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Regio- and Stereoselective Hydrosilation of α,β-Unsaturated Carbonyl Compounds

A thesis submitted to the
Faculty of Graduate Studies and Research
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in the
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Montréal

by

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For my beloved wife Zhili, our son David,

my parents and the rest of the family.

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ABSTRACT:

Hydrosilation of α,β-unsaturated carbonyl compounds catalyzed by hydrido*tetrakis*(triphenylphosphine)rhodium(I) (**2.20**) was found to be highly regioselective, depending on the type of silicon hydrides used. Diphenylsilane was found to give 1,2-hydrosilation (100%), whereas dimethylphenylsilane and other monohydrosilanes gave 1,4-addition (100%).

The kinetic isotope effect of the hydrosilation reaction was examined. A kinetic isotope effect of $k_H/k_D = 2$ was observed in the hydrosilation of acetophenone (**2.78**) by dihydrosilane, H_2SiPh_2 (**2.21**) and D_2SiPh_2 (**2.83**), catalyzed by the complex **2.20**. While a mixture of 1 : 1 labeled and unlabeled *sec*-phenethyl alcohols was obtained for the same reaction with monohydrosilane, $HSiMe_2Ph$ (**2.14**) and $DSiMe_2Ph$ (**2.86**).

A mechanism was proposed to account for the regioselection and the kinetic isotope effect. With the proposed intermediate **O** in Chart 2.5, (), when R ≠ H, the hydrosilation proceeds at the rhodium center to give the 1,4- selection product; when R = H, the reaction occurs at the silicon center to generate the 1,2-reduction product.

The reaction catalyzed by **2.20** was also diastereoselective, in both 1,2-hydrosilation (up to 100% de) and 1,4-hydrosilation (84% de) of α,β-unsaturated ketones.

A moderate enantiomeric excess was achieved in the asymmetric hydrosilation of prochiral ketones with chiral complexes derived from complex **2.20** with chiral phosphine ligands (up to 78% ee), and with chiral oxazolinyl compound **2.139** (up to 46% ee). Two C_3 symmetric ligands have been designed and synthesized, which were found to be too unstable to form C_3-metal complexes.

RÉSUMÉ:

L'hydrosilylation de composés carbonylés α,β-insaturés catalysés par l'hydrure de *tetrakis*(triphenylphosphine)rhodium(I) (**2.20**) est hautement régiosélective, dependant de la nature de l'hydrure de silicium utilisé. L'hydrure de diphenylsilane conduit spécifiquement à l'hydrosilylation de type 1-2, alors que l'usage de monohydrures de silanes donne uniquement l'addition de type 1-4.

L'effet isotopique cinétique de la réaction d'hydrosilylation a été étudié. Un rapport de 2 pour les constantes de vitesse k_H/k_D a été obtenu dans le cas de l'hydrosilylation de l'acétophénone (**2.78**) par l'hydrure de diphenylsilane (H_2SiPh_2) et son pendant deutérié (D_2SiPh_2) en présence du catalyseur **2.20**. Dans une expérience de compétition entre les monohydrures $HSiMe_2Ph$ et $DSiMe_2Ph$ pour la réduction de l'acétophénone, un taux d'incorporation de deutérium de 50% a été obtenu.

Un mécanisme a été proposé pour tenir compte de la régiosélectivité et de l'effet cinétique isotopique observé. En ayant recours à l'intermédiaire **O** du diagramme 2.5 (), lorsque R ≠ H l'hydrosilylation procède à partir du centre rhodium et conduit au produit d'addition 1-4 sélectivement; lorsque R = H, la réaction prend place au niveau du centre silicium ce qui mène au produit d'addition 1-2.

Une forte diastéréosélectivité lors de ces réactions a aussi été observée. Ainsi des excès diastéréomériques (ed) allant jusqu'à 100% furent obtenus lors des additions de type 1-2, alors qu'ils atteignent 84% pour les additions de type 1-4 lorsque le catalyseur utilisé est **2.20**.

L'usage de phosphines chirales comme ligands dans les complexes catalytiques de rhodium permet des inductions assymetriques [excès enantiomérique (ee) jusqu'à 78%] lorsque appliqué à des cétones prochirales. Le ligand chiral comportant un groupement oxazolinyl (**2.139**) conduit à l'obtention d'ee allant jusqu'à 46%. Deux ligands comportant une symétrie C_3 ont été conçus et synthéstisés; ces derniers ne forment toutefois pas un complexe assez stable avec le rhodium.

TABLE OF CONTENTS

CONTRIBUTION TO ORIGINAL KNOWLEDGE:

The achievement of regiocontrolled (1,2-/1,4-) hydrosilation of α,β-unsaturated carbonyl compounds provides a reliable means to access important Si-containing precursors. The established hydrosilation system can also provide an alternative route to reduce carbonyl compounds diastereoselectively. Compared to similar catalytic systems, our chiral complexes produce higher enantiomeric excess in the reduction of prochiral ketones. Our proposal that the migration of the hydride group from the silicon center in a sila-metal complex during the course of hydrosilation of carbonyl groups is a new contribution in the field of hydrosilation chemistry. The observation of η^2-complex **V** (Figure 2.44), as well as metal insertion to the Si-O bond have enriched silicon chemistry in this area. The direct coupling of amine to the chloromethyl moiety of silane is the first example for the synthesis of aminomethylsilanes. The concept of quadrants of carbonyl groups in the explanation of asymmetric reduction of prochiral ketonic substrates has been introduced for the first time, and it may provide some guidance for other related systems. The design and the first synthesis of two new C_3 ligands, which could find potential application in the field of asymmetric synthesis, is presented.

LIST OF TABLES:

LIST OF ABBREVIATIONS

Ac	acetyl
n-BuLi	*n*-butyllithium
Bz	benzyl
CH&N	carbon, hydrogen and nitrogen analysis
COD	cyclooctadiene
d	dextrorotatory (+)
DCC	dicyclohexylcarbodiimide
de	diastereomeric excess
DIBAH	diisobutylaluminum hydride
DMF	N,N-dimethylformamide
DMAP	4-dimethylaminopyridine
EDCI	3-ethyl-1-(3-dimethylaminopropyl)carbodiimide
ee	enantiomeric excess
EE	ethoxyethyl
Et	ethyl
EPC	enantiomerically pure compound
GC	gas chromatography
HOBT	1-hydroxybenzotriazole
IR	infrared absorption spectroscopy
l	levorotatory (-)
L	ligand
LAH	lithium aluminum hydride

LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilylamide
Me	methyl
Men	menthyl
MS	mass spectrometry
NBH	Sodium (Na) borohydride
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser enhancement
Nor	2,5-Norbonadiene
Ph	phenyl
THF	tetrahydrofuran
THP	tetrahydropyranyl
TLC	thin layer chromatography
TMEDA	N,N,N,N-tetramethylethalenediamine
TMS	trimethylsilyl
UV	ultraviolet

I INTRODUCTION

1.1 Hydrosilation

1.1.1 Definition

Hydrosilation is, by definition, the addition of a silicon-hydride bond, Si-H, to unsaturated functionalities, such as carbon-carbon double bonds, triple bonds, carbonyl groups, imine, nitrile or azo groups.[1] *Hydrosilation* is also called *hydrosilylation* in Europe. The reaction can be initiated *via* free radicals[1b] generated by radical initiators,[2] UV light,[3] γ-irradiation[4] or heat.[5] It can also be carried out under nucleophilic or electrophilic conditions.[1b] Mediated by transition metals and/or their complexes, catalytic hydrosilation is the most important and widely used method for making organosilicon compounds and derivatives.[6]

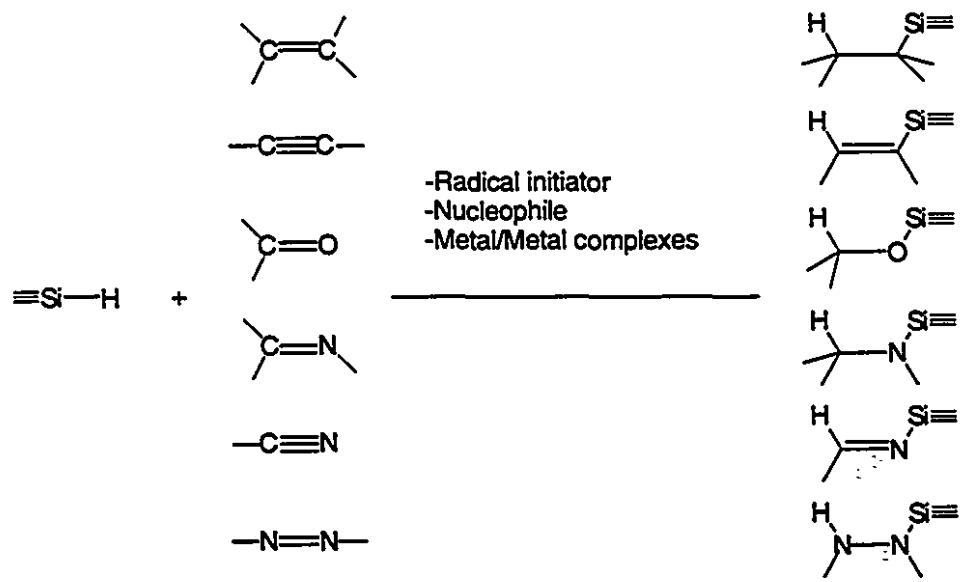


Chart 1.1

The synthetic significance of organosilicon compounds in modern synthetic chemistry has received increasing attention.[7] Since a large number of different unsaturated functionalities can be involved in hydrosilation, it can provide a powerful method for the synthesis of a wide variety of Si-containing organic molecules, and a convenient means of reducing organic compounds. The subject has been extensively reviewed,[8] and it has been estimated that there are over 4000 papers that have been published on hydrosilation during the past thirty years.[9]

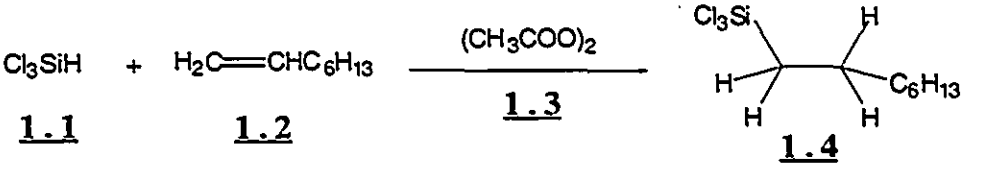
According to theoretical estimations,[10] the reaction may proceed without the assistance of catalysts. However, hydrosilation reactions can only, sometimes, be carried out without the presence of catalysts under drastic conditions (> 250 °C).[11] In the cases where catalysts are used, hydrosilation reactions are usually exothermic,[12] and can be carried out under quite mild conditions. The reactions are often highly selective. Compared with the energies of C-H and H-H bonds, the characteristic low energy of the Si-H bond makes it much easier to activate, especially, by transition metals and their complexes.[13] Hydrosilation is one of the most active areas of research in the fields of organic and organometallic chemistry.

1.1.2 Historical Overview

1.1.2.1 Radical Catalyzed Hydrosilation

In 1947, Sommer's group reported a new type of reaction between hydrosilane (1.1) and 1-octene (1.2).[2a] The reaction

proceeded with the hydride of hydrosilane adding to one end of the carbon-carbon double bond, while the silyl moiety attached to the other side of the olefin. The reaction was carried out with a radical initiator, $(CH_3COO)_2$ (**1.3**). The other possible isomer, $CH_3CH(SiCl_3)$-C_6H_{13} (**1.5**) was not formed.



1.1 **1.2** **1.3** **1.4**

Scheme 1.1

Other initiators, such as *tert*-butyl peroxide (**1.6**),[2c-e] benzoyl peroxide (**1.7**)[2f-h] and azobisisobutyronitrile (**1.8**)[2i] have been used to initiate hydrosilation reactions. A silyl radical is formed after a radical initiator has abstracted a hydrogen from the hydrosilane. The silyl radical is then involved in radical chain reactions as illustrated in Chart 1.2.

The radical initiator forms radical at relatively low temperatures (usually < 100 °C). The newly formed radical then abstracts a hydrogen atom from a hydrosilane to generate a silyl radical. The silyl radical is subsequently involved in the chain propagation step, where it attacks at one side of unsaturated functionalities to form an alkyl radical. The latter abstracts a hydrogen atom from another molecule of hydrosilane to generate the hydrosilation product and another silyl radical for further product formation. The process is repeated and more and more product is therefore produced. Telomerization and/or polymerization often

accompany the chain propagation step. These problems can be alleviated by using excess silane in the reaction systems.[2e]

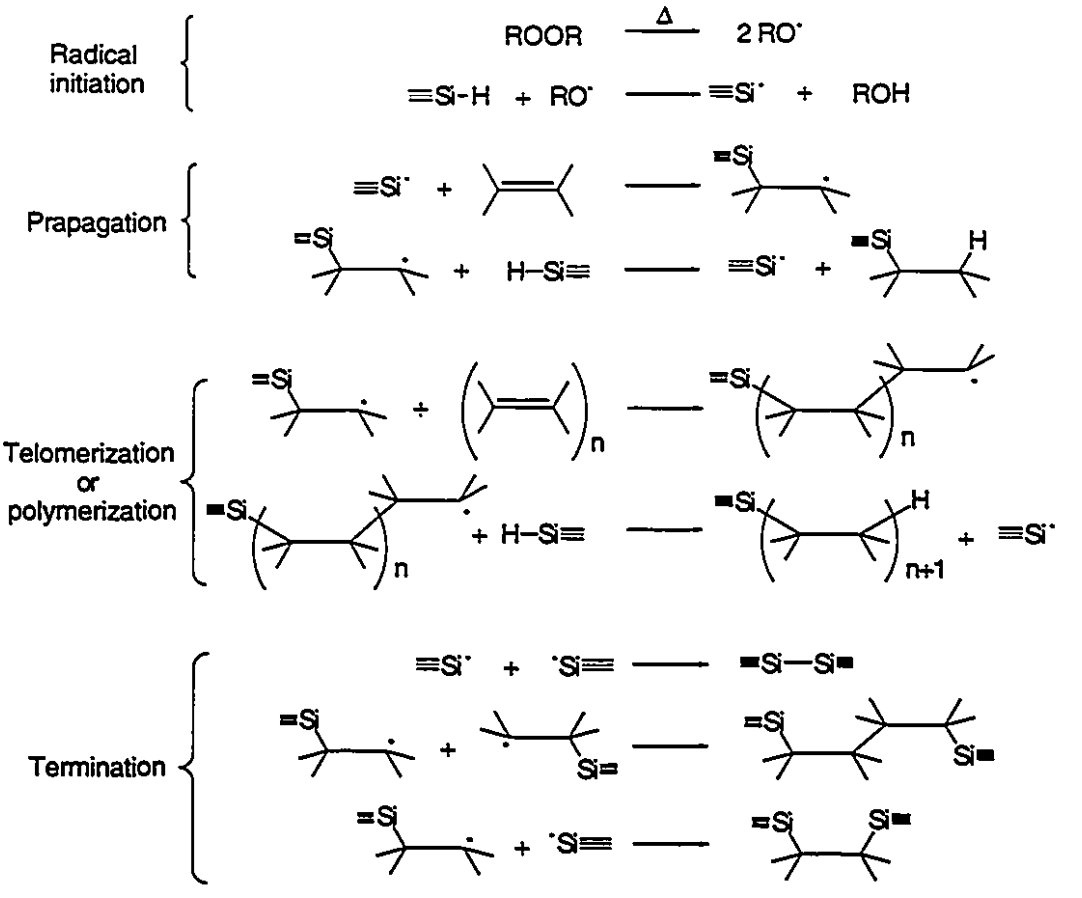
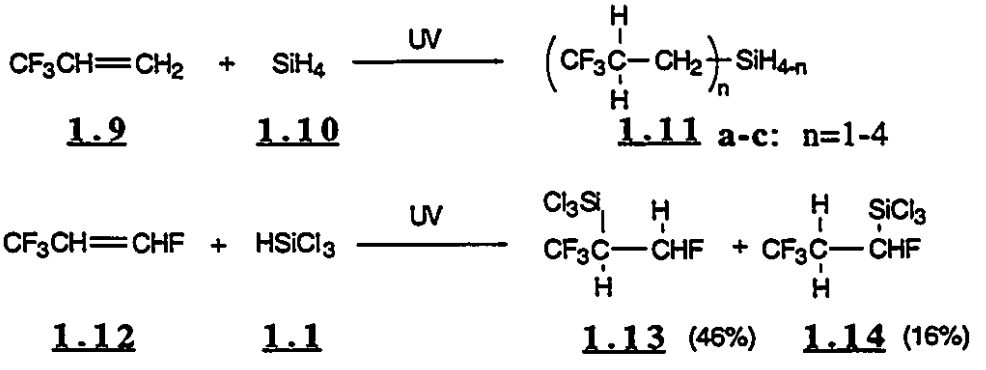


Chart 1.2

In the case of an unsymmetrical alkene involved in a hydrosilation reaction, the addition of a silyl radical occurs according to anti-Markovnikov's rule, *i.e.* the silyl group attaches to the carbon atom of the unsymmetrical olefin with more hydrogen substituents. This is known as Farmer's rule for hydrosilation.[14] Obviously, the preference of the silyl group to occupy the less substituted side of a double bond is mainly due to the relative stabilities of the radical

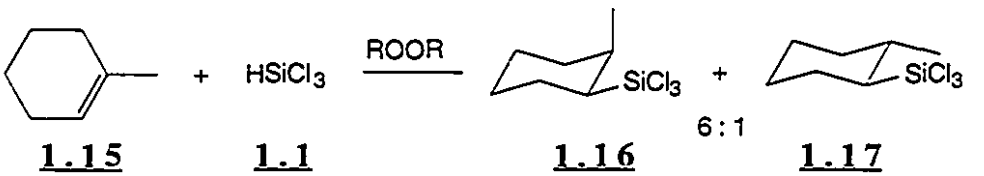
intermediates. Radicals formed at more substituted carbon centers are more stable than those formed at less substituted centers. Interestingly, trialkylsilyl radicals react with alkenes much slower than trichlorosilyl radical.[2c] This is due to the fact that the more stable trichlorosilyl radical is less bulky than trialkylsilyl radical.[2c]

As shown in Scheme 1.2, hydrosilation of 3,3,3-trifluoro-1-propene (**1.9**) generated **1.11** with the silyl radical attaching to the less substituted carbon atom of the double bond.[15] When a proton of the double bond of the olefin was replaced by a strong electron withdrawing group, such as F in **1.12**, hydrosilation resulted in the silyl radical attaching to the more hindered side of the double bond.[16] This change in regioselectivity suggests that electronic factors play an important role in the addition of silyl radicals to unsymmetrical double bonds.



Scheme 1.2

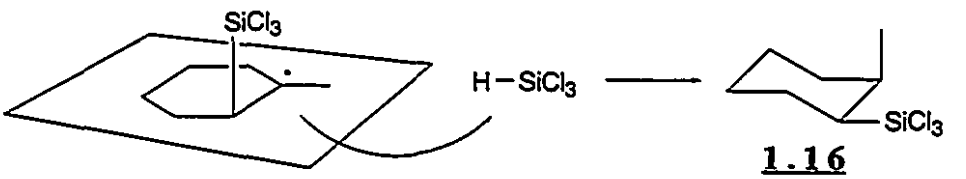
Radical initiated hydrosilation is also stereoselective. Hydrosilation of 1-methyl-1-cyclohexene (**1.15**)[3c] generated *cis* and *trans* products in a ratio of 6 : 1 (Scheme 1.3).



1.15 **1.1** **1.16** **1.17**

Scheme 1.3

After the addition of the silyl radical to substrate **1.15**, the newly formed radical intermediate **1.18** has two diastereotopic faces. The less hindered face is *trans* to the silyl moiety. This face would be expected to be more reactive towards the Si-H bond than the other face which is *cis* to the silyl moiety. Therefore, more *cis* product was generated as a result of *trans* attack (Scheme 1.4).

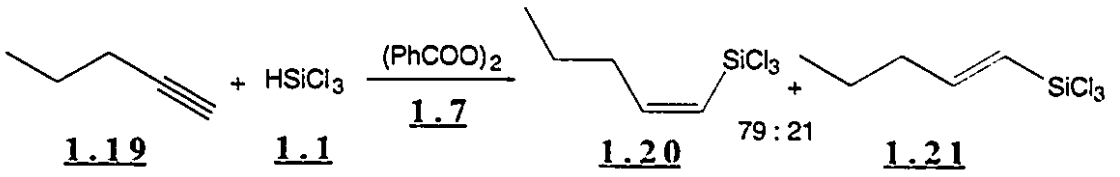


1.18 **1.16**

Scheme 1.4

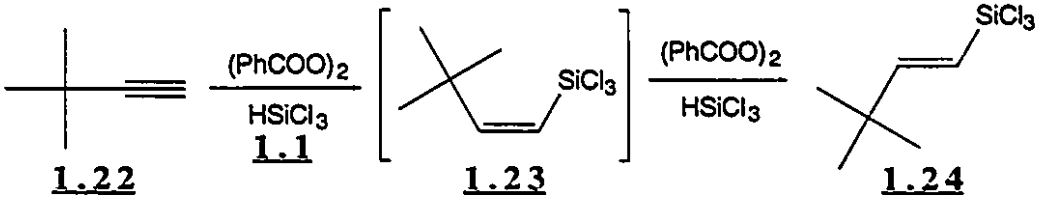
Reaction of hydrosilanes with alkynes is more complicated. In addition to the formation of vinylsilanes, if there is enough hydrosilane in the reaction system the reaction can continue further to generate saturated products. The latter reaction would follow the same mechanism as hydrosilation of alkenes mentioned above.

Hydrosilation of 1-pentyne (**1.19**) in the presence of radical initiator, benzoyl peroxide (**1.7**), gave *cis*-vinylsilane **1.20** as the major product.[8r] The *trans* product was believed to be generated from a subsequent isomerization step rather than at the addition step (Scheme 1.5).



Scheme 1.5

The isomerization becomes significant when the alkyl group in the above *cis*-product is sterically hindered. Hydrosilation of 3,3-dimethyl-1-butyne (**1.22**) for a prolonged reaction time (20 h) using the same radical initiator gave only the *trans* product (Scheme 1.6).[8r] Reactions that follow this radical pathway usually produce mixtures of *cis* and *trans* products.[17]



Scheme 1.6

In the case of hydrosilation of carbonyl compounds, the silyl radical attacks at the oxygen atom, since the Si-O bond is much stronger than the Si-C bond. This is followed by the subsequent formation of a favorable radical intermediate at the carbon atom.[18] This explains why hydrosilation of carbonyl functionalities is always regiospecific leading to the formation of alkyl silyl ethers (Chart 1.3).

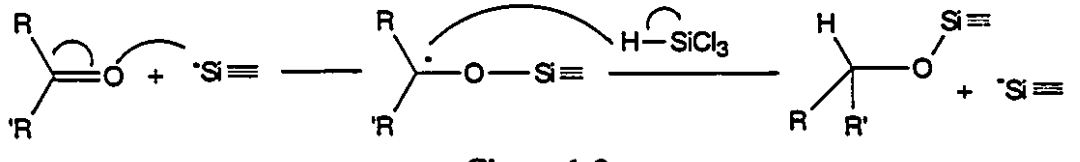
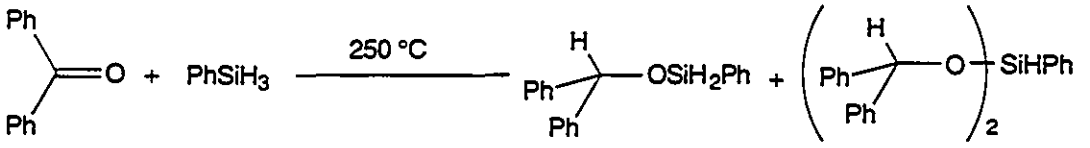


Chart 1.3

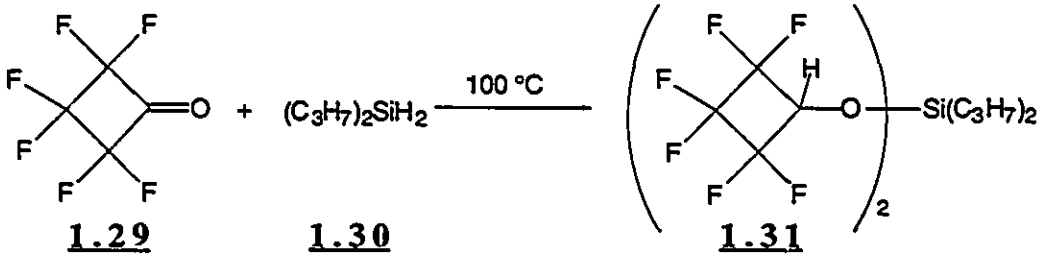
Active silicon hydrides (di- or trihydrosilanes) are required for the hydrosilation reaction to be carried out under thermal conditions. Hydrosilation of benzophenone (**1.25**) by phenylsilane (**1.26**) can proceed by heating the reaction mixture up to 250 °C[2i] (Scheme 1.7).



1.25 **1.26** **1.27** **1.28**

Scheme 1.7

When the activated ketone **1.29** was used in the thermal hydrosilation reaction, a much lower temperature (100 °C) was needed for the reaction to proceed.[19]



1.29 **1.30** **1.31**

Scheme 1.8

1.1.2.2 Nucleophilic Activation

Due to the physicochemical properties of the Si-H bond, it can be heterogeneously cleaved by nucleophiles to become a source of hydride. Nucleophilic activation of silanes can lead to hydrosilation of C=C, C≡C and C=O bonds.[8r,20] The most commonly employed

nucleophiles are amino compounds,[21] phosphino compounds,[22] fluoride[23] and alkoxide ions.[24] In most cases, nucleophilic activation is believed to occur *via* the formation of penta- and/or hexacoordinated silicon hydride species leading to a hydride being delivered to the unsaturated functionalities.[23c]

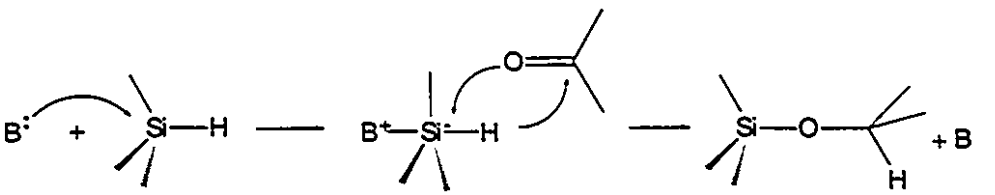
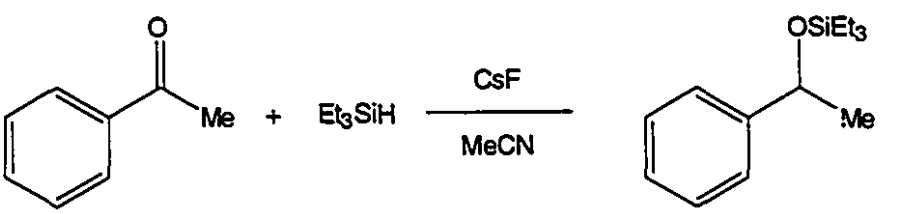


Chart 1.4

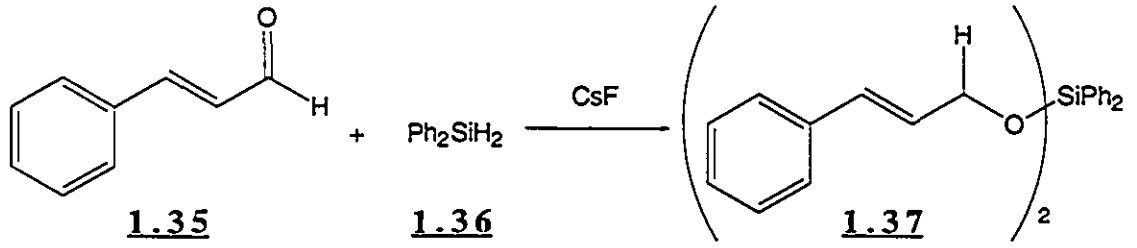
Hydrosilation of acetophenone (**1.32**) by triethylsilane (**1.33**), in the presence of cesium fluoride, generated alkyl silyl ether **1.34**[23c,25] (Scheme 1.9).



1.32 **1.33** **1.34**

Scheme 1.9

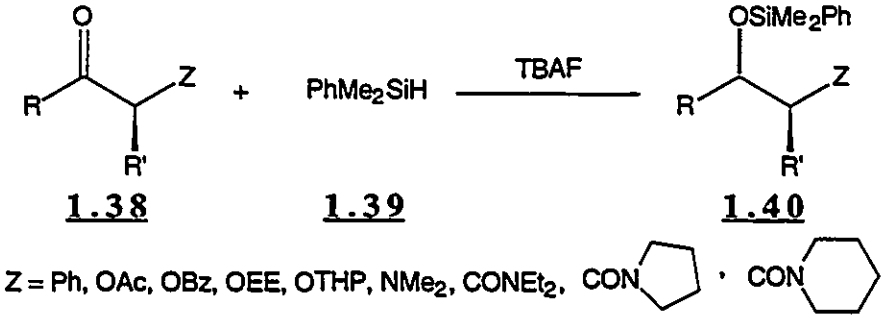
Under the same conditions, only the 1,2-hydrosilation product was obtained for the hydrosilation of α,β-unsaturated carbonyl compound **1.35** with diphenylsilane (**1.36**).[25a]



1.35 1.36 1.37

Scheme 1.10

Activated by nucleophiles, the reaction is quite stereoselective. Hydrosilation of compound **1.38** by dimethylphenylsilane (**1.39**) gave *threo* product **1.40** (Scheme 1.11),[23f,26] which is consistent with the Felkin-Anh model.[27] On the other hand, intramolecular hydrosilation of compound **1.41** yielded mainly *anti*-product **1.42**[25b] (Scheme 1.12).



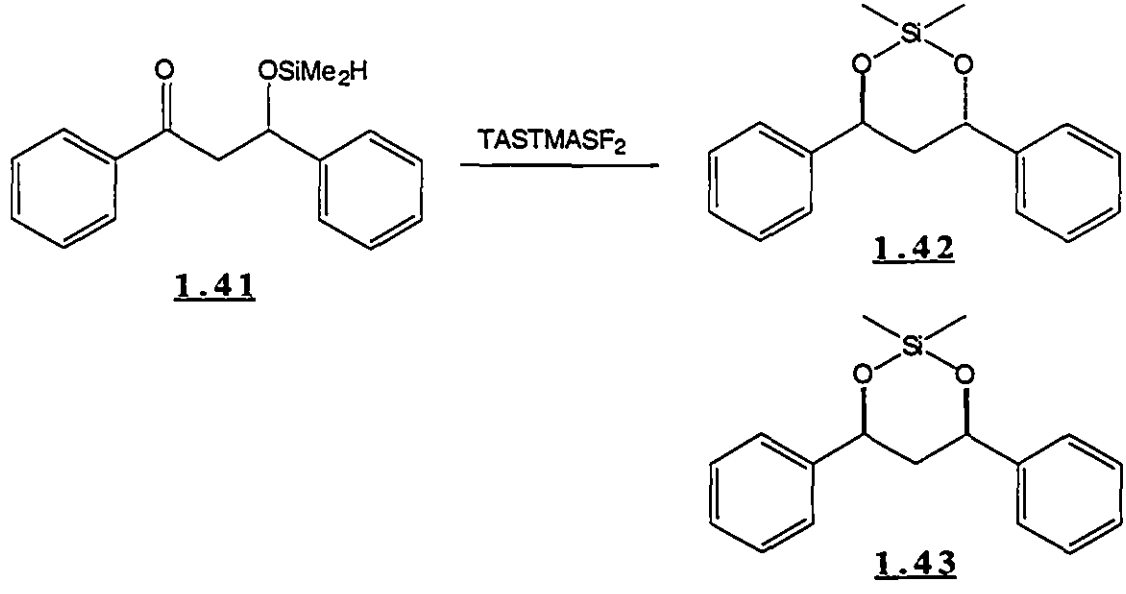
1.38 1.39 1.40

Scheme 1.11

The reaction tolerates the presence of carbon-carbon double bonds, bromo, nitro, amido or ester groups in the substrate, and reduces the carbonyl group selectively.[28] Moreover, it can selectively reduce aldehydes in the presence of ketones.[28]

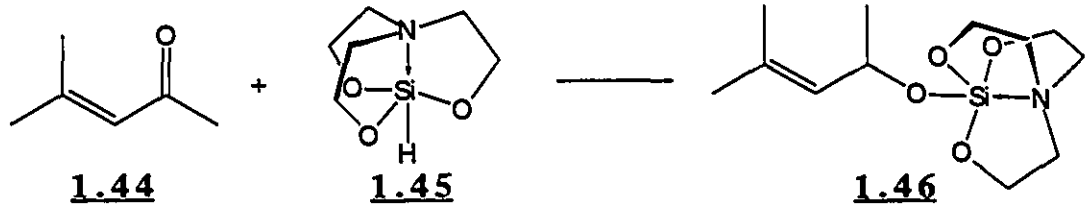
Silicon hydrides containing a nucleophilic functionality do not need external nucleophiles to catalyze the reaction.[20b,29]

Hydrosilation of 4-methyl-3-penten-2-one (**1.44**) with silatrane **1.45** yielded the 1,2-reduction product **1.46** (Scheme 1.13).[30]



1.41 **1.42** **1.43**

Scheme 1.12



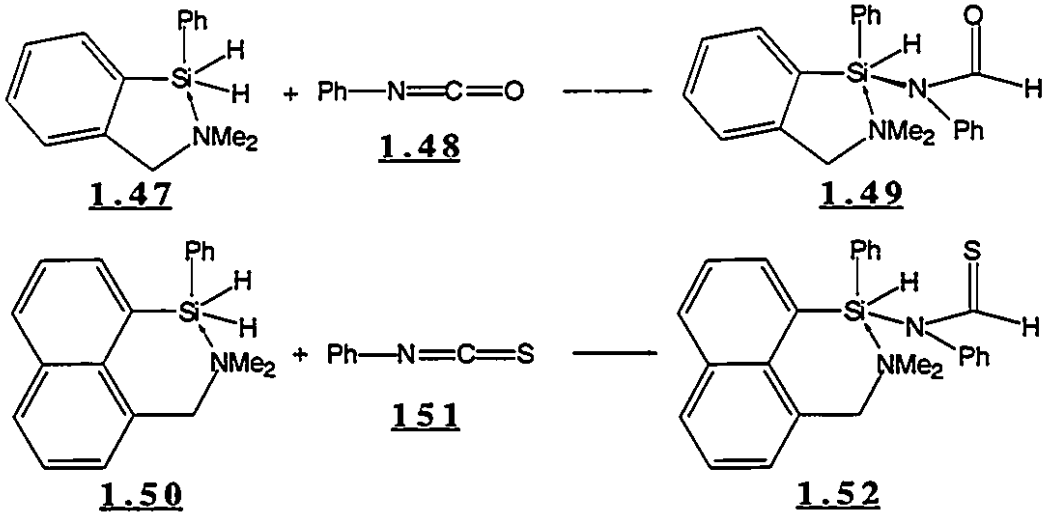
1.44 **1.45** **1.46**

Scheme 1.13

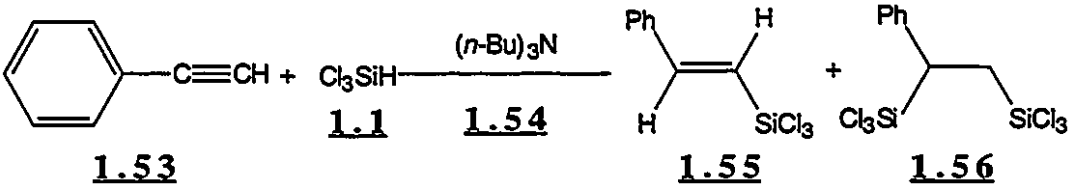
Other unsaturated functionalities, such as isocyanates and isothiocyanates, can be reduced under similar conditions (Scheme 1.14).[31]

On the other hand, hydrosilation of alkenes and alkynes may sometimes involve a different mechanism. For example, the reaction between 1-hexyne (**1.53**) and trichlorosilane (**1.1**) catalyzed by tri-

n-butylamine (**1.54**) gave mainly the *trans* product **1.55** and a small amount of diadduct **1.56** (Scheme 1.15).[32]



Scheme 1.14



Scheme 1.15

An ionic pair, $R_3N^+HSi^-Cl_3$, was believed to be formed in the reaction mixture.[33] Due to the strong electron withdrawing property of the chloride group, the hydrogen atom at the silicon center has less hydride character than that of the trialkylsilane. Therefore, the reaction is believed to proceed *via* a cyclic intermediate shown in Scheme 1.16.

1.53 1.55

Scheme 1.16

1.1.2.3 Metal and Metal Complexes Catalyzed Hydrosilation

The discovery of the efficient hydrosilation catalyst, hexachloroplatinic acid (1.56),[12a] by Speier in 1957 is a land-mark for catalytic hydrosilation involving transition metals, metal salts and metal complexes. Subsequently, Wagner and Strother applied supported platinum in the hydrosilation of carbon-carbon double and triple bonds with trichlorosilane.[34] The most commonly used metals are Pt,[34] Rh,[35] Ru,[35] Pd,[36] Ni,[37] and Ir,[38] while the most frequently used supports are active carbon, γ-Al_2O_3, SiO_2 and $CaCO_3$. Platinum supported on carbon (5%) is very efficient for the hydrosilation of alkenes, alkynes,[8p,39] carbonyl groups,[34] and cyano groups.[36b]

The catalytic activity of metals is dependant on the support material.[38] For instance, when carbon was used as support, the order of activity is: Rh > Ir > Pd > Ru > Pt, while with γ-Al_2O_3 as the support, the order changes to: Pd > Pt > Ru > Rh > Ir.

Metal salts can also catalyze hydrosilation. Reduced metal colloids are believed to be the true catalyst for hydrosilation by many metal salts[40] and even some metal complexes.[40,41]

The idea of homogeneous catalysis has been greatly extended[39,42] since the proposal by Chalk and Harrod in 1965 of a general mechanism for catalytic hydrosilation mediated by transition metal complexes.[43]

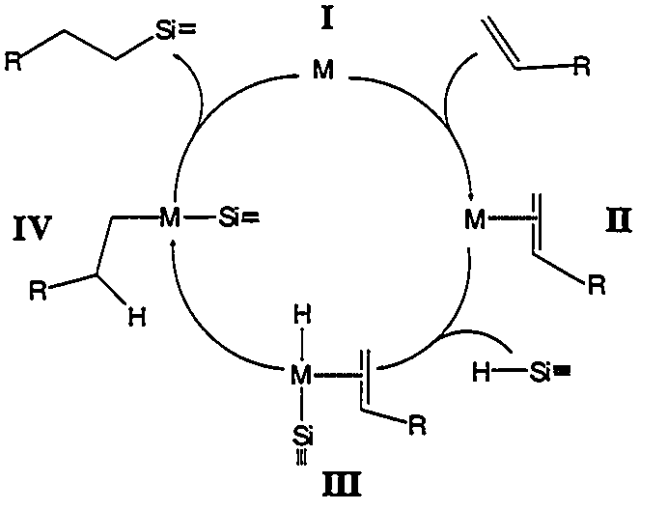


Chart 1.5

The alkene substrate forms a π-complex (**II**) with metal complex **I** in the first step of the hydrosilation reaction. This step is normally accomplished by losing at least one ligand in complex **I** to make coordination site available for the incoming alkene substrate:

$$\underset{\textbf{(I)}}{L_nM} + RCH{=}CH_2 \rightleftharpoons \underset{\textbf{(II)}}{(RCH{=}CH_2)ML_{n-m}} + mL \qquad (1)$$

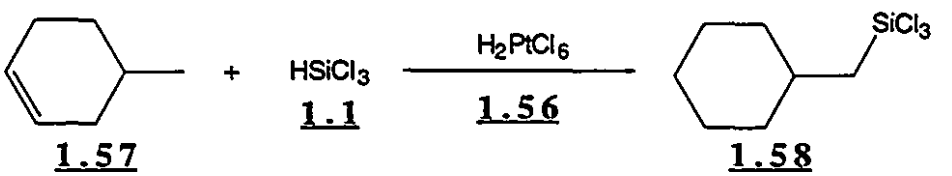
The following step involves oxidative insertion of the Si-H bond by complex **II**. This process is reversible.[42c] The stability of the newly formed complex, **III**, depends largely on the nature of the ligands attached at the metal center, as well as the steric hindrance at the reaction site:

$$\underset{\textbf{(II)}}{(RCH{=}CH_2)ML_{n\text{-}m}} + \equiv Si\text{-}H \rightleftharpoons \underset{\textbf{(III)}}{(RCH{=}CH_2)MH(Si)L_{n\text{-}m\text{-}1}} + L \quad (2)$$

Migration of the hydride group in the metal center of **III** to the carbon-carbon double bond (*cis* insertion) leads to a $\pi - \sigma$ rearrangement from the π-complex, **III**, to the σ-complex, **IV**:

$$\underset{\textbf{(III)}}{(RCH{=}CH_2)MH(Si)L_{n\text{-}m\text{-}1}} + L \rightleftharpoons \underset{\textbf{(IV)}}{(RCH_2\text{-}CH_2)M(Si)L_{n\text{-}m}} \quad (3)$$

This reversible step is believed to be the rate-determining step. Abstraction of a β-hydrogen by the metal of complex **IV** may account for the observed migration of the double bond during catalysis. This is illustrated in Scheme 1.17.[44]



1.57 + **1.1** → **1.56** → **1.58**

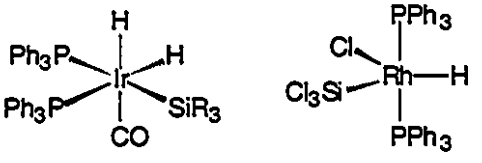
Scheme 1.17

In the last step of the catalytic cycle, coordination of a free ligand, L, or another alkene substrate, $RCH{=}CH_2$, to the metal center of complex **IV** leads to the reductive elimination of product, $RCH_2\text{-}CH_2SiR'_3$, and complex, $XML_{n\text{-}m}$ (X = L, or $RCH{=}CH_2$), to start another catalytic cycle.

This general mechanism can accommodate many features observed during catalytic hydrosilation under homogeneous conditions, such as the retention of stereochemistry at the silicon center[45] during the oxidative insertion of the Si-H bond and

reductive elimination of the C-Si bond,[46] *cis*-addition of M-H to C=C (or C≡C) bond,[47] etc.

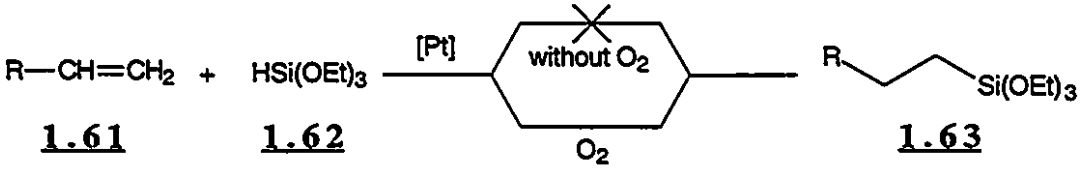
Complex **III** is believed to be the key intermediate in the catalytic cycle. Only the formation of complex **III** can lead to an effective hydrogen group *cis*-migration onto the π-coordinated double bond. Compounds that can not form this type of complex, such as trialkylsilyldihydridebis(triphenylphosphine)iridium(III) (**1.59**),[48] or those that form a π-complex leading to the reductive elimination of Si-H at the metal center [e.g. hydrido(chloro)-(trichlorosilyl)bis(triphenylphosphine)rhodium(III) (**1.60**)],[49] are inactive towards hydrosilation reactions.



1.59 **1.60**

Figure 1.1

This proposal can not, however, account for the cocatalytic effect of O_2 in hydrosilation reactions catalyzed by many metal complexes, especially platinum complexes,[8k] in conjunction with certain silicon hydrides, such as triethoxysilane (**1.62**, Scheme 1.18).



1.61 **1.62** **1.63**

Scheme 1.18

Despite the obscure role of molecular O_2, the widely accepted Chalk-Harrod mechanism of hydrosilation is the most successful proposal to account for and predict many observations of these reactions. Further to this, many modifications and new postulations have been proposed lately.[9,50]

Chart 1.6 shows the modified proposal,[8r,51] in which, an alternative silyl migration pathway is considered as one of the features to account for the observations in hydrosilation reactions catalyzed by $Fe(CO)_5$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Co(CO)_4$.[50a-b,52] Hydrosilation of alkenes catalyzed by these catalysts normally generates vinylsilanes and saturated products.[53]

After the alkene inserts into the M-Si bond, complex **VIII** (Chart 1.6) is formed. The latter can undergo various reactions to give allylsilane, **XIV**, vinylsilane, **XV**, the normal hydrosilation product, **VII**, as well as the hydrogenated product, **XIII**, and the isomerized olefin, **XVII**. Although the modification can explain many observations that the original Chalk-Harrod proposal can not, the variant is still unable to explain the role of O_2 in the catalytic hydrosilation reactions.

Relative to heterogeneous catalysis, homogeneous catalytic hydrosilation provides many advantages in the study of hydrosilation mechanisms.[50c] They are also useful in the search for new reactions, as well as in modifying selectivities of hydrosilation reactions. As many side reaction pathways have been elucidated,[8c,54] modifications can be directed towards avoiding or enhancing side reactions.

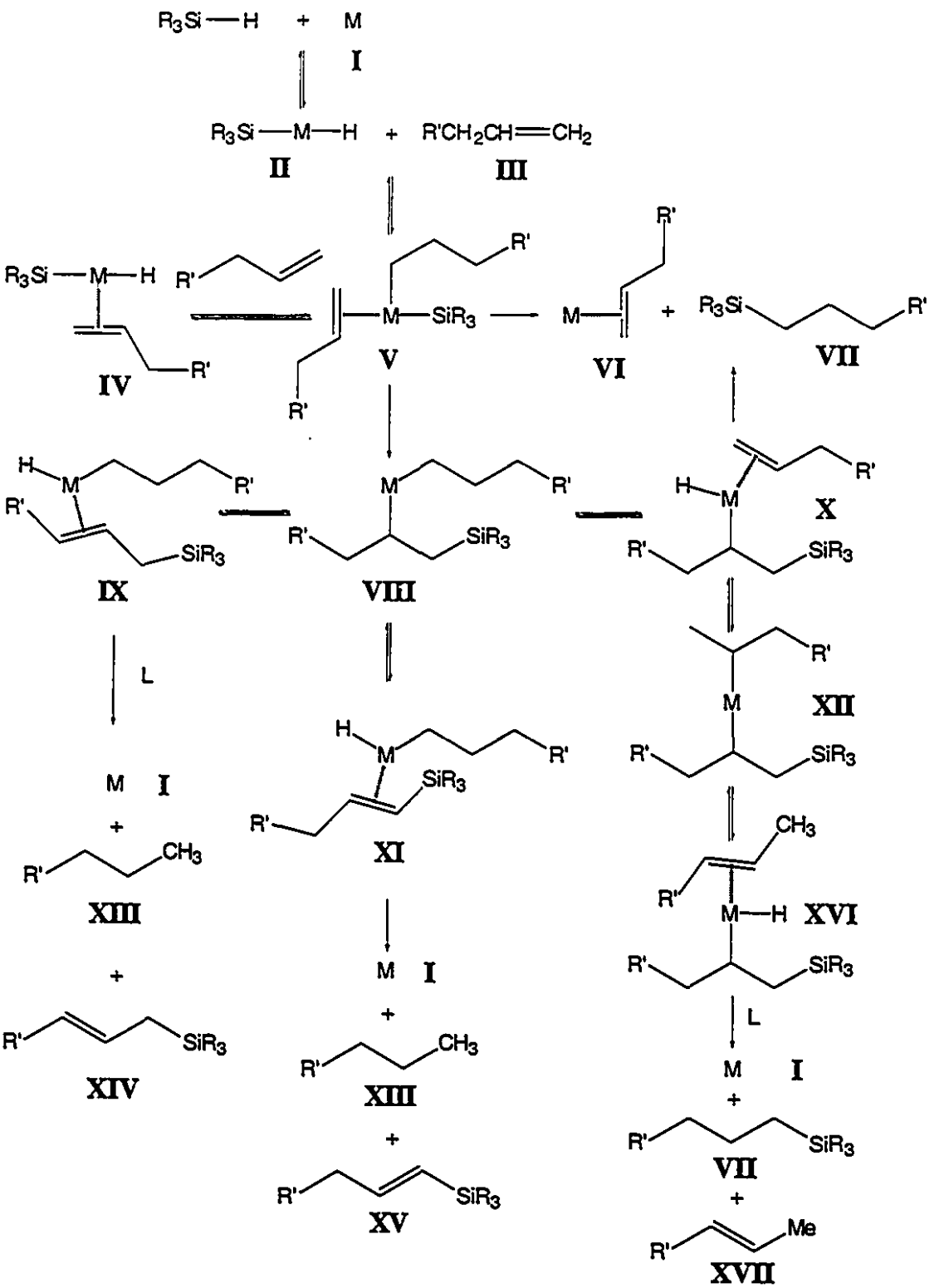

R3Si—H + M
I
R3Si—M—H + R'CH2CH=CH2
II
III
R3Si—M—H
R'
IV
M—SiR3
V
VI
R3Si
VII
H
M
R'
SiR3
IX
VIII
X
L
M I
+
CH3
XIII
XI
XII
XIV
XV
M—H
XVI
VII
Me
XVII

Chart 1.6

Among the many transition metal complexes discovered as active hydrosilation catalysts, platinum[55] and rhodium[15,49,56] metal complexes are the most common. Their catalytic pathways have been studied extensively during the past three decades. Other metal complexes, such as iridium,[57] cobalt,[58] ruthenium,[53g,59] osmium,[60] nickel,[46b,61] palladium,[62] and titanium[63] have also been used to catalyze hydrosilation reactions.

Like many other useful transformations in organic synthesis, hydrosilation reactions are usually both regio- and stereoselective. The nature of this selectivity has been extensively studied, especially in the case of homogeneous catalytic hydrosilation.[1b] The nature of these selectivities depends on the electronic properties of the metal center, the reactivity of the silicon hydride and the nature of the substrate involved.

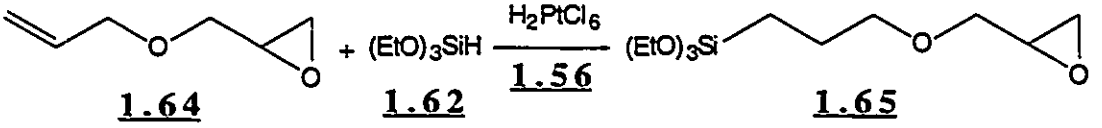
Among the many features of homogeneous catalytic hydrosilation, an important application is the hydrosilation of carbonyl compounds. Hydrosilation provides an alternative to the hydrogenation and metal hydride reduction of C=O functionalities. In 1972, Yamamoto and co-workers reported the first enantioselective hydrosilation of acetophenone.[55l] Much attention has since been directed towords this area (*vide infra*).

1.1.2.3.1 Regioselective Hydrosilation

When unsymmetric carbon-carbon double or triple bonds, or heteroatom substituted functionalities, such as C=O and C≡N, are subjected to hydrosilation with hydrosilane, the reaction proceeds

regioselectively depending on the nature of the substrate and silicon hydride and, most importantly, the intrinsic nature of the transition metal complex (catalyst).[42,51,64]

Hydrosilation of alkenes catalyzed by metal complexes is usually quite regioselective.[12a,65] The silyl group is normally added to the least substituted side of the double bond (Farmer's rule). Compound **1.65** was the only product obtained from the hydrosilation of olefin **1.64** by triethoxysilane (**1.62**) catalyzed by $H_2PtCl_6 \cdot 6H_2O$ (**1.56**).[65a]

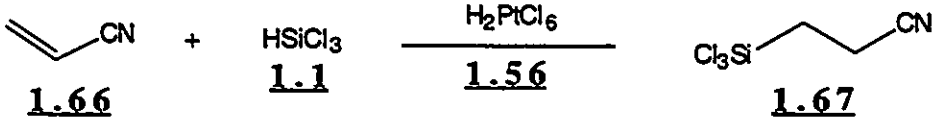


1.64 **1.62** **1.65**

Scheme 1.19

The epoxide functionality remained intact during the reaction. Many other functionalities are tolerated under similar reaction conditions, such as acetal,[65g] ester,[66] nitrile,[67] imine[68] and amide[69] groups.

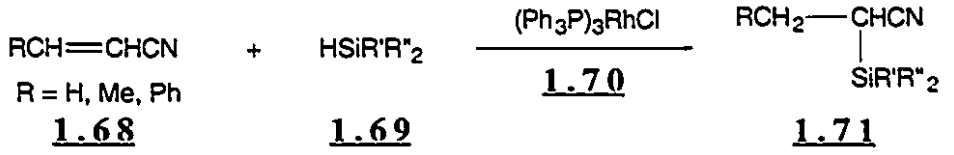
The nature of the catalyst appears to be important for the regioselectivity. Hydrosilation of compound **1.66** catalyzed by $H_2PtCl_6 \cdot 6H_2O$ (**1.56**) gave only the β-adduct **1.67**.[67]



1.66 **1.1** **1.56** **1.67**

Scheme 1.20

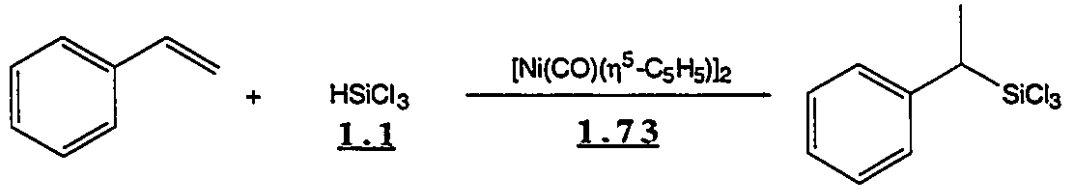
On the other hand, hydrosilation of the similar substrate **1.68** catalyzed by Wilkinson's complex $RhCl(PPh_3)_3$ (**1.70**) yielded exclusively the α-product **1.71**.[56e,i]



1.68 **1.69** **1.70** **1.71**

Scheme 1.21

With complex $[Ni(CO)(\eta^5\text{-}C_5H_5)]_2$ (**1.73**) as catalyst,[70] hydrosilation of styrene (**1.72**) by trichlorosilane (**1.1**) gave α-adduct **1.74** (Scheme 1.22).



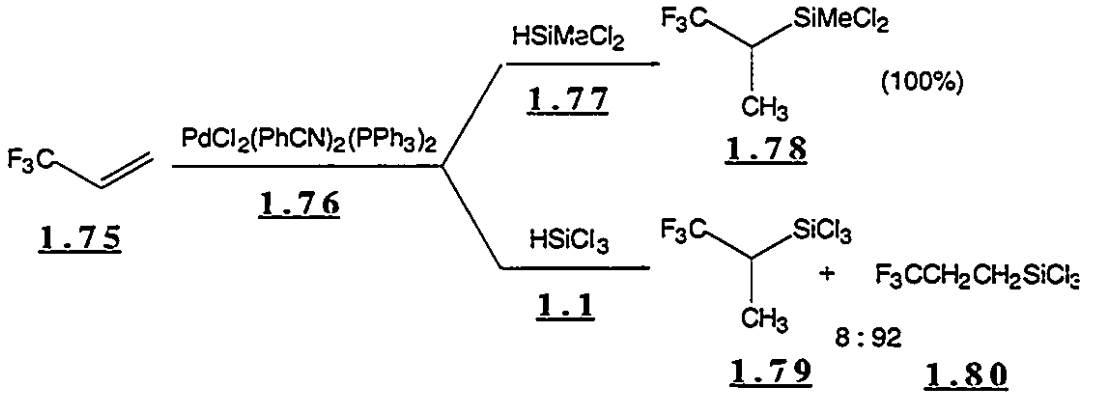
1.72 **1.1** **1.73** **1.74**

Scheme 1.22

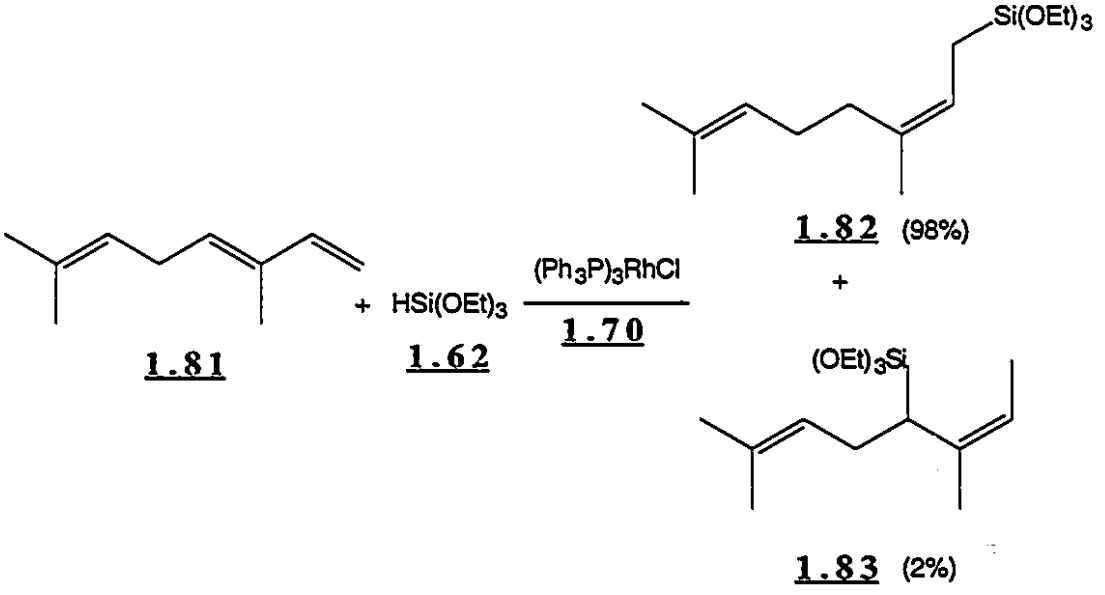
Silicon hydrides have a great effect on the regioselectivity. α-Addition product **1.78** was the only product obtained when dichloromethylsilane (**1.77**) was used in the reaction.[53g] In contrast, β-product **1.80** was predominant in the same reaction when trichlorosilane (**1.1**) was used (Scheme 1.23).[53g]

The addition of Si-H to a conjugated diene proceeds mainly with 1,4-selection. Hydrosilation of compound **1.81** by

triethoxysilane (**1.62**) catalyzed by Wilkinson's catalyst (**1.70**) produced predominantly compound **1.82** (98%, Scheme 1.24).[71]

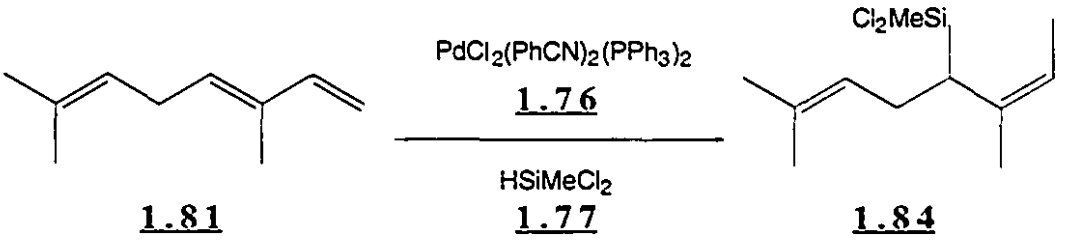


Scheme 1.23



Scheme 1.24

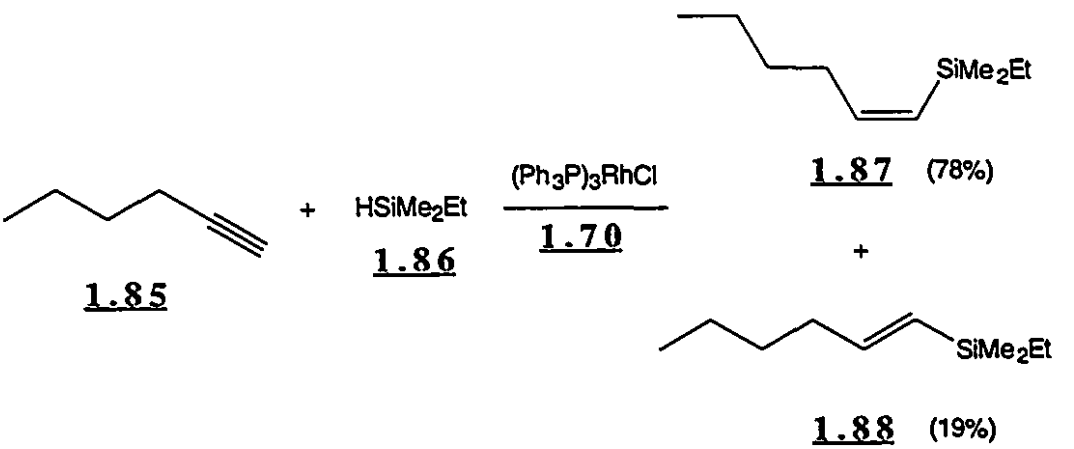
With $Pd(PhCN)_2Cl_2(PPh_3)$ (**1.76**) as catalyst, the same substrate, **1.81**, was converted to compound **1.84** exclusively with methyldichlorosilane (Scheme 1.25).[71]



1.81 1.77 1.84

Scheme 1.25

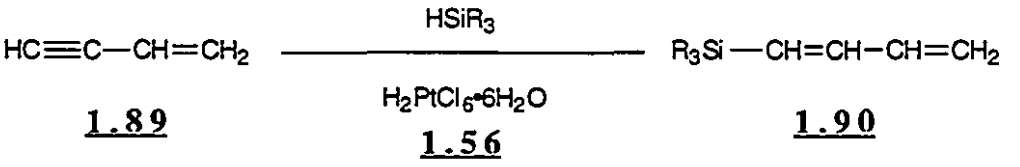
Hydrosilation of alkynes proceeds mainly according to Farmer's rule for regioselectivity.[72] The reaction usually produces both *cis* and *trans* products with the same regiochemistry. For example, hydrosilation of alkyne **1.85** gave both *cis* and *trans* products, where the regiochemistry of both products is the same (Scheme 1.26).[42b,52b,73]



1.85

Scheme 1.26

The reaction can proceed chemoselectively to reduce the carbon-carbon triple bond without interfering with the olefin functionality (Scheme 1.27).[74]



1.89 **1.56** **1.90**

Scheme 1.27

When a heteroatom, such as O or N, is part of the unsaturated functionality, hydrosilation proceeds regiospecifically. As oxygen or nitrogen forms stronger bonds with silicon atoms than carbon does,[75] the silyl group is exclusively attached to the hetero atoms of the products.[8i,q] This regiospecificity makes hydrosilation of the carbonyl group an important alternative method for the reduction of ketones. However, it was not until the 1972 discovery that Wilkinson's catalyst is effective for hydrosilation of ketones,[76] that remarkable progress in this area was made. Later, some other metal complexes were shown to demonstrate good activity in mediating hydrosilation of ketones (Chart 1.7).

