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CATALYTIC ASYMMETRIC HYDROSILYLATION OF KETONES

I. CHIRAL PHOSPHINE—PLATINUM(II) COMPLEX-CATALYZED HYDROSILYLATION *,**

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Summary

Dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum(II) was found to be an effective catalyst for the hydrosilylation of alkyl phenyl ketones with methyldichlorosilane to give the corresponding silyl ethers of 1-phenylalkanols. In the case of dialkyl ketones, the reaction was accompanied by formation of silyl enol ethers in considerable amounts. Asymmetric hydrosilylation of a series of alkyl phenyl ketones catalyzed by chiral phosphine—platinum(II) complexes was undertaken. The products were readily converted into partially active 1-phenylalkanols.

Introduction

Although homogeneous hydrogenation catalyzed by various transition metal complexes has been extensively studied [2], it has been confined mostly to that of carbon—carbon multiple bonds. There had been only a few papers on hydrogenation of carbon—oxygen double bonds [3] before Schrock and Osborn reported in 1970 [4] that cationic rhodium complexes with relatively basic phosphines as ligands catalyze the reduction of ketones under mild conditions. On the basis of these findings, a catalytic asymmetric hydrogenation of ketones was achieved, but with low optical yield [5].

Zinc chloride [6] and chloroplatinic acid [7] were found to catalyze the hydrosilylation of carbonyl compounds, though their applicability was limited. Recently, Ojima and coworkers have reported [8] that chlorotris(triphenylphosphine)-rhodium(I) is very effective for the hydrosilylation of carbonyl compounds. Corriu and Moreau also have studied [9] the addition of diarylsilanes to ketones in the presence of dichlorotris(triphenylphosphine)ruthenium(II) as well as the

* For a preliminary communication see [1].

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rhodium complex. The transition metal-catalyzed hydrosilylation of carbonyl compounds may be considered as a synthetic equivalent of C=O-reduction.

We have shown that platinum(II) [10], nickel(II) [11], and rhodium(I) [12] complexes with chiral phosphines as ligands catalyze the enantioselective addition of hydrosilanes to prochiral olefins. With the aim of developing an asymmetric hydrosilylation of ketones, we have independently examined the behavior of several ketones toward addition of hydrosilanes in the presence of a variety of transition metal complexes with phosphine ligands. In this paper, it is reported that the hydrosilylation of ketones with methyldichlorosilane proceeds under mild conditions by the use of $[(PhMe_2P)PtCl_2]_2$, and that one of its chiral phosphine analogs is useful for the asymmetric hydrosilylation of a series of alkyl phenyl ketones. Some chiral phosphine—rhodium complexes also have been found [13] to catalyze the reaction, with higher enantioselectivity than observed with the platinum(II) system, cf. [22].

Results and discussion

Hydrosilylation of ketones catalyzed by platinum(II) complexes

All experiments were carried out in degassed sealed glass tubes. In typical runs the catalyst concentration was about 10^{-3} mole per mole of the ketone and 1.3 equivalent of the hydrosilane was used for each equivalent of the ketone. The mixture was allowed to stand at room temperature or heated, if necessary, for a given period of time. The addition products were isolated by distillation, and characterized by their IR and NMR spectra and elemental analyses.

To begin with, various Group VIII transition metal complexes were examined for their catalytic activities in the addition reaction of methyldichlorosilane to acetophenone (eq. 1). Dichlorodi(phosphine)-palladium(II) and -nickel(II) complexes exhibited no appreciable effect on the reaction even under forcing conditions. Chlorotris(triphenylphosphine)rhodium(I) also did not catalyze the hydro-

$$PhCOMe + HSiMeCl_2 \xrightarrow{\text{catalyst}} \underset{\text{(IV)}}{PhMeCHOSiMeCl_2} \qquad (1)$$

