CATALYTIC ASYMMETRIC HYDROSILYLATION OF OLEFINS.

I. CHIRAL PHOSPHINE-PLATINUM(II) COMPLEXES AS HYDROSILYLATION CATALYSTS*,**

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Summary

Several platinum(II) complexes containing chiral phosphines, (R)-benzyl-methylphenylphosphine (BMPP), (R)-methylphenyl-n-propylphosphine (MPPP), and menthyldiphenylphosphine (MDPP), were prepared. Catalytic asymmetric hydrosilylation has been achieved for the first time in the reaction of methyldichlorosilane with 1,1-disubstituted prochiral olefins, α-methyl-styrene, 2,3-dimethyl-1-butene, and 2-methyl-1-butene, using a platinum catalyst precursor $[L^*PtCl_2]_2$ (L^* = BMPP and MPPP), and partly optically active adducts of the type $RMe\overset{*}{C}HCH_2SiMeCl_2$ (R = Ph, *i*-Pr, and Et) have been obtained. With trichlorosilane, the asymmetric addition reaction was always accompanied by isomerization or dimerization of the olefins. The chiral platinum complex-catalyzed addition-cyclization of 4-pentenyldimethylsilane also gave rise to an optically active 2-methyl-1-silacyclopentane derivative.

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* For a preliminaly communication see Ref. 1.

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Introduction

There has been a considerable interest in hydrosilylation of olefins in the presence of various Group VIII metal complexes as homogeneous catalysts [2]. A mechanism for the platinum(II) complex-catalyzed hydrosilylation has been proposed on the basis of coordination catalysis of d^8 metal complexes [3,4]. It is similar to the mechanism proposed for rhodium-(I)-catalyzed hydrogenation of olefins mostly advanced by Wilkinson and his coworkers [5]. In the last few years, several asymmetric hydrogenation catalysts, all of which are chiral phosphine complexes of rhodium, have been described [6].

In view of the formal resemblance in mechanisms between transition metal-catalyzed hydrogenation and hydrosilylation, it seemed of particular interest to explore asymmetrically catalyzed hydrosilylation of prochiral olefins using d^8 metal complexes with chiral ligands.

Few of the platinum complexes with phosphine ligands as effective catalysts for hydrosilylation had been recorded in the literature until 1971, when Fink [7a] and we [7b] found independently that some of them can catalyze the reaction, whereas there appeared several papers in 1968-1970 which dealt with certain phosphine complexes of palladium [8], nickel [9], and rhodium [10] as the hydrosilylation catalysts.

The present study was undertaken to investigate the use of chiral phosphine-platinum(II) complexes as asymmetric hydrosilylation catalysts with particular emphasis on the addition of methyldichlorosilane to 1,1-disubstituted olefins. Some nickel and rhodium complexes with chiral phosphines as catalysts will be described in the succeeding papers.
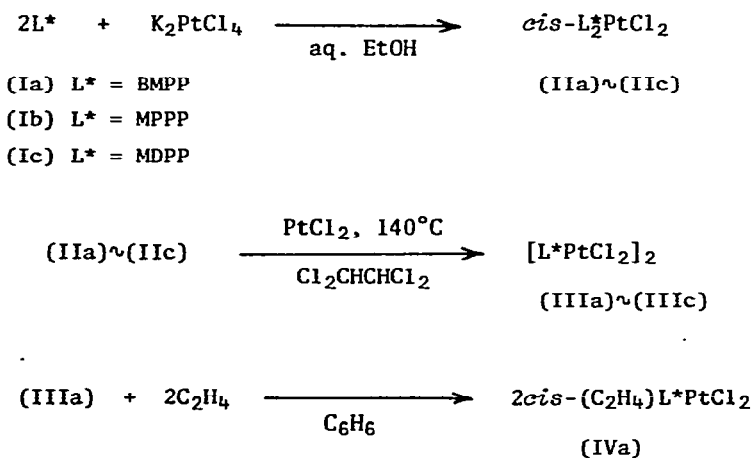
Results and Discussion

Platinum(II) complexes with chiral phosphines as catalysts

cis-Dichloro(ethylene)[(S)-1-phenylethylamine]platinum(II) [11] is
known to undergo exchange of the coordinated ethylene with a prochiral
olefin (such as *tert*-butylethylene and *trans*-2-butene) while giving rise to
an asymmetric induction of the latter. Although this complex showed an
efficient catalytic activity in hydrosilylation of α-methylstyrene and some
other olefins (in essentially quantitative yield; see Experimental), the
adducts were always racemic.

On the other hand, cis-dichloro(ethylene)phosphineplatinum(II) and
related complexes containing a chiral phosphine have been found to act as
effective catalysts for the aimed reaction, so our interest centered on
these complexes.

It has already been established that optically active phosphines, (R)-
benzylmethylphenylphosphine (BMPP) [12], (R)-methylphenyl-n-propylphosphine
(MPPP) [12,13], and menthyldiphenylphosphine (MDPP) [14,15], can readily be
obtained. The platinum complexes with these phosphines were prepared by the
following reaction sequences (Chart 1).