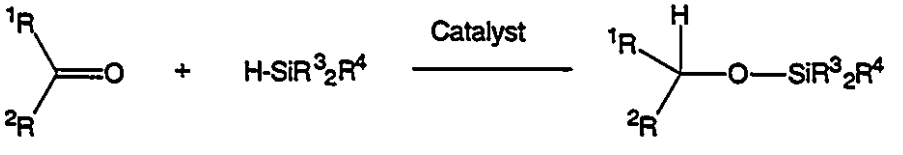
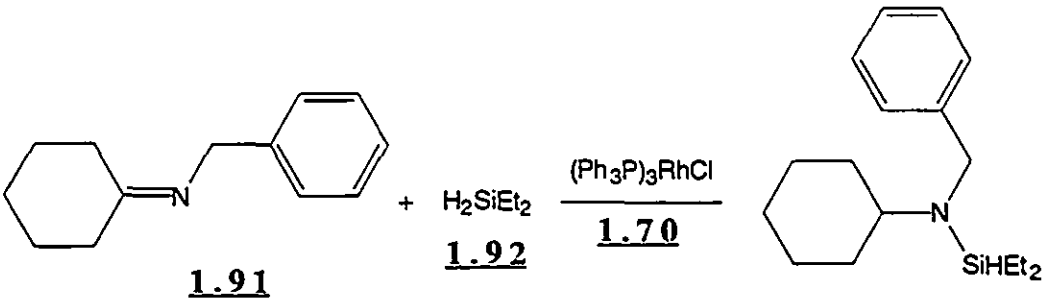


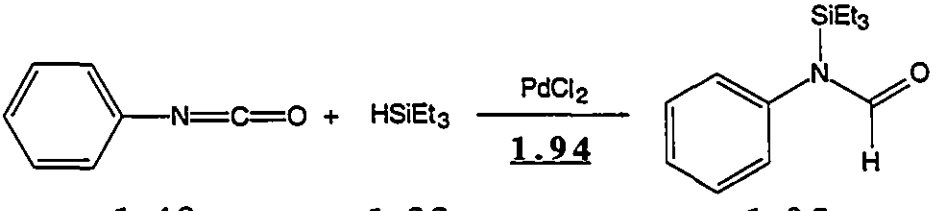
Chart 1.7

Accordingly, hydrosilation of N-containing unsaturated bonds proceeds regiospecifically (Scheme 1.28).[77] When the substrate is isocyanate, similar addition of Si-H was observed (Scheme 1.29).[36b,78]



1.91 + 1.92 → 1.70 → 1.93

Scheme 1.28

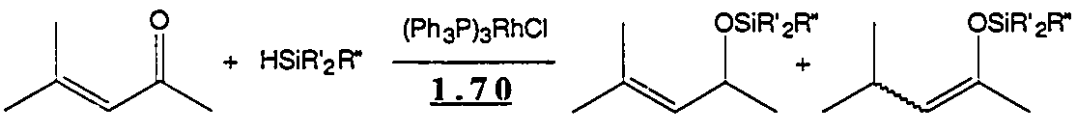


1.48 + 1.33 → 1.94 → 1.95

Scheme 1.29

In the case of α,β-unsaturated carbonyl compounds, the regioselectivities are largely dependent on the silicon hydrides used in the reactions. The silicon hydride used seems to be a decisive factor in determining the regioisomers produced in hydrosilation, regardless of the nature of substrate, and sometimes, catalyst. When monohydrosilane is used, hydrosilation of α,β-unsaturated carbonyl compounds undergoes 1,4-addition. Otherwise, 1,2-addition of the Si-H bond to the α,β-unsaturated carbonyl compounds is the major pathway of hydrosilation, when di- or trihydrosilane is used[79] (Scheme 1.30).

The mechanism underlying this kind of selectivity has been the subject of extensive studies,[80] and is part of the present investigation (*vide infra*).



1.96 **1.97** **1.98**

$PhMe_2SiH$	**(1.39)**	1 : 99
Ph_2SiH_2	**(1.36)**	93 : 7
$PhSiH_3$	**(1.26)**	99 : 1

Scheme 1.30

Regiocontrolled hydrosilation of α,β-unsaturated carbonyl compounds is of considerable use in organic synthesis since it can generate synthons such as allyl alcohols or silyl enol ethers.[8i] However, only a few catalytic systems,[56h,i,79,82] mainly Wilkinson's catalyst, $RhCl(PPh_3)_3$,[56h,i,79,82a,b] and some platinum complexes,[82c] have been developed to specifically control regiochemistry during hydrosilation of α,β-unsaturated carbonyl compounds. Further study in the area is clearly required.

1.1.2.3.2 Stereoselective Hydrosilation

i) Diastereoselective Hydrosilation

It has been noted that hydrosilation of hydrocarbon multiple bonds, C=C[83] and C≡C,[47] occurs mainly with *cis*- stereochemistry.[12b,84] It is understandable from a mechanistic point of view that the addition of a Si-H bond should be, in principle, to the same side of the π–complex as shown in Chart 1.8.[37]

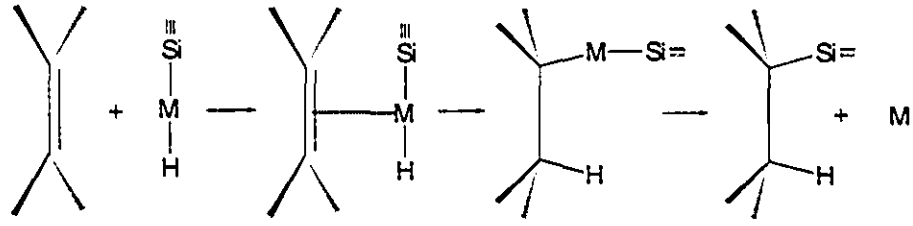
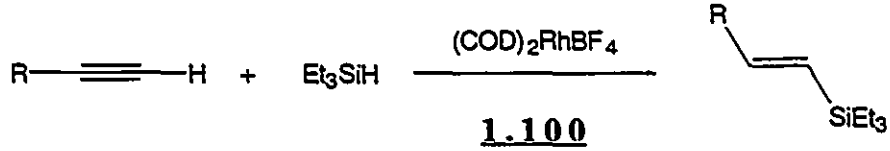


Chart 1.8

For example, hydrosilation of 1-alkynes **1.99** by triethylsilane (**1.33**) catalyzed by $(COD)_2RhBF_4$ (**1.100**) generated exclusively *E*-product.[85]



1.99 **1.33** **1.100** **1.101**

Scheme 1.31

There is, however, alternative stereochemistry in the hydrosilation of alkynes.[56b,c] Mainly *trans* addition of the Si-H bond to alkynes has been observed, when Wilkinson's catalyst[56b,c] or iridium complexes are used.[57c] The *trans* addition product is believed to be a result of *cis* addition of the M-H or M-Si bond to the alkyne, followed by isomerization before the silyl or hydride group migrates from the metal center to the carbon atom.[73,86] Among several proposals to account for this observation, the mechanism proposed by Ojima appears most reasonable (Chart 1.9).[86]

The key intermediate, zwitterionic carbene **V**, is formed after the electron at the metal center delocalizes to the vinyl group. As both the metal and silyl moieties are sterically hindered, the silyl

group tends to turn away from the metal moiety to alleviate the steric congestion.

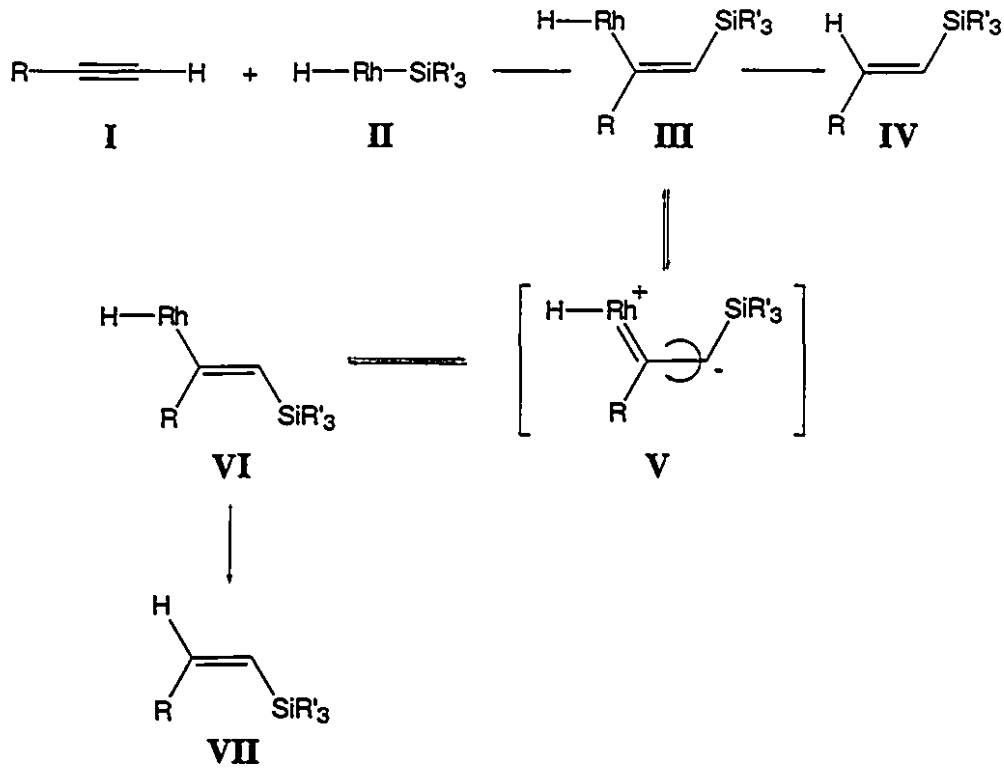
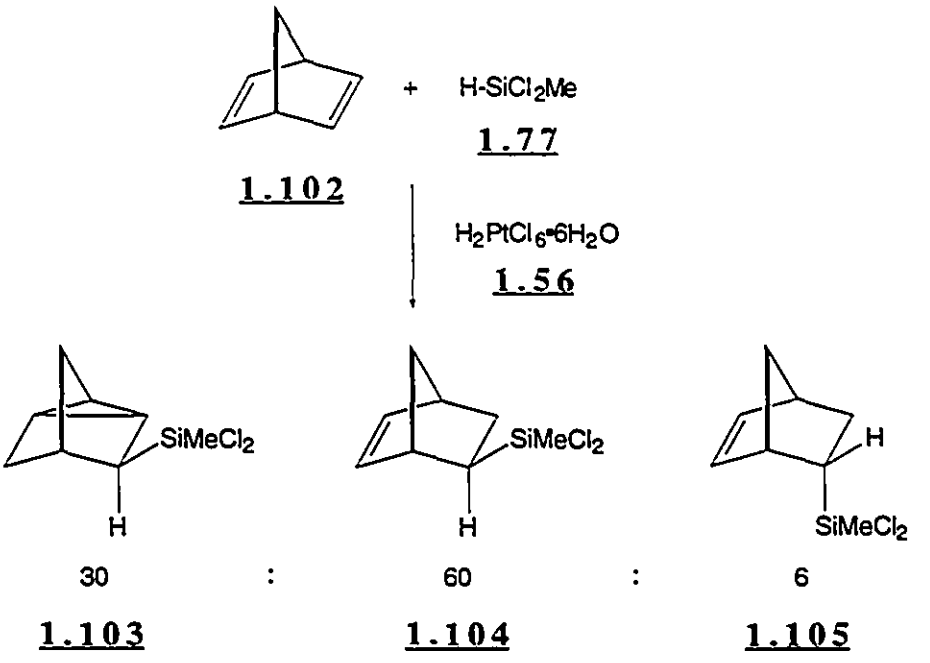


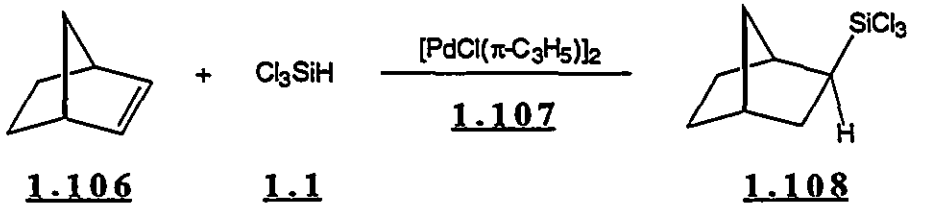
Chart 1.9

In the case where a carbon-carbon double bond has two diastereotopic faces, silicon hydrides add mainly from the less hindered face to form hydrosilation products. Hydrosilation of norbornadiene (**1.102**) catalyzed by $H_2PtCl_6 \cdot 6H_2O$ (**1.56**) yielded mainly *exo*-products **1.103** and **1.104** (Scheme 1.32).[87]



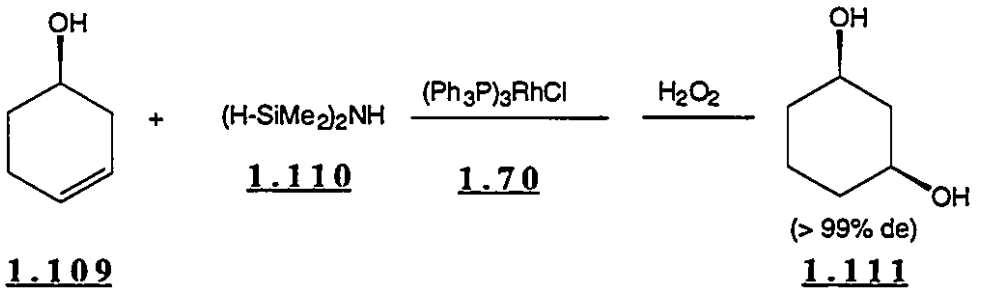
Scheme 1.32

When a palladium complex was used in the reaction, norborene (**1.106**) was hydrosilated from the *exo*-face again, and only one product was obtained (Scheme 1.33).[88]



Scheme 1.33

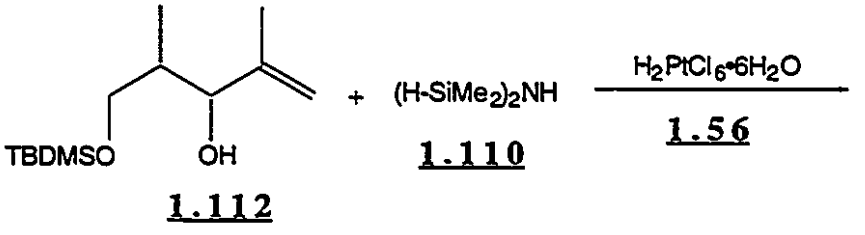
If there is a directing group in the substrate, such as OH, Si-H will be added to the carbon-carbon double bond from the same face where the directing group is located. *cis*-Diol **1.111** was obtained after oxidation of the hydrosilation product of cyclohexenol (**1.109**).[89]



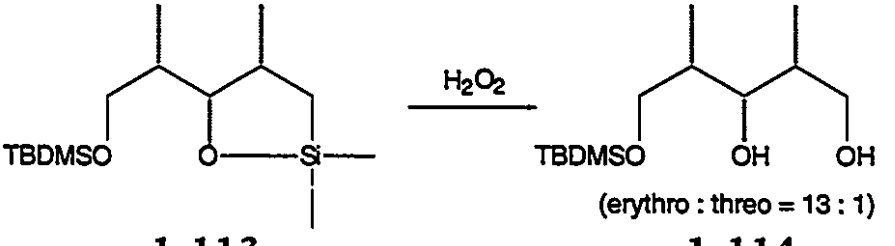
1.109 1.110 1.70 1.111

Scheme 1.34

Similarly, intramolecular hydrosilation of allylic alcohol 1.112 gave mainly erythro product 1.114 (*erythro : threo* = 13 : 1).[89]



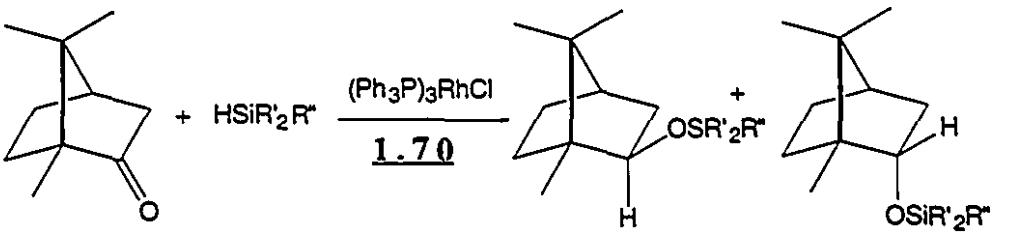
1.112 1.110 1.56



1.113 1.114

Scheme 1.35

Hydrosilation of carbonyl compounds are also quite diastereoselective. The diastereoselectivity, however, is largely dependant on the silicon hydride and the catalyst that is used. Hydrosilation of camphor (1.115) gave two diastereomers ranging from 91 : 9 to 30 : 70 (*exo : endo*) depending on the silicon hydride used in the reaction (Scheme 1.36).[8j,90]

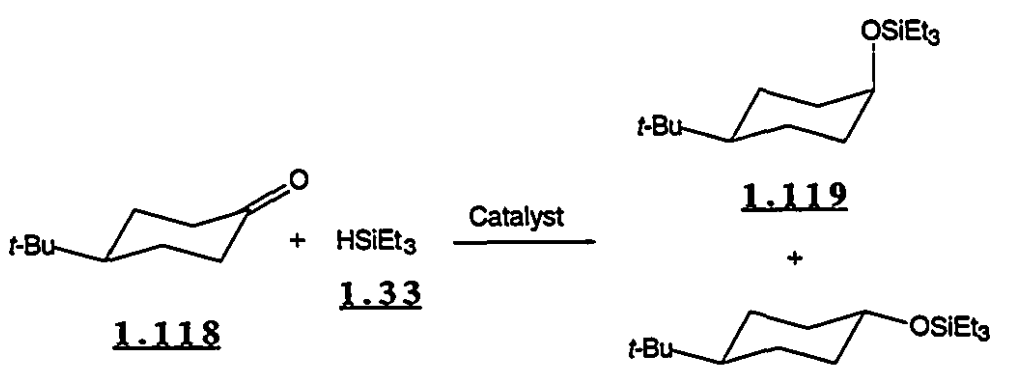


1.115 1.116 1.117

H_2SiEt_2	(1.92)	91	:	9
H_2SiPh_2	(1.36)	73	:	27
$HSiEt_3$	(1.33)	30	:	70

Scheme 1.36

Catalyst also affects the diastereoselectivity. During the reduction of 4-*tert*-butylcyclohexanone, (1.118),[91] catalyzed by $RhCl(PPh_3)_3$ (1.70), two diastereomers were produced with a ratio of 11 : 89 (*cis : trans*),[91a] while a ratio of 5 : 95 (*cis : trans*) was obtained using $RuCl_2(PPh_3)_3$ (1.121) as the catalyst.[91b]

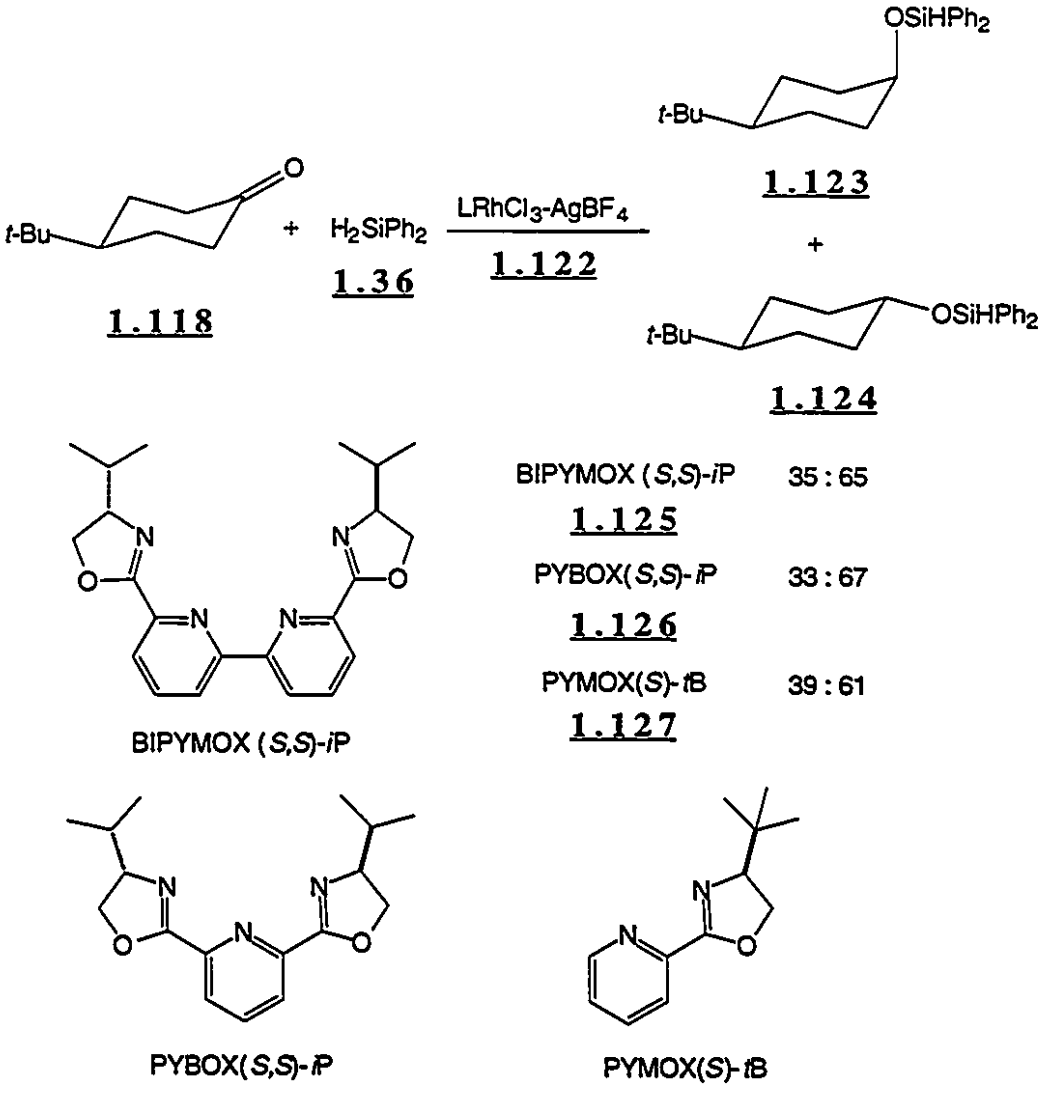


1.118 1.33 1.119 1.120

$(Ph_3P)_3RhCl$	(1.70)	11	:	89
$RuCl_2(PPh_3)_3$	(1.121)	5	:	95

Scheme 1.37

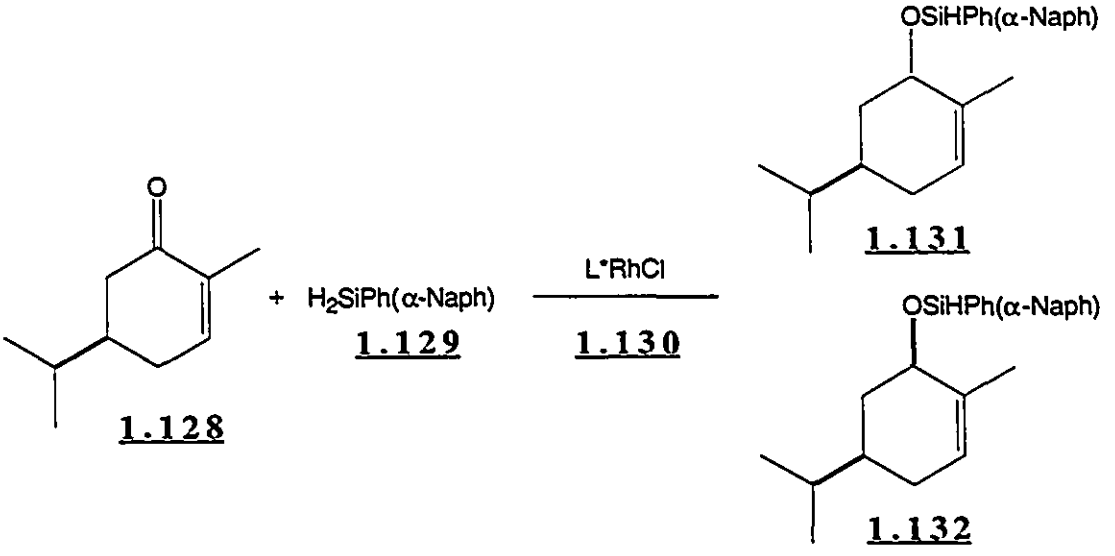
Much lower *cis/trans* ratios were obtained when chiral catalysts were used in the reduction of the same substrate **1.118**.[92]



Scheme 1.38

The chirality of the catalyst affects the stereochemical outcome in the hydrosilation of carbonyl groups with diastereotopic faces. Hydrosilation of carvone (**1.128**) by dihydrosilane **1.129** catalyzed by a chiral catalyst made from (+)-DIOP gave a *cis/trans* isomeric

ratio of 21 : 79. The diastereomeric ratio was inverted to 79 : 21 (*cis : trans*) when the opposite enantiomeric catalyst, made with (-)-DIOP, was used in the reaction[80a,93] (Scheme 1.39).



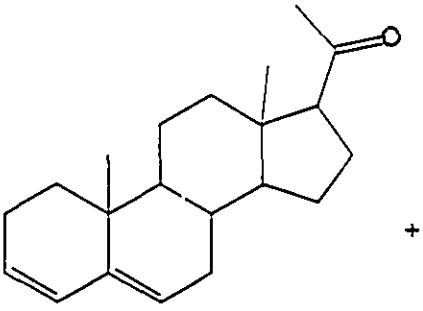
1.128 **1.129** **1.130** **1.131** **1.132**

L*: (+)-DIOP **1.133** 79 : 21 *(trans : cis)*

(-)-DIOP **1.133** 21 : 79 *(trans : cis)*

Scheme 1.39

Surprisingly, the similar catalytic system applied to substrate **1.134** had almost no effect in altering the stereochemical outcome of the products (Scheme 1.40).[94]

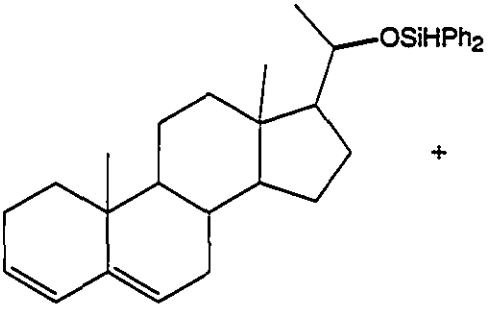


+ H_2SiPh_2 **1.36**

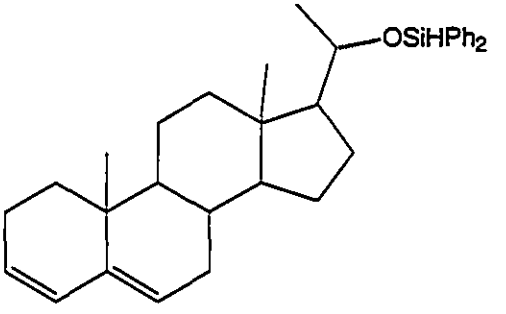
L*RhCl

1.130

1.134



+



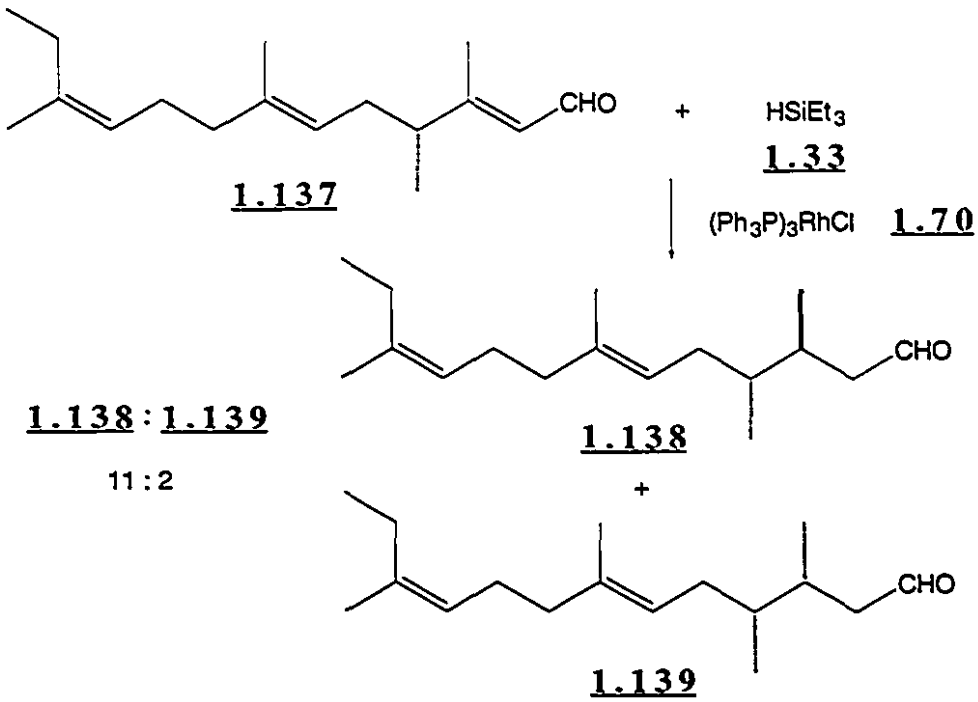
1.135 **1.136**

L*: (+)-DIOP **1.133** 70 : 30

(-)-DIOP **1.133** 73 : 27

Scheme 1.40

1,4-Diastereoselective hydrosilation of compound **1.137** yielded mainly the insect pheromone faranal (**1.138**) which has *anti*-stereochemistry at the newly formed stereogenic center (Scheme 1.41).[95]



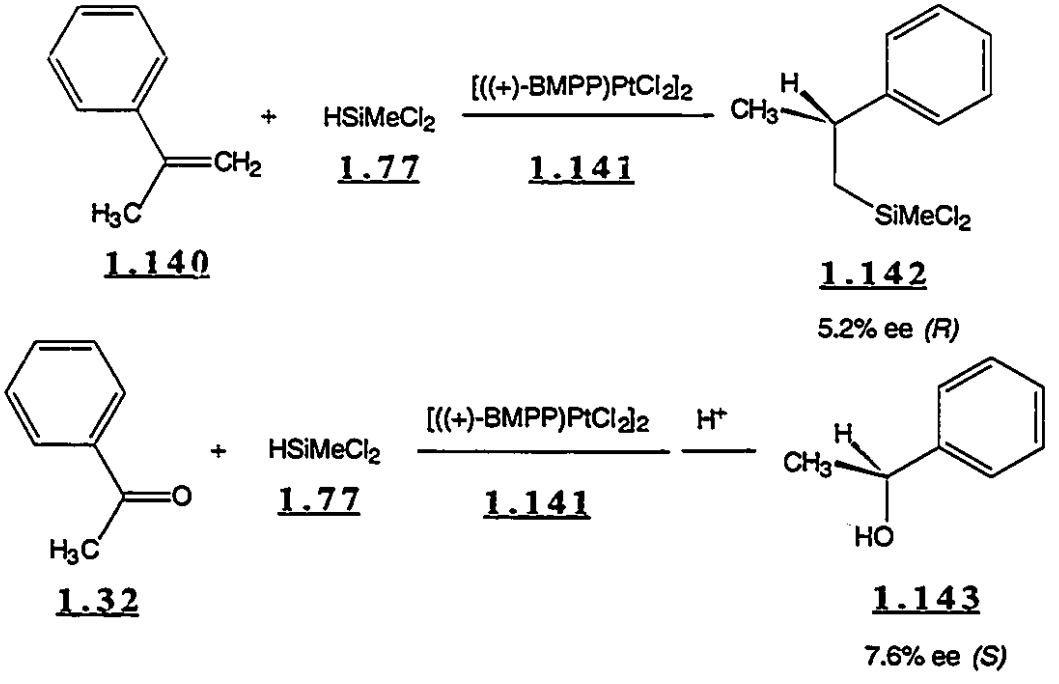
Scheme 1.41

ii) Enantioselective Hydrosilation

Enantioselective hydrosilation has become an important route to optically active silicon compounds and their derivatives.[96] Much progress has been made since the first report on the asymmetric hydrosilation of α-methylstyrene (**1.140**) and acetophenone (**1.32**) in 1972 (Scheme 1.42).[55l]

Most of the early chiral catalysts employed for hydrosilation were transition metals with chiral phosphine ligands.[8c,j] Many P-containing chiral ligands have been prepared for the purpose of asymmetric catalysis.[97] Figure 1.2 shows some of the ligands that have been used in asymmetric hydrosilation reactions. These chiral ligands are: monodentate phosphine, BMPP (**1.144**),[98] bidentate

ligand DIOP (**1.133**)[99] and its derivative **1.145**,[100] CHIRAOPHOS (**1.146**),[101] chiral ferrocenyl phosphine [PPFA (**1.147**),[102] MPFA (**1.148**),[102] BPPFA (**1.149**)[102]], BINAP (**1.150**),[9] NAPHOS (**1.151**),[103] glucophinite (**1.152**),[104] camphinite (**1.153**),[104] Amphos (**1.154**),[105] TRAP [R=*n*-Bu: (**1.155**),[106] R=Ph: (**1.156**)[107]], MOP (**1.157**),[108] TADDOL derivatives (**1.158**,[88,109] **1.159**[109]), NORPHOS (**1.160**),[102,110] and methonylphosphine (**1.161**,[111] **1.162**[111]).



1.140 + **1.77** → (**1.141**) → **1.142** 5.2% ee *(R)*

1.32 + **1.77** → (**1.141**, H+) → **1.143** 7.6% ee *(S)*

Scheme 1.42

Asymmetric hydrosilation of cyclopentadiene (**1.163**) with dichloromethylsilane (**1.77**) catalyzed by chiral catalyst, *(R,S)*-PPFA-$RdCl_2$ (**1.164**), yielded a 1,4-addition product, **1.165**, with an enantiomeric excess of 25% in favor of the *(S)*-enantiomer (Scheme 1.43).[112]

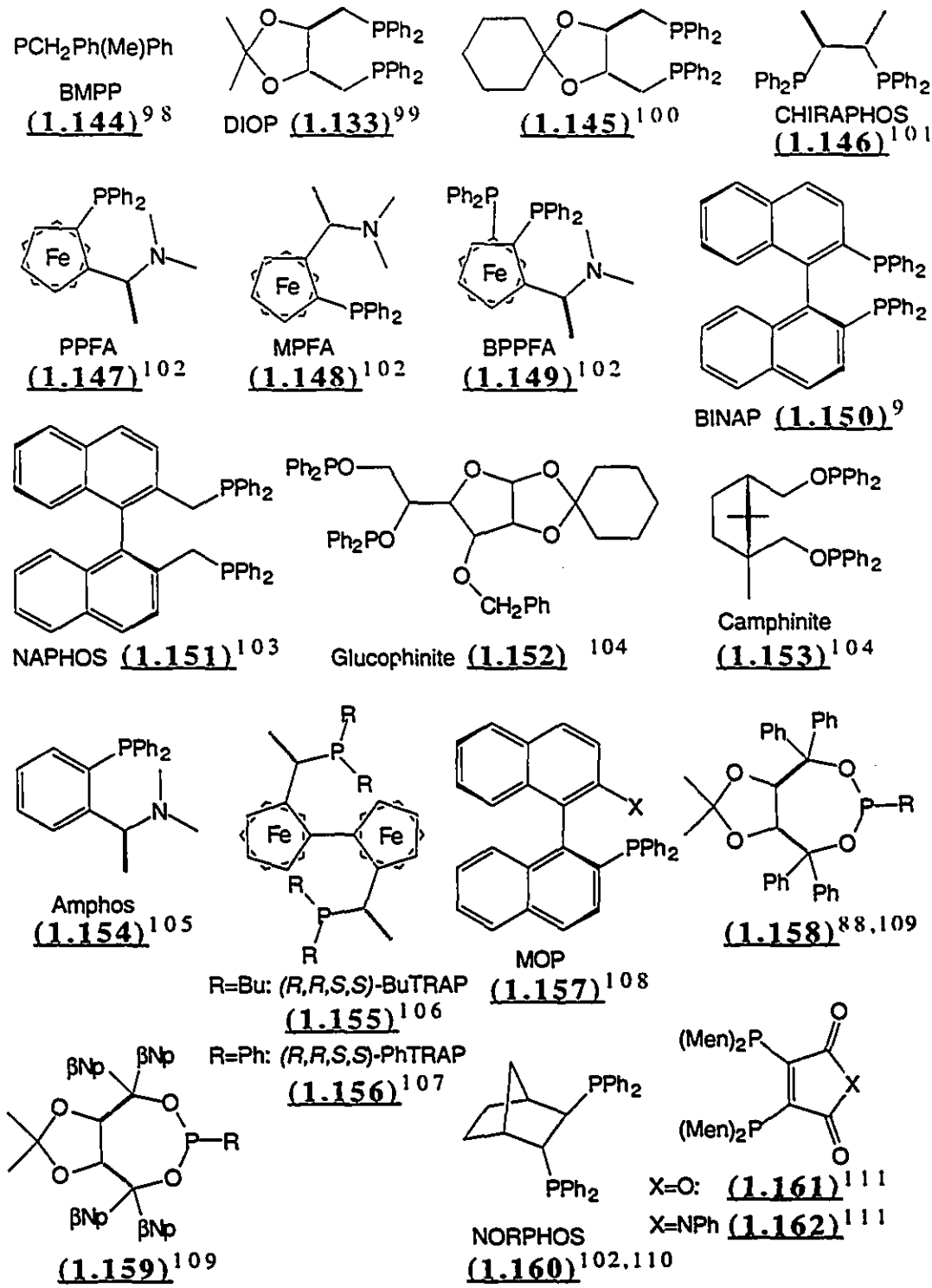
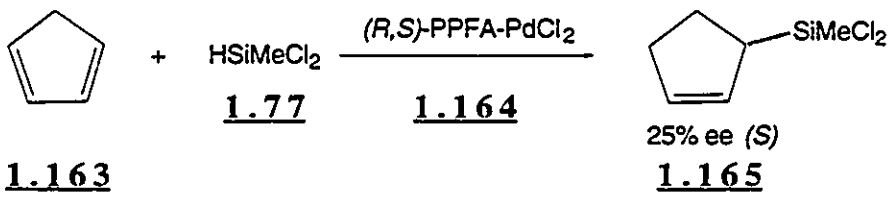

PCH2Ph(Me)Ph
BMPP
(1.144)98
DIOP (1.133)99
(1.145)100
CHIRAPHOS
(1.146)101
PPFA
(1.147)102
MPFA
(1.148)102
BPPFA
(1.149)102
BINAP (1.150)9
NAPHOS (1.151)103
Glucophinite (1.152) 104
Camphinite
(1.153)104
Amphos
(1.154)105
R=Bu: (R,R,S,S)-BuTRAP
(1.155)106
R=Ph: (R,R,S,S)-PhTRAP
(1.156)107
MOP
(1.157)108
(1.158)88,109
(1.159)109
NORPHOS
(1.160)102,110
X=O: (1.161)111
X=NPh (1.162)111

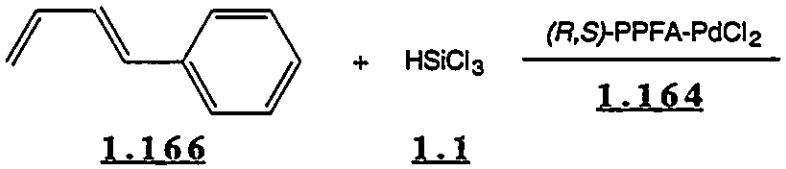
Figure 1.2



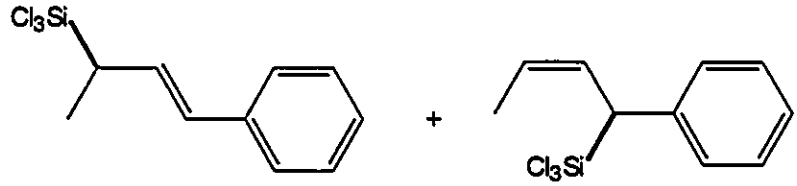
1.163 1.77 1.164 1.165

Scheme 1.43

Enantioselective hydrosilation of 1-phenyl-1,3-butadiene (**1.166**) by trichlorosilane (**1.1**) catalyzed by the chiral complex *(R,S)*-PPFA-$PdCl_2$ (**1.164**) generated two regioisomers, **1.167** and **1.168**. The 1,2-addition product **1.167** had a much lower enantiomeric excess [30% ee *(R)*] than that of the 1,4-product [64% ee *(S)*].[113]



1.166 1.1 1.164



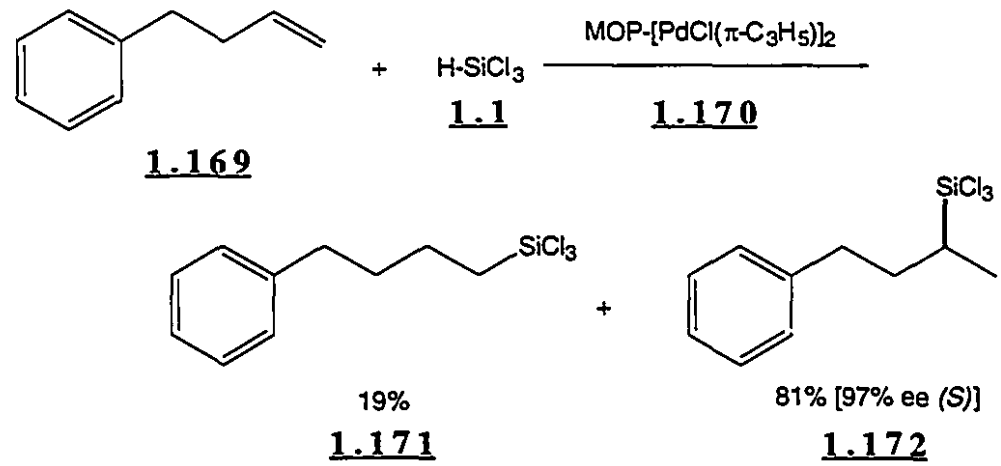
30% ee *(R)* 64% ee *(S)*

1.167 1.168

Scheme 1.44

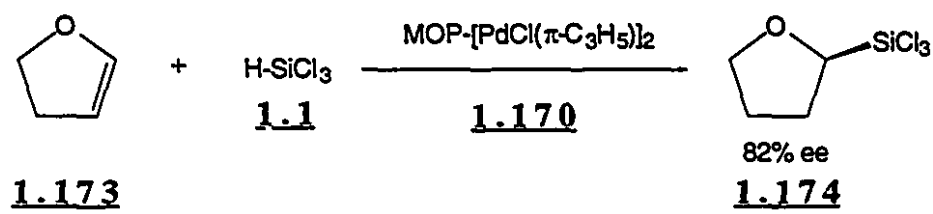
The use of chiral catalysts derived from the chiral ligand MOP with palladium complexes has boosted the enantiomeric excess for hydrosilation of alkenes to a much higher level than ever before.[108] Enantiomeric excess of the chiral product **1.172** was as high as 97%

(*S*)[108c] in the hydrosilation of alkene **1.169** with chiral catalyst **1.170**.



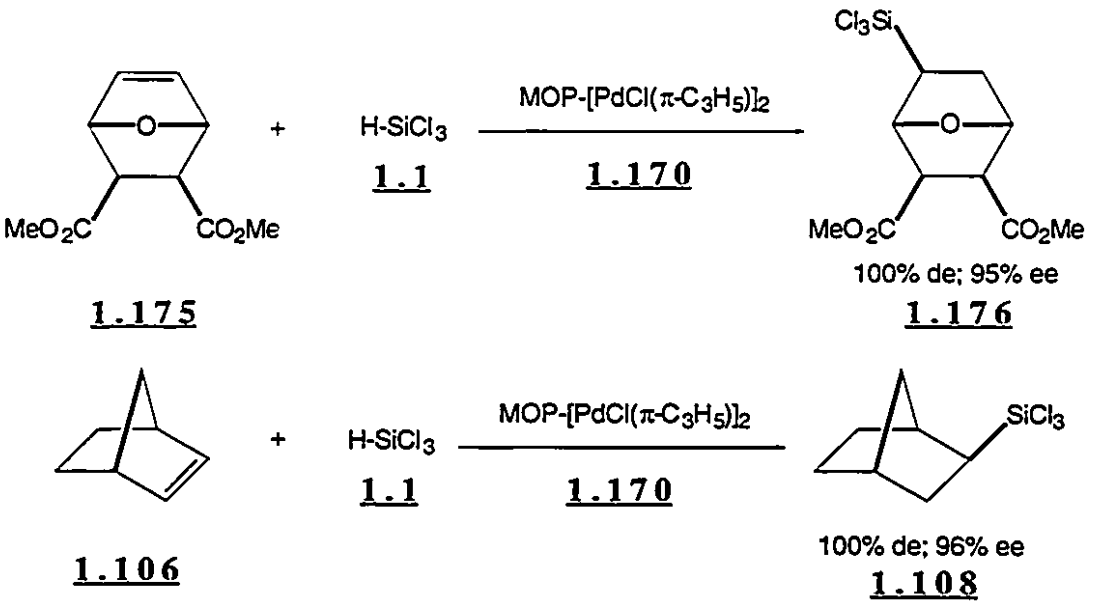
Scheme 1.45

The regiochemistry was much better defined in the hydrosilation of substrate **1.173**. Only one regioisomer, **1.174**, was obtained with high optical yield (82% ee) in the reaction mediated by the same MOP-Pd catalyst, **1.170**.[108d]



Scheme 1.46

Hydrosilation of compounds **1.175**[108d] and **1.106**[88] generated products with exclusive diastereoselectivities (100% de). Furthermore, the enantiomeric excess (< 96% ee) induced by this chiral catalyst **1.170** was excellent (Scheme 1.47).



Scheme 1.47

In the case of hydrosilation of prochiral ketones, optically active alcohols are obtained after hydrolysis of the resulting products.[114] Table 1.1 summarizes some results obtained by asymmetric hydrosilation of prochiral ketones catalyzed by chiral P-containing transition metal catalysts.

Although the average optical yield generated by P-containing ligands is moderate, excellent enantiomeric excess (92% ee) can be obtained by using chiral complexes derived from the C_2 symmetric ligand *n*-BuTRAP.[106,107]

Monodentate chiral ligands normally induce low to moderate enantiomeric excess. However, with the TADDOL derivatives, **1.158** and **1.159**, as chiral ligands in the asymmetric hydrosilation of prochiral ketones, enantiomeric excess can reach as high as 82 %.[109]

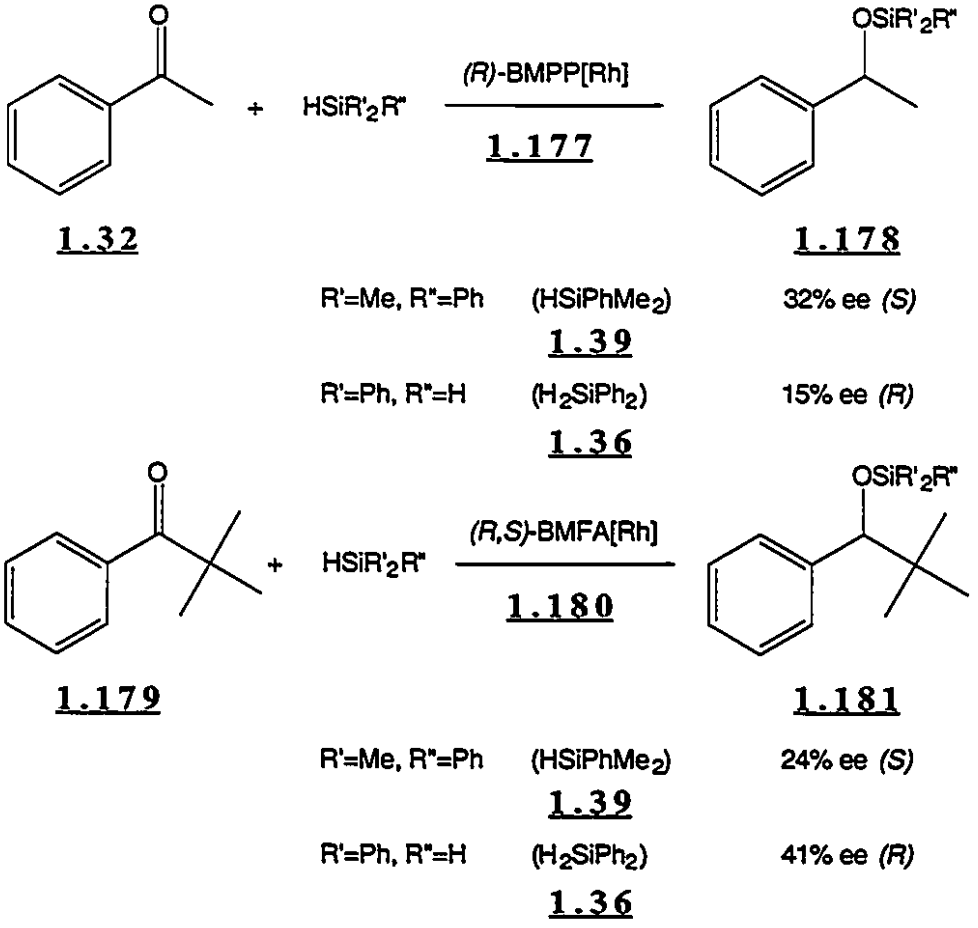
Table 1.1: Asymmetric hydrosilation of ketones using chiral phosphine complexes.

Ligand	Metal Complex	Silane	Yield	% ee
(R)-BMPP[115]	$(Nor)_2RhClO_4$	$PhMe_2SiH$	97%	32% *(S)*
(R)-BMPP[115]	$(Nor)_2RhClO_4$	Ph_2SiH_2	84%	15% *(R)*
1.158[109]	$[Rh(COD)Cl]_2$	"	59%	55% *(R)*
1.159[109]	$[Rh(COD)Cl]_2$	"	91%	82% *(R)*
(S)-Amphos[116]	$[Rh(C_2H_4)_4Cl]_2$	"	90%	27% *(S)*
(R,S)-MPFA[102]	$[Rh(C_6H_{10})_4Cl]_2$	"	89%	49% *(R)*
(S,R)-BPPFA[102]	$[Rh(C_6H_{10})_4Cl]_2$	"	72%	29% *(R)*
(S,R)-PPFA[102]	$[Rh(C_6H_{10})_4Cl]_2$	"	61%	11% *(R)*[b]
(S,S)-CHIRAPHOS[116]	$[Rh(C_2H_4)_4Cl]_2$	"	60%	4% *(S)*
(R,R)-DIOP[116]	$[Rh(C_2H_4)_4Cl]_2$	"	95%	23% *(S)*
1.145[100]	$[Rh(C_2H_4)_4Cl]_2$	"	87%	24% *(S)*
(R,R)-Norphos[8q]	$[(COD)RhCl]_2$	"		16%
Glucophinite[104]	$Rh(COD)_2BF_4$	"	65%	55%
Camphinite[104]	$Rh(COD)_2BF_4$	"	64%	42%
(R,R,S,S)-nBuTRAP[106c]	$Rh(COD)_2BF_4$	"	98%	92% *(S)*
1.161[111]	$[(COD)RhCl]_2$	"	79%	33% *(R)*
1.162[111]	$[Rh(COD)Cl]_2$	"	74%	31% *(R)*
(S)-NAPHOS[76a,115a]	$[Rh(COD)Cl]_2$	$\alpha NpPhSiH_2$		16% *(S)*

a) all substrates are PhCOMe except b); b) PhCOEt

It is interesting to note that with the chiral complex BMPP-Rh, where the chirality is located at the phosphorous center, hydrosilation of acetophenone (**1.32**) by monohydrosilane (**1.39**) induced higher enantiomeric excess [32 % ee *(S)*] than by

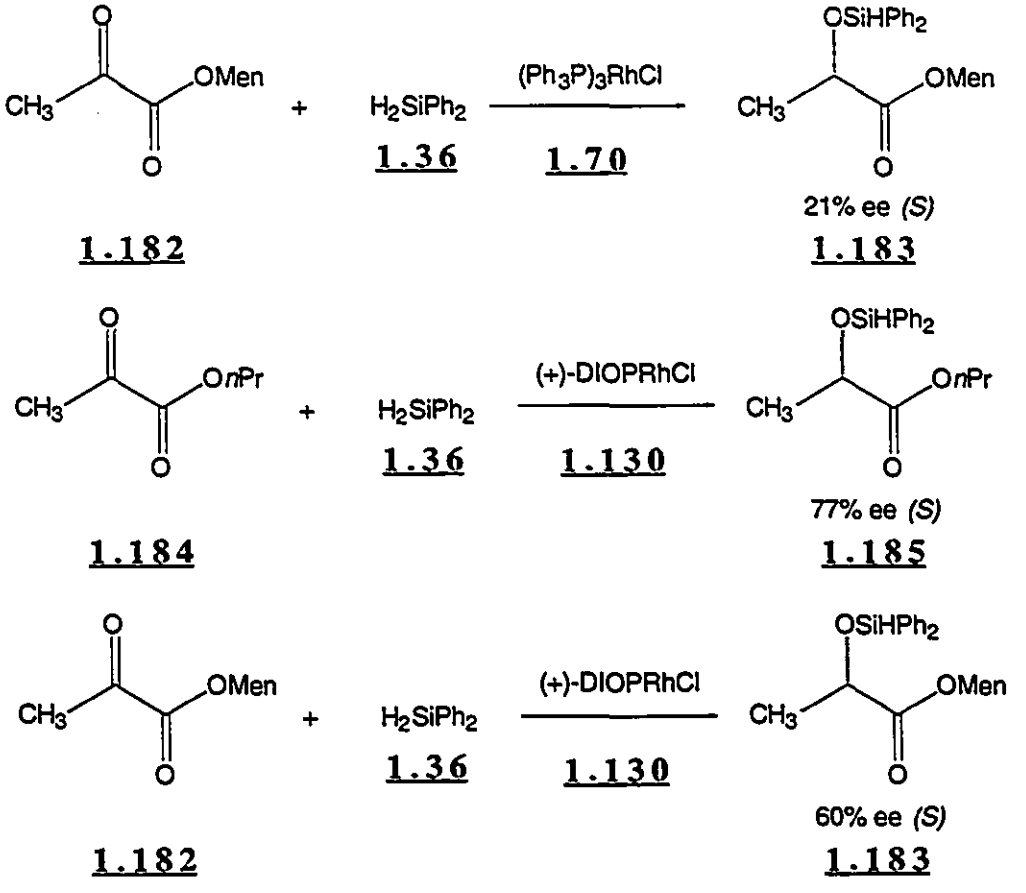
dihydrosilane [**1.36**; 15 % ee *(R)*].[115] When the chiral complex, MPFA-Rh, where the chirality is located at the carbon centers, was used in the hydrosilation of compound **1.179**, opposite results were obtained, *i.e.* dihydrosilane created higher optical yield than monohydrosilane for the same asymmetric hydrosilation system (Scheme 1.48).[102]



Scheme 1.48

In a double asymmetric hydrosilation of chiral substrate **1.182**, the results were not very encouraging.[117] Hydrosilation of chiral substrate **1.182** by diphenylsilane (**1.36**) catalyzed by achiral

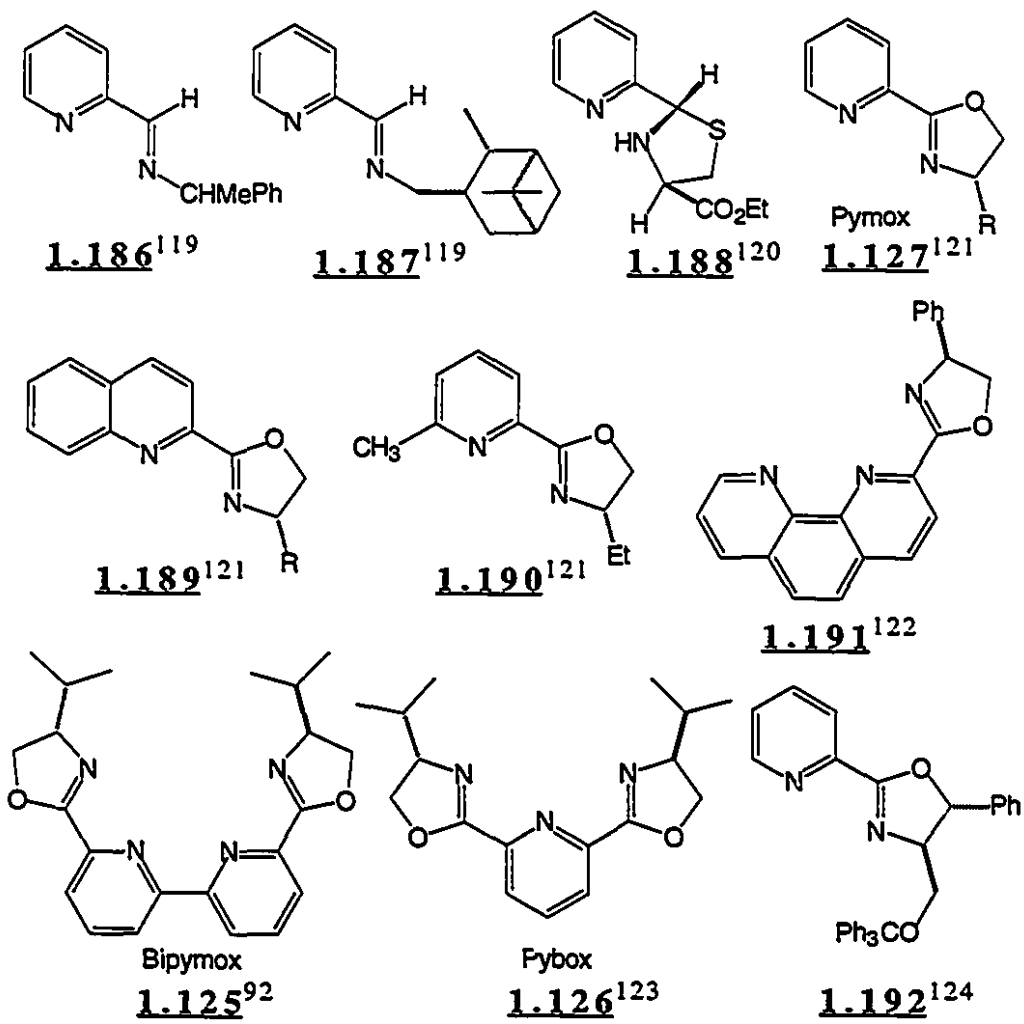
catalyst, $RhCl(PPh_3)_3$ (**1.70**), offered a product with an enantiomeric excess of only 21% *(S)*. On the other hand, reduction of prochiral ketone **1.184** by the same silane **1.30** catalyzed by chiral catalyst (+)-DIOP-RhCl, (**1.130**), generated product **1.185** with an optical purity of 77% ee *(S)*. However, combination of these two matched chiralities did not produce higher enantiomeric excess [60 % ee *(S)*].



Scheme 1.49

Nitrogen containing chiral ligands demonstrated high efficiency in asymmetric induction during hydrosilation of prochiral ketones.[118] Figure 1.3 shows some of the nitrogen-containing chiral ligands used in the asymmetric hydrosilation of prochiral ketones. These types of

chiral ligands (**1.186**,[119] **1.187**,[119] **1.188**,[120] **1.127**,[121] **1.189**,[121] **1.190**,[121] **1.191**,[122] **1.125**,[92] **1.126**,[123] **1.192**,[124]) have some common fertures: they are relatively easy to make, the chiral starting materials are readily available from chiral amino acid, and they are relatively stable. The average enantiomeric excess induced by this type of chiral ligand in the hydrosilation of prochiral ketones is somewhat higher compared to that induced by chiral phosphine ligands.



1.186[119] **1.187**[119] **1.188**[120] **1.127**[121]

1.189[121] **1.190**[121] **1.191**[122]

1.125[92] **1.126**[123] **1.192**[124]

Figure 1.3

Table 1.2 summarizes some results obtained from the asymmetric hydrosilation of acetophenone (**1.32**) with dihydrosilane catalyzed by catalysts derived from different chiral ligands. The results clearly indicated that high to excellent asymmetric induction can be achieved with this type of chiral ligand.

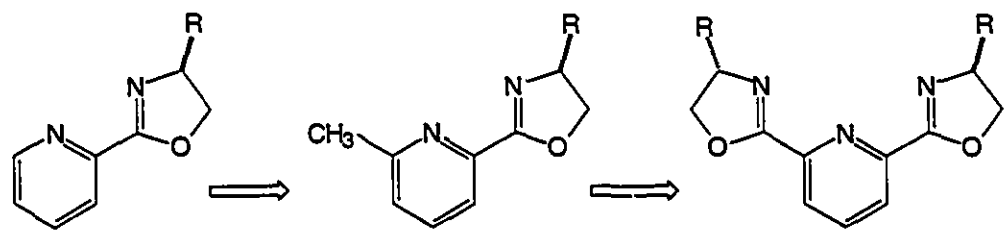
Table 1.2: Asymmetric hydrosilation of acetophenone using chiral oxazolinyl complexes.

Ligand	Metal complex	Silane	Yield	% ee
1.186[119]	$[(COD)RhCl]_2$	Ph_2SiH_2	96%	57% *(R)*
1.187[119]	$[(COD)RhCl]_2$	Ph_2SiH_2	99%	79% *(S)*
1.188[120]	$[(COD)RhCl]_2$	Ph_2SiH_2	99%	98% *(R)*
1.127[121]	$[(COD)RhCl]_2$	Ph_2SiH_2	90%	83% *(R)*
1.190[121b]	$[(COD)RhCl]_2$	Ph_2SiH_2	84%	48% *(S)*
1.189[121b]	$[(COD)RhCl]_2$	Ph_2SiH_2	79%	79% *(S)*
1.125[92]	$RhCl_3$-$AgBF_4$	Ph_2SiH_2	98%	90% *(S)*
1.126[123]	$RhCl_3$-$AgBF_4$	Ph_2SiH_2	91%	94% *(S)*
1.192[124]	$[(C_2H_4)_4RhCl]_2$	$\alpha NpPhSiH_2$	100%	80% *(R)*

The thiazolidine ligand, (**1.188**), could furnish an optical yield up to 98% ee *(R)* in the enantioselective reduction of acetophenone, (**1.32**), by diphenylsilane, (**1.36**).

Enantiomerically pure 2-(2-pyridinyl)oxazoline ligand (**I**, Chart 1.20) was introduced by Brunner's group in 1986 for the Cu-catalyzed enantioselective monophenylation of diols.[125] These

ligands have been shown to induce high enantiomeric excesses in the hydrosilation of prochiral ketones.[121b] Many modifications have been made based on these findings.[126] An extra methyl group at the C(6) position of the 2-(2-pyridinyl)oxazoline (**II**) was shown to enhance asymmetric induction.[121b,127] These ligands have evolved into the C_2 symmetric, tridentate, **III**,[123a,b,128] and tetradentate[92] chelating ligands which give excellent optical yields (up to 99% ee) in asymmetric hydrosilation reactions (Chart 1.10).



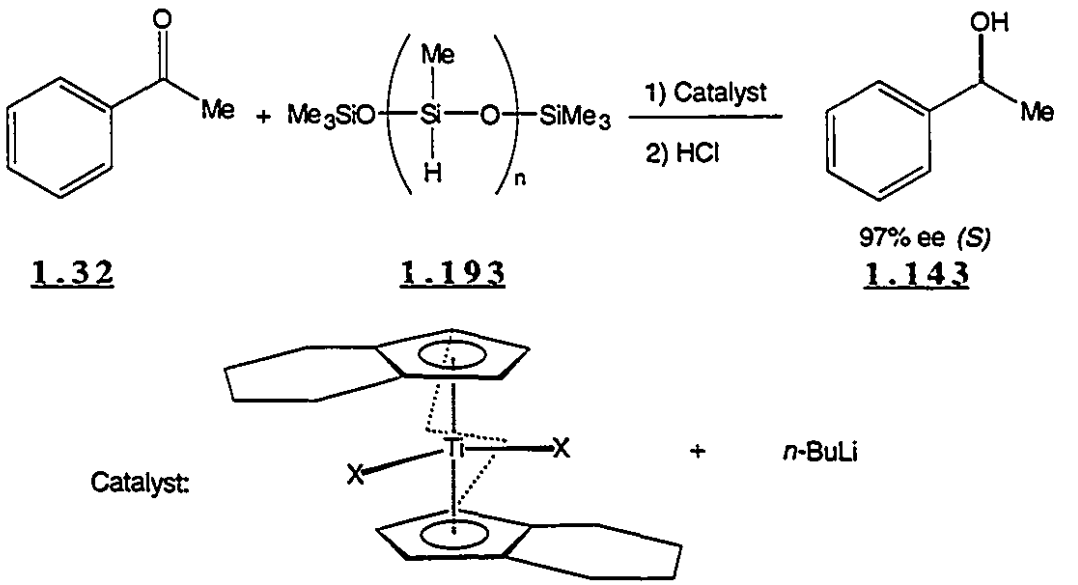
I **II** **III**

Chart 1.10

There are also some other ligands, containing both N and P, which have been used for the asymmetric hydrosilation of prochiral ketones.[129] As a matter of fact, over 200 chiral bidentated N- based ligands have been synthesized in the past decade.[130] Most of them were derived from the inexpensive and readily available chiral pool: α-amino acids.