silylation of acetophenone with methyldichlorosilane at all, though trialkylsilanes and dialkylsilanes were later found to react under mild conditions [8,9]. Platinum complexes seemed to be the only satisfactory catalysts for the reaction of methyldichlorosilane with acetophenone, so that several phosphine—platinum complexes were examined in some detail. The yield of the silyl ether of 1-phenylethanol varied markedly, depending on the nature of the catalyst used. As shown in Table 1, dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum(II) (I) was the most effective catalyst, whereas its triphenylphosphine analog had little catalytic activity. In accord with the nature of cationic rhodium complexes [4] with more basic phosphines, these facts may suggest that a relatively electron-donating phosphine ligand plays an important role in facilitating the coordination of a carbonyl moiety to the coordinatively unsaturated platinum complex and, as a result, giving rise to the addition of methyldichlorosilane to the ketone. Dichlorodi(phosphine)platinum(II) was of no use as a catalyst precursor for the hydrosilylation of ketones, nor for that of prochiral olefins [10].

The addition of other hydrosilanes, such as dialkyl- and trialkylsilanes, to acetophenone catalyzed by I was carried out (eq. 2). The ease with which the addition

$$PhCOMe + HSiR_3 \xrightarrow[\text{room temp., 40 h}]{I} PhMeCHOSiR_3 \quad (2)$$

reaction occurred was dependent strongly on the nature of silanes employed; methylphenylsilane added readily to the ketone at room temperature to give the corresponding silyl ether in 80% yield. Phenylsilane also added, the major product being not the 1 : 1 adduct of phenylsilane but the 1 : 2 adduct. On the other hand trimethylsilane, dimethylphenylsilane, diethoxymethylsilane, and dichlorophenylsilane did not react at all when the platinum(II) catalyst I was used.

The hydrosilylation of a few dialkyl ketones with methyldichlorosilane was rather complicated, always being accompanied by the formation of silyl enol ethers [14] as indicated in the following equations.

$$EtCOMe + HSiMeCl_2 \xrightarrow[\text{room temp.}]{I} EtMeCHOSiMeCl_2$$

(V (31%))

$$+ \underset{H}{\overset{Me}{\diagdown}}C=C\underset{OSiMeCl_2}{\overset{Me}{\diagup}} \quad + \underset{H}{\overset{Me}{\diagdown}}C=C\underset{Me}{\overset{OSiMeCl_2}{\diagup}} \quad (3)$$

(*E*-VI (3%)) (*Z*-VI (2%))

$$t\text{-BuCOMe} + HSiMeCl_2 \xrightarrow[\text{room temp.}]{I} t\text{-BuMeCHOSiMeCl}_2 + \underset{MeCl_2SiO}{\overset{t\text{-Bu}}{\diagdown}}C=CH_2 \quad (4)$$

(VII (9%)) (VIII (4%))

$$PhCH_2COMe + HSiMeCl_2 \xrightarrow[\text{room temp.}]{I} PhCH_2MeCHOSiMeCl_2$$

(IX (29%))

$$+ \underset{H}{\overset{Ph}{\diagdown}}C=C\underset{OSiMeCl_2}{\overset{Me}{\diagup}} \quad + \underset{H}{\overset{Ph}{\diagdown}}C=C\underset{Me}{\overset{OSiMeCl_2}{\diagup}} \quad (5)$$

(*E*-X (8%)) (*Z*-X (3%))

Since the formation of silyl enol ethers should take place with concomitant evolution of hydrogen, it is conceivably possible to argue that the silyl ethers of alkanols might arise from some catalytic hydrogenation of silyl enol ethers initially formed. However, attempted hydrogenation of α-trimethylsiloxystyrene gave no appreciable amount of the silyl ether of 1-phenylethanol under the same conditions as mentioned above, so that the possibility of silyl enol ether intermediates may be ruled out. The formation of silyl enol ethers in the presence of platinum complex I and the catalytic hydrosilylation of ketones most likely are competing processes. At least two possible mechanisms exist for the formation of silyl enol ethers on the basis of known homogeneous catalysis; (*a*) a pathway involving dehydrogenative condensation [15] between the hydrosilane and the enol present in equilibrium with the ketone, and (*b*) one involving the well-recogniz-

