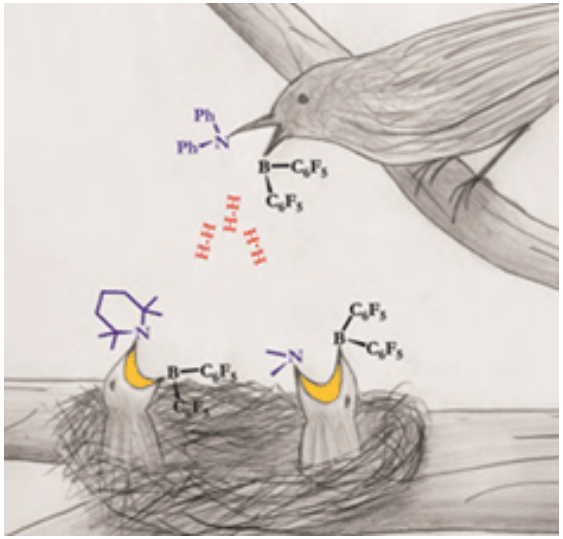
The Chemistry of Frustrated Lewis Pairs



MacMillan Group Meeting

Tracy Liu

4 December 2013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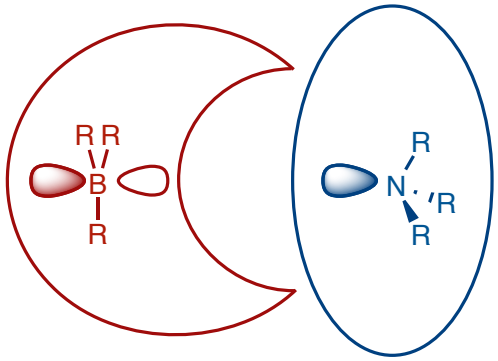
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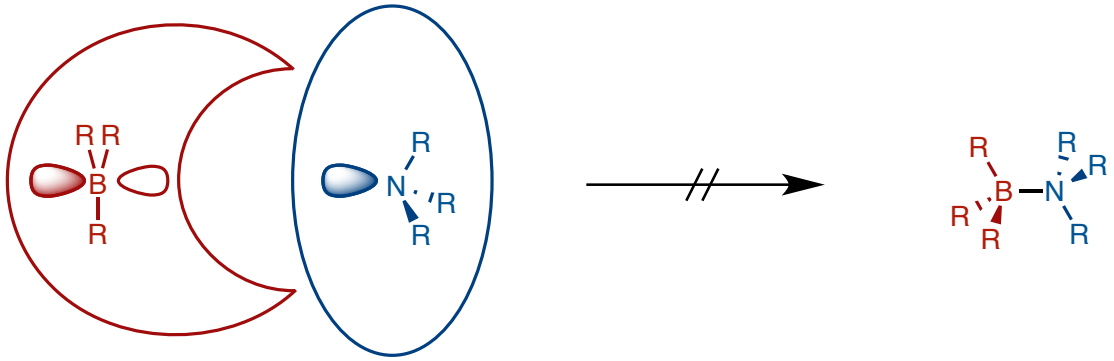
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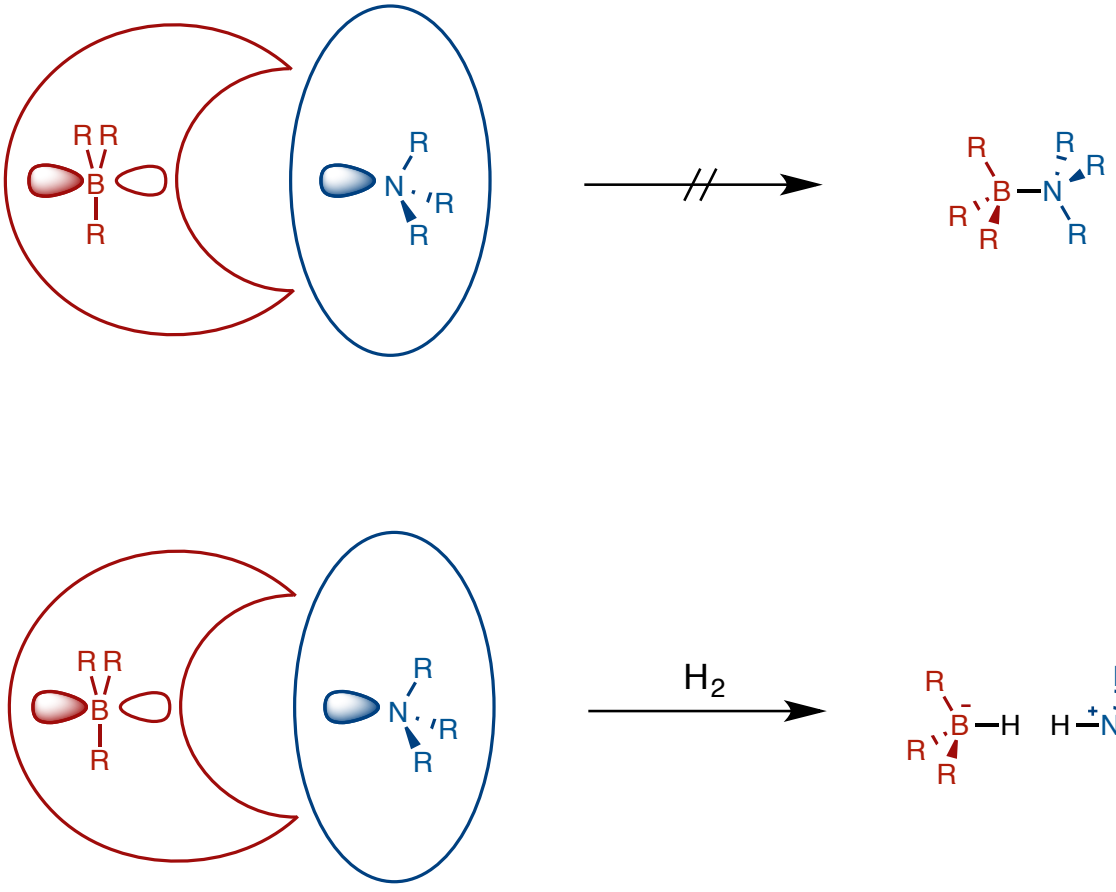
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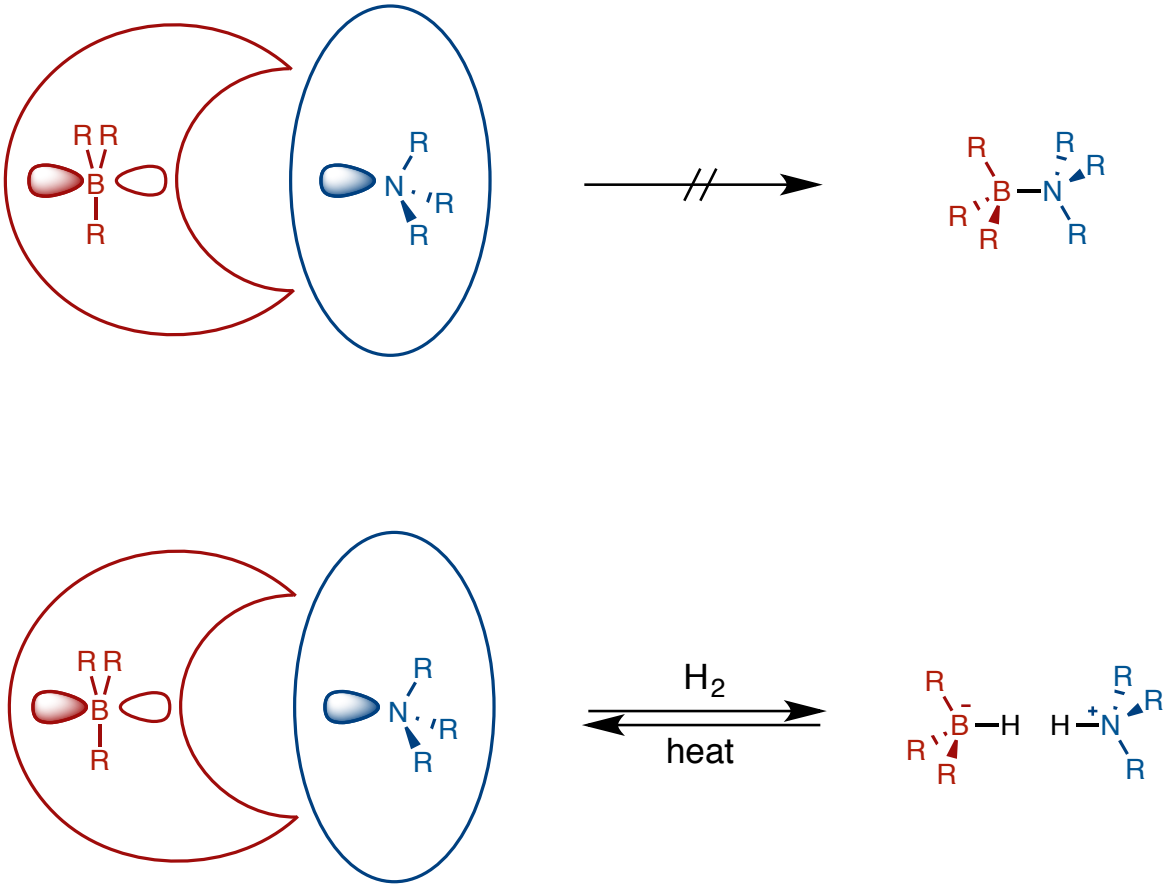
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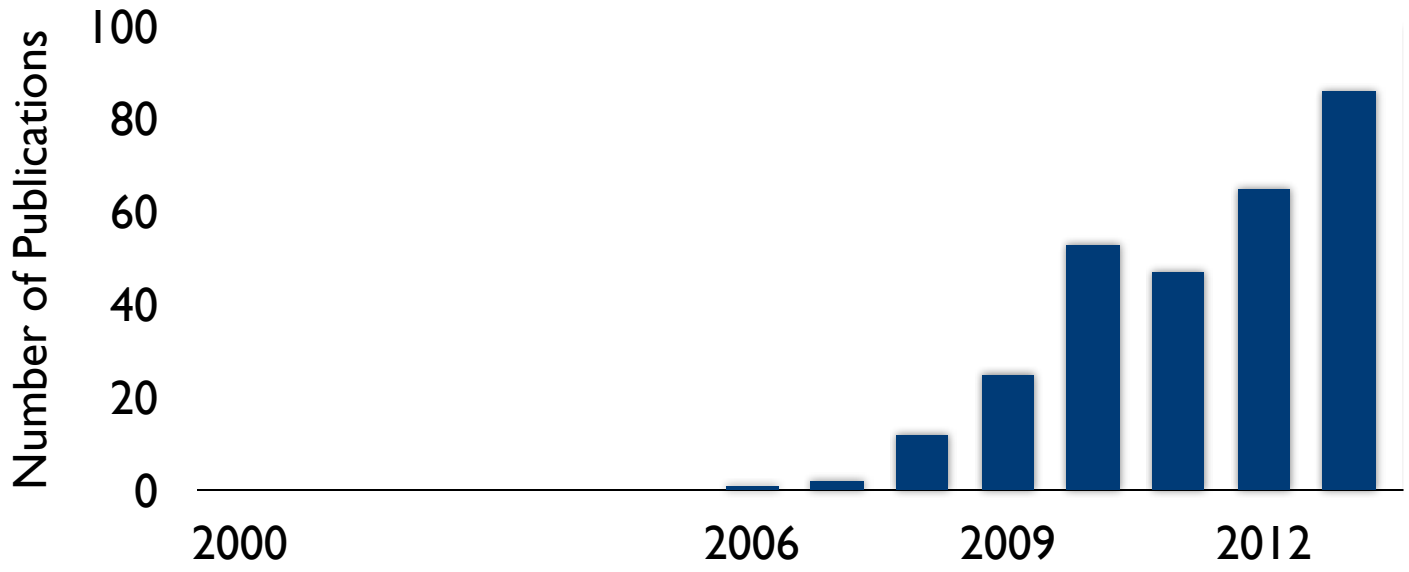
Rapid Emergence of FLP Chemistry



- 289 total publications in FLP chemistry
- Leading Academics:

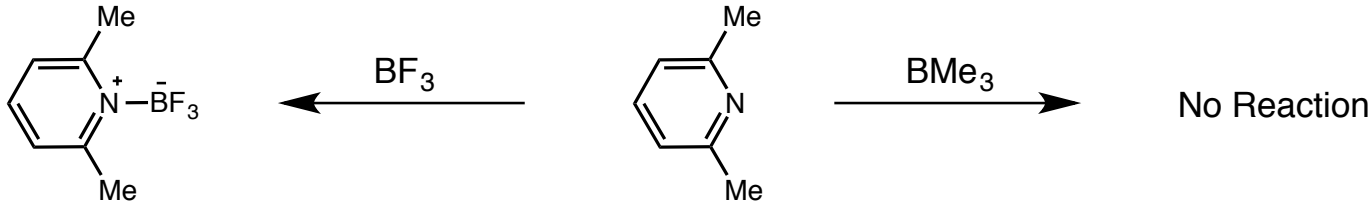
  Douglas W. Stephan, University of Toronto, Canada

  Gerhard Erker, Westfälische Wilhelms-Universität Münster, Germany

  Imre Pápai, Chemical Research Cent. of the Hungarian Acad. of Sciences, Hungary

The Advent of FLP Chemistry

1942 - Brown makes an interesting observation



Brown, H. C.; Schlesinger, H. I. *JACS*, **1942**, *64*, 325-329.

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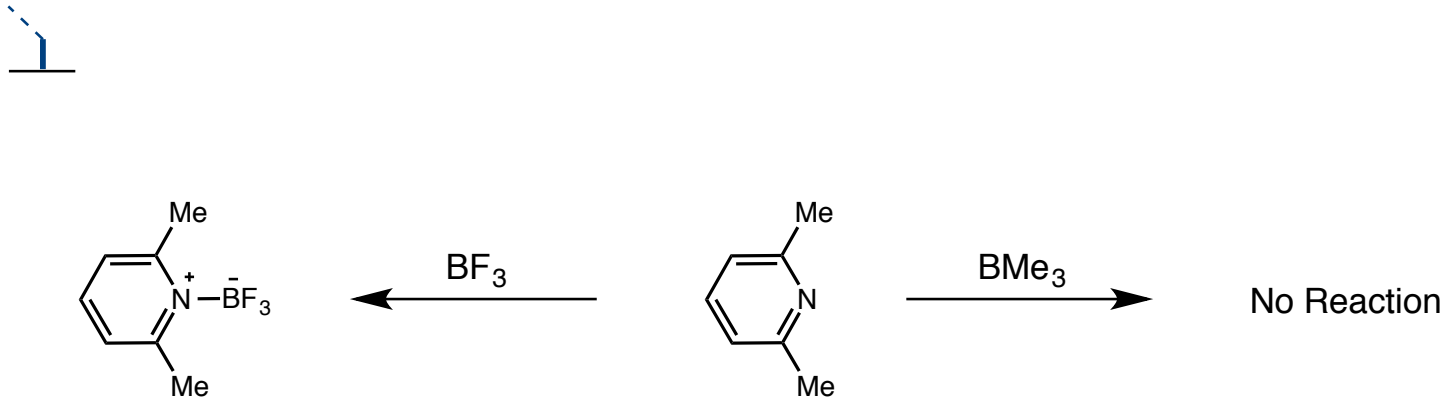

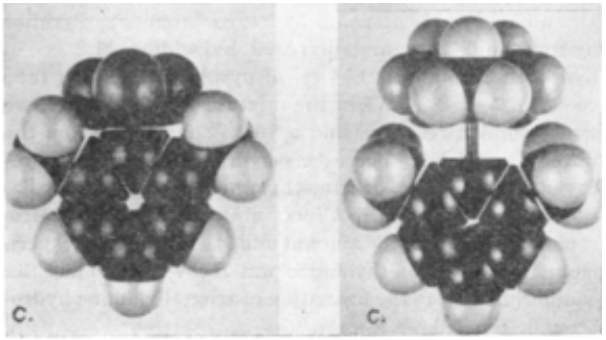

Fig. 1.—Molecular models of the coördination compounds of boron fluoride with (a) trimethylamine, (b) pyridine and (c) α,α′-lutidine.

Fig. 2.—Molecular models of the coördination compounds of trimethylboron with (a) trimethylamine, (b) pyridine and (c) α,α′-lutidine.

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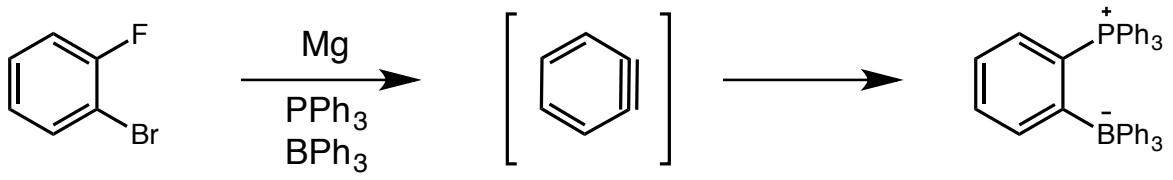

No formation of classical Lewis Acid/Base adduct

Wittig, G.; Benz, E. *Chem. Ber.*, **1959**, *92*, 1999-2013.

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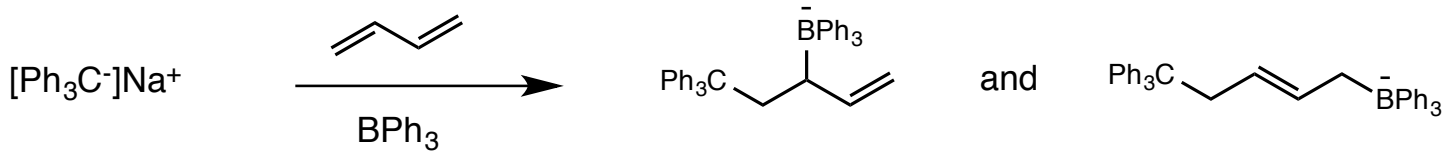

no observation of polybutadiene

Tochtermann, W. *ACIE*, **1966**, *5*, 351-371.

The Advent of FLP Chemistry

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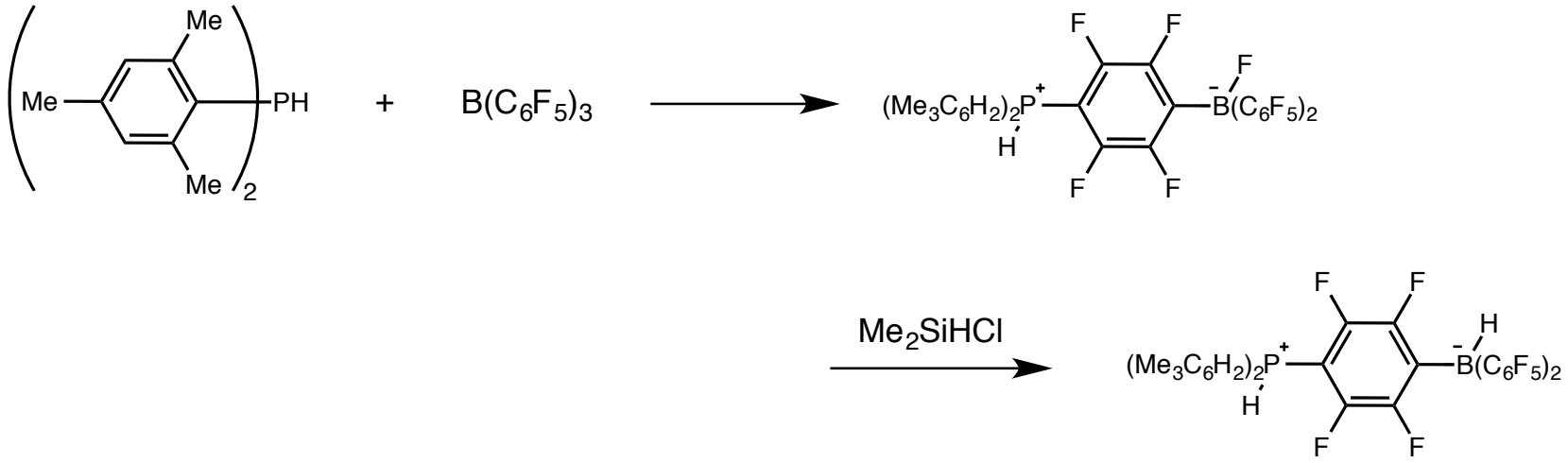

Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science*, **2006**, *314*, 1124-1126.

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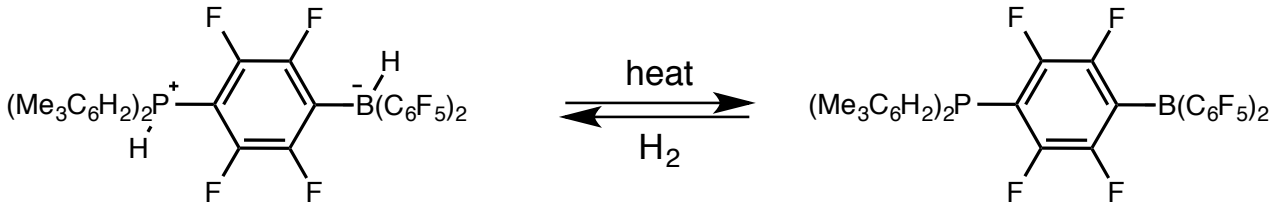

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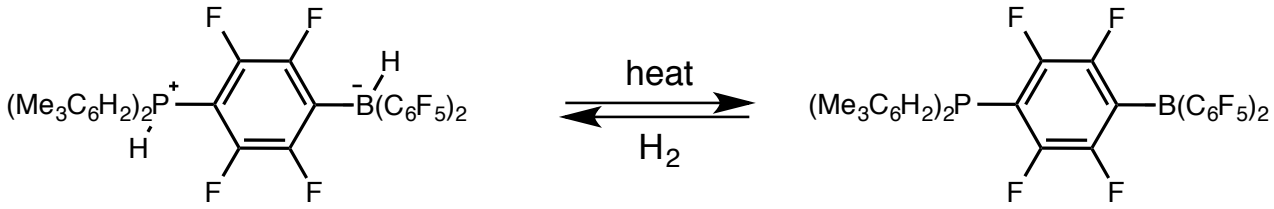

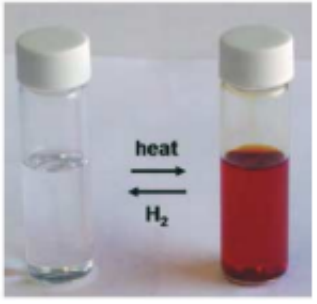

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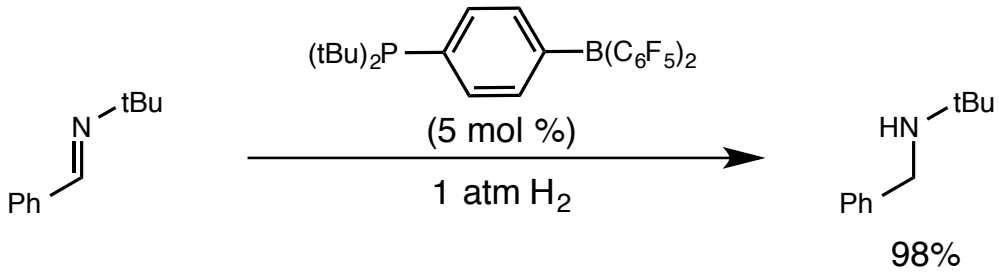
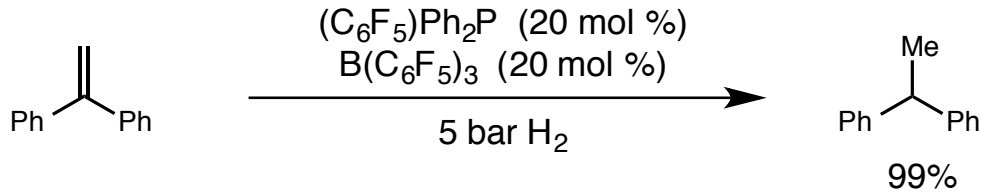
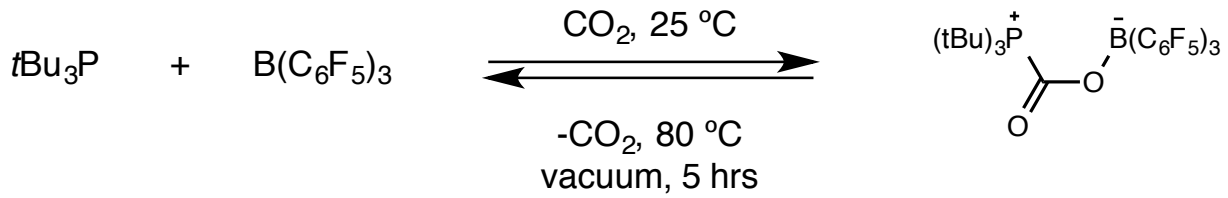




Chase, P.A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

Greb, L.; Ona-Burgos, P.; Schirmer, B.; Grimme, S.; Stephan, D. W.; Paradies, J. *ACIE*, **2012**, *51*, 10164-10168.

The Advent of FLP Chemistry



Mömming, C. M.; Otten, E.; Kehr, G.; Frölich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *ACIE*, **2009**, *48*, 6643-6646.

