

Boranes as Z-type Ligands for Transition Metal Complexes

2015/2/11

Zhi Ren

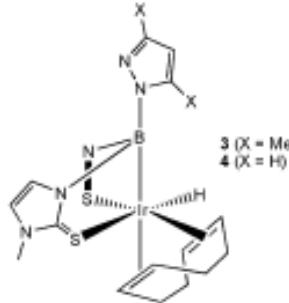
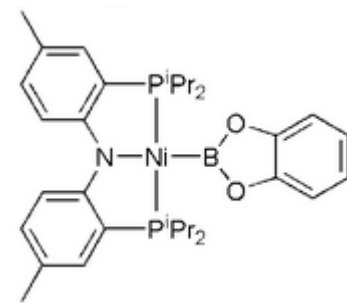
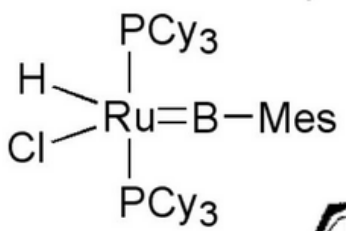
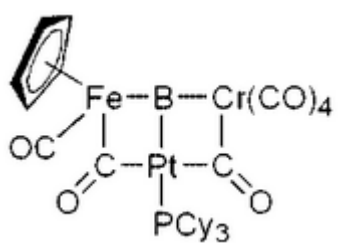
Overview

- 1. Introduction
- 2. Metal complexes
- 3. Catalytic reactions
- 4. Brief summary

1. Introduction

- 1.1. Borane ligands
- 1.2. Z-type ligands
- 1.3. Electronegativities
- 1.4. Electron count for Z type ligands

1.1. Borane ligands

| Ligand name | Coordinate with metals | Metal complexes |
|--|---|---|
| $\begin{array}{c} R \\ \diagdown \\ B \\ \diagup \\ R \\ \\ R \end{array}$ | $\begin{array}{c} M \\ \downarrow \\ R \\ \diagdown \\ B \\ \diagup \\ R \\ \\ R \end{array}$ |  |
| $\begin{array}{c} \ominus \\ \\ B \\ \\ R \\ \\ R \end{array}$ | $\begin{array}{c} M \\ \uparrow \\ R \\ \diagdown \\ B \\ \diagup \\ R \\ \\ R \end{array}$ |  |
| $R-B:$ | $\begin{array}{c} M \\ \\ R-B \end{array}$ |  |
| $\cdot B \cdot$ | $\begin{array}{c} M \\ \\ M-B \end{array}$ |  |

Braunschweig, H. *et al Chem. Rev.* **2010**, *110*, 3924.

For boryl metal complexes: Irvine, G.J. *et al Chem. Rev.* **1998**, *98*, 2685.

