 11.6% ee, with a reproducibility of ±2.3% in 23 separate experiments (run 1). Surprisingly, lowering the reaction temperature to 0 and −5 °C, an effect, which usually increases selectivity, led to a drastic drop of enantioselectivity to 1.2 and 0.7% ee (runs 2 and 3). In benzene solution an intermediate value of 8.0% ee was obtained (run 4). Imines **16** and **17** under comparable conditions gave 13.8 and 4.4% ee (runs 5 and 6). For imine **17** enantioselectivity increased slightly if the hydrosilylation was carried out in benzene solution (run 7). The highest optical inductions of all the imines studied were achieved with imines **18** and **19** with 13.2 and 23.1% ee (runs 8 and 9), although it should be noted that the reproducibility was poor. This was perhaps due to impurities in the relatively unstable imines **18** and **19**, accessible only in low yields.

Runs 12–15 (Table IV). Similar to the hydrosilylation of ketoximes (Tables I and III), imines **15** and **16** gave reduced enantioselectivities with (-)-Norphos as a cocatalyst compared to (-)-diop (runs 10 and 11). (-)-Prophos yielded no enantioselectivity with imine **15**, whereas with (-)-BPPFA 5.6% ee were observed (runs 12 and 13). The use of a pyridine imine derivative and a pyridinethiazolidine derivative, powerful procatalysts in the hydrosilylation of ketones,[8–10,13] resulted in only low optical inductions with imine **15** as a substrate, even if used in higher ligand/Rh ratios (runs 14 and 15).

Compared to oximes, ketimines were hydrosilylated in short reaction times of 24–48 h. with chemical yields of 50–70% exceeding those obtained for oximes. Only for the hydrosilylation of the sterically hindered *o*-tolyl *tert* butyl ketimine **17** were higher temperatures necessary (runs 6 and 7).

Discussion

Trends in the Hydrosilylation of Ketoximes 1–14. The catalytic hydrosilylation of oximes is a reaction system very sensitive to changes in the structure of substrate and catalyst affecting both chemical yield and optical induction. Remarkable trends are the increase of enantiomeric excess with increasing size of the alkyl substituent in the alkyl phenyl ketoximes **1–4** and the reversal of enantioselectivity in the case of *tert*-butyl phenyl ketoxime **4** compared to the oximes **1–3**. Addition of NH_4PF_6 to the in situ catalyst $[Rh(cod)Cl]_2$/(-)-diop increases the optical induction for acetophenone oxime; however, for *tert*-butyl phenyl ketoxime **4** it inverts the product configuration.

Methyl and methoxy substituents in the aryl group of aryl alkyl ketoximes gave optical inductions similar to the phenyl derivatives with strongly prolonged reaction times. Electron-withdrawing substituents like the nitrofunction in the aryl group or a 2-pyridyl group prevented the catalytic hydrosilylation completely, a fact which can be explained by the strong tendency to form stable complexes.

Higher optical inductions combined with slower reaction rates compared to **1–4** were found for the oximes **10** and **11** of indanone and tetralone. Both effects probably are due to the reduced flexibility of the alkyl substituent in these cyclic aryl alkyl ketoximes. Similarly, the higher optical induction of 1-naphthyl methyl ketoxime **12** with respect to the corresponding 2-isomer **13** can be rationalized on the basis of increased steric hindrance due to the peri H in **12** in the selectivity-determining step.

Simple dialkyl ketoximes cannot be hydrosilylated catalytically. Aryl substituents proximate to the oxime function appear to be essential. For the benzyl derivative **14**, however, which gives optically active amphetamine, reaction times are very long with the more active Wilkinson catalyst[19] and even longer with the less active in situ system $[Rh(cod)Cl]_2$/(-)-diop.

