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CATALYTIC ASYMMETRIC HYDROSILYLATION OF OLEFINS.

II. CHIRAL PHOSPHINE-NICKEL(II) AND -RHODIUM(I) COMPLEX-CATALYZED REACTION*,**

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Summary

Dichlorobis[(*R*)-benzylmethylphenylphosphine]nickel(II) was found to be a good catalyst precursor for the asymmetric hydrosilylation of 1,1-disubstituted prochiral olefins with methyldichlorosilane. The addition products were obtained in much higher optical yields than those obtained using chiral platinum(II) complexes. Trimethylsilane and phenyldimethylsilane were found to add readily to α-methylstyrene in the presence of chiral phosphine-rhodium complexes. Optical yields were not significantly affected by changes in structure of the hydrosilanes. Asymmetric induction was also observed in the nickel-catalyzed hydrosilylation of 1,4-cyclohexadiene. The stereochemical course of the asymmetric hydrosilylation of olefins is discussed.

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* A preliminaly account of this work appeared in [1].

** Taken from the Ph.D. thesis of T. Hayashi, 1975.

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Introduction

In a previous paper [2] an exploratory study on the catalytic asymmetric hydrosilylation of certain prochiral olefins has been concentrated on seeking effective chiral platinum catalysts. It has been shown that a dichlorobis(phosphine)di-μ-chlorodiplatinum(II) containing an optically active tertiary phosphine as ligand is generally useful for a chiral catalyst precursor in asymmetric addition of methyldichlorosilane to 1,1-disubstituted olefins, though the extent of asymmetric induction is very low.

Since the potential catalytic activity of various phosphine-complexes of nickel(II) [3], palladium(II) [3a,4], rhodium(I) [5] as well as platinum(II) [2] for the hydrosilylation is now well documented in the literature, it seems likely that asymmetric addition of a silicon hydride to certain olefins might be better achieved by using one of these d^8 metal complexes with chiral phosphine ligands.

In the present paper we describe that chiral phosphine-nickel and -rhodium complexes catalyze the reaction with higher asymmetric bias than the platinum(II) system.

Results and Disscussion

Asymmetric hydrosilylation of 1,1-disubstituted olefins

(1) Nickel complex-catalyzed reaction

In the presence of dichlorobis[(*R*)-benzylmethylphenylphosphine]nickel(II) (I), the reaction of α-methylstyrene (IIa) with methyldichlorosilane was carried out at 90°C for 60 h, to give two types of addition products in 39% combined yield; one was the expected 2-phenylpropylmethyldichlorosilane (IIIa) as a major product and the other was anomalous 2-phenylpropylmethylchlorosilane (IVa), an addition product of methylchlorosilane. The latter may be formed *via* a nickel-catalyzed redistribution of methyldichlorosilane during the course of hydrosilylation (eqn. 1). This SiH/SiCl interchange has extensively been examined in our laboratories [3c] with a variety of phosphine-nickel(II) complexes as hydrosilylation catalysts.

$$\mathrm{RMeC{=}CH_2} + \mathrm{HSiMeCl_2} \xrightarrow{\mathrm{I}} \mathrm{RMe\overset{*}{C}HCH_2SiMeCl_2} + \mathrm{RMe\overset{*}{C}HCH_2SiMeClH} \qquad (1)$$

(IIa) R = Ph (IIIa)$\sim$(IIIc) (IVa)$\sim$(IVc)
(IIb) R = *i*-Pr
(IIc) R = Et

By fractional distillation, IIIa and IVa were obtained pure in optically active forms, having the almost identical degree of rotation (see Table 1). IIIa was converted into 2-phenylpropyltrimethylsilane (V), $[\alpha]_D^{15}$ +4.10° (neat), which was in 16.9% enantiomeric excess of the *R*-isomer, on the basis of a maximum rotation of (*R*)-(+)-V, $[\alpha]_D^{15}$ +24.3° (neat) [2]. Taking account of an optical purity of the chiral phosphine used, the present asymmetric hydrosilylation may well proceed in 20.9% optical yield.

We have been unable to compare directly the catalytic activity of the phosphine complexes of the nickel triad (Ni, Pd, and Pt), because neither platinum(II) [2] nor palladium(II) analog [6] of I has been found to be effective as a catalyst precursor for the addition of methyldichlorosilane to IIa. It is noted, however, that the use of I with the same chiral phosphine as one used in the case of platinum(II) complexes resulted in giving much improved optical yields of the addition products. Although the exact structure of the catalytically active nickel species is uncertain, it is likely that the presence of two chiral phosphines per metal atom in the nickel complex is advantageous for asymmetric induction (20.9% optical yield) compared with the dichlorobis(phosphine)di-μ-chlorodiplatinum(II) (5.2% optical yield) [2].