Chart 1

$$2L^* \ + \ K_2PtCl_4 \ \xrightarrow[\text{aq. EtOH}]{} \ cis\text{-}L_2^*PtCl_2$$

(Ia) L* = BMPP   (IIa)∿(IIc)

(Ib) L* = MPPP

(Ic) L* = MDPP

$$(IIa)\text{∿}(IIc) \ \xrightarrow[\text{Cl}_2\text{CHCHCl}_2]{\text{PtCl}_2, \ 140°C} \ [L^*PtCl_2]_2$$

(IIIa)∿(IIIc)

$$(IIIa) \ + \ 2C_2H_4 \ \xrightarrow[\text{C}_6\text{H}_6]{} \ 2cis\text{-}(C_2H_4)L^*PtCl_2$$

(IVa)

Dichlorobis[(*R*)-benzylmethylphenylphosphine (BMPP)]di-μ-chlorodi-platinum(II) (IIIa) and its MPPP analog (IIIb) were prepared according to a modified procedure of Orchin *et al.* [16] involving a reaction of the mono-nuclear complex, IIa or IIb, and platinum(II) chloride in tetrachloroethane solution, instead of melting them together as originally reported by Chatt and Venanzi [17]. This was in order to avoid possible racemization of the phosphine ligand, since the optically active phosphine Ib was found [18] to undergo considerable racemization with a half-life of 5 h at 130°C. It was confirmed that no appreciable decrease in optical activity of IIa resulted when IIa dissolved in tetrachloroethane was heated even at 155°C for 5 h.

The chlorine-bridged complex of MDPP (IIIc) was also prepared in order to compare the effectiveness of asymmetric induction in the hydrosilylation, since a complex with ligands that are asymmetric remote from phosphorus does fulfil the necessary conditions for asymmetric catalysis [6].

One particular ethylene complex of the *cis* configuration IVa was pre-pared by direct interaction of ethylene with IIIa under mild conditions [19].

Of these platinum complexes prepared here, IIa-IIc were found to be ineffective as catalyst precursors (probably due to insolubility). Complex IVa exhibited an efficient catalytic activity for hydrosilylation of various prochiral olefins. IIIa was as effective a chiral catalyst precursor as the ethylene complex IVa, presumably due to its possible interaction with an olefin substrate to form the same catalyst species.

Physical data of all complexes thus prepared are listed in Table 1.
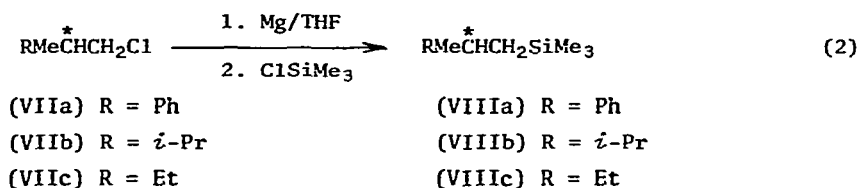
Asymmetric hydrosilylation of 1,1-disubstituted olefins

In typical runs, a 1:1 mixture of an olefin and methyldichlorosilane was heated in the presence of a catalyst (10^{-3} mole per mole of olefin) at 40°C over a period of 24 h. The hydrosilylation proceeded smoothly (eqn.

1).* The addition products were isolated by distillation in moderate yields

$$RMeC=CH_2 \quad + \quad HSiMeCl_2 \quad \xrightarrow{\text{chiral Pt}} \quad R\overset{*}{Me}CHCH_2SiMeCl_2 \qquad (1)$$

(Va) R = Ph   (VIa) R = Ph

(Vb) R = i-Pr   (VIb) R = i-Pr

(Vc) R = Et   (VIc) R = Et

and characterized by IR and NMR spectral data and elemental analyses for new compounds. Optical yields of the products were determined, after methylation to their trimethylsilyl derivatives, by comparison of specific rotations of the latter with those of the authentic substances, which were prepared by the unambiguous route shown by eqn. 2. Actual conversions were carried out

$$R\overset{*}{Me}CHCH_2Cl \quad \xrightarrow[\text{2. ClSiMe}_3]{\text{1. Mg/THF}} \quad R\overset{*}{Me}CHCH_2SiMe_3 \qquad (2)$$

(VIIa) R = Ph   (VIIIa) R = Ph

(VIIb) R = i-Pr   (VIIIb) R = i-Pr

(VIIc) R = Et   (VIIIc) R = Et

with chlorides of lower activity and the maximum rotations of the resulting trimethylsilyl·derivatives VIIIa-VIIIc were calculated on the basis of optical purity of the starting chlorides.

The data obtained for asymmetric hydrosilylation of Va-Vc and for the authentic substances VIIIa-VIIIc are summarized in Tables 2 and 3, respectively.

The extent of asymmetric induction in the hydrosilylation was considerably low and a nickel complex with the same chiral phosphine as one used here has been found to catalyze the reaction with higher asymmetric bias
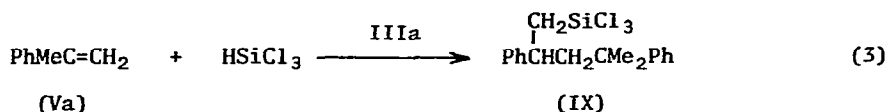
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* There seems to be no racemization arising from dehydrosilylation of the adducts, since (S)-(+)-methylbutyltrichlorosilane does not racemize at all in the presence of chloroplatinic acid even at 180°C [20].