Mechanism. In the Beckmann rearrangement of oximes cleavage of the N–O bonds and alkyl/aryl migration take place. Since in the catalytic hydrosilylation of oximes the N–O bond is also cleaved, the reaction was carried out under conditions which favor the Beckmann rearrangement. However, addition of the strong Lewis acid BF_3, known to catalyze the Beckmann rearrangement,[39] did not change reaction rate and product composition significantly. Specifically, starting with acetophenone oxime only pure 1-phenylethylamine was isolated. Secondary amines, resulting from a Beckmann rearrangement, could not be detected. Also compounds with good leaving groups such as 3,4-dinitrophenyl or *p*-tolylsulfonyl at the oxime O atom did not undergo the catalytic hydrosilylation reaction. Therefore we favor a reaction course via nitrene inter-

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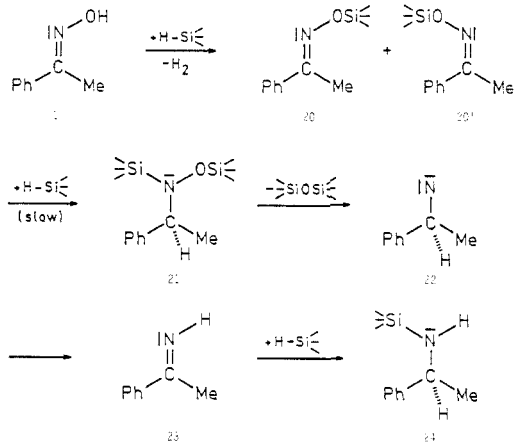
Scheme III



mediates, although we cannot exclude other possible mechanisms or even variants of the mechanism proposed in Scheme III.

The first step in Scheme III, formulated for acetophenone oxime **1**, is the formation of molecular hydrogen by reaction of one of the Si–H bonds of the first equivalent of diphenylsilane with the OH group of **1** to give the silyl oxime **20**. Similar dehydrocondensations are known for the catalyzed preparation of alkoxysilanes from alcohols.[40-44] ^{1}H NMR studies had shown that at 0 °C first only one (**20**) of the two syn–anti isomers is formed. The signals of the other (**20′**) grow in at 0 °C in the course of 2 h.[17]

The next step is proposed to be the addition of one of the Si—H bonds of the second equivalent of diphenylsilane to the C=N double bonds of the syn-anti isomers **20** and **20′** with formation of the hydroxylamine derivative **21**. α-Elimination of $SiHPh_2$ and $OSiHPh_2$ from the N atom of **21** yields tetraphenyldisiloxane, which can be observed by ^{1}H NMR spectroscopy and the nitrene **22**. Similar reactions are described in the literature.[45-48] One of the possible pathways from the nitrene **22** to the silylamine **24** is a 1,2-hydrogen shift from the asymmetric center to the N atom giving the imine **23**. Addition of one of the Si–H bonds of the third equivalent of diphenylsilane to **23** leads to the final product, silylamine **24**, observable by ^{1}H NMR spectroscopy. It is the enantioselectivity of the step imine **23** → silylamine **24** which is reflected in the enantiomeric excess of the primary amines obtained after hydrolysis. Other pathways to the silylamine **24** could be the insertion of the nitrene **22** into a Si–H bond of excess diphenylsilane or H abstraction by the nitrene **22** from other molecules in the reaction mixture to give a primary amine which is catalytically silylated with excess H_2SiPh_2 to give **24** similar to step **1** → **20**.

Comparison of the Hydrosilylation of Oximes and Imines. We tried to find evidence in favor of the mechanism of Scheme III by a separate study of the step imine **23** → silylamine **24** under the conditions of the catalytic enantioselective hydrosilylation. Imines **15–19**, stable enough to be isolated, gave optical inductions between 5 and 23% ee, similar to the corresponding ketoximes, however, with increased chemical yields and distinctly reduced reaction times.

The lower chemical yields in the hydrosilylation reaction of ketoximes compared to imines can be attributed to the formation of a nitrene intermediate of the type **22**. Besides giving silylamines of the kind **24** these reactive species can undergo a variety of reactions forming products[49] not isolated with the amine fraction after hydrolytic workup.

