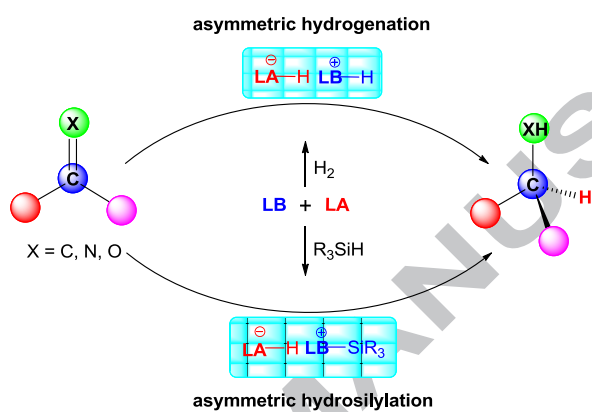# Accepted Manuscript

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Graphical Abstract

**Metal-free Asymmetric Hydrogenation and Hydrosilylation Catalyzed by Frustrated Lewis Pairs**

Xiangqing Feng and Haifeng Du∗

asymmetric hydrogenation

LA—H LB—H

X = C, N, O

LB + LA

$H_2$

$R_3SiH$

LA—H LB—SiR₃

asymmetric hydrosilylation

# Metal-free Asymmetric Hydrogenation and Hydrosilylation Catalyzed by Frustrated Lewis Pairs

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ARTICLE INFO

ABSTRACT

The activation of $H_2$ for the catalytic hydrogenation of unsaturated compounds is one of the most useful reactions in both academia and chemical industry, which has long been predominated by the transition-metal catalysis. However, metal-free hydrogen activation represents a formidable challenge, and has been less developed. The recent emerging chemistry of frustrated Lewis pairs (FLPs) with a combination of sterically encumbered Lewis acids and Lewis bases provides a promising approach for metal-free hydrogenation due to their amazing abilities for the challenging $H_2$ activation. In the past several years, the hydrogenation of a wide range of unsaturated compounds using FLP catalysts has been successfully developed. Despite of these advances, the corresponding asymmetric hydrogenation is just in its start-up step. Similar with the mode of H-H bond activation, Si-H bond can also be activated by FLPs for the hydrosilylation of ketones and imines. But its asymmetric version is also not well-solved. This paper will outline the recent important progress of metal-free catalytic asymmetric hydrogenation and hydrosilylation using FLP catalysts.
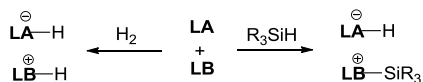
∗ Corresponding author. Tel.: +86-10-6265-2117; fax: +86-1-6255-4449; e-mail: haifengdu@iccas.ac.cn

## Introduction

The activation of inert chemical bonds for further useful transformation is an extremely important subject in synthetic chemistry. As a representative example, the activation of $H_2$ for the catalytic hydrogenation of unsaturated compounds has become one of the most useful reactions in both academia and industry, which has long been predominated by the transition-metal catalysis.[1,2] The mechanism for the metal homolytic or heterolytic cleavage of H-H bond is generally believed to involve the formation of a σ complex between $H_2$ and the metal, the electron donation to the σ* ($H_2$) orbital from the metal or an external/internal base, and the electron acceptance of the metal from the σ ($H_2$) orbital.[1-3] In contrast to this well-established metal activation, the metal-free activation of $H_2$ has been a formidable challenge. In 2006, Stephan and co-workers reported the first metal-free reversible hydrogen activation with the combination of sterically encumbered Lewis acid and Lewis base,[4] in which Lewis acid accepts electron of the σ ($H_2$) orbital and Lewis base donates electron to the σ* ($H_2$) orbital. This seminal work quickly opens an interesting area of frustrated Lewis pairs (FLPs). In 2007, Bertrand and co-workers described a hydrogen activation using (alkyl)(amino) carbenes, in which the carbene carbon serves as both Lewis acid and base.[5] Besides the activation of $H_2$, FLPs can also activate other small molecules including $CO_2$, NO, $N_2O$, $SO_2$ and so on.[6]

One of the most promising issues for the lately emerging FLP chemistry is that it provides an important approach for the metal-free homogeneous hydrogenation. Although the organocatalyzed transfer hydrogenation using Hantzsch esters as hydrogen sources have made great progress in recent years, stoichiometric amount of organic molecules make it less atomic economy and likely restricts its application.[7] In the past several years, a wide range of unsaturated compounds have been successfully hydrogenated with $H_2$ using either stoichiometric or catalytic amounts of FLP catalysts.[8,9] Despite of the rapid growth of FLP catalysis, the asymmetric hydrogenation has less been developed.