[21] than the present platinum(II) system. However, the fact that the platinum complexes contain only one chiral phosphine molecule may allow one to scrutinize the net contribution of the chiral information of the catalyst to the present asymmetric hydrosilylation. First, a system with one asymmetric center as close to the platinum atom as possible may be advantageous for the purpose of sustaining the asymmetric bias, though this is not always necessary for asymmetric synthesis in general [14]. Morrison and coworkers [22] have reported that a chiral rhodium complex with the neomenthyldiphenylphosphine (NMDPP) ligand, which is not asymmetric at phosphorus, is very effective as an asymmetric homogeneous hydrogenation catalyst. However, a platinum(II) complex with epimeric chiral phosphine MDPP proved to be less useful for the asymmetric hydrosilylation studied here. Second, in Table 2 it is seen that the extent of asymmetric induction depends on the structure of both the phosphine ligand with an asymmetric phosphorus atom and the olefinic substrate. BMPP is positively a better chiral ligand than MPPP to induce asymmetry in hydrosilylation of α-methylstyrene (Va). In addition, a preferred configuration of addition products, VIa-VIc, was consistently of the R isomer. Thus, in the light of current views of the mechanisms of metal-catalyzed hydrosilylation [3,4], we may assume that, in all cases, a similar stereochemical sequence of coordination of the olefin to platinum followed by addition of the silane occurs, viz. a similar diastereomeric transition state is involved.
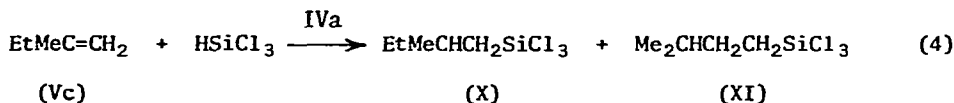
Effects of silanes on the asymmetric hydrosilylation

Methyldichlorosilane was by far the most reactive in the hydrosilylation of 1,1-disubstituted olefins (Va-Vc). Trialkylsilanes did not add at all to such olefins with the chiral platinum catalysts even at 120°C, whereas the addition of trimethylsilane and diethylmethylsilane to 1-hexene (but not to internal olefins such as 2-hexene) was reported previously to

proceed smoothly at 40°C in the presence of *trans*-dichloro(ethylene)pyridine-
platinum(II) [23] or bis(triphenylphosphine)ethyleneplatinum(0) [7] as
catalyst. Moreover, in the case where trichlorosilane was used, hydrosilyla-
tion of Va-Vc gave rather complicated results, involving some isomerization
or dimerization of olefins. Thus, in the addition of trichlorosilane to
Va in the presence of IIIa or IVa at 90°C, a 1:2 adduct (IX) was a major
product, which was isolated in 52% yield and optically inactive (eqn. 3).

$$PhMeC=CH_2 \quad + \quad HSiCl_3 \quad \xrightarrow{\text{IIIa}} \quad \overset{\overset{\displaystyle CH_2SiCl_3}{|}}{PhCHCH_2CMe_2Ph} \qquad (3)$$

$$\text{(Va)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(IX)}$$

When 2-methyl-1-butene (Vc) was used, two products were obtained in
comparable amounts (54% combined yield), one being the expected 2-methyl-
butyltrichlorosilane (X) and the other isoamyltrichlorosilane (XI). The
latter obviously came from 3-methyl-1-butene, which was formed by isomeriza-
tion of Vc under the conditions used, and might be sterically less hindered
with respect to the addition reaction of the silane (eqn. 4). Finally, with

$$EtMeC=CH_2 \quad + \quad HSiCl_3 \quad \xrightarrow{\text{IVa}} \quad EtMeCHCH_2SiCl_3 \quad + \quad Me_2CHCH_2CH_2SiCl_3 \qquad (4)$$

$$\text{(Vc)} \qquad\qquad\qquad\qquad\qquad \text{(X)} \qquad\qquad\qquad \text{(XI)}$$

2,3-dimethyl-1-butene (Vb) the hydrosilylation gave a sole product, slightly
active 2,3-dimethylbutyltrichlorosilane, in 70% yield. Although some iso-
merization would also take place in this case, the isomerized olefin is
identical with the original one. After methylation of the adduct, the
optical yield was found to be 0.8% of the *R* isomer.

All results described here indicate a significant electronic rather
than steric effect of the substituents of silanes on the platinum-catalyzed
hydrosilylation. In a previous paper [7b], it has been claimed that the

stability of the silylplatinum intermediates formed upon treatment of Pt(PPh$_3$)$_2$(C$_2$H$_4$) with a series of silanes is in the order SiCl$_3$ > SiMeCl$_2$ > SiMe$_3$, which is the same as that for the oxidative addition of these silanes to RhCl(PPh$_3$)$_3$ [10]. This appears to be the reason why some isomerization or dimerization of an olefin substrate on the platinum catalyst precedes the addition of trichlorosilane to the olefin, whereas with methyldichlorosilane there is no appreciable isomerization under the conditions used.

Asymmetric hydrosilylation of other olefins

The asymmetric hydrosilylation of prochiral olefins other than, 1,1-disubstituted ones was unsuccessful, since highly substituted olefins did not undergo addition of methyldichlorosilane under the conditions employed.

With a simple terminal olefin a terminal adduct is usually the major product. Hydrosilylation of styrene with methyldichlorosilane readily took place in the presence of IIIa even at room temperature to give 2-phenylethylmethyldichlorosilane (50% yield) and 1-phenylethylmethyldichlorosilane (20% yield),* but the latter was optically inactive.

