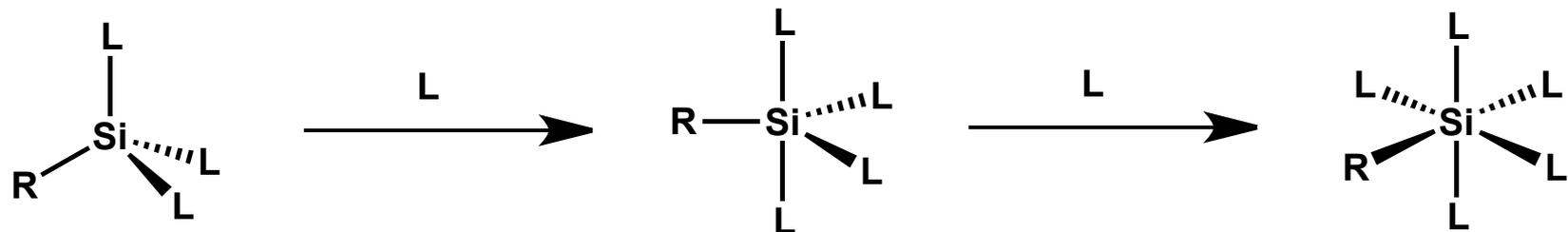


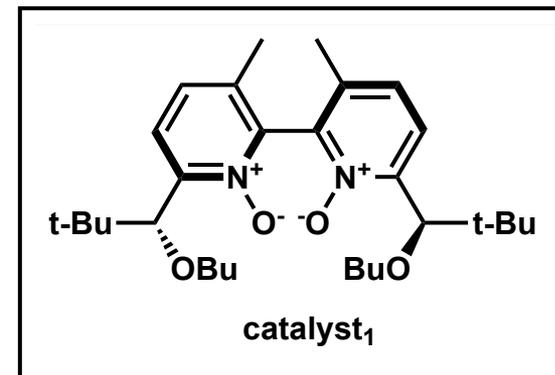
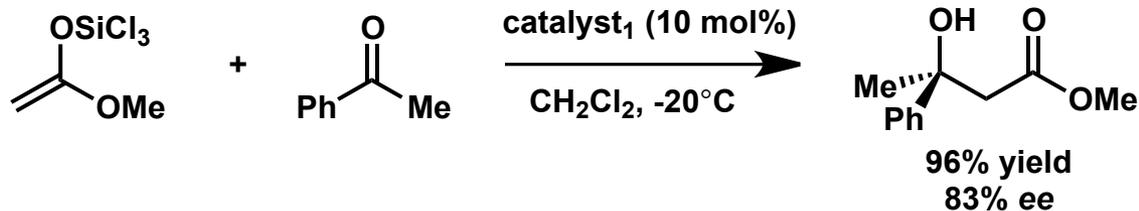
# Hypervalent Silicon in Organic Chemistry



Literature Seminar  
January 5, 2013  
Taisuke Itoh (B4)

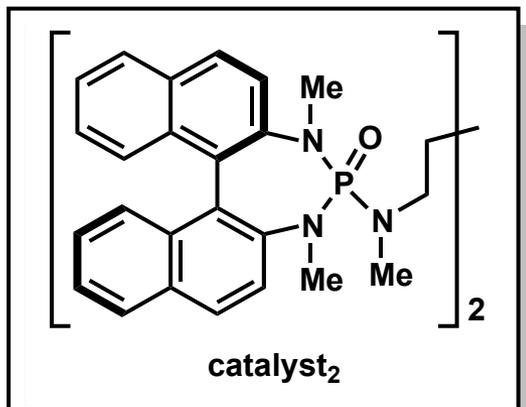
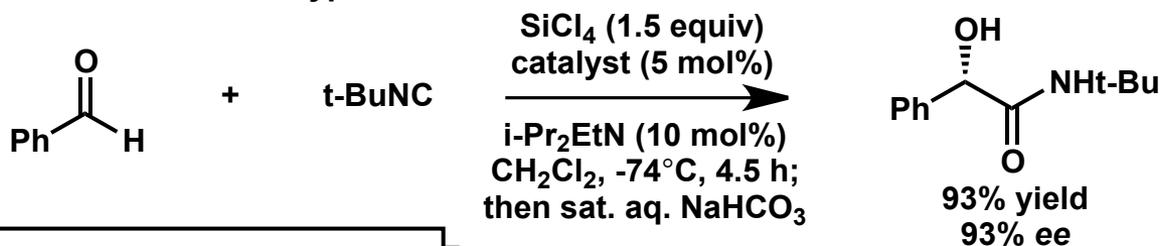
## Introduction

## Catalytic Enantioselective Aldol Reaction to Ketones



Denmark, S. E.; Fan, Y. *J. Am. Chem. Soc.* **2002**, *124*, 4233.

## Enantioselective Passerini-Type Reaction



The first catalytic asymmetric  $\alpha$ -addition of isocyanides.

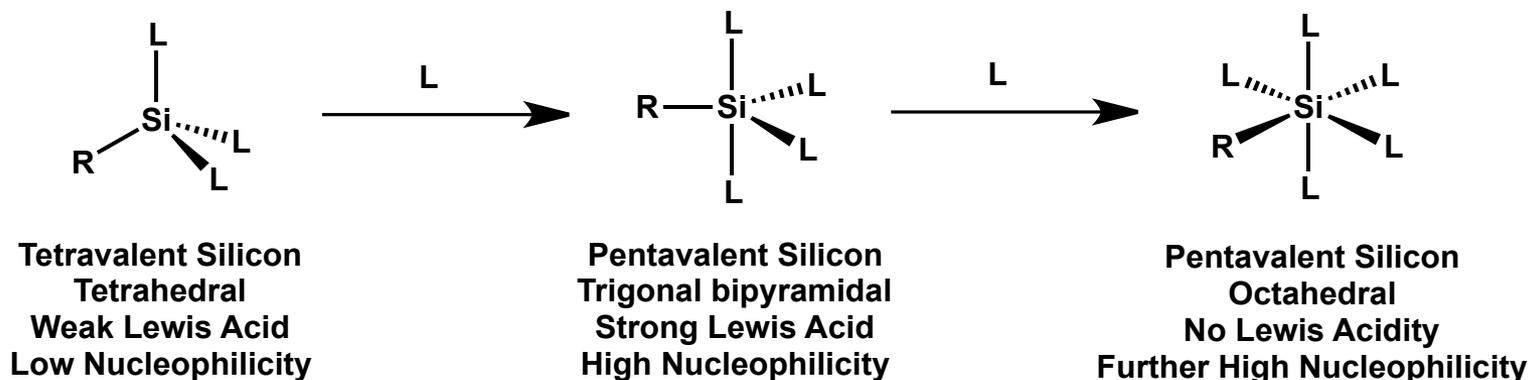
Denmark, S. E.; Fan, Y. *J. Am. Chem. Soc.* **2003**, *125*, 7825.  
 Denmark, S. E.; Fan, Y. *J. Org. Chem.* **2005**, *70*, 9667.

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- **Structure and Property of Hypervalent Silicon**
- Hydrosilylation as a Hypervalent Silicon Example
- Lewis Base Catalyzed Allylsilylation
- Denmark's Contribution to Lewis Base Catalyzed Aldol Reaction and Allylsilylation
- Other Examples of Hypervalent Silicon  
Nucleophilicity
- Hypervalent Silicon as a Chiral Lewis Acid

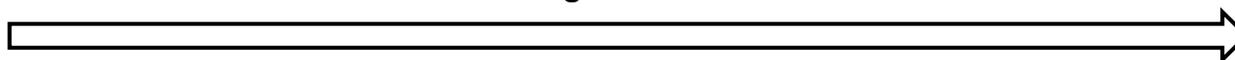
## Structure and Property of Hypervalent Silicon

### Structure and Property of Hypervalent Silicon



L = negatively charged or neutral silaphilic ligands  
such as F, Cl, OR and OAr or Lewis bases  
R = H or C

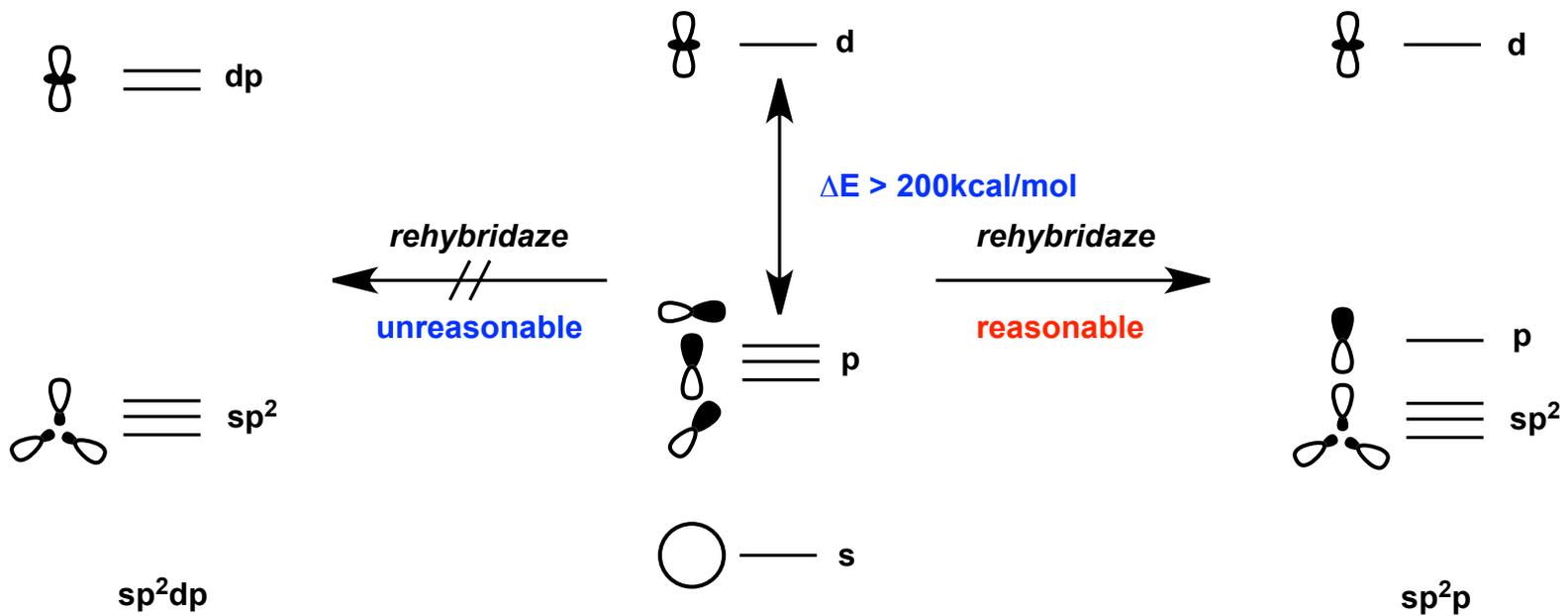
$\delta^+$  at silicon  
 $\delta^-$  at ligands L and R



Lewis acidity  
nucleophilicity of R

## Structure and Property of Hypervalent Silicon

### The Molecular Orbital of Pentavalent Silicon (Trigonal bipyramidal)



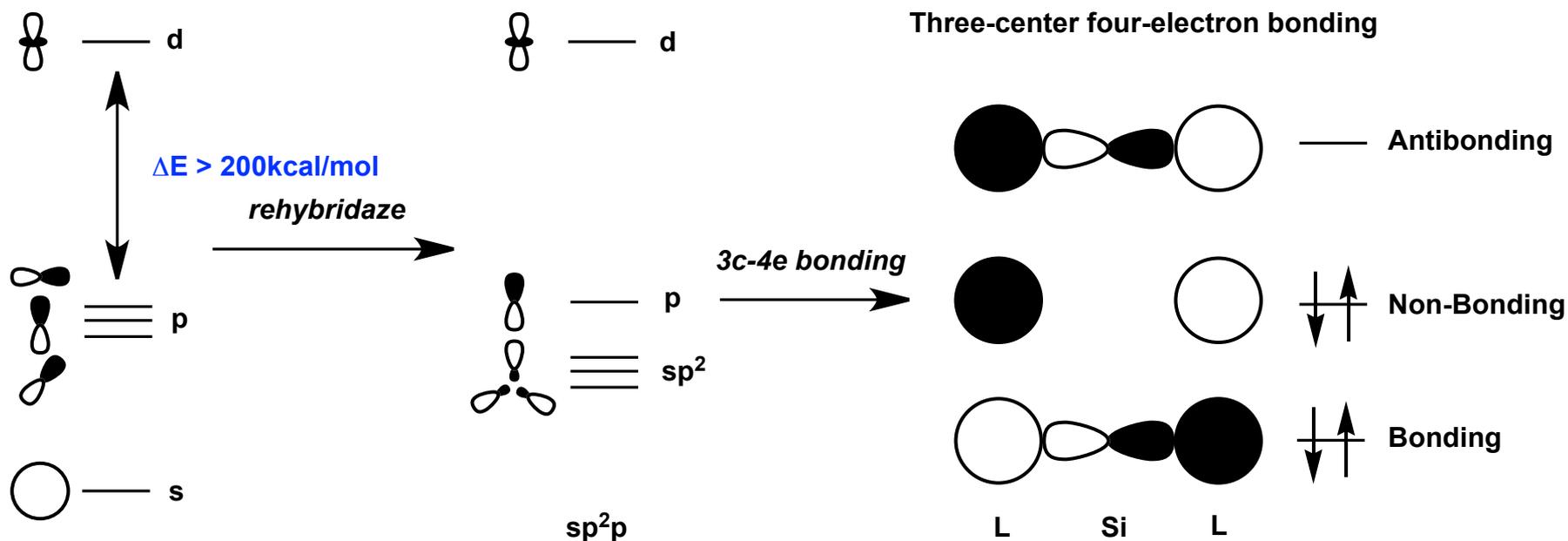
Older models for explaining hypervalency invoked d orbitals. However, quantum chemical calculations suggest that d-orbital participation is negligible due to the large energy difference between the relevant p and d orbitals.



