Asymmetric Syntheses. 20.[1] Enantioselective Hydrosilylation of Ketones with $[Rh(cod)Cl]_2$/Thiazolidine Catalysts

Henri Brunner,* Richard Becker, and Georg Riepl

Institut für Anorganische Chemie, Universität Regensburg, D-8400 Regensburg, Germany

Received February 27, 1984

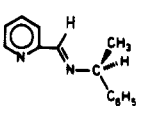
Optically active thiazolidines are new cocatalysts for the Rh-catalyzed enantioselective hydrosilylation of acetophenone with diphenylsilane. Compounds 1–17 are easily prepared in one-step condensations from carbonyl components and cysteine derivatives. Thiazolidine 3, derived from 2-pyridinecarbaldehyde and L-cysteine ethyl ester, with the procatalyst $[Rh(cod)Cl]_2$ gives 97% ee and quantitative chemical yield. Compounds 1–17 contain the (*R*)-cysteine chirality at C4 of the five-membered ring and during thiazolidine formation a new asymmetric center at C2 is formed. Diastereomers 2*R*,4*R* and 2*S*,4*R* can be separated but are epimerized at C2 in a fast Rh-catalyzed reaction. Therefore, the high ee's with cocatalysts 1–17 are achieved with diastereomer mixtures 2*R*,4*R*/2*S*,4*R* close to 1:1. Similarly, the hydrosilylations of the prochiral ketones benzyl methyl ketone, *tert*-butyl methyl ketone, and β-phenylethyl methyl ketone with $[Rh(cod)Cl]_2$/thiazolidine catalysts give higher ee's than with transition metal/phosphine catalysts.

Introduction

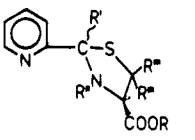
In enantioselective homogeneous catalysis chelate phosphine ligands in transition-metal complexes play a dominating role.[2] Some time ago we showed that in certain catalytic reactions optically active phosphine ligands can be replaced by nitrogen ligands.[3-8] As most of these nitrogen ligands derive from primary amines, the vast number of optically active primary amines available[9] can be used for their synthesis. Therefore, these nitrogen ligands are much less expensive and easier to prepare than optically active phosphines. In a recent review[10] arguments have been given in favor of a better chirality transmission within the catalyst from optically active nitrogen ligands to the prochiral substrate compared to optically active phosphorus ligands.

Chelating nitrogen ligands, derived from optically active primary amines, give high ee's in asymmetric hydrosilylation reactions.[3-7] The pyridine imine skeleton in ligands of type 0 has proved especially fruitful.[3,5] Varying the optically active amino component in these pyridine imine derivatives 0, we also used L-cysteine methyl ester which, however, does not form an imine of type 0 but, due to the additional SH group, thiazolidine 1. Surprisingly, thiazolidine 1 as a cocatalyst together with the procatalyst $[Rh(cod)Cl]_2$ gave the highest ee in the hydrosilylation of acetophenone with diphenylsilane reported up to now, as described in a short communication.[4] In this paper we give our results for the hydrosilylation of four prochiral ketones with diphenylsilane using thiazolidines 1–17 as cocatalysts in in situ catalysts with $[Rh(cod)Cl]_2$.[11,12]

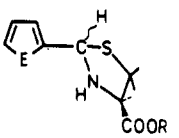
Chart I

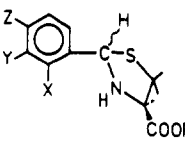


0



	1	2	3	4	5	6	7	8
R	CH_3	CH_3	C_2H_5	H	CH_3	C_2H_5	H	CH_3
R'	H	CH_3	H	H	H	H	H	CH_3
R''	H	H	H	H	$COCH_3$	$COCH_3$	H	CH_3
R'''	H	H	H	H	H	H	CH_3	H





	9	10
E	NH	S
R	CH_3	H

	11	12	13	14	15	16	17
R	H	C_2H_5	C_2H_5	C_2H_5	H	C_2H_5	CH_3
X	H	H	H	H	OH	OH	$P(C_6H_5)_2$
Y	H	H	OCH_3	OH	H	H	H
Z	H	H	OH	OCH_3	H	H	H

Results

Synthesis and Stereochemistry of Thiazolidines 1–17. Thiazolidines 1–17 (Chart I) were synthesized by using the corresponding aldehydes or ketones and L-cysteine, L-cysteine methyl ester, or L-cysteine ethyl ester, following established procedures.[13,14] For the preparation of 7 D-penicillamine was used. The carbonyl components in 1–8 are 2-pyridinecarbaldehyde or 2-acetylpyridine and in 9 and 10 are 2-pyrrolecarbaldehyde and 2-thienylcarbaldehyde. 11–16 are derived from benzaldehyde and OH- and OCH_3-substituted benzaldehydes, including salicylaldehyde in derivatives 15 and 16. Compound 17, con-

(1) Part 19: Brunner, H.; Vitulli, G.; Porzio, W.; Zocchi, M. *Inorg. Chim. Acta*, in press.
(2) Kagan, H. B. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, A. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 464.
(3) Brunner, H.; Riepl, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 377; *Angew. Chem. Suppl.* **1982**, 769.
(4) Brunner, H.; Riepl, G.; Weitzer, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 331; *Angew. Chem. Suppl.* **1983**, 445.
(5) Brunner, H.; Reiter, B.; Riepl, G. *Chem. Ber.* **1984**, *117*, 1330.
(6) Brunner, H.; Rahman, A. F. M. M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1332.
(7) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.* **1984**, *117*, 710.
(8) Brunner, H.; Hammer, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 312.
(9) Newman, P. "Optical Resolution Procedures for Chemical Compounds"; Optical Resolution Information Center: New York, 1979; Vol. 1.
(10) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897.
(11) Riepl, G. Ph. D. Thesis, University of Regensburg, 1983.
(12) Becker, R. Diploma Thesis, University of Regensburg, 1983.
(13) Soloway, H.; Kipnis, F.; Ornfelt, J.; Spoerri, P. E. *J. Am. Chem. Soc.* **1948**, *70*, 1667.
(14) Asinger, F.; Gluzek, K. H. *Monatsh. Chem.* **1983**, *114*, 47.