We have observed the asymmetric induction in one particular case, where a ring-closure occurs to give a 2-methyl-1-silacyclopentane. Thus, the hydrosilylatio₁ of 4-pentenyldimethylsilane in benzene solution using IIIa as catalyst gave two products, 1,1,2-trimethyl-1-silacyclopentane (XII) [25], $[\alpha]_D^{20}$ +0.24° (neat), and 1,1-dimethyl-1-silacyclohexane (XIII) [25], with the former in an overwhelming quantity. The same two compounds were produced by the use of *cis*-dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II) as catalyst, but this chiral amine complex did not cause any asymmetric bias in XII.

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* The ratio of two isomeric products thus obtained was in good accord with that obtained by Speier and Musolf in the presence of chloroplatinic acid [24].

$$CH_2=CHCH_2CH_2CH_2SiMe_2H \xrightarrow[90°]{[Pt*]} \text{(XII)} \ SiMe_2 \ + \ \text{(XIII)} \ SiMe_2 \quad (5)$$

The preferred formation of the silacyclopentane structure may reasonably be explained by the key intermediate of a six-membered ring involving the platinum center, whereas a seven-membered ring would be required for the formation of the silacyclohexane [26].

Experimental

General comments

All melting and boiling points are uncorrected. A Varian Aerograph Model 90P, equipped with a 20-ft column packed with Silicone DC-550 (30% on Celite), was used, if necessary, for isolation and purification. NMR spectra were recorded with a Varian T-60 spectrometer, IR spectra with a Hitachi EPI G-3 Grating spectrophotometer, and optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter (accuracy ±0.003°).

Preparation of platinum(II) complexes with chiral ligands

1. *(-)-cis-Dichloro(ethylene)[(S)-1-phenylethylamine]platinum(II).* This was prepared in accordance with the procedure by Panunzi and Paiaro [11]

2. *Dichlorobis[(R)-benzylmethylphenylphosphine]di-μ-chlorodiplatinum(II) (IIIa).* According to the procedure [36] for preparing the complexes of the type cis-dichlorobis(phosphine)platinum(II), 0.98 g (2.4 mmoles) of K_2PtCl_4 was treated with 0.99 g (4.8 mmoles) of BMPP [12] ($[\alpha]_D^{20}$ +92.8° (c 0.50,

toluene)) with an 81% optical purity* in 30 ml of aqueous ethanol under an argon atmosphere. The precipitate formed was washed with four portions of each 20 ml of ether and dried *in vacuo* to give 1.10 g (66%) of the crude *cis*-dichlorobis[(R)-benzylmethylphenylphosphine]platinum(II) (IIa). A pure sample was obtained as colorless needles by recrystallization from CH_2Cl_2/EtOH (1/1); m.p. 249-250°C (in a sealed tube), 430-450 cm^{-1} (ν(Pt-P), doublet), $[\alpha]_D^{15}$ -57.4° (*c* 1.00, CH_2Cl_2). (Found: C, 48.71; H, 4.62; Cl, 10.50. $C_{28}H_{30}Cl_2P_2Pt$ calcd.: C, 48.42; H, 4.35; Cl, 10.21%.)

Repeated recrystallization of this complex should be avoided, since a slight decrease in optical rotation was observed, *e.g.* after the third recrystallization from dry ethanol, $[\alpha]_D^{25}$ -52.0° (*c* 0.30, CH_2Cl_2). This is presumably due to some resolution of possible diastereomers of IIa arising from the partially active phosphine used (81% optical purity).

In accordance with the procedure by Orchin *et al.* [16], 0.58 (0.84 mmole) of IIa and 0.28 g (1.05 mmoles) of platinum(II) chloride suspended in 24 ml of freshly distilled tetrachloroethane was heated to reflux with occasional shaking for 1.5 h under an argon atmosphere. The resulting solution was separated by filtration from the black residue, and the filtrate was condensed *in vacuo* to a minimum volume. By dissolving the crude product in dichloromethane (3 ml) followed by trituration with 40 ml of *n*-hexane, 0.66 g (82%) of IIIa as a yellow powder was obtained; m.p. 125-127°C. (Found: C, 35.98; H, 3.45; Cl, 13.89. $C_{28}H_{30}Cl_4P_2Pt_2$ calcd.: C, 35.02; H, 3.14; Cl, 14.77%.)

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* The optical purity of (R)-benzylmethylphenylphosphine was determined by converting it into (S)-[(PhCH$_2$)MePh-n-PrP]$^+$Br$^-$, $[\alpha]_D^{22-24}$ +29.8° (*c* 1.20, MeOH); the maximum rotation reported for this compound is +36.8° [13]. Mislow and coworkers [12a] have reported the optical rotation of the tertiary phosphine with 95% optical purity, based on the same quaternization, to be +81°, but this figure seems to be too low [12b].

3. cis-Dichloro(ethylene)[(R)-benzylmethylphenylphosphine]platinum(II)

(IVa). The reported procedure by Chatt *et al.* [19] for preparing ethylene

complexes was modified as follows. A solution of 0.29 g (0.30 mmole) of

IIIa in 10 ml of purified benzene was placed in a micro autoclave with a

glass lining, and magnetically stirred under an ethylene atmosphere at 40

kg/cm^2. After three days, 0.25 g (82%) of crude IVa was collected. It was

too soluble in usual organic solvents to purify by further recrystalliza-

tion, and was reprecipitated from a dichloromethane solution with *n*-pentane.

