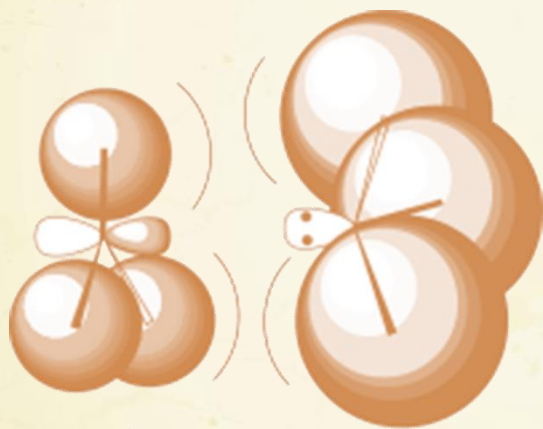


Frustrated Lewis Pairs in Hydrogen Splitting and Metal-Free Hydrogenation



报告人：姜范洲

2015-06-01



Introduction and Background

Frustrated Lewis Pairs in Metal-free Hydrogenation

Summary and Outlook

Introduction and Background

- 👉 **Lewis Base: Electron-pair Donors**
Lewis Acid: Electron-pair Acceptors
- 👉 **Lewis acids are characterized by LUMOs which can interact with the lone electron-pair in HOMOs of Lewis bases.**

Lewis Acid



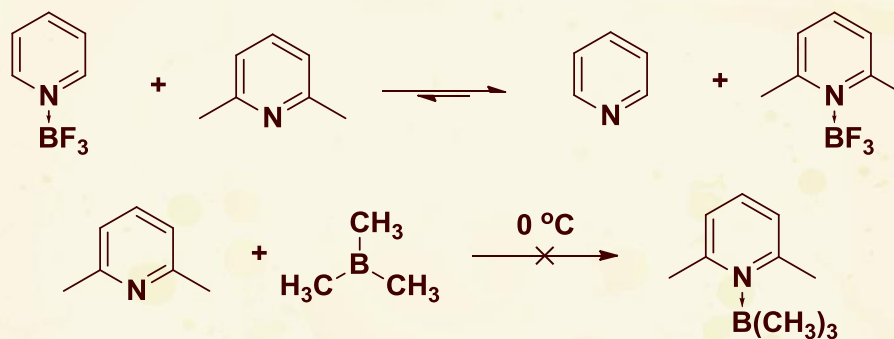
Lewis Base



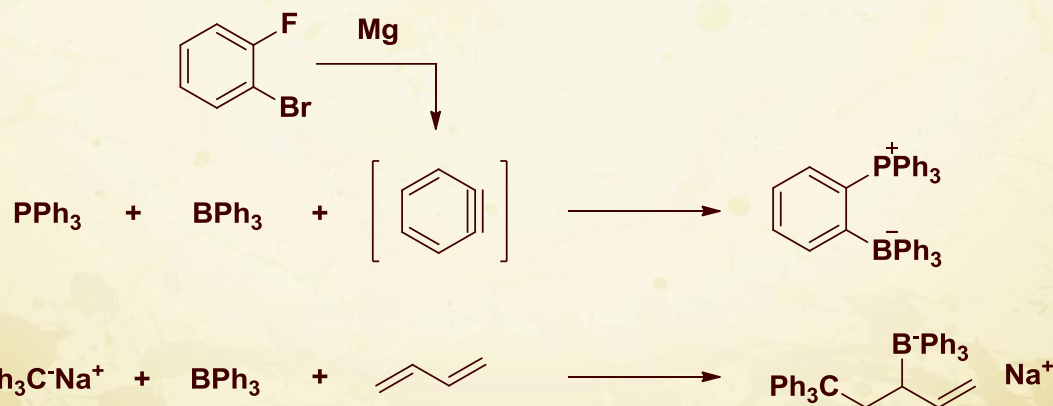
Introduction and Background

Not all Lewis acid/Lewis base combinations form strong adducts.

H. C. Brown, 1942

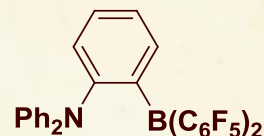
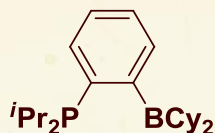
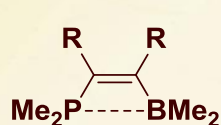


G. Wittig, 1959

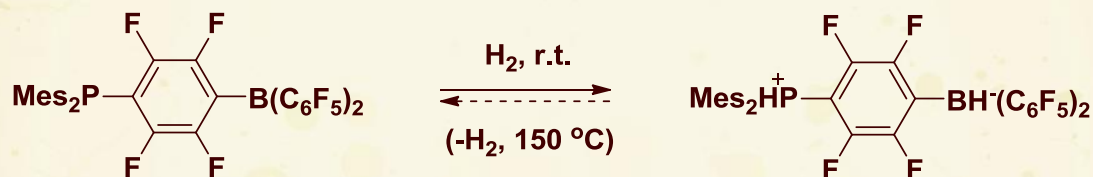


Introduction and Background

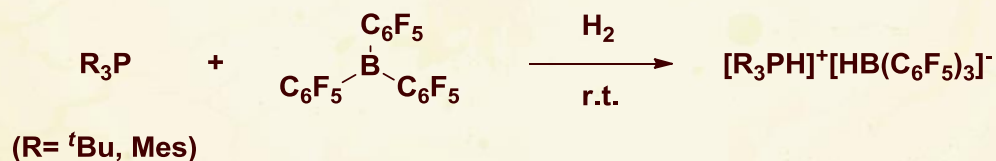
The combination of Lewis acid and Lewis base functional groups into single molecules.



