

# **Chemistry of Boryl Anion -focusing on M. Yamashita's work-**

**2014/12/13 (Sat.)**

**Literature Seminar**

**Yuya Morita (D1)**

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3. Other Borylmetals
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# 1. Introduction

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# Boron Chemistry

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Lewis acidic boron-mediated chemistry

Hydroboration chemistry

**Boron  
Chemistry**

Boron-enolate chemistry

Suzuki-Miyaura cross-coupling chemistry

The boron atom is **electrophilic** in all cases shown above.

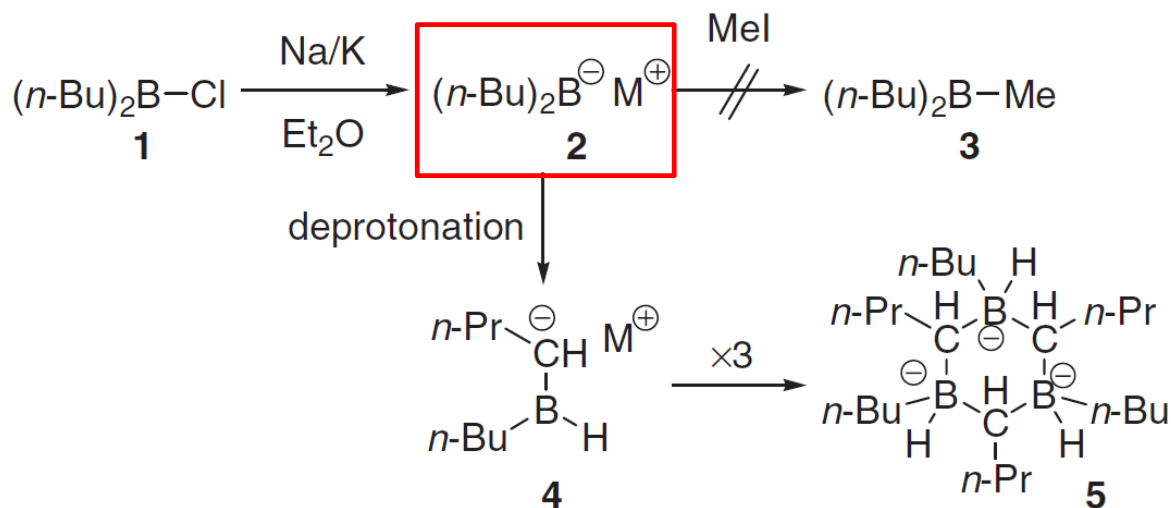


A boron-centered **nucleophile** has been a challenging target.

# Early Attempts to Prepare the Boryl Anion

Three examples had been reported asserting the existence of alkali metal salts of anionic organoboron compounds as reactive intermediates.

## 1) Reduction of dialkylchloroborane

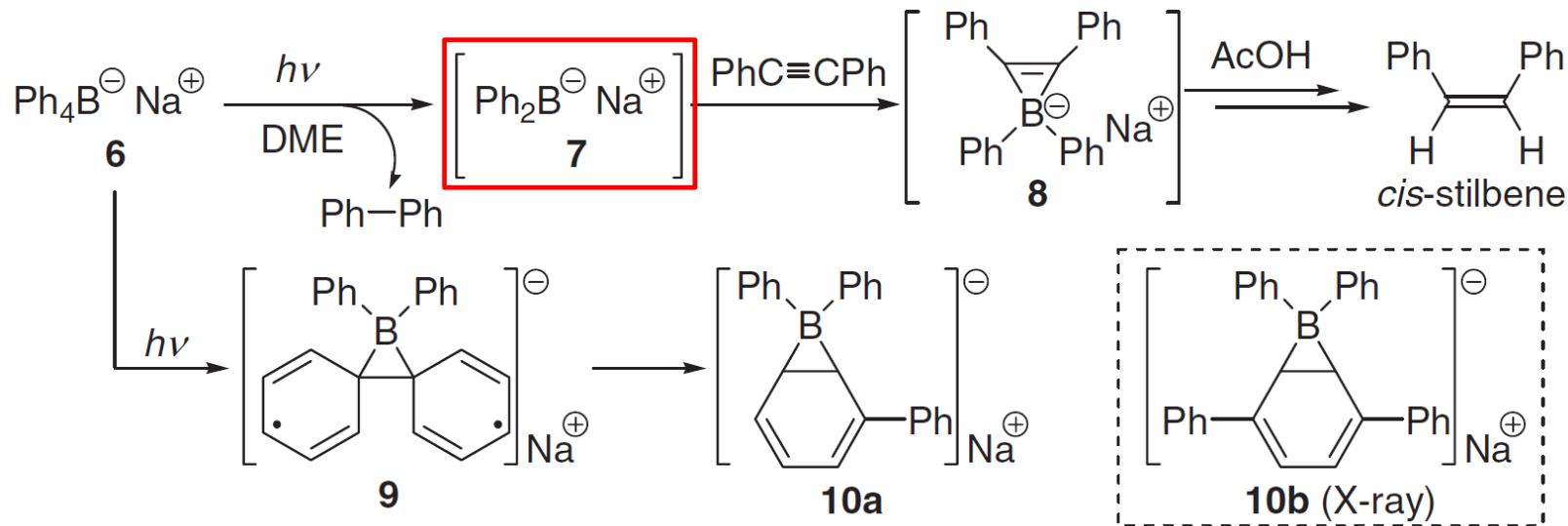


R. W. Auten, C. A. Kraus,  
*J. Am. Chem. Soc.* **1952**, *74*, 3398.

K. Smith, K. Swaminathan,  
*J. Chem. Soc., Dalton Trans.* **1976**, 2297.

# Early Attempts to Prepare the Boryl Anion

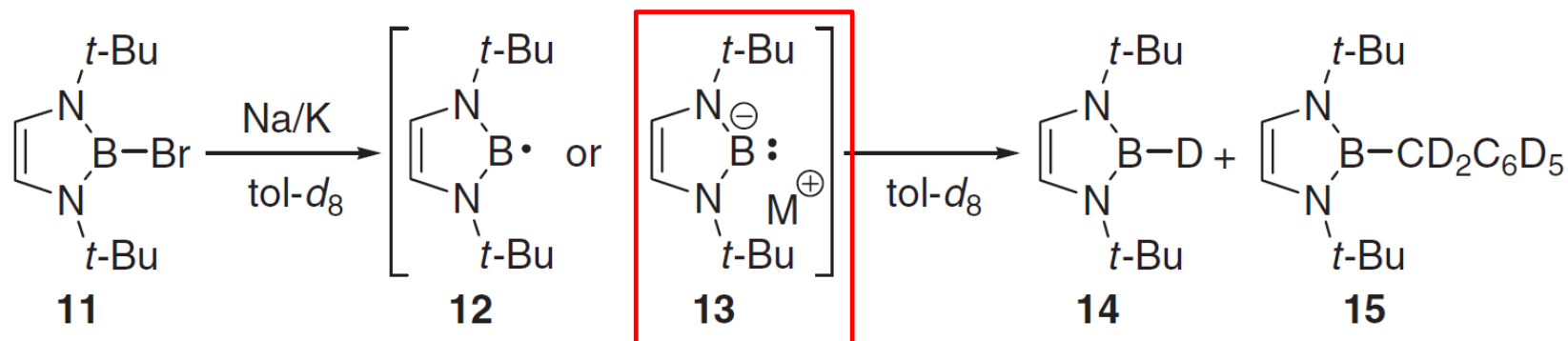
## 2) Photolysis of sodium tetraphenylborate



J. J. Eisch, *et al. J. Org. Chem.* **1989**, *54*, 1627.

G. B. Schuster, *et al. J. Am. Chem. Soc.* **1991**, *113*, 2149.

## 3) Reduction of bromoborane

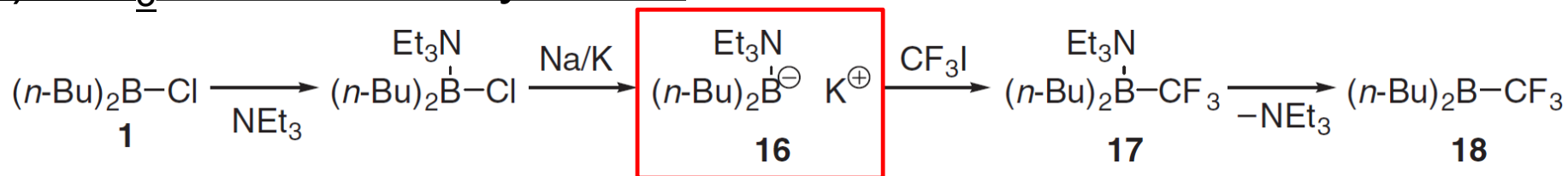


L. Weber, *et al. J. Chem. Soc., Dalton Trans.* **2001**, 3459.

# Base-Stabilized Boryl Anion

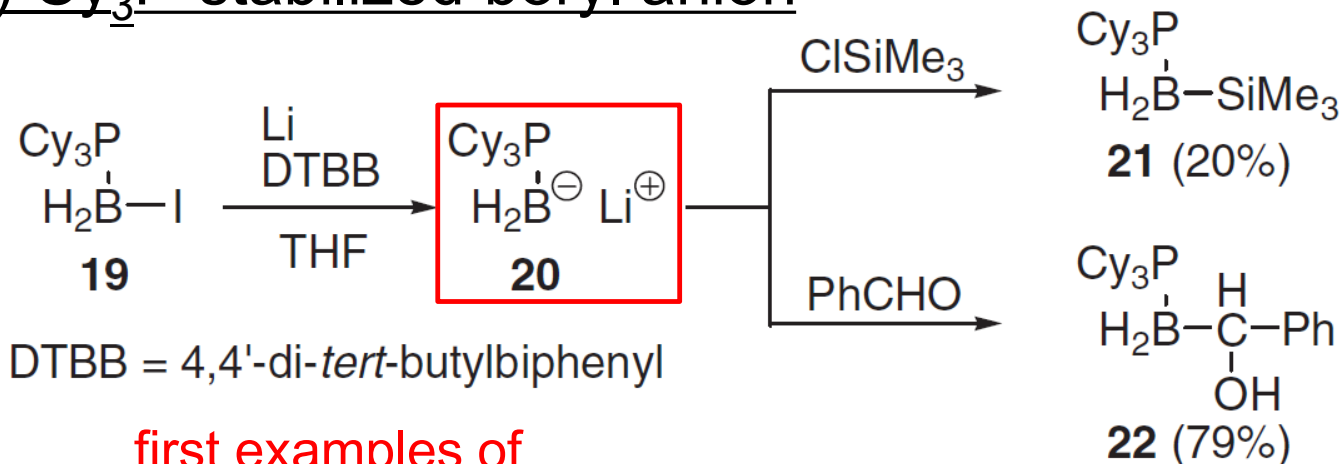
Filling the vacant p-orbital of boron with Lewis base makes the boron atom  $sp^3$ , similar to carbon, to provide a good strategy for preparation of nucleophilic boryl anions as carbanion can be made from haloalkanes.

## 1) $NEt_3$ -stabilized boryl anion



T. D. Parsons, *et al. J. Am. Chem. Soc.* 1967, 89, 3446.

## 2) $Cy_3P$ -stabilized boryl anion



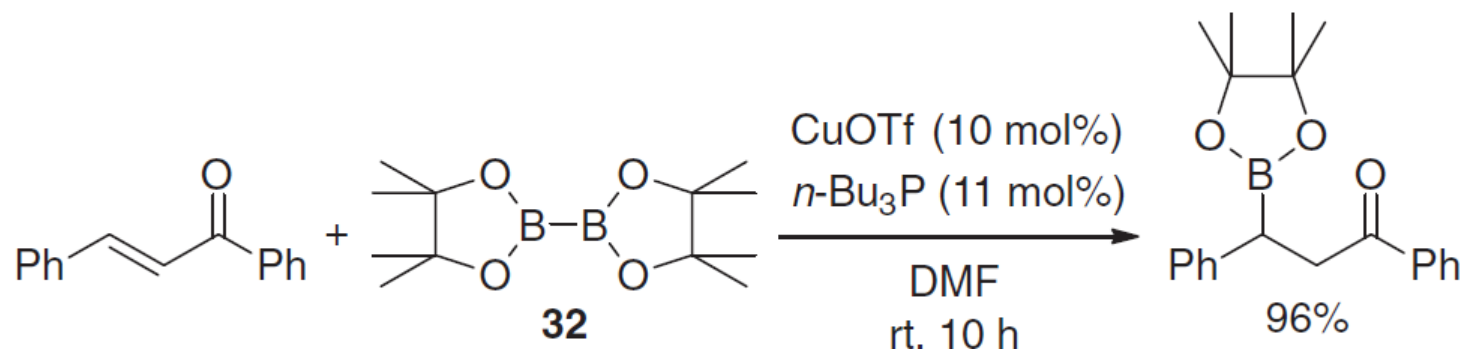
first examples of  
nucleophilic boron reagent

H. Schmidbaur, *et al. J. Organomet. Chem.* 1993, 462, 107.  
T. Iwamoto, T. Hikosaka, *J. Org. Chem.* 1994, 59, 6753.

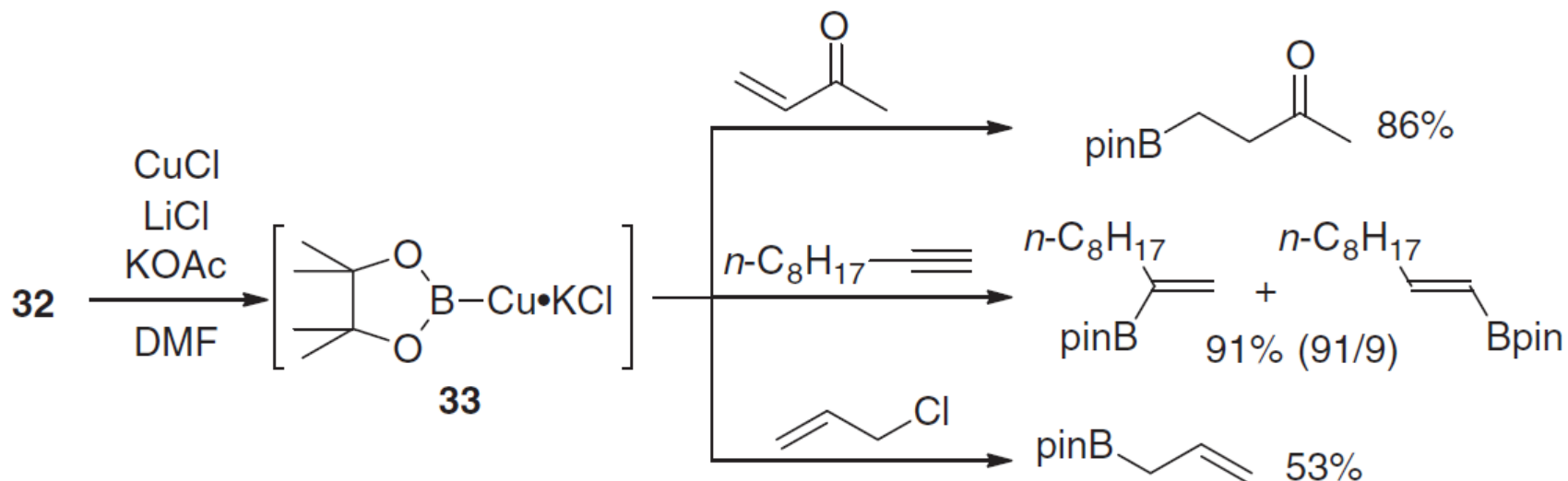
# Borylcopper

## 1) Borylcopper intermediate generated from diboron

The catalyst system Cu(I)/diborane(4) could mediate nucleophilic borylation.