(Found: C, 37.61; H, 4.33; Cl, 13.05. $C_{16}H_{19}Cl_2PPt$ calcd.: C, 37.81; H,

3.77; Cl, 13.95%.)

4. Dichlorobis[(R)-methylphenyl-n-propylphosphine]di-μ-chlorodi-

platinum(II) (IIIb). In a similar manner to that described for IIa, *cis-*

dichlorobis[(R)-methylphenyl-*n*-propylphosphine]platinum(II) (IIb) was

prepared from 1.00 g (2.4 mmoles) of K_2PtCl_4 and 0.80 g (4.8 mmoles) of

MPPP (93% optical purity [12]) in 70% yield. (Found: C, 40.20; H, 5.22;

Cl, 12.13. $C_{20}H_{30}Cl_2P_2Pt$ calcd.: C, 40.14; H, 5.05; Cl, 11.85%.)

Complex IIb (0.60 g, 1.00 mmole) was then treated with 0.33 g (1.23

mmoles) of $PtCl_2$ in 25 ml of freshly distilled $Cl_2CHCHCl_2$ to give 0.61 g

(70%) of crude IIIb. The latter was dissolved in a hot mixture of CH_2Cl_2

(10 ml) and *n*-hexane (15 ml) and subsequently part of CH_2Cl_2 was removed by

distillation until clouding began. On keeping the mixture in a refrigerator,

pure IIIb was obtained as orange yellow prisms. (Found: C, 27.74; H, 3.35;

Cl, 16.58. $C_{20}H_{30}Cl_4P_2Pt_2$ calcd.: C, 27.79; H, 3.50; Cl, 16.41%.) Melting

points and optical rotations of IIb and IIIb are listed in Table 1.

5. Dichlorobis[(-)-menthyldiphenylphosphine]di-μ-chlorodiplatinum(II)

(IIIc). Similarly, from 0.50 g (1.2 mmoles) of K_2PtCl_4 and 1.85 g (2.6

mmoles) of ·MDPP ($[\alpha]_D^{20}$ -95.7° (*c* 1.07, CH_2Cl_2)) [14], was obtained 0.45 g

(41%) of *cis*-dichlorobis[(-)-menthyldiphenylphosphine]platinum(II) (IIc) as

yellow crystals. (Found: C, 57.68; H, 6.38; Cl, 7.70. $C_{44}H_{58}Cl_2P_2Pt$ calcd.

C, 57.77; H, 6.39; Cl, 7.75%.)

TABLE 1

MELTING POINTS AND OPTICAL ROTATIONS OF PLATINUM(II) COMPLEXES OF CHIRAL
PHOSPHINES

Complex		Color	M.p. $(°C)^a$	$[\alpha]_D^{15b}$
No.	Formula			deg.
IIa	cis-(BMPP)$_2$PtCl$_2{}^c$	colorless	249-250	-57.4^d
IIb	cis-(MPPP)$_2$PtCl$_2{}^e$	colorless	171-172	-24.6
IIc	cis-(MDPP)$_2$PtCl$_2{}^f$	pale yellow	243-244	-145
IIIa	[(BMPP)PtCl$_2$]$_2{}^c$	yellow	125-127	——
IIIb	[(MPPP)PtCl$_2$]$_2{}^e$	orange yellow	134-135	-15.0
IIIc	[(MDPP)PtCl$_2$]$_2{}^f$	off-white	299-300	-27.0^g
IVa	cis-(C$_2$H$_4$)(BMPP)PtCl$_2{}^c$	pale yellow	——	-49.4^g

^{a} Measured in a sealed tube. ^{b} In dichloromethane (c 1.00-1.60).
^{c} BMPP = (R)-(+)-(PhCH$_2$)MePhP (81% optical purity) (ref. [12]). ^{d} $-56.7°$
when BMPP (79% optical purity) was used. ^{e} MPPP = (R)-(-)-MePh-n-PrP (93%
optical purity) (ref. [12]). ^{f} MDPP = (-)-Menthyldiphenylphosphine.
^{g} Analytically not pure.

IIc (0.31 g, 0.34 mmole) was then allowed to react with 0.11 g (0.41
mmole) of PtCl$_2$ to give 0.31 g of crude IIIc, which was recrystallized twice
from EtOH/CH$_2$Cl$_2$ (2/1) to afford IIIc as off-white prisms in 56% yield.
(Found: C, 41.38; H, 4.17; Cl, 13.67. C$_{44}$H$_{58}$Cl$_4$P$_2$Pt$_2$ calcd.: C, 44.75; H,
4.69; Cl, 12.01%.)

Asymmetric hydrosilylation of 1,1-disubstituted olefins

1. *α-Methylstyrene (Va).* (a) *With methyldichlorosilane.* The follow-
ing procedure for an asymmetric hydrosilylation of Va is typical. In a

sealed degassed glass tube, a mixture of 3.60 g (30 mmoles) of Va, 3.50 g (30 mmoles) of methyldichlorosilane and 10 mg ($ca.$ 2×10^{-2} mmoles) of IVa was heated at 40°C over a period of 24 h. The product was isolated by distillation through a short Vigreux column to give 3.0 g (43%) of 2-phenylpropyldichloromethylsilane (VIa), b.p. 55°C/2 Torr, n_D^{15} 1.5151, d_4^{15} 1.1110, (lit. [27]: b.p. 148-149°C/42 Torr, n_D^{25} 1.5082, d_4^{25} 1.100), $[\alpha]_D^{15}$ +1.93° (neat); NMR (CCl$_4$/TMS): δ 0.34 (s, 3H, SiCH$_3$), 1.37 (d, J = 7.4 Hz, 3H, CCH$_3$), 1.52 (d, J = 7.4 Hz. 2H, CH$_2$), 3.11 (ill resolved sextet, 1H, CH), and 7.19 (s, 5H, C$_6$H$_5$).

