# Literature Report 3

## A Crystalline Aluminium-Carbon-Based Ambiphile Capable of Activation and Catalytic Transfer of Ammonia in Non-aqueous Media

Reporter: Na Li
Date: 2024-07-30

Krämer, F.; Paradies, J.; Fernández, I.; **Breher, F.** *Nat. Chem.* **2024**, *16*, 63-69

# CV of Prof. Dr. Frank Breher

## Background:

- ☐ **1998-2001** Ph.D., Oldenburg University and Marburg University
- ☐ **2001-2005** Postdoctoral Fellow, ETH Zürich
- ☐ **2005-2010** Assistant Professor, Universität Karlsruhe
- ☐ **2010-now** Professor, Karlsruhe Institute of Technology

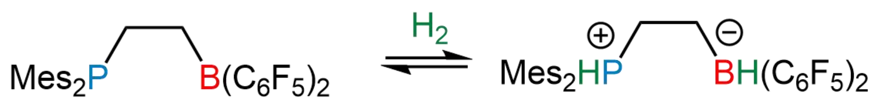
## Research Interests:

- ➢ **Reactivity of Organometallic and Coordination Compounds**
- ➢ **Spectroscopic Techniques**
- ➢ **Density Functional Theory Calculations**

# Contents

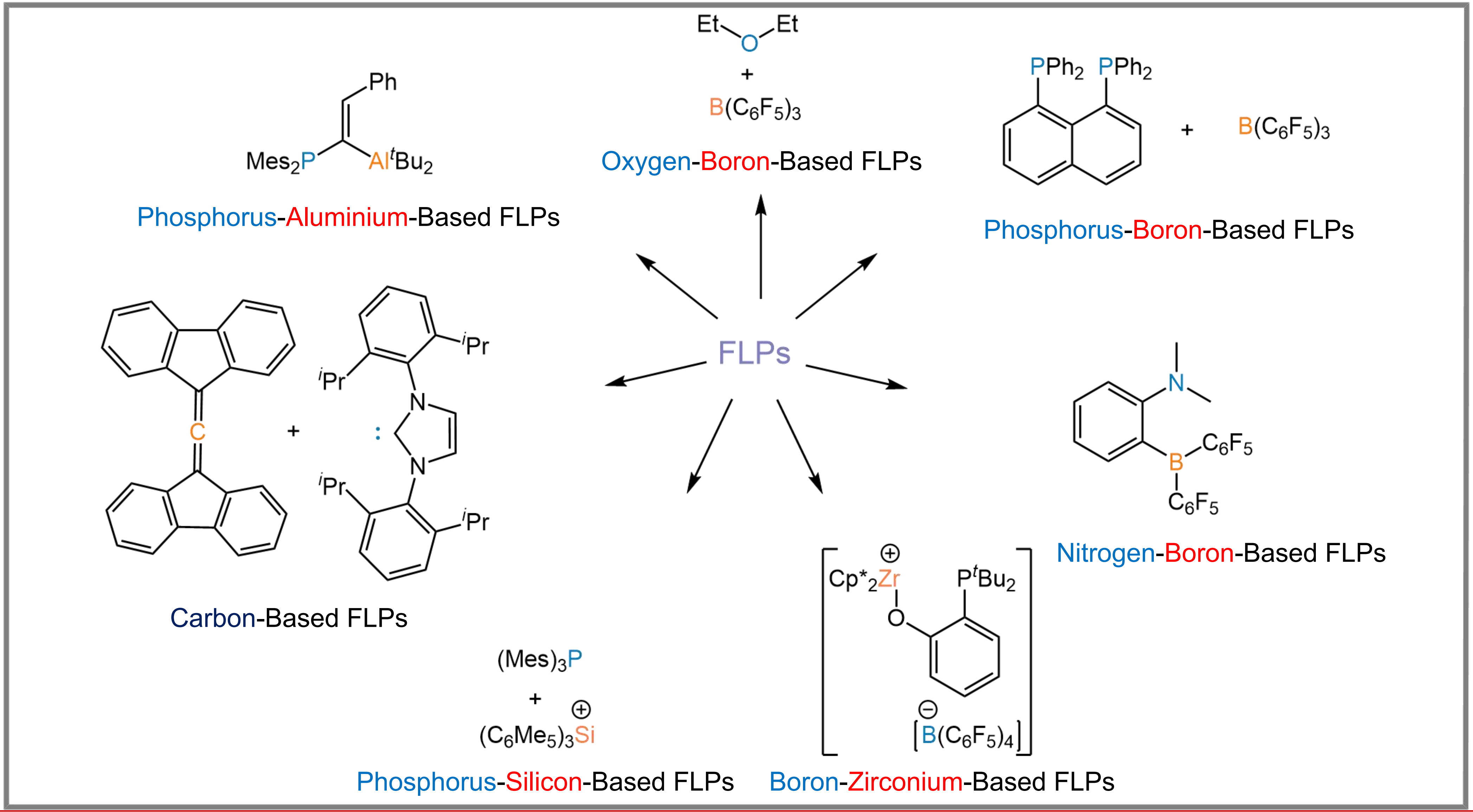
# Introduction: The Concept of FLPs

受阻路易斯酸碱对(Frustrated Lewis Pairs, FLPs)即在一个或一对分子中同时存在Lewis酸中心和Lewis碱中心，但由于位阻等某些原因使得这两个中心不能接触，这样得到的化合物称为受阻路易斯酸碱对。受阻路易斯酸碱对具有催化功能。