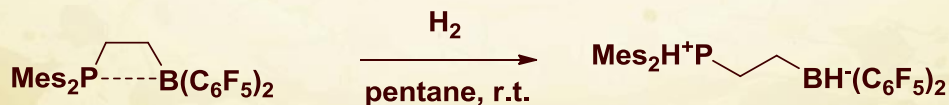
D. W. Stephan, 2006



D. W. Stephan, 2007

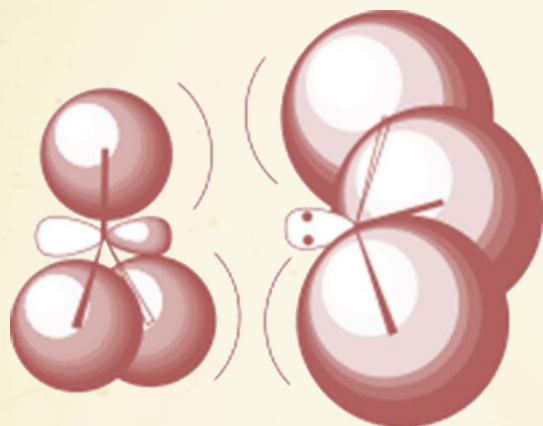


G. Erker, 2007



Introduction and Background

- Frustrated Lewis Pairs (FLPs):** the combination of a bulky Lewis base with a bulky, electrophilic Lewis acid.



Lewis Acid

Lewis Base



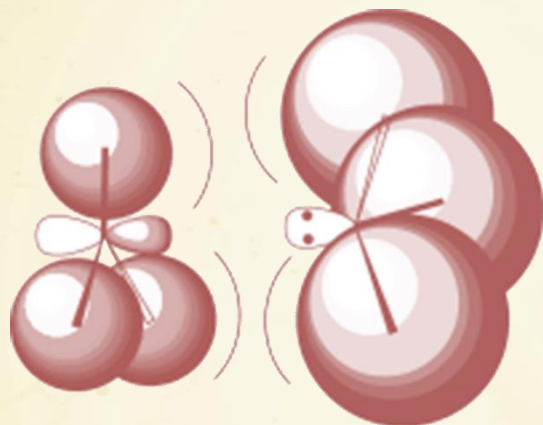
To heterolytically cleave the strong H-H bond

Frustrated Lewis Pairs in Metal-free Hydrogenation

Hydrogen activation



Metal-free FLP-catalyzed hydrogenations



Lewis Acid

Lewis Base



Variability of FLPs

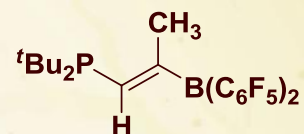
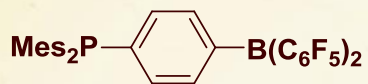
Different substrates



Leading to small-molecule binding and activation

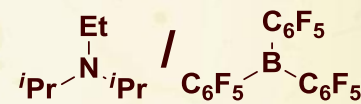
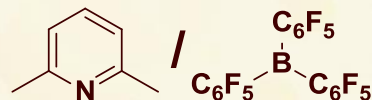
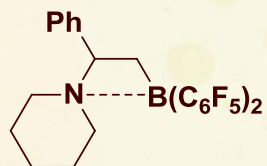
Frustrated Lewis Pair Systems

P/B FLPs



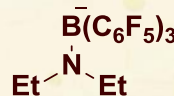
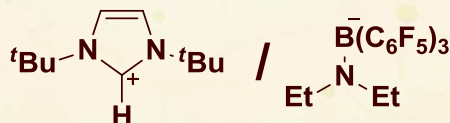
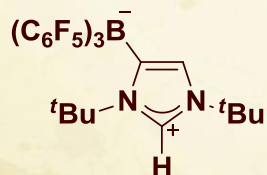
...

N/B FLPs



...