In the hydrosilylation of oximes the only intermediates observable by ^{1}H NMR spectroscopy are (i) the syn–anti isomers of type **20** and **20′** and (ii) the silylamine of type **24**. This is in accord with the assumption that the step silyloxime **20** → hydroxylamine **21** in Scheme III is rate-determining. It is also in accord with the observation that the hydrosilylation of imines, a fast step in Scheme III, needs shorter reaction times than that of ketoximes, which comprise the slow step of the Si–H addition to intermediates of the kind **21**.

With respect to enantioselectivity oxime **5**/imine **15** have to be compared with each other. Oxime **5** in toluene solution gave 13.9% ee and the corresponding imine **15** in benzene solution under comparable conditions gave 8% ee for amine **5a** = **15a** (Table II, run 1; Table IV, run 4). In both cases the product configuration was the same (*R*). The difference in enantioselectivity (13.9 and 8.0 % ee) is of the order of the solvent effect found in the present study. The reaction media to be compared are (i) in case of oxime **5** in toluene solution: 3 equiv of diphenylsilane, 1 equiv of oxime **5**, and only a small concentration of imine **15** which is formed as an intermediate and which is rapidly hydrosilylated and (ii) in the case of imine **15** in benzene solution: 1 equiv of diphenylsilane and 1 equiv of imine 15. Taking into account these differences in the reaction media, the two values 13.9% ee (*R*) and 8% ee (*R*) for oxime **5** and imine **15** are evidence in favor of the mechanism in Scheme III involving imine intermediates of the type **23** in the catalytic hydrosilylation of oximes.

4/**19** is another pair of corresponding oximes/imines with comparable enantioselectivities (Table I, runs 6 and 7; Table IV, run 9) and the same product configuration (*S*). Interestingly, for both oximes and imines the product configuration changes from *R* to *S* on going from the isopropyl derivatives **5** and **15** to the *tert*-butyl derivatives **4** and **19**, thus supporting the mechanism in Scheme III.

Experimental Section

Measurements. For analytical gas chromatography a Varian 1820 gas chromatograph with FID and the Spectra Physics SP 4000 and SP 4100 integration system were used. Enantiomers were separated on glass capillary columns (25 mm × 0.5 mm) and fused silica columns (50 mm × 0.22 mm) coated with Chirasil-L-Val.[30] The nuclear magnetic resonance spectra were measured with a Varian T-60 spectrometer, using Me_4Si as internal standard.

Materials. Diphenylsilane was prepared from dichlorodiphenylsilane.[50] Rhodium trichloride trihydrate and bis[(μ-chloro)(η^4-1,5-cyclooctadiene)rhodium], $[Rh(cod)Cl]_2$, were gifts from BASF AG. Tris(triphenylphosphine)chlororhodium,[51] (4*R*,5*R*)-(−)-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane, (−)-diop,[24,25] and (2*R*,3*R*)-(−)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene, (−)-Norphos,[26,27] were prepared following literature procedures. (2*S*,4*S*)-4-(Diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine, (−)-PPM, was commercially available from Merck Inc. The oximes **1–15**

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Table V. ^{1}H NMR Parameters (δ, Me_4Si Internal Standard, 60 MHz) and Melting Points/Boiling Points of Oximes/Imines 1-19