TABLE 1

HYDROSILYLATION OF ACETOPHENONE WITH METHYLDICHLOROSILANE CATALYZED BY TRANSITION METAL COMPLEXES

Catalyst	Conditions		Yield [a] (%)
	Temp. (°C)	Time (h)	
cis-(C_2H_4)Am*$PtCl_2$ [b]	room temp.	40	51
cis-$(R_3P^*)_2PtCl_2$ [c]	room temp.	90	3
$[(PhMe_2P)PtCl_2]_2$	room temp.	40	80
$[(Ph_3P)PtCl_2]_2$	room temp.	60	4
$(PhMe_2P)_2PdCl_2$	120	40	0
$[(PhMe_2P)PdCl_2]_2$	120	40	0
trans-$(R_3P^*)_2NiCl_2$ [c]	90	20	0
$(Ph_3P)_3RhCl$	50	40	0

[a] Yields were determined by GLC based on acetophenone used. [b] Am*: (*S*)-$PhMeCHNH_2$. [c] R_3P^*: (*R*)-$(PhCH_2)MePhP$.

ed β-elimination of platinum—hydride from an α-siloxyalkylplatinum intermediate, which, if not isolated, would be formed via migration of the silyl ligand from the metal to the coordinated carbonyl oxygen atom. Although, at present, these two alternatives cannot be differentiated, we are inclined to believe that the latter pathway may be of significance when more substituted silyl enol ethers are formed exclusively.

Asymmetric hydrosilylation of ketones catalyzed by chiral phosphine—platinum complexes

Dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum(II) (I) is found to be a specifically effective catalyst for the hydrosilylation of alkyl phenyl ketones as mentioned above. Accordingly, dichlorobis[(*R*)-benzylmethylphenylphosphine]di-μ-chlorodiplatinum(II) (II) [10] or its (*R*)-methylphenyl-*n*-propylphosphine analog (III) [10] would be suitable for the asymmetric hydrosilylation of the prochiral ketones. Indeed, the addition of methyldichlorosilane to a series of alkyl phenyl ketones catalyzed by these chiral phosphine—platinum(II) complexes gave partially optically active silyl ethers of 1-phenylalkanols, and the silyl ethers were readily converted into the corresponding 1-phenylalkanols by treatment with methyllithium (eq. 6).

$$PhCOR + HSiMeCl_2 \xrightarrow{[L^*PtCl_2]_2} PhR\overset{*}{C}HOSiMeCl_2 \xrightarrow[2)\ H_3O^+]{1)\ MeLi} PhR\overset{*}{C}HOH \qquad (6)$$

(R = Me, Et, n-Pr, i-Pr, i-Bu, t-Bu; L* = chiral phosphine)

The results for a series of alkyl phenyl ketones examined are summarized in Table 2. It is noteworthy that the platinum(II) complex II catalyzes the asymmetric addition of methyldichlorosilane to the ketones to give predominantly (*S*)-1-phenylalkanols, whereas III gives the (*R*)-enantiomers, except in the case of pivalophenone.

The results clearly indicate that in the two phosphines employed it is the only chiral nature at the phosphorus atom to be transmitted in the diastereomeric transition states that is opposite. This is not the case for the asymmetric hydrosilyla-

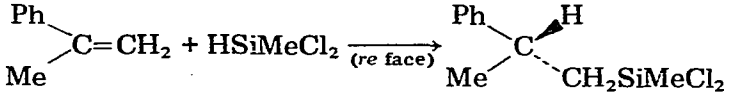
TABLE 2

ASYMMETRIC HYDROSILYLATION OF RCOPh WITH $HSiMeCl_2$ CATALYZED BY $[L^*PtCl_2]_2$ AT ROOM TEMPERATURE [a]