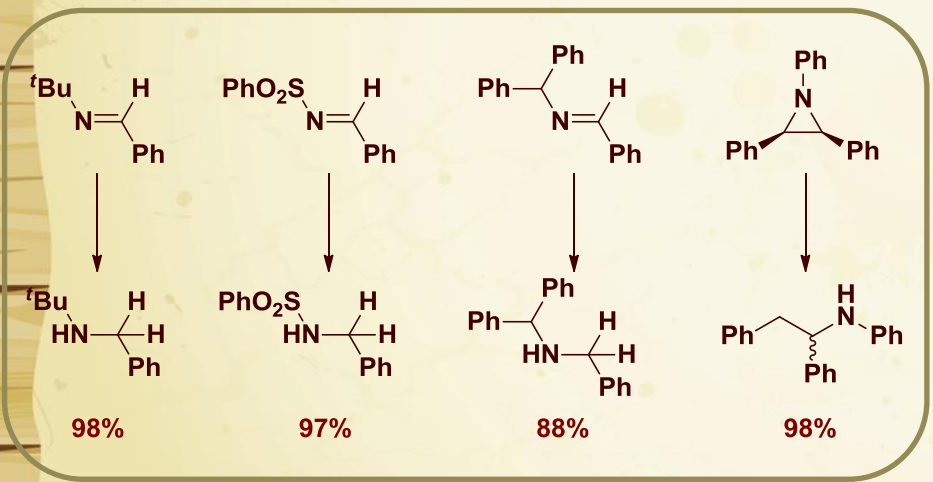
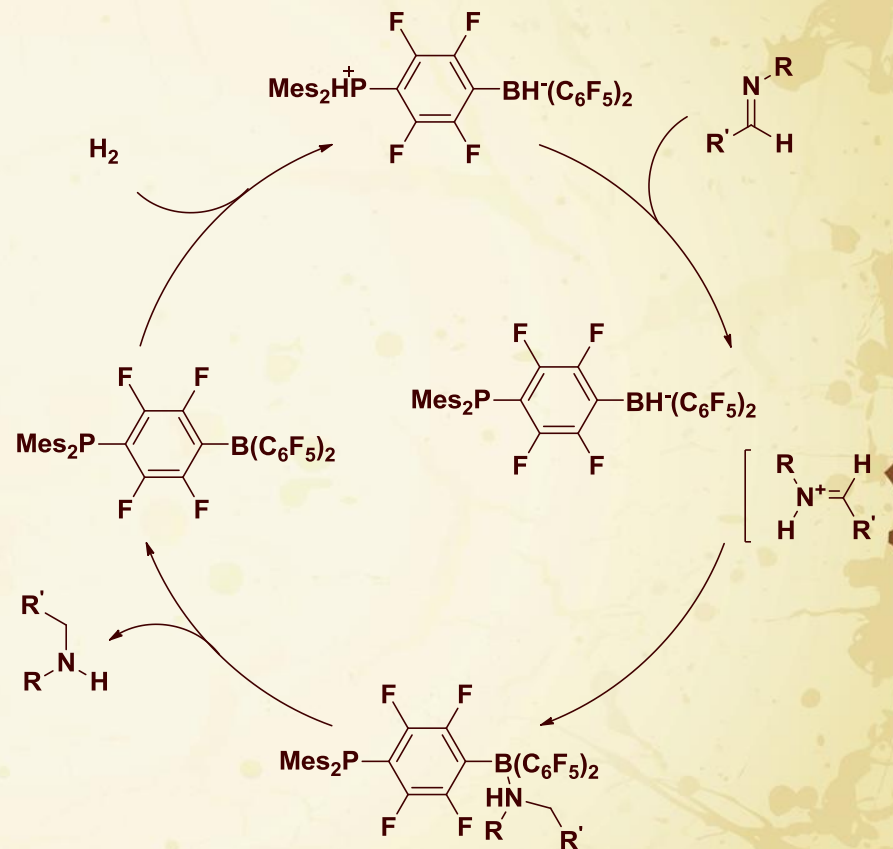
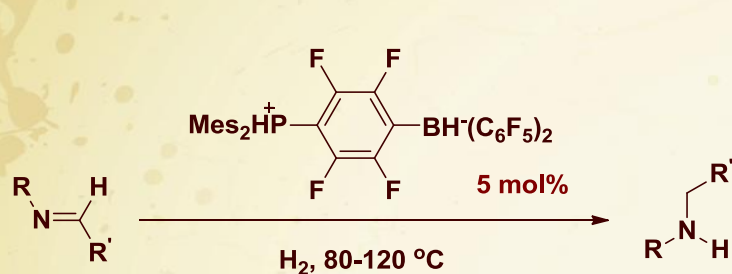
C/B FLPs