no.	solv	C=NOH	C=NH	aryl H	alkyl H	mp/bp, °C
1	CCl_4	10.10 (br, 1, OH)		7.07–7.68 (m, 5, Ph)	2.23 (s, 3, CH_3)	55–58 (EtOH/H_2O) (ref 55: 57.5–57.8)
2	CCl_4	10.17 (br, 1, OH)		7.13–7.75 (m, 5, Ph)	2.83 (q, 2, CH_2CH_3), 1.17 (t, 3, CH_2CH_3)	53–54 (EtOH/H_2O) (ref 56: 53–55)
3	CCl_4	9.40 (br, 1, OH)		7.08–7.48 (m, 5, Ph)	2.83/3.57 (h/h, 1, $CH(CH_3)_2$), 1.13/1.20 (d/d, 6, $CH(CH_3)_2$)	55.5–56 (EtOH/H_2O) (ref 57: 58–59)
4	$CDCl_3$	9.33 (br, 1, OH)		7.46–8.00 (m, 5, Ph)	1.63 (s, 9, $C(CH_3)_3$)	167–168 (EtOH/H_2O) (ref 58: 167)
5	$CDCl_3$	8.20 (br, 1, OH)		6.83–7.33 (m, 4, Ph)	2.72/3.57 (h/h, 1, $CH(CH_3)_2$), 2.23/2.26 (s/s, 3, CH_3), 1.05/1.13 (d/d, 6, $CH(CH_3)_2$)	66–77 (EtOH/H_2O)
6	$CDCl_3$	9.60 (br, 1, OH)		6.92–7.62 (m, 4, Ph)	2.32/2.37 (s/s, 6, $PhCH_3/CCH_3$)	62 (EtOH/H_2O) (ref 59: 61)
7	$CDCl_3$	9.40 (br, 1, OH)		6.70–7.73 (m, 4, Ph)	3.87 (s, 3, OCH_3), 2.33 (s, 3, CH_3)	88–89 (EtOH/H_2O) (ref 60: 86–87)
8	$CDCl_3$	9.67 (br, 1, OH)		6.77–7.57 (m, 4, Ph)	3.72 (s, 3, OCH_3), 2.33 (s, 3, CH_3)	94–96 (EtOH/H_2O) (ref 60: 96–96.5)
9	MeOH-d_4			6.85–7.42 (m, 3, Ph)	3.92 (s, 6, OCH_3), 2.28 (s, 3, CH_3)	145–146 (EtOH/H_2O) (ref 61: 144)
10	MeOH-d_4			7.30–7.10 (m, 4, Ph)	3.10–2.83 (m, 4, CH_2CH_2)	146 (EtOH/H_2O) (ref 62: 146)
11	$CDCl_3$	9.60 (br, 1, OH)		6.87–7.38 (m, 4, Ph)	2.50–3.03 (m, 4, CH_2CH_2), 1.57–2.08 (m, 2, $C(NOH)CH_2$)	101.5–102.5 (EtOH/H_2O) (ref 63: 102)
12/13	$CDCl_3$	8.90 (br, 1, OH)		7.25–8.15 (m, 7, Naph)	2.37 (s, 3, CH_3)	115–125 (EtOH/H_2O)
14	$CDCl_3$	9.13 (s, 1, OH)		7.06–7.33 (m, 5, Ph)	3.50 (s, 2, $PhCH_2$), 1.80 (s, 3, CH_3)	68–70 (petroleum ether) (ref 64: 69–71)
15	neat		9.30 (br, 1, NH)	6.67–7.25 (m, 4, Ph)	2.68 (h, 1, $CH(CH_3)_2$), 1.08/2.18 (d/d, 6, $CH(CH_3)_2$), 1.35/1.62 (s/s, 3, $PhCH_3$)	70–72 (0.1 torr) ref 36: 86–87 (5 mm))
16	neat		9.60 (br, 1, NH)	6.75–7.75 (m, 4, Ph)	3.02 (h, 1, $CH(CH_3)_2$), 2.20 (s, 3, $PhCH_3$), 1.06/1.63 (d/d, 6, $CH(CH_3)_2$)	89–91 (0.1 torr) (ref 36: 87–88 (5 mm)) 84–86 (0.1 torr) (ref 36: 93–94(5 mm))
17	$CDCl_3$		9.20 (br, 1, NH)	6.80–7.30 (m, 4, Ph)	1.18 (s, 9, $C(CH_3)_3$), 1.15 (s, 3, $PhCH_3$)	
18	neat		8.80 (br, 1, NH)	6.65–6.99 (m, 4, Ph)	2.25 (s, 3, $PhCH_3$), 1.20 (s, 9, $C(CH_3)_3$)	75–78 (0.1 torr) (ref 36: 91–93 (5 mm))
19	neat		9.17 (br, 1, NH)	6.78–7.48 (m, 5, Ph)	1.20 (s, 9, $C(CH_3)_3$)	71–74 (0.1 torr)

