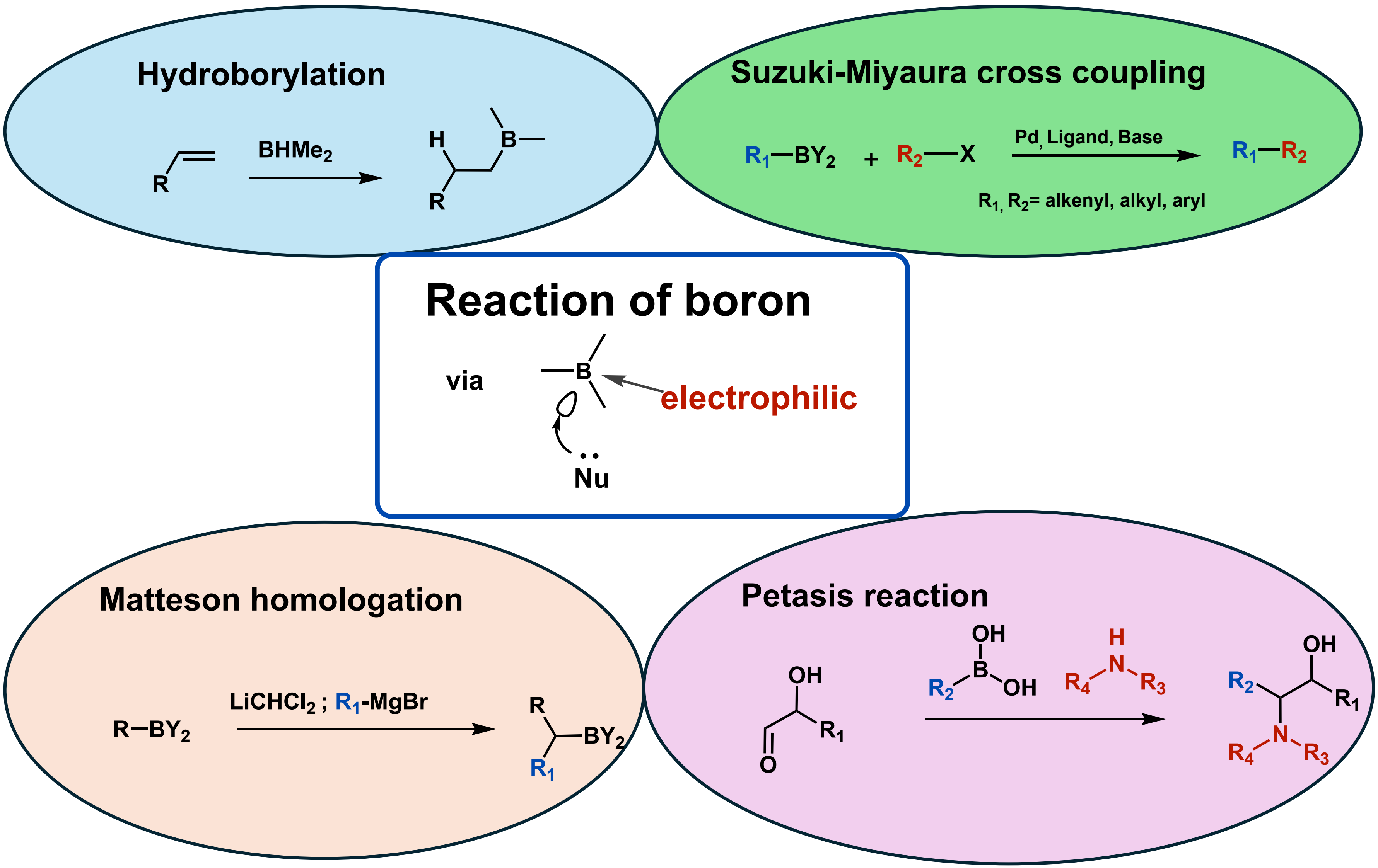
Reactivity of metal boryl complex

Literature Seminar #2

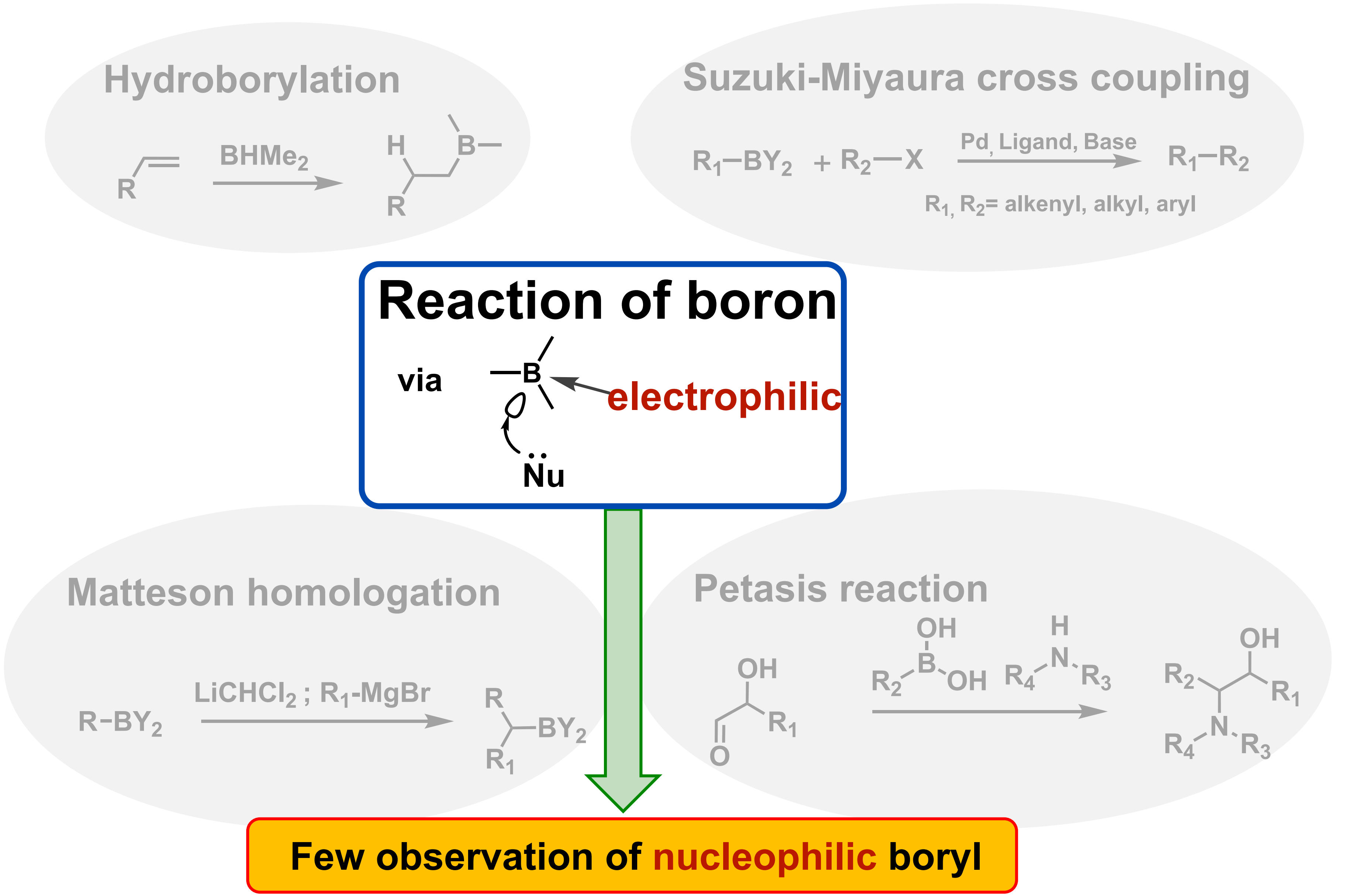
M1 Yuta Kasamoto

Contents

Reaction of boron

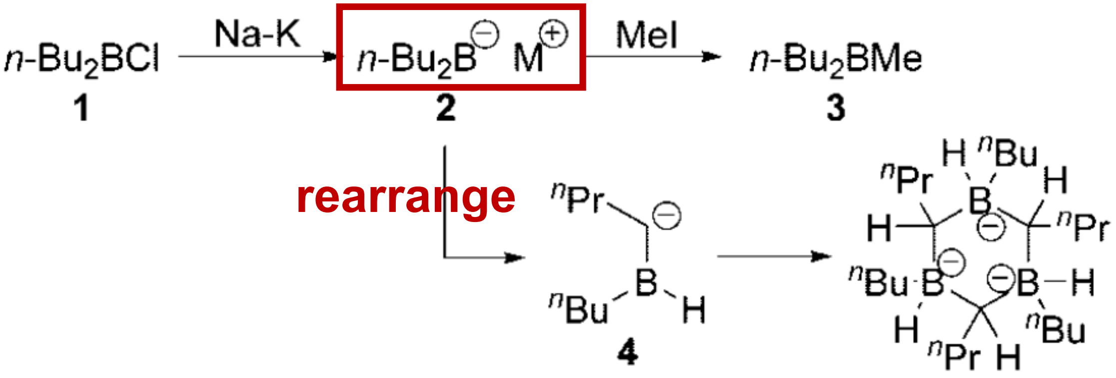


Reaction of boron



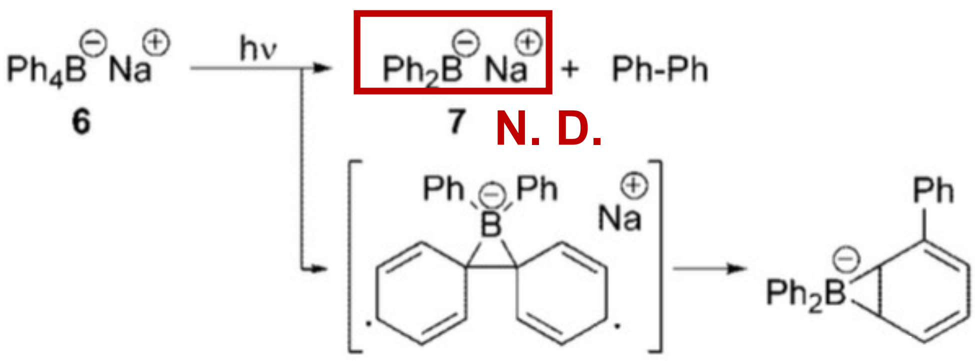
Early attempts of boryl anion

Attempt ①



C. A. Kraus, *et al. J. Am. Chem. Soc*. **1952**, *74*, 3398.
K. Swaminathan, *et al. J. Chem. Soc.,Dalton Trans.* **1976**, 2297.

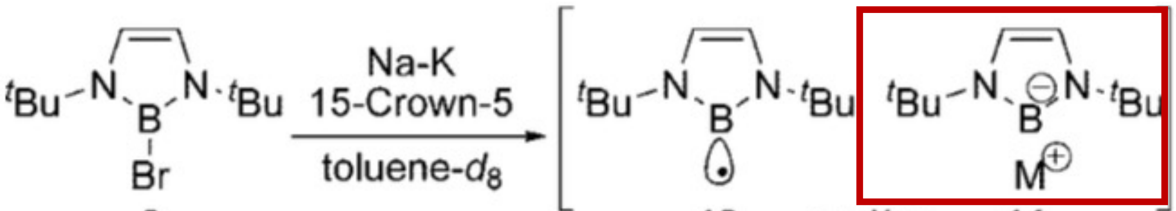
Attempt ②



D. P. Maier, *et al. J. Am. Chem. Soc*. **1967**, *89*, 5153–5157.

Early attempts of boryl anion

Attempt ③



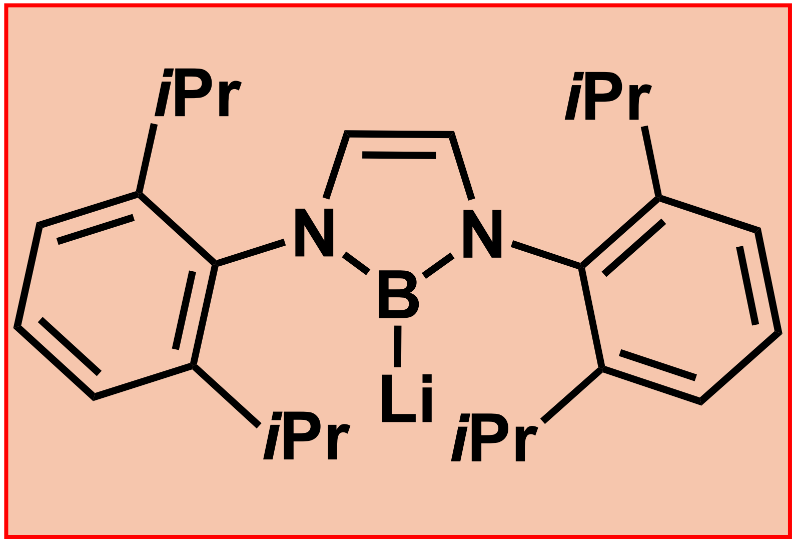
9 **10** and/or **11**

L. Weber, *et al. J. Chem. Soc. Dalton Trans*. **2001**, 3459.

Boryl lithium could not be isolated and structurally analyzed.

Boryl lithium

First example of isolated boryl anion

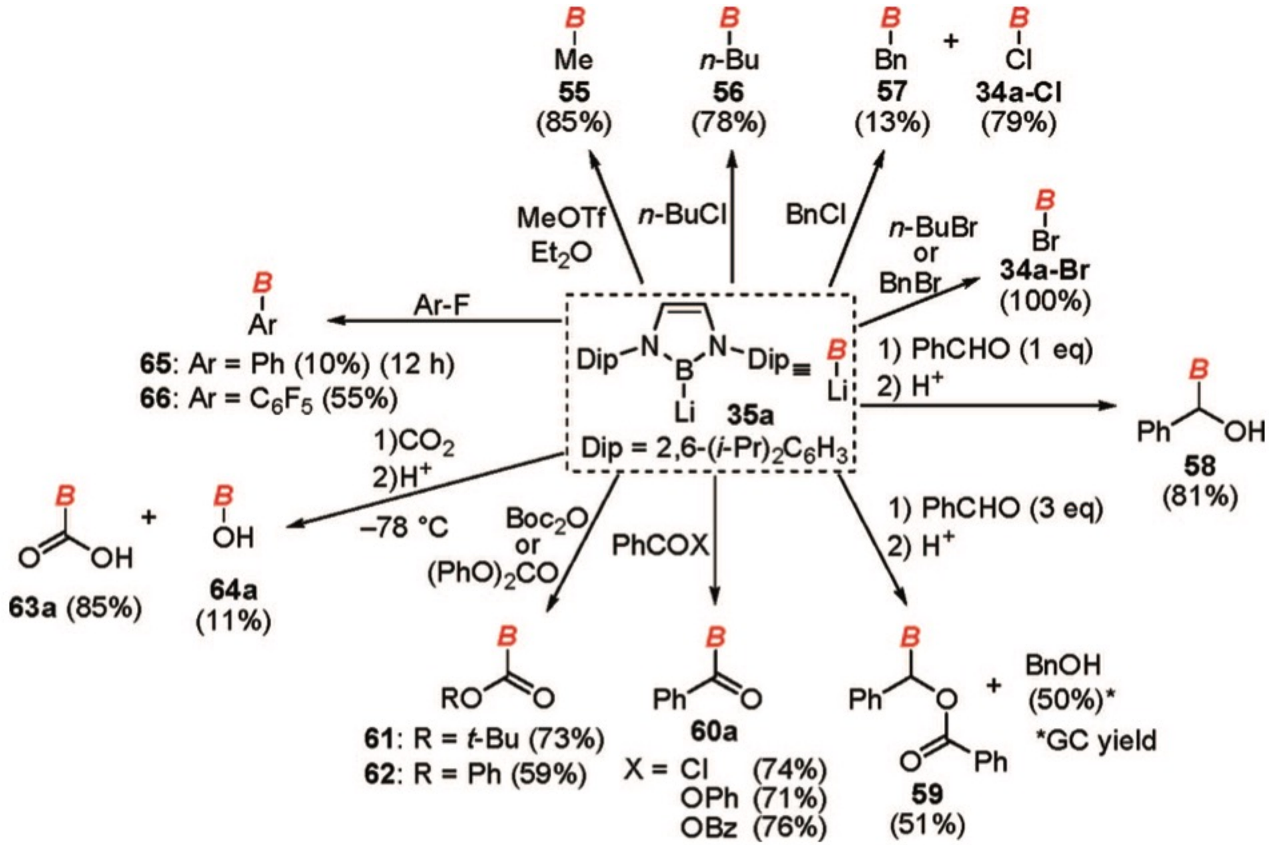


- **X-ray crystallography**
- **Bond length and angle**
- **NMR**
- **Reaction with several electrophiles**