Chiral titanocene has gained much attention recently as another type of chiral catalyst.[63c,131] These chiral complexes have their chirality directly attached to the metal center, and are C_2 symmetric. In most cases low to moderate optical yields are induced by these chiral catalysts.[131a-c] Excellent enantiomeric excess has recently

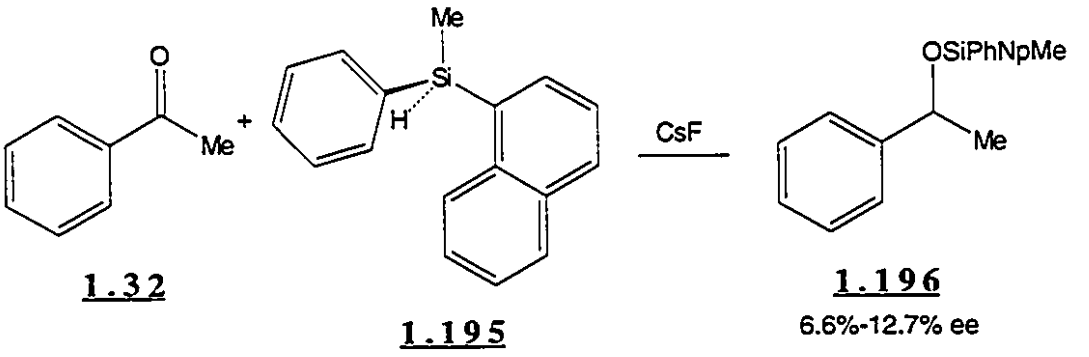
been achieved by Buchwald's group using complex **1.194** as catalyst (up to 97% ee: Scheme 1.50).[63c]



Scheme 1.50

An alternative method to achieve asymmetric induction is to use chiral silicon hydrides and achiral catalysts in the hydrosilation of prochiral ketones.[132] However, only low to moderate enantiomeric excess has been obtained thus far with this approach. When the chirality is located at the silicon center, only poor to low optical yields were obtained when catalyzed by cesium fluoride (Scheme 1.51).[132b]

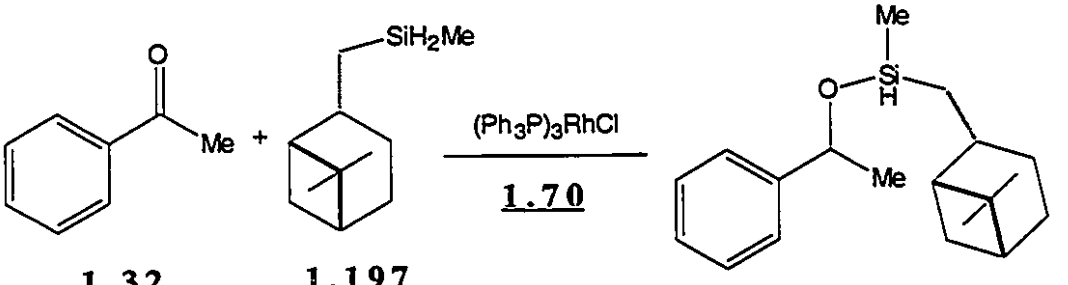
The use of C-centered chiral silicon hydrides has only improved the enantiomeric excess in the reduction of prochiral ketones to a limited extent (Scheme 1.152).[132a,c]



1.32 **1.195** **1.196**

6.6%-12.7% ee

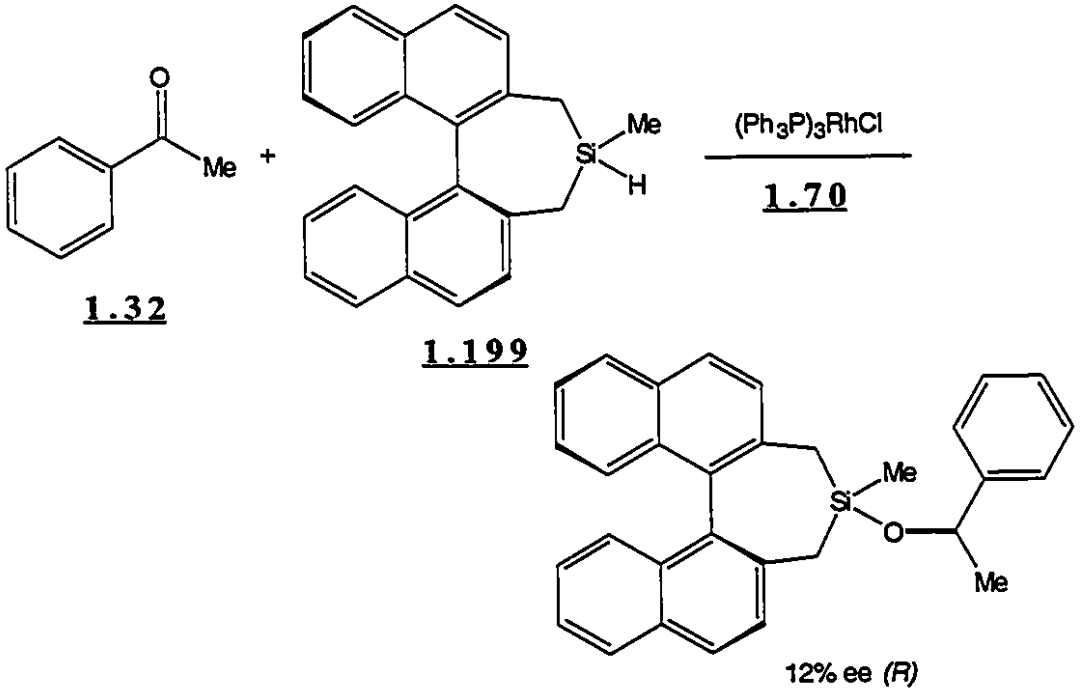
Scheme 1.51



1.32 **1.197** **1.70**

16% ee *(S)*

1.198



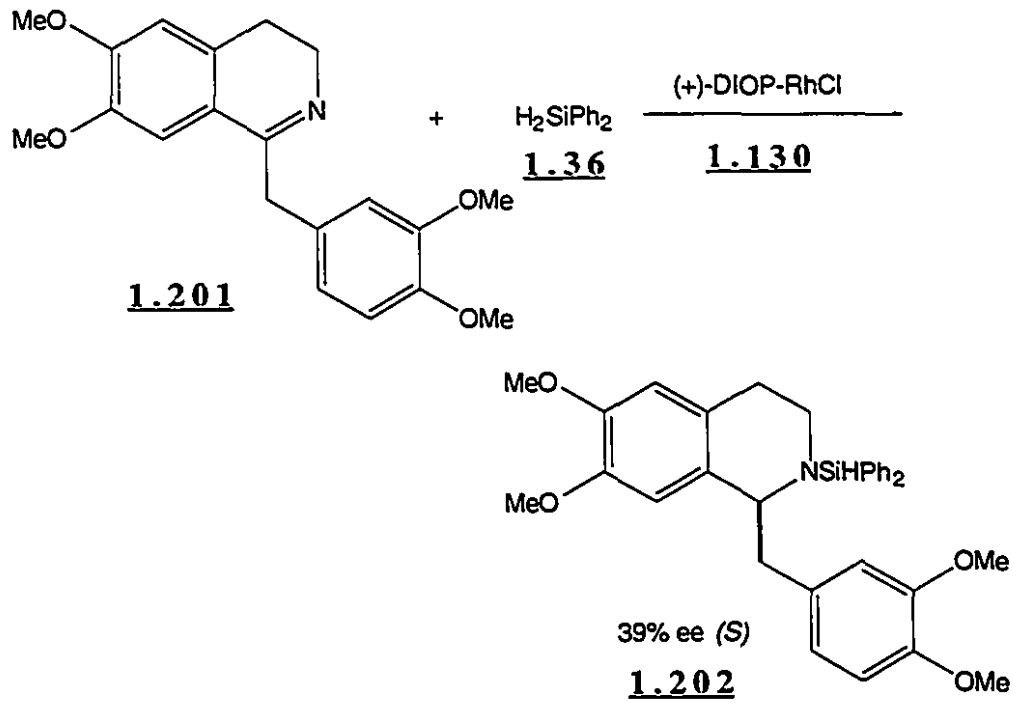
1.32 **1.199** **1.70**

12% ee *(R)*

1.200

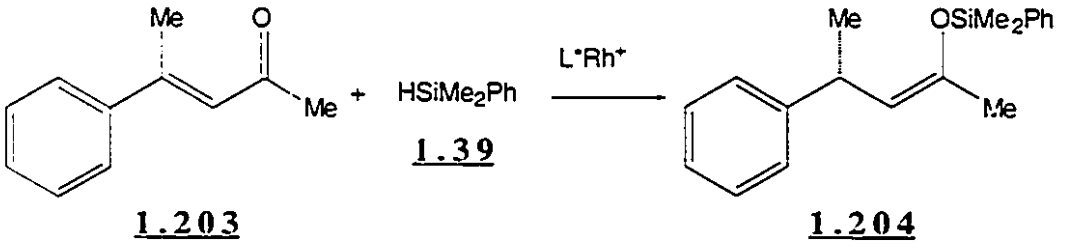
Scheme 1.52

Asymmetric hydrosilation of imines provides a convenient method to access N-containing chiral compounds.[133] A typical example is the reduction of substrate **1.201** under the influence of (+)-DIOP-RhCl (**1.130**) as catalyst (Scheme 1.53).[133a]



Scheme 1.53

Less attention has been placed on the area of asymmetric 1,4-hydrosilation of α,β-unsaturated ketones.[134] The reaction usually gives quite low enantiomeric excess at the newly generated chiral center at the β-position. 1,4-Hydrosilation of compound **1.203** by dimethylphenylsilane (**1.39**) catalyzed by chiral rhodium complexes produced only poor to low enantiomeric excess at the β-position (Scheme 1.54).[134a,b]



1.203 **1.39** **1.204**

L*= (+)-BMPP **1.144** 16% ee *(R)*

(-)-DIOP **1.133** 6% ee *(R)*

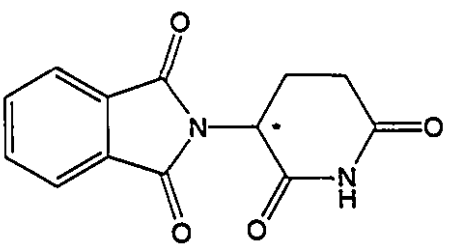
Scheme 1.54

1.2 Plan and Targets

1.2.1 Synthesis of Enantiomerically Pure Alcohols

Asymmetric synthesis has attracted tremendous attention during the past several decades.[135] Since many bioactive natural products and synthetic drugs contain stereogenic center(s), it is quite obvious that the demand for reliable methods to make enantiomerically pure compounds has increased rapidly. EPC (enantiomerically pure compound) synthesis can lead to a new age for the pharmaceutical industry, which produces only about 1/5 of their chiral drugs used in the current market in their enantiomerically pure forms. Concerns have been raised about racemic drugs, which can be considered to be contaminated with 50% of their corresponding distomer, the less active enantiomer. After a racemic chiral drug is administered, the two enantiomers of the

racemate are no longer the same since they become diastereomeric once they interact within the body. These two enantiomers could have different potency,[136] different therapeutic activities,[137] or opposite effects.[138] Sometimes these contaminant distomers could be responsible for unwanted side effects.[139] For example, thalidomide (**1.205**) was a hypnotic agent and also used to treat leprosy.[140a] However, the *(S)*-enantiomer is teratogenic, and the teratogenicity could be removed when the *(R)*-enantiomer is used (Figure 1.4).[140]



1.205

Figure 1.4

Compounds with a chiral center bearing a hydroxy group are ubiquitous.[141] Asymmetric synthesis of optically pure alcohols has been, and continues to be, a major preoccupation in organic synthesis.[135] General methods which yield high levels of asymmetric induction are always desirable for academic and industrial research and development.

1.2.2 Asymmetric Synthesis

EPC can be prepared in many ways: chemically,[142] biochemically or biologically.[143] In the early days, practical access to EPC from prochiral precursor was considered possible only by using

biochemical or biological methods. Methods using enzymes, cell cultures, or whole micoorganisms are powerful tools to produce optically active compounds, especially naturally occurring products. The scope of these approaches is somewhat restricted, as most of these systems can only access one enantiomer,[143] and the compound in question must be a substrate in the biological system used.

In terms of chemical methods, classical resolution of racemates has its obvious limitation in giving, in general, poor recovery. The chiron approach to obtain EPC by transformation of readily available optically active natural products relies on the application of chemical synthesis, and the availability of appropriate precursors. Alternatively, a variety of versatile enantioselective reactions using chiral auxiliaries have been discovered, which can be quite useful.[135c]

One approach to EPC synthesis of alcohols is based on asymmetric hydrosilation of prochiral ketones. Unlike hydroboration, hydrosilation is much more difficult without the presence of catalyst.[10] The need for catalysts in hydrosilation reactions is thus inevitable. The goal of the present research is to examine transition metal complexes as catalysts to mediate hydrosilation of prochiral ketones, and to study factors affecting asymmetric induction in these reactions.

1.2.2.1 The Search for Active Hydrosilation Catalysts

Although there are many transition metal complexes which can serve as good catalysts for the hydrosilation of ketones, most of them

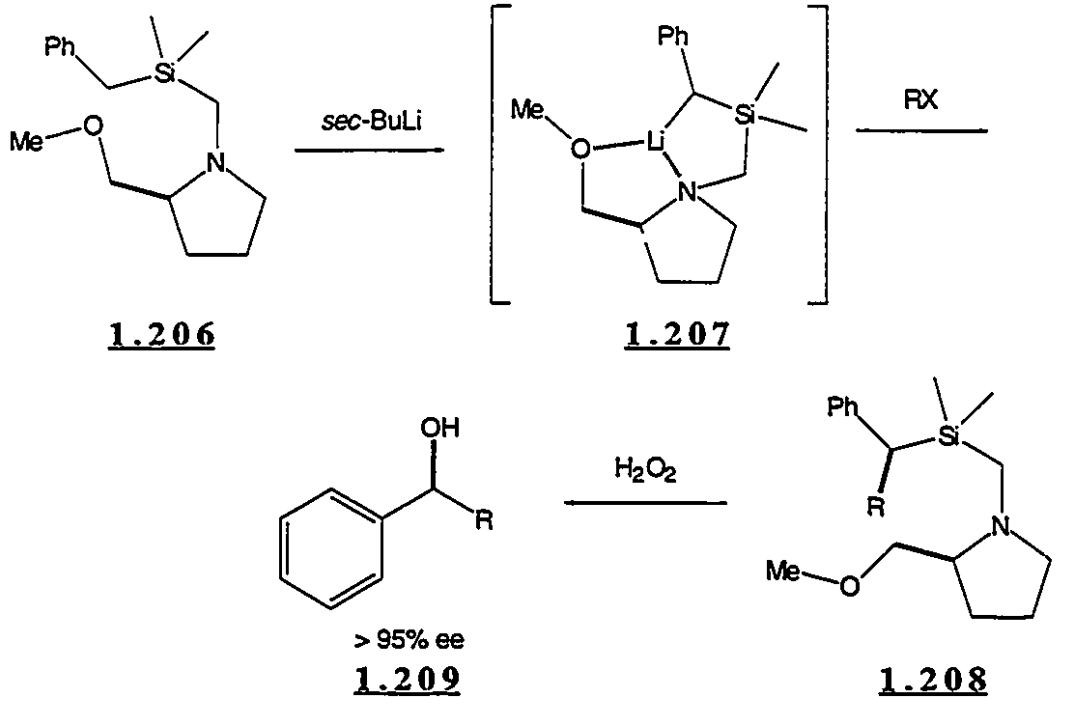
are not efficient enough, in terms of their potency and selectivity (*vide supra*). Our research plan is to first find a system which is potent and selective enough to carry out hydrosilation of α,β-unsaturated ketones in a regiocontrolled manner, *i.e.* 1,2- or 1,4-regiospecific, under very mild reaction conditions. Based on this catalytic system, we want to develop regiocontrolled asymmetric hydrosilation of prochiral ketones to obtain alcohols and their derivatives.

1.2.2.2 Catalytic Hydrosilation with Chiral Silicon Hydride

In this approach, the chirality is transferred from enantiomerically pure silicon hydride to the product mediated by achiral metal catalysts. Asymmetric hydrosilation of prochiral ketones using enantiomerically pure silicon hydride can have the chirality of the silane preserved throughout the reaction (see section 1.1.2.3.2). Therefore, the chirality at silane remains intact, and the chiral silane can be reused after recovery.

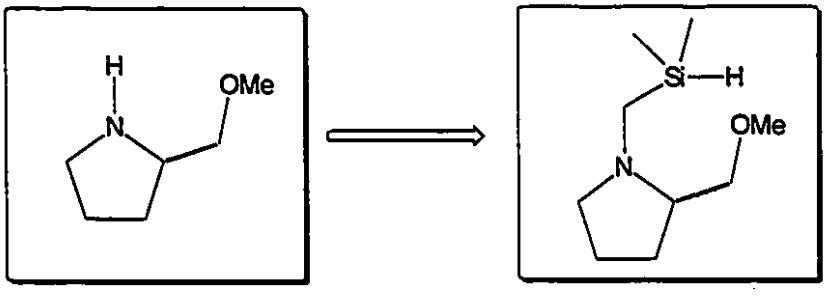
As discused in section 1.1.2.3.2, asymmetric hydrosilation using chiral silanes with the chiral center located at silicon generally gave products with low enantiomeric excess.[132b] Our approach was to use C-center chiral silicon hydrides[132a,c] to engage in the hydrosilation of prochiral ketones. The major benefit of this approach is that the chiral silane can be prepared in enantiomerically pure forms without the need for resolution. The chiral silane should be designed to be recyclable after use.

Based on the excellent enantioselectivities exhibited with the chiral moiety of pyrrolidinyl, **1.210**,[144] as shown in Scheme 1.55,[144b] chiral silane **1.211** was designed as a candidate for the investigation of enantioselectivity in the regiocontrolled hydrosilation of prochiral carbonyl compounds catalyzed by an achiral metal catalyst.



1.206 **1.207** **1.209** **1.208**

Scheme 1.55



1.210 **1.211**

Figure 1.5

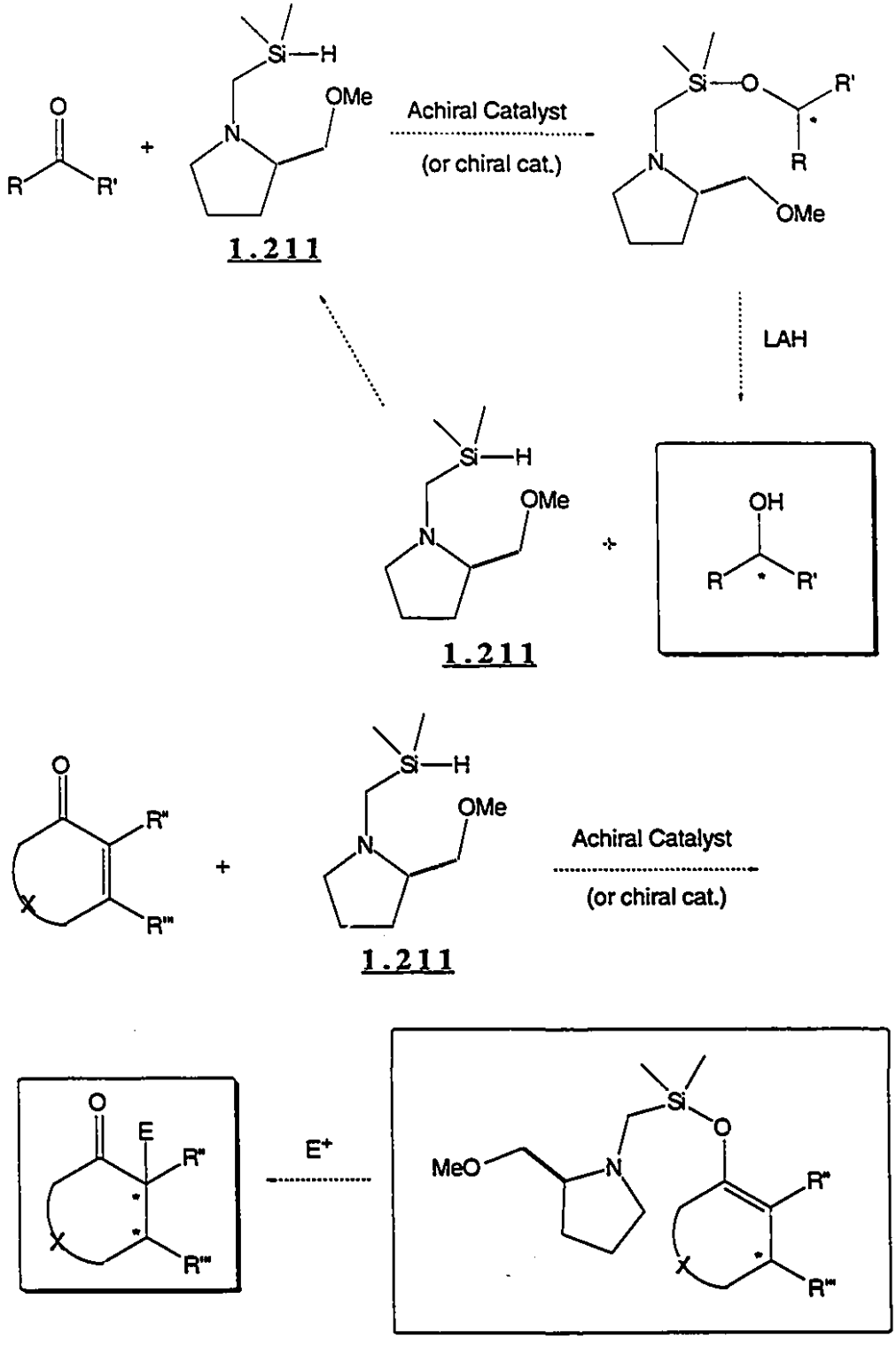

Achiral Catalyst
(or chiral cat.)
LAH
1.211
1.211
Achiral Catalyst
(or chiral cat.)
1.211
E+

Chart 1.11

The same chiral silane can also be used for the hydrosilation of alkenes. Optically active alcohols can be obtained after oxidation of the resulting products (Chart 1.12).

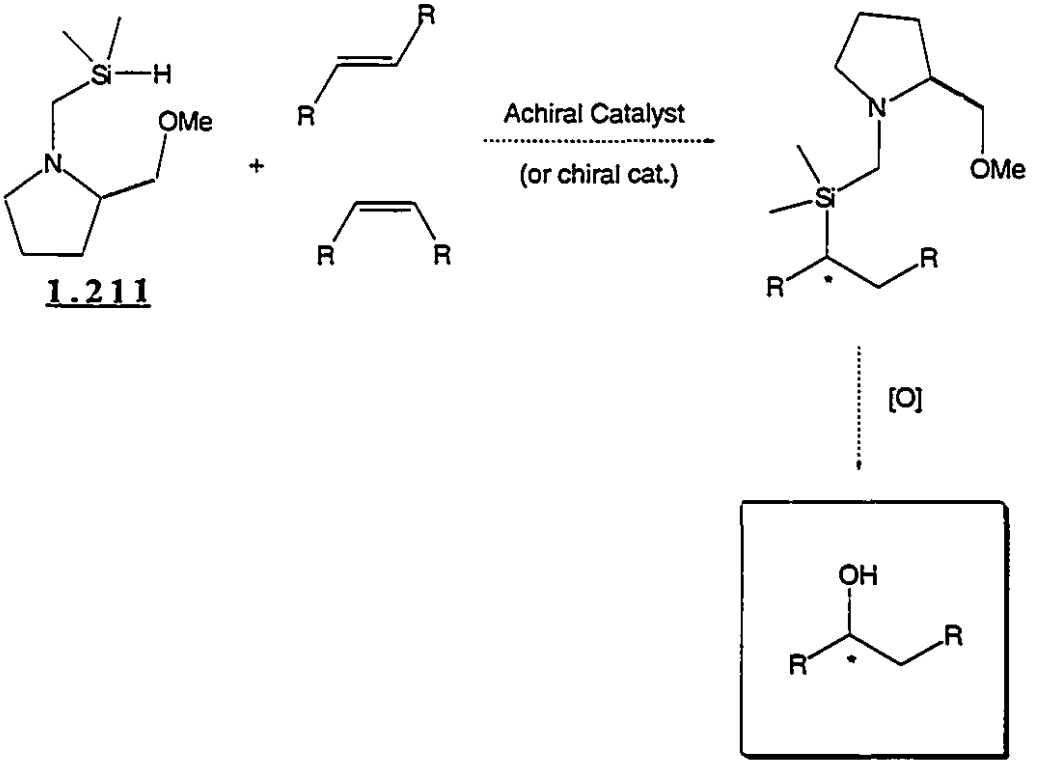


Chart 1.12

1.2.2.3 Asymmetric Catalysis

Asymmetric catalysis is an ideal method for EPC synthesis.[142] This approach can allow chirality multiplication by using small amounts of chiral catalyst to produce EPC in large quantities. The efficiency of chiral multiplication, defined as [(major enantiomer-minor enantiomer)/chiral source], could be infinite for asymmetric catalysis. Recent advances in this area are turning chemists' dreams into reality at both the academic and industrial levels.

Research in this field is growing due to the demand for more general and high enantioselective catalytic systems for the synthesis of a wider range of EPCs.[142] Our plan for EPC synthesis is to build a catalytic system for asymmetric hydrosilation of prochiral ketones with a wider spectrum of substrates, and more importantly, to gain higher levels of asymmetric induction (Chart 1.13).

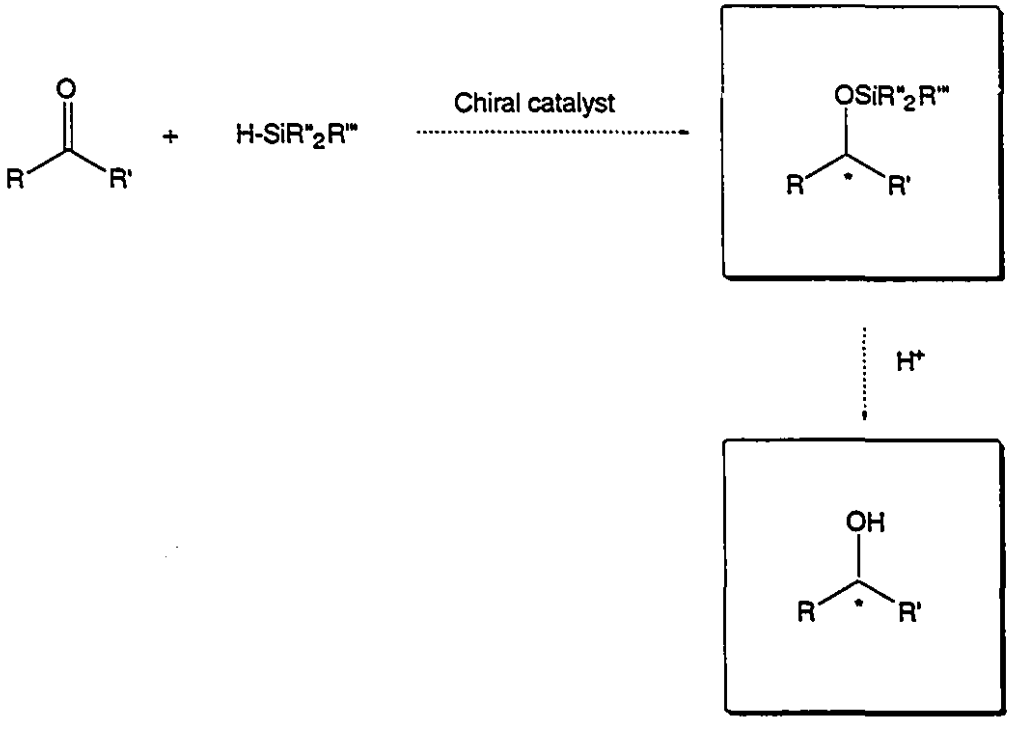


Chart 1.13

Also, this approach could introduce a chiral center(s) at the α- and/or β-position of α,β-unsaturated carbonyl compounds *via* asymmetric 1,4-hydrosilation of α,β-unsaturated carbonyl compounds. The products generated from 1,4-hydrosilation are an important class of precursors in organic synthesis.[81] This type of asymmetric induction is usually difficult as shown in section 1.2.2.[134]

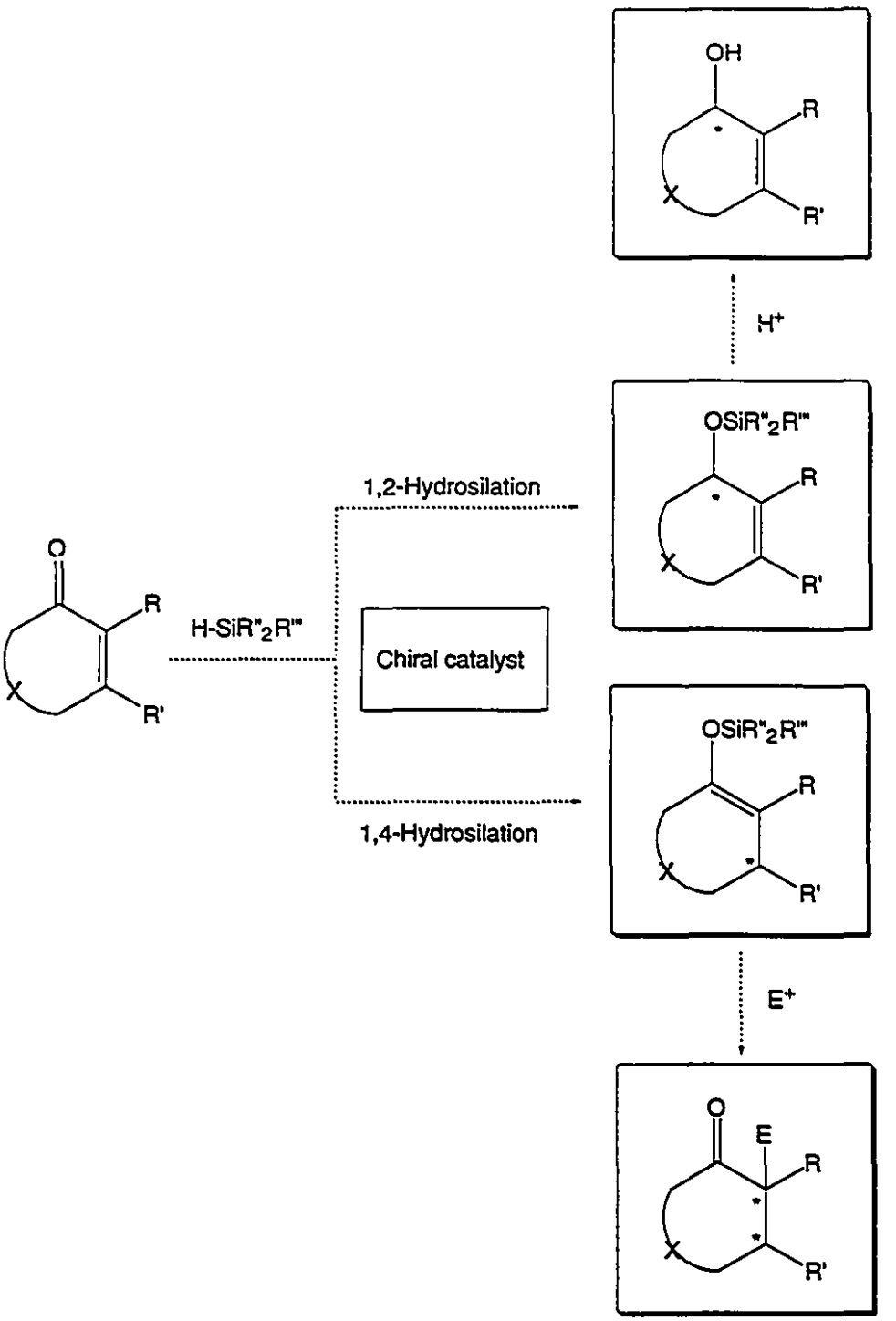


Chart 1.14

In general, this approach allows the generation of stereogenic centers at C(1), C(2) and C(3) of α,β-unsaturated carbonyl compounds regio- and stereoselectively, as illustrated in Chart 1.14.

II. REGIO- AND STEREOSELECTIVE HYDROSILATION OF KETONES

2.1. The Search for Active, Homogeneous Hydrosilation Catalysts

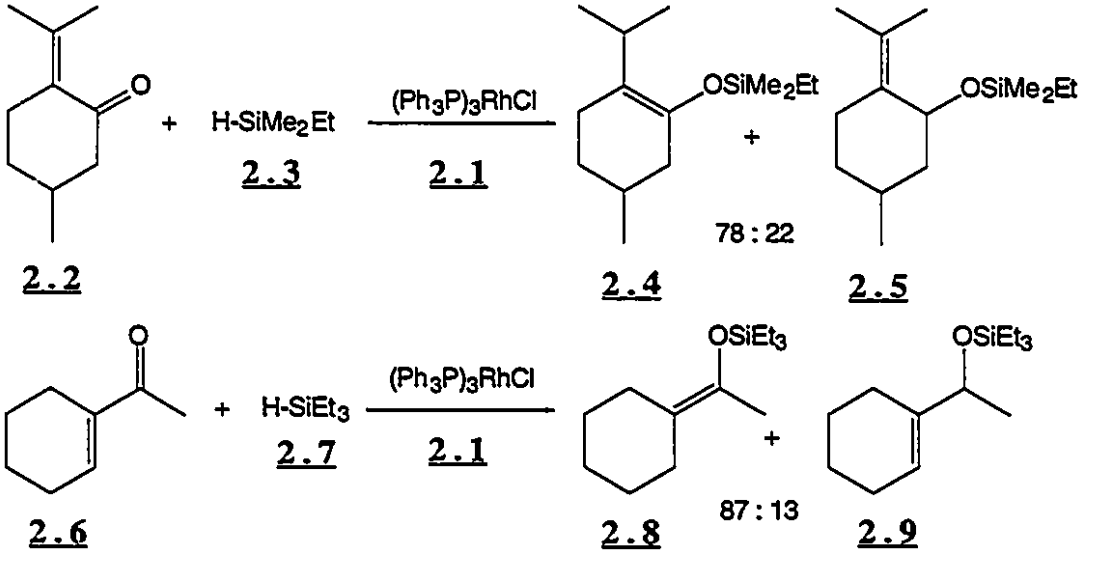
Many active catalysts used currently for hydrosilation are often not quite selective in the production of pure products (section 1.1.2.3). Some of them mediated hydrosilation reactions *via* heterogeneous pathways.[40,41] In such a pathway, chiral induction with chiral ligands (in practical terms, it should be called an enantiomerically pure ligand) can be difficult.

Our attention is focused on late transition metals, such as cobalt, rhodium and iridium, which are well studied and known as good catalysts for hydrosilation of ketones. Their behaviors can more likely be interpreted by well established mechanisms, which may provide guidance to modify and improve chiral induction (*vide infra*).

The type of complexes we are looking for should be capable of mediating hydrosilation under mild reaction conditions, and most importantly, in a regio- and stereoselective manner. The preferred complexes should have very similar electronic structures as the desired chiral complexes so that reactivities, regioselectivities and stereoselectivities of the complexes would not change to a great extent after chiral modification.

2.1.1 Rhodium Complexes

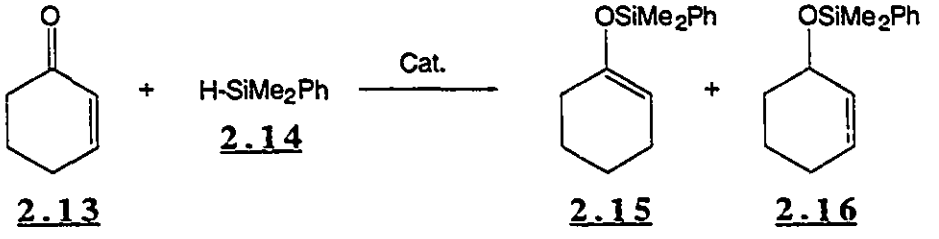
Our search began by examining a number of rhodium complexes. It has been known for some time that many rhodium metal complexes are good catalysts for the hydrosilation of olefins, alkynes and carbonyl functionalities.[145] The well known Wilkinson's catalyst, chloro(triphenylphosphine)rhodium(I) (**2.1**),[15,49,56,146] is one example. However, it is not quite efficient in terms of reactivities and selectivities (regio- and stereoselectivities). For instance, for the hydrosilation of pulegone (**2.2**) or 1-acetylcyclohexene (**2.6**) catalyzed by Wilkinson's catalyst, the regioselectivities (1,2-/1,4-) were only 1 : 3.5 and 1 : 6.7, respectively (Scheme 2.1).[80a]



Scheme 2.1

There are three rhodium complexes, μ-dichlorotetra(ethylene)dirhodium (**2.10**),[147] chlorobis(cyclooctene)rhodium(I) dimer

(2.11)[148] and chloro(1,5-cyclooctendiene)rhodium(I) dimer (2.12),[149] which serve as precursors for many other rhodium catalysts,[150] and are very closely related to Wilkinson's complex. They are very active catalysts for hydrosilation of α,β-unsaturated carbonyl compounds. The difference in reaction times for the three precursors (Scheme 2.2) was probably caused partially by low solubilities of these complexes in benzene, which is used to minimize the reactions between solvent and complexes. Although complex 2.1 was soluble in benzene, it is much less reactive than the three precursors (Scheme 2.2).



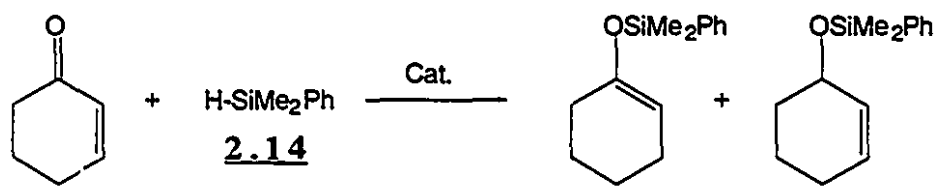
2.13 2.15 2.16

		time, rt	
$(Ph_3P)_3RhCl$	(2.1)	5.5 days	97 : 3
$[(C_2H_4)_2RhCl]_2$	(2.10)	3 min	100 : 0
$[(C_8H_{12})_2RhCl]_2$	(2.11)	70 min	100 : 0
$[(COD)RhCl]_2$	(2.12)	40 min	100 : 0

Scheme 2.2

Although these complexes are quite potent for hydrosilation of ketones under much milder conditions than Wilkinson's catalyst, they may not be ideal for asymmetric catalysis since these complexes are relatively unstable. Introduction of chiral ligands may also affect greatly their reactivities.

Attempts were made to modify Wilkinson's catalyst by removing the chloride from the complex with silver salt to form cationic species. The resulting solution in THF was dark red and homogeneous. However, the addition of silane to this solution led to precipitation of a dark solid. The dark solid was presumably rhodium metal. Nevertheless, the cationic species were much more active towards hydrosilation of α,β-unsaturated ketone, 2-cyclohexen-1-one (**2.13**), with mono-hydrosilane than the corresponding neutral Wilkinson's complex. The cationic rhodium(I) complexes, bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (**2.17**),[151] bis(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) perchlorate (**2.18**)[152] and (1,5-cyclooctadiene)bis(triphenylphosphine)rhodium-(I) hexafluorophosphonate (**2.19**)[153] were thus tested for the hydrosilation of ketone, **2.13**. All of them were found to be active and also highly regioselective yielding only the 1,4-adduct **2.15**. They could be good candidates for future investigations on asymmetric catalysis (Scheme 2.3).

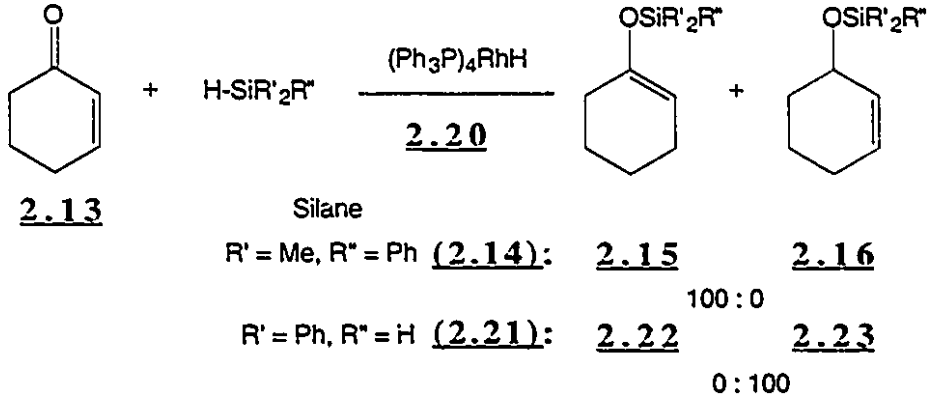


2.13 **2.15** **2.16**

		time, rt	
$(COD)_2RhBF_4$	**(2.17)**	40 min	100 : 0
$(Nor)_2RhClO_4$	**(2.18)**	70 min	100 : 0
$(COD)_2Rh(PPh_3)_2^+$	**(2.19)**	40 min	100 : 0

Scheme 2.3

The rhodium complex, hydridotetrakis(triphenylphosphine)-rhodium(I)[154] (**2.20**) was found to be fairly potent and highly regioselective for both 1,2- and 1,4-hydrosilation of α,β-unsaturated ketones (Scheme 2.4).[80b]



Scheme 2.4

The complex was originally made by Yamamoto's group[154a] and Dewkirst's group[154b] independently in 1968. One year later, the structure was determined by Baker and Pauling by X-ray defraction analysis.[155] The complex has a slightly distorted tetrahedral geometry with two kinds of triphenylphosphine ligands occupying four tetrahedral positions [P(1)-Rh-P(2): 107°; P(2)-Rh-P(2): 111°]. The complex could be considered as an analog of Wilkinson's catalyst with the chloride replaced by a hydride. Although it has never been reported that this catalyst could mediate hydrosilation of ketones, the complex was known to be a catalyst for hydrosilation of alkenes[156] and for the migration of double bonds in olefins.[157] Compared to most other metal catalysts, this complex achieved much higher regioselection in the reduction of α,β-unsaturated ketones

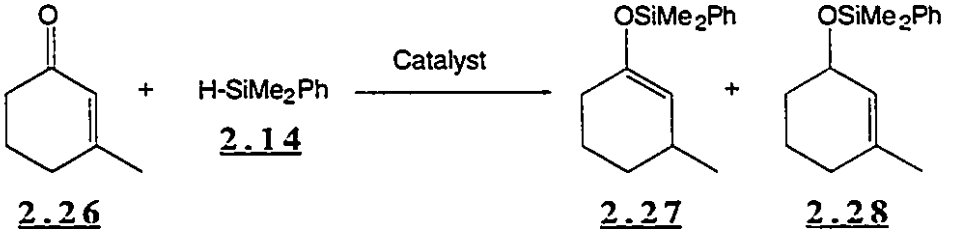
(*vide infra*). Furthermore, unlike complexes 2.10-2.12 and 2.17-2.19 mentioned above, this complex has phosphine ligands already attached. One would expect the electronic structure to be very similar after chiral phosphine modification. Thus the reactivities, regioselectivities and stereoselectivities may not change drastically after using chiral phosphine ligands to replace the achiral triphenylphosphine ligands. It is therefore a good candidate to study for the regio- and stereoselective hydrosilation of α,β-unsaturated ketones.

2.1.2 Iridium Complexes

Iridium complexes are also known as potent hydrosilation catalysts.[57] However, the results of 1,4-hydrosilation of α,β-unsaturated ketones with monohydrosilane catalyzed by chlorobis(cyclooctene)iridium(I) dimer (2.24)[158] or chloro(1,5-cyclooctadiene)iridium(I) dimer (2.25)[158a] was not quite satisfactory. A mixture of 1,2- and 1,4- hydrosilation products was generated. To our surprise, the modification of this complex with phosphine ligands, or with nitrogen bases, formed new iridium species which were inactive towards hydrosilation of ketones. It has been reported that the ratio of phosphino or amino bases to metal is crucial for the activity of these complexes.[57c]

On the other hand, the iridium complexes 2.24 and 2.25 were more efficient catalysts for β-substituted, α,β-unsaturated ketones. For example, the hydrosilation of 3-methyl-2-cyclohexen-1-one

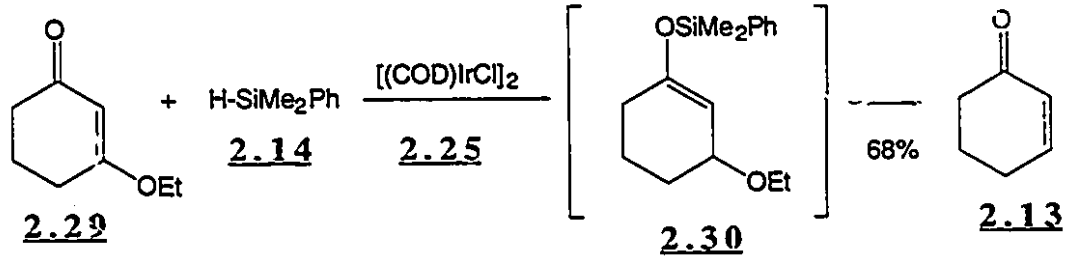
(2.26) by dimethylphenylsilane (2.14) catalyzed by $(Ph_3P)_4RhH$ (2.20) took 24 hours at 50 °C to furnish a clean 1,4-hydrosilation product. With iridium complex 2.25 as the catalyst, the reaction was complete in 5 hours at room temperature (Scheme 2.5).



$(Ph_3P)_4RhH$	2.20	24 h, 50 °C	100 : 0
$[(COD)IrCl]_2$	2.25	5 h, rt	95 : 5

Scheme 2.5

1,4-Hydrosilation of α,β-unsaturated ketones with an alkoxy group substituted at the β-position catalyzed by iridium complex 2.25 proceeded quite well and provided a means of reducing the 3-substituted alkoxy group (Scheme 2.6).



Scheme 2.6

In general, the iridium complexes seem to be inferior to rhodium complexes in catalyzing clean, regiocontrolled hydrosilation of α,β-unsaturated ketones.

2.2 Regioselective Hydrosilation of α,β-Unsaturated Carbonyl Compounds

Reactions which selectively reduce α,β-unsaturated carbonyl compounds are of considerable interest for organic synthesis. Among many procedures available, metal complex catalyzed homogeneous hydrosilation[8f,80a] offers some interesting advantages. For example, regioselective 1,4-reduction of α,β-unsaturated carbonyl compounds with hydrosilane gives the corresponding silyl enol ethers, which are themselves useful precursors for many reactions.[81] Having found that the rhodium complex, hydridotetrakis(triphenylphosphine)-rhodium(I) (**2.20**), is a good catalyst for hydrosilylation of ketones,[82d] our further investigations revealed that silicon hydrides played a crucial role in 1,2- and 1,4-regioselectivity during the course of hydrosilation of α,β-unsaturated carbonyl compounds.[80a] When monohydrosilane was used, the reaction gave exclusively silyl enol ether by 1,4-addition of silicon hydride. While if di- or trihydrosilane was used in the above reaction, only 1,2-reduction of the carbonyl group took place. Comparing rhodium complex **2.20** with Wilkinson's catalyst, chlorotris(triphenylphosphine)rhodium(I) (**2.1**), studied by Ojima,[79] complex **2.20** seems to be more potent, and provides much better regioselectivity.

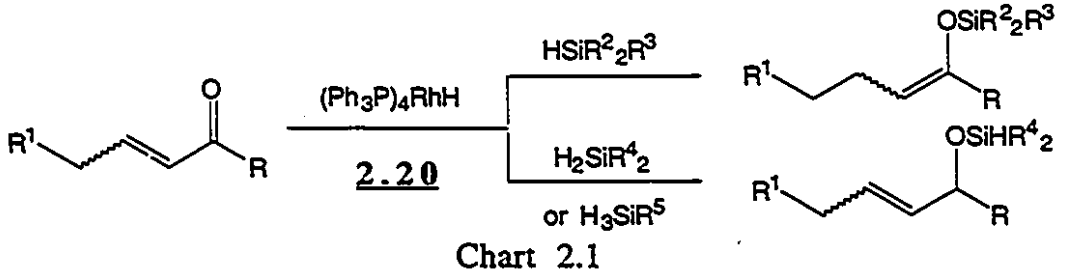


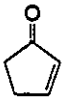
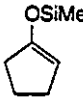
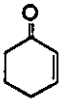
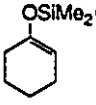
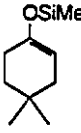
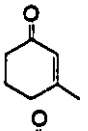
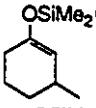
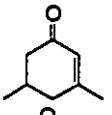
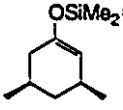
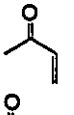
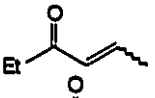
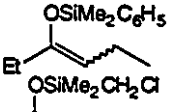
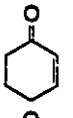
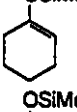
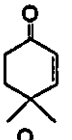
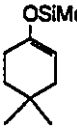
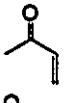
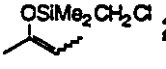
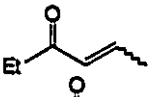
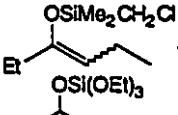
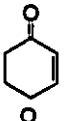
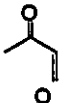
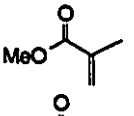
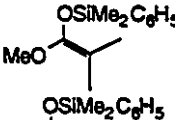
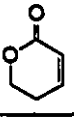
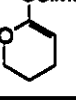
Chart 2.1

The mechanism of catalytic hydrosilation is a subject of much discussion.[43,50b,51,53a,64c,159] In most cases, the organosilyl group has been considered simply as a ligand attached to the metal center or a bimetallic complex. The role of the organosilyl moiety in this type of complex has been largely ignored. The properties of the dimetallic organosilicon-metal complexes are probably more complicated than what has been considered up to now. Our studies to control regioselectivities of hydrosilation reactions led us to wonder whether the silicon moiety in the silyl-metal complexes had any effect on regiochemistry. A new hydrosilation mechanism has been proposed based on our observations.[80a] The role of the silyl moiety in this mechanism has been amplified.

2.2.1 1,4-Hydrosilation of α,β-Unsaturated Carbonyl Compounds

A number of α,β-unsaturated carbonyl compounds were reduced by various monohydrosilanes with rhodium catalyst **2.20**, to give the corresponding silyl enol ethers. The results summarized in Table 2.1 clearly indicate that only 1,4-reduction was observed in all cases.[80a,82d] Products generated from 1,2- reduction could not be detected in any of the experiments. The reaction proceeded under mild conditions and generated clean products.

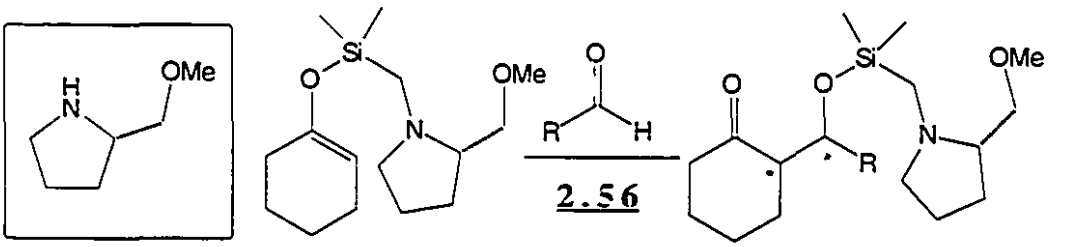
Table 2.1: 1,4-Hydrosilation of α,β-unsaturated carbonyl compounds

entry	substrate	[Rh] M%; cond.	silane	product	yield*
1	 **2.31**	0.3; rt, 12 h	**2.14**	 **2.32**	83%
2	 **2.13**	0.3; rt,12 h	**2.14**	 **2.15**	84%
3	 **2.33**	0.4; rt, 12 h	**2.14**	 **2.34**	96%
4	 **2.26**	0.5; 50 °C, 24 h	**2.14**	 **2.27**	89%
5	 **2.35**	0.5; 50 °C, 24 h	**2.14**	 **2.36**	87% (*cis:trans*=92:8)
6	 **2.37**	0.2; rt, 6 h	**2.14**	 **2.38**	73% (*E/Z*=33:67)
7	 **2.39**	0.2; rt, 6 h	**2.14**	 **2.40**	82% (*E/Z*=77:23)
8	 **2.13**	0.1; rt, 0.5 h	**2.41**	 **2.42**	83%
9	 **2.33**	0.3; rt, 4 h	**2.41**	 **2.43**	80%
10	 **2.37**	0.2; rt, 1.5 h	**2.41**	 **2.44**	85% (*E/Z*=1:2)
11	 **2.39**	0.3; rt, 10 h	**2.41**	 **2.45**	83% (*E/Z*=4:1)
12	 **2.13**	0.3; rt, 12 h	**2.46**	 **2.47**	93%
13	 **2.37**	0.3; rt, 20 h	**2.46**	 **2.48**	75% (*E/Z*=56:44)
14	 **2.49**	0.3; rt, 1.5 h	**2.14**	 **2.50**	91%
15	 **2.51**	0.3; rt, 12 h	**2.14**	 **2.52**	85%

*) The products were distilled *via* Kugelröhr apparatus.

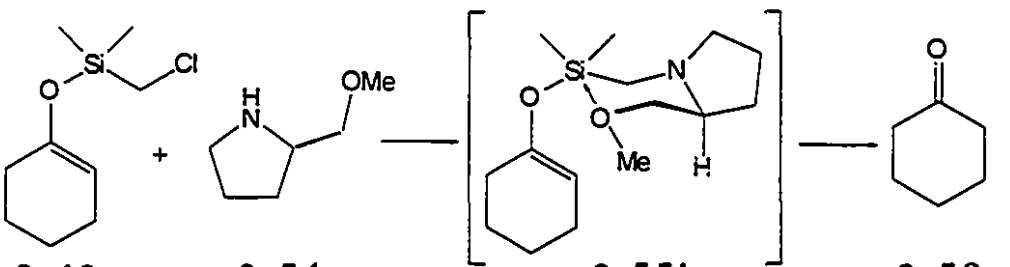
The nature of the substrate greatly affected the reaction rate, but not the regioselectivity. Steric hindrance at the C(3) or C(4) positions of **2.26**, **2.35** and **2.33** (entries 3-5) did retard the reaction, but no decrease in 1,4-selectivity was observed. In the case of 3,5-dimethyl-2-cyclohexen-1-one (**2.35**), interesting results were obtained. Hydrosilation proceeded quite well to give the 1,4-hydrosilation product, **2.36**, in yield of 87% with high diastereoselectivity (*cis* : *trans* = 92 : 8). While it was reported in the literature[160] that this substrate only underwent isomerization of the C=C bond to form 3,5-dimethyl-3-cyclohexen-1-one (**2.53**) regardless of what kind of silicon hydrides were used. Hydrosilation with (chloromethyl)dimethylsilane yielded intermediates in which the chloromethyl group at the silyl moiety might be further functionalized.

In the hopes of obtaining optically active compounds *via* diastereoselective Mukayama reactions,[81a] chiral pyrrolidinyl compound (**2.54**) was used to couple with silyl enol ether **2.42** (Scheme 2.7). It was found that the starting silyl enol ether (**2.42**) decomposed to cyclohexanone very quickly under the reaction conditions used. It was not clear, however, whether or not the coupled product was generated *in situ*. It is possible that the newly formed product, **2.55**, might be unstable, and quickly decompose to cyclohexanone with the help of the neighboring amino, or methoxy groups as indicated in **2.55'** (Scheme 2.8). To test this theory, a bulkier base, diisopropylamine, was used in place of **2.54** to prevent or reduce this neighboring group effect. Although no coupling product was observed, the silyl enol ether remained intact.



2.54 2.55 2.57

Scheme 2.7



2.42 2.54 2.55' 2.58

Scheme 2.8

On the basis of these observations, the (chloromethyl)-dimethylsilyl moiety could be developed as a new type of protecting group, which can be deprotected with certain amino bases. We have not developed this idea fully at the present time.

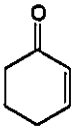
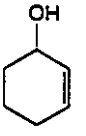
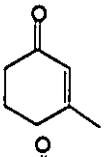
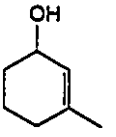
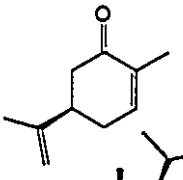
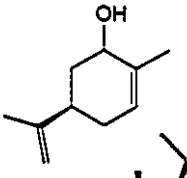
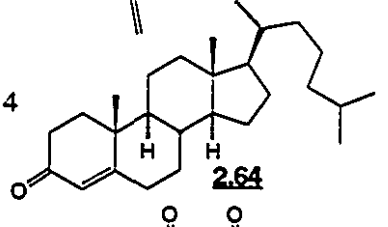
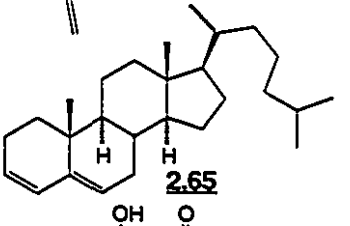
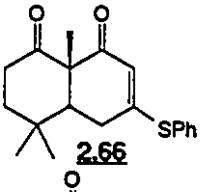
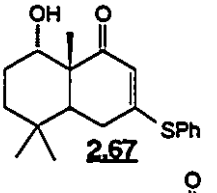
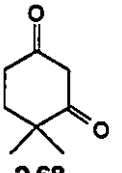
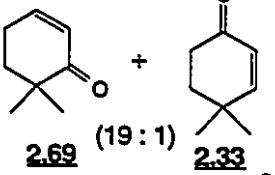
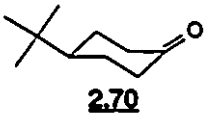
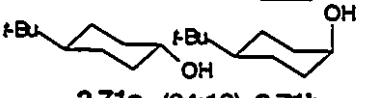
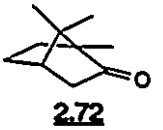
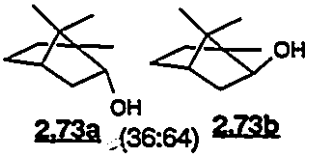
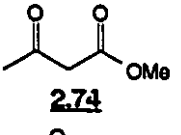
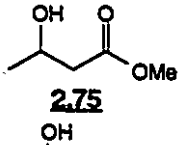
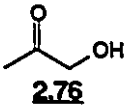
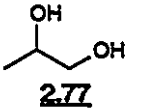
The catalyst **2.20** is also capable of performing hydrosilation of α,β-unsaturated esters with good yields (entries 14 and 15, Table 2.1). α,β-Unsaturated ester, **2.49**, and α,β-unsaturated lactone, **2.51**, were reduced regiospecifically. Transition metal catalyzed hydrosilation of α,β-unsaturated esters have previously been reported.[56i,161] Since silyl ketene acetals are useful as synthons as well as in group transfer polymerization,[162] the present catalyst may find considerable applications.

2.2.2 1,2-Hydrosilation of α,β-Unsaturated Ketones

Hydrosilation of ketones by diphenylsilane (2.21) or phenylsilane (2.59) catalyzed by hydridotetrakis(triphenylphosphine)rhodium(I) (2.20) proceeded smoothly under very mild reaction conditions (Table 2.2). Using 2.20 as catalyst, hydrosilations of α,β-unsaturated ketones by diphenylsilane (2.21) or phenylsilane (2.59) yielded clean 1,2-reduced products. No detectable 1,4-reduced products were observed in the ^{1}H NMR spectra of the crude product mixtures, and GC analysis of the allylic alcohols 2.60, 2.61 and 2.63 showed the absence of the corresponding saturated ketones (entries 1-3, Table 2.2).

In the case of carvone (2.62) (entry 3), both the conjugated and the isolated double bonds were unaffected. Hydrosilation seemed to proceed chemoselectively between the saturated carbonyl group and the enone functionality (entry 5). Only the saturated carbonyl group was reduced exclusively to give 2.67. α,β-Unsaturated carbonyl groups are usually more electron-rich than saturated ones, *i.e.* enones are less activated than saturated carbonyl groups. Steric hindrance could also affect chemoselectivity. Substrate 2.68 was subjected to hydrosilation with diphenylsilane (2.21). The less hindered carbonyl group at C(1) was reduced much faster than the carbonyl group at C(3) (19 : 1). The latter had two methyl groups at C(4) which presumably accounts for the hindrance.

Table 2.2: 1,2-Hydrosilation of α,β-unsaturated ketones

entry	substrate	Rh(I), (% M); time[a]	product[b]	yield[c]
1	 2.13	0.4; 4 h	 2.60	83%
2	 2.26	0.3; 4 h	 2.61	86%
3	 2.62	0.4; 12 h	 2.63	84% *cis: trans*=65:35
4	 2.64	0.4; 12 h	 2.65	76%
5	 2.66	0.5; 12 h	 2.67	56%
6	 2.68	0.5; 12 h	 2.69 (19 : 1) 2.33	49%
7	 2.70	0.3; 5 h	 2.71a (84:16) 2.71b	81%
8	 2.72	0.4; 7 h	 2.73a (36:64) 2.73b	85%
9	 2.74	0.3; 4 h	 2.75	86%
10	 2.76	0.4; 12 h	 2.77	80%

a) CH_2Cl_2 as solvent. b) hydrolyzed product. c) purified yield.

Hydrosilation of cholestenone (2.64) gave a diene product 2.65 after hydrolysis. Presumably, elimination of the allylic intermediate generated in the reaction was the cause for the production of this diene product. The catalyst 2.20 tolerated the presence of a hydroxy group, thioether and ester functions in substrates 2.76, 2.66 and 2.74 respectively.

Hydrosilation of ketones catalyzed by rhodium complex 2.20 is also diastereoselective as shown in Table 2.1 and 2.2, which will be discussed in section 2.4.

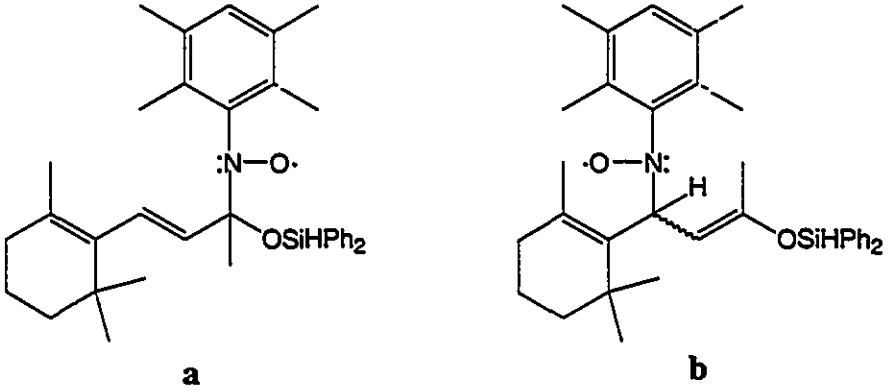
2.2.3 Mechanism

Since the general mechanism for the hydrosilation of alkenes was proposed by Chalk and Harrod (section 1.1.2.3),[43] homogeneous catalysis of hydrosilation has become one of the most important reactions catalyzed by metal complexes.[1,2] The ideas in the original proposal have also been adopted for the hydrosilation of ketones. Many modifications have since been made to accommodate the regiospecificity for the addition of the Si-H bond to the carbonyl group. The silyl group has always ended up bonding to the oxygen atom of the carbonyl group in both 1,2- and 1,4-hydrosilation reactions. Although it has been noted for a long time that the 1,2- and 1,4-regioselectivities depend on the kind of silicon hydrides used in the reactions, none of the proposals were able to intergrate this observation in their mechanisms. In the widely accepted mechanism for the hydrosilation of ketones proposed by Ojima[80a] in 1982, the

role of silicon hydride was not made explicit, and the regioselectivity of the reaction was hardly explained.