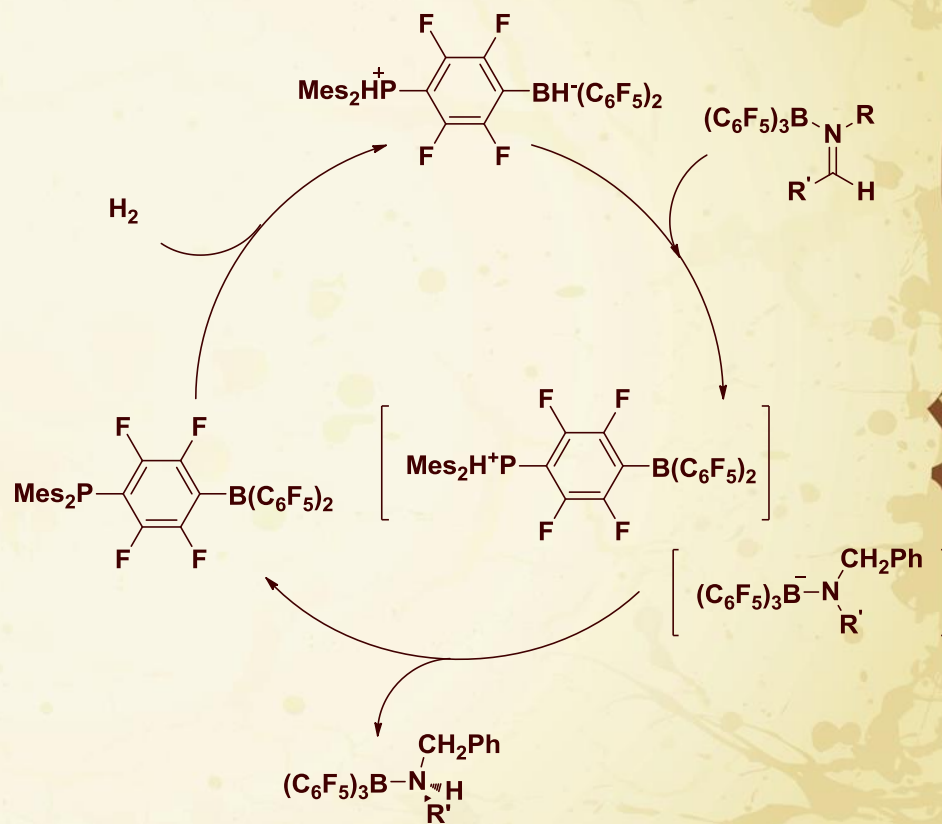
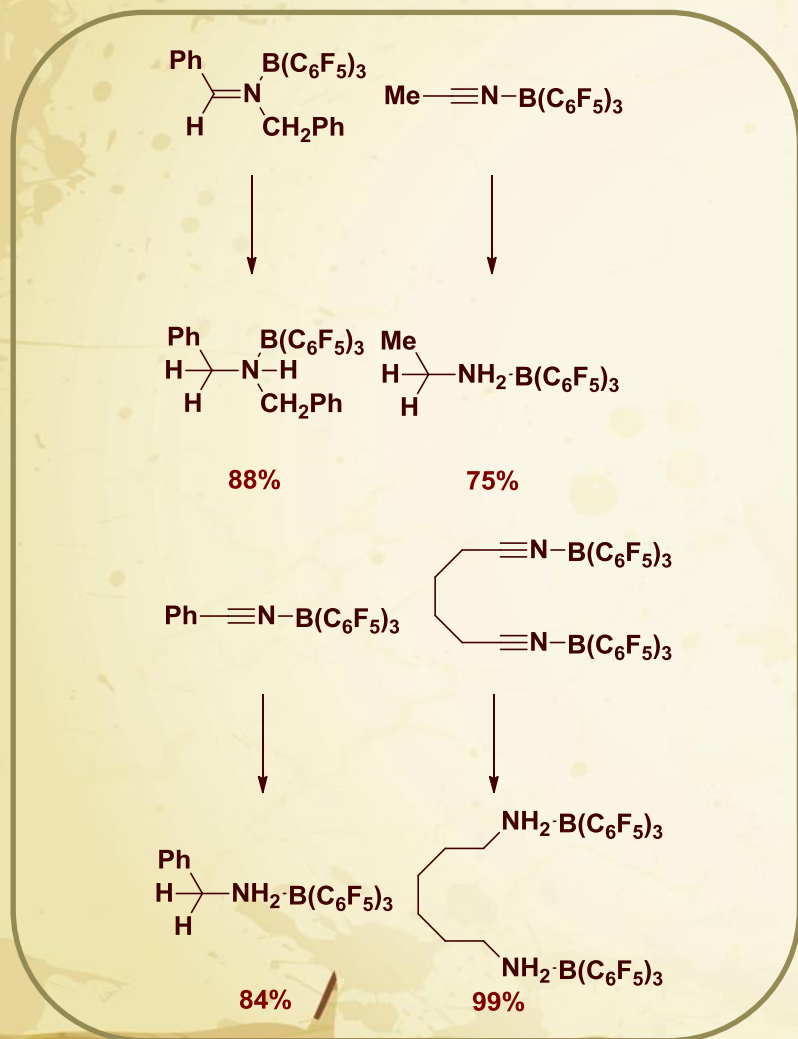
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Frustrated Lewis Pairs in Metal-free Hydrogenation