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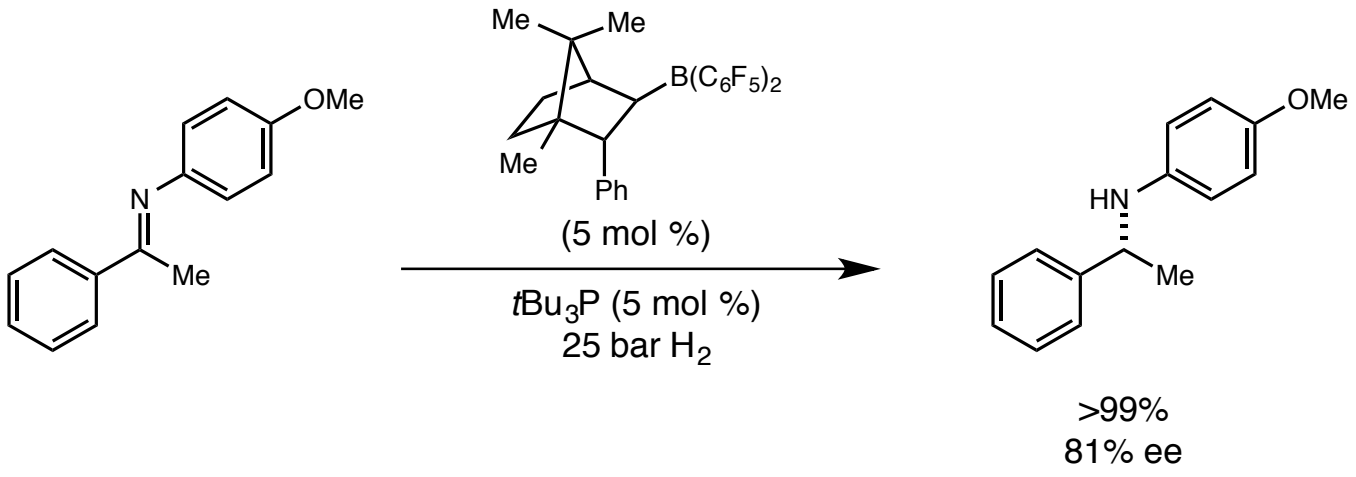
2006 - Stephan finds FLPs can reversibly split H_2

2007 - FLPs catalytically perform hydrogenations

2008 - FLPs reversibly bind CO_2

2010 - Asymmetric hydrogenation of imines with FLPs



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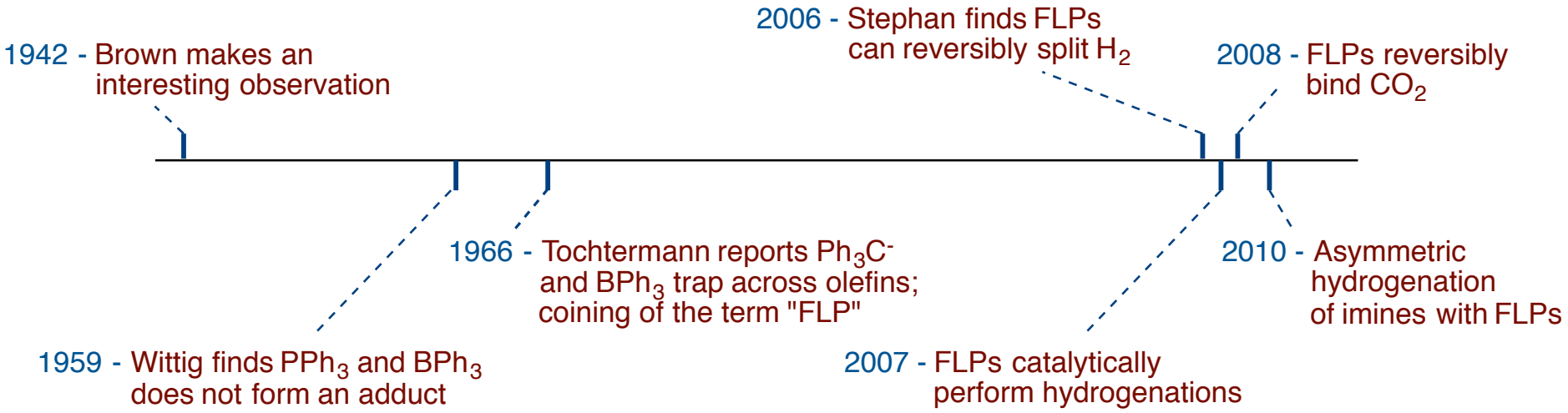
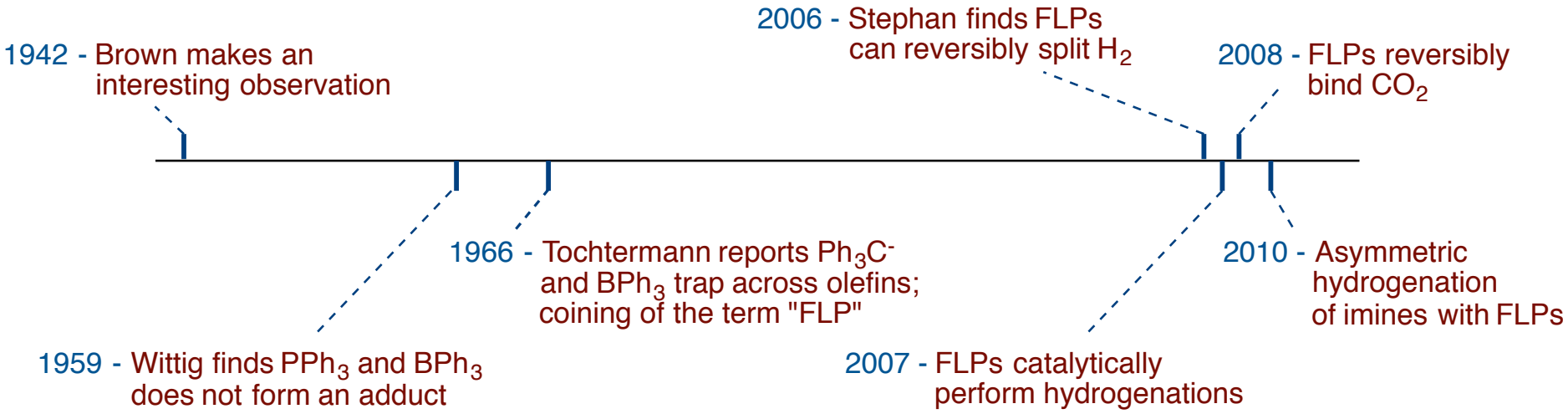
Chen, D.; Wang, Y.; Klankermeyer, J. *ACIE*, **2010**, *49*, 9475-9578.

The Advent of FLP Chemistry



- I. Theories on the Mechanism of H_2 Activation
- II. Applications of FLPs in Hydrogenation Reactions and Storage of Small Molecules

The Advent of FLP Chemistry



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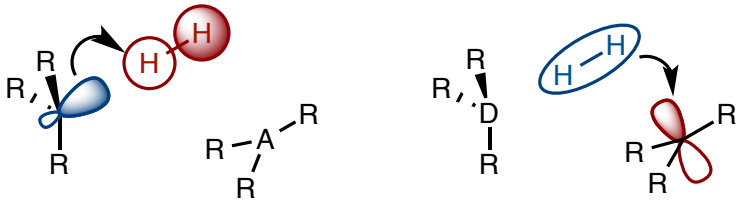
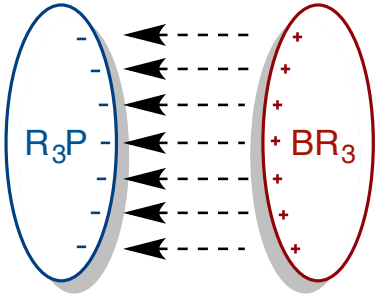
Two Competing Models on the Mechanism of H_2 Activation



D → σ* donation

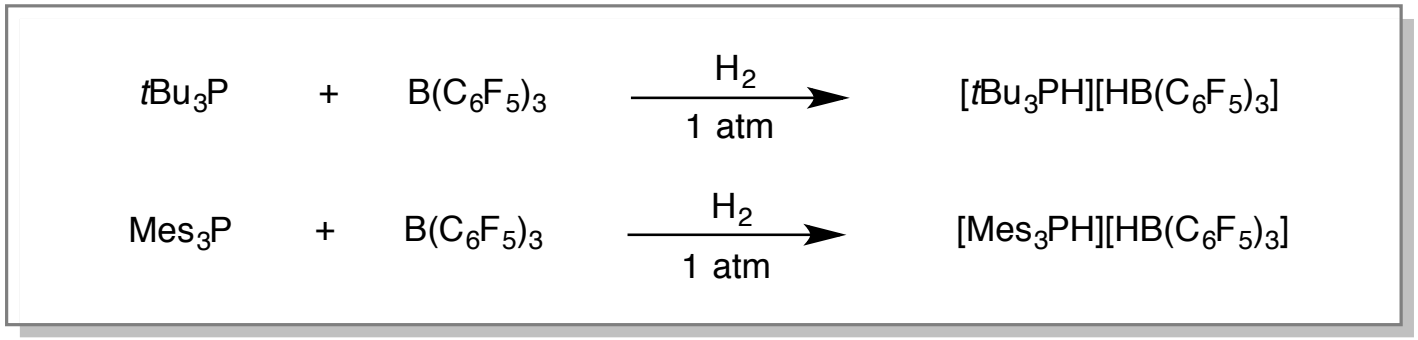
σ → A donation

Electron Transfer Model



Electric Field Model

Initial Hypotheses on the Mechanism of H_2 Activation



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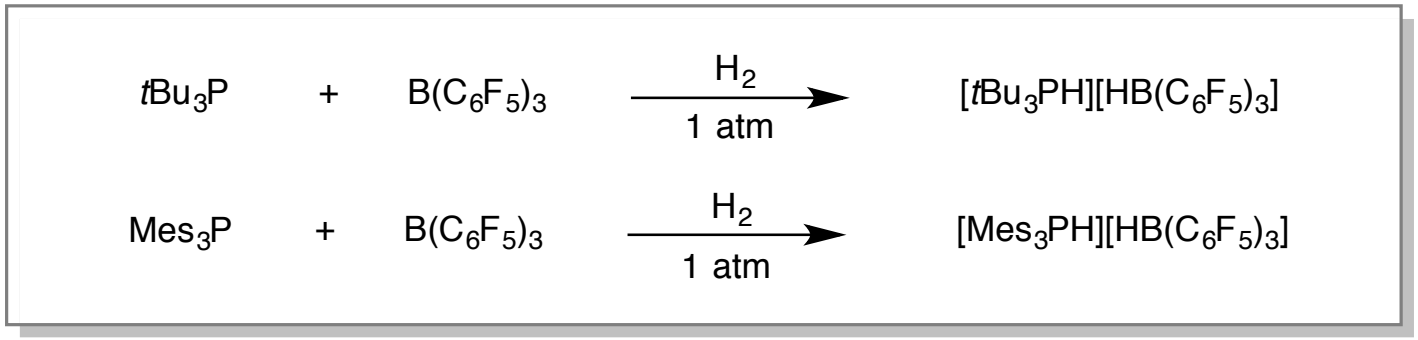

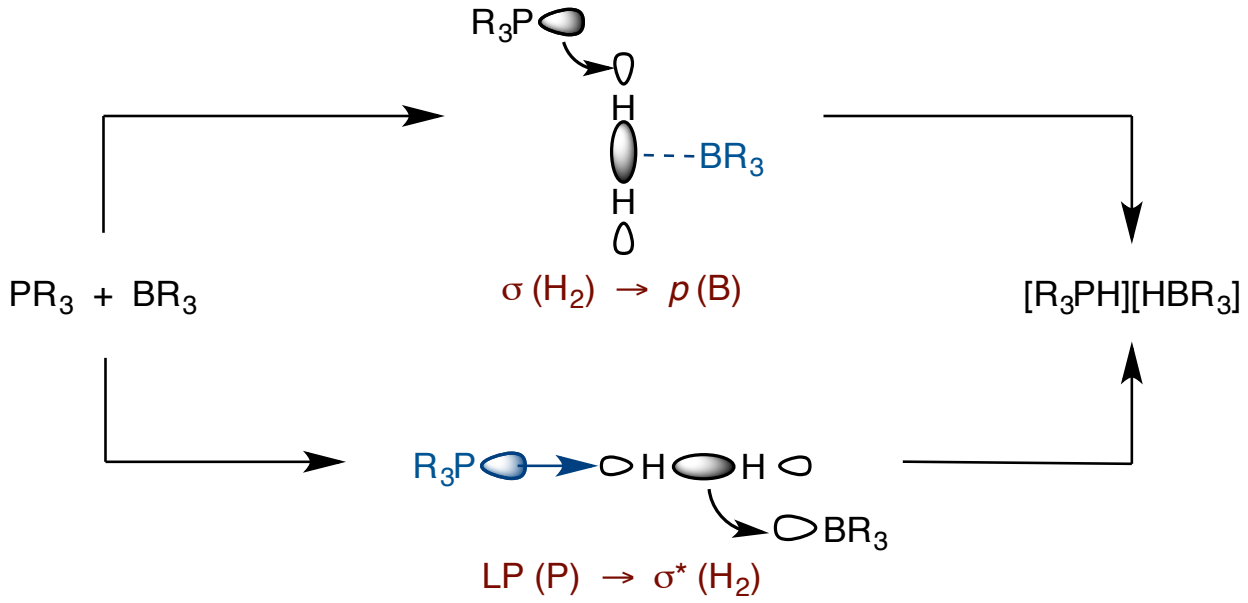

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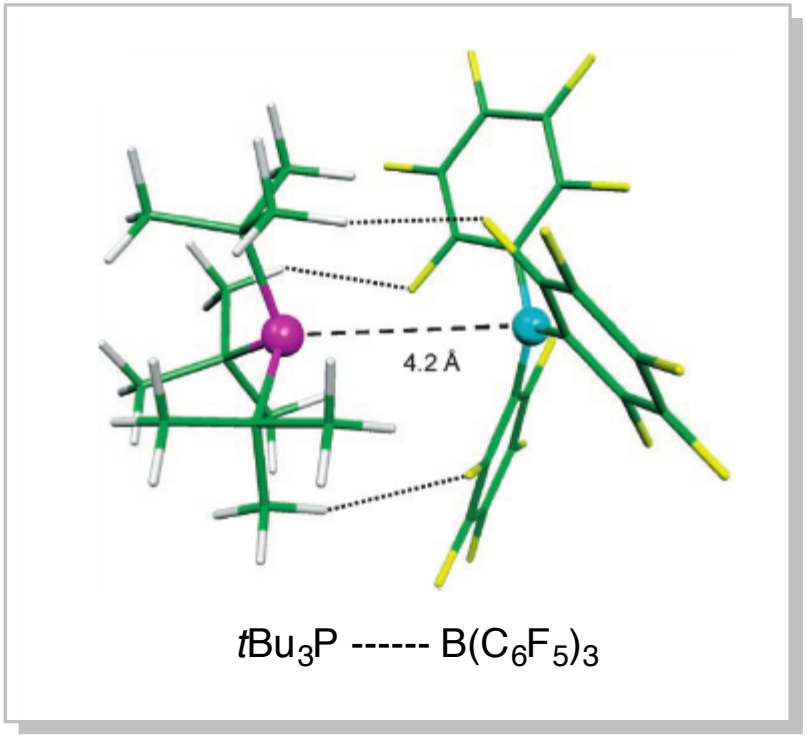
First DFT Study on the Mechanism of H_2 Activation



tBu_3P ------ $B(C_6F_5)_3$

- Multiple H-bonds between C–H---F groups give rise to a preorganized complex
- Non-directional dispersion forces between *t*Bu and C_6F_5 groups render the complex flexible

Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *ACIE*, **2008**, *120*, 2469-2472.

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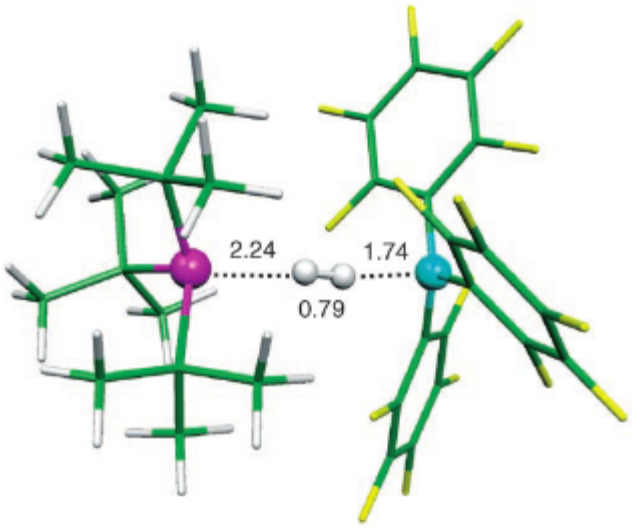

tBu_3P --- H–H --- $B(C_6F_5)_3$

- Located T.S. features a nearly linear P–H–H–B axis
- H_2 bond elongated from 0.74 A to 0.79 A indicative of an early T.S.
- 10.4 kcal/mol higher than t*B*u_3P---$B(C_6F_5)_3$ + H_2

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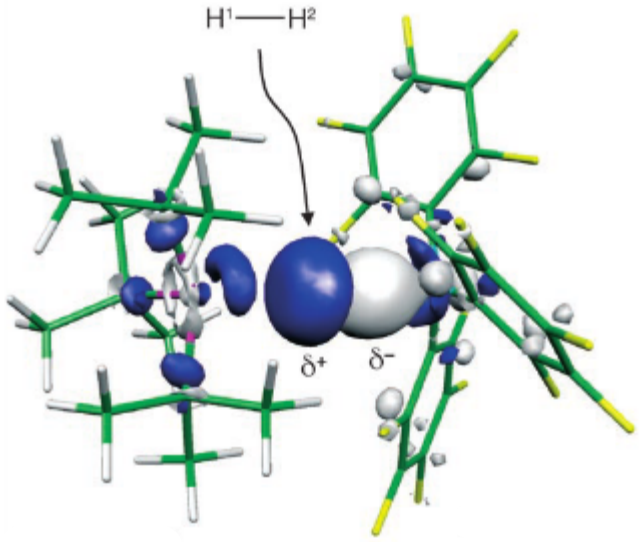


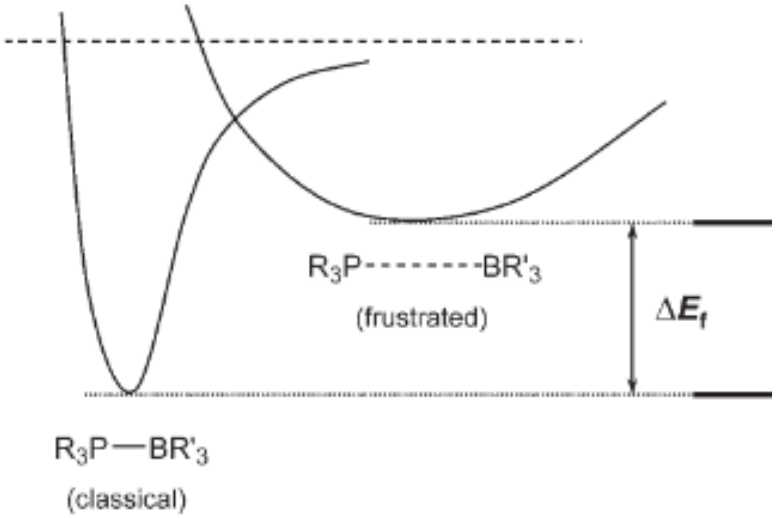
tBu_3P --- H–H --- $B(C_6F_5)_3$

- Discovered significant H_2 polarization
- Electron transfer proceeds via simultaneous *t*$Bu_3P \rightarrow \sigma*(H_2)$ and $\sigma(H_2) \rightarrow B(C_6F_5)_3$ donation

Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *ACIE*, **2008**, *120*, 2469-2472.

First DFT Study on the Mechanism of H_2 Activation

The Electron Transfer Model



- Non-bonding interactions between bulky substituents lead to a higher E frustrated complex

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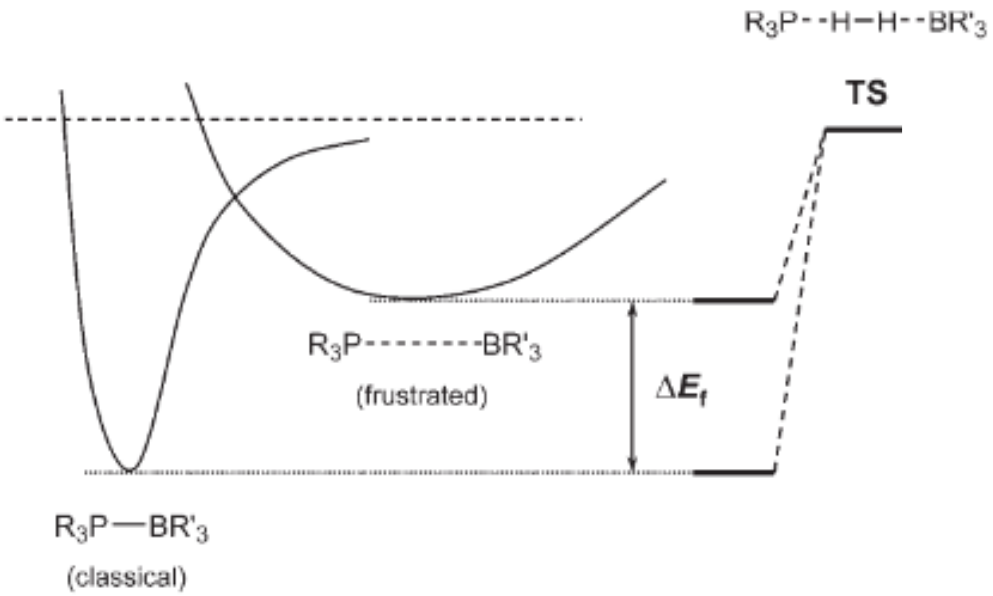

- Non-bonding interactions between bulky substituents lead to a higher E frustrated complex
- Frustration energy, ΔE_t, decreases the activation energy and renders hydrogen splitting facile and highly exothermic via reactant state destabilization

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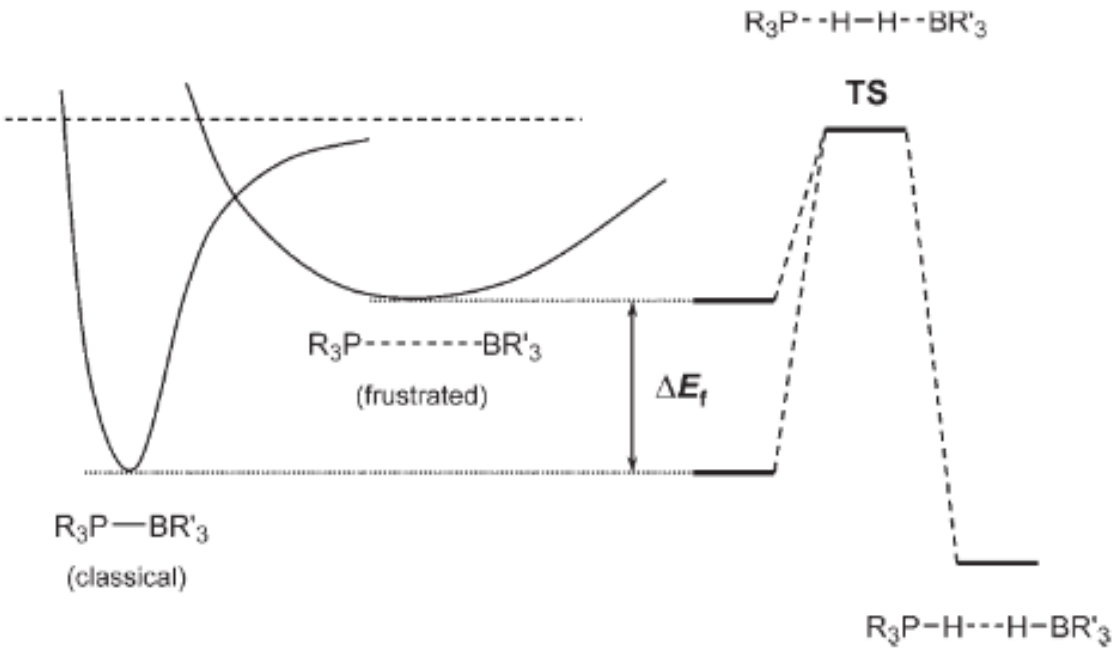

- Non-bonding interactions between bulky substituents lead to a higher E frustrated complex
- Frustration energy, ΔE_t, decreases the activation energy and renders hydrogen splitting facile and highly exothermic via reactant state destabilization
- Non-bonding interactions between bulky substituents stabilizes both the T.S. and product

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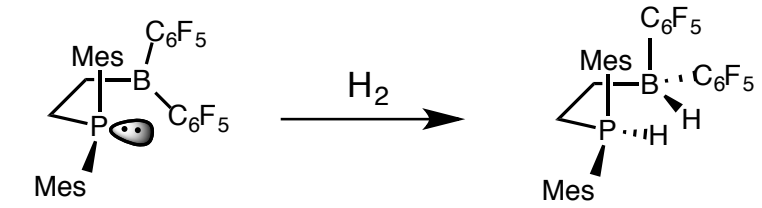
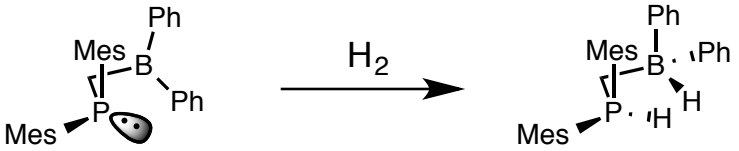
An Alternative Mechanism of H_2 Activation



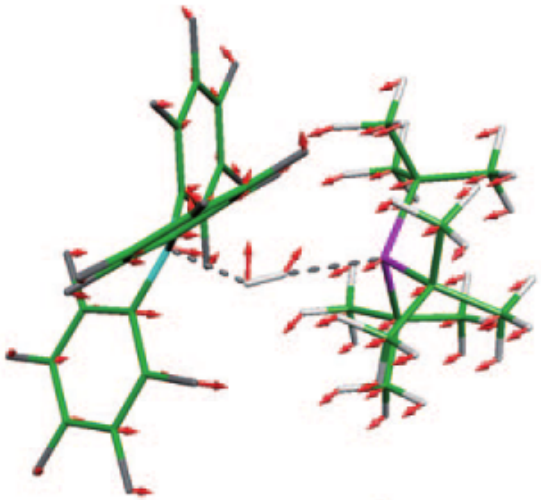


Linear T.S. not possible for certain tethered FLPs

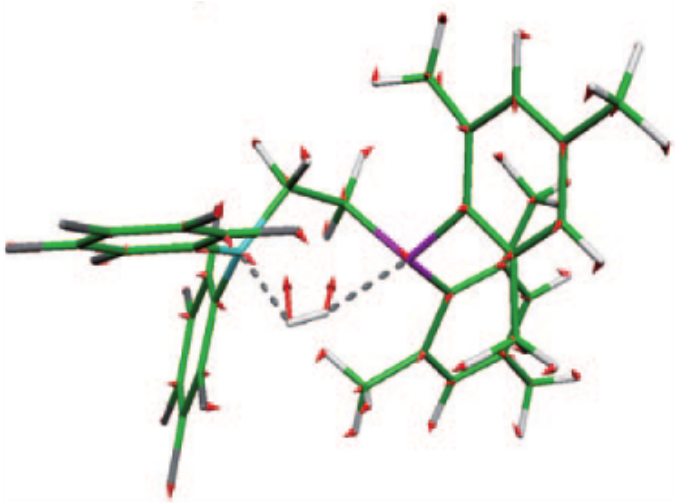
Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

Calculated T.S. employing a dispersion corrected DFT model:



$(C_6F_5)_3B$ ---- P*t*Bu$_3$ + H_2

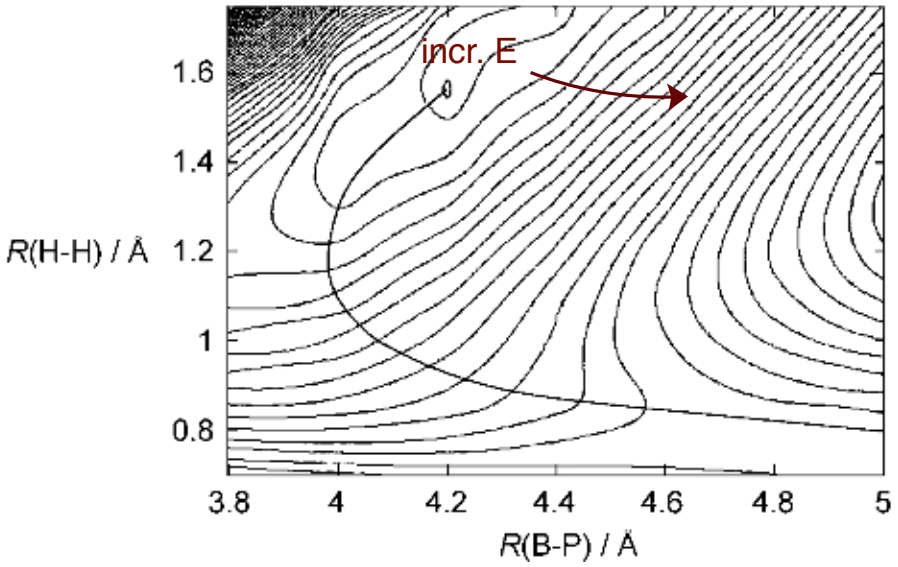


$(C_6F_5)_2B$ PMes$_2$ + H_2

Calculated T.S. do not have a linear relationship along P–H–H–B axis

Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation



2 kcal/mol between each line

2-D potential E surface for tBu$_3$P + B(C$_6$F$_5$)$_3$ system

Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

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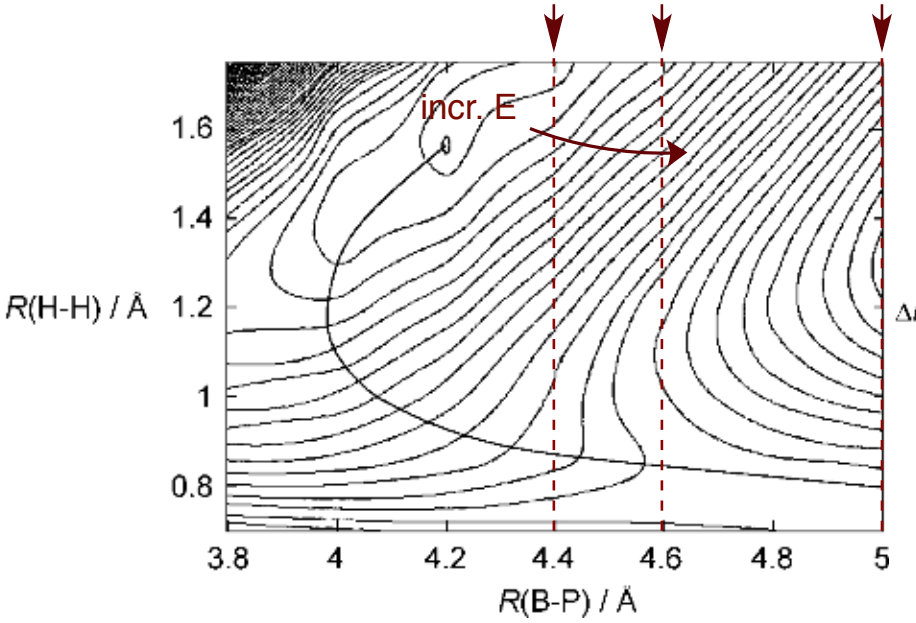

