Reactivity Promoted by Using Boron Groups as Secondary Coordination Sphere

Speaker：Tianlin Zhang（张天麟）
Supervisor：Prof. Zhangjie Shi

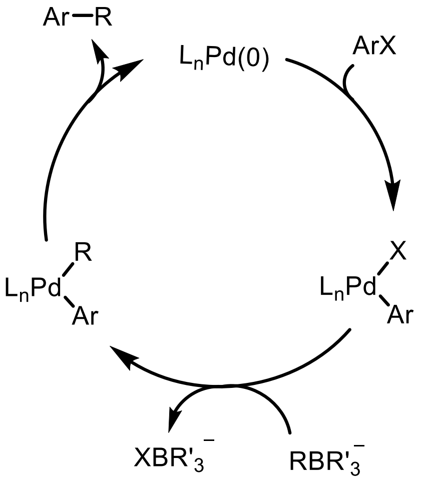
2025.09.26

Contents

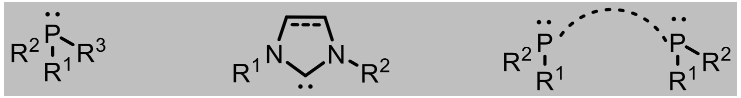
Contents

1.1 The Role of Ligands

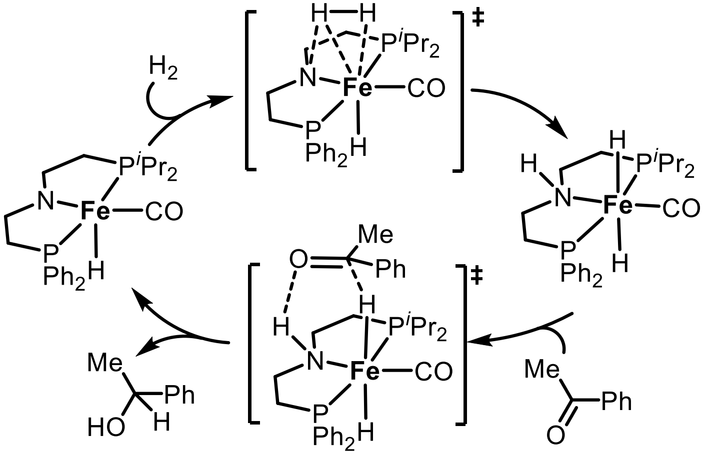
Suzuki-Miyaura cross-coupling reaction



Preferred Ligands: no direct interaction with substrates



Outer-sphere hydrogenation reaction



- Metal–ligand cooperation， MLC
- Non-innocent Ligands
- High reactivity, High efficiency

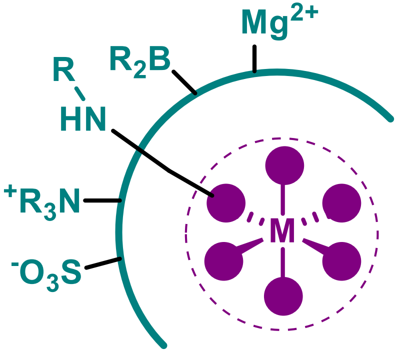
R. H. Morris et. al., *J. Am. Chem. Soc.*, **2014**, *136*, 1367–1380

1.2 Secondary Coordination Sphere

Secondary Coordination Sphere:

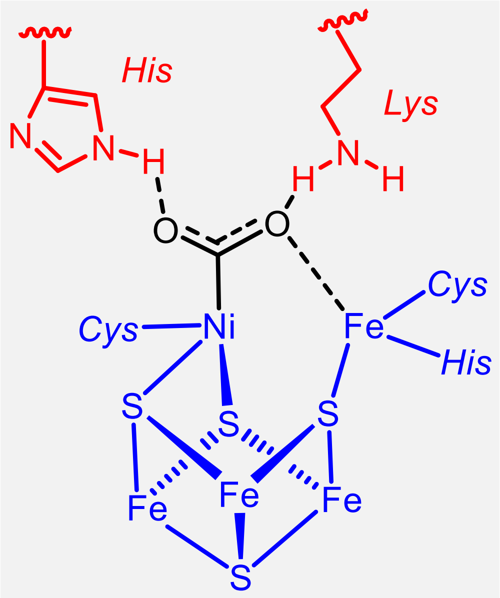
Groups that are not directly bound to the metal center.

It affects reactivity through hydrogen bond, electrostatic effects, π-π stack, acid-base interaction



Primary Coordination Sphere:

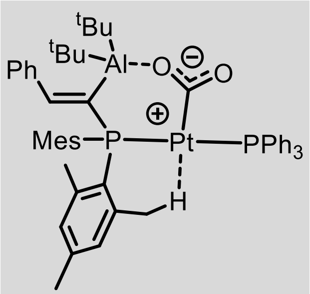
The molecules that are attached directly to the metal



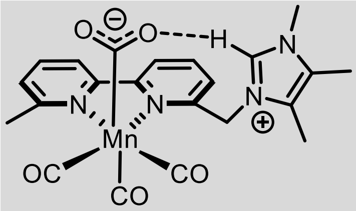
Ni-Fe CODH site

Marcus W. Drover et. al., *Chem. Soc. Rev.*, **2022**, *51*, 1861

1.3 Acidic group as Secondary Coordination Sphere



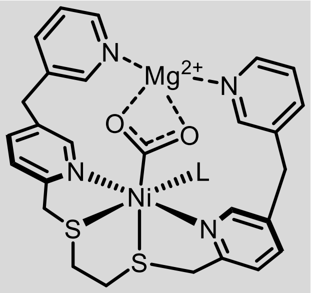
2016 **Bourissou**



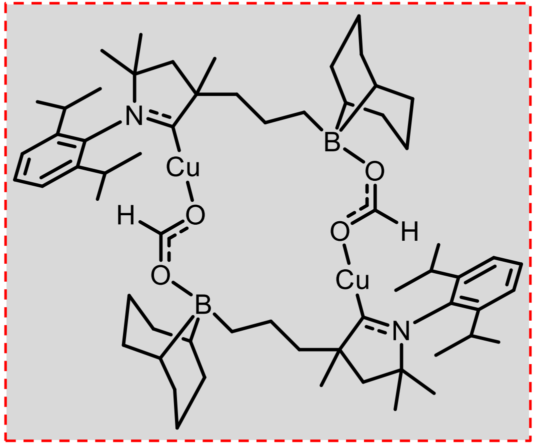
2019 **Nippe**

Advantages of Boron Group

- **Simple Synthetic Route**
- **Appropriate Lewis Acidity**
- **High Chemical Stability**
- **Easy to Characterize**



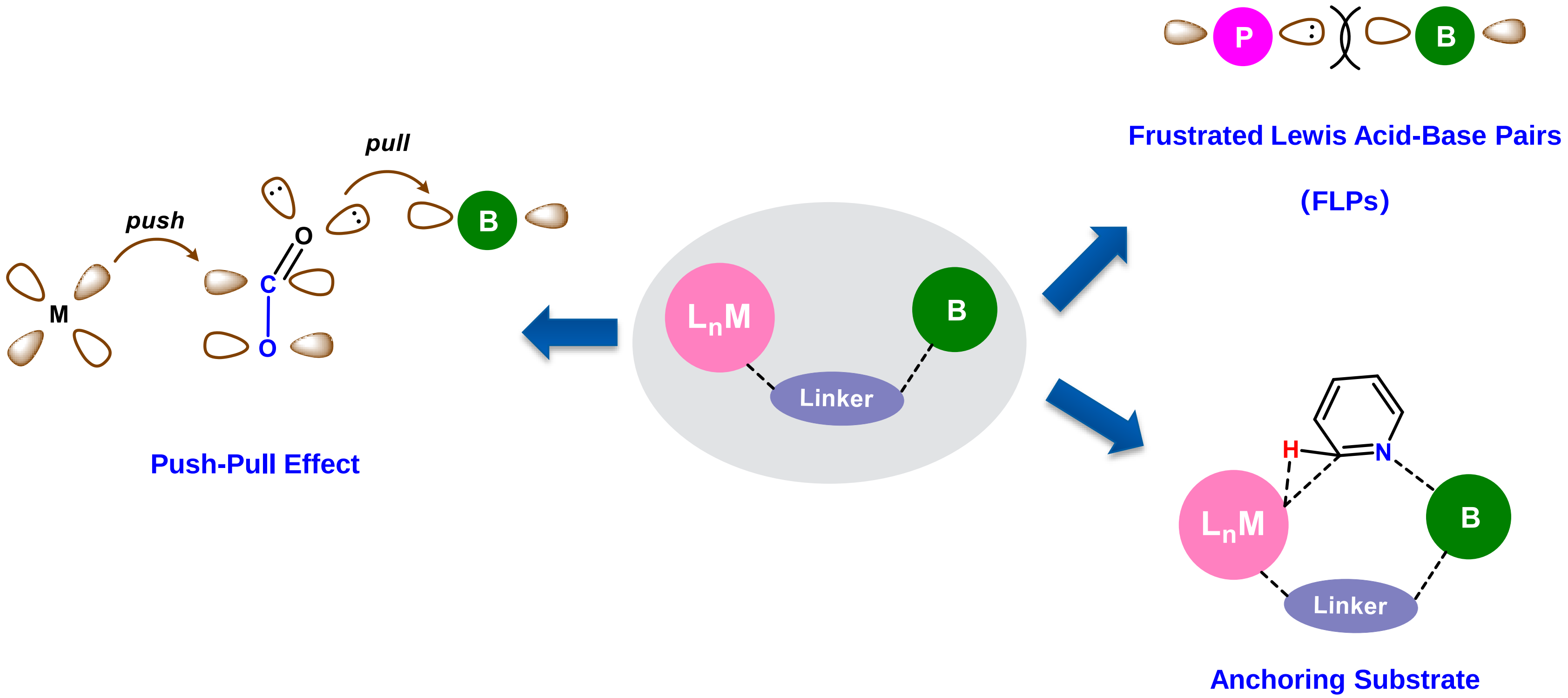
2019 **Kojima**



2024 **Szymczak**

D. Bourissou et. al., *J. Am. Chem. Soc.* **2016**, *138*, 4917–4926; T. Kojima et. al., *J. Am. Chem. Soc.* **2019**, *141*, 20309–20317;
M. Nippe et. al., *J. Am. Chem. Soc*., **2017**, *139*, 13993–13996; Nathaniel Szymczak et. al., *Angew. Chem. Int. Ed.*, **2024**, *136*, e202411099

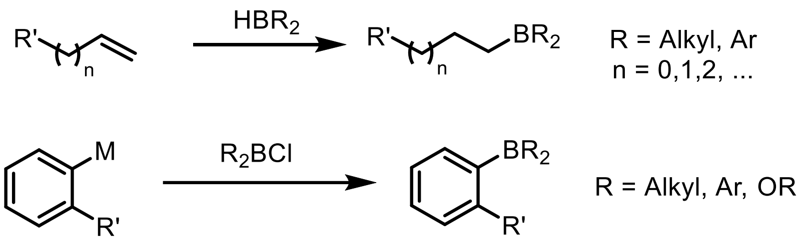
1.4 Boron-metal cooperative reaction patterns



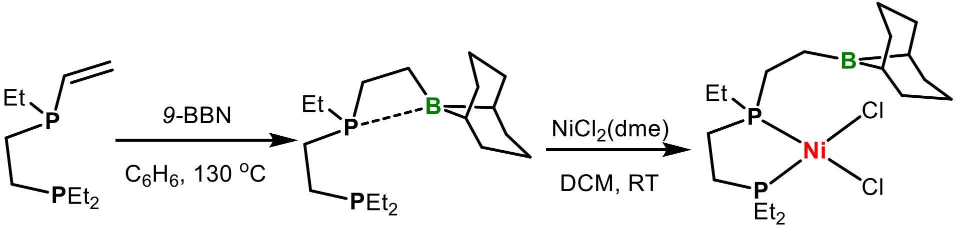
Contents

2.1 Common Methods to Synthesize [Metal-Linker-Boron] System

Synthesis Methods of borane-tethered ligands:

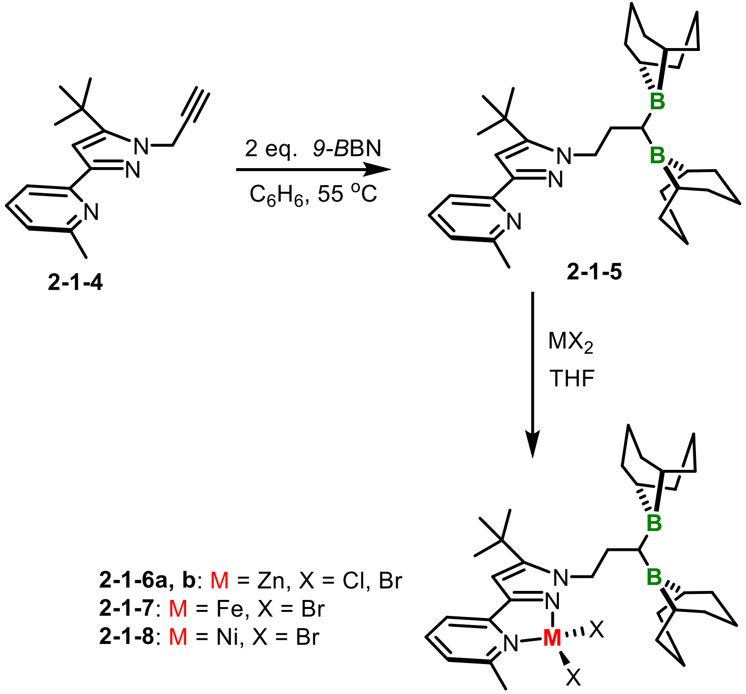


2022 **Chu**



2-1-1 **2-1-2** **2-1-3**

2023 **Szymczak**

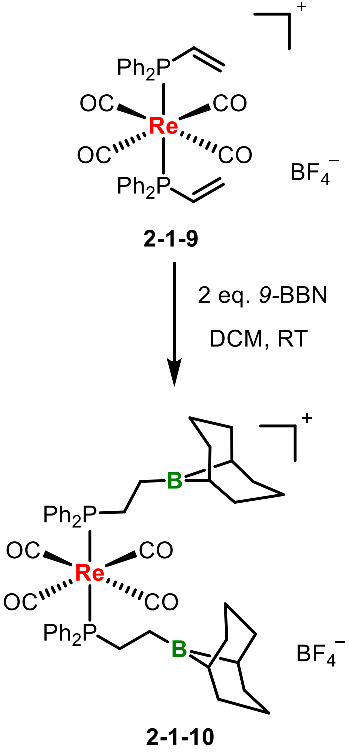


Jiaxiang Chu et. al., *J. Am. Chem. Soc.*, **2022**, *144*, 15793–15802

Nathaniel Szymczak et. al., *Angew. Chem. Int. Ed.*, **2023**, *62*, e202218907

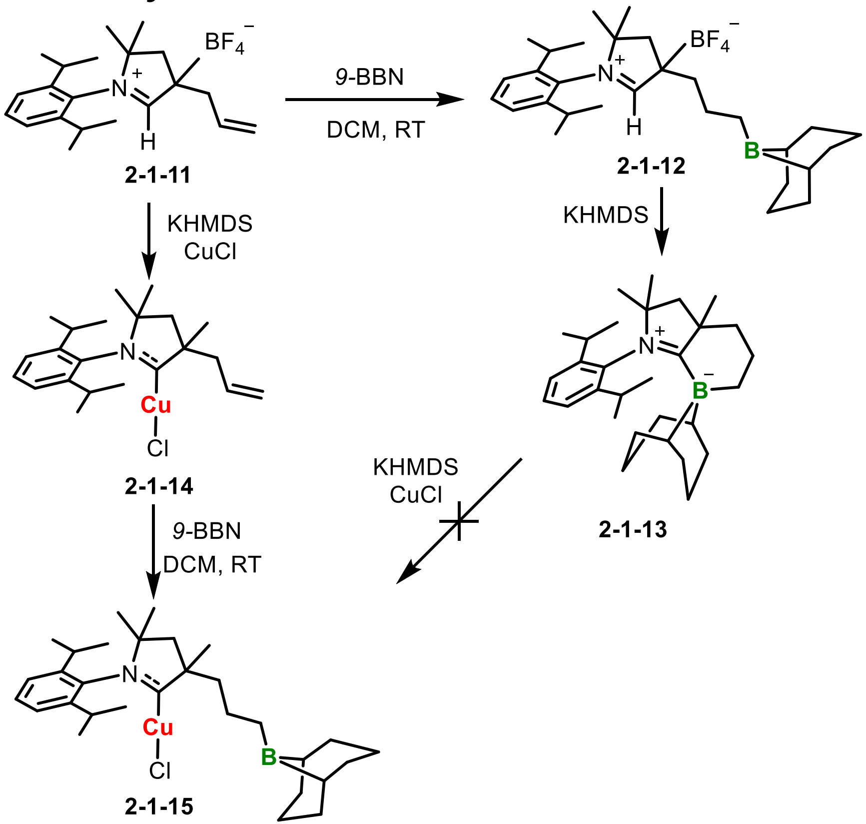
2.1 Common Methods to Synthesize [Metal-Linker-Boron] System

2008 **Bercaw**



John E. Bercaw et. al., *J. Am. Chem. Soc.*, **2008**, *130*, 11874–11875

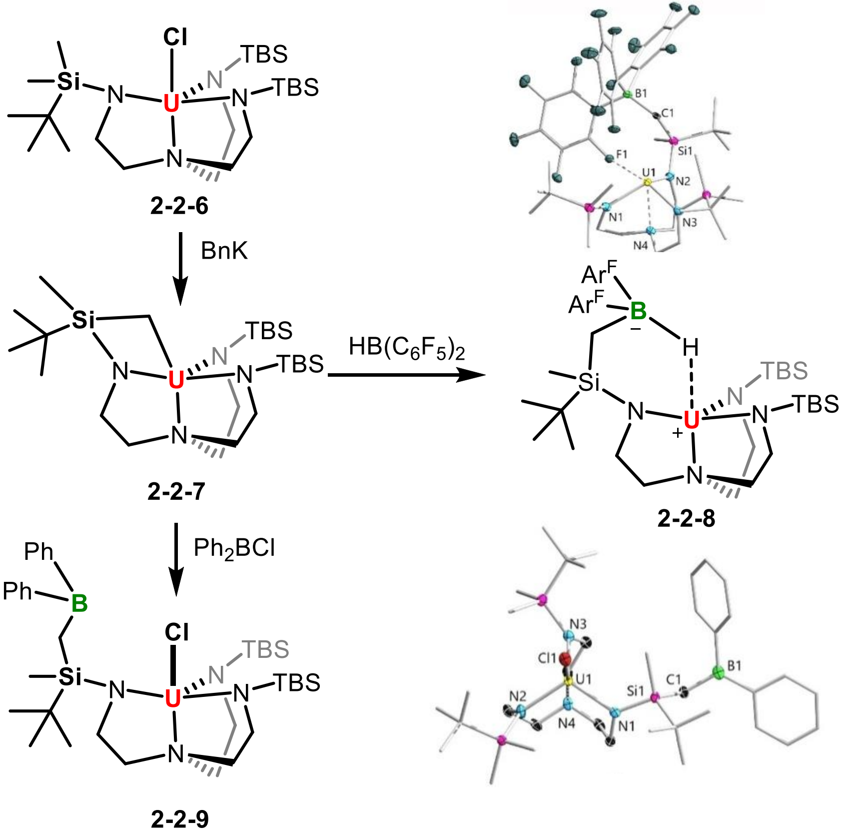
2024 **Szymczak**



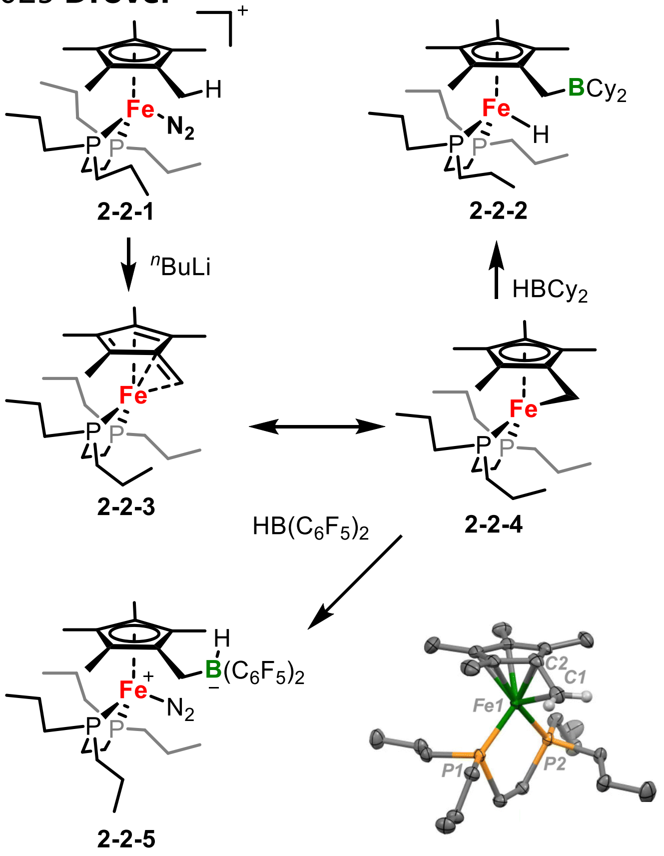
Nathaniel Szymczak et. al., *Angew. Chem. Int. Ed.*, **2024**, *136*, e202411099

2.2 Synthesize [Metal-Linker-Boron] System By R-M

2022 **Ye**



2025 **Drover**



Ye Qing et. al., *Angew. Chem. Int. Ed.*, **2022**, *61*, e202212823

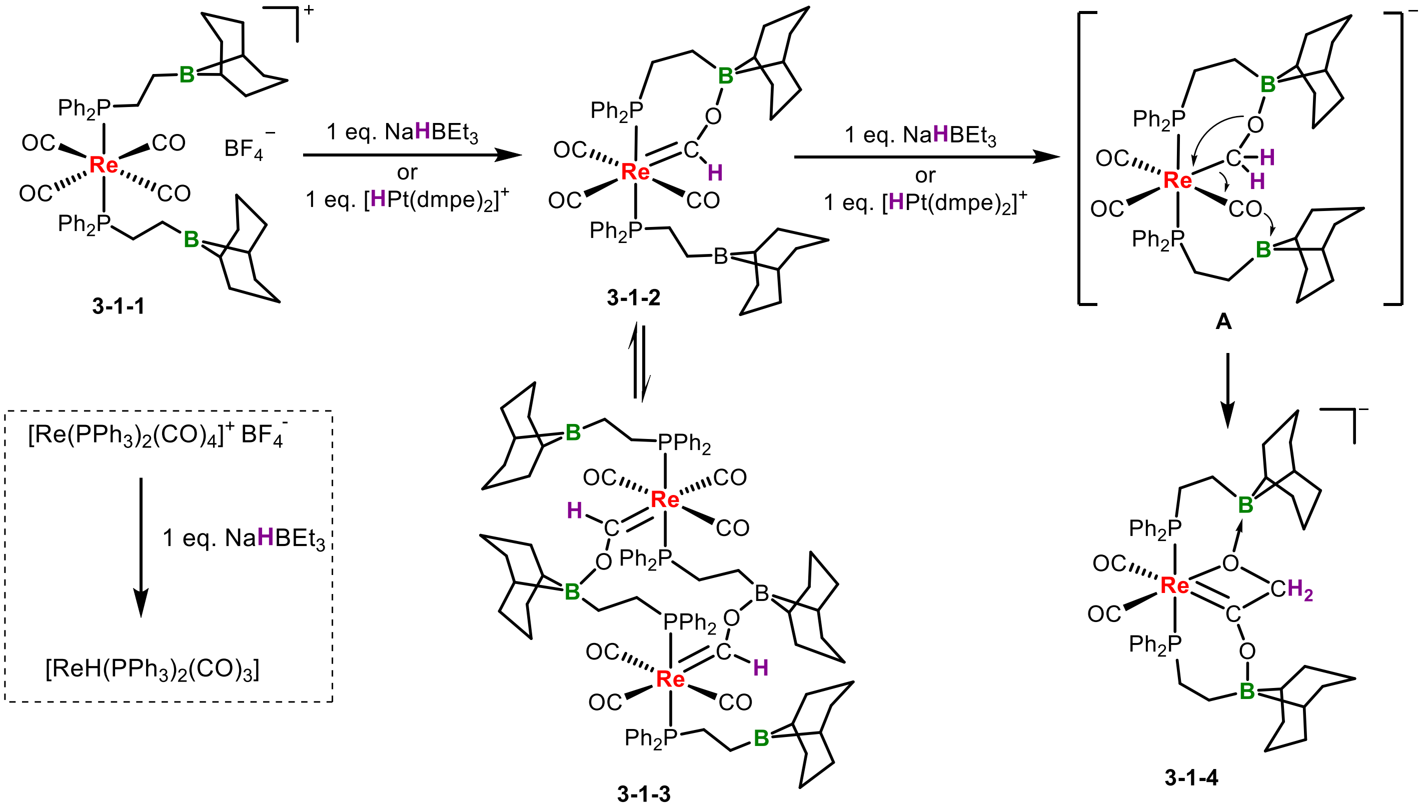
Marcus W. Drover et. al., *Angew. Chem. Int. Ed.* **2025**, *64*, e202421599