*How does  $sp^2p$  molecular orbital engage in hypervalent bonding?*

## Structure and Property of Hypervalent Silicon

## The Molecular Orbital of Pentavalent Silicon (Trigonal bipyramidal)

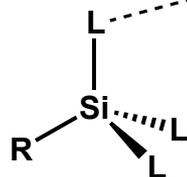


- The filled non-bonding molecular orbital has all of the electron density on the ligand atoms.
- Thus, highly electronegative atoms stabilize 3c-4e bonding and hypervalent molecules and electron density of axial position is higher than that of equatorial position.
- This is why most hypervalent molecules have F, Cl or OR in ligand atoms.
- Consequently, hypervalent molecules get more Lewis acidic.

## Structure and Property of Hypervalent Silicon

How do we have access to hypervalent silicon?

### Electronegative Ligands

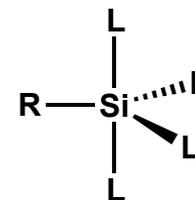


Tetravalent silicon  
Rather strong Lewis acid  
because of electronegative ligands.

Bent's rule : Atomic p character tends to concentrate in orbitals that are directed toward electronegative groups.

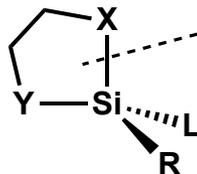


L : Electronegative ligand



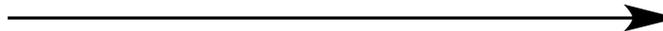
Pentavalent silicon  
Stabilized by electronegative ligands  
Strong Lewis acid

### Strain Release

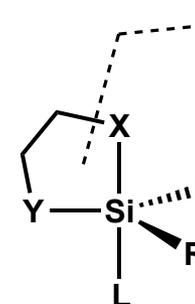


Tetravalent silicon  
Strain release Lewis acidity

Bond angle  $\sim 90^\circ$  : Longer Si-X and Si-Y bond than C-X and C-Y bond.



L



Pentavalent silicon  
Strain released  
Strong Lewis acid

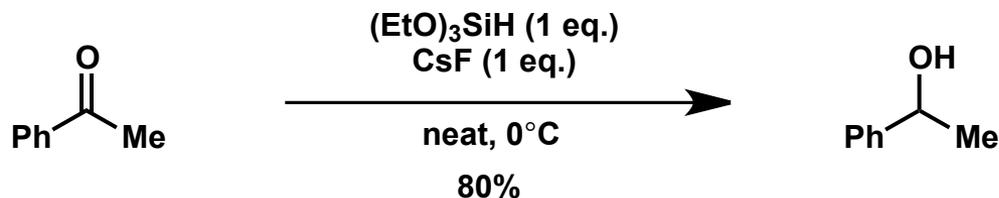
Bond angle : eq-ax  $90^\circ$

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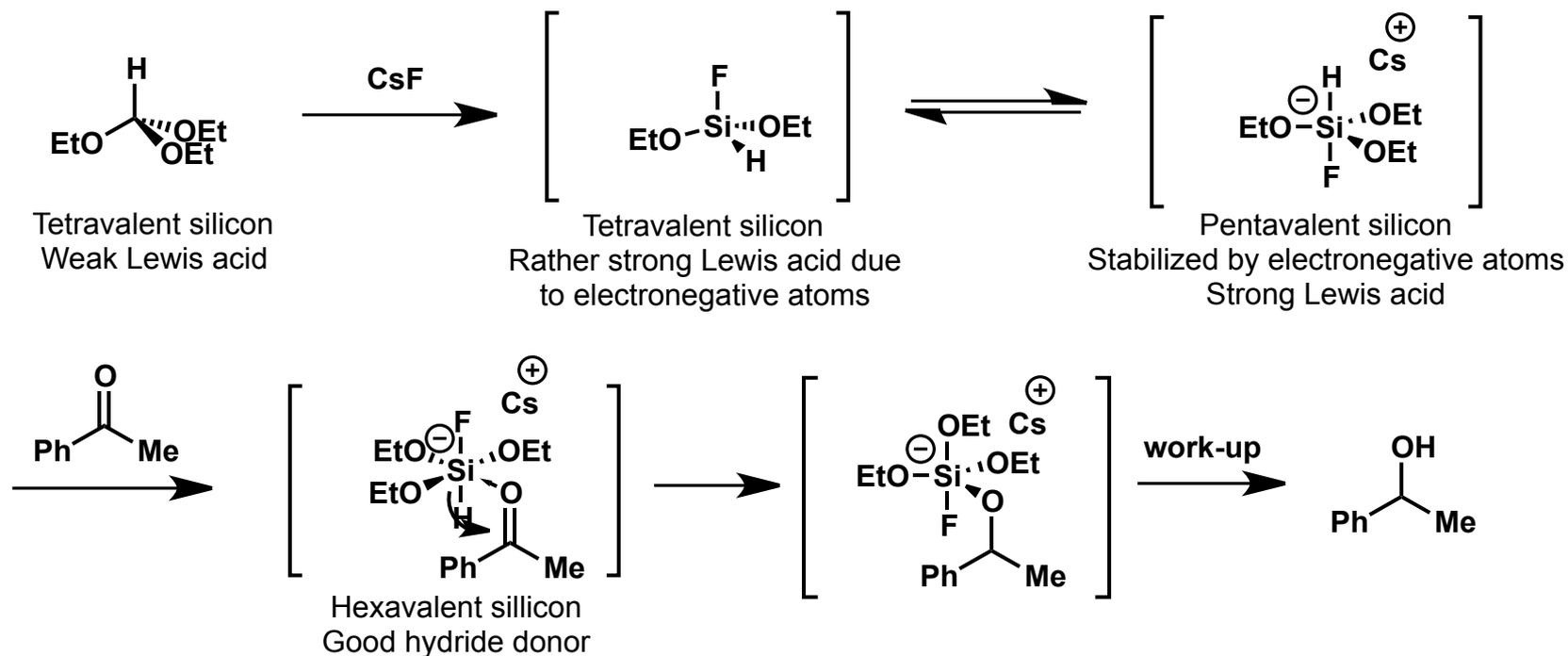
## Hydrosilylation as a Hypervalent Silicon Example

## First Lewis Base Catalyzed Hydrosilylation



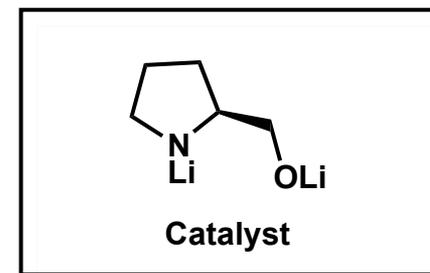
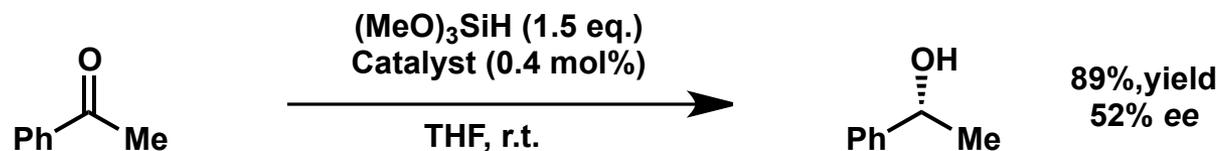
Boyer, J.; Corriu, R. J. P.; Perz, C. *Tetrahedron*, **1981**, 37, 2165.

## Probable reaction mechanism



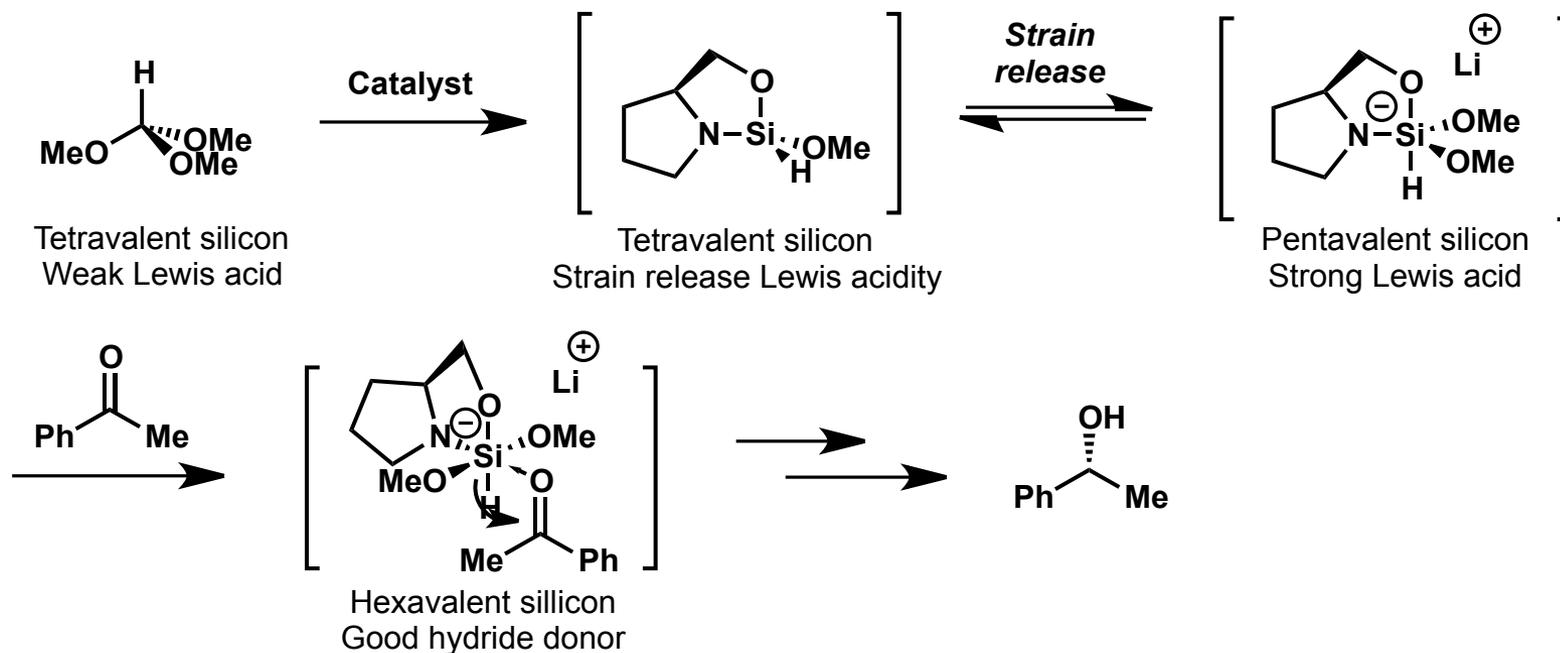
## Hydrosilylation as a Hypervalent Silicon Example

## Chiral Lewis Base Catalyzed Assymmetric Hydrosilylation



Kohra, S.; Hayashida, H.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett*, **1988**, 29, 89.

## Probable reaction mechanism



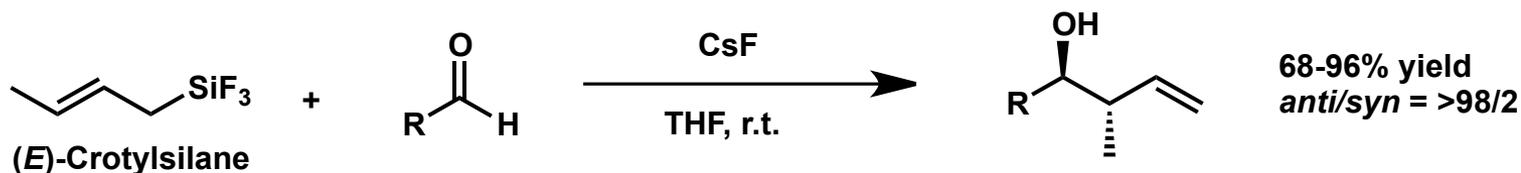
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- Hypervalent Silicon as a Chiral Lewis Acid



## Lewis Base Mediated Diastereoselective Allylation

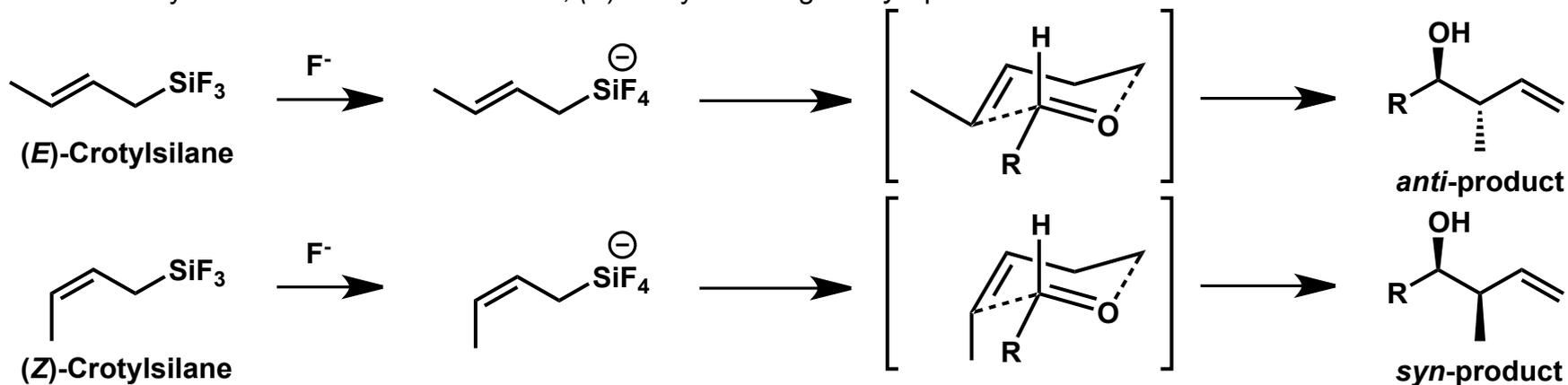
## Lewis Base Mediated Addition of Crotylsilanes to Aldehydes



Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, 28, 4081.