M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

Boryl lithium

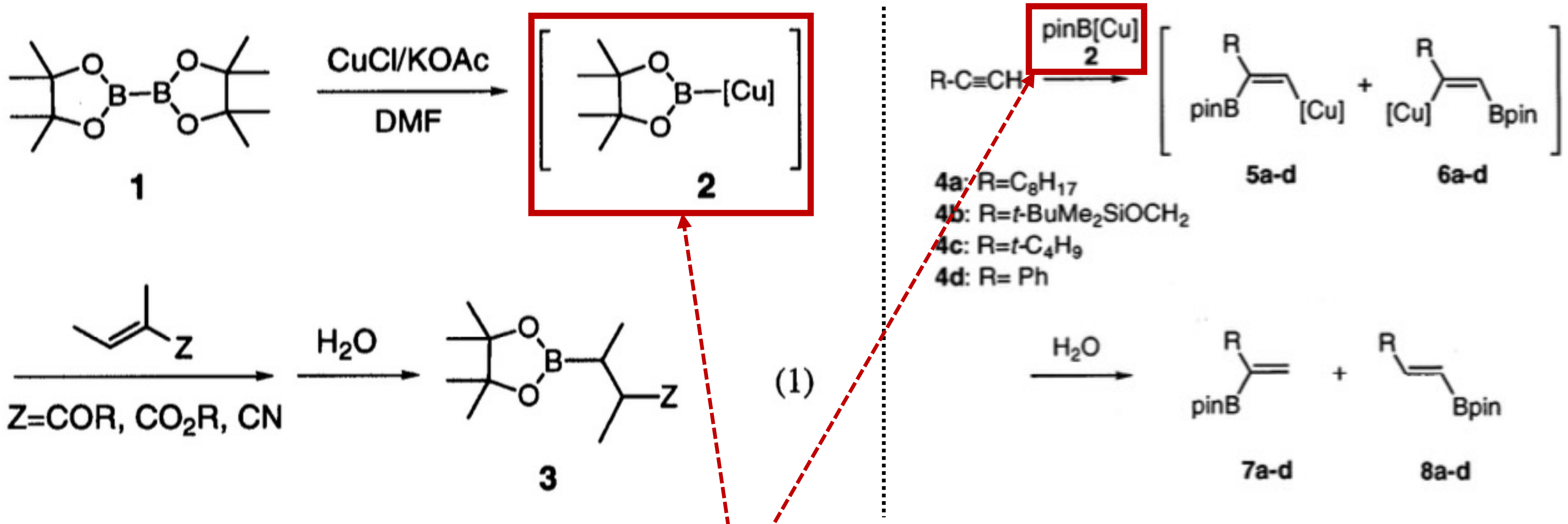
Boryl lithium can react with various electrophiles.



M. Yamashita, K. Nozaki, *et al.* *J. Am. Chem. Soc.* **2008**, *130*, 16069.

Boryl copper complex

Addition of boryl copper complex to alkenes and alkynes



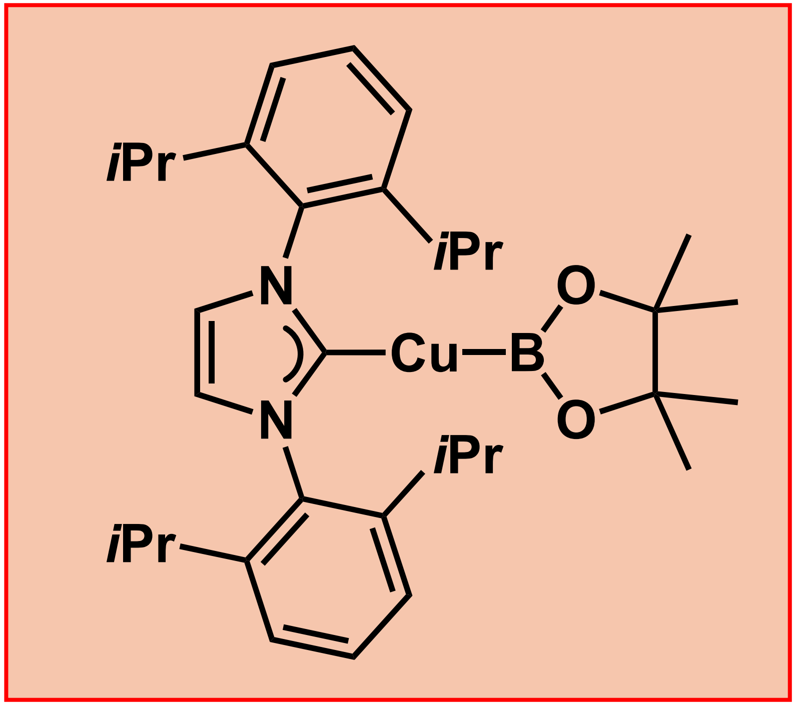
Nucleophilicity of boron center in copper boryl complex was suggested.

N. Miyaura, *et al. Chem. Lett.* **2000**, 982.

N. Miyaura, *et al. J. Organomet. Chem.* **2001,** *625*, 47.

Boryl copper complex

First example of isolated boryl anion

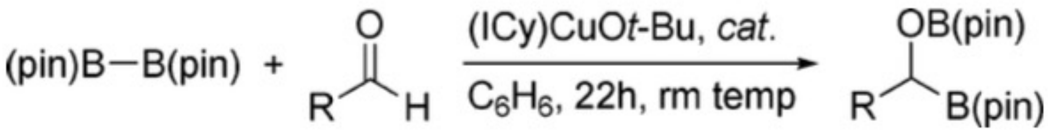


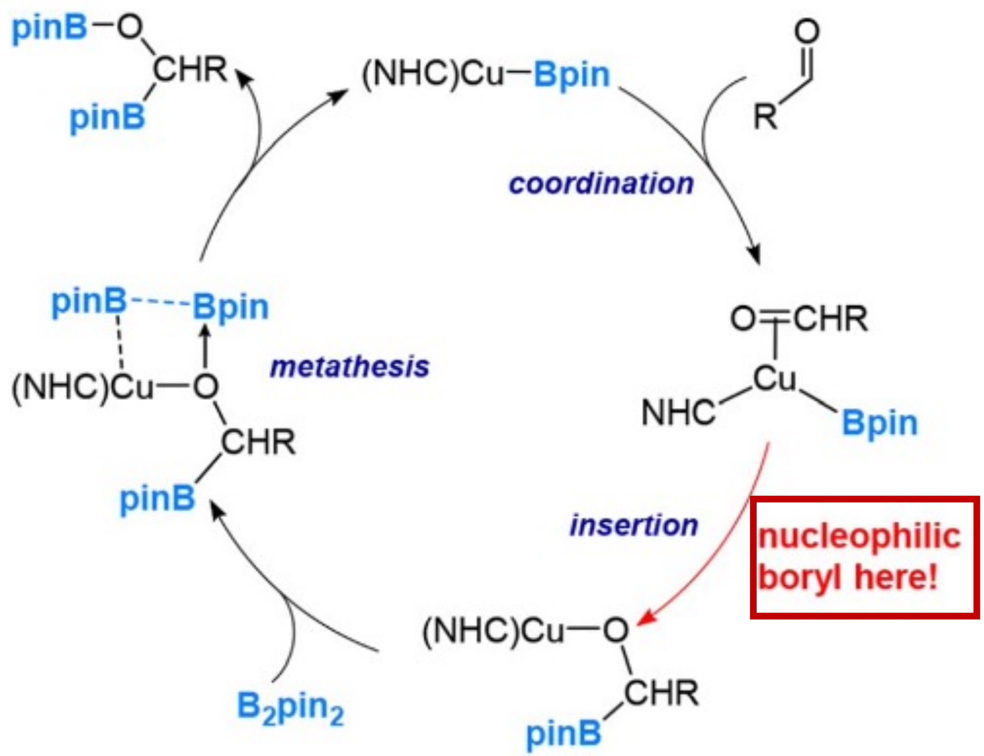
- X-ray crystallography
- Bond length and angle
- NMR
- Reaction with CO_2 and aldehydes as electrophiles

J. P. Sadighi, *et al. J. Am. Chem. Soc.* **2005**, *127*, 17196.
J. P. Sadighi, *et al. J. Am. Chem. Soc.* **2006**, *128*, 11036.

Boryl copper complex

Borylation of aldehydes



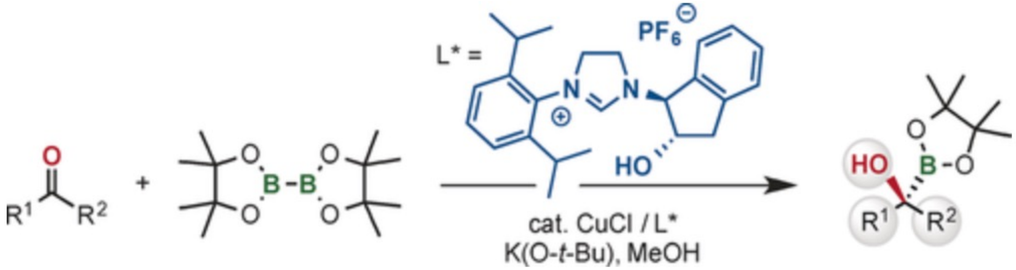


J. P. Sadighi, *et al. J. Am. Chem. Soc.* **2006**, *128*, 11036.

Boryl copper complex

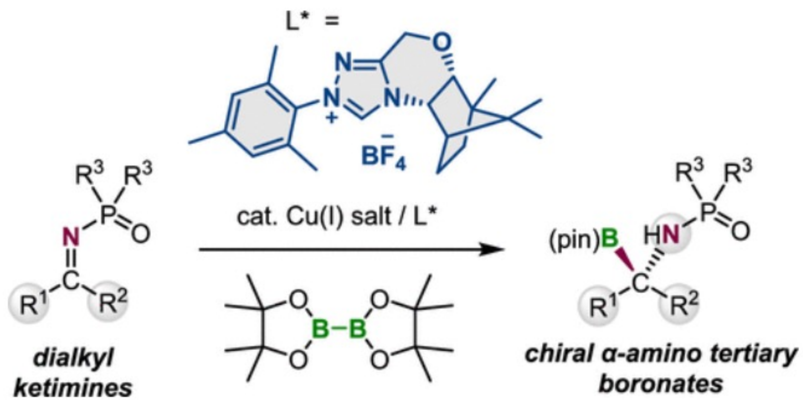
Boryl copper complex can react with various electrophiles.

Borylation of ketone



H. Ito, *et al. Angew. Chem. Int. Ed.* **2017***, 56,* 6646.

Borylation of dialkyl ketimine



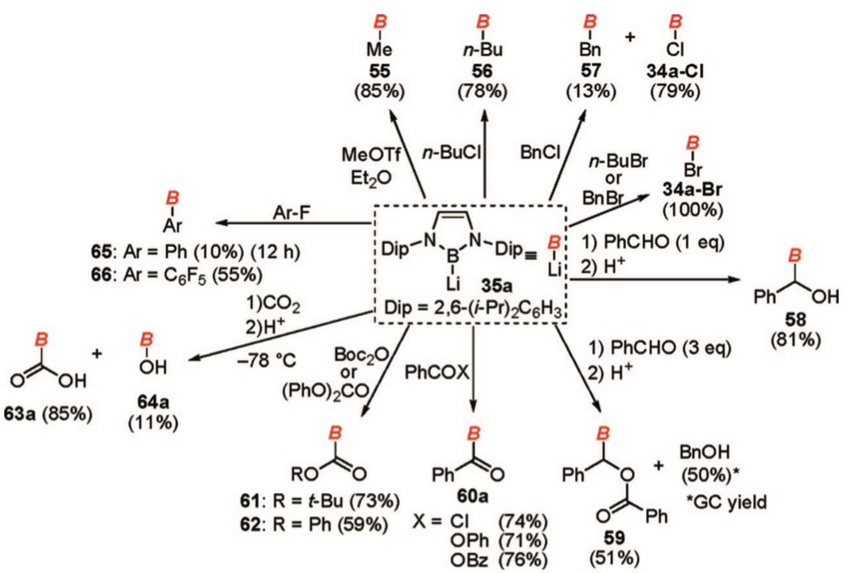
H. Ito*, et al. ACS Catal*. **2021**, *11, 11*, 6733.

Nucleophilic boryl

Application to nucleophilic boryl

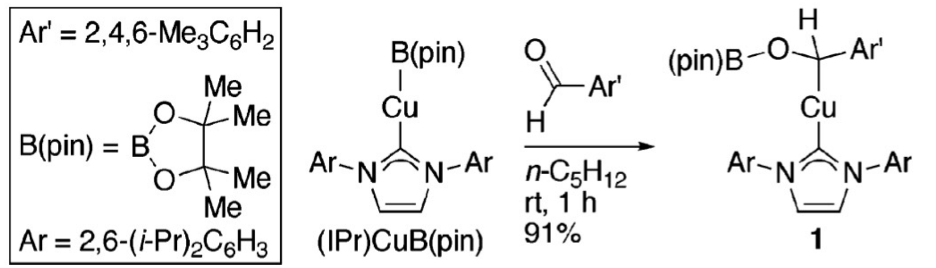
Borylation of electrophiles

Boryl lithium

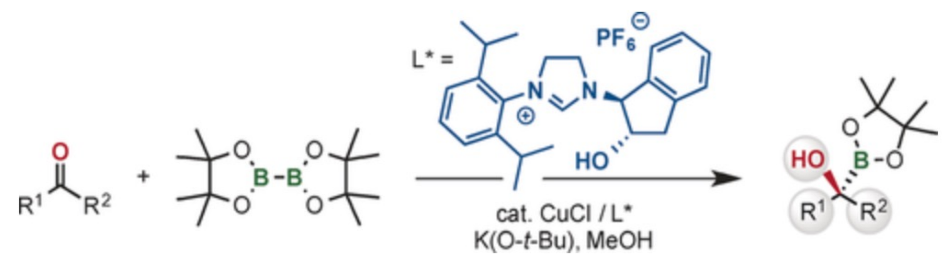


K. Nozaki, *et al. J. Am. Chem. Soc.* **2008**, *130*, 16069.

Boryl copper complex



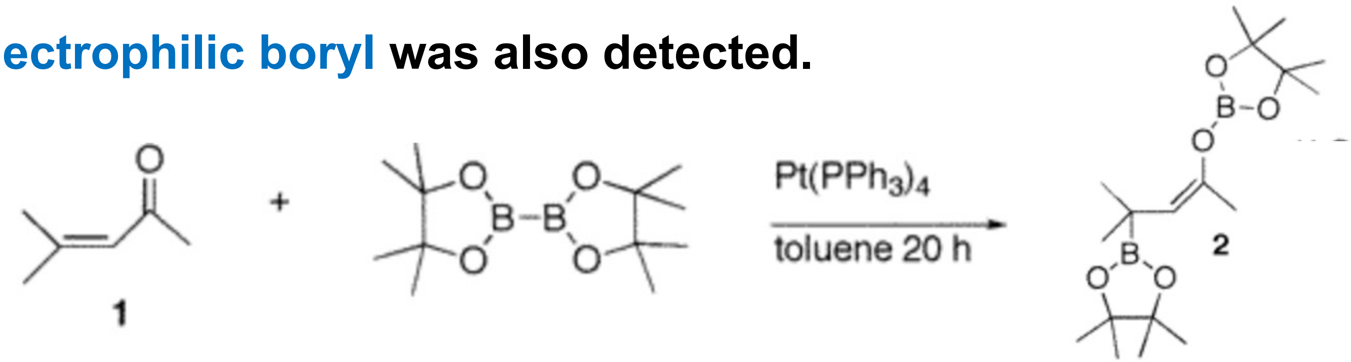
J. P. Sadighi, *et al. J. Am. Chem. Soc.* **2006**, *128*, 11036.