R	Yield (%)	Silyl ether [b] $[\alpha]_D^{20}$ (neat)	Carbinol [b] $[\alpha]_D^{20}$	Optical yield (%) [c] (configuration)
L*: (*R*)-(+)-($PhCH_2$)MePhP (79% optical purity)				
Me	81	−4.60	−2.61	7.6 (*S*)
Et	81	−6.11	−2.21	10.0 (*S*)
n-Pr	77	−5.21	−3.0 [d]	8.4 (*S*)
i-Pr	55 [e]	—	−1.7 [f]	4.5 (*S*)
i-Bu	65	—	−4.74 [g]	18.6 (*S*)
t-Bu [h]	33	−6.74	−3.8 [i]	18.6 (*S*)
L*: (*R*)-(−)-MePh-n-PrP (93% optical purity)				
Me	71	+3.81	+2.24	5.5 (*R*)
Et	83	+5.13	+1.94	7.4 (*R*)
n-Pr	74	+3.82	+2.0 [d]	4.7 (*R*)
i-Pr	57 [e]	—	+1.1 [f]	2.5 (*R*)
i-Bu	54	—	+0.03 [g]	0.1 (*R*)
t-Bu [h]	24	−2.62	−1.5 [i]	6.2 (*S*)

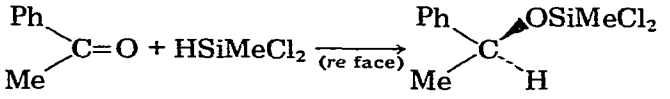
[a] $[L^*PtCl_2]_2 = 6.7 \times 10^{-2}$ mol%. [b] Specific rotation was measured neat unless otherwise noted. [c] Optical yields are calculated from the specific rotation of the pure enantiomers which are reported in the literature (lit. [16]), and calibrated for the optical purity of chiral phosphines used. [d] Specific rotation in benzene; maximum rotation $[\alpha]_D^{27}$ −45.9° (*c* 6, benzene) (lit. [17]). [e] Contaminated with ca. 10% of $Ph(MeCl_2Si-O)C{=}CMe_2$. [f] Specific rotation in ether. [g] Specific rotation in n-heptane. [h] Heated at 90°C for 10 days. [i] Specific rotation in benzene.

tion of, for example, α-methylstyrene with methyldichlorosilane [10]. Furthermore, the latter reaction catalyzed by II gives rise to the (*R*)-adduct predominantly, while (*S*)-1-phenylethanol is the preferred enantiomer in the case of asymmetric addition of methyldichlorosilane to acetophenone as given in Table 2. These facts may well imply that the stereoselectivity for the addition of a hydrosilane to the enantiotopic faces of a ketone is different from that of an olefin which is undoubtedly π-coordinated to the chiral catalyst (eq. 7 and 8).



(7)

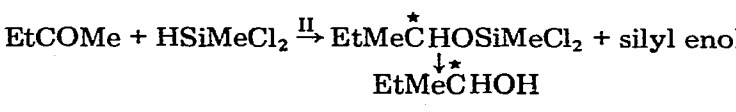
(5.2% optical yield, *R*)



(8)

(7.6% optical yield, *S*)

An asymmetric induction also was observed in the hydrosilylation of 2-butanone, but the optical yield was only 3.6% of the *S* configuration as shown in eq. 9.



(9)

$[\alpha]_D^{20}$ + 0.40° (neat)

TABLE 3

ASYMMETRIC HYDROSILYLATION OF RCOPh WITH $H_2SiMePh$ CATALYZED BY $[\{(R)\text{-}(PhCH_2)MePhP\}PtCl_2]_2$ (II) AT ROOM TEMPERATURE [a]

R	Yield (%)	Silyl ether [b] α_D^{20} (0.1 dm, neat)	Carbinol $[\alpha]_D^{20}$ (neat)	Optical yield (%) (configuration)
Me	90	−0.204	−1.32	3.8 (*S*)
t-Bu	59	+0.020	+0.15 [c]	0.7 (*R*)

[a] II = 6.7×10^{-2} mol%. [b] A mixture of two diastereomeric isomers. [c] Specific rotation in benzene.

The addition of methylphenylsilane to acetophenone and to pivalophenone in the presence of II also was carried out, and the results are shown in Table 3. The optical purity of the resulting alcohol was much lower in both cases than that with methyldichlorosilane. The marked dependence of the extent of asymmetric induction on the structure of the hydrosilanes employed, which seems to be notable in chiral phosphine—rhodium system, will be fully discussed in a following paper [22].

When *cis*-dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II) [18] is used as a catalyst instead of chiral tertiary phosphine—platinum complexes, the adduct was obtained in very low optical purity. For example, the silyl ether from acetophenone and methyldichlorosilane had $[\alpha]_D^{20}$ + 0.34°.