Kira, M.; Hino, T.; Sakurai, H. *Tetrahedron Lett.* **1989**, 30, 1099.

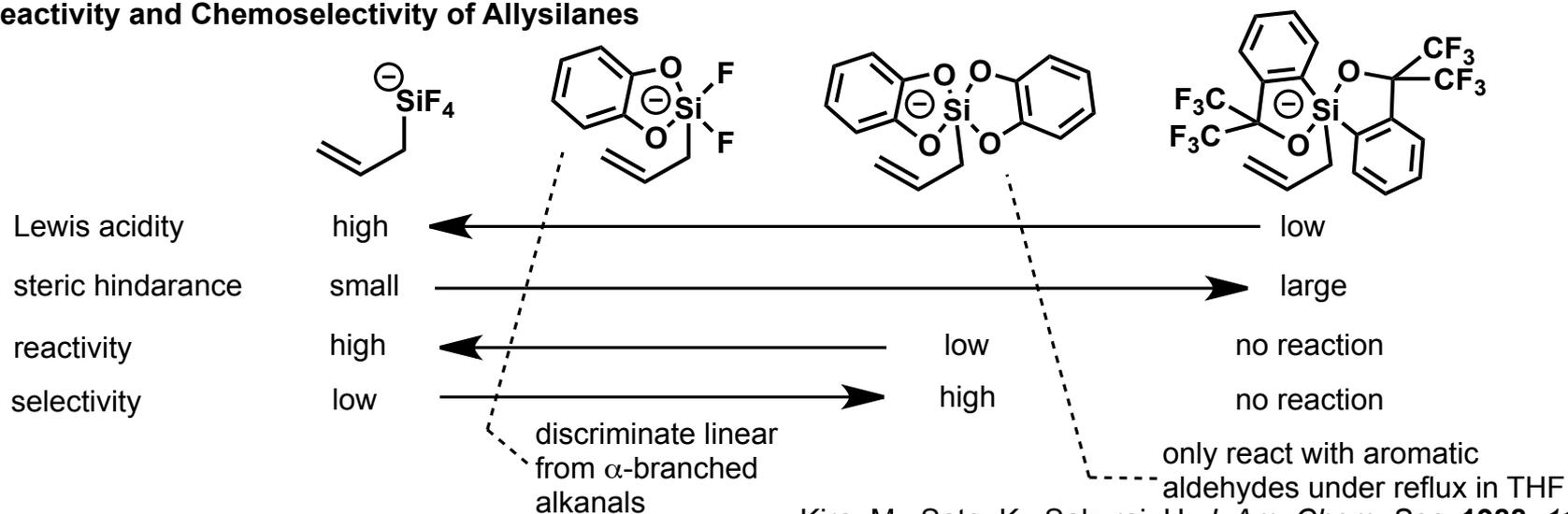
Lewis acid catalyzed addition of crotylsilanes to aldehyde generally gives *syn*-products via linear transition state regardless of starting *E/Z* isomers. In contrast, Lewis base mediated addition of (*E*)-Crotylsilanes gave *anti*-products via 6-membered cyclic transition state. Of course, (*Z*)-Crotylsilanes gave *syn*-products.



This result strongly suggests that this reaction occurs via 6-membered transition state.

## Lewis Base Catalyzed Allylation via Hypervalent Silicon Intermediates

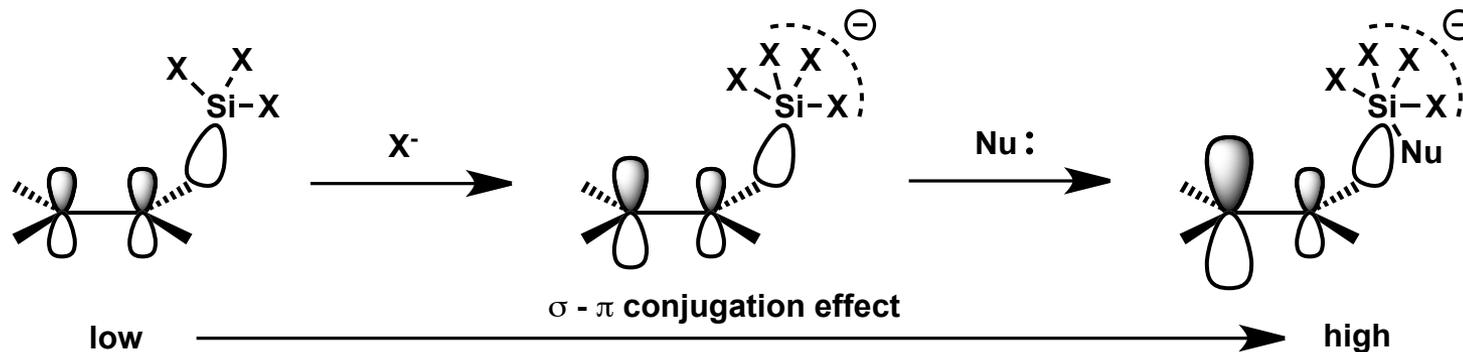
### Reactivity and Chemoselectivity of Allylsilanes



Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599.

Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1990**, *112*, 257.

### Does $\gamma$ -position of hypervalent allylic silanes really possess high reactivity?

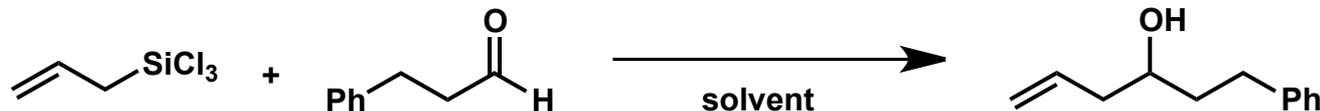


$^{13}\text{C}$ -NMR chemical shift of the  $\gamma$ -carbon showed a higher field shift as silicon's electron-donating ability increased.

Grishin, Y. K.; Sergeyev, N. M.; Ustynyuk, Y. A. *Org. Magn. Reson.* **1972**, *4*, 377.

## Neutral Lewis Base Mediated Allylsilylation

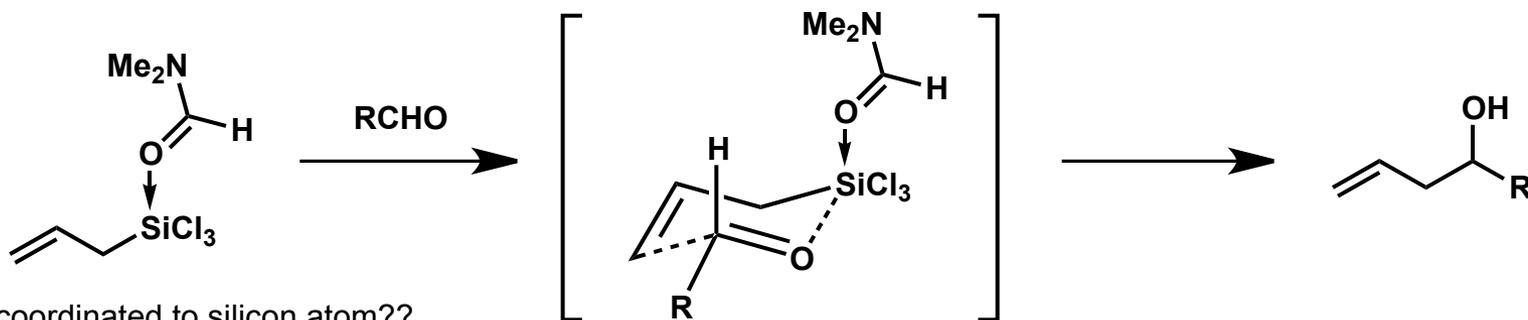
## Dramatic Solvent Effect on Allylsilylation of Aldehydes



solvent	temp. (°C)	time (h)	yield (%)
CH <sub>2</sub> Cl <sub>2</sub>	r.t.	24	trace
CH <sub>3</sub> CN	r.t.	24	trace
benzene	r.t.	24	trace
Et <sub>2</sub> O	r.t.	24	trace
THF	r.t.	24	trace
<b>DMF</b>	<b>0</b>	<b>2</b>	<b>90</b>
HMPA	0	3	28
CH <sub>2</sub> Cl <sub>2</sub> -HMPA (2:1)	0	18	97

The allylation of aldehydes using allyltrichlorosilanes proceeded smoothly in DMF or HMPA as a solvent without any additives!

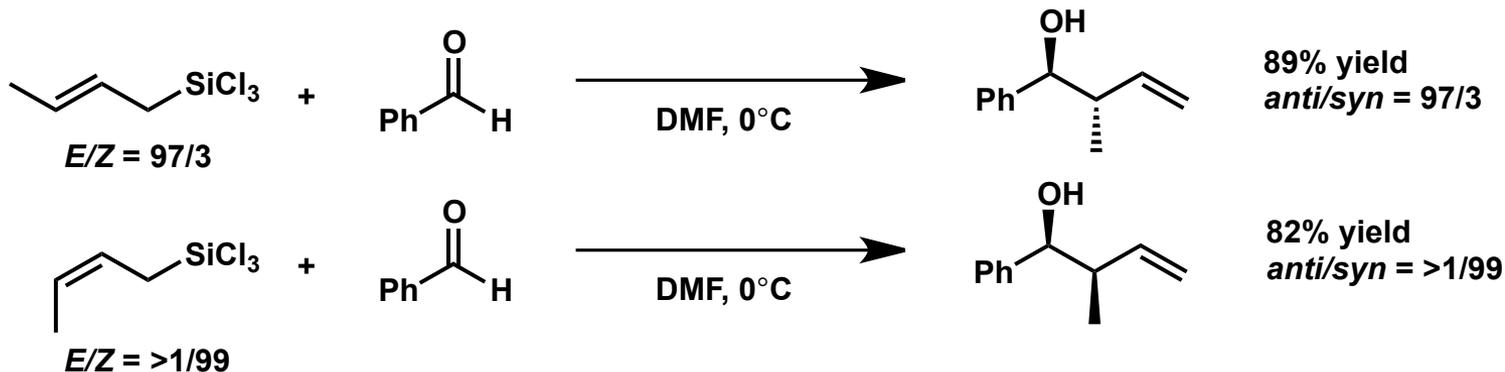
Does this allylation reaction in DMF proceed via the neutral hypervalent silicon intermediate as shown below?



DMF coordinated to silicon atom??

## Neutral Lewis Base Catalyzed Allylsilylation

Diastereoselective Allylation of Aldehydes using Crotyltrichlorosilanes in DMF

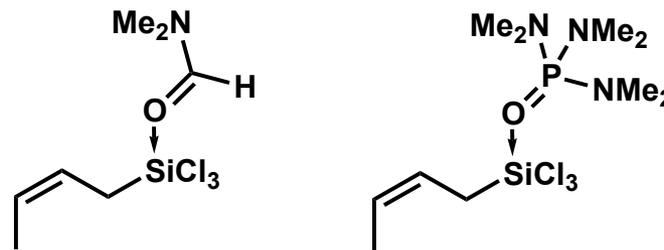


These high diastereoselectivities can be explained by 6-membered cyclic transition state.

<sup>29</sup>Si-NMR Chemical Shifts of (Z)-Crotyltrichlorosilane in Several Solvents

solvent	chemical shift (ppm)
CDCl <sub>3</sub>	+8.0
CD <sub>3</sub> CN	+8.6
C <sub>6</sub> D <sub>6</sub>	+7.9
THF-d <sub>8</sub>	+8.5
<b>DMF-d<sub>7</sub></b>	<b>-170</b>
<b>HMPA</b>	<b>-22</b>

This <sup>29</sup>Si-NMR spectra of (Z)-crotyltrichlorosilane indicated that DMF or HMPA coordinated to the silicon atom of (Z)-crotyltrichlorosilane to form the corresponding penta- or hexavalent silicate.



Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, 34, 3453.  
 Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, 59, 6620.