Similar with the FLP activation of H-H bond, Si-H bond can also be activated (Scheme 1). In fact, as early as 1996, Piers and co-workers discovered that tris(pentafluorophenyl)borane $B(C_6F_5)_3$ was an effective catalyst for hydrosilylation of ketones and imines, in which Lewis acid activated silane rather than the substrate.[10] This Piers type hydrosilylation is the first example of FLP chemistry, and attracts intensive interests.[11] However, the asymmetric reaction is still not well-solved. This paper will therefore outline the present progress of metal-free catalytic asymmetric hydrogenation and hydrosilylation using FLP catalysts.
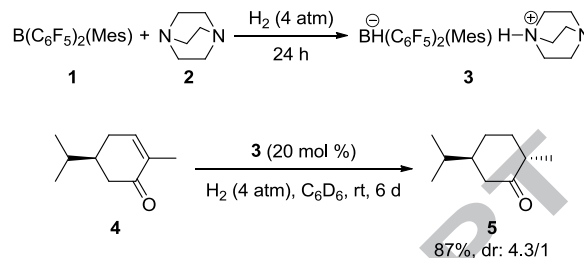


**Scheme 1.** Metal-free activation of H-H and Si-H bonds.

## 1. FLPs catalyzed asymmetric hydrogenation

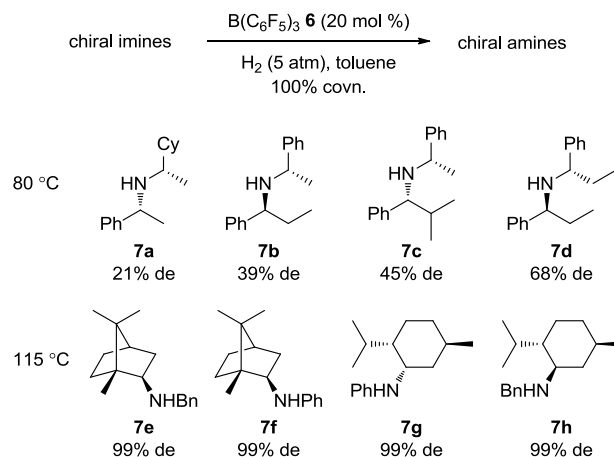### 1.1 The chiral substrate induced asymmetric hydrogenation

In 2010, the first example of chiral substrate induced asymmetric hydrogenation catalyzed by a FLP catalyst was reported by Soós and co-workers. As shown in Scheme 2, with the using 20 mol % the zwitter-ion **3** generated from the heterolytic cleavage of $H_2$ with the FLP of mesityl borane $B(C_6F_5)_2(Mes)$ **1** and DABCO, the conjugated double bond of

D-carvone **4** was selectively hydrogenated with the carbonyl group untouched to furnish the desired product **5** in 87% yield with a 4.3/1 diastereoselectivity.[12]