2.2.3.1 Ojima's Mechanism of Hydrosilation of Carbonyl Compounds

In adopting the hydrosilation mechanism outlined by Chalk and Harrod to the reduction of carbonyl compounds, Ojima proposed a general mechanism for the hydrosilation of carbonyl compounds as depicted in Chart 2.2.[80a] Using spin trapping technique, Ojima believed that they observed two possible intermediates, **D** and **E** in Chart 2.2, trapped as intermediates **a** and **b** shown in Figure 2.1, during the course of hydrosilation of α,β-unsaturated ketones catalyzed by Wilkinson's catalyst. Their proposal shown in Chart 2.2, indicated that hydrosilation of α,β-unsaturated carbonyl compounds could be regioselective.



a **b**

Figure 2.1

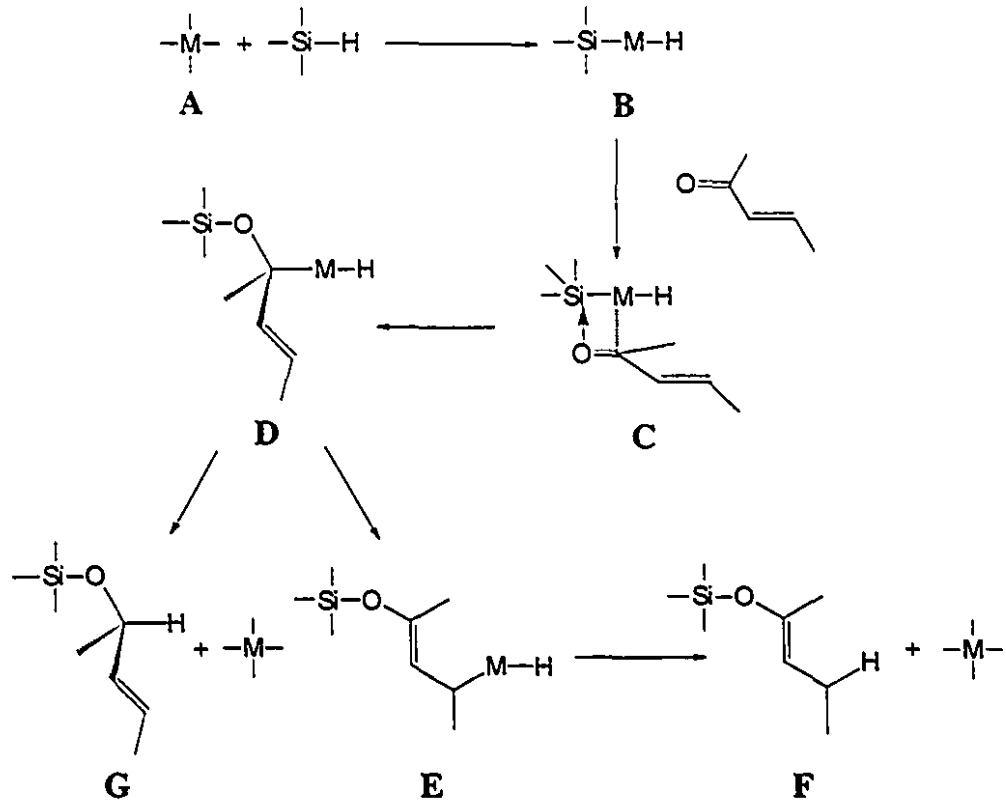


Chart 2.2

The metal complex **A** undergoes insertion into a Si-H bond to give the silyl metal hydride complex **B**. Coordination of **B** with a carbonyl substrate gives complex **C**, where there is a four-membered ring structure. In the next step, the four-membered ring is transformed into an α-metalated silyl ether intermediate **D**. Reductive elimination of **D** gives the 1,2-addition product **G** with regeneration of the metal complex **A** to start another catalytic cycle. Alternatively, **D** can undergo an allylic rearrangement to give the intermediate **E**, which on reductive elimination gives a 1,4-addition product **F**. Spin trapping experiments were used by Ojima to provide evidence for the intermediary of **D** and **E**.

In trying to adopt Ojima's mechanism to the observed regioselection in our experiments, we were puzzled by several points. The most glaring one is the fact that monohydrosilane gave exclusively 1,4-addition, while di- or trihydrosilane resulted in 1,2-addition. It is difficult to understand why the isomerization of **D** to **E** or their subsequent elimination should be drastically altered by the presence (or absence) of a hydrogen on silicon in Ojima's mechanism. Regardless of the role of the silicon moiety in **D** and **E**, the driving force which governs the equilibrium between intermediates **D** and **E** is not clear. On the other hand, the hydride group in the intermediate **C** could migrate to the carbonyl group to form the 1,2-addition product (Chart 2.3). This process could always compete with the 1,4-hydrosilation to prevent the 1,4-addition product being formed exclusively.

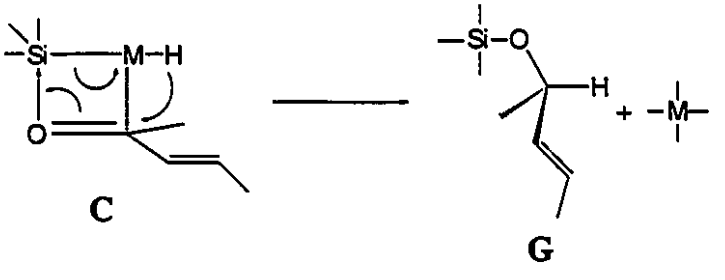


Chart 2.3

The second point is that in a substrate where only 1,2-addition is possible, for example, in the hydrosilation of acetophenone (**2.78**), diphenylsilane (**2.21**; 4 h, rt) was found to react much faster than dimethylphenylsiiane (**2.14**; 96 h, rt) using the same catalyst **2.20**.

Again, this is difficult to reconcile on the basis of the proposed mechanism.

The third point is that when there is an additional substituent in the β-position of the C=C bond, one would expect the isomerization of **D** to **E** to be diminished on both kinetic and thermodynamic grounds, thus reducing the regioselectivity. Our observation is that regioselection was not affected (Table 2.1). We seek, therefore, an alternative explanation to accommodate these observations, at least for complex **2.20** as the catalyst.[80a]

2.2.3.2 New Proposal

For the 1,2-hydrosilation of carbonyl compounds with di- and trihydrosilanes, a possible mechanism is outlined in Chart 2.4. The critical feature in this proposal is that, in the step from the complex **J** to the intermediate **K**, it is the hydride on the silicon that is transferred. When the silane used is a monohydrosilane, this pathway is not available. Complex **J** then rearranges to the intermediate **L**, which reductively eliminates to the silyl ether product **N**. The mechanism accounts for the substantial difference in rates in the 1,2-reduction of carbonyl compounds with diphenylsilane versus dimethylphenylsilane (Chart 2.4).

The oxidative insertion of metal complex **A** to the Si-H bond forms silyl metal hydride complexes, such as **B**, which have been studied by many groups.[163] Our NMR studies indicated that the oxidative insertion step was fairly effective (section 2.3.3).

Furthermore, dimethylphenylsilane reacted with rhodium complex **2.20** in dichloromethane as fast as diphenylsilane. Clearly, the formation of the dimetallic silyl metal hydride complex **B** was not a decisive factor to account for the huge differences in reaction rates when different silicon hydrides were used in the hydrosilation of ketones. Catalyzed by rhodium complex **2.20**, hydrosilation of acetophenone with diphenylsilane took four hours to complete, whereas the same reaction with dimethylphenylsilane required four days for the reaction to finish.

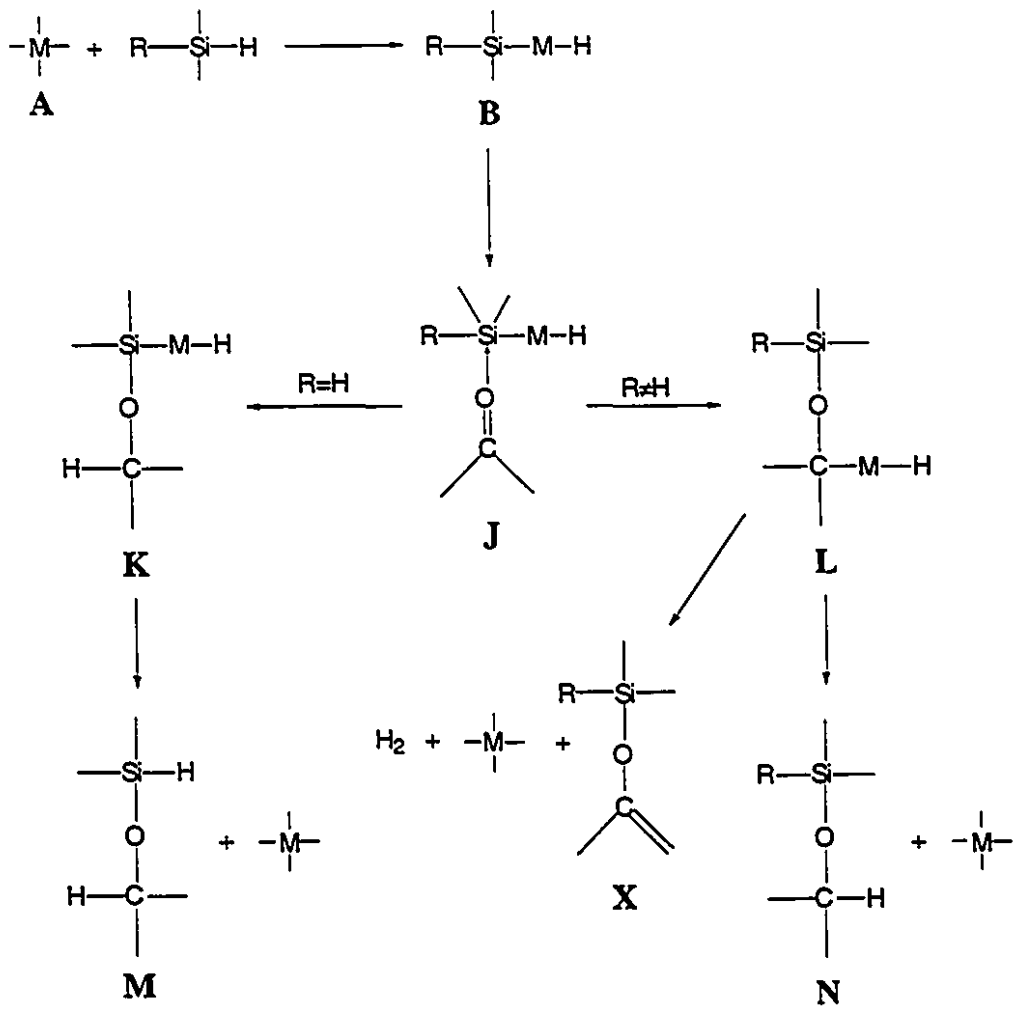
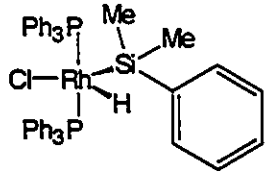


Chart.2.4

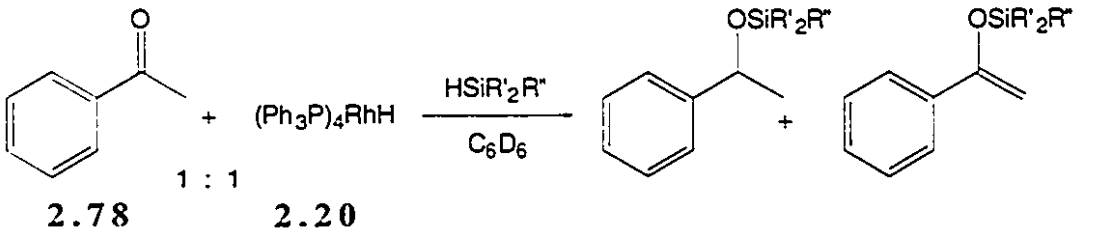
The next step to consider is the coordination of the carbonyl group to the dimetallic complex **B**. The metal center that the incoming carbonyl group should coordinate with in order to induce further reaction (effective coordination) is a key issue. If an effective coordination is to occur at the rhodium center, then the carbonyl group has to rearrange from a σ-complex to a π-complex to explain the regiochemistry. Normally, one would expect the silyl moiety in the dimetallic complex **B** to be activated by the adjacent rhodium metal, which could donate its d orbital electrons to the empty d^0 orbital of silicon. In the dimetallic complex **B'** formed by rhodium complex **2.20** and dimethylphenylsilane in dichloromethane, the methyl group at the silyl moiety had a chemical shift of 0.04 ppm, shifted upfield by 0.31 ppm from the methyl signal of free dimethylphenylsilane, *i.e.* the silyl group has become more electron rich. On the other hand, it is known that a silyl center may coordinate with σ donors to form the penta- or hexacoordinated species, **J**. The postulated pentacoordinate silicon intermediate **J** is therefore compatible with well known organosilicon chemistry. Depending on the silicon hydride used, **J** can react *via* two different pathways. When di- or trihydrosilane is used, the silicon still has at least one hydrogen and the intermediate **J** proceeds to the intermediate **K**. Otherwise, in the absence of a hydrogen on silicon, **J** gives **L**.



B'

Intermediate **L** is probably also responsible for the formation of silyl enol ether,[164] a side product which is often observed in hydrosilation of saturated, enolizable ketones. This can be considered as a β-elimination of **L** to give the silyl enol ether **X**. Although the side product silyl enol ether was previously considered to be derived from ketone enolisation,[21a,165] our studies indicated that this may not be the case. This is based on our observation that alcohols react much faster than ketones with silicon hydride under our catalytic conditions. If ketonic enolization is the pathway for the formation of enol silyl ether, the rapid reaction between the newly formed enol and silicon hydride should drive this side reaction to completion, and **X** should become the predominant product. The fact is that, in most hydrosilation reactions, this side product (**X**) was observed as a minor product. Very often, the silyl enol ether was not observed at all during the course of hydrosilation of ketones.

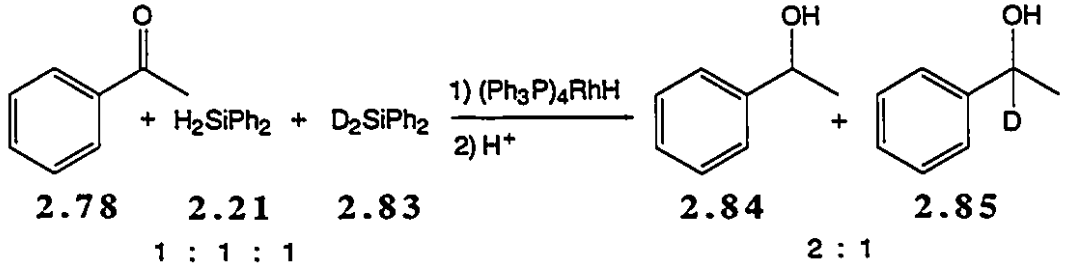
If complex **L** is indeed responsible for the formation of the silyl enol ether side product **X**, using monohydrosilane and/or large amounts of catalyst should favor the side reaction. Hydrosilation of acetophenone (**2.78**) with dimethylphenylsilane (**2.14**) using a stoichiometric amount of rhodium complex **2.20** in benzene, indeed produced up to 50% silyl enol ether **2.80**, in agreement with our prediction. When diphenylsilane (**2.21**) was used under the same conditions, no detectable silyl enol ether was observed (Scheme 2.9).



HSiR'$_2$R": R' = Me, R" = Ph (2.14): 2.79 50 : 50 2.80
R' = Ph, R" = H (2.21): 2.81 100 : 0 2.82

Scheme 2.9

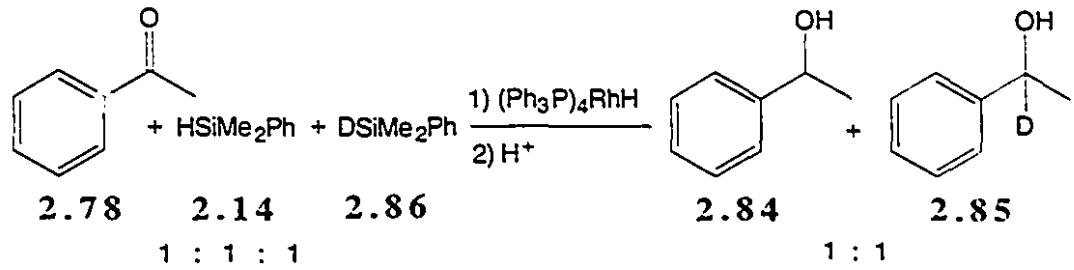
We have examined the kinetic isotope effect in the hydrosilation of acetophenone, and the results appear to be more compatible with the mechanism in Chart 2.4 than with Ojima's mechanism. When dideuteriodiphenylsilane (2.83; 1 mmol) and diphenylsilane (2.21; 1 mmol) were reacted with acetophenone (2.78; 1 mmol) using 2.20 as the catalyst, after hydrolysis, the product *sec*-phenethyl alcohol (2.84 and 2.85) had a ratio of 2 : 1 for proton and deuterium incorporation in the methine carbon. This gives an isotope effect of k_H/k_D = 2 (Scheme 2.10).



Scheme 2.10

In contrast, when deuteriodimethylphenylsilane (2.86; 1 mmol) and dimethylphenylsilane (2.14; 1 mmol) were reacted with acetophenone (2.78; 1 mmol) using catalyst 2.20 under identical

conditions, the product ratio was 1 : 1 for hydrogen and deuterium incorporation, giving a kinetic isotope effect of k_H/k_D = 1 (Scheme 2.11).



Scheme 2.11

The primary kinetic isotope effect depends generally on the strength of the bond cleaved in the rate determining step. The limiting k_H/k_D ratio can be estimated by the equation, k_H/k_D = exp{(hc/2kT)Δv}, where Δv is the difference in the frequencies of the X-H and X-D stretching vibrations.[166] It can be estimated from stretching vibrational frequencies of silanes and rhodium hydrides[156,167] that in a rate-determining step where a Si-H or Rh-H bond is broken, the primary kinetic isotope effect would be k_H/k_D = 3-4. The absence of any significant kinetic isotope effect in the reaction of dimethylphenylsilane with acetophenone suggests that neither the formation of silylhydrido-rhodium complex **B** nor the elimination of **L** to **N** can be the rate-determining step. On the other hand, the observation of a significant primary kinetic isotope effect in the reduction of acetophenone by diphenylsilane is consistent with the possibility that the rate-determining step is the formation of the intermediate **K** from the complex **J**. The observed k_H/k_D of 2 is

similar to the primary kinetic isotope effect observed in the reduction of sulfoxide by silane, where cleavage of a Si-H bond in a four-membered ring transition state is believed to be the rate-determining step.[168]

A possible mechanism for the 1,4-hydrosilation reaction is outlined in Chart 2.5. When the substrate is an α,β-unsaturated carbonyl compound, it complexes with **B** to form **O**, where there is σ-coordination between oxygen and silicon and π-coordination between the metal and the double bond. When the silane used is a di- or trihydrosilane, the hydrogen on silicon migrates as in Chart 2.4 to give **P** and then the 1,2-reduction product, **Q**. On the other hand, when the silane used is a monohydrosilane, complex **O** rearranges with Si-M cleavage to give the intermediate **R**, which then reductively eliminates to give the enol silyl ether **S**. Alternatively the hydride at the metal center of complex **O** can migrate directly to the double bond to form product **S**. In such a mechanism, one can readily rationalize the divergent regioselection of di- versus monohydrosilane (Chart 2.5).

We have also examined the isotope effect of the 1,4-hydrosilation reaction. When deuteriodimethylphenylsilane (**2.86**; 1 mmol) and dimethylphenylsilane (**2.14**; 1 mmol) were reacted with 4,4-dimethyl-2-cyclohexen-1-one (**2.33**; 1 mmol) using catalyst **2.20**, the product enol silyl ether was obtained as a 1 : 1 mixture of the non-deuterated, **2.34**, and the monodeuterated, **2.87**, compounds (Scheme 2.12).

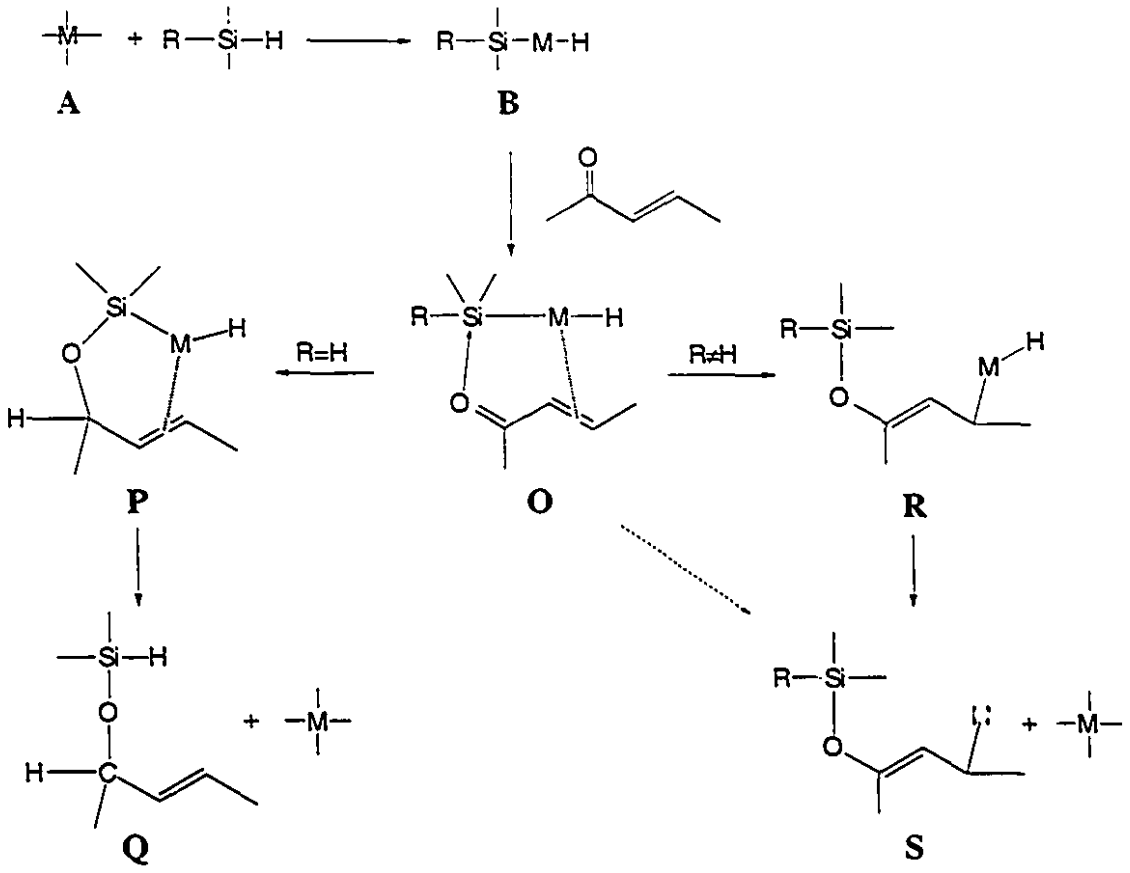
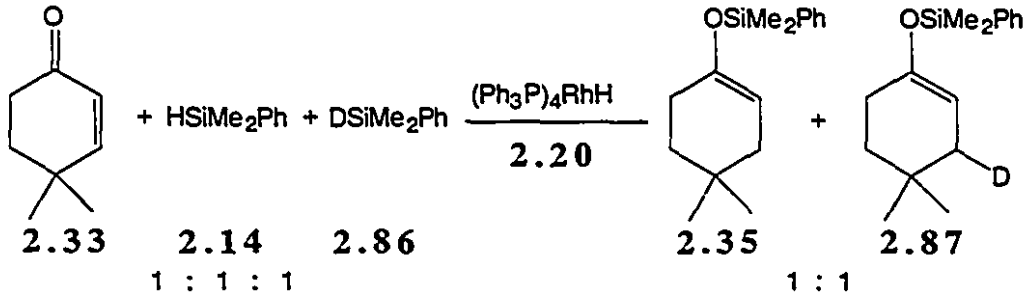


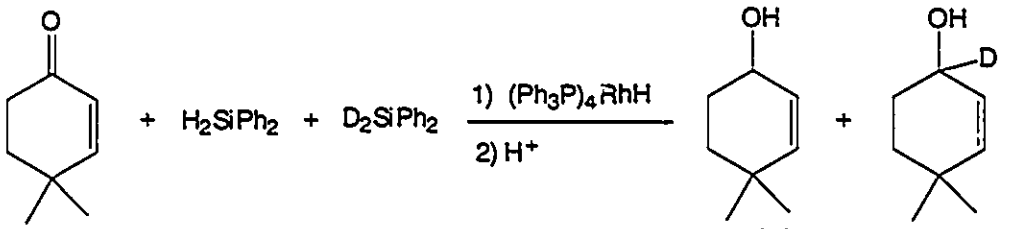
Chart 2.5



Scheme 2.12

The absence of a significant primary kinetic isotope effect suggested that the rate-determining step is either the formation of the complex **O** or the formation of the intermediate **R**. In a kinetic study of the hydrosilation of *tert*-butyl phenyl ketone using a [Rh(1,5-COD)((-)-

DIOP)]$^+ClO_4^-$ catalyst. Kolb and Hetflejs[159b] were able to show that the coordination of the ketone with the silylhydridorhodium species was the rate-determining step in the reaction. It is possible that in the present case the coordination of the α,β-unsaturated ketones with the silylhydridorhodium species **B** to form **O** is the rate determining step. This is also consistent with the absence of a primary kinetic isotope effect in the 1,2-hydrosilation of 4,4-dimethyl-2-cyclohexen-1-one (2.33) with an equal mixture of dideuteriodiphenylsilane and diphenylsilane using complex 2.20 as catalyst where a 1 : 1 mixture of 1-deuterio-4,4-dimethyl-2-cyclohexen-1-ol (2.89) and 4,4-dimethyl-2-cyclohexen-1-ol (2.88) was obtained (Scheme 2.13).



2.33 2.21 2.83 (1 : 1 : 1) 2.88 2.89 (1 : 1)

Scheme 2.13

2.2.3.3 NMR Studies

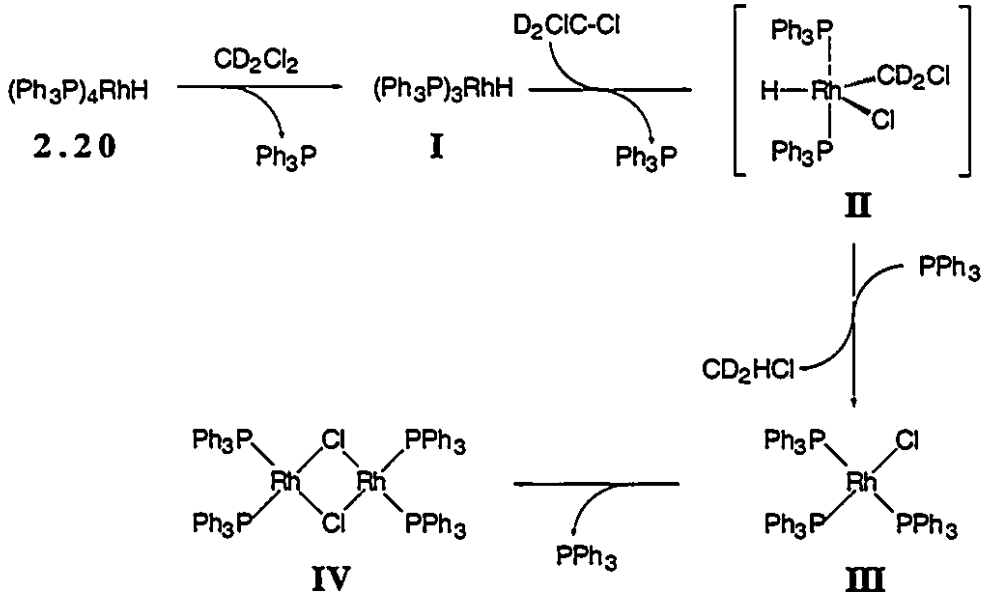
NMR studies of catalytic hydrosilation of ketones could provide crucial and decisive information concerning reaction intermediates. It is sometimes possible to deduce a reaction pathway through the information gathered from NMR studies. In a catalytic reaction, active intermediates which may exist in trace amounts in a catalytic

system, are responsible for product generation. They can be distinguished from the inactive intermediates which may be found in the reaction and are not responsible for the desired product. The active intermediates often have lifetimes shorter than the limits of the NMR time scale. It is therefore not always possible to follow a catalytic process using existing NMR techniques. Nevertheless, NMR studies can provide useful information concerning reaction intermediates and products.

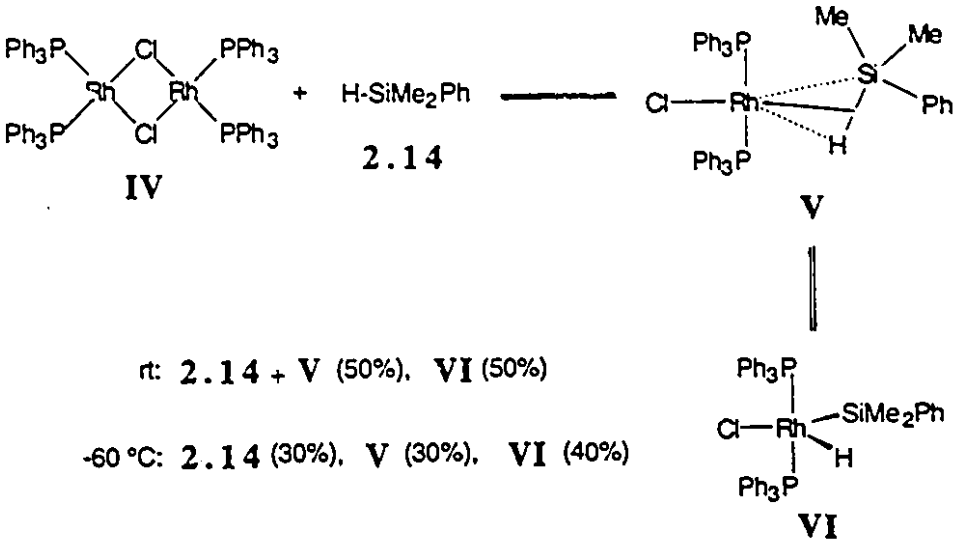
In a solution, such as benzene, toluene and CH_2Cl_2, complex **2.20** [hydridotetrakis(triphenylphosphine)rhodium(I)] mainly exists as $[(Ph_3P)_3RhH]$ (**I**).[154b,169] Complex **I** was relatively stable in non-halogenated solvents, such as benzene and toluene [^{1}H (Rh-H): δ = -8.119 ppm, d, J = 12.4 Hz (C_6D_6); δ = -8.057 ppm, d, J = 12.5 Hz (toluene-d_8)]. However, in the halogenated solvent, CD_2Cl_2, complex **I** [^{1}H (Rh-H): δ = -8.545 ppm, d, J = 14.0 Hz] reacted with the solvent to form Wilkinson's complex, $(Ph_3P)_3RhCl$ [$^{31}P\{^1H\}$: δ = 31.807 ppm, dd, J_{RhP} = 143.0 Hz, J_{PP} = 38.4 Hz 2P; 48.496 ppm, dt, J_{RhP} = 190.1 Hz, J_{PP} = 38.4 Hz 1P],[170] and reduced product chloromethane [^{1}H (CD_2HCl): δ = 2.990 ppm, m, J = 1.5 Hz] (Scheme 2.14).

Addition of stoichiometric amounts of a monohydrosilane, dimethylphenylsilane (**2.14**), to a solution of complex **2.20** in deuterated dichloromethane at room temperature instantly generated the silyl rhodium hydride complex **VI** (50 %) [^{1}H (Rh-H): δ = -15,212 ppm, dt, J_{RhH} = 23.0 Hz, J_{PH} = 15.0 Hz. $^{31}P\{^1H\}$: δ = 37.803 ppm, d, J_{RhP} = 125.8 Hz].[171] The other half of the starting silane remained in a fast equilibrium with complex **V**, since the hydride Si-H and methyl Si-CH_3 signals became broad singlets [^{1}H (Si-H): δ =

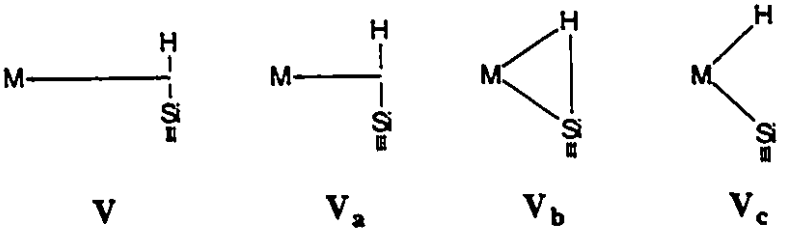
4.405 ppm (br) s; (Si-CH_3): 0.349 ppm, s]. Upon cooling the mixture to -60 °C, the three components of this equilibrium were observed clearly. About 30% starting silane **2.14** remained intact [^{1}H (Si-H): δ = 4.332 ppm, sept, J = 3.5 Hz; (Si-CH_3): 0.308 ppm, d, J = 3.5 Hz], another 40% starting silane **2.14** was converted to the silyl rhodium hydride complex **VI** [^{1}H (Rh-H): δ = -15.272 ppm, dt, J_{RhH} = 23.0 Hz, J_{PH} = 15.0 Hz; (Si-CH_3): δ = -0.126 ppm, s], and the remaining 30% silane may belong to the intermediary **V**, in which the Si-H was a η^2 σ-donor towards the rhodium center of complex **IV** [^{1}H (Si-H): δ = 4.475 ppm (br) s; (Si-CH_3): 0.273 ppm, s; Scheme 2.15]. In all three known forms of Si-H metal complexes $\mathbf{V_a}$-$\mathbf{V_c}$,[63b,172] the proton signals of the Si-H were normally shifted upfield to the hydride region. While in intermediate **V**, the proton signal Si-H shifted downfield, opposite to that in complexes $\mathbf{V_a}$-$\mathbf{V_c}$ (Figure 2.2).



Scheme 2.14



Scheme 2.15



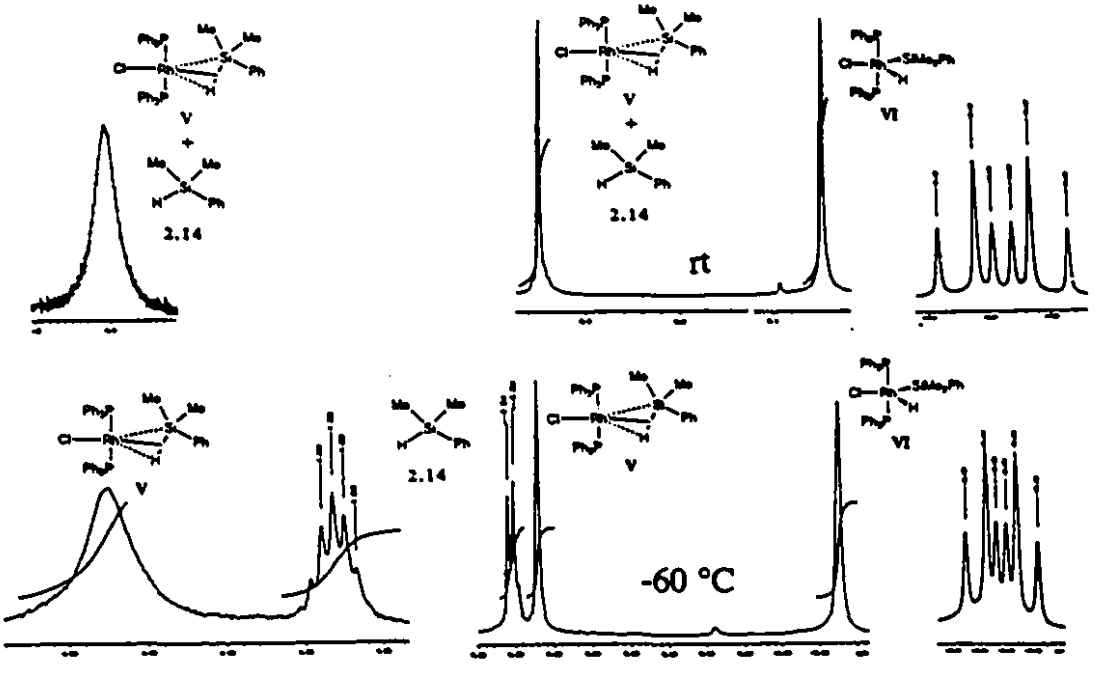


Figure 2.2

Probably, there is another form of η^2 Si-H metal interaction prior to the formation of complex $\mathbf{V_a}$ as depicted in Figure 2.2. This type of interaction is very weak, and is an intermediary between free Si-H with **IV** and complex $\mathbf{V_a}$ in Figure 2.2.

The silyl rhodium hydride complex **VI** was relatively stable at room temperature. The hydride (Rh-H) signals (doublet of triplets) collapsed into a doublet when ^{31}P decoupling was used [$^{1}H\{^{31}P\}$ (Rh-H): δ = -15.215 ppm, d, J_{RhH} = 22.5 Hz], which indicated that there were two phosphine ligands at the metal center of complex **VI**. The number of hydride groups at the metal center was unambiguously detrmined by $^{31}P\{^{1}H\}$ NMR experiments partial decoupled at the phenyl region in the corresponding ^{1}H NMR. The doublet of the phosphine ligands in $^{31}P\{^{1}H\}$ NMR were split into a doublet of doublets [$^{31}P\{^{1}H\}_{partial}$: δ = 37.80 ppm, dd, J_{RhP} = 125.8 Hz, J_{HP} = 14.9 Hz], indicating that there is only one hydride group present in the rhodium center of complex **VI**. The symmetrically substituted phosphine and proton (M-H) signals suggested that complex **VI** could be one of the isomers depicted in Figure 2.3, but probably not isomer $\mathbf{VI_c}$. The latter has its hydride and silyl group *trans* at the metal center. After the oxidative insertion of Si-H with complex **IV**, the silyl and the hydride groups are more likely *cis* at the metal center in the newly formed complex **VI**. In fact, the NMR spectra could be a result of an equilibrium of all the possible isomers $\mathbf{VI_a}$-$\mathbf{VI_d}$ formed with the assistance of solvent (**VI'**, Figure 2.3).

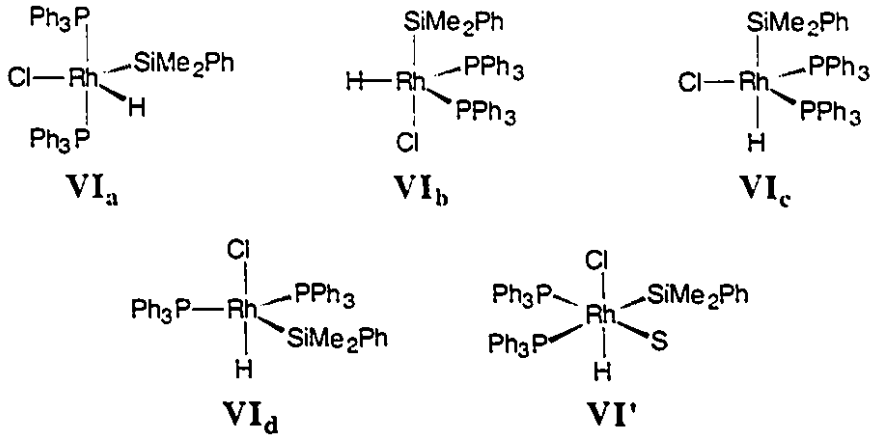
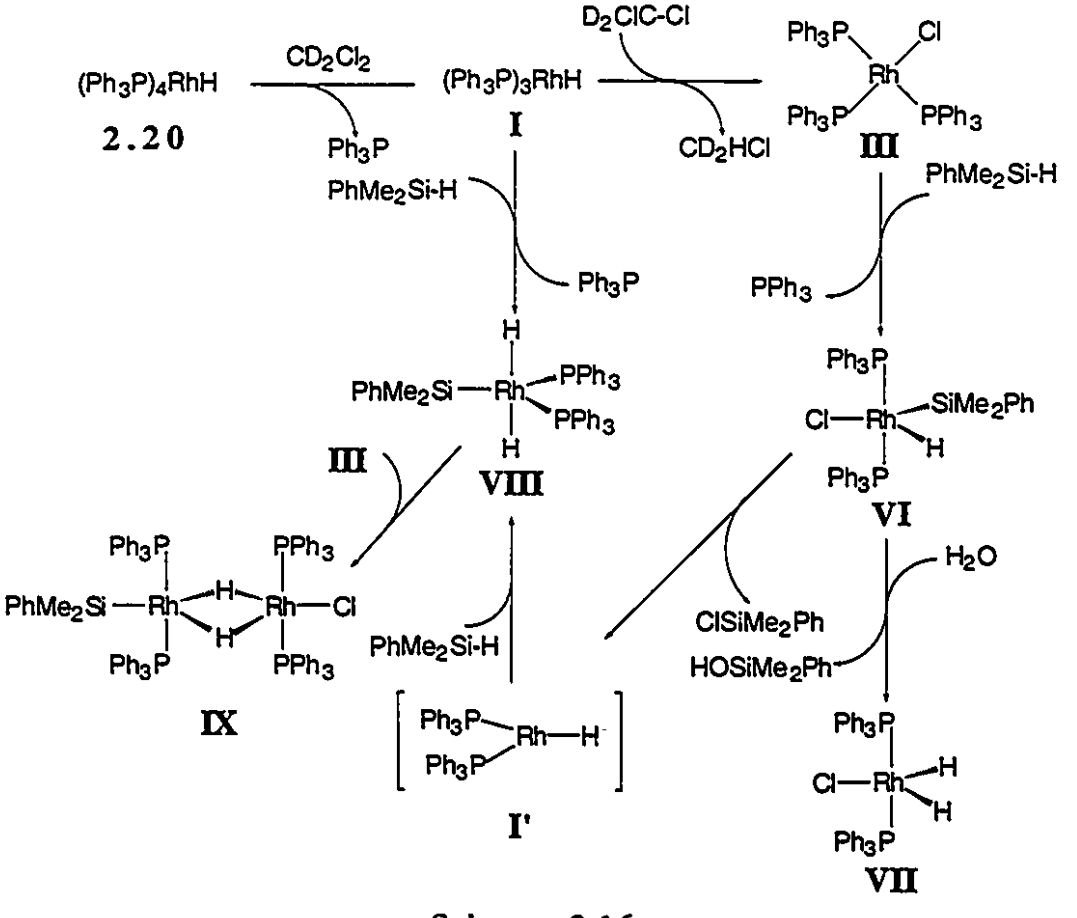


Figure 2.3

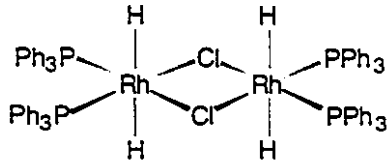
There were two sets of ill-resolved hydride peaks at -9.78 ppm (d) and -17.38 ppm (s), which had a ratio of 1 : 1. These signals were due to rhodium dihydride **VII**.[171d,173] The presence of small amounts of water in the system was probably the main cause for the generation of this rhodium dihydride complex **VII**.[171d] Apparently, this rhodium dihydride **VII** was inactive in the reduction of carbonyl compounds for it survived more than one week in the presence of excess acetophenone (Scheme 2.16).

When the reaction mixture was allowed to stand at room temperature for 2-3 days, complex **VI** disappeared. Instead, a new metal hydride species was formed. The hydride signals of this new complex showed up as a doublet of triplets very similar to that of complex **VI**, except that the former has its chemical shift further upfield [^{1}H (Rh-H): δ = -19.890 ppm, dt, J_{RhH} = 22.0 Hz, J_{PH} = 17.0 Hz; ^{31}P{^{1}H}: δ = 37.560 ppm, d, J_{RhP} = 117.4 Hz]. Surprisingly, two hydride groups were found in complex **VIII** *via* ^{31}P{^{1}H}$_{partial}$ NMR. The splitting pattern of the ^{31}P NMR signals changed from a simple doublet to a doublet of triplets [^{31}P{^{1}H}$_{partial}$: δ = 37.56 ppm, dt, J_{RhP} =

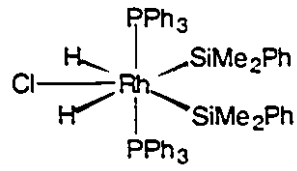
117.4 Hz, J_{HP} = 17.0 Hz]. This new complex was not dimer **X**, $[(Ph_3P)_2RhH_2Cl]_2$, derived from complex **VII**.[173] The new complex was unlikely the heptavalent rhodium(V) complex **XI**, as its structural nonrigidity would not result in signals with fine splitting (Figure 2.4).[174] The new rhodium hydride was probably complex **VIII**,[175] formed from the oxidative insertion of the Si-H bond by complex **I** or **I'**. This complex **VIII** was quite stable in the presence of acetophenone in the reaction mixture.



Scheme 2.16



X



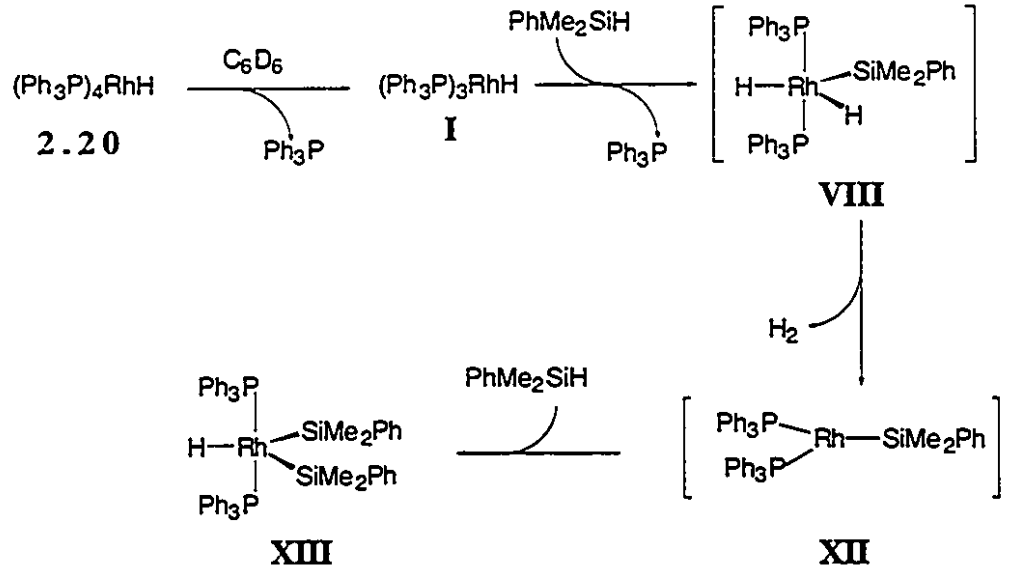
XI

Figure 2.4

There were small amounts of other hydrides formed after the reaction mixture stood at room temperature for several days. One of them, had a triplet of multiplets splitting pattern [^{1}H (Rh-H): δ = -10.823 ppm, tm, J_{RhH} = 75.0 Hz, J_{PH} = 9.5 Hz], assigned as complex **IX** due to the unsymmetric substitution at the two rhodium centers. If the two rhodium centers in the complex were symmetrically substituted, the splitting patern should be a clear triplet of quintets.[176]

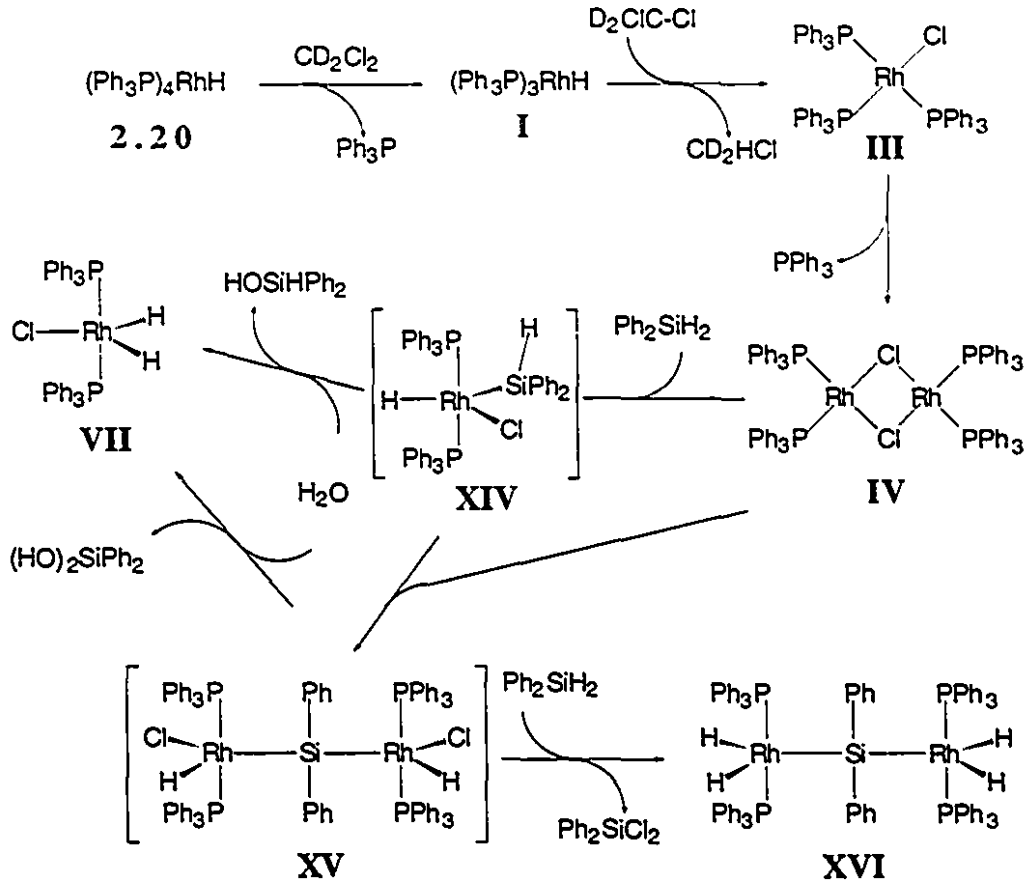
Complex **VIII** was thought to be the major product of oxidative insertion of the Si-H bond by complex **I** in benzene. However, addition of dimethylphenylsilane to a solution of complex **2.20** in deuterated benzene resulted in a doublet of triplets in the hydride region [^{1}H (Rh-H): δ = -14.575 ppm, dt, J_{RhH} = 22.5 Hz, J_{PH} = 15.5 Hz], which was clearly not the same as that of complex **VIII**. $^{31}P\{^1H\}$ partial decoupling experiments revealed that only one hydride group was present at the rhodium center [$^{31}P\{^1H\}$: δ = 37.34 ppm, d, J_{RhP} = 127.1 Hz; $^{31}P\{^1H\}_{partial}$: dd, J_{HP} = 15.5 Hz]. Complex **VIII** may be formed at the very beginning of the reaction, but in benzene it quickly decomposed to complex **XII** and molecular hydrogen. The oxidative insertion of the Si-H bond by the newly formed species **XII**

gave complex **XIII**, which was a disilyl rhodium hydride complex (Scheme 2.17).



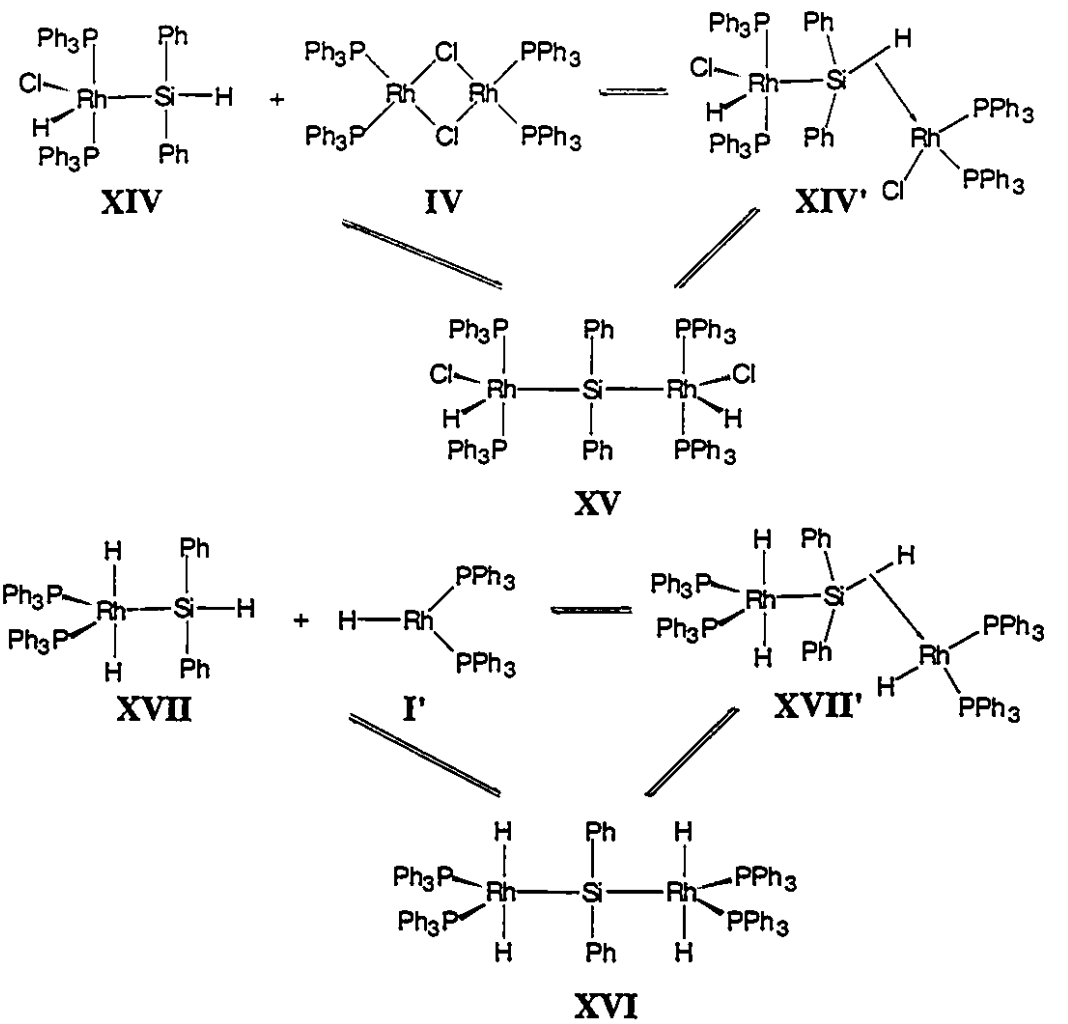
Scheme 2.17

The reactions between dihydrosilane and complex **2.20** were slightly more complicated than that of monohydrosilane with the same complex in deuterated dichloromethane. The oxidative insertion of the Si-H bond by the dimeric complex **IV** initially formed a species **XIV** [^{1}H (Rh-H): δ = -15.103 ppm, dt, J_{RhH} = 23.0 Hz, J_{PH} = 15.0 Hz] similar to complex **VI**, which was quickly converted to a new complex in less than 5 minutes to form complex **IIV** [^{1}H (Rh-H): δ = -14.493 ppm, dt, J_{RhH} = 24.0 Hz, J_{PH} = 14.5 Hz]. The former complex was assigned as complex **XIV** as shown in Scheme 2.18, in which the rhodium moiety is the same as that of complex **VI**, but differing only in the silyl moiety (Scheme 2.18).



Scheme 2.18

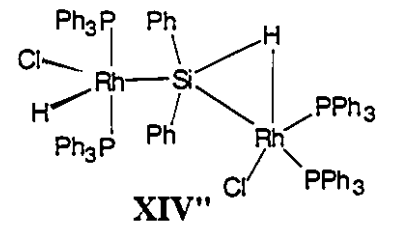
The hydride Rh-H could be coupled to the extra hydride group at the silicon center of the silyl rhodium hydride **XIV** to cause further splitting of the M-H hydride signals.[172h,177] But in our case, the hydride signals were not split further by this hydride. This spin-spin coupling was not observed even at -60 °C. The implication of this observation was that the equilibrium between complex **XIV** and **XIV'** was so fast that no extra coupling is observed (Scheme 2.19).



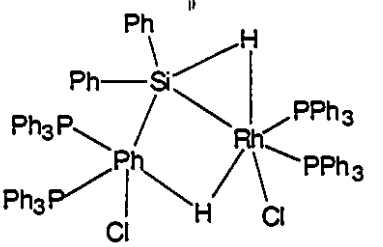
Scheme 2.19

Since complex **XIV'** may have a similar structure as complex **XIV"**, which equilibrates with **XIV'"**, complex **XIV** may actually have a similar structure as the reported complex **XXVII** (Figure 2.5).[178] The latter has an interesting bi-rhodium-μ^2-H-μ-Si structure (Figure 2.5).

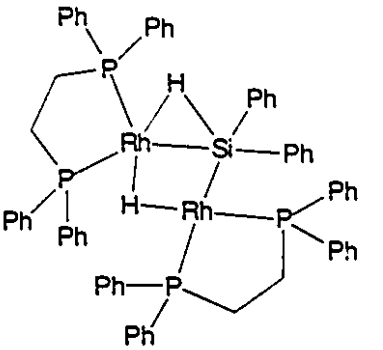
At low temperature (-60 °C), complex **XIV** was the major product (**XIV** : **XV** = 92 : 8). At room temperature complex **XIV** quickly vanished, and only **XV** was observed. By analogy, complex **XVII** could also be equilibrating with complex **XVII'** (Scheme 2.19).



XIV"



XIV"'

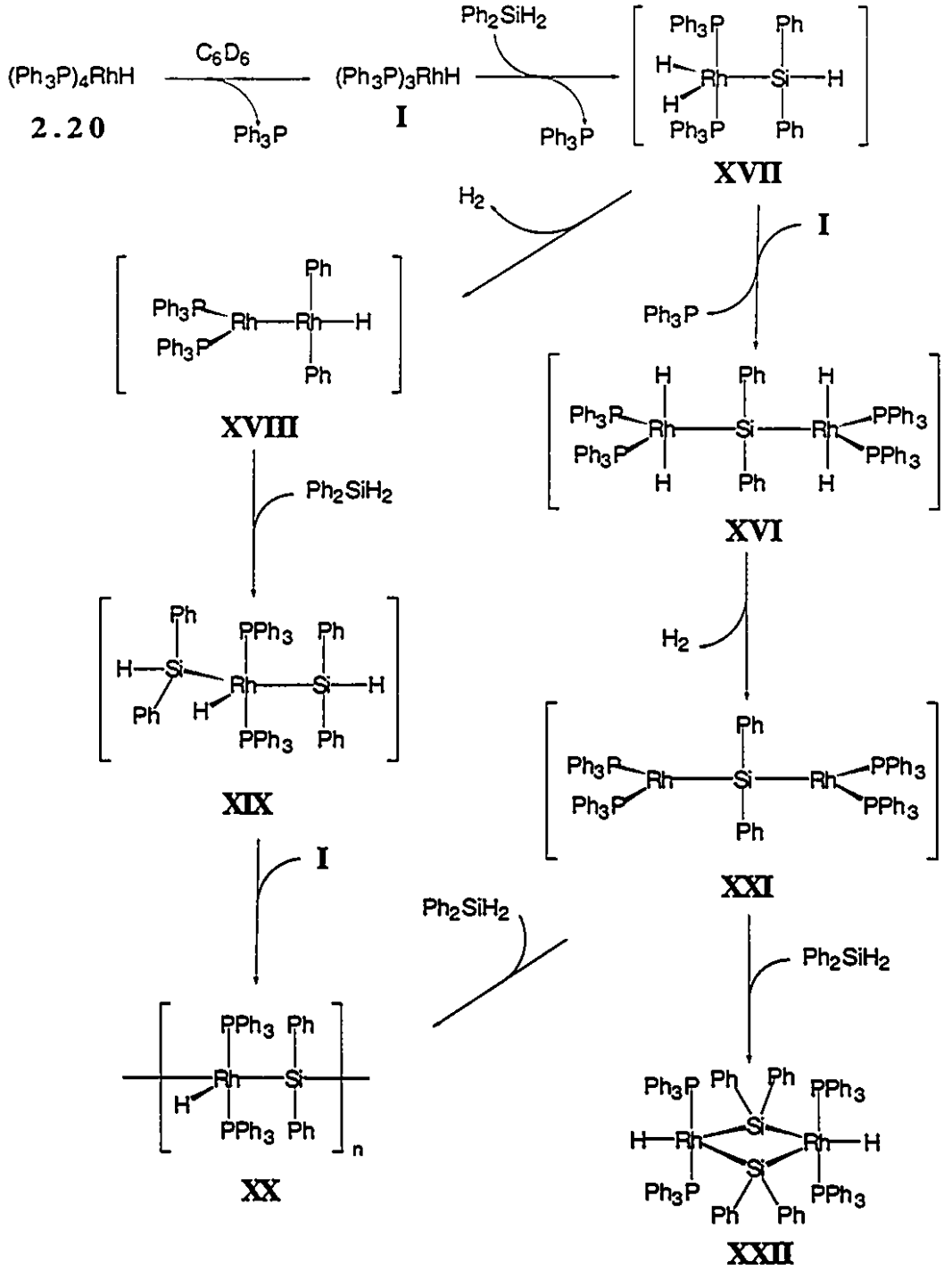


XXVII

Figure 2.5

The dihydride complex **XVI** appeared to be inactive towards the reduction of carbonyl groups since it was stable in the presence of acetophenone. Again, the rhodium dihydride complex **VII** was always present in the reaction mixture.

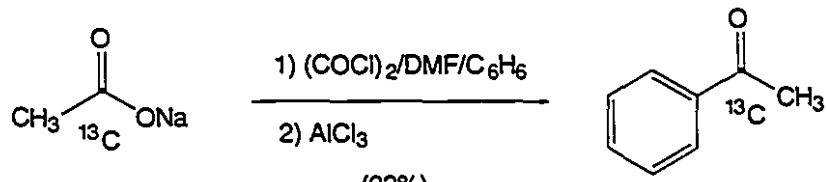
The reaction of dihydrosilane with complex **2.20** in benzene was quite complicated and may involve polymeric silyl rhodium hydride complexes. Except for a set of well resolved hydride signals observed in the hydride region with low intensities [^{1}H (Rh-H): δ = -13.785 ppm, dt, J_{RhH} = 22.5 Hz, J_{PH} = 15.0 Hz], there were no other obvious signals. By analogy with the results from the reactions of monohydrosilane with complex **2.20** in benzene, the observed hydride signals were probably due to small amounts of complex **XXII** formed in the reaction mixture. The other complex may primarily involve polymeric rhodium hydride complexes **XX** (Scheme 2.20).



Scheme 2.20

Hydrosilation of acetophenone (**2.78**) was carried out in all the previously mentioned systems. To facilitate observations, C(1)-^{13}C

labeled acetophenone, **2.91**, was used in some of the experiments. The C(1)-^{13}C labeled acetophenone was made *via* the C(1)-^{13}C labeled acetyl chloride. Formation of acid chloride in benzene using oxalyl chloride/DMF,[179] followed by addition of $AlCl_3$[180] gave the ^{13}C labeled acetophenone in good yield (92%; Scheme 2.21).



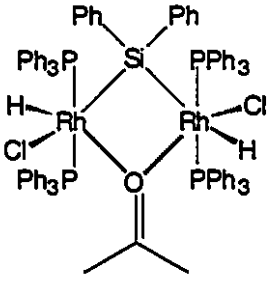
2.90 **2.91**

Scheme 2.21

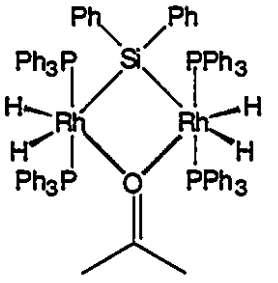
The use of C(1)-^{13}C labeled acetophenone (**2.91**) could help to detect whether the carbonyl group was coordinated with the silyl metal hydride species from ^{13}C NMR experiments. Should the proposed coordination occur, the splitting pattern of the C=O signal in ^{13}C NMR could distinguish whether the carbonyl group was attached to the silyl or rhodium center. Further information on the type of coordination (σ or π) could be revealed.

Unfortunately, the addition of C(1)-^{13}C labeled acetophenone (**2.91**) to the mixture of catalyst and silane did not cause any detectable changes in chemical shifts of the carbonyl group in ^{13}C NMR, or in ^{1}H NMR for the signals of silylmetal hydride. Presumably, the detected complexes were already in their equilibria with solvent and addition of small amounts of acetophenone did not affect the chemical shifts of these complexes. Alternatively, the reactions were too fast to be detected on the normal NMR time scale.

It is interesting to note that the dihydride rhodium complexes **VII**, **VIII** and **XVI** did not seem reactive towards the reduction of carbonyl groups. Although the hydride groups are necessary for the reduction of carbonyl groups, they are not the only requirement for the the reaction to proceed. The silyl moiety may play a decisive role in the complexes. On the other hand, hydrosilation of ketones proceeds with great variation in rates depending on the different kinds of silicon hydrides used. The cause of this rate difference was not quite clear. In the case of diphenylsilane, if complex **XV** is responsible for the great rate acceleration *via* intermediate **XXIII**, then intermediate **XXIV** should react much faster than the former as more hydrides are present at the rhodium centers. The latter seemed to be inactive for the reduction of carbonyl groups (Figure 2.6).



XXIII



XXIV

Figure 2.6

There is some concern that a heptavalent rhodium(V) species is involved in hydrosilation.[51,159c-e,181] As the oxidative insertion of the Si-H bond of mono- or di- hydrosilane with rhodium complexes occurs quite readily, both can easily form heptavalent rhodium(V). It is very difficult to rationalize that the rate differences in using

different silicon hydrides were actually caused by the heptavalent rhodium(V) species.

Without a silyl moiety present at the metal hydrides, complexes 2.20, I, II and VII are all inactive in the reduction of carbonyl groups. Comparing the silyl metal hydride complexes to $LiAlH_4$ for the reduction of carbonyl compounds, the function of the silyl group may be similar to the lithium cation in the corresponding metal hydrides. Weakening the Lewis acidity of the lithium ion in $LiAlH_4$ led to a reduced reactivity of the complex towards carbonyl groups.[182] It is possible that the silyl moiety plays a similar role in reducing carbonyl compounds in the silyl metal hydride complexes.