A. Hosomi, *et al. Tetrahedron Lett.* 2000, 41, 6821.



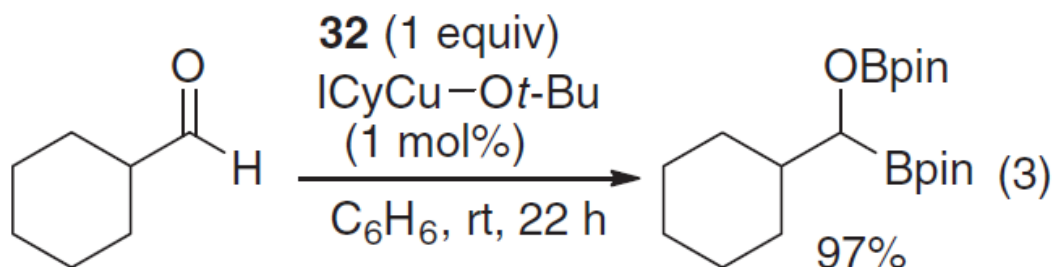
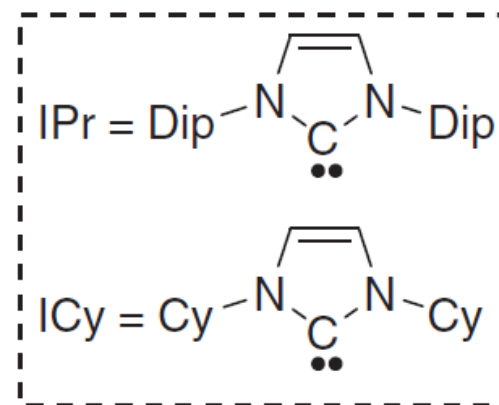
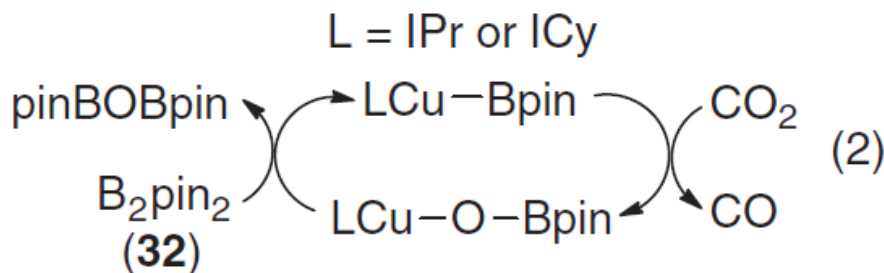
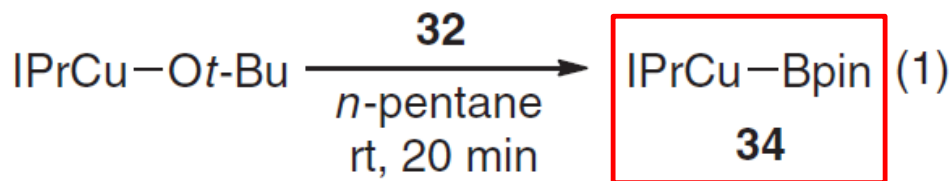
N. Miyaura, *et al. Chem. Lett.* 2000, 982.  
*J. Organomet. Chem.* 2001, 625, 47.



# Borylcopper

## 2) Isolated borylcopper species

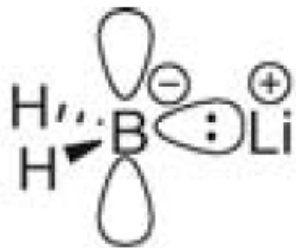
Borylcopper possessing NHC ligand was isolated.



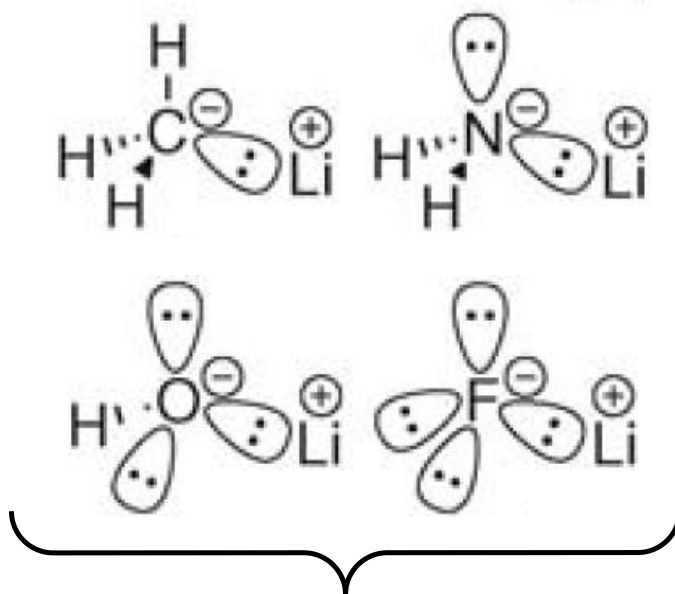
Borylcopper have opened a new area of organoboron chemistry. However the application of the boron nucleophile was still limited.

# Lithium Salts of Second-Row $p$ -Block Elements

For most of the  $p$ -block elements in the second row of the periodic table, anions can be prepared as lithium salts, such as LiF, LiOH, LiNH<sub>2</sub> and H<sub>3</sub>CLi. However, **there had been no direct observations of the lithium salt of anionic boron atom, boryllithium.**



6 valence electrons

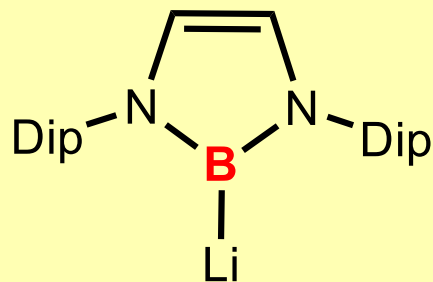


satisfy the Octet (8 electrons) rule

Pauling's electronegativity

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

# Isolated Nucleophilic Boryl Anions



M. Yamashita, K. Nozaki, *et al.*  
*Science* **2006**, 314, 113.



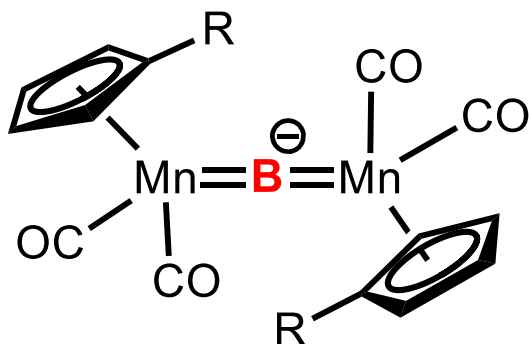
Kyoko Nozaki



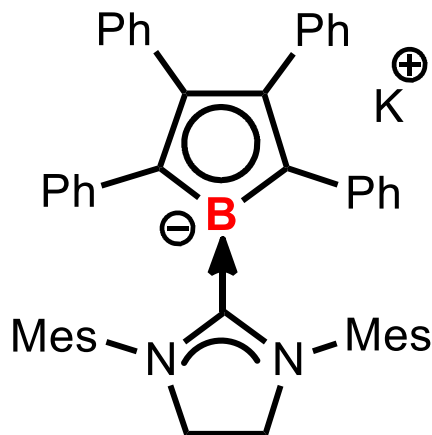
Makoto Yamashita

Makoto Yamashita, born in 1974 in Hiroshima, received his Ph.D. from Hiroshima University in 2002 under the guidance of Professor Yohsuke Yamamoto and Professor Kin-ya Akiba. He spent two years as a JSPS research fellow under the supervision of Professor John F. Hartwig at Yale University and Professor Takayuki Kawashima at the University of Tokyo. He started his academic career appointment as a research associate, an assistant professor, and a lecturer with Professor Kyoko Nozaki at the University of Tokyo in 2004. Then he moved to Chuo University in April 2011 to manage his own research group as an associate professor. His current research interests are organometallic chemistry, molecular catalysts for petrochemistry, and main group chemistry. He has been awarded the Inoue Research Award for Young Scientist (2005), the Chemical Society of Japan Award for Young Chemists (2008), The Young Scientists' Prize from the Minister of Education, Culture, Sports, Science and Technology (2009), and Banyu Chemist Award (2010).

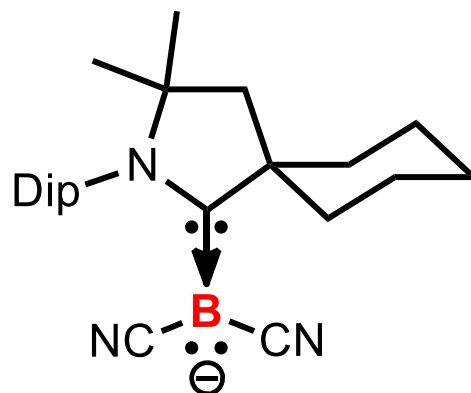
# Other Isolated Nucleophilic Boryl Anions



H. Braunschweig, *et al.*  
*Angew. Chem. Int. Ed.* **2008**, 47, 5650.



H. Braunschweig, *et al.*  
*Angew. Chem. Int. Ed.* **2010**, 49, 2041.

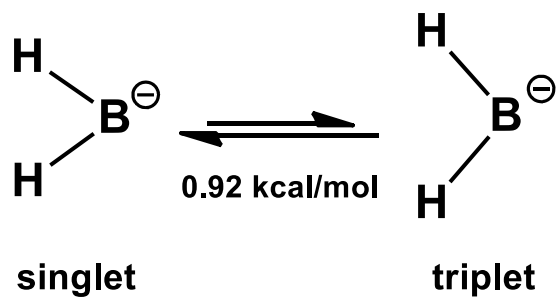
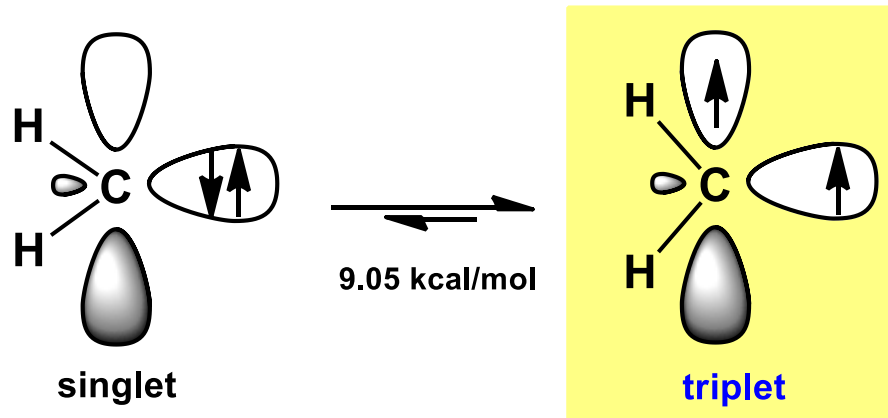


G. Bertrand, *et al.*  
*Angew. Chem. Int. Ed.* **2013**, 52, 7590.

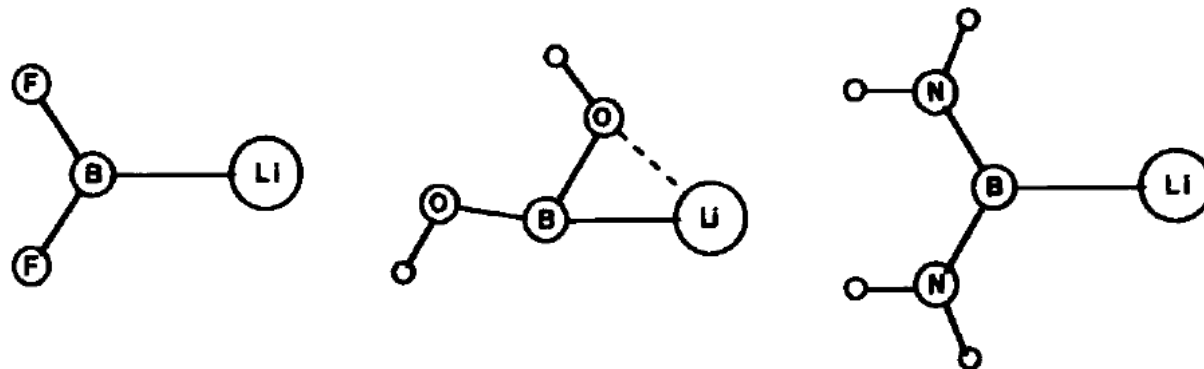
- 
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# What is the Ground State of Boryllithium?

The  $\text{H}_2\text{B}^-$  anion is isoelectronic with  $\text{CH}_2^-$ , which has a triplet ground state. What is the ground state of  $\text{H}_2\text{B}^-$ ?

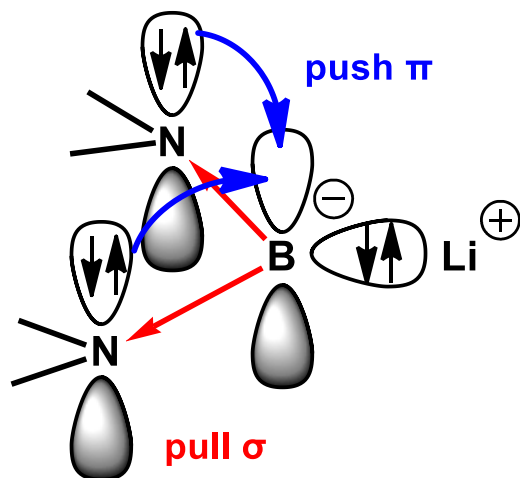


# Rational Design for Boryllithium



NBO charges $X^a$	-0.61	-1.13, -1.00	-1.20
boron $p_z$ occ <sup>b</sup>	0.18	0.19	0.30

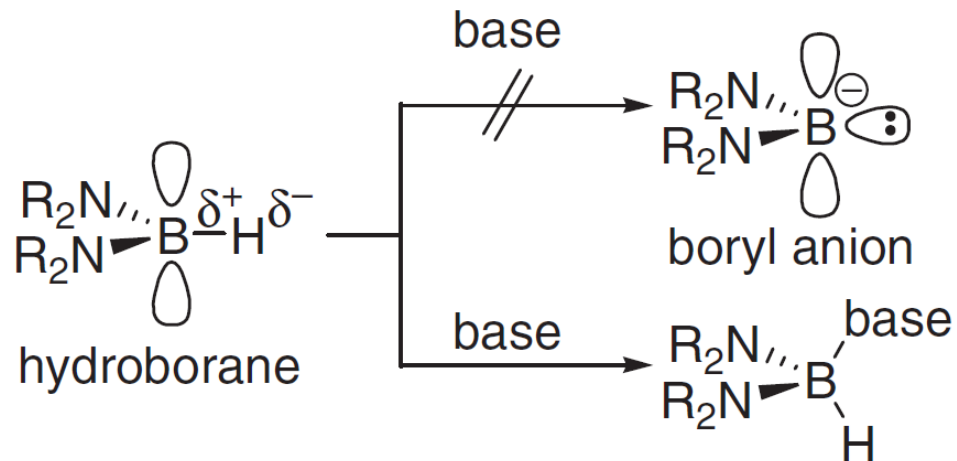
<sup>a</sup>X = central atom of substituent. <sup>b</sup>Occupancy of the boron  $p_z$  orbital.