**Scheme 2.** Hydrogenation of D-carvone by a $B(C_6F_5)_2(Mes)$/ DABCO catalyst.

A highly diastereoselective catalytic hydrogenation of enantiomeric pure ketimines using 10-20 mol % $B(C_6F_5)_3$ (**6**) as a catalyst was successfully achieved by Stephan and co-workers in 2011 (Scheme 3).[13] For α-phenethylimines (**7a-d**), in which the chiral center is adjacent to the nitrogen center, low to moderate diastereoselectivities were achieved (Scheme 1). While, camphor or menthone derived imines (**7e-h**) with the chiral center near the unsaturated carbon center can give quantitative conversions and 95-99% de even at a very high temperature. It is likely attributed to the large effect of proximity of the chiral center on the approach of the steric bulky $[HB(C_6F_5)_3]^-$ anion. A plausible mechanism was shown in Figure 1. The combination of chiral imines **8** and $B(C_6F_5)_3$ **6** as a FLP catalyst heterolytically cleavage $H_2$ to form the zwitter-ion **A**. Then the hydride of $[HB(C_6F_5)_3]^-$ anion is transferred to the carbon atom of the iminium cation from the less steric side. The corresponding amines **7** are afforded and $B(C_6F_5)_3$ regenerates to complete a catalytic cycle.



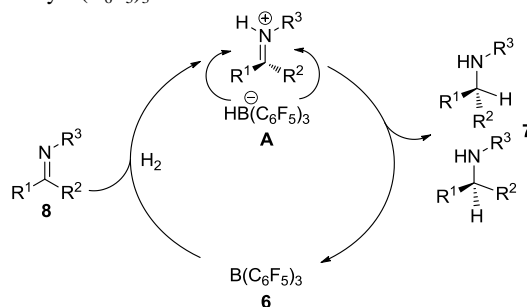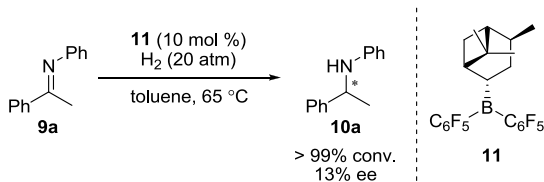**Scheme 3.** Diastereoselective hydrogenation of chiral imines catalyzed by $B(C_6F_5)_3$.



**Figure 1.** A plausible mechanism for $B(C_6F_5)_3$ catalyzed diastereoselective hydrogenation of chial imines.
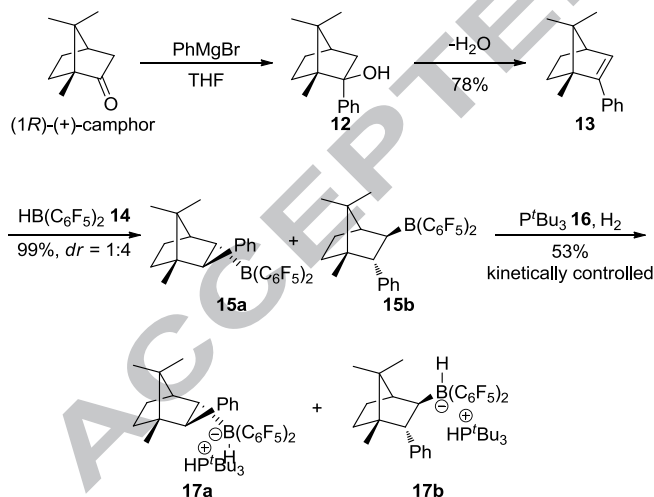
## 1.2 Chiral frustrated Lewis pairs catalyzed asymmetric hydrogenation

In comparison with the chiral-substrate-controlled asymmetric hydrogenations, the chiral-catalyst-controlled reactions are undoubtedly much more efficient. The first chiral FLP catalyzed asymmetric hydrogenation of imine **9a** was reported by Klankermayer in 2008.[14] It was found that chiral borane **11** prepared from (+)-α-pinene can promote the hydrogenation at 65°C and 20 bar hydrogen pressure in a quantitative conversion with 13% ee (Scheme 4). Although the enantioselectivity is very low, this study provides a possibility for the metal-free asymmetric hydrogenation with the use of chiral FLP catalysts.