Contents

3.1 CO Activation

2008 **Bercaw**

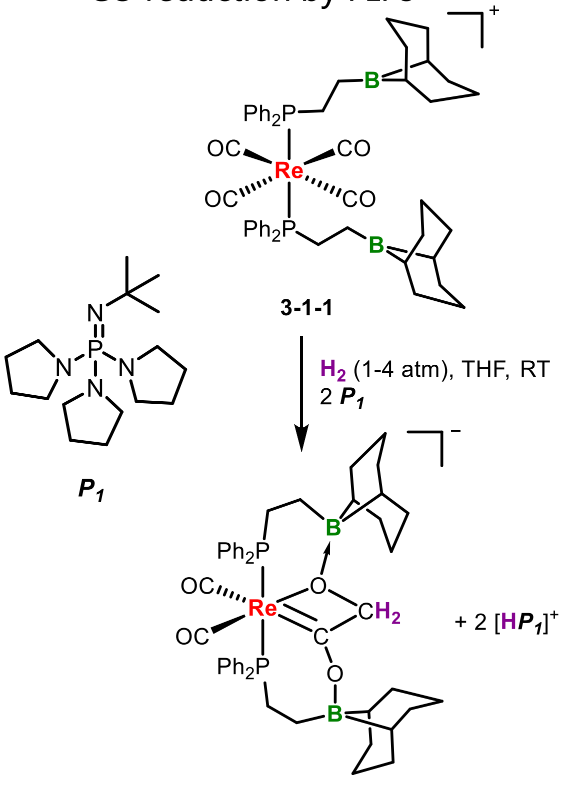
Reductive coupling reaction of CO

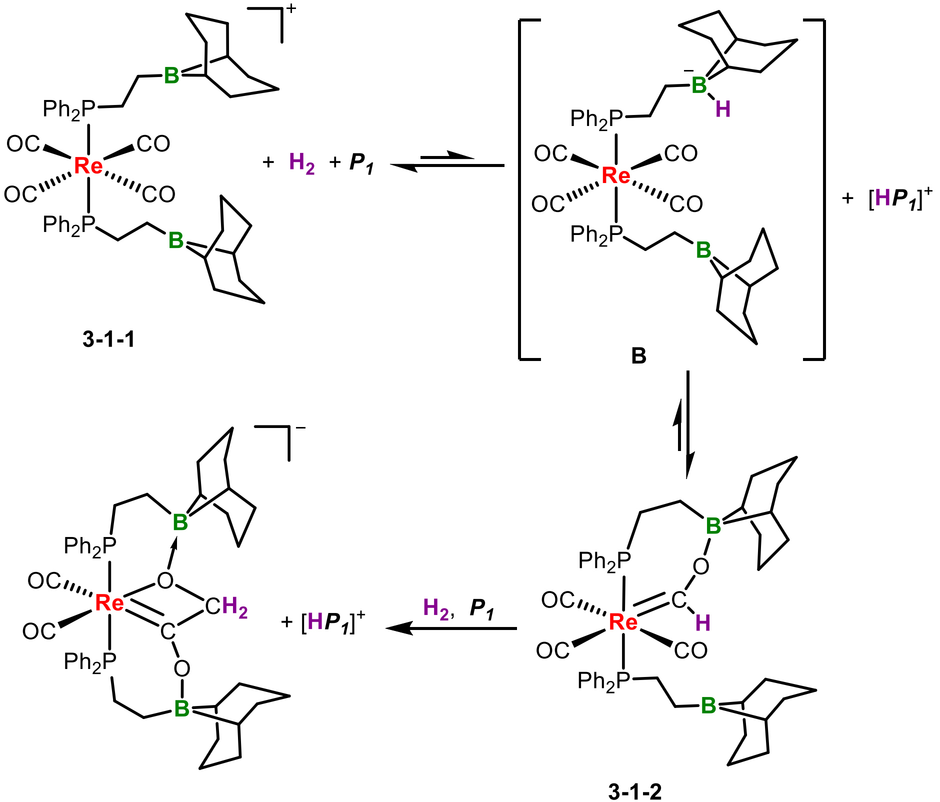


John E. Bercaw et. al., *J. Am. Chem. Soc.*, **2008**, *130*, 11874–11875

3.1 CO Activation

2010 **Bercaw**
CO reduction by FLPs

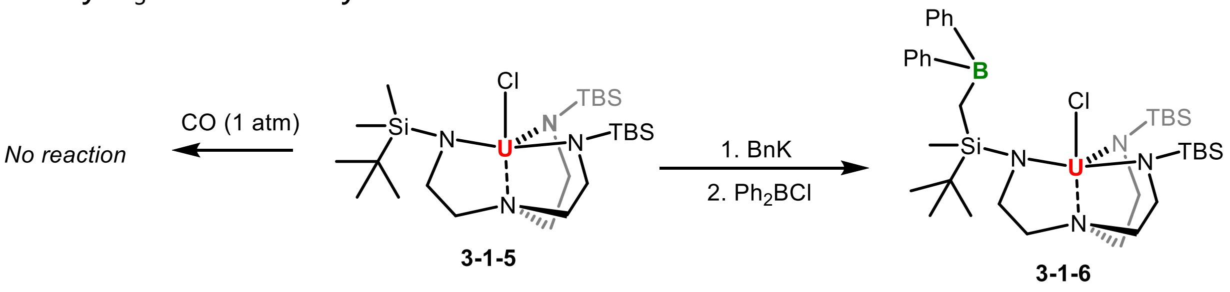


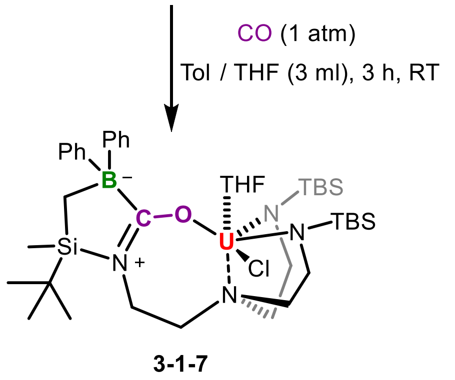


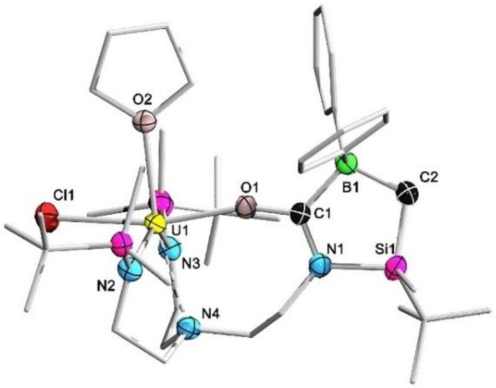
John E. Bercaw et. al., *J. Am. Chem. Soc.*, **2010**, *132*, 3301–3303