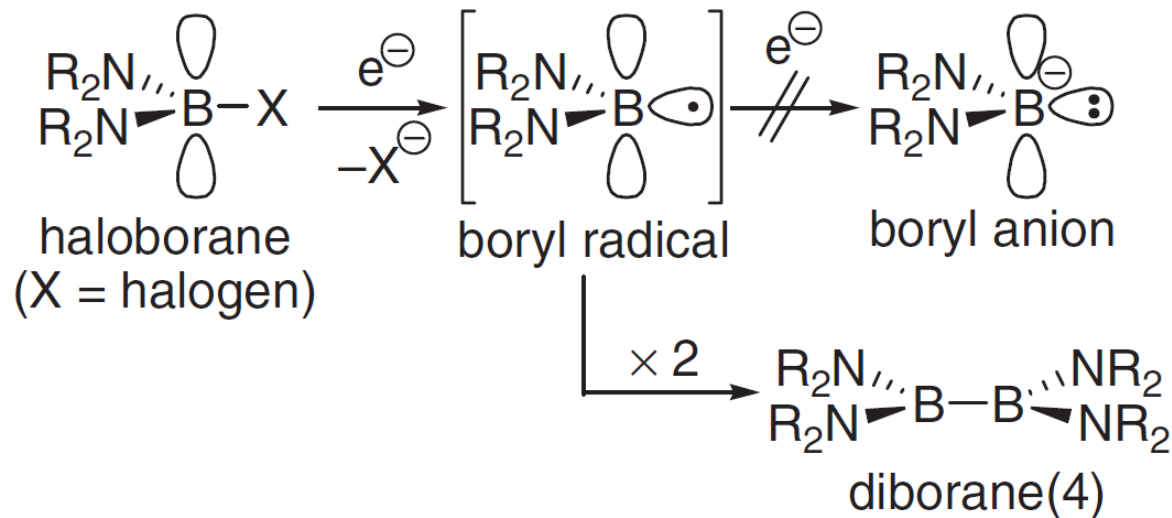
stabilization effect of nitrogen atoms through their  $\pi$ -donor and  $\sigma$ -acceptor characters

# Strategy for Generating a Boryllithium

## 1) Deprotonation of hydroborane with base



## 2) Reductive dehalogenation of haloborane with alkali metal

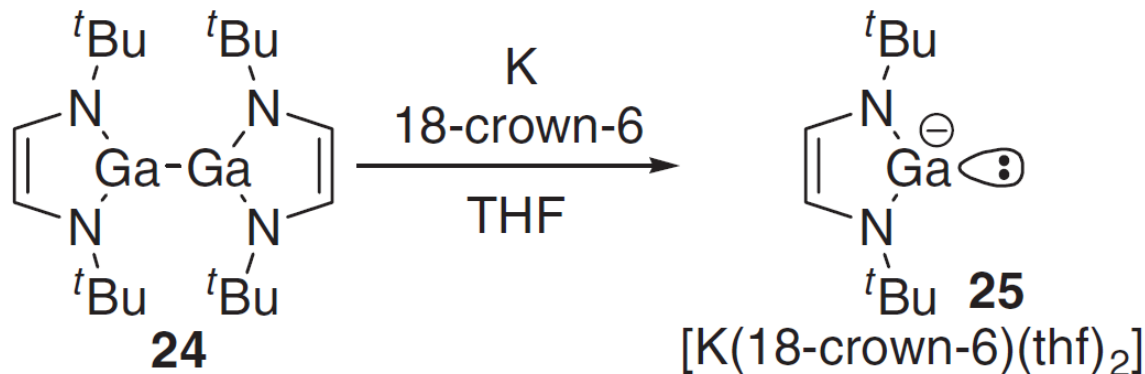




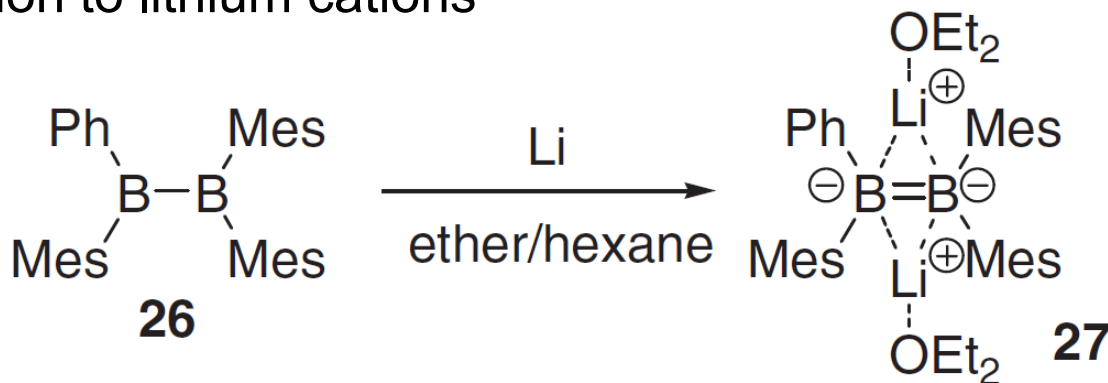
# Strategy for Generating a Boryllithium

## 3) Reductive cleavage of a B-B single bond of diborane(4)

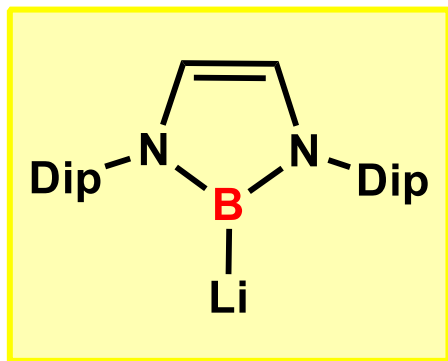
Synthesis of gallyl anion **25** was performed by reductive cleavage of the Ga-Ga single bond of digallane(4) **24**.



However the reduction of the diborane(4) **26** led to the formation of isolable diborane(4) dianion **27**, having a B=B double bond character with  $\pi$ -coordination to lithium cations



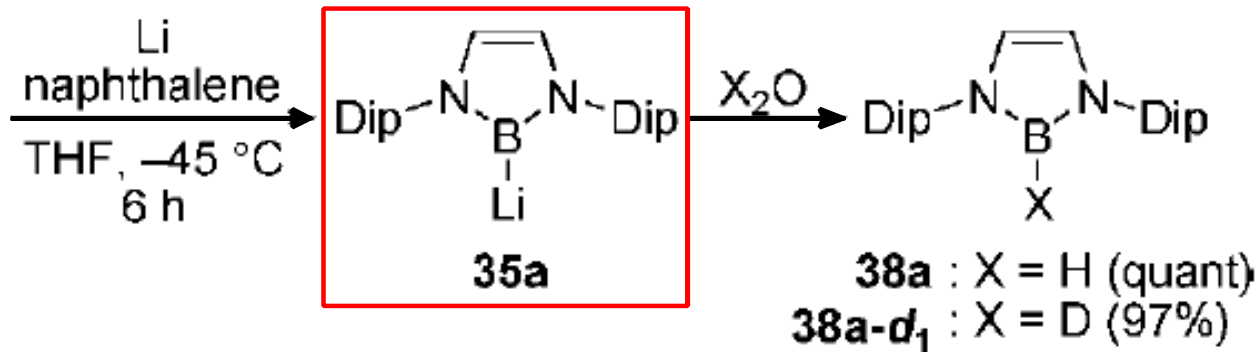
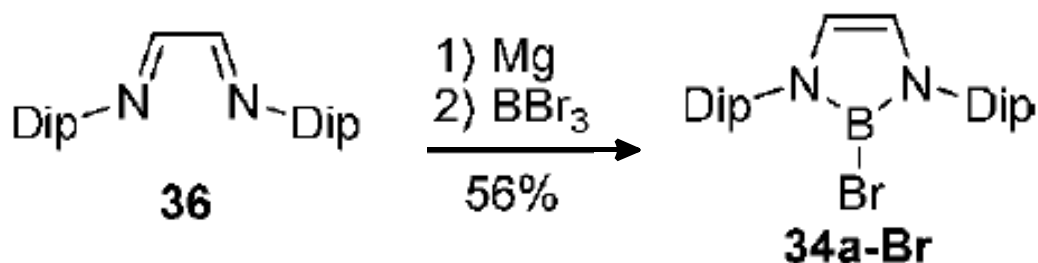
# Synthesis of Boryllithium



aromatic stabilization by the five-membered ring

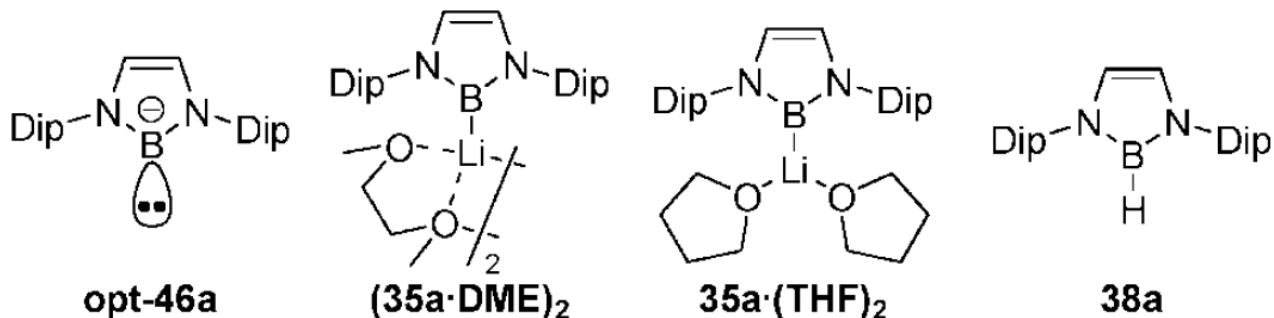
large substituents on the nitrogen atoms  
(prevent the dimer formation via boryl radical)

Dip = 2,6-(*i*Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

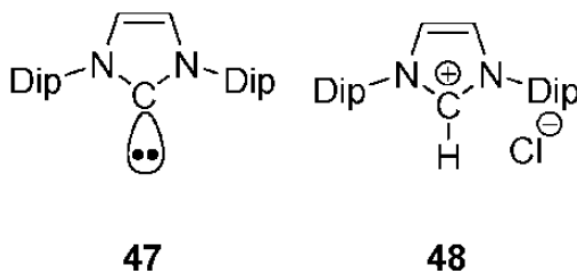
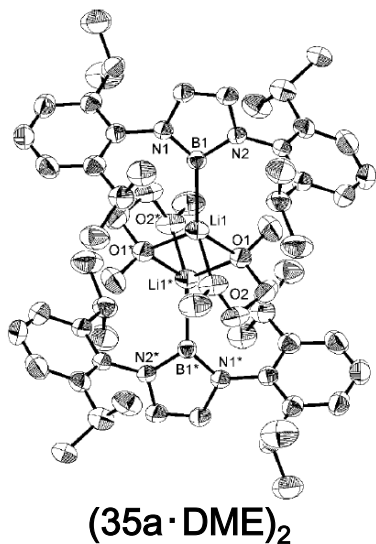


M. Yamashita, K. Nozaki, *et al. Science* 2006, 314, 113.  
*J. Am. Chem. Soc.* 2008, 130, 16069.

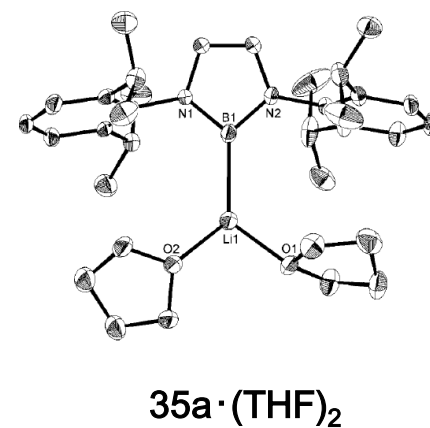
# Crystallographic Study: Solid State Structures



B-Li (Å)		2.291(6)	2.276(5)	
B-N (Å)	1.496	1.465(4) 1.467(4)	1.474(3) 1.480(4)	1.418(3) 1.423(3)
N-B-N (°)	97.79	99.2(2)	98.7(2)	105.25(16)



C-N (Å)	1.365(3) 1.369(3)	1.341(4) 1.339(4)
N-C-N (°)	101.4(2)	107.6(3)



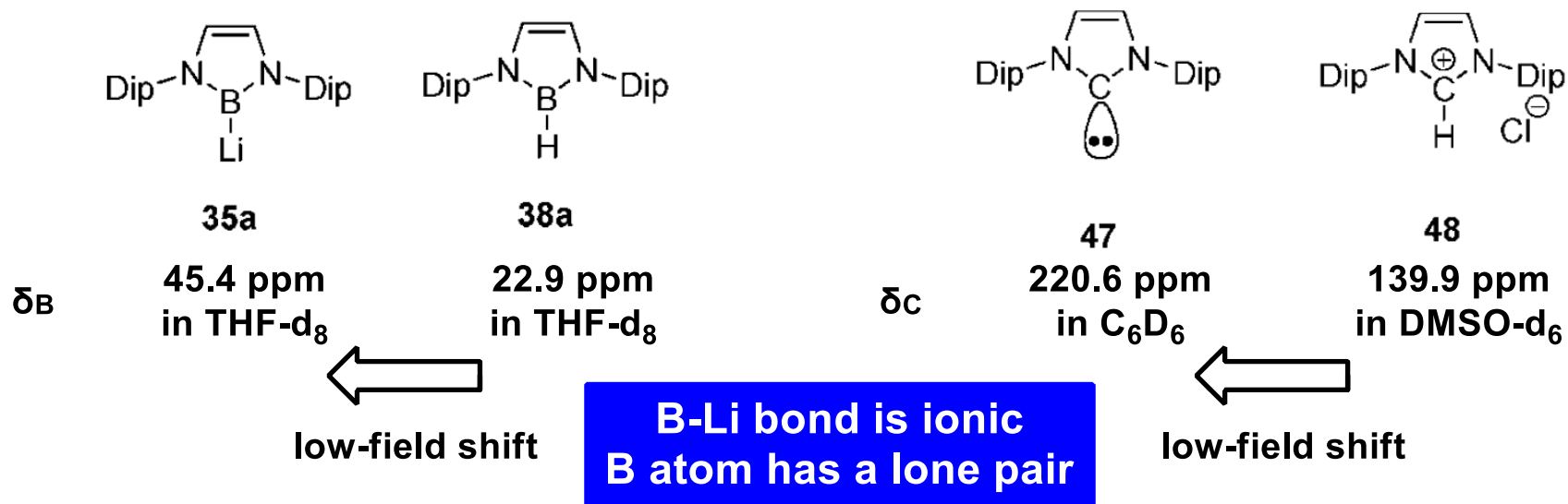
**B-Li bond is ionic**  
**B atom has a lone pair**

M. Yamashita, K. Nozaki, *et al. Science* 2006, 314, 113.  
*J. Am. Chem. Soc.* 2008, 130, 16069.

# NMR Spectroscopic Study: Structure in Solution

To clarify the solution structure of boryllithium, several spectroscopic studies were performed.

## 1) Comparison with carbene **47** and imidazolium salt **48**



## 2) $^7Li$ -NMR spectroscopic study

$35a \cdot (THF)_2$	LiCl
$\nu_{1/2} = 36$ Hz	$\nu_{1/2} = 1.2$ Hz

$\nu_{1/2}$  = half-width of the signal

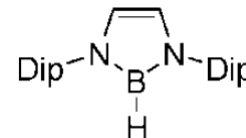
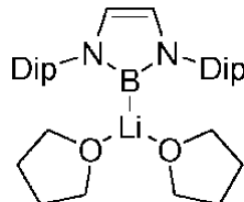
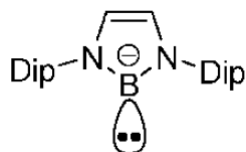
The large half-width may originate from the interaction of the Li atom with the quadrupolar B nucleus.