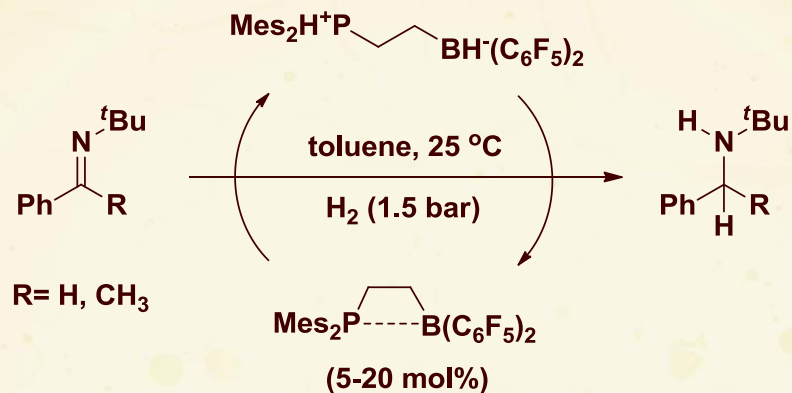
Hydrogenation of Imines and Aziridines



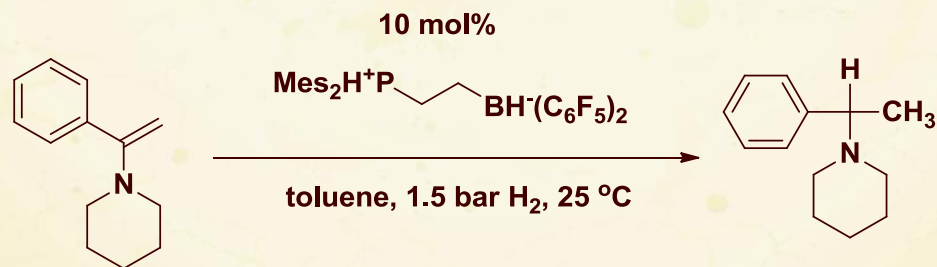
Hydrogenation of Borane-protected Imines and Nitriles