**Scheme 4.** Asymmetric hydrogenation of an imine catalyzed by chiral borane **11**.

Subsequently, the enantioselectivity was largely improved using novel chiral boranes **17** derived with (1$R$)-(+)-camphor as the starting material.[15] Reaction of (1$R$)-(+)-camphor with phenylmagnesium bromide gave alcohol **12**. Subsequent dehydration resulted in chiral olefin **13**. The hydroboration of **13** using bis(perfluorophenyl)borane (Piers borane) (**14**) gave the diastereomeric boranes **15a** and **15b** in a 1:4 ratio. Due to the difficulty for the separation of the two diastereomers **15a** and **15b**, this mixture was treated with hydrogen at room temperature in the presence of $^t$Bu$_3$P (**16**) to afford the activated FLP salts **17a** and **17b** as a mixture. The optical pure chiral catalysts **17a** and **17b** could be isolated by kinetically controlled product formation (Scheme 5).
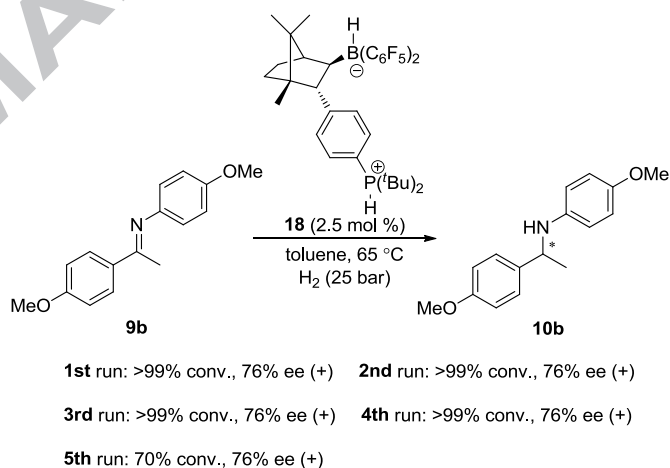


**Scheme 5.** The preparation of chiral FLP catalyst **17**.

The catalysts were applied in the hydrogenation of prochiral ketimines **9**. It is interesting to find that catalyst **17a** gave 48% ee, but catalyst **17b** gave 79% ee in a reverse configuration, which resulted in a very low ee when 1:1 mixture of **17a** and **17b** was used (Table 1). It is therefore very important to obtain the highly optical pure chiral catalyst **17b** for asymmetric hydrogenations. Several ketimines **9** were suitable substrates for this asymmetric reaction to give the products **10** in 74-83% ee's.[15] This work represents the first highly enantioselective hydrogenation catalyzed by chiral FLPs.

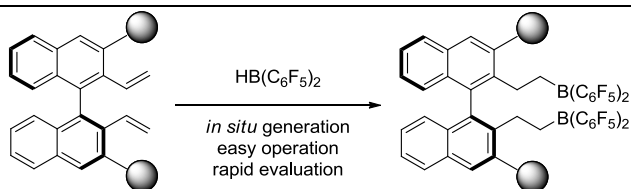**Table 1.** Asymmetric hydrogenation of imines catalyzed by chiral **17**.



| Entry | R$^1$ = | R$^2$ = | Cat. (**17**) | Yield (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | Ph | Ph | **17a/17b** = 1/1 | >99 | 20 ($S$) |
| 2 | Ph | Ph | **17a** | >99 | 48 ($S$) |
| 3 | Ph | Ph | **17b** | 95 | 79 ($R$) |
| 4 | Ph | 2-Me-C$_6$H$_4$ | **17b** | 37 | 74 (-) |
| 5 | Ph | 4-MeO-C$_6$H$_4$ | **17b** | >99 | 81 ($R$) |
| 6 | 4-MeO-C$_6$H$_4$ | Ph | **17b** | 96 | 81 (-) |
| 7 | 2-Naphthyl | Ph | **17b** | 93 | 80 (-) |
| 8 | 2-Naphthyl | 4-MeO-C$_6$H$_4$ | **17b** | 96 | 83 (+) |