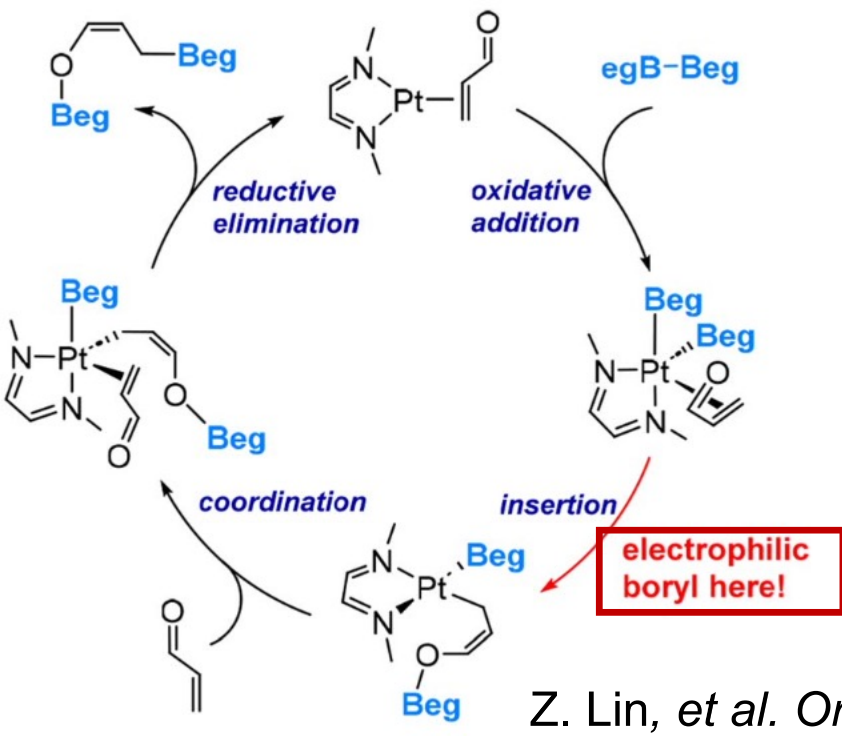
H. Ito, *et al. Angew. Chem. Int. Ed.* **2017**. *56*, 6646.

Other metal boryl complex

Electrophilic boryl was also detected.



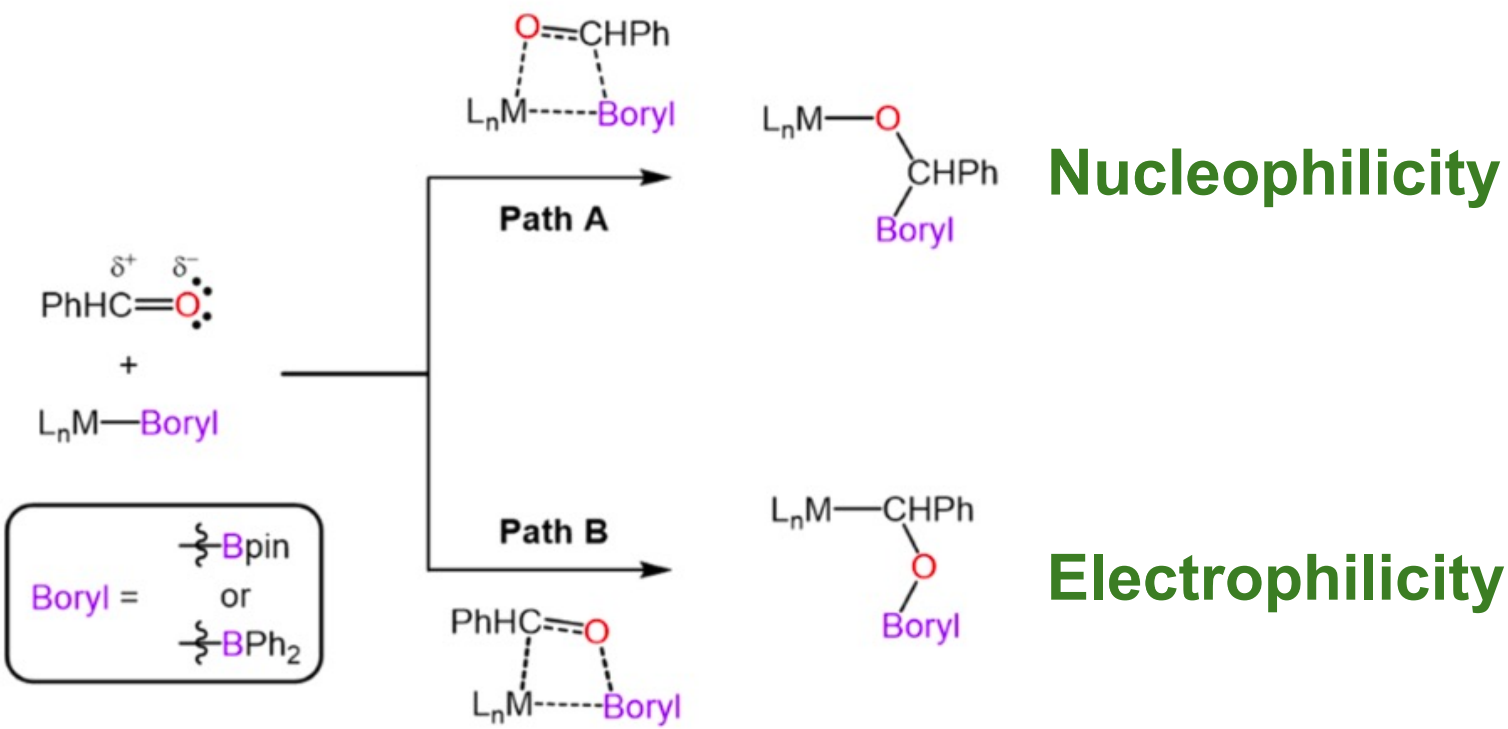
M. Srebnlik, *et al.* Organometallics. **2001**, *20, 18*, 3962.



Z. Lin, *et al. Organometallics.* **2012**, *31*, 3410.

Transition metal boryl complex

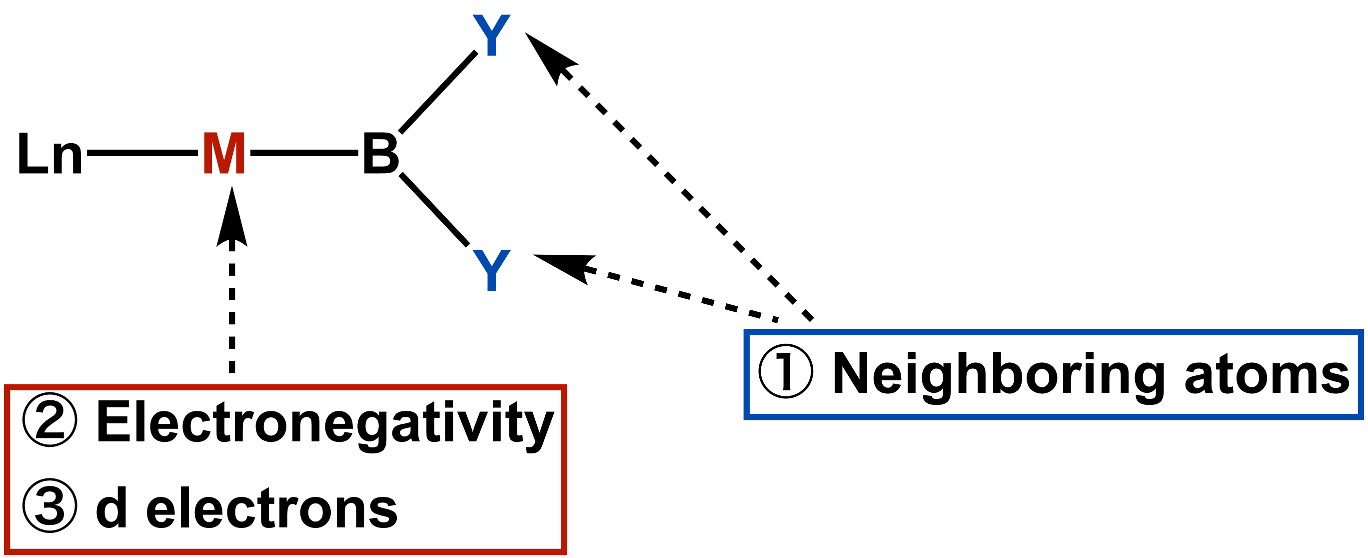
Difference of reactivity of transition metal boryl complex



Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

Transition metal boryl complex

Reactiyity of metal boryl complex is affected by 3 factors below.



Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

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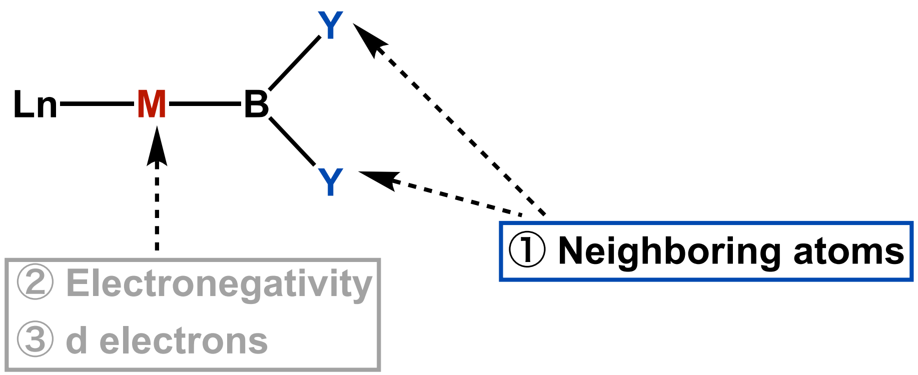
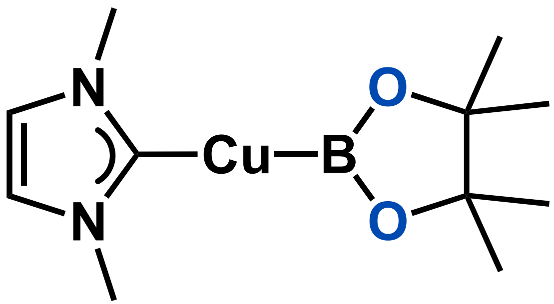


Ln
M
B
Y
Y
① Neighboring atoms
② Electronegativity
③ d electrons

Model

<u>**Neighboring atom is O**</u>

(NHC)Cu-Bpin

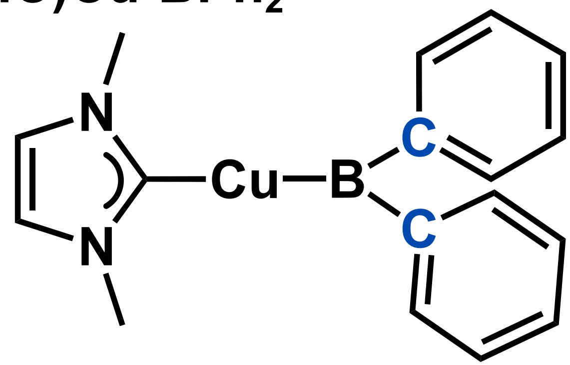


Isolated as
(Icy)Cu-Bpin (J. P. Sadighi, 2005)

Many application
to borylation of electrophiles

<u>**Neighboring atom is C**</u>

(NHC)Cu-BPh$_2$

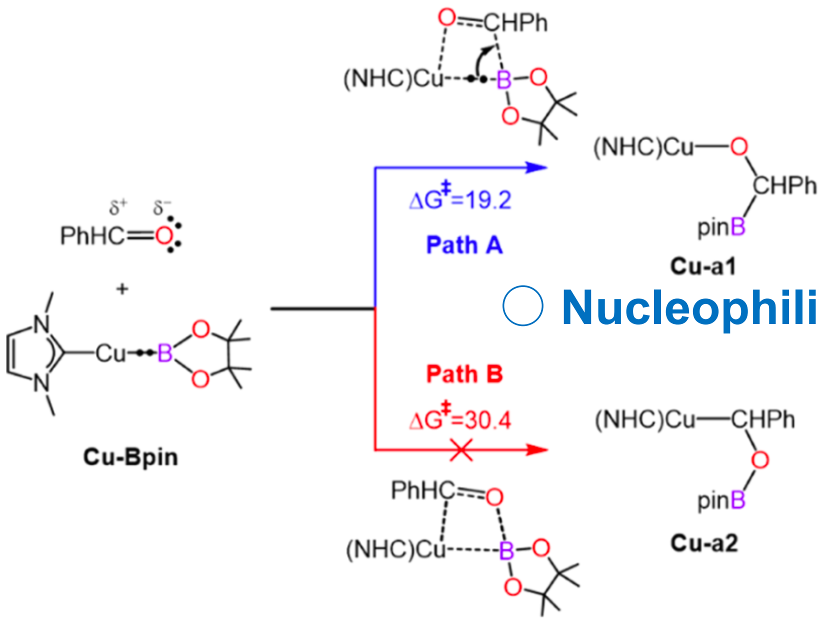


Not isolated

Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

DFT calculation

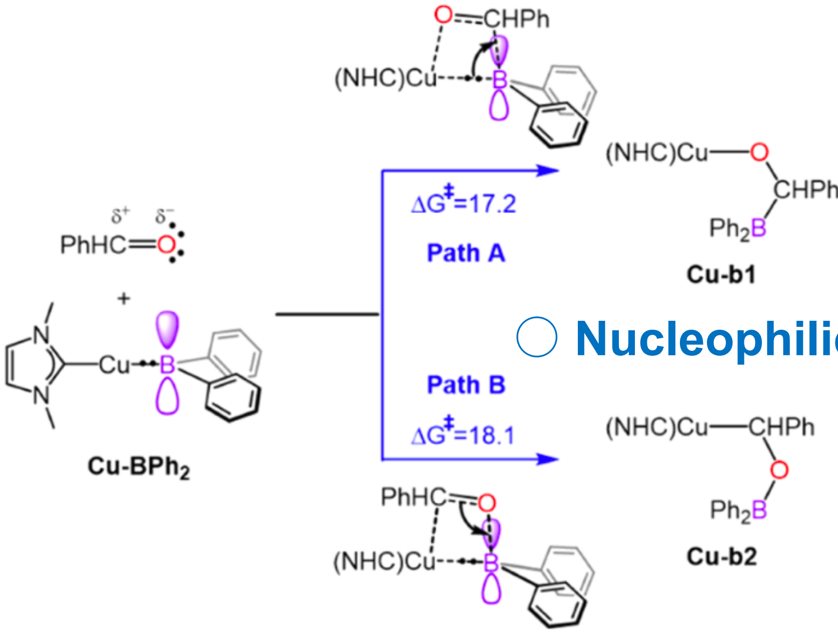
(NHC)Cu-Bpin



○ Nucleophilicity

✕ Electrophilicity

(NHC)Cu-BPh$_2$



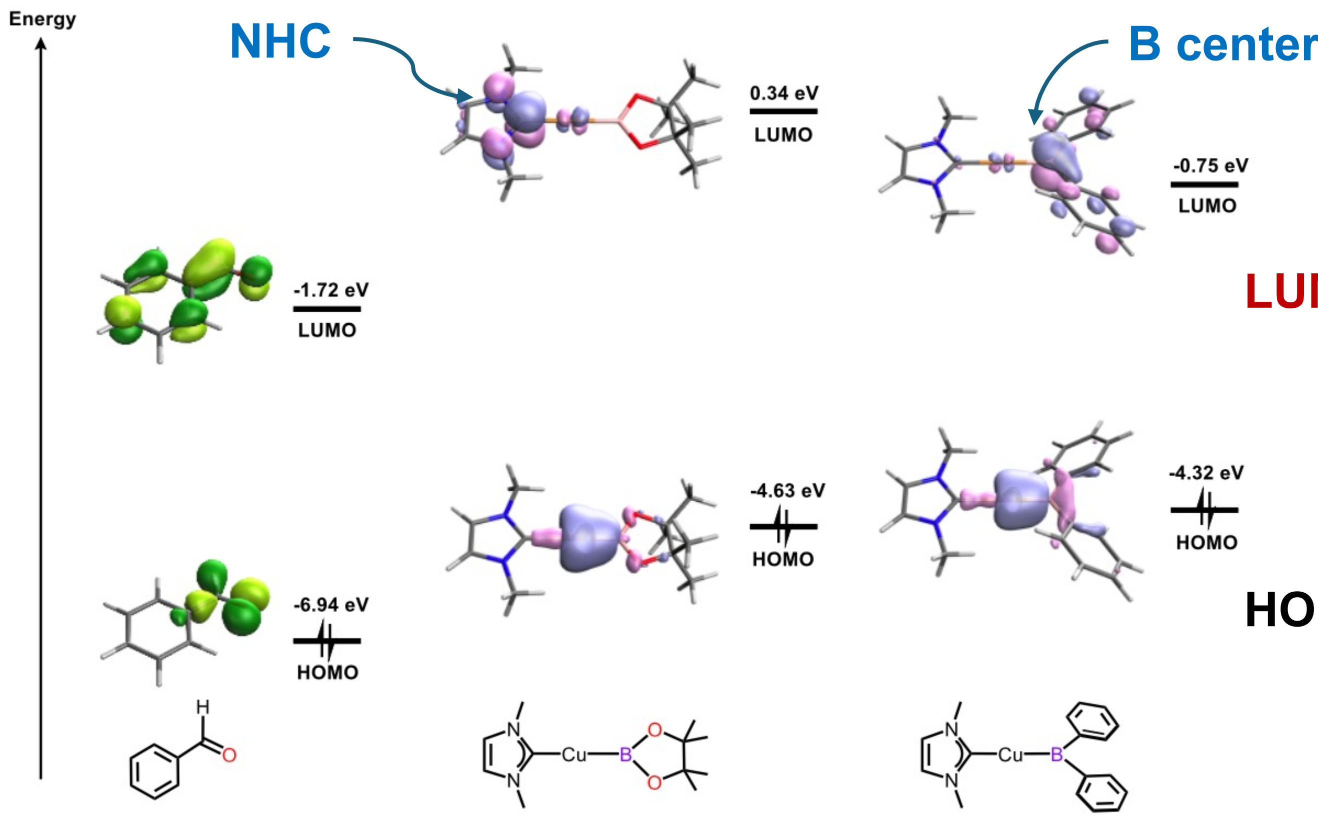
○ Nucleophilicity

○ Electrophilicity

Neighboring atoms affect electrophilicity of boryl.