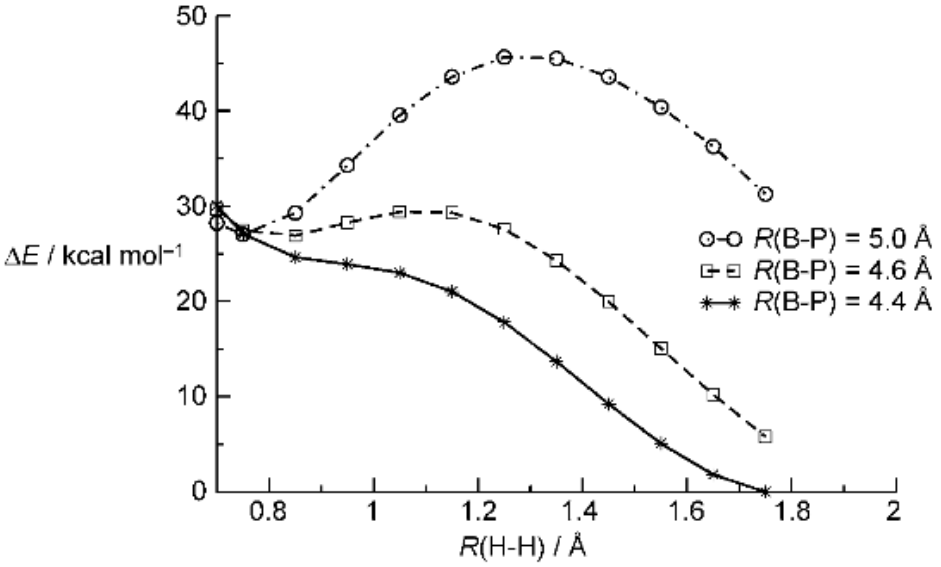

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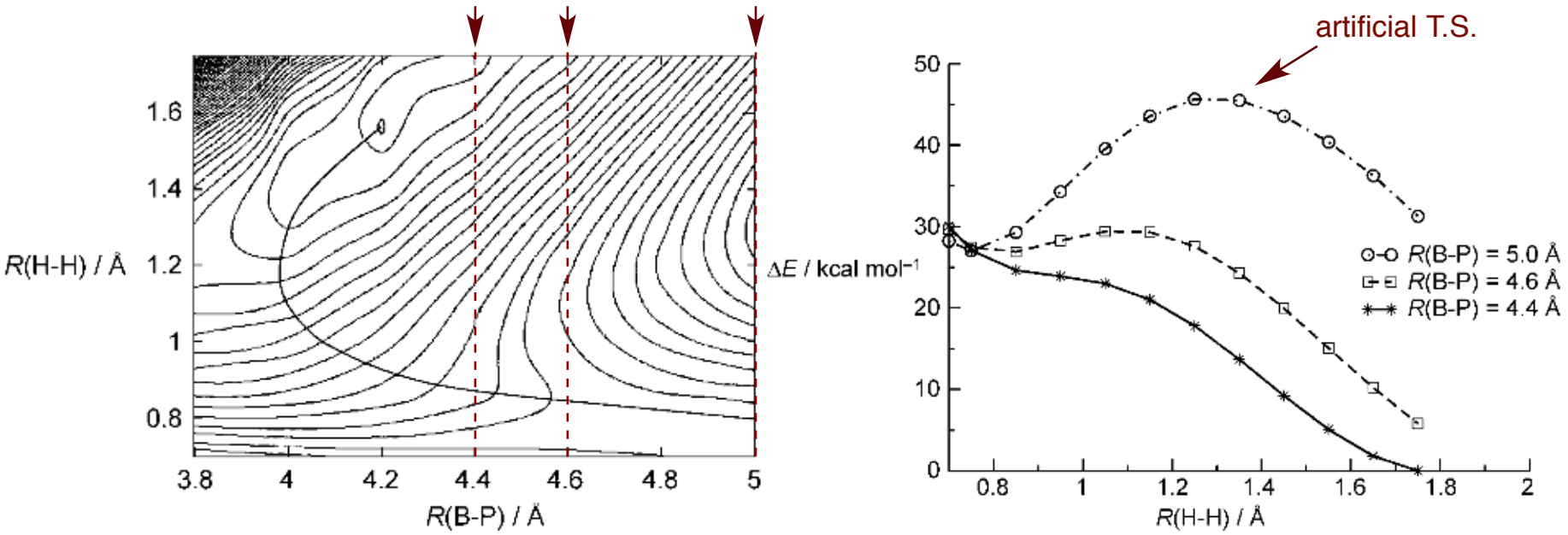
Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

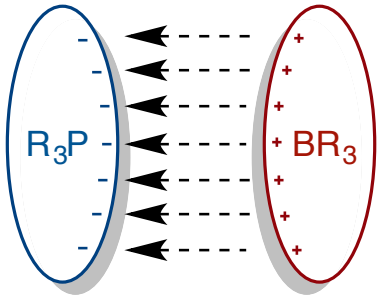


Pápai's non-dispersion corrected DFT model overestimated the P–B bond distance resulting in a T.S. that is otherwise not present

Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

The Electric Field Model



- Neglect the FLP as a molecular species and replace it by an electric field
- Polarization from electric field generated in the interior of the FLP cavity allows for H_2 splitting

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An Alternative Mechanism of H_2 Activation

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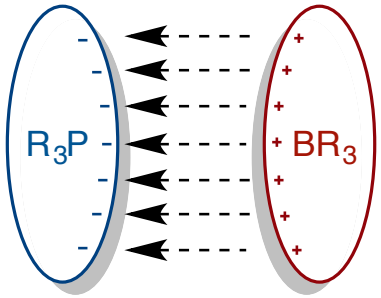

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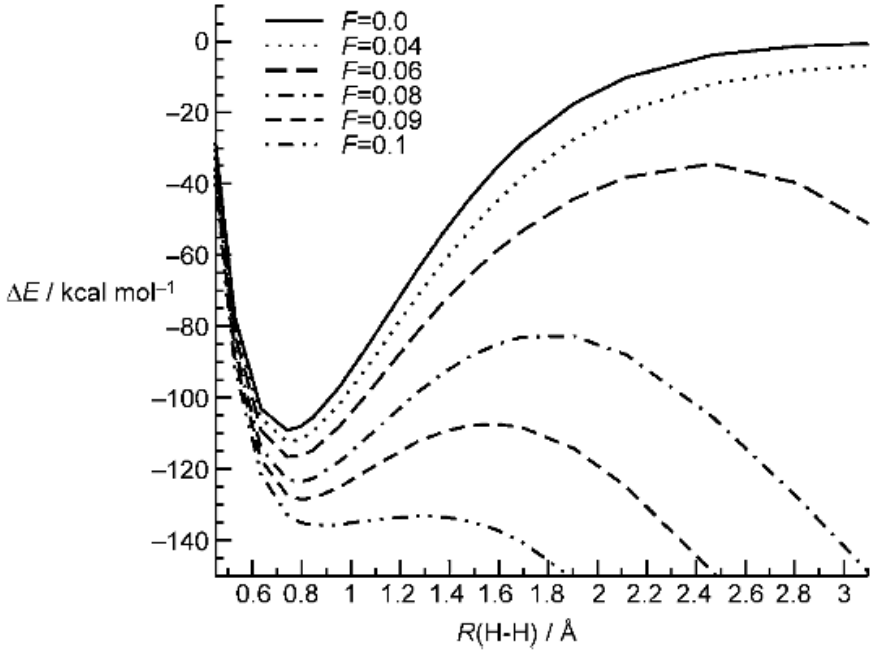


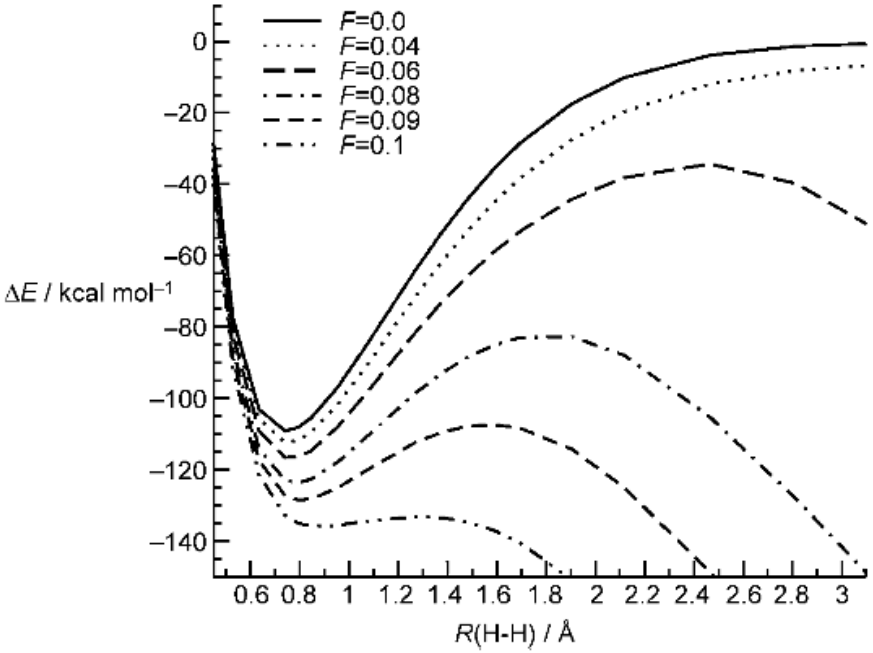
F = Electric field strength (a.u.)
(1 a.u. = 5.1422×10^{11} Vm^{-1})

Critical field strength needed for H_2 splitting is 0.05 – 0.06 a.u.

Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

The Electric Field Model



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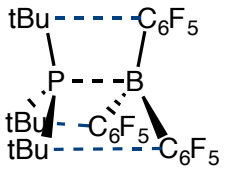
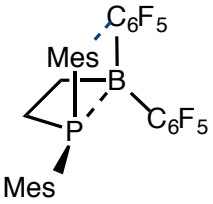


0.04 - 0.06 a.u.



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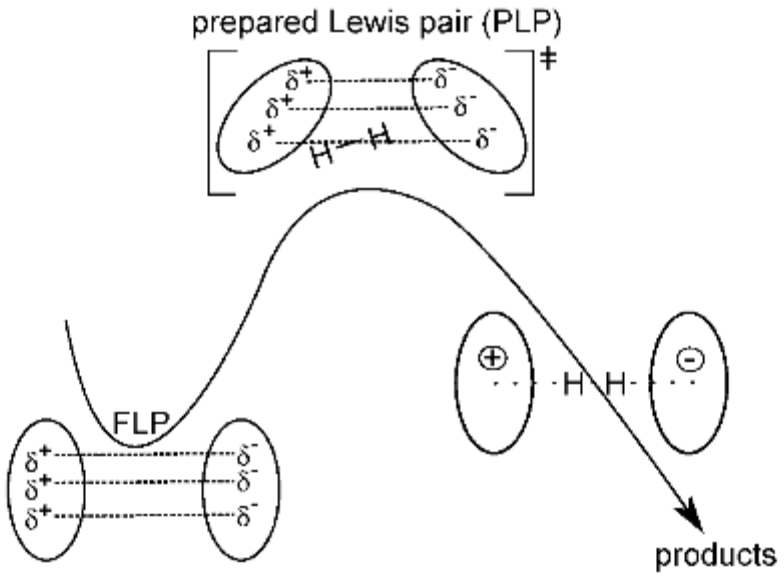
Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

The Electric Field Model

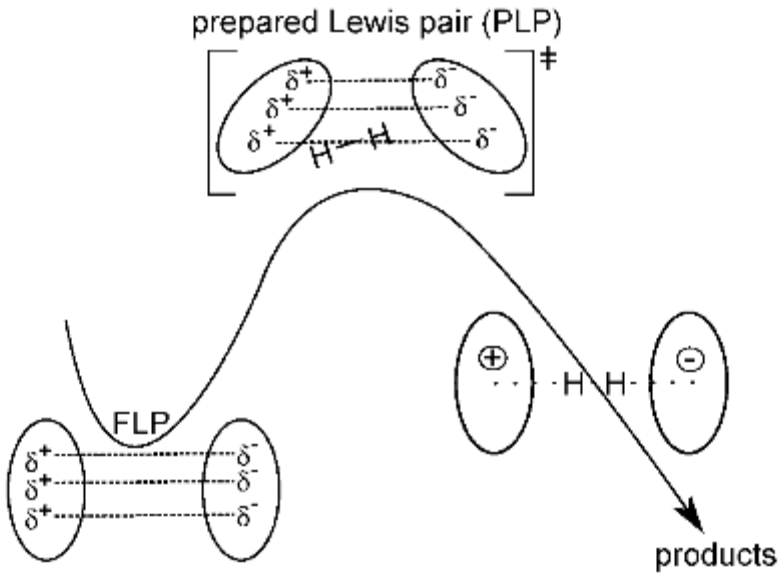


- H-bonding interactions form the FLP while non-directional dispersion forces instill flexibility allowing H_2 entry – termed the "preparation step"

Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

The Electric Field Model



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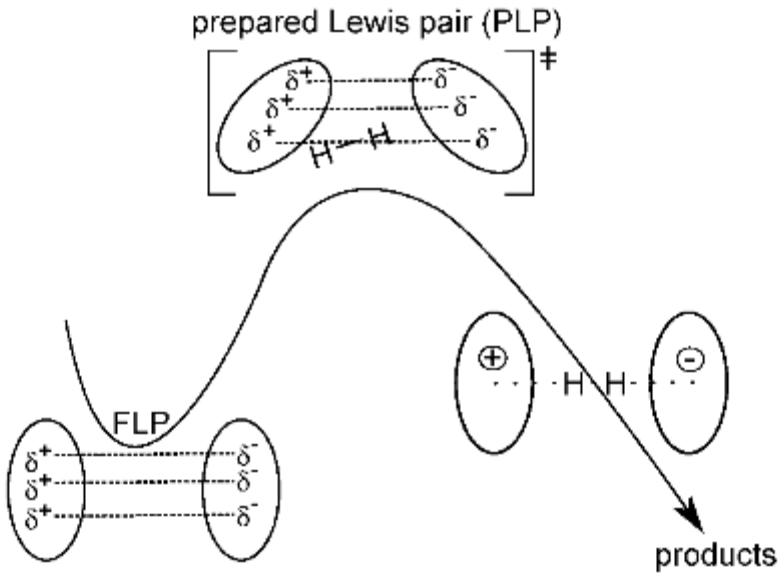
Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

An Alternative Mechanism of H_2 Activation

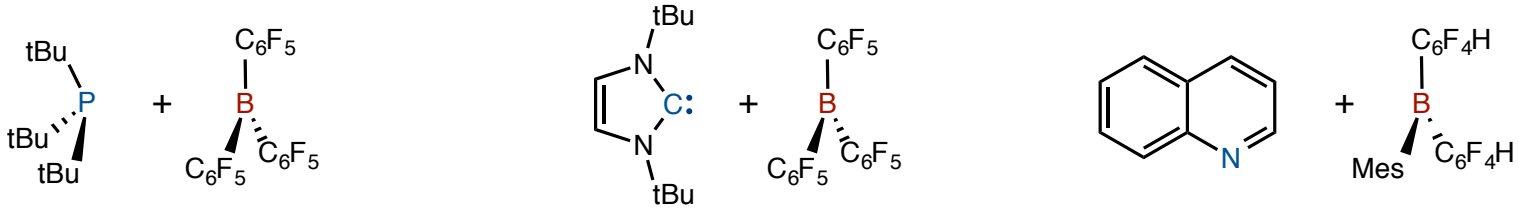
The Electric Field Model



- H-bonding interactions form the FLP while non-directional dispersion forces instill flexibility allowing H_2 entry – termed the "preparation step"
- Activation energy is the "preparation step"; after entrance H_2 splitting is barrierless
- No molecular orbitals arguments invoked; believe this accounts for the similar reactivity of chemically different FLPs

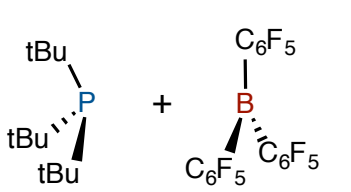
Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.

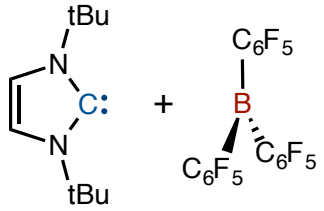
The Electron Transfer Model Revisited

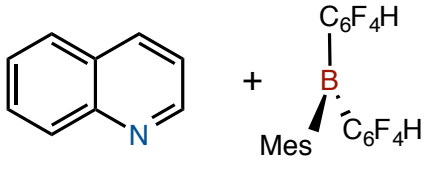


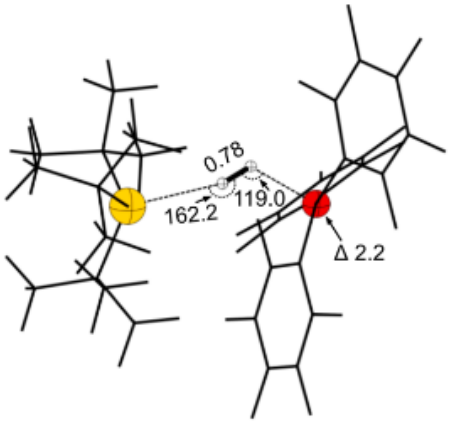
Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *JACS*, **2013**, *135*, 4425-4437.

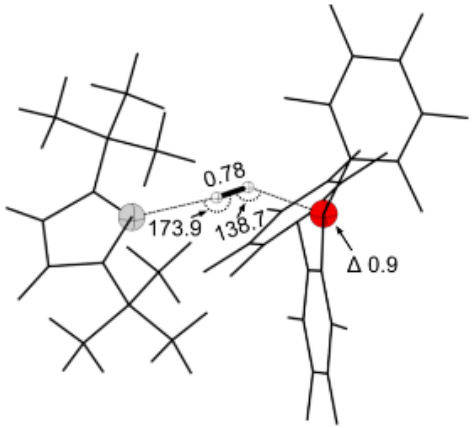
The Electron Transfer Model Revisited

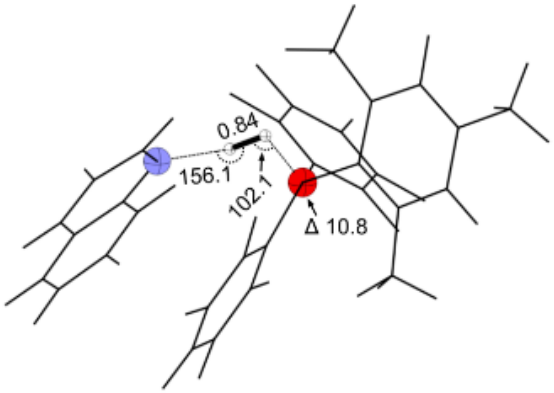












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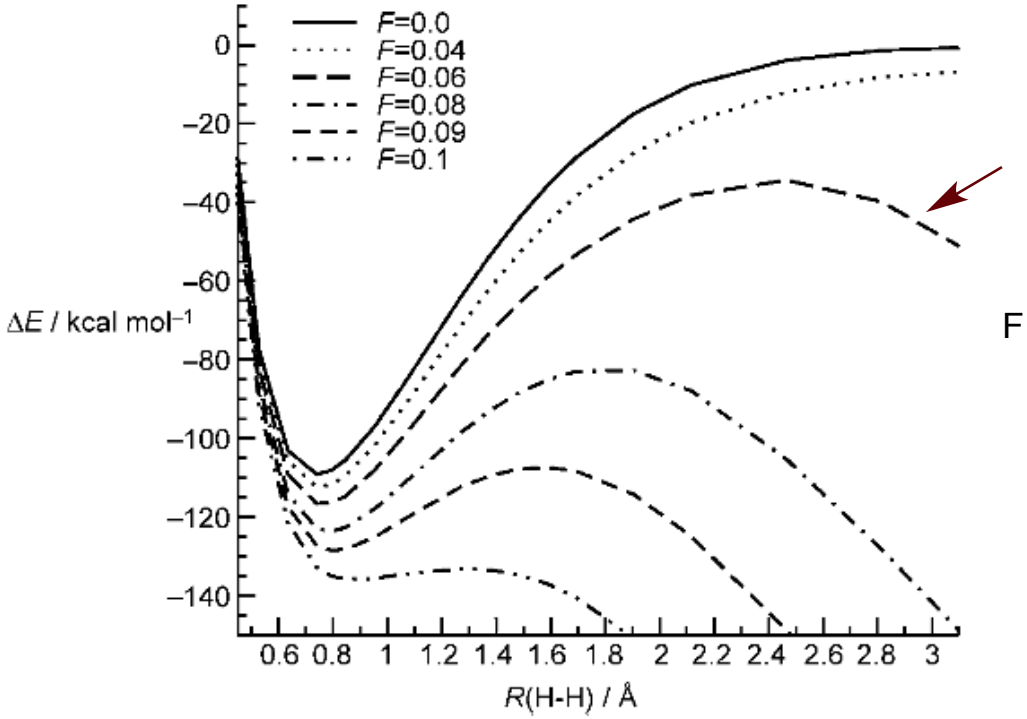
The Electron Transfer Model Revisited



F = Electric field strength (a.u.)
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- At the "critical field" of 0.06 a.u., the activation energy is 75 kcal/mol

Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.
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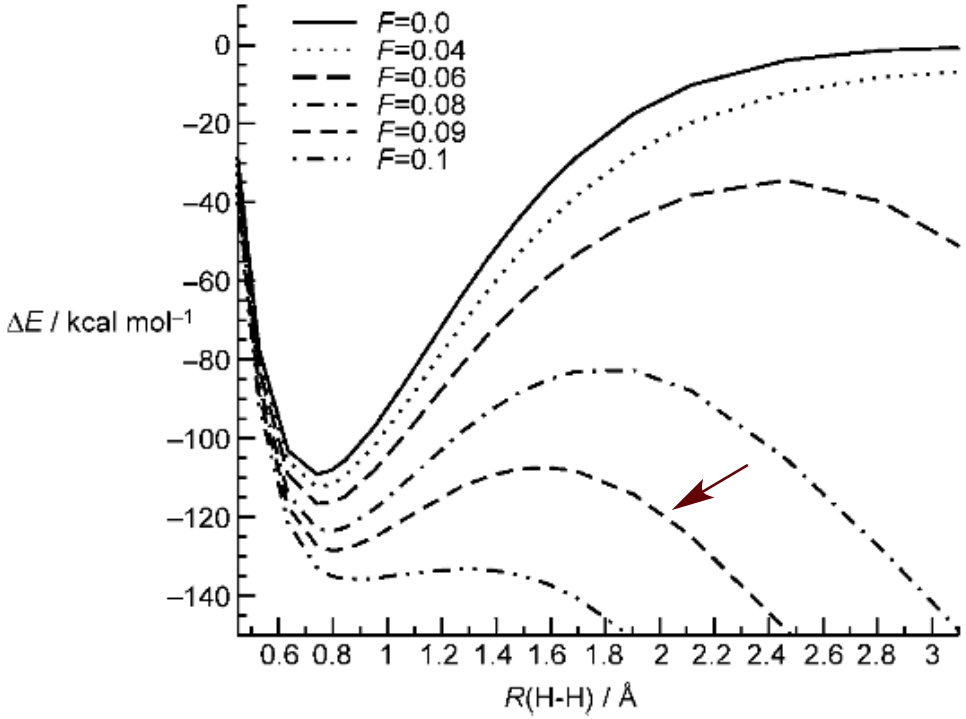
The Electron Transfer Model Revisited



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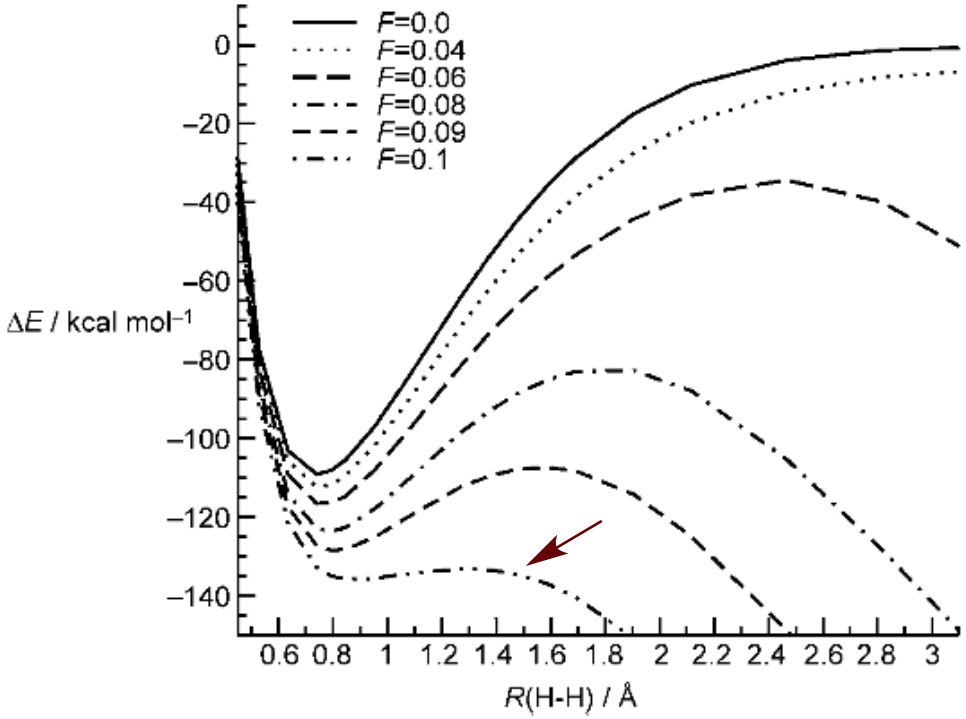
The Electron Transfer Model Revisited



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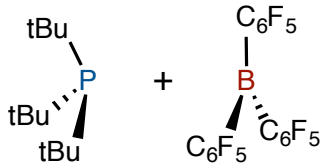
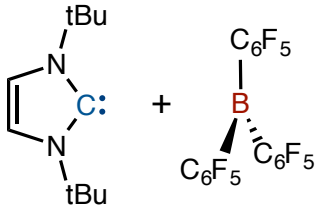
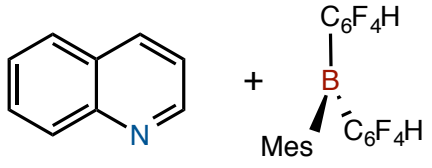
- Only at higher electric fields, 0.09 a.u. and above, does the activation energy lower to a reasonable range (20 kcal/mol or lower)
- Only at field strengths above 0.1 a.u., does H_2 splitting become "barrierless"

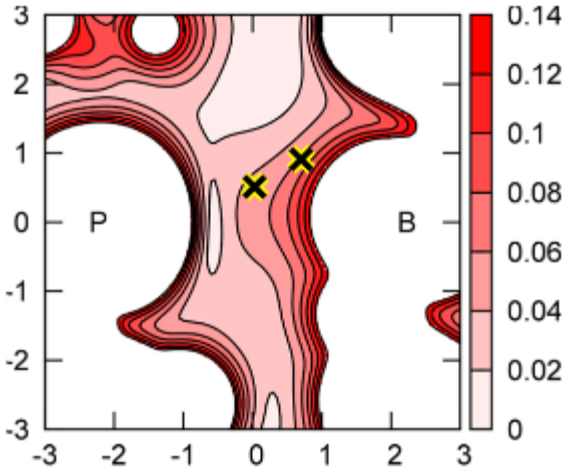
Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *ACIE*, **2010**, *49*, 1402-1405.
Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *JACS*, **2013**, *135*, 4425-4437.