In 2012, Klankermayer and co-workers reported an intramolecular phosphine-borane FLP catalyst **18** derived from (1$R$)-(+)-camphor. With a 2.5 mol % catalyst loading, the enantioselective hydrogenation of imines can give up to 76% ee (Scheme 6).[16] Catalyst **18** is very stable in air condition, and can be recycled for four times without loss of any activity and enantioselectivity. Further reducing the catalyst loading to 0.5 mol %, the desired product was obtained in 95% yield with 76% ee.
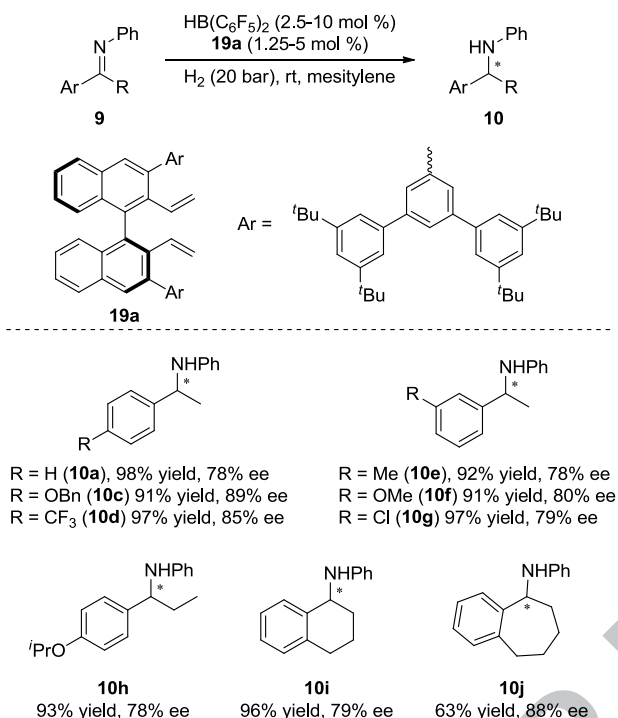


**1st** run: >99% conv., 76% ee (+)    **2nd** run: >99% conv., 76% ee (+)

**3rd** run: >99% conv., 76% ee (+)    **4th** run: >99% conv., 76% ee (+)

**5th** run: 70% conv., 76% ee (+)

**Scheme 6.** Recycling experiments with an intramolecular phosphine-borane FLP catalyst.

The aforementioned chiral borane or FLP catalysts were exclusively used after purification, which may restrict further application of the catalysts. Very recently, Du and co-workers described a novel strategy for the development of chiral boranes. In this strategy, the chiral olefin[17] acted like a "ligand" in the transition-metal catalysis to generate chiral borane catalysts *in situ* without further isolation, which made this process easy operation and rapid evaluation (Scheme 7). Moreover, the use of terminal olefins ensured the optical purity of boranes by the hydroboration with Piers borane and avoided to produce diastereoisomers for the case of internal olefins. After screening a variety of chiral dienes, binaphthyl-based chiral diene **19a** bearing a large steric hindrance in 3,3'-positions proved to be highly effective for the metal-free asymmetric hydrogenation of ketimines **9** at room temperature, the corresponding amine products **10** were produced in excellent yields and with up to 89% ee (Scheme 8).[18]
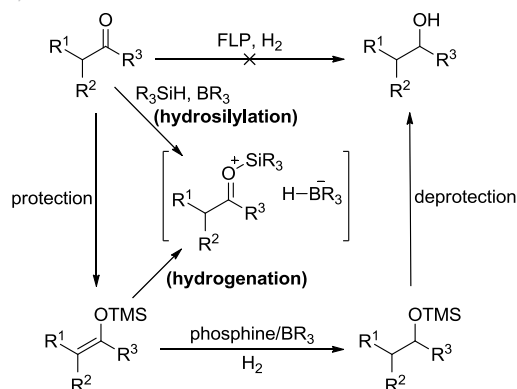
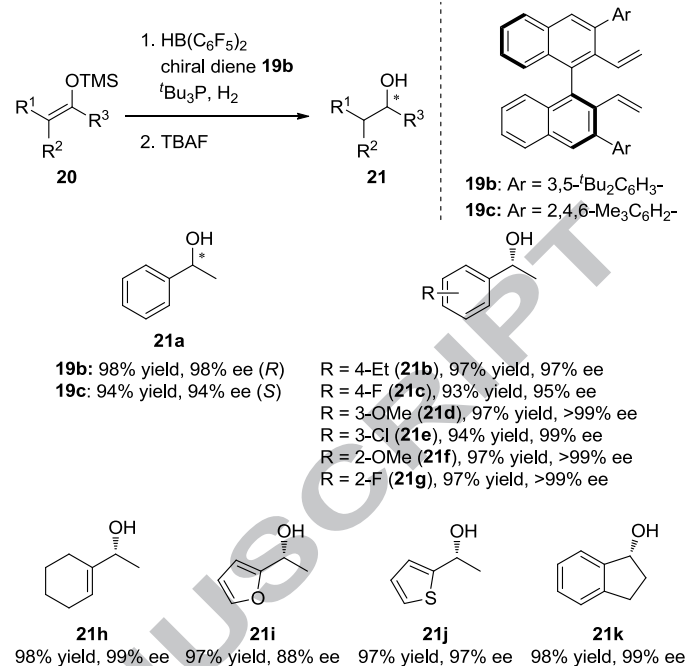**Scheme 7.** New strategy for the development of chiral FLP catalysts.