Z. Lin, *et al. ACS Catal.* **2021**, *11*, 5061.

FMO calculation



LUMO is different.

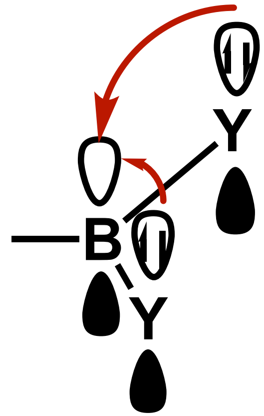
HOMO is almost same.

Neighboring atoms affect electrophilicity of boryl.

Z. Lin, *et al. ACS Catal.* **2021**, *11*, 5061.

Effects of neighboring atoms

Push π electron ⇨ **Stabilization (Lose electrophilicity)**



<u>Example of stabilization of boryl lithium</u>

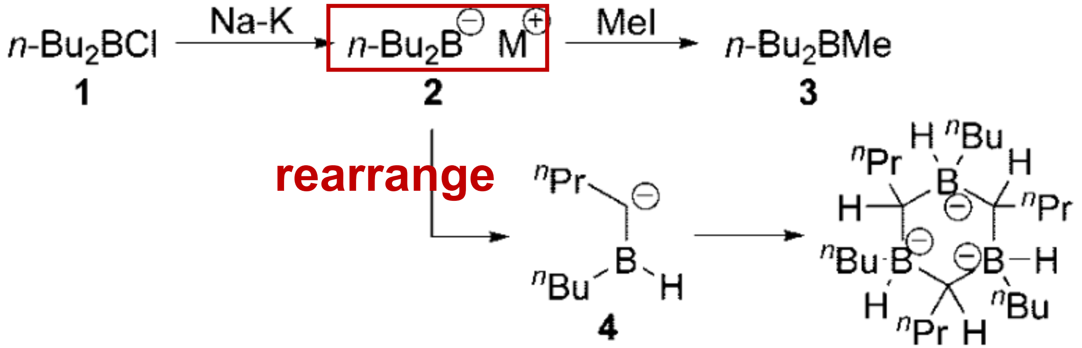
	$Li-B(CH_3)_2$	$Li-B(NH_2)_2$	$Li-B(OH)_2$	$Li-BF_2$
Boron p_z occ	–	0.30	0.19	0.18

(occ= occupancy of boron p_z orbital)

R. Schleyer, *Inorg. Chem*. **1995**, *34* , 607.

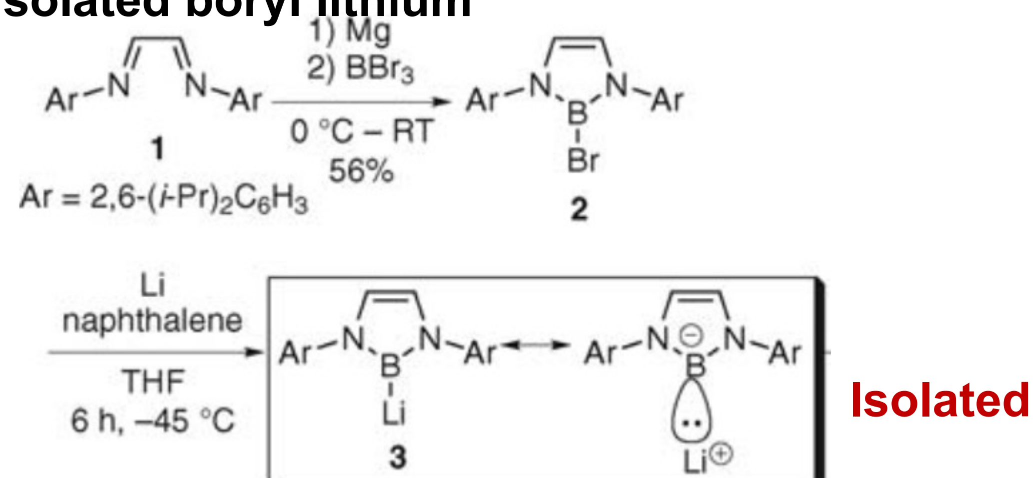
Stable boryl lithium

Early attempt to generate boryl anion



C. A. Kraus, *et al. J. Am. Chem. Soc*. **1952**, *74*, 3398.
K. Swaminathan, *et al. J. Chem. Soc.,Dalton Trans.* **1976**, 2297.

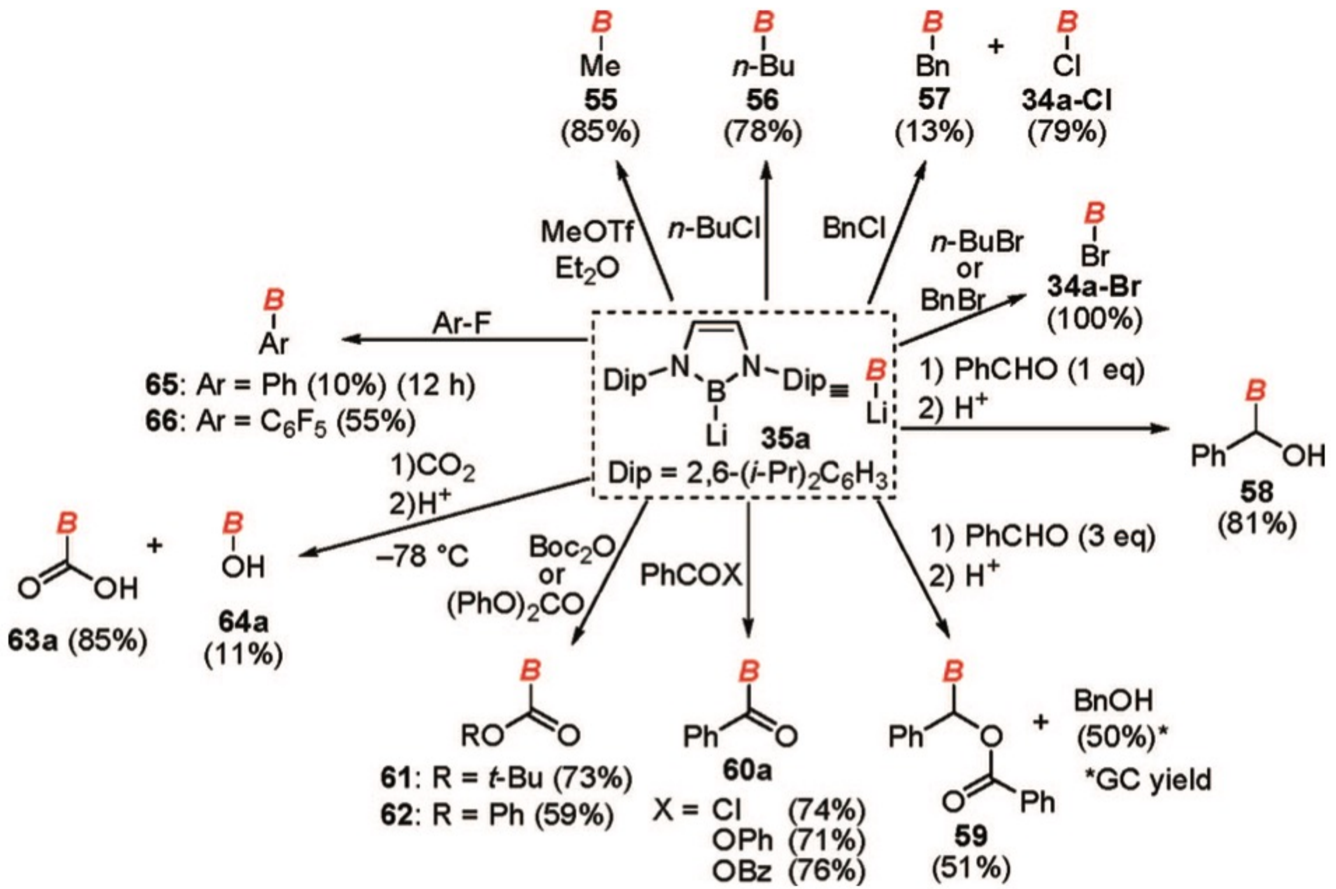
First example of isolated boryl lithium



M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

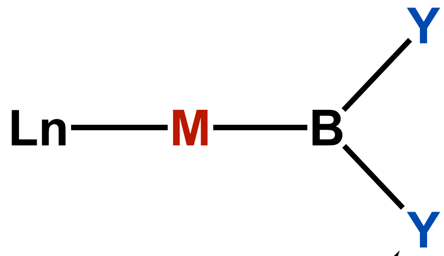
Stable boryl lithium

Boryl lithium can react with various electrophiles.



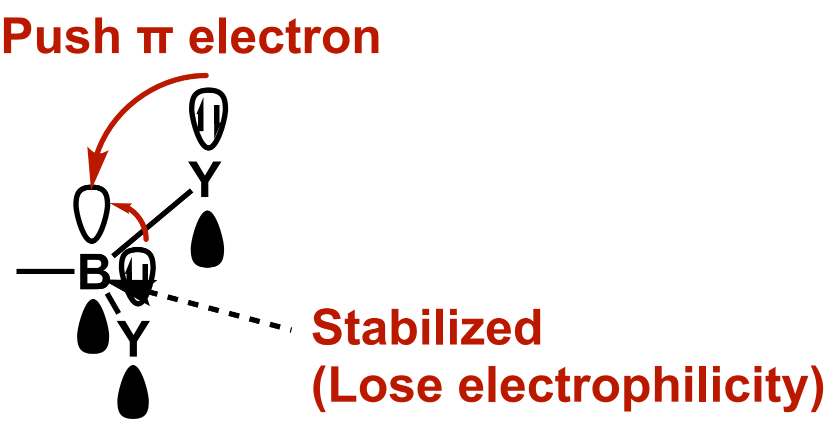
M. Yamashita, K. Nozaki, *et al.* *J. Am. Chem. Soc.* **2008**, *130*, 16069.

Short summary



① **Neighboring atoms**

Y= N, O, F



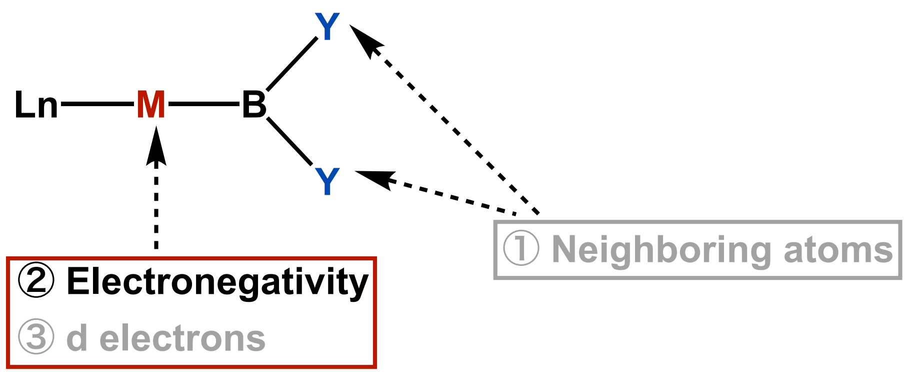
Z. Lin*, et al. ACS Catal*. **2021**, *11*, 5061.

Contents

1. Introduction: Nucleophilic boryl

2. Contents: Factors of reactivity of metal boryl complex
   - 2-1. Stabilization of neighboring atoms
   - 2-2. Electronegativity of metal
   - 2-3. d electrons of metal

3. Summary

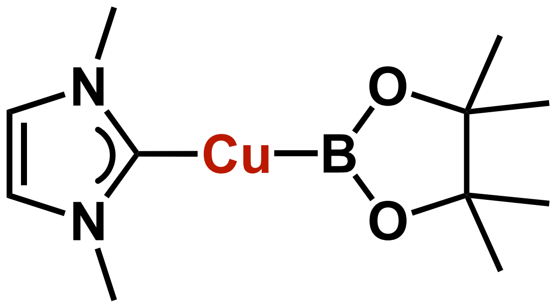


Model

Electronegativity (Pauling)
Cu: 1.90   B: 2.04   Au: 2.54

Electropositive metal (Cu)

(NHC)Cu-Bpin

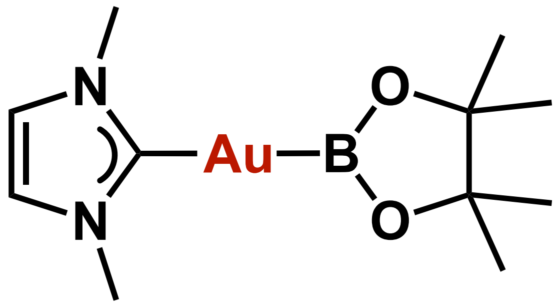


Isolated as
(Icy)Cu-Bpin   (J. P. Sadighi, 2005)

Many application
to borylation of electrophiles

Electronegative metal (Au)

(NHC)Au-Bpin

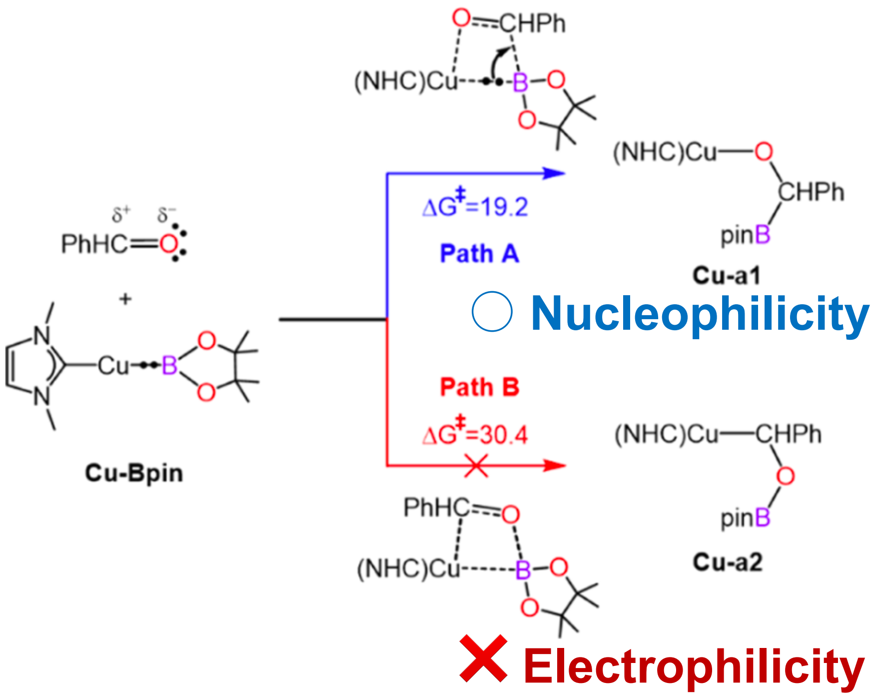


Isolated as
(IPr)Au-Bpin (S. P. Nolan, 2019)