Table VI. ^{1}H NMR Parameters (δ, Internal Standard Me_4Si, 60 MHz) and Retention Times of Amines 1a–19a

no.	solv	aryl H	alkyl H, NH_2	RT, min (T_c)[a]
1a	$CDCl_3$	6.93–7.38 (m, 5, Ph)	3.93 (q, 1, $CHCH_3$), 1.28/1.37 (d/s, 5, $CHCH_3/NH_2$)	13.5 (105)
2a	neat	6.97–7.45 (m, 5, Ph)	3.60 (t, 1, $CHCH_2$), 1.11–1.87 (m, 4, CH_2CH_3, NH_2), 0.77 (t, 3, CH_2CH_3)	21.5 (105)
3a	$CDCl_3$	6.97–7.43 (m, 5, Ph)	3.48 (d, 1, $CHCH(CH_3)_2$), 1.35–2.12 (m, 3, NH_2, $CH(CH_3)_2$), 0.70/0.88 (d/d, 6, $CH(CH_3)_2$)	25.4 (105)
4a = 19a	neat	6.92–7.53 (m, 5, Ph)	3.53 (s, 1, $CHC(CH_3)_3$), 1.17 (s, 2, NH_2), 0.82 (s, 9, $C(CH_3)_3$)	13.2 (145)
5a = 15a	$CDCl_3$	6.92–7.52 (m, 4, Ph)	3.78 (d, 1, $CHNH_2$), 2.28 (s, 3, $PhCH_3$), 1.75 (h, 1, $CH(CH_3)_2$), 1.25 (s, 2, NH_2), 0.75/0.95 (d/d, 6, $CH(CH_3)_2$)	16.9 (153)
6a	$CDCl_3$	6.83–7.35 (m, 4, Ph)	3.93 (q, 1, $CHCH_3$), 2.25 (s, 3, $PhCH_3$), 1.27/1.37 (d/s, 5, $CHCH_3/NH_2$)	12.5 (125)
7a	$CDCl_3$	6.58–7.38 (m, 4, Ph)	3.57/3.90 (s/q, 4, $OCH_3/CHCH_3$), 1.22/1.52 (d/s, 5, $CHCH_3/NH_2$)	18.4 (110)
8a	$CDCl_3$	6.60–7.43 (m, 4, Ph)	4.33 (q, 1, $CHCH_3$), 3.82 (s, 3, OCH_3), 1.63 (s, 2, NH_2), 1.37 (d, 3, $CHCH_3$)	49.6 (125)[b]
9a	$CDCl_3$	6.58–7.07 (m, 3, Ph)	3.88/3.92/4.08 (s/s/q, 7, $OCH_3/OCH_3/CHCH_3$), 1.43/1.47 (d/s, 5, $CHCH_3/NH_2$)	23.9 (170)
10a	neat	6.80–7.30 (m, 4, Ph)	4.30 (m, 1, $CHNH_2$), 1.46 (s, 2, NH_2), 1.90–2.86 (m, 4, CH_2CH_2)	18.3 (110)
11a	neat	6.83–7.43 (m, 4, Ph)	3.66–4.00 (m, 1, $CHNH_2$), 1.30–2.10 (m, 8, $(CH_2)_3$, NH_2)	12.8 (120)
12a/13a	$CDCl_3$	7.17–8.17 (m, 7, Naph)	4.75/4.17 (q/q, 1, $CHCH_3$), 1.16–1.60 (d/d/s, 5, CH_3/NH_2)	15.3/21.0 (150)
14a	$CDCl_3$	6.96–7.10 (m, 5, Ph)	2.66–3.20 (m, 1, CH), 2.46 (d, 2, CH_2), 1.96 (s, 2, NH_2), 0.90 (d, 3, CH_3)	c
16a	$CDCl_3$	6.75–7.28 (m, 4, Ph)	3.90 (s, 3, $PhCH_3$), 1.48–2.15 (m, 1, $CH(CH_3)_2$), 1.77 (s, 2, NH_2), 1.30 (d, 1, $NCHCH(CH_3)_2$), 0.75/0.95 (d/d, 6, $CH(CH_3)_2$)	8.5 (125)
17a	$CDCl_3$	6.85–7.57 (m, 4, Ph)	4.00 (s, 1, $NCHC(CH_3)_3$, 2.32 (s, 3, $PhCH_3$), 1.22 (s, 2, NH_2), 0.88 (s, 9, $C(CH_3)_3$)	7.2 (125)
18a	$CDCl_3$	6.85–7.50 (m, 4, Ph)	3.58 (s, 1, $NCHC(CH_3)_3$), 2.30 (s, 3, $PhCH_3$), 1.32 (s, 2, NH_2), 0.85 (s, 9, $C(CH_3)_3$)	7.0 (125)