3.1 CO Activation

2022 **Ye**
CO fixation By N_3N-U-Boron system

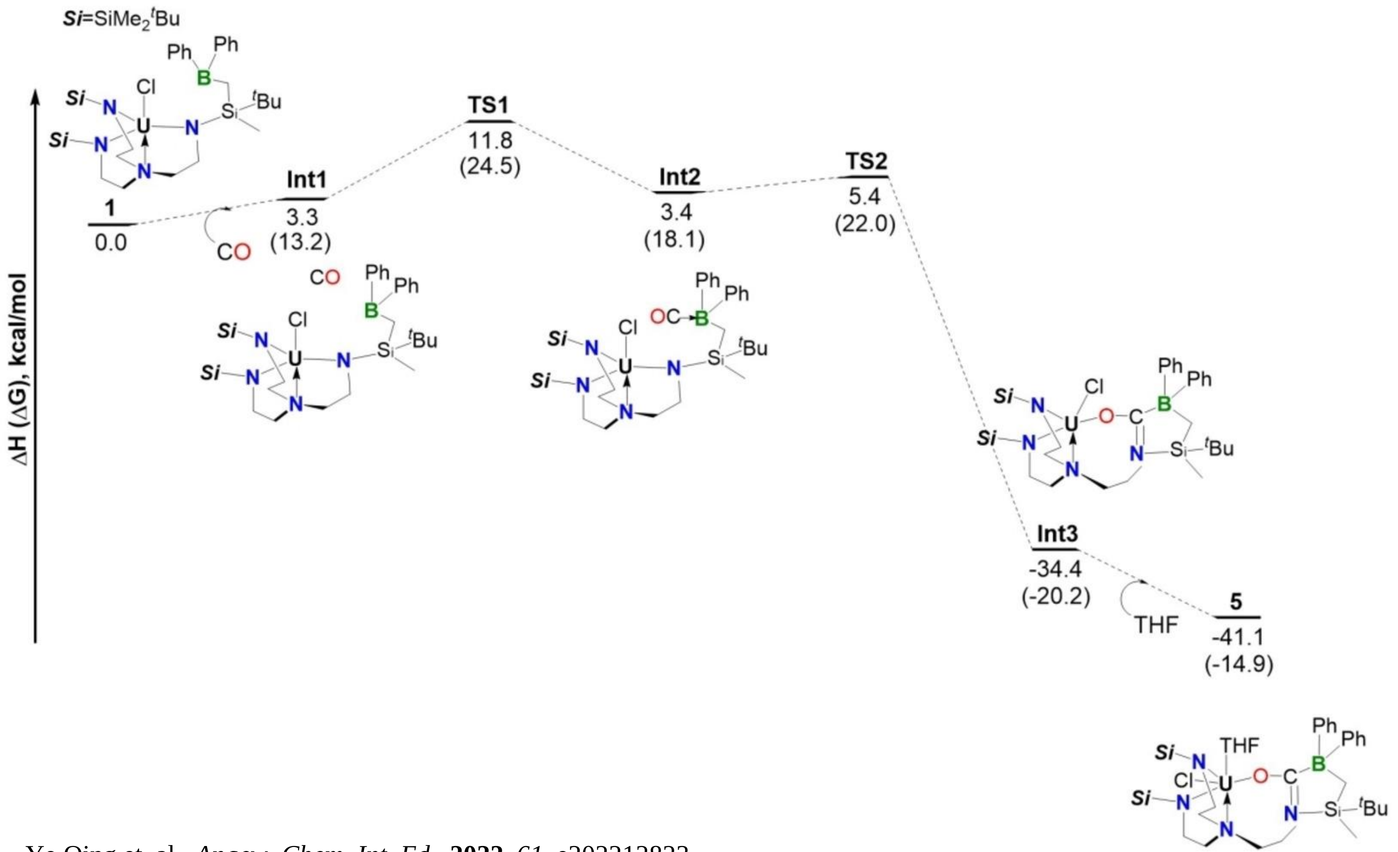






Ye Qing et. al., *Angew. Chem. Int. Ed.*, **2022**, *61*, e202212823

3.1 CO Activation

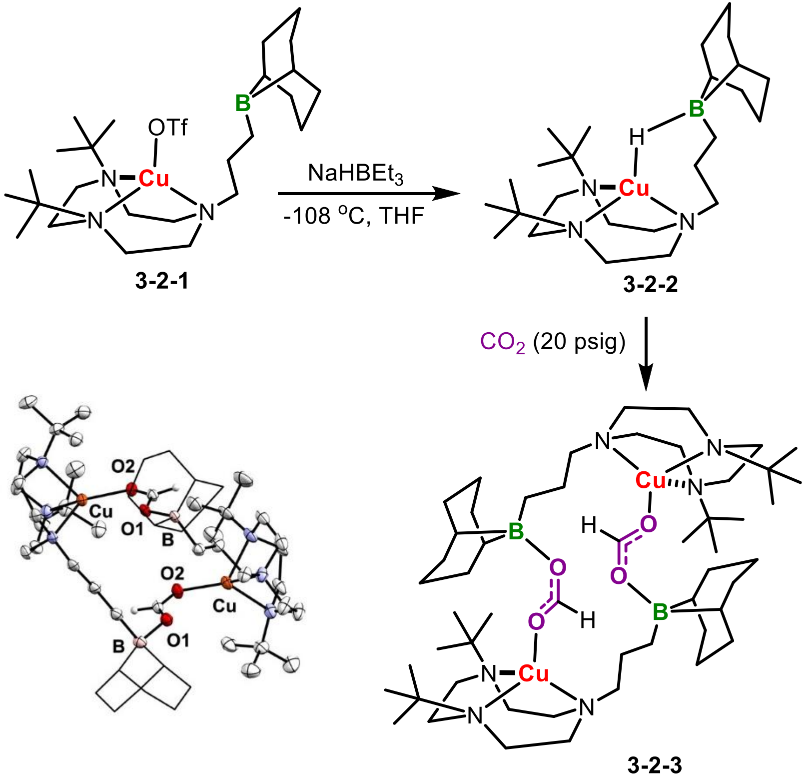


Ye Qing et. al., *Angew. Chem. Int. Ed.*, **2022**, *61*, e202212823

3.2 CO_2 Activation

2022 **Szymczak**

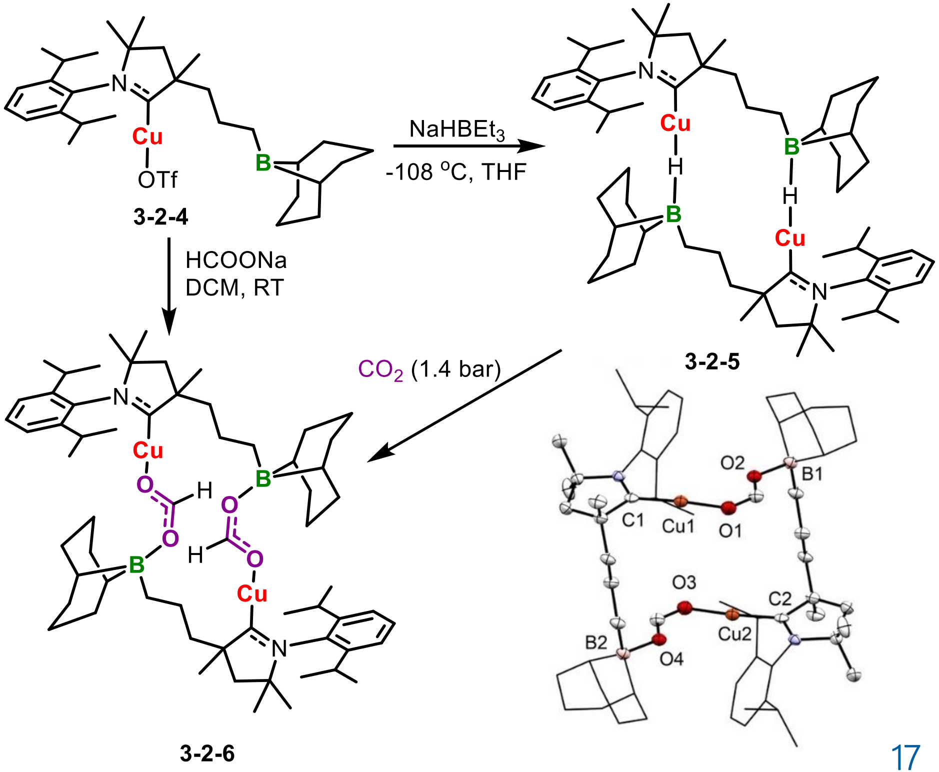
CO_2 reduction with TACN-Cu-Borane system



Nathaniel Szymczak et. al., *J. Am. Chem. Soc.*, **2022**, *144*, 15038–15046

2024 **Szymczak**

CO_2 reduction with cAAc-Cu-Borane system



Nathaniel Szymczak et. al., *Angew. Chem. Int. Ed.*, **2024**, *136*, e202411099

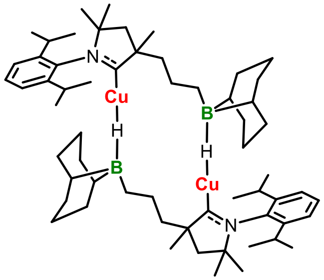
3.2 CO_2 Activation

Catalytic reduction of carbon dioxide to formate anion

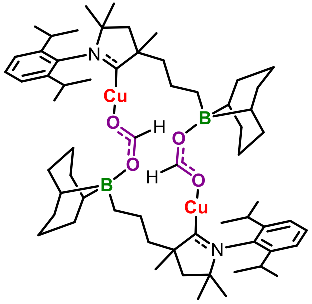
$$CO_2 / H_2\ (1/3) + \textbf{DBU}\ \underset{\text{4 mmol}}{} \xrightarrow[\text{THF, 100 °C, 24 h}]{\text{Cat.}} [HCOO]^- [\textbf{HDBU}]^+$$

entry	Cat.	mol%	Pressure/CO_2:H_2 (bar)	Additive (eq.)	TON
1	3-2-6	0.1	16:48		241
2	3-2-6	0.001	16:48		375
3	3-2-6	0.0001	16:48		**738**
4	3-2-5	0.1	16:48		140
5	3-2-6	0.1	8:24		77
6	3-2-6	0.1	8:24	$B(C_6F_5)_3$ (0.1)	**76**
7	3-2-7[a]	0.1	16:48	$B(C_6F_5)_3$ (0.1)	75

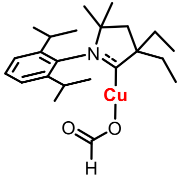
a: Literature reported reaction



3-2-5



3-2-6



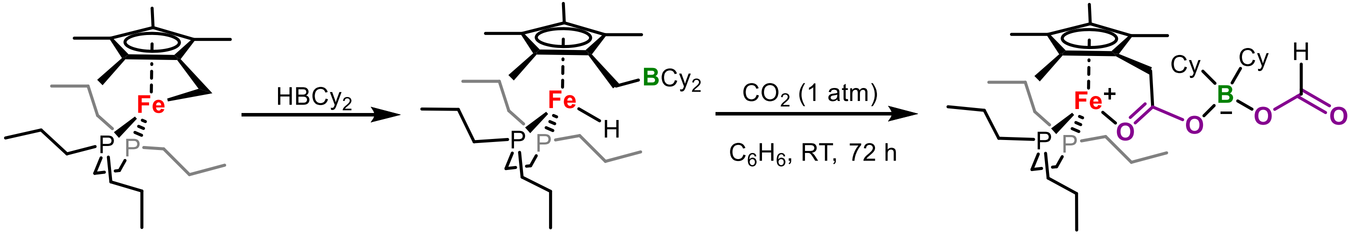
3-2-7

Nathaniel Szymczak et. al., *Angew. Chem. Int. Ed.*, **2024**, *136*, e202411099

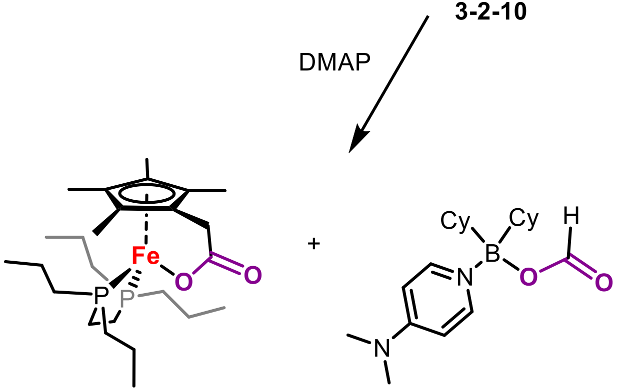
3.2 CO_2 Activation

2025 **Drover**

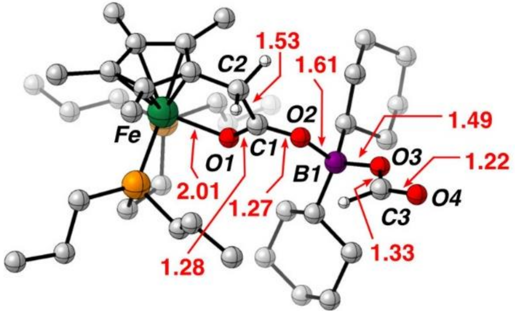
CO_2 Fixation with Fe-Borane system



3-2-8 **3-2-9** **3-2-10**



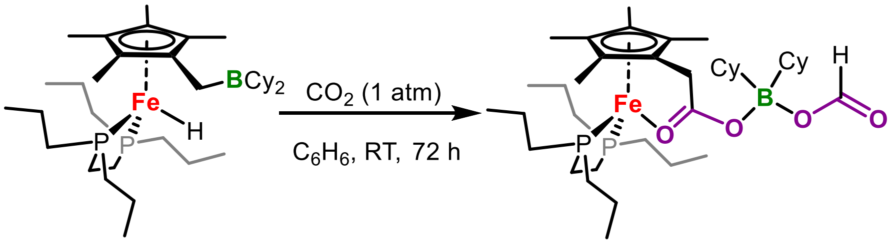
3-2-11 **3-2-12**



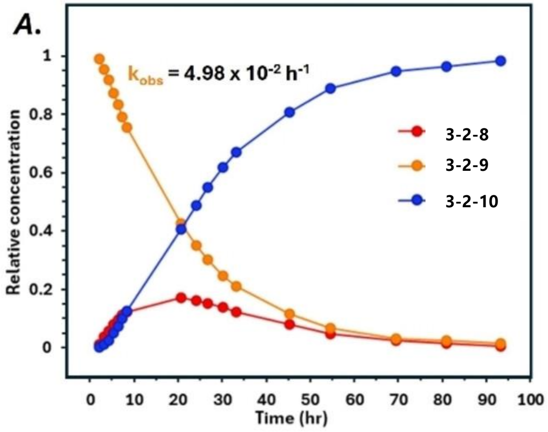
Marcus W. Drover et. al., *Angew. Chem. Int. Ed.* **2025**, *64*, e202421599

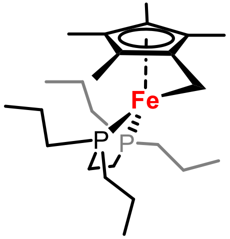
3.2 CO_2 Activation

Reaction monitoring



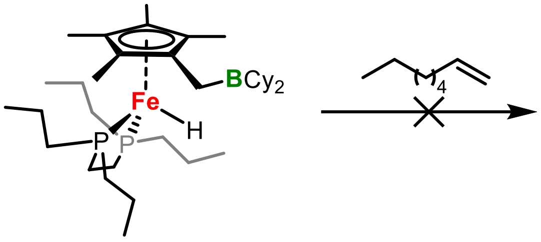
3-2-9 **3-2-10**





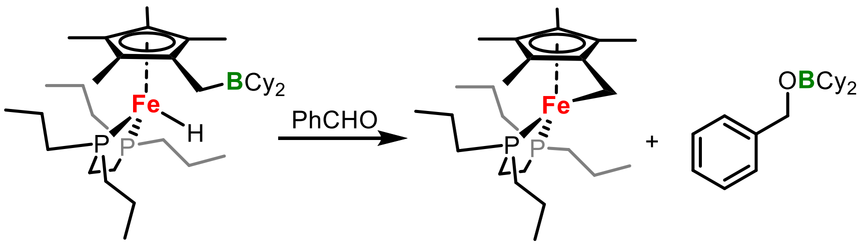
3-2-8

a. Alkene hydroboration is not observed



3-2-9

b. $HBCy_2$ transfer to benzaldehyde

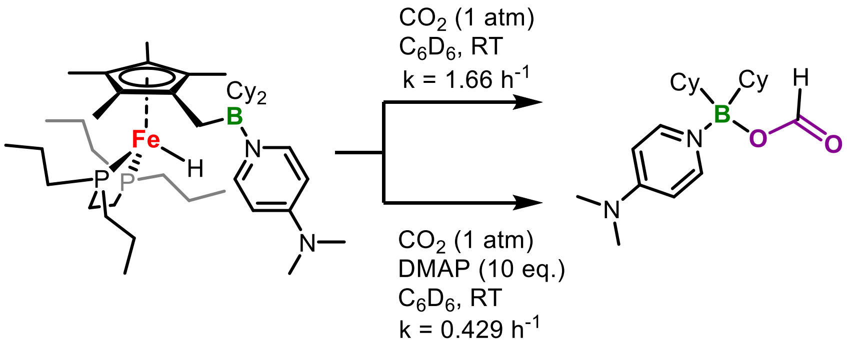


3-2-9 **3-2-8**

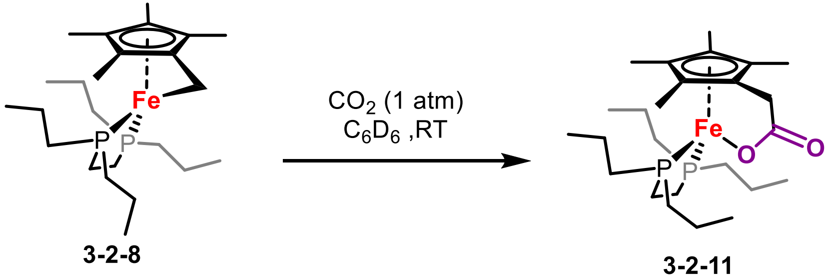
Marcus W. Drover et. al., *Angew. Chem. Int. Ed.* **2024**, *64*, e202421599