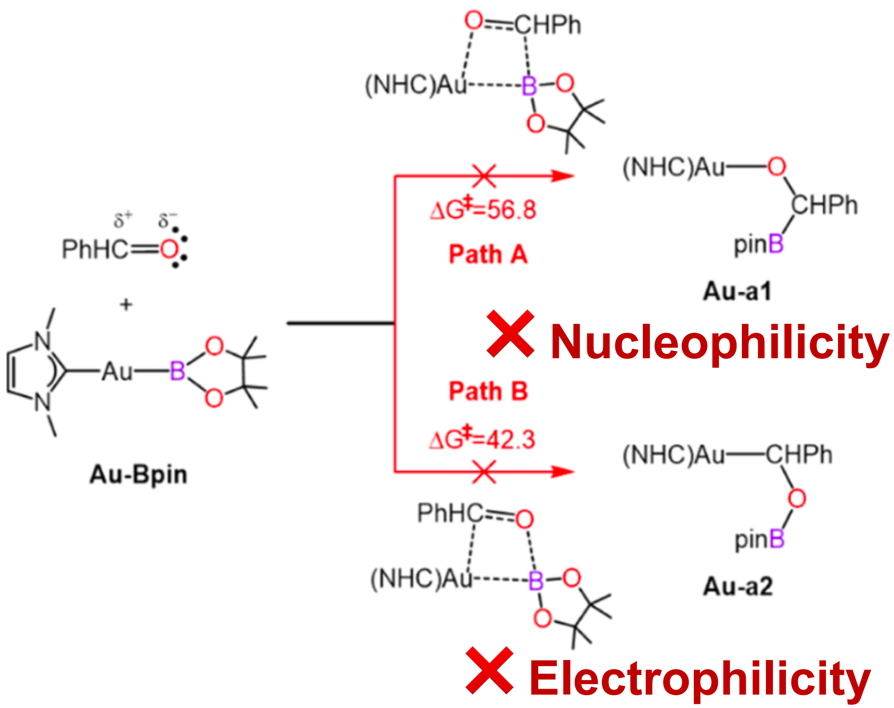
Low reactivity and high stability

DFT calculation

(NHC)Cu-Bpin



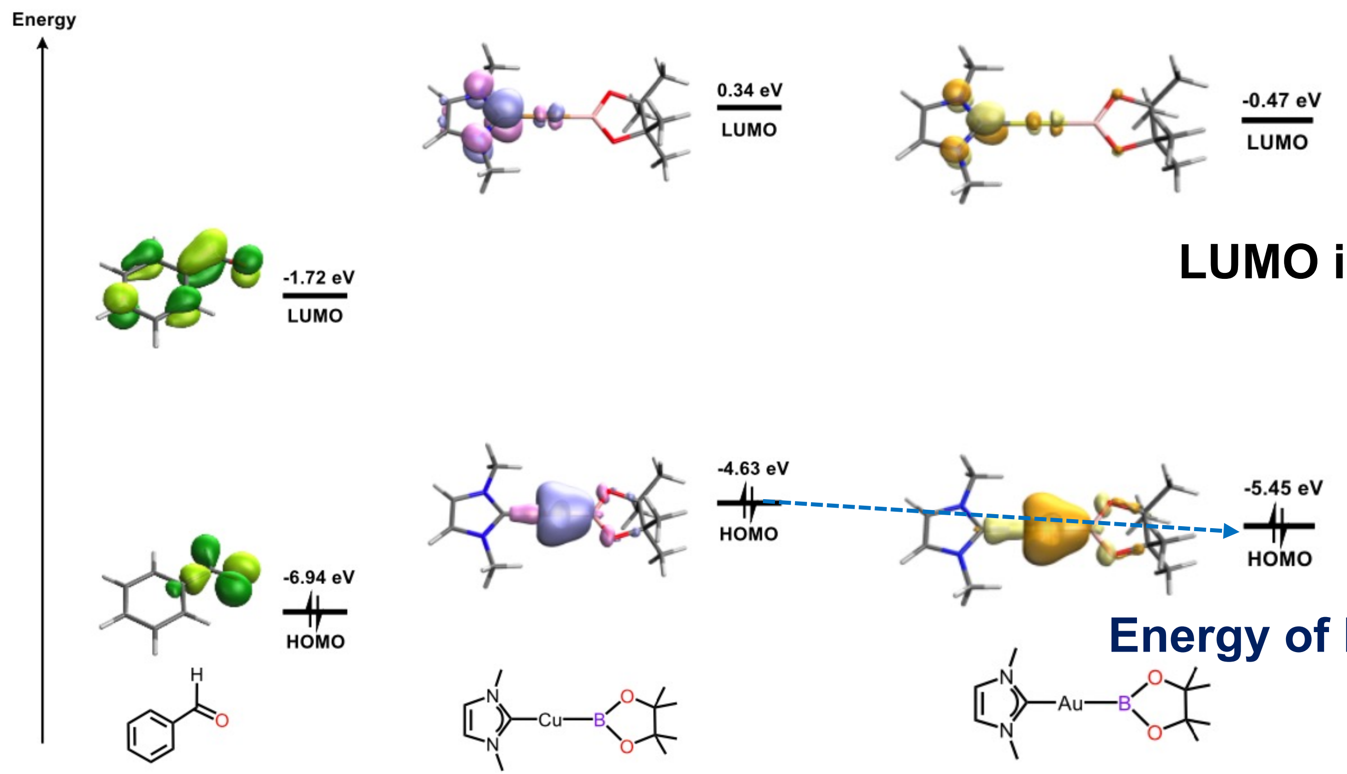
(NHC)Au-Bpin



Transition metal affect nucleophilicity of boryl.

Z. Lin, *et al. ACS Catal.* **2021**, *11*, 5061.

FMO calculation



LUMO is almost same.

Energy of HOMO is lower.

Transition metal affect nucleophilicity of boryl.

Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

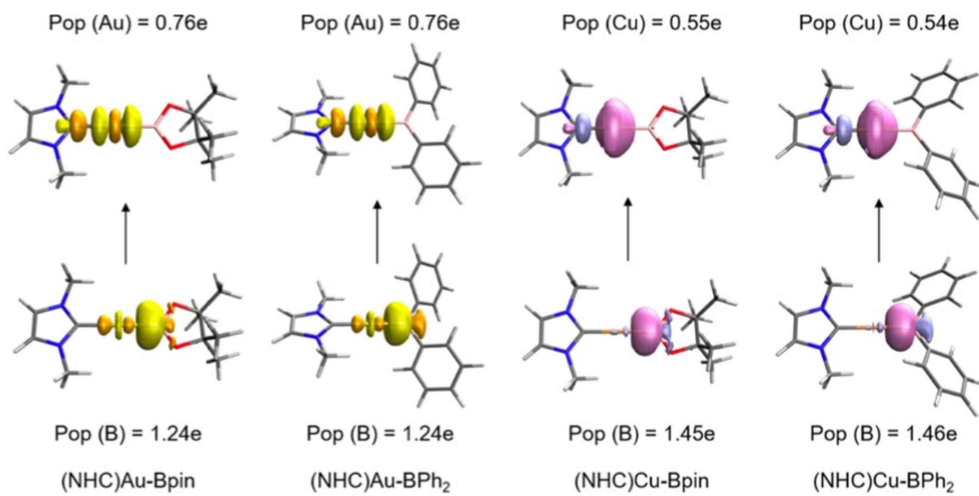
Electronegativity of metal

The charge population calculated by NBO analysis

species	population of M (%)	population of B (%)
[Au]−Bpin	43.69	56.31
[Au]−BPh_2	43.70	56.30
[Cu]−Bpin	31.02	68.98
[Cu]−BPh_2	30.74	69.26

B of electron population
→ lower

PIO analysis



Due to Electronegativity
Cu: 1.90 B: 2.04 Au: 2.54 (Pauling)

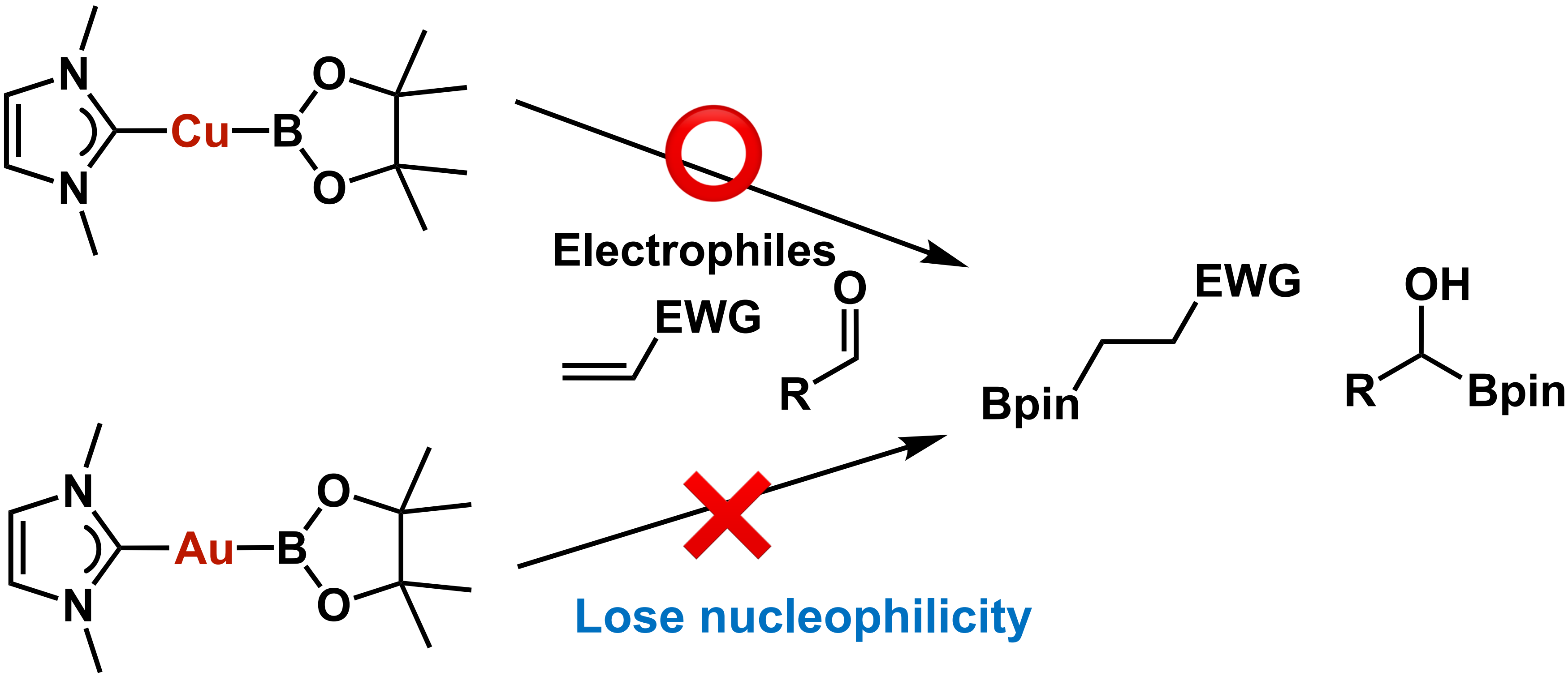
Electronegative metal loses nucleophilicity of metal boryl complex

B of Pop (Occupation number of electron)
→ lower

Z. Lin, *et al. ACS Catal.* **2021**, *11*, 5061.

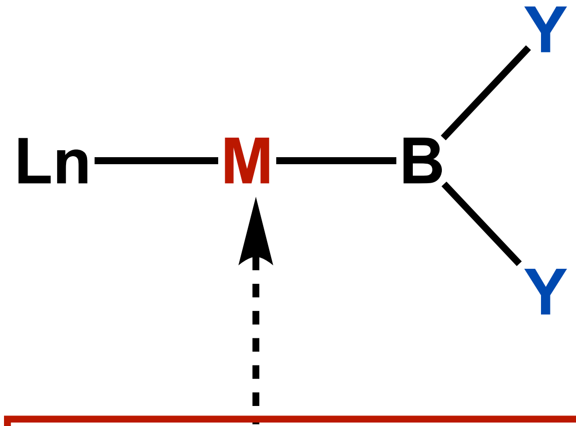
Au(NHC)Bpin complex

Reaction with electrophiles



S. P. Nolan, *et al. Chem. Commu*n. **2019**, *55*, 6799.

Short summary



② **Electronegativity**

M<B (M: electropositive)

→B gets nucleophilicity

M>B (M: electronegative)

→B loses nucleophilicity

Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

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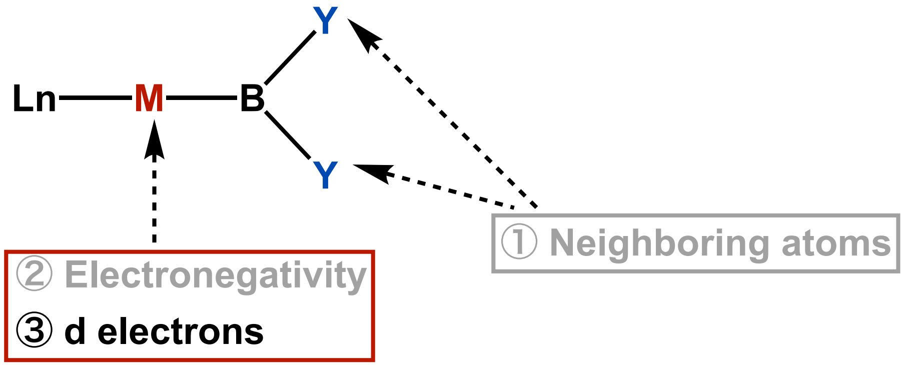
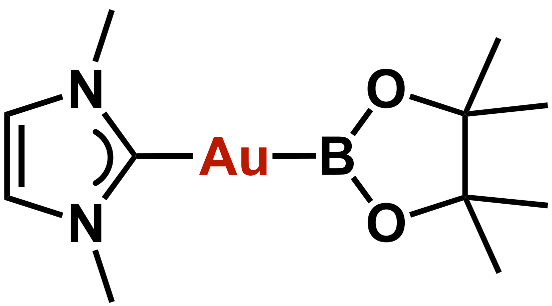


3. Summary

Model

Electronegativity (Pauling)
B: 2.04 Rh: 2.28 Au: 2.54

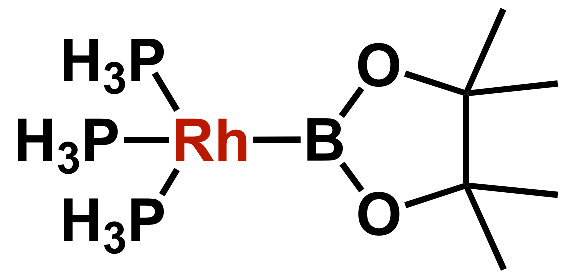
(NHC)Au-Bpin



Isolated as
(IPr)Au-Bpin (S. P. Nolan, 2019)

Low reactivity and high stability

$(PH_3)_3$Rh-Bpin

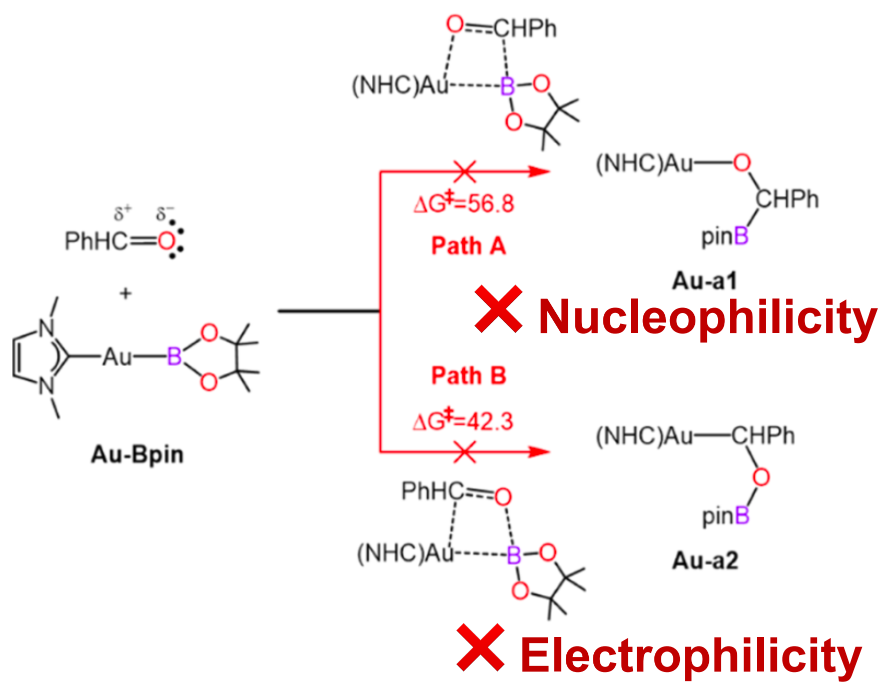


Use as catalyze
Rh-Bpin (W. Zhao 2020)