[a] RT = retention time of the *N*-TFA amides for 25-m Chirasil-L-Val; oven-temperature T_c (°C) in parentheses. RT = [RT(*R*) + RT(*S*)]/2 − RT(LM), where RT(*R*) and RT(*S*) are the retention times of the *R* and *S* enantiomers and RT(LM) is the retention time of the solvent. [b] 50-m Chirasil-L-Val. [c] No base-line separation of *R* and *S* enantiomers. Enantiomeric excess (ee) was determined polarimetrically, based on $[\alpha]^{15}_D$ +37.6°.[65]

were prepared from the corresponding ketones and hydroxylamine, liberated from hydroxylammonium chloride. The ketones for the synthesis of oximes **1–3**, **6–12**, and **14** were commercial products. *tert*-Butyl phenyl ketone for the preparation of **4** was obtained by methylation of isobutyrophenone.[52] Oxime **5** was synthesized by reacting NH_2OH with the ketimine **15**. Starting material for **13** was 1-indanone, obtained from 3-phenylpropionic acid.[53] ^1H NMR data and melting points for the oximes are given in Table V.

Ketimines **15–19** were prepared by addition of alkyl Grignard reagents to the corresponding aromatic nitriles followed by methanolysis according to literature procedures.[36-38] ^1H NMR data and boiling points for the imines are given in Table V.

Catalytic Procedures. Hydrosilylation of Oximes. Method A. Oxime (16 mmol) and catalyst were dissolved in 5 mL of solvent and stirred at room temperature for 10 min. Then the mixture was cooled to −10 °C. After 5 min 9.9 mL of diphenylsilane (52.4 mmol) was added to the stirred solution. The mixture was slowly warmed to room temperature and stirred until diphenylsilane had reacted completely as monitored by ^1H NMR spectroscopy.

For workup the reaction mixture was cooled to 0 °C, 50 mL of methanol was added, and the mixture was refluxed for 2 h. The solvent was evaporated, and the viscous residue was treated with 15 mL of 20% aqueous HCl at 0 °C and shaken with 30 mL of ether. The ether was washed with 15 mL of water and discarded. The combined water phases at 0 °C were made alkaline by addition of 15 mL of aqueous KOH. The amine fraction which separated on the surface was extracted with 50 and 30 mL of ether. The combined ether extracts were dried with anhydrous $MgSO_4$. After evaporation of the solvent the product was distilled in vacuo by using a microdistillation apparatus.

For the determination of the enantiomeric purity 200 mg of the isolated product was dissolved in 2 mL of THF, 0.4 mL of trifluoroacetic anhydride was added, and the mixture was stirred for 10 min. Addition of 5 mL of an aqueous solution saturated with $NaHCO_3$ increased the pH to >7. After extraction with 3 mL of ether and drying with anhydrous Na_2CO_3 the ether solution was directly used for GLC measurement.

Method B. The reaction was carried out as described for method A except with 2 mmol of oxime in 2 mL of solvent and 6.5 mmol of diphenylsilane. After completion of the reaction an accurately weighed amount (ca. 100 mg) of the internal standard 2,6-dimethylnaphthalene and 2 mL of THF were added. The mixture was stirred until the standard was fully dissolved. Trifluoracetylation of amines in this solution, its neutralization, and the preparation of the anhydrous ether solution for the GLC measurement were performed as described for method A. The GLC analysis was carried out by using a back-flush technique, in which a capillary precolumn (2-m SE 30) was inserted between the injector and the 50-m Fused-Silica Chirasil-L-Val column. A part of the eluate was passed through a detector after the precolumn. When the solvent, the trifluoracetamides, and the standard had passed through the precolumn and arrived in the main column, a carrier gas stream was flushed backward through the precolumn to elute higher boiling compounds through the injector and split system. After passage through the main column optical yields were determined as described for method A. Chemical yields were calculated relative to the internal standard.[54]