The reaction of monohydrosilane, diphenyl(1-phenylethoxy)-silane (2.92), with complex 2.20 generated some interesting results. Addition of monohydrosilane 2.92 to a solution of complex 2.20 in deuterated dichloromethane led to the oxidative insertion of the RO-Si bond by metal complex IV and formed a RO-M-SiX structure. In the $PhCH(ORhSi)CH_3$ moiety of the newly formed complex both proton signals of the methine and methyl groups shifted upfield [^1H ($PhCH(ORhSi)CH_3$): δ = 4.314 ppm, q, J = 6.5 Hz; 0.476 ppm, d, J = 6.5 Hz]. Compared with that of the starting silane [^1H ($PhCH(OSi)CH_3$): δ = 5.011 ppm, q, J = 6.5 Hz; 1,501 ppm, d, J = 6.5 Hz], the proton signals of the newly formed complex shifted ca. 0.7 and 1.0 ppm upfield for the methine and methyl groups, respectively. This was a strong indication that the rhodium metal was attached directly at the oxygen atom of the $PhCH(ORhSi)CH_3$ species.[183] Although metal complexes inserting into Si-R bonds (other than Si-H bonds) is a known-phenomena,[184] the observation of oxidative insertion of a Si-

OR bond by metal complexes was quite surprising, as the Si-OR bond is much stronger than Si-H and Si-R bonds (Scheme 2.22, Figure 2.7).

2.92 XXV

Scheme 2.22

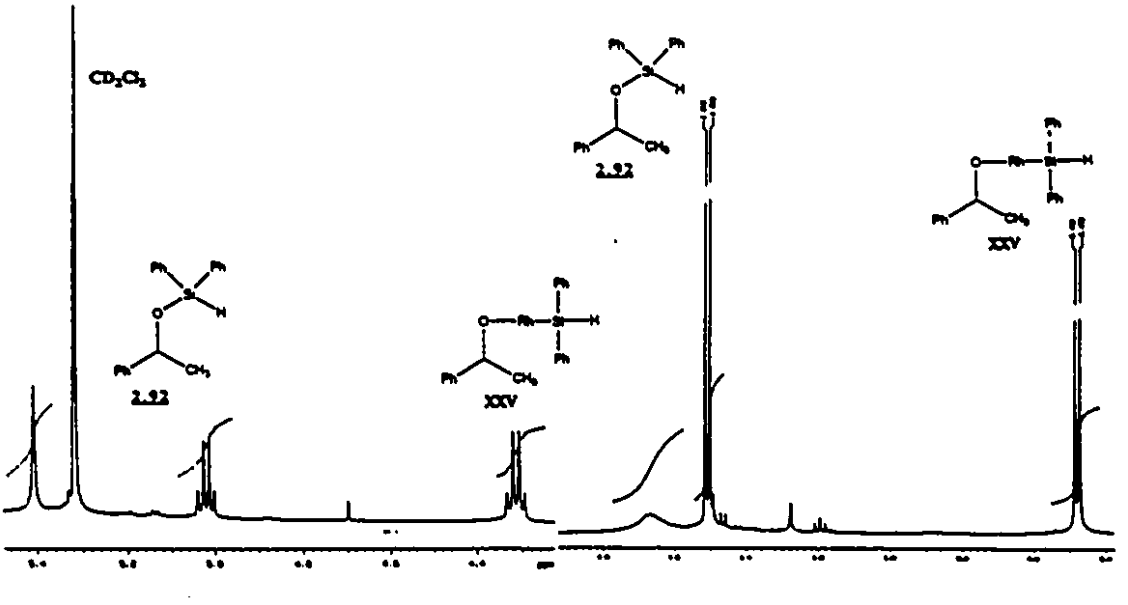


Figure 2.7

The alkoxy group bound directly to the rhodium metal center was not observed in all the reactions of the hydrosilation of acetophenone mentioned above. This implies that the RO-Rh moiety was not generated in the hydrosilation of acetophenone under these reaction conditions, including different kinds of silicon hydrides,

solvents etc. In other words, the direct formation of RO-Rh type complexes *via* hydride migration from the metal center to the carbonyl group may not be the pathway for hydrosilation of ketones (Chart 2.6).

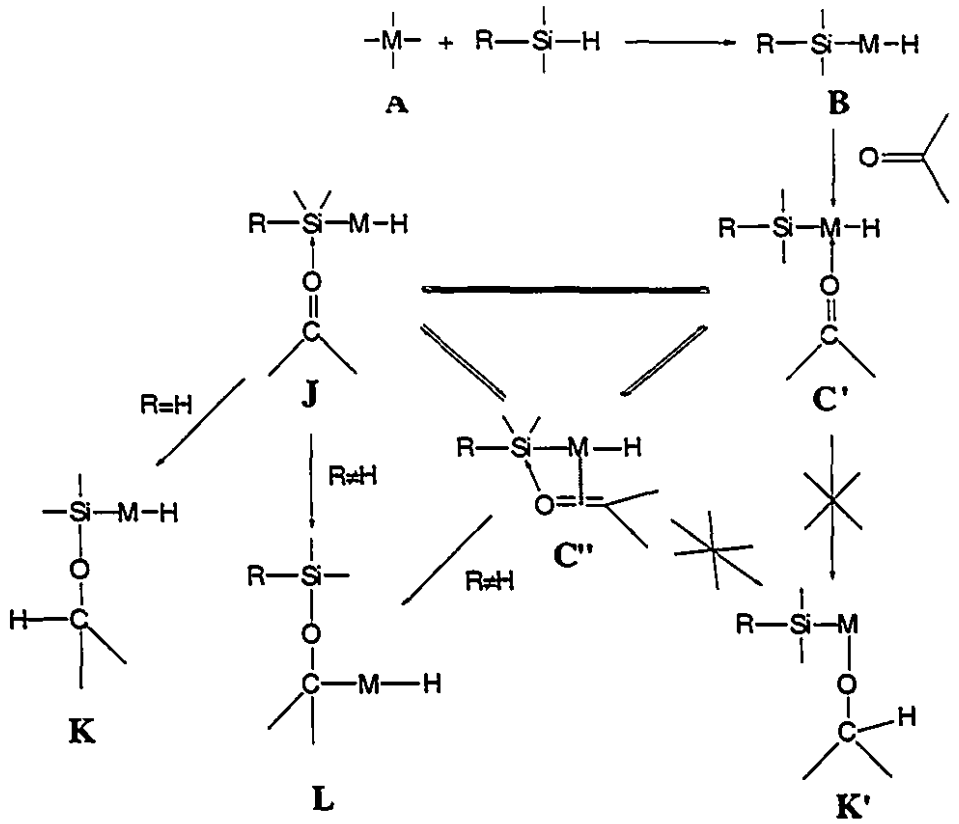


Chart 2.6

The observation mentioned above seems to disfavor the possible dirhodium carbonyl intermediate **XXIII**, which could be responsible for the greater reaction rates. After one hydride migrated from one of the rhodium centers, an alkoxy rhodium complex (RO-RhSi) was formed, which was not observed in all cases of hydrosilation of acetophenone. Since both **C'** and **C"** to **K'** pathways do not occur, the remaining possibilities are the pathways

from **C"** or **J** ($R \neq H$) to **L**, or the pathway from **J** ($R = H$) to **K** (Chart 2.6). As both pathways **C"** and **J** ($R \neq H$) to **L** do not explain the rate differences between mono- and di- hydrosilane created in the hydrosilation of ketones, the pathway **J** ($R = H$) to **K** has again some advantages over the other pathways. On the other hand, the alternative species, $PhCH(OSiX)CH_3$ (**K**; X = Rh, O etc), were observed in all hydrosilations of acetophenone mentioned above, regardless of the different solvents and silanes used in the reactions [^1H ($PhCH(OSiX)CH_3$, X = Rh, O etc): $PhMe_2SiH/CD_2Cl_2$: δ = 4.876 ppm, q, J = 6.5 Hz, 1.458 ppm, d, J = 6.5 Hz; Ph_2SiH_2/CD_2Cl_2: δ = 4.871 ppm, q, J = 6.5 Hz, 1.455 ppm, d, J = 6.5 Hz; $PhMe_2SiH/Ph^{13}C(O)CH_3/C_6D_6$: δ = 4.621 ppm, dq, J_{CH} = 142.5 Hz, J_{HH} = 6.5 Hz, 1.348 ppm, dd, J_{CH} = 4.5 Hz, J_{HH} = 6.5 Hz; $Ph_2SiH_2/Ph^{13}C(O)CH_3/C_6D_6$: δ = 4.995 ppm, dq, J_{CH} = 142.0 Hz, J_{HH} = 6.5 Hz, 1.465 ppm, dd, J_{CH} = 4.0 Hz, J_{HH} = 6.5 Hz etc]. Whether this type of substructure was formed directly from pathway **J** to **K**, or *via* reductive elimination of intermediate **L** was not quite clear at this stage.

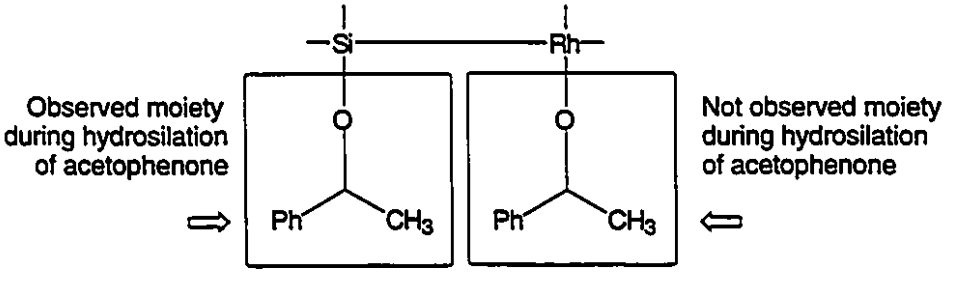


Figure 2.8

The conclusions made from the above studies were that the oxidative insertion of the Si-H bond by rhodium complexes was rapid

and reversible, regardless of the kind of silicon hydrides used in the reactions. Hydrosilation of ketones may not proceed *via* pathways **C'** to **K'** or **C"** to **K'** (Chart 2.6). For the same reason, the di- or poly-rhodium hydride complex, **XV** or **XX** may not be the key intermediates in the hydrosilation of ketones. Although there was no evidence for the actual active intermediate(s), the above observations imply that intermediates with H-Si-M-H substructure, such as **XIV** and **XIX**, can be the active species responsible for the great reaction rate enhancement in the course of hydrosilation of carbonyl groups with dihydrosilane.

2.3 Stereoselective Hydrosilation of Ketones

2.3.1 Diastereoselective Hydrosilation of Ketones

Hydrosilation of ketones catalyzed by hydridotetrakis-(triphenylphosphine)rhodium(I) (**2.20**) proceeds with good to excellent diastereoselectivities. Comparing complex **2.20** with Wilkinson's catalyst, the subtle difference between the hydride and the chloride groups greatly affects their catalytic activities propably through a combination of steric and electronic factors. Although hydride has smaller electronegativity than that of chloride, it has no lone electron pair to contribute to the empty d orbitals of the metal center as chloride does in the corresponding complexes. As a consequence, the rhodium metal in the Wilkinson's complex might

not have the same affinity to form π-complexes with carbon-carbon double bonds as that of **2.20** due to these electronic and steric differences. This partially accounts for the differences in regioselectivities for these complexes. The steric and electronic properties of complex **2.20** also affected diastereoselectivities in both 1,2- and 1,4-hydrosilation of ketones.

The reduction of carvone (**2.62**) by diphenylsilane (**2.21**) catalyzed by complex **2.20** generated *cis*- and *trans*- carveol (**2.63**) in a ratio of 65 : 35, similar to the results obtained by using chiral (+)-DIOP-Rh as a catalyst.[93a] The reduction of 4-*tert*-butyl-cyclohexanone (**2.70**) led to two diastereomers, **2.71a,b**, with a ratio of 84 : 16 (*trans : cis*), which is better than most reported results.[185] The major *cis*-product **2.63** from carvone (**2.62**) and the major *trans* product **2.71a** from substrate **2.70**, were the results of axial attack during the course of hydrosilation, which implied that stereoelectronic factors were more important than steric factors in the hydrosilation of ketones with diphenylsilane (**2.21**) mediated by complex **2.20**. A bulky metal hydride usually attacks the carbonyl group from the less hindered equatorial direction,[186] while less bulky reducing reagents approach the C=O bond *via* the stereoelectronic favored axial direction.[187] This is explained by the argument that the σ–π* interaction distorts the π* orbital of the carbonyl group such that the largest density of the π* orbital lies to the side of the σ orbital of the carbon-carbon bond as shown in Chart 2.7.[188] Thus, hydrosilation of compounds **2.62** and **2.70** by diphenylsilane (**2.21**) catalyzed by $(Ph_3P)_4RhH$ (**2.20**), appeared to prefer the stereoelectronic controlled axial attack to form predominantly *cis*-

2.63 and *trans*-2.71a, respectively. Interestingly, substrate 2.70 has about twice as much σ–π* interactions as that in carvone (2.62), and the hydrosilation of the former substrate produced a diastereomeric excess (68% de) which is about twice as high as that in the reduction of carvone (2.62; 30% de) (Chart 2.7).

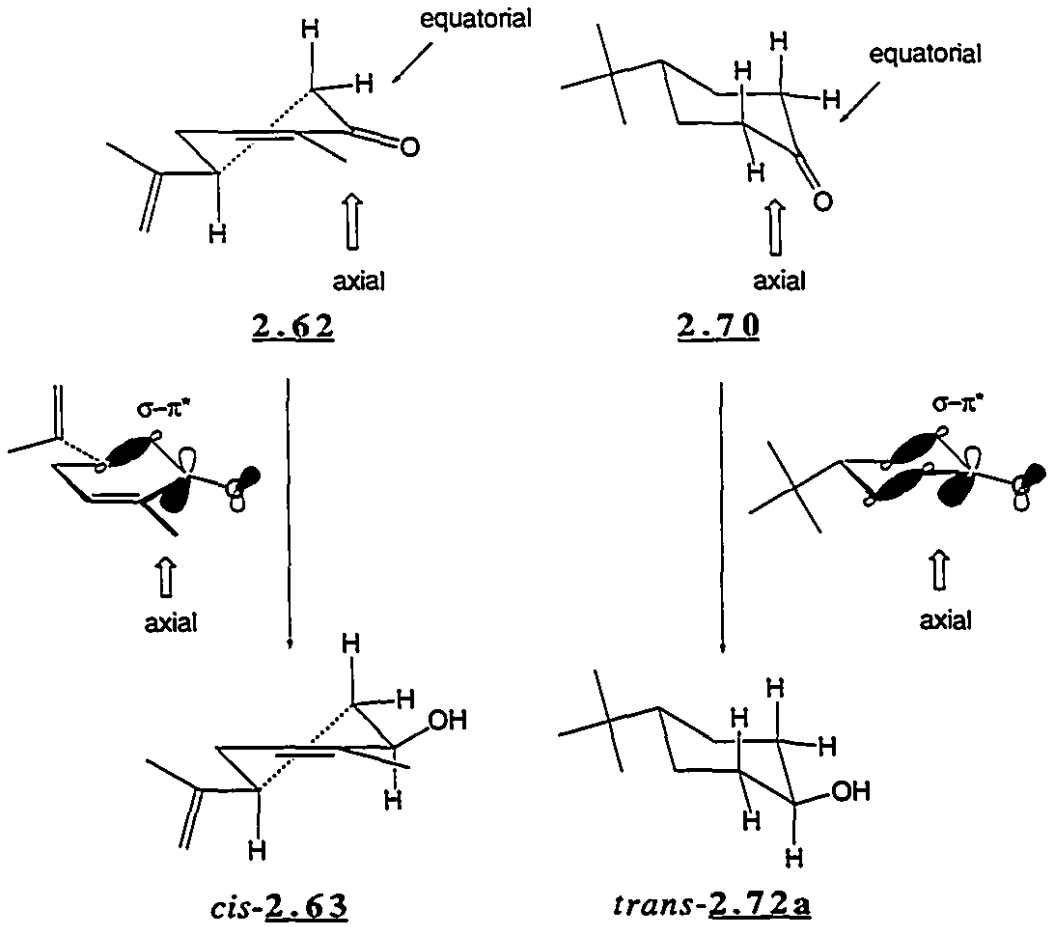


Chart 2.7

On the other hand, the hydrosilation of 2.66 (page 72; entry 5, Table 2.2) yielded one single stereoisomer as a result of the attack of bicyclic substrate on the convex face. Hydrosilation of camphor could give high diastereoselectivity (91 : 9 = isoborneol : borneol)[189] using

diethylsilane (2.93) catalyzed by Wilkinson's catalyst, 2.1. However, a much lower diastereomeric ratio (73 : 27) was obtained when diphenylsilane (2.21) was used in the same reaction. Similar results were generated in our case. Two diastereomers were formed with low selectivity (64 : 36 = isoborneol : borneol; entry 8, Table 2.2).

In view of the diastereomeric ratios generated by this complex in the hydrosilation of ketones, it seemed that the ratio is governed by the relative importance of stereoelectronic factors versus that of the steric factors. In the reduction of camphor (2.72), steric effects were expected to dominate, and the reaction gave two diastereomers with a ratio of less than 2 : 1. On the other hand, hydrosilation of 4-*t*-butylcyclohexanone (2.70), governed mainly by stereoelectronic effects, yielded two diastereomers with a ratio of more than 5 : 1.

The 1,4-hydrosilation of α,β-unsaturated ketones were also highly diastereoselective. In the reduction of 3,5-dimethyl-2-cyclohexen-1-one (2.35), the *cis* and *trans* product ratio is 92 : 8; which is impressive for this type of reaction (entry 5, Table 2.1). The major *cis*-product (2.36) was presumably formed *via* intermediate **T** (Chart 2.8). The alternative, intermediate **U** has a serious *pseudo* 1,3-interaction between the axial methyl group and the organometallic moiety. This interaction made it unfavorable to obtain the *trans*-dimethyl product (Chart 2.8).

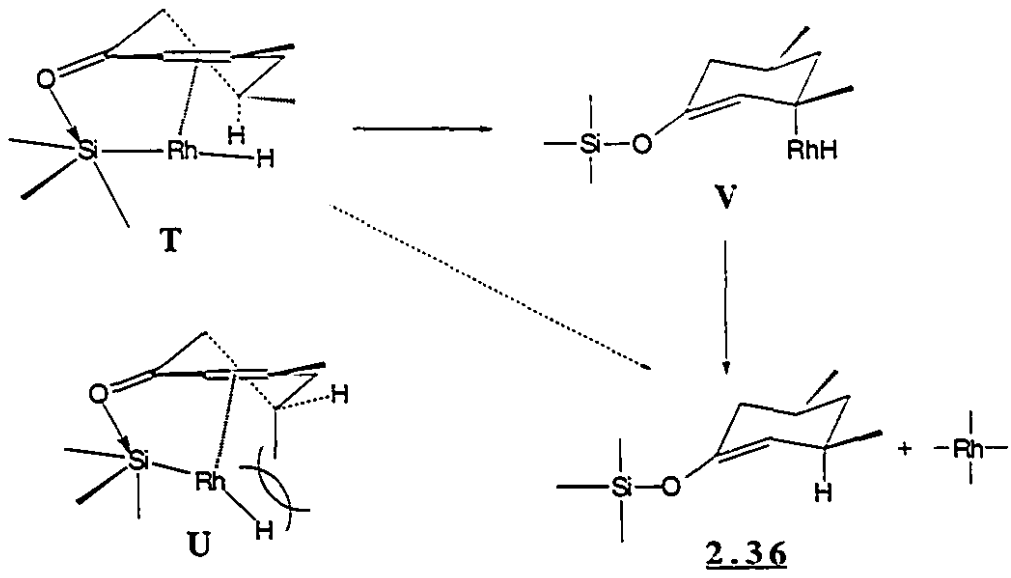


Chart 2.8

2.3.2 Enantioselective Hydrosilation of Prochiral Ketones

One of the potential applications of catalytic hydrosilation is the production of optically active alcohols *via* reduction of prochiral ketones. The first report on enantioselective hydosilation of ketones[551] attracted attention for the search for new methods to achieve high asymmetric induction (*vide supra*).

2.3.2.1 Strategies in Asymmetric Hydrosilation

There are several ways to achieve asymmetric induction in catalytic hydrosilation of prochiral ketones with silicon hydrides. The optimal goal, of course, is to obtain enantiomerically pure

alcohols. In an asymmetric catalysis, the chemical yield of the reaction is defined as [(amount of product)/(theoretical amount of product)]X100%; the enantiomeric excess of the product is [(major enantiomer - minor enantiomer)/(major enantiomer + minor enantiomer)]X100%, and the optical yield of the product is [(optical purity of product)/(optical purity of starting material)]X100%. Asymmetric induction is a term that is used to describe the ability of a reaction to produce one enantiomer over the opposite one under the influence of a chiral environment, such as a chiral auxillary, a chiral additive, or a chiral solvent. It is always difficult to find the ideal combination to induce high levels of enantiomeric excess due to the obscure nature of the four-dimensional chemistry, a chemistry which contains three-dimentional structure (x,y,z) and suitable kinetics (t). Cost is another consideration in the choice of asymmetric catalytic systems.

In terms of our approach, the chiral environment is a chiral catalyst and/or a chiral silicon hydride. We will examinine them separately: (I) hydrosilation of prochiral ketones by a chiral silane mediated with achiral catalysts; or (II) hydrosilation of prochiral ketones by achiral silane catalyzed by chiral catalysts.

2.3.2.2 Hydrosilation Using Chiral Silane

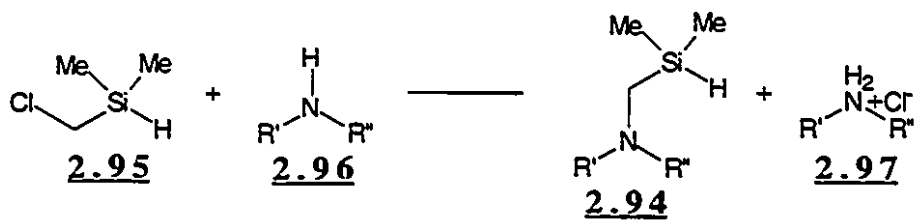
One disadvantage in using a chiral silane in the catalytic hydrosilation of prochiral ketones is that it will consume stoichiometric amounts of the precious enantiomerically pure silane during the course of reduction. At first glance, this does not seem

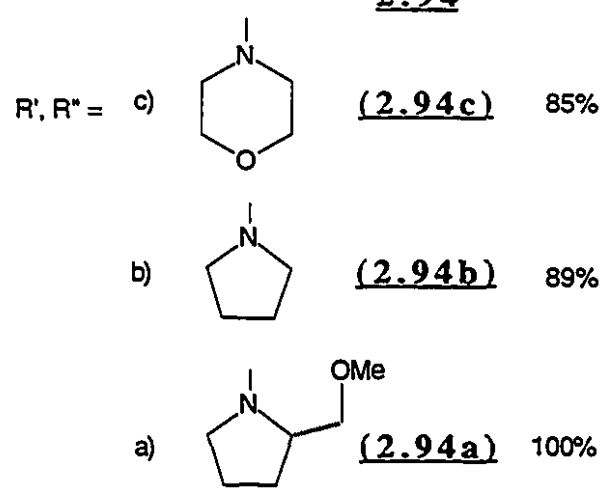
elegant for this type of design. It does, however, have some benefits over the use of chiral metal catalysts. First, a chiral silane can be prepared in pure form relatively easier than a chiral metal catalyst. Secondly, although enantiomerically pure chiral ligands are used in the synthesis of chiral metal catalysts, or catalyst precursors, the newly formed chiral metal complexes are often a mixture of several diastereomeric forms. Purification of these diastereomeric forms is difficult, and sometimes, impossible. If a chiral metal catalyst is made *in situ*, it is often used as a mixture of these diastereomers. The unwanted isomers could be problematic in terms of the stereochemical outcome as they may compete with the active isomer during the course of asymmetric hydrosilation *via* similar and/or different pathways. Thirdly, as both the achiral catalyst and chiral silane are relatively pure, their behavior may be monitored and understood more readily than that of chiral catalysts. Such understanding may lead to modifications that improve enantiomeric excess.

Since it is known that chiral silanes with chirality at the silicon center usually give quite poor enantioselectivities in asymmetric hydrosilation of prochiral ketones (section 1.2.2.2),[132b] we decided to try the C-centered chiral silane, **2.94**. The same methoxymethyl-pyrrolidinyl chiral moiety has induced excellent stereoselectivities in the asymmetric synthesis of optically active alcohols (section 1.2.2.2).[144]

2.3.2.2.1 Synthesis of Chiral Silane

Although, the chiral silane **2.94a** can be made *via* another route,[190] our approach to synthesize this product, **2.94a**, was to use substrate **2.95**, to couple with *(S)*-methoxymethylpyrrolidine (**2.54**). This one step synthesis provides a reliable route to this type of silane (Scheme 2.23).



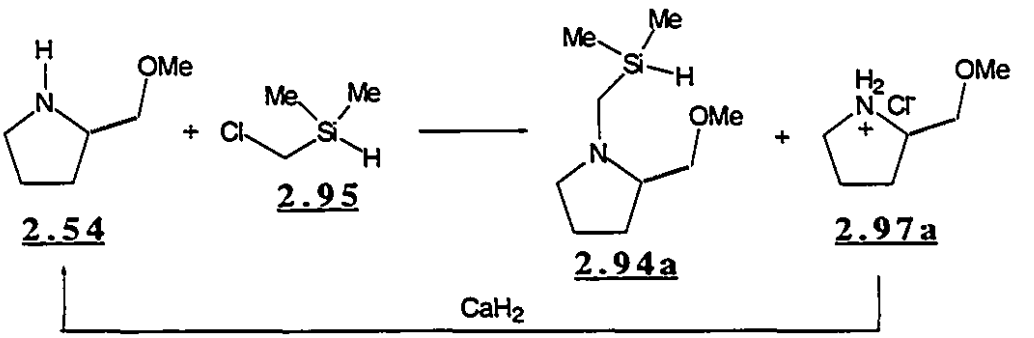


Scheme 2.23

The reaction proceeded under very mild conditions with high chemical yield (>85%). The crude product, which was almost pure, could be obtained by simple filtration. One drawback of this approach was that at least two equivalents of amine were needed to drive the reaction to completion. We tried to replace the excess one equivalent of the amine with a tertiary amine (e.g. pyridine, DMAP,

TEA, TMEDA etc) but none were basic enough to free all of the protonated secondary amine, **2.97**, to force the reaction to completion.

Although the second equivalent of amine could be retrieved in the ammonium salt form, it would be more ideal if only one equivalent of secondary amine was required in the reaction. Metal hydrides were introduced to the reaction mixture to slowly neutralize the ammonium salt, so that only one equivalent of starting amine would be needed (Scheme 2.24).



Scheme 2.24

Calcium hydride seemed to be better than other metal hydrides, such as sodium hydride or potassium hydride. The latter two hydrides might react with the silicon hydrides (both the starting material and the product) over a prolonged period of time. An optimized chemical yield as high as 85% was obtained by using calcium hydride.

Using this approach mentioned above, the chiral silane **2.94a** was easily prepared.

2.3.2.2.2 *Hydrosilation Using Chiral Silane*

Having chiral silane **2.94a** in hand, we wanted to investigate its asymmetric 1,2-hydrosilation of saturated prochiral ketones, and 1,4-hydrosilation of α,β-unsaturated carbonyl compounds.

Unfortunately, 1,4-hydrosilation of 3-methyl-2-cyclohexen-1-one (**2.26**), as well as 1,2-hydrosilation of acetophenone (**2.78**) with chiral silane **2.94a** catalyzed by rhodium catalyst **2.20** did not proceed as expected. Chiral silane **2.94a** deteriorated very fast in the presence of catalyst **2.20**. Similar problems occurred when other rhodium complexes, such as **2.11**, **2.12**, **2.17**, **2.19** and iridium complex **2.25**, were used. Although it was not clear what the cause for the decomposition of the chiral silane was, the presence of the amino and the methoxy group in the chiral silane might weaken the Si-H bond by forming a penta- and/or hexavalent silicate to facilitate the hydrolysis process (Figure 2.9). Furthermore, the presence of metal catalysts may accelerate this hydrolysis reaction. The chiral silane **2.94a** could survive much longer when mixed with acetophenone (**2.78**) without the presence of metal catalyst. However, no reaction was observed even at elevated temperatures (<80 °C).

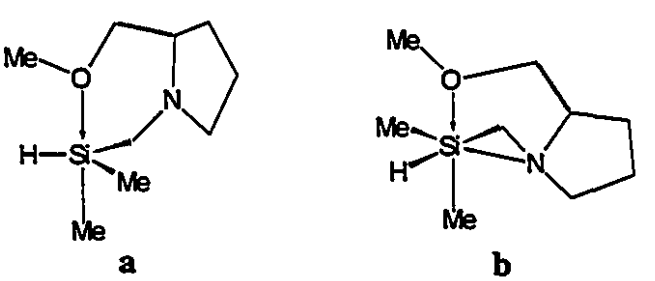
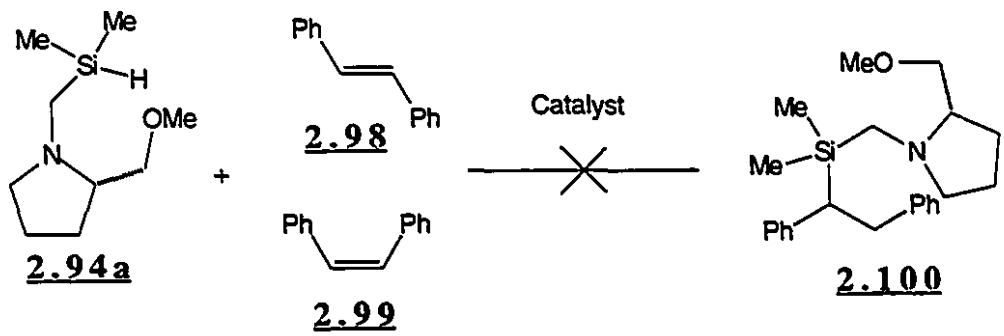


Figure 2.9

We are still looking for a suitable metal catalyst, which could allow the chiral silane **2.94a** to survive long enough to carry out the proposed 1,2- and 1,4-hydrosilation of prochiral ketones.

An alternative application of this chiral silane **2.94a** was the hydrosilation of alkenes. The products could be converted to alcohols stereospecifically.[191] Because there could be a problem of regio-chemistry in the addition of a Si-H bond to the C=C functionality, symmetric alkenes, such as **2.98** and **2.99** were used to react with the chiral silane **2.94a** catalyzed by various metal complexes. Again, both reactions did not proceed (Scheme 2.25).



2.94a + **2.98** + **2.99** → **2.100**

Scheme 2.25

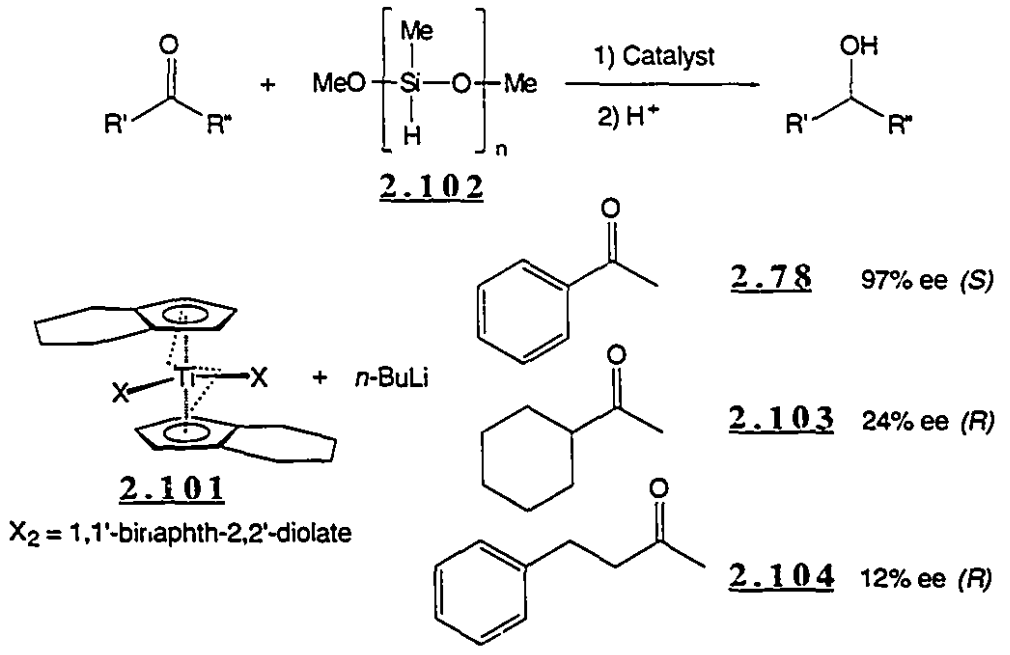
2.3.2.3 Hydrosilation Using Chiral Catalysts

An advantage for this type of asymmetric synthesis using chiral catalysts is that the reaction does not need stoichiometric amounts of chiral reactant to be consumed in order to make optically active and preferrably optically pure products. It is believed that this approach is better than using stoichiometric amounts of chiral

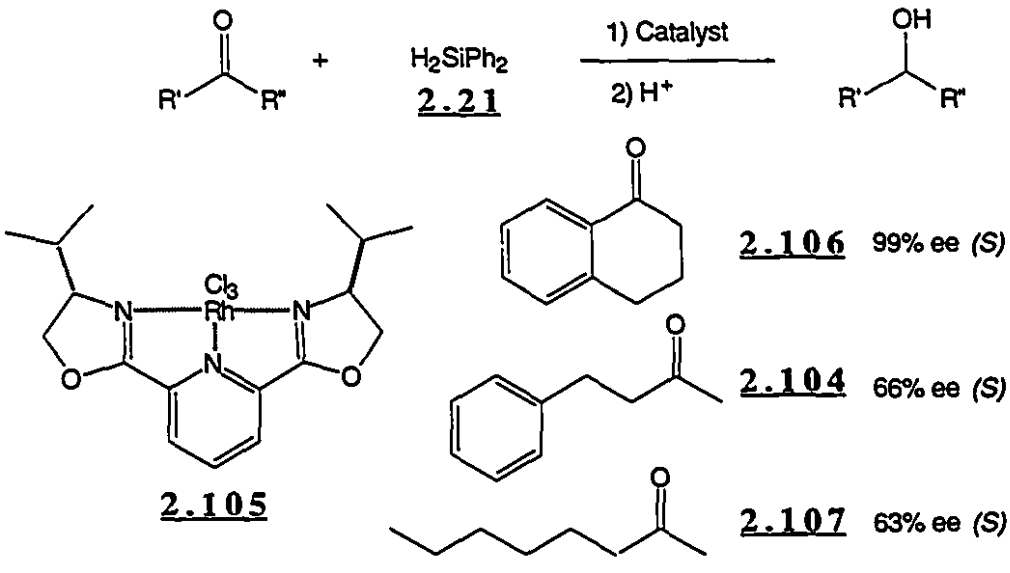
reactant because less of the precious chiral materials are required during the chemical process. The growing concerns of cost and, especially, environmental contamination make this type of asymmetric synthesis the choice in the future. The growing progress in this area could one day make rational design of asymmetric catalytic systems possible.

As the origin of asymmetric induction in hydrosilation of prochiral ketones is not quite clear, rational design of chiral catalyst is a real challenge. Systems used for asymmetric catalysis are largely empirical. Serendipitous discoveries are still essential to advance technologies in this field. As discussed in section 1.1.2.3.2 (Table 1.1, 1.2), many systems for asymmetric catalysis induce only poor to low enantiomeric excess in hydrosilation of prochiral ketones. Some generate high to excellent enantiomeric excess in products of hydrosilation of prochiral ketones, but their generality is limited.[96,97,118] For example, C_2 symmetric catalyst precursor titanocene (**2.101**) with the chirality directly associated with the metal center, could produce high optical yield when used for the asymmetric hydrosilation of prochiral, aromatic ketones. When the substrates were dialkyl ketones, the enantiomeric excess of the products dropped substantially[63c] (Scheme 2.26).

Similar results were obtained when catalyst procursor **2.105** was used in asymmetric hydrosilation of prochiral ketones. Although the catalyst precursor **2.105** is stable and can be purified by column chromatography, the need of silver cation to activate the precursor is a drawback. Substrates containing halogen may not be suitable for this type of catalytic system[123] (Scheme 2.27).



Scheme 2.26



Scheme 2.27

Our search for an effective catalytic system was also mainly empirical. Our attention was focused on those chiral ligands which normally induce high ee in the products when used in related

catalytic systems (e.g. hydrogenation). It is important to emphasize that there may not be a direct relationship between the two systems in terms of their stereochemical outcomes.

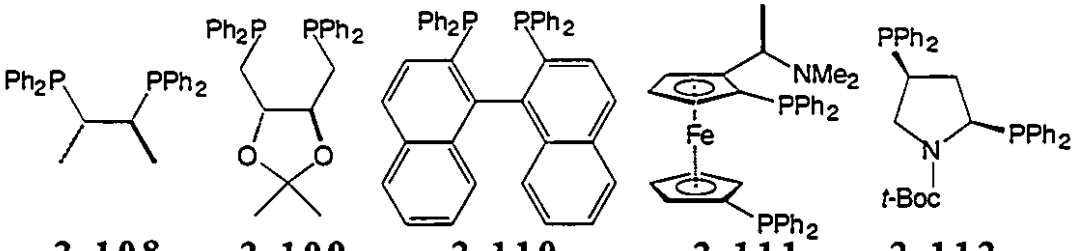
There are mainly two types of ligands widely used in asymmetric catalysis. One type is the chiral phosphino ligand, and the other type is the nitrogen containing chiral ligand (section 1.1.2.3.2) Enantiomerically pure chiral phosphine ligands, with the stereogenic center located either at phosphorous or in the backbone, are usually air and moisture sensitive, while most nitrogen contained chiral ligands are relatively stable. Some nitrogen containing chiral metal complexes could be purified by column chromatography.[123] The advantage of the purified catalysts or catalyst precursors is that impurities which may be detrimental to the reaction can be eliminated. In theory, the number of unwanted competing reactions caused by the impurities and the isomeric forms of the catalyst will decrease, and the total optical yield of the reaction could thus be favored.

In trying to gather more information concerning the origin of chiral induction in the course of asymmetric hydrosilation of prochiral ketones, our search covered both chiral phosphine ligands and chiral N-containing oxazolinyl compounds. We have also tried to improve the optical yield of the reaction based on our interpretation of the mechanism of hydrosilation.

2.3.2.3.1 Chiral Phosphine Ligands

There are many enantiomerically pure phosphine ligands which could be used in the investigation of hydrosilation of prochiral ketones. It has been documented that chiral monophosphino ligands with the stereogenic center at phosphorous generate poor to low enantiomeric excess in the hydrosilation of prochiral ketones [section 1.1.2.3.2 (ii)]. Better results were obtained when bi- and tridentate chiral ligands were used in asymmetric hydrosilations. In our case, it is also advantageous that bi-, tri- or polydentate chiral phosphino ligands be used to make chiral metal complexes *in situ* with achiral precursors (e.g. rhodium complex **2.20**). The chelation effect should certainly favour the displacement of mono- achiral ligand with chiral chelating ligands. Since rhodium complex **2.20** had not been previously used as a catalyst for hydrosilation of ketones, its chiral complexes are relatively unknown[192] in asymmetric hydrosilation. We therefore investigated its reactions.

Enantiomerically pure chiral phosphine ligands, **2.108**-**2.112** (Figure 2.10) were used to generate chiral catalysts *in situ* in order to mediate asymmetric hydrosilation of prochiral ketones. The results are summarized in Table 2.3. Although the results ranged from poor to good in our investigation, the average seemed to be better than that of previously reported results.[98-111] For example, the results for the hydrosilation of acetophenone (**2.78**) by diphenylsilane (**2.21**) catalyzed by other rhodium chiral catalysts derived from chiral phosphines, **2.108-2.112**, are summarized in Table 2.4.



2.108 2.109 2.110 2.111 2.112

Figure 2.10

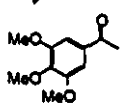
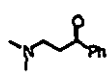
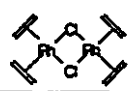
Table 2.4: Comparison of %ee for hydrosilation of acetophenone*

chiral ligand	This work metal complex	% ee	Literature metal complex	% ee	ref.
CHIRAPHOS	$(Ph_3P)_4RhH$	6 %	$[(C_2H_4)_2RhCl]_2$	4 %	116
BINAP	$(Ph_3P)_4RhH$	10 %	-		
DIOP	$(Ph_3P)_4RhH$	46 %	$[(C_2H_4)_2RhCl]_2$	23 %	116
BPPFA	$(Ph_3P)_4RhH$	46 %	$[(C_8H_{14})_2RhCl]_2$	29 %	102
BPPM	$(Ph_3P)_4RhH$	33 %	-		

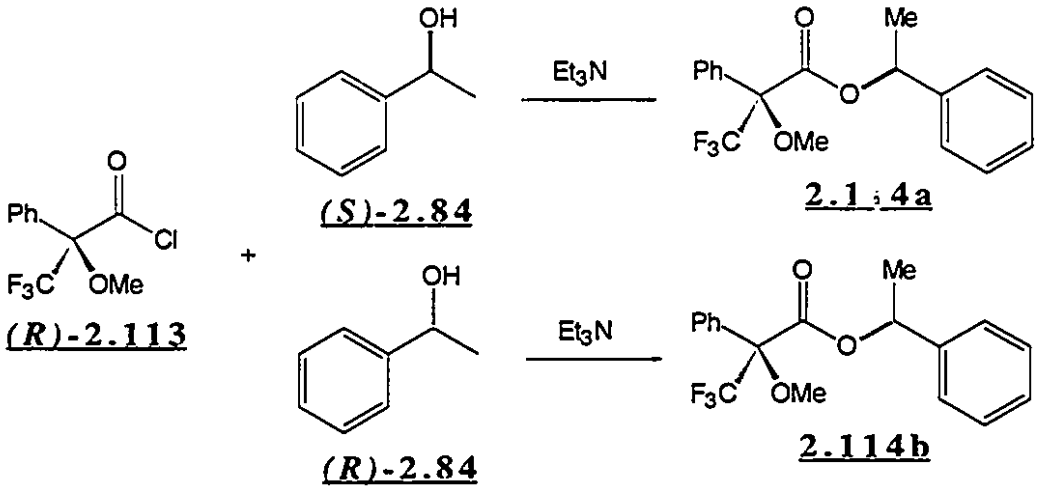
*) H_2SiPh_2 was used in all the cases.

The enantiomeric excesses were determined *via (S)*-Mosher's ester [*(S)*-α-methoxy-α-(trifluoromethyl)phenylacetate].[193] The absolute stereochemistry of *sec*-phenethyl alcohol (2.84) was confirmed by comparison with authentic *(R)*- and *(S)-sec*-phenethyl alcohol-*(S)*-Mosher's esters using ^1H NMR spectroscopy (Scheme 2..28).

Table 2.3: Enantioselective hydrosilation of ketones

entry	ligand	substrate	complex (Rh:L*)	[Rh](% mol); cond. time (h)	yield	% ee[b]
1	(+)-CHIRAPHOS	 (2.78)	$(Ph_3P)_4RhH$ (1:3)	0.4; rt, 336 h, neat	81%	6% *(R)*
2	*(R)*-BINAP	"	" (1:2)	0.4%; rt, 72 h, "	72%	10% *(R)*
3	(+)-DIOP	"	" (1:5)	0.3%; rt, 12 h, "	83%	46% *(S)*
4	(-)-BPPFA	"	" (1:3)	0.4; rt, 5.5 h, CH_2Cl_2	95%	46% *(S)*
5	(-)-BPPM	"	" (1:2)	0.4%; rt, 8 h, neat	84%	33% *(R)*
6	(+)-DIOP	 (2.13)	" (1:3)	0.7%; rt, 12 h, "	76%	6%
7	"	 (2.26)	" (1:3)	0.4%; rt,12 h, CH_2Cl_2	83%	6%
8	(-)-BPPFA	 (2.13)	" (1:3)	0.4%; rt, 7 h, "	78%	4%
9	"	 (2.115)	" (1:3)	0.4%; rt, 5 h, "	94%	24% *(S)*
10	"	 (2.116)	" (1:3)	0.4%; rt, 8 h, "	85%	10%
11	"	 (2.117)	" (1:3)	0.4%; rt, 8 h, "	84%	14%
12	"	 (2.118)	" (1:3)	0.4%; rt, 8 h, "	93%	56%
13	"	 (2.119)	" (1:3)	0.4%; rt, 12 h, "	93%	28% *(S)*
14	"	 (2.120)	" (1:4)	0.7%; rt, 12 h, THF	83%	16% *(S)*
15	"	 (2.121)	" (1:4)	1%; 5 °C, 10 h, "	84%	78% *(S)*
16	"	 (2.122)	" (1:4)	0.7%; rt, 10 h, "	76%	20%
17	(-)-BPPM	 (2.123)	" (1:2)	0.9%; rt,12 h, CH_2Cl_2	71%	32% *(R)*
18	"	 (2.124)	" (1:3)	1.2%; rt, 12 h, "	78%	44% *(R)*
19	*(S)*-BINAP	 (2.78)	 (1:3)	0.4%; rt, 12 h, neat	83%	26% *(S)*
20	(-)-BPPFA	"	" (1:4)	0.3%; 0°C,12 h, "	85%	30% *(S)*
21	"	"	 (1:2)	0.8%; rt, 12 h, "	87%	8% *(S)*

a) H_2SiPh_2 was used in all cases. b) measured by ^1H NMR with Mosher's ester



Scheme 2.28

The absolute stereochemistry of the other products were assigned based on the empirical rule derived from Mosher's esters, as shown in Figure 2.11.[194]

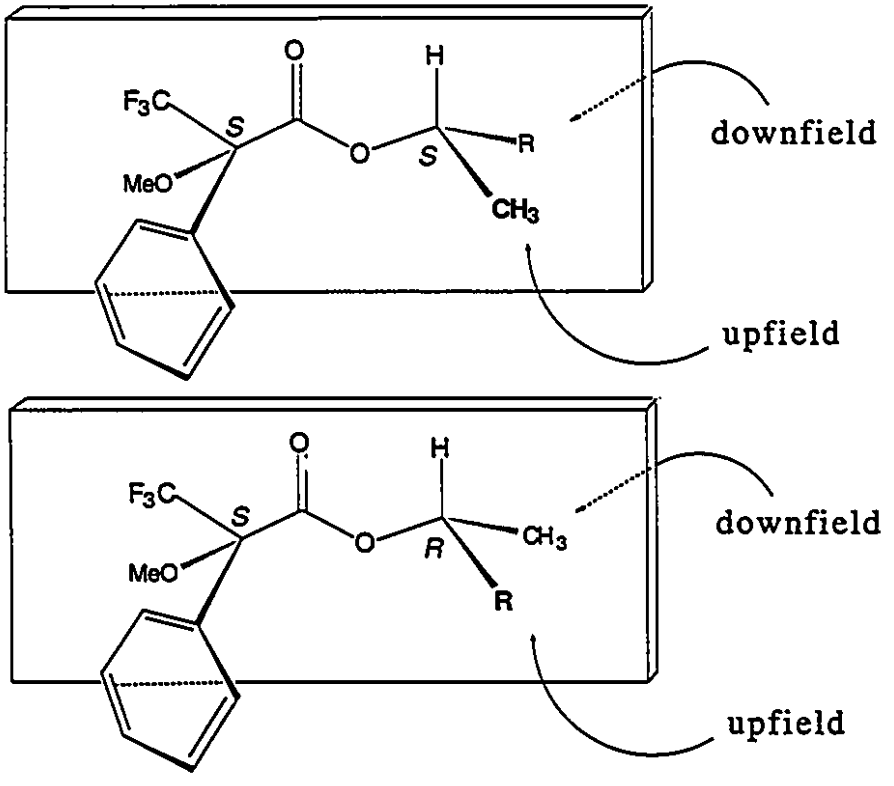


Figure 2.11

The chiral rhodium complex derived from *(R,R)*-CHIROPHOS (**2.108**)[101,195] and complex **2.20** is expected to have a rigid backbone.[101,196] The chiral ligand chelates with the metal to form a five-membered ring. The rigid backbone of this ligand forces the four phenyl groups at the two phosphorous centers to get close to each other with a small Δ angle, which is the angle between the axis bisecting the two phenyl groups at the phosphorous centers (Figure 2.12). The influence of the chiral center transformed to the two phenyl groups at the corresponding phosphorous center is diminished. This may explain why the chiral complex derived from CHIRAPHOS and **2.20** generated only 6% ee *(R)* in the reduction of acetophenone (**2.78**) with diphenylsilane (**2.21**).

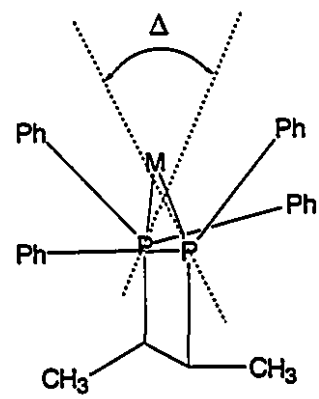


Figure 2.12

The chiral complex CHIRAPHOS-RhH also had a low reactivity. Hydrosilation of acetophenone (**2.78**) with diphenylsilane (**2.21**) catalyzed by this chiral species took one week to achieve *ca.* 80% conversion. By comparison, the same reaction was completed in less than 10 hours with the achiral catalyst **2.20**. The small angle, Δ

(Figure 2.12), was probably a reason that the newly formed chiral complex had low reactivity. The rigid backbone forced the four phenyl groups to be in close proximity so that the reaction was partially blocked.

Increasing the Δ angle could probably enhance the chiral influences and the reaction rate. This can be realized by altering the size of the backbone in the chiral ligands. Enantiomerically pure BINAP,[197] which could form a rigid, but larger metallocyclic ring[159h,198] compared to that of CHIROPHOS-RhH, was then used to form the chiral complex. The latter was expected to have a larger Δ angle than that of the CHIROPHOS-RhH complex. This change resulted in a better enantiomeric excess (10% ee) in the product of hydrosilation of acetophenone, but the increase in ee was still insignificant. (+)-DIOP[99] was then used to form the chiral rhodium catalyst. The backbone of this ligand is more flexible than that of BINAP.[199] The optical yield of the same reaction reached 40% ee, which is relatively high compared to the results from the previous two chiral phosphino ligands associated with the rhodium hydride complexes. Presumably, the bicyclic DIOP-RhH complex might reinforce its chiral influence on the metal center with the assistance of the rigid *exo*- ring system. With a large excess of chiral ligand to metal (RhH : L = 1 : 5), the enantiomeric excess reached as high as 46% ee.

After oxidative insertion of the Si-H bond with a rhodium complex, the newly formed dimetallic, silyl metal hydride species could have several diastereomeric forms. Each of these diastereomeric forms may have several conformational isomers due

to the rotation of the M-Si bond alone. Each rotamer caused by rotation of the Si-M bond is a distinct chiral catalyst,[200] which contributes to the overall optical yield of the asymmetric hydrosilation. In most cases, the overall optical yield is lowered due to the existance of these competing diastereomeric catalysts. To limit this usually disfavored rotation of the silyl moiety in dimetallic species, an extra intramolecular σ-donor is needed in the chiral ligand to coordinate at the silicon center of the dimetallic complex to restrict the Si-M rotation. As a result of this internal coordination, fewer distinct comformers will be formed. The overall optical yields may therefore increase (Figure 2.13).

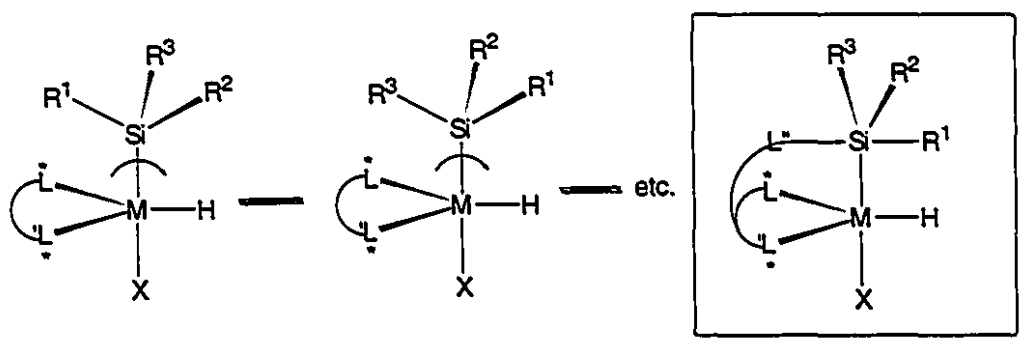
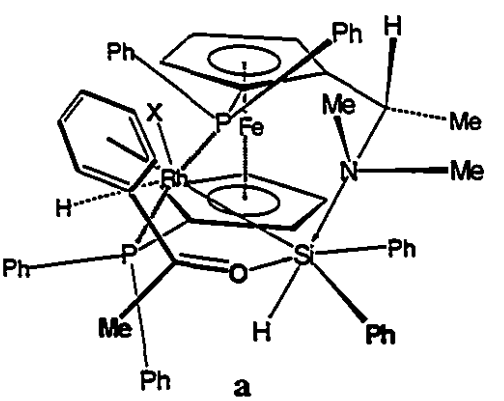


Figure 2.13

The phosphine ligands, BPPFA[201] and BPPM[202] having an extra σ-donor were used to form chiral rhodium hydride complexes for asymmetric hydrosilation. Indeed, the average optical yields were higher using chiral catalysts derived from these types of ligands than those from simple bidentate ligands. A good enantiomeric excess was achieved (78% ee *(S)*) when the substrate was compound **2.121**.

Furthermore, the chiral complexes of **2.111** and **2.112** seemed to be more reactive in the hydrosilation of prochiral ketones with the

same silicon hydride, diphenylsilane (**2.21**), than those of CHIROPHOS, BINAP or DIOP. The reactions were completed in less than 5 hours when acetophenone (**2.78**) was used as the substrate. While chiral complexes of bidentate ligand **2.108-2.110** needed much longer times to complete the same reaction (CHIROPHOS: 336 h; BINAP: 72 h; DIOP: 12 h). It is not quite clear whether the amino group in BPPFA (or, the carbonyl group in BPPM) facilitates the hydride transfer (as depicted in Figure 2.14), or coordinates to the metal center to alter its reactivity. However, it is believed that the former is the more likely explanation. First of all, it is known that the presence of nucleophiles in the reaction of silicon hydrides with ketones or aldehydes, hydrosilation can proceed *via* nucleophilic activation (section 1.1.2.2)[24] This is also in agreement with the observation that when monohydrosilane, **2.14**, was used in the hydrosilation of acetophenone (**2.78**), the reaction rates were very similar when comparing the BPPFA system (192 h) to that of the DIOP system (240 h). The presence of the extra amino group in the chiral ligand clearly did not affect the reactivities of the catalysts *via* coordination at rhodium centers (Figure 2.14).



a

Figure 2.14

We propose that differences in the steric hindrance of the two groups in unsymmetric ketones are important for the generation of enantiomeric excess in hydrosilation reactions. To summarize the results in Table 2.3, we divided the carbonyl group into quadrants: **a**, **b**, **c** and **d** (Figure 2.15).

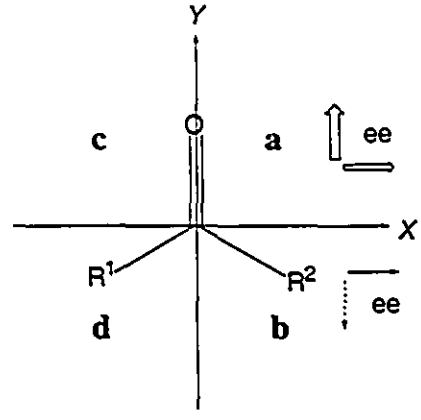


Figure 2.15

A difference between areas **a**, **b** and **c**, **d** is necessary to create enantiomeric excess in the reaction. Increasing the difference in bulkiness along the *x* direction enhances enantiomeric excess. Thus, compound **2.117** gave better optical yield (14% ee) than substrate **2.13** (6% ee). However, Enhancing bulkiness of a substrate along the -*y* direction seemed to have little influence on the enantioselectivity. For example, the same enantiomeric excess was obtained in the hydrosilation of ketones **2.13** and **2.26** (Figure 2.16).

It is interesting to note that bulkiness in the area **a** is the most important factor in getting high enantiomeric excess in the reduction. Compounds **2.116**, **2.117** and **2.118**, all have an α-benzo group; but with different orientations relative to the C=O bond (Fig 2.17). With

the absence of steric hindrance in the area **a**, substrate **2.116** was reduced with only 10% ee. On the other hand, bulkiness is clearly present in the area **a** of substrate **2.118**. Reducing this compound with diphenylsilane (**2.21**) mediated by (-)-BPPFA-RhH gave a moderate 56% ee, which was the highest among the substrates **2.116**-**2.118**. The implication of this observation is that the hydride probably migrates from the silyl rhodium hydride complex to the carbonyl carbon directly when the carbonyl group σ-coordinates with the complex (Figure 2.18).

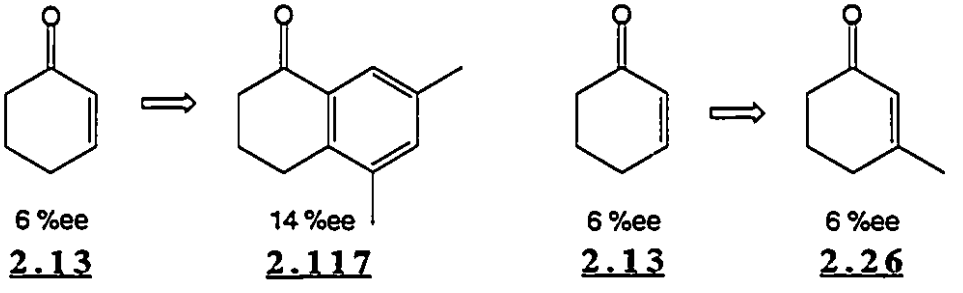


Figure 2.16

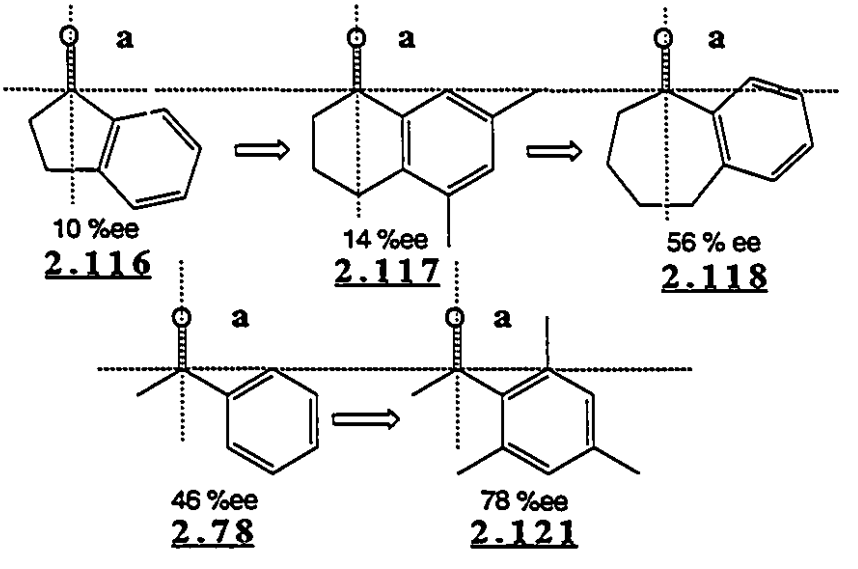


Figure 2.17

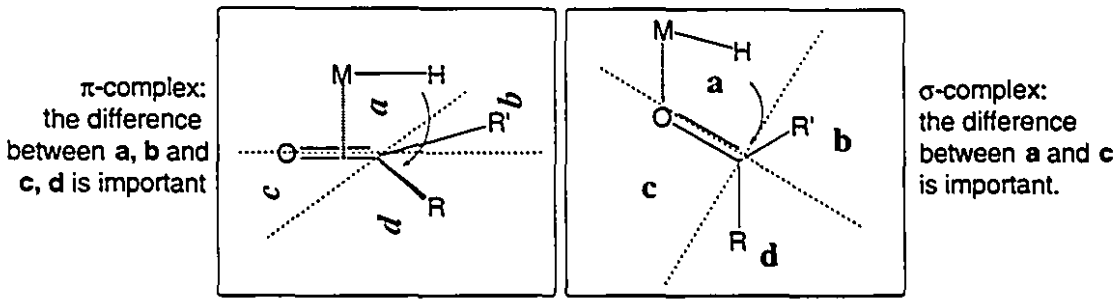


Figure 2.18

The major influence on the preferred steric hindrance seems to be two dimensional. For example, the sterically hindered adamantyl group in compound **2.119** was not as 'large' as the phenyl group of acetophenone in terms of their chiral inductions. The former produced 18% ee less than the latter. Whether there was a $\pi-\pi$ interaction between the phenyl groups of acetophenone with the diphenylphosphino group, or a π-metal complexation was not quite clear. When the *(S,S)*-BPPM-RhH complex was used as the chiral catalyst, the dimethylamino group in substrate **2.123** appeared to have a similar effect as that of the phenyl group in acetophenone (**2.78**). Both substrates gave the same optical yields with the same stereochemical outcomes (Figure 2.19).

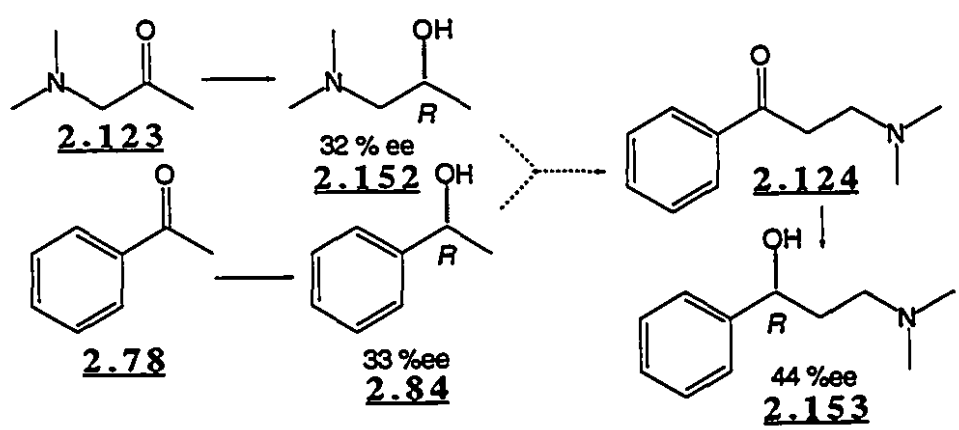


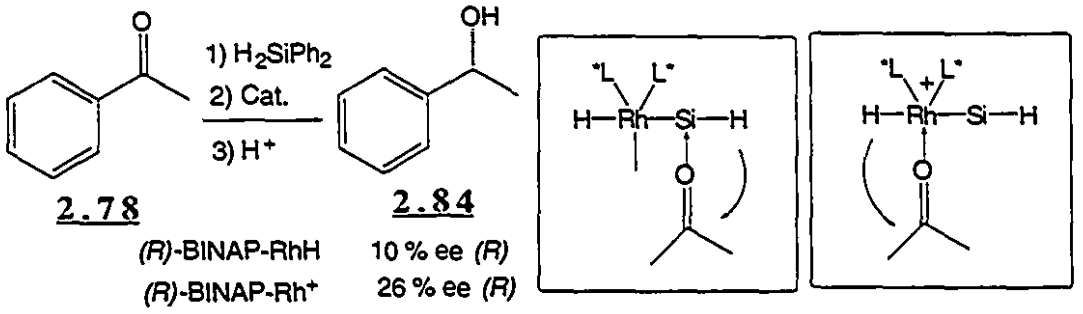
Figure 2.19

Interestingly, these two factors did not cancel each other when both groups were put together on the same substrate **2.124**. Instead, moderate enantiomeric excess (44% ee) was generated in the reaction.

If the reaction did occur at the silicon center in the sila-rhodium complex as proposed, the chiral influence from the chiral ligand could only be transmitted through a long distance induction. The use of rhodium cation to form chiral metal complexes might shift the reaction center from the proposed silicon center to the rhodium center. Asymmetric induction could thus be reinforced. With this premise in mind, chiral rhodium cationic complexes were made in the hope that higher optical yields would be generated in the asymmetric hydrosilation of prochiral ketones. The cationic rhodium(I) complex of BINAP did induce higher enantiomeric excess (26% ee) than the corresponding neutral complex (10% ee) for the reduction of acetophenone. However, the cationic complex of BPPFA had its chiral induction reduced from 46% ee to 30% ee in the same reaction. In this case, the amino group of BPPFA might be forced to coordinate with the cationic rhodium center and leave the silyl group free to rotate due to the removal of the internal chelation with silicon. Thus the optical yields were disfavored (Scheme 2.29).