## Chiral Lewis Base Mediated Asymmetric Allylation of Aldehydes

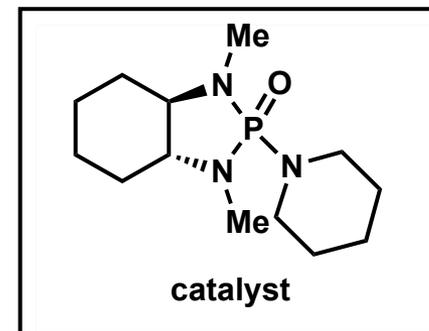
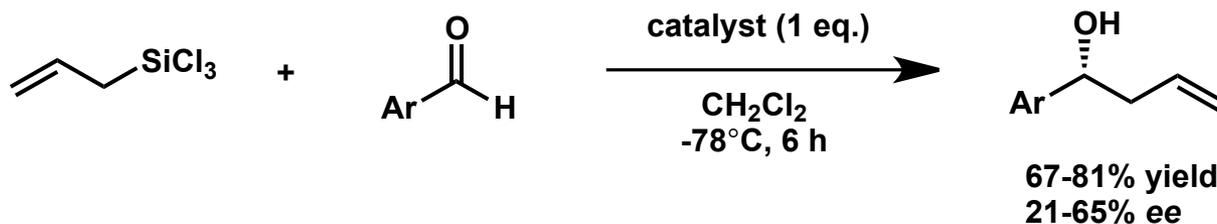
Allylation of Benzaldehyde using Allyltrichlorosilane and 1 equiv of Additives



additive	solvent	t <sub>1/2</sub> (min)	conversion (%)	isolated yield (%)
DMF	C <sub>6</sub> D <sub>6</sub>	-	83 (70 h)	-
HMPA	C <sub>6</sub> D <sub>6</sub>	18	-	77
HMPA	CDCl <sub>3</sub>	-	63 (4 min)	85
HMPA	CD <sub>3</sub> CN	-	63 (4 min)	86

Kobayashi has shown that DMF is an efficient promoter as solvent. However, Denmark found that 1 equiv of DMF in benzene is relatively less effective than that of HMPA, which promoted complete conversion within minutes.

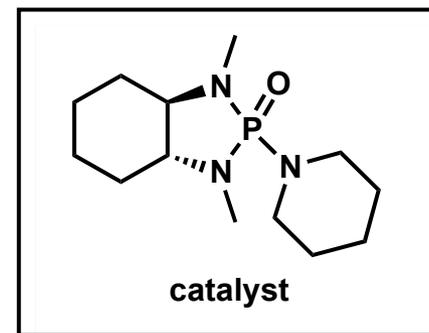
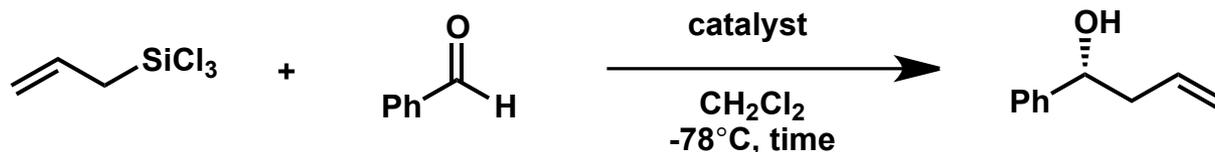
Chiral Phosphoramidate Mediated Asymmetric Allylation of Aromatic Aldehydes using Allyltrichlorosilanes



Only aromatic aldehyde underwent allylation in good yields, but electron-donating and electron-withdrawing substituents dramatically reduced enantioselectivity.

## Chiral Lewis Base Catalyzed Asymmetric Allylation of Aldehydes

Denmark also tried catalytic amount of chiral phosphoramidate

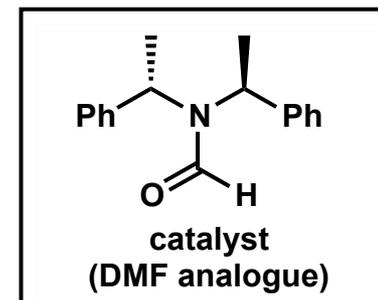
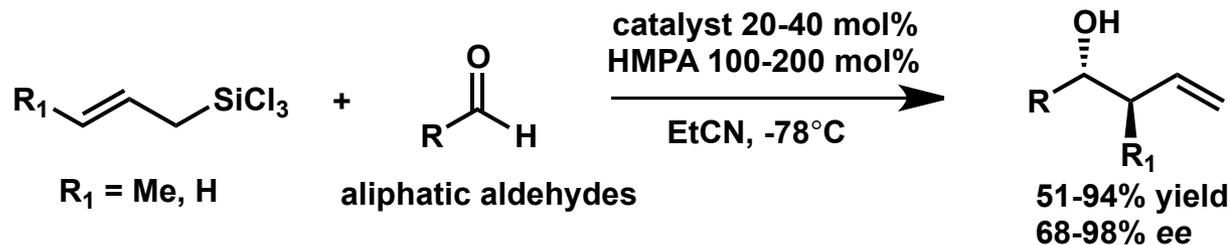


catalyst (equiv)	time (h)	yield (%)	ee (%)
<b>1.0</b>	6	<b>81</b>	<b>60</b>
0.5	24	78	57
<b>0.25</b>	24	<b>74</b>	<b>59</b>
0.1	24	40	53

With as little as 25 mol% of catalyst, the yield is only slightly reduced and the enantioselectivity essentially the same.

Denmark, S. E.; Coe, D. A.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161.

## Chiral Formamide Catalyzed Asymmetric Allylation of Aliphatic Aldehyde

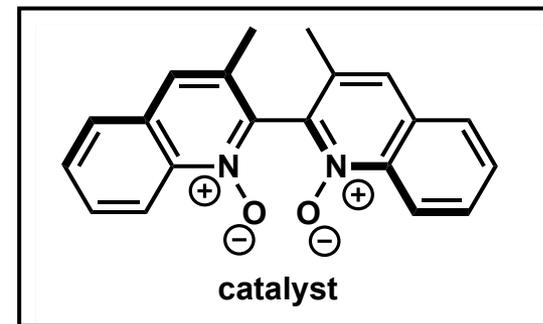
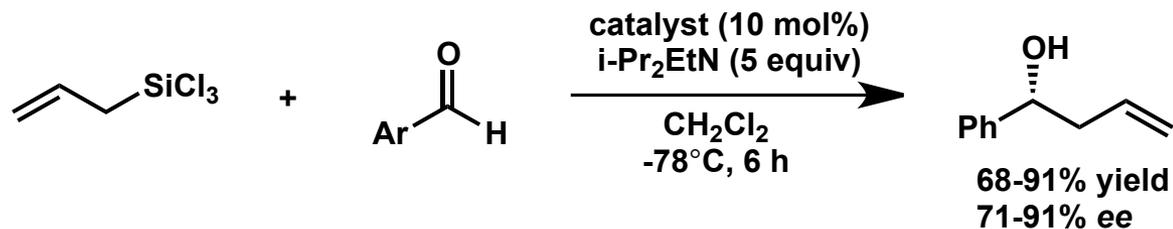


HMPA can promote a diassociation of the chiral formamide from silicon atom in the product by ligand exchange to regenerate the chiral formamide. Only aliphatic aldehydes gave good to high enantioselectivity. Aromatic aldehyde also gave good yield but low enantioselectivity was observed.

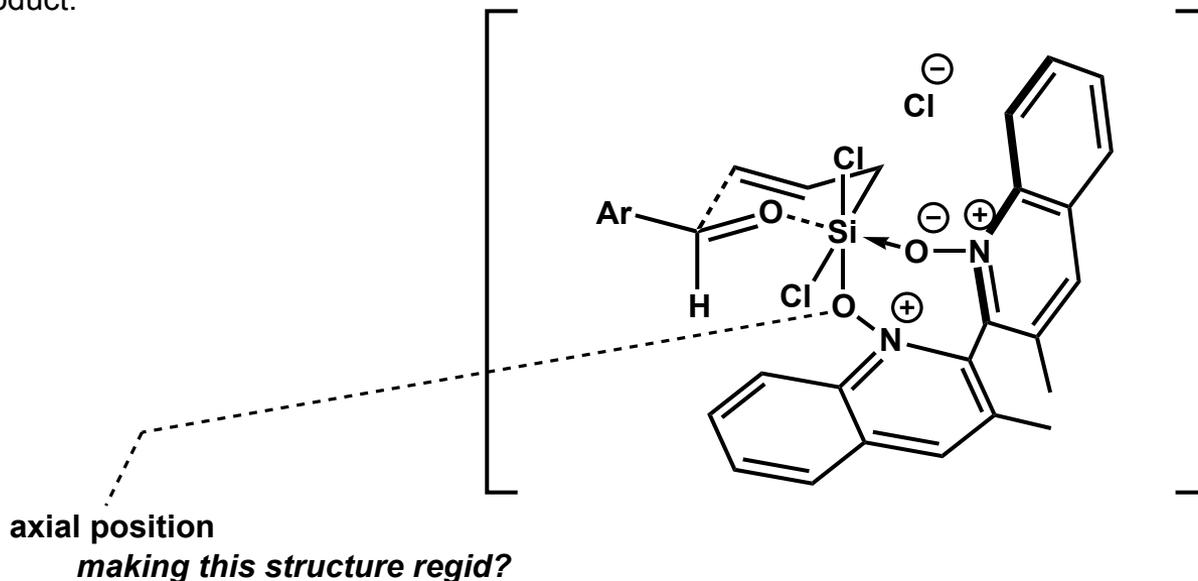
Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron Lett.* **1998**, *39*, 2767.

Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron Lett.* **1999**, *55*, 977.

## Chiral Bidentate Lewis Base Catalyzed Asymmetric Allylation of Aldehydes

Chiral *N*-Dioxide Catalyzed Asymmetric Allylation of Aromatic Aldehyde

Bidentate Lewis base enhanced the enantioselectivity. This is probably because the allylation mediated by the bidentate *N*-dioxide catalyst proceeds via rigid 6-membered cyclic chairlike transition state as shown below, where one of a pair of *N*-oxide moieties occupies an axial position. DIPEA can promote a dissociation of the chiral catalyst from silicon atom in the product.

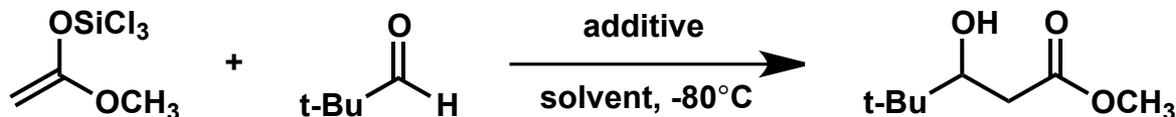


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Nucleophilicity
- Hypervalent Silicon as a Chiral Lewis Acid

## Lewis Base Catalyzed Aldol Reaction via Hypervalent Silicon Intermediates

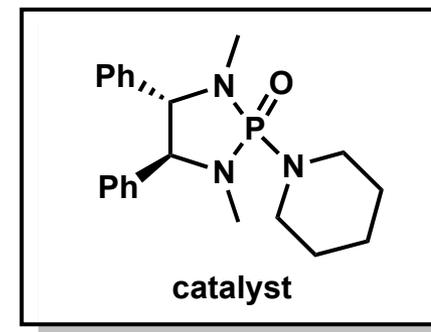
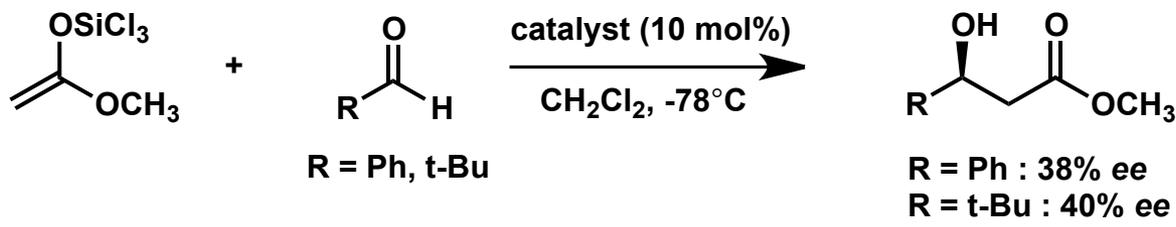
Denmark thought if Lewis base catalyzed allylation strategies could apply to aldol reaction.



solvent	additive	time (h)	conversion (%)
toluene-d <sub>8</sub>	none	120	18
CD <sub>2</sub> Cl <sub>2</sub>	none	120	50
THF-d <sub>8</sub>	none	120	69
CD <sub>2</sub> Cl <sub>2</sub>	<b>HMPA 0.1 eq.</b>	<b>&lt;3</b>	<b>100</b>

Surprisingly, **trichlorosilyl ketene acetal reacted spontaneously** with a number of aldehydes at -80°C. Only pivalaldehyde reacted slowly enough to be followed spectroscopically. On pivalaldehyde, **the acceleration was observed with a catalytic amount of HMPA.**

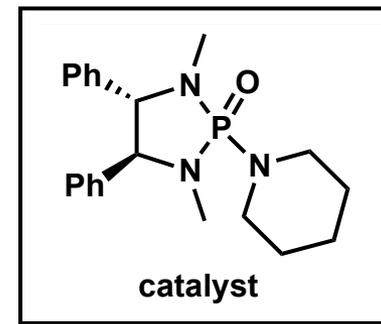
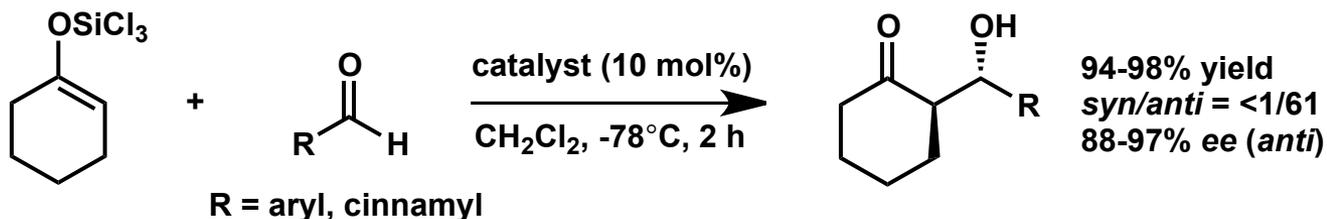
Denmark also tried chiral phosphoramidate.