1.1. Borane ligands

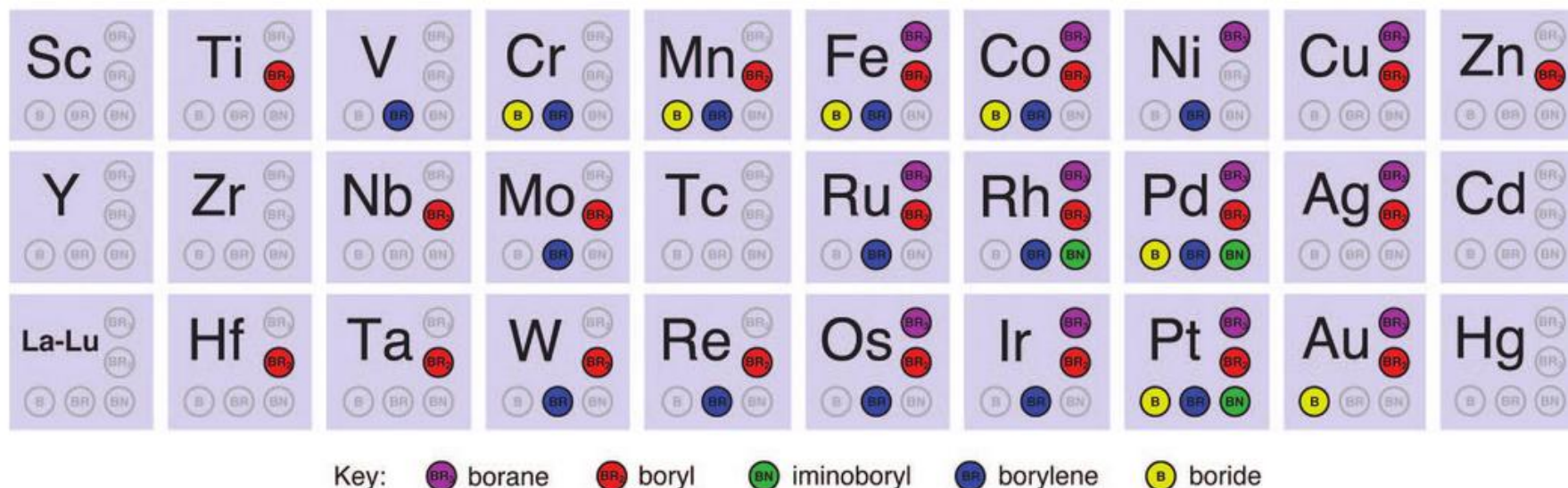
| Ligand name | Coordinate with metals | Properties |
|--|---|----------------------------------|
| $\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{B} \\ / \quad \diagdown \\ \text{R} \end{array}$ | $\begin{array}{c} \text{M} \\ \downarrow \\ \begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{B} \\ / \quad \diagdown \\ \text{R} \end{array} \end{array}$ | σ -acceptor |
| $\begin{array}{c} \ominus \\ \\ \text{B} \quad \text{R} \\ \\ \text{R} \end{array}$ | $\begin{array}{c} \text{M} \\ \uparrow \\ \begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{B} \\ / \quad \diagdown \\ \text{R} \end{array} \end{array}$ | σ -donor, π -acceptor |
| $\text{R}-\text{B}:$ | $\begin{array}{c} \text{M} \\ \\ \text{R}-\text{B} \end{array} \quad \begin{array}{c} \text{M} \\ \\ \text{B} \\ \\ \text{R} \end{array} \quad \begin{array}{c} \text{M} \\ \\ \text{R}-\text{B}-\text{M} \end{array}$ | |
| $\cdot\text{B}\cdot$ | $\begin{array}{c} \text{M} \\ \\ \text{M}-\text{B} \end{array} \quad \begin{array}{c} \text{M} \\ \\ \text{B} \\ \\ \text{M} \end{array} \quad \begin{array}{c} \text{M} \\ \\ \text{M}-\text{B}-\text{M} \end{array}$ | |

Braunschweig, H. *et al Chem. Rev.* **2010**, *110*, 3924.

For boryl metal complexes: Irvine, G.J. *et al Chem. Rev.* **1998**, *98*, 2685.

1.1. Borane ligands

- Summary of known boron-metal complexes



1.2. Z-type ligands

- Three type of metal-ligand interactions



2e donor

L = phosphines, amines, CO,
N-heterocyclic carbenes...



1e donor

X = H, halogen,
aryl, alkyl...