**B-Li bond remains in solution**

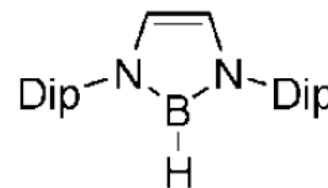
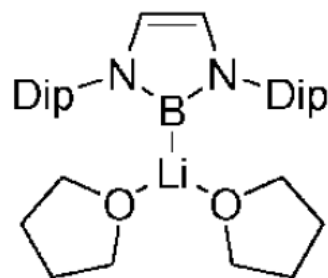
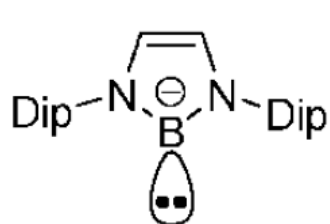
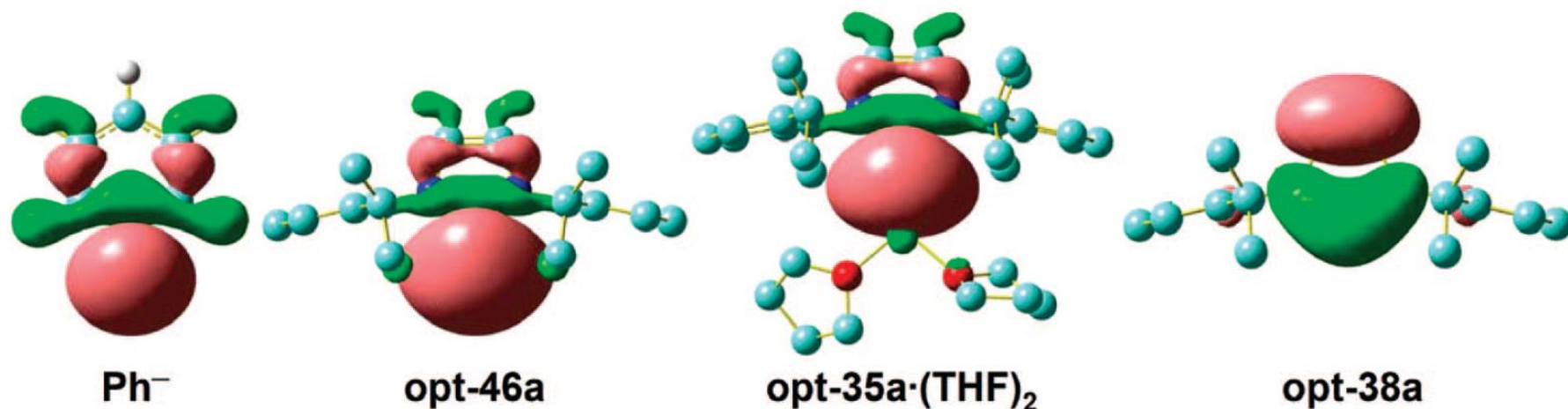
# DFT Study

**Table 2.** Structural Parameters (Å and deg), NPA Charges of B, Li, and N Atoms, and Calculated  $^{11}\text{B}$  NMR Chemical Shift (ppm) for Optimized Boryllithium and Related Compounds

	opt-46a	opt-35a	opt-35a•(THF) <sub>2</sub>	opt-35a•(THF) <sub>3</sub>	opt-38a
B–Li		2.159	2.268	2.363	
B–N	1.495	1.467	1.481	1.491	1.436
N–B–N	97.74	101.02	99.22	1.487	105.28
B	0.104	0.032	0.072	0.084	0.656
Li		0.769	0.755	0.768	
N	–0.770	–0.712	–0.728	–0.742	–0.663
$\delta_{\text{B}}$	51.3	36.1	41.4	–0.739	19.6



# DFT Study: Lone Pair Character in the HOMO Orbital



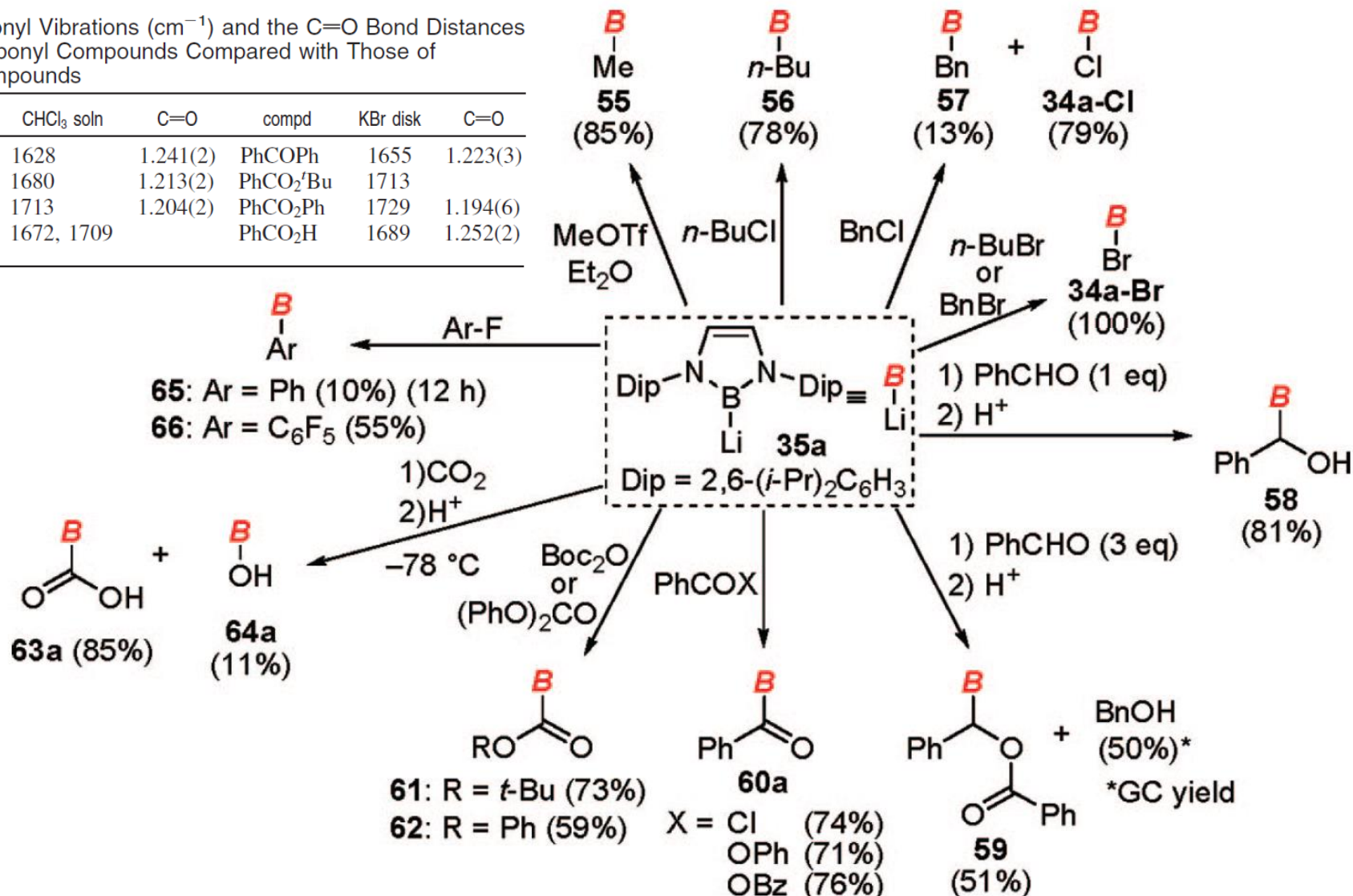
**B-Li bond is ionic**  
**B atom has a lone pair**

# Reactions of Boryllithium

## Reaction of boryllithium with various electrophiles

**Table 3.** Carbonyl Vibrations ( $\text{cm}^{-1}$ ) and the C=O Bond Distances ( $\text{\AA}$ ) of Borylcarbonyl Compounds Compared with Those of Reference Compounds

compd	KBr disk	$\text{CHCl}_3$ soln	C=O	compd	KBr disk	C=O
<b>60a</b>	1618	1628	1.241(2)	PhCOPh	1655	1.223(3)
<b>61</b>	1690	1680	1.213(2)	PhCO <sub>2</sub> <sup>t</sup> Bu	1713	
<b>62</b>	1719	1713	1.204(2)	PhCO <sub>2</sub> Ph	1729	1.194(6)
<b>63a</b>	1666	1672, 1709		PhCO <sub>2</sub> H	1689	1.252(2)

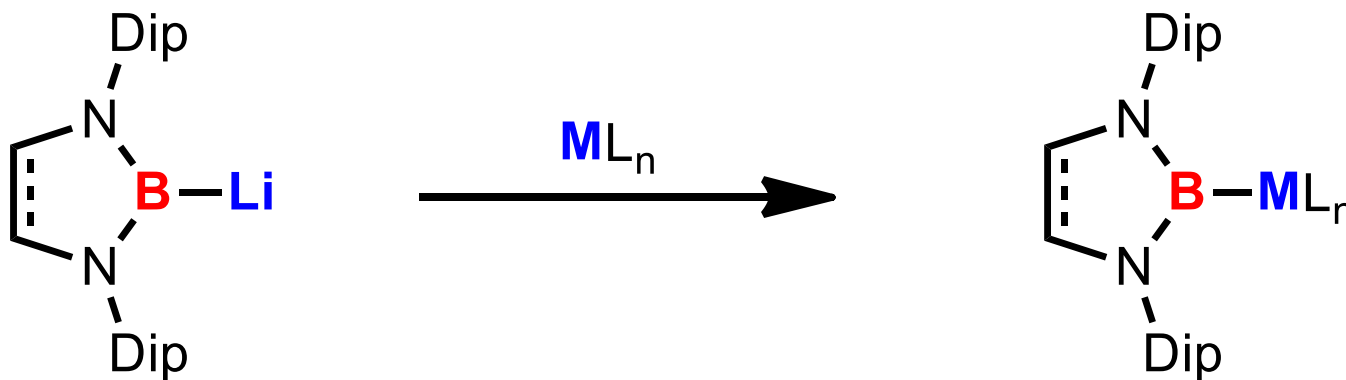


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# Transmetalation of Boryllithium to Other Metals

Based on the high reactivity of boryllithium, transmetalation to other metals enables synthesis of a series of borylmetals.

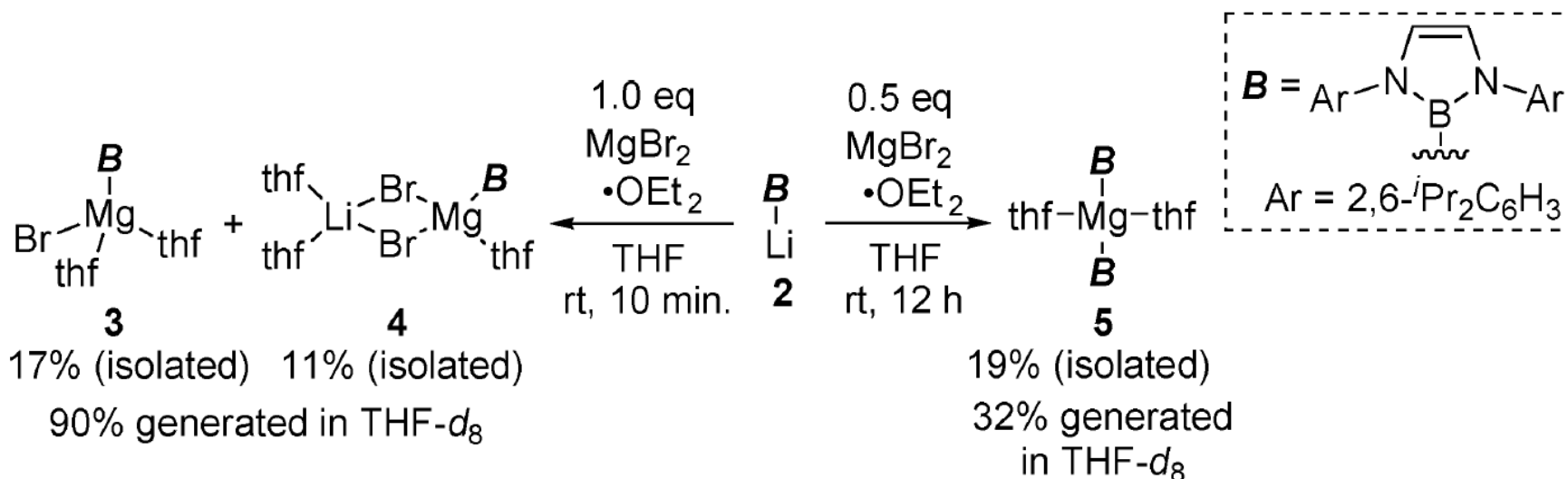


**M = Mg, Zn, Cu, Ag, Au, Ti, Hf**

# Borylmagnesium

## Synthesis of borylmagnesium compounds

The discovery of boryllithium prompted them to synthesize new anionic boron nucleophile, borylmagnesium species.

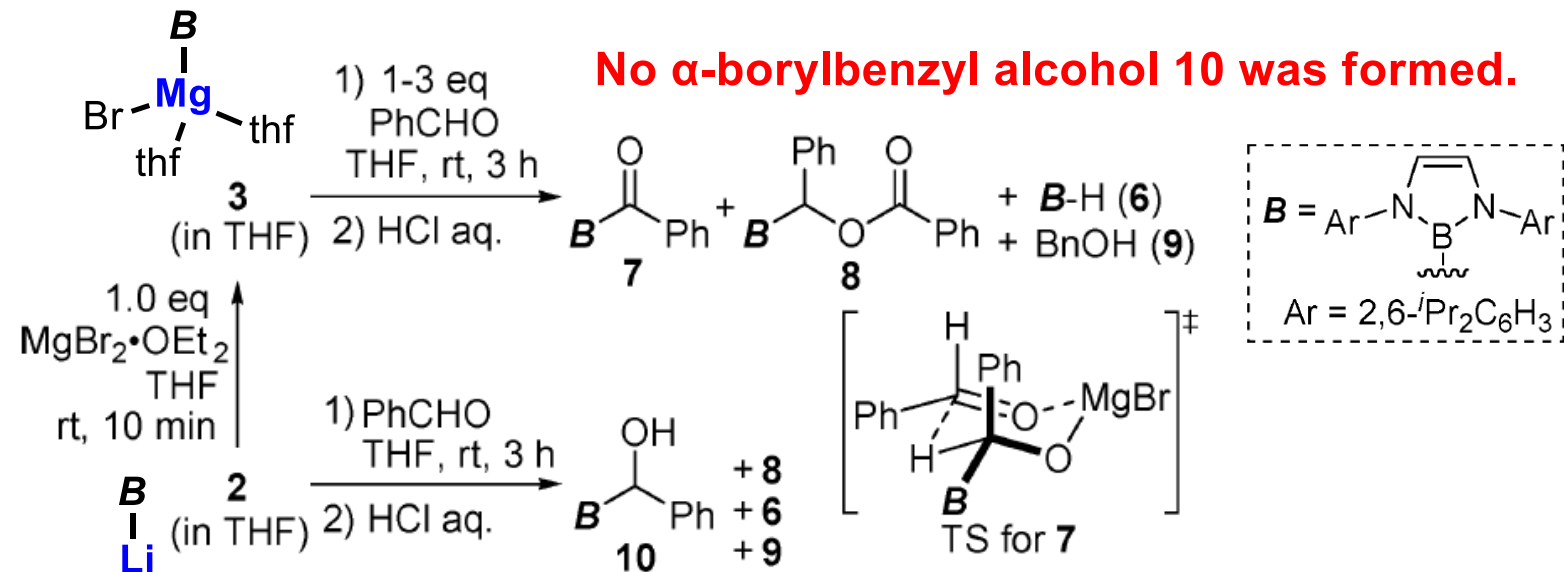


Structure of **3**, **4**, and **5** in the crystals and solutions indicated the **ionic character** of the **B-Mg bond**.

M. Yamashita, K. Nozaki, *et al. J. Am. Chem. Soc.* **2007**, *129*, 9570.

# Borylmagnesium

## Reaction of borylmagnesium bromide to benzaldehyde



run	reactant	PhCHO (equiv)	7 (%) <sup>a</sup>	8 (%) <sup>a</sup>	6 (%) <sup>a</sup>	9 (%) <sup>b</sup>	10 (%) <sup>a</sup>
1	3	1	18	18	56	27	0
2	3	2	34	24	32	47	0
3	3	3	22	40	16	55	0
4	2	1	0	0	6	0	81
5	2	3	0	51	10	50	0