0276-7333/84/2303-1354$01.50/0

Table I. Hydrosilylation of 2 mL of Acetophenone A with 3.4 mL of Diphenylsilane without Solvent[a]

run	ligand	Rh/ligand	Rh/substrate	reactn time, h	% hydrosilylation	% ee
1	1	1/9	1/210	38	99	83.2 (*R*)
2	1[b]	1/9	1/210	235	98	86.7 (*R*)
3	1[c]	1/9	1/450	100	86	87.2 (*R*)
4	1	1/1.6	1/210	43	95	72.3 (*R*)
5	1	1/5	1/860	65	94	78.2 (*R*)
6	1	1/5	1/1710	65	92	78.9 (*R*)
7	1	1/5	1/2800	40	43	73.6 (*R*)
8	2	1/4	1/420	45	99	73.5 (*R*)
9	2	1/5	1/200	57	93	80.1 (*R*)
10	2[c]	1/5	1/240	87	90	84.1 (*R*)
11	2[d]	1/8	1/170	120	99	80.3 (*R*)
12	2[f]	1/8	1/210	93	45	45.5 (*R*)
13	3	1/2	1/440	63	95	75.6 (*R*)
14	3[e]	1/2	1/440	63	95	73.3 (*R*)
15	3[d]	1/13	1/140	120	99	97.6 (*R*)
16	4	1/7	1/410	63	93	76.6 (*R*)
17	5	1/7	1/390	23	40	14.5 (*S*)
18	6	1/8	1/450	65	28	6.0 (*S*)
19	7	1/2	1/400	23	32	5.0 (*S*)
20	7	1/9	1/420	65	32	9.0 (*S*)
21	8	1/8	1/230	100	95	69.8 (*R*)
22	9	1/10	1/390	48	65	17.0 (*R*)
23	10	1/5	1/410	24	31	1.0 (*R*)
24	11	1/5	1/420	24	35	2.0 (*S*)
25	12	1/6	1/230	40	59	3.0 (*R*)
26	13	1/5	1/210	38	72	18.6 (*R*)
27	14	1/6	1/210	40	61	10.3 (*R*)
28	15	1/5	1/420	63	78	0.4 (*S*)
29	16	1/7	1/370	24	19	0.7 (*S*)
30	17	1/1	1/420	24	97	3.2 (*S*)
31	17	1/1.4	1/420	24	85	3.9 (*S*)
32	17	1/6	1/420	24	94	2.6 (*R*)

[a] In situ catalysts from [Rh(cod)Cl]$_2$ and thiazolidines 1-17. Reaction temperature 0 → 25 °C.[3] [b] Reaction temperature −15 °C. [c] Reaction temperature −20 °C. [d] Diastereomer mixture epimerized at C2, reaction temperature −20 °C. [e] Diastereomer mixture epimerized at C2. [f] Hydrosilylation with phenyl-1-naphthylsilane.

Table II. Hydrosilylation of 2.7 mL of 1-Phenylpropan-2-one, B (Benzyl Methyl Ketone), 2.5 mL of 3,3-Dimethylbutan-2-one, C (*tert*-Butyl Methyl Ketone), or 3 mL of 4-Phenylbutan-2-one, D (β-Phenylethyl Methyl Ketone), with 4 mL of Diphenylsilane without Solvent[a]

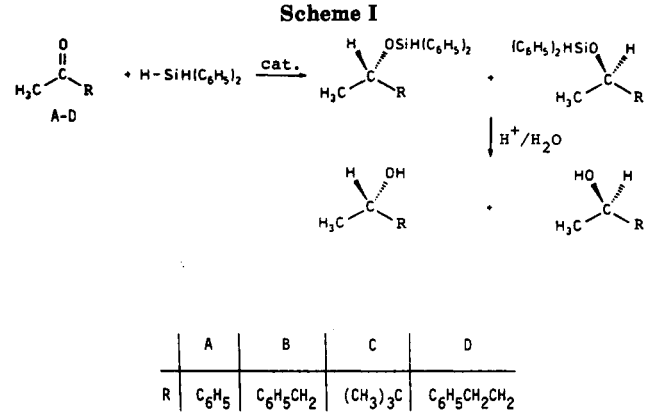
no.	ketone	ligand	Rh/ligand	Rh/ketone	reactn time, h	% hydrosilylation	% ee
1	B	1	1/2	1/190	44	97	7.1 (*R*)
2	B	1	1/10	1/190	42	91	52.7 (*R*)
3	B	2	1/8	1/190	72	94	39.5 (*R*)
4	C	1	1/9	1/300	40	98	31.5 (*R*)
5	C	2	1/8	1/300	64	100	68.5 (*R*)
6	D	2	1/9	1/360	48	99	55.0 (−)
7	D	3	1/2	1/200	48	98	26.9 (−)

[a] In situ catalysts from [Rh(cod)Cl]$_2$ and thiazolidines 1-3. Reaction temperature 0 → 25 °C.[3,5]

taining an *o*-P(C$_6$H$_5$)$_2$ substituent, can be regarded as a triphenylphosphine with a thiazolidinyl substituent in the ortho position of one of its phenyl rings. All the compounds are H substituted at the thiazolidine nitrogen except **5** and **6** which are acetylated and **8** which is methylated at the ring nitrogen atom.

All the thiazolidines **1–17** contain the original amino acid chirality *R* at C4 of the ring. During thiazolidine formation, however, a new asymmetric center at C2 of the ring, the C atom of the former carbonyl group, is formed.[15-17] Therefore, two diastereomers 2*R*,4*R* and 2*S*,4*R* arise that only differ in the configuration at C2, indicated in Chart I by the winding line. As the diastereomers exhibit different ^{1}H NMR spectra, the diastereomer ratio can be determined by the integration of appropriate signals. In some cases the diastereomers could be enriched by fractional crystallization and some were obtained optically pure. The optical rotations of the best enrichments achieved are given in the Experimental Section. If not otherwise stated, these diastereomer mixtures have been used for the asymmetric hydrosilylations.

Scheme I



	A	B	C	D
R	C_6H_5	$C_6H_5CH_2$	$(CH_3)_3C$	$C_6H_5CH_2CH_2$

(15) Parthasarathy, R.; Paul, B.; Korytnyk, W. *J. Am. Chem. Soc.* **1976**, *98*, 6634.
(16) Pesek, J. J. *Anal. Chem.* **1978**, *50*, 787.
(17) Nagasawa, H. T.; Goon, D. J. W.; Shirota, F. N. *J. Heterocycl. Chem.* **1981**, *18*, 1047.