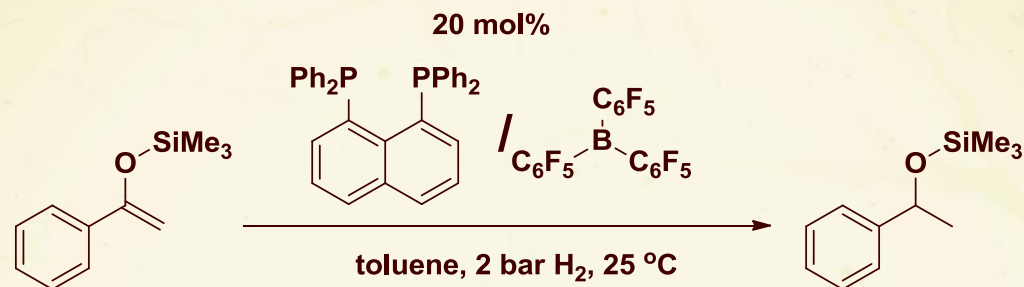
Hydrogenation of Imines



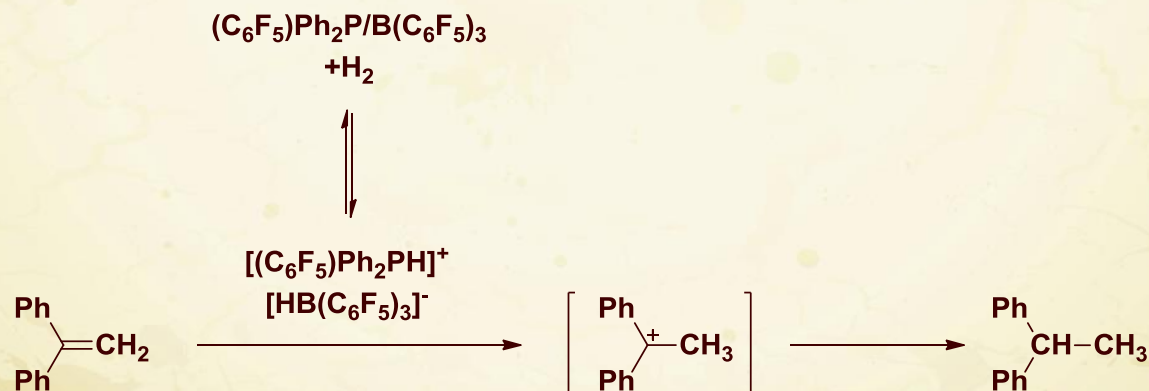
Hydrogenation of Enamines



Hydrogenation of Silylenoethers

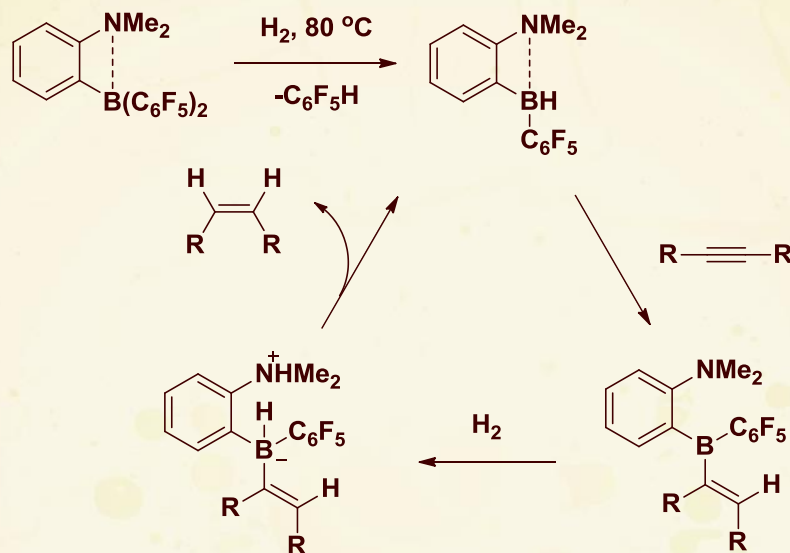


Hydrogenation of Non-functionalized Alkenes

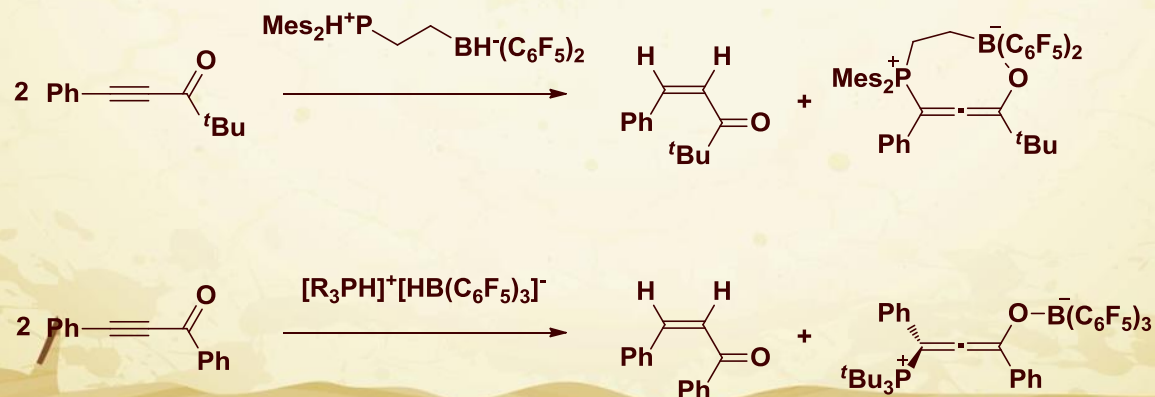


Frustrated Lewis Pairs in Metal-free Hydrogenation

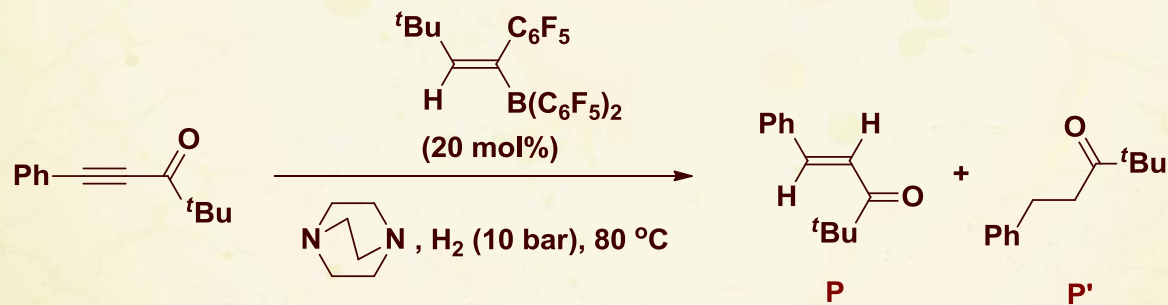
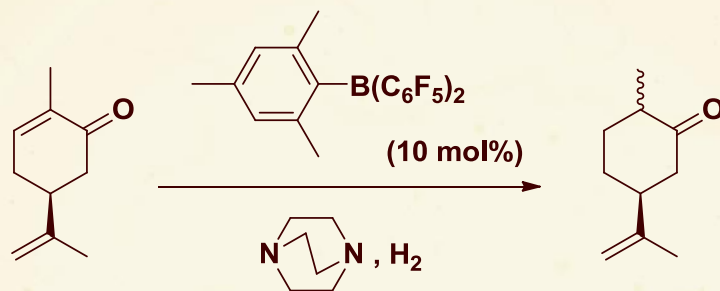
cis-Hydrogenation of Alkynes



Hydrogenation of Conjugated Ynones

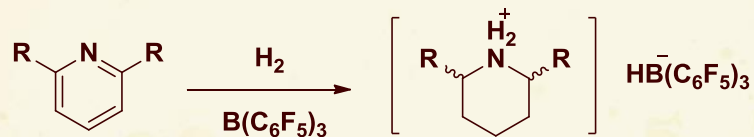
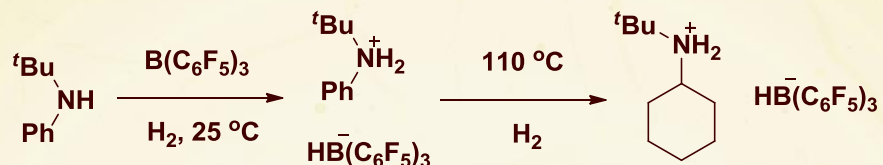