The Electron Transfer Model Revisited









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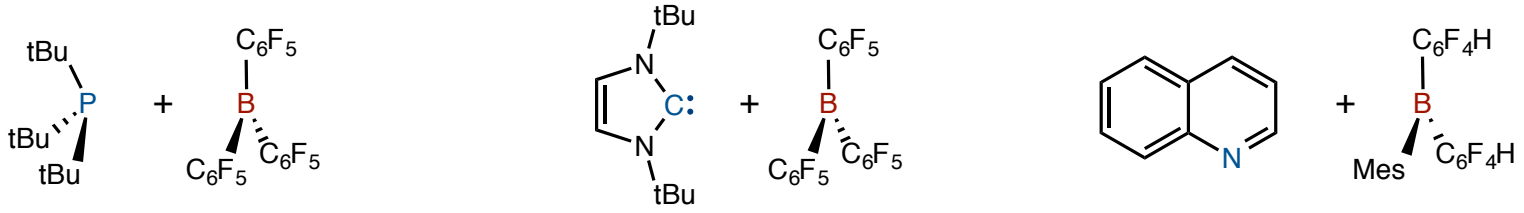
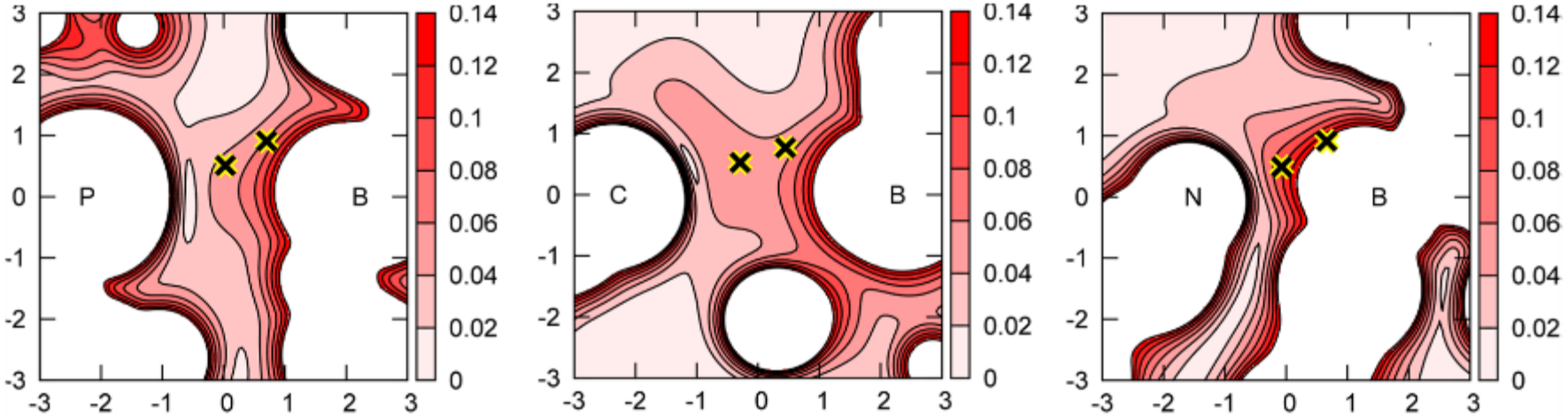
The Electron Transfer Model Revisited





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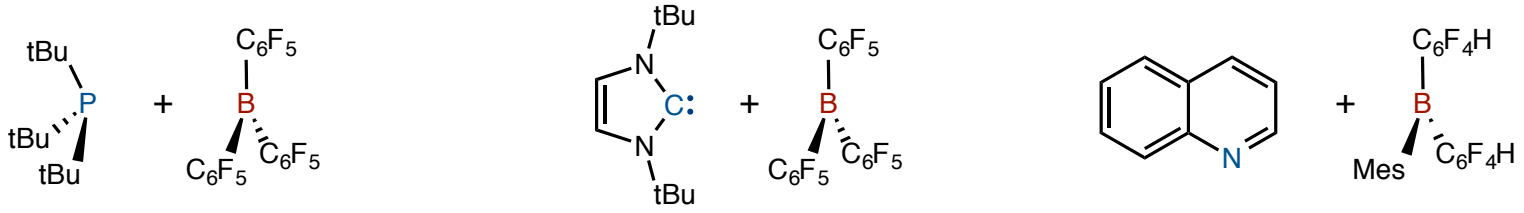
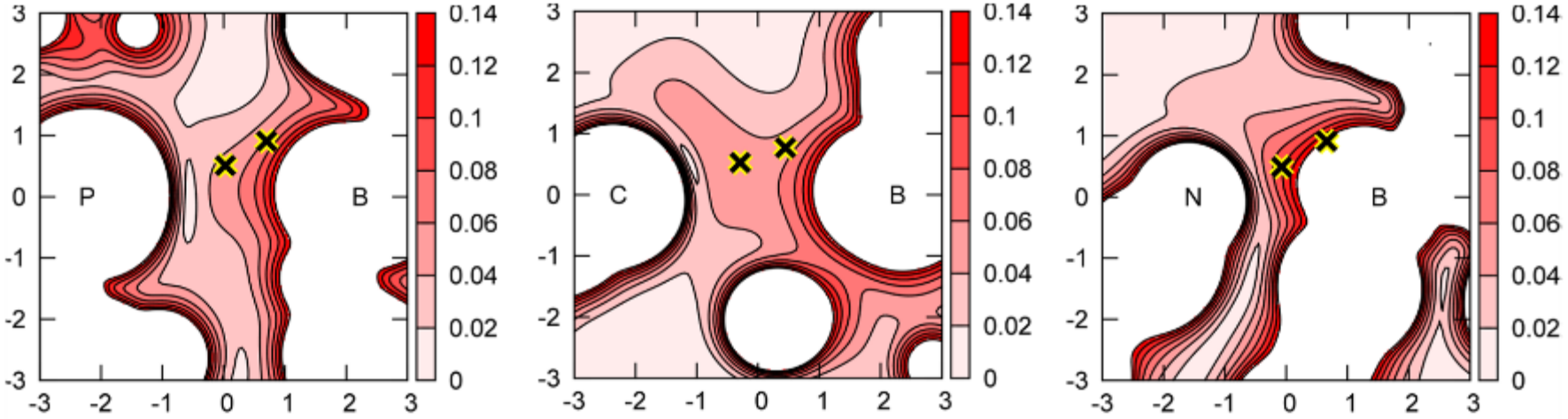
The Electron Transfer Model Revisited

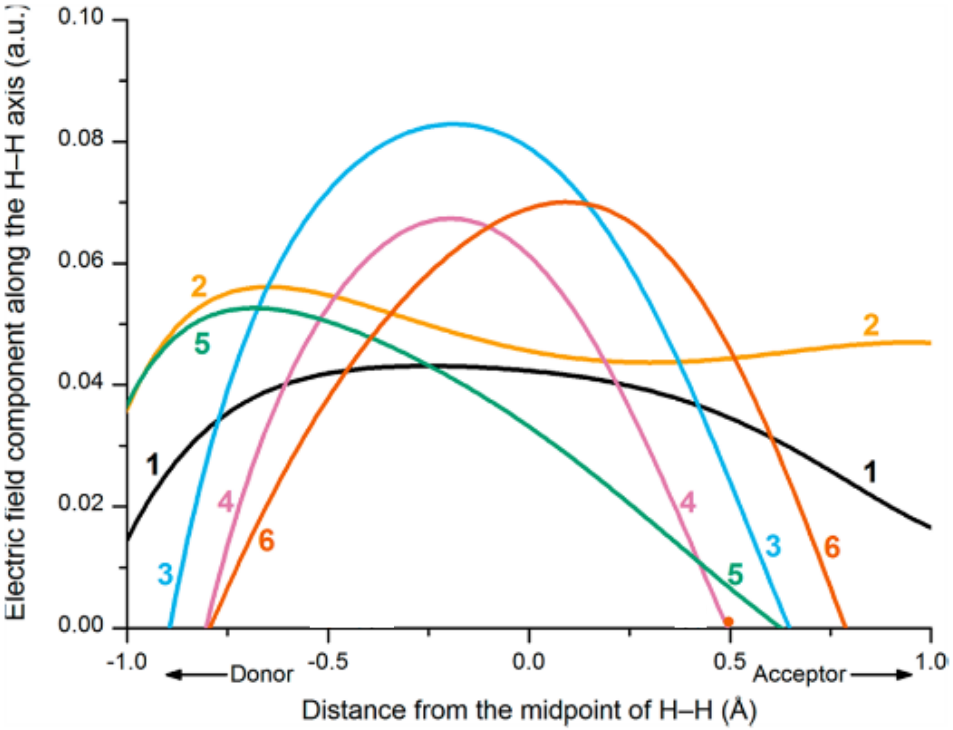


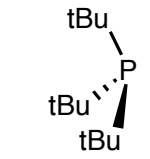


EFs within FLP cavities are not homogeneous and are not always strong enough to effect H_2 splitting

Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *JACS*, **2013**, *135*, 4425-4437.

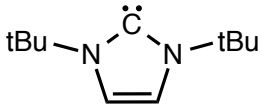
The Electron Transfer Model Revisited





+ $B(C_6F_5)_3$

1



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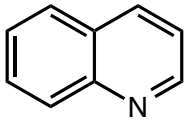
2



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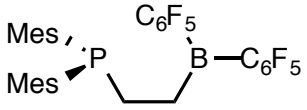
3



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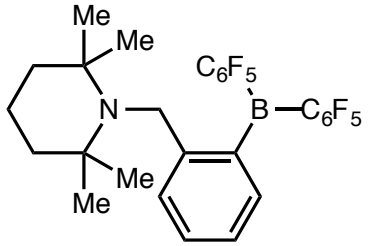
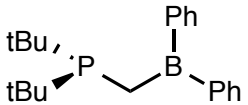


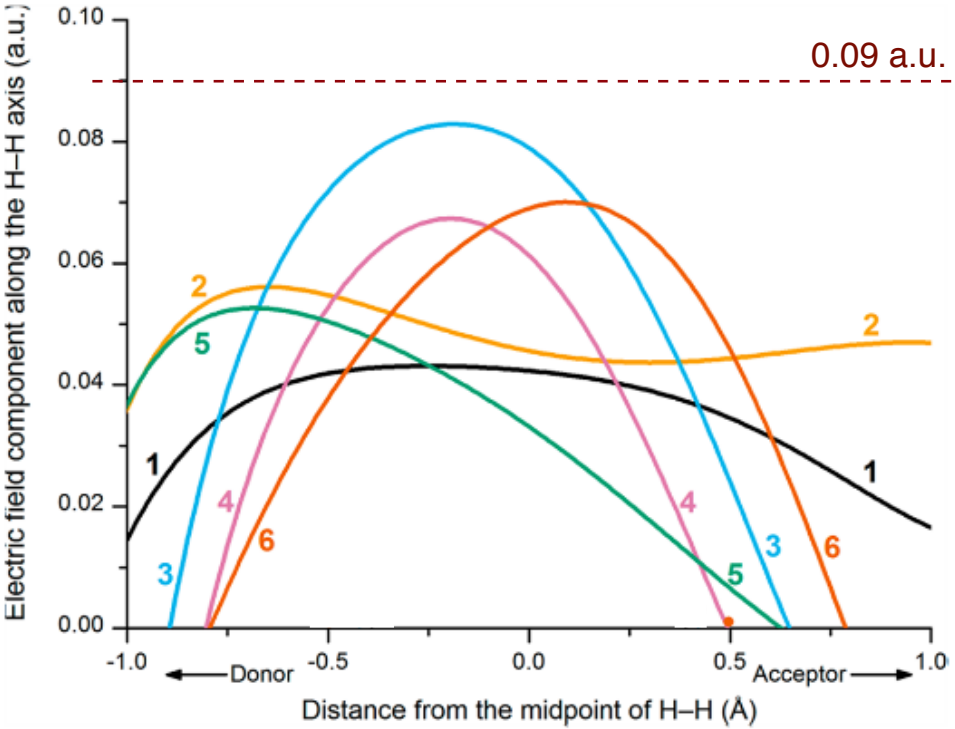
5



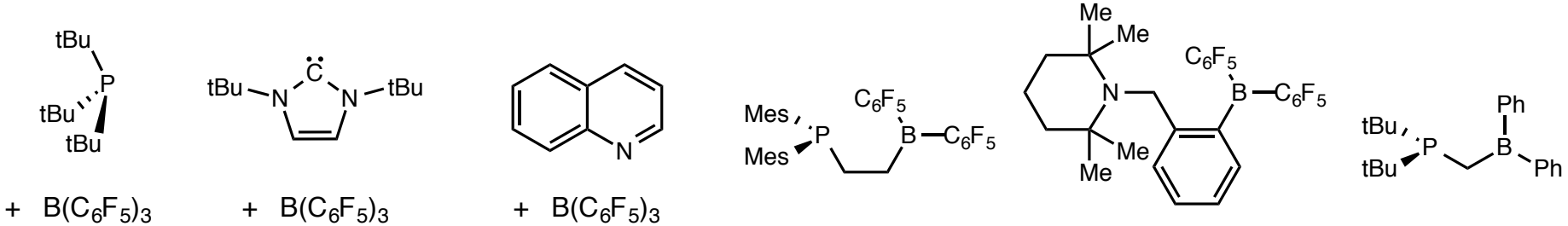
6

Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *JACS*, **2013**, *135*, 4425-4437.

The Electron Transfer Model Revisited



For none of the FLPs studied is the EF along the H_2 axis high enough to permit H_2 splitting



Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *JACS*, **2013**, *135*, 4425-4437.

The Electron Transfer Model Revisited

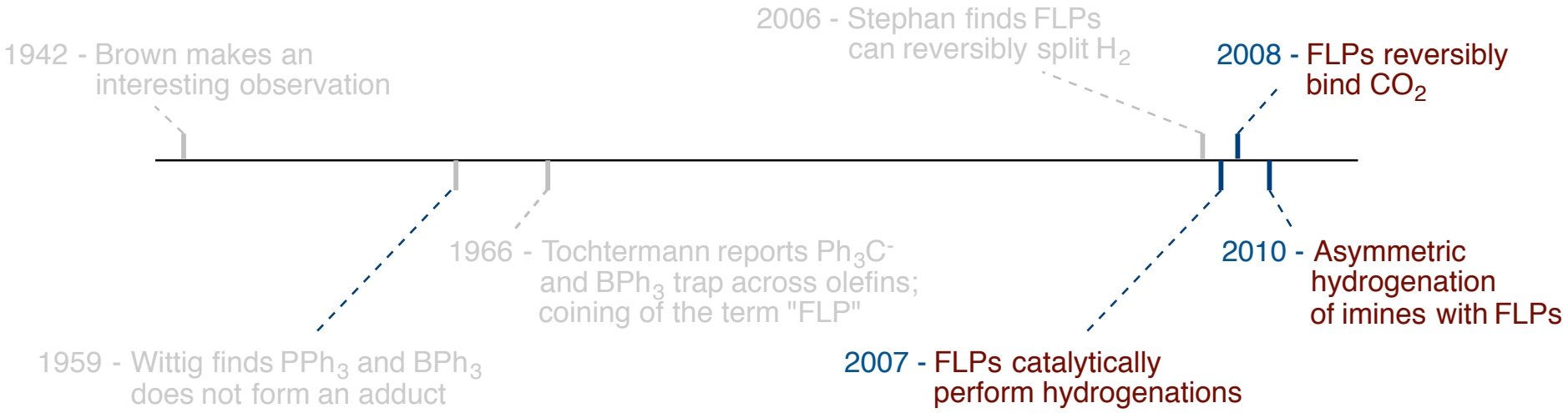
D → σ* donation

σ → A donation

- Use of dispersion corrected DFT basis set results in a generally bent D–H–H–A geometry explained by frontier orbitals aligning themselves for optimal orbital overlap
- Deviation from ideal 180° D---H_2 angle and 90° H_2---A angle due to polarization of the σ / σ* orbitals of H_2

Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *JACS*, **2013**, *135*, 4425-4437.

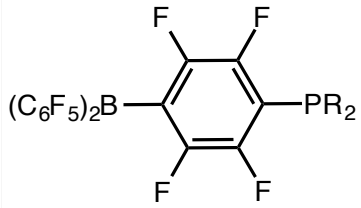
The Advent of FLP Chemistry



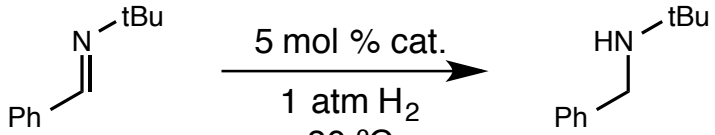
- I. Theories on the Mechanism of H_2 Activation
- II. Applications of FLPs in Hydrogenation Reactions and Storage of Small Molecules

The First Example of Catalytic Hydrogenations with FLPs

Hydrogenation of Imines, Nitriles, and Aziridines



1 R = Mes
2 R = *t*Bu



79% (**1**)
98% (**2**)

Chase, P. A.; Welch, C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

The First Example of Catalytic Hydrogenations with FLPs

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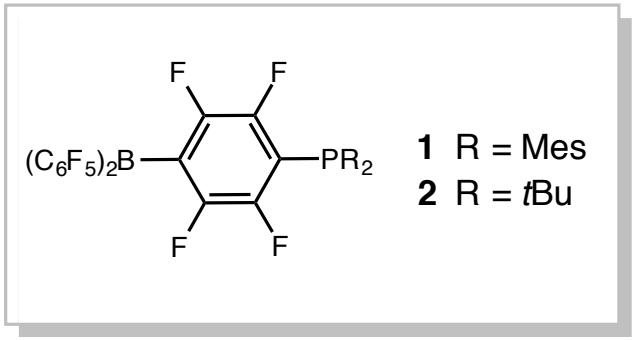

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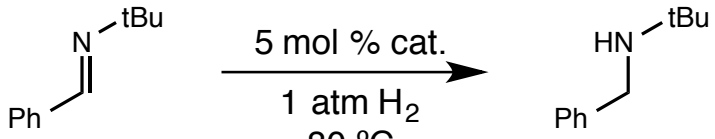

79% (1)
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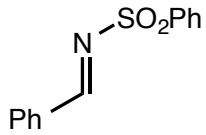

97% (1)
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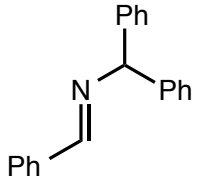
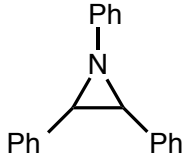


88% (1)



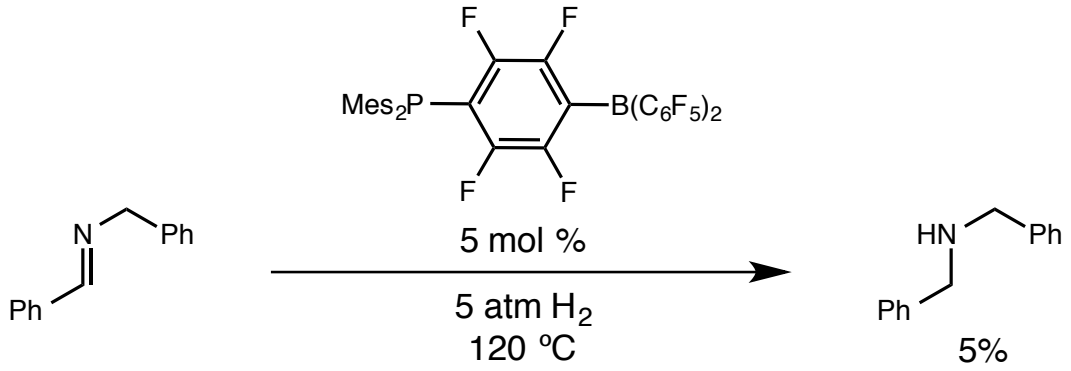
98% (1)

Chase, P. A.; Welch, C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

The First Example of Catalytic Hydrogenations with FLPs

Hydrogenation of Imines, Nitriles, and Aziridines

- Catalytic hydrogenation only possible for sterically hindered imines



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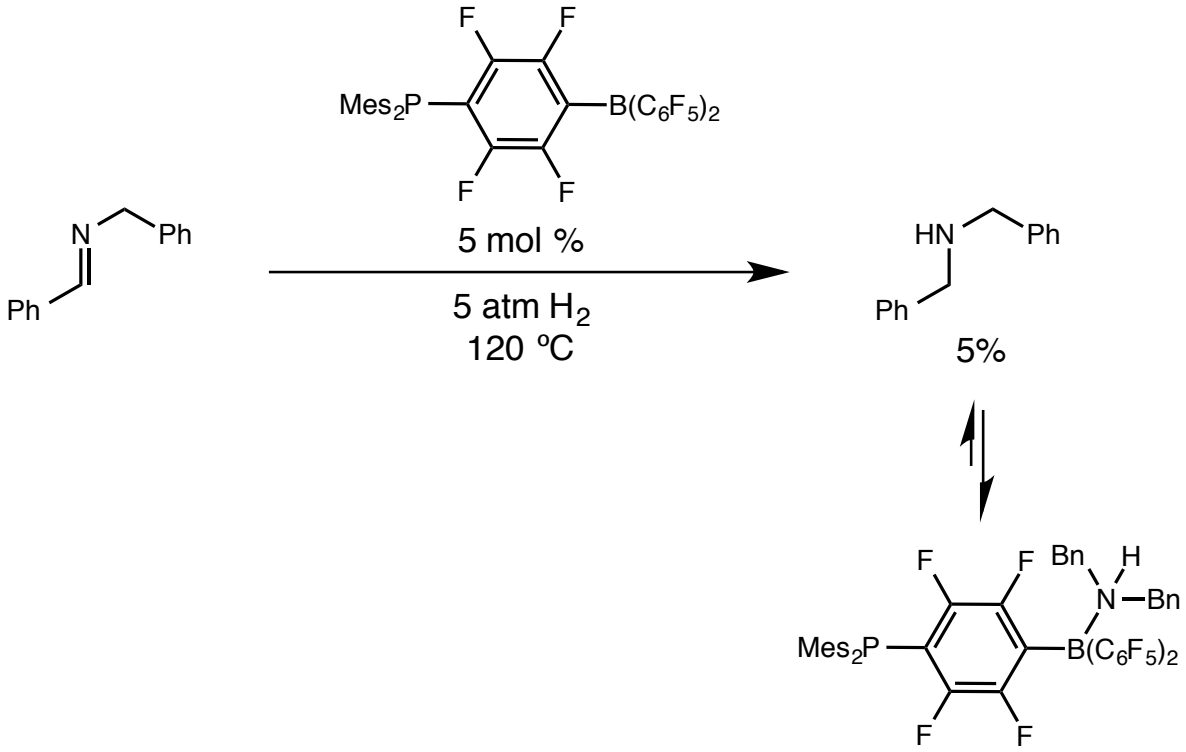

adduct formation between Lewis Basic product and FLP shuts down catalytic activity

Chase, P. A.; Welch, C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

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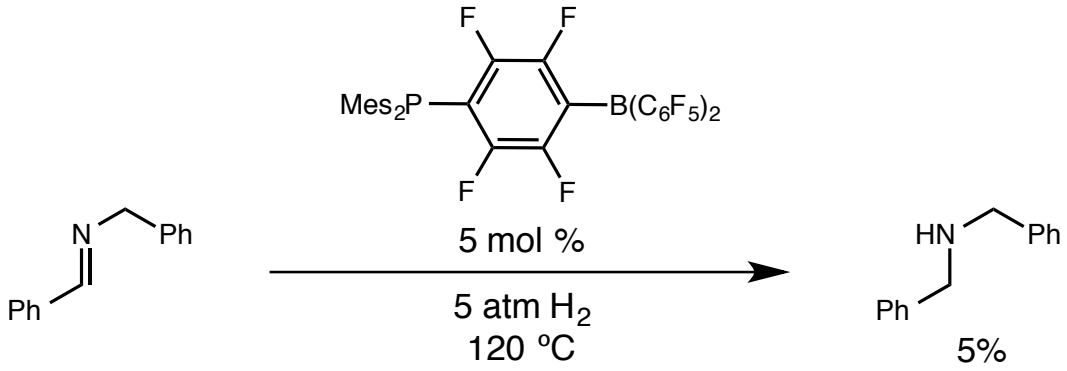
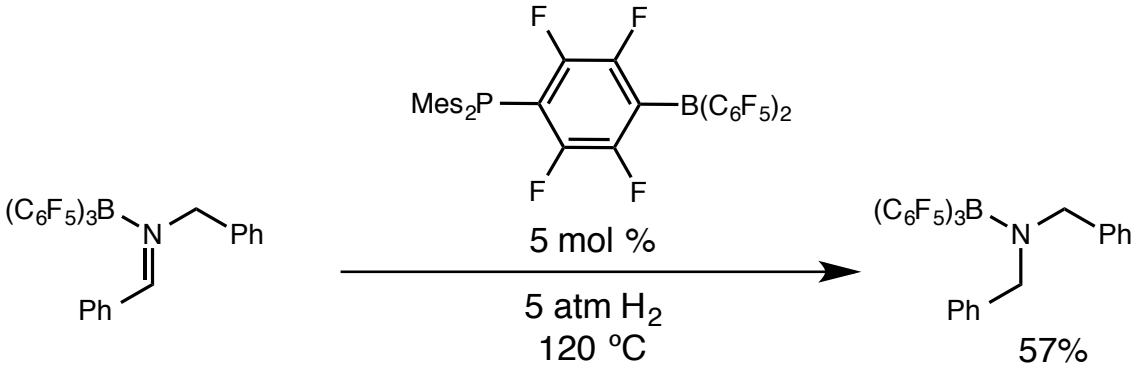


- Protecting Imine with $B(C_6F_5)_3$ recovers catalytic activity



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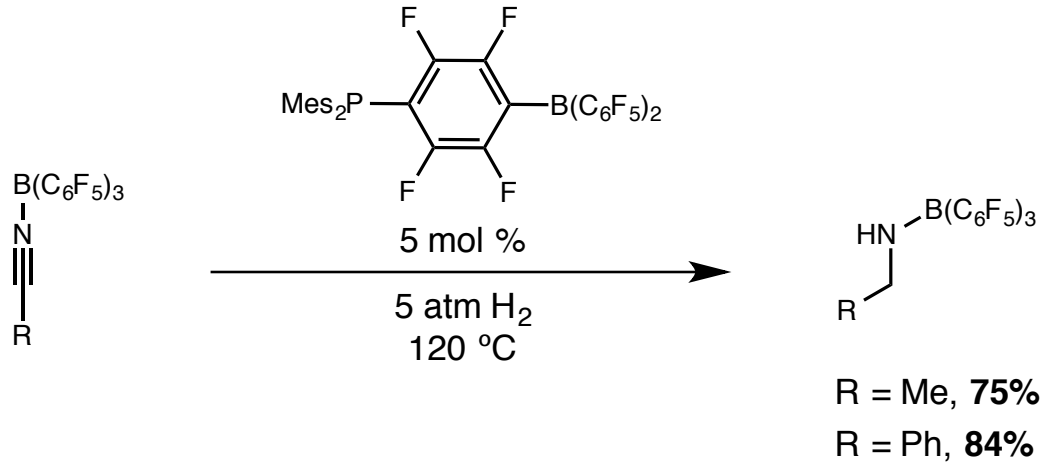
The First Example of Catalytic Hydrogenations with FLPs

Hydrogenation of Imines, Nitriles, and Aziridines

- Catalytic hydrogenation only possible for $B(C_6F_5)_3$ protected nitriles



R = Me, **75%**

R = Ph, **84%**

Only the amine is isolated (cannot isolate imine)

Chase, P. A.; Welch, C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

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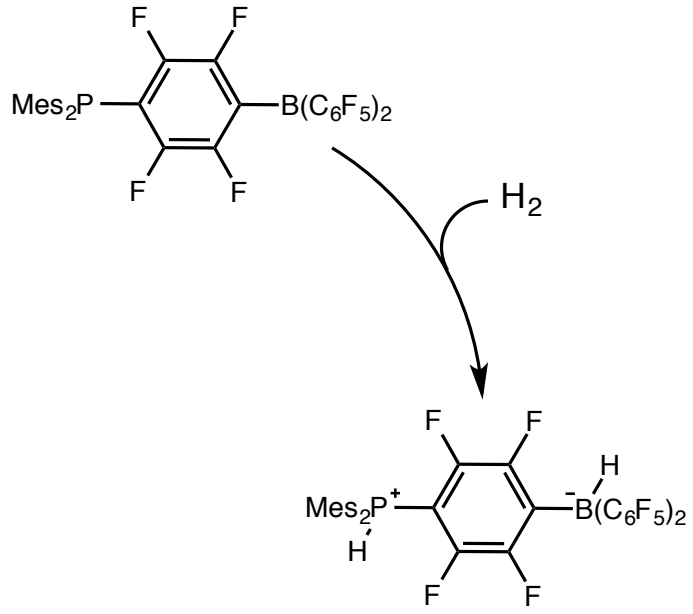