The adduct thus obtained was treated with a large excess of methylmagnesium bromide in ether solution to give 2.4 g (98%) of 2-phenylpropyltrimethylsilane (VIIIa), b.p. 98°C/17 Torr, n_D^{15} 1.4900, d_4^{15} 0.8681 (lit. [27], b.p. 217°C/750 Torr, n_D^{25} 1.4841, d_4^{25} 0.8619), $[\alpha]_D^{15}$ +1.20° (neat), NMR (CCl$_4$/TMS): δ 0.03 (s, 9H, SiCH$_3$), 1.09 and 1.11 (a pair of d, J = 7.6 Hz, 2H, CH$_2$), 1.45 (d, J = 6.8 Hz, 3H, CCH$_3$), 3.00 (sextet, 1H, CH), and 7.24 (s, 5H, C$_6$H$_5$).

The results of asymmetric hydrosilylation of Va using IIIa, IIIb, and IIIc as catalysts are listed in Table 2.

(b) *With trichlorosilane.* A mixture of 3.6 g (30 mmoles) of Va, 4.1 g (30 mmoles) of trichlorosilane, and 10 mg of IVa was heated at 90°C for 24 h. The reaction mixture was distilled to give 0.2 g (3%) of the expected 2-phenylpropyltrichlorosilane [28], NMR (CCl$_4$/TMS): δ 1.42 (d, J = 6.6 Hz, 3H, CCH$_3$), 1.78 (d, J = 6.8 Hz, 2H, CH$_2$), 3.19 (ill-resolved sextet, 1H, CH), and 7.29 (s, 5H, C$_6$H$_5$); and 3.0 g (52%) of 2,4-diphenyl-4-methylpentyltrichlorosilane (IX) as a major product, b.p. 125-130°C/1.3 Torr. The latter was converted into the trimethylsilyl derivative, b.p. 121-122°C/2 Torr, n_D^{20} 1.5280, α_D^{20} nil (neat), NMR (CCl$_4$/C$_6$H$_{12}$): δ -0.40 (s, 9H, SiCH$_3$), 1.05 and 1.21 (a pair of s, 6H, CCH$_3$), 2.01 (d, J = 6.4 Hz, 2H, CCH$_2$C), and 6.79-7.34 (diffused m, 10H, C$_6$H$_5$). (Found: C, 80.96; H, 9.82. C$_{21}$H$_{30}$Si calcd.: C, 81.22; H, 9.74%.)

TABLE 2

ASYMMETRIC HYDROSILYLATION OF OLEFINS WITH $HSiMeCl_2$ CATALYZED BY CHIRAL PHOSPHINE-PLATINUM(II) COMPLEXES AT 40°C

Olefin	Catalyst[a]	Yield (%)	$[\alpha]_D^{15}$, deg of product[b]	$[\alpha]_D^{15}$, deg methylated[b]	Optical yield (%)[c] (Configuration)	
PhMeC=CH$_2$	IIIa	56	+1.65	+1.03	5.2	(R)
PhMeC=CH$_2$	IVa	43	+1.93	+1.20	6.1	(R)
PhMeC=CH$_2$	IIIb	64	+0.38		1.1	(R)
PhMeC=CH$_2$	IIIc	33[d]	0		—	
i-PrMeC=CH$_2$	IIIa	83	-0.17	-0.27	1.4	(R)
i-PrMeC=CH$_2$	IVa	76	-0.16	-0.24	1.2	(R)
i-PrMeC=CH$_2$	IIIb	86	-0.19		1.3	(R)
i-PrMeC=CH$_2$	IIIc	70[e]	-0.14		0.9	(R)
EtMeC=CH$_2$	IIIa	68	-0.13	-0.15	1.2	(R)
EtMeC=CH$_2$	IVa	69	-0.12	-0.14	1.1	(R)
EtMeC=CH$_2$	IIIb	55	-0.08		0.6	(R)
EtMeC=CH$_2$	IIIc	35[e]	0		—	

[a] See Table 1. [b] Neat. [c] Based on the maximum rotation of authentic samples and calibrated for the optical purity of the chiral phosphines used. [d] Heated at 120°C for 60 h. [e] Heated at 90°C for 40 h.

   2. *2,3-Dimethyl-1-butene (Vb)*. *(a) With methyldichlorosilane*. From a mixture of 2.5 g (30 mmoles) of Vb, 3.5 g (30 mmoles) of methyldichloro-silane, and 10 mg of IVa was obtained 4.5 g (76%) of 2,3-dimethylbutyl-methyldichlorosilane (VIb), b.p. 69°C/16 Torr, n_D^{15} 1.4466, d_4^{15} 1.0111, $[\alpha]_D^{15}$ -0.16° (neat), NMR (CCl$_4$/TMS): δ 0.79 (s, SiCH$_3$) and diffused

multiplets of all other protons. (Found: C, 42.49; H, 8.29. $C_7H_{16}Cl_2Si$

calcd.: C, 42.21; H, 8.10%.)