Hydrosilylation of Acetophenone with Diphenylsilane. The in situ catalysts were prepared from the procatalyst $[Rh(cod)Cl]_2$ and cocatalysts **1–17** in acetophenone solution. As educts and products are liquids, no other solvent was used.[3] The standard hydrosilylation was started on addition of diphenylsilane at 0 °C. Then, the reaction mixture was slowly warmed up to room temperature and stirred for the reaction time indicated in Tables I and II. In the hydrosilylation reaction, shown in Scheme I one of the Si–H bonds of diphenylsilane adds to the C=O bond of acetophenone to give the silyl ether that is hydrolyzed to 1-phenylethanol. After distillation the chemical and optical yields were determined by GC and polarimetry as described previously.[3,5]

In Table I the ratio of Rh/thiazolidine is given, a 3–10-fold ligand excess being beneficial for high enantiomeric excess.[5,11,12] The Rh/acetophenone ratio in Table I shows that 0.5–0.2 mol % of catalyst has been used. The chemical yields were close to 100% for those catalysts that gave high ee's. Chemical yields in low-temperature hydrosilylations can be increased by longer reaction times. However, if the low chemical yields are due to the formation of the silyl enol ether of acetophenone,[18–20] which on hydrolysis regenerates acetophenone, they cannot be increased by longer reaction periods.

In the following the results of experiments 1–32 of Table I are discussed, each of which has been carried out several times (ee ± 1.5%).[5] With a 9-fold excess of thiazolidine **1** quantitative yields of 1-phenylethanol with 83.2% ee were obtained (run 1). Reducing the temperature to −15 and −20 °C increased the optical yield to 86.7 and 87.2% ee (runs 2, 3), although in run 3 less catalyst was used. For the pyridine imine containing catalyst $[Rh(cod)Cl]_2/0$ it was found that decreasing ligand excess led to a reduction of the optical yield.[5] However, run 4 shows that for the corresponding thiazolidine-containing catalyst $[Rh(cod)Cl]_2/1$ even with a ligand excess as low as 1.6-fold the optical yield only dropped to 72.3% ee. Furthermore the new thiazolidine-derived catalyst was remarkably active even at low concentrations (runs 5–7). Chemical yields of over 90% and high ee's could be achieved for catalyst concentrations down to 0.05 mol %.

For thiazolidine **2** an increase of the catalyst concentration increased the optical yields slightly (runs 8, 9); at a reaction temperature of −20 °C a further increase to 84.1% ee took place (run 10). Surprisingly, run 11 shows that a 60:40 diastereomer mixture of **2**, obtained by thermal epimerization of the pure diastereomer, under conditions comparable to run 10 gave only a slightly reduced enantiomeric excess. In transition metal/phosphine complex catalyzed hydrosilylations the prochiral phenyl-1-naphthylsilane sometimes gave higher ee's than diphenylsilane.[21–26] With regard to the catalyst $[Rh(cod)Cl]_2/2$ however, phenyl-1-naphthylsilane was inferior to diphenylsilane as far as yield and optical induction were concerned (runs 11, 12).

Thiazolidine **3** behaves similar to **2**. The optically pure diastereomer yielded 75.6% ee and the epimerized 50:50 mixture 73.3% ee (runs 13, 14). Experiment 15 in Table I contains the best result obtained up to now. A 13-fold excess of the 50:50 epimer mixture of **3** and $[Rh(cod)Cl]_2$ at −20 °C gave 99% chemical yield and 97.6% optical induction for a catalyst/substrate ratio of 1:140. The carboxylic acid **4** linked up with the esters **1–3** in giving good chemical and optical yields (run 16).

Acetyl substituents at the ring nitrogen atoms in thiazolidines **5** and **6** reduced conversion and enantiomeric excess drastically (runs 17, 18). This was also true for the penicillamine derivative **7** (runs 19, 20). In contrast to ligands **1–4** thiazolidines **5–7** favored the *S* configuration in 1-phenylethanol. With thiazolidine **8**, methylated at the ring nitrogen, ee's came up to 70% (run 21).

The pyrrole derivative **9**[27] gave a 65% yield with 17% *R*, the corresponding thienyl derivative **10**,[13] structurally similar to the pyridyl derivative **4**, however, only 31% yield and 1.0% *S* (runs 22, 23). It was not surprising that thiazolidines **11** and **12**, derived from benzaldehyde,[14] lacking the coordination possibilities of an additional pyridine, pyrrole, or thiophene group, gave only low optical inductions with the *S* or *R* configurations preferred (runs 24, 25). Although the OH and OCH_3 substituents in **13** and **14** are in the meta and para positions of the phenyl ring, relatively high optical inductions of 18.6% and 10.3% *R* were obtained with 60–70% chemical yields (runs 26, 27). The salicylaldehyde derivatives **15** and **16**, with the OH group in a position suitable for coordination, however, gave an enantiomeric excess below 1%, the catalyst derived from the acid **15** reacting much faster than the catalyst derived from the ester **16** (runs 28, 29). The reason for the low enantioselectivity in the catalysis with **15** might have been its low solubility. Run 28 was the only one that was not homogeneous due to undissolved **15** during the whole reaction time. Therefore dissolved and uncomplexed $[Rh(cod)Cl]_2$ might have catalyzed an achiral hydrosilylation giving the observed high chemical yield. With the triphenylphosphine derivative **17**[28] almost quantitative chemical yields with optical inductions between 3 and 4% were achieved (runs 30–32).

Hydrosilylation of Other Prochiral Ketones. Besides the system acetophenone/diphenylsilane, frequently used as a model system, the hydrosilylation of three other methyl ketones, containing *tert*-butyl, benzyl, and β-phenylethyl substituents, were investigated by using in situ catalysts $[Rh(cod)Cl]_2$/thiazolidines **1–3** (Table II).[20,21,24,29–36] For the reduction of benzyl methyl ketone B with the Rh complex of thiazolidine **1** the optical yield is strongly dependent on excess ligand, a 2-fold excess giving only 7.1% ee, whereas with a 10-fold excess 52.7% ee is achieved (no. 1, 2). Compared to thiazolidine **1** the enantiomeric excess obtainable with thiazolidine **2** is lower (no. 2, 3). For *tert*-butyl methyl ketone C it is the other

(18) Benes, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2264.
(19) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 38.
(20) Payne, N. C.; Stephan, D. W. *Inorg. Chem.* **1982**, *21*, 182.
(21) Dumont, W.; Poulin, I. C.; Dang, T. P.; Kagan, H. *J. Am. Chem. Soc.* **1973**, *95*, 8295.
(22) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671.
(23) Masuda, T.; Stille, I. K. *J. Am. Chem. Soc.* **1978**, *100*, 268.
(24) Peyronel, I. F.; Kagan, H. B.; Fiaud, I. C. *J. Chem. Soc. Minipr.* **1980**, 4057; *J. Chem. Res., Synop.* **1980**, 320.
(25) Johnson, T. H.; Klein, K. C.; Thomen, S. *J. Mol. Catal.* **1981**, *12*, 37.
(26) Kogure, T.; Ojima, I. *J. Organomet. Chem.* **1982**, *234*, 249.
(27) Brunner, H.; Weber, H., unpublished results.
(28) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.*, in press.
(29) Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1972**, *46*, C65.
(30) Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1973**, *54*, C45.
(31) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, *49*, 4405.
(32) Ojima, I.; Nagai, Y. *Chem. Lett.* **1974**, 223.
(33) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1975**, *85*, 19.
(34) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83.
(35) Hayashi, T.; Mise, T.; Kumada, M. *Tetrahedron Lett.* **1976**, 4351.
(36) Hayashi, T.; Yamamoto, K.; Kasuga, K.; Omizu, H.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 127.

way round. The optical induction for ligand **2** with 68.5% ee exceeds that for ligand **1** with 31.5% by far (no. 4, 5). Thiazolidine **2** also gives 55% ee with β-phenylethyl methyl ketone D, compared to thiazolidine **3** with only 26.9% ee. The chemical yields for ketones B–D are close to 100%.