Poor enantioselectivity was observed probably because of **the intervention of the uncatalyzed pathway.**

## Lewis Base Catalyzed Asymmetric Aldol Reaction

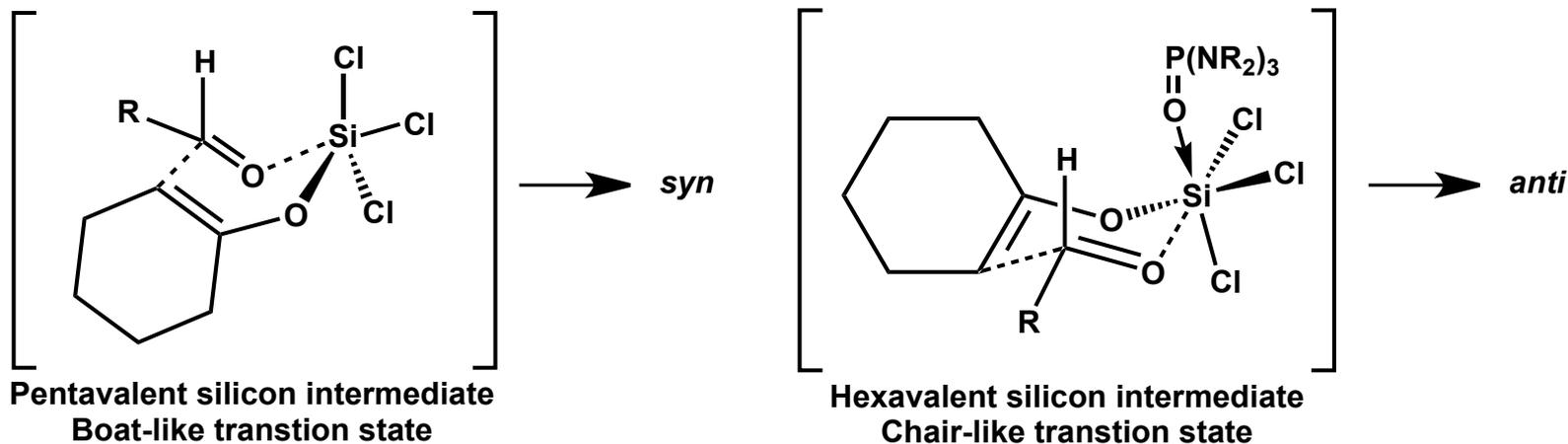
Chiral Phosphoramidate Catalyzed Asymmetric Aldol Reaction of Trichlorosilyl Ketone Enolates



The corresponding uncatalyzed reaction at  $0^\circ\text{C}$  gave high *syn* selectivity ( $\text{syn/anti} = >5.7/1$ ).

Trichlorosilyl ketone enolates were also highly reactive but much less reactive than trichlorosilyl ketene enolates. Thus, chiral phosphoramidate catalyzed aldol reaction proceeded with high selectivity. Surprisingly, **uncatalyzed aldol reaction of *E*-enolate gave *syn* adduct** while **Lewis base catalyzed reaction gave *anti* adduct**.

This is because **pentavalent silicate** transition structures were shown computationally to **prefer boat-like arrangements** while **hexavalent silicate** to prefer **chair-like arrangements**.

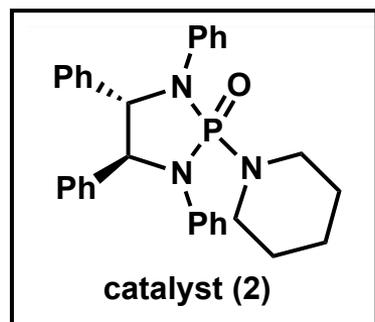
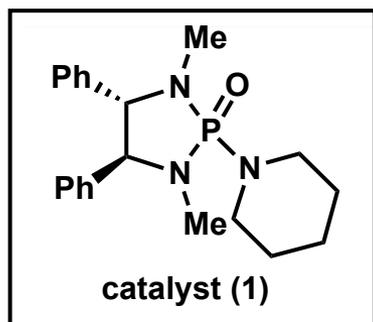
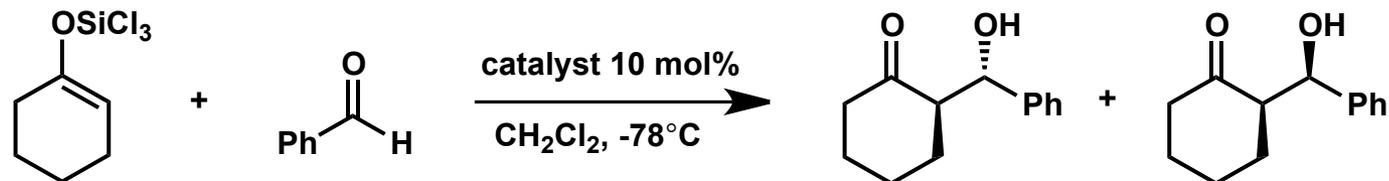


Denmark, S. E.; Wong, K.-T.; Stavenger, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 2333.

Denmark, S. E.; Stavenger, R. A.; Wong, K.-T. *J. Org. Chem.* **1998**, *63*, 918.

## Mechanistic Duality in the Lewis Base Catalyzed Aldol Reaction

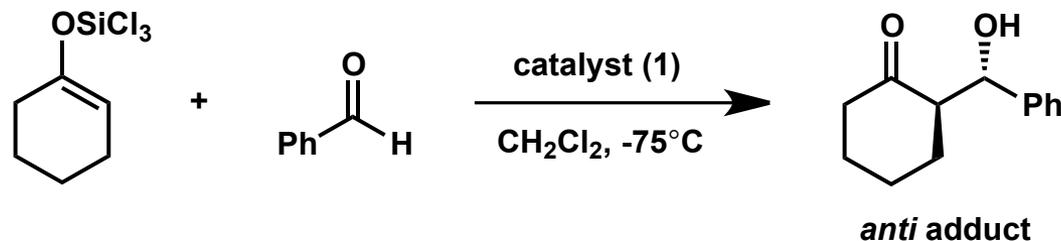
## Dramatic Switch in Diastereoselectivity with Phosphoramidate Structures



catalyst	yield (%)	<i>anti/syn</i>	ee
(1)	95	<b>60/1</b>	92 ( <i>anti</i> )
(2)	94	<b>1/97</b>	51 ( <i>syn</i> )

Lewis base catalyzed aldol reaction proceeds via different transition states due to phosphoramidate structures??

## Denmark's Observation on the Influence of the Catalyst Concentration on Selectivity



catalyst (1)	<i>anti/syn</i>
10 mol%	>50/1
2 mol%	28/1
0.5 mol%	5/1

**The *syn/anti* selectivity dramatically decreased with decreased loading of catalyst (1).**

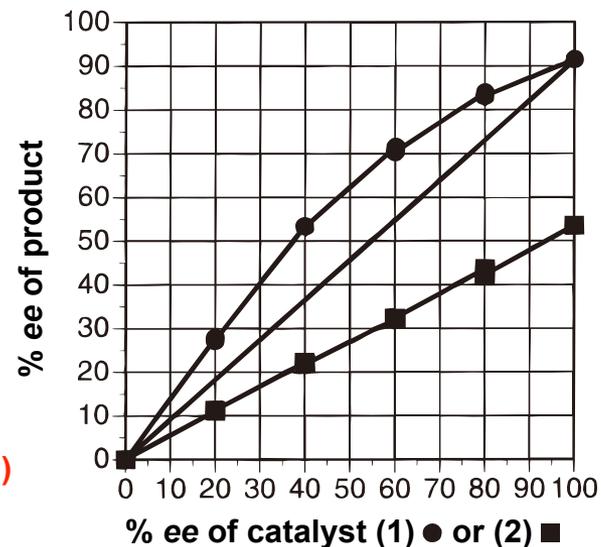
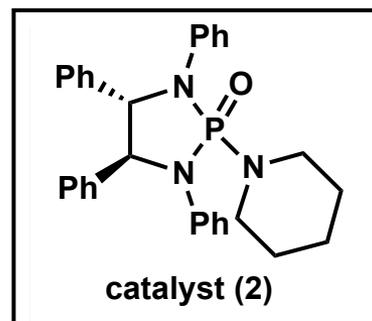
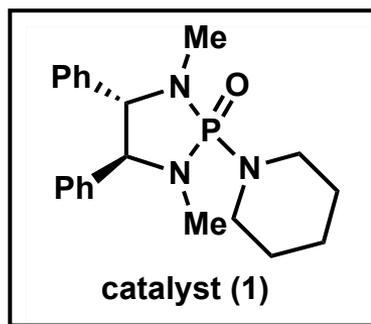
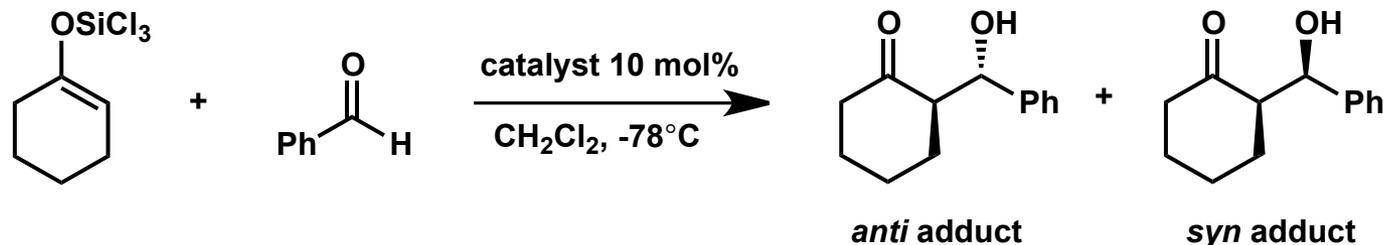
Lewis base catalyzed aldol reaction proceeds via different competitive transition states due to catalyst concentration??

Denmark, S. E.; Su, X.; Nishigaichi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12990.

Denmark, S. E.; Stavenger, R. A. *Acc. Chem. Res.* **2000**, *33*, 432.

## Mechanistic Duality in the Lewis Base Catalyzed Aldol Reaction

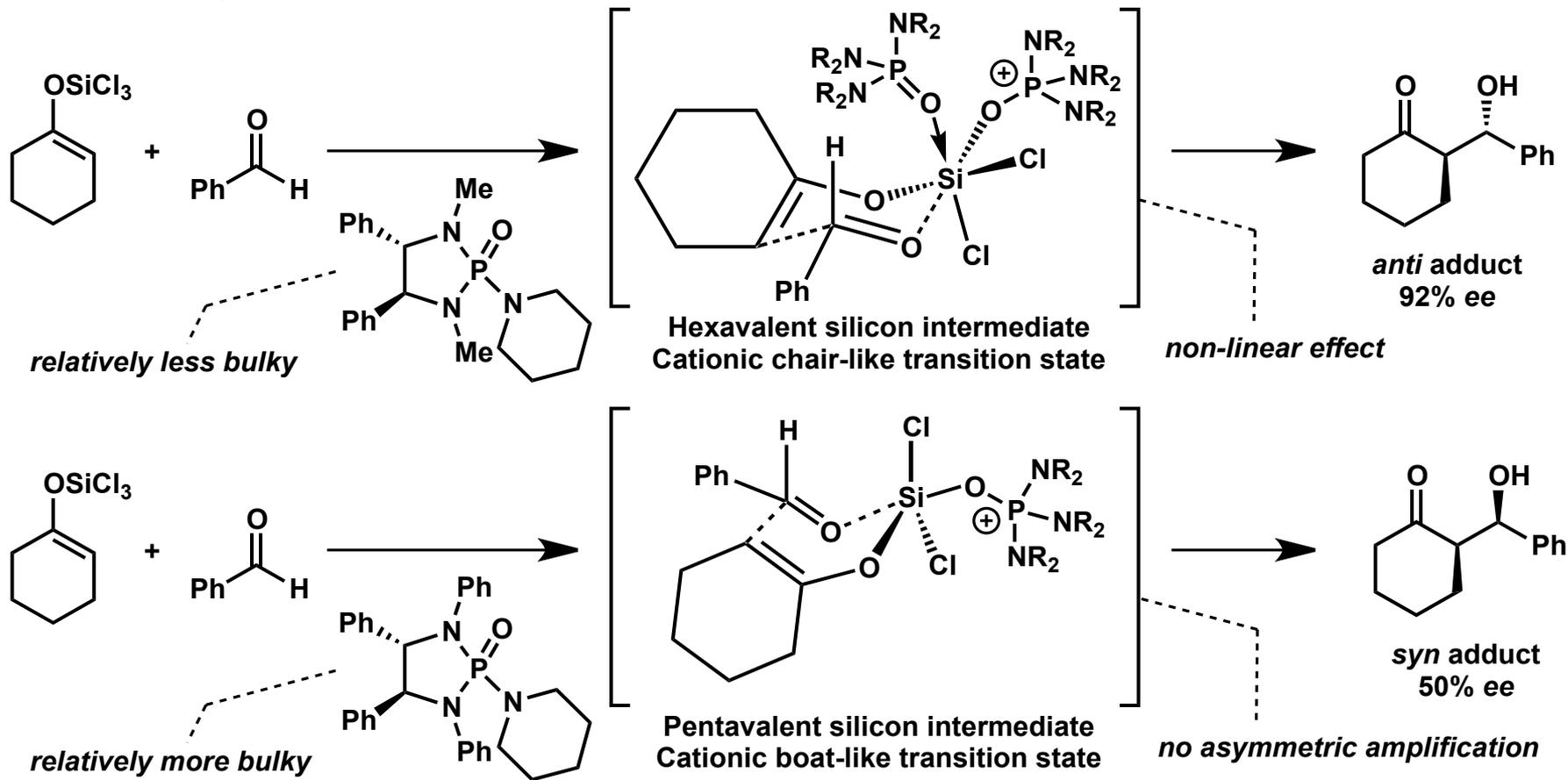
Denmark's Observation on Non-linear Effect of Chiral Phosphoramidate Catalyzed Aldol Reaction



**A positive non-linear effect was only measured using catalyst (1)** and no asymmetric amplification was seen using catalyst (2). Those results strongly suggest that relatively less bulky phosphoramidate catalyzed aldol reaction proceeds via a transition state including more than one phosphoramidate molecule.