The adduct was methylated to give quantitatively 2,3-dimethylbutyl-trimethylsilane (VIIIb), b.p. 149.5°C, n_D^{15} 1.4232, d_4^{15} 0.7557, $[\alpha]_D^{15}$ -0.24° (neat), NMR (CCl_4/C_6H_6): δ 0.00 (s, $SiCH_3$) and diffused multiplets. (Found: C, 68.09; H, 13.78. $C_9H_{22}Si$ calcd.: C, 68.26; H, 14.00%.)

Other results using IIIa-IIIc as catalysts are given in Table 2.

(b) With trichlorosilane. Similarly but with 4.1 g (30 mmoles) of trichlorosilane, 2,3-dimethylbutyltrichlorosilane (4.6 g 70%), b.p. 75°C/22 Torr, α_D^{15} -0.012° (0.1 dm, neat), was obtained. (Found: C, 33.10; H, 6.15. $C_6H_{13}Cl_3Si$ calcd.: C, 32.82; H, 5.97%.) After methylation the optical rotation of the trimethylsilyl derivative was $[\alpha]_D^{15}$ -0.15° (neat).

3. 2-Methyl-1-butene (Vc). (a) With methyldichlorosilane. From a mixture of 2.1 g (30 mmoles) of Vc, 3.5 g (30 mmoles) of methyldichloro-silane, and 10 mg of IVa, was obtained 3.8 g (69%) of 2-methylbutylmethyl-dichlorosilane (VIc), b.p. 62°C/22 Torr, n_D^{15} 1.4408, d_4^{15} 1.0166 (lit. [29]: b.p. 167°C, n_D^{25} 1.4357, d_4^{25} 1.007), $[\alpha]_D^{15}$ -0.12° (neat), NMR (CCl_4/TMS): δ 0.78 (s, $SiHC_3$). Treatment of VIc with excess of methylmagnesium bromide in ether gave 2-methylbutyltrimethylsilane (VIIIb), b.p. 132.0°C, n_D^{15} 1.4158 d_4^{15} 0.7420 (lit. [29]: b.p. 134°C, n_D^{25} 1.4095, d_4^{25} 0.7343), $[\alpha]_D^{15}$ -0.14° (neat), NMR (CCl_4/TMS): δ -0.03 (s, $SiCH_3$).

Other results using catalyst precursors IIIa-IIIc are given in Table 2.

(b) With trichlorosilane. 2-Methylbutyltrichlorosilane (X) and isoamyltrichlorosilane (XI) were obtained in 54% combined yield. The GLC area ratio of isomeric products was 2:1. The products were methylated to give (by preparative GLC) VIIIc, n_D^{20} 1.4124 (lit. [30]: n_D^{20} 1.4120) and isoamyltrimethylsilane, n_D^{20} 1.4089 (lit. [31]: n_D^{20} 1.4064).

Asymmetric hydrosilylation of other olefins

1. Styrene. A mixture of 12.5 g (0.12 mole) of freshly distilled
styrene, 13.8 g (0.12 mole) of methyldichlorosilane, and 23 mg (2.4×10^{-2}
mmoles) of IIIa (with the phosphine of 79% optical purity) was allowed to
stand at room temperature for 12 h. The reaction mixture was distilled at
140-143°C/37 Torr, to give 20.1 g (76% combined yield) of 1-phenylethyl-
and 2-phenylethylmethyldichlorosilane [27]. The GLC area ratio of the
isomers was 1:3.2 (cf. [23]). The products were methylated and the result-
ant 1-phenylethyltrimethylsilane was isolated by preparative GLC. It was
optically inactive.

2. 4-Pentenyldimethylsilane. Methyldichlorosilane was treated with
4-pentenylmagnesium bromide to give 64% yield of 4-pentenylchloromethyl-
silane, b.p. 143°C, NMR (CCl_4/TMS): δ 0.48 (d, J = 3.0 Hz, 3H, $SiCH_3$),
0.6-2.3 (diffused m, 6H, $(CH_2)_3$), 4.77 (d, J = 3.0 Hz, 1H, SiH), and 5.4-6.1
(m, 3H, vinylic protons); IR (neat): 2160 (ν(Si-H)) and 1685 cm^{-1} (ν(C=C)).
(Found: C, 50.20; H, 9.15. $C_6H_{13}ClSi$ calcd.: C, 48.45; H, 8.81%.) Methyla-
tion of this compound gave known 4-pentenyldimethylsilane, b.p. 118.5-122.5°C
(Found: C, 65.40; H, 12.80. $C_7H_{16}Si$ calcd.: C, 65.54; H, 12.57%.) (lit.
[25]: prepared by other ways, b.p. 120-121°C, n_D^{20} 1.4219, d_4^{20} 0.7436).