It is also noteworthy that the two addition products obtained, IIIa, and IVa, have almost the same degree of optical rotation, despite adding silanes, $MeCl_2SiH$ and $MeClSiH_2$, are different. In view of the fact that an optically active dialkylchlorosilane readily racemizes [7], under the reaction conditions used there might be an extensive epimerization of IVa resulting from addition of $MeClSiH_2$. We did not pursue further this aspect.

Asymmetric hydrosilylation of 2,3-dimethyl-1-butene (IIb) and 2-methyl-1-butene (IIc) was also carried out under the same conditions as described above. In either case, it was observed that the expected addition product (IIIb or IIIc) was accompanied by a comparable amount of another anomalous adduct (IVb or IVc) which came from SiH/SiCl interchange of methyldichlorosilane (eqn. 1).

Data obtained for asymmetric hydrosilylation of these 1,1-disubstituted olefins are summarized in Table 1.

Although the nickel complex-catalyzed hydrosilylation of IIa-IIc required higher temperature to give rather low reaction yield of addition products than for the platinum system, as far as the asymmetric induction is concerned, the nickel catalyst always effected larger asymmetric bias onto the *R* configuration of the adducts than the platinum one. In addition, the extent of asymmetric induction was consistently in the order IIa > IIb > IIc in both cases.

The fact that (*R*)-benzylmethylphenylphosphine (BMPP) coordinated to the metal center can induce asymmetric addition of methyldichlorosilane across the carbon-carbon double bond of prochiral olefins may be explained in terms of the current views of mechanism on metal-catalyzed hydrosilylation [8] where the following processes may be involved: (a) insertion of the metal center into the silicone-hydrogen bond; (b) addition of the resulting hydridometal moiety to the coordinated olefin preferentially from its *re* face (in a *cis* manner) to convert it into an alkyl-metal species; and (c) transfer of the silicon from the metal center to the alkyl carbon

TABLE 1

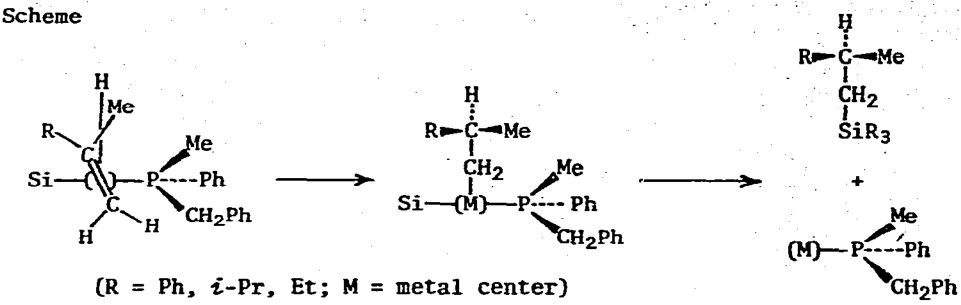
ASYMMETRIC HYDROSILYLATION OF OLEFINS WITH $HSiMeCl_2$ CATALYZED BY $Ni(BMPP)_2Cl_2$[a] (I) AT 90°C

Olefin	Product	Yield (%)	$[\alpha]_D^{15}$, deg of product	$[\alpha]_D^{15}$, deg methylated	Optical yield (%)[b] (Configuration)
$PhMeC=CH_2$	$PhMeCHCH_2SiMeCl_2$	31	+6.50	+4.10	20.9 (*R*)
	$PhMeCHCH_2SiMeClH$	8	+6.43	—	
i-$PrMeC=CH_2$	*i*-$PrMeCHCH_2SiMeCl_2$	21[c]	-0.79	-1.00	6.2 (*R*)
	i-$PrMeCHCH_2SiMeClH$	26[c]	-0.90	—	
$EtMeC=CH_2$	$EtMeCHCH_2SiMeCl_2$	17[c]	—	-0.27	2.5 (*R*)
	$EtMeCHCH_2SiMeClH$	19[c]	-0.22	—	

[a] BMPP = (*R*)-(+)-$(PhCH_2)MePhP$ (67% or 81% optical purity). [b] Based on the maximum rotation of authentic samples and calibrated for the optical purity of the chiral phosphine used. [c] Based on GLC analysis.

to give the product. Since process (b) most likely involves diastereomeric transition states or intermediates, the overall asymmetric bias onto the *R* configuration at the chiral carbon would have already been determined prior to process (c). A schematic view of such a process is shown in the Scheme.