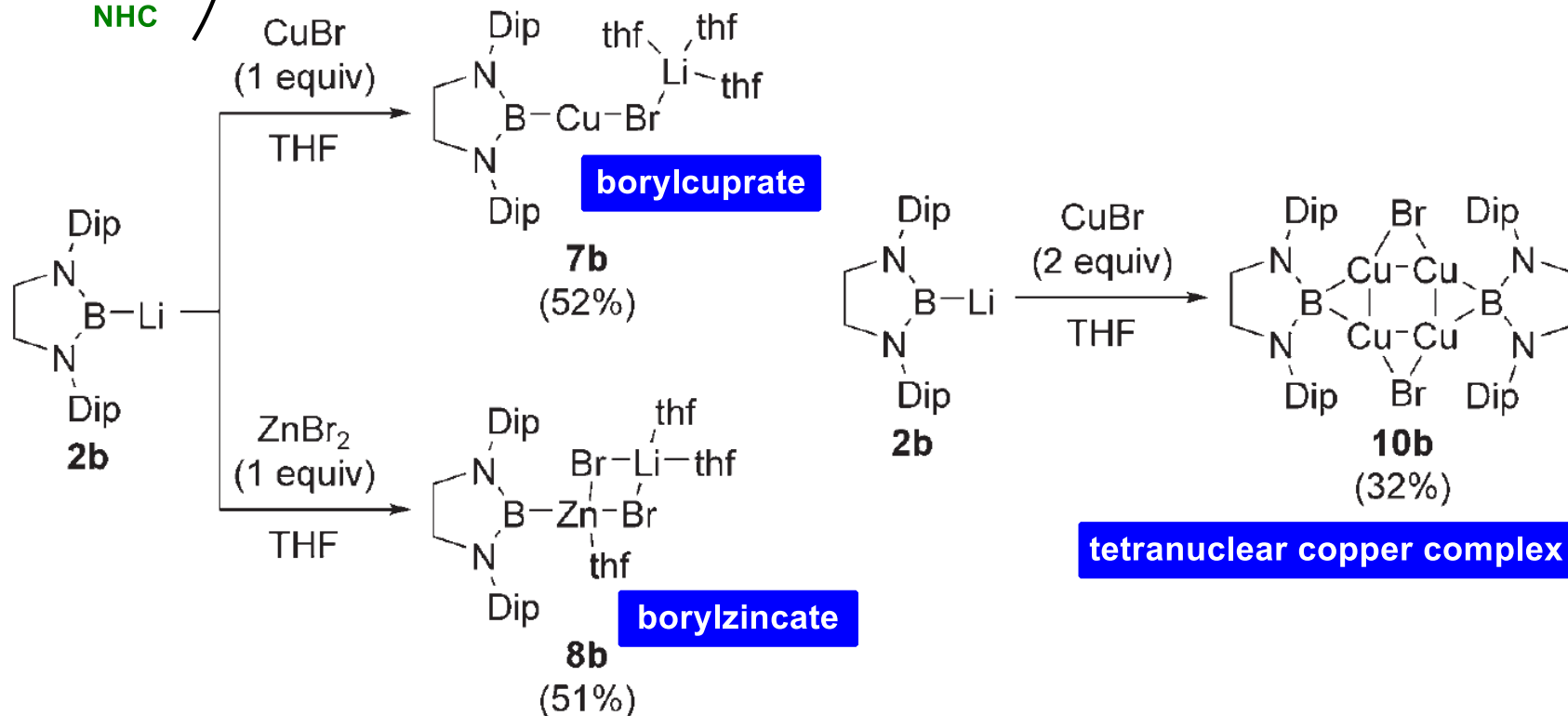
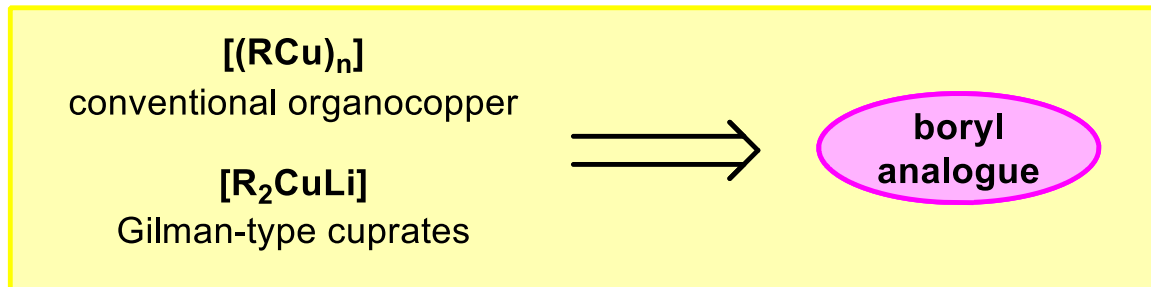
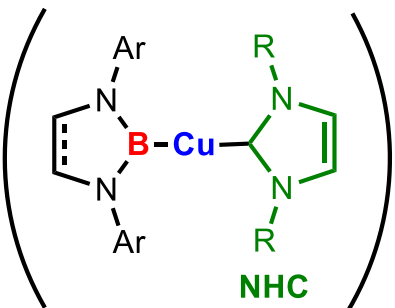
<sup>a</sup> <sup>1</sup>H NMR yield. <sup>b</sup> GC yield.

**The counter metal cation affects the reactivity of  $\alpha$ -borylbenzyloxide intermediated.**

# Borylcopper (and Borylzinc)

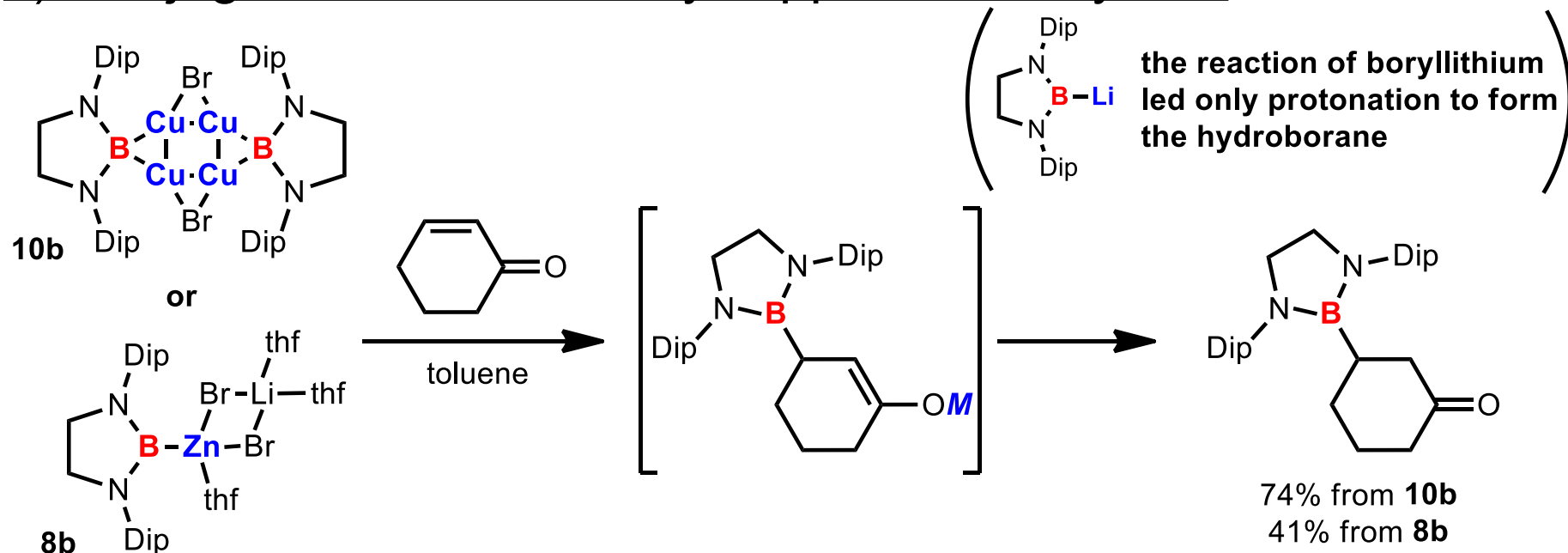
## Synthesis of borylcopper and borylzinc compounds

previous borylcopper

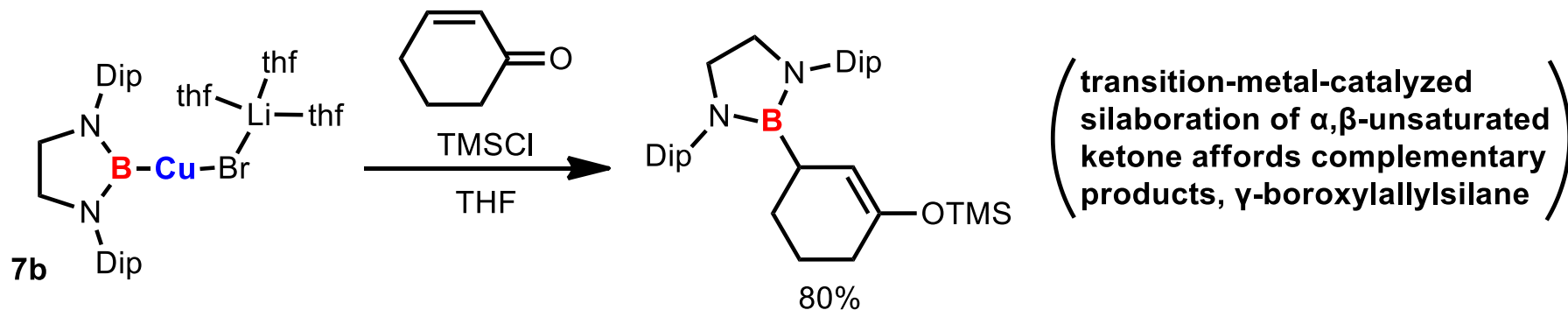


# Borylcopper (and Borylzinc)

## 1) Conjugate addition of borylcopper and borylzinc

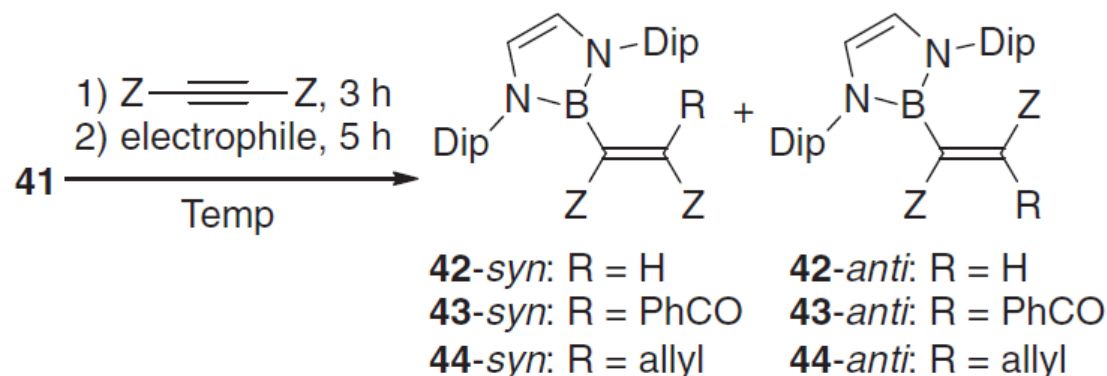
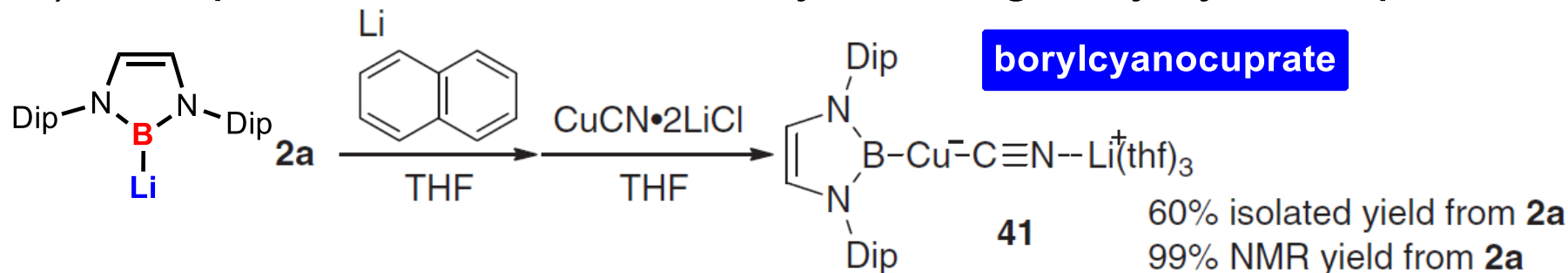


## Trapping the copper enolate intermediate with TMSCl



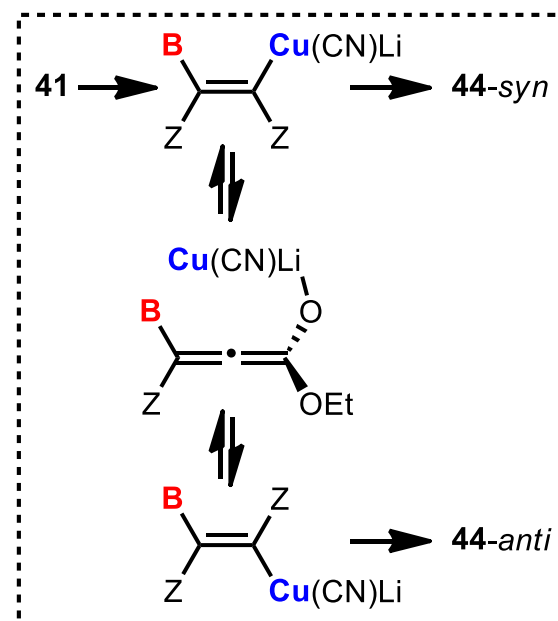
# Borylcopper (and Borylzinc)

## 2) One-pot carboboration of alkyne using borylcyanocuprate



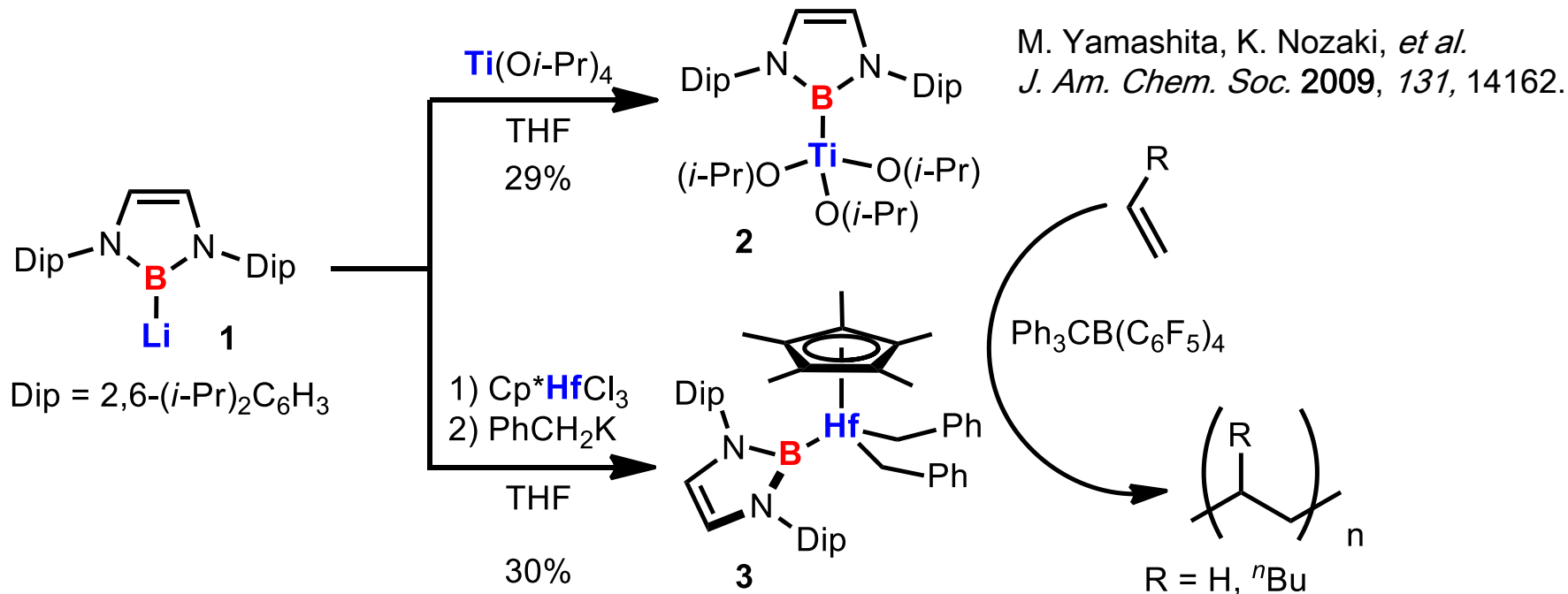
Entry	Electrophile	Temp/°C	Products (Yield <sup>a</sup> )/%	syn/anti
1	PhCOCl	-78	<b>42-syn</b> (48), <b>42-anti</b> (32)	60/40
2	PhCOCl	RT	<b>43-anti</b> (71)	1/99>
3	allylBr	-78	<b>44-syn</b> (93)	99>/1
4	allylBr	RT	<b>44-syn</b> (36), <b>44-anti</b> (60)	38/62

a) Isolated yield based on the added DEAD.