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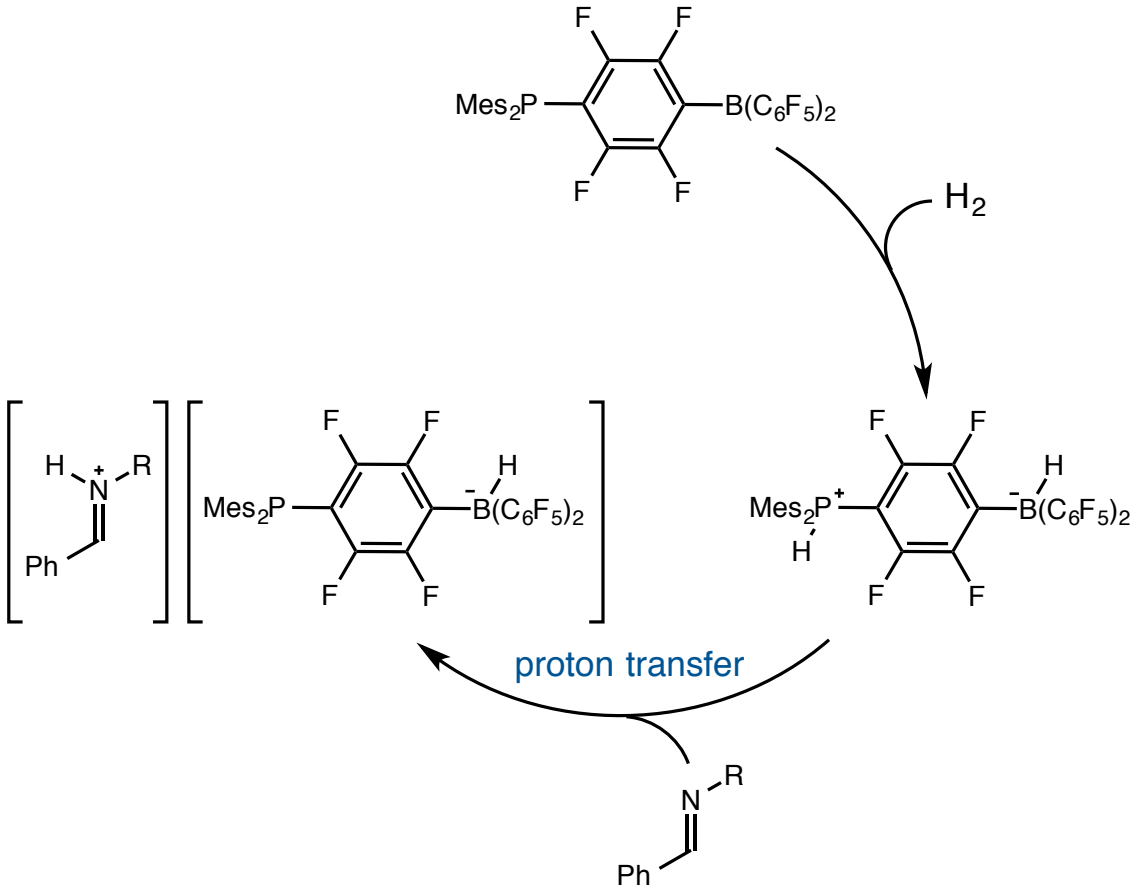

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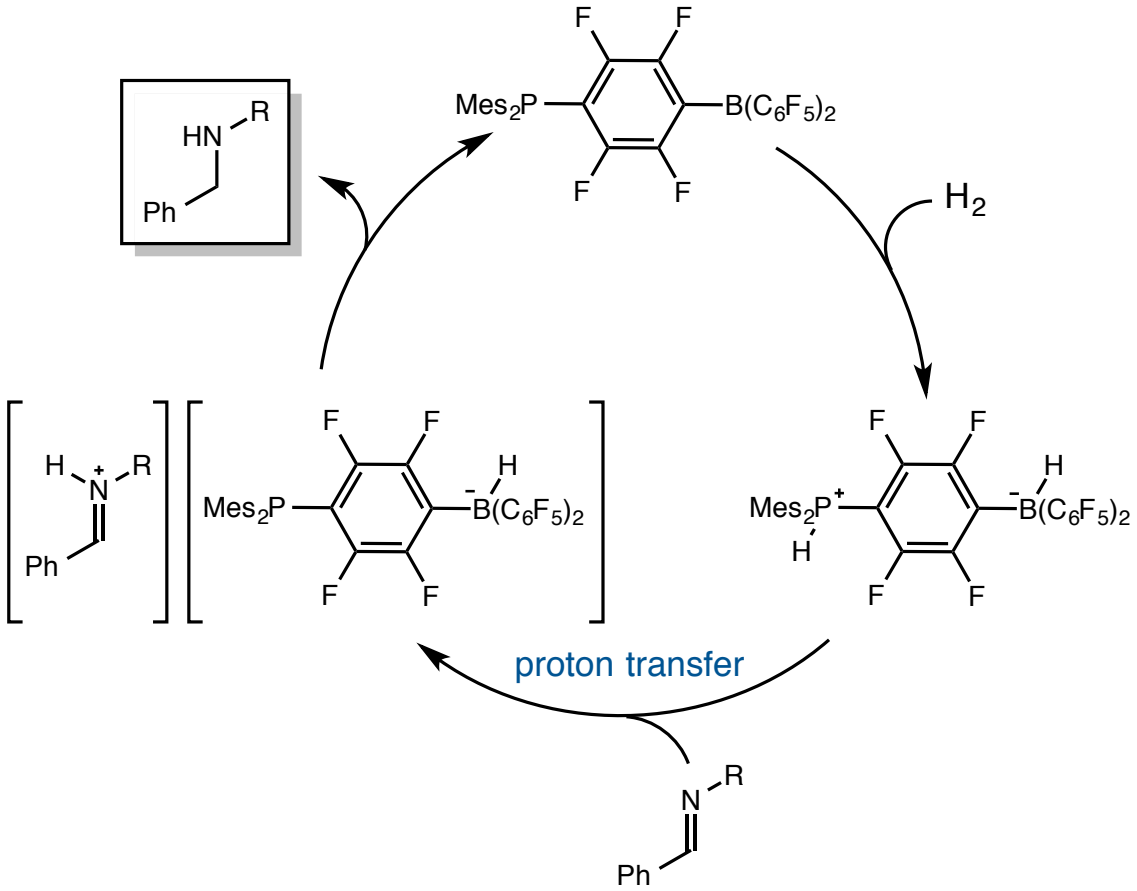

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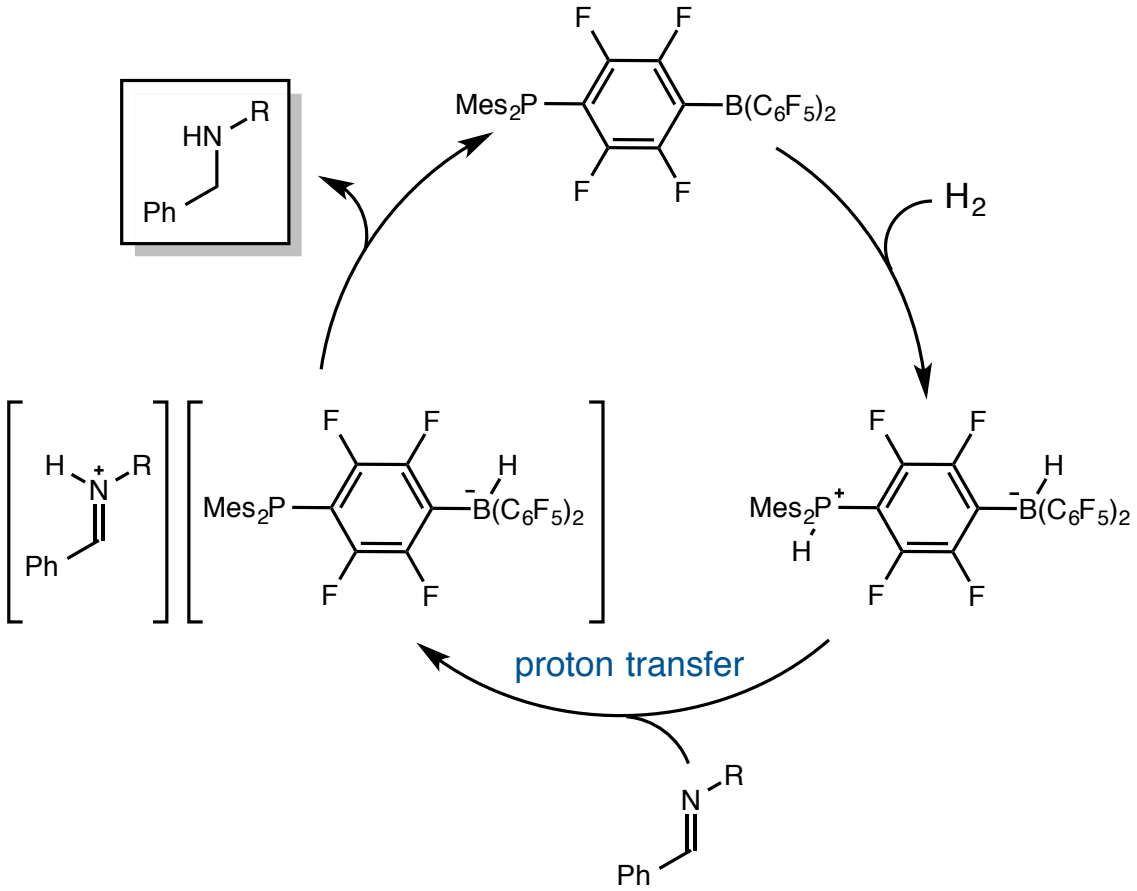


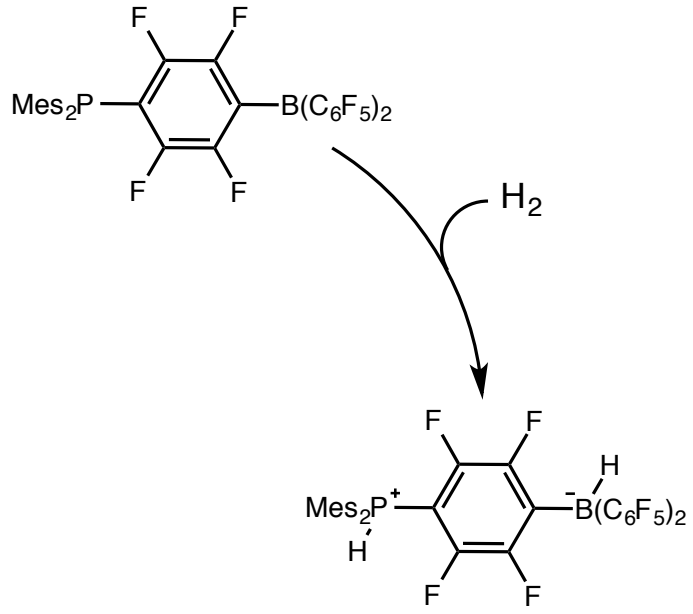
Proton transfer precedes hydride delivery

Increased rates with electron rich imines (R = *t*Bu, 1 hr vs. R = SO_2Ph, >10 hrs)

Chase, P. A.; Welch, C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

The First Example of Catalytic Hydrogenations with FLPs

Hydrogenation of Imines, Nitriles, and Aziridines



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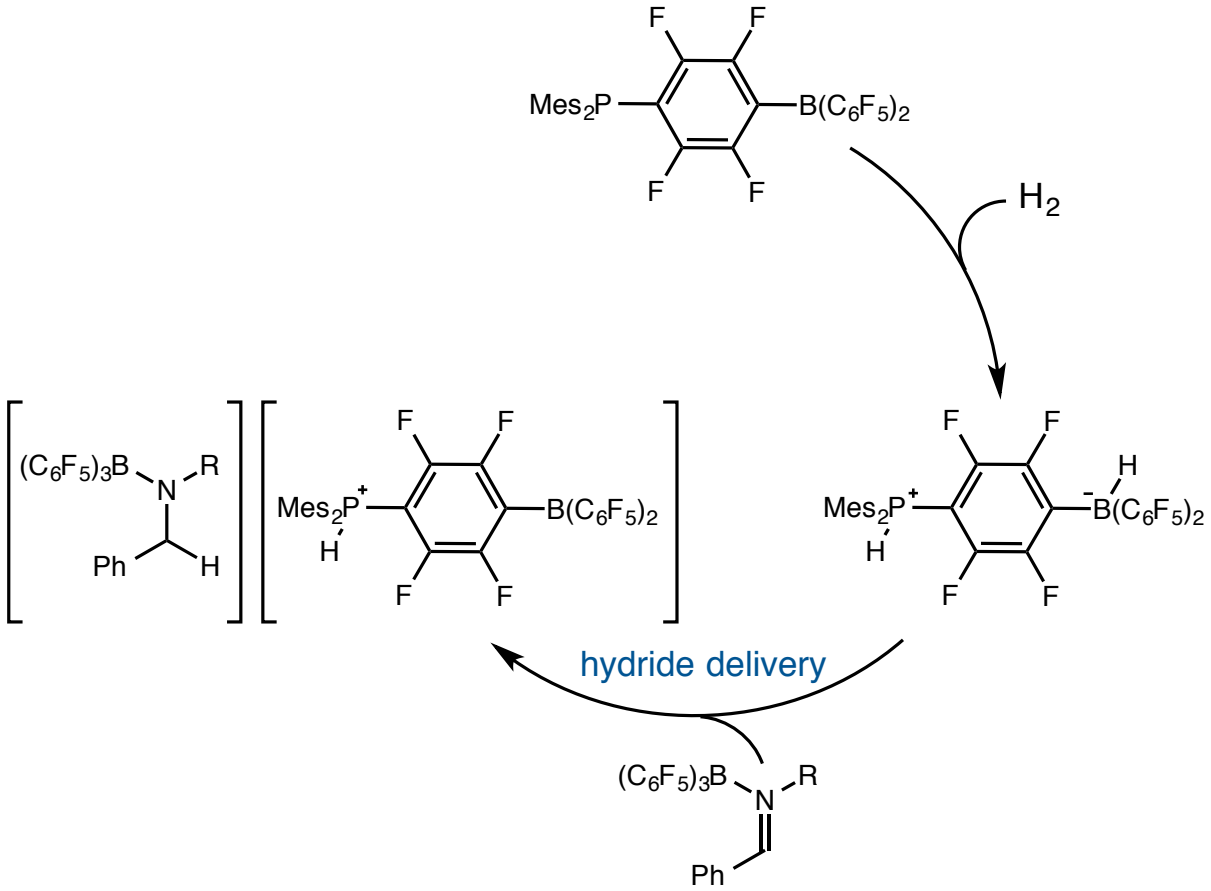

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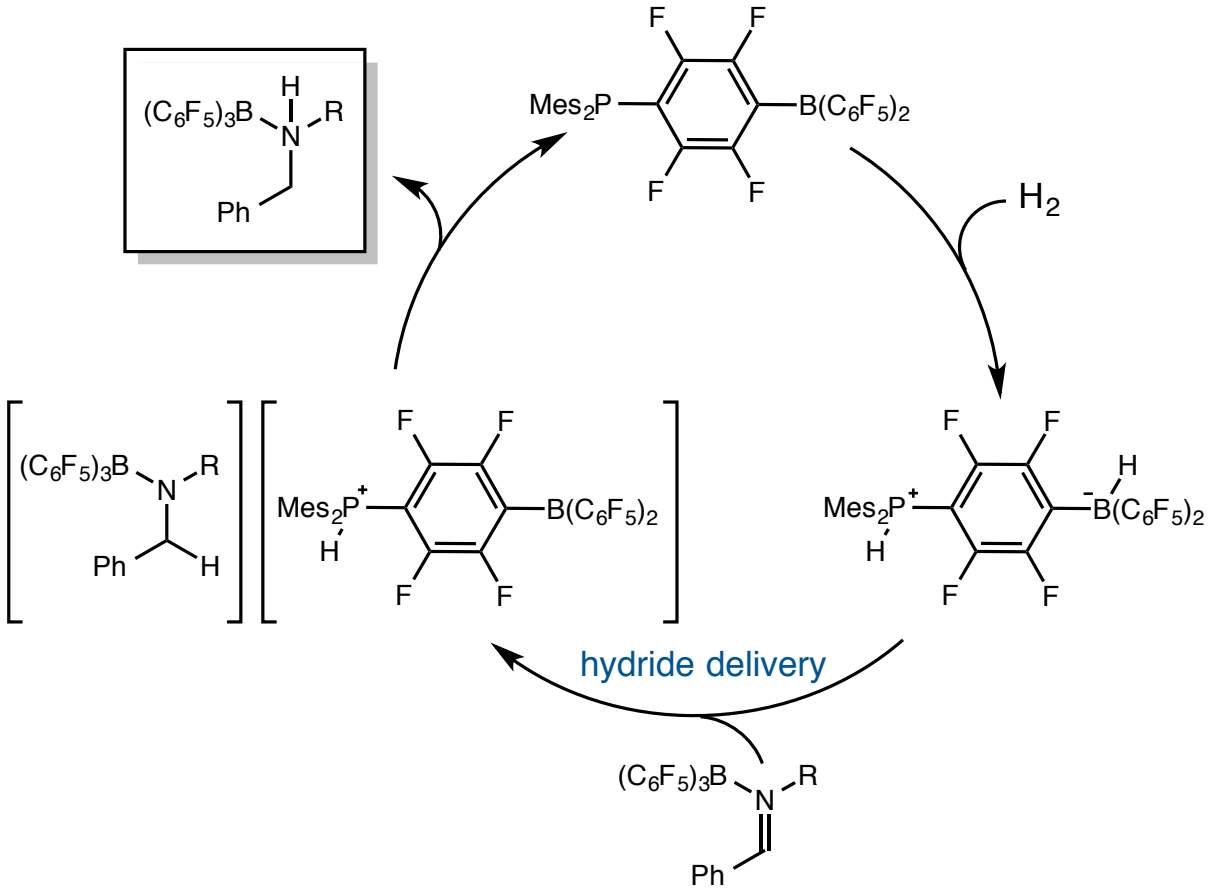

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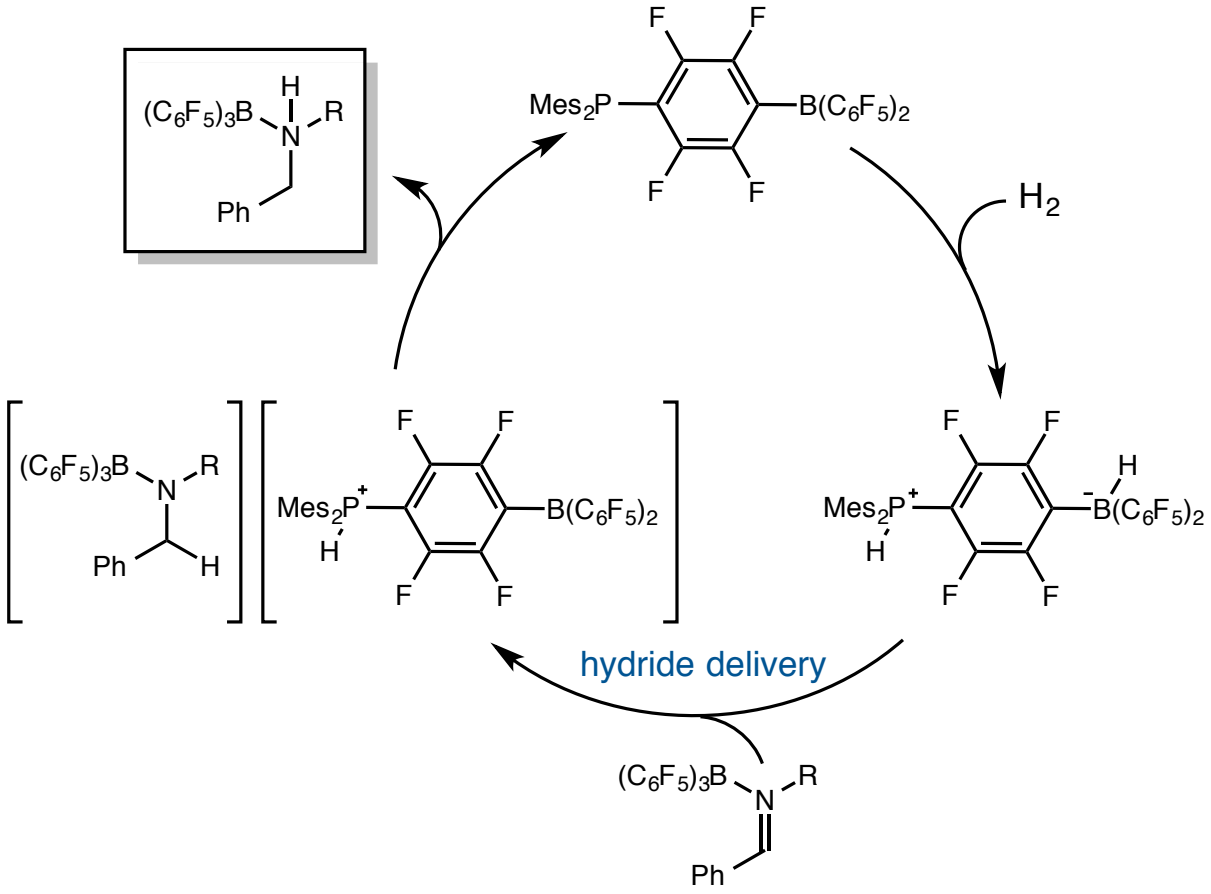
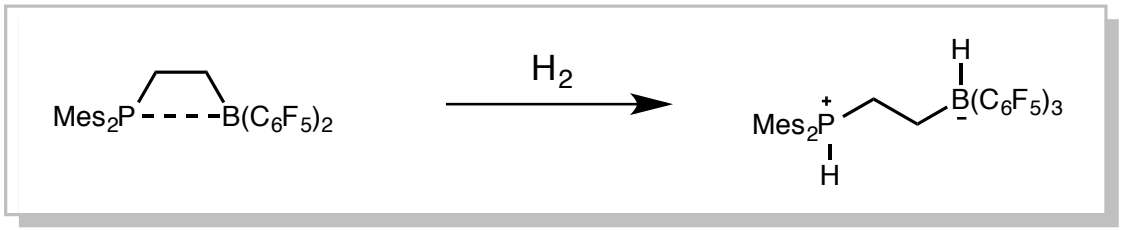


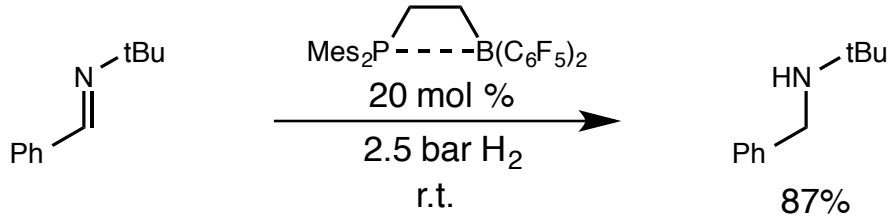
Hydride delivery precedes proton transfer

Chase, P. A.; Welch, C.; Jurca, T.; Stephan, D. W. *ACIE*, **2007**, *46*, 8050-8053.

An Improved FLP

Hydrogenation of Ketimines and Enamines





Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *ACIE*, **2008**, *47*, 7543-7546.

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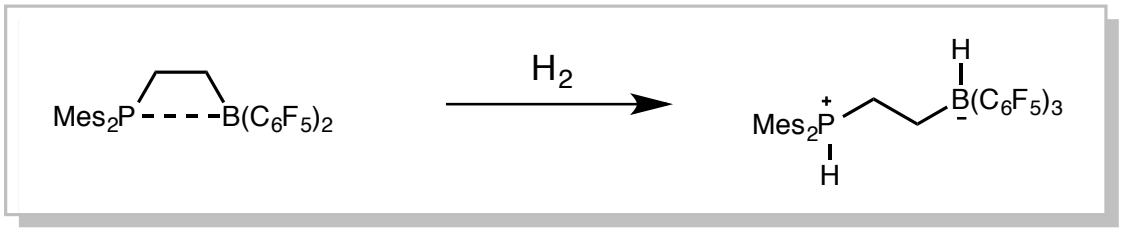
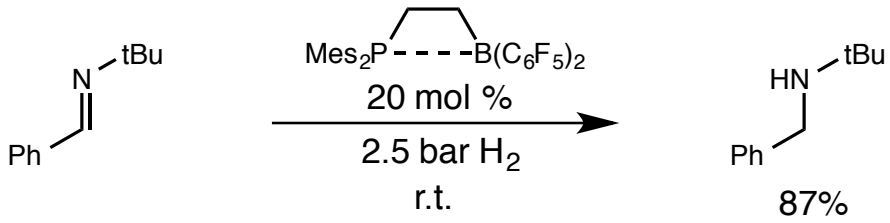
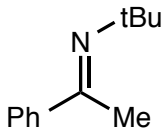
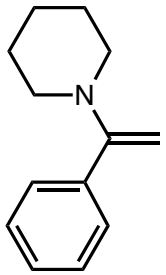




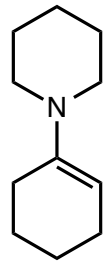
87%



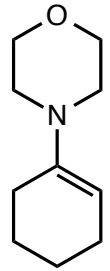
70%
(5 mol %)



70%
(10 mol %)



70%
(5 mol %)

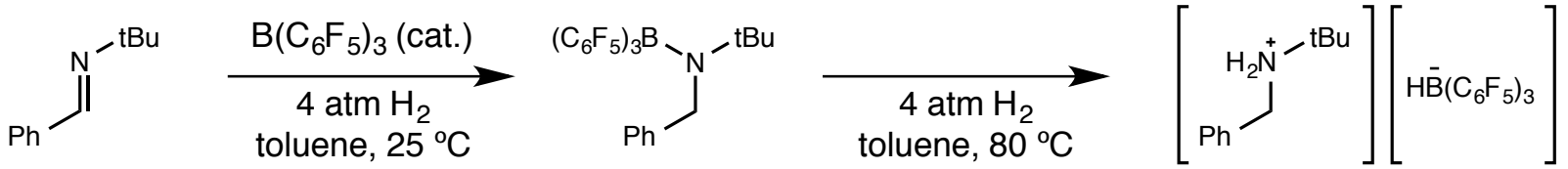


70%
(3 mol %)

Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *ACIE*, **2008**, *47*, 7543-7546.

Catalytic Hydrogenations Using only $B(C_6F_5)_3$

Hydrogenation of Imines



Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Comm.*, **2008**, 1701-1703.