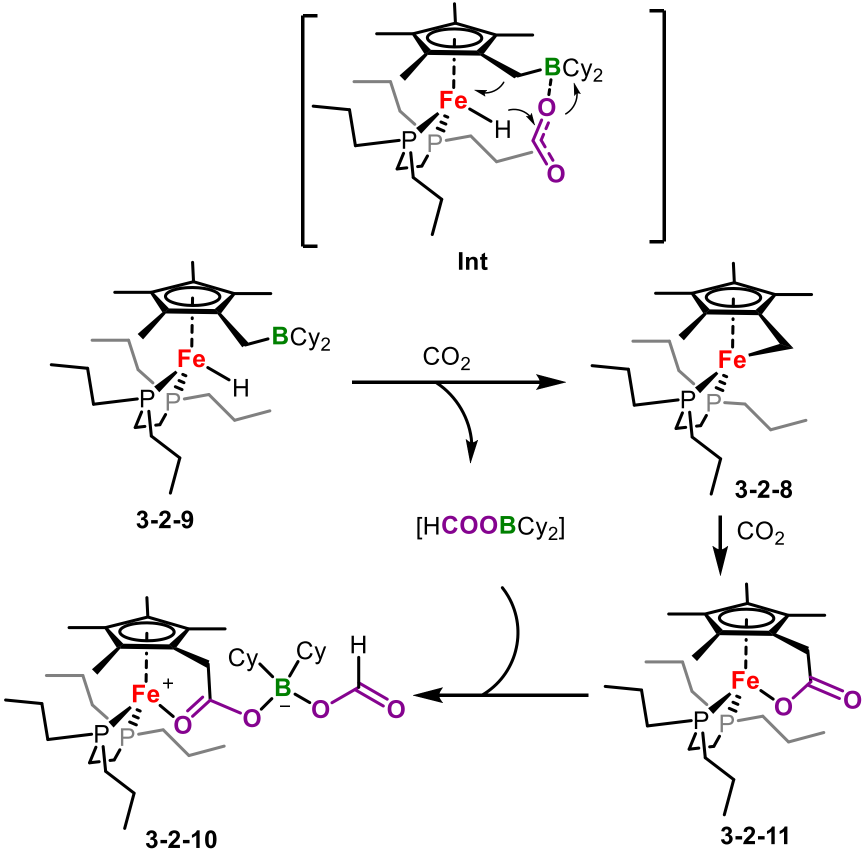
3.2 CO_2 Activation

c. Excess DMAP decrease rate of CO_2 reduction



d. CO_2 reduced by Alkyl-ion intermediate



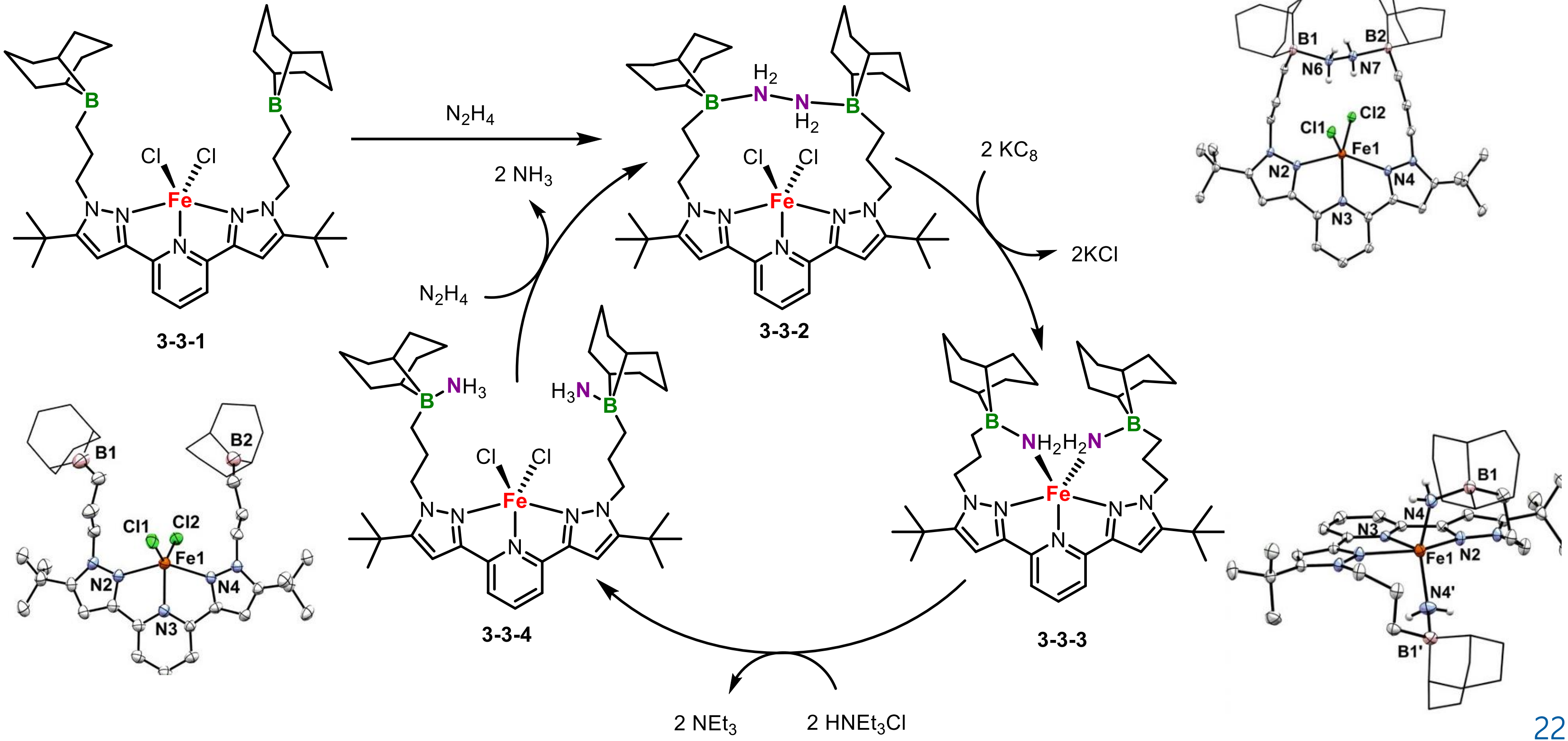


Marcus W. Drover et. al., *Angew. Chem. Int. Ed.* **2024**, *64*, e202421599

3.3. N_2H_4 Activation

2017 **Szymczak**

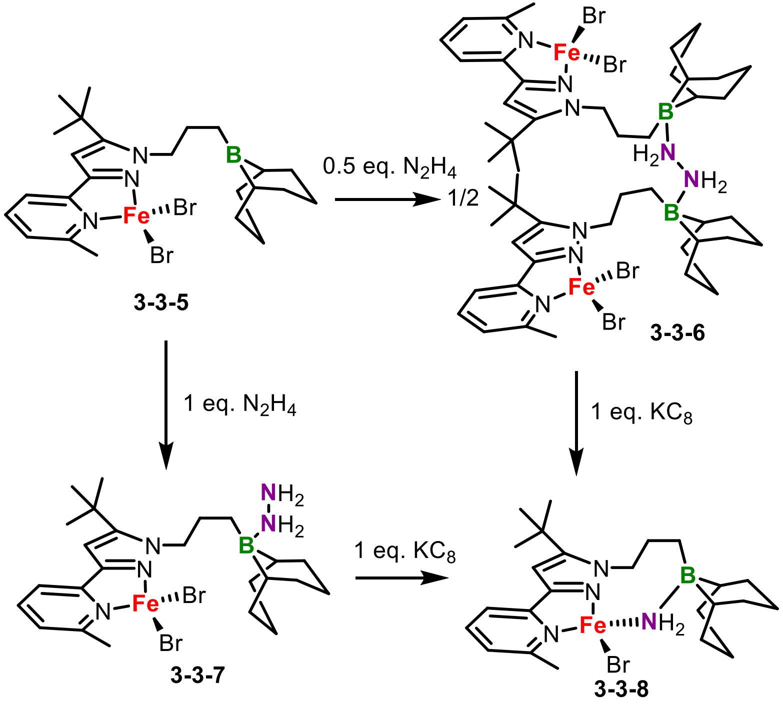
N_2H_4 reduction with pincer-Fe-diborane system