Hydrosilylation of Ketimines. Method A. To the catalyst system was added the liquid imine (16 mmol) without using a solvent in the standard procedure. After being stirred for 10 min at room temperature, the mixture was cooled to 0 °C. Then 3.3 mL of diphenylsilane (17.5 mmol) was added. Workup followed the procedure for oxime hydrosilylation (method A).

Method B. The same procedure as in method A was employed, except that 3 mmol of imine and 1.2 mL of diphenylsilane were used. Workup, including the addition of the standard, followed the procedure for oxime hydrosilylation (method B).

^1H NMR data of amines obtained after hydrolysis of the hydrosilylation products and microdistillation are given in Table VI.

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Registry No. (*E*)-**1**, 10341-75-0; (*Z*)-**1**, 50314-86-8; **1a**, 3886-69-9; (*E*)-**2**, 23517-42-2; (*Z*)-**2**, 23517-38-6; **2a**, 3082-64-2; (*E*)-**3**, 72846-70-9; (*Z*)-**3**, 72846-71-0; **3a**, 23844-66-8; (*E*)-**4**, 100485-49-2; (*Z*)-**4**, 69498-76-6; **4a**, 82729-98-4; (*E*)-**5**, 100485-50-5; (*Z*)-**5**, 100485-56-1; **5a**, 100485-64-1; (*E*)-**6**, 54582-23-9; (*Z*)-**6**, 54582-30-8; **6a**, 4187-38-6; (*E*)-**7**, 26358-63-4; (*Z*)-**7**, 73744-32-8; **7a**, 22038-86-4; (*E*)-**8**, 54582-21-7; (*Z*)-**8**, 54582-28-4; **8a**, 68285-23-4; (*E*)-**9**, 75906-45-5; (*Z*)-**9**, 75906-46-6; **9a**, 100570-24-9; (*E*)-**10**, 68253-35-0; (*Z*)-**10**, 100485-57-2; **10a**, 10277-74-4; (*E*)-**11**, 68253-36-1; (*Z*)-**11**, 100485-58-3; **11a**, 23357-46-2; (*E*)-**12**, 100485-51-6; (*Z*)-**12**, 100485-59-4; **12a**, 3886-70-2; (*E*)-**13**, 100485-52-7; (*Z*)-**13**, 100485-60-7; **13a**, 3906-16-9; (*E*)-**14**, 10048-64-3; (*Z*)-**14**, 10048-65-4; **14a**, 51-64-9; (*E*)-**15**, 100570-83-0; (*Z*)-**15**, 100570-84-1; (*E*)-**16**, 100485-53-8; (*Z*)-**16**, 100485-61-8; **16a**, 100485-65-2; (*E*)-**17**, 100485-54-9; (*Z*)-**17**, 100485-62-9; **17a**, 100485-66-3; (*E*)-**18**, 100485-55-0; (*Z*)-**18**, 100485-63-0; **18a**, 100485-67-4; (*E*)-**19**, 100570-82-9; (*Z*)-**19**, 100570-81-8; (−)-diop, 37002-47-4; (−)-Norphos, 71042-55-2; (−)-PPM, 61478-29-3; (−)-Prophos, 67884-33-7; $[Rh(Cod)Cl]_2$, 12092-47-6; H_2SiPh_2, 775-12-2; Me_2SiHCl, 1066-35-9; $MeSiHCl_2$, 75-54-7; Et_3SiH, 617-86-7; $(EtO)_3SiH$, 998-30-1; Zeise's salt, 16405-35-9; (*S*)-(−)-*N*-((2-pyridinyl)methylene)-α-methylbenzenamine, 51705-23-8; methyl 2-methyl-2-(2-pyridinyl)thiazolidine-4-carboxylate, 90697-22-6.

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