Scheme



(R = Ph, *i*-Pr, Et; M = metal center)

(2) Rhodium complex-catalyzed reaction

$[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (VI) [9] (S = solvent) and ((−)-DIOP)-Rh(S)Cl (VII), where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [10a], were used as catalysts for the present reaction. These complexes have been effectively used for asymmetric hydrogenation of olefins [10] and hydrosilylation of ketones [9,11].

It should be mentioned that in the hydrosilylation of α-methylstyrene catalyzed by VI or VII, methyldichlorosilane, which adds readily to several prochiral olefins in the presence of platinum(II) [2] and nickel(II) complexes, scarcely reacted even under forced conditions. However, trialkylsilanes such as trimethylsilane and phenyldimethylsilane were found to be moderately reactive.

$$\underset{\text{(IIa)}}{PhMeC{=}CH_2} + HSiMe_2R \xrightarrow[120°]{\text{VI or VII}} PhMe\overset{*}{C}HCH_2SiMe_2R \qquad (2)$$

(V) R = Me

(VIII) R = Ph

Adduct VIII was converted into known compound V *via* a dimethylchlorosilyl derivative (IX) in order to determine the enantiomeric excess (eqn. 3).

$$\underset{\text{(VIII)}}{\text{PhMe}\overset{*}{\text{C}}\text{HCH}_2\text{SiMe}_2\text{Ph}} \xrightarrow[\text{CHCl}_3]{\text{HCl-AlCl}_3} \underset{\text{(IX)}}{\text{PhMe}\overset{*}{\text{C}}\text{HCH}_2\text{SiMe}_2\text{Cl}} \xrightarrow{\text{MeMgBr}} \underset{\text{(V)}}{\text{PhMe}\overset{*}{\text{C}}\text{HCH}_2\text{SiMe}_3} \qquad (3)$$

The results obtained are summarized in Table 2. It is of interest that, unlike the hydrosilylation of ketones [9,11], changes in structure of hydrosilanes used do not significantly affect the extent of asymmetric induction in the rhodium complex-catalyzed hydrosilylation of α-methylstyrene. It follows that the steric effect of a trialkylsilyl group bound to the rhodium catalyst on a stereochemical outcome for hydrosilylation of the prochiral olefin should be a minor one, scarcely assisting the steric control by the chiral phosphine-rhodium moiety which operates throughout the processes. These arguments, in agreement with the mechanism proposed for asymmetric hydrosilylation of olefins (*vide supra*), insist that the

TABLE 2

ASYMMETRIC HYDROSILYLATION OF α-METHYLSTYRENE CATALYZED BY CHIRAL RHODIUM COMPLEXES AT 120°C

Silane	Catalyst[a]	Yield (%)	$[\alpha]_D^{20}$, deg[b] of product	Optical yield (%) (Configuration)
$HSiMe_3$	VI	63	+1.19	7.0 (*R*)[c]
$HSiMe_2Ph$	VI	25	+1.07	5.2 (*R*)[c]
$HSiMe_3$	VII	63	-2.54	10.4 (*S*)
$HSiMe_2Ph$	VII	19	-1.97	6.7 (*S*)

[a] Catalyst = 0.05 mol%. [b] Neat. [c] Calibrated for the optical purity of the chiral phosphine used (70%).

extent of asymmetric induction is already fixed in the process of forming diastereomeric alkyl-rhodium intermediates by way of the insertion of an olefin into the hydride-rhodium moiety, rather than during the reductive elimination process where alkyl and trialkylsilyl groups both bound to the rhodium leave to form the final product.

Asymmetric hydrosilylation of other olefins

Two additional olefins, styrene and 1,4-cyclohexadiene, were also examined with respect to the asymmetric hydrosilylation since different modes of asymmetric induction from that discussed above seem to be operative for these olefins.