## Mechanistic Duality in the Lewis Base Catalyzed Aldol Reaction

Proposed Pathway to the Two Diastereomers



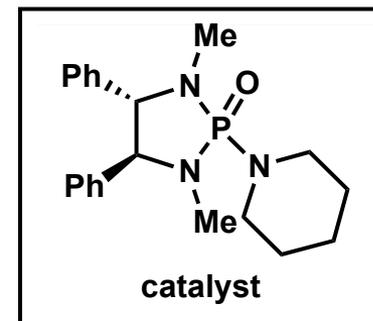
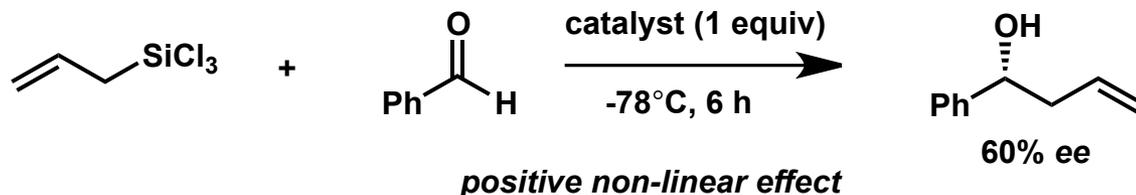
This mechanism explains the different diastereoselectivity by phosphoramidate structures and concentration, non-linear effect by relatively less bulky phosphoramidate, and low enantioselectivity of *syn* adduct.

Denmark, S. E.; Su, X.; Nishigaichi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12990.

Denmark, S. E.; Stavenger, R. A. *Acc. Chem. Res.* **2000**, *33*, 432.

## Mechanistic Duality in the Lewis Base Catalyzed Allylsilylation

Denmark thought the same mechanistic duality in allylsilylation as aldol reaction.



A positive non-linear effect was measured on allylation reaction, too. This result suggests the presence of two molecules of catalyst in the stereochemically determining transition structure.

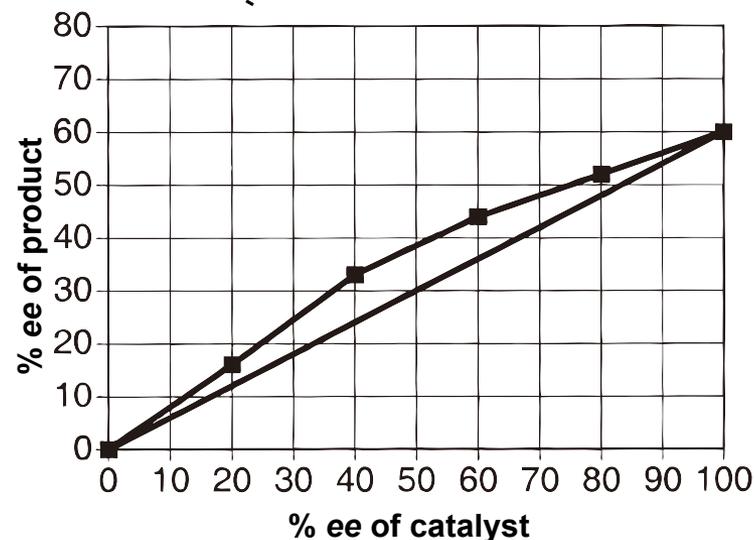
### The rate expression

$$v = k[\text{allylsilane}][\text{benzaldehyde}]$$

A plot of  $k$  versus  $[\text{catalyst}]^2$  give a straight line.

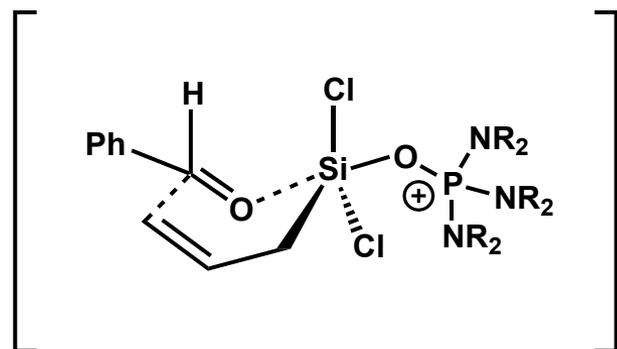
Denmark also determined the overall rate expression. According to that, the reaction is overall second order, and first order in allylsilane and benzaldehyde.

A  $\ln(k)$  versus the catalyst concentration ( $\ln[\text{catalyst}]$ ) gave a straight line with a slope of 1.77. This result also suggests the presence of more than one molecules of catalyst in the stereochemically determining transition structure.



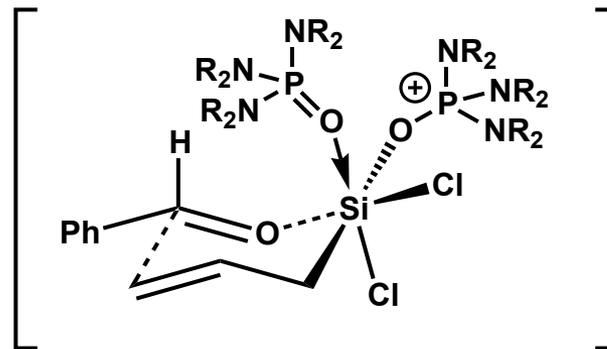
## Mechanistic Duality in the Lewis Base Catalyzed Allylsilylation

Proposed Two Transition Structures in the Lewis Base Catalyzed Allylsilylation



Pentavalent silicon intermediate  
Cationic boat-like transition state

*less selective pathway*

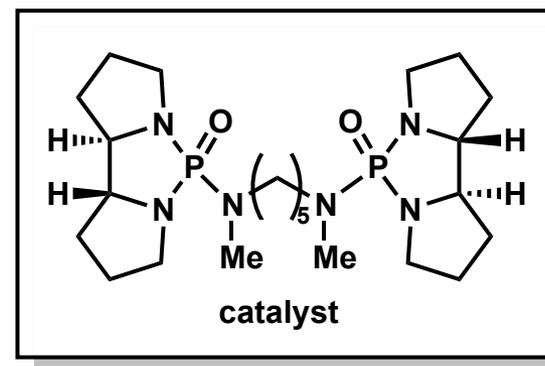
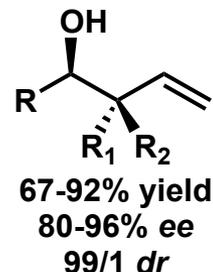
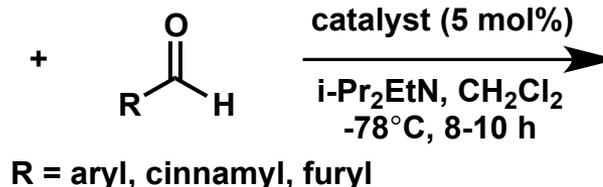
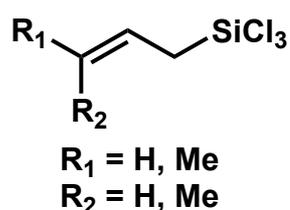


Hexavalent silicon intermediate  
Cationic chair-like transition state

*high selective pathway*

*A competing less selective pathway would reduce the enantioselectivity of this phosphoramidate catalyzed reaction??*

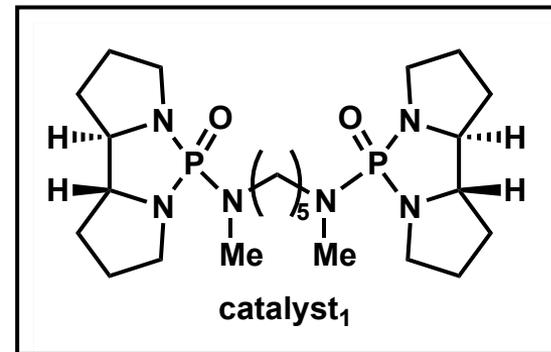
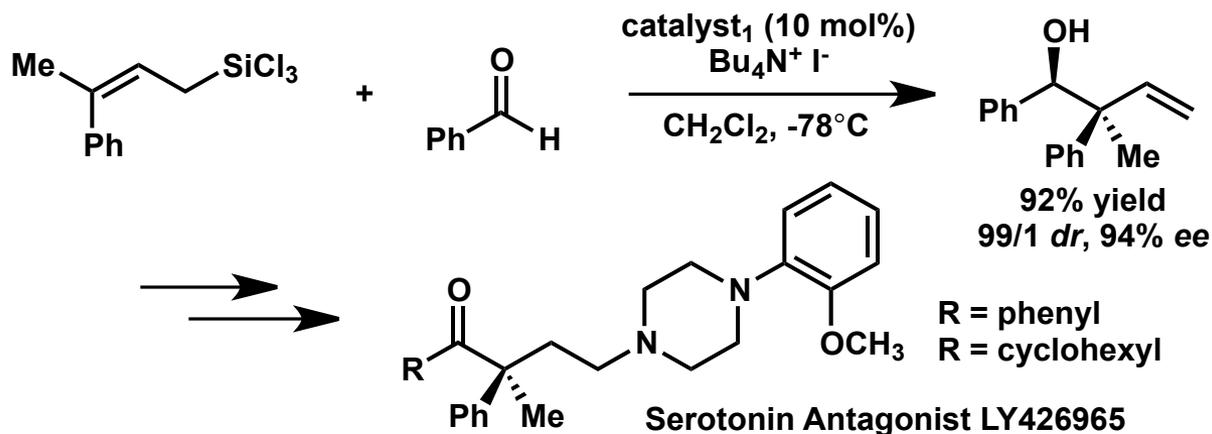
Thus, Denmark tried a bidentate chiral phosphoramidate catalyst.



*Denmark's well thought-out bidentate chiral phosphoramidate strategy successfully gave high enantioselectivity!*

## Synthetically Useful Application of Denmark's Bisphosphoramidate Catalyst

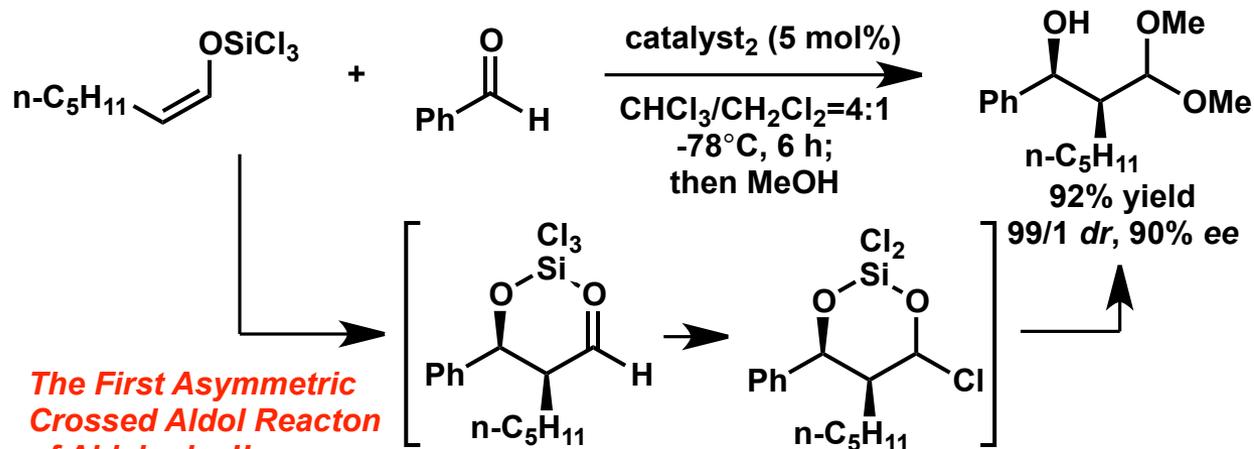
## Asymmetric Construction of Quaternary Centers



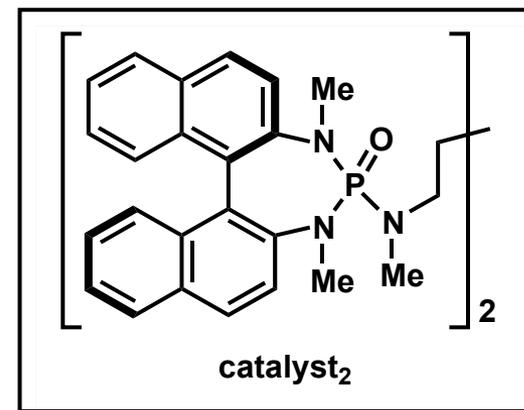
*The first application of catalytic, enantioselective allylation to generate quaternary carbon centers!!*

Denmark, S. E.; Fu, J. *Org. Lett.* **2002**, 4, 1951.