Discussion

Most surprising in the use of thiazolidine ligands as cocatalysts in rhodium complexes is the fact that optically pure thiazolidines and diastereomer mixtures, completely epimerized at C2 of the thiazolidine ring, give very similar or identical optical inductions in the hydrosilylation reaction of Scheme I. This is demonstrated by thiazolidine **2**. The optically pure, less-soluble diastereomer (+)-**2**, obtained by fractional crystallization, gives an enantiomeric excess of 84.1% (Table I, run 10). (+)-**2** can be thermally epimerized at C2. By heating its solution in $CHCl_3$ to 50 °C for 8 h, an equilibrium mixture of (+)-**2**/(−)-**2** = 40:60 is obtained. With this diastereomer mixture as a cocatalyst 80.3% ee is achieved (Table I, run 11), almost the same value as with optically pure (+)-**2**. Similarly, a diastereomer mixture of **1** as low as 58:42 gives an optical induction of up to 87.2% (Table I, run 3). Thiazolidine **3** is analogous to **2**. By crystallization from ether/pentane it can be obtained optically pure. In $CHCl_3$ solution at room temperature it epimerizes in the course of hours to give a 50:50 diastereomer mixture. Runs 13 and 14 of Table I show that for thiazolidine **3** the optically pure diastereomer and the 50:50 mixxture give almost the same results. Furthermore, the best enantioselectivity of 97.6% ee, obtained for the model reaction in Scheme I up to now, was achieved with a 50:50 diastereomer mixture of **3** (run 15, Table I).

It is known that acids and bases catalyze the opening and closing of the five-membered ring in 4-carboxy-1,3-thiazolidine,[17,37-39] We could show that small quantities of [Rh(cod)Cl]$_2$ catalyze the epimerization of thiazolidines at C2 at room temperature within minutes,[39] probably also via ring opening to imine–thiol intermediates. So it must be assumed that in enantioselective catalyzes, in which thiazolidines of type **1**–**17** are used, after some minutes the mixture, epimerized at C2, is present and all the results refer to such an equilibrium mixture. The only advantage of using optically pure diastereomers is the fact that they are sometimes solids whereas diastereomer mixtures are oils, e.g., in the case of **2**.

The high enantiomeric excess in the hydrosilylation reaction of Scheme I, using as a cocatalyst a diastereomer mixture close to 1:1, can be explained on the basis that one of the diastereoisomers leads to a catalyst with an appreciably reduced conversion rate. Another explanation involves the assumption that one of the diastereoisomers does not coordinate at all. This could be due to increased steric hindrance, e.g., for the diastereomer in which the COOR group of the thiazolidine ring points toward the metal. As for high ee's an excess of thiazolidine is required (Tables I and II), the latter assumption explains the necessity of at least part of it.

As the carboxylic acid **4** with regard to chemical and optical yield gives similar results as the esters **1**–**3**, the COOH and COOR substituents at C4 of the thiazolidine ring do not play an active role during catalysis.

The acetylation of the ring nitrogen in the thiazolidine system should prevent the epimerization at C2. In crystalline **5** and **6** two sets of signals appear in the ^{1}H NMR spectra with the intensities 14:86 and 86:14. This can be attributed either to the presence of two diastereomers or to a hindered rotation in the acid amide part of the molecules.[37] The drop in enantioselectivity for **5** and **6** can be ascribed to the fact that the nitrogen atom of the thiazolidine ring no longer is a good donor atom when acetylated compared to its protonated or methylated form. The drop in the conversion of acetophenone to 1-phenylethanol in the catalysts with **5** and **6** is due to the side reaction, mentioned above. By ^{1}H NMR spectroscopy it could be shown that large amounts of the silyl enol ether $C_6H_5C[OSiH(C_6H_5)_2]{=}CH_2$ are formed, which lead to the observed reduction in yield.[12]

The strong influence of steric effects on catalytic activity and enantioselectivity of the hydrosilylation is demonstrated by the penicillamine derivative **7**. As observed for imine ligands of type O, the replacement of the 2-pyridyl group by other coordinating aromatic systems like pyrrole or thiophene in thiazolidines **9** and **10** reduces the optical induction in the hydrosilylation of acetophenone appreciably.[5] The triphenylphosphine-derived thiazolidine **17** behaves like other P,N ligands.[7] On increasing the Rh/ligand ratio the stereoselectivity changes from preferred *S* to *R* in the 1-phenylethanol formed.

For the hydrosilylation of acetophenone with diphenylsilane (run 10, Table I) and similarly for benzyl methyl ketone, *tert*-butyl methyl ketone, and β-phenyl ethyl methyl ketone (Table II) the new catalytic systems [Rh(cod)Cl]$_2$/thiazolidine give much higher optical inductions than reported in the literature for transition-metal complexes with optically active phosphines.[20,21,24,29-36] However, whereas for acetophenone the best results are achieved with thiazolidine **3**, for benzyl methyl ketone it is thiazolidine **1** and for *tert*-butyl methyl ketone it is thiazolidine **2** that give the best results. So, for different substrates different thiazolidines seem to be the best cocatalysts.

Experimental Section

2-(2-Pyridyl)-4-carbomethoxy-1,3-thiazolidine (1). To the solution of 10.0 g (58.3 mmol) of L-(−)-cysteine methyl ester hydrochloride in methanol/benzene (20 mL/40 mL) were added 8 ml of triethylamine and 6.2 g (57.9 mmol) of 2-pyridinecarbaldehyde. After 15 h of stirring at room temperature the solvent was removed and the residue was treated with 150 mL of ether. Triethylammonium hydrochloride was filtered off, and the ether was dried with Na_2SO_4. Evaporation of the solvent gave the crude compound **1**.