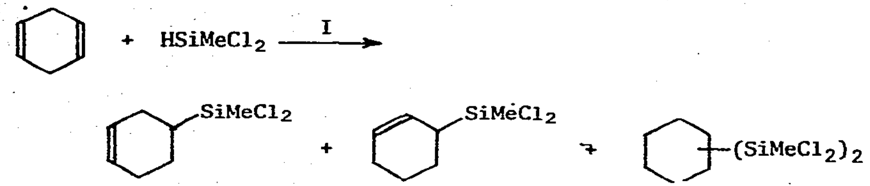
Addition of methyldichlorosilane to styrene catalyzed by nickel complex I at 120°C for 12 h gave 1-phenylethylmethyldichlorosilane (X) [12] and isomeric 2-phenylethylmethyl derivative (XI) [12] in 24% combined yield, and some polymeric substances. The GLC area ratio of the two products was 46:54. No SiH/SiCl interchange as described above was observed in this case (eqn. 4). The optical yield of the product X was estimated to be 0.9% of

$$\mathrm{PhCH{=}CH_2} + \mathrm{HSiMeCl_2} \xrightarrow{\mathrm{I}} \underset{(\mathrm{X})}{\mathrm{PhMe\overset{*}{C}HSiMeCl_2}} + \underset{(\mathrm{XI})}{\mathrm{PhCH_2CH_2SiMeCl_2}} \qquad (4)$$

the *R* isomer, on the basis of an empirical value of molecular rotations of 1-phenylethyl systems reported by Davis and Jensen [13].

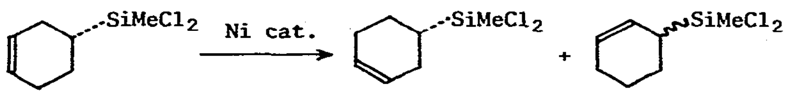
The hydrosilylation of styrene with trimethylsilane or phenyldimethylsilane in the presence of rhodium catalyst VI resulted in giving exclusively the 2-phenylethylsilyl derivatives, and the 1-isomer which might be also expected to be formed was found only in a trace amount.

Of significance is the fact that hydrosilylation of 1,4-cyclohexadiene under the influence of I gave rise to some extent of asymmetric induction in one of three addition products. Thus, addition of methyldichlorosilane



(XII) (XIII) (XIV) (5)

to 1,4-cyclohexadiene was carried out in the presence of I at 90°C for 40 h, to give 4-(methyldichlorosilyl)cyclohexene (XII) and 3-(methyldichlorosilyl)-cyclohexene (XIII), in a ratio of 2.7:1, and bis(methyldichlorosilyl)cyclohexane (XIV) (eqn. 5). The isomeric mixture of XII and XIII was treated with methylmagnesium bromide and then with trifluoroacetic acid [14] to give pure 4-trimethylsilylcyclohexene (XV), $[\alpha]_D^{20}$ +3.69° (neat). On the basis of an empirical rule of conformational asymmetry of endocyclic olefinic compounds [15], XV was estimated to be at least of 4% enantiomeric purity with respect to the *R* isomer. It should be mentioned that the formation of XIII is attributed to an isomerization of XII (*vide infra*) and that this isomerization inevitably results in some racemization of optically active XII by a process shown in eqn. 6.



(*R*)-(XII) (*S*)-(XII) (XIII) (6)

Hydrosilylation of 1,3-cyclohexadiene under the same conditions did not appreciably occur, while at elevated temperature (120°C) giving XII and XIII in a ratio of 1:2.7. Therefore, the nickel complex-catalyzed isomerization of 1,4-cyclohexadiene to the 1,3-isomer would be slow (and *vice versa*) under the present conditions. The isomeric mixture of XII and XIII, after methylation, had a slight optical activity (α_D^{20} -0.023° (0.1 dm, neat)).

TABLE 3

HYDROSILYLATION OF 1,4- AND 1,3-CYCLOHEXADIENE CATALYZED BY CHIRAL PHOSPHINE COMPLEXES OF NICKEL TRIAD

Catalyst	Silane	Temp. (°C)	Time (h)	Yield[a] (%)	Product ratio[b]		Optical activity
					XII	XIII	
1,4-Cyclohexadiene							
Ni[c]	$HSiMeCl_2$	90	40	37	73	27	yes
Pd[d]	$HSiCl_3$	135	66	80	10[e]	90[e]	yes
Pt[f]	$HSiMeCl_2$	90	43	90	14	86	no
Pt[g]	$HSiMeCl_2$	90	28	83	nil	100	no
1,3-Cyclohexadiene							
Ni[c]	$HSiMeCl_2$	120	40	38	27	73	yes
Pd[d]	$HSiCl_3$	120	63	64	10[e]	90[e]	yes