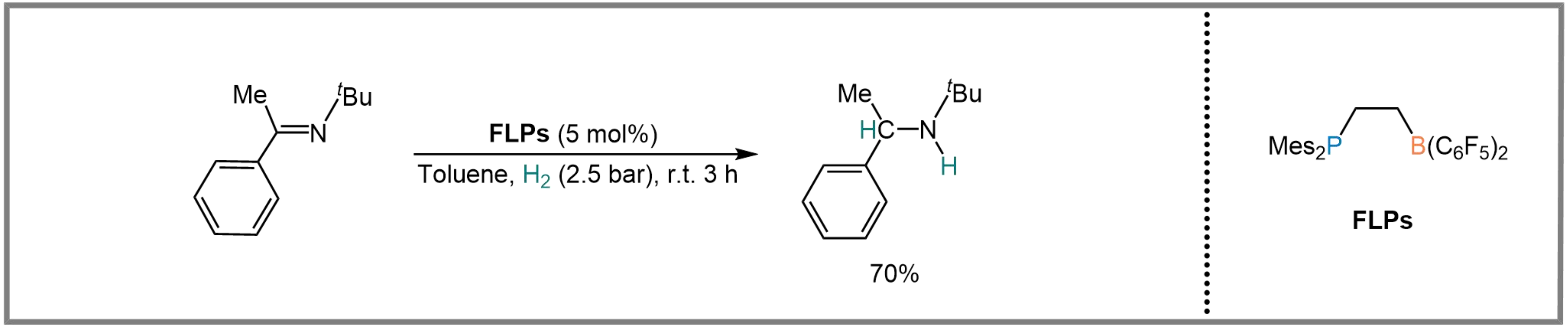

FLPs

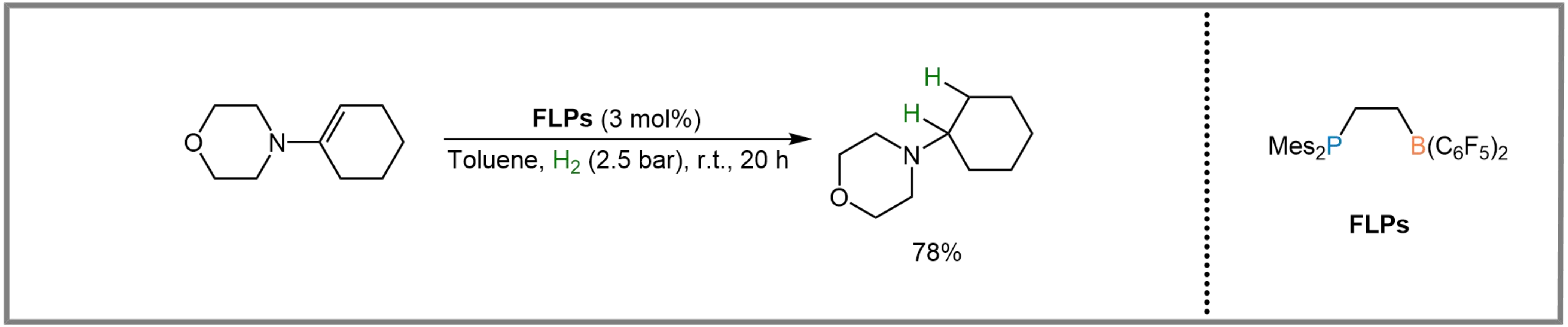
# Introduction: The Types of FLPs



# **Introduction:** FLPs Chemistry of $H_2$

## Reduction of Imines and Enamines

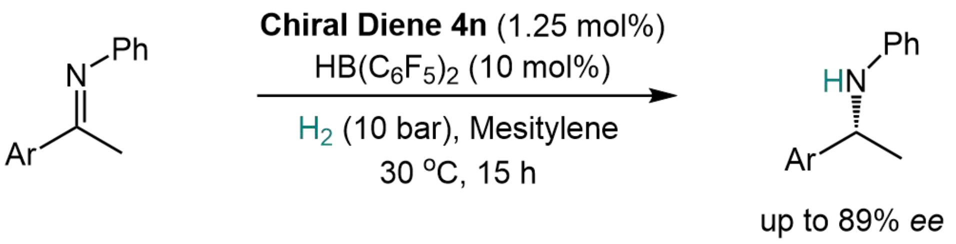


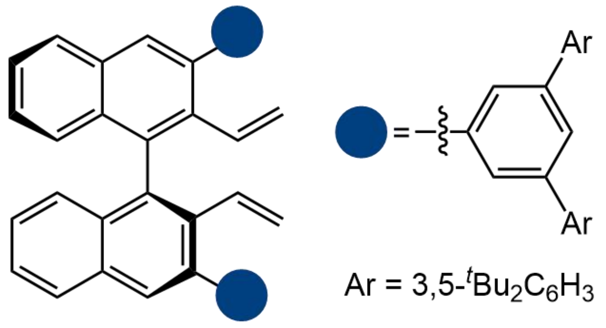




Spies, P.; Schwendemann, S.; **Erker, G.** *Angew. Chem. Int. Ed.* **2008**, *47*, 7543-7546

# Introduction: FLPs Chemistry of $H_2$

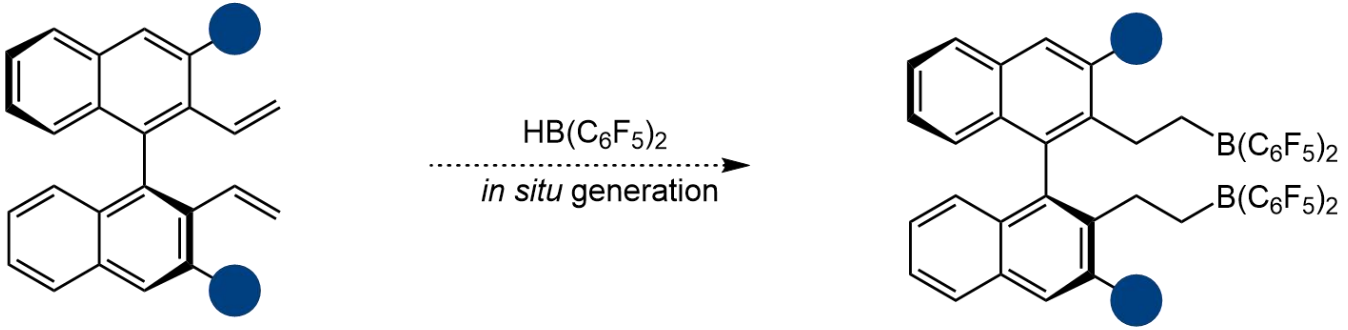
## Asymmetric Reductions



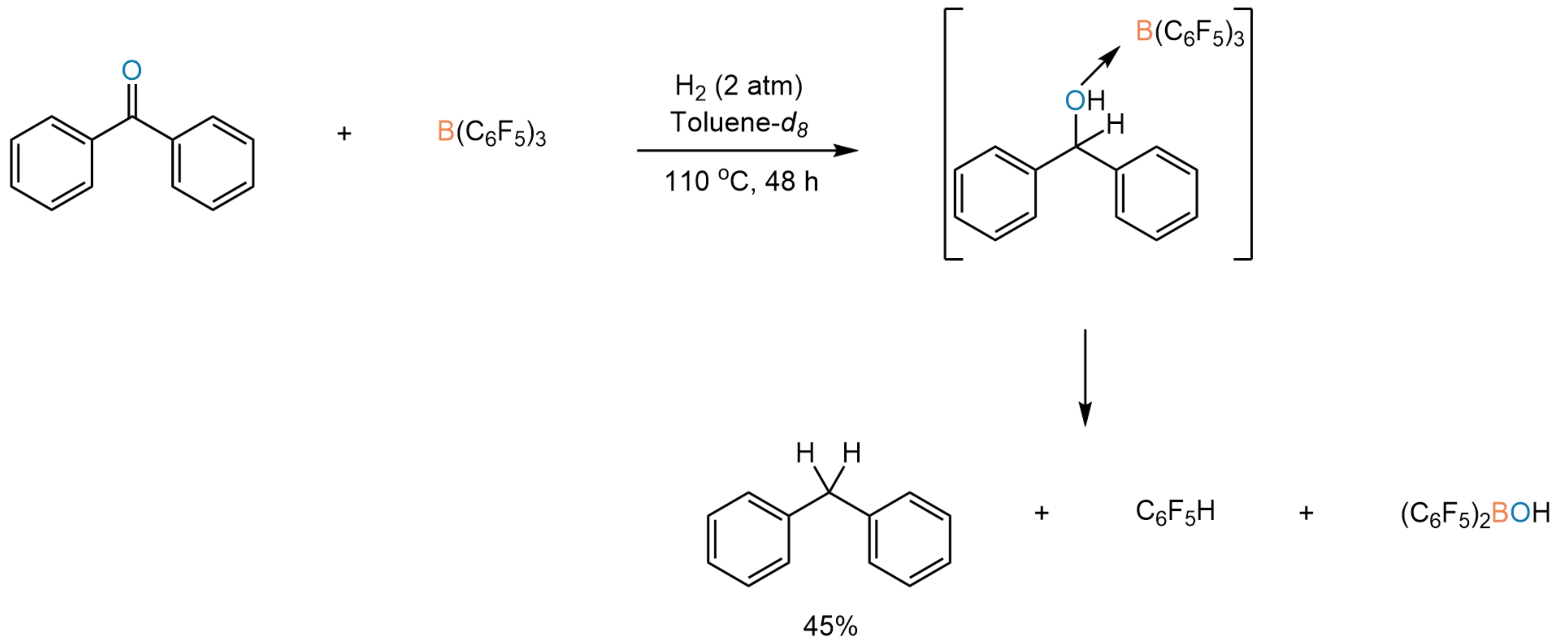

**Chiral Diene 4n**

Note:



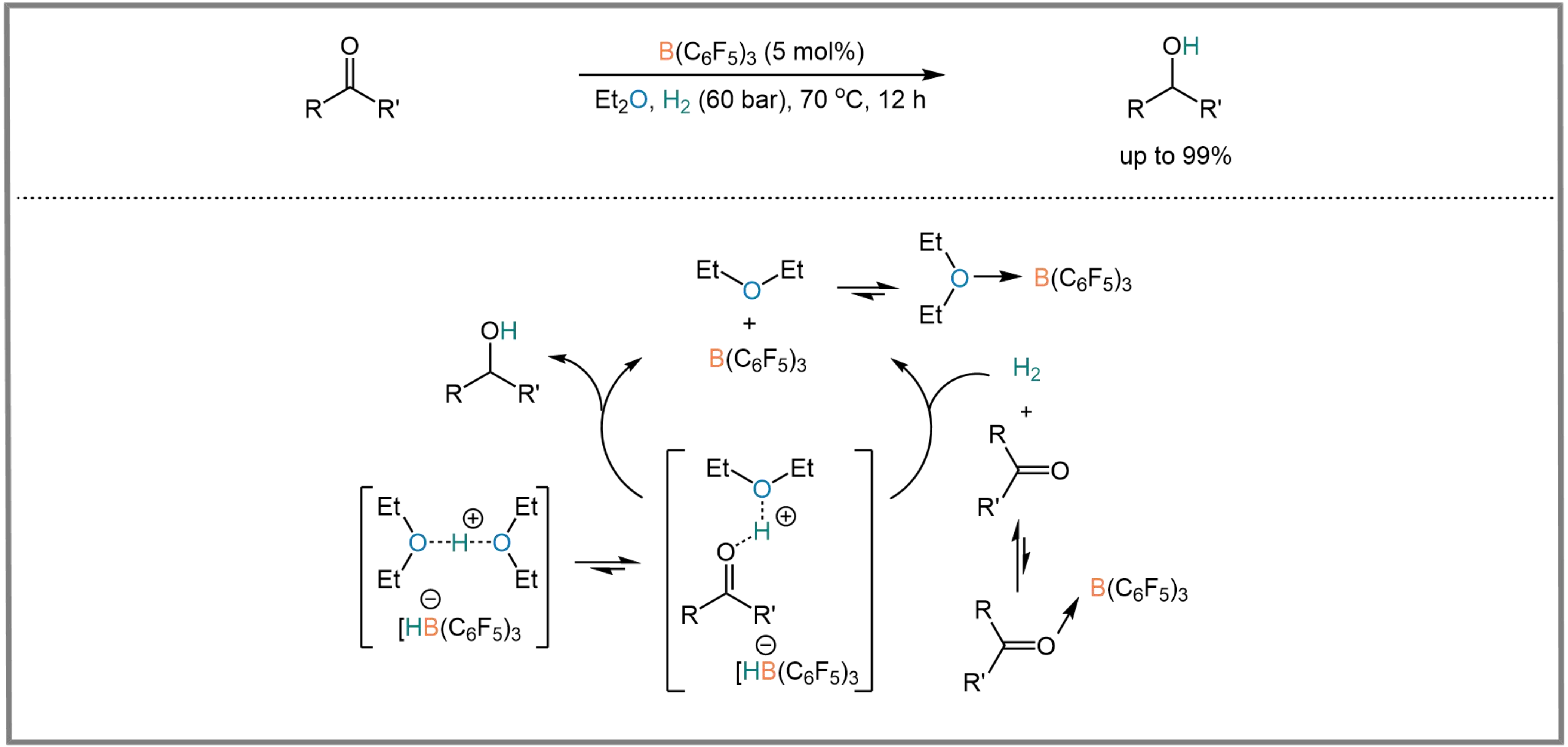

Liu, Y.-B.; **Du, H.-F.** *J. Am. Chem. Soc.* **2013**, *135,* 6810-6813

## The Borane Degradation in Reduction of Carbonyl Derivatives




Lindqvist, M.; Sarnela, N.; **Repo, T.** *Dalton Trans.* **2012**, *41*, 4310-4312