For purification **1** was passed through a 8-cm silica layer with petroleum ether/benzene (2:1): yield 7.1 g (63%); diastereomer ratio 58:42; yellow oil; ^{1}H NMR (250 MHz/$CDCl_3$/Me_4Si/296 K) δ 3.80 + 3.83 (s, 3, $COOCH_3$, ratio 42:58), 5.84 + 5.66 (d, J = 11.4 Hz, 1, pyC*H*, ratio 42:58), 7.6 (m, 1, pyH^3), 7.2–7.4 (m, 2, pyH^4 + pyH^5), 8.58 (m, 1, pyH^6), 3.1–4.6 (m, 3, SCH_2CH); IR (neat) 3310 (br, NH), 1745 (CO) cm^{-1}; optical rotation (*c* 6.8, acetone) $[\alpha]^{20}_{589}$ −33.5°, $[\alpha]^{20}_{578}$ −35.3°, $[\alpha]^{20}_{546}$ −41.6°, $[\alpha]^{20}_{436}$ −83.7°. Anal. Calcd for $C_{10}H_{12}N_2O_2S$: C, 53.55; H, 5.39. Found: C, 53.36; H, 5.27.

2-Methyl-2-(2-pyridyl)-4-carbomethoxy-1,3-thiazolidine (2). Same procedure as for **1** was used except heating 3 h at reflux and passing the condensing solvent through a Soxhlet filled with dry $CaSO_4$ to remove the water. After evaporation of the solvent from the filtrate the oily residue was treated with petroleum ether to give a white solid, which was recrystallized from $CHCl_3$/ether (1:1). Data for **2**: yield 80%; pure diastereomer; white crystals; mp 91–93 °C; ^{1}H NMR (250 MHz/$CDCl_3$/Me_4Si/297 K) δ 3.83 (s, 3, $COOCH_3$), 1.94 (s, 3, $pyCCH_3$), 3.07 (t, J = 9.8 Hz, 1, CHCOO), 3.48 (m, 1, SCH), 4.23 (m, 1, SCH), 4.74 (br, 1, NH), 7.48 (m, 1, pyH^3), 7.70 (m, 1, pyH^4), 7.23 (m, 1, pyH^5), 8.70 (m, 1, pyH^6); IR (KBr) 3285 (NH), 1745 (CO) cm^{-1}; optical rotation (*c* 9.1, acetone) $[\alpha]^{20}_{589}$ +125.4°, $[\alpha]^{20}_{578}$ +133.3°, $[\alpha]^{20}_{546}$ +153.3°,

(37) Szilâgyi, L.; Györgydeâk, Z. *J. Am. Chem. Soc.* **1979**, *101*, 427.
(38) Pesek, J. J; Frost, J. H. *Tetrahedron* **1975**, *31*, 907.
(39) Brunner, H.; Riepl, G.; Kunz, M., unpublished results.

$[\alpha]^{20}_{436}$ +238.6°, $[\alpha]^{20}_{365}$ +507.1°. Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92; N, 11.76. Found: C, 55.38; H, 5.96;, N, 11.81.

2-(2-Pyridyl)-4-carbethoxy-1,3-thiazolidine (3). Same procedure as for 1 was used. The oily residue was treated with ether/petroleum ether (2:1). Data for 3: yield 23%; white solid; pure diastereomer; mp 81–83 °C; ^{1}H NMR (250 MHz/C_6D_6/Me_4Si/297 K) δ 0.90 (t, J = 7.1 Hz, 3, CH_2CH_3), 3.91 (q, J = 7.1 Hz, 2, CH_2CH_3), 2.94–4.26 (m, 4, SCH_2CH + NH), 6.04 (d, J = 9.8 Hz, 1, pyCH), 6.51–8.37 (m, 4, py); IR (KBr) 3290 (NH), 1447 (CO) cm^{-1}; optical rotation (c, 4.1, acetone) $[\alpha]^{20}_{578}$ −296.3°, $[\alpha]^{20}_{546}$ −341.4°, $[\alpha]^{20}_{436}$ −614.0°, $[\alpha]^{20}_{365}$ −1043.3°. Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92. Found: C, 55.35; H, 5.62.

2-(2-Pyridyl)-3-carboxy-1,3-thiazolidine (4). To the solution of 15.2 g (125 mmol) of L-cysteine in 75 mL of water was added 12 mL (125 mmol) of 2-pyridinecarbaldehyde in 75 mL of ethanol. After 2 h at 55 °C the solution was cooled to room temperature giving a crystalline, white precipitate, which was recrystallized from water/ethanol. Data for 4: yield 11.0 g (42%); white crystals; mp 62–64 °C; ^{1}H NMR (250 MHz/D_2O/297 K) δ 3.33–4.58 (m, 4, SCH_2CH + NH), 6.05 + 6.15 (s, 1, pyCH, ratio 35:65), 7.4–8.72 (m, 4, py); IR (KBr) 3400 (NH), 1647 (CO) cm^{-1}; optical rotation (c 4.4, ethanol) $[\alpha]^{20}_{578}$ −87.7°, $[\alpha]^{20}_{546}$ −100.6°, $[\alpha]^{20}_{436}$ −184.5°, $[\alpha]^{20}_{365}$ −329.0°.

2-(2-Pyridyl)-4-carbomethoxy-3-acetyl-1,3-thiazolidine (5). To a solution of 3.94 g (11.5 mmol) of 1 in 75 mL of benzene was added 4.2 mL of acetic acid anhydride. After the solution was heated for some minutes to 60 °C, the solvent was removed and the oily residue was treated with 20 mL of ether. Data for 5: yield 2.93 g (96%); white crystals; mp 88 °C; ^{1}H NMR (60 MHz/$CDCl_3$/Me_4Si/300 K) δ 1.95 + 2.17 (s, 3, $COCH_3$, ratio 86:14), 3.8 (s, 3, $COOCH_3$), 3.3–5.1 (m, 3, SCH_2CH), 6.13 + 6.48 (s, 1, pyCH, ratio 86:14), 7.03–8.67 (m, 4, py); IR (KBr) 1743 (CO), 1665 (CO) cm^{-1}; optical rotation (c 7.2, $CHCl_3$) $[\alpha]^{20}_{578}$ +9.9°, $[\alpha]^{20}_{546}$ +11.5°, $[\alpha]^{20}_{436}$ +21.4°. Anal. Calcd for $C_{12}H_{14}N_2O_3S$: C, 54.12; H, 5.30. Found: C, 54.06; H, 5.29.