Nathaniel Szymczak et. al., *J. Am. Chem. Soc.*, **2017**, *139*, 18194–18197

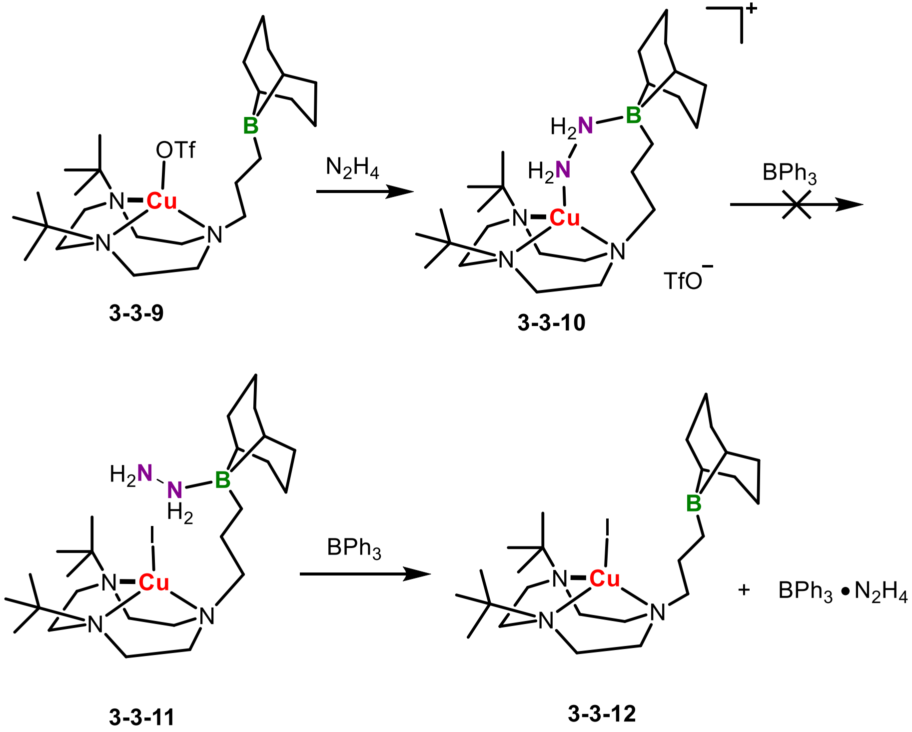
3.3. N_2H_4 Activation

2019 **Szymczak**



Nathaniel Szymczak et. al., *Chem. Commun.*, **2019**, *55*, 11896-11899

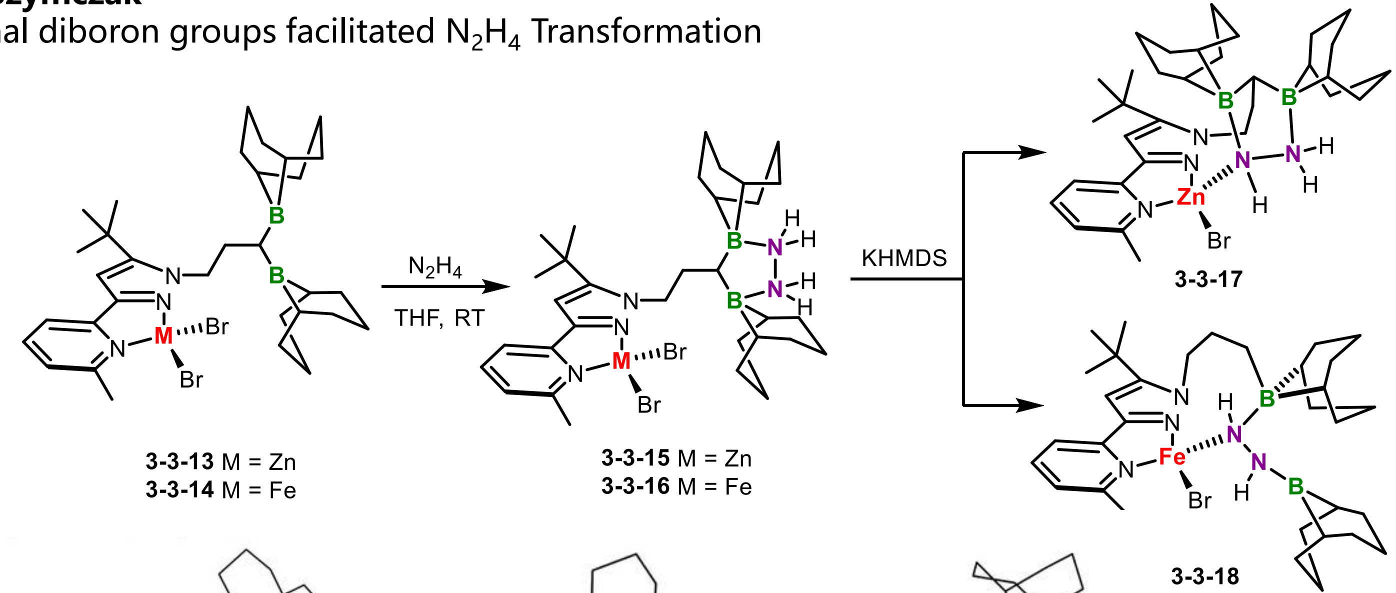
2024 **Szymczak**



Nathaniel Szymczak et. al., *Inorg. Chem.*, **2024**, *63*, 18519–18523

3.3. N_2H_4 Activation

2023 **Szymczak**
Geminal diboron groups facilitated N_2H_4 Transformation

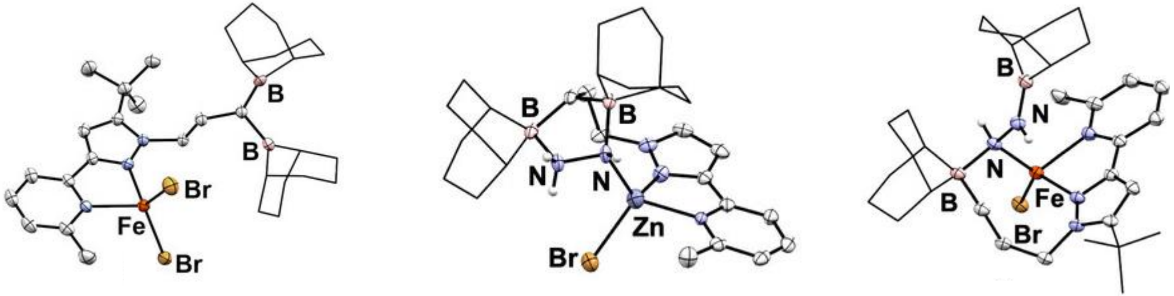


3-3-13 M = Zn
3-3-14 M = Fe

3-3-15 M = Zn
3-3-16 M = Fe

3-3-17

3-3-18

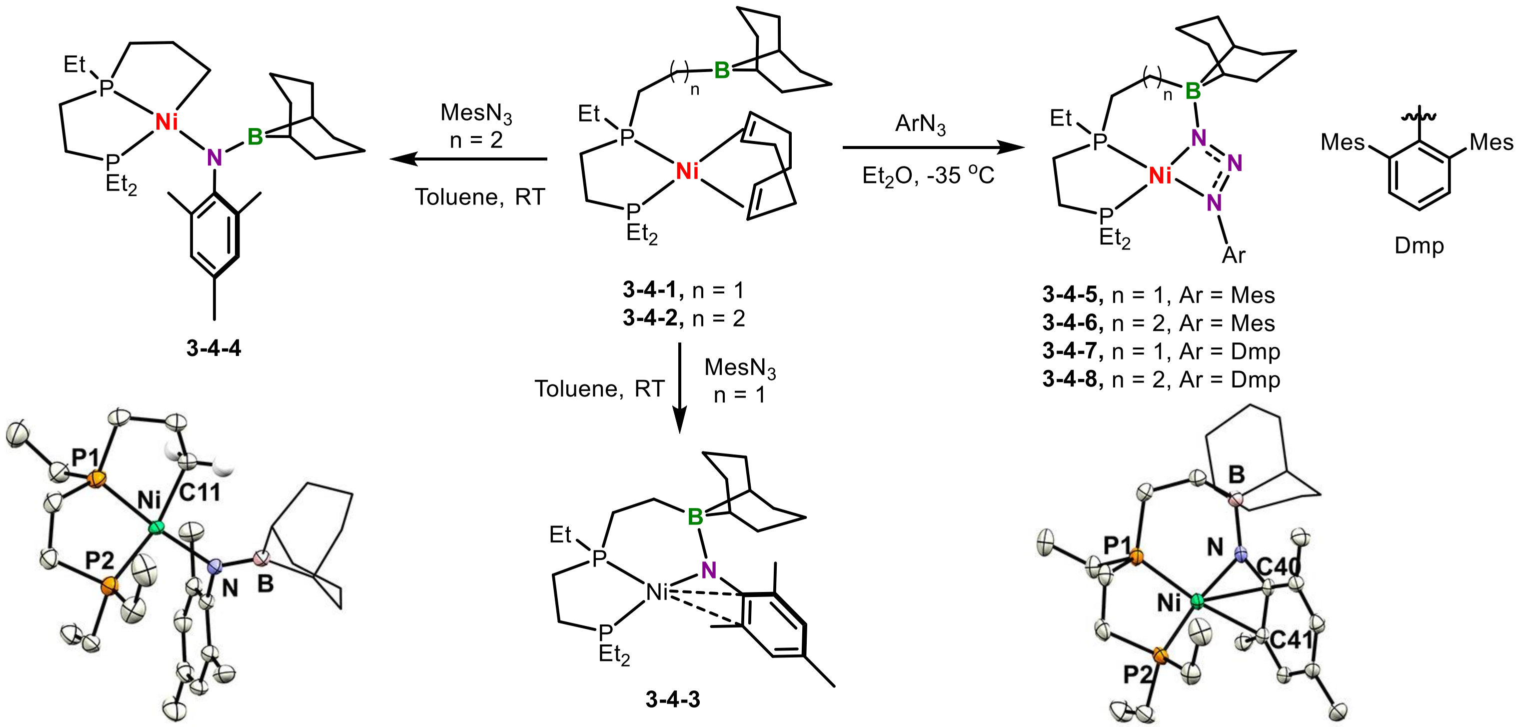


Nathaniel Szymczak et. al., *Angew. Chem. Int. Ed.*, **2023**, *62*, e202218907

3.4. Azide Activation

2022 **Chu**

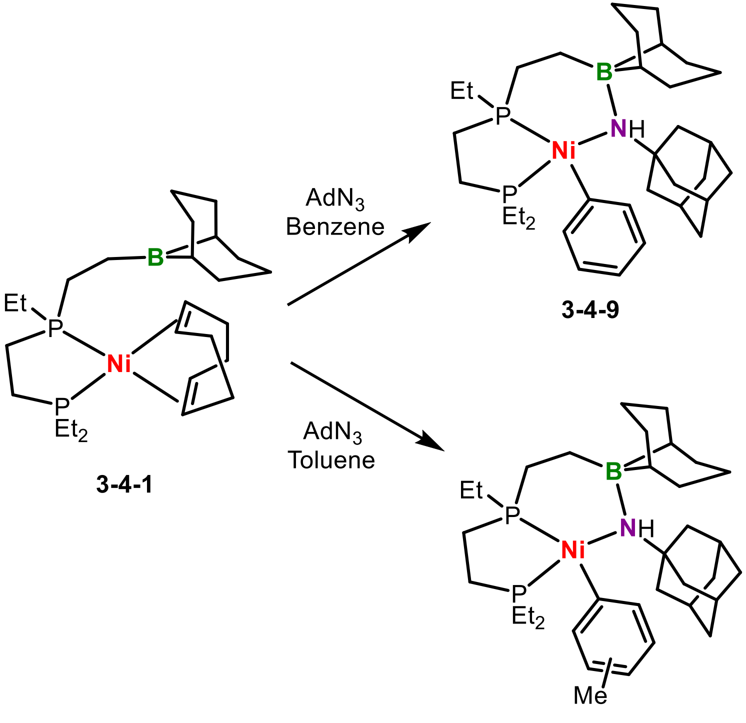
a. Reaction of Borane-functionalized Diphosphine Ni complexes with Aryl Azides



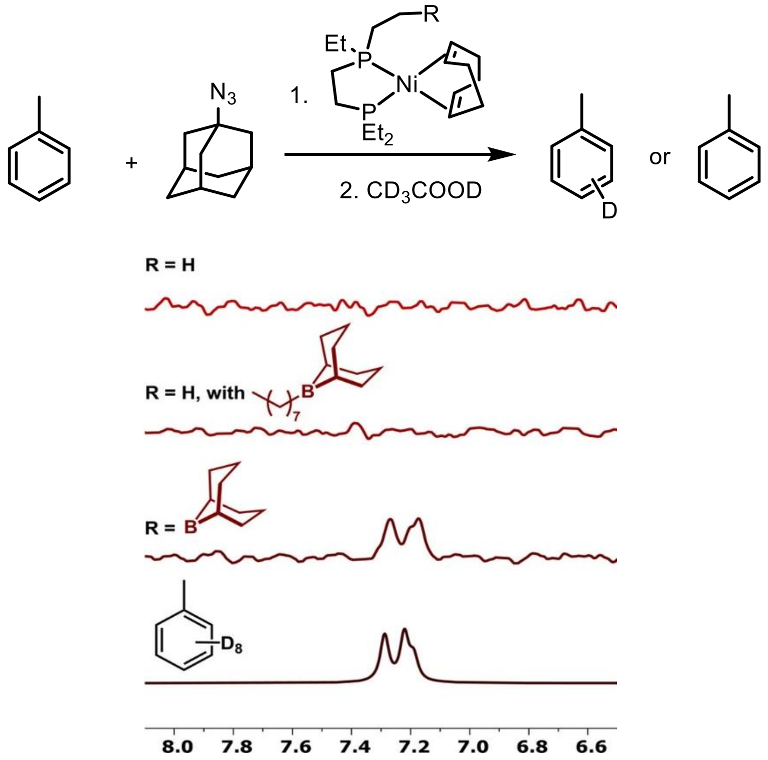
Jiaxiang Chu et. al., *J. Am. Chem. Soc.*, **2022**, *144*, 15793–15802

3.4. Azide Activation

b. Reaction with Alkyl Azides in aromatic solvents



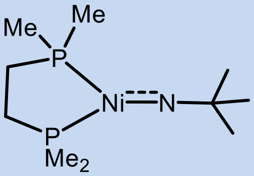
c. Control experiments about borane substituent



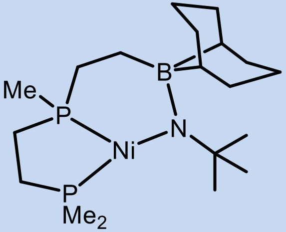
Jiaxiang Chu et. al., *J. Am. Chem. Soc.*, **2022**, *144*, 15793–15802