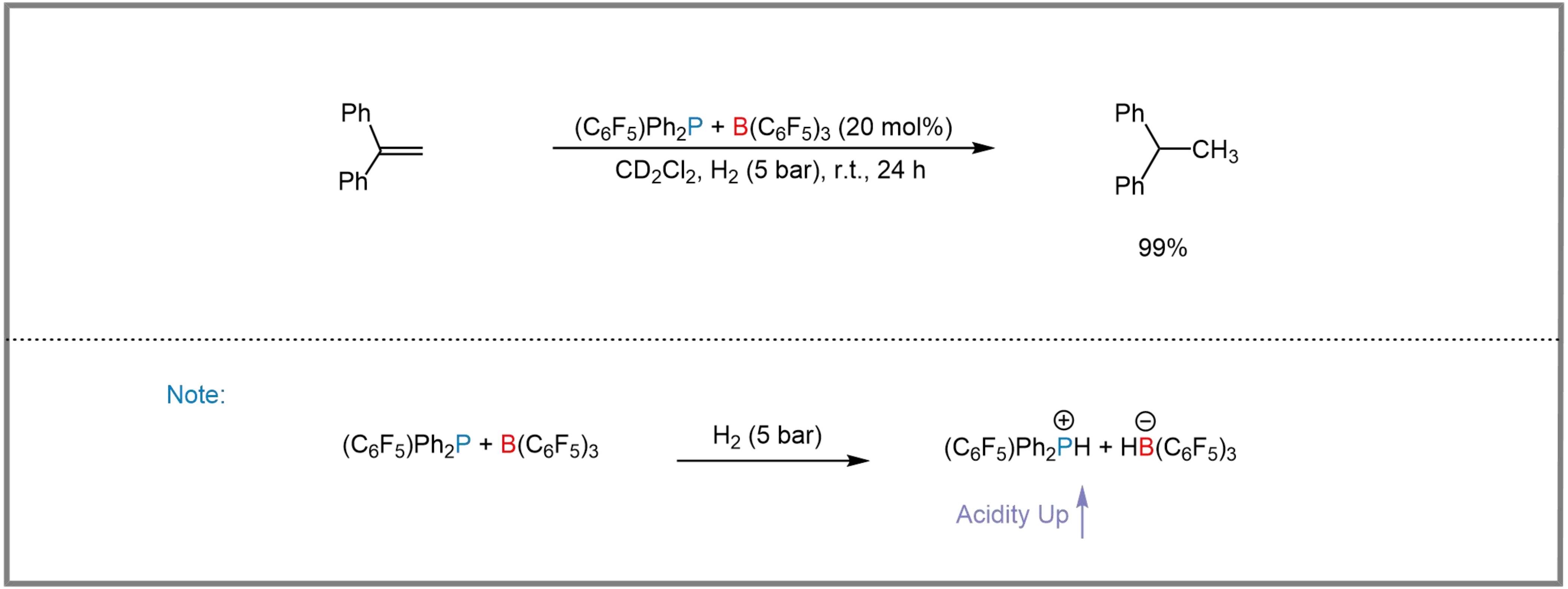
## Reduction of Carbonyl Derivatives




Mahdi, T.; **Stephan, D. W.** *J. Am. Chem. Soc.* **2014**, *136*, 15809-15812

# Introduction: FLPs Chemistry of $H_2$

## Reduction of Olefins

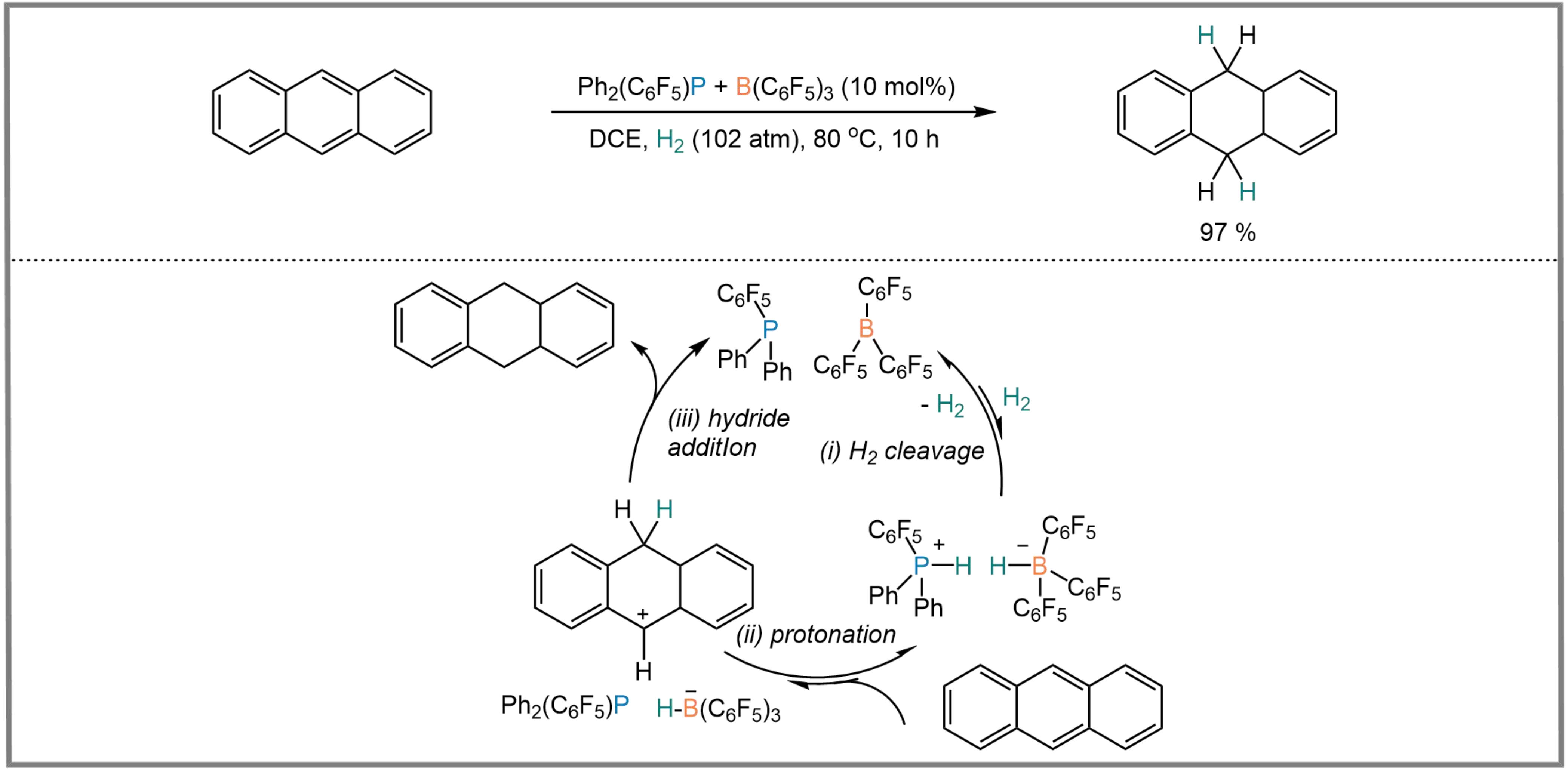



✓ Weakly basic phosphine can enhance the Brønsted acidity of the cation generated by the FLPs activation of hydrogen.

Greb, L.; Schirmer, B.; **Paradies, J.** *Angew. Chem. Int. Ed.* **2012**, *51*, 10164-10168

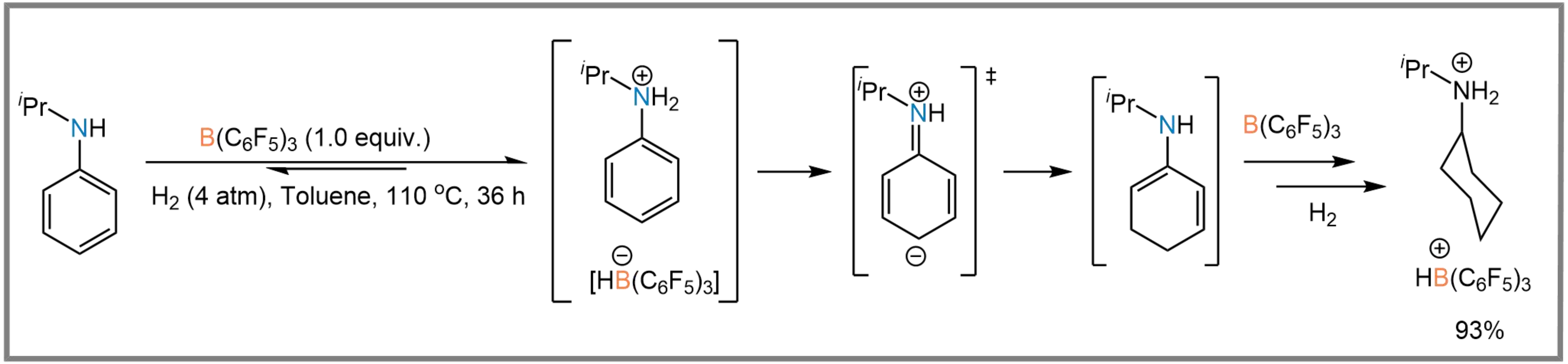
# Introduction: FLPs Chemistry of $H_2$

## Reduction of Arene




Segawa, Y.; **Stephan, D. W.** *Chem. Commun.* **2012**, *48*, 11963-11965

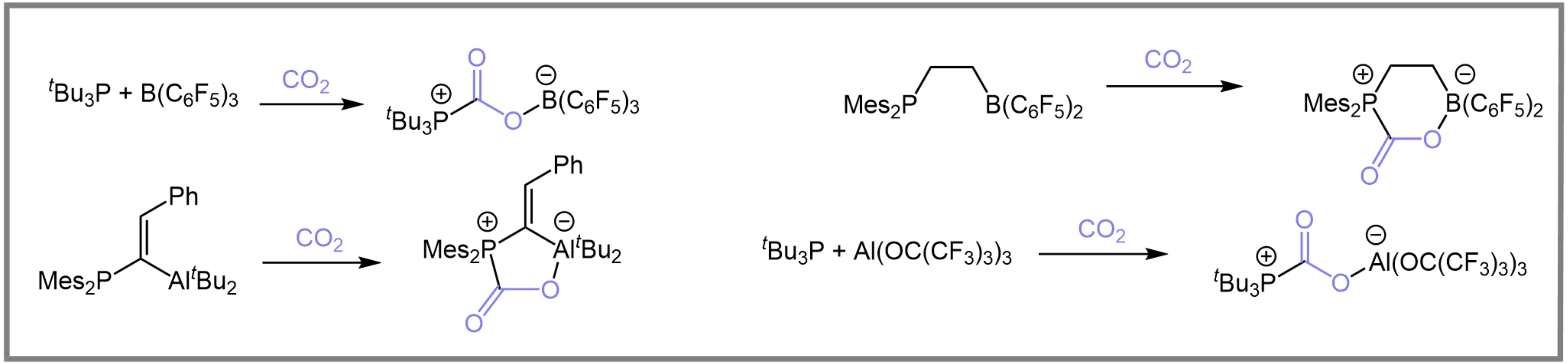
## Reduction of Arene




Mahdi, T.; Heiden, Z. M.; **Stephan, D. W.** *J. Am. Chem. Soc.* **2012**, *134*, 4088-4091