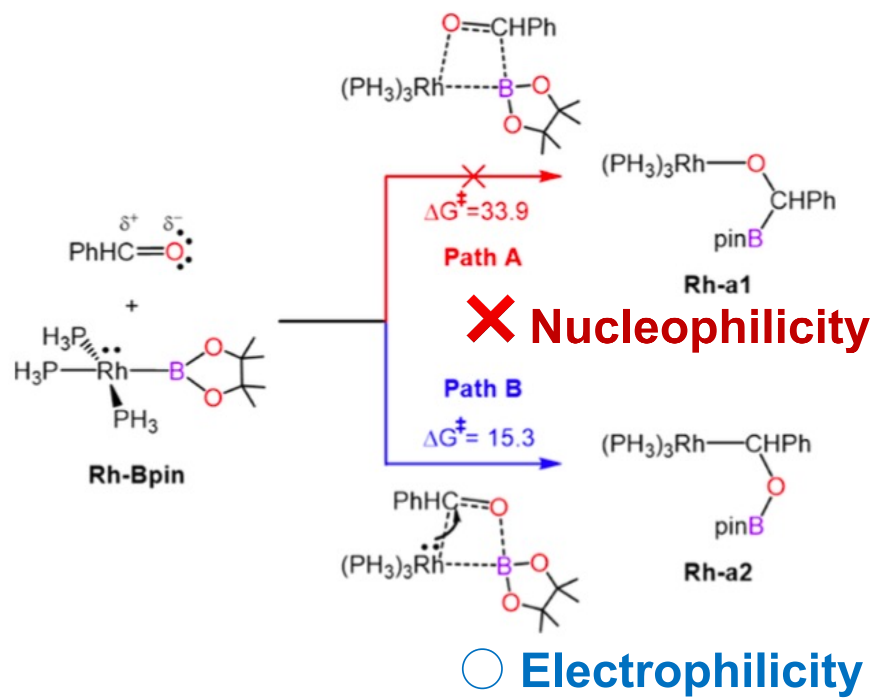
B exhibits electrophilicity

DFT calculation

(NHC)Au-Bpin



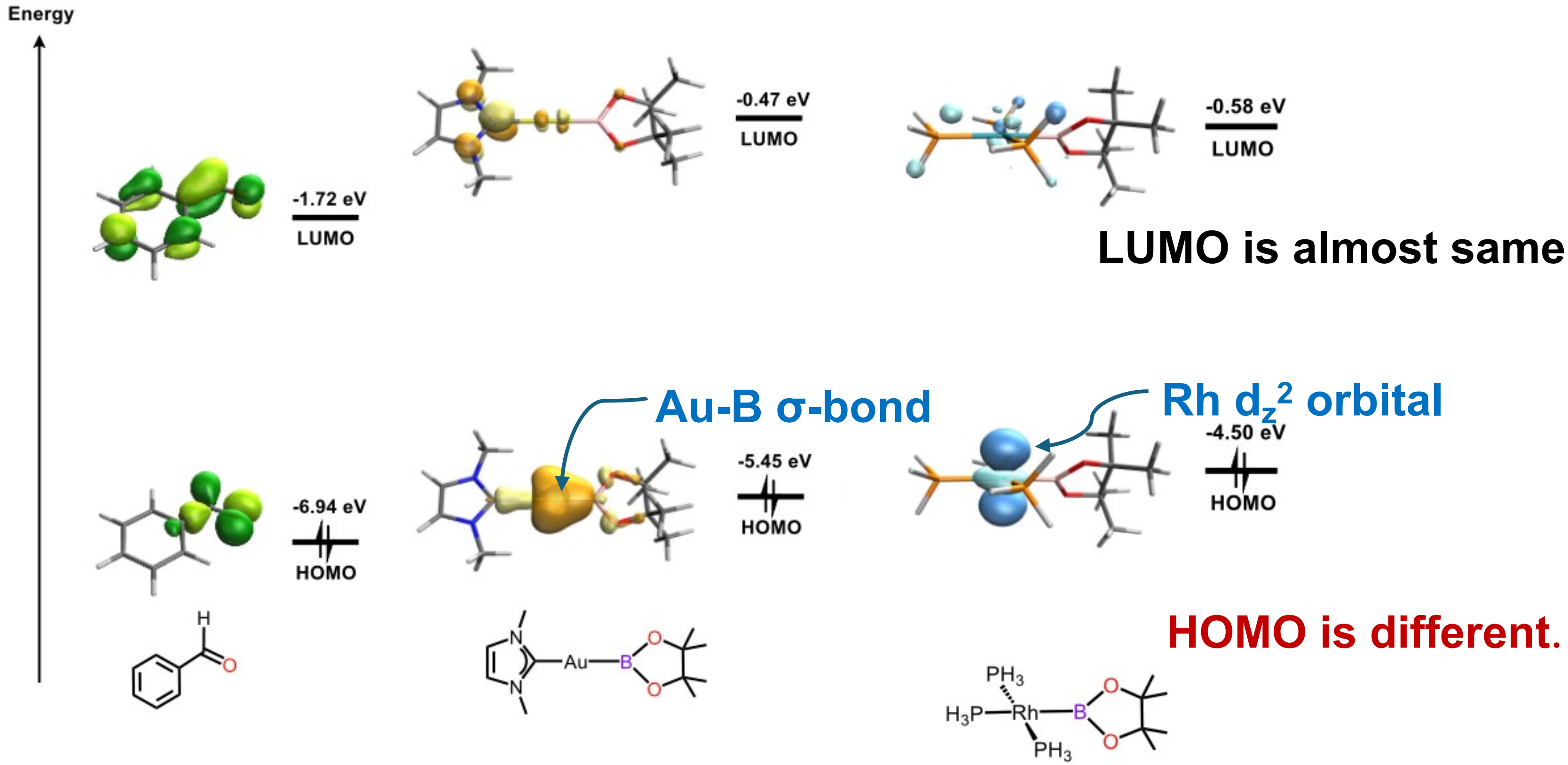
$(PH_3)_3$Rh-Bpin



Transition metal affect electrophilicity of boryl.

Z. Lin, *et al. ACS Catal.* **2021**, *11*, 5061.

FMO calculation



Have nucleophilicity of d orbital in transition metal depending on transition metals

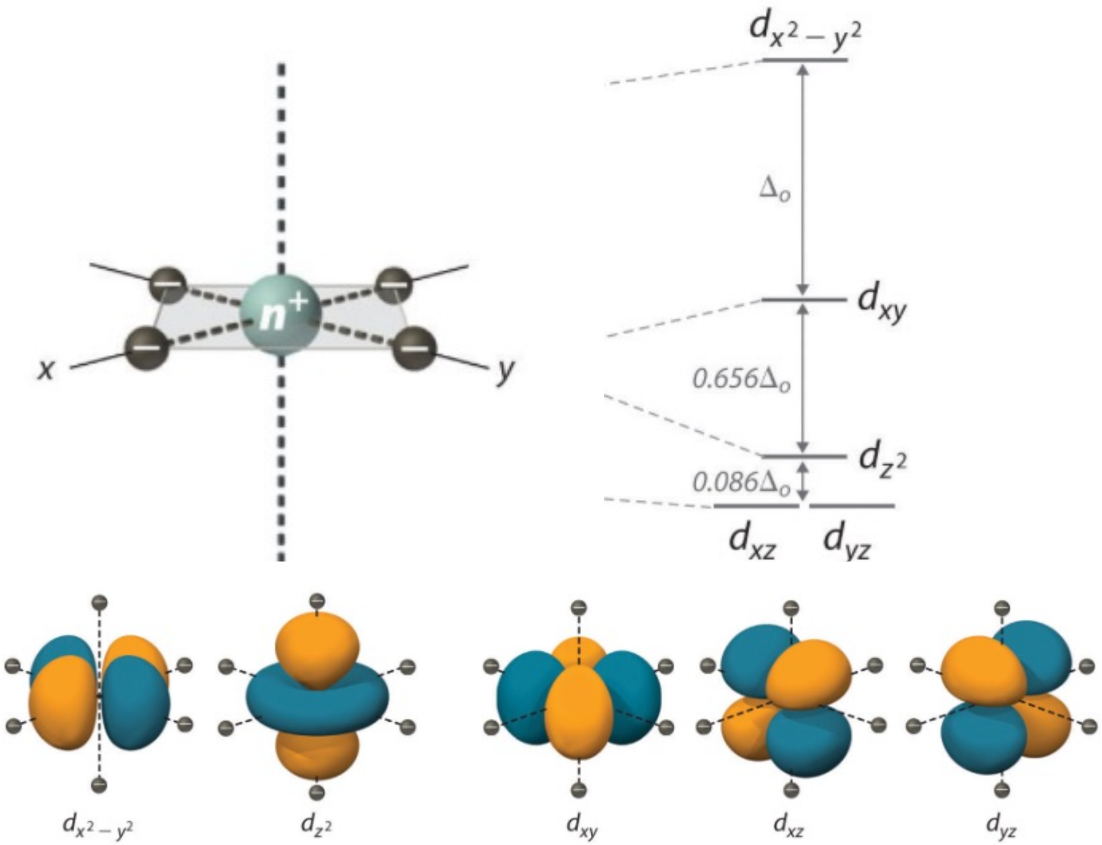
Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

8 d electrons metal complex

Pt(Ⅱ), Pd(Ⅱ), Ir(Ⅰ) , Rh(Ⅰ)

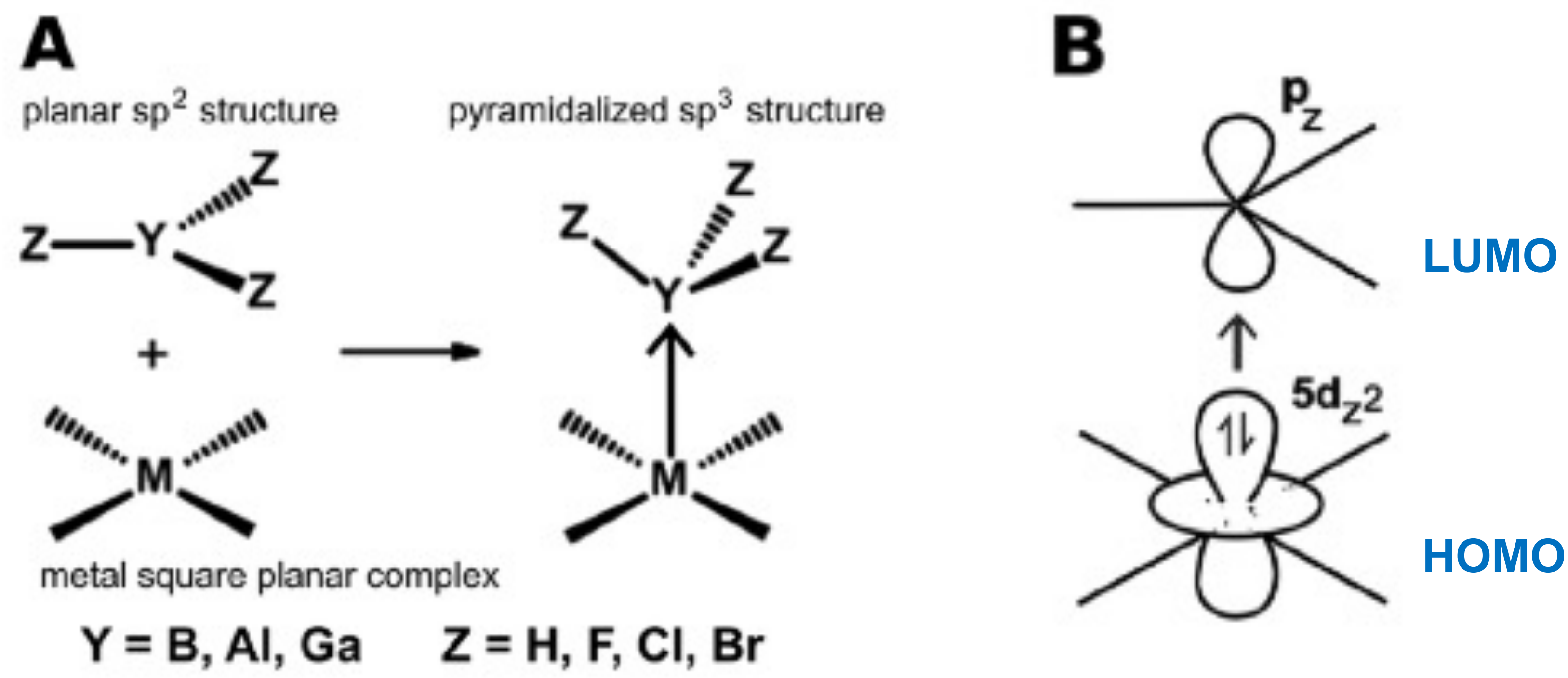
(Tetracoordination complex of 8 d electrons metal)

→Form square planar complex



https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s27-05-crystal-field-theory.html

8 d electrons metal complex

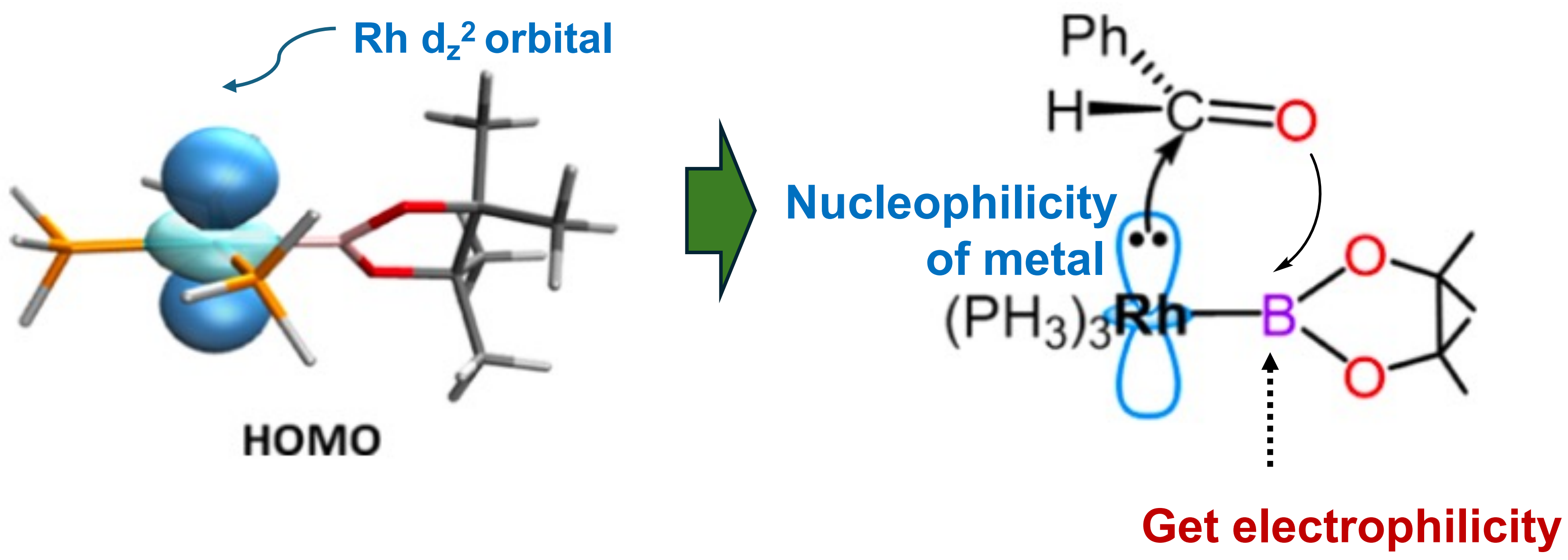


d_{z^2} orbital of square planar complex (Pt(Ⅱ), Ir(Ⅰ)) has nucleophilicity showed by natural atomic orbital analysis.