Although the optical yields obtained are rather low in the present platinum(II) catalyst system compared with a cationic rhodium complex [13a] of the same chiral phosphine as one used here, the fact that the platinum complexes contain only one chiral phosphine molecule allows one to discuss a simple correlation of given chiral information with the stereoselective addition to enantiotopic faces of the substrate.

Experimental

General comments

All boiling points described here are uncorrected. The ^1H NMR spectra were obtained on a Varian T-60 or HA-100 spectrometer in carbon tetrachloride solution containing TMS as an internal standard. Infrared spectra were measured on a Hitachi EPI-G3 grating spectrometer. A Varian Aerograph Model 90P, equipped with a 20 ft. column packed with Apiezon-L (30% on Celite) or Silicone DC550 (30% on Celite) was used, if necessary, for isolation and purification of products. The optical rotations were measured with a Yanagimoto OR-50 polarimeter.

The preparation of metal complexes with chiral ligands has been described in other papers [10,11], and other phosphine complexes were prepared by literature methods: $[(PhMe_2P)PtCl_2]_2$ [19], $[(Ph_3P)PtCl_2]_2$ [20], and $[(PhMe_2P)PdCl_2]_2$ [19].

Hydrosilylation of acetophenone with methyldichlorosilane catalyzed by some transition metal complexes

All reactions were carried out by the following procedure. In a degassed sealed glass tube was heated a mixture of acetophenone (1 part), methyldichlorosilane

TABLE 4

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR HYDROSILYLATION PRODUCTS

Compound	B.p. (°C/Torr)	n_D^{20}	d_4^{20}	Found (calcd.) (%)		
				C	H	Cl
RPhCHOSiMeCl$_2$						
R = Me	97/17	1.4920	1.1464	46.43 (45.96)	5.12 (5.14)	29.89 (30.15)
R = Et	124/22	1.4910	1.1251	48.40 (48.20)	5.80 (5.66)	28.38 (28.45)
R = n-Pr	79/3	1.4888	1.1022	50.45 (50.19)	6.39 (6.13)	26.66 (26.49)
R = t-Bu	77/2	1.4904	1.0831	53.02 (51.98)	6.76 (6.54)	25.43 (25.57)
RPhCHOSiHMePh [a]						
R = Me	107—11/3	—	—	73.98 (74.32)	7.62 (7.48)	
R = t-Bu	120—37/3	—	—	75.75 (76.00)	8.80 (8.50)	

[a] A mixture of diastereoisomers.

(1.3 parts), and a catalyst (0.7×10^{-3} part) for a given period of time. 1-Phenylethyl methyldichlorosilyl ether (IV) was isolated by fractional distillation. The ^{1}H NMR, physical constants, and analytical data of IV are listed in Tables 4 and 5. The yield in each case was generally determined by GLC, and the results obtained for hydrosilylation of acetophenone with methyldichlorosilane are summarized in Table 1.

The reaction with other hydrosilanes was carried out in the same way as in the case with methyldichlorosilane.

TABLE 5

^{1}H NMR DATA FOR RPhCHOSiMeCl$_2$

R	Chemical shifts (δ) [a]		
	SiC$\underline{H}_3$	OC$\underline{H}$	Others [b]
Me	0.76 (s)	5.25 (q, J = 6.4 Hz)	1.56 (d, J = 6.4 Hz, C$\underline{H}_3$)
Et	0.71 (s)	4.98 (t, J = 6.3 Hz)	0.89 (t, J = 7.0 Hz, C$\underline{H}_3$) 1.61—2.11 (m, C$\underline{H}_2$)
n-Pr	0.71 (s)	5.05 (t, J = 6.3 Hz)	0.92 (t, J = 7.2 Hz, C$\underline{H}_3$) 0.9—2.4 (m, C$\underline{H}_2$C$\underline{H}_2$)
i-Pr	0.69 (s)	4.73 (d, J = 6.2 Hz)	0.81 and 0.92 (pair of d, J = 6.4 Hz, 2C$\underline{H}_3$) 1.95 (sep, J = 6.4 Hz, C$\underline{H}$)
i-Bu	0.68 (s)	5.12 (t, J = 6.2 Hz)	0.95 (d, J = 6.0 Hz, 2C$\underline{H}_3$) 0.8—2.6 (m, C$\underline{H}_2$C$\underline{H}$)
t-Bu	0.68 (s)	4.71 (s)	0.94 (s, C(C$\underline{H}_3$)$_3$)