[a] Combined yield of XII and XIII. [b] By GLC analysis. [c] $Ni(BMPP)_2Cl_2$ (I); BMPP = (*R*)-$(PhCH_2)MePhP$. [d] $Pd(PhCN)_2Cl_2$ plus 2 MDPP; MDPP = (-)-Menthyldiphenylphosphine (see ref. 6). [e] Trichlorosilyl analog of XII and XIII, respectively. [f] *cis*-$(C_2H_4)\overset{*}{Am}PtCl_2$; $\overset{*}{Am}$ = (*S*)-$PhMeCHNH_2$. [g] *cis*-$(C_2H_4)(BMPP)PtCl_2$.

All results as well as those obtained with palladium and platinum catalysts for comparison are summarized in Table 3.

In contrast to the use of a nickel catalyst, hydrosilylation of 1,4-cyclohexadiene catalyzed by *cis*-dichloro(ethylene)[(*S*)-1-phenylethylamine]-platinum(II) or its chiral phosphine analog readily took place to give XII and XIII in 90% or 83% combined yield, respectively, but XIII was always predominant and optically inactive.

Finally, when a *cis* olefin of C_{2v} symmetry is coordinated to the metal center, the two asymmetric carbon atoms formed have opposite configurations, yielding a *meso* compound [16]. Hence, the asymmetric induction in hydrosilylation of 1,4-cyclohexadiene should take place during and/or after formation of the diastereomeric alkyl-metal intermediates which arise from a stereoselective *cis* addition of hydridometal moiety to the coordinated *meso* diene. It may be, therefore, concluded that the asymmetric induction in the step of coordination of an olefin to the chiral complex catalyst is not necessarily an essential factor for the process of asymmetric hydrosilylation in general [17].

Experimental

Preparation of dichlorobis[(R)-benzylmethylphenylphosphine]nickel(II) (I)

To a solution of 1.00 g (4.2 mmoles) of nickel chloride hydrate in 15 ml of. dry ethanol under an agron atmosphere was added 2.0 ml (8.8 mmoles) of (*R*)-benzylmethylphenylphosphine (BMPP) [18] (67% optical purity) in one portion and the mixture was magnetically stirred overnight. The precipitates formed were taken up with methylene chloride. After removal of the solvent, the residue was recrystallized from CH_2Cl_2/petroleum ether (1/5) to give 1.45 g (58%) of pure I as deeply purple plates, m.p. 132-133°C (in an evacuated tube). The optical rotation of this complex in methylene chloride could hardly be measured due to deeply red-colored solution. (Found: C, 60.49; H, 5.64; Cl, 13.11. $C_{28}H_{30}Cl_2NiP_2$ calcd.: C, 60.26; H, 5.42; Cl, 12.70%.)

The same complex but with the phosphine of 81% optical purity was also prepared.

Asymmetric hydrosilylation of 1,1-disubstituted olefins catalyzed by I

The following procedure is typical: In a degassed sealed glass tube a mixture of an appropriate olefin (90 mmoles), methyldichlorosilane (90 mmoles) and the catalyst I (3.6×10^{-2} mmoles) was heated at 90°C for 60 h. The reaction mixture was fractionally distilled to give two types of addition products. In some cases the product ratio was determined by GLC analysis prior to distillation. The normal adduct (with no SiCl/SiH exchange) was then treated with excess of methylmagnesium bromide to convert it into the trimethylsilyl derivative, with which the optical yield was determined on the basis of the maximum rotation of authentic samples [2]. Optical data are given in Table 1.