2-(2-Pyridyl)-3-acetyl-4-carbethoxy-1,3-thiazolidine (6). Same procedure as for 5 was used. The oily residue was dissolved in acetic acid ester/petroleum ether (1:1) and crystallized at −30 °C. Recrystallization was from acetic acid ester/petroleum ether (1:1). Data for 6: yield 65%, white crystals; mp 96–97 °C; ^{1}H NMR (250 MHz/$CDCl_3$/Me_4Si/297 K) δ 1.35 (t, 3, CH_2CH_3), 1.98 + 2.18 (s, 3, $COCH_3$, ratio 86:14) 3.15–4.3 (m, 5, SCH_2CH + $COOCH_2CH_3$), 6.13 + 6.50 (s, 1, pyCH, ratio 14:86), 7.12–8.60 (m, 4, py); IR (KBr) 1750 (CO), 1680 (CO) cm^{-1}; optical rotation (c 2.9, methanol) $[\alpha]^{20}_{578}$ +25.9°, $[\alpha]^{20}_{546}$ +42.1°, $[\alpha]^{20}_{436}$ +93.5°, $[\alpha]^{20}_{365}$ +179.7°. Anal. Calcd for $C_{13}H_{16}N_2O_3S$: C, 55.70; H, 5.75. Found: C, 55.66; H, 5.63.

2-(2-Pyridyl)-4-carboxy-5,5-dimethyl-1,3-thiazolidine (7). A 2.05-g sample of sodium acetate and 2.5 mL of concentrated HCl were added to 3.73 g (25 mmol) of D-penicillamine in water/ethanol (62 mL/44 mL). On addition of 2.4 mL (25 mmol) of 2-pyridinecarbaldehyde a yellow color resulted. After 3 h at room temperature the solution was cooled to 0 °C. Data for 7: crystalline white precipitate; yield 3.17 g (53%); mp 164 °C dec; ^{1}H NMR (60 MHz/Me_2SO-d_6/Me_4Si/300 K) δ 1.47 (s, 3, CH_3), 1.82 (s, 3, CH_3), 2.68 (br, 1, NH), 3.73 (s, 1, $CHCOOH$), 5.92 (s, 1, pyCH), 7.3–8.77 (m, 4, py); IR (KBr) 3450 (OH), 3260 (NH), 1745 (CO) cm^{-1}; optical rotation (c 5.9, Me_2SO) $[\alpha]^{20}_{578}$ −19.4°, $[\alpha]^{20}_{546}$ −22.2°, $[\alpha]^{20}_{436}$ −38.8°, $[\alpha]^{20}_{365}$ −62.1°. Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92. Found: C, 55.38; H, 5.83.

2-Methyl-2-(2-pyridyl)-3-methyl-4-carbomethoxy-1,3-thiazolidine (8). To a stirred solution of 2.5 g (10 mmol) of optically pure (+)-2 and 4 mL (50 mmol) of 37% aqueous formaldehyde in 20 mL of acetonitrile was added 950 g (15 mmol) of $NaBH_3CN$. A 0.5-mL sample of glacial acetic acid was added dropwise over 10 min, and the reaction mixture was stirred at room temperature for 2 h. After addition of another 0.5 mL of glacial acetic acid, stirring was continued for another hour. The reaction mixture was then poured into 100 mL of ether and washed with three 20-mL portions of 1 N KOH and one 20-mL portion of brine. The ether layer was dried over K_2CO_3 and filtered and the solvent removed. 8 was crystallized from 3 mL of ether at −30 °C: yield 2.0 g (80%); pure diastereomer; white crystals; mp 82–83 °C; ^{1}H NMR (250 MHz/$CDCl_3$/Me_4Si/297 K) δ 1.88 (s, 3, $pyCCH_3$), 2.38 (s, 3, NCH_3), 3.77 (s, 3, $COOCH_3$), 3.21 (d, J = 7.2 Hz, 2, SCH_2), 3.91 (t, J = 7.3 Hz, 1, SCH_2CH), 8.02 (m, 1, pyH^3), 7.13 (m, 1, pyH^4), 7.65 (m, 1, pyH^5), 8.52 (m, 1, pyH^6); IR (KBr) 1755 (CO) cm^{-1}; optical rotation (c 7.1, acetone) $[\alpha]^{20}_{589}$ +111.0°, $[\alpha]^{20}_{578}$ +118.5°, $[\alpha]^{20}_{546}$ +140.0°, $[\alpha]^{20}_{436}$ +306.6°, $[\alpha]^{20}_{365}$ +714.0°. Anal. Calcd for $C_{12}H_{16}N_2O_2S$: C, 57.12; H, 6.38. Found: C, 56.98; H, 6.32.

2-(2-Pyrrolyl)-4-carbomethoxy-1,3-thiazolidine (9). Under N_2 protection 2.37 g (13.8 mmol) of L-cysteine methyl ester and 1.39 g (13.8 mmol) of triethylamine were dissolved in 20 mL of methanol and heated to reflux. A 1.31-g (13.8-mmol) sample of 2-pyrrolecarbaldehyde in 20 mL of toluene was added dropwise. After 1 h reflux the solvent was removed and the residue was dissolved in ether and passed through a layer of SiO_2. Data for 9: red solidifying oil; recrystallization from THF; yield 1.55 g (53%); white crystals; ratio 52:48; mp 76–79 °C; ^{1}H NMR (250 MHz/$CDCl_3$/Me_4Si/297 K) δ 2.72 (br, 1, NH), 3.05–4.11 (m, 3, SCH_2CH), 3.77 + 3.78 (s, 3, $COOCH_3$, ratio 48:52), 5.64 + 5.83 (s, 1, NSCH, ratio 48:52), 6.13–6.76 (m, 3, pyrr), 8.64 + 8.84 (br, 1, pyrrNH, ratio 48:52); IR (KBr) 3350 + 3330 (NH), 1740 (CO) cm^{-1}; optical rotation (c 0.3, acetone) $[\alpha]^{20}_{578}$ −112.7°, $[\alpha]^{20}_{546}$ −129.0°, $[\alpha]^{20}_{436}$ −232.9°, $[\alpha]^{20}_{365}$ −394.9°. Anal. Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.66; N, 13.21. Found: C, 50.68; H, 5.46; N, 13.02.

2-(2-Thienyl)-4-carboxy-1,3-thiazolidine[13] (10). The solution of 4.5 g (37.1 mmol) of L-cysteine in 35 mL of water at room temperature was reacted with 3.5 mL (37.1 mmol) of distilled 2-thiophenecarbaldehyde, dissolved in 35 mL of ethanol. Immediately a white precipitate was formed. After 5 h the reaction mixture was cooled to −30 °C. The precipitate was recrystallized from ethanol. Data for 10: yield 5.13 g (64%); white solid; mp 144–145 °C; ^{1}H NMR (250 MHz/Me_2SO-d_6/Me_4Si/297 K) δ 3.09 + 3.41 (m, 2, SCH_2, ratio 34:66), 3.92 + 4.10 (t, 1, $CHCOOH$, ratio 34:66), 5.76 + 5.94 (s, 1, thienyl-CH, ratio 34:66), 6.93–7.55 (m, 3, thienyl); IR (KBr) 3440 (br, OH), 1590 (CO) cm^{-1}; optical rotation (c 3.3, Me_2SO) $[\alpha]^{20}_{578}$ −165.0°, $[\alpha]^{20}_{546}$ −189.5°, $[\alpha]^{20}_{436}$ −343.3°. Anal. Calcd for $C_8H_9NO_2S_2$: C, 44.65; H, 4.21. Found: C, 44.69; H, 4.23.