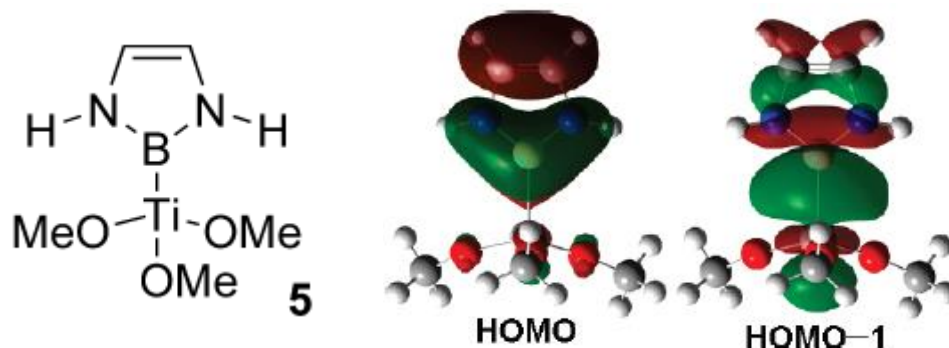


# Boryltitanium and Borylhafnium

## Synthesis of boryltitanium and borylhafnium



## The nature of the group-4 transition metal-boron bond



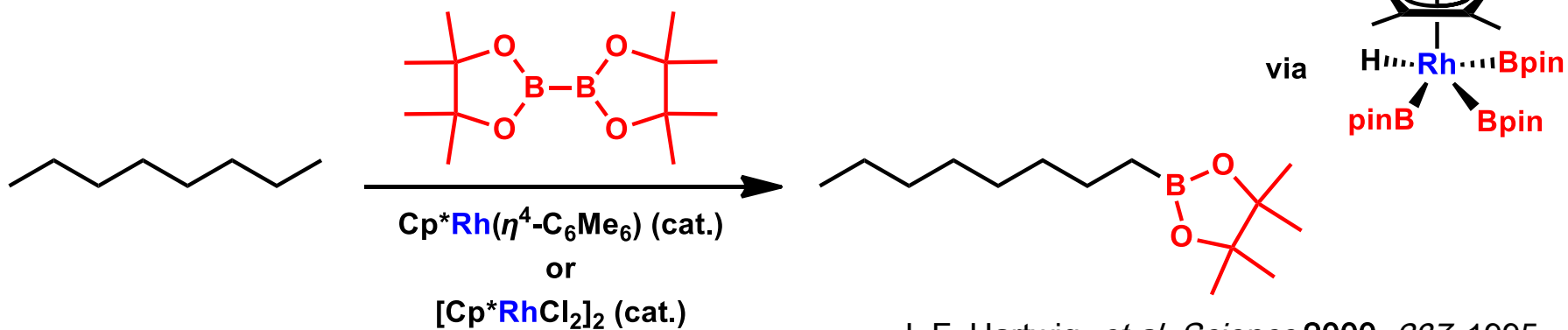
**B-Ti bonds have  
covalent character**

- 
1. Introduction
  2. Boryllithium
  3. Other Borylmetals
  - 4. PBP Pincer Ligands**
  5. Summary

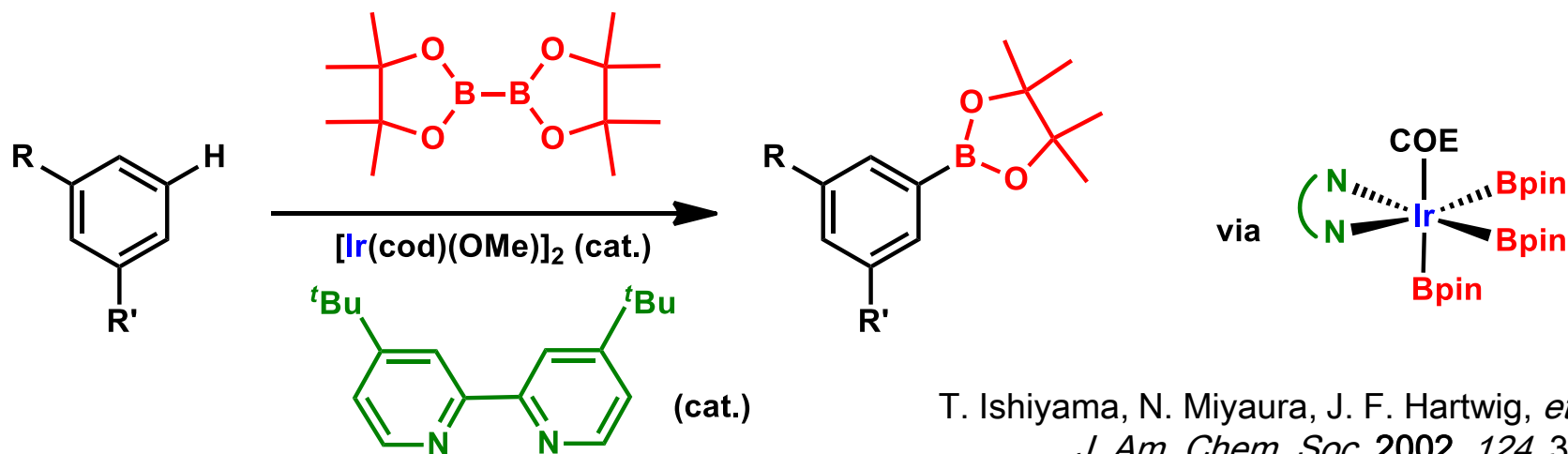


# Background

Transition metal boryl complexes have been widely synthesized and applied to catalytic **borylation reactions**.



J. F. Hartwig, *et al.* *Science* 2000, 287, 1995.  
*J. Am. Chem. Soc.* 2005, 127, 2538.



T. Ishiyama, N. Miyaura, J. F. Hartwig, *et al.*  
*J. Am. Chem. Soc.* 2002, 124, 390.

boryl ligands act as **“reactive”** ligands

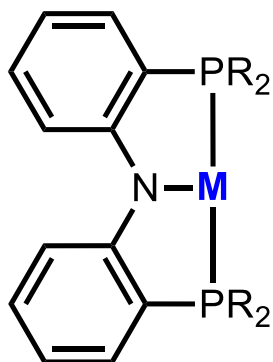
# Background

It is known that the boryl ligand has a greater  $\sigma$ -donor ability than other monoanionic ligand of carbon, nitrogen and oxygen.

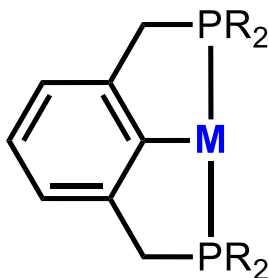


If the boryl ligand is stabilized and acts as “supporting” ligand, the strong electron-releasing property of the boryl ligand would be applied to functionalization other than borylation.

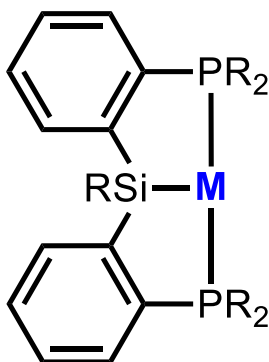
## PXP pincer ligands



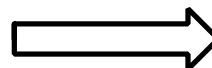
PNP



PCP

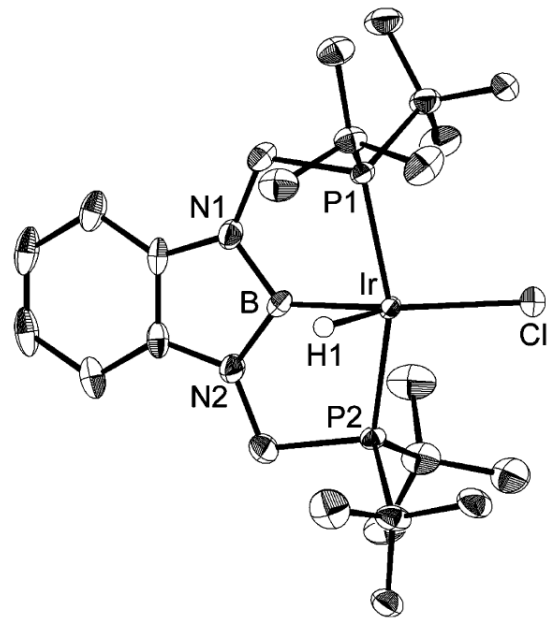
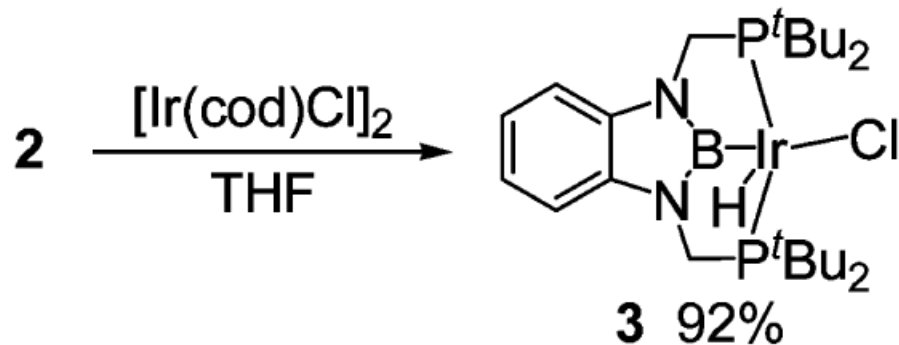
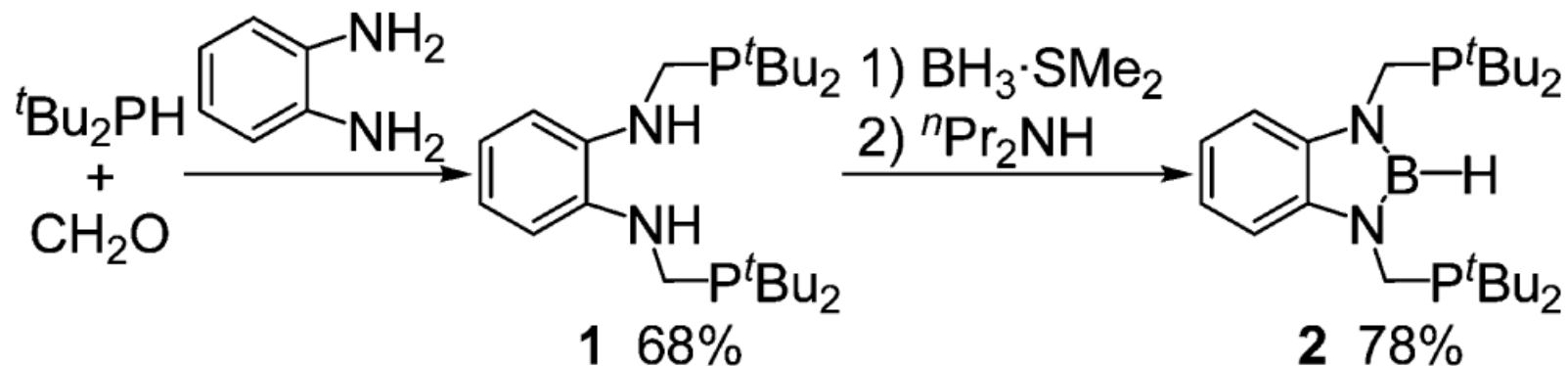


PSiP



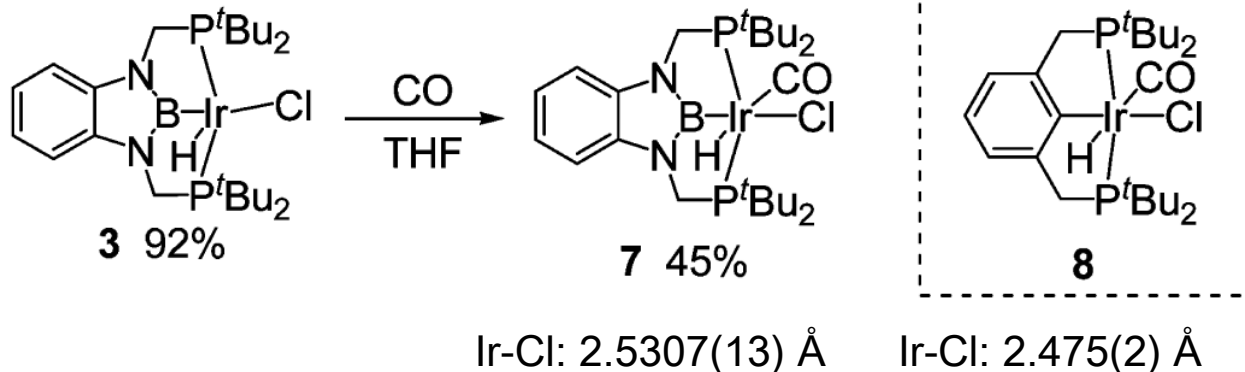
- retain highly reactive anionic ligands on metal center
- provide remarkable thermodynamic stability

# Synthesis of PBP Pincer Iridium Complexes



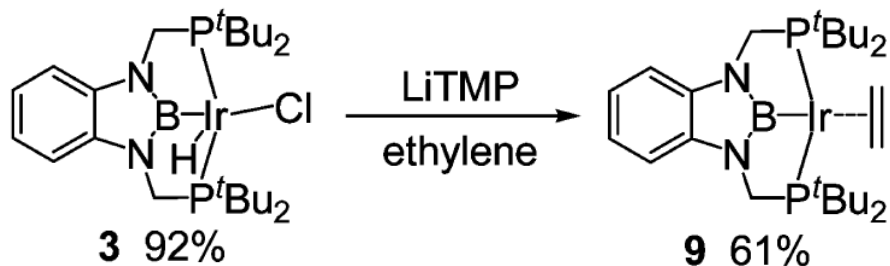
# Synthesis of PBP Pincer Iridium Complexes

## Carbonyl complex



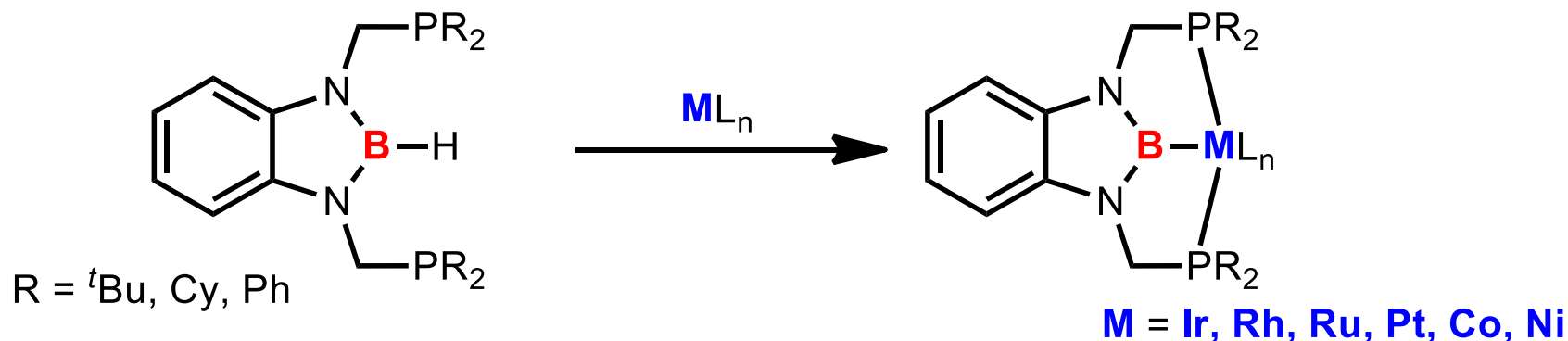
**PBP ligand has stronger  $\sigma$ -donor ability**

## Ethylene complex



Applications of these easily prepared PBP pincer complexes to catalytic reactions are under investigation.