From our NMR studies, Wilkinson's catalyst readily reacted with silicon hydrides to form silyl rhodium hydride complexes (section 2.2.3.3). Since this process was quite clean, and only one major sila-metallic complex was observed, using a chiral catalyst of this complex may provide some advantages for asymmetric hydrosilation of ketones. Despite the fact that chiral catalysts

derived from Wilkinson's complex usually gave quite poor enantiomeric excess in asymmetric hydrosilation of prochiral ketones,[551] a chiral BINAP-RhCl complex was made to catalyze the hydrosilation of acetophenone. Unfortunately, only 6% ee (*S*) was generated in the reaction. Another rhodium complex precursor, **2.10**, was used to form a complex with chiral ligand BPPFA and similar results were obtained [8% ee (S)].



Scheme 2.29

Altering the electronic properties of the carbonyl group by introducing methoxy groups in compound **2.120**, and trifluoromethyl in substrate **2.122**, did not help to enhance the enantiomeric excess. It appeared that steric effects were essential for enhancing enantioselectivity in the reduction of carbonyl groups. Interestingly, stereoelectronic effects played a significant role in the diastereo-selective reduction of ketones as discussed earlier (section 2.3.1).

There are many other factors which affect the stereochemical outcome of the asymmetric hydrosilation of prochiral ketones. Some of which were investigated.

i) Solvent Effects

Solvent often has a substantial effect on the optical yield of the reaction in asymmetric catalysis. As we already know from NMR studies, chlorinated solvents, such as CH_2Cl_2, can react with rhodium complex **2.20** to form new complexes (section 2.2.3.3). In the present case, Wilkinson's catalyst was the major complex formed when **2.20** was dissolved in dichloromethane. Although complex **2.20** was detected as $(PPh_3)_3RhH$ in dichloromethane (^1H: δ = -8.55 ppm, (br)d, J = 14.0 Hz), the oxidative insertion of the solvent C-Cl bond by the complex was quite fast. The product from the following reductive elimination step, CHD_2Cl, was observed instantly after the complex was dissolved in dichloromethane-d_2. The original rhodium hydride complex **2.20** was then converted to mainly Wilkinson's catalyst. On the other hand, the catalyst **2.20** was relatively stable in non-chlorinated solvents, such as benzene or THF (Scheme 2.14).

Complex **2.20** appeared to be the catalyst responsible for the hydrosilation of ketones, in both chlorinated and non-chlorinated solvents, but probably *via* different active species. The same level of chiral induction was observed in all solvent systems shown in Table 2.5. The enantiomeric excess was slightly higher in CH_2Cl_2. It has been reported that higher enantiomeric excess could be achieved by using carbon tetrachloride as solvent in asymmetric hydrosilation of ketones.[21a] Due to solublity problems, we used a mixed solvent of CCl_4 and THF (about 2 : 1) in the reaction. Similar chiral induction [40% ee *(S)*] was obtained (Table 2.5).

Table 2.5: Enantiomeric excess affected by different solvents

entry[a]	L*: Rh[b]	[Rh] (% mol)	time (h); cond.	solvent	yield	% ee
1	1 : 3	0.4 %	rt, 5.5 h	CH_2Cl_2	95 %	46 % (*S*)
2	1 : 3.5	0.7 %	rt, 10 h	THF	95 %	38 % (*S*)
3	1 : 3.5	0.7 %	rt, 10 h	C_6H_6	95 %	38 % (*S*)
4	1 : 3.5	0.7 %	rt, 10 h	CCl_4/THF	95 %	40 % (*S*)

a) acetophenone was reduced by H_2SiPh_2. b) (-)-BPPFA-$(Ph_3P)_4RhH$.

ii) Structure of Silicon Hydrides

Silicon hydride tremendously affects the hydrosilation reaction rate. The enantiomeric excess generated in the asymmetric hydrosilation of prochiral ketones also depends on the type of silicon hydrides used in the reduction. In general, symmetrically substituted dihydrosilane produced the highest enantiomeric excess among all the silicon hydrides.[102] It has been noted that the enantiomeric excess decreased following the sequence of: R_2SiH_2 > $RSiH_3$ > RR'_2SiH. This sequence was observed when the chiral DIOP-RhH complex was used in the hydrosilation of acetophenone in our studies (Table 2.6).

It was quite difficult to explain this observation according to Ojima's mechanism (section 2.2.3.1). However, this observation can be rationalized by our new proposal. As the reaction center is at the silyl moiety of dimetallic complexes, the coordination of a carbonyl

group with these complexes can form a reactive intermediate, **J**, as depicted in Figure 2.19. If a dihydrosilane (diphenylsilane for instance) is used in the reaction (R^1 = H), the hydride at the silicon center is the only hydride available to transfer to the carbonyl group. In contrast, if phenylsilane is used, a competing migration of the two diastereomeric hydrogens (R^1 and R^2 = H) in complex **J** can occur. Therefore, diphenylsilane could, in principle, generate higher enantiomeric excess than trihydrosilane. The latter can also be involved in a mismatched double asymmetric induction, which can sometimes decrease the optical yield (*vide infra*). However, the low enantiomeric excess generated by monohydrosilane was more difficult to explain. As different hydride migratory pathways may be involved, it is not suitable to compare with the above situations, where di- and trihydrosilane are used (Figure 2.20).

Table 2.6: Enantiomeric excess affected by different silanes

entry[a]	silane	L*: Rh[b]	[Rh] (% mol)	t (h); cond.[c]	yield	% ee
1	$PhMe_2SiH$	1 : 5	0.3 %	rt, 240 h	80 %	2 % *(R)*
2	Ph_2SiH_2	1 : 5	0.3 %	rt, 8 h	83 %	46 % *(S)*
3	$PhSiH_3$	1 : 4	0.6 %	rt, 8 h	83 %	22 % *(R)*

a) substrate: acetophenone. b) (+)-DIOP-$(Ph_3P)_4RhH$. c) neat.

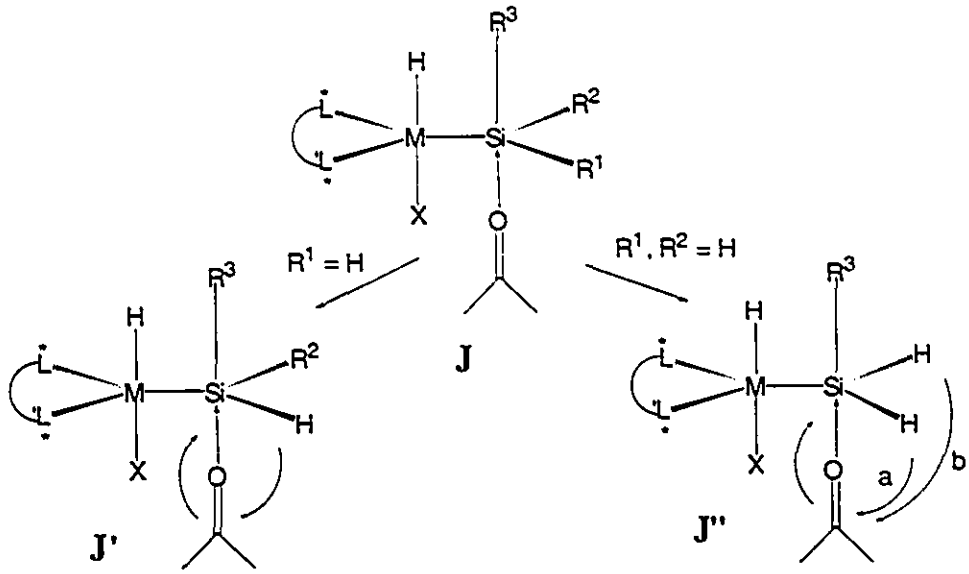


Figure 2.20

iii) Reaction Conditions

Apart from the inherent nature of the chiral catalyst, the substrate, and the silicon hydride in the asymmetric inductions, the reaction conditions also affect the stereochemical outcome of the reactions. Reaction conditions affect the optical yields and the chiralities of the newly generated stereogenic centers of the products. The amounts of reactants and catalyst have certain effects on the final optical yields of asymmetric hydrosilation. Variation of the ratios of catalyst, ketone and silane in the reaction mixture, along with variations of the solvent and the reaction temperature, could change the reaction rate, percentage of conversion and most importantly, the enantiomeric excess.

a) Amount of Catalyst

The amount of catalyst present in the reaction mixture did affect the optical yields of the products. In general, higher concentrations of catalyst increases enantiomeric excess, even though the effect is not very pronounced (Table 2.7).[121b] During reaction, a catalyst will become less effective after a certain number of catalytic cycles (catalyst deterioration). Since a chiral catalyst generated *in situ* is normally a mixture of diastereomers and/or rotamers, each of them deteriorates differently. Although all the components of the mixture should be proportionally increased when a relatively large amount of chiral catalyst is used, the optical yields of the reactions are somehow usually favored (Table 2.7).

Table 2.7: Enantiomeric excess affected by amount of catalyst

entry[a]	Rh:L*[b]	[Rh] (% mol)	cond., time (h)	yield	% ee
1	1 : 3	0.2 %	rt, 6 h	90 %	30 % *(S)*
2	1 : 3	0.4 %	rt, 4 h	79 %	34 % *(S)*
3	1 : 3	0.9 %	rt, 4 h	78 %	38 % *(S)*
4	1 : 3	1.3 %	rt, 3.5 h	82 %	40 % *(S)*

a) acetophenone/H_2SiPh_2/THF. b) (-)-BPPFA-$(Ph_3P)_4RhH$.

After oxygen, silicon hydride may be a major cause for chiral catalyst deterioration, since more silicon hydride was needed to complete the reaction when the catalyst to ketone ratio was high.

The chiral induction appeared to be similar throughout the reaction (Table 2.8).

Table 2.8: Enantiomeric excess during hydrosilation

entry[a]	Rh:L*[b]	[Rh] (% mol)	cond., time (h)	yield	% ee
1	1 : 3	1.0 %	rt, 1 h	22 %	36 % *(S)*
2	1 : 3	0.9 %	rt, 2 h	53 %	40 % *(S)*
3	1 : 3	0.9 %	rt, 3 h	68 %	40 % *(S)*
4	1 : 3	0.9 %	rt, 4 h	78 %	38 % *(S)*

a) acetophenone/H_2SiPh_2/THF. b) (-)-BPPFA-$(Ph_3P)_4RhH$.

b) Amount of Chiral Ligands

The amount of chiral phosphine ligand used relative to the metal complex affected only slightly enantiomeric excess. As long as the required stoichiometric amount of ligand was reached, excess chiral ligand is not crucial to the stereochemical outcome.[124,127] Still, excess chiral ligand was used to ensure complete formation of the chiral complexes. Also, excess chiral ligand could prevent the chiral metal complex from dissociating in the reaction mixture. These could be the reasons which favored the optical yields of the reaction when excess ligand is used (Table 2.9).

Table 2.9: Enantiomeric excess affected by amount of ligand

entry[a]	ligand	Rh:L*[b]	[Rh] (% mol)	cond., t. (h)	yield	% ee
1	(+)-DIOP	1 : 2.7	0.4 %	rt, neat,12 h	91 %	40 % *(S)*
2	(+)-DIOP	1 : 5	0.3 %	rt, neat, 8 h	83 %	46 % *(S)*
3	(-)-BPPFA	1 : 2	0.4 %	rt, CH_2Cl_2, 4 h	87 %	42 % *(S)*
4	(-)-BPPFA	1 : 3	0.4 %	rt, CH_2Cl_2, 5 h	80 %	46 % *(S)*
5	(-)-BPPFA	1 : 5	0.4 %	rt, CH_2Cl_2, 10 h	84 %	46 % *(S)*

a) acetophenone was reduced by H_2SiPh_2. b) $(Ph_3P)_4RhH$.

c) Amount of Silane

It was known that increasing the amount of silane in the reaction mixture could enhance the chemical yield. The optical yield was also affected by the amount of silane used in the asymmetric hydrosilation. Excess of silane had a negative effect on the stereochemical outcome. The same negative effect has been observed in the asymmetric hydrosilation of prochiral ketones using chiral oxazolinyl compounds by Brunner's group[121b] (*vide infra*). It is not quite clear why excess silane in the reaction mixture decreased the enantiomeric excess. The problem caused by the excess silane was probably related to the catalyst deterioration. (Table 2.10).

Table 2.10: Enantiomeric excess affected by amount of silane

entry[a]	Rh:L*[b]	[Rh] (% mol)	S : SiH[a]	cond., time (h)	yield	% ee
1	1 : 2.3	0.4 %	1 : 0.5	rt, 10 h	79 %	36 % *(R)*
2	1 : 2.3	0.4 %	1 : 1	rt, 8 h	84 %	33 % *(R)*
3	1 : 2.3	0.4 %	1 : 1.5	rt, 8 h	81 %	30 % *(R)*
4	1 : 2.3	0.4 %	1 : 2	rt, 8 h	89 %	28 % *(R)*

a) acetophenone/H_2SiPh_2/neat. b) (-)-BPPM-$(Ph_3P)_4RhH$.

d) Amount of Ketone

Variation of the amount of ketone in the reaction mixture had a minor effect on the optical yield of the reaction. The enantiomeric excesses of the reactions shown in Table 2.11 were almost the same, despite an eight fold increase in the amount of ketone used.

Table 2.11: Enantiomeric excess affected by amount of ketone

entry[a]	Rh:L*[b]	[Rh] (% mol)	S,[a] mmol	cond., time(h)	yield	% ee
1	1 : 3.5	1.4 %	0.5	rt, 10 h	66 %	40 % *(S)*
2	1 : 3.5	0.7 %	1.0	rt, 10 h	91 %	38 % *(S)*
3	1 : 3.5	0.5 %	1.5	rt, 10 h	86 %	40 % *(S)*
4	1 : 3.5	0.3 %	2.0	rt, 10 h	90 %	41 % *(S)*
5	1 : 3.5	0.2 %	4.0	rt, 10 h	88 %	38 % *(S)*

a) acetophenone/H_2SiPh_2/THF. b) (-)-BPPFA-$(Ph_3P)_4RhH$.

e) Amount of Solvent

Small amounts of chlorinated solvent helped to increase the enantiomeric excess. However, larger amounts of solvent had a negative effect. When the substrate was compound **2.118**, the optical yield decreased from 56% ee (2 mL CH_2Cl_2) to 32% ee (15 mL, CH_2Cl_2). Small amounts of chlorinated solvent may convert an ideal amount of a chiral complex of **2.20** to a new active chiral complex, which is responsible for the stereochemical outcome of the reaction. When a large amount of chlorinated solvent was used, dissociation of the chiral complex, especially of the active species, may become more significant. The latter could lead to a decrease in optical yields.

The same negative effect was observed when the non-chlorinated solvent, benzene, was used in the asymmetric hydrosilation of acetophenone. (Table 2.12)

f) The Effect of Temperature

Temperature affected the optical yields of hydrosilation reactions in a more complicated manner. It is known that low temperatures usually favor the enhancement of enantiomeric excess. As a matter of fact, lowering the reaction temperature to gain enhancement of optical yields of a reaction is a common practice. On the other hand, hydrosilation of ketones usually needs a short induction period for the reaction to proceed. The hydrosilation would not proceed if the reaction mixture was first pre-cooled to a certain

temperature, and later warmed up. Sometimes, the reaction did proceed after being warmed up, but needed much longer times for completion. The latter led to a relatively low optical yield.

Table 2.12: Enantiomeric excess affected by amount of solvent

entry[a]	substrate	Rh:L[b]	[Rh] % mol; cond. t (h)	solvent (ml)	yield	% ee
1	 (2.78)	1:3	0.4; rt, 4 h	-	79%	34% *(S)*
2	"	1:2	0.4%; rt, 5.5 h	CH_2Cl_2 (2 ml)	80%	46% *(S)*
3	"	1:3.5	0.7%; rt, 10 h	C_6H_6 (2 ml)	97%	38% *(S)*
4	"	1:3.5	0.7; rt, 12 h	" (5 ml)	84%	35% *(S)*
5	"	1:3.5	0.7%; rt, 24 h	" (10 ml)	80%	33% *(S)*
6	 (2.118)	1:3	0.7%; rt, 8 h	CH_2Cl_2 (2 ml)	92%	56%
7	"	1:3	0.4%; rt, 12 h	" (5 ml)	75%	50%
8	"	1:3	0.4%; rt, 15 h	" (10 ml)	83%	40%
9	"	1:3	0.4%; rt, 24 h	" (15 ml)	88%	32%

a) H_2SiPh_2 was used. b) (-)-BPPFA-$(Ph_3P)_4RhH$

The explanation for these observations is not clear. If the reaction was carried out at a temperature just above the no-reaction temperature, it proceeded with no problem. An enhancement in optical yield was obtained in such a case (Table 2.13).

Table 2.13: Enantiomeric excess affected by temperature

entry[a]	substrate	Rh:L[b]	[Rh] % mol; cond. t (h)	yield	% ee
1	 (2.78)	1:3	0.4; rt, 4 h, neat	79%	34% *(S)*
2	"	1:2	0.4; 0 °C → rt, 10 h, neat	81%	16% *(S)*
3	 (2.121)	1:3.4	0.7; rt, 12 h, THF	84%	60% *(S)*
4	"	1:4	0.7; 5 °C, 16 h, THF	79%	74% *(S)*

a) H_2SiPh_2 was used. b) (-)-BPPFA-$(Ph_3P)_4RhH$

2.3.2.3.2 Modification Strategies

Apart from manipulating reaction conditions, attempts to modify the optical yield of the asymmetric hydrosilation of prochiral ketones have also been made based on our mechanistic studies. As the hydride may actually be transferred from the silicon center of a silicon-metal intermediate to the carbonyl group, one can try to modify the reaction intermediate so that unnecessary competing reactions can be reduced or hopefully eliminated.

i) Addition of Monohydrosilane

So far, we haven't fully been convinced as to the identity of the true active intermediate(s). However, there may exist one intermediate, **D** (**XIX**, Scheme 2.20) as depicted in Chart 2.9, which is active towards hydrosilation of ketones. Insertion of the Si-H bond of another silane by complex **C** would form a bis-silametal complex

intermediate (Chart 2.9). Similar to that of Brunner's proposal, this intermediate **D** presents two diastereotopic silyl groups to the incoming carbonyl group. To alleviate this potential problem, small amounts of monohydrosilane, dimethylphenylsilane (**2.14**), was introduced to the solution of complex **2.20** prior to the addition of ketone and diphenylsilane. According to our observations, dimethylphenylsilane could react with complex **2.20** instantly in CH_2Cl_2 to form intermediate **E** in Chart 2.9. The intermediate **F** could be formed after reductive elimination of HCl. The complex **F** has no extra hydrogen on the silicon group available for reduction of the carbonyl group at this point. Once diphenylsilane is introduced, the intermediate **G** can be formed. The coordination of a carbonyl group on the newly formed intermediate **G** would make the reduction effective, as this intermediate **G** has a transferable hydride on only one of the silyl groups. At this stage, there are always two silicons attached to the metal center, but only one of them posseses a transferrable hydride. If complex **G** is the active intermediate which is responsible for the stereochemical outcome, this modification may alleviate the problem caused by bis-silyl metal complex **D** (Chart 2.9). The formation of intermediate **G** has actually turned the competition between two dihydrosilanes in intermediate **D** into the competition between monohydrosilane and dihydrosilane in intermediate **G**. The reaction rate of the latter (monohydrosilane versus dihydrosilane) could alleviate the problem due to intermediate **D** (Chart 2.9).

The results obtained do not seem to support this approach. The enantiomeric excess of the product remained the same regardless of the amounts of monosilane **2.14** added to the reaction system (Table

2.14). The results indicated that intermediate **D**, if formed as proposed, was not a major reason for the stereochemical outcome in the asymmetric hydrosilation of prochiral ketones (Table 2.14).

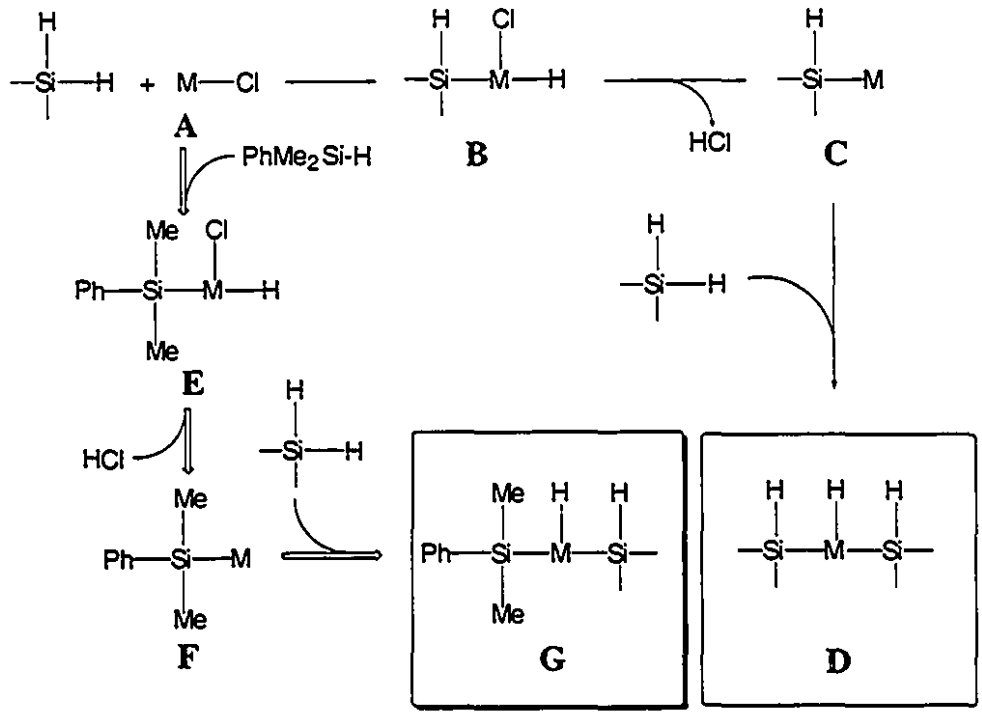


Chart 2.9

Table 2.14: Hydrosilation with two different silanes

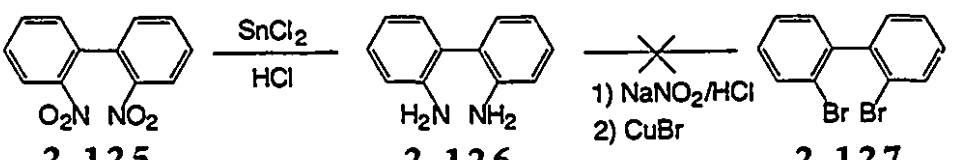
entry[a]	[Rh][b] (% mol)	cond., time (h)	monosilane	yield	% ee
1	1.4 %	rt, 10 h	-	91 %	38 % *(S)*
2	0.7 %	rt, 10 h	0.15 mmol	85 %	36 % *(S)*
3	0.5 %	rt, 10 h	0.30 mmol	82 %	38 % *(S)*
4	0.3 %	rt, 10 h	0.60 mmol	91 %	38 % *(S)*

a) acetophenone/H_2SiPh_2/THF
b) (-)-BPPFA-$(Ph_3P)_4RhH$ (L : M = 1 : 3.9).

ii) Cyclic Silane

On the other hand, if there is only one silicon atom in the silametal complex, the silicon center itself also is a key factor for the stereochemical outcome of the reaction. Several comformers may exist due to the rotation of the M-Si bond. Many additional possibilities exist because the incoming carbonyl group can coordinate with the silicon center *via* the penta- and/or hexa-coordinated metalo-silicates. One way to reduce the number of possible diastereomeric intermediates at the silicon center, is to tie together phenyl groups on the silicon center in a cyclic structure. In light of this rationale, a cyclic silane of structure **2.130** was synthesized.

The first attempt to synthesize the cyclic silane was to start from α,α'-dinitrobiphenyl. Reduction of the dinitro to the diamino groups by stannous chloride/HCl was carried out under mild conditions with high yield (98%).[203] However, using the diazonium salt method to convert the diamino groups to the dibromo groups proved to be a problem.[204] The product **2.127** was generated in low chemical yield (<10%; Scheme 2.30).

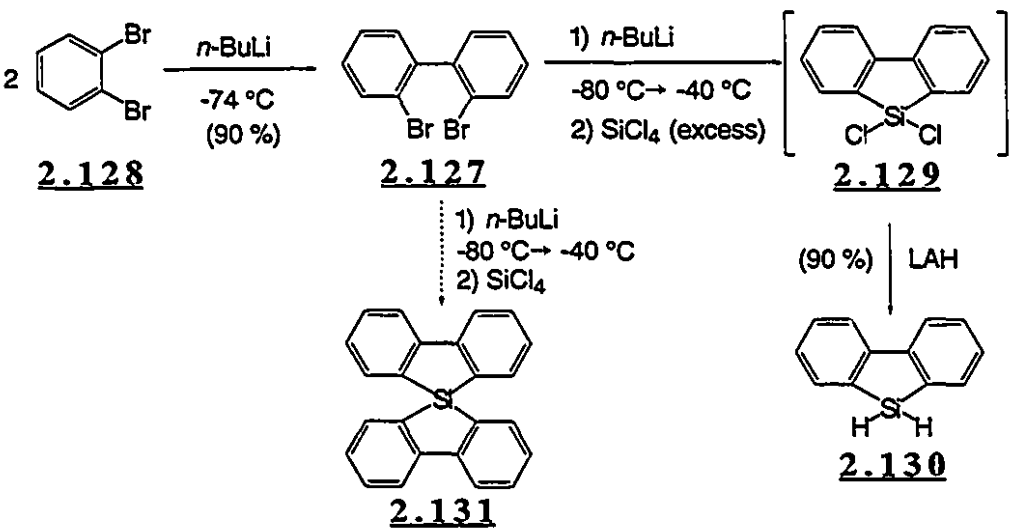


2.125 **2.126** **2.127**

Scheme 2.30

An alternative approach to obtain **2.130** is shown in Scheme 2.30. 2,2'-Dibromobiphenyl (**2.128**) was made with excellent yield

(90%) from 1,2-dibromobenzene and *n*-butyllithium at -74 °C.[205] Half of the starting dibromobenzene was smoothly converted into 2-bromo-1-lithiobenzene at low temperature, which was then coupled with the other half of the starting material to form biphenyl **2.127** in excellent yield (90%). Lithiation of this dibromobiphenyl, **2.127**, with *n*-butyllithium[206] at low temperature (-80 °C to -40 °C) afforded a yellow precipitate. Tetrachlorosilane, freshly distilled from calcium hydride, was added to this reaction mixture at -80 °C in large excess (10 equivalents). The reaction mixture was stirred at low temperature for about 30 minutes, and the mixture become clear. The clear solution was then allowed to stir below -30 °C for 1 hour. The excess tetrachlorosilane was removed at low temperature *in vacuo*. One pot reduction of this dichlorosilabiphenyl intermediate, **2.129**, with $LiAlH_4$, *in situ*, afforded the final product **2.130** with an excellent chemical yield (90%; Scheme 2.31).



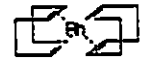
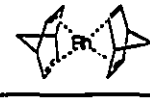
2.128 **2.127** **2.129** **2.131** **2.130**

Scheme 2.31

It was interesting to note that when less than two equivalents of tetrachlorosilane was used to quench the dilithiobiphenyl *in situ*, the reaction gave the sila-spiro compound **2.131** as the major product as shown in Scheme 2.31.

With the cyclic silane **2.130** in hand, we tried the hydrosilation of acetophenone catalyzed by the BINAP-Rh^+ system. This modification gave the reaction a relatively high optical yield [44% ee *(S)*], compared to that of the diphenylsilane in the same catalytic system [10% ee *(S)*]. This was quite an encouraging result for this catalytic system. Surprisingly, the enantiomeric excess decreased substantially when the chiral complex was made from BINAP and complex **2.19**, where one of the COD ligands was replaced by two triphenylphosphine ligands. The BPPFA-RhH complex, which usually gave relatively high enantiomeric excess, produced only 8% ee with this cyclic silane. Apparently, this cyclic silane, **2.130**, is not compatible with the chiral complex BPPFA-RhH (Table 2.15).

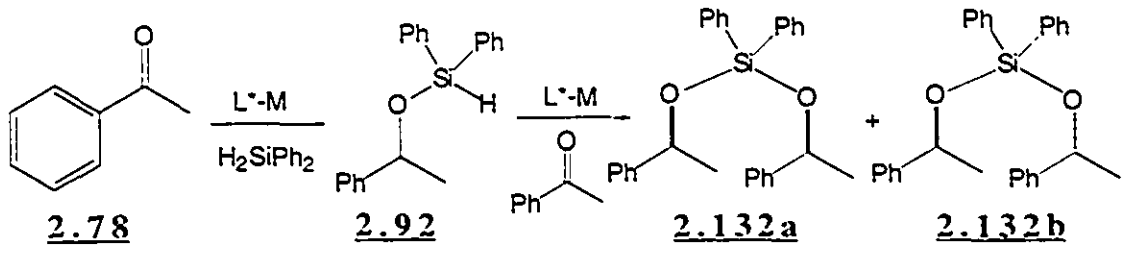
Table 2.15: Hydrosilation with cyclic silane

entry*	substrate	[M]	ligand	Rh:L	[Rh] (% mol)	t (h), cond.	yield	% ee
1	 (2.78)	$(Ph_3P)_4RhH$	*(S)*-BINAP	1:3.5	3 %	6 h, rt	72 %	8 % *(S)*
2	•		•	1:2.3	3 %	6 h, rt	70 %	44 % *(S)*
3	•		•	1:4	5 %	4 h, rt	66 %	8 % *(S)*
4	 (2.121)		(-)-BPPFA	1:3	11 %	10 h, rt	64 %	60 % *(S)*

*) cyclic silane **2.130** /THF.

2.3.2.3.3 Chiral Amplification

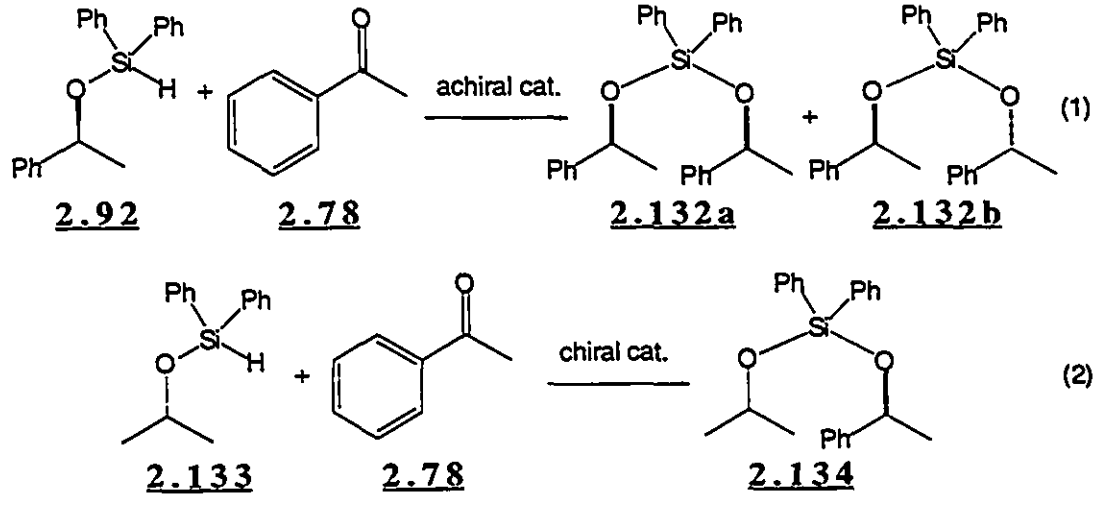
Asymmetric hydrosilation of acetophenone (**2.78**) with diphenylsilane (**2.21**) catalyzed by a chiral complex of **2.20** can be treated as a two-step reaction if less than half an equivalent of diphenylsilane is used in the process. First, the asymmetric addition of the Si-H bond to the carbonyl group of acetophenone gives the chiral (phenylethoxy)diphenylsilane (**2.92**). Since monohydrosilane is much less reactive than dihydrosilane, the reaction of **2.92** with the excess of acetophenone (**2.78**) is too slow relative to the first step and all the diphenylsilane should be converted to the optically active monohydrosilane product, **2.92**. The second step involves the optically active monohydrosilane **2.92** reacting with the second acetophenone to form diastereomeric dialkoxysilanes **2.132**. This time, the reaction is influenced by both the chiral silane **2.92** and the chiral catalyst, *i.e.* double asymmetric induction.[207] The net chiral induction of the reaction could be amplified through this second step. Although acetophenone is used for the purpose of this analysis, the approach could be applied to other prochiral ketones in asymmetric hydrosilation reactions. It was found that the chiral silane, (phenylethoxy)diphenylsilane (**2.92**), could produce diastereomeric excess in asymmetric hydrosilation of acetophenone catalyzed by the achiral catalyst **2.20**. The local configuration of the major diastereomer formed from the asymmetric hydrosilation appeared to be the same as that of the starting chiral silane **2.92** (Scheme 2.32).



2.78 2.92 2.132a 2.132b

Scheme 2.32

The chiral induction of the reaction will be amplified only if in the second step, the effects of the chiral silane, 2.92, and the chiral catalyst are matched. To find out whether or not the effects of these two agents are matched, the following reactions were conducted. The chiral silane 2.92 was allowed to react with acetophenone catalyzed by achiral catalyst 2.20 [$(PPh_3)_4RhH$]. The chiral complex of 2.20 was then used to catalyze the hydrosilation of the same substrate 2.78, but this time, an achiral silane 2.133 was used to estimate the asymmetric induction of the reaction (Scheme 2.33).



2.92 2.78 2.132a 2.132b

2.133 2.78 2.134

Scheme 2.33

This approach also includes another important component, in which the minor enantiomer produced in the first step may react to produce mainly the opposite enantiomer (mismatched double asymmetric induction) in the second step. This part of the design prevents the minor enantiomer produced in the first step to be amplified in the second step, which could make the whole approach meaningless (Chart 2.10).

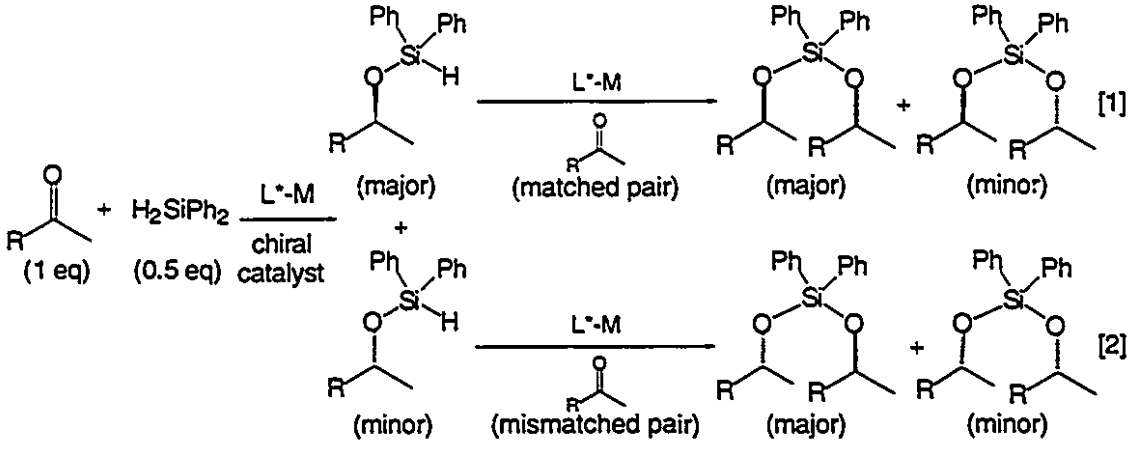
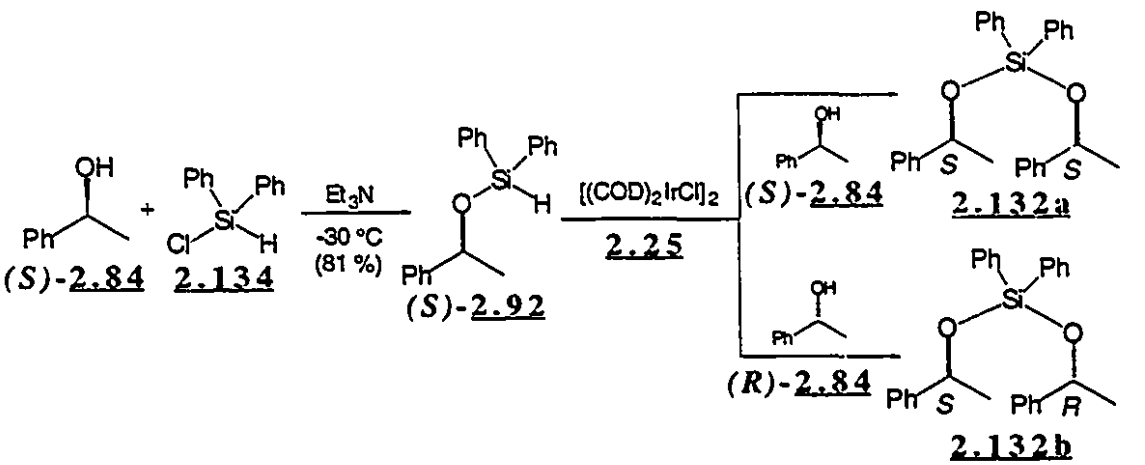


Chart 2.10

To check the first equation, we used C(1)-^{13}C labelled acetophenone as the starting material, so that we can use ^{13}C NMR to determine the ratio of the two diatereomeric products **2.132a** and **2.132b**. The natural abundance of ^{13}C (1.1%) is relatively low so that the signals derived from the unlabeled chiral silane become insignificant, and within the limit of error of NMR spectroscopy (< 5%).

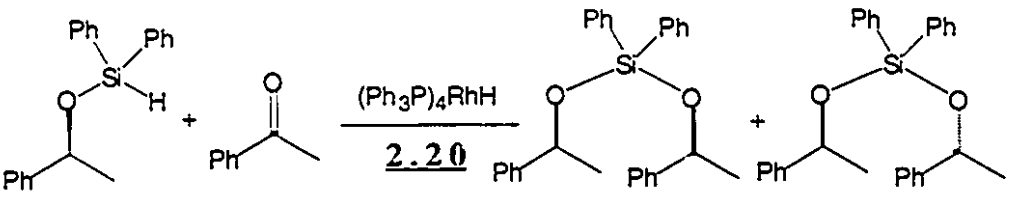
The absolute stereochemistry of these two diastereomers were assigned using ^{13}C NMR compared with that of authentic *(S,S)*- and *(S,R)*- diastereomers made according to Scheme 2.34. The *(S)*-

phenylethoxydiphenylsilane (2.92) was coupled with *(S)-sec*-phenethyl alcohol *via* the metal catalyst chloro(1,5-cyclooctediene)iridium(I) dimer (2.25). As it was very difficult to purify the dialkoxysilane products 2.132, the crude products were used in the measurements. The *(S,S)*- or *(R,R)*- diastereomer (2.132a) had a signal at 71.19 ppm for the alkoxy methine. The signal belongs to the same carbon as for the *(S,R)*- or *(R,S)*-diastereomer (2.132b) at 71.24 ppm (Scheme 2.34).



Scheme 2.34

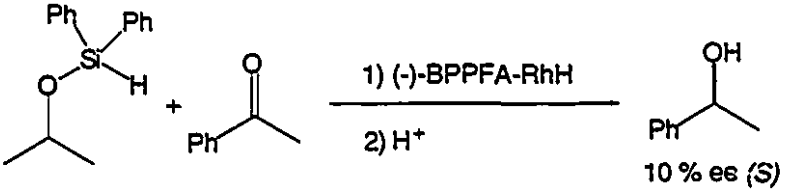
The intermediate monohydrosilane, *(S)*-phenylethoxydiphenyisilane 2.92, was used in the hydrosilation of acetophenone in the presence of achiral catalyst 2.20. The result was quite encouraging. The product 2.132 had a diastereomeric excess of 48% in favor of the *(S,S)*-diastereomer (2.132a; Scheme 2.35).



(S)-2.92 2.78 *(S,S)*-2.132a *(S,R)*-2.132b

Scheme 2.35

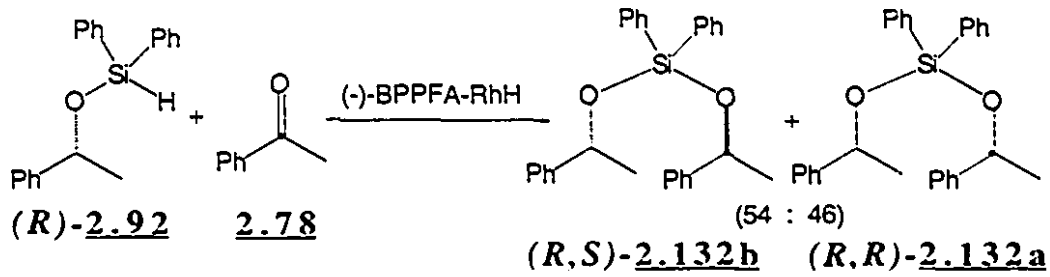
To check the second equation in Scheme 2.10, the reaction of the achiral silane, isopropoxydiphenylsilane (2.133), with acetophenone catalyzed by the chiral catalyst, (-)-BPPFA-RhH, gave a product 2.84 with an enantiomeric excess of 10% in favor of the *(S)*-enantiomer. It appeared that the effects of the chiral silane and the chiral catalyst were matched (Scheme 2.36).



2.133 2.78 2.84

Scheme 2.36

To test the mismatched double asymmetric induction for the minor enantiomer generated in the first step as shown in Chart 2.9, the enantiomer *(R)*-2.92 was used in the hydrosilation of acetophenone in the presence of the same chiral complex (-)-BPPFA-RhH. The reaction produced only 8% de in favor of the *(R,S)*-isomer, 2.132b (Scheme 2.37).



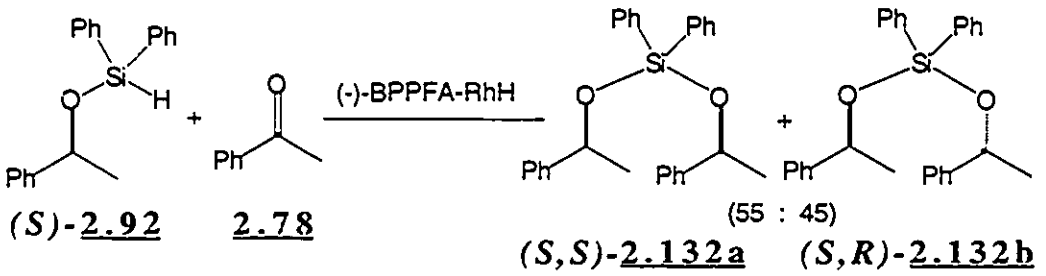
(R)-2.92 2.78 *(R,S)*-2.132b *(R,R)*-2.132a

Scheme 2.37

Having these results in hand, we knew then that there was a possibility to develop a system which could perform hydrosilation of prochiral ketones using double asymmetric induction. The magnitude of double asymmetric induction can be estimated.[208] For the chiral silane, the local enantiomeric ratio of the product was 74 *(S)* : 26 *(R)* = 2.8 : 1; while for the chiral catalyst, the enantiomeric ratio of the product was 55 *(S)* : 45 *(R)* = 1.2 : 1. The combined double asymmetric induction can produce a product with an enantiomeric ratio of 77 *(S)* : 23 *(R)* (1.2 X 2.8 : 1 = 3.4 : 1), *i.e.* the final enantiomeric excess of the second step is about 54% ee *(S)* (Scheme 2.38).

Unfortunately, when a double asymmetric hydrosilation of acetophenone with *(S)*-phenylethoxydiphenylsilane (**2.92**) catalyzed by the chiral catalyst, (-)-BPPFA-RhH, was carried out under identical reaction conditions as discussed above, the reaction gave only poor diastereomeric excess in favor of the *(S,S)*-diastereomer, **2.131a** (10% de), far from the predicted result (Scheme 2.38).

Due to this poor result for the double asymmetric induction, the enantiomeric excess produced in the first step is unlikely to be amplified in the second step.



(S)-2.92 2.78 *(S,S)*-2.132a *(S,R)*-2.132b

Scheme 2.38

2.3.2.3.4 Chiral Oxazolinyl Ligands

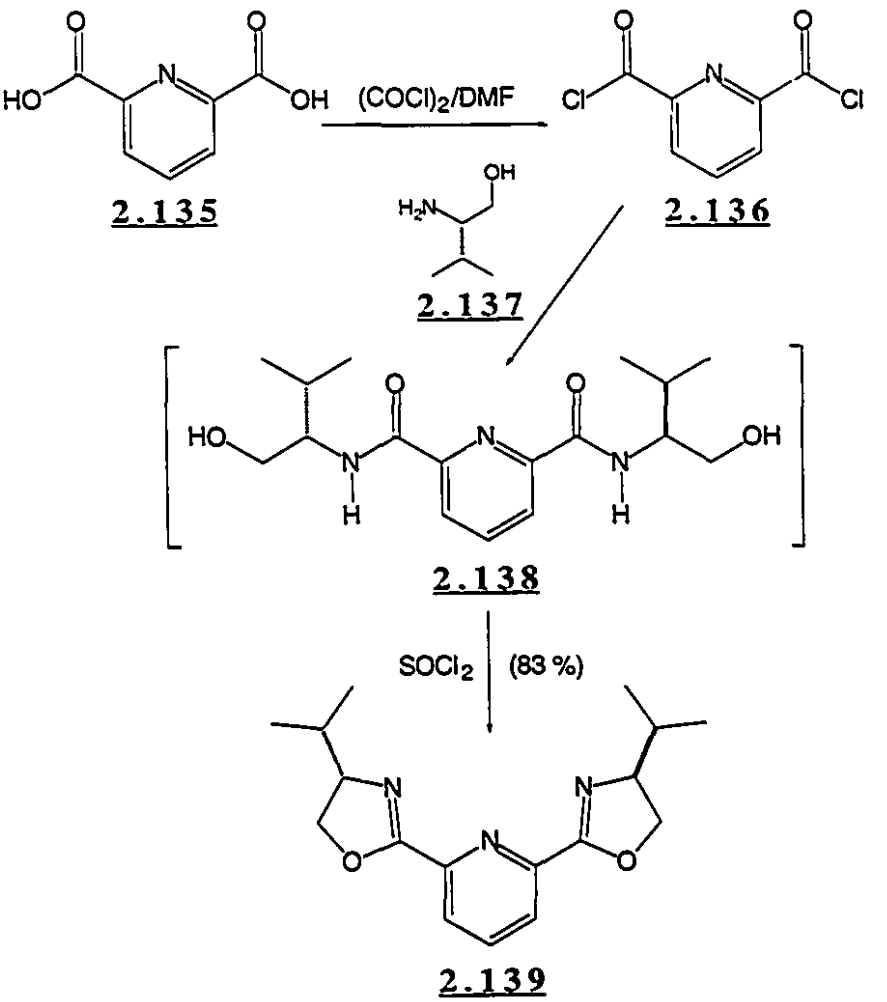
Recently, the use of chiral oxazolinyl ligands has attracted much attention for several reasons (section 1.1.2.3.2). This type of ligand has been reported to induce relatively higher enantiomeric excess in asymmetric catalysis than chiral phosphino ligands. Also, this type of ligand is usually easy to make from readily available natural animo acids, and they are more stable than chiral phosphine ligands. The applications of this type of chiral ligand have been extensively reviewed.[118]

i) C_2 Symmetry Ligands

a) Chiral Rhodium Complexes

Among these known chiral oxazolinyl ligands, the C_2 symmetric ligand **2.139** has been reported to give very high enantiomeric excess in the asymmetric hydrosilation of ketones in the form of the C_2-$RhCl_3$ complex as the catalyst precursor.[123] The advantages of this

catalyst precursor are: the ligand is stable and easy to make and the precursor can be purified by silica gel column chromatography which eliminates competing impurities for future reactions. The same ligand was synthesized and used in our investigations on asymmetric hydrosilation of prochiral ketones (Scheme 2.39).



Scheme 2.39

The acid chloride **2.136** was made from the corresponding dicarboxylic acid **2.135** using oxalyl chloride and catalytic amounts of DMF at 0 °C.[179] It was then coupled with *(S)*-valinol (**2.137**) to

generate the diamide **2.138** as an intermediate, which was further converted, *in situ*, to the final product **2.139** with thionyl chloride in chloroform. After recrystalization, a white crystalline product was obtained in good yield (83% in three steps; Scheme 2.39).

The drawback of the reported catalytic system, which used silver tetrafluoroborate to activate the catalyst precursor, is that the system has difficulty accommodating substrates containing halide groups. Also, the system requires a relatively large excess of chiral ligand to subdue the catalytic activity of the silver salt.[123] To avoid these problems caused by the presence of silver salt, chiral complexes were generated in activated forms with the chiral ligand, C_2 symmetric **2.139**, in our investigations of the asymmetric hydrosilation of prochiral ketones.

The chiral complex C_2-RhH, formed by reacting the C_2 ligand with the complex hydridotetrakis(triphenylphosphine)rhodium(I) (**2.20**), gave only 6% ee *(S)* in the reduction of acetophenone (**2.78**) with diphenylsilane (**2.21**).

The same chiral ligand was used to form the C_2-RhCl complexes *in situ* with the complex μ-dichlorotetraethylenedirhodium(I) (**2.10**) and the complex chloro(1,5-cyclooctadiene)rhodium(I) dimer (**2.12**). The optical yields induced by these two chiral complexes in the hydrosilation of acetophenone were relatively low [18% ee *(S)* and 8% ee *(S)*, respectively (Table 2.12)].

Since we noticed that the chiral catalytic system, C_2-$RhCl_3/AgBF_4$, could generate high enantiomeric excess during asymmetric hydrosilation of ketones, the cationic rhodium complexes bis(1,5-cyclooctendiene)rhodium(I) tetrafluoroborate (**2.17**) and

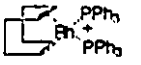
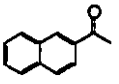
(1,5-cyclooctadiene)bis(triphenylphosphine)rhodium(I) hexafluorophosphonate (**2.19**) were used to form the chiral C_2-Rh^+ complexes *in situ* for mediating hydrosilation reactions. The tridentate C_2 symmetric ligand **2.139** has the tendency to replace one of the COD ligands in bis(COD)rhodium(I) to form the C_2 symmetric complex. Apparently, the COD ligand was replaced easier by the C_2 symmetric **2.139** than the monodentate triphenylphosphine ligand when complex **2.19** was the precursor. Upon heating at 90 °C, the displacement of the COD ligand of complex **2.19** with the C_2 symmetric ligand **2.139** occured smoothly, as indicated by the formation of free COD [^{1}H: δ = 5.53 ppm (s), 2.34 ppm (s)], as well as formation of the corresponding chiral complex (the characteristic isopropyl signals at δ = 0.53 ppm (d) and 0.11 ppm (d) were observed). The results listed below show only poor to moderate enantiomeric excess have been generated with these catalytic systems (Table 2.16, 2.17).

Table 2.16: Hydrosilation fo acetophenone with C_2 ligand (**2.139**) complexes

No*	complex	Rh:L*	[Rh] (% mol); cond., t. (h)	yield	% ee
1	$(Ph_3P)_4RhH$	1 : 2.8	0.8 %; rt, CH_2Cl_2,48 h	78 %	6 % *(S)*
2	$[(C_2H_4)_2RhCl]_2$	1 : 4.6	1.9 %; rt, THF, 72 h	80 %	18 % *(S)*
3	$[(COD)RhCl]_2$	1 : 3.0	0.5 %; -5 °C, THF, 12 h	90 %	8 % *(S)*
4	$(COD)_2RhBF_4$	1 : 3.3	0.6 %; 0 °C, THF, 12 h	90 %	46 % *(S)*
5	$(COD)Rh(PPh_3)_2$	1 : 6.5	0.4 %; 0 °C, THF, 12 h	74 %	22 % *(S)*

*) acetophenone was reduced by H_2SiPh_2; L = **2.139**

Table 2.17: Hydrosilation of ketones with C_2 ligand (**2.139**) complexes

entry[a]	substrate		[M]	Rh:L[b]	[Rh] (% mol)	t (h), cond.	yield	% ee
1		(2.78)		1:6.5	1 %	6 h,-14→ 0 °C ($CDCl_3$)	74 %	22 % *(S)*
2	"			1:3.3	0.5 %	rt, 0 °C 12 h (neat)	90 %	46 % *(S)*
3		(2.116)	"	1:2.3	1 %	rt, 12 h ($CDCl_3$)	77 %	2 %
4		(2.117)	"	1:2.3	1 %	rt, 12 h ($CDCl_3$)	80 %	4 %
5		(2.118)	"	1:2.3	1 %	rt, 12 h ($CDCl_3$)	87 %	32 %
6		(2.140)	"	1: 5	0.7 %	rt, 12 h ($CDCl_3$)	88 %	30 % *(S)*
7		(2.122)	"	1:2.7	1 %	rt, 7 h ($CDCl_3$)	72 %	24 %

a) H_2SiPh_2 was used. b) C_2 **2.139** was used in all cases.

Compared with C_2-$Rh^+(PPh_3)_2$, the chiral complex C_2-Rh^+(COD) induced higher enantiomeric excess in the reduction of acetophenone. The reduction of ketones **2.116**-**2.118**, again demonstrated that the steric hindrances in the area **a** in Figure 2.15 was important for the stereochemical outcome of the reactions (Figure 2.21).

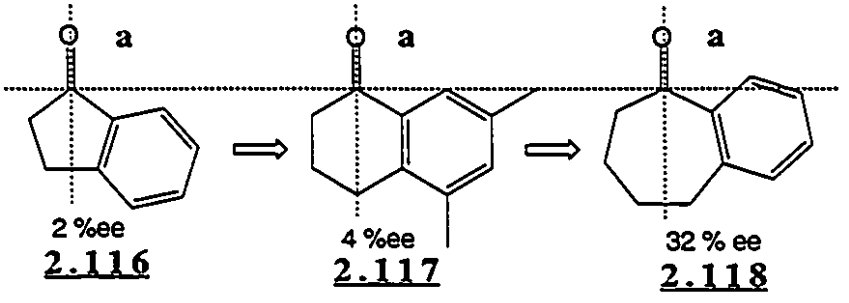


Figure 2.21

Modification of the electronic properties of the carbonyl group of acetophenone by incorporating a benzo group or α-trifluoride as in substrates **2.140** and **2.122**, did not enhance the optical yields (Table 2.17).

Unlike chiral phosphine ligands (section 2.3.2.2.2), where a proper amount of chlorinated solvent can enhance optical yield, both chlorinated and non-chlorinated solvents decrease the enantiomeric excess of the product with the C_2-M system. However, the non-chlorinated solvent affected the optical yield (46% to 10% ee) substantially more than the chlorinated solvent (46% to 36% ee; Table 2.18)

Table 2.18: Enantiomeric excess affected by solvents

No[a]	Rh:L*[b]	[Rh] (% mol);	cond., t. (h)	yield	% ee
1	1 : 3.3	0.5 %	0 °C, neat,12 h	90 %	46 % *(S)*
2	1 : 3.0	0.5 %	0 °C, $CDCl_3$, 12 h	81 %	36 % *(S)*
3	1 : 7.0	1.0 %	0 °C, THF, 12 h	90 %	10 % *(S)*

a) acetophenone was reduced by H_2SiPh_2. b) $(COD)_2RhBF_4$ and **2.139**.

Similar to the situation observed for chiral complexes derived from chiral phosphine ligands, dilution of the reaction system also had a negative effect on chiral induction for chiral oxazolinyl metal complexes. The optical yield of the hydrosilation reaction mediated by the chiral oxazolinyl metal complexes dropped substantially when the reaction mixture was diluted with solvent (Table 2.19).

Table 2.19: Enantiomeric excess affected by amount of solvent

No[a]	Rh:L*[b]	[Rh] (% mol);	cond., t. (h); sol (ml)	yield	% ee
1	1 : 5	0.7 %	rt, 12 h; $CDCl_3$ (0.5)	88 %	30 % *(S)*
2	1 : 5	0.7 %	rt, 12 h; $CDCl_3$ (2.0)	83 %	24 % *(S)*
3	1 : 5	0.7 %	rt, 12 h; $CDCl_3$ (5.0)	80%	18 % *(S)*

a) 2-acetonaphthone (**2.140**) was reduced by H_2SiPh_2.
b) $(COD)_2RhBF_4$ and **2.139**.

The presence of excess chiral ligand increased the enantiomeric excess generated in the hydrosilation reaction using chiral oxazolinyl compounds.[121b] However, once the ratio of M/L reached a certain point, further addition of ligand had little effect on the optical yield of the reaction (Table 2.20).

Table 2.20: Enantiomeric excess affected by amount of ligand

No[a]	Rh:L*[b]	[Rh] (% mol);	cond., t. (h); sol	yield	% ee
1	1 : 5	1 %	rt, 12 h; $CDCl_3$	91 %	36 % *(S)*
2	1 : 10	0.5 %	rt, 12 h; $CDCl_3$	82 %	42 % *(S)*
3	1 : 55	0.5 %	rt, 12 h; $CDCl_3$	87%	44 % *(S)*

a) acetophenone (**2.78**) was reduced by H_2SiPh_2.
b) $(COD)_2RhBF_4$ and **2.139**.

Apparently, the dissociation of the chiral oxazolinyl metal complexes seemed to be a problem in the asymmetric hydrosilation of prochiral ketones. Brunner's proposal indicates that the formation of complex **IX**[121b] in Chart 2.11, which could generate high enantiomeric excess in the reaction, was favored by the presence of

excess chiral ligand, L-L'. This argument was not very plausible since it is unclear how the second liagnd, L-L' added to the intermedirte **IX**, L-L' could help to enhance to optical yield of the reaction. The above mentioned solvent and chiral ligand effects could be an indication of the dissociation of chiral oxazolinyl metal complexes. Dilution with solvent may increase the concentration of the 'naked' intermediate **IV**, which certainly disfavors the optical yield of the reaction. Although, more chiral ligand presented in the reaction mixture could help the generation of chiral intermediates **V**, **VI**, **VII** and **VIII**, the enhancement of chiral induction is limited by the formation of isomeric intermediates **V/VI** and **VII/VIII** (Chart 2.11).

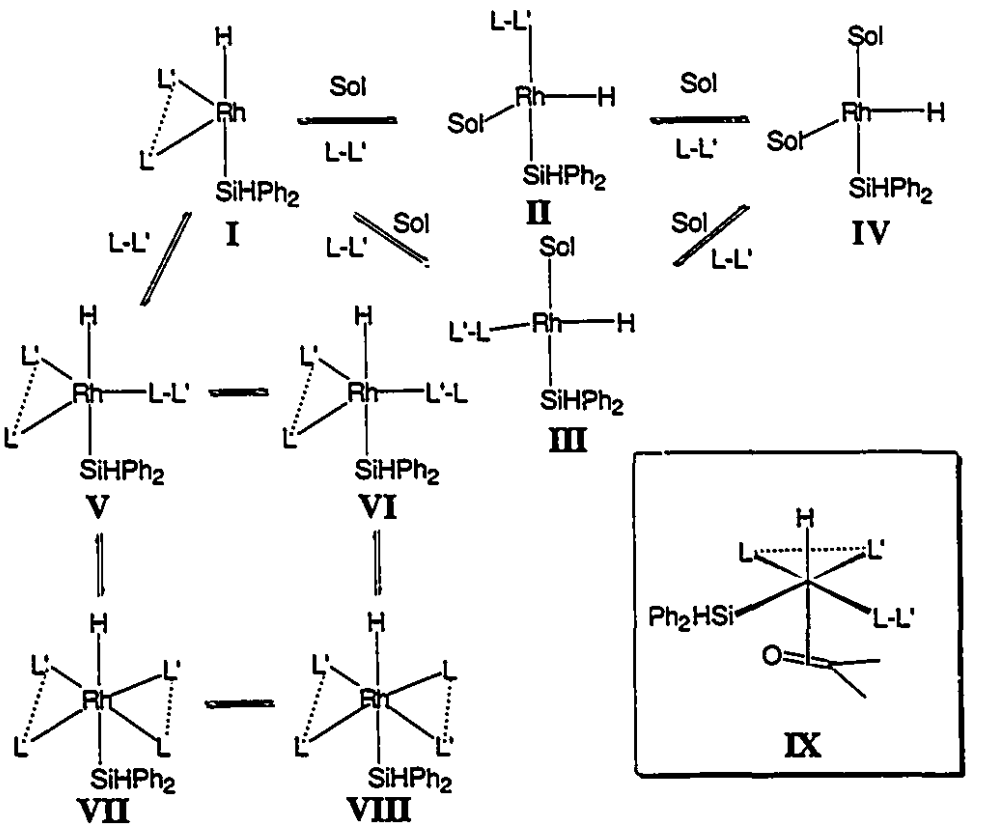


Chart 2.11

The hydrosilation of acetophenone proceeded much slower when monohydrosilane was used in the reaction instead of diphenylsilane. The enantiomeric excess of the reaction with the monohydrosilane was also very poor compared with the results derived from diphenylsilane. It is interesting to note that, in general, the stereochemical outcome of the reaction with monohydrosilane [*(R)*-enantiomer in favor] was opposite to that with diphenylsilane [*(S)*-enantiomer in favor] (Table 2.21).

Table 2.21: Enantiomeric excess affected by different silanes

No[a]	Rh:L*[b]	[Rh] (% mol);	silane	cond., t. (h)	yield	% ee
1	1 : 5	2 %	Ph_2SiH_2	rt, 72 h	80 %	18 % *(S)*
2	1 : 6	5 %	$PhMe_2SiH$	rt, 336 h	82 %	4 % *(R)*

a) acetophenone (**2.78**)/THF.
b) C_2-**2.139**/$[(C_2H_4)_2RhCl]_2$.

The reaction temperature was crucial for hydrosilation to be carried out sucessfully. For instance, no reaction occured at -20 °C (8 h) and -5 °C (8 h) for hydrosilation of acetophenone (**2.78**) with diphenylsilane (**2.21**) catalyzed by the C_2-Rh^+(COD) complex. On the other hand, the reaction proceeded smoothly at 0 °C and was complete in 12 hours. For reasons unknown, the enantiomeric excess of the reaction was low. Only 6% ee was obtained from this pre-cooled reaction mixture (Table 2.22). A similar result was obtained with the chiral C_2-RhCl complex derived from precursor **2.10**.

Table 2.22: Enantiomeric excess affected by temperature

No[a]	complex	Rh:L*[b]	[Rh] (% mol);cond.; t. (h)	yield	% ee
1	$(COD)_2RhBF_4$	1 : 3	0.5 %; 0 °C, 12 h, $CDCl_3$	81 %	40 % (*S*)
2	$(COD)_2RhBF_4$	1 : 20	0.3 %; -20 °C (8 h)→ -5 °C (8 h) → 0 °C, 12 h, $CDCl_3$	82 %	6 % (*S*)
3	$[(C_2H_4)_2RhCl]_2$	1 : 5	2 %; rt, 72 h, THF	80 %	18 % (*S*)
4	$[(C_2H_4)_2RhCl]_2$	1 : 5	2 %; -25 °C (72 h)→ -10 °C (24h) → 0 °C (12 h)→ rt, 72 h, THF	80 %	10 % (*S*)

a) acetophenone (**2.78**) was reduced by H_2SiPh_2.
b) C_2-**2.139** was the chiral ligand.

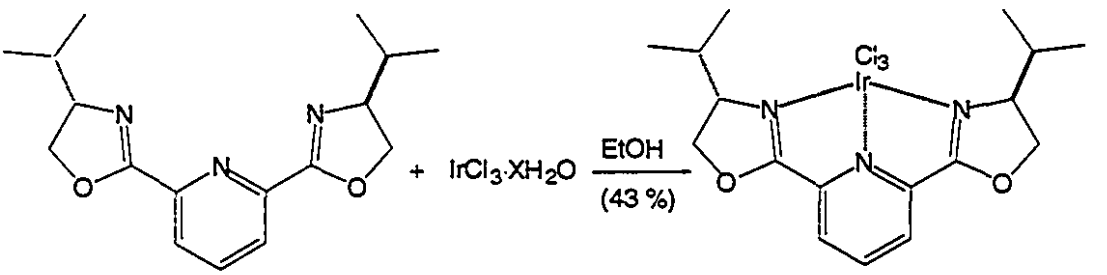
However, if the reaction was allowed to proceed directly at low temperatures without cooling the reaction mixture further below the no-reaction temperature, the optical yield slightly increased (Table 2.22). This observation is in agreement with that of the chiral phosphine ligand system discussed in section 2.3.2.3.

b) Iridium Complexes

The iridium complexes, **2.24** and **2.25** are active towards hydrosilation of ketones. The chiral modification with either chiral phosphine ligands or chiral oxazolinyl compounds, however, led to inactive chiral iridium complexes for the hydrosilation of ketones.[57c]

Interestingly, the chiral C_2-$IrCl_3$ complex (**2.141**), made by reacting the C_2 ligand (**2.139**) with $IrCl_3$ in ethanol, was found active in mediating hydrosilation of prochiral ketones. Like the

corresponding rhodium(III) complex, this complex is also stable in air, and can be purified by silica gel column chromatography (Scheme 2.40).