2-Phenyl-4-carboxy-1,3-thiazolidine[14] (11). A 3.04-g (25-mmol) sample of L-cysteine was suspended in 35 mL of water and 35 mL of ethanol. On addition of 2.6 mL (25 mmol) of distilled benzaldehyde a clear solution was formed from which white crystals separated after some time. After 3 h at room temperature and 3 h at 0 °C the solid was filtered and washed with ethanol. Data for 11: yield 4.42 g (84%); mp 158–159 °C dec; ^{1}H NMR (250 MHz/Me_2SO-d_6/Me_4Si/297 K) δ 3.12–4.25 (m, 5, SCH_2CH + COOH + NH), 5.51 + 5.68 (s, 1, PhCH, ratio 43:57), 7.26–7.54 (m, 5, Ph); IR (KBr) 3460 (NH, OH), 1580 (CO) cm^{-1}; optical rotation (c 4.0, Me_2SO) $[\alpha]^{20}_{578}$ −139.0°, $[\alpha]^{20}_{546}$ −161.3°, $[\alpha]^{20}_{436}$ −293.4°, $[\alpha]^{20}_{365}$ −508.9°. Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.40; H, 5.30. Found: C, 57.10; H, 4.92.

2-Phenyl-4-carbethoxy-1,3-thiazolidine (12). Same procedure as for 1 was used, with L-(−)-cysteine ethyl ester hydrochloride and benzaldehyde as starting materials. Data for 12: yield 80%; diastereomer ratio 37:63; colorless oil; ^{1}H NMR (60 MHz/$CDCl_3$/Me_4Si/300 K) δ 1.27 (t, 3, J = 7 Hz, CH_3), 4.22 (q, 2, J = 7 Hz, $CHCH_3$), 3.0–4.2 (m, 4 H, SCH_2CH + NH), 5.53 + 5.80 (s, 1, PhCH, ratio 63:37), 7.1–7.6 (m, 5, Ph); IR (neat) 3330 (NH), 1740 (CO) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.93; H, 6.36; N, 6.00.

2-(4-Hydroxy-3-methoxyphenyl)-4-carbethoxy-1,3-thiazolidine (13). Same procedure as for 1, was used, with L-(−)-cysteine ethyl ester hydrochloride and vanillin as starting materials. Data for 13: yield 83%; diastereomer ratio 68:32; white solid; mp 78–82 °C; ^{1}H NMR (60 MHz/$CDCl_3$/Me_4Si/300 K) δ 1.27 (t, 3, J = 7 Hz, CH_3), 3.83 (s, 3, OCH_3), 3.0–4.0 (m, 5, SCH_2CH + NH + OH), 4.26 (q, 2, J = 7 Hz, CH_2CH_3), 5.5 + 5.77 (s, 1, NSCH, ratio 68:32), 6.7–7.1 (m, 3, Ph). Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.11; H, 6.05; N, 4.94. Found: C, 55.19; H, 5.90; N, 5.20.

2-(3-Hydroxy-4-methoxyphenyl)-4-carbethoxy-1,3-thiazolidine (14). Same procedure as for 1 was used with L-(−)-cysteine ethyl ester hydrochloride and isovanillin as starting materials. Data for 14: solidifying oil; recrystallization from ether/petroleum ether (1:1); yield 85%; white solid; diastereomer ratio 67:33; mp 67–69 °C; ^{1}H NMR (60 MHz/$CDCl_3$/Me_4Si/300 K) δ 1.28 (t, 3, J = 7 Hz, CH_3), 3.0–4.0 (m, 4, SCH_2CH + NH), 3.83 (s, 3, OCH_3), 4.25 (q, 2, J = 7 Hz, CH_2CH_3), 5.47 + 5.73 (s, 1, NSCH, ratio 67:33), 6.6–7.1 (m, 3, Ph). Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.11; H,

6.05. Found: C, 54.97; H, 5.84.

2-(2-Hydroxyphenyl)-4-carboxy-1,3-thiazolidine (15). Same procedure as for **4** was used. After 3 h at room temperature water/ethanol (30 mL/30 mL) was added to the white precipitate. The suspension was cooled to 0 °C for 2 h. Data for **15**: recrystallization from ethanol/water (1:1); yield 8.52 g (92%); colorless crystals; mp 170–171 °C dec; ^{1}H NMR (250 MHz/Me_2SO-d_6/Me_4Si/297 K) δ 2.94–3.45 (m, 2, SCH_2), 3.86 + 4.24 (t, 1, C*H*COOH, ratio 46:54), 5.65 + 5.84 (s, 1, PhCH, ratio 46:54), 6.74–7.36 (m, 4, Ph); IR (KBr) 3600–3250 (OH, NH), 1640 (CO) cm^{-1}; optical rotation (*c* 1.7, Me_2SO) $[\alpha]^{20}_{578}$ −184.1°, $[\alpha]^{20}_{546}$ −217.2°, $[\alpha]^{20}_{436}$ −411.0°, $[\alpha]^{20}_{365}$ −764.3°. Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92. Found: C, 53.27; H, 4.92.

2-(2-Hydroxyphenyl)-4-carbethoxy-1,3-thiazolidine (16). Same procedure as for **1** was used. Data for **16**: yield 42%; yellow solid; diastereomer ratio 67:33; ^{1}H NMR (60 MHz/$CDCl_3$/Me_4Si/300 K) δ 1.27 (t, 3, J = 7 Hz, CH_3), 2.98–4.07 (m, 4, SCH_2CH + NH), 5.57 + 5.87 (s, 1, NSCH, ratio 33:67), 6.72–7.3 (m, 4, Ph); IR (KBr) 3460 (OH), 3340 (NH), 1750 (CO) cm^{-1}; optical rotation (*c* 3.6, methanol) $[\alpha]^{20}_{578}$ −29.8°, $[\alpha]^{20}_{536}$ −34.4°. Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97. Found: C, 56.72; H, 5.80.