# **Introduction:** FLPs Chemistry of $CO_2$

## $CO_2$ Capture

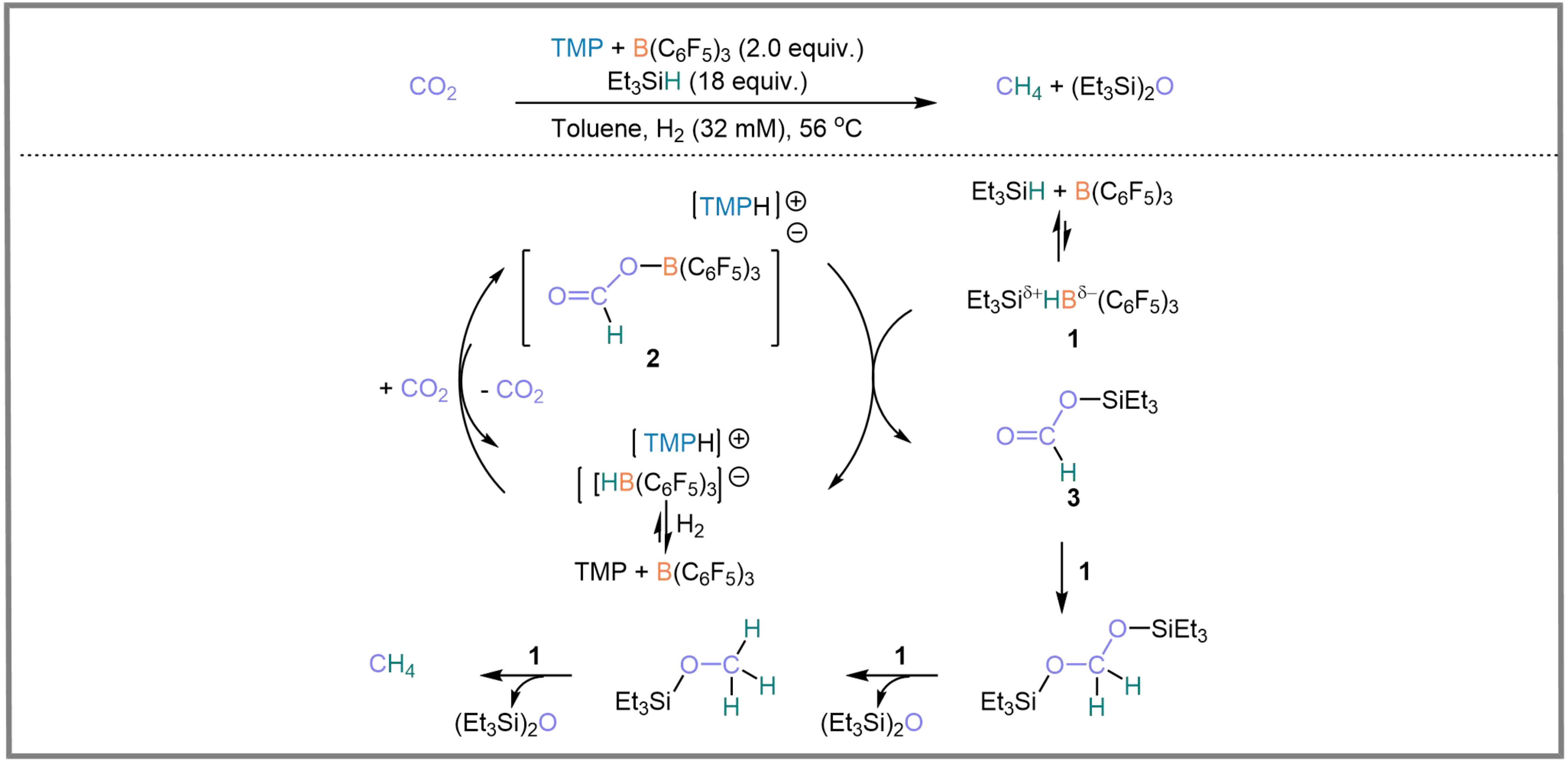




Momming, C. M.; Otten, E.; Kehr, G.; **Stephan, D. W.** *Angew. Chem. Int. Ed.* **2009**, *48*, 6643-6646
Appelt, C.; Westenberg, H.; Lammertsma, K.; **Uhl, W.** *Angew. Chem. Int. Ed.* **2011**, *50*, 3925-3928

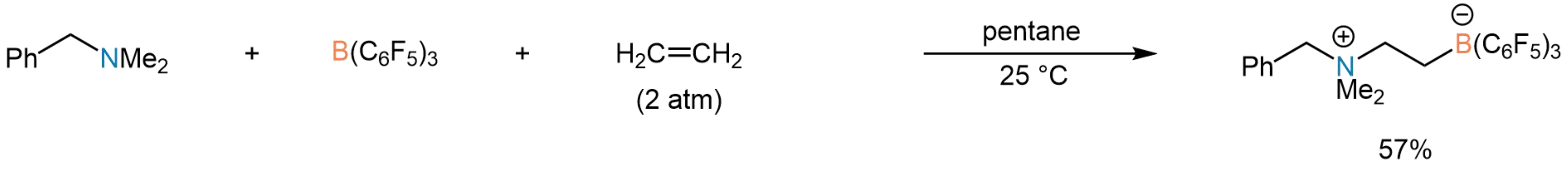
# Introduction: FLPs Chemistry of $CO_2$

## Reduction of $CO_2$




Berkefeld, A.; Piers, W. E. **Parvez, M.** *J. Am. Chem. Soc.* **2010**, *132*, 10660-10661

# **Introduction:** FLP Addition Reactions

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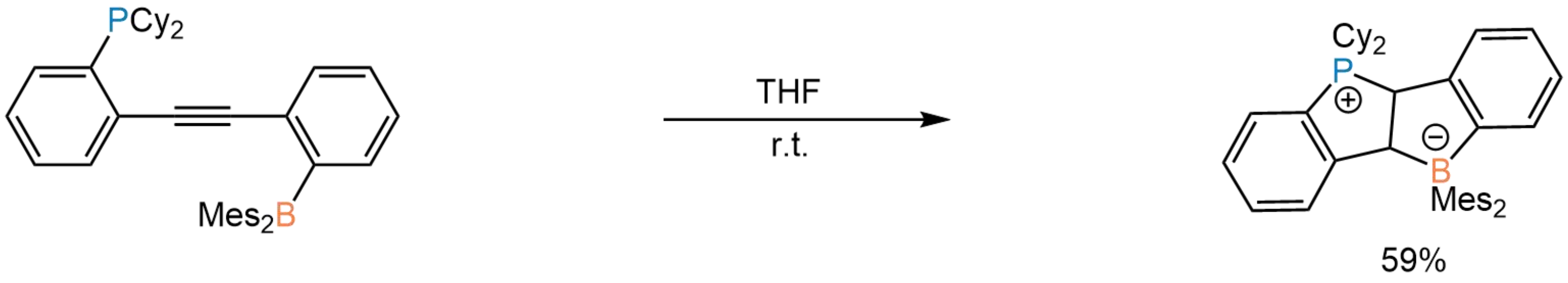
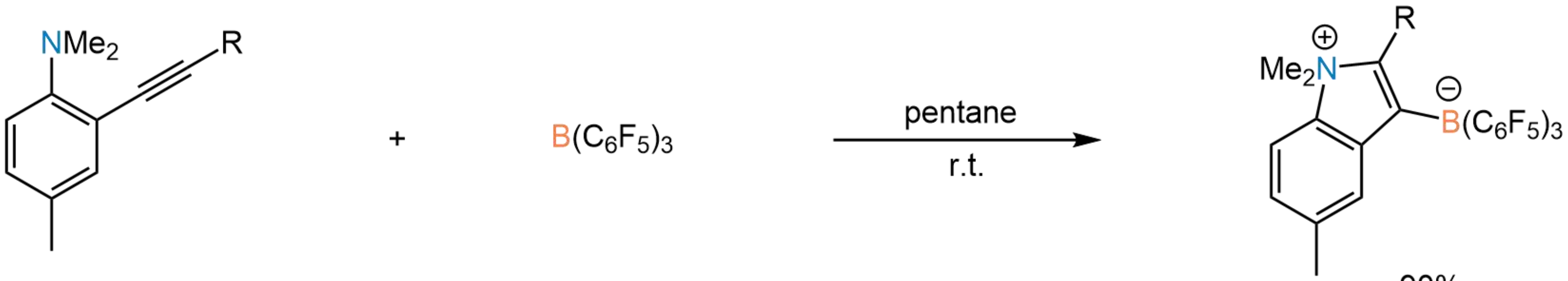


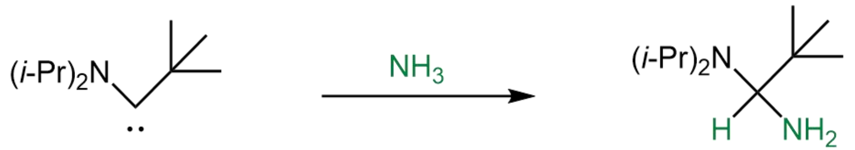

Fukazawa, A.; Yamada, H.; **Yamaguchi, S.** *Angew. Chem. Int. Ed.* **2008**, *47*, 5582-5585