2.139 2.141

Scheme 2.40

The chiral iridium complex 2.141 was able to catalyze hydrosilation reactions without the presence of silver salts. The reaction proceeded smoothly at room temperature. However, the asymmetric induction was not high (< 8% ee; Table 2.23). In the presence of silver salt, the complex became more potent for the hydrosilation of ketones with diphenylsilane (2.21). Excess chiral ligand in the reaction mixture did not help to enhance the enantiomeric excess in this case. Increasing the amounts of silver salt led to no improvement in the optical yield. As a consequence of using a large excess of silver salt, a dark, shiney metal deposit was observed. In this case, part of the hydrosilation of acetophenone (2.78) with diphenylsilane (2.21) was probably catalyzed by the newly generated iridium metal instead of the chiral iridium complex. A racemic product was obtained (Table 2.24).

Table 2.23: Hydrosilation of acetophenone with C_2-iridium complex

No[a]	[Rh] (% mol);	silane	cond., t. (h)	yield	% ee
1	5.8 %	Ph_2SiH_2	rt, neat, 36 h	92 %	6 % *(S)*
2	1.8 %	$PhSiH_3$	rt, neat, 36 h	78 %	8 % *(R)*

a) acetophenone (**2.78**) was the substrate.
b) iridium complex **2.141** was used in all cases.

Table 2.24: Enantiomeric excess affected by silver salts

No[a]	[M] : L : Ag^+	[Rh] (% mol)	cond., t. (h)	yield	% ee
1	1 : - : 3.4	1 %	rt, neat, 36 h	78 %	2 % *(S)*
1	1 : 2.8 : 3.4	1 %	rt, neat, 36 h	87 %	2 % *(S)*
1	1 : 3.6 : 5.5	1 %	rt, neat, 36 h	81 %	2 % *(S)*
1	1 : 3.5 : 6.5	0.5 %	rt, neat, 36 h	78 %	0 %

a) acetophenone (**2.78**) was the substrate.
b) iridium complex **2.141** was used in all cases.

ii) C_3 Ligands

a) Motivation of Design

Since the first use of C_2 symmetric ligands in asymmetric induction, many fruitful results in the field of asymmetric synthesis have been obtained.[208] The application of this type of ligand in enantiomeric deprotonation,[209] protonation,[210] elimination,[211]

hydrogenation,[212] hydroformylation,[213] hydroboration[214] and hydrosilation[123] has been quite successful in terms of optical yields. Although the reasons behind this success are too complicated to simply rationalize, symmetry could play a key role in this type of asymmetic induction.

During the course of asymmetric catalysis, the catalyst should form less competing diastereomeric transition states and/or key intermediates, which could lead to the desired final products. By introducing C_2 symmetry in the metal complexes, the possible number of intermediates and/or transition states is reduced by about one half. This is an important reason for the enhancement of the optical yield generally observed in asymmetric catalysis.

Different ligands should have different electronic and stereoelectronic effects on the metal center of a chiral complex resulting from different bond angles, σ-bonding and π-back bonding etc. Once an incoming substrate is coordinated at the metal center, a mixture of diastereomeric intermediates are formed. The subtle electronic and stereoelectronic distortions of the newly formed diastereomeric intermediates affect their reactivities. However, not all of the diastereomeric intermediates formed are active. Only those that are reactive enough can lead to product. The final optical yield of the reaction is dominated by the most active intermediate, and less dependent on the relative concentration in the reaction mixture. Different substrates will certainly disturb the electronic and stereoelectronic balances at the metal center differently, which changes the reaction rates for every newly formed diastereomeric intermediate. Different enantiomeric excesses are thus generated for

the very same catalytic system with different substrates. Therefore, the term chiral template is only a practical term for chiral catalysts, since the stereochemical outcome also depends largely on the substrates themselves for the same catalytic systems. In other words, the fourth dimension of the four-dimensional asymmetric catalysis is quintessential for the stereochemical outcome.

Modification of chiral ligands *via* altering steric hindrances will risk the delicate electronic and stereoelectronic balance at the metal center of the chiral complex established for the best stereochemical outcome of the reaction. Any complex generated from a different type of ligand after modification is new in terms of the electronic properties at the metal center. Therefore, any alterations will not necessarily lead to an enhancement of optical yield of the reactions.

It is, however, believed that for every reaction, there is a suitable system for asymmetric catalysis which could produce enantiomerically pure product. It is up to researchers to discover each specific system.[8q] As there are too many possibilities to establish a suitable system for the asymmetric hydrosilation of prochiral ketones, random screening for a suitable system for asymmetric catalysis is time consuming. Inspired by the good results of the C_2 symmetric ligands, we decided to synthesize C_3 symmetric ligands in our pursuit. There are few reported results in asymmetric catalysis concerning C_3 symmetric compounds for chiral phosphine ligands,[215] and no reports on C_3 symmetric oxazolinyl ligands in the asymmetric catalysis of hydrosilation of prochiral ketones. The major benefit of this type of C_3 symmetric ligand is that the potential number of diastereomeric intermediates and/or transition states is

reduced. Furthermore, the C_3 symmetric ligand may chelate to the metal center stronger than the corresponding C_2 symmetric ligands. Therefore, the chiral induction could be re-inforced in the C_3- M complexes due to the three dimensional chelation of the C_3 ligands. Also, dissociation of chiral complexes in the reaction mixture may be alleviated due to the strengthened chelation of chiral C_3 ligands with the metal center. Moreover, the chiral influence of the C_3 chiral ligands is expected to extend to the silyl moiety after the formation of the silyl-metal hydride complex. If the reaction takes place at the silicon center of the complex, as proposed, the chiral induction can be enhanced. Therefore, the C_3 symmetric ligand might induce high enantiomeric excess during the asymmetric catalysis (Figure 2.22).

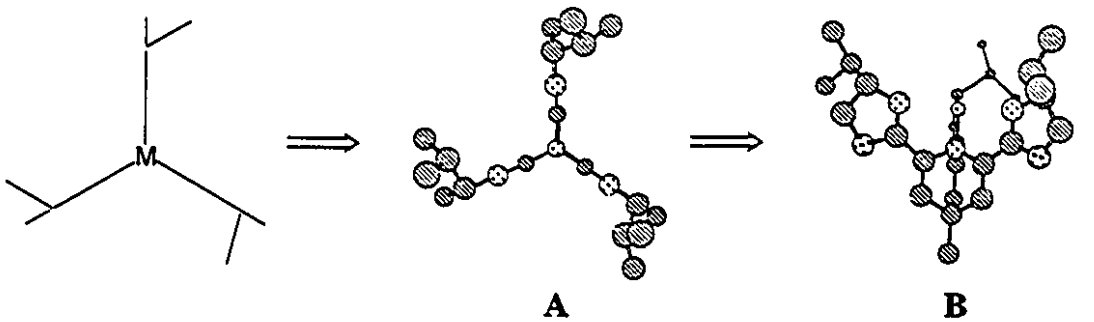


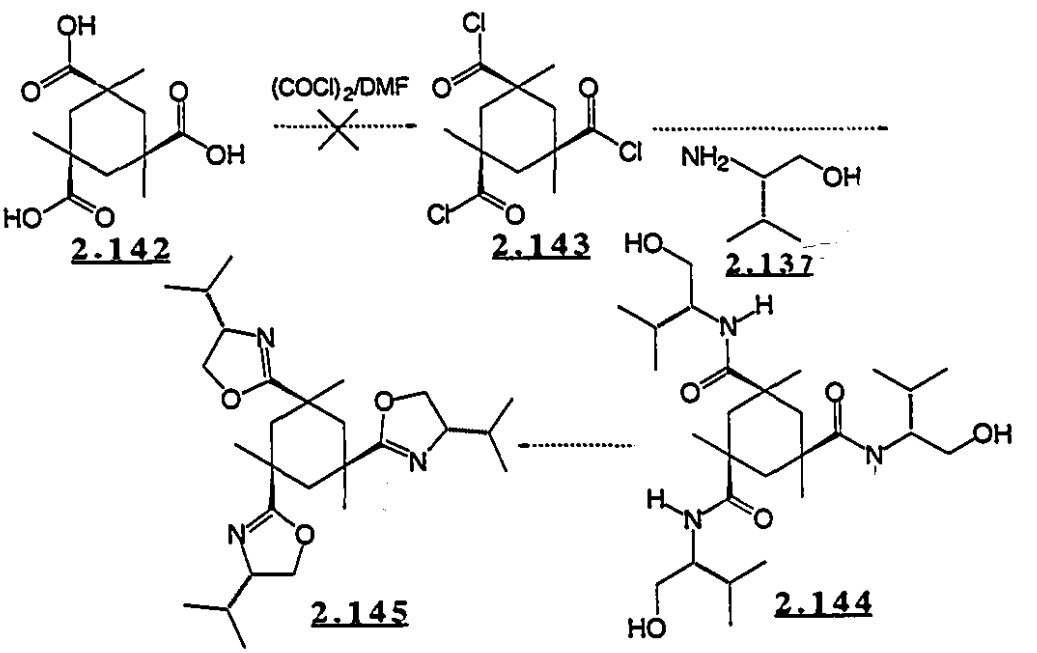
Figure 2.22

Two C_3 symmetric ligands have been designed. One was made from Kemp's triacid (**2.142**), and another was synthesized from nitrotriacetic acid (**2.148**). A transition metal can be set in the middle of the ligands to form C_3 complexes (Figure 2.22). These types of ligands may have less free space for the incoming substrates than that of the corresponding C_2 symmetric ligands. The chiral induction can therefore be reinforced. According to our proposed

mechanism in section 2.2.3.2, the hydride at the silyl moiety of the silicon metal complex is crucial for the reduction of the carbonyl group. Therefore, the protruding isopropyl group attached at the chiral center of the ligand can extend the chiral environment to the silyl group in the silyl metal hydride complex.

b) Strategies of Synthesis

We attempted to prepare the C_3 symmetry ligand derived from Kemp's triacid (**2.142**) *via* the formation of triacid chloride **2.143** under oxalyl chloride/DMF conditions, followed by coupling with amino alcohol, **2.137**, and then cyclisation to the oxazolinyl product, **2.145** (Scheme 2.41).



Scheme 2.41

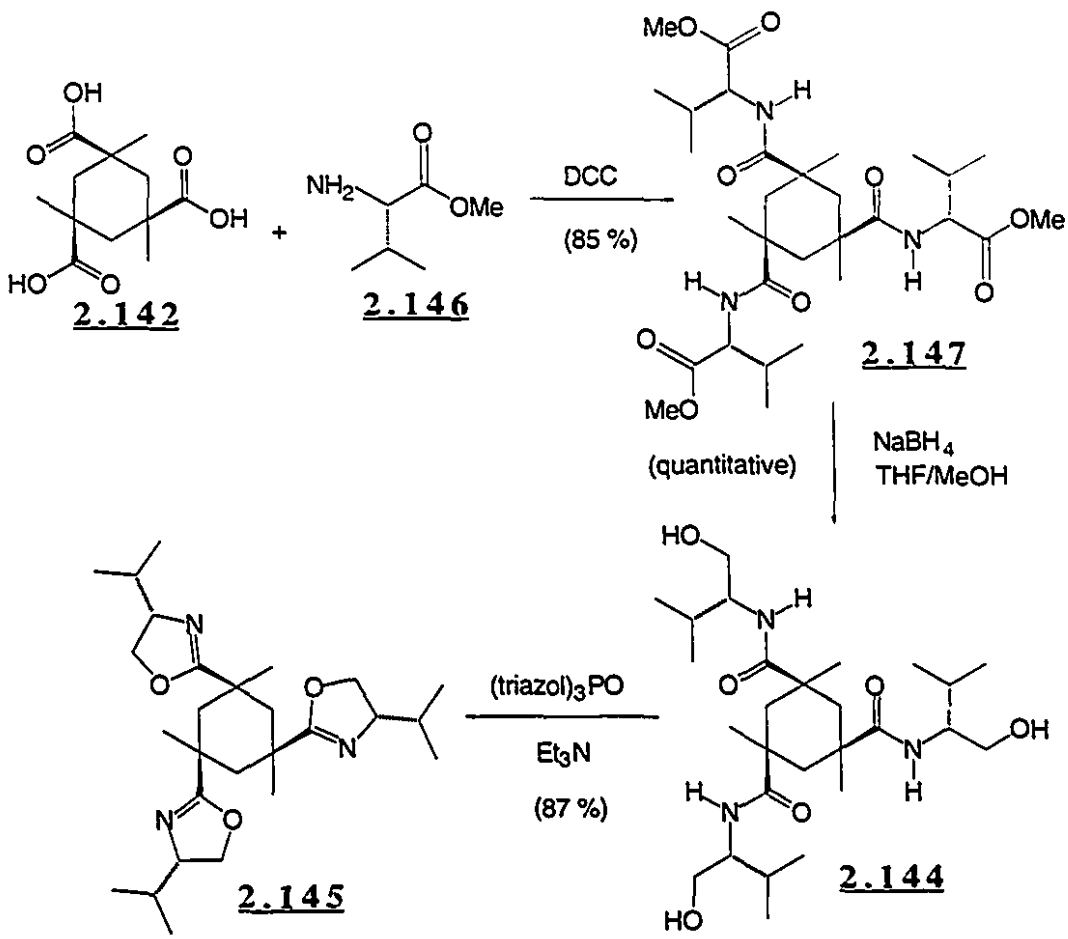
This attempt to generate the triacid chloride **2.143** was not quite successful. Presumably, reaction of triacid with oxalyl chioride/DMF may produce an intramolecular anhydride, which did not allow complete amidation of *(S)*-valinol (**2.137**).

To avoid this problem, another route was chosen to form triamide **2.144** (Scheme 2.42). DCC was used as a coupling reagent to give compound **2.147** in high yield (85%).[216] As three chiral centers have been implanted into compound **2.147**, any recemization should be easy to detect by ^1H NMR spectroscopy. The results show that the coupling reaction with DCC has no significant recemization at the amino attached chiral center, with or without the presence of 1-hydroxybenzotriazole (HOBT), a reagent reported to prevent racemization at the α-chiral center during coupling reactions (Scheme 2.42).[217]

Selective reduction of the ester function to the alcohol was relatively easy to achieve. Sodium borohydride was used to reduce the ester group without attacking the amide function.[218] The reaction had to be carried out in a mixed solvent system (MeOH : THF = 50 : 50). A large excess (5-10 eq.) of sodium borohydride was used to drive the reduction to completion (100%).

Cyclisation of the α-hydroxy amide **2.144** proved to be problematic. The procedure for making C_2 symmetric ligand **2.139**, which used thionyl chloride to promote sucessful cyclisation, was not satisfactory for substrate **2.144**. The reaction gave a mixture of products. Other reagents, such as $(CF_3CO)_2O/Et_3N$,[219] N,N-dimethyl-chloromethyleneammonium chloride[220] and $(CF_3SO_2)_2O/Ph_3PO$[221]

gave similar results. No significant desired product was produced in any of these attempts.



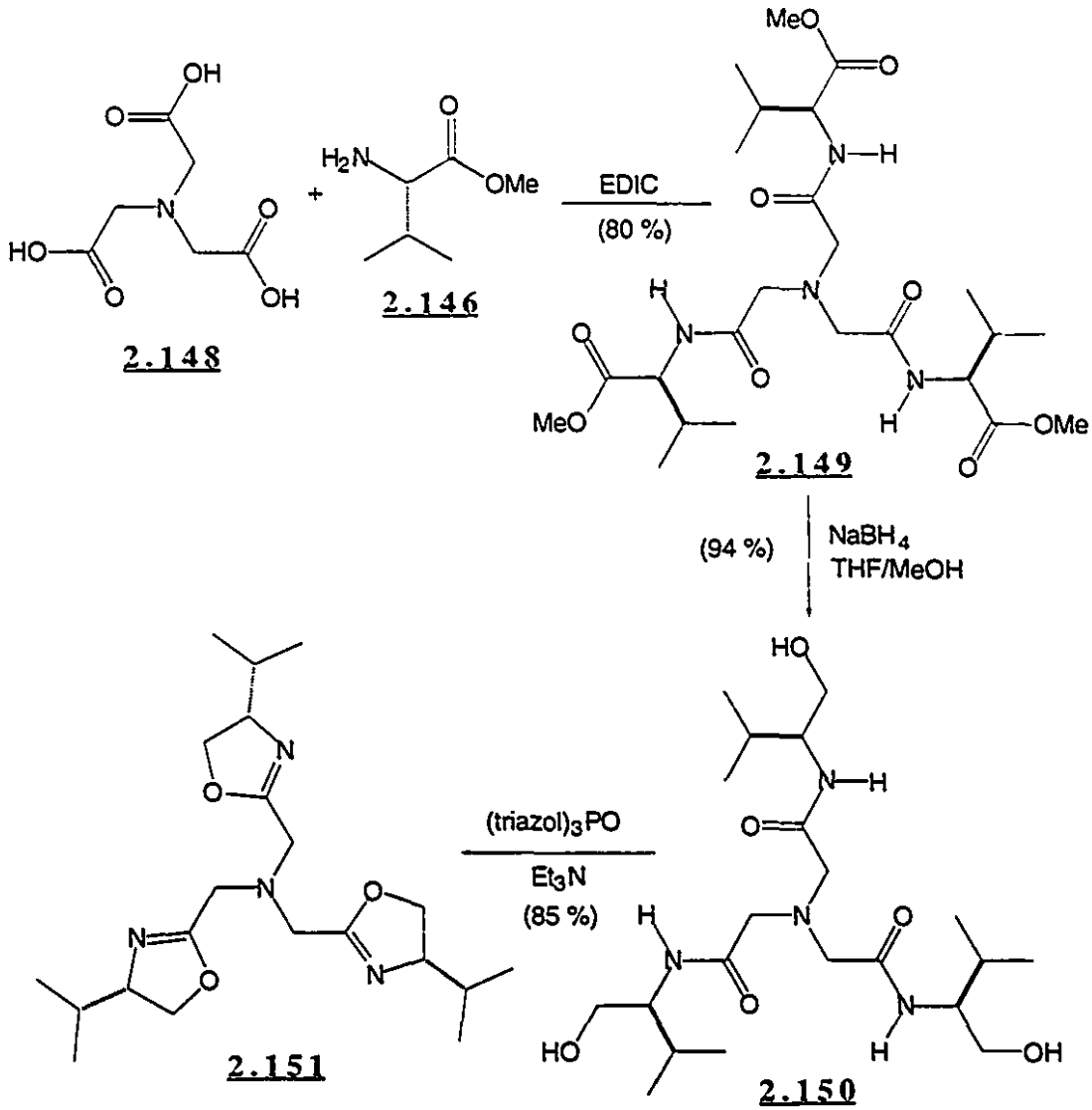
Scheme 2.42

The product was finally obtained with high yield when the mild and potent dehydration reagent, tris(triazole)phosphorite,[222] was used to promote cyclisation. The reagent was prepared by reaction of phosphoryl chloride with 1,2,4-triazole in the presence of triethylamine followed by filtration directly to the reaction flask under argon. Cyclisation proceeded instantly with high chemical yield (87%).

Purification was difficult, as the product decomposed on silica gel and to a lesser degree on neutral alumina gel. Many unwanted by-products were present even after chromatography by neutral alumina. After chromatography on deactivated silica gel with triethylamine, the final product was purified.

The C_3 ligand **2.151** was synthesized *via* the same approach. The coupling reaction of the triacid **2.148** with *(S)*-valine methyl ester (**1.146**) was realized by using the coupling agent EDCI,[223] which is water soluble (Scheme 2.43). After the coupling reaction was completed, saturated ammonium chloride in aqueous solution was added to the reaction mixture. The reaction mixture was then washed with water to give a reasonably pure product **2.149** (80%). The reduction of **2.149** using $NaBH_4$ converted the ester function to an alcohol (**2.150**; 94%). The alcohol, **2.144**, was subsequently cyclized to give the final C_3 product **2.151** with high yield (85%; Scheme 2.43).

It was then found that the product **2.151** was too unstable to be purified by conventional silica or alumina chromatography, even under deactivated conditions. The purified product was always contaminated with some decomposed impurities during the course of purification. However, the pure product could be obtained using gel filtration (Saphedex LH-20) separation.[224]



Scheme 2.43

c) Applications

Unfortunately, attempts to make C_3-complexes, C_3-$RhCl_3$, of **2.145** and **2.151** in the same manner as the corresponding C_2 complex (C_2-$RhCl_3$) were unsuccessful. Presumably, these C_3 ligands can not withstand the reaction conditions and decomposed.

The alternative method, to generate the complexes *in situ*, was also fruitless. The reaction of the C_3 ligand and rhodium complex **2.10** resulted in a mixture of decomposition products. Nevertheless, a mixture of C_3 compound **2.144** and complex **2.10** were used to catalyze hydrosilation of acetophenone (**2.78**) with diphenylsilane (**2.21**). Very poor enantiomeric excess was generated with this mixture [4% ee *(S)*]. The C_3 symmetric ligand **2.151** was even worse. The ligand decomposed rapidily under the reaction conditions used. Further studies involving the asymmetric hydrosilation of prochiral ketones will required chemically stable C_3 symmetric ligands.

III CONCLUSIONS

Hydridotetrakis(triphenylphosphine)rhodium(I), **2.20**, was found to be a very efficient catalyst for the regiocontrolled hydrosilation of α,β-unsaturated carbonyl compounds. The NMR studies indicate that: (i) the reduction of the carbonyl group does not proceed *via* the migration of the hydride group directly from the metal center; (ii) rhodium hydride intermediates (**2.20**, **I**, **I'**, **VII** in section 2.2.3.3) without silyl moiety attached at metal center of the complexes are inactive towards the reduction of carbonyl compounds; and (iii) the substructure, H-Si-Rh-H (**XIV**, **XVII**, **XIX** in section 2.2.3.3), seems to be the one responsible for the great rate acceleration incured in the hydrosilation of ketones with di- or trihydrosilane. The proposed mechanism can thus far acommodate the observed regioselectivity and (1,4-) diastereoselectivity, as well as the difference in reaction rates observed when using different silicon hydrides in the reaction.

The major geometric requirements of the carbonyl compounds for the best enantiomeric excess in asymmetric hydrosilation is the bulkiness presented in quadrant a (Figure 2.14) of the substrate. Higher enantiomeric excess (up to 78%) was realized by chiral ligands with an internal σ-donor, such as BPPFA (**2.111**) and BPPM (**2.112**). In the hopes of decreasing diastereomeric intermediates formed during the reaction, a cyclic dihydrosilane, **2.130**, was synthesized

and used in asymmetric hydrosilation of prochiral ketones. Higher asymmetric induction was achieved in some cases with this cyclic silane (up to 60% ee). Two C_3 symmetric ligands (**2.145** and **2.151**) were designed, synthesized and used in an attempt to make new, C_3 symmetric metal complexes. The latter was not successful due to the decomposition of the C_3 chiral ligands under reaction conditions.

I V EXPERIMENTAL SECTION

General considerations: Most of the chemicals used were purchased from Aldrich. Hydridotetrakis(triphenylphosphine)rhodium(I), chloro(1,5-cyclooctadiene)iridium(I) dimer was purchased from Johnson Matthey. Diphenylchlorosilane, diphenylsilane, triethoxysilane, *t*-butyldimethylsilane and triethylsilane were purchased from Hüls America. THF was distilled over sodium/benzophenone ketyl radical[225] prior to use. Hexanes, ethyl acetate, dichloromethane,[226] triethylamine,[227] pyridine[232a] DMF[228] and acetonitrile were distilled over calcium hydride. 1,2,4-Triazole was recrytalized from CH_2Cl_2/*n*-pentane. Thionyl chloride, phosphoryl chloride, oxalyl chloride were distilled prior to use. *n*-Butyllithium was titrated periodically using 2,5-dimethyoxybenzyl alcohol as indicator.[229] Nuclear magnetic resonance spectra were recorded on VARIAN Gemini 200 (^1H 200 MHz, ^{13}C 50 MHz), XL-200 (^1H 200 MHz, ^{13}C 50 MHz), XL-300 (^1H 300 MHz, ^{13}C 75 MHz) and Unity 500 (^1H 500 MHz, ^{13}C 125 MHz, ^{31}P 202 MHz). Chemical shifts are expressed in parts per million (ppm) and the references are the residual proton signals of $CDCl_3$ (δ = 7.24 ppm for ^1H, δ = 77.00 ppm for ^{13}C NMR), CD_3OD (δ = 3.30 ppm for ^1H NMR), CD_2Cl_2 (δ = 5.32 ppm for ^1H NMR), C_6D_6 (δ = 7.15 ppm for ^1H NMR) and toluene-d_8 (δ = 2.09 ppm for ^1H NMR). ^{31}P NMR chemical shifts are given with respect to aqueous phosphoric acid (H_3PO_4, 85%; δ = 0.0 ppm). The following

abbreviations were used for NMR spectra: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. IR spectra were recorded on an Analet FT A25-18 spectrometer between NaCl plates (neat liquids) or a film on a NaCl plate or as KBr disk. Mass spectra were recorded on a Kratos MS25RFA mass spectrometer. Melting points were determined on a Gallenkamp block and are uncorrected. Elemental analyses were obtained on a CEC 240XA elemental analyzer in the Department of Chemical Engineering, McGill University. Analytical samples for elemental analysis were obtained via column chromatography (silica gel, deactivated with 2% triethylamine in hexanes) using hexanes as eluent.

All the solvents, liquid reagents and substrates used in asymmetric hydrosilation were degassed *via* freeze-thaw cycle under argon prior to use. All asymmetric hydrosilation reactions were carried out under an inert atmosphere (argon). The glassware, syringes, needles and magnetic stirring bars (teflon coated) were dried at 120 °C overnight or longer and were then allowed to cool over Drierite in a glass desiccator. Enantiomeric excess was determined via *(S)*-Mosher's esters of the products using ^{1}H NMR. The cooresponding *(R)*-α-methoxy-α-trifluoromethylphenylacetyl chloride was prepared from *(S)*-α-methoxy-α-trifluoromethyl-phenylacetic acid and thionyl chloride.[194]

Flash column chromatographic separations were performed with Merck Kieselgel 60 (230-400 mesh ASTM) under air pressure. All thin layer chromatography (TLC) was carried out using pre-coated cellular plates with Silica Gel 60 F254. The spots were detected by using UV light, or phosphomolybdic acid/Ce_2SO_4 solution

followed by charring with a hot air gun. Gel filtration was performed using Sephardex LH-20.

Low temperature reactions were carried out in a dry ice-acetone bath (-78 °C), and in methanol baths cooled by NESLAB Cryocool CC-100 II (-20 °C to -100 °C) and Cryocool PBC-75 II (20 °C to -20 °C).

General Procedure for 1,4-Reduction of α,β-Unsaturated Carbonyl Compounds: In a 5 mL flask furnished with a magnetic stirring bar and sealed with a rubber septum, hydridotetrakis(triphenylphosphine)rhodium(I) (**2.20**; ca 5 mg) was placed under argon. The α,β-unsaturated ketone (1 mmol) was introduced to the flask via a syringe followed by the silane (1.1 mmol). The reaction mixture was stirred at room temperature for 12 h and then hexanes (1 mL) were added. The mixture was filtered and the solvent was removed to get the crude product which was purified by distillation using a Kugelröhr distillation apparatus.

1-Cyclopenten-1-yl Dimethylphenylsilyl Ether (2.32): Catalyst **2.20** (4 mg, 0.0035 mmol) and 2-cyclopenten-1-one (84 μL, 82 mg, 1.0 mmol) were treated with dimethylphenylsilane (169 μL, 150 mg, 1.1 mmol) at room temperature for 12 h. After standard work up, the crude mixture was distilled at 95 °C / 5 mm Hg (Kugelröhr) to give **2.32** as a colorless liquid (182 mg, 83% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 7.68 (m, 2H), 7.46 (m, 3H), 4.66 (m, 1H), 2.33

(m, 4H), 1.89 (q, J = 7.0 Hz, 2H), 0.55 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 154.8, 137.4, 133.3, 129.7, 127.8, 102.7, 33.4, 28.7, 21.2, -1.3; IR (neat): 2958.0, 2850.5, 1645.9, 1428.4, 1344.9, 1253.0, 1119.3, 831.4, 699.2 cm^{-1}; MS (EI): calcd for $C_{13}H_{18}OSi$ 218.1127, found 218.1139; Anal. calcd. for $C_{13}H_{18}OSi$: C 71.52, H 8.32; found: C 71.48, H 8.37.

1-Cyclohexen-1-yl Dimethylphenylsilyl Ether (2.15). Catalyst **2.20** (4 mg, 0.0035 mmol) and 2-cyclohexen-1-one (97 µL, 96 mg, 1.0 mmol) were treated with dimethylphenylsilane (169 µL, 150 mg, 1.1 mmol) at room temperature for 12 h. After standard work up, the crude mixture was distilled at 90 °C / 5 mm Hg (Kugelröhr) to give **2.15** as a colorless liquid (195 mg, 84% yield). ^1H NMR (200 MHz, $CDCl_3$): 7.66 (m, 2H), 7.42 (m, 3H), 4.91 (m, 1H), 2.03 (m, 4H), 1.68 (m, 2H), 1.55 (m, 2H), 0.49 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 170.9, 158.8, 154.0, 150.2, 148.5, 125.4, 50.5, 44.5, 43.8, 43.0, 19.7; IR (neat): 2930.5, 1669.4, 1252.6, 1186.8, 1169.9, 893.6 cm^{-1}; MS (EI): calcd for $C_{14}H_{20}OSi$ 232.1283, found 232.1288; Anal. calcd. for $C_{14}H_{20}OSi$: C 72.37, H 8.68; found: C 71.97, H 8.70.

4,4-Dimethyl-1-cyclohexen-1-yl Dimethylphenylsilyl Ether (2.34). Catalyst **2.20** (5 mg, 0.0043 mmol) and 4,4-dimethyl-2-cyclohexen-1-one (132 µL, 124 mg, 1.0 mmol) were treated with dimethylphenylsilane (169 µL, 150 mg, 1.1 mmol) at room temperature for 12 h. After standard work up, the crude mixture was distilled at 100 °C / 5 mm Hg (Kugelröhr) to give **2.34** as a colorless liquid (250 mg, 96% yield). ^1H NMR (200 MHz, $CDCl_3$): 7.66 (m, 2H), 7.41 (m, 3H), 4.82 (m, 1H), 2.03 (m, 2H), 1.82 (m, 2H), 1.42 (t,

J = 6.5 Hz, 2H), 0.93 (s, 6H), 0.50 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 149.2, 138.0, 133.3, 129.6, 127.7, 103.6, 37.8, 35.8, 28.5, 27.9, 27.5, -1.0; IR (neat): 2952.0, 2919.9, 1669.6, 1366.3, 1197.3, 1167.7, 1119.1, 889.2, 873.3, 834.2, 784.8 cm^{-1}; MS (EI): calcd for $C_{16}H_{24}OSi$ 260.1596, found 260.1595. Anal. calcd. for $C_{16}H_{24}OSi$: C 73.80, H 9.30; found: C 73.82, H 9.34.

Deuterium Isotope Effect for the 1,4-Reduction of 4,4-Dimethyl-2-cyclohexen-1-one: Catalyst **2.20** (5 mg, 0.0043 mmol) and 4,4-dimethyl-2-cyclohexen-1-one (132 µL, 124 mg, 1.0 mmol) were treated with dimethylphenylsilane (98%, 140 mg, 1 mmol) and deuterodimethylphenylsilane (96%-D; 140 mg, 1 mmol) at room temperature for 12 h. After standard work up, the crude product was distilled at 100 °C / 5 mm Hg (Kugelröhr) to give a colorless liquid (237 mg, ca. 91% yield) as a mixture of **2.34** and its 3-deuterated compound. The amounts of deuterium incorporation was determined by comparing the signal at 1.82 ppm (m, 1.52H) and that at 2.03 ppm,(m, 2.00H). The ratio of nondeuterated : deuterated products was 50.6 : 47.3 (1.1 : 1).

3-Methyl-1-cyclohexen-1-yl Dimethylphenylsilyl Ether (2.27): Catalyst **2.20** (6 mg, 0.0052 mmol) and 3-methyl-2-cyclohexen-1-one (114 µL, 110 mg, 1.0 mmol) were treated with dimethylphenylsilane (199 µL, 177 mg, 1.3 mmol) at 50 °C for 24 h. After standard work up, the crude mixture was distilled at 110 °C / 5 mm Hg (Kugelröhr) to give **2.27** as a colorless liquid (220 mg, 89% yield). ^1H NMR (300 MHz, $CDCl_3$): 7.70 (m, 2H), 7.45 (m, 3H), 4.83 (d,

J = 1.4 Hz, 1H), 2.28 (m, 1H), 2.04 (m, 2H), 1.70-1.86 (m, 2H), 1.59 (m, 1H), 1.11 (m, 1H), 0.99 (d, J = 7.0 Hz, 3H), 0.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.9, 137.9, 133.3, 129.5, 127.7, 111.5, 31.0, 29.7, 29.4, 22.4, 21.7, -1.0, -1.1; IR (neat): 2952.0, 2930.3, 2864.5, 2853.0, 1664.5, 1455.8, 1428.5, 1252.8, 1185.0, 1119.4, 1063.9, 1047.9, 886.4, 831.4, 786.8, 699.4 cm^{-1}; MS (EI): calcd for $C_{15}H_{22}OSi$ 246.1440, found 246.1443. Anal. calcd. for $C_{15}H_{22}OSi$: C 73.13, H 9.01; found: C 73.22, H 9.28.

3,5-Dimethyl-1-cyclohexen-1-yl Dimethylphenylsilyl Ether (2.36): Catalyst **2.20** (6 mg, 0.0052 mmol) and 3,5-dimethyl-2-cyclohexen-1-one (141 µL, 124 mg, 1.0 mmol) were treated with dimethylphenylsilane (199 µL, 177 mg, 1.3 mmol) at 50 °C for 48 h. After standard work up, the crude mixture was distilled at 90 °C / 1 mm Hg (Kugelröhr) to give **2.36** as a colorless liquid (225 mg, 87% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 7.58 (m, 2H), 7.37 (m, 3H), 4.66 (s, 1H), 2.21 (br, 1H), 1.93 (m, 1H), 1.63 (m, 4H), 0.90 (d, J = 7.9 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H), 0.43 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 149.7, 138.0, 133.4, 129.5, 127.7, 111.3, 40.8, 38.4, 30.3, 29.6, 22.6, 22.0, -0.9, -1.0; IR (neat): 2952.0, 2917.6, 2912.9, 2901.5, 2870.0, 1666.1, 1428.4, 1368.9, 1252.9, 1196.8, 1182.4, 1120.8, 1079.3, 826.2, 786.5, 699.3 cm^{-1}; MS (EI): calcd for $C_{16}H_{24}OSi$ 260.1596, found 260.1584. Anal. calcd. for $C_{16}H_{24}OSi$: C 73.80, H 9.30; found: C 73.78, H 9.25.

2-Buten-2-yl Dimethylphenylsilyl Ether (2.38): Catalyst **2.20** (2 mg, 0.0017 mmol) and 3-buten-2-one (83 µL, 70 mg, 1.0 mmol) were treated with dimethylphenylsilane (169 µL, 150 mg, 1.1

mmol) at room temperature for 6 h. After standard work up, the crude mixture (205 mg, *E/Z* = 33 : 67) was distilled at 60 °C / 5 mm Hg (Kugelröhr) to give a colorless liquid (151 mg, 73% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 7.66 (m, 2H), 7.42 (m, 3H), 4.70 (dq, J = 6.9, 1.0 Hz, 0.33H), 4.52 (dq, J = 6.6, 1.0 Hz, 0.67H), 1.74 (m, 3H), 1.53 (m, 3H), 0.49 (s, 4.02H), 0.46 (s, 1.98H); ^{13}C NMR (50 MHz, $CDCl_3$): 147.9, 147.2, 138.1, 138.0, 133.3, 129.6, 127.8, 103.0, 102.3, 22.6, 17.3, 12.1, 10.7, -0.7, -1.1; IR (neat): 2960.8, 2944.1, 1682.4, 1428.4, 1383.8, 1316.0, 1252.9, 1119.2, 1100.5, 1048.0, 834.2, 784.9, 699.2 cm^{-1}; MS (EI): calcd for $C_{12}H_{18}OSi$ 206.1127, found 206.1117.

3-Hexen-3-yl Dimethylphenylsilyl Ether (2.40): Catalyst **2.20** (2 mg, 0.0017 mmol) and 4-hexen-3-one (114 μL, 98 mg, 1.0 mmol) were treated with dimethylphenylsilane (169 μL, 150 mg, 1.1 mmol) at room temperature for 6 h. After standard work up, the crude mixture (*E/Z* = 77 : 23) was distilled at 70 °C / 5 mm Hg (Kugelröhr) to give a colorless liquid (192 mg, 82% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 7.70 (m, 2H), 7.46 (m, 3H), 4.68 (t, J = 7.6 Hz, 0.77H), 4.54 (t, J = 7.0 Hz, 0.23H), 2.17 (m, 2H), 2.00 (m, 2H), 1.12 (m, 3H), 0.99 (m, 3H), 0.54 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 152.3, 151.1, 138.2, 138.1, 133.4, 133.3, 129.6, 129.5, 127.7, 109.2, 109.1, 29.3, 24.3, 20.1, 18.7, 15.4, 14.4, 12.0, 11.7, -0.8, -1.0; IR (neat): 2963.3, 1662.1, 1654.0, 1458.3, 1428.5, 1252.6, 1199.3, 1119.2, 1084.5, 831.4, 786.5 cm^{-1}; MS (EI): calcd for $C_{14}H_{22}OSi$ 234.1440, found 234.1437.

1-Cyclohexen-1-yl (Chloromethyl)dimethysilyl Ether (2.42): Catalyst 2.20 (12 mg, 0.010 mmol) and 2-cyclohexen-1-one (968 μL, 960 mg, 10.0 mmol) were treated with (chloromethyl)-dimethylsilane (1.34 mL, 1.196 g, 11.0 mmol) at 0 °C. The mixture was then warmed up to room temperature and stirred for 30 min. After standard work up, the crude mixture (2.3681 g) was distilled at 70 °C / 5 mm Hg (Kugelröhr) to give 2.42 as a colorless liquid (1.6852 g, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): 4.87 (m, 1H), 2.82 (s, 2H), 1.98 (m, 4H), 1.62 (m, 2H), 1.51 (m, 2H), 0.28 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 149.8, 104.9, 29.6, 29.5, 23.7, 23.0, 22.1, -2.9; IR (neat): 2931.1, 1669.8, 1265.1, 1255.1, 1190.0, 1169.8, 987.8, 898.4 cm^{-1}; MS (EI): calcd for $C_9H_{17}OSiCl$ 204.0737, found 204.0742.

4,4-Dimethyl-1-cyclohexen-1-yl (Chloromethyl)dimethylsilyl Ether (2.43): Catalyst 2.20 (7 mg, 0.0061 mmol) and 4,4-dimethyl-2-cyclohexen-1-one (264 μL, 248 mg, 2.0 mmol) were treated with (chloromethyl)dimethylsilane (292 μL, 261 mg, 2.4 mmol) at room temperature for 4 h. After standard work up, the crude mixture (488 mg) was distillated at 70 °C / 5 mm Hg (Kugelröhr) to give 2.43 as a colorless liquid (371 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 4.75 (m, 1H), 2.79 (s, 2H), 1.96 (m, 2H), 1.76 (m, 2H), 1.37 (t, J = 6.5 Hz, 2H), 0.88 (s, 6H), 0.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 148.7, 103.7, 37.7, 35.7, 29.4, 28.5, 27.8, 27.3, -3.0; IR (neat): 2952.0, 2923.6, 1673.8, 1366.4, 1255.2, 1196.8, 1167.5, 898.3, 876.3, 847.4, 825.1 cm^{-1}; MS (EI): calcd for $C_{11}H_{21}OClSi$ 232.1050, found 232.1051.

2-Buten-2-yl (Chloromethyl)dimethylsilyl Ether (2.44): Catalyst **2.20** (5 mg, 0.0043 mmol) and 3-buten-2-one (167 µL, 140 mg, 2.0 mmol) were treated with (chloromethyl)dimethylsilane (268 µL, 239 mg, 2.2 mmol) at room temperature for 1.5 h. After standard work up, the crude mixture (350 mg, *E/Z* = 1 : 2) was distilled at 60 °C / 15 mm Hg (Kugelröhr) to give **2.44** as a colorless liquid (305 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): *(E)*-isomer (33%), 4.65 (q, J = 6.7 Hz, 1H), 2.79 (s, 2H), 1.69 (d, J = 1.0 Hz, 3H), 1.48 (d, J = 6.8 Hz, 3H), 0.25 (s, 6H), *(Z)*-isomer (67%), 4.48 (q, J = 6.6 Hz, 1H), 2.80 (s, 2H), 1.73 (d, J = 1.0 Hz, 3H), 1.45 (dd, J = 6.7, 1.4 Hz, 3H), 0.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *(E)*-isomer, 147.5, 102.6, 29.4, 17.1, 11.9, -3.1, *(Z)*-isomer, 146.5, 103.3, 29.6, 22.4, 10.5, -2.8; IR (neat): 2963.3, 2922.5, 1685.8, 1384.2, 1315.5, 1255.6, 1202.0, 1107.0, 1100.0, 1048.3, 1003.0, 888.9, 847.5, 823.1, 799.7 cm^{-1}. MS (EI): calcd for $C_7H_{15}OSiCl$ 178.0581, found 178.0571.

3-Hexen-3-yl (Chloromethyl)dimethylsilyl Ether (2.45). Catalyst **2.20** (6 mg, 0.005 mmol) and 4-hexen-3-one (229 µL, 196 mg, 2.0 mmol) were treated with (chloromethyl)dimethylsilane (293 µL, 261 mg, 2.4 mmol) at room temperature for 10 h. After standard work up, the crude product mixture (400 mg, *E/Z* = 4 : 1) was distilled at 40 °C / 5 mm Hg (Kugelröhr) to give **2.45** as a colorless liquid (342 mg, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 4.55 (t, J = 7.6 Hz, 0.75H), 4.42 (t, J = 6.7 Hz, 0.25H), 2.79 (s, 1.50H), 2.78 (s, 0.50H), 2.03 (q, J = 7.6 Hz, 2H), 1.89 (p, J = 7.6 Hz, 2H), 0.84-1.00 (m, 6H), 0.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *(E)*-isomer, 151.9, 109.2, 29.4, 24.1, 20.0, 15.2, 11.8, -3.1, *(Z)*-isomer, 150.5, 109.4, 29.6, 24.1, 18.5,

14.2, 11.6, -2.9; IR (neat): 2965.6, 2935.4, 1668.7, 1654.0, 1465.6, 1458.4, 1255.5, 1196.8, 1086.2, 1064.0, 1044.9, 876.3, 847.2, 821.1 cm^{-1}; MS (EI): calcd for $C_9H_{19}OClSi$ 206.0894, found 206.0894

1-Cyclohexen-1-yl Triethoxysilyl Ether (2.47): Catalyst 2.20 (3 mg, 0.0026 mmol) and 2-cyclohexen-1-one (97 µL, 96 mg, 1 mmol) were treated with triethoxysilane (207 µL, 181 mg, 1.1 mmol) at room temperature for 12 h. After standard work up, the crude product (242 mg, 93%) was distilled at 70 °C / 5 mm Hg (Kugelröhr) to give 2.47 as a colorless liquid (202 mg, 78%). ^1H NMR (200 MHz, $CDCl_3$): 5.05 (m, 1H), 3.84 (q, J = 7.0 Hz, 6H), 2.04 (m, 4H), 1.64 (m, 2H), 1.48 (m, 2H), 1.21 (t, J = 7.0 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): 148.8, 104.5, 59.4, 28.9, 23.6, 23.0, 22.1, 18.0; IR (neat): 2978.0, 2930.2, 2859.7, 1674.7, 1368.5, 1199.4, 1167.9, 1105.0, 1083.7, 524.6 cm^{-1}; MS (EI): calcd for $C_{12}H_{24}O_4Si$ 260.1444, found 260.1453. Anal. calcd. for $C_{12}H_{24}O4Si$: C 55.35, H 9.30; found: C 55.33, H 9.35.

2-Buten-2-yl Triethoxysilyl Ether (2.48): Catalyst 2.20 (3 mg, 0.0026 mmol) and 3-buten-2-one (83 µL, 70 mg, 1 mmol) were treated with triethoxysilane (207 µL, 181 mg, 1.1 mmol) at room temperature for 20 h. After standard work up, the crude product (E/Z = 56 : 44) was distilled at 60 °C / 5 mm Hg (Kugelröhor) to give 2.48 as a colorless liquid (176 mg, 75%): ^1H NMR (200 MHz, $CDCl_3$): 4.82 (q, J = 6.9 Hz, 0.56H), 4.40 (q, J = 6.6 Hz, 0.44H), 3.81 (m, 6H), 1.78 (s, 1.32H), 1.72 (s, 1.68H), 1.47 (m, 3H), 1.16 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): 146.4, 145.8, 102.6, 102.1, 59.2, 21.5, 18.1, 17.9, 16.4, 11.8; IR (neat): 2978.1, 2926.1, 2895.9, 1722.1, 1682.7,

1388.6, 1106.8, 1083.6, 792.0 cm^{-1}; MS (EI): calcd for $C_{10}H_{22}O_4Si$ 234.1287, found 234.1295.

1-Methoxy-1-dimethylphenylsiloxy-2-methyl-1-propene (2.50): Catalyst **2.20** (8 mg, 0.0069 mmol) and methyl methacrylate (214 μL, 200 mg, 2.0 mmol) were treated with dimethylphenylsilane (337 μL, 300 mg, 2.2 mmol) at room temperature for 1.5 h. After standard work up, the crude mixture was distilled at 85 °C / 5 mm Hg (Kugelröhr) to give a colorless liquid (430 mg, 91% yield). ^1H NMR (200 MHz, $CDCl_3$): 7.63 (m, 2H), 7.39 (m, 3H), 3.41 (s, 3H), 1.55 (s, 3H), 1.50 (s, 3H), 0.47 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 149.4, 137.2, 133.4, 129.8, 127.8, 91.4, 56.9, 16.9, 16.1, -1.5; IR (neat): 2962.4, 2933.2, 2917.6, 2858.4, 1706.5, 1428.6, 1253.1, 1204.6, 1173.8, 1147.3, 1121.1, 1026.1, 943.0, 859.8, 834.2, 789.7 cm^{-1}; MS (EI): calcd for $C_{13}H_{20}O_2Si$ 236.1233, found 236.1229.

5,6-Dihydro-*4H*-pyran-2-yl Dimethylphenylsilyl Ether (2.52): Catalyst **2.20** (8 mg, 0.0069 mmol) and 5,6-dihydro-*2H*-pyran-2-one (172 μL, 196 mg, 2.0 mmol) were treated with dimethylphenylsilane (337 μL, 300 mg, 2.2 mmol) at room temperature for 12 h. After standard work up, the crude mixture was distilled at 110 °C / 5 mm Hg (Kugelröhr) to give **2.52** as a colorless liquid (398 mg, 85% yield). ^1H NMR (200 MHz, $CDCl_3$): 7.67 (m, 2H), 7.44 (m, 3H), 4.04 (dd, J = 5.1, 5.1 Hz, 2H), 3.88 (t, J = 3.7 Hz, 1H), 2.04 (dt, J = 6.3, 3.9 Hz, 2H), 1.76 (m, 2H), 0.53 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 154.2, 137.0, 133.2, 129.6, 127.6, 74.3, 67.1, 22.2, 19.7, -1.3; IR (neat): 2955.1, 2932.9, 2850.5, 1736.0, 1688.6, 1428.5,

1386.3, 1278.5, 1250.1, 1209.8, 1121.1, 1063.2, 911.9, 844.6, 821.1, 792.4 cm^{-1}; MS (EI): calcd for $C_{13}H_{18}O_2Si$ 234.1076, found 234.1078.

General Procedure for the 1,2-Reduction of α,β-Unsaturated Ketones: Hydridotetrakis(triphenylphosphine)-rhodium(I) (ca. 5 mg) was placed in a 10 mL flask furnished with a magnetic stirring bar, sealed with a rubber septum under argon. Dried CH_2Cl_2 (1 mL) was added via a syringe followed by the α,β-unsaturated ketone (1 mmol). After 10 min, diphenylsilane (1.3 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 4 h and then transferred to a 25 mL flask with a solution of HCl (2N, 3 mL)-acetone (3 mL). The mixture was stirred at room temperature for 2 h. Acetone was removed via rotary evaporation. The aqueous residue was then extracted with dichloromethane (4 X 5 mL). The combined organic layers were dried over Na_2SO_4. Removal of solvent gave the crude product, which was purified by flash column chromatography separation or Kugelröhr distillation.

2-Cyclohexen-1-ol (2.60)[230]: Compound **2.60** was obtained from 2-cyclohexen-1-one (97%; 100 μL, 99 mg, 1 mmol) as a yellowish liquid, which was subjected to flash column chromatography separation (hexanes : ethyl acetate = 6 : 1) to give product **2.60** (81 mg, 83% yield). ^1H NMR (200 MHz, $CDCl_3$): 5.82 (dt, J = 3.0, 10.1 Hz, 1H), 5.72 (m, 1H), 4.17 (m, 1H), 1.97 (m, 2H), 1.45-1.92 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): 130.0, 129.2, 65.6, 32.5, 25.7, 19.6; IR (neat) 1054.2, 1435.6, 1451.9, 1651.4, 1706.3, 2864.4,

2935.7, 3024.6, 3363.5 cm^{-1}; MS (EI) 99 (4), 98 (54, M), 97 (41), 83 (35), 70 (100), 55 (22).

3-Methyl-2-cyclohexen-1-ol[231] (**2.61**): Compound **2.61** was obtained from 3-methyl-2-cyclohenen-1-one (98%; 116 μL, 112 mg, 1 mmol) as a yellowish liquid, which was subjected to flash column chromatography separation (hexanes : ethyl acetate = 6 : 1). Compound **2.61** was obtained as a colorless liquid (96 mg, 86% yield). ^1H NMR (200 MHz, $CDCl_3$): 5.47 (m, 1H), 4.12 (m, 1H), 1.89 (m, 2H), 1.75 (m, 2H), 1.67 (s, 3H), 1.56 (m, 2H), 1.55 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): 137.7, 123.7, 65.7, 32.1, 30.5, 24.2, 19.7; IR (neat) 957.9, 993.1, 1034.6, 1436.5, 1448.3, 1671.6, 2867.1, 2875.6, 2895.5, 2925.5 cm^{-1}; MS (EI) 112 (17, M), 97 (100), 84 (30), 79 (22), 69 (18).

***(1R,5R)*-5-Isopropenyl-2-cyclohexen-1-ol**[232] **(Carveol, 2.63)**: Compound **2.63** was obtained from (*R*)-(-)-carvone (127 mg, 84% yield) as a colorless liquid with a ratio for *cis : trans* isomers of 65 : 35. ^1H NMR (200 MHz, $CDCl_3$): 5.58 (m, 35% of 1H), 5.48 (m, 65% of 1H), 4.71 (s, 4H), 4.18 (m, 65% of 1H), 4.01 (m, 35% of 1H), 1.87-2.40 (m, 6H), 1.68-1.84 (m, 12H), 1.40-1.65 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): 148.3, 148.1, 135.4, 133.6, 124.8, 123.3, 108.7, 108.6, 71.0, 68.6, 40.8, 38.4, 37.2, 35.7, 31.5, 21.6, 21.5, 21.3, 19.7; IR (neat) 1035.0, 1439.1, 1645.3, 2858.3, 2884.2, 2915.8, 2940.1, 2967.7, 3319.5 cm^{-1}; MS (EI): 152 (23, M), 137 (16), 134 (58), 109 (100), 93 (28), 84 (99).

3,5-Cholestadiene[233] (**2.65**): Compound **2.65** was obtained from (+)-4-chlotesten-3-one (**2.64**, 385 mg, 1.0 mmol) as a solid, which was recrystallized from CH_2Cl_2-MeOH (281 mg, 76% yield). m.p. 76.5-77.5 °C ^{1}H NMR (200 MHz, $CDCl_3$): 5.91 (d, J = 10.0 Hz, 1H), 5.58 (m, 1H), 5.38 (m, 1H), 2.14 (m, 2H), 2.00 (dt, J = 3.4, 12.3 Hz, 1H), 0.96-1.88 (m, 23H), 0.94 (s, 3H), 0.90 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 6H), 0.67 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 140.7, 128.4, 124.4, 122.6, 57.2, 56.4, 48.7, 42.9, 40.3, 40.0, 36.7, 36.3, 35.7, 34.3, 32.3, 28.8, 28.6, 24.8, 24.6, 24.0, 23.5, 23.2, 21.6, 19.5, 19.4, 12.8; IR (KBr): 1333.5, 1374.6, 1463.9, 1650.6, 2857.5, 2908.8, 2962.3, 3017.7 cm^{-1}; MS (EI): 370 (16), 369 (30), 368 (100, M), 353 (20), 260 (19), 255 (16), 147 (43), 107 (27), 105 (30).

***cis*-3-(Phenylthio)-1,4,4a,5,6,7,8,8a-octahydro-8α-hydroxy-5,5,8a-trimethylnaphthalen-1-one**[234] (**2.67**): Compound **2.67** was obtained from *cis*-3-(phenylthio)-1,4,4a,5,6,7,8,8a-octahydro-5,5,8a-trimethylnaphthalen-1,8-dione[237] (**2.66**, 18 mg, 0.06 mmol) as a yellowish solid, which was subjected to flash column chromatography purification (hexanes : ethyl acetate = 6 : 1) to give white solid α-isomer (10.5 mg, 56% yield). m.p. 183.0-184.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$): 7.44 (m, 5H), 5.32 (d, J = 2.4 Hz, 1H), 4.77 (d, J = 11.0 Hz, 1H), 3.13 (td, J = 11.3, 4.6 Hz, 1H), 2.87 (ddd, J = 19.0, 6.4, 2.4 Hz, 1H), 2.48 (dd, J = 19.0, 1.1 Hz, 1H), 1.24-1.86 (m, 5H), 1.44 (s, 3H), 0.92 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 202.2, 163.2, 134.9, 129.6, 129.3, 127.2, 119.9, 78.6, 52.8, 47.7, 40.7, 35.2, 31.7, 29.6, 29.4, 25.0, 24.0; IR (film) 1030.7, 1222.4, 1341.9, 1378.3, 1433.8, 1580.3, 1618.8, 1713.6, 2863.9, 2930.2, 2955.8, 3449.1 cm^{-1};

MS (EI): 316 (7, M), 219 (6), 218 (16), 217 (100), 176 (24), 139 (19), 108 (11).

6,6-Dimethyl-2-cyclohexen-1-one[235] (2.69) **and 4,4-Dimethyl-2-cyclo-hexen-1-one**[236] (2.33): Compounds 2.69 and 2.33 were obtained from 4,4-dimethylcyclohexan-1,3-dione (98%, 143.0 mg, 1 mmol) as a yellowish liquid which was subjected to Kugelröhr distillation (90 °C / 20 mm Hg) to give a mixture of 2.69 and 2.33 (95 : 5; 61 mg, 49% yield) [or flash column chromatography separation (hexanes : ethyl acetate = 10 : 1)]:

6,6-Dimethyl-2-cyclohexen-1-one (2.69): ^{1}H NMR (200 MHz, $CDCl_3$): 6.84 (dt, J = 10.0, 4.0 Hz, 1H), 5.89 (dt, J = 10.0, 2.0 Hz, 1H), 2.35 (m, 2H), 1.81 (t, J = 6.0 Hz, 2H), 1.09 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 203.1, 147.7, 127.7, 41.8, 36.7, 24.7, 24.0; IR (neat): 1125.9, 1301.9, 1385.5, 1427.4, 1453.9, 1679.1, 1708.5, 2867.3, 2930.5, 2963.4, 3033.7 cm^{-1}; 126 (5); 124 (41, M), 109 (11), 96 (18), 69 (11), 68 (100).

4,4-Dimethyl-2-cyclohexen-1-one (2.33): ^{1}H NMR (200 MHz, $CDCl_3$): 6.62 (d, J = 10.0 Hz, 1H), 5.80 (d, J = 10.0 Hz, 1H), 2.42 (t, J = 6.5 Hz, 2H), 1.83 (t, J = 6.7 Hz, 2H), 1.13 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 198.1, 158.8, 126.2, 36.5, 34.9, 33.3, 28.3; IR (neat): 803.6, 1122.0, 1236.5, 1418.9, 1467.0, 1618.4, 1687.9, 2930.1, 2962.7 cm^{-1}; 125 (7), 124 (72, M), 109 (13), 96 (67), 82 (100), 81 (48).

***cis*-4-*tert*-Butyl-1-cyclohexanol**[237] (2.71b) **and *trans*-4-*tert*-Butyl-1-cyclohexanol**[238] (2.71a): Compounds 2.71a and 2.71b were obtained from 4-*tert*-butylcyclohexan-1-one (99%; 156

mg, 1 mmol) as a solid (*cis* : *trans* = 16 : 84), which was subjected to flash column chromatography separation (hexanes : ethyl acetate = 6 : 1). White solids were obtained (*cis*: 27 mg, *trans:* 100 mg, 81% yield):

trans-4-*tert*-Butyl-1-cyclohexanol (**2.71a**). m.p. 80.5-81.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$): 3.43 (m, 1H), 2.47 (br, 1H), 1.93 (m, 2H), 1.71 (m, 2H), 0.87-1.27 (m, 5H), 0.78 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): 71.0, 47.4, 36.3, 32.7, 28.1, 26.1; IR (KBr): 1068.5, 1367.6, 1450.7, 1473.3, 2862.8, 2917.8, 2964.4, 3215.0 cm^{-1}; MS (CI): 174 (33, M+18), 156 (2, M), 155 (5), 139 (35), 138 (100), 123 (83).

cis-4-*tert*-Butyl-1-cyclohexanol (**2.71b**). m.p. 82.0-83.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$): 4.00 (br, 1H), 1.80 (m, 2H), 1.50 (m, 2H), 1.29-1.54 (m, 5H), 0.96 (tt, J = 11.4, 2.9 Hz, 1H), 0.83 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): 66.0, 48.3, 33.9, 33.1, 28.0, 21.5; IR (KBr): 960.5, 1007.3, 1032.5, 1114.3, 1147.4, 1180.5, 1232.1, 1275.0, 1337.3, 1365.9, 1439.9, 1476.3, 2839.6, 2866.8, 2952.5, 3287.4 cm^{-1}; MS (CI): 174 (8, M+18), 155 (3), 139 (15), 123 (21).

(*1S,2R,4S*)-1,7,7-Trimethylbicyclo[2.2.1]hepten-2-ol[243] **(Isoborneol, 2.73a) and (*1S,2S,4S*)-1,7,7-Trimethylbicyclo-[2.2.1]hepten-2-ol**[243] **(Borneol, 2.73b)**: Compounds **7c** and **7d** were obtained from (-)-camphor (99%; 154 mg, 1 mmol) as a yellowish solid, which was subjected to flash column chromatography separation (hexanes : ethyl acetate = 6 : 1). White solid products were obtained (83.8 mg exo-isomer **7d**, 47.2 mg endo-isomer **7c**, 85% yield):

Isoborneol (2.73a). m.p. 218.0-219.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$): 3.61 (m, 1H), 1.40-1.74 (m, 8H), 1.00 (s, 3H), 0.86 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 79.7, 49.2, 46.6, 45.3, 40.8, 34.4, 27.8, 21.1, 20.7, 12.1; IR (KBr): 1005.1, 1070.3, 1455.9, 1477.7, 2875.0, 2955.0, 3434.3 cm^{-1}; MS (EI): 154 (3, M), 139 (16), 136 (27), 121 (21), 110 (32), 96 (10), 95 (100), 93 (22).

Borneol (2.73b). m.p. 206.0-208.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$): 4.01 (m, 1H), 2.26 (m, 1H), 1.56-1.94 (m, 3H), 1.14-1.38 (m, 3H), 0.92 (dd, J = 13.5, 3.6 Hz, 1H), 0.85 (s, 3H), 0.84 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 77.4, 49.8, 48.4, 45.5, 39.5, 28.9, 26.5, 20.9, 19.4, 14.1; IR (KBr): 1024.5, 1056.8, 1109.7, 1455.6, 2874.0, 2952.0, 3305.6 cm^{-1}; MS (EI): 154 (2, M), 139 (15), 136 (11), 110 (32), 95 (100),93 (8).

Methyl 3-hydroxybutyrate[239] (2.75): Compound 2.75 was obtained from methyl acetoacetate (109 µL, 117 mg, 1 mmol) as a yellowish liquid, which was subjected to Kugelröhr distillation (50 °C / 10 mm Hg, 101 mg, 86% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 4.18 (m, 1H), 3.69 (s, 3H), 2.95 (m, 1H), 2.49 (dd, J = 16.5, 4.3 Hz, 1H), 2.37 (dd, J = 16.5, 8.0 Hz, 1H), 1.21 (d, J = 6.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 172.0, 64.3, 51.9, 43.0, 23.0; IR (neat): 1007.2, 1072.3, 1087.9, 1174.0, 1197.4, 1296.9, 1440.0, 1742.7, 2973.7, 3459.0 cm^{-1}; MS (CI): 136 (5, M+18), 120 (5), 119 (100, M+1), 101 (15), 74 (12).

1,2-Propanediol[240] (2.77): Compound 2.77 was obtained (at -78°C, and then room temperature) from acetol (90%, 76 µL, 82 mg, 1 mmol) as a yellowish liquid, which was subjected to Kugelröhr

distillation (80 °C / 20 mm Hg; 61 mg, 80% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 3.86 (m, 1H), 3.58 (d, J = 10.9 Hz, 1H), 3.38 (d, J = 8.1 Hz, 1H), 3.25 [s(br), 2H], 1.12 (d, J = 6.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 68.4, 68.1, 19.4; IR (neat): 1037.6, 1052.6, 1079.5, 1139.0, 1414.9, 1458.9, 2879.8, 2929.0, 2974.4, 3313.6 cm^{-1}; MS (EI): 76 (1, M), 61 (6), 45 (100), 44 (9), 43 (14), 40 (10).

1-Phenylethanol[241] (**2.84**): Catalyst **2.20** (5 mg, 0.0043 mmol) and acetophenone (118 µL, 121 mg, 1 mmol) were treated with diphenylsilane (250 µL, 245 mg, 1.3 mmol) at room temperature for 4 h. After standard work up, the crude product was distillated at 75 °C / 5 mm Hg (Kugelröhr) to give **2.84** as a colorless liquid (100 mg, 82% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 7.22-7.38 (m, 5H), 4.88 (q, J = 6.5 Hz, 1H), 1.87 (s, 1H), 1.45 (d, J = 8.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 145.0, 127.9, 126.9, 124.8, 70.5, 25.8; IR (neat): 699.4, 1077.1, 1452.1, 1493.3, 1603.6, 2875.1, 2927.5, 2974.4, 3366.4 cm^{-1}; MS (EI): 122 (39, M), 107 (100), 79 (67), 77 (36), 51 (14).

Deuterium Isotope Effects for the Reduction of Acetophenone: (a) With dideuterodiphenylsilane-diphenylsilane (2.83/2.21): Catalyst **2.20** (3 mg, 0.0026 mmol) and acetophenone (118 µL, 121 mg, 1 mmol) were treated with diphenylsilane (245 mg, 1.3 mmol) and dideuterodiphenylsilane (96%-D, 245 mg, 1.3 mmol) at room temperature for 12 h. The crude mixture was used to measure the products ratio by 500 MHz NMR: δ 1.46, s, 33.6%; δ 1.47, d, 7.0 Hz, 67.7%. The ratio of nondeuterated-deuterated 1-phenylethyl diphenylsilyl ether was 65.1 : 33.6 (1.9 :

1). Hydrolysis of the product with HCl (2N), and distillation (Kugelröhr) at 75 °C / 5 mm Hg gave 1-phenylethanol and its 1-deuterated compound (103 mg, ca 84% yield).