1. α-Methylstyrene (IIa). Using complex I with BMPP of 81% optical purity, two addition products, 2-phenylpropylmethyldichlorosilane (IIIa) [2] and 2-phenylpropylmethylchlorosilane (IVa), were obtained by fractional distillation of the reaction mixture; IVa: b.p. 51-52°C/0.8 Torr, 1.4 g (8% yield) 95+% pure), n_D^{15} 1.5138, d_4^{15} 1.0119; NMR (CCl_4/TMS): δ 0.25 (d, J = 2.8 Hz, 3H, $SiCH_3$), 1.31 (d, 2H, CH_2), 1.35 (d, J = 6.8 Hz, 3H, CCH_3) 3.04 (ill resolved m, 1H, CH), 4.67 (sextet, J =2.8 Hz, 1H, SiH), and 7.16 (s, 5H, C_6H_5). (Found: C, 61.19; H, 7.59; Cl, 17.30. $C_{10}H_{15}ClSi$ calcd.: C, 60.42; H, 7.61; Cl, 17.83%.) IIIa: b.p. 66.0-66.5°C/0.6 Torr, 6.6 g (31%), n_D^{15} 1.5151, d_4^{15} 1.1110 (lit. [12]: b.p. 148-149°C/42 Torr, n_D^{25} 1.5082, d_4^{25} 1.100). IIIa was methylated to give 2-phenylpropyltrimethylsilane (V) [2]; b.p. 100-100.5°C/19 Torr, n_D^{15} 1.4900, d_4^{15} 0.8681.

From another run of the same reaction but in 45 mmol-scale was obtained 4.4 g (42%) of the adducts, which gave, on direct methylation followed by preparative GLC, pure V; $[\alpha]_D^{15}$ +3.89° (neat). Taking account of an optical purity of the phosphine (81%), the optical yield of the addition product is 19.8%.

2. *2,3-Dimethyl-1-butene (IIb).* Complex I with BMPP of 67% optical purity was used as catalyst. Simple distillation of the reaction mixture gave 8.2 g (47% combined yield) of two addition products, and the GLC area ratio of the products was 56:44. The distillate was then fractionally redistilled to isolate each adduct in the pure state. (i) *i*-$PrMeCHCH_2SiMeClH$ (IVb), b.p. 64-66°C/18 Torr, 3.5 g, n_D^{20} 1.4354, d_4^{20} 0.8818; NMR (CCl_4/TMS): δ 0.47 (d, *J* = 3.2 Hz, $SiCH_3$), 4.83 (m, SiH), and other protons as diffused multiplets; IR (liquid film): 2167 cm^{-1} (ν(Si-H)). (Found: C, 50.44; H, 10.53; Cl, 20.01. $C_7H_{17}ClSi$ calcd.: C, 51.03; H, 10.40; Cl, 21.52%.) (ii) *i*-$PrMeCHCH_2SiMeCl_2$ [2] (IIIb), b.p. 74-76°C/18 Torr, 3.3 g, (97+% pure). Methylation of the adducts gave *i*-$PrMeCHCH_2SiMe_2H$, b.p. 70°C/73 Torr, n_D^{20} 1.4211; NMR (CCl_4/TMS): δ 0.13 (d, *J* =3.4 Hz, $SiCH_3$), 3.97 (m, SiH); IR: 2124 cm^{-1} (ν(Si-H)) (Found: C, 66.75; H, 14.00. $C_8H_{20}Si$ calcd.: C, 66.57; H, 13.97%.), and *i*-$PrMeCHCH_2SiMe_3$ [2], b.p. 96.5°C/137 Torr.

3. *2-Methyl-1-butene (IIc).* Similarly, simple distillation of the reaction mixture gave 7.5 g of addition products, which boiled over a range of 59-78°C/32 Torr and consisted of four components. The GLC area ratio of the products was 42:37:16:5. The major two were separated and identified as follows, while the other two could not be obtained pure.

The major adducts were: (i) $EtMeCHCH_2SiMeClH$ (IVc), b.p. 43°C/20 Torr, n_D^{20} 1.4274, d_4^{20} 0.8813; NMR (CCl_4/TMS): δ 0.52 (d, *J* = 3.6 Hz, $SiCH_3$), 4.83 (m, SiH), and other protons as diffused multiplets; IR: 2172 cm^{-1} (ν(Si-H)). (Found: C, 47.38; H, 10.36; Cl, 23.02. $C_6H_{15}ClSi$ calcd.: C, 47.81; H, 10.03; Cl, 22.54%.) Methylation followed by preparative GLC gave 2-methylbutyldimethylsilane, n_D^{20} 1.4151; NMR (CCl_4/TMS): δ 0.12 (d, J = 3.9 Hz, $SiCH_3$) and 3.96 (m, SiH). (Found: C, 64.06; H, 14.06. $C_7H_{18}Si$ calcd.: C, 64.52; H, 13.92%.) (ii) $EtMeCHCH_2SiMeCl_2$ [2] (IIIc), which was directly converted into trimethylsilyl derivative and purified by preparative GLC. The optical retations were as indicated in Table 1.