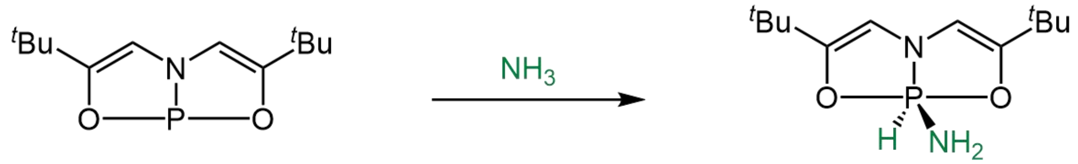

90%

Voss, T.; Chen, C.; **Stephan, D. W.** *Chem. Eur. J.* **2010**, *16*, 3005-3008

# Project Synopsis

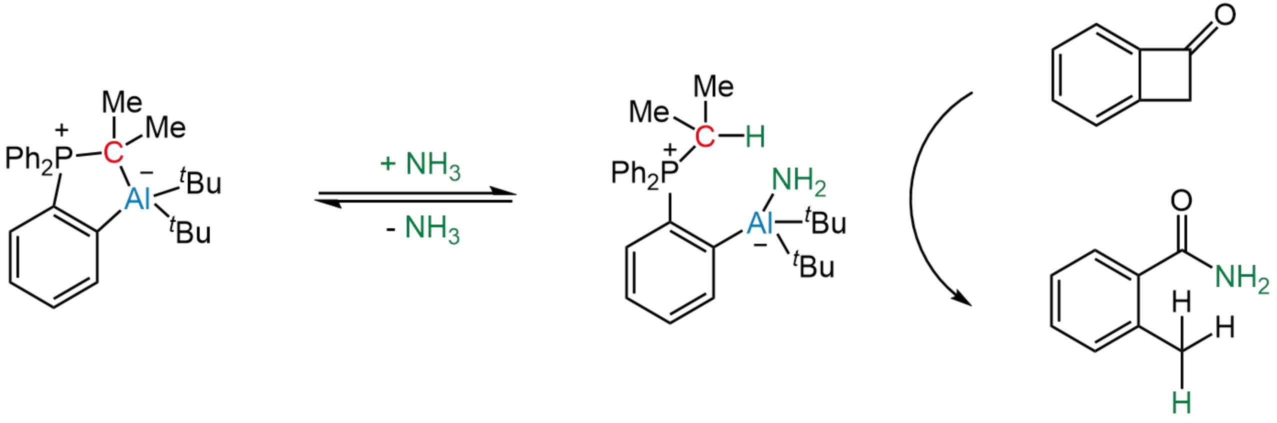



Frey, G. D.; Lavallo, V.; **Bertrand, G.** *Science.* **2007**, *316*, 439-441




Abbenseth, J.; Townrow, O. P. E.; **Goicoechea, J. M.** *Angew. Chem. Int. Ed.* **2021**, *60*, 23625-23629