J. V. Burda, *et al. Inorg. Chem.* **2019**, *58,* 3616.

Nucleophilicity of transition metal

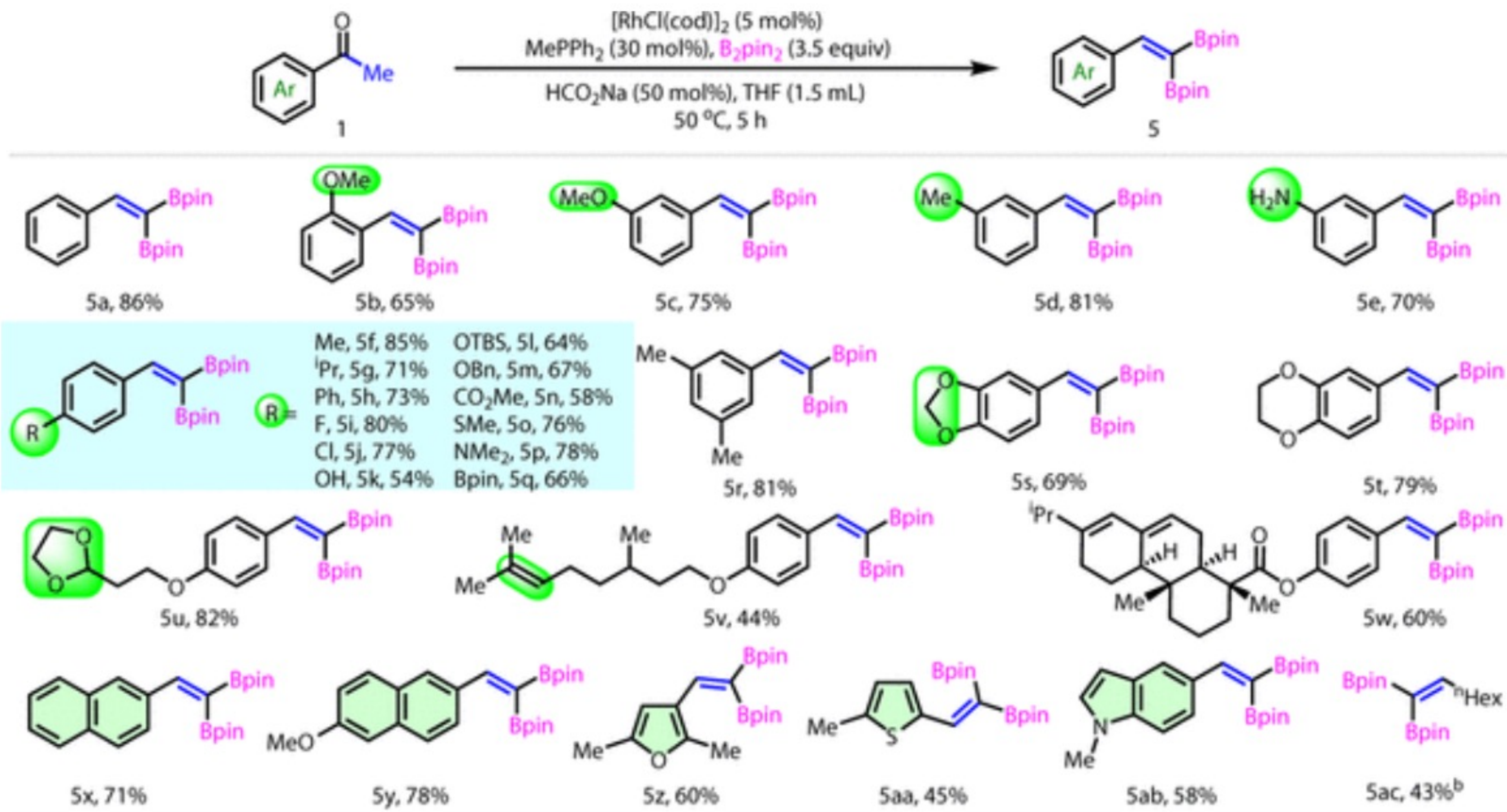
$(PH_3)_3$Rh-Bpin



Z. Lin, *et al. ACS Catal*. **2021**, *11*, 5061.

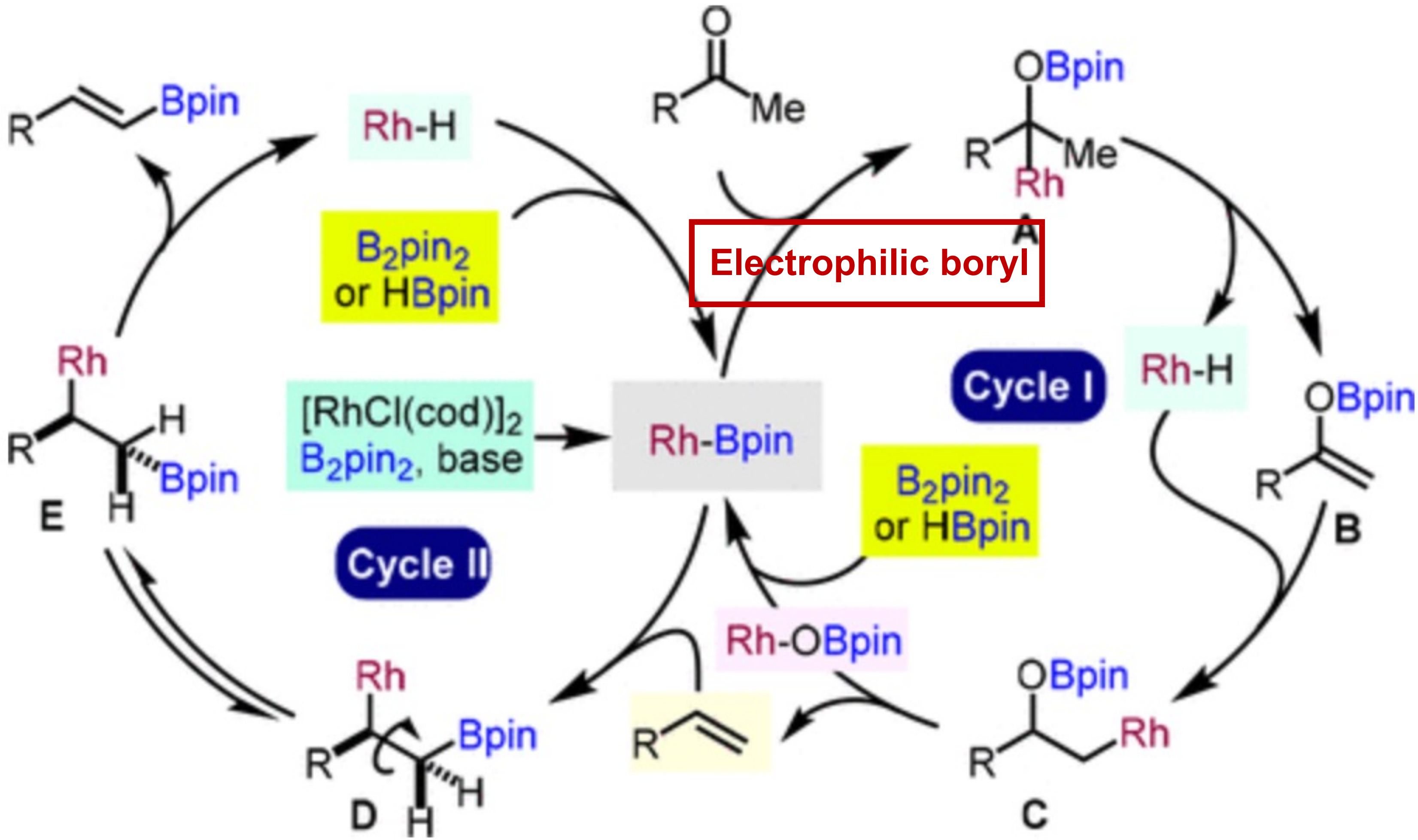
Rh boryl complex

Via Rh (Ⅰ) boryl complex **(8 d electrons)**



W. Zhao, *et al. J. Am. Chem. Soc.* **2020**, *142, 42*, 18118.

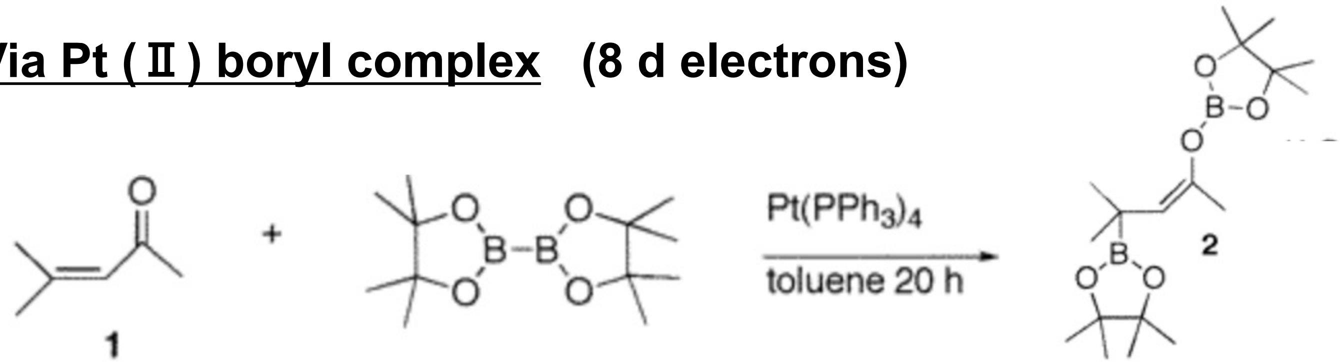
Rh boryl complex



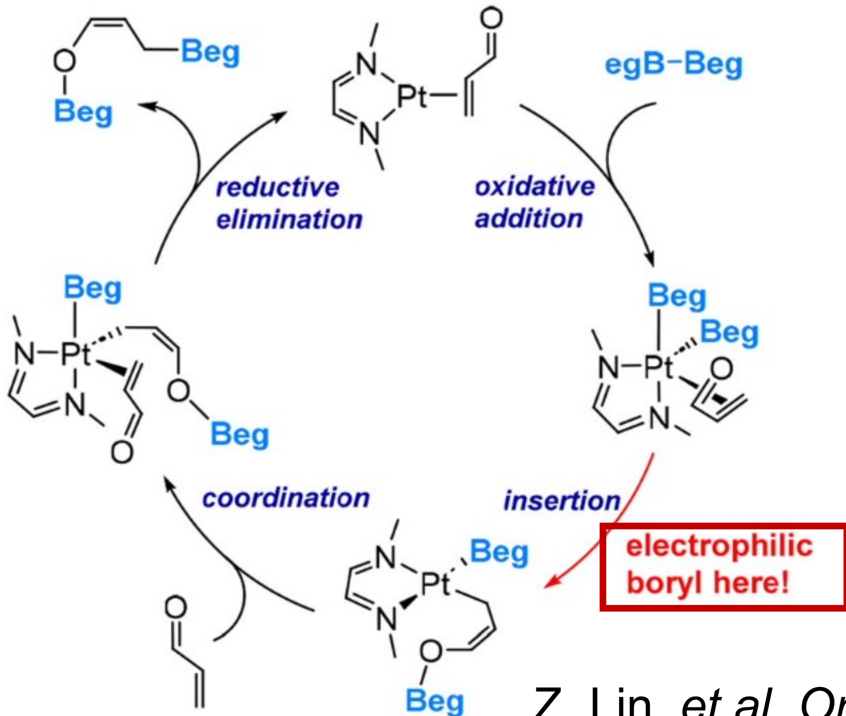
W. Zhao, *et al. J. Am. Chem. Soc.* **2020**, *142, 42*, 18118.

Pt boryl complex

<u>Via Pt (Ⅱ) boryl complex</u>   (8 d electrons)

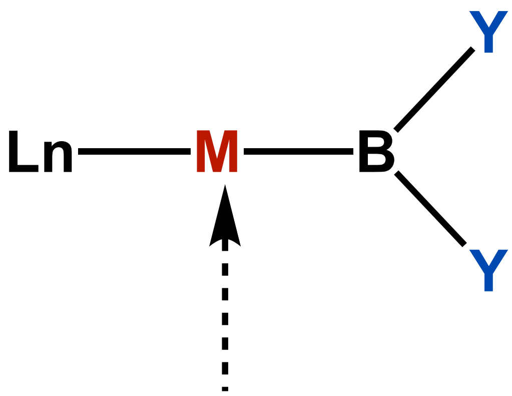


M. Srebnlik, *et al.* Organometallics. **2001**, *20, 18*, 3962.



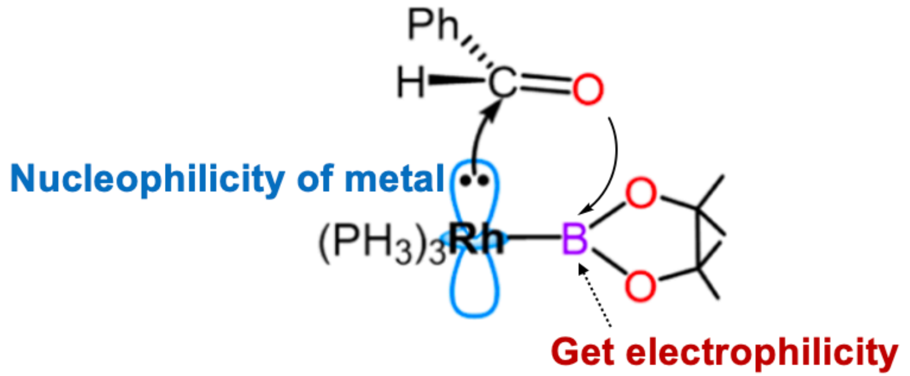
Z. Lin, *et al. Organometallics.* **2012**, *31*, 3410.

Short summary



③ d electrons

8 d electrons metal（square planar complex)

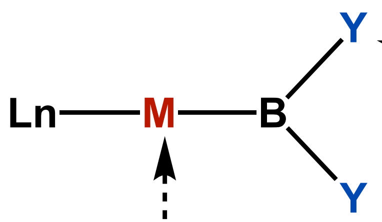


Z. Lin, *et al. ACS Catal.* **2021**, *11*, 5061.

Contents

Summary

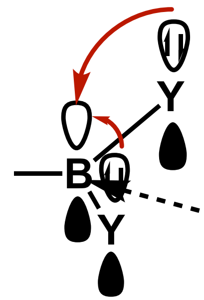
Reavtivity of metal boryl complex



① Neighboring atoms

Y= N, O, F

Push π electron



Stabilized
(Lose electrophilicity)

② Electronegativity

M<B (M: electropositive)

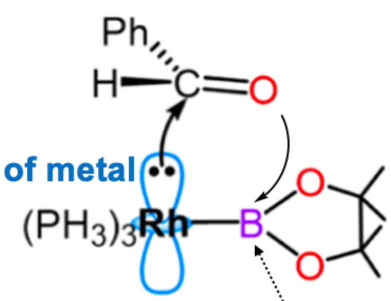
→B gets nucleophilicity

M>B (M: electronegative)

→B loses nucleophilicity

③ d electrons

8 d electrons metal (square planar complex)



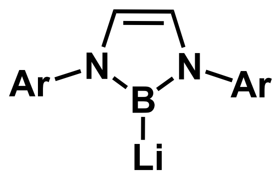
Get electrophilicity

Appendix

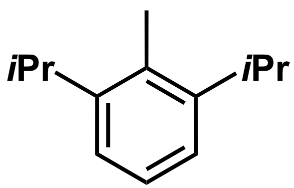
Nucleophilic boryl

Example of nucleophilic boryl

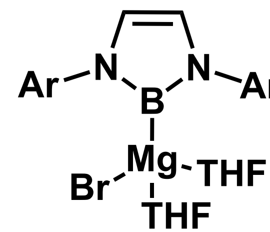
Boryl lithium (K. Nozaki, 2006)



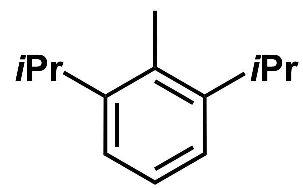
Ar =



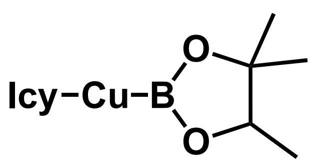
Boryl magnesium (K. Nozaki, 2007)



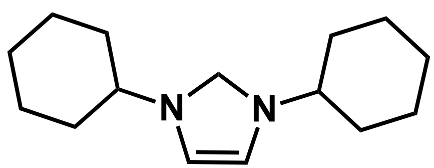
Ar =



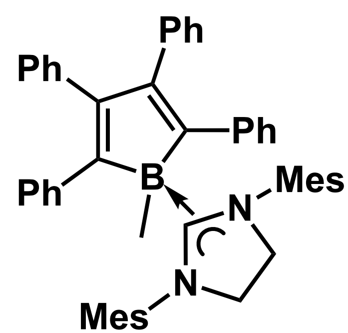
Boryl copper (J. P. Sadighi, 2005)