Asymmetric hydrosilylation of α-methylstyrene (IIa) catalyzed by VI and VII

The chiral cationic complex VI was prepared *in situ* from $[Rh\{(R)-(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (NBD = 2,5-norbornadiene) according to the reported procedure [9,19]. A 1:2 mixture of di-μ-chlorobis(1,5-hexadiene)dirhodium and (-)-DIOP was used as catalyst VII.

1. *With trimethylsilane.* In 2.0 ml of degassed dry benzene containing 0.4 ml of dichloromethane, 14 mg (2×10^{-2} mmoles) of $[Rh\{(R)-(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (with the phosphine of 70% optical purity) was dissolved, and molecular hydrogen was bubbled through the solution for 10 min. Then 4.7 g (40 mmoles) of α-methylstyrene and 3.7 g (50 mmoles) of trimethylsilane were added successively. The mixture was heated at 120°C for 40 h in a degassed sealed glass tube. Isolation of the product by preparative GLC (Silicone DC550) after distillation (57°C/4 Torr) gave 4.8 g (63%) of 2-phenylpropyltrimethylsilane (V) [2], $[\alpha]_D^{20}$ +1.19° (neat). Since the specific rotation of optically pure (R)-V is $[\alpha]_D^{20}$ +24.3° (neat) [2], the enantiomeric excess of the product is 4.9% (R).

2. *With phenyldimethylsilane.* Similarly, a mixture of 7.1 g (60 mmoles) of α-methylstyrene and 10.0 g (75 mmoles) of phenyldimethylsilane was heated in the presence of VI (3×10^{-2} mmoles) at 120°C for 40 h to give 3.8 g (25%) of 2-phenylpropylphenyldimethylsilane (VIII), b.p. 132-134°C/4 Torr, n_D^{20} 1.5455, d_4^{20} 0.9630, $[\alpha]_D^{20}$ +1.07° (neat); NMR (CCl_4/TMS): δ 0.05 and 0.09 (a pair of s, $Si(CH_3)_2$), 1.16 (d, J = 6.6 Hz, CH_2), 1.22 (d, J = 6.4 Hz, CCH_3), 2.81 (sextet, CH), 7.11 (s, CC_6H_5), and 7.29 (broad s,

SiC_6H_5). (Found: C, 79.61; H, 8.80. $C_{17}H_{22}Si$ calcd.: C, 80.25; H, 8.71%.)

VIII was treated with dry hydrogen chloride in 15 ml of chloroform in the presence of a catalytic amount of aluminum chloride to give 2.3 g (70%) of 2-phenylpropyldimethylchlorosilane (IX), b.p. 73-75°C/4 Torr, n_D^{20} 1.5033, d_4^{20} 0.9899, $[\alpha]_D^{20}$ +1.47° (neat); NMR (CCl_4/TMS): δ 0.15 and 0.19 (a pair of s, $Si(CH_3)_2$), 1.12 (d, J = 7.2 Hz, CH_2), 1.30 (d, J = 7.2 Hz, CCH_3), 3.01 (sextet, CH), and 7.19 (s, C_6H_5). (Found: C, 62.27: H, 8.20; Cl, 16.01. $C_{11}H_{17}ClSi$ calcd.: C, 62.09; H, 8.05; Cl, 16.66%.)

IX was then methylated with excess of methylmagnesium bromide in ether solution to obtain V, $[\alpha]_D^{20}$ +0.88° (neat).

The results of asymmetric hydrosilylation of α-methylstyrene using VII as catalyst are listed in Table 2.

Asymmetric hydrosilylation of styrene catalyzed by I

A mixture of 18.8 g (0.18 mole) of freshly distilled styrene, 20.8 g (0.18 mole) of methyldichlorosilane and 40 mg (7×10^{-2} mmoles) of I (with BMPP of 67% optical purity) was heated at 120°C over a period of 12 h. The reaction mixture was distilled to give 9.6 g (24% combined yield) of 1-phenylethyl- (X) and 2-phenylethylmethyldichlorosilane (XI) [12]. The GLC area ratio of isomeric products was 46:54. The mixture was methylated. 1-Phenylethyltrimethylsilane was obtained by preparative GLC in optically active from, $[\alpha]_D^{20}$ +0.62° (neat); $[M]_D^{20}$ +1.11°, 0.9% optical yield of the *R* isomer, which was estimated on the basis of the optical purity of the chiral phosphine used and of an empirical value of molecular rotation of (*S*)-(-)-1-phenylethyltrimethylsilane, $[M]_D^{20}$ -184° [13].