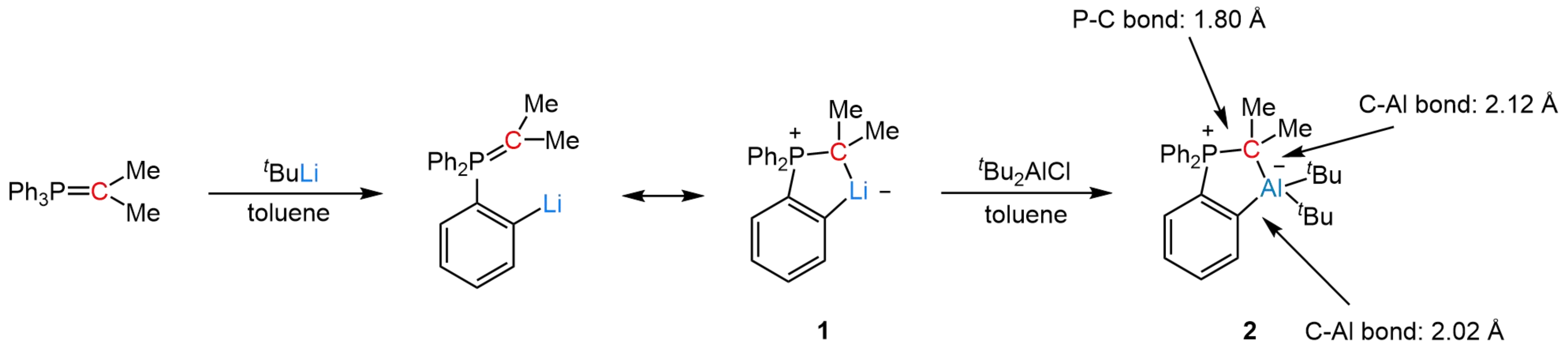
**This Work:**



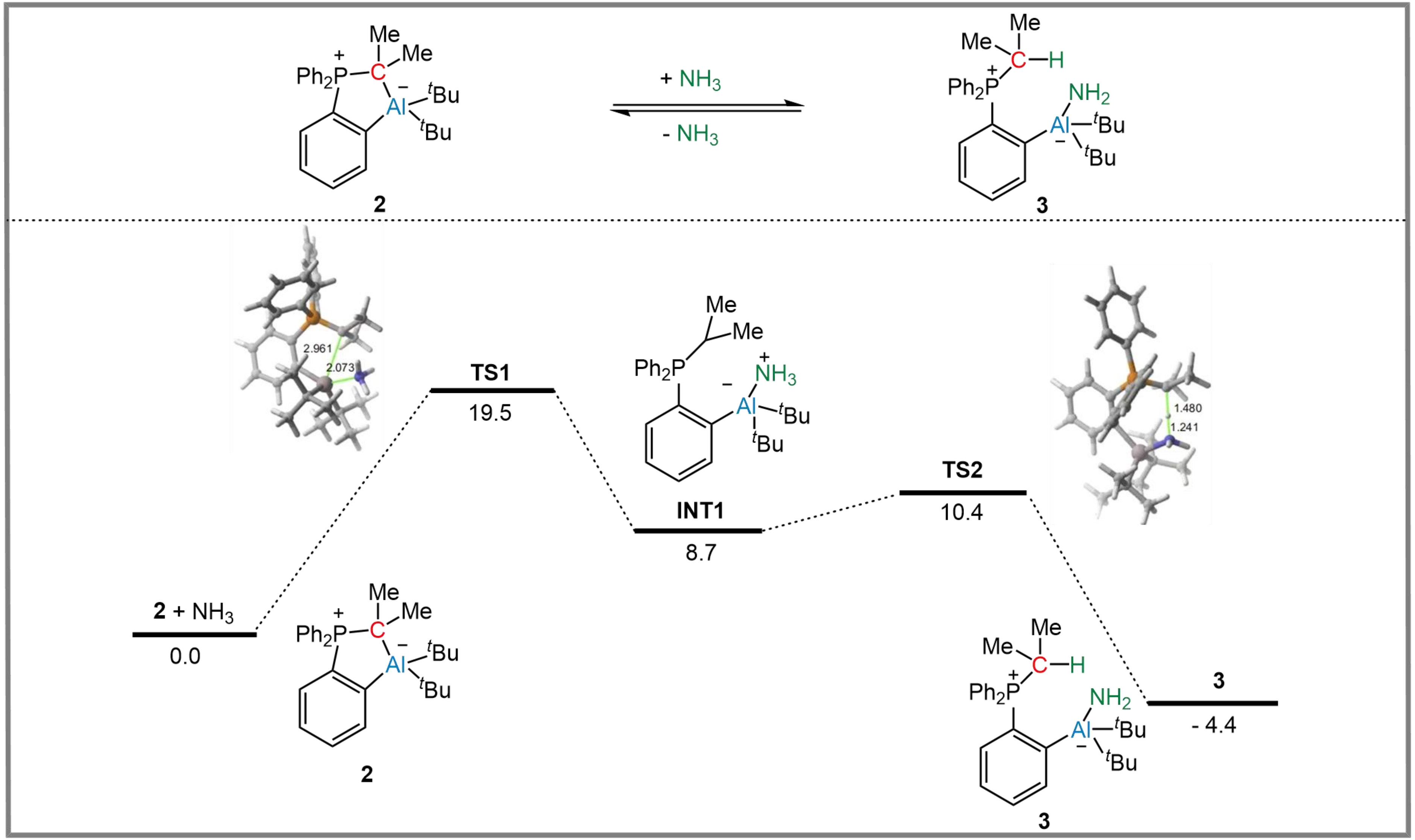

**Ammonia Activation**

**Catalytic Transfer**

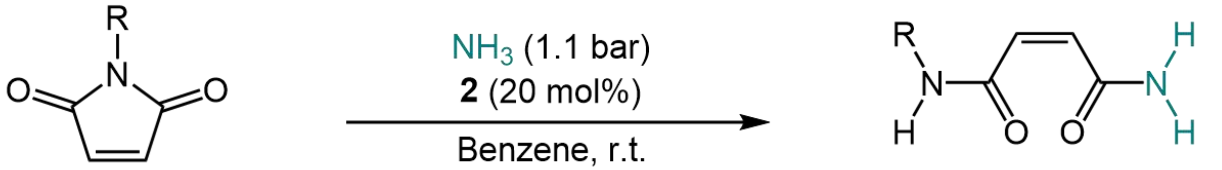
# The Synthesis of Aluminium–Carbon-Based FLPs



# The N–H Bond Activation by Aluminium–Carbon-Based FLPs



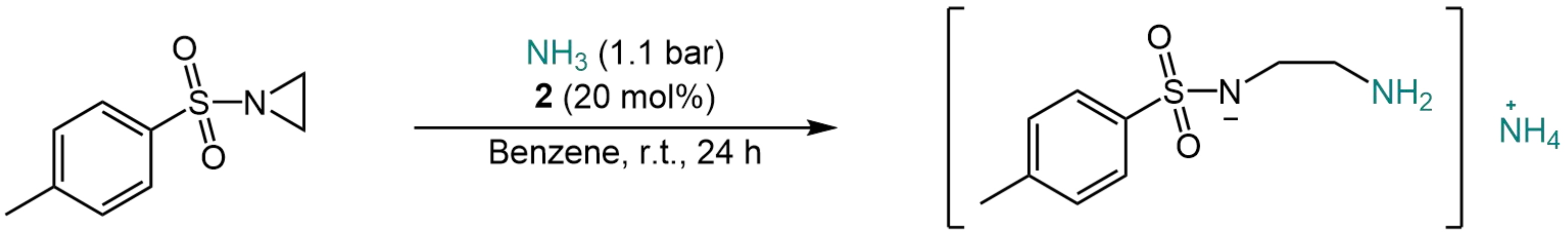
# Catalytic Ammonia Transfer by Aluminium–Carbon-Based FLPs




R = H (**I**), 48 h; R = Ph (**II**), 20 h

R = H (**Ia**); R = Ph (**IIa**)