ICy=

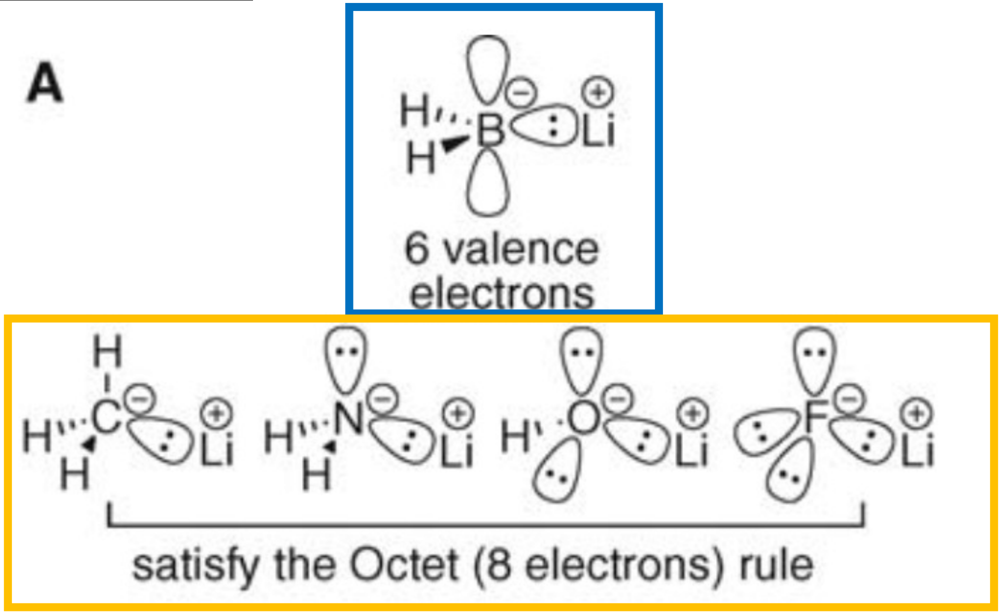


Carben stabulized π-boryl anion (H. Braunschweig, 2010)



Difficulty of boryl anion

Difficulty ①: <u>6e⁻ structure</u>



Difficulty ②: <u>Low electronegativity</u>

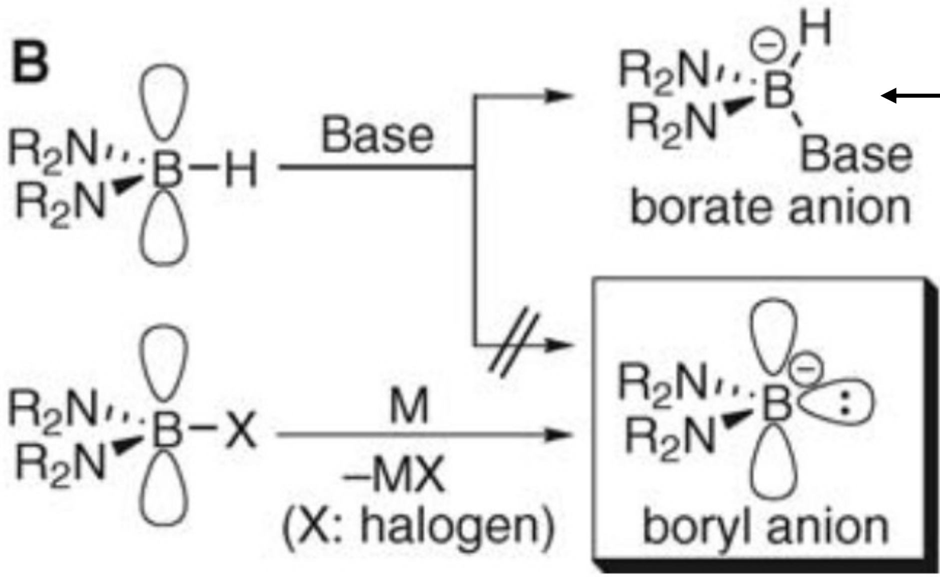
→Lower stability for boryl anions

B: 2.04 C: 2.55 N: 3.04 O: 3.44 F: 3.98

M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

Difficulty of boryl anion

Difficulty ③: <u>Synthesis (Can't use base)</u>



Satisfy the octet rule

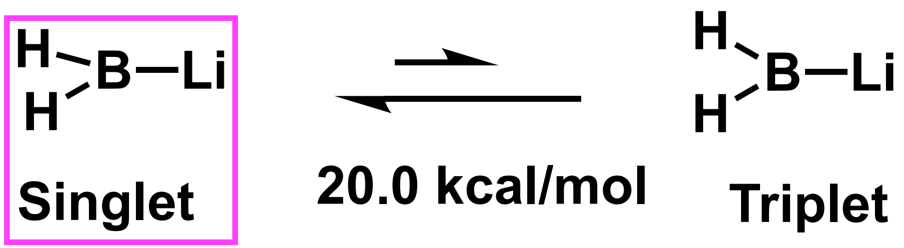
Reduction of halogen borane

M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

Design for boryl lithium

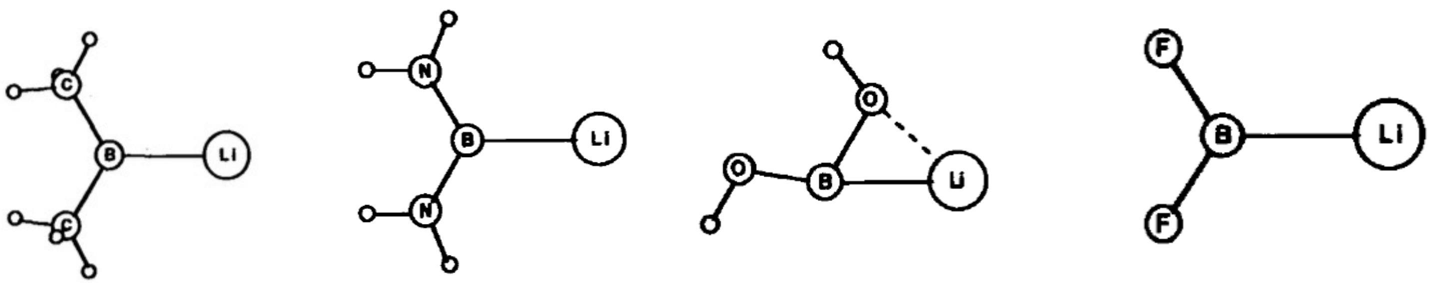
Design ①

Boryl lithium has a singlet grand state.



Design ②

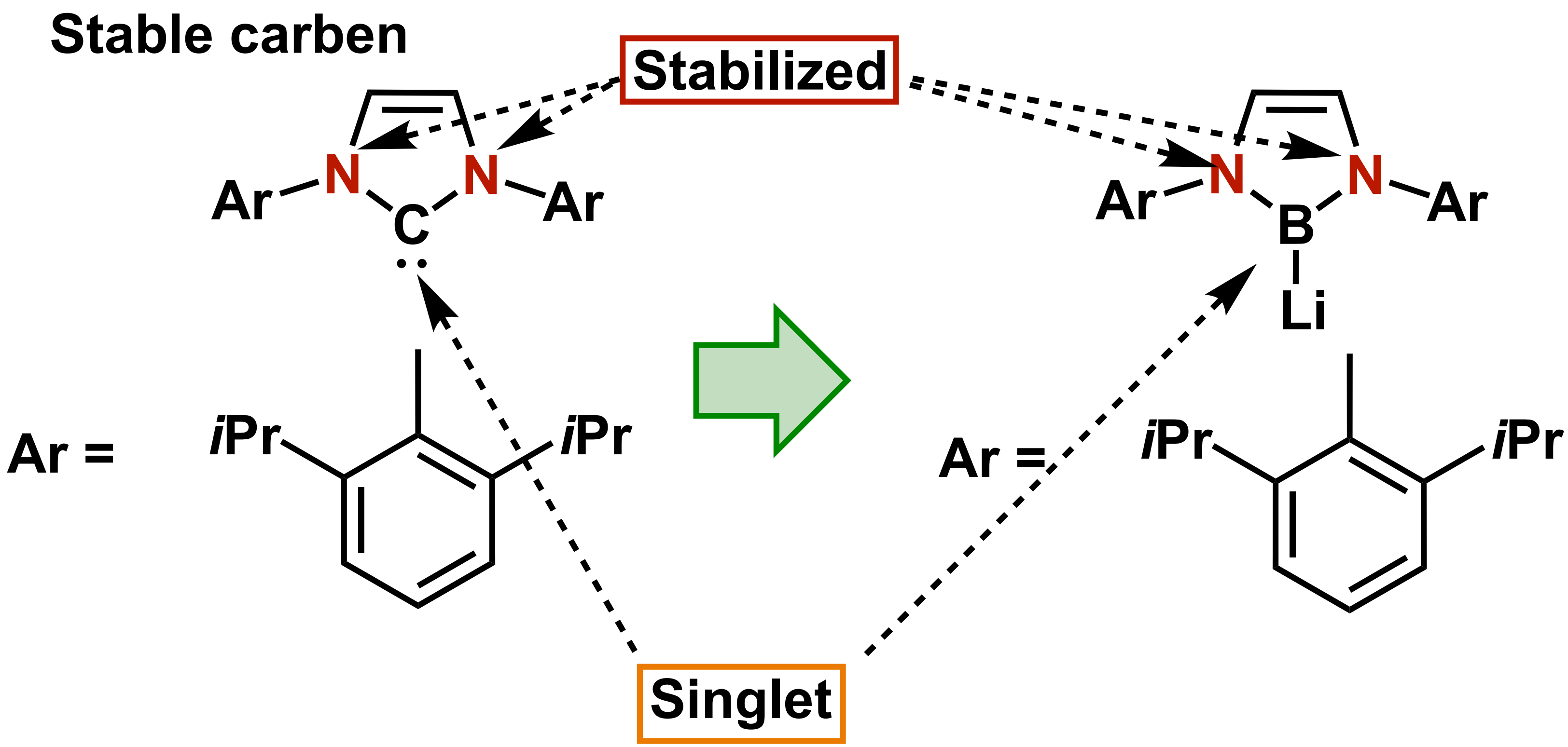
Boryl lithium is more stabilized by N than O, F.



NBO charges Y	**-0.99**	**-1.20**	**-1.00**	**-0.61**
NBO charges B	**0.19**	**0.36**	**0.50**	**0.58**
Boron p^z occ	**—**	**0.30**	**0.19**	**0.18**

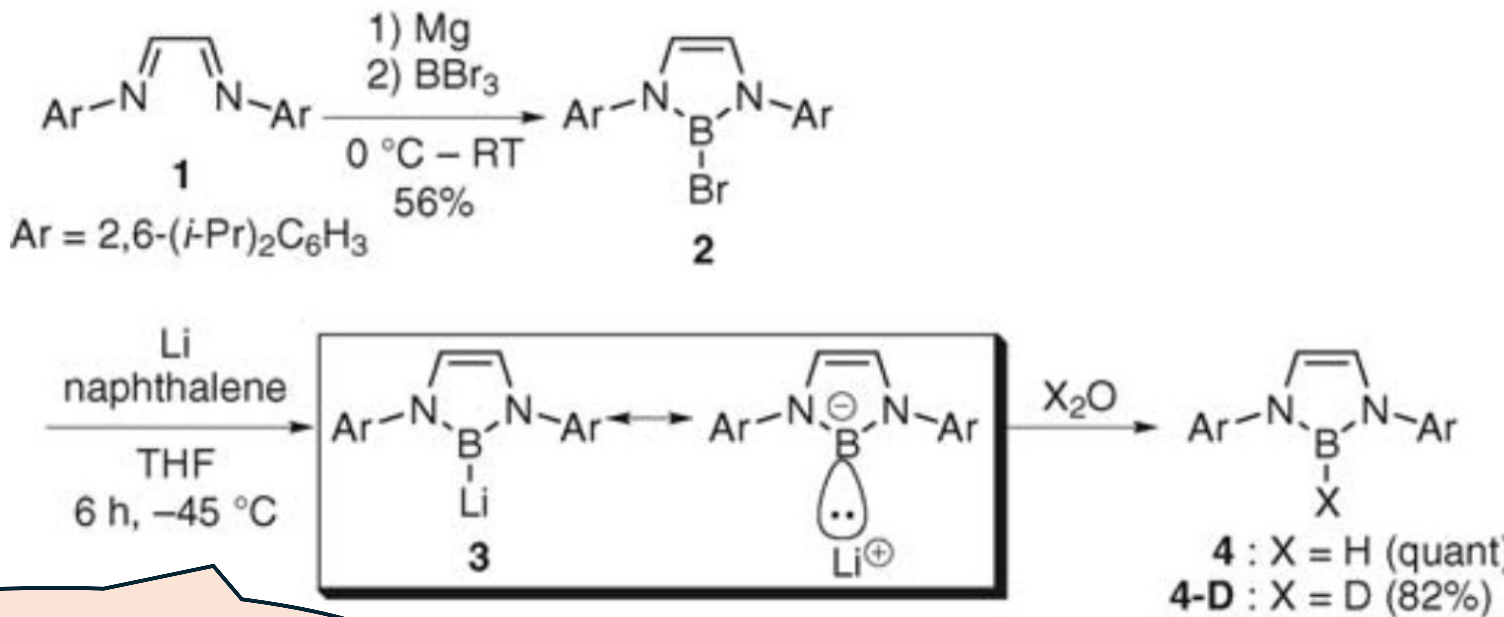
R. Schleyer, *Inorg. Chem.* **1995**, *34*, 607.

Design for boryl lithium



M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

Synthesis of boryl lithium



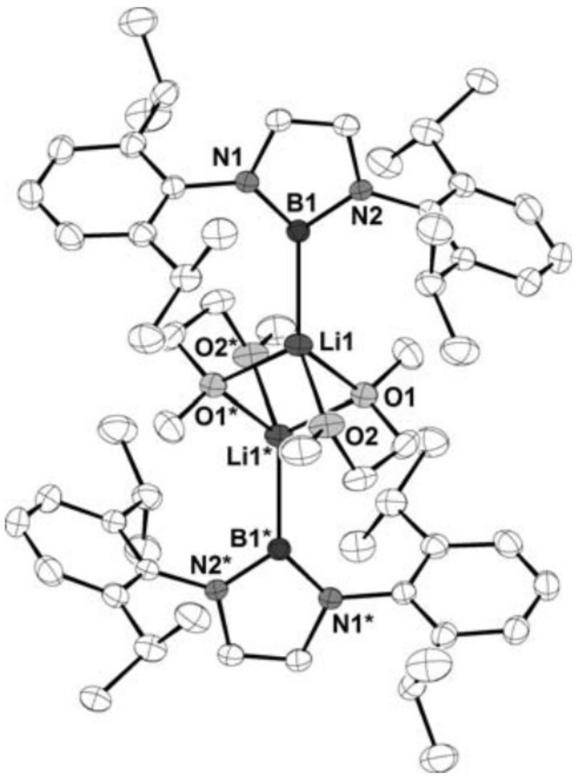
Reduction of halogen borane

M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

X-ray crystallography

Crystal structure of the boryl lithium

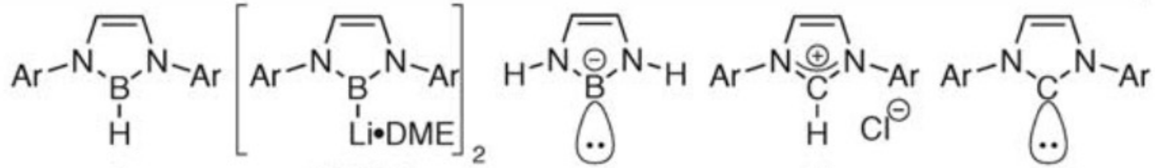
with an included DME(1,2-dimethoxyethane) molecule.



∠ N1-B1-Li1 + ∠ N2-B1-Li1
= 359.2°
→ sp² character of boron center of 3-DME

M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.

X-ray crystallography



compounds	4	3-DME	6	8	5
B(or C)-N (Å)	1.418(3) 1.423(3)	1.465(4) 1.467(4)	1.475	1.341 1.338	1.364 1.369
N-B(or C)-N (°)	105.25(16)	99.2(2)	97.72	107.6	101.4
reference	this work	this work	23	34	34

B-N length and N-B-N angle

- **3-DME is closer to 6 than 4.**
- **Structural change from 4 to 3-DME is similar to that from 8 to 5.**

→ **Anionic character of boron center of 3-DME**

Reference

23: N. Metzler-Nolte, *New J. Chem*. **1998**, *22*, 793.

34: R. Schmutzler, *et al,* Tetrahedron. **1999**, *55*, 14523.

M. Yamashita, K. Nozaki, *et al.* Science. **2006**, *314*, 5796.