(b) With Deuterodimethylphenylsilane-Dimethylphenylsilane (2.86/2.14): Catalyst **2.20** (11 mg, 0.0095 mmol) in CH_2Cl_2 (0.5 μL) and acetophenone (118 μL, 121 mg, 1 mmol) were treated with deuterodimethylphenylsilane (96%-D; 140 mg, 1 mmol) and dimethylphenylsilane (140 mg, 1 mmol) at room temperature for 4 days. The crude mixture was used for measuring the products ratio by 500 MHz NMR: δ 1.40, s, 49%; δ 1.47, d, 6.5 Hz, 51%. The ratio of nondeuterated-deuterated 1-phenylethyl dimethylphenylsilyl ether was 49 : 51 (1 : 1). Distillation (Kugelröhr) at 105 °C / 5 mm Hg gave products (112 mg, ca 91% yield), which was contaminated with some disiloxane.

4,4-Dimethyl-2-cyclohexen-1-ol (2.88): Catalyst **2.20** (4 mg, 0.0034 mmol) and 4,4-dimethyl-2-cyclohexen-1-one (136 μL, 128 mg, 1 mmol) were treated with diphenylsilane (250 μL, 245 mg, 1.3 mmol) at room temperature for 12 h. After standard work up, the crude product was distilled at 80 °C / 5 mm Hg (Kugelröhr) to give **2.88** (109 mg, 87% yield). ^1H NMR (200 MHz, $CDCl_3$): 5.56 (dd, J = 10.1, 2.6 Hz, 1H), 5.47 (d, J = 10.3 Hz, 1H), 4.11 (m, 1H), 1.85 (m, 1H), 1.28-1.70 (m, 4H), 0.98 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 139.8, 126.7, 66.0, 34.1, 32.3, 29.7, 29.6; IR (neat) 1055.6, 1366.4, 1458.1, 1650.9, 2864.7, 2955.6, 3317.1 cm^{-1}; MS (EI): 126 (18, M), 111 (30), 92 (18), 84 (11), 70 (100).

Deuterium Isotope Effect for the 1,2-Reduction of 4,4-Dimethyl-2-cyclohexen-1-one (2.88/2.89): Catalyst **2.20** (5 mg, 0.0043 mmol) in CH_2Cl_2 (2 mL) and 4,4-dimethyl-2-cyclohexen-1-one (136 µL, 128 mg, 1 mmol) were treated with diphenylsilane (250 mg, 1.3 mmol) and dideuterodiphenylsilane (96%-D, 250 mg, 1.3 mmol) at room temperature for 12 h. After standard work up, the crude mixture was distilled (Kugelröhr; 80 °C / 5 mm Hg) to give **2.88** and **2.89** (107 mg, ca. 85% yield). The ^1H NMR signal of HOCH at 4.11 had 54% of the intensity of the signal (100%) at 5.47 ppm. The ratio of nondeuterated/deuterated products was therefore 52 : 48 (1.1 : 1).

Deuterodimethylphenylsilane (2.86): Chlorodimethylphenylsilane (99%, 1.72 g, 10 mmol) was placed in a 150 mL flask with 40 mL diethyl ether. $LiAlD_4$ (96%-D, 210 mg, 5 mmol) was added at room temperature. The reaction mixture was stirred for 3 h at room temperature and then quenched with saturated aqueous NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted by diethyl ether (2 X 10 mL). The combined organic layers were dried over Na_2SO_4 and filtered. Removal of ether gave a colorless liquid, which was purified via Kugelröhr distillation (55 °C / 5 mm Hg) to give 1.10 g of **2.86** (80% yield) which contained about 95% deuterated product. ^1H NMR (200 MHz, $CDCl_3$): 7.53 (m, 2H), 7.36 (m, 3H), 0.33 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 142.2, 133.3, 128.5, 127.2, -2.9; IR (neat): 699.5, 732.3, 794.1, 836.3, 1116.1, 1252.6, 1541.1, 1589.4, 2119.7, 2960.6, 3016.0, 3052.1, 3068.7 cm^{-1}; HRMS: calcd for $C_8H_{11}DSi$ 137.0771, found 137.0774.

Dideuterodiphenylsilane[242] (2.83): Dichlorodiphenylsilane (97%, 1.27 g, 4.9 mmol) was placed in a 150 mL flask with 40 mL diethyl ether. $LiAlD_4$ (96%-D, 210 mg, 5 mmol) was added at room temperature. The reaction mixture was stirred for 3 h at room temperature and then quenched with saturated aqueous NH_4Cl solution. The reaction mixture was worked up as in 2.86. This gave a colorless liquid which was purified via Kugelröhr distillation (100 °C / 5 mm Hg) to give 0.84 g of 2.83 (90% yield) which contained about 96% dideuterated product. ^1H NMR (200 MHz, $CDCl_3$): 7.61 (m, 4H), 7.41 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): 134.9, 130.7, 129.2, 127.4; IR (neat) 1121.4, 1428.3, 1548.3, 1655.5, 1819.6, 1884.8, 1956.8, 2140.7, 3016.3, 3050.0, 3066.9 cm^{-1}; HRMS calcd for $C_{12}H_{10}D_2Si$ 186.0834, found 186.0832.

Dimethyl(1-morpholinomethyl)silane (2.94c). Compound (chloromethyl)dimethylsilane (2.18 g, 20.0 mmol) was added to a 25 mL flask containing morpholine (3.83 g, 44.0 mmol). The mixture was stirred at room temperature for 12 h before diethyl ether was added. The white precipitate was separated by filtration, and the filtrate was concentrated. A pure, colorless product was obtained after distillation (Kogelröhr: 50 °C / 15 mm Hg; 2.8 g, 88%): ^1H NMR (200 MHz, $CDCl_3$) δ 3.92 (m, 1H), 3.67 (m, 4H), 2.40 (m, 4H), 1.97 (d, J = 3.1 Hz, 2H), 0.11 (d, J = 3.7 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 67.2, 57.3, 49.4, -3.7; IR (neat) 842, 868, 889, 927, 1119, 1250, 1283, 1295, 2117, 2798, 2854, 2934, 2960 cm^{-1}; MS *m/z* calcd for $C_7H_{17}ONSi$: 159.1079, found 159.1076.

Dimethyl(1-pyrrolidinomethyl)silane (2.94b). Compound (chloromethyl)dimethylsilane (2.18 g, 20.0 mmol) was added to a 25 mL flask containing pyrrolidine (4.55 g, 64.0 mmol). The mixture was stirred at room temperature for 12 h before diethyl ether was added. The white precipitate was separated by filtration, and the filtrate was concentrated. A pure, colorless product was obtained after distillation (Kogelrohr: 38 °C / 15 mm Hg; 2.6 g, 91%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.22 (m, 1H), 2.42 (m, 4H), 2.00 (d, J = 3.1 Hz, 2H), 1.62 (m, 4H), 0.10 (d, J = 3.7 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 58.1, 45.9, 24.5, -3.5; IR (neat) 841, 894, 1250, 1413, 1458, 2119, 2778, 2960 cm^{-1}; MS (EI): calcd for $C_7H_{17}NSi$ 143.1130, found 143.1132.

Dimethyl(N-*(2S)*-methoxymethylpyrrolidinomethyl)silane (2.94a). Compound (chloromethyl)dimethylsilane (108.5 mg, 1.0 mmol) was added to a 25 mL flask containing a solution of 2-*(S)*-methyoxymethylpyrrolidine (115 mg, 1.0 mmol). The mixture was stirred at 50 °C for 6 h. The excess of silane and solvent were removed in vacuo. The white solid was then triturated with diethyl ether (5 X 15 mL). Removal of solvent gave a pure product (90 mg, 96%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.94 (m, 1H), 3.18-3.45 (m, 2H), 3.32 (s, 3H), 3.09 (m, 1H), 2.49 (dd, J = 14.2, 3.7 Hz, 1H), 2.34 (m, 1H), 2.12 (q, J=8.5 Hz, 1H), 1.46-1.84 (m, 5H), 0.10 (d, J = 1.9 Hz, 3H), 0.08 (d, J = 1.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 76.5, 67.7, 59.5, 57.7, 44.9, 28.8, 23.4, -3.4; IR (neat) 841, 889, 1109, 1250, 2117, 2809, 2960 cm^{-1}; MS (EI): calcd for $C_9H_{21}NOSi$ 187.1392, found 187.1393; $[\alpha]_D^{20}$ -109.2° (c = 0.1051 g/ml, CH_2Cl_2).

General Procedure for Asymmetric Hydrosilation of Ketones with Chiral Phosphine Ligands and Rhodium Hydride Complex: a) *sec*-Phenethyl alcohol (2.84): Hydridotetrakis(triphenylphosphine)rhodium(I) (10 mg, 0.009 mmol), *(2R,3R)*-(+)-bis(diphenylphosphino)butane (10 mg, 0.024 mmol) and THF (2 mL) were placed in a 5 mL flask under argon. The reaction mixture became orange-red. The mixture was heated at 60 °C for 10 min, and then allowed to be stirred at room temperature for 2 h before the solvent was removed in vacuo.

To the newly formed chiral complex, acetophenone (240 mg, 2.0 mmol) was added to the solid complex in the reaction flask. The resulting solution was then stirred at room temperature for 1 h. Diphenylsilane (390 mg, 2.1 mmol) was added dropwise to the reaction at room temperature. The reaction was monitored by TLC or/and ^{1}H NMR. The reaction was stirred at room temperature for 14 days to completion.

The reaction mixture was then transferred to a 25 mL flask, which contained a solution of HCl (2 N, 5 mL) and acetone (5 mL). The mixutre was stirred at room temperature for 5 h. Na_2CO_3 was added at 0 °C to neutralize the reaction mixture. Acetone was removed via rotatory evaporator, and the residual aqueous mixture was then extracted with chloroform (5 X 5 mL). The combined organic layers were dried over Na_2SO_4. The chloroform was removed via rotary evaporator, and the residue was extracted with *n*-pentane. Removal of *n*-pentane gave a reasonable pure product, which was purified by distillation (Kugelröhr: 65 °C / 5 mm Hg; 198 mg, 81%).

Small amount of this product (ca 5 mg, 0.04 mmol) and deuteratd chloroform (0.5 mL) were placed in a clean NMR tube. A small piece of crystal of 4-dimethylaminopyridine (DMAP) was added to this NMR tube followed by small amounts of pyridine (10 μL). After the mixture was well mixed, *(R)*-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (ca. 12 mg, 0.05 mmol) was added. The reaction mixture was then allowed to stand in an oil bath at about 40 °C for 5 h. The methyl groups of the newly formed *(S)*-Mosher's esters were detected in ^{1}H NMR spectrum. *(S,S)*-Mosher's ester (^{1}H, 500 MHz): δ = 7.30-7.46 ppm (m, 10H), 6.12 (q, J = 6.5 Hz, 1H), 3.46 (s, 3H), 1.57 [d, J = 6.5 Hz, 3H, 47% *(R)*]; *(R,S)*-Mosher's ester: 7.20-7.40 ppm (m, 10H), 6.07 (q, J = 6.5 Hz, 1H), 3.54 (s, 3H), 1.62 [d, J = 6.5 Hz, 3H; 53% *(S)*]. The enantiomeric excess of the reaction was 6% ee *(R)*.

b) *(R)*-(+)-Bis(diphenylphosphino)-1,1'-binaphthyl [*(R)*-BINAP]: *sec*-Phenethyl alcohol (2.84): Chiral complex was made by $(Ph_3P)_4RhH$ (10 mg, 0.009 mmol) and *(R)*-(+)-bis(diphenylphosphino)-1,1'-binaphthyl (13 mg, 0.021 mmol) in THF (2 mL) (wine-red). Hydrosilation of acetophenone (240 mg, 2.0 mmol) by diphenylsilane (390 mg, 2.1 mmol) catalyzed by the newly formed chiral complex was completed in 3 days at room temperature. Standard work-up gave an optically active product [187 mg, 77% yield, 10% ee *(R)*].

c) (+)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)-DIOP]: *sec*-Phenethyl alcohol

(2.84): Chiral complex was made by $(Ph_3P)_4RhH$ (7 mg, 0.006 mmol), (+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (15 mg, 0.030 mmol) in THF (2 mL) (orange-red). Hydrosilation of acetophenone (240 mg, 2.0 mmol) by diphenylsilane (390 mg, 2.1 mmol) catalyzed by the newly formed chiral complex was completed in 12 h at room temperature. Standard work-up gave an optically active product [203 mg, 83% yield, 46% ee *(S)*].

2-Cyclohexen-1-ol (2.60) The chiral complex was made by complex $(Ph_3P)_4RhH$ (8 mg, 0.007 mmol) and (+)-DIOP (10 mg, 0.02 mmol) in THF (2 mL). Hydrosilation of 2-cyclohexen-1-one (96 mg, 1.0 mmol) by diphenylsilane (200 mg, 1.1 mmol) catalyzed by the newly formed chiral complex was completed in 12 h at room temperature. Standard work-up gave an opticaly active product (74 mg, 76% yield, 6% ee).

3-Methyl-2-cyclohexen-2-ol (2.61) The chiral complex was made by complex $(Ph_3P)_4RhH$ (10 mg, 0.009 mmol) and (+)-DIOP (12 mg, 0.024 mmol) in THF (2 mL). Hydrosilation of 3-methyl-2-cyclohexen-1-one (220 mg, 2.0 mmol) by diphenylsilane (460 mg, 2.5 mmol) catalyzed by the newly formed chiral complex was completed in 12 h at room temperature. Standard work-up gave an optically active product (187 mg, 83% yield, 6% ee).

Hydrosilation of acetophenone by monohydrosilane: The chiral complex was made by complex $(Ph_3P)_4RhH$ (7 mg, 0.006 mmol) and (+)-DIOP (16 mg, 0.032 mmol) in THF (2 mL).

Hydrosilation of acetophenone (240 mg, 2.0 mmol) by dimethylphenylsilane (341 mg, 2.5 mmol) catalyzed by the newly formed chiral complex was completed in 10 days at room temperature. Standard work-up gave an optically active product [203 mg, 83% yield, 2% ee *(R)*].

***Hydrosilation of acetophenone by trihydrosilane:*:** The chiral complex was made by complex $(Ph_3P)_4RhH$ (13 mg, 0.011 mmol) and (+)-DIOP (20 mg, 0.040 mmol) in THF (2 mL). Hydrosilation of acetophenone (240 mg, 2.0 mmol) by phenylsilane (272 mg, 2.5 mmol) catalyzed by the newly formed chiral complex was completed in 8 h at room temperature. Standard work-up gave an optically active product [203 mg, 83% yield, 22% ee *(R)*].

d) (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine [(-)-BPPFA]: *sec*-Phenethyl alcohol (2.84): The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (7 mg, 0.011 mmol) in THF (2 mL). Hydrosilation of acetophenone (120 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex was completed in 5.5 h at room temperature. Standard work-up gave an optically active product [97 mg, 80% yield, 46% ee *(S)*].

2-Cyclohexen-1-ol (2.60): The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (7 mg, 0.011

mmol) in THF (2 mL). Hydrosilation of 2-cyclohexen-1-one (100 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (2 mL) was completed in 7 h at room temperature. Standard work-up gave an optically active product (76 mg, 78% yield, 4% ee).

6-Methyl-5-hepten-2-ol (2.115'). The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (7 mg, 0.011 mmol) in THF (2 mL). Hydrosilation of 6-methyl-5-hepten-2-one (126 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (0.5 mL) was completed in 5.5 h at room temperature. Standard work-up gave an optically active product [120 mg, 94% yield, 24% ee *(S)*]: ^1H NMR (200 MHz, $CDCl_3$) δ 5.11 (t, J = 7.3 Hz, 1H), 3.77 (m, 1H), 2.05 (q, J = 7.3 Hz, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.45 (m, 2H), 1.17 (d, J = 6.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.3, 123.4, 68.0, 39.4, 26.3, 25.1, 24.0, 18.3; IR (neat) 1074, 1129, 1376, 1453, 1458, 2925, 2968, 3344 cm^{-1}; MS (EI) *m/z* 67 (15.7), 69 (28.4), 71 (14.1), 95 (100.0), 110 (25.4), 128 (18.9, M).

1-Indanol (2.116'). The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (7 mg, 0.011 mmol) in THF (2 mL). Hydrosilation of 1-indanone (132 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1 mL) was completed in 8 h at room

temperature. Standard work-up gave an optically active product (114 mg, 85% yield, 10% ee): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41 (m, 1H), 7.25 (m, 3H), 5.24 (dd, J = 6.6, 5.6 Hz, 1H), 3.04 (ddd, J = 15.9, 8.5, 3.6 Hz, 1H), 2.81 (m, 1H), 2.44 (m, 1H), 1.87 (m, 1H), 1.68 (br, 1H, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.1, 142.3, 127.4, 125.9, 124.1, 123.5, 76.1, 36.1, 30.2; IR (neat) 742, 754, 764, 1056, 1459, 1479, 2941, 3371 cm^{-1}; MS (EI) *m/z* 77 (12.3), 91 (13.2), 105 (20.9), 115 (24.5), 116 (20.5), 117 (12.2), 133 (100.0), 134 (56.3, M), 135 (5.4).

1,2,3,4-Tetrahydro-5,7-dimethyl-1-naphthol (**2.117'**). The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)-ferrocenyl]ethylamine (7 mg, 0.011 mmol) in THF (2 mL). Hydrosilation of 5,7-dimethyl-1-tetralone (175 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 8 h at room temperature. Standard work-up gave an optically active product (151 mg, 86% yield, 14% ee): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.10 (s, 1H), 4.73 (t, J = 4.8 Hz, 1H), 2.56 (m, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.90 (m, 4H), 1.62 (s, 1H, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.8, 135.6, 134.4, 131.7, 129.3, 126.2, 68.5, 32.2, 26.8, 21.5, 20.1, 19.2; IR (Film) 858, 1033, 1061, 1074, 1438, 1479, 2863, 2934, 3334 cm^{-1}; MS (EI) *m/z* 115 (21.6), 119 (45.7), 143 (77.3), 147 (31.8), 148 (57.8), 158 (96.5), 161 (62.0), 176 (100.0, M), 177 (12.8).

1-Benzosuberol (**2.118'**). The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-

[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (7 mg, 0.011 mmol) in THF (2 mL). Hydrosilation of 1-benzosuberone (160 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (0.5 mL) was completed in 8 h at room temperature. Standard work-up gave an optically active product (150 mg, 92% yield, 56% ee): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 (dd, J = 6.6, 2.2 Hz, 1H), 7.19-7.37 (m, 3H), 5.03 (d, J = 7.5 Hz, 1H), 3.50 (ddd, J = 14.2, 8.1, 1.8 Hz, 1H), 2.84 (ddd, J = 14.2, 10.3, 1.8 Hz), 1.80-2.30 (m, 5H), 1.64 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 140.0, 128.8, 126.3, 125.4, 124.0, 73.9, 37.0, 36.2, 28.4, 28.1; IR (film) 624, 737, 748, 761, 1016, 1037, 1055, 1069, 1104, 1199, 1213, 1240, 1448, 1453, 1676, 1718, 1736, 2853, 2928, 3421 cm^{-1}; MS (EI) *m/z* 91 (67.4), 105 (35.8), 116 (23.4), 120 (22.3), 129 (70.1), 131 (23.0), 133 (73.1), 144 (100.0), 162 (21.9).

1-(1'-Adamantyl)ethanol (2.119'). The chiral complex was made by complex $(Ph_3P)_4RhH$ (5 mg, 0.004 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (7 mg, 0.011 mmol) in THF (2 mL). Hydrosilation of 1-adamantyl methyl ketone (178 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 12 h at room temperature. Standard work-up gave an optically active product [167 mg, 93% yield, 28% ee *(S)*]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.26 (q, J = 6.4 Hz, 1H), 1.98 (m, 3H), 1.43-1.74 (m, 12H), 1.08 (d, J = 6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 75.8, 38.2, 37.7, 37.0, 28.9, 17.2; IR (Film) 739, 1074, 1449, 2848, 2889,

2915, 3328 cm^{-1}; MS (EI) *m/z* 79 (16, 0), 93 (15.2), 135 (100.0), 136 (20.6), 180 (3.5, M).

1-(3',4',5'-Trimethoxyphenyl)ethanol (2.120'). The chiral complex was made by complex $(Ph_3P)_4RhH$ (8 mg, 0.007 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (16 mg, 0.026 mmol) in THF (2 mL). Hydrosilation of 3',4',5'-trimethyoxyacetophenone (210 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in THF (2.0 mL) was completed in 12 h at room temperature. Standard work-up gave an optically active product [175 mg, 83% yield, 16% ee *(S)*]: ^1H NMR (200 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.81 (q, J = 6.5 Hz, 1H), 3.84 (s, 6H), 3.80 (s, 3H), 1.46 (d, J = 6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.2, 140.9, 136.2, 101.8, 70.5, 60.9, 56.2, 25.8; IR (neat) 1105, 1127, 1155, 1235, 1421, 1458, 1463, 1593, 2941, 2970, 3408 cm^{-1}; MS (EI) *m/z* 138 (40.2), 139 (14.8), 154 (35.1), 155 (10.4), 169 (88.2), 195 (13.3), 197 (64.9), 212 (100.0, M), 213 (12.2).

1-(2',4',6'-Trimethylphenyl)ethanol (2.121'). The chiral complex was made by complex $(Ph_3P)_4RhH$ (8 mg, 0.007 mmol) and (-)-*(R)*-N,N-Dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]-ethylamine (15 mg, 0.024 mmol) in THF (2 mL). Hydrosilation of 2',4',6'-trimethylacetophenone (162 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in THF (2.0 mL) was completed in 10 h at room temperature. Standard work-up gave an optically active product [139 mg, 84% yield, 78% ee

(S)]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.81 (s, 2H), 5.35 (q, J = 6.8 Hz, 1H), 2.40 (s, 6H), 2.24 (s, 3H), 1.70 [s(br, OH)], 1.51 (d, J = 6.8 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.9, 135.7, 134.9, 129.5, 67.6, 22.3, 21.4, 21.2; IR (Film) 891, 1073, 1092, 1449, 1612, 2926, 2970, 3356 cm^{-1}; MS (EI) *m/z* 105 (35.0), 115 (11.5), 119 (15.4), 121 (55.9), 131 (25.9), 146 (40.2), 147 (17.8), 149 (100.0), 150 (11.1), 164 (32.9, M).

2,2,2-Trifluoro-1-phenylethanol (2.122'.) The chiral complex was made by complex $(Ph_3P)_4RhH$ (8 mg, 0.007 mmol) and (-)-*(R)*-N,N-dimethyl-1-[*(S)*-1',2-bis(diphenylphosphino)ferrocenyl]-ethylamine (17 mg, 0.027 mmol) in THF (2 mL). Hydrosilation of 2,2,2-trifluoroacetophenone (174 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in THF (2.0 mL) was completed in 10 h at room temperature. Standard work-up gave an optically active product (133 mg, 76% yield, 20% ee): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41 (m, 5H), 5.01 (dq, J = 4.6, 6.8 Hz, 1H), 2.48 (d, J = 4.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.2, 128.9, 128.0, 126.8, 123.7 (q, 278.6), 72.8 (q, 31.6); IR (neat) 633.4, 705.6, 1063.4, 1123.5, 1178.9, 1207.2, 1268.3, 1458.0, 3390.6 cm^{-1}; MS (EI) m/z 51 (10.6), 77 (37.8), 79 (57.4), 107 (100.0), 176 (46.3, M), 177 (4.1).

d) *(2S,4S)*-*tert*-Butyl 4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)-1-pyrrolidinecarboxylate [*(2S,4S)*-BPPM] as chiral ligand: *sec*-Phenethyl alcohol (2.84)**:** The chiral complex was made by complex $(Ph_3P)_4RhH$ (10 mg, 0.009 mmol) and *(2S,4S)*-*tert*-butyl 4-(diphenylphosphino)-2-(diphenylphosphinome-

thyl)-1-pyrrolidine-carboxylate (11 mg, 0.02 mmol) in THF (2 mL). Hydrosilation of acetophenone (240 mg, 2.0 mmol) by diphenylsilane (400 mg, 2.2 mmol) catalyzed by the newly formed chiral complex was completed in 8 h at room temperature. Standard work-up gave an optically active product [204 mg, 84% yield, 33% ee *(R)*]

1-N,N-Dimethylamino-2-propanol (2.152). The chiral complex was made by complex $(Ph_3P)_4RhH$ (10 mg, 0.009 mmol) and *(2S,4S)-tert*-butyl 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-1-pyr-rolidinecarboxylate (11 mg, 0.02 mmol) in THF (2 mL). Hydrosilation of 1-N,N-dimethyl-2-propanone (101 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex was completed in 12 h at room temperature. Standard work-up gave an optically active product [73 mg, 71% yield, 32% ee *(R)*]: ^1H NMR (200 MHz, $CDCl_3$) δ 3.79 (m, 1H), 2.95 (br, 1H), 2.12-2.41 (m, 2H), 2.27 (s, 6H), 1.11 (d, 6.2, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 67.1, 63.2, 45.7, 20.7; IR (neat) 1039, 1099, 1134, 1458, 1463, 2778, 2824, 2944, 2970, 3375 cm^{-1}; MS (EI) *m/z* 58 (100.0), 70 (14.2), 72 (31.1), 102 (100.0), 103 (6.8, M).

3-Dimethylamino-1-phenylpropan-1-ol (2.153). The chiral complex was made by complex $(Ph_3P)_4RhH$ (14 mg, 0.01 mmol) and *(2S,4S)-tert*-butyl 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-1-pyrrolidinecarboxylate (17 mg, 0.03 mmol) in THF (2 mL). Hydrosilation of 3-dimethylaminopropiophenone (177 mg, 1.0 mmol) by diphenylsilane (300 mg, 1.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 12 h at

room temperature. Standard work-up gave an optically active product [139 mg, 78% yield, 44% ee *(R)*]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (m, 5H), 4.92 (dd, J = 7.0, 4.7 Hz, 1H), 2.66 (ddd, J = 12.7, 8.2, 5.6 Hz, 1H), 2.46 (m, 1H), 2.29 (s, 6H), 1.82 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.4, 127.6, 126.3, 125.0, 75.5, 58.5, 45.7, 35.2; IR (Film) 701, 1051, 1064, 1453, 1458, 1464, 2825, 2948, 3238 cm^{-1}; MS (EI) *m/z* 58 (100.0), 77 (13.9), 179 (28.1, M), 180 (3.7).

e) Hydrosilation of Acetophenone Catalyzed by Miscellenious Chiral Phosphine Rhodium Complexes: i) The chiral complex was made by complex (1,5-cycloocta-diene)bis(triphenylphosphine)rhodium(I) hexafluorophosphate, di-chloromethane (7 mg, 0.007 mmol) and *(S)*-BINAP (12 mg, 0.019 mmol) in CH_2Cl_2 (2 mL). Hydrosilation of acetophenone (**2.78**, 240 mg, 2.0 mmol) by diphenylsilane (500 mg, 2.7 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 12 h at 0 °C. Standard work-up gave an optically active product [203 mg, 83% yield, 26% ee *(S)*].

ii) The chiral complex was made by complex (1,5-cyclooctendiene)bis(triphenylphosphine)rhodium(I) hexafluorophos-phate, dichloromethane (5 mg, 0.005 mmol) and (-)-BPPFA (11 mg, 0.018 mmol) in CH_2Cl_2 (2 mL). Hydrosilation of acetophenone (240 mg, 2.0 mmol) by diphenylsilane (500 mg, 2.7 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 12 h at 0 °C. Standard work-up gave an optically active product [208 mg, 85% yield, 30% ee *(S)*].

iii) The chiral complex was made by complex μ-dichlorotetraethenedirhodium (3 mg, 0.009 mmol) and (-)-BPPFA (11 mg, 0.018 mmol) in THF (1 mL). Hydrosilation of acetophenone (240 mg, 2.0 mmol) by diphenylsilane (500 mg, 2.7 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 12 h at 0 °C. Standard work-up gave an optically active product [210 mg, 87% yield, 8% ee *(S)*].

f) Hydrosilation of Acetophenone with Cyclic Silane (2.130) Catalyzed by Various Chiral Catalysts: i) The chiral complex was made by complex chlorotris(triphenylphosphine)rhodium(I) (12 mg, 0.013 mmol) and *(S)*-BINAP (22 mg, 0.035 mmol) in THF (2 mL). Hydrosilation of acetophenone (60 mg, 0.5 mmol) by 2,2'-sila-1,1'-biphenyl (100 mg, 0.6 mmol) catalyzed by the newly formed chiral complex in THF (1.0 mL) was completed in 6 h at room temperature. Standard work-up gave an optically active product [47 mg, 77% yield, 6% ee *(S)*].

ii) The chiral complex was made by complex bis(1,5-cyclooctendiene)rhodium(I) tetrafluoroborate hydrate (6 mg, 0.015 mmol) and *(S)*-BINAP (22 mg, 0.035 mmol) in THF (2 mL). Hydrosilation of acetophenone (60 mg, 0.5 mmol) by 2,2'-sila-1,1'-biphenyl (100 mg, 0.6 mmol) catalyzed by the newly formed chiral complex in THF (1.0 mL) was completed in 6 h at room temperature. Standard work-up gave an optically active product [43 mg, 70% yield, 44% ee *(S)*].

iii) The chiral complex was made by complex (1,5-cyclooctendiene)bis(triphenylphosphine)rhodium(I) hexafluorophosphate dichloromethane (12 mg, 0.012 mmol) and *(S)*-BINAP (36 mg, 0.058 mmol) in CH_2Cl_2 (1 mL). Hydrosilation of acetophenone (30 mg, 0.25 mmol) by 2,2'-sila-1,1'-biphenyl (100 mg, 0.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 8 h at room temperature. Standard work-up gave an optically active product [20 mg, 66% yield, 8% ee *(S)*].

iv) The chiral complex was made by complex $(Ph_3P)_4RhH$ (8 mg, 0.007 mmol) and (-)-BPPFA (15 mg, 0.024 mmol) in THF (1 mL). Hydrosilation of acetophenone (30 mg, 0.25 mmol) by 2,2'-sila-1,1'-biphenyl (100 mg, 0.6 mmol) catalyzed by the newly formed chiral complex in CH_2Cl_2 (1.0 mL) was completed in 10 h at room temperature. Standard work-up gave an optically active product [22 mg, 72% yield, 8% ee *(S)*].

_(S)_-(1-Phenyl-1-ethoxy)diphenylsilane (2.92) *(S)-sec*-Phenethyl alcohol (367 mg, 3.0 mmol) was placed in a 50 mL flask containing *n*-pentane (15 mL). The solution was then cooled to -30 °C. Chlorodiphenylsilane (656 mg, 3.0 mmol) was added to this solution followed by triethylamine (2 mL). White solid precipitated. The reaction mixture was stirred at -30 °C for 3 h, and then warmed up to room temperature, and kept stirring for 30 min at this temperature. The white precipitate was removed by filtration. The filtrate was washed with water (2 X 5 mL), and then dried over Na_2SO_4. The solvent was removed *in vacuo*. A colorless product was

obtained after Kugelröhr distillation (140 °C / 2 mm Hg, 766 mg, 84%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18-7.68 (m, 15H), 5.40 (s, 1H), 4.99 (q, J = 6.5 Hz, 1H), 1.50 (d, J = 6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.41, 139.96, 133.61, 133.54, 133.33, 129.64, 129.58, 127.58, 127.36, 127.30, 126.50, 124.94, 72.72, 26.83; IR (neat) 698, 733, 820, 840, 961, 1034, 1069, 1087, 1114, 1121, 1429, 1448, 1493, 1590, 2126, 2974, 3069 cm^{-1}; MS (EI) *m/z* 79 (39.0), 105 (27.2), 107 (49.1), 122 (27.8), 183 (31.0), 199 (100.0), 200 (20.0), 304 (1.2, M).

***(R)*-(1-Phenyl-1-ethoxy)diphenylsilane (2.92):** *(R)*-1-Phenyl-1-ethoxydiphenylsilane was obtained by reaction of *(R)-sec*-phenethyl alcohol (450 mg, 3.7 mmol) with chlorodiphenylsilane (805 mg, 3.7 mmol) in *n*-pentane (25 mL) at -30 °C for 3 h (140 °C / 2 mm Hg, 907 mg, 81%).

Iospropoxydiphenylsilane (2.133). Iospropoxydiphenylsilane was obtained by reaction of 2-propanol (0.5 mL, 393 mg, 6.5 mmol) with chlorodiphenylsilane (656 mg, 3.0 mmol) in *n*-pentane (10 mL) at -30 °C for 3 h. After standard work-up, a colorless aproduct was obtained using Kugelröhr distillation (110 °C / 2 mm Hg, 653 mg, 90%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.61 (m, 4H), 7.38 (m, 6H), 5.43 (s, 1H), 4.15 (m, J = 6.1 Hz, 1H), 1.22 (d, J = 6.1 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.9, 133.6, 129.5, 127.3, 67.5, 25.9; IR (neat) 699, 733, 820, 837, 881, 1023, 1032, 1121, 1429, 1590, 2117, 2875, 2973 cm^{-1}; MS (EI) *m/z* 105 (27.1), 122 (62.0), 123 (38.5), 164 (100.0), 183 (54.9), 199 (27.1), 242 (6.8, M).

Acetophenone-*carbonyl*-^{13}C (2.91): To the mixture of $CH_3{}^{13}CO_2Na$ (150 mg, 1.8 mmol) and benzene (10 mL) in a 25 mL flask equipped with a drying tube filled with Derierte, oxaly chloride (251 mg, 2.0 mmol) was added at 0 °C, followed by catalytic amount of DMF (ca. 10 μL). The reaction was completed in 3 h. The reaction mixture became clear. To this clear solution, aluminun trichloride (530 mg, 4.0 mmol) was added at room temperature. The mixture was allowed to stir for 7 h at room temperature.

Saturated aqueous ammonium chloride solution was added to the reaction mixture, followed by HCl (6N, 5 mL). The acidic solution was neutralized by potassium carbonate powder at 0 °C, and was then extracted with diethyl ether (5 X 10 mL). The combined organic extracts were dried over Na_2SO_4. After removal of solvent, the crude product was purified by distillation (Kugelröhr, 65 °C / 5 mm Hg; 200 mg, 92%): ^1H NMR (200 MHz, $CDCl_3$): 7.95 (m, 2H), 7.50 (m, 3H), 2.58 (d, J = 6.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 196.6, 136.3 (d, J = 51.8 Hz), 127.7 (dd, J = 12.5, 4.1 Hz), 27.1 (d, J = 42.1 Hz); IR (neat) 639, 703, 762, 942, 1243, 1278, 1318, 1448, 1578, 1599, 1646, 1651, 1657, 3029, 3061, 3083 cm^{-1}; MS (EI) *m/z*: 51 (12.6), 77 (62.6), 106 (100.0), 121 (43.2, M), 122 (3.3).

2,2'-Diaminobiphenyl (2.126). Tin(II) chloride (34.1 g, 90 mmol) was placed in a 250 mL flask equipped with a thermometer. Concentrated HCl (46 mL) was added to the flask at 0 °C. 2,2'-Dinitrobiphenyl (7.32 g, 30 mmol) was introduced to the reaction mixture at room temperature followed by ethanol (50 mL). After a while, the temperature of the stirred reaction mixture reached 36 °C.

After 12 h, the stirred reaction mixture became a clear solution. The solution was then neutralized by NaOH (20%) at 0 °C. After most of the solvent was removed via a rotary evaporator, the mixture was then filtrated using a sintered glass Buchner funnel. The filtrate was extracted by chloroform (5 X 100 mL), and the combined organic layers were dried over Na_2SO_4. Removal of solvent gave a pure product (5.401 g, 98%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20 (dd, J = 7.5, 1.6 Hz, 2H), 7.11 (dm, J = 7.8 Hz, 2H), 6.84 (dd, J = 7.5, 1.2 Hz, 2H), 6.77 (dm, J = 7.8 Hz, 2H), 3.70 ((br)s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 130.4, 128.2, 124.0, 118.3, 115.1; IR (film) 751, 1299, 1445, 1484, 1614, 2853, 3024, 3061 cm^{-1}; MS (EI) *m/z* 166 (18.9), 167 (46.9), 168 (35.7), 183 (41.1), 184 (100.0, M), 185 (13.6).

2,2'-Dibromobiphenyl (2.127). To a solution of 1,2-dibromobenzene (20.76 g, 88.0 mmol) in THF (550 mL), *n*-butyllithium (1.85 M, 21.7 mL, 40.1 mmol) in hexanes was added using a syringe pump under argon at -80 °C for a period of 2 h. The reaction mixture was then slowly warmed up to 5 °C during 2 h, and was stirred at 5 °C for another 30 min. Saturated aqueous ammonium chloride solution was added to the reaction flask at about -10 °C. The mixture was slowly warmed up to room temperature. Organic layer was separated and the solvent was removed via rotary evaporator. The reddish crude product was then purified by a short column chromatography (silica gel, hexanes). A white solid product was obtained (11.2 g, 90%): mp: 86.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.8, 1.5 Hz, 2H), 7.40 (td, J = 7.0, 1.9 Hz, 2H), 7.27 (td, J = 6.8, 1.8 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.2, 131.9, 130.3, 128.7,

126.5, 122.9; IR (film) 761, 1003, 1025, 1422, 1434, 1455, 1616, 16356, 2915, 2970, 3055 cm^{-1}; MS (EI) *m/z* 76 (32.7), 151 (20.7), 152 (100.0), 231 (47.1), 233 (45.8), 400 (21.5), 312 (41.3, M), 313 (5.6), 314 (5.6).

9-Silafluorene (2.130). To a solution of 2,2'-dibromobiphenyl (6.85 g, 22.0 mmol) in THF (400 mL), *n*-butyllithium (26.2 mL, 1.85 M, 48.5 mmol) in hexanes was added via a syringe pump under argon at -80 °C for a period of 2 h. The reaction mixture was then allowed to warm up to 0 °C, and was stirred at 0 °C for 15 min before cooled down to -80 °C again.

The cooled reaction mixture was then siphonated to a solution of tetrachlorosilane (37.5 g, 221 mmol) in THF (200 mL) dropwise at -80 °C. After the addition was completed, the reaction mixture was stirred at -50 °C for about 2 h. The reaction mixture became clear. The clear solution was then stirred at -30 °C for another 30 min.

The excess of tetrachlorosilane was removed in vacuo under -5 °C. After addition of extra THF (200 mL), the reaction mixture was then cooled to -80 °C again. $LiAlH_4$ (5.5 g, 145 mmol) was added to the reaction flask in small portions at -80 °C. After stirring at -80 °C for 3 hour, the reaction mixture was allowed to warm up slowly to 0 °C, and stirred for another hour at 0 °C. Ethyl acetate was added very slowly at -10 °C to quench the excess $LiAlH_4$, followed by methanol and saturated ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 X 100 mL). The combined organic layers were dried over Na_2SO_4. Removal of solvents gave a crude product, which was purified by distillation

(Kugelröhr: 110 °C / 2 mm Hg; 3.605 g, 90%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 7.3 Hz, 2H), 7.47 (td, J = 7.7, 1.4 Hz, 2H), 7.30 (td, J = 7.2, 1.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.5, 133.6, 130.7, 130.1, 126.9, 120.7; IR (neat) 728, 750, 784, 943, 1061, 1127, 1433, 1593, 2149, 3047, 3063, 3071 cm^{-1}; MS *m/z* calcd for $C_{12}H_{10}Si$: 182.0552, found 182.0555.

9,9'-Silabisfluorene (2.131). To a solution of 2,2'-dibromobiphenyl (624 mg, 2.0 mmol) in THF (50 mL), *n*-butyllithium (1.85 M, 2.4 mL, 4.4 mmol) in hexanes was added via a syringe under argon at -50 °C. The reaction mixture was then allowed to warm up to 0 °C, and was stirred at 0 °C for 1 h. An off-white precipitate appeared. The reaction mixture was then cooled down to -50 °C again.

To this cooled reaction mixture, silicon tetrachloride (170 mg, 1.0 mmol) in THF (1 mL) was added dropwise at -50 °C. After the addition was completed, the reaction mixture was stirred at -20 °C for about 2 h. The reaction mixture became clear. Methanol was added to this reaction mixture followed by saturated ammonium chloride in aqueous solution. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 X 50 mL). The combined organic layers were dried over Na_2SO_4. Removal of solvents gave a crude product, which was purified by flush column chromatography (silica gel, hexanes : ethyl acetate = 50 : 1; 604 mg, 91%): mp: 222 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 4H), 7.48 (td, J = 7.4, 1.4 Hz, 4H), 7.39 (dm, J = 6.6 Hz, 4H), 7.19 (t, J = 7.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.1, 133.6, 132.0, 130.6, 127.3,

120.5; IR (film) 725 (32.6), 749 (23.5), 1066 (48.8), 1256 (49.5), 1430 (40.8), 1592 (45.7), 2923 (59.7) cm^{-1}; MS *m/z* calcd for $C_{24}H_{16}Si$: 332.1021, found 332.1013.

2,6-Bis[*(4'S)*-isopropyl-2'-oxazolin-2'-yl]pyridine (2.139). 2,6-Pyridinedicarboxylic acid (1.002 g, 6.0 mmol) and CH_2Cl_2 (50 mL) were placed in a 250 mL flask. Oxalyl chloride (1.15 mL, 1.675 g, 13.2 mmol) was added dropwise at 0 °C to the reaction mixture followed by catalytic amount of DMF (2 μL, 2 mg, 0.03 mmol). The reaction mixture was then stirred at room temperature for 10 h. Small portion of this clear solution was taken and quenched with large excess of methanol. TLC indicated that the reaction was completed.

The solvent was then removed in vacuo, and the crude product (1.1289 g, 99%) was dissolved in CH_2Cl_2 (12 mL) again. A solution of *(S)*-(+)-2-amino-3-methyl-1-butanol (1.26 g, 12.2 mmol) in CH_2Cl_2 (22 mL) was added at 0 °C, followed by triethylamine (4.7 mL, 3.41 g, 33.7 mmol). The reaction mixture was stirred at 0 °C for 24 h.

Thionyl chloride (5 mL, 8.16 g, 68.5 mmol) was added to the reaction flask. The reaction mixture became cloudy. After refluxed for 2 h, the reaction mixture was poured into a beaker containing ice and water. The mixture was then extracted with CH_2Cl_2 (5 X 50 mL). Removal of solvent gave a crude product, which was purified by short column chromatography (silica gel, CH_2Cl_2). A reasonably pure product was obtained (1.8416 g, 83% for 3 steps).

The product was then dissolved in a solution of NaOH (1.2 g, 30 mmol) in water (16 mL) and methanol (34 mL) at room temperature.

The solution was stirred at room temperature for 3 days. The reaction mixture was then extracted by CH_2Cl_2 (6 X 20 mL), and the combined organic layers were dried over Na_2SO_4. An off-white solid was obtained after removal of solvent. The solid was recrystallized using ethyl acetate/hexanes to give a white needle crystalline product (0.6340 g, 43%): m.p. 155.5°; ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 7.8 Hz, 2H), 7.83 (t, J = 7.7 Hz, 1H), 4.50 (t, J = 9.2 Hz, 2H), 4.20 (t, J = 8.5 Hz, 2H), 4.13 (dd, J = 9.3, 6.3 Hz, 2H), 1.84 (m, J = 6.6 Hz, 2H), 1.02 (d, J = 6.8 Hz, 6H), 0.91 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 146.8, 137.2, 125.6, 72.9, 71.0, 32.8, 19.0, 18.3; IR (Film) 1071, 1100, 1379, 1636, 1640, 2958, 2976 cm^{-1}; MS (EI) *m/z* 301 (3.7), 259 (25.6), 258 (100.0), 230 (22.6), 145 (14.1); $[\alpha]_D^{20}$ -132.9° (c = 0.0539, CH_2Cl_2).

General Method for Asymmetric Hydrosilation of Ketones Using Chiral Oxazolinyl Ligand, *(S,S)*-2,6-Bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine, and Metal Complex, Bis(1,5-cyclooctadiene)rhodium(I) Tetrafluoroborate Hydrate: *sec*-Phenethyl alcohol (2.84): Bis(1,5-cyclooctadiene)-rhodium(I) tetrafluoroborate hydrate (4 mg, 0.01 mmol), *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (11 mg, 0.03 mmol) and methanol (1 mL) were placed in a 5 mL flask sealed with a glass adaptor furnished with a teflon valve under argon. The mixture was heated at 80 °C for 30 min. After removal of solvent in vacco, a orange solid was obtained. Acetophenone (240 mg, 2.0 mmol) was added to the reaction flask, and the mixture was stirred at room temperature for 30 min then cooled to 0 °C. Diphenylsilane (460 mg,

2.5 mmol) was added to the reaction mixture at 0 °C. The reaction was completed in 12 h.

The reaction mixture was transferred to a 25 mL flask with HCl (2N, 5 mL) and acetone (5 mL). The mixutre was stirred at room temperature for 3 h. Na_2CO_3 was added to neutralize the reaction mixture. The mixture was then extracted with chloroform (5 X 10 mL). The combined organic layers were dried over Na_2SO_4. The chloroform was removed *via* rotary evaporator, and the crude product was purified by distillation [Kugelröhr, 65 °C / 5 mm Hg; 220 mg, 90% yield, 46% ee *(S)*].

1-Indanol (2.116'): The chiral catalyst was made by complex bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate hydrate (4 mg, 0.01 mmol) and *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyrridine (7 mg, 0.023 mmol) in methanol (1 mL). Hydrosilation of 1-indanone (132 mg, 1.0 mmol) by diphenylsilane (250 mg, 1.4 mmol) catalyzed by the newly formed chiral complex in $CHCl_3$ (1 mL) was completed in 12 h at room temperature. Standard work-up gave an optically active product (103 mg, 77% yield, 2% ee).

1,2,3,4-Tetrahydro-5,7-dimethyl-1-naphthol (2.117'): The chiral catalyst was made by complex bis(1,5-cyclooctadiene)rhodium(I) tetrafluoro-borate hydrate (4 mg, 0.01 mmol) and *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (7 mg, 0.023 mmol) in methanol (1 mL). Hydrosilation of 5,7-dimethyl-1-tetralone (174 mg, 1.0 mmol) by diphenylsilane (250 mg, 1.4 mmol) catalyzed by the newly formed chiral complex in $CHCl_3$ (1 mL) was

completed in 12 h at room temperature. Standard work-up gave an optically active product (141 mg, 80% yield, 4% ee).

1-Benzosuberol (2.118'): The chiral catalyst was made by complex bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate hydrate (4 mg, 0.01 mmol) and *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (7 mg, 0.023 mmol) in methanol (1 mL). Hydrosilation of 1-benzosuberone (160 mg, 1.0 mmol) by diphenylsilane (250 mg, 1.4 mmol) catalyzed by the newly formed chiral complex in $CHCl_3$ (1 mL) was completed in 12 h at room temperature. Standard work-up gave an optically active product (141 mg, 87% yield, 32% ee).

1-(2'-naphthyl)ethanol (2.140): The chiral catalyst was made by complex bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate hydrate (3 mg, 0.007 mmol) and *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (11 mg, 0.04 mmol) in methanol (1 mL). Hydrosilation of 2'-acetonaphthone (170 mg, 1.0 mmol) by diphenylsilane (250 mg, 1.4 mmol) catalyzed by the newly formed chiral complex in $CHCl_3$ (0.5 mL) was completed in 12 h at room temperature. Standard work-up gave an optically active product [152 mg, 88% yield, 30% ee *(S)*]: ^1H NMR (200 MHz, $CDCl_3$) δ 7.80 (m, 4H), 7.48 (m, 3H), 5.06 (q, J=6.6 Hz, 1H), 1.64 (s(br), 1H), 1.57 (d, J=6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.3, 132.5, 132.1, 127.5, 127.2, 126.9, 125.4, 125.0, 123.2, 123.1, 70.3, 25.6; IR (film) 741.3, 822.2, 1073.5, 2973.0, 3052.9, 3325.5 cm^{-1}; MS (EI) *m/z* 128 (40.9), 129 (100.0), 156 (11.7), 157 (48.5), 172 (40.6, M), 173 (5.5).

2,2,2-Trifluoro-1-phenylethanol (2.122'): The chiral catalyst was made by complex bis(1,5-cyclooctadiene)rhodium(I) tetrafluoro-borate hydrate (4 mg, 0.01 mmol) and *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (8 mg, 0.027 mmol) in methanol (1 mL). Hydrosilation of 2,2,2-trifluoroacetophenone (174 mg, 1.0 mmol) by diphenylsilane (250 mg, 1.4 mmol) catalyzed by the newly formed chiral complex in $CHCl_3$ (1 mL) was completed in 7 h at room temperature. Standard work-up gave an optically active product [127 mg, 72% yield, 24% ee *(S)*].

***(S,S)*-2,6-Bis(4'-Isopropyl-2'-oxazolin-2'-yl)pyridinyl-iridium Trichloride** (2.141): *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (129 mg, 0.43 mmol) and iridium trichloride hydrate (173 mg, 0.58 mmol) were dissolved in ethanol (10 mL) in a 25 mL flask furnished with a condenser. The solution was heated at 80 °C for 12 h, and the solvent was removed in vacuo. A pure product was obtained after flash column chromatography purification (silica gel, ethyl acetate : methanol = 10 : 1; 156 mg, 61%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (m, 3H), 5.08 (dd, J = 8.0, 8.0 Hz, 2H), 4.99 (dd, J = 8.0, 8.0 Hz, 2H), 4.48 (ddd, J = 3.0, 8.0, 11.0 Hz, 2H), 3.08 (m, 2H), 0.99 (d, J = 3.0 Hz, 6H), 0.98 (d, J = 3.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 148.0, 138.1, 126.0, 73.1, 69.3, 28.0, 19.5, 15.2; IR (film) 733, 924, 956, 1255, 1283, 1391, 1409, 1496, 1572, 1576, 1598, 2873, 2961, 3066 cm^{-1}; MS (FAB) *m/z* 136 (100.0), 137 (97.9), 138 (32.6), 139 (27.6), 154 (89.8), 155 (50.1), 289 (16.1), 307 (36.1), 460 (3.3), 564 (9.2), 565 (4.0), 566 (4.9), 599 (2.6, M).

General Method for Asymmetric Hydrosilation of Acetophenone Using Chiral Iridium Complex, *(S,S)*-2,6-bis(4'-iospropyl-2'-oxazolin-2'-yl)pyridinyliridium Trichloride: *sec*-Phenethyl alcohol (2.84): Chiral iridium complex *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridinyliridium trichloride (35 mg, 0.05 mmol) was placed in a 5 mL flask sealed with a glass adaptor with a teflon valve under argon. Acetophenone (120 mg, 1.0 mmol) was added to the flask to dissolve the solid. The mixture was stirred at room temperature for 1 h. Diphenylsilane (300 mg, 1.6 mmol) was added to the reaction mixture at room temperature. The reaction was completed in 36 h.

The reaction mixture was transferred to a 25 mL flask with HCl (2N, 5 mL) and acetone (5 mL). The mixutre was stirred at room temperature for 3 h. Na_2CO_3 was added to neutralize the reaction mixture. The mixture was then extracted with chloroform (5 X 10 mL). The combined organic layers were dried over Na_2SO_4. The chloroform was removed *via* rotary evaporator, and the crude product was purified by distillation [Kugelröhr, 65 °C / 5 mm Hg; 112 mg, 92% yield, 6% ee *(S)*].

Hydrosilation of acetophenone with trihydrosilane: Hydrosilation of acetophenone (120 mg, 1.0 mmol) by phenylsilane (120 mg, 1.1 mmol) catalyzed by chiral catalyst *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridinyliridium trichloride (11 mg, 0.018 mmol) was completed in 36 h at room temperature. Standard work-up gave an optically active product [95 mg, 78% yield, 8% ee *(R)*].

General Method for Asymmetric Hydrosilation of Acetophenone Using Chiral Iridium Complex, *(S,S)*-2,6-Bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridinyliridium Trichloride, Activated by $AgBF_4$: *sec*-Phenethyl alcohol (2.84): Chiral iridium complex *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridinyliridium trichloride (7 mg, 0.01 mmol), chiral ligand *(S,S)*-2,6-bis(4'-isopropyl-2'-oxazolin-2'-yl)pyridine (10 mg, 0.03 mmol) and silver tetrafluoroborate (8 mg, 0.04 mmol) were placed in a 5 mL flask sealed with a glass adaptor with a teflon valve under argon. Acetophenone (120 mg, 1.0 mmol) was added to the flask. The mixture was stirred at room temperature for 1 h. Diphenylsilane (300 mg, 1.6 mmol) was added to the reaction mixture at room temperature. The reaction was completed in 36 h.

The reaction mixture was transferred to a 25 mL flask with HCl (2N, 5 mL) and acetone (5 mL). The mixutre was stirred at room temperature for 3 h. Na_2CO_3 was added to neutralize the reaction mixture. The mixture was then extracted with chloroform (5 X 10 mL). The combined organic layers were dried over Na_2SO_4. The chloroform was removed *via* rotary evaporator, and the crude product was purified by distillation [Kugelröhr, 65 °C / 5 mm Hg; 106 mg, 87% yield, 2% ee *(S)*].

1,3,5-Tris[*(4'S)*-isopropyl-2'-oxazolin-2'-yl)-1,3,5-trimethylcyclohexane (2.145). 1,2,4-Triazole (6.95 g, 100.6 mmol) was dissolved in acetonitrile (135 mL) in an 500 mL flask furnished with a Drierite drying tube. Phosphorus oxychloride (3.1 mL, 5.10 g, 33.3 mmol) was added at 0 °C, followed by triethylamine (14.5 mL,

10.53 g, 104 mmol) dropwise. The reaction mixture was then stirred at 0 °C for 2 h. The mixture was siphonated through a cannula to a sealed sintered glass filter, which was placed in a neck of a 1 L flask, so that the clear filtrate could be added directly to the solution of compound N,N,N-tris[2'-((*2'S*)-1'-hydroxy-3'-methylbutyl)]-1,3,5-methyl-1,3,5-cyclohexanetriamide (3.11 g, 6.1 mmol) in triethylamine (150 mL) and acetonitrile (50 mL). After the addition was finished, the reaction mixture was allowed to be stirred another 30 min before saturated $NaHCO_3$ aqueous solution (70 mL) was introduced to the reaction flask. The organic solvents were removed via a rotary evaperator, and the remaining mixture was extracted with CH_2Cl_2 (10 X 50 mL). The combined organic layers were washed with water (3 X 40 mL) and then dried over Na_2SO_4. Removal of solvent gave a reasonable pure product (2.42 g, 87%). : ^1H NMR (200 MHz, $CDCl_3$) δ 4.12 (dd, J = 8.1, 7.6 Hz, 3H), 3.87 (dd, J = 7.6, 7.2 Hz, 3H), 3.76 (m, 3H), 2.64 (d, J = 14.3 Hz, 3H), 1.73 (m, 3H), 1.50 (d, J = 14.3 Hz, 3H), 1.33 (s, 9H), 0.89 (d, J = 6.7 Hz, 9H), 0.79 (d, J = 6.8 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.9, 71.8, 69.6, 40.6, 36.6, 32.9, 30.1, 19.9, 18.3; IR (neat) 1040, 1079, 1121, 1150, 1185, 1371, 1385, 1463, 1656, 1736, 2931, 2963 cm^{-1}; MS *m/z* calcd for $C_{27}H_{45}O_3N_3$: 459.3461, found 459.3451; $[\alpha]_D^{20}$ -48.8° (c = 0.1968 g/ml, CH_2Cl_2).

N,N,N-Tris[2'-((*2'S*)-1'-hydroxy-3'-methylbutyl)]-1,3,5-methyl-1,3,5-cyclohexanetriamide (2.144). In a 500 mL, three-neck flask equipped with a condensor, N,N,N-tris[1'-((*1'S*)-methoxycarbonyl-2'-methylpropyl)]-1,3,5-trimethyl-1,3,5-cyclohexanetriamide (4.23 g, 7.1 mmol) was dissolved in methanol (120 mL)

and THF (120 mL) under argon. $NaBH_4$ (4.4 g, 115.8 mmol) was added in small portions to the solution at room temperature. The reactiom mixture was stirred at room temperature for 2 days before being quenched with saturated aqueous ammonium chloride solution at 0 °C. A clear solution was obtained after HCl (2N, 30 mL) was added at 0 °C. The later was then neutrolized by saturated K_2CO_3 aqueous solution. The organic solvents were removed via rotary evaporator, and the aqueous residue was extracted with ethyl acetate (10 X 40 mL). The combined organic layers were washed with saturated K_2CO_3 aqueous solution (2 mL), water (3 X 10 mL), and then dried over Na_2SO_4. Removal of solvent gave a reasonably pure product (4.31 g, quantitative yield). The product can be purified by flash chromatography (silica gel; ethyl acetate : methanol = 10 : 1; 3.56 g, 98 %): ^1H NMR (200 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 3H), 4.32 (t, J = 6.7 Hz, 3H), 3.45-3.75 (m, 9H), 2.94 (d, J = 15.4 Hz, 3H), 1.87 (m, 3H), 1.28 (s, 9H), 1.10 (d, 15.4. 3H), 0.90 (d, J = 7.1 Hz, 9H), 0.86 (d, J = 7.2 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.4, 62.5, 58.0, 44.2, 42.5, 35.7, 30.4, 20.2, 19.7; IR (Film) 1071, 1458, 1466, 1535, 1541, 1558, 1626, 1636, 2934, 2961, 3325 cm^{-1}; MS [CI(NH_3)] *m/z* calcd for $C_{27}H_{52}O_6N_3$ (M+1): 514.3856, found 514.3818; $[\alpha]_D^{20}$ + 25.2° (c = 0.2289 g/ml, CH_2Cl_2).

N,N,N-Tris[1'-((*1'S*)-methoxycarbonyl-2'-methylpropyl)]-1,3,5-trimethyl-1,3,5-cyclohexanetriamide (2.147). 1,3,5-Trimethyl-1,3,5-cyclohexanetricarboxylic acid (2.20 g, 8.5 mmol) was placed in a 250 mL flask with THF (45 mL) under argon. L-Valine methyl ester hydrochloride (4.45 g, 26.7 mmol) in THF (10

mL) was added to the mixtre at 0 °C followed by 4-methylmorpholine (3.0 mL, 2.76 g, 27.3 mmol). 1,3-Dicyclohexylcarbodiimide (5.67 g, 27.5 mmol) was added to this mixture, which was stirred at room temperature for 3 days. The resulting white solid was filtrated, and the filtrate was subjected to flash chromatography (silica gel; hexanes : ethyl acetate: 4 : 1, then 2: 1, and then 1 : 1). A pure product was obtained (4.33 g, 85%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (d, J = 6.7 Hz, 3H), 4.18 (dd, J = 6.7, 4.8 Hz, 3H), 3.66 (s, 9H), 2.88 (d, J = 15.0 Hz, 3H), 2.09 (m, 3H), 1.27 (s, 9H), 1.16 (d, J = 15.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 9H), 0.92 (d, J = 6.9 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.5, 170.4, 58.9, 52.0, 43.3, 41.6, 33.8, 30.8, 19.4, 19.3; IR (Film): 1200, 1260, 1471, 1540, 1558, 1646, 1651, 1747, 2876, 2936, 2963, 3281 cm^{-1}; MS (EI): calcd for $C_{30}H_{51}N_3O_9$: 597.3625, found 597.3634; $[\alpha]_D^{20}$ -31.1° (c = 0.1306 g/ml, CH_2Cl_2).

N,N,N-Tris[1-((*S*)-1-methoxycarbonyl-2-methylpropyl)]nitrilotriacetamide (2.149). L-Valine methyl ester hydrochloride (7.50 g, 44.7 mmol), nitrilotriacetic acid (2.48 g, 13.0 mmol), 1-(3'-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (7.5 g, 39.1 mmol) and DMAP (0.12 g, 0.1 mmol) were dissolved in CH_2Cl_2 (250 mL) in a 500 mL flask under argon. 4-Methylmorpholine (6 mL, 5.52 g, 55 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 2 days. To the clear, light yellow solution, saturated aqueous ammonium chloride solution was added. The organic layer was washed with water (2 X 30 mL) and dired over Na_2SO_4. Removal

of solvent gave a reasonably pure product (5.51 g, 80%).: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.63 (d, J = 9.0 Hz, 3H), 4.53 (dd, J = 8.8, 5.2 Hz, 3H), 3.72 (s, 9H), 3.44 (d, J = 15.2 Hz, 3H), 3.28 (d, J = 15.2 Hz, 3H), 2.20 (m, 3H), 0.96 (d, J = 6.3 Hz, 9H), 0.92 (d, J = 6.6 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.1, 169.4, 58.3, 57.6, 52.4, 30.6, 19.7, 18.5; IR (Film) 1116, 1154, 1210, 1530, 1535, 1543, 1649, 1656, 1742, 2938, 2964, 3263 cm^{-1}; MS *m/z* calcd for $C_{24}H_{42}O_9N_4$: 530.2952, found 530.2959; $[\alpha]_D^{20}$ +9.1° (c = 0.0527 g/ml, MeOH).

N,N,N-Tris[2-((*S*)-1-hydroxy-3-methylbutyl)]nitrilotriacetamide (2.150). In a 500 mL, three-neck flask equipped with a condenser, N,N,N-tris[1-((*S*)-1-methoxycarbonyl-2-methylpropyl)-]nitrilotriacetamide (5.40 g, 10.2 mmol) was dissolved in methanol (50 mL) and THF (50 mL) under argon. $NaBH_4$ (3.0 g, 78.9 mmol) was added in small portions to the solution at room temperature. Another portion of $NaBH_4$ (3.0 g, 78.9 mmol) was added to the reaction mixture 2 h later ar room temperature. The reactiom mixture was stirred at room temperature for 3 h before being quenched with saturated aqueous ammonium chloride solution at 0 °C. A clear solution was obtained after HCl (2N, 30 mL) was added at 0 °C. The latter was then neutralized by saturated K_2CO_3 aqueous solution. The organic solvents were removed via rotary evaporator, and the aqueous residue was extracted with ethyl acetate (10 X 40 mL). The combined organic layers were washed with saturated K_2CO_3 aqueous solution (2 mL), water (3 X 10 mL), and then dried over Na_2SO_4. Removal of solvent gave a reasonably pure product (4.33 g, 96%). The product can be purified by flash chromatography

(silica gel; ethyl acetate : methanol = 10 : 1). : ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (d, 3H), 4.21 (br, 3H), 3.73 (m, 6H), 3.52 (dd, J = 10.1, 8.3 Hz, 3H), 3.39 (d, J = 5.9 Hz, 6H), 1.77 (m, 3H), 0.91 (d, J = 5, 1 Hz, 9H), 0.88 (d, J = 5.1 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.5, 62.9, 59.9, 57.3, 29.9, 20.1, 19.6; IR (Film) 1076, 1371, 1389, 1466, 1558, 1657, 2934, 2963, 3280, 3294, 3318 cm^{-1}; MS *m/z* calcd for $C_{21}H_{40}O_5N_4$-(M-H_2O): 428.2999, found 428.3003; $[\alpha]_D^{20}$ - 13.7° (c = 0.0648 g/ml, MeOH).

N,N,N-Tris[((*4S*)-isopropyl-2-oxazolin-2-yl)methyl]-amine (2.151). 1,2,4-Triazole (21.9 g, 317 mmol) was dissolved in acetonitrile (425 mL) in an 1 L flask furnished with a Drierite drying tube. Phosphorus oxychloride (9.7 mL, 15.96 g, 104 mmol) was added at 0 °C, followed by triethylamine (50 mL, 36.3 g, 359 mmol) dropwise. The reaction mixture was then stirred at 0 °C for 2 h. The mixture was siphonated through a cannula to a sealed sintered glass filter, which was placed in a neck of a 2 L flask, so that the clear filtrate could be added directly to the solution of compound N,N,N-tris[2-((*S*)-1-hydroxy-3-methyl-butyl)]nitrilotriacetamide. (4.07 g, 9.1 mmol) in triethylamine (900 mL) and acetonitrile (100 mL). After the addition was finished, the reaction mixture was stirred another 20 min before saturated $NaHCO_3$ aqueous solution (100 mL) was introduced to the reaction flask. The organic solvents were removed *via* a rotary evaperator, and the remaining mixture was extracted with CH_2Cl_2 (10 X 50 mL). The combined organic layers were washed with water (3 X 40 mL) and then dried over Na_2SO_4. Removal of solvent gave a reasonably pure product (3.04 g, 85%).

The product could be further purified using gel filtration method (Sephardex LH-20, ethyl acetate): ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.21 (m, 3H), 3.89 (m, 6H), 3.59 (s, 6H), 1.69 (m, 3H), 0.91 (d, J = 6.7 Hz, 9H), 0.83 (d, J = 6.8 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 72.0, 67.0, 50.3, 32.4, 18.7, 18.1; IR (Film) 983, 1145, 1194, 1386, 1468, 1672, 2873, 2963, 33.52 cm^{-1}; MS *m/z* calcd for $C_{21}H_{36}N_4O_3$: 392.2787, found 392.2785; $[\alpha]_D^{20}$ -73.7° (c = 0.1191 g/ml, CH_2Cl_2).

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