>99% Conversion
0% Preparative Yield

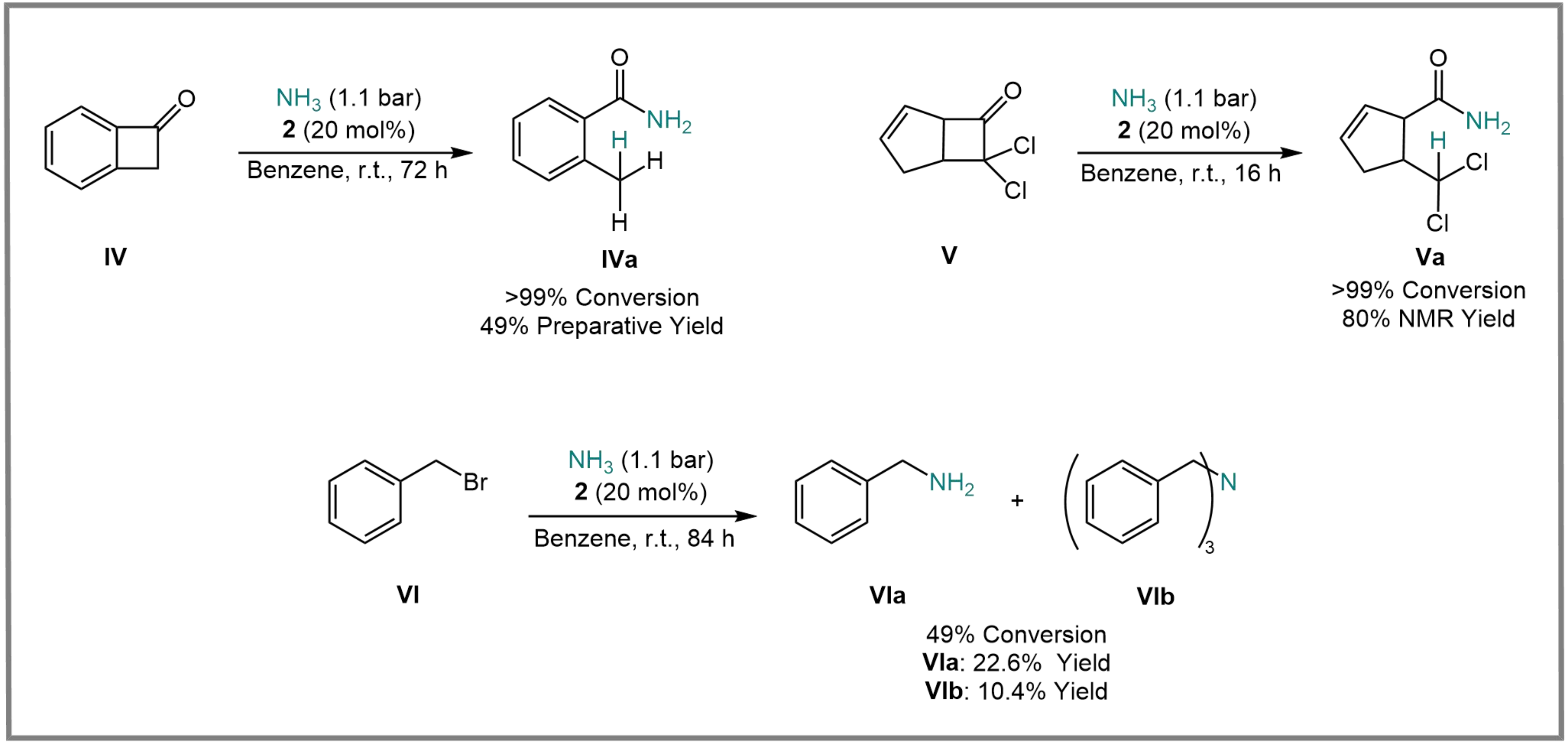



**III**

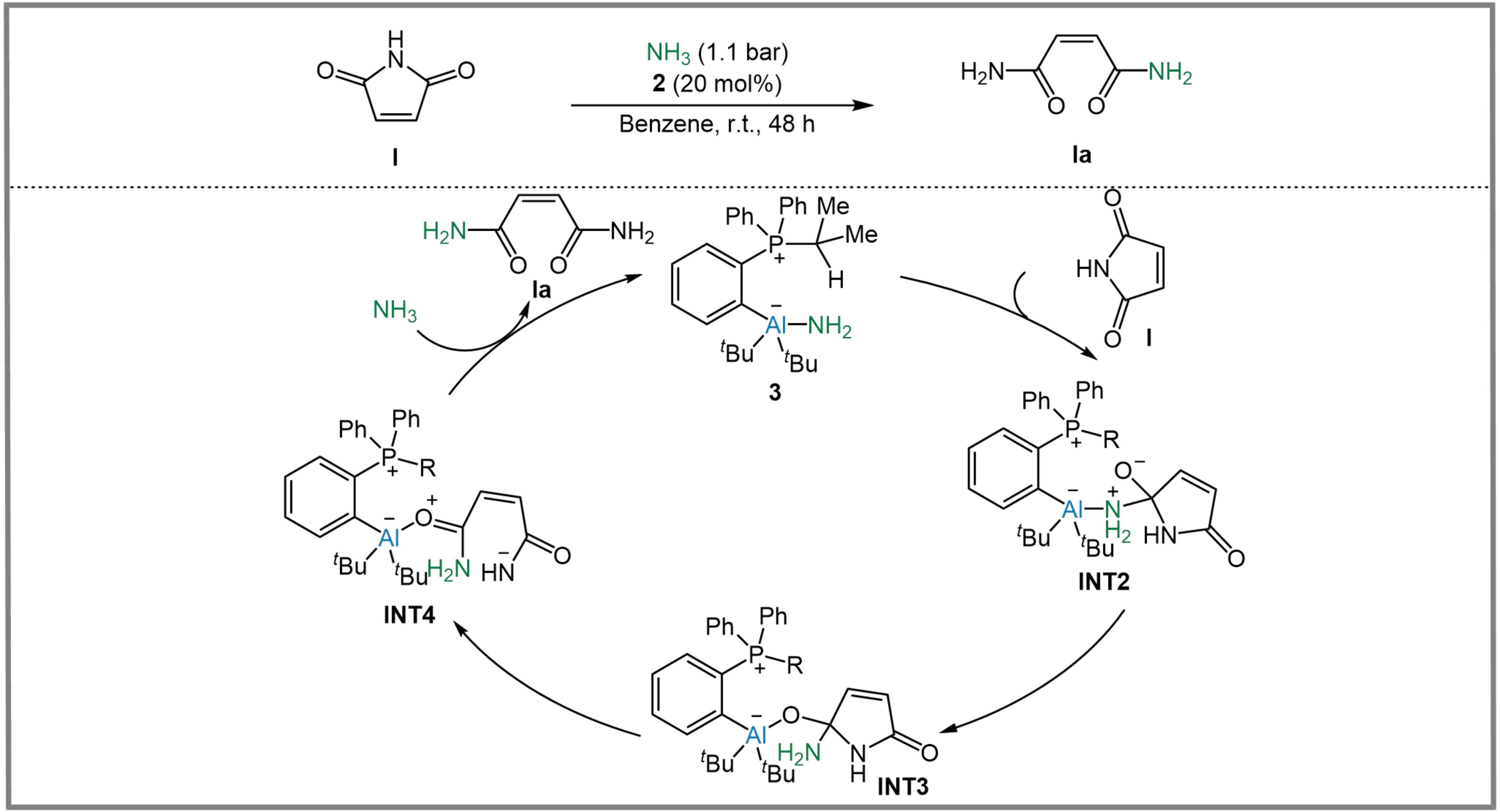
**IIIa**

>99% Conversion
72% Preparative Yield

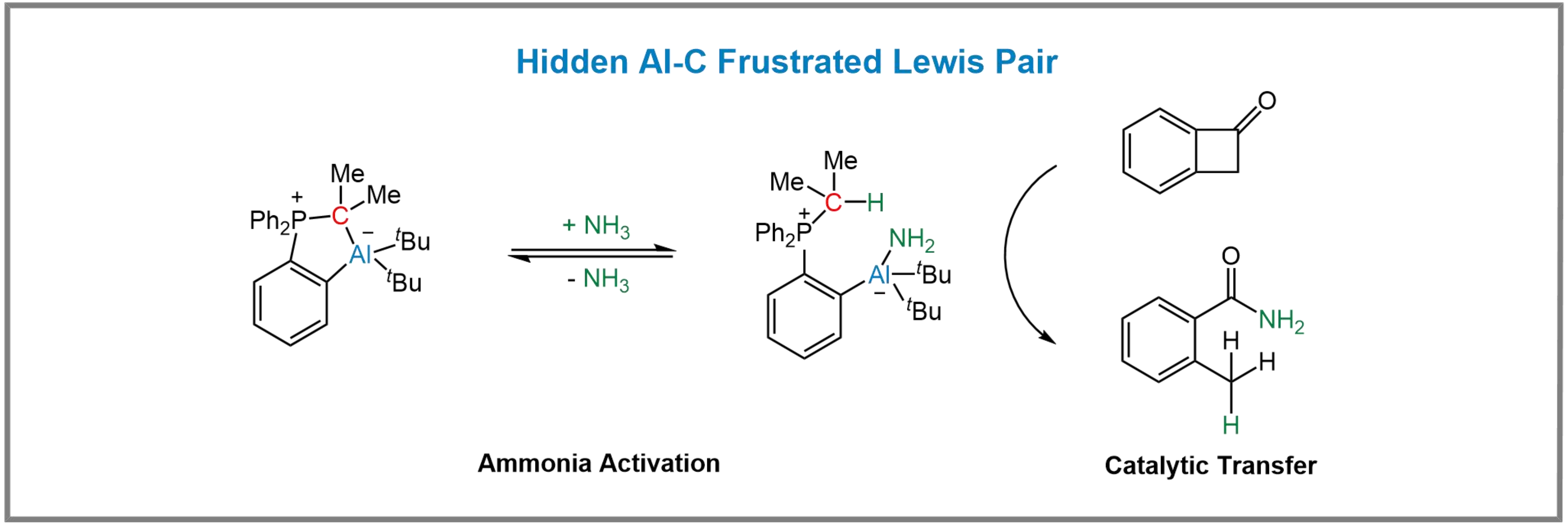
# Catalytic Ammonia Transfer by Aluminium–Carbon-Based FLPs



# The Mechanism for the Catalytic Ammonia Transfer



# Summary




- ✓ Main-group Element-derived Catalyst.
- ✓ Hidden FLPs Consisting of an Aluminium Lewis Acid and a Carbon Lewis Base.
- ✓ Activation and Transfer of Non-aqueous Ammonia.
- ✓ The Reversibility of The $NH_3$ Activation.

# Strategy for Writing the First Paragraph

**Activation of Ammonia by Non-metallic Compounds**

➢ Non-metallic compounds that mimic the reactivity of transition metal complexes have attracted considerable interest.

↓

**The Importance of Frustrated Lewis Pairs (FLPs)**

➢ Since its first report, the use of so-called frustrated Lewis pairs (FLPs), consisting of sterically hindered Lewis acids and Lewis bases to prevent adduct formation in the activation of small molecules, has increased considerably.

↓

**Introduce The Work of This Article**

➢ Therefore, the cooperative action of an aluminium Lewis acid and a Lewis basic phosphorus ylide appears to be a promising approach for achieving the challenging N-H bond activation.

# Strategy for Writing the Last Paragraph

**Highlights**

- We present the first example of a main-group element-derived catalyst for the activation and transfer of non-aqueous ammonia.

**The Conclusion of This Work**

- The uncommon combination of an aluminium Lewis acid and adjacent carbon Lewis base in the form of a phosphorus ylide bearing an aluminium fragment in the *ortho* position of a phenyl ring reacts reversibly with ammonia under heterolytic splitting of one N-H bond at ambient conditions. Moreover, the catalytic $NH_3$ transfer to a variety of electrophiles including maleimide, phenylmaleimide, tosylazirinel, cyclobutenones and benzylbromide was demonstrated in the presence of 20 mol% **2**, which in the presence of $NH_3$, forms the catalytically active $NH_3$ activation product **3**.

# Representative Examples

- This proof-of-principle study is expected to initiate further activities in utilizing N–H-activated ammonia as a readily available, atom-economical nitrogen source. (proof-of-principle study, *n.* 原理论证研究)
- In addition quantum chemical studies present FLPs as promising candidates in the dehydrogenation of ammonia borane involving N–H bond activation. (quantum, *n.* 量子)
- The reaction product 3 was unequivocally characterized by X-ray diffraction studies and NMR spectroscopic analysis as the product of the heterolytic splitting of the N–H bond. (unequivocally, *adv.* 明确的, 毫不含糊的，斩钉截铁的)

# Acknowledgement

Thanks for your attention