2-(2-(Diphenylphosphino)phenyl)-4-carbomethoxy-1,3-thiazolidine (17). To a solution of 0.89 g (5.17 mmol) of L-(−)-cysteine methyl ester hydrochloride in methanol/benzene (7.5 mL/15 mL) were added 0.52 g (5.17 mmol) of triethylamine and in small portions 1.5 g (5.17 mmol) of 2-(diphenylphosphino)-benzaldehyde. After the solution was stirred for 10 h, the solvent was removed and the residue was treated with 150 mL of ether. Triethylamonium chloride was filtered off, and evaporation of the ether gave 1.4 g of the crude compound **16**. For purification **16** was dissolved two times in 5 mL of CH_2Cl_2 and precipitated with 40 mL of petroleum ether. Data for **17**: yield 0.75 g (37%); white solid; ^{1}H NMR (60 MHz/$CDCl_3$/Me_4Si/300 K) δ 3.0–4.47 (m, 4, SCH_2CH + NH), 3.68 + 3.73 (s, 3, $COOCH_3$), 6.22 + 6.35 (s, 1, NSCH), 6.78–7.98 (m, 14, Ph); IR (KBr) 3460 (br, NH), 1750 (CO) cm^{-1}; optical rotation (*c* 2.6, benzene) $[\alpha]^{20}_{578}$ −143.6°, $[\alpha]^{20}_{546}$ −167.8°, $[\alpha]^{20}_{436}$ −321.1°, $[\alpha]^{20}_{365}$ −607.8°. Anal. Calcd for $C_{23}H_{21}NO_2PS$: C, 67.00; H, 5.37. Found: C, 67.32; H, 5.18.

Catalytic Procedures. The enantioselective hydrosilylations were carried out as described in ref 3 and 5 under the conditions given in Tables I and II. After hydrolysis and distillation chemical and optical yields of 1-phenylethanol were determined by GC and polarimetry as given in ref 3 and 5. Workup and product analysis for benzyl methyl ketone and *tert*-butyl methyl ketone were reported in ref 5. In ref 15 the ee's for the hydrosilylation of *tert*-butyl methyl ketone referred to much too high optical rotations of the isolated silyl ether. This problem was discussed in ref 5. Workup for β-phenylethyl methyl ketone was analogous; the optical yield was determined polarimetrically and refers to the optical rotation for 4-phenylbutan-2-ol given in ref 40.

Attempts To Isolate the Catalysts. In the reaction of $[Rh(cod)Cl]_2$ with a slight excess of thiazolidines **1–3** brown noncrystalline solids were obtained that could be converted into PF_6 derivatives. On chromatography at SiO_2 or Al_2O_3 the compounds were strongly adsorbed and slowly changed or decomposed. The reaction of $[Rh(cod)Cl]_2$ with thiazolidine **9** gave a red-brown solid that after chromatography at SiO_2 with CH_2Cl_2/THF led to a yellow solid exhibiting IR bands for the ester carbonyl group and an imine group (1740 (C=O), 1630 (C=N) cm^{-1}). The reaction product of $[Rh(cod)Cl]_2$, thiazolidine **16**, and triethylamine in benzene after chromatography at SiO_2 with benzene/ether yielded a yellow solid (IR 1735 (C=O), 1615 (C=N) cm^{-1}) whose NMR ($CDCl_3$) contained signals for an imine proton (CH=N δ 8.4), and a phenol proton (OH δ 12.7) besides the aliphatic, aromatic, and cod protons.

Similar products, frequently oils, were obtained in the reaction of $[Rh(cod)Cl]_2$ with other thiazolidines, the presence or absence of a C=N vibration in the IR spectrum indicating an opening of the thiazolidine ring or an intact thiazolidine system. None of the complexes could be characterized unambiguously.[11,12]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG, Ludwigshafen, for support of this work.

Registry No. (2*R*,4*R*)-**1**, 90819-83-3; (2*S*,4*R*)-**1**, 90761-64-1; (2*R*,4*R*)-**2**, 90697-21-5; (2*S*,4*R*)-**2**, 90697-22-6; (2*R*,4*R*)-**3**, 90697-23-7; (2*S*,4*R*)-**3**, 90697-24-8; (2*R*,4*R*)-**4**, 90697-25-9; (2*S*,4*R*)-**4**, 90697-26-0; (2*R*,4*R*)-**5**, 90718-45-9; (2*S*,4*R*)-**5**, 90697-27-1; (2*R*,4*R*)-**6**, 90697-28-2; (2*S*,4*R*)-**6**, 90697-29-3; (2*R*,4*R*)-**7**, 90697-30-6; (2*S*,4*R*)-**7**, 90697-31-7; (2*R*,4*R*)-**8**, 90697-32-8; (2*S*,4*R*)-**8**, 90697-33-9; (2*R*,4*R*)-**9**, 90697-34-0; (2*S*,4*R*)-**9**, 90697-35-1; (2*R*,4*R*)-**10**, 90697-36-2; (2*S*,4*R*)-**10**, 90697-37-3; -(2*R*,4*R*)-**11**, 64970-78-1; (2*S*,4*R*)-**11**, 59999-67-6; (2*R*,4*R*)-**12**, 90697-38-4; (2*S*,4*R*)-**12**, 90697-39-5; (2*R*,4*R*)-**13**, 90697-40-8; (2*S*,4*R*)-**13**, 90697-41-9; (2*R*,4*R*)-**14**, 90697-42-0; (2*S*,4*R*)-**14**, 90697-43-1; (2*R*,4*R*)-**15**, 82562-55-8; (2*S*,4*R*)-**15**, 82562-56-9; (2*R*,4*R*)-**16**, 90697-44-2; (2*S*,4*R*)-**16**, 90697-45-3; (2*R*,4*R*)-**17**, 90697-46-4; (2*S*,4*R*)-**17**, 90697-47-5; A, 98-86-2; (*R*)-A (alcohol), 1517-69-7; (*S*)-A (alcohol), 1445-91-6; B, 103-79-7; (*R*)-B (alcohol), 1572-95-8; C, 75-97-8; (*R*)-C (alcohol), 1572-96-9; D, 2550-26-7; (−)-D (alcohol), 39516-03-5; $[Rh(cod)Cl]_2$, 12092-47-6; diphenylsilane, 775-12-2; phenyl-1-naphthylsilane, 21701-61-1; L-(−)-cysteine methyl ester hydrochloride, 18598-63-5; L-cysteine, 52-90-4; D-penicillamine, 52-67-5; 2-pyridine carbaldehyde, 1121-60-4; 2-pyrrolecarbaldehyde, 1003-29-8; 2-thiophenecarbaldehyde, 98-03-3; benzaldehyde, 100-52-7; vanillin, 121-33-5; isovanillin, 621-59-0; 2-(diphenylphosphino)benzaldehyde, 50777-76-9.

(40) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, *105*, 1115.