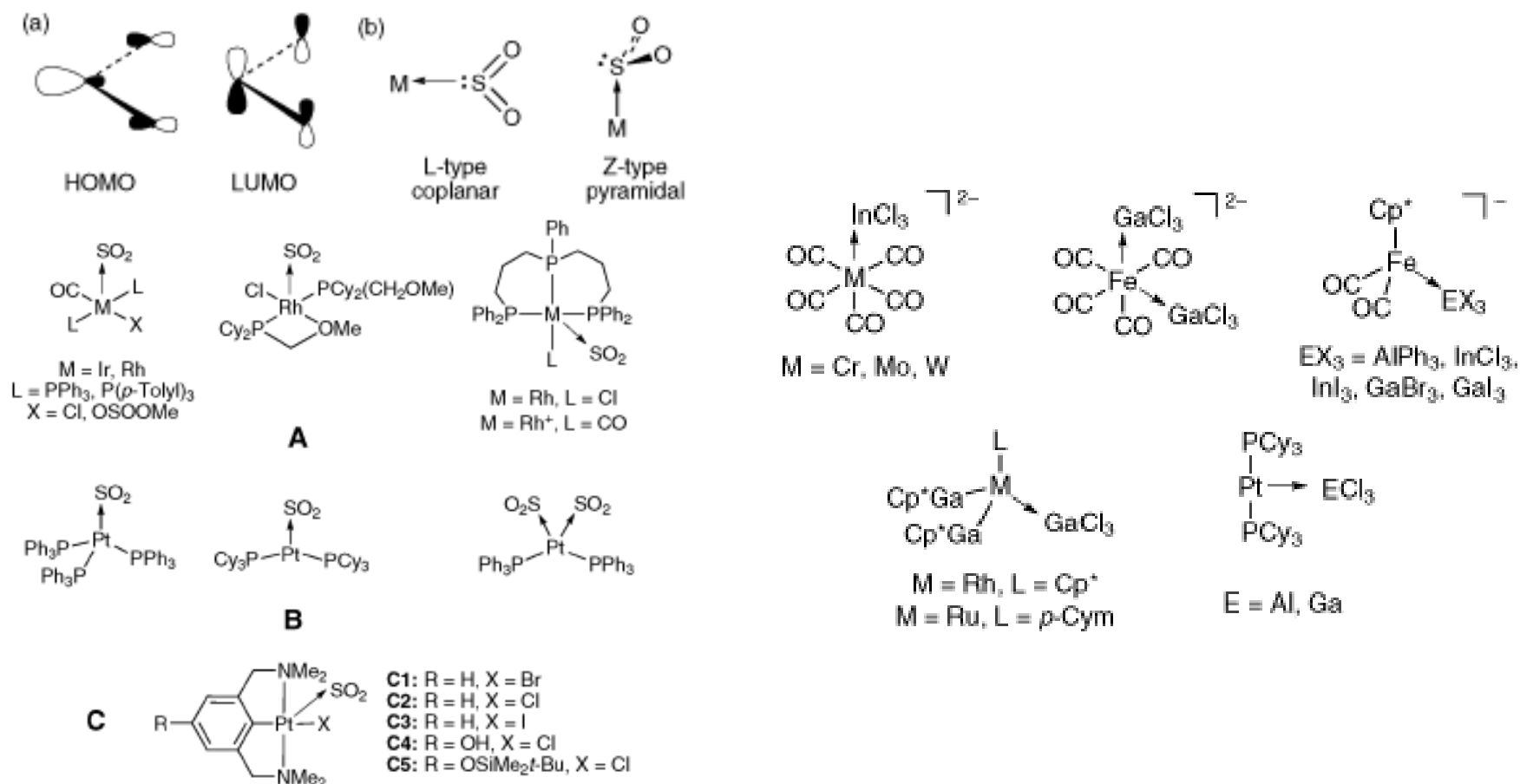


2e acceptor

Z = Lewis acids
(SO₂, boranes...)