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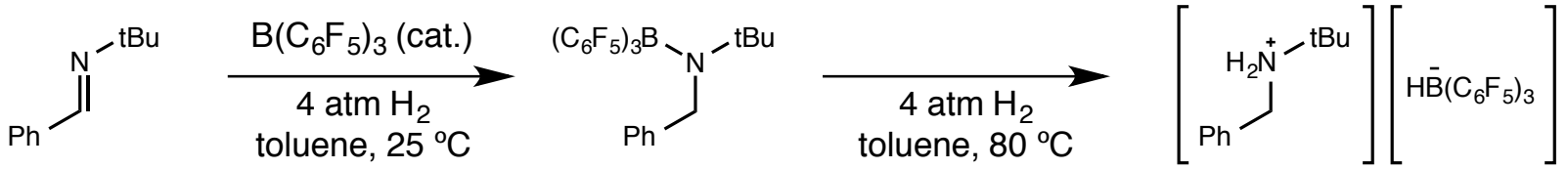

Isolation of zwitterion suggests adduct formation with the product is reversible and that the $B(C_6F_5)_3$ catalyst can be recycled

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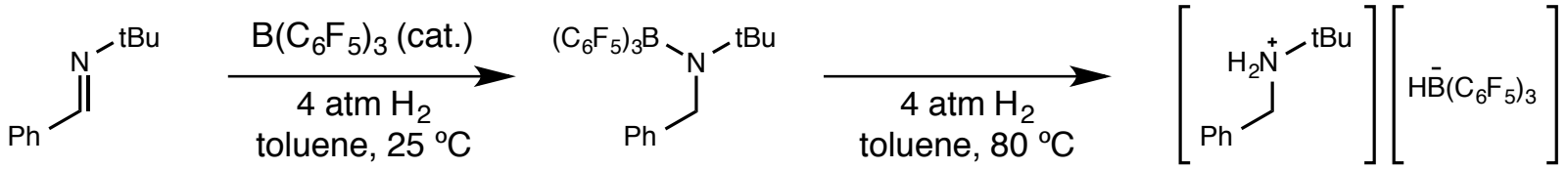

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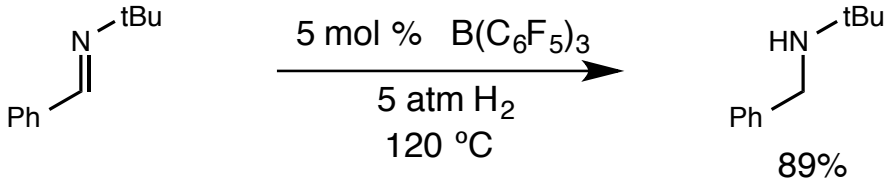

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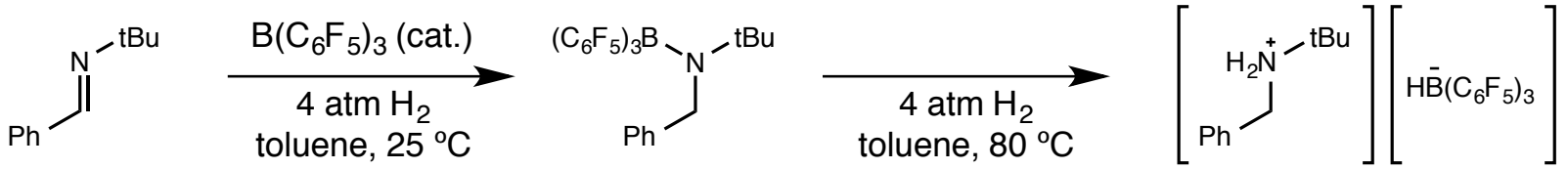

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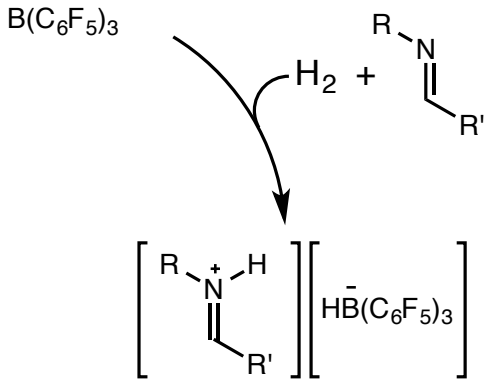

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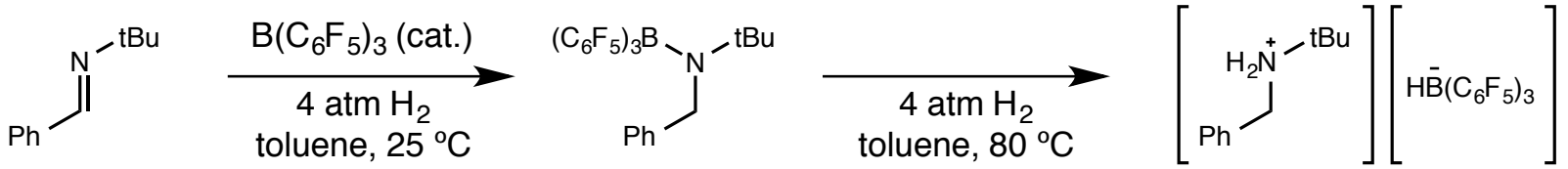

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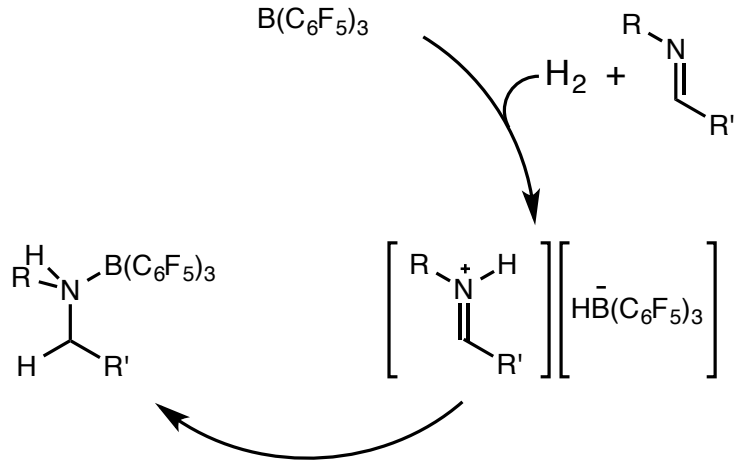

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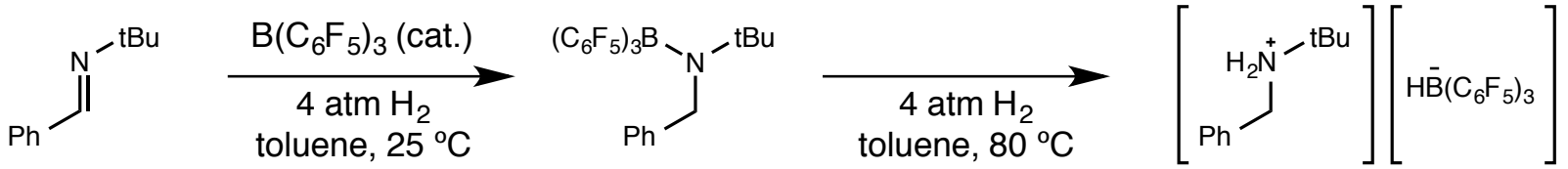

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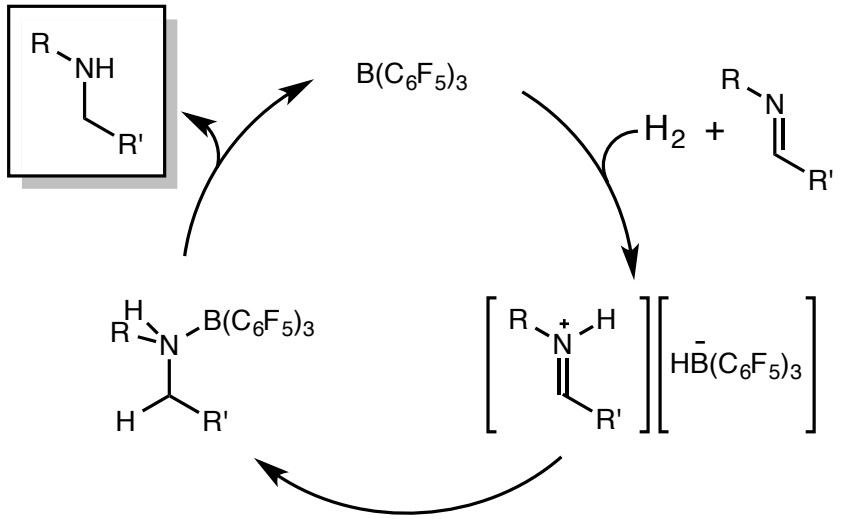

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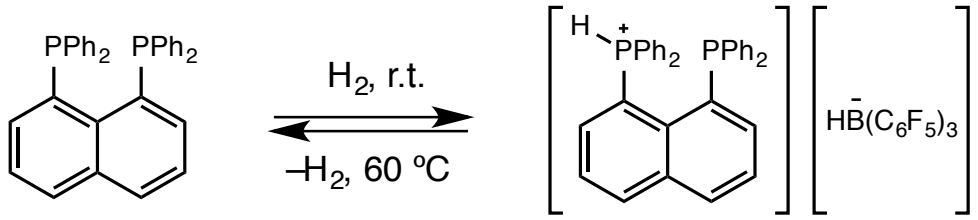
Expanding the Scope to Oxygenated Substrates

Hydrogenation of Silyl Enol Ethers



Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Comm.*, **2008**, 5966-5968.

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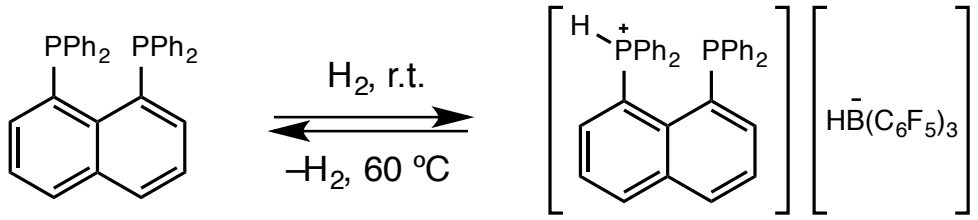

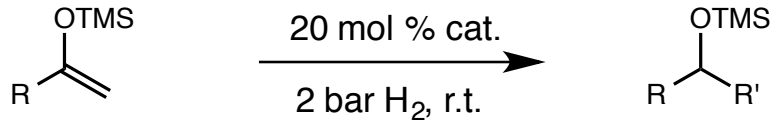

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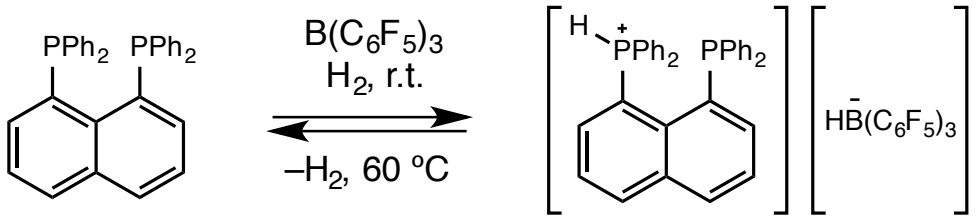
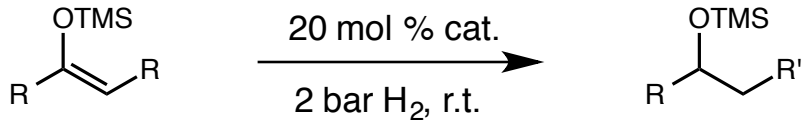
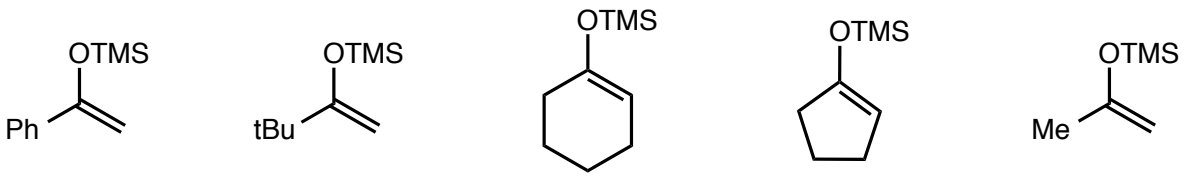




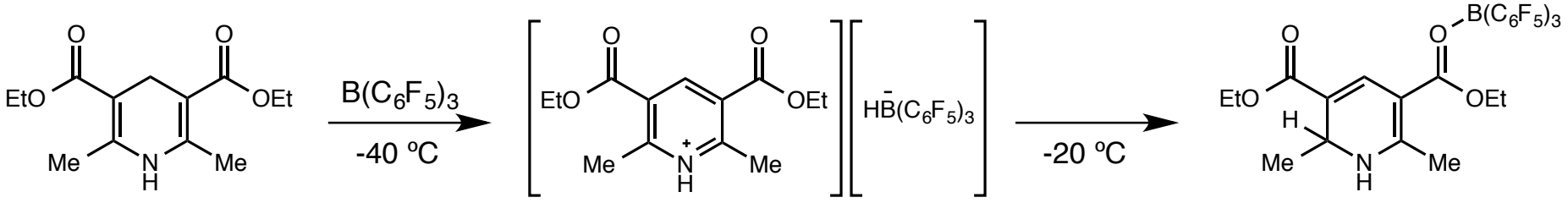


93% **89%** **86%** **85%** **>99%**

Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Comm.*, **2008**, 5966-5968.

Studies of Hantzsch Ester with $B(C_6F_5)_3$ Unveils New Substrates

Hydrogenation of N-heterocycles



Webb, J. D.; Laberge, V. S.; Geier, S. J.; Stephan, D. W.; Crudden, C. M. *Chem. Eur. J.*, **2010**, *16*, 4895-4902.
Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Comm.*, **2010**, *46*, 4884-4886.

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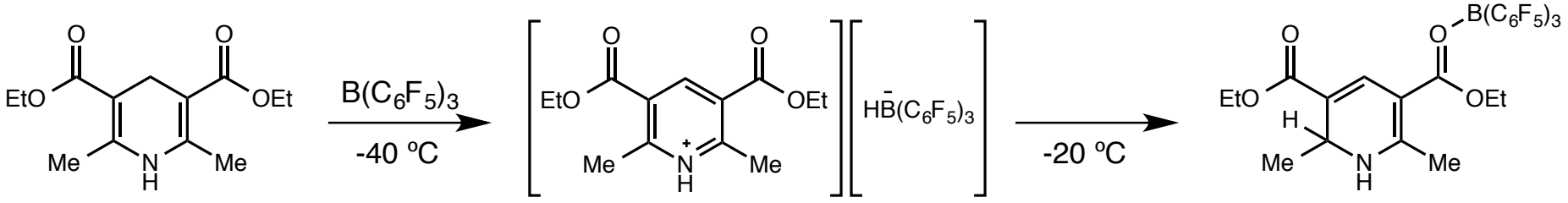

60%

55%
(70% at r.t.)

Observation of hydride delivery into pyridinium inspired experimentation with N-heterocycle substrates

Webb, J. D.; Laberge, V. S.; Geier, S. J.; Stephan, D. W.; Crudden, C. M. *Chem. Eur. J.*, **2010**, *16*, 4895-4902.
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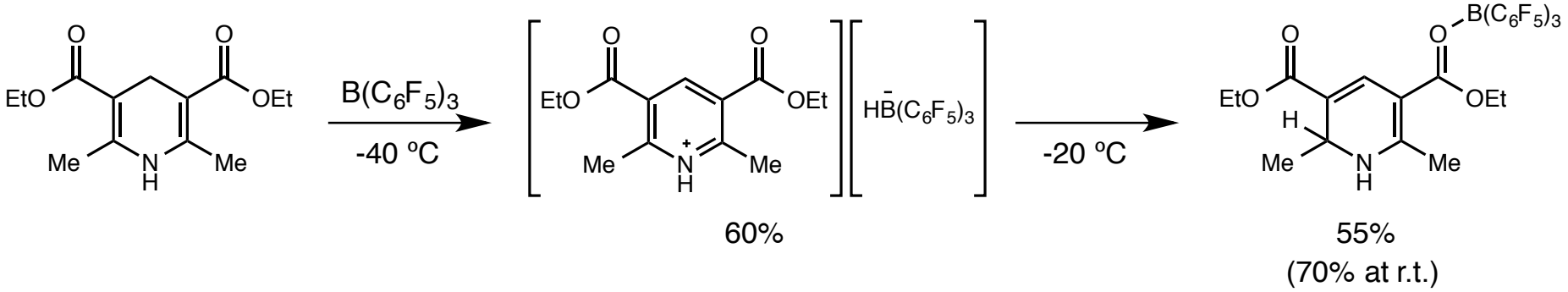

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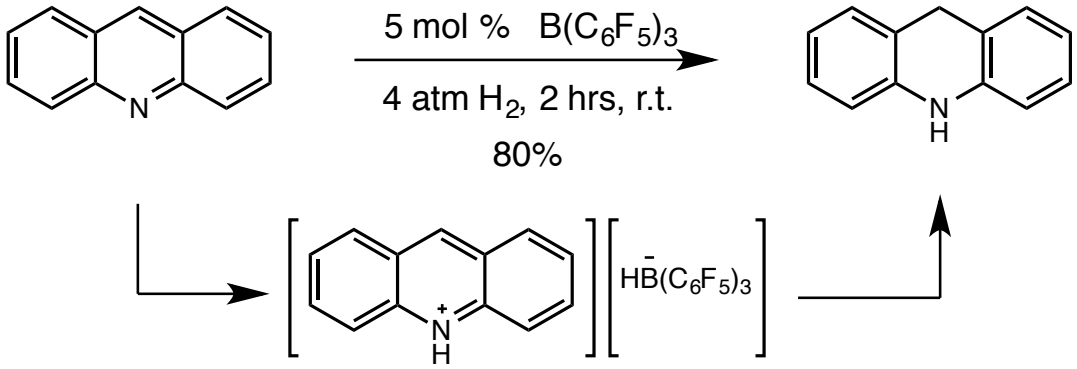
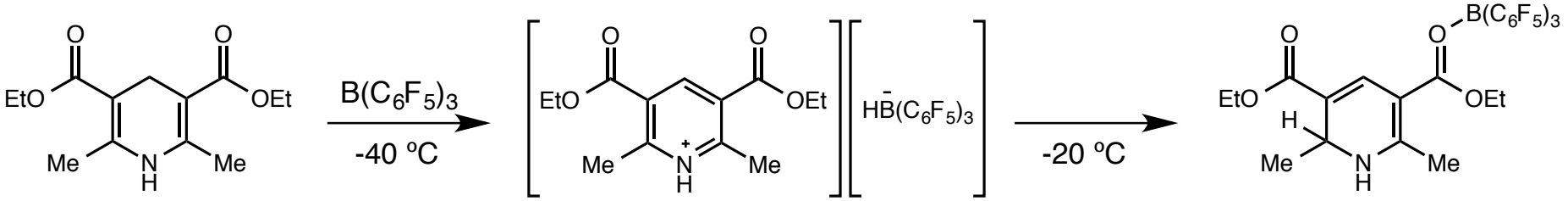


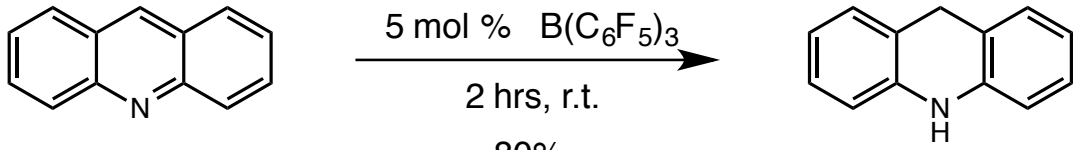
Webb, J. D.; Laberge, V. S.; Geier, S. J.; Stephan, D. W.; Crudden, C. M. *Chem. Eur. J.*, **2010**, *16*, 4895-4902.
Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Comm.*, **2010**, *46*, 4884-4886.

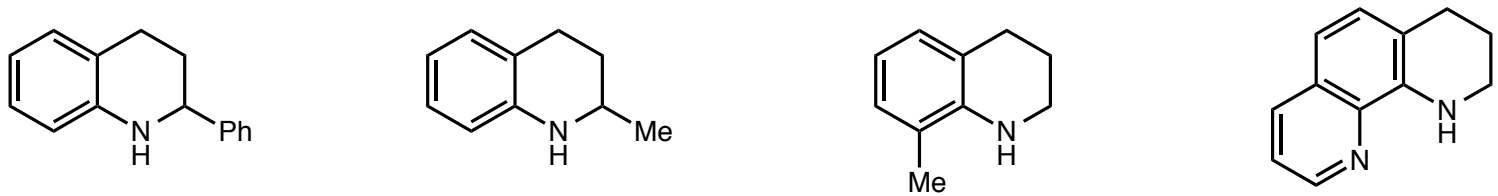
Studies of Hantzsch Ester with $B(C_6F_5)_3$ Unveils New Substrates

Hydrogenation of N-heterocycles



Observation of hydride delivery into pyridinium inspired experimentation with N-heterocycle substrates





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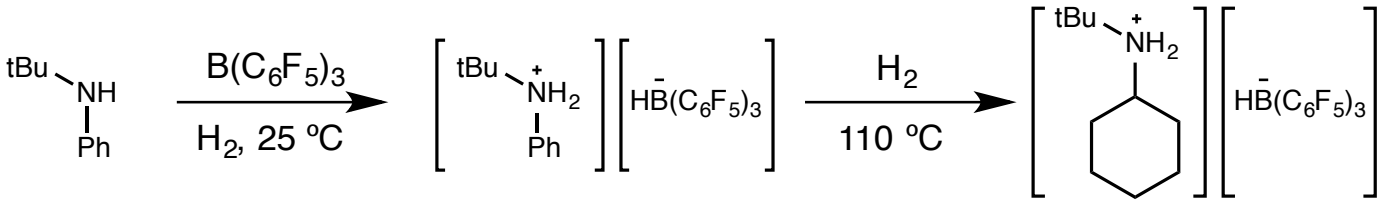
Aromatic Hydrogenation

Hydrogenation of Anilines to Cyclohexylamines



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Mahdi, T.; Heiden, Z. M.; Grimme, S.; Stephan, D. W. *JACS*, **2012**, *134*, 4088-4091.

Aromatic Hydrogenation

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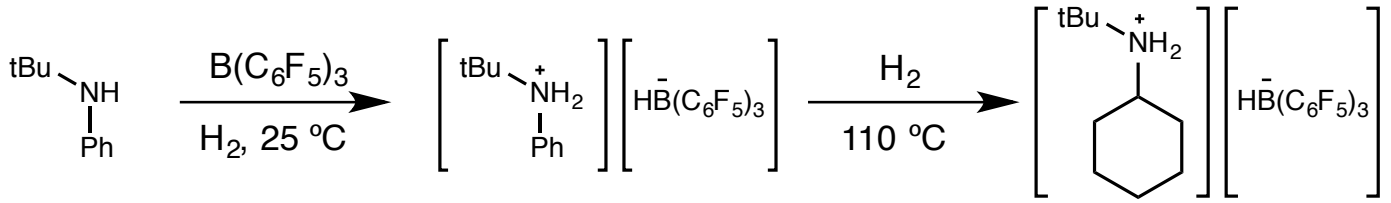

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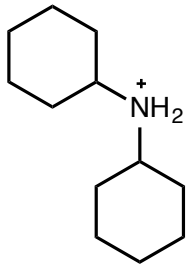
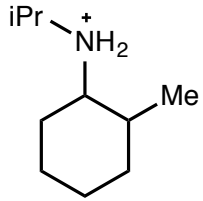
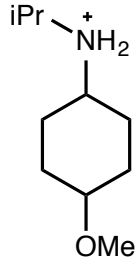


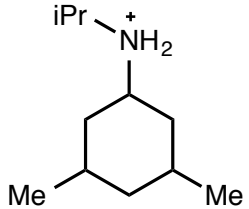
65%, 96 hrs



77%, 36 hrs



61%, 36 hrs

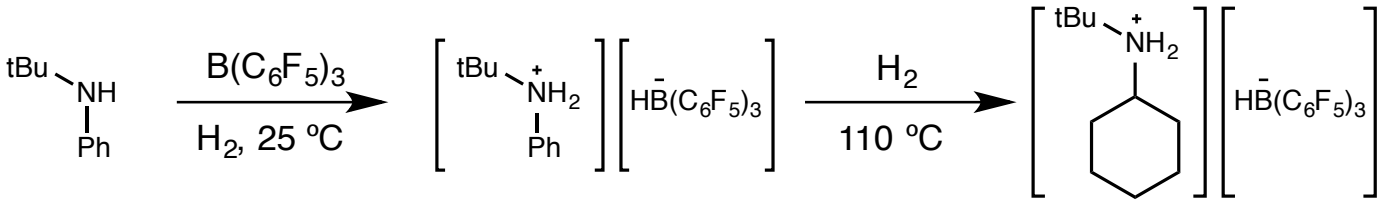


48%, 72 hrs

Mahdi, T.; Heiden, Z. M.; Grimme, S.; Stephan, D. W. *JACS*, **2012**, *134*, 4088-4091.

Aromatic Hydrogenation

Hydrogenation of Anilines to Cyclohexylamines



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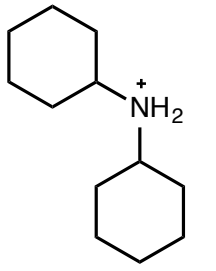
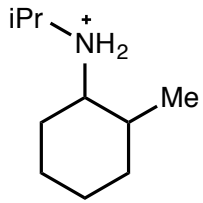
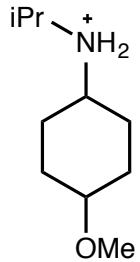


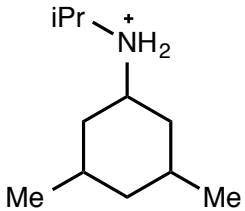
65%, 96 hrs



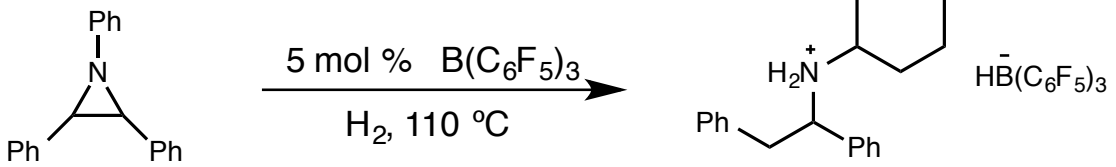
77%, 36 hrs



61%, 36 hrs



48%, 72 hrs

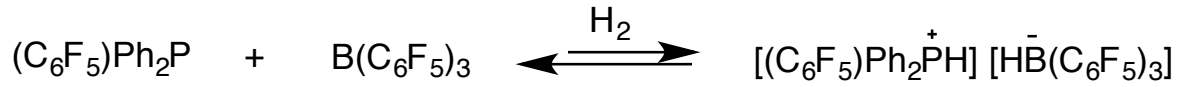


50%, 96 hrs

Mahdi, T.; Heiden, Z. M.; Grimme, S.; Stephan, D. W. *JACS*, **2012**, *134*, 4088-4091.

Hydrogenation of Non-Polar Substrates

Hydrogenation of Olefins

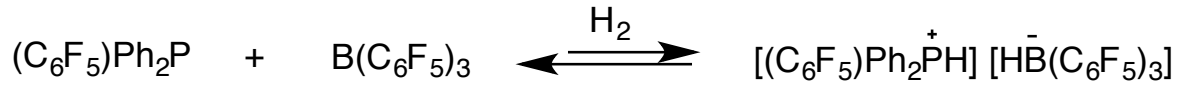


cation posseses much greater bronsted acidity

Greb, L.; Ona-Burgos, P.; Schirmer, B.; Grimme, S.; Stephan, D. W.; Paradies, J. *ACIE*, **2012**, *51*, 10164-10168.