**Scheme 8.** Catalytic asymmetric hydrogenation with chiral dienes as "ligands".

The direct hydrogenation of ketones under FLP catalysis still remains as an unsolved problem. Using silyl enol ethers instead of ketones for the FLP catalysis is a clever detour. Erker and Paradies reported the hydrogenation of silyl enol ethers utilizing the combination of phosphine and broane as a FLP catalyst, respectively.[19] It is noteworthy that hydrogenation and Piers type hydrosilylation possess a similar intermediate (Scheme 9). Very recently, Du and co-worker reported the first highly enantioselective hydrogenation of silyl enol ethers using a simple combination of $^tBu_3P$ and boranes generated by the *in situ* hydroboration of chiral dienes with $HB(C_6F_5)_2$ as FLP catalysts.[20] A variety of optically active secondary ahcohols **21** were furnished in 93-99% yields and with 88->99% ee's (Scheme 10). The readily available of the *in situ* prepared boranes and the diverse combination with Lewis bases make them a promising class of catalysts for metal-free asymmetric hydrogenations.
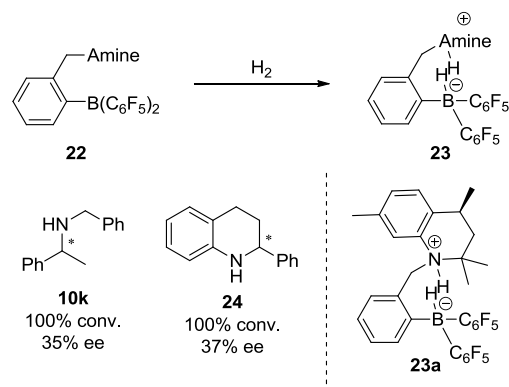


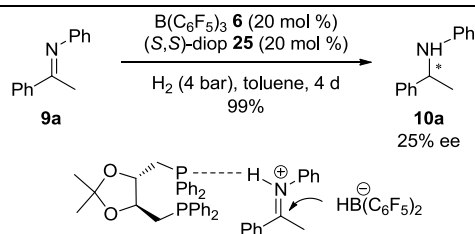**Scheme 9.** Catalytic asymmetric hydrogenation of silyl enol ethers.



**Scheme 10.** Catalytic asymmetric hydrogenation of silyl enol ethers.

In the aforementioned FLP catalytic systems, the asymmetric induction comes from the chiral Lewis acid component. As a two-component catalyst, chiral Lewis base is also likely to control the asymmetric process. Repo and co-workers designed a novel class of intramolecular *ansa*-aminoborates **22**. After treated with $H_2$, the resulting *ansa*-ammonium catalysts were highly effective in the hydrogenation of imines. It was found that the basicity of the amine moiety had a great influence on the activity. Weaker basicity gave a higher activity. Installed with a chiral amine moiety, a chiral *ansa*-aminoborate **23a** was obtained. The corresponding chiral *ansa*-aminoborate **23a** was effective for the asymmetric hydrogenation of ketimines and quinolines to give up to 37% ee (Scheme 11).[21]