3.4. Azide Activation

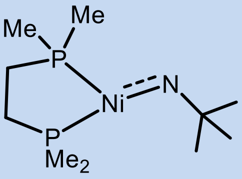
d. Calculation



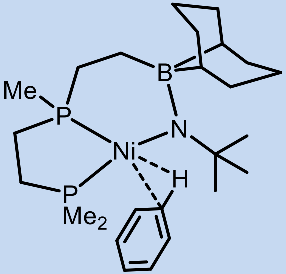
$\Delta q_{(Ni\text{-}N)}$ = 0.172
Ni-N = 1.660 Å
$BO_{(Ni\text{-}N)}$ = 1.436



$\Delta q_{(Ni\text{-}N)}$ = 0.622
Ni-N = 1.782 Å
$BO_{(Ni\text{-}N)}$ = 0.776

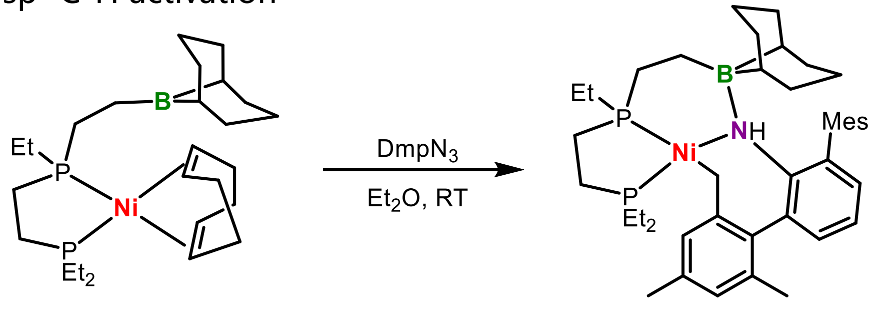


$\Delta q_{(Ni\text{-}N)}$ = 0.430
Ni-N = 1.728 Å
$BO_{(Ni\text{-}N)}$ = 1.214



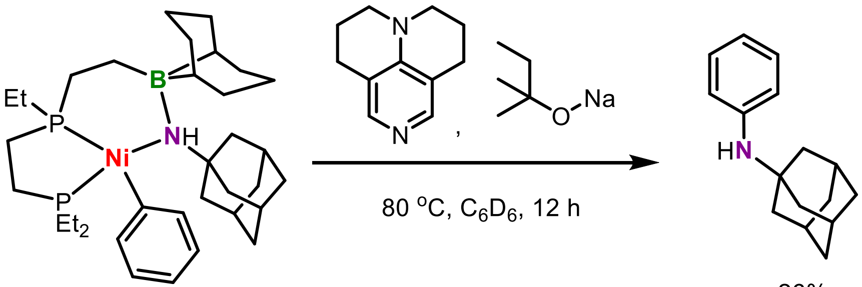
$\Delta q_{(Ni\text{-}N)}$ = 0.716
Ni-N = 1.786 Å
$BO_{(Ni\text{-}N)}$ = 0.704

e. sp^3 C-H activation



3-4-1 **3-4-11**

e. Reductive elimination



26%

3-4-9

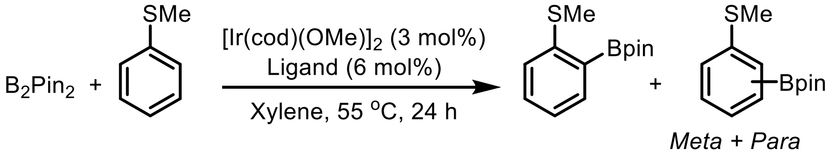
Jiaxiang Chu et. al., *J. Am. Chem. Soc.*, **2022**, *144*, 15793–15802

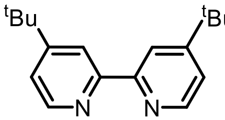
Contents

4. Catalytic Reactivity of [Metal-Linker-Boron] System

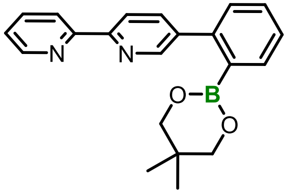
2017 Kanai

Boron-promoted regioselective borylation reaction

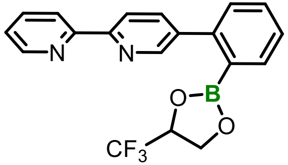




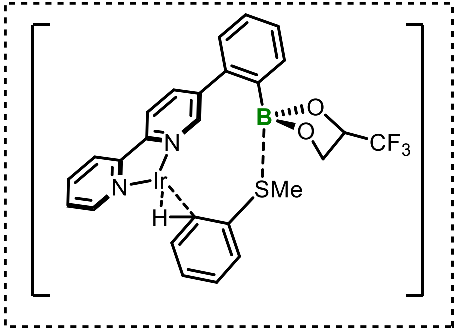
L1 70% (0.22 : 1)



L2 64% (2.8 : 1)

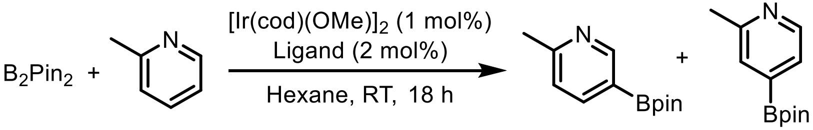


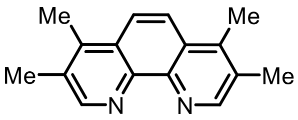
L3 64% (>30 : 1)

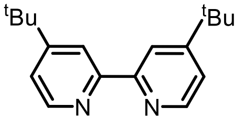


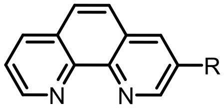
2019 Nakao

Regioselective borylation with appropriate chain length



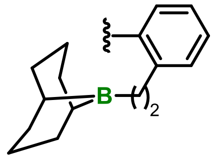


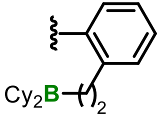


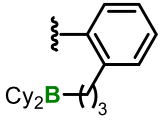


L4 88% (42:58) **L5** 71% (27:73)

R =







L6 83% (76:24) **L7** 99% (98:2) **L8** 82% (71:29)

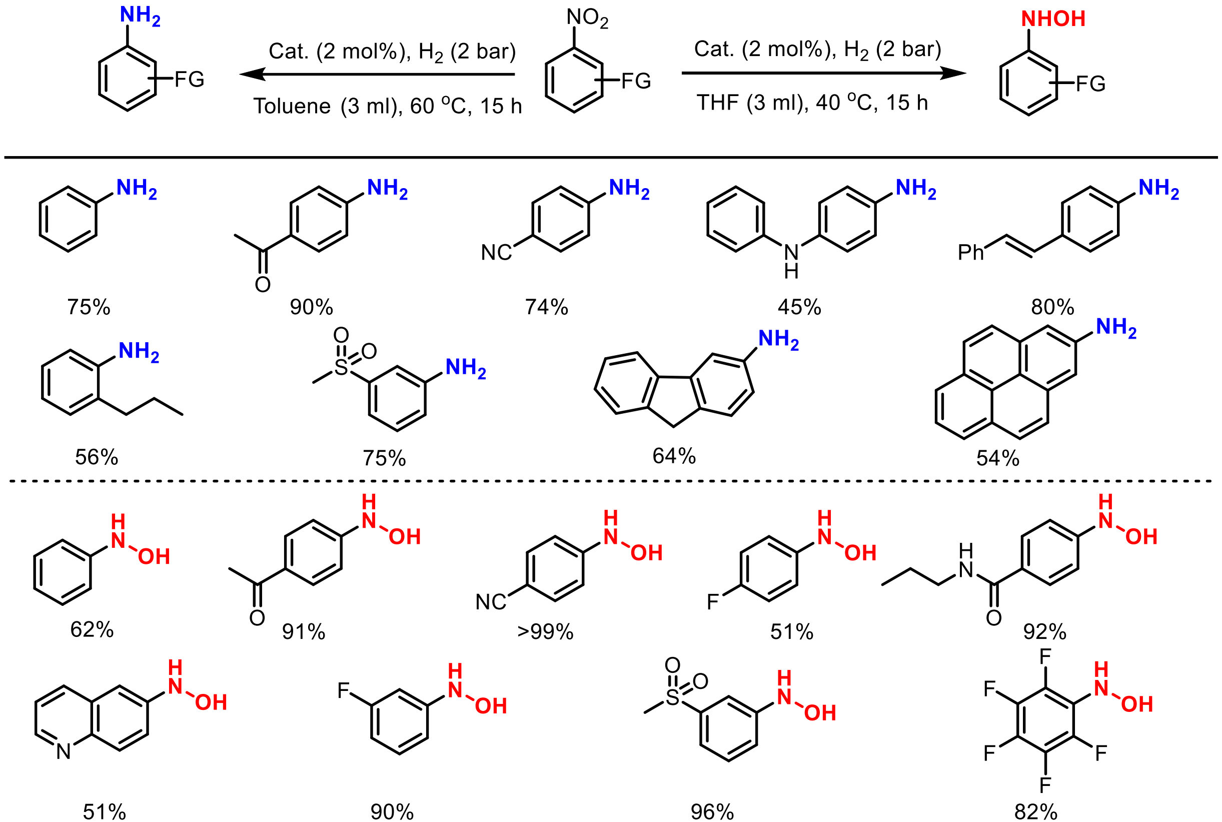
Motomu Kanai et. al., *Angew. Chem. Int. Ed.*, **2017**, *56*, 1495–1499

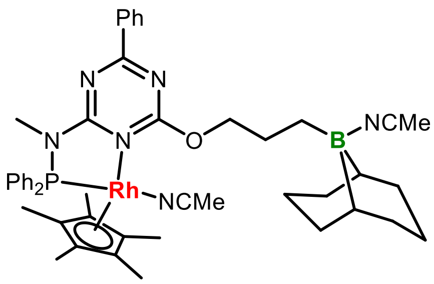
Yoshiaki Nakao et. al., *J. Am. Chem. Soc.* **2019**, *141*, 7972–7979

4. Catalytic Reactivity of [Metal-Linker-Boron] System

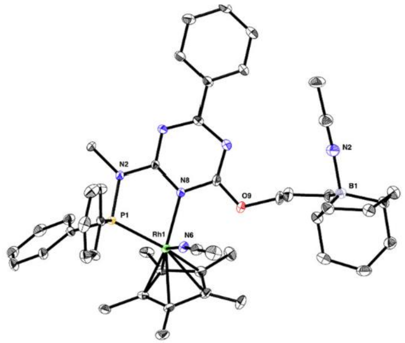
2022 **Werlé**

Borane-mediated selective reduction of nitroaranes under different conditions



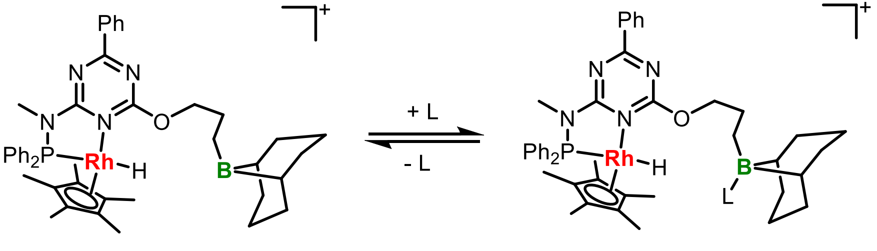


4-1-1-MeCN

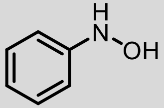


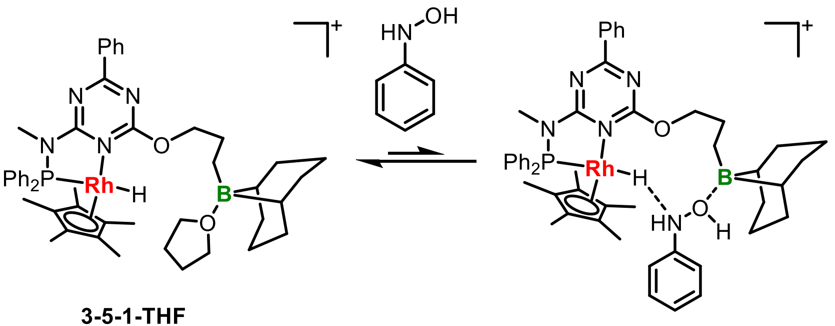
Christophe Werlé et. al., *Angew. Chem. Int. Ed.*, **2022,** *61*, e202205515