Hydrogenation of Conjugated Enones

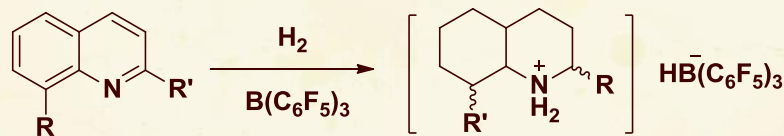


$\text{tran-P} : \text{cis-P} : \text{P}' \approx 50 : 1.5 : 1$

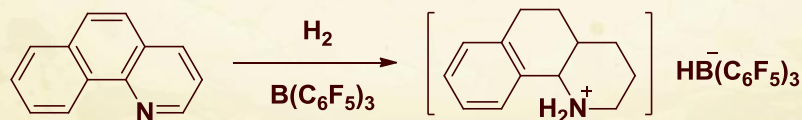
Hydrogenation of Arenes



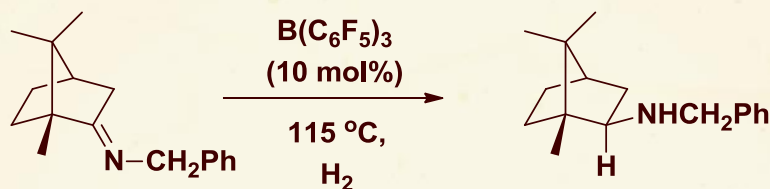
R= Me, Ph



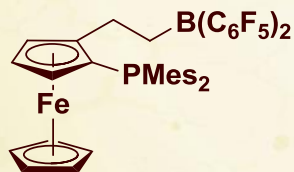
R=H, R'=H, Ph
R=Me, R'=H



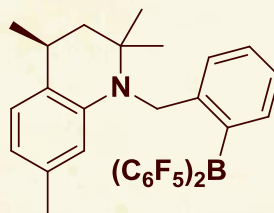
Diastereoselective Hydrogenation



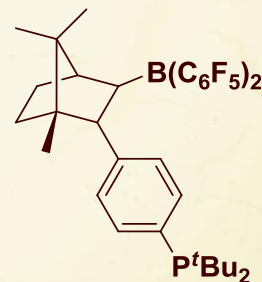
Chiral FLPs for Asymmetric Hydrogenation