A mixture of 2.56 g (20 mmoles) of 4-pentenyldimethylsilane and 6 mg
(10^{-2} mmole) of IIIa dissolved in 5 ml of dry benzene was heated at 90°C for
40 h. At this point the addition-cyclization was complete. The GLC area
ratio of isomeric products was 28:1. 1,1,2-trimethyl-1-silacyclopentane
(XII) as a major component was isolated by preparative GLC, n_D^{20} 1.4402, d_4^{20}
0.7968 (lit. [25]: b.p. 125°C, n_D^{20} 1.4380, d_4^{20} 0.7954), $[\alpha]_D^{20}$ +0.24° (neat);
NMR (CCl_4/TMS): δ 0.05 and 0.10 (two s, $Si(CH_3)_2$), and 1.00 (broad s, CCH_3),
and diffused multiplets assignable to ring protons. The known 1,1-dimethyl-
1-silacyclohexane (XIII) was also obtained in a trace amount.

The same reaction using *cis*-$(C_2H_4)[(S)$-PhMeCHNH$_2]PtCl_2$ as catalyst

took place readily to give the isomeric products in a ratio of 24:1, but the isolated 1-silacyclopentane derivative was racemic.

Preparation of chiral authentic substances

1. *(R)-2-Phenylpropyltrimethylsilane (VIIIa)*. (R)-2-phenyl-1-propanol ($[\alpha]_D^{20}$ +16.6° (neat)), 95.4% optical purity [32] was converted by treatment with thionyl chloride and pyridine into (R)-2-phenyl-1-chloropropane (VIIa) ($[\alpha]_D^{20}$ +13.4° (neat)), which was contaminated with *ca.* 7% of 1-phenyl-2-chloropropane [33]. The latter was not readily romoved, and the impure chloride (VIIa) was used for the following Grignard reaction without further purification.

To a tetrahydrofuran solution of (R)-2-phenylpropylmagnesium chloride, prepared from 4.8 g (31 mmoles) of the chloride VIIa and 0.9 g (37 mg-atom) of magnesium turnings, was added 6.4 g (59 mmoles) of trimethylchlorosilane over a period of 0.5 h. The mixture was heated to reflux for 7 h, and then hydrolyzed with dilute hydrochloric acid. After work-up in the usual manner, fractional distillation gave 1.1 g (20%) of pure (R)-2-phenylpropyltrimethyl-silane, b.p. 98°C/17 Torr, $[\alpha]_D^{15}$ +23.3° (neat). Assuming that an optical purity of the product is exactly the same as that of the starting (R)-alcohol the maximum rotation of VIIIa is $[\alpha]_D^{15}$ +24.3° (neat).

2. *(R)-2,3-Dimethylbutyltrimethylsilane (VIIIb)*. In accordance with the procedure by Pino *et al.* [34], partially resolved (R)-2,3-dimethyl-1-butanol ($[\alpha]_D^{20}$ -2.39° (neat), 43.0% optical purity) was converted into (R)-2,3-dimethyl-1-chlorobutane (VIIb) in 62% yield; b.p. 120-124°C, d_4^{20} 0.8890, $[\alpha]_D^{20}$ -4.22° (neat) (the maximum rotation, [34], $[\alpha]_D^{25}$ -9.91°).

In a similar manner to the preparation of VIIIa, reaction of (R)-2,3-dimethylbutylmagnesium chloride, prepared from 5.3 g (44 mmoles) of the chloride VIIb (42.6% optical purity), with 17.0 g (65 mmoles) of trimethyl-chlorosilane gave 3.1 g (44%) of crude VIIIb which was purified by prepara-tive GLC, b.p. 149.5°C, $[\alpha]_D^{15}$ -10.3° (neat).

3. (S)-2-Methylbutylmethyldichlorosilane (VIc) and -trimethylsilane

(VIIIc). After the procedure by Mosher *et al.* [35], (S)-2-methyl-1-butanol of 98% optical purity was converted into (S)-2-methylbutyl chloride (VIIc) in 75% yield, b.p. 99.0°C, $[\alpha]_D^{15}$ +1.68° (neat).

To a solution of 22.5 g (0.15 mole) of freshly distilled trichloro-methylsilane dissolved in 130 ml of dry ether/benzene (2/3) was added under gentle reflux (S)-2-methylbutylmagnesium chloride prepared from 16.0 g (0.15 mole) of the chloride VIIc in ether. The ether was distilled off through a 30-cm Vigreux column and the residue was filtered. The filtrate was distilled under reduced pressure to give 15.5 g (56%) of VIc, b.p. 76.5-77.0°C/ 37 Torr, $[\alpha]_D^{15}$ +12.8° (neat).

The product (9.2 g) was converted by treating with methylmagnesium bromide into VIIIc in 83% yield, b.p. 132°C, $[\alpha]_D^{15}$ +15.8° (neat).

The calculated maximum rotations of these authentic substances are given in Table 3.

TABLE 3

DATA OF MAXIMUM ROTATION OF THE AUTHENTIC SAMPLES

Compound	B.p. (°C/Torr)	d_4^{15}	n_D^{15}	$[\alpha]_D^{15}$, max[a]
(R)-PhMeCHCH$_2$SiMe$_3$	98/17	0.8681	1.4900	+24.3
(R)-i-PrMeCHCH$_2$SiMe$_3$	149.5	0.7557	1.4232	-24.1
(S)-EtMeCHCH$_2$SiMeCl$_2$[b]	77/37	1.0166	1.4408	+13.1
(S)-EtMeCHCH$_2$SiMe$_3$	132.0	0.7420	1.4158	+16.0

[a] Neat and based on the optical purity of starting chlorides used.

[b] Cl$_3$SiMe was used instead of ClSiMe$_3$.

Acknowledgements

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