[a] Carbon tetrachloride solution with tetramethylsilane as an internal standard; s, singlet, d, doublet, t, triplet, q, quartet, sep, septet, m, multiplet. [b] The chemical shift for phenyl protons is 7.23—7.29 ppm (s).

Hydrosilylation of dialkyl ketones with methyldichlorosilane

2-Butanone. A mixture of 4.3 g (60 mmol) of 2-butanone, 9.2 g (80 mmol) of methyldichlorosilane, and 16 mg (4×10^{-2} mmol) of dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum (I) was allowed to stand at room temperature over a period of 40 h to give, by distillation (60—64°C/50 Torr), 4.0 g (36% combined yield) of a mixture of three products, which were isolated with difficulty. On the basis of NMR analysis, this consisted of sec-butyl methyldichiorosilyl ether (V) and (*E*)- and (*Z*)-2-methyldichlorosiloxybut-2-ene (VI) in a ratio of 31 : 3 : 2. NMR : V: δ 0.77 (s, $SiCH_3$), 0.93 (t, $J = 6.6$ Hz, CH_2CH_3), 1.27 (d, $J = 6.0$ Hz, $CHCH_3$), 1.50 (q, $J = 6.4$ Hz, CH_2CH_3), and 4.20 (sextet, OCH). (*E*)-VI: δ 0.82 (s, $SiCH_3$), 1.58 (double q, $J = 1.0$ and 7.2 Hz, $=CHCH_3$), 1.82 (overlapping q, $OCCH_3$), and 4.98 (q of q, $J = 1.0$ and 6.8 Hz, =CH). (*Z*)-VI: δ 1.52 (double q, ill-resolved, $CHCH_3$), 1.89 (broad s, $OCCH_3$), and 4.62 (diffuse q, =CH).

3,3-Dimethyl-2-butanone. From a mixture of 6.0 g (60 mmol) of 3,3-dimethyl-2-butanone; 9.2 g (80 mmol) of methyldichlorosilane, and 16 mg (4×10^{-2} mmol) of I was obtained 1.7 g (13% combined yield) of a mixture of 2-methyldichlorosiloxy-3,3-dimethylbutane (VII) and 2-methyldichlorosiloxy-3,3-dimethylbut-1-ene (VIII), b.p. 73—77°C/44 Torr. NMR : VII: δ 0.76 (s, $SiCH_3$), 0.91 (s, $C(CH_3)_3$), 1.21 (d, $J = 6.2$ Hz, $CHCH_3$), and 3.94 (q, OCH). VIII: δ 0.86 (s, $SiCH_3$), 1.11 (s, $C(CH_3)_3$), and 4.37 (*AB*, $J = 2.0$ Hz, $\Delta\nu = 3.6$ Hz, $=CH_2$).

1-Phenyl-2-propanone. Similarly, by fractional distillation over a range of 79—86°C/4 Torr of the reaction mixture, 1-phenyl-2-methyldichlorosiloxypropane (IX) and (*E*)- and (*Z*)-1-phenyl-2-methyldichlorosiloxypropene (X) were obtained in 40% combined yield. NMR : IX: δ 0.64 (s, $SiCH_3$), 1.27 (d, $J = 6.0$ Hz, $CHCH_3$), 2.71—2.88 (double d, CH_2), 4.43 (sextet, $J = 6.2$ Hz, OCH), and 7.19 (s, C_6H_5). (*E*)-X: δ 0.97 (s, $SiCH_3$), 2.05 (s, $=CCH_3$), 6.09—6.17 (broad s, =CH), and 7.15 (broad s, C_6H_5). (*Z*)-X: δ 0.80 (s, $SiCH_3$), 2.14 (s, $=CCH_3$), 5.52—5.60 (broad s, =CH), and 7.15 (broad s, C_6H_5).