# Other Metal Complexes Possessing PBP Pincer Ligand



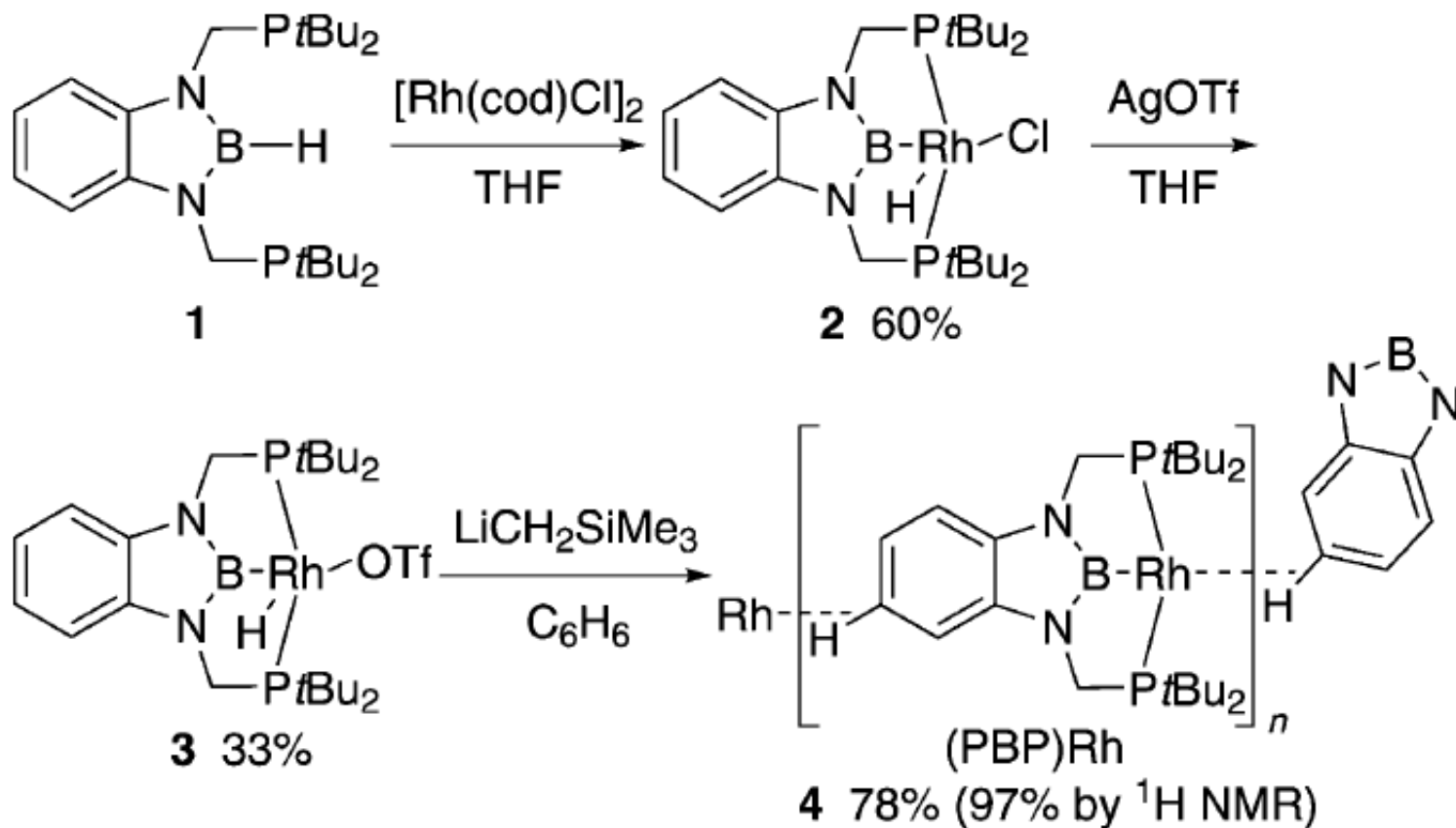
**Ir** complex: M. Yamashita, K. Nozaki, *et al. Organometallics* **2009**, *28*, 6234.

**Ru** complex: M. Yamashita, *et al. Organometallics* **2014**, *33*, 6760.

**Pt** complex: M. Yamashita, *et al. Dalton Trans.* **2013**, *42*, 625.

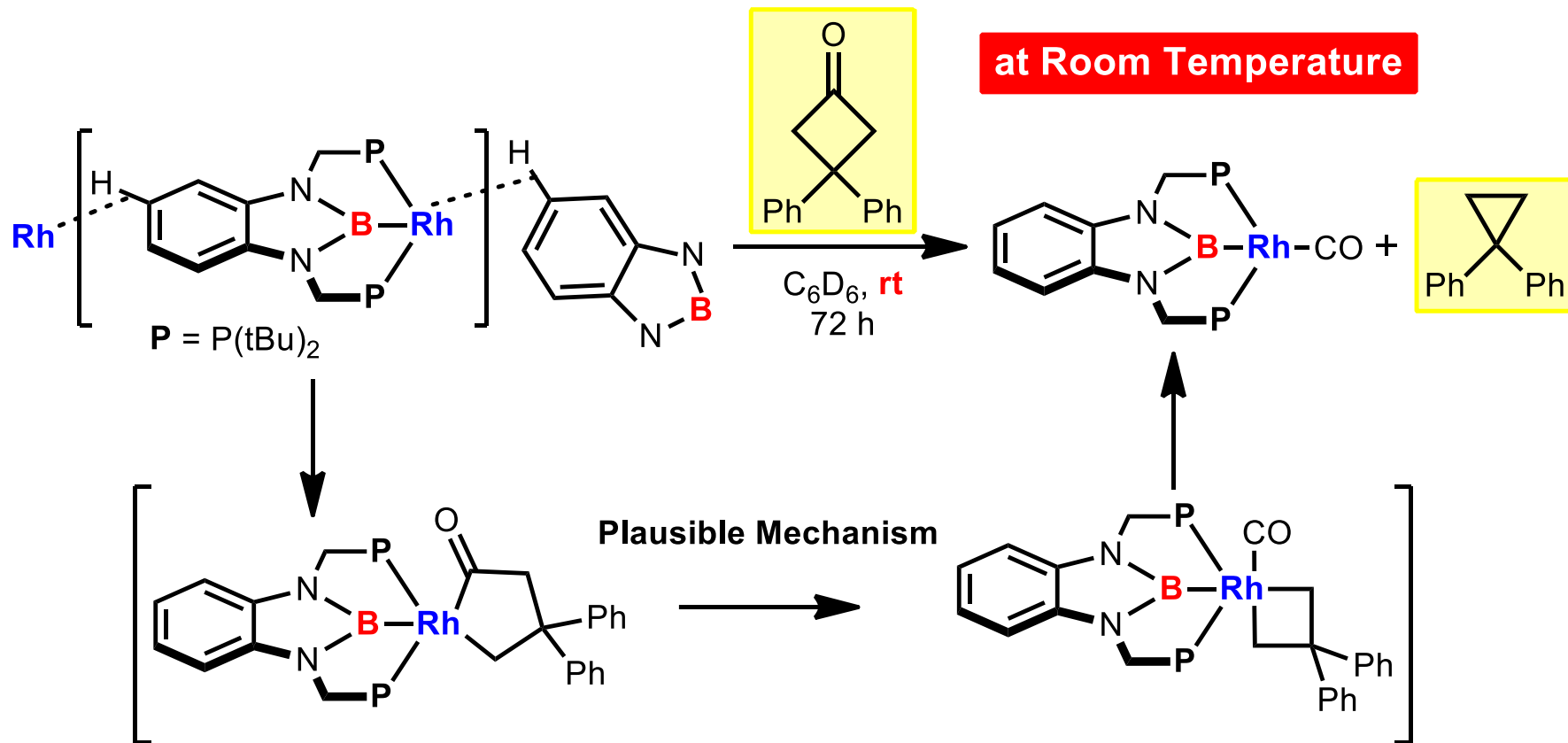
# PBP Rhodium Complex

## Synthesis of PBP rhodium complex



# PBP Rhodium Complex

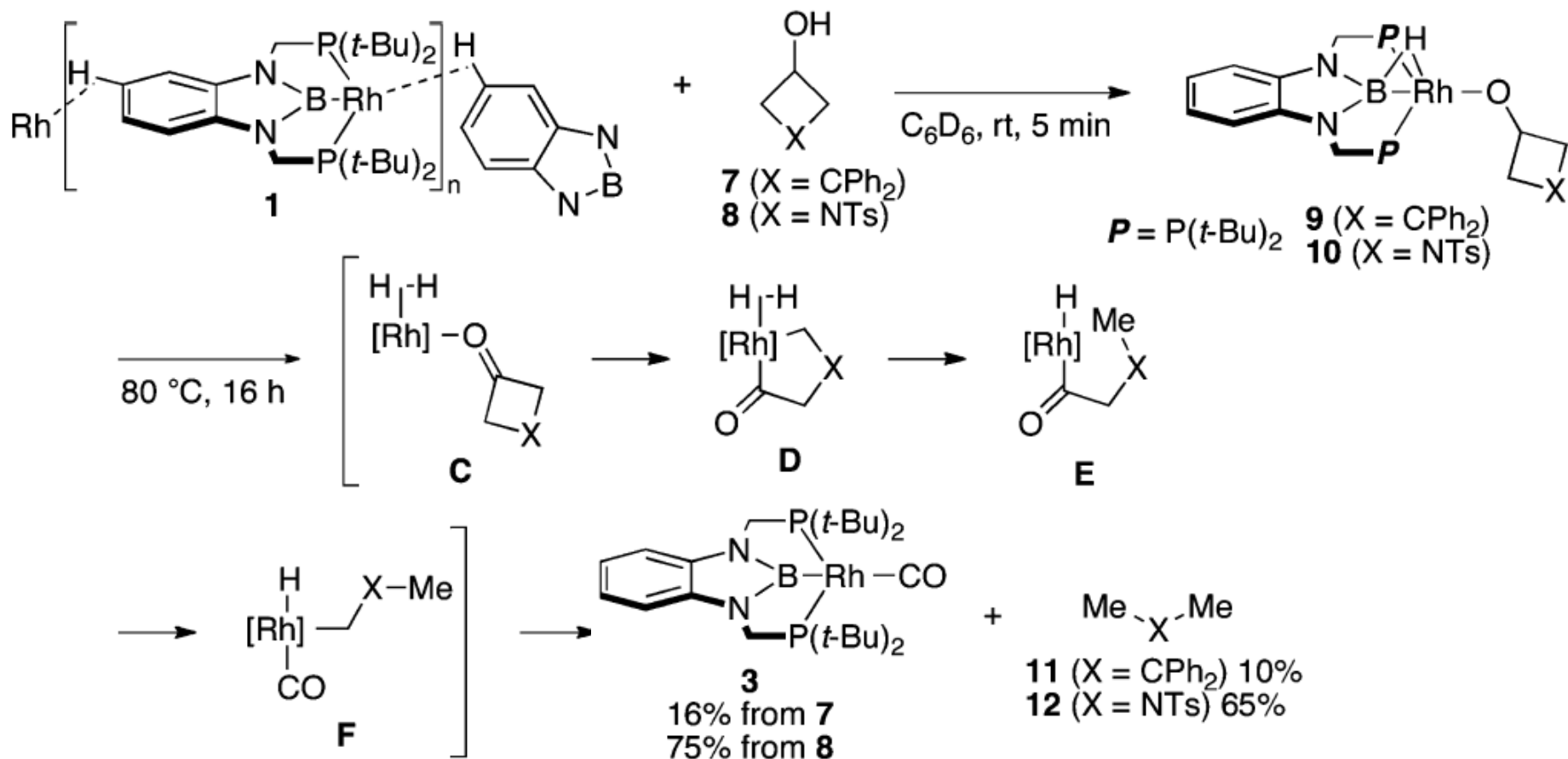
## Oxidative addition of a strained C-C bond at room temperature



An analogous decarbonylation reaction of cyclobutanone mediated by Rh(I) complexes bearing PPh<sub>3</sub> or NHC ligands generally requires reflux conditions even when a stoichiometric amount of Rh(I) complex is used.

# PBP Rhodium Complex

## Reaction with *sec*-Alcohols

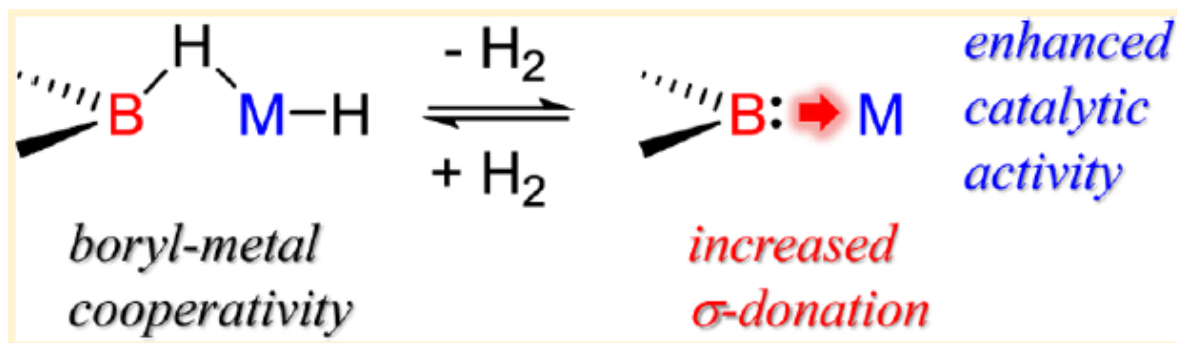


PBP Rh(I) complexes possess a high propensity for oxidative addition of nonpolar C-C  $\sigma$ -bonds as well as polar O-H bonds

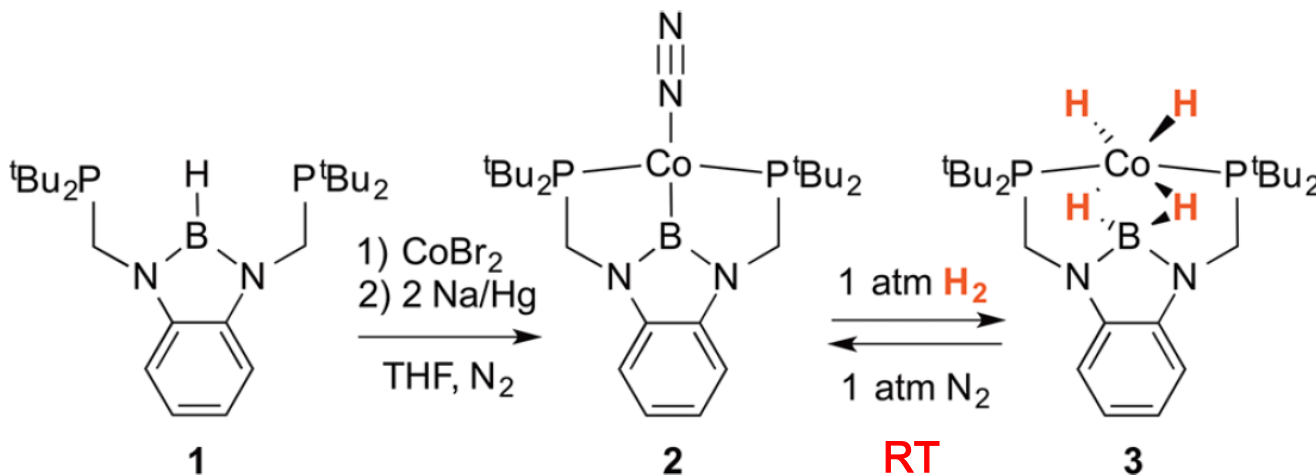


# PBP Cobalt Complex

New approaches toward the generation of late first-row metal catalysts that facilitate **two-electron reductive transformations** (e.g., hydrogenation) more typical of noble-metal catalysts is important goal.