## Asymmetric Crossed Aldol Reaction of Aldehydes



*The First Asymmetric Crossed Aldol Reaction of Aldehydes!!*



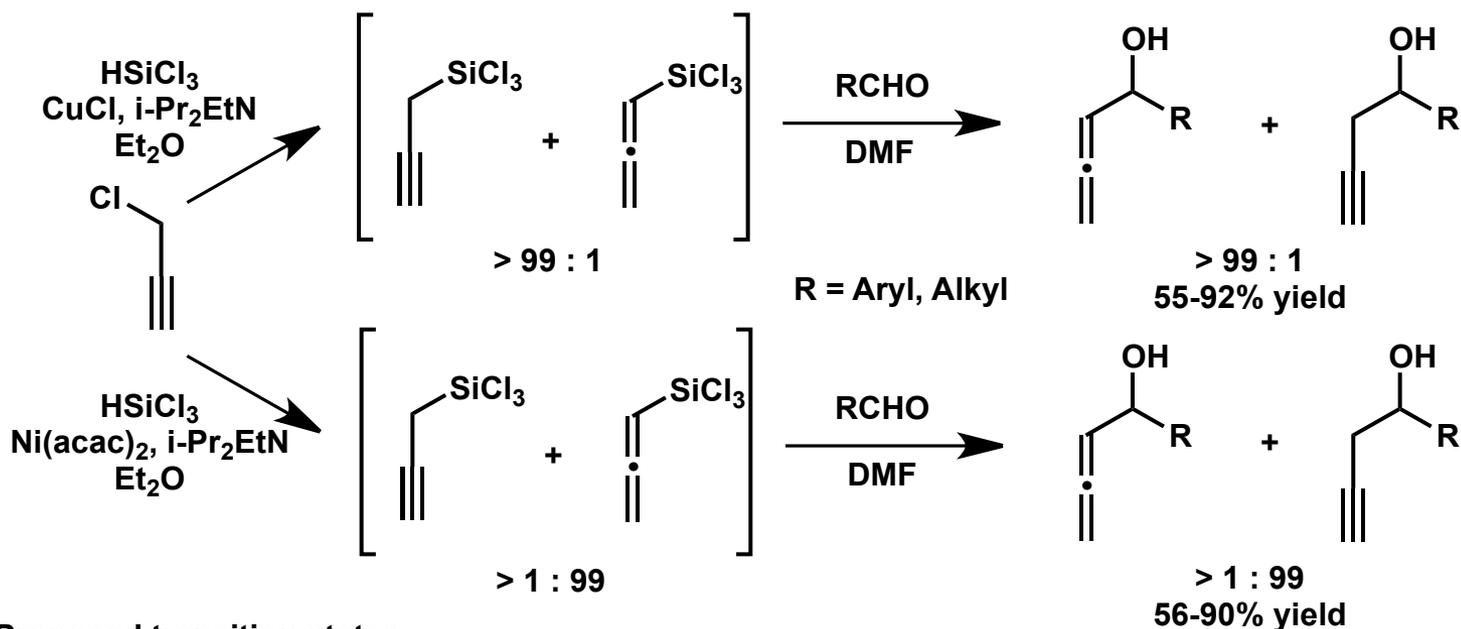
Denmark, S. E.; Gosh, S. K. *Angew. Chem. Int. Ed.* **2001**, 40, 4759.

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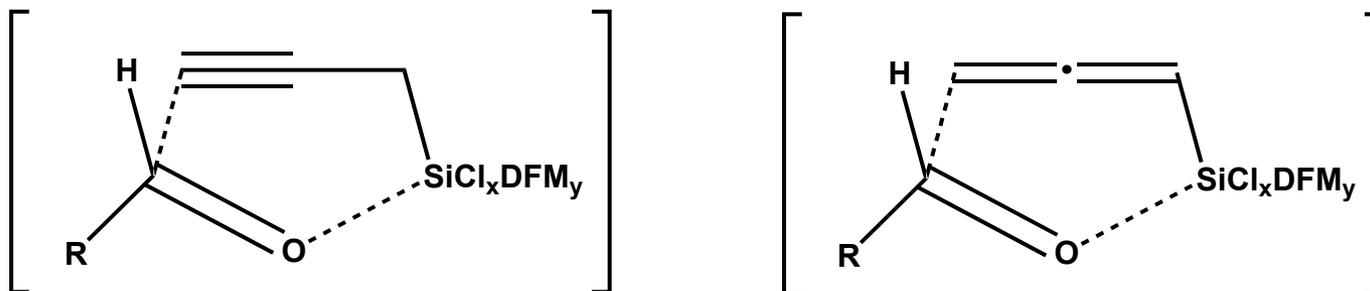
- Structure and Property of Hypervalent Silicon
- Hydrosilylation as a Hypervalent Silicon Example
- Lewis Base Catalyzed Allylsilylation
- Denmark's Contribution to Lewis Base Catalyzed Aldol Reaction and Allylsilylation
- **Other Examples of Hypervalent Silicon Nucleophilicity**
- Hypervalent Silicon as a Chiral Lewis Acid

## Lewis Base Catalyzed Propargylation and Allenylation of Aldehydes

## The Addition of Allenyl- and Propargyltrichlorosilanes to Aldehydes

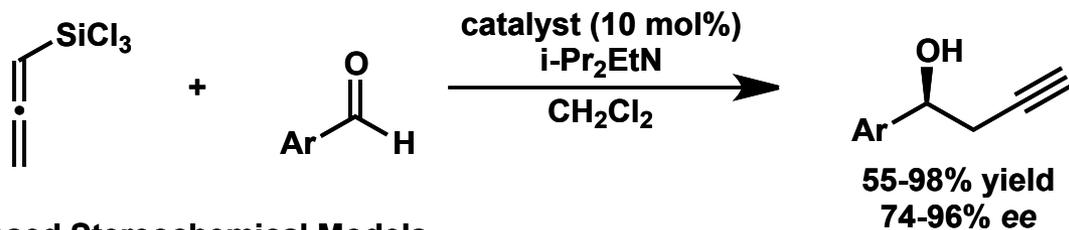


## Proposed transition states

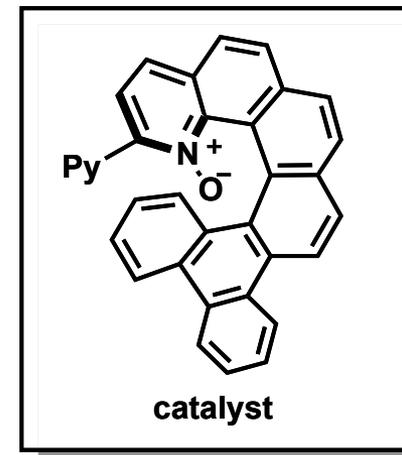
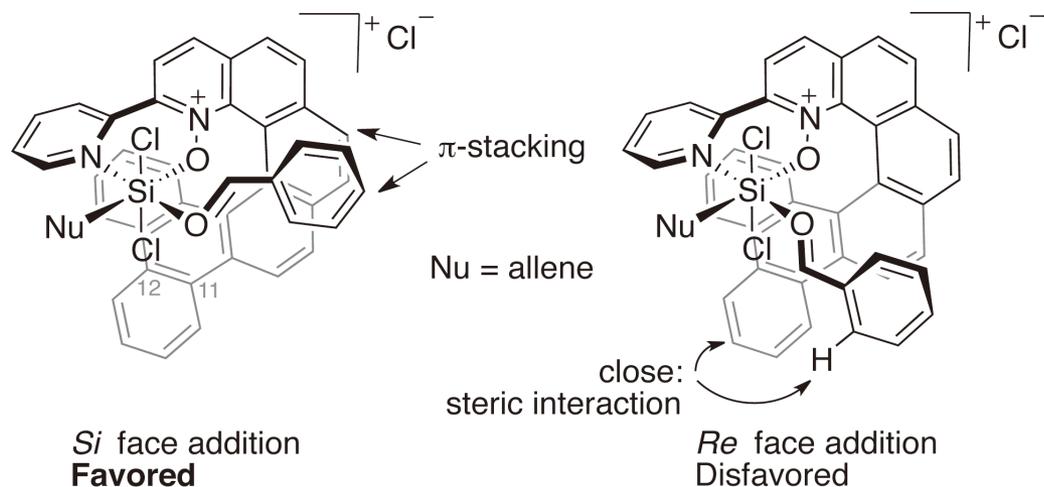


## Lewis Base Catalyzed Asymmetric Propargylation of Aldehydes

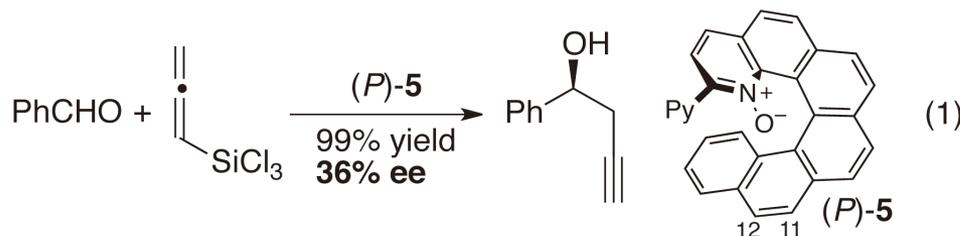
Asymmetric Propargyltrichlorosilanes to Aldehydes with Allenyltrichlorosilane



## Proposed Stereochemical Models

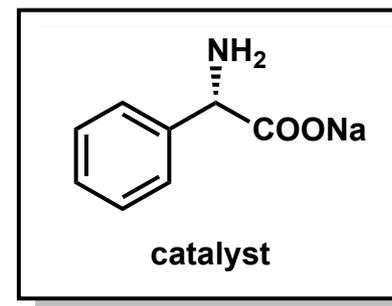
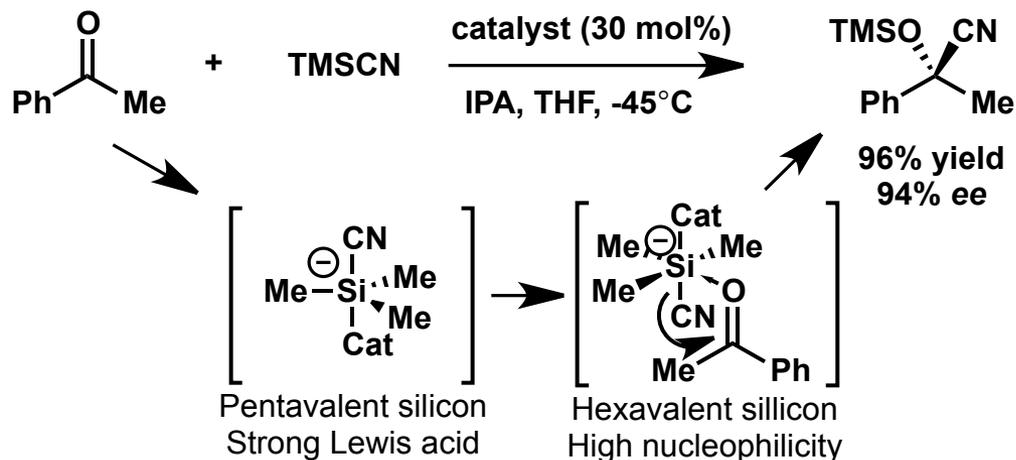


The *Si* face addition is favored due to the expected  $\pi$ -stacking between the bound aldehyde and the helicene framework. In contrast, the 11, 12- benzo unit is very close to the aldehyde bound in the *Re* face addition mode.



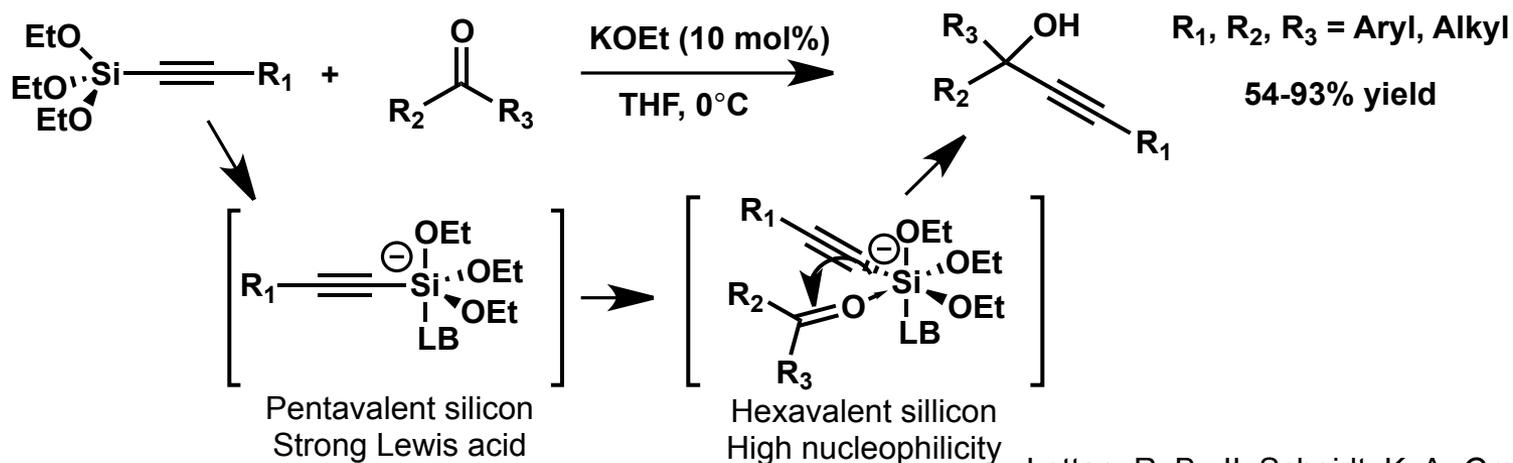
## Lewis Base Catalyzed Other C-C Bond-Forming Reactions via Hypervalent Silicon

## Chiral Amino Acid Salt Catalyzed Asymmetric Cyanosilylation to Ketones



Liu, X.; Oin, B.; Zhou, X.; He, B.; Feng, X.  
*J. Am. Chem. Soc.* **2005**, *127*, 12224.