**Scheme 11.** Asymmetric hydrogenation catalyzed by *ansa*-ammonium borate catalyst.
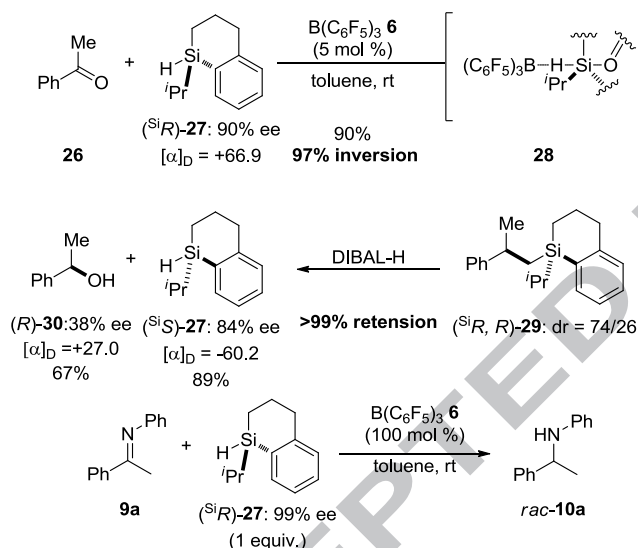
In 2011, Stephan and co-workers employed (*S*,*S*)-diop (**25**) and $B(C_6F_5)_3$ (**6**) as an intermolecular FLP catalyst for the asymmetric hydrogenation of ketimine **9a** to result in a promising 25% ee (Scheme 12).[22] The proton was transferred from the phosphonium cation to the imine, and the chirality may be induced by the weak effect between the chiral phosphines and the iminium.

**Scheme 12.** Asymmetric hydrogenation with a chiral P/B catalyst.

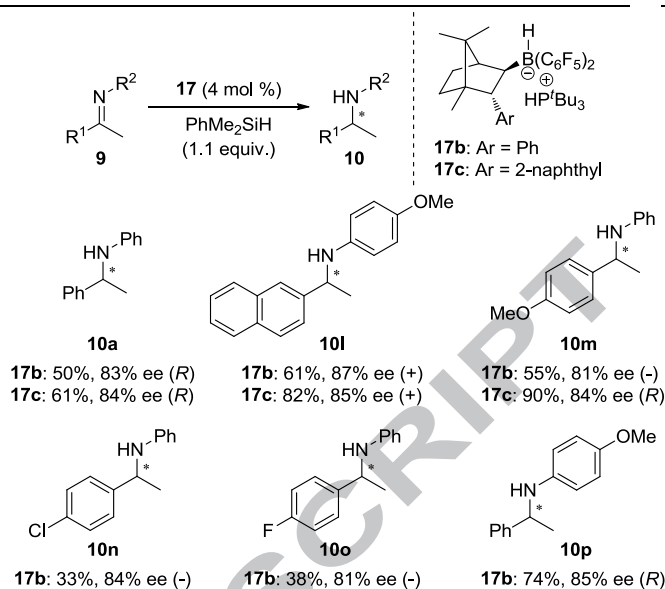## 2. FLPs catalyzed asymmetric hydrosilylation

Although Piers type hydrosilylation was reported as early as 1996, the first asymmetric transformation was reported until 2008. Oestreich and co-workers described a $B(C_6F_5)_3$-catalyzed hydrosilylation of prochiral acetophenone using a chiral silane.[11b] Treated the prochiral ketone **26** with silane ($^{Si}R$)-**27** in the presence of 5 mol % of $B(C_6F_5)_3$ (**6**) to give a mixture of diastereomers **29**, after a racemization-free reductive cleavage, the ($^{Si}S$)-**27** was recovered in 89% yield and with an inverse configuration. Chiral alcohol ($R$)-**30** was obtained in good yield and with 38% ee. An attempt for the hydrosilylation of imine **9a** by the same strategy gave racemic amine **10a** (Scheme 13).[23]



**Scheme 13.** $B(C_6F_5)_3$-catalyzed hydrosilylation of a prochiral acetophenone.

The first chiral FLPs catalyzed asymmetric hydrosilylation was developed by Klankermayer and co-workers in 2012. The camphor derived catalysts **17** were applied in the hydrosilylation of imines, using dimethylphenyl silane as a hydrogen source, several amines were obtained with up to 87% enantioselectivity, which demonstrated the effectiveness of the chiral FLP catalysts for this transformation (Scheme 14).[24] It should be noted that using chiral borane without the addition of phosphine resulted in a racemic product.