In another run of the same reaction catalyzed by I with BMPP of 81% optical purity, the optical rotation of 1-phenylethyltrimethylsilane was $[\alpha]_D^{20}$ +0.79° (*c* 6.09, benzene). With trichlorosilane the reaction did not take place under the conditions employed (*cf*. ref. 3b).

Hydrosilylation of styrene catalyzed by VI

1. *With phenyldimethylsilane.* A mixture of 5.2 g (50 mmoles) of freshly distilled styrene, 7.5 g (55 mmoles) of phenyldimethylsilane, and 2.5×10^{-2} mmoles of VI was heated at 110°C for 7 days. The reaction mixture was distilled (b.p. 117-120°C/2 Torr) to give 8.4 g (70%) of 2-phenylethylphenyldimethylsilane, n_D^{20} 1.5502. GLC analysis indicated that only a trace amount of 1-isomer was present. NMR (CCl_4/TMS): δ 0.25 (s, 6H, $SiCH_3$), 0.96-1.32 (m, 2H, CH_2Si), 2.45-2.81 (m, 2H, $PhCH_2$), 7.09 (s, 5H, CC_6H_5), 7.0-7.6 (broad s, 5H, SiC_6H_5). (Found: C, 79.63; H, 8.33. $C_{16}H_{20}Si$ calcd.: C, 79.93; H, 8.38%.)

2. *With trimethylsilane.* From a mixture of 3.1 g (30 mmoles) of styrene, 3.0 g (40 mmoles) of trimethylsilane and 1.5×10^{-2} mmoles of VI, was obtained 3.4 g (63%) of 2-phenylethyltrimethylsilane, b.p. 100-102°C/20 Torr, n_D^{20} 1.4880, (lit. [12]: b.p. 117°C/40 Torr, n_D^{25} 1.4840); NMR (CCl_4/TMS): δ 0.11 (s, $SiCH_3$), 0.81-1.03 (m, CH_2Si), 2.53-2.85 (m, $PhCH_2$), 7.15 (s, C_6H_5).

Asymmetric hydrosilylation of 1,4- and 1,3-cyclohexadiene

A mixture of 4.1 ml of 1,4-cyclohexadiene (containing 20% of benzene), 3.5 g (30 mmoles) of methyldichlorosilane and 10 mg of I (with 81% optically pure BMPP) was heated at 90°C for 40 h. Fractional distillation of the reaction mixture gave two fractions: (i) b.p. 86-88°C/16 Torr, 2.1 ml, a mixture of 3-(XII) and 2-cyclohexenylmethyldichlorosilane (XIII), α_D^{20} +0.691° (0.1 dm, neat); and (ii) b.p. 108-109°C/3 Torr, 0.9 ml, bis(methyldichlorosilyl)cyclohexane (XIV). After methylation of the first fraction was obtained trimethylsilyl derivatives of XII and XIII in a ratio of 73:27, b.p. 62-63°C/20 Torr, 1.0 ml, α_D^{20} +0.492° (0.1 dm, neat).

A similar mixture (2.2 ml) of 4- and 3-trimethylsilylcyclohexene from another run was treated with trifluoroacetic acid (1.8 ml), and the mixture was distilled to give pure 4-trimethylsilylcyclohexene (XV) [3c], b.p.

58-60°C/17 Torr, 0.9 ml, n_D^{20} 1.4580, d_4^{20} 0.8428, $[\alpha]_D^{20}$ +3.69° (neat), $[M]_D^{20}$ +5.68°; NMR: δ -0.05 (s, $SiCH_3$) and 5.64 (broad s, CH=CH). (Found: C, 70.19: H, 11.62. $C_9H_{18}Si$ calcd.: C, 70.05; H, 11.76%.)

Similarly, from a mixture of 2.8 g (35 mmoles) of 1,3-cyclohexadiene and 3.5 g (30 mmoles) of methyldichlorosilane were obtained XII (10%), XIII (28%), and XIV (10%). An isomeric mixture of XII and XIII, upon methylation, showed a slightly negative rotation, α_D^{20} -0.023° (0.1 dm, neat) Furthermore, the similar reaction of 1,4-cyclohexadiene catalyzed by chiral platinum complexes (see Table 3) yielded XII and XIII in high yield, and there was no disilylated product. Neither of two isomeric products showed optical activity.

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