G. Erker



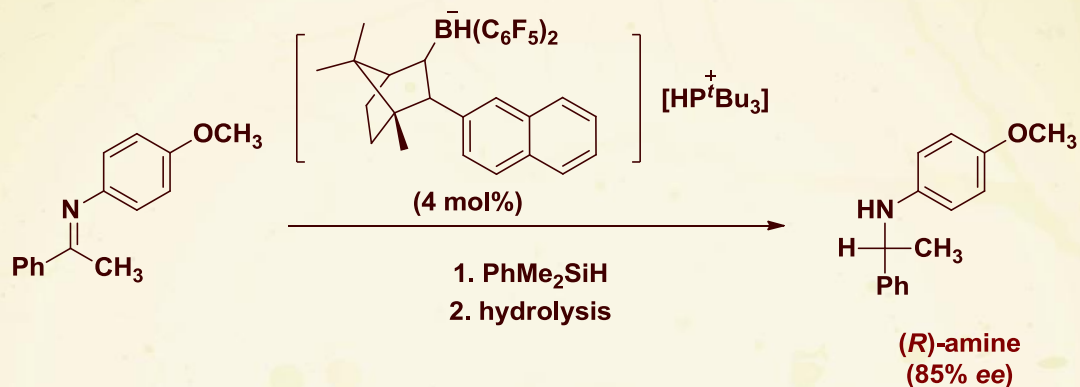
T. Repo



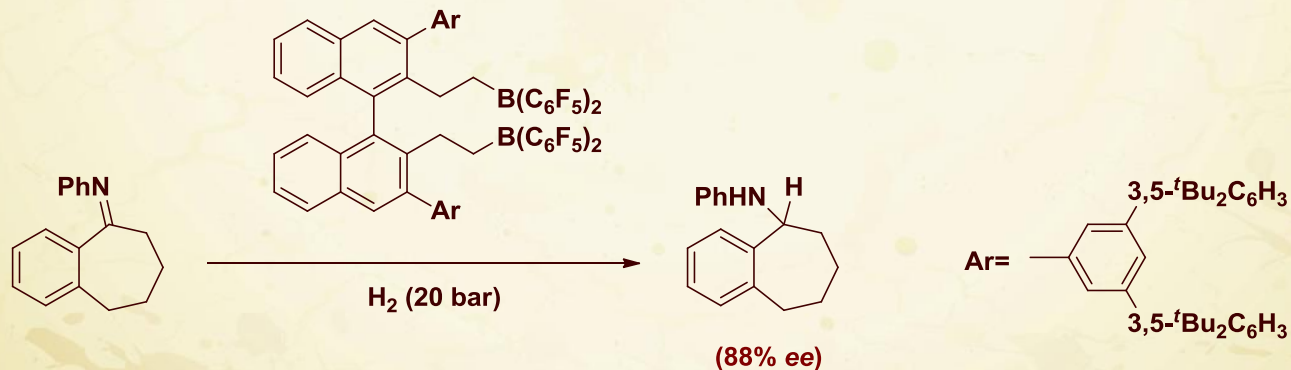
J. Klankermayer

Frustrated Lewis Pairs in Metal-free Hydrogenation

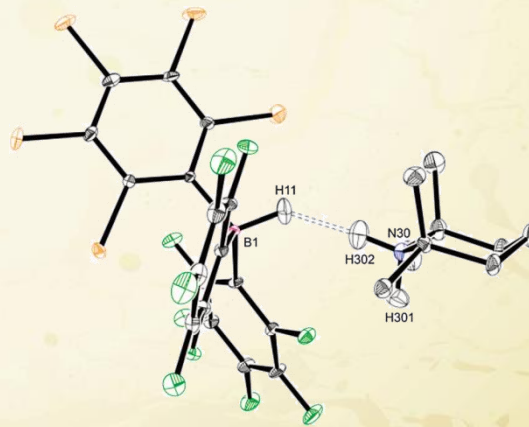
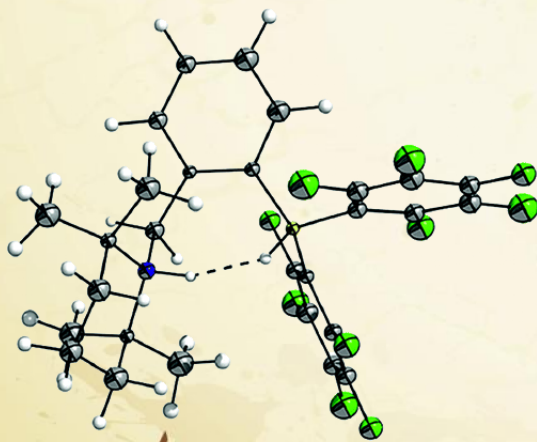
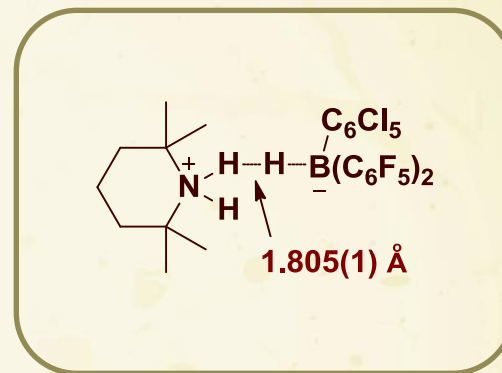
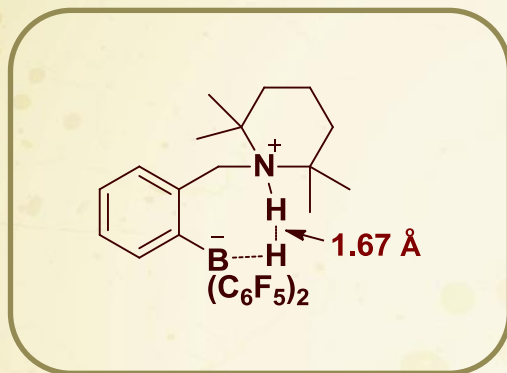
Asymmetric Hydrosilylation/Hydrolysis Sequence



Asymmetric Hydrogenation of Imines



Ammonium/Hydridoborate Zwitterions Characterized by Neutron Diffraction

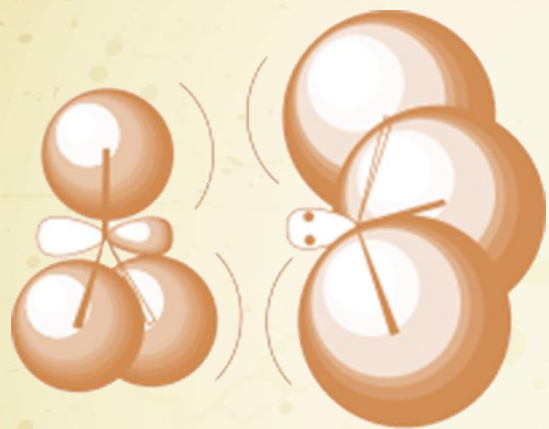


Frustrated Lewis Pairs

The cooperation of active nonquenched Lewis acids and Lewis bases has led to some remarkable discoveries in small-molecule activation.

The heterolytic cleavage of dihydrogen is under very mild conditions, proceeding in many cases with remarkable ease and high reaction rates,

The resulting proton/hydride pair has been transferred to a variety of unsaturated substrates leading to the development of metal-free catalytic hydrogenation.



Thanks for your attention!



Jiang Fanzhou



中国科学院上海有机化学研究所
SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, CAS

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