In 2012, Oestreich and co-worker demonstrated an axially chiral $C_6F_5$-substituted borane ($S$)-**31**. With this catalyst, a phenyl-substituted imine **9a** could be reduced to amine **10a** with 33% ee. For the acetophenone derived imine with a benzyl protection, a promising 62% ee was obtained. Combined ($S$)-**31** with the novel axially chiral silanes **32**, distinct matched/mismatched selectivities were observed in the hydrosilylations (Table 2).[25]



**Scheme 14.** Hydrosilylation of imines by chiral FLP catalyst **17**.

**Table 2.** Hydrosilylation of imines.



| Entry | Substrate | Silane | Temp. (h) | Conv. (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | **9a** | **33** | 66 | 84 | 33 ($S$) |
| 2 | **9k** | **33** | | | 62 |
| 3 | **9a** | ($R$)-**32** | 96 | 57 | 22 ($S$) |
| 2 | **9a** | ($S$)-**32** | 96 | 60 | 2 ($R$) |
| 3 | **9q** | ($R$)-**32** | 22 | 92 | 13 ($S$) |
| 4 | **9q** | ($S$)-**32** | 23 | 90 | 16 ($R$) |

## Conclusion and outlook

The FLP chemistry provides a promising approach for the metal-free asymmetric reduction of unsaturated compounds. Some important progress has been made for hydrogenation and hydrosilylation in recent years. Especially for the asymmetric hydrogenation, >99% ee has been achieved for the reaction of silyl enol ethers. It is noteworthy that silyl enol ethers are ineffective substrates for the transition-metal catalyzed hydrogenations up to date. For the asymmetric hydrosilylation, up to 87% ee has also been obtained for the imine substrates. Despite these advances, there still remain numerous problems and challenges for this lately emerging area, such as the difficulty for the catalyst synthesis, the relatively narrow substrate scope, and the absence of highly efficient and diverse catalysts. The development of new catalysts as well as novel strategies for the catalyst synthesis, and the expanding their application for asymmetric reduction of other unsaturated compounds are two important subjects in the field of FLP catalysis.
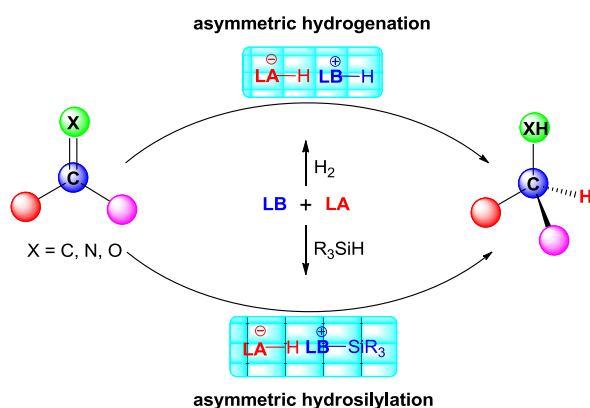
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Graphical Abstract

The metal-free hydrogenation utilizing molecular hydrogen is a challenging and unsolved problem. The development of Frustrated Lewis pairs (FLPs) provides a novel access to the metal-free homogeneous hydrogenation. In the past several years, the hydrogenation of a wide range of unsaturated compounds using FLP catalysts has been successfully developed, and the asymmetric hydrogenation has also witnessed great progress. Similarly, Si-H bond can also be activated by FLPs for hydrosilylation of ketones and imines. This paper will outline the present progress of metal-free catalytic asymmetric hydrogenation and hydrosilylation using FLP catalysts.