## Lewis Base Catalyzed Alkynylsilylation to Ketones



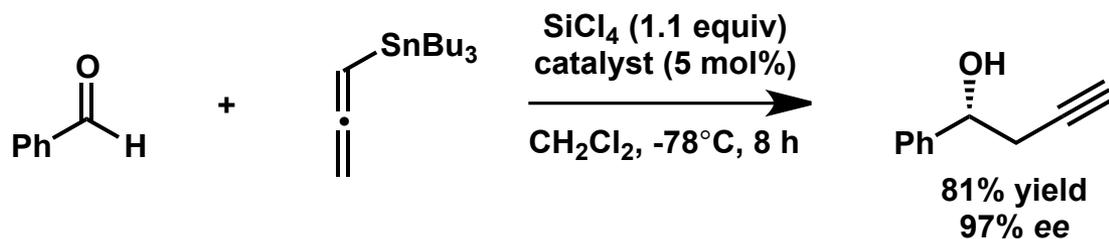
Lettan, R. B., II; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 3227.

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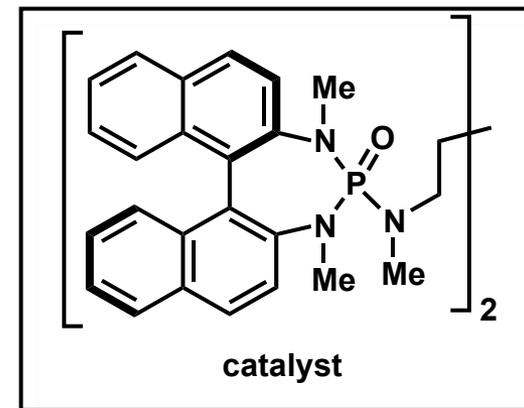
- Structure and Property of Hypervalent Silicon
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Nucleophilicity
- **Hypervalent Silicon as a Chiral Lewis Acid**

## Hypervalent Silicon as a Chiral Lewis Acid

## Asymmetric Propargylation of Aldehydes

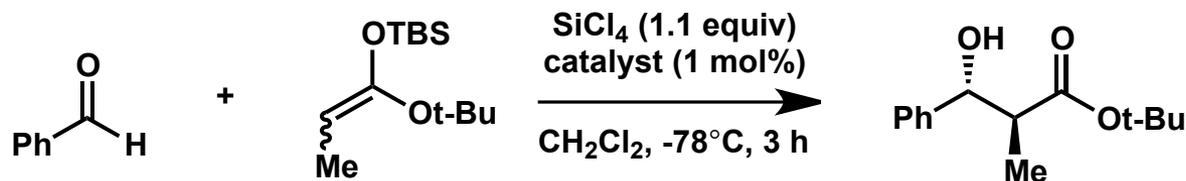


Allyltributyltin also gave the homoallylic alcohol with high yield and enantioselectivity.



Denmark, S. E.; Wynn, T. *J. Am. Chem. Soc.* **2001**, 123, 6199.

## Asymmetric Addition of Silyl Ketene Acetals to Aldehydes



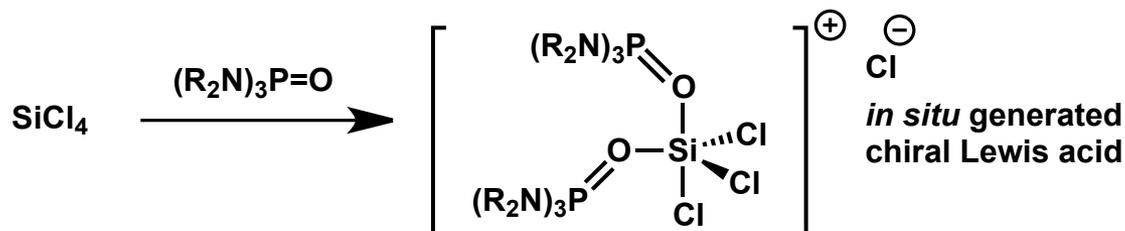
Addition of silyl ketene acetals proceeded via acyclic transition state to give **anti products**.

*E/Z* = 95/5 : 93% yield, 99% ee, 99/1 *dr*

*E/Z* = 12/88 : 73% yield, 99% ee, 99/1 *dr*

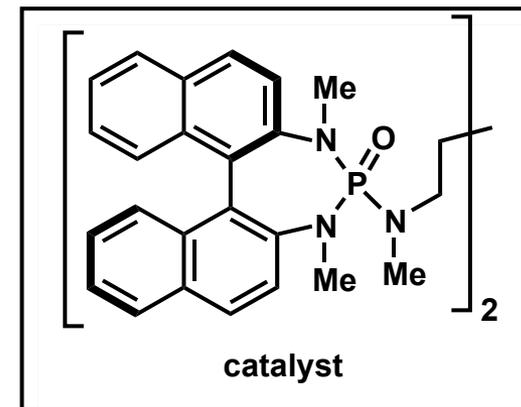
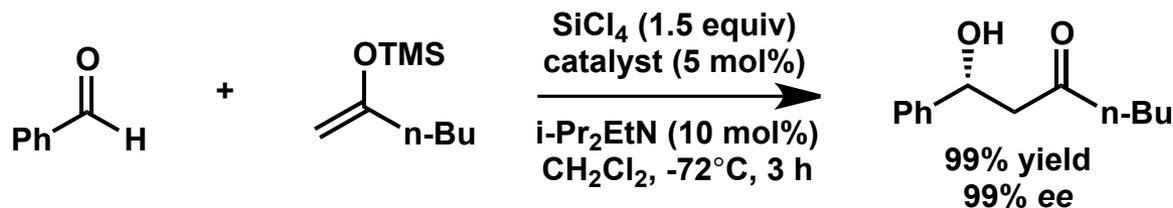
Denmark, S. E.; Wynn, T.; Beutner, G. L. *J. Am. Chem. Soc.* **2002**, 124, 13405.

Denmark, S. E.; Beutner, G. L.; Wynn, T.; Eastgate, M. D. *J. Am. Chem. Soc.* **2005**, 127, 3774.

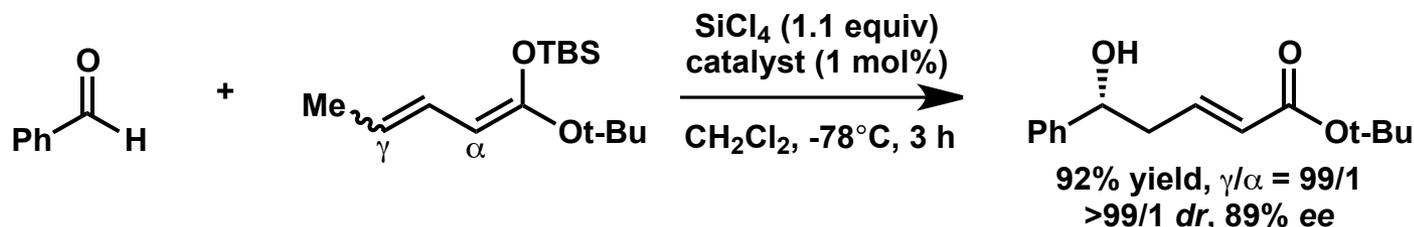


## Hypervalent Silicon as a Chiral Lewis Acid

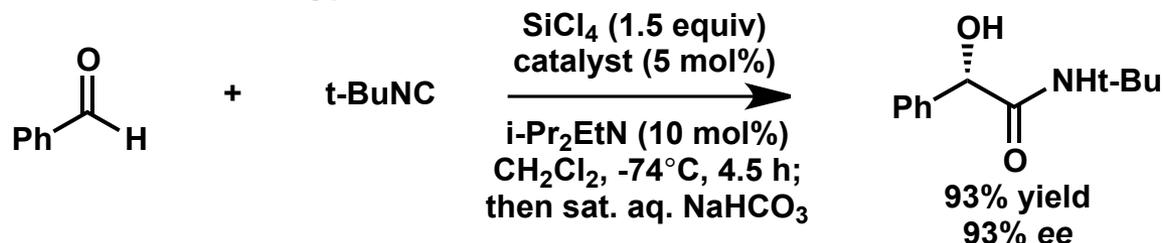
## Asymmetric Addition of Silyl Enol Ethers of Aldehydes

Denmark, S. E.; Heemstra, Jr., J. R.; *Org. Lett.* **2003**, 5, 2303.

## Asymmetric Vinylogous Aldol Reaction

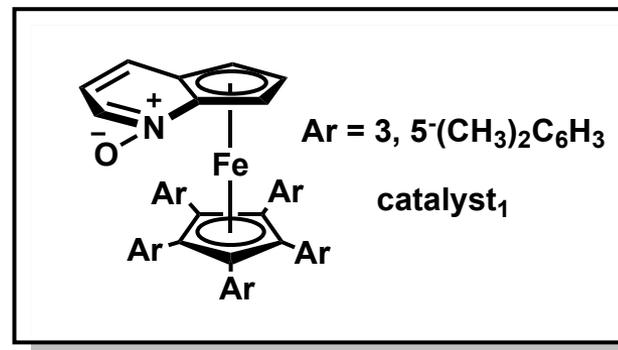
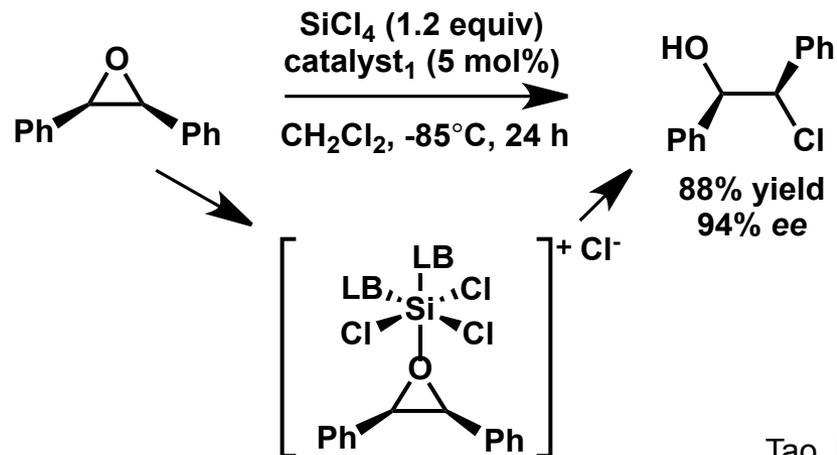
Denmark, S. E.; Beutner, G. L. *J. Am. Chem. Soc.* **2003**, 125, 7800.  
Denmark, S. E.; Heemstra, Jr., J. R. *J. Am. Chem. Soc.* **2006**, 128, 1038.

## Enantioselective Passerini-Type Reaction

The first catalytic asymmetric  $\alpha$ -addition of isocyanides.Denmark, S. E.; Fan, Y. *J. Am. Chem. Soc.* **2003**, 125, 7825.  
Denmark, S. E.; Fan, Y. *J. Org. Chem.* **2005**, 70, 9667.

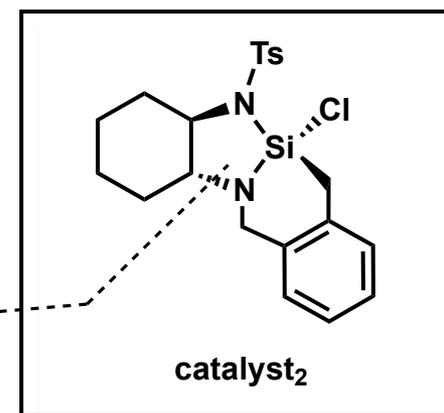
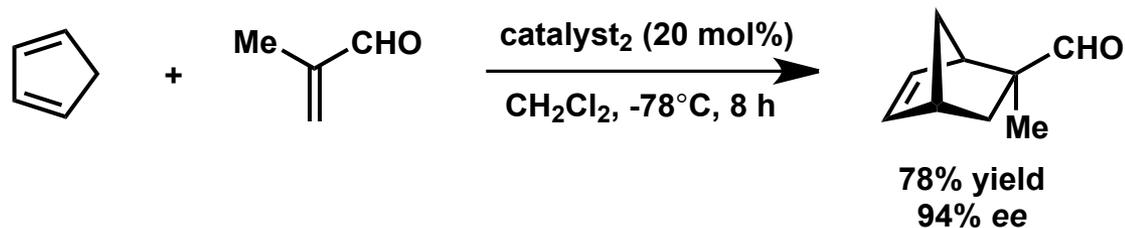
## Hypervalent Silicon as a Chiral Lewis Acid

### Enantioselective Ring Opening of Epoxides



Tao, B.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, 123, 353.

### Strained Silacycle-Catalyzed Asymmetric Diels-Alder Cycloaddition



**Strain release Lewis acidity!!**  
 Ring strain exists including silicon.

Kubota, K.; Hamblett, C. L.; Wang, X.; Leighton, J. L. *Tetrahedron* 2006, 62, 11397.

## Summary

- Hypervalent silicon is crucial intermediate in Lewis base catalyzed allylsilylation and aldol reaction. Using chiral Lewis bases, these reactions could give high diastereo- and enantioselectivity.
- Hypervalent silicon is also used as chiral Lewis acid catalyst in aldol reaction, ring opening of epoxides, Diels-Alder cycloaddition and so on.