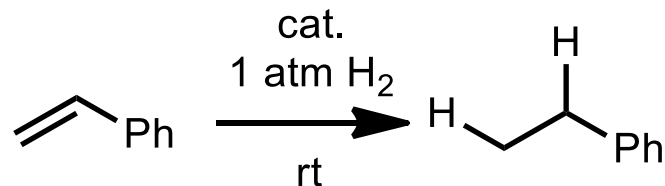


## Synthesis of PBP cobalt complex and reversible H<sub>2</sub> activation



# PBP Cobalt Complex

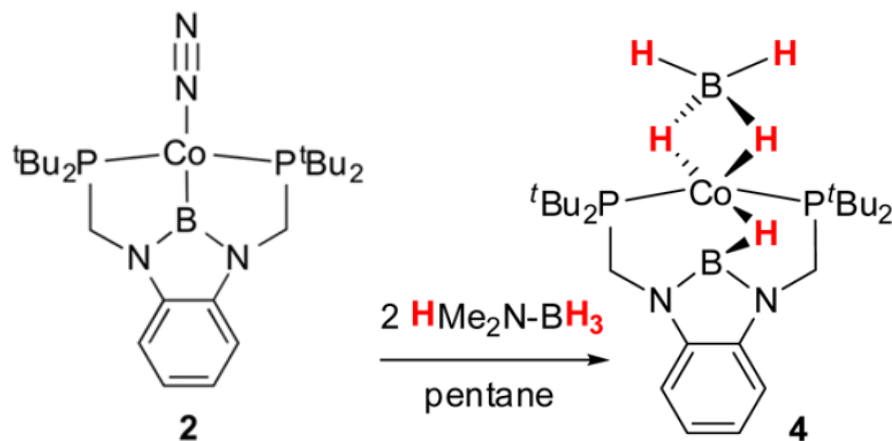
## 1) Hydrogenation of styrene with H<sub>2</sub>



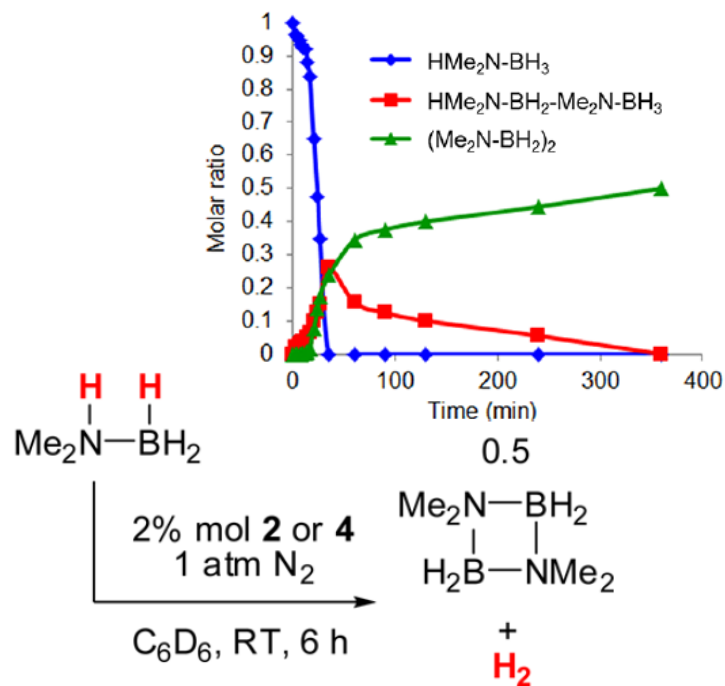
catalyst	TOF (h <sup>-1</sup> )	catalyst	TOF (h <sup>-1</sup> )
<b>2</b>	1000 <sup>b</sup>	( <sup>Mes</sup> DPB <sup>Ph</sup> )Ni	20 <sup>d</sup>
( <sup>Cy</sup> PNP)CoR	25 <sup>b</sup>	( <sup>iPr</sup> TPB)Fe(N <sub>2</sub> )	0.27 <sup>c</sup>
( <sup>iPr</sup> PDI)Fe(N <sub>2</sub> ) <sub>2</sub>	1344 <sup>a</sup>	(PPh <sub>3</sub> ) <sub>3</sub> RhCl	100 <sup>b</sup>

Conditions: RT, 1 atm H<sub>2</sub>, organic solvents. Catalyst loading: <sup>a</sup>0.3% mol; <sup>b</sup>2% mol; <sup>c</sup>3.3% mol; <sup>d</sup>5% mol. PNP = bis-phosphino-amido; PDI = pyridyl-diimine; DPB = bis-phosphino-borane; TPB = tris-phosphino-borane.

## 2) Amine-borane dehydrogenation



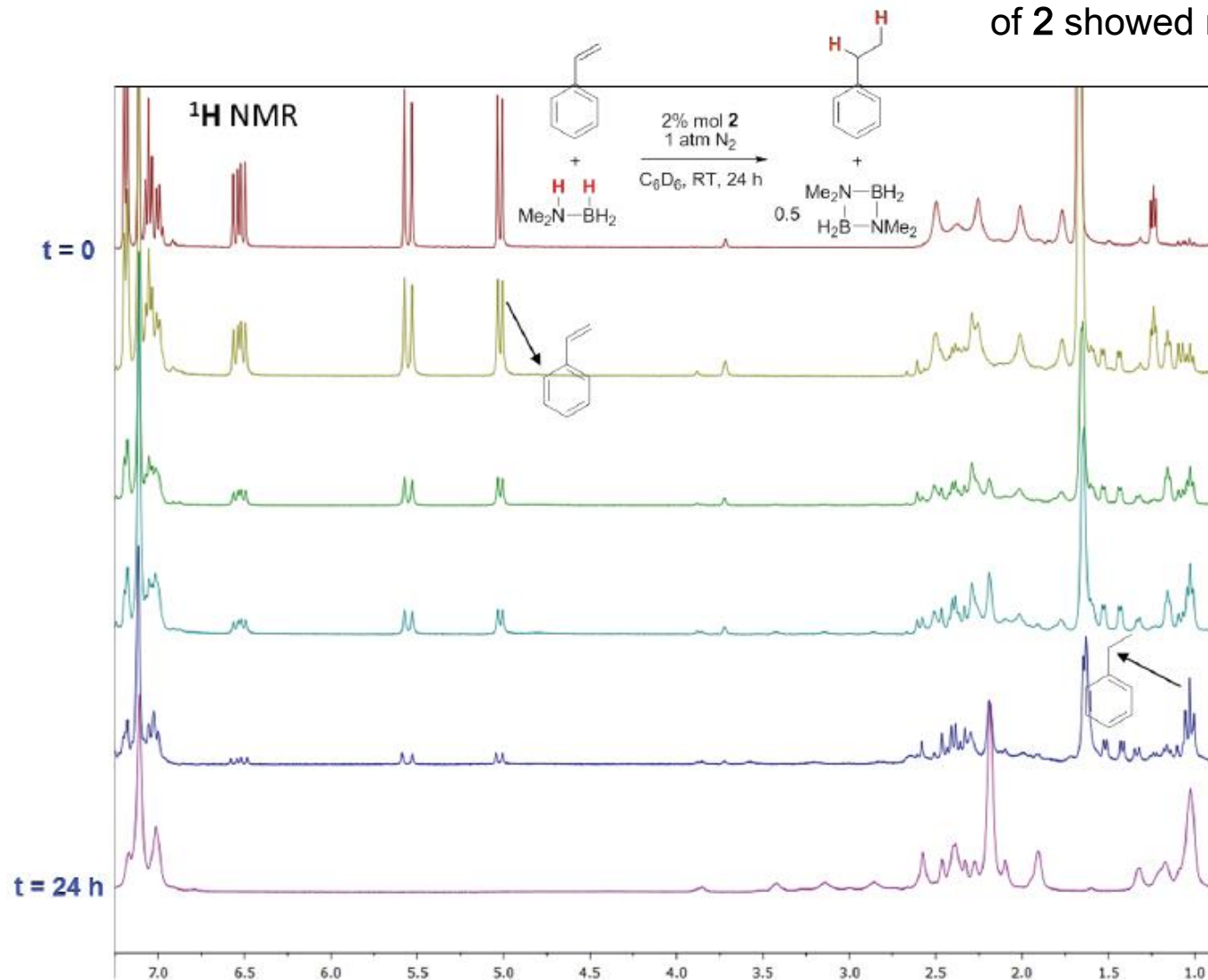
equilibrium between 2 and 4  
in the presence of excess Et<sub>3</sub>N



# PBP Cobalt Complex

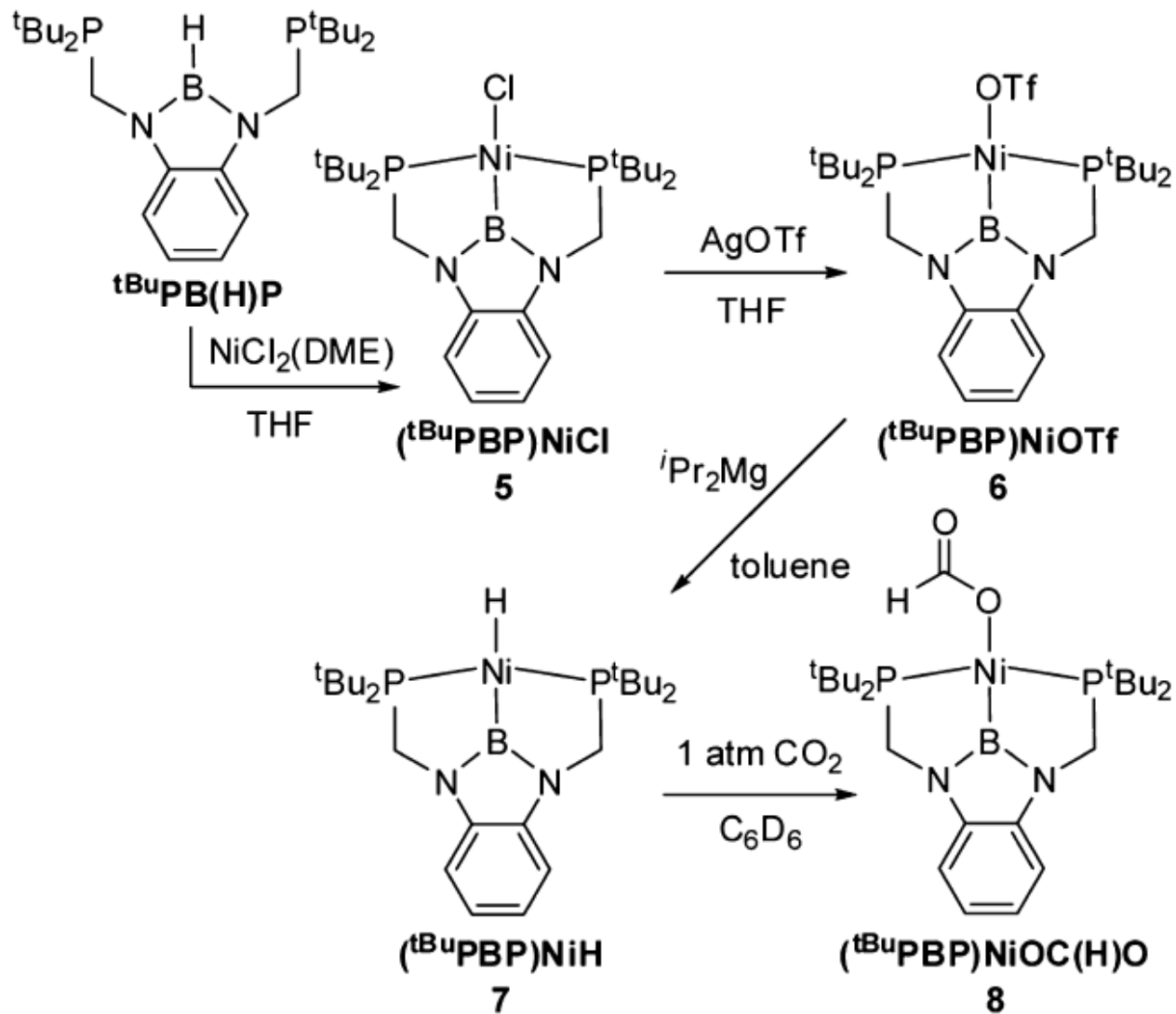
## 3) Transfer hydrogenation reaction

Control experiments in the absence of **2** showed no reactivity.



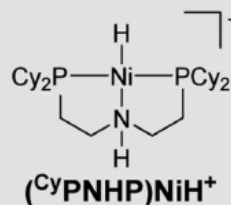
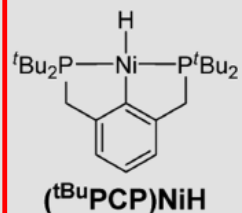
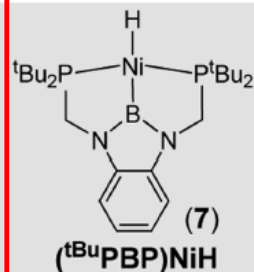
# PBP Nickel Complex

## Synthesis of PBP nickel complex



# PBP Nickel Complex

## Turnover frequency (TOF) of catalytic olefin hydrogenation

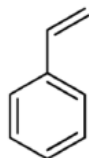


Conditions:

1 atm H<sub>2</sub>, RT

1 atm H<sub>2</sub>, RT

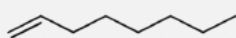
4 atm H<sub>2</sub>, 80 °C



25 h<sup>-1</sup>  
(100%)<sup>a</sup>

0.7 h<sup>-1</sup>  
(100%)<sup>a</sup>

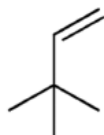
0.4 h<sup>-1</sup>  
(100%)<sup>b</sup>



25 h<sup>-1</sup>  
(64%)<sup>a</sup>

0 h<sup>-1</sup>  
-<sup>a</sup>

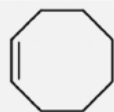
0.4 h<sup>-1</sup>  
(70%)<sup>b</sup>



5 h<sup>-1</sup>  
(100%)<sup>a</sup>

0 h<sup>-1</sup>  
-<sup>a</sup>

0.2 h<sup>-1</sup>  
(97%)<sup>b</sup>



0.6 h<sup>-1</sup>  
(100%)<sup>a</sup>

0 h<sup>-1</sup>  
-<sup>a</sup>

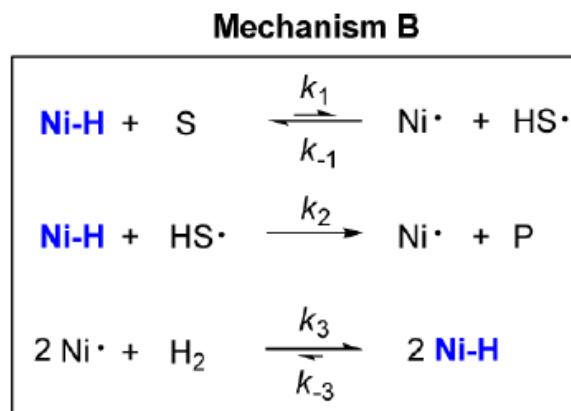
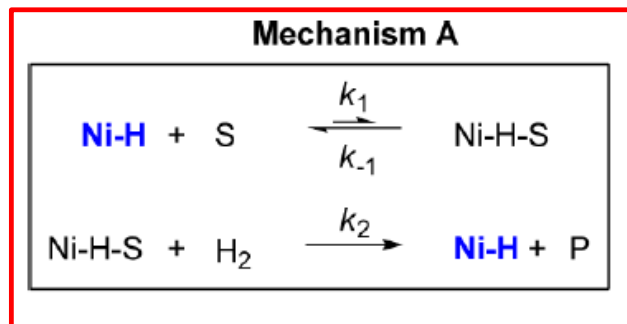
not  
reported

<sup>a</sup>Conditions: 2 mol % catalyst relative to olefin, C<sub>6</sub>D<sub>6</sub>. The yield (given in parentheses) was determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The turnover frequency (h<sup>-1</sup>) was calculated at the end of the reaction when the starting olefin was not detectable. <sup>b</sup>As reported by Hanson:<sup>5c</sup> 10 mol % catalyst relative to olefin, THF-*d*<sub>8</sub>.

PBP Nickel complex **7** is a more active olefin hydrogenation catalyst compared with its isoelectronic/isostructural phenyl and amino analogues.

# PBP Nickel Complex

## Proposed mechanism



Ni-H = catalyst **7**  
S = olefin  
P = hydrogenated product

<sup>a</sup>The catalyst resting state is highlighted in blue.

Why PBP Nickel complex **7** is a more active olefin hydrogenation catalyst compared with phenyl and amino analogues?

strong *trans* influence of the boryl group destabilizes the Ni-H and Ni-alkyl bond



kinetically more favorable migratory insertion ( $k_1$ ) and  $\sigma$ -bond metathesis ( $k_2$ ) step

- 
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  - 5. Summary**

# Summary

## Boryllithium

- First isolation and structural analysis of boryllithium was performed.
- Boryllithium reacts with various electrophile as alkyl lithium does.

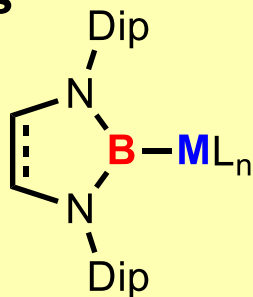
## Borylmetals other than lithium

- Transmetalation of boryllithium to other metals enables synthesis of a series of borylmetals.
- However useful reactions taking advantage of isolable borylmetals were under development.

## PBP pincer ligand

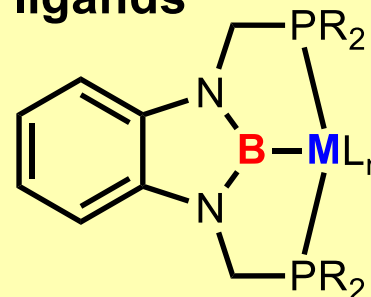
- PBP ligand has higher  $\sigma$ -donor ability than PCP and PNP ligand.
- Some useful reactions taking advantage of higher  $\sigma$ -donor ability were developed.

### Borylmetals



**M = Li, Mg, Zn, Cu, Ag, Au, Ti, Hf**

### PBP pincer ligands



**M = Ir, Rh, Ru, Pt, Co, Ni**