The ratio of these compounds thus obtained is shown in the text.

Asymmetric hydrosilylation of ketones with methyldichlorosilane

Alkyl phenyl ketones. The reaction conditions, yields, and optical data of the products are summarized in Table 2. Some physical constants, analytical data, and ^1H NMR spectra for the silyl ethers are listed in Tables 4 and 5. The following procedure for an asymmetric hydrosilylation of acetophenone is typical. Under a nitrogen atmosphere 9.2 g (80 mmol) of methyldichlorosilane was added to 7.2 g (60 mmol) of acetophenone in the presence of 20 mg (4×10^{-2} mmol) of II (with phosphine of 79% optical purity). The reaction mixture was stirred at room temperature over a period of 40 h. The product was isolated by distillation through a short Vigreux column to give 11.4 g (81% yield) of 1-phenylethyl methyldichlorosilyl ether (IV), b.p. 109°C/18 Torr, $[\alpha]_D^{20}$ —4.60° (neat).

To the adduct thus obtained was added dropwise excess methyllithium in ether solution with stirring at 0°C. After 2 h reflux, the reaction mixture was hydrolyzed with dilute hydrochloric acid. The organic products were extracted with ether and this ether extract was dried over sodium sulfate. After evaporation of ether, distillation under reduced pressure gave almost quantitatively 1-phenylethanol, $[\alpha]_D^{20}$ —2.61° (neat), (lit. [16]: maximum rotation $[\alpha]_D^{21}$ —43.5° (neat)). Considering an optical purity of the phosphine (79%), the optical yield of the addition

product is 7.6%. The alcohol was identified by comparison of the GLC retention time and the NMR spectrum with those of an authentic sample.

The reaction of isobutyrophenone with methyldichlorosilane catalyzed by II or III was accompanied by the formation of ca. 10% of 2-methyl-1-methyldichlorosiloxy-1-phenylpropene, NMR: δ 0.63 (s, $SiCH_3$), 1.74 and 1.86 (a pair of s, $C(CH_3)_2$), and 7.32 (s, C_6H_5).

2-Butanone. From a mixture of 8.8 g (120 mmol) of 2-butanone, 18.4 g (160 mmol) of methyldichlorosilane, and 39 mg (8×10^{-2} mmol) of II was obtained 7.5 g (39% combined yield) of the mixture of sec-butyl methyldichlorosilyl ether and silyl enol ethers in the same proportion as described above, α_D^{20} +0.055° (0.1 dm, neat). The adducts were treated with excess methyllithium in ether solution and then hydrolyzed to give, after preparative GLC, 2-butanol, $[\alpha]_D^{20}$ +0.40° (neat), (lit. [21]: maximum rotation, $[\alpha]_D^{20}$ +13.83° (neat).

Asymmetric hydrosilylation of acetophenone and pivalophenone with methylphenylsilane

The procedure for the reaction with methyldichlorosilane was followed except that 9.0 g (75 mmol) of methylphenylsilane was used. Yields and optical data are summarized in Table 3.

The silyl ether was obtained as a mixture of two diastereoisomers. GLC and NMR analyses indicated that the diastereoisomers were formed in nearly equal amounts in both cases. Boiling points and analytical data of silyl ethers are shown in Table 4. NMR(CCl_4/TMS): PhMeCHOSiHMePh; δ 0.34 and 0.37 (d, J = 2.9 Hz, $SiCH_3$), 1.40 and 1.43 (d, J = 6.3 Hz, $CHCH_3$), 4.81 (q, OCH), 4.93 and 5.02 (q, SiH), 7.12 and 7.20 (s, CC_6H_5), and 7.06—7.57 (m, SiC_6H_5). t-BuPhCHOSiHMePh; δ 0.23 and 0.31 (d, J = 2.9 Hz, $SiCH_3$), 0.85 and 0.86 (s, CCH_3), 4.26 (s, OCH), 4.86 and 4.92 (q, SiH), 7.14 and 7.18 (s, CC_6H_5), and 7.06—7.54 (m, SiC_6H_5).

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