Hydrogenation of Non-Polar Substrates

Hydrogenation of Olefins



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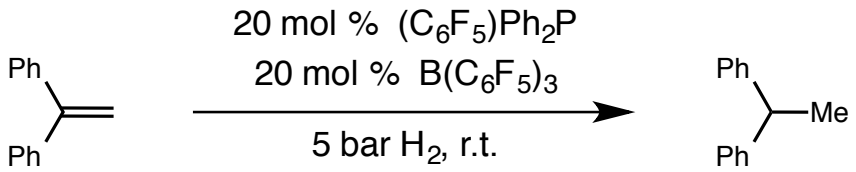

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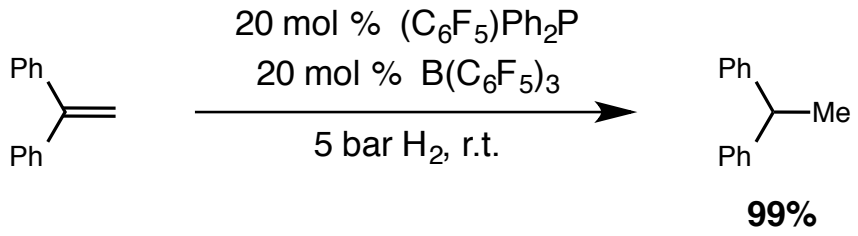
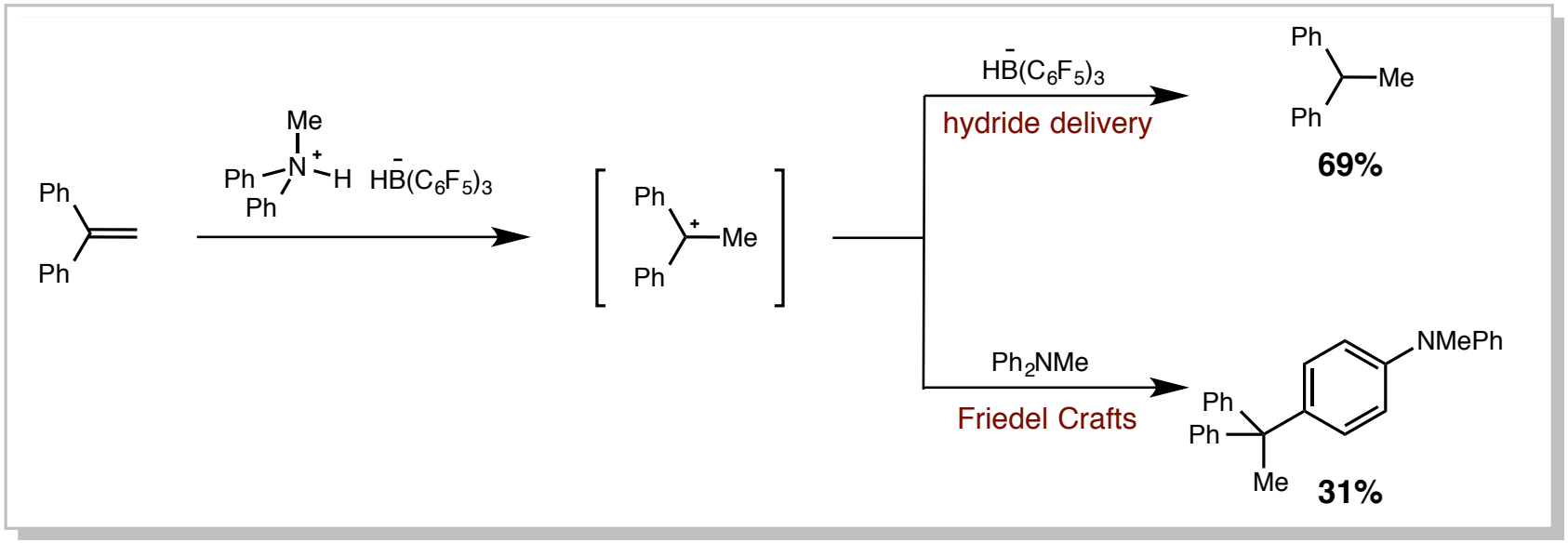
Hydrogenation of Non-Polar Substrates

Hydrogenation of Olefins

$(C_6F_5)Ph_2P$ + $B(C_6F_5)_3$ $\overset{H_2}{\rightleftharpoons}$ $[(C_6F_5)Ph_2\overset{+}{P}H]\ [H\overset{-}{B}(C_6F_5)_3]$

cation posseses much greater bronsted acidity





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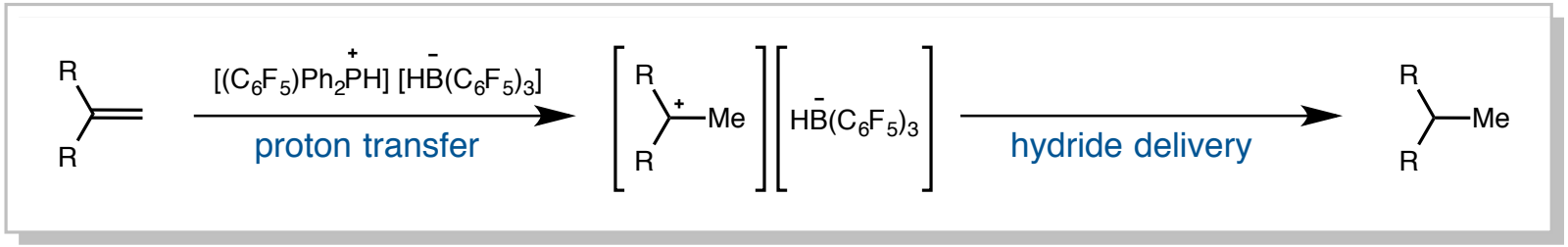

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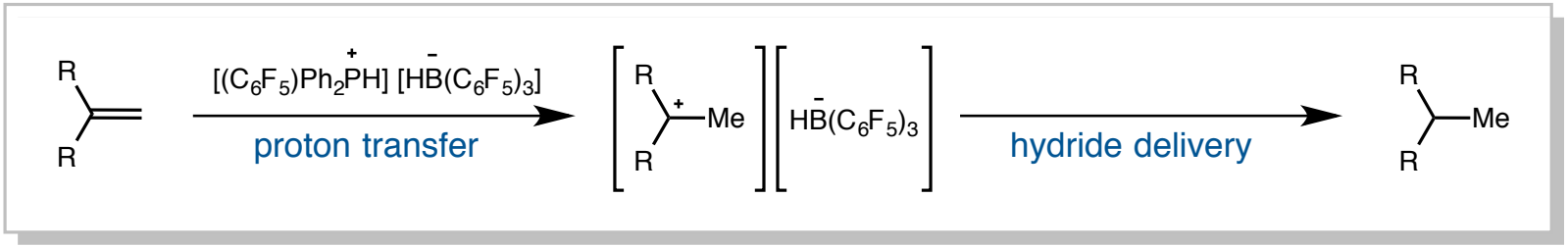

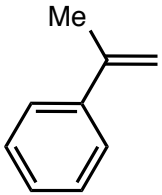

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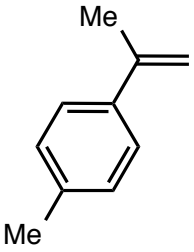

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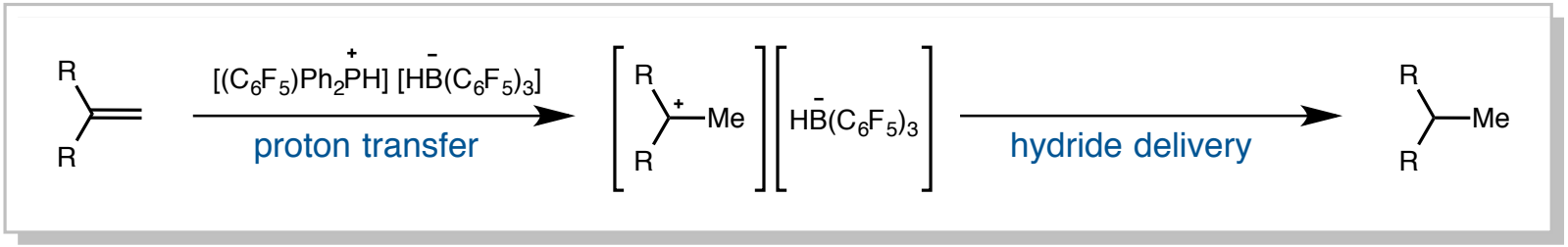
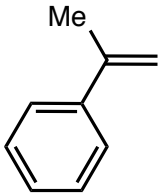
Hydrogenation of Non-Polar Substrates

Hydrogenation of Olefins





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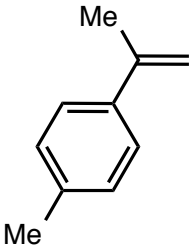

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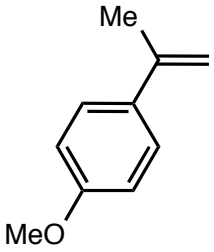

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Hydrogenation of Non-Polar Substrates

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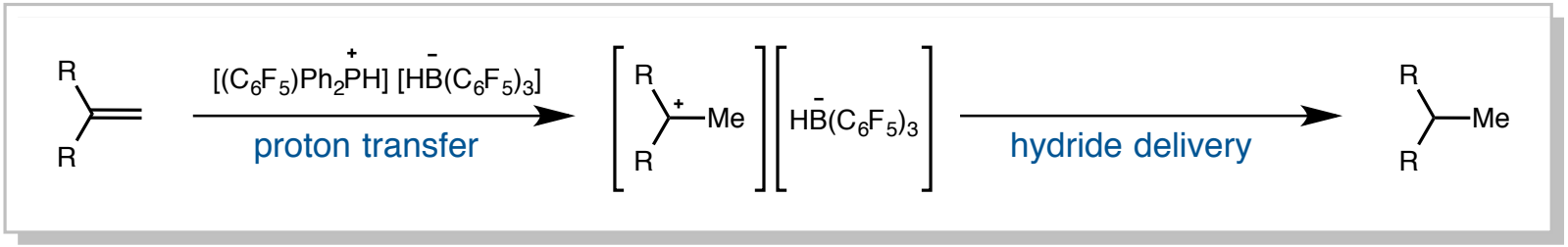

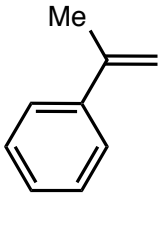

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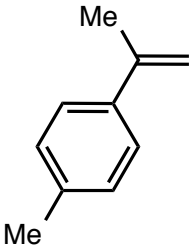

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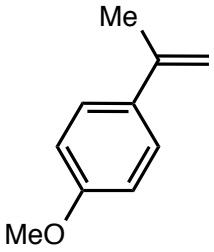

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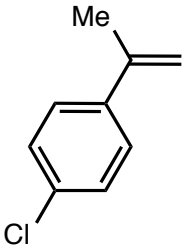

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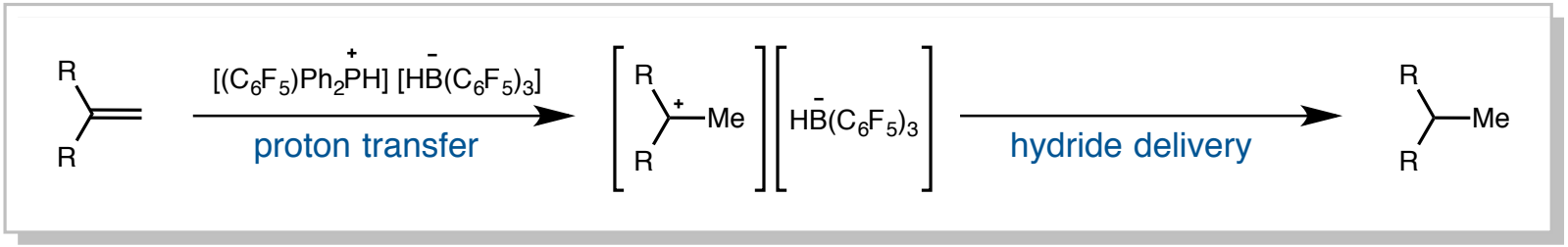
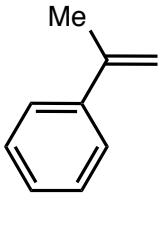
Hydrogenation of Non-Polar Substrates

Hydrogenation of Olefins





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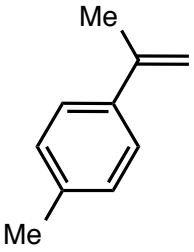

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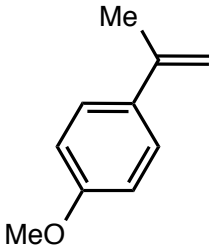

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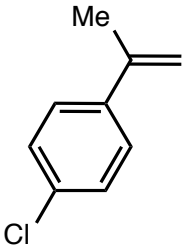

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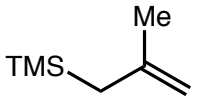

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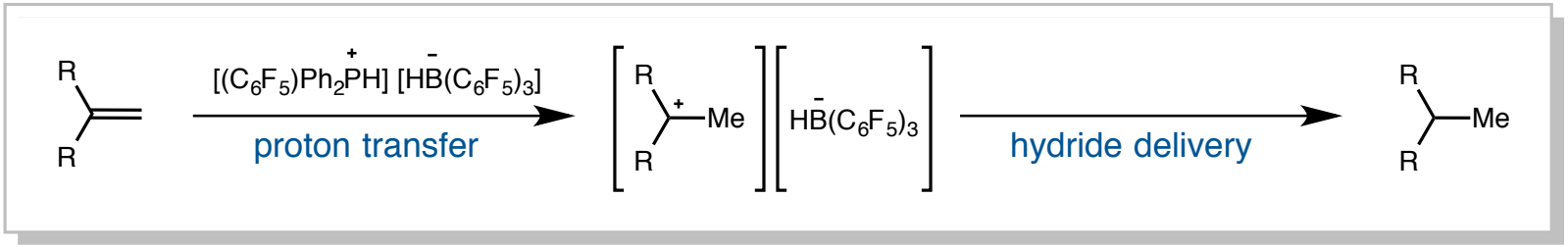
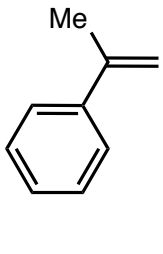
Hydrogenation of Non-Polar Substrates

Hydrogenation of Olefins





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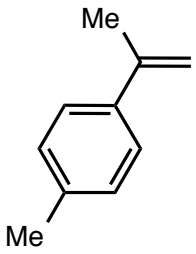

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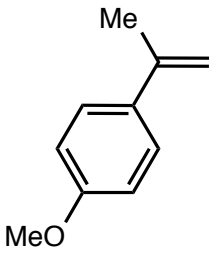

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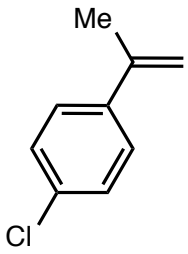

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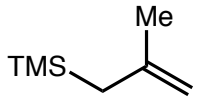

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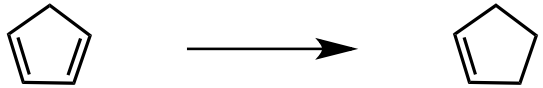

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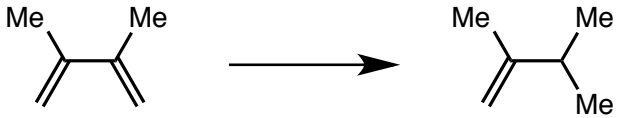

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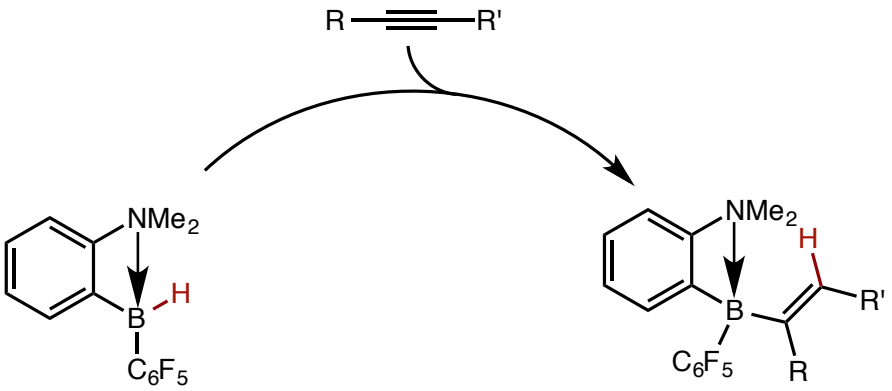
Hydrogenation of Non-Polar Substrates

Hydrogenation of Alkynes to Cis-Alkenes



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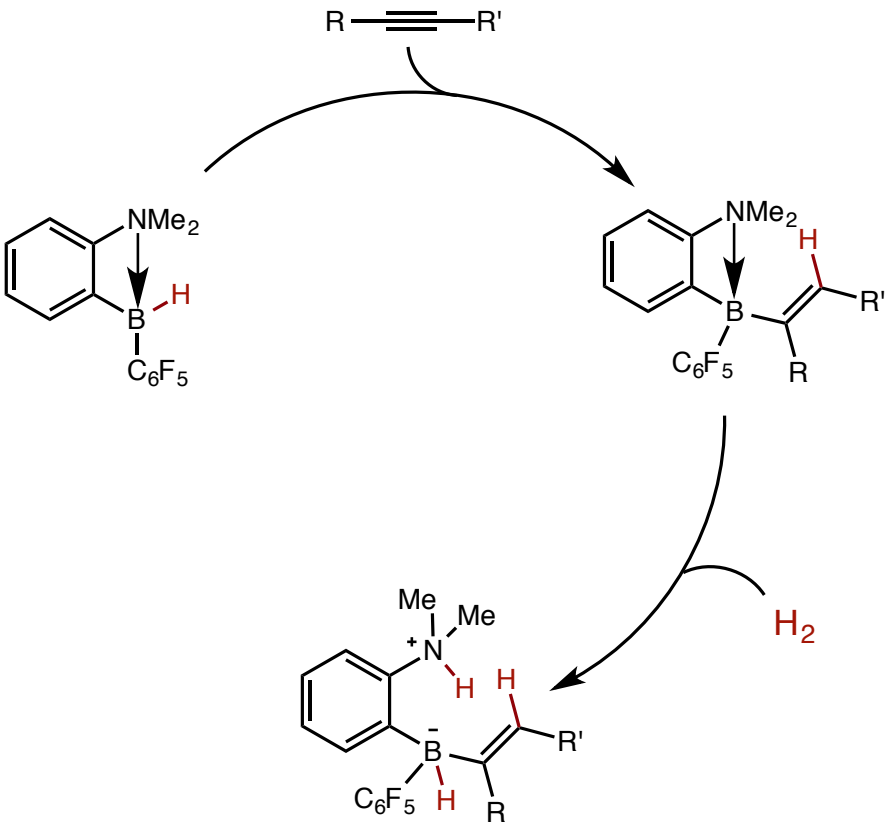

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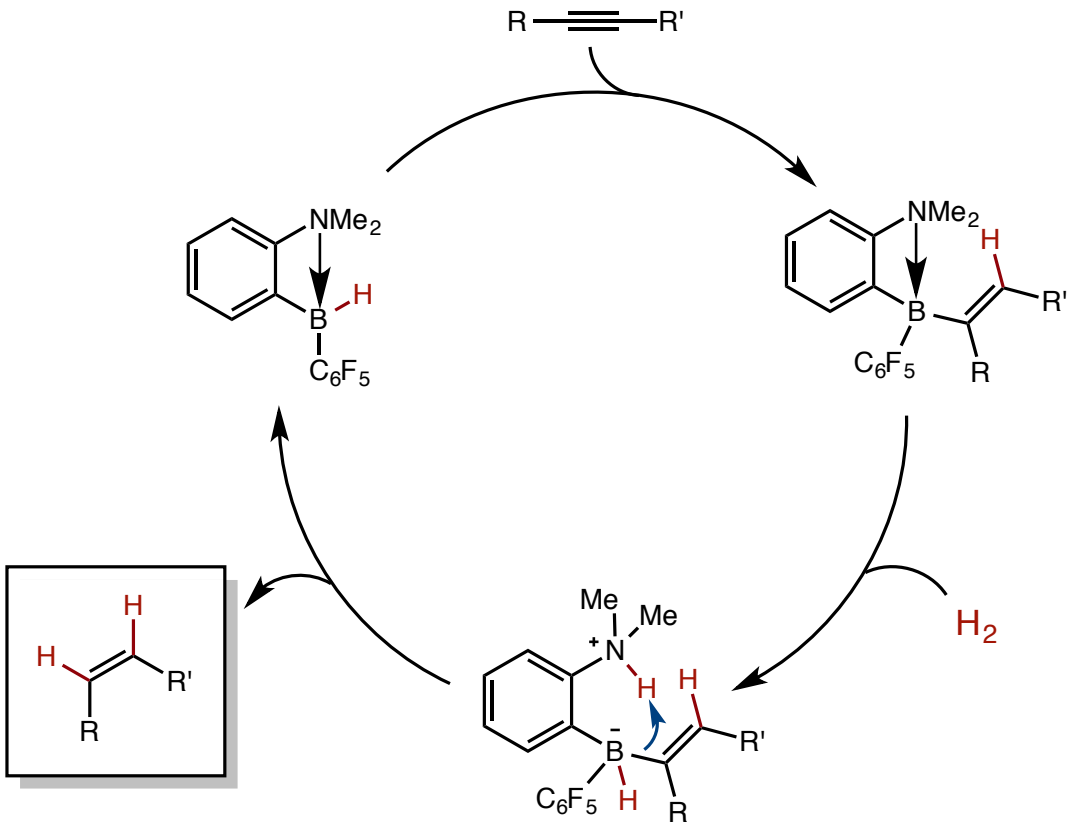
Hydrogenation of Non-Polar Substrates

Hydrogenation of Alkynes to Cis-Alkenes



Chernichenko, K.; Madarász, A.; Pápai, I.; Nieger, M.; Leskela, M.; Repo, T. *Nat. Chem.*, **2013**, *5*, 718-723.

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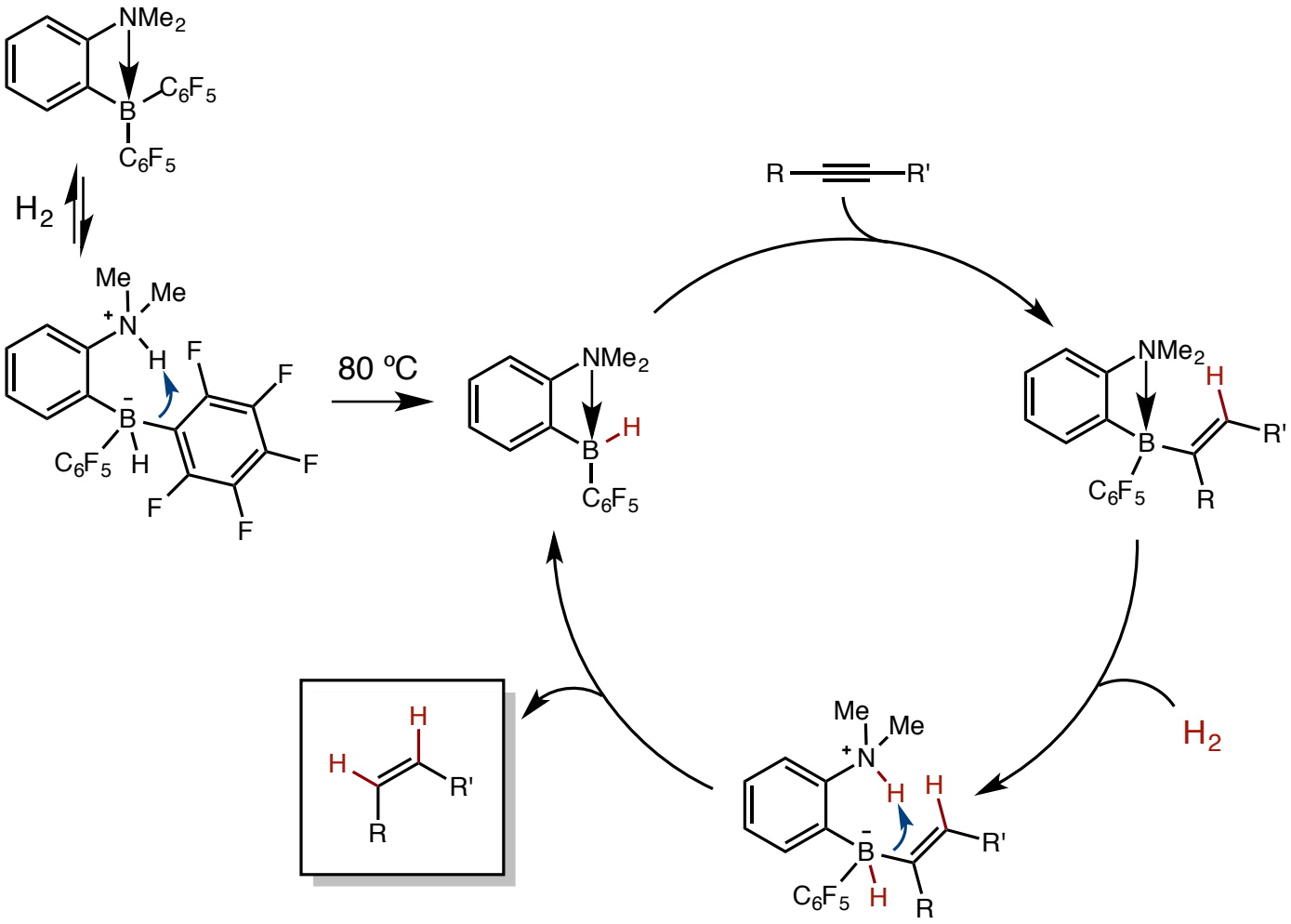

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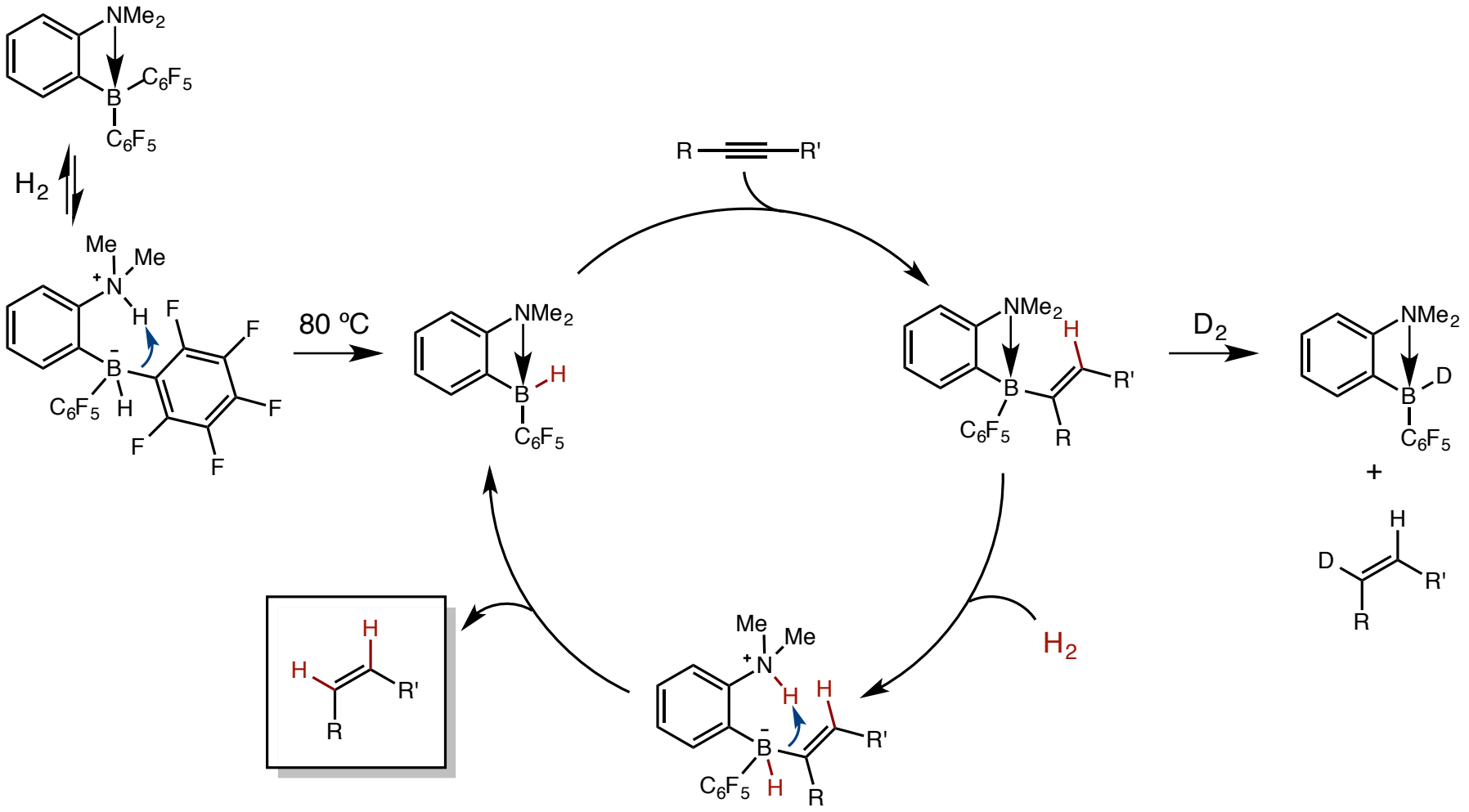
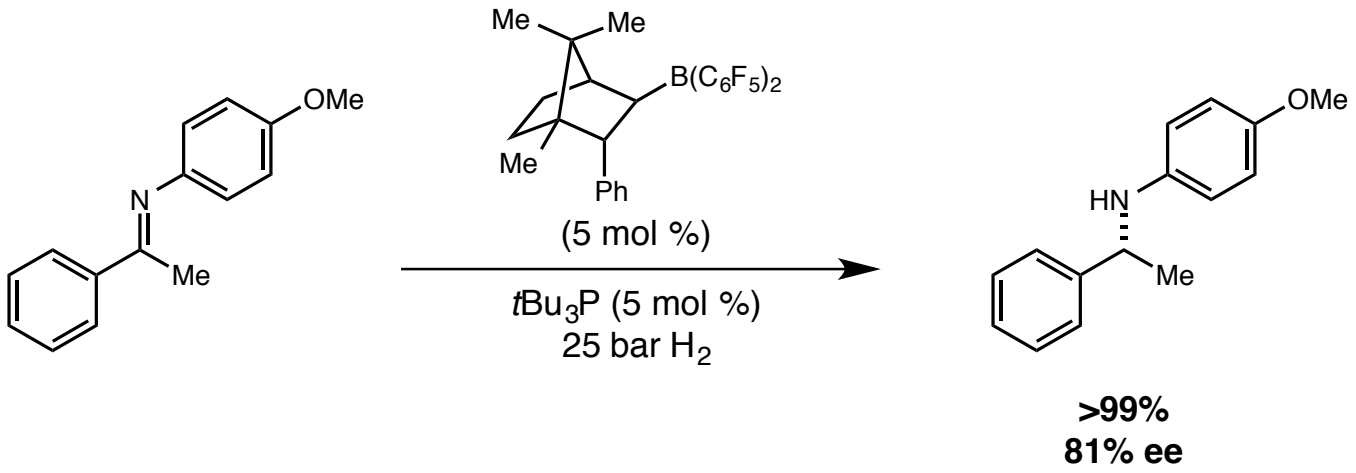


Chernichenko, K.; Madarász, A.; Pápai, I.; Nieger, M.; Leskela, M.; Repo, T. *Nat. Chem.*, **2013**, *5*, 718-723.