4. Catalytic Reactivity of [Metal-Linker-Boron] System

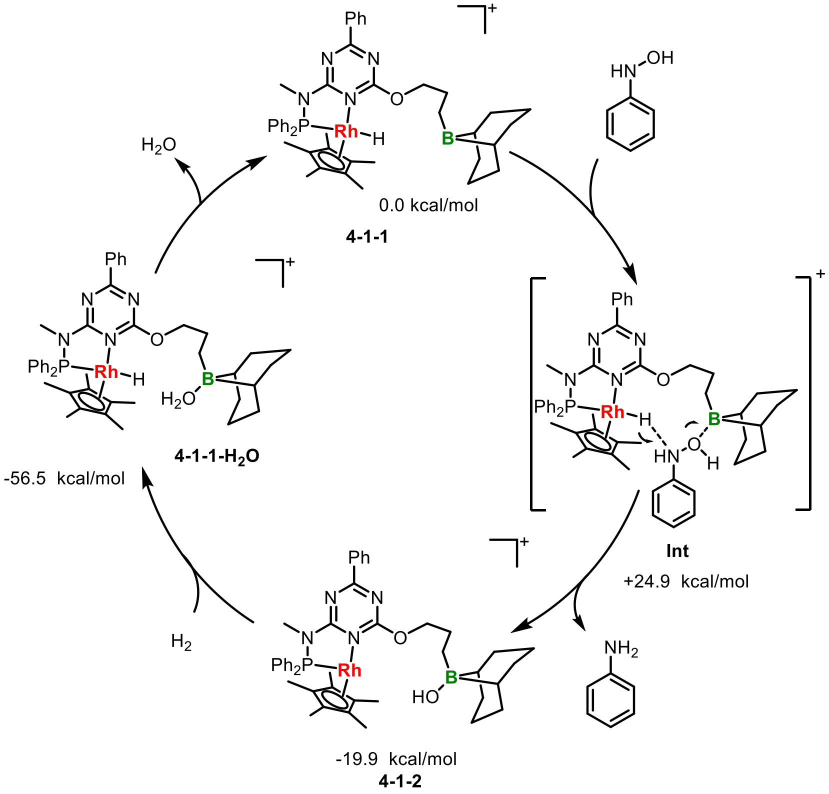


4-1-1 **4-1-1-L**

L:	MeOH	THF	MeCN		
ΔG(Kcal/mol):	-2.3	-1.2	1.5	6.6 (NH)	11.0 (OH)



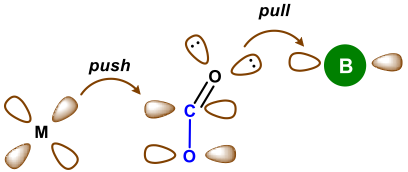
3-5-1-THF



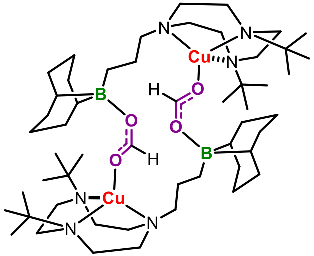
Christophe Werlé et. al., *Angew. Chem. Int. Ed.*, **2022,** *61*, e202205515

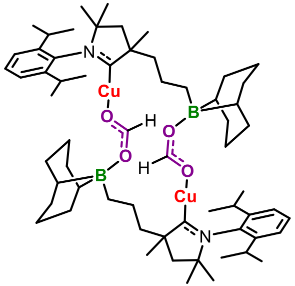
Contents

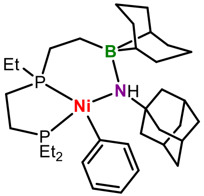
5.1 Summary

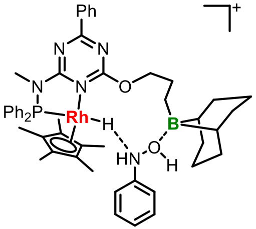


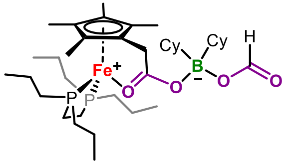
Push-Pull Effect

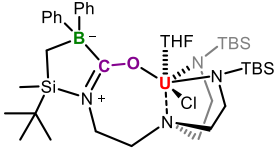


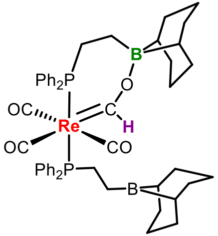


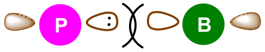




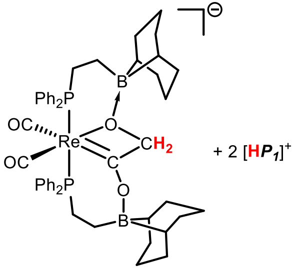


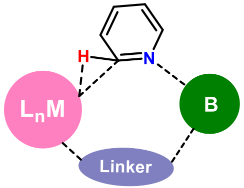




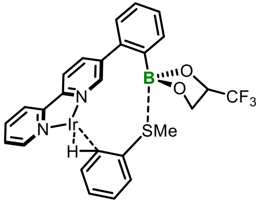


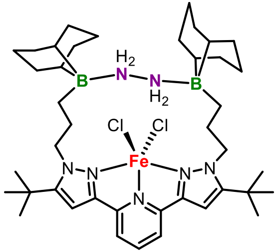
Frustrated Lewis Acid-Base Pairs (FLPs)





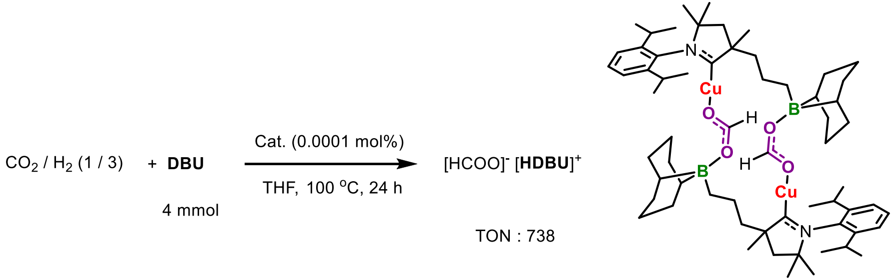
Anchoring Substrate



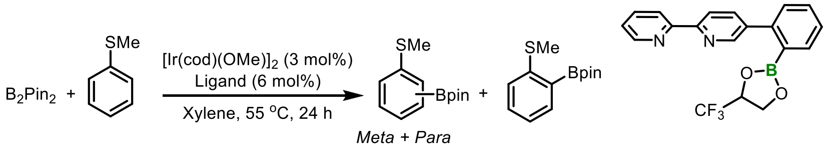


5.1 Summary

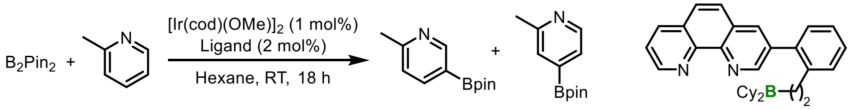
Reactivity or selectivity improved by Boron groups



3-2-6

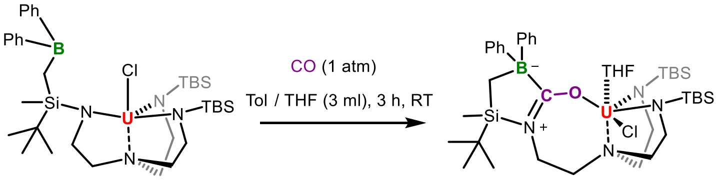


L3 64% (> 1 : 30)

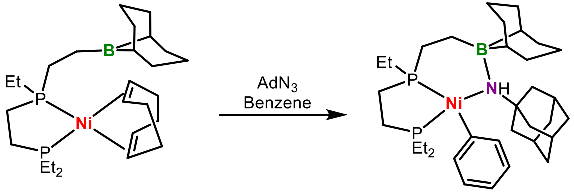


L7 99% (98:2)

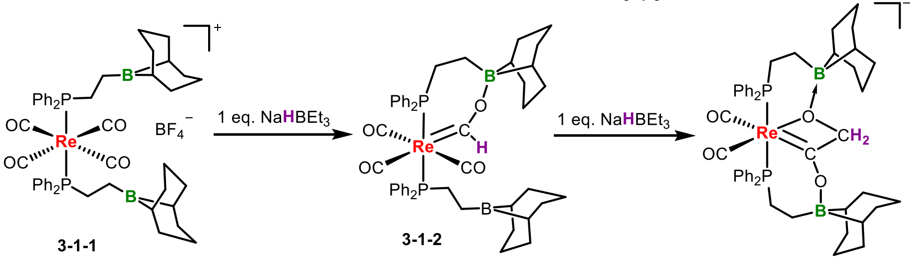
Unique Reactivity led by Boron groups



3-1-6 3-1-7

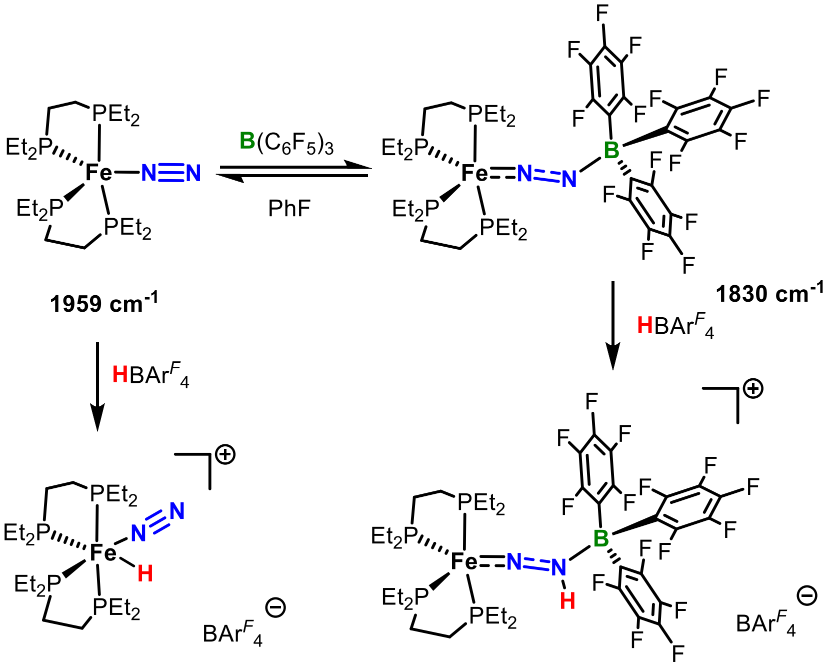


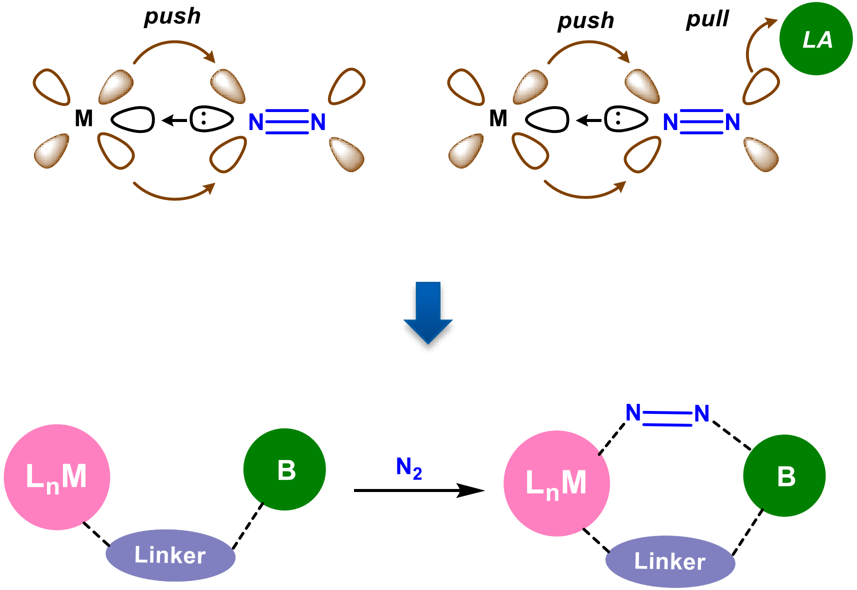
3-4-1 3-4-9



3-1-1 3-1-2 3-1-4

5.2 Prospect





Nathaniel K. Szymczak et. al. *J. Am. Chem. Soc.* **2017**, *139*, 5952–5956

感谢倾听，

敬请各位老师同学批评指正！