Asymmetric Catalytic Hydrogenation

Hydrogenation of Imines



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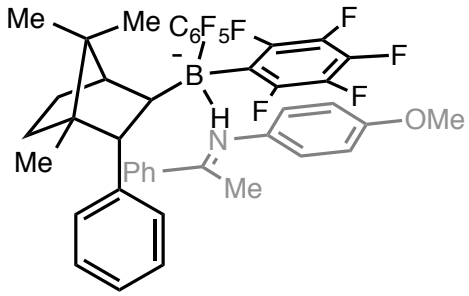
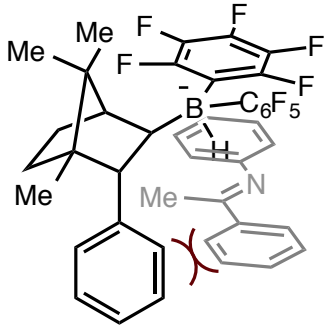


favored approach

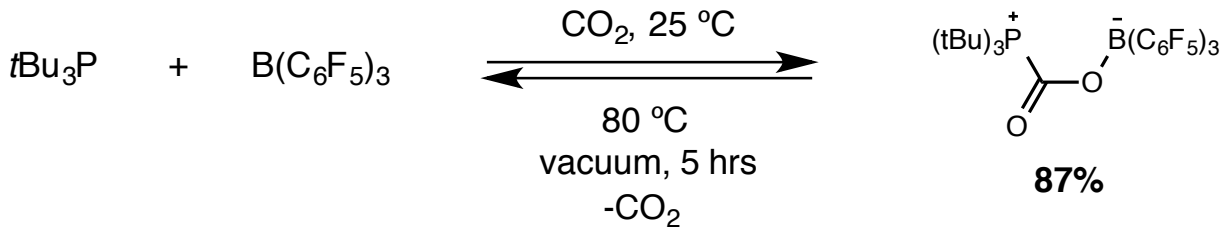


disfavored approach

Chen, D.; Wang, Y.; Klankermeyer, J. *ACIE*, **2010**, *49*, 9475-9578.

Applications in Green Chemistry

Reversible CO_2 Binding



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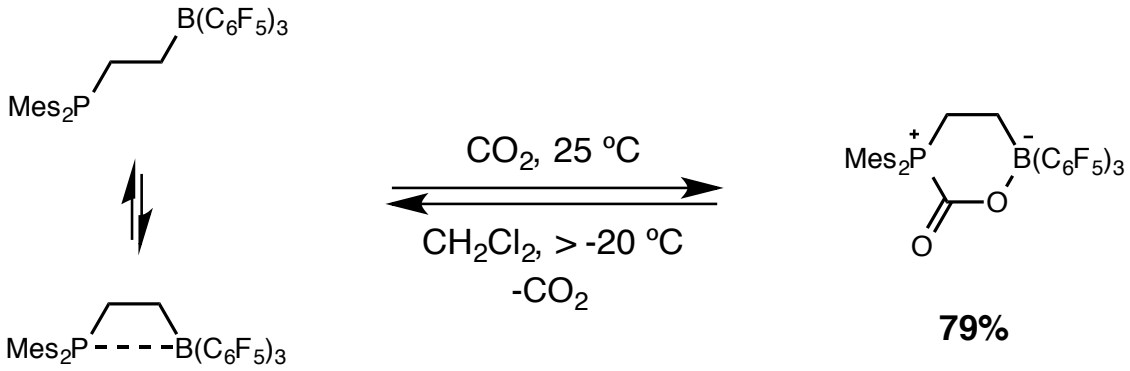


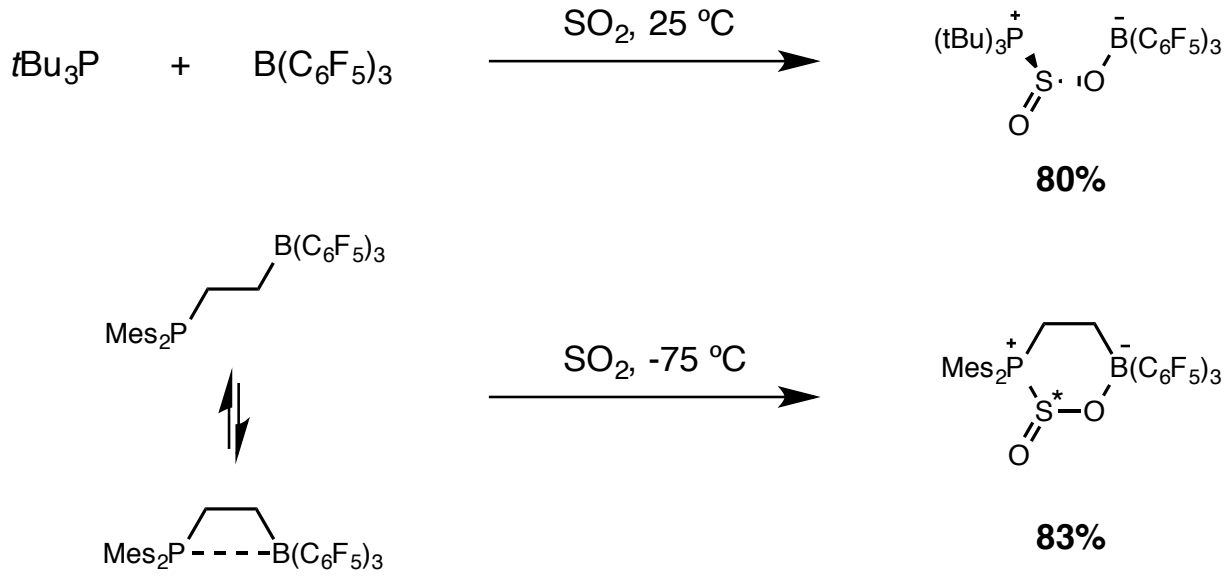
79%

Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *ACIE*, **2009**, *48*, 6643-6646.

Applications in Green Chemistry

SO_2 and N_2O Binding

- SO_2 is a major air pollutant, precursor to acid rain



Sajid, M. et. al. *Chem. Sci.*, **2013**, *4*, 213-219.

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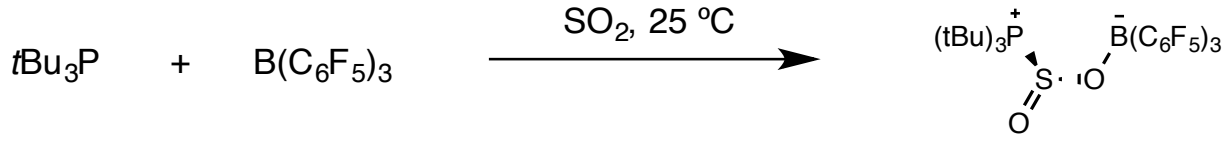

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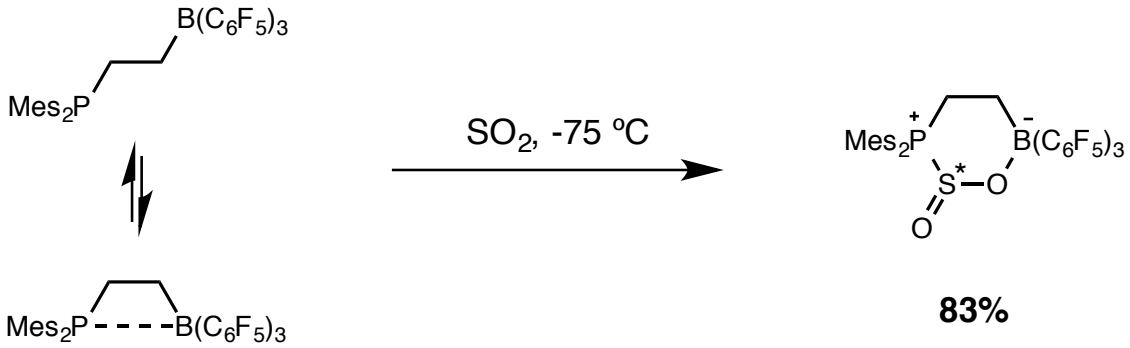
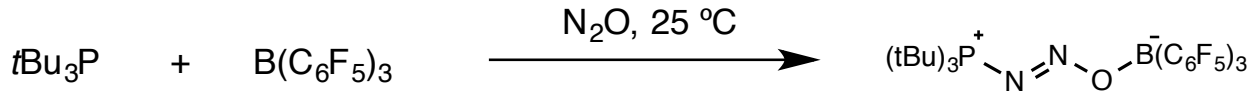


83%

- N_2O is a minor constituent in the atmosphere, but ~300x more potent as a greenhouse gas



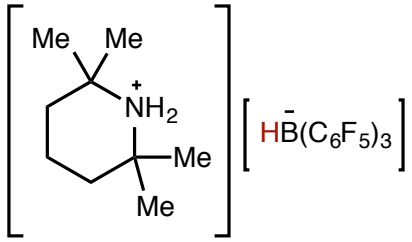
76%

Sajid, M. et. al. *Chem. Sci.*, **2013**, *4*, 213-219.
Otten, E.; Neu, R. C.; Stephan, D. W. *JACS*, **2009**, *131*, 9918-9919.

Applications in Green Chemistry

Converting CO_2 to Fuels

- Addition of Et_3SiH to CO_2 in the presence of an FLP efficiently reduces CO_2 to CH_4



Berkefeld, A.; Piers, W. E.; Parvez, M. *JACS*, **2010**, *132*, 10660-10661.

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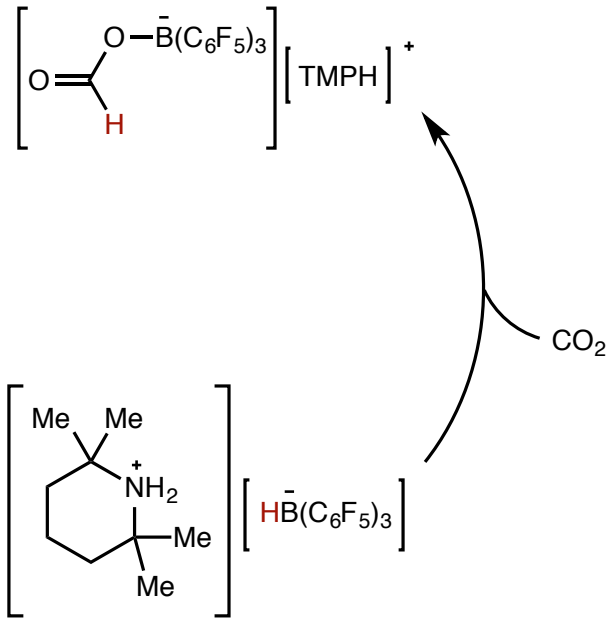

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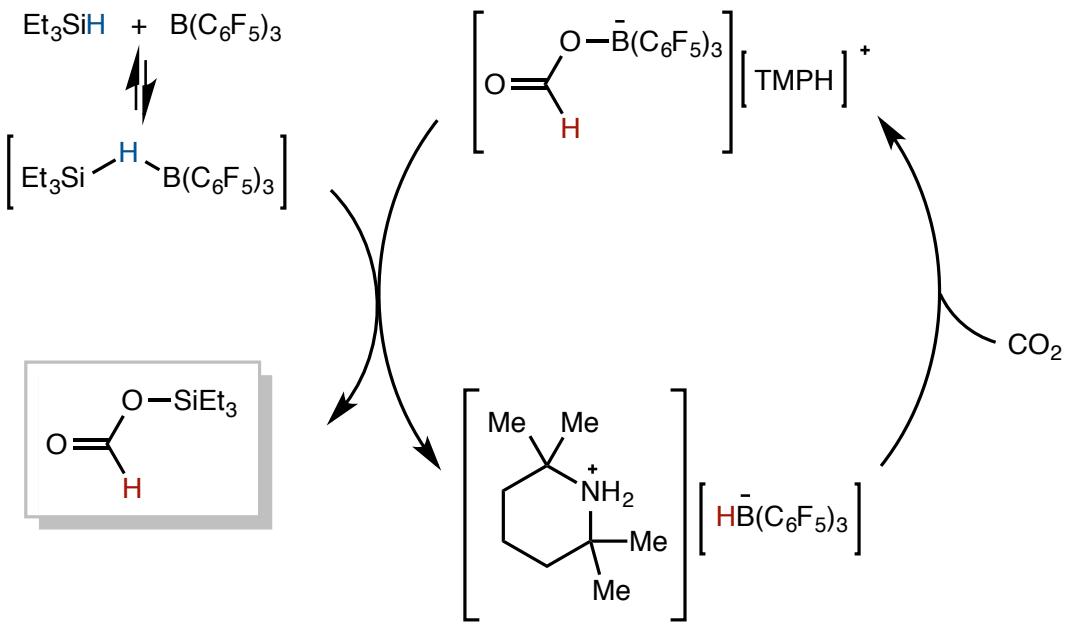

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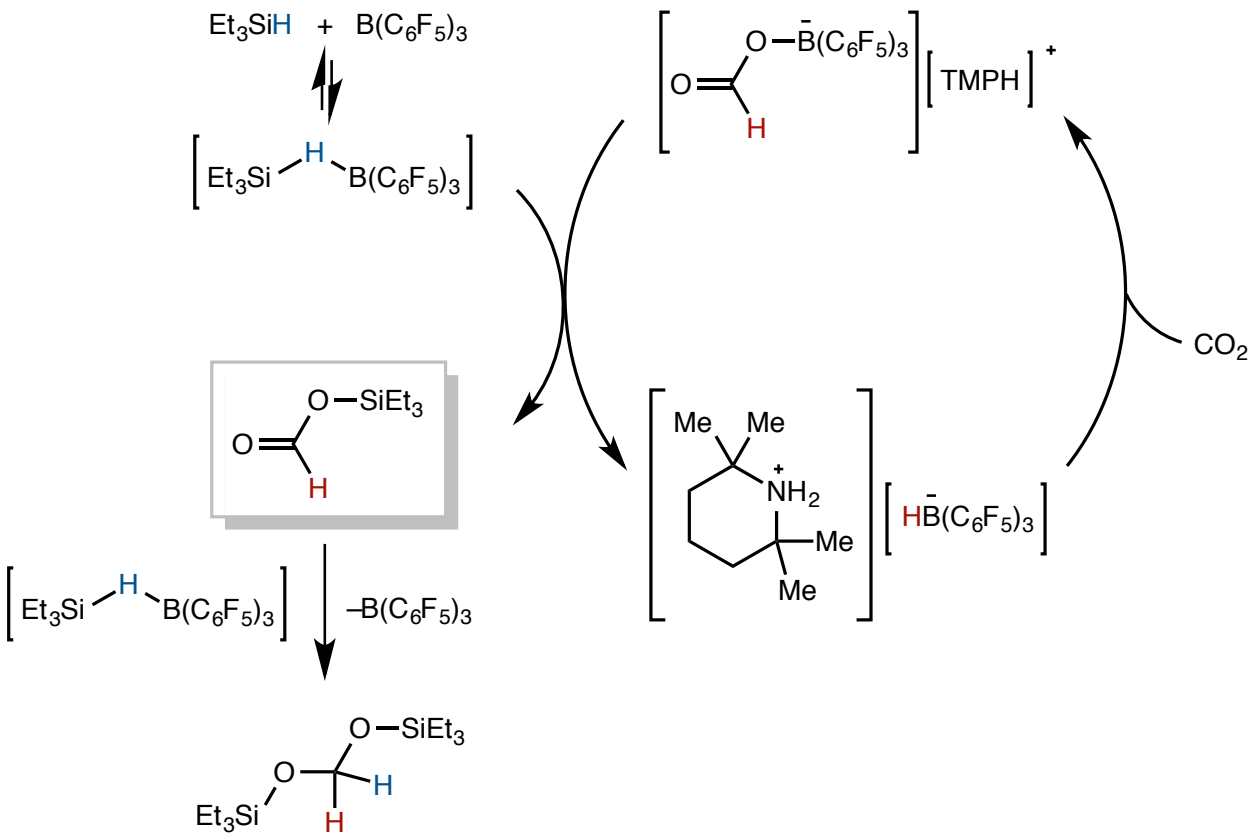

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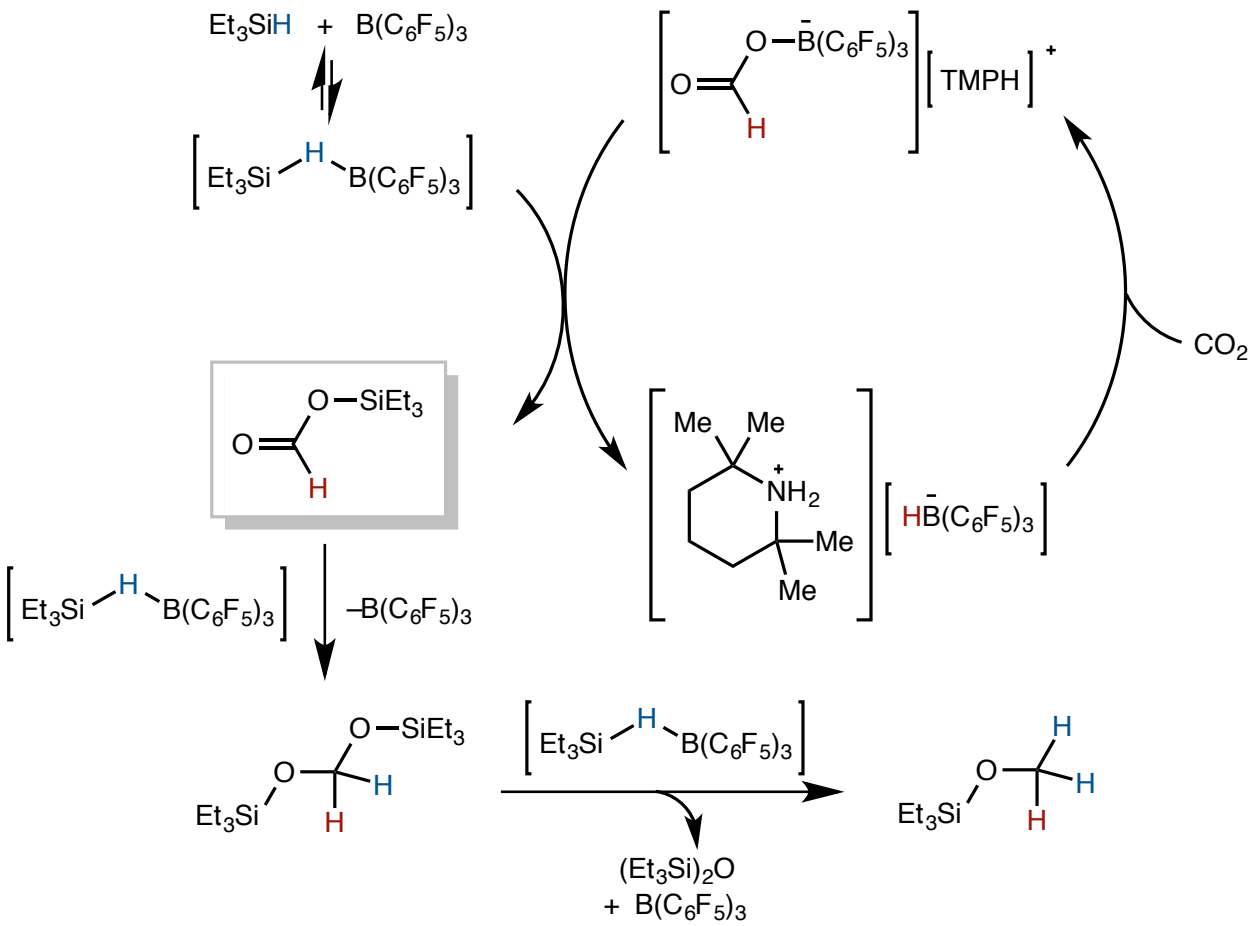

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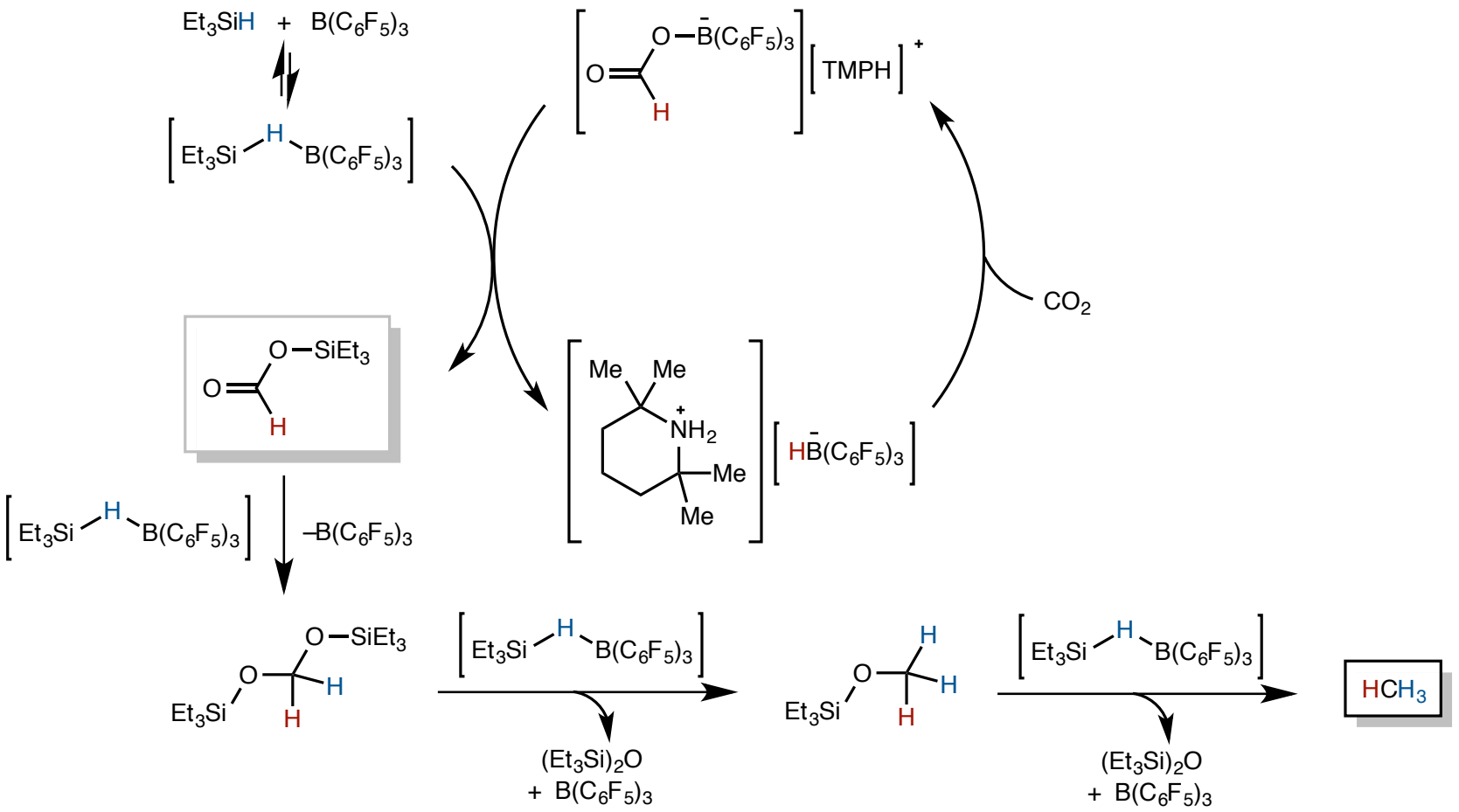
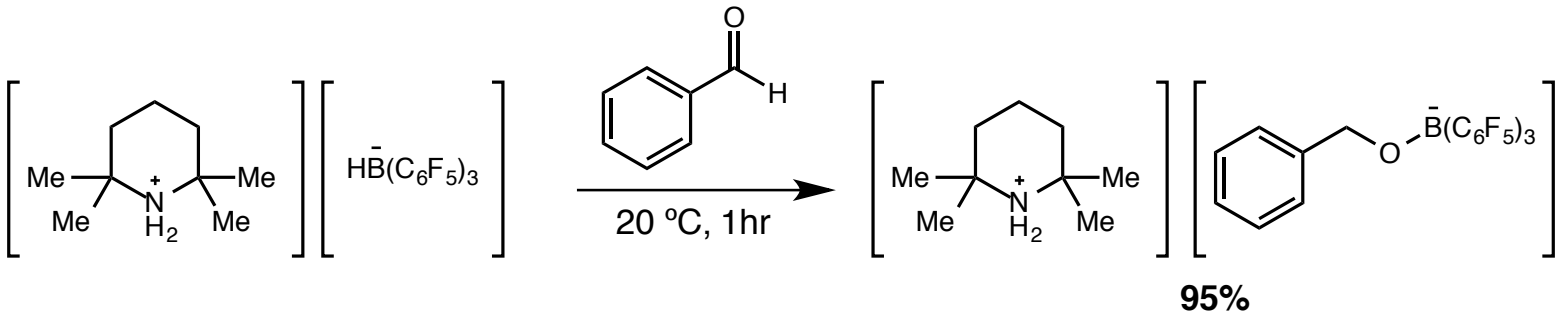


Berkefeld, A.; Piers, W. E.; Parvez, M. *JACS*, **2010**, *132*, 10660-10661.

Limitations and Future Directions

- Currently cannot hydrogenate aldehydes or ketones catalytically



95%

- Discovery of better FLP catalysts for asymmetric induction; expanding the scope to olefin hydrogenations

- Hydrogen gas storage - currently FLPs can achieve 0.25 wt % H_2; whereas to be practical need 6 - 9 wt % H_2 (i.e. ammonia-borane)

Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *ACIE*, **2008**, *47*, 6001-6003.

Summary

- *I. Theories on the Mechanism of H_2 Activation*
  - Electron Transfer Model that Invokes Frontier Molecular Orbitals
  - Electric Field Model that disregards Frontier Molecular Orbitals
  - Secondary non-covalent interactions play key role in lowering H_2 activation barrier

- *II. Applications of FLPs in Hydrogenation Reactions and Storage of Small Molecules*
  - Catalytic hydrogenation of imines, enamines, nitriles, aziridines, silyl enol ethers, cyclic ethers, alkenes, alkynes, ynones
  - Stoichiometric hydrogenations of aldehydes, ketones
  - Asymmetric imine hydrogenations
  - Advances in area of green chemistry