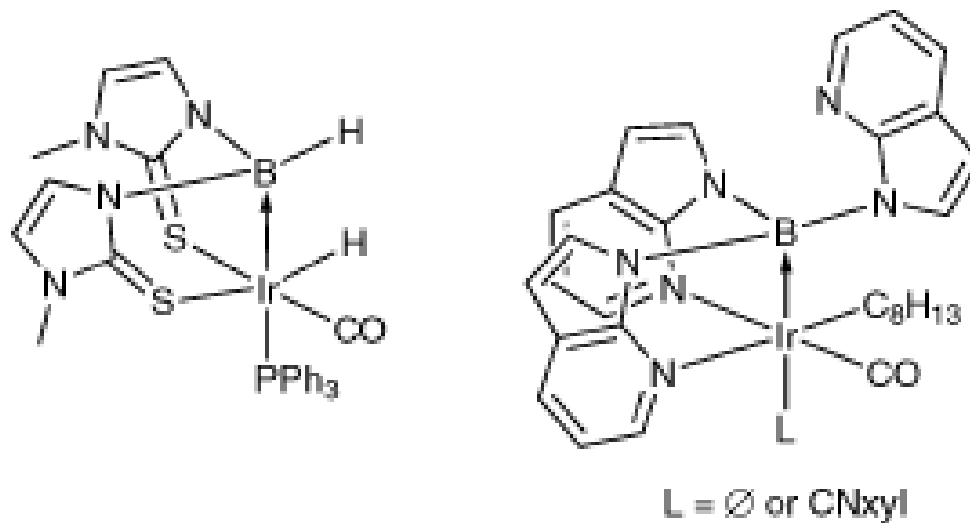
1.2. Z-type ligands

- Unsupported M \rightarrow Z interactions



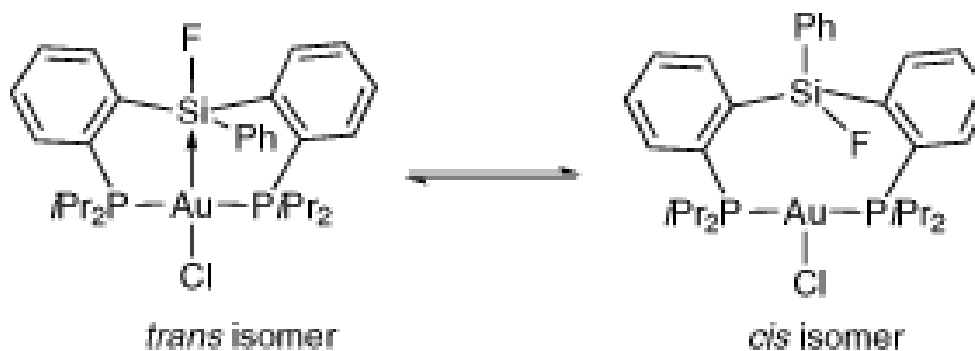
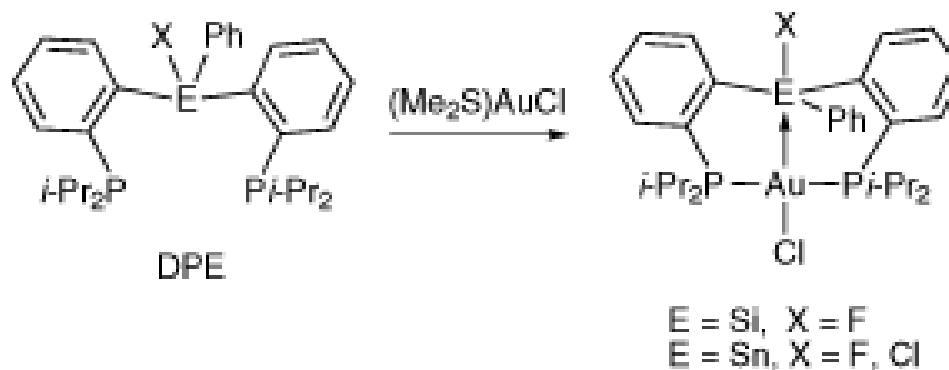
1.2. Z-type ligands

- Supported M \rightarrow Z interactions: borane ligands



1.2. Z-type ligands

- Supported M \rightarrow Z interactions: other ligands



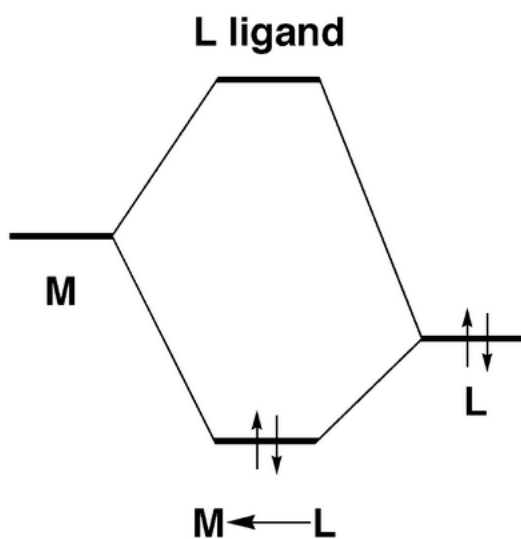
1.3. Electronegativities

- Gold: Give me your electrons!
- Boron: Sorry I don't have any left...

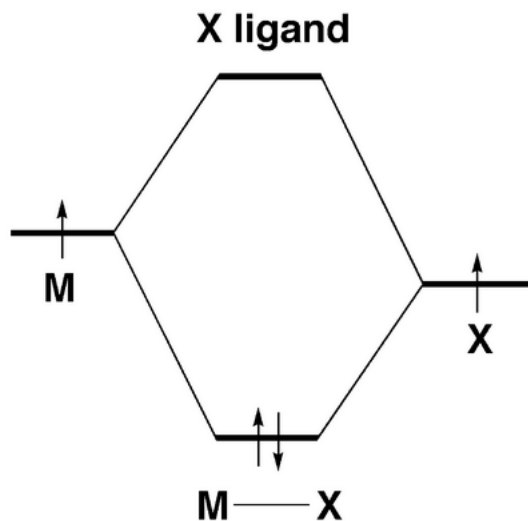
| | | | | | | | | | | | | | |
|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| | | | | | | | | | | B | C | N | O |
| | | | | | | | | | | 2.04 | 2.55 | 3.04 | 3.44 |
| | | | | | | | | | | Al | Si | P | S |
| | | | | | | | | | | 1.61 | 1.90 | 2.19 | 2.58 |
| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se |
| 1.36 | 1.54 | 1.63 | 1.66 | 1.55 | 1.83 | 1.88 | 1.91 | 1.90 | 1.65 | 1.81 | 2.01 | 2.18 | 2.55 |
| Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te |
| 1.22 | 1.33 | 1.6 | 2.16 | 1.9 | 2.2 | 2.28 | 2.20 | 1.93 | 1.69 | 1.78 | 1.96 | 2.05 | 2.1 |
| * | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | |
| | 1.3 | 1.5 | 2.36 | 1.9 | 2.2 | 2.20 | 2.28 | 2.54 | 2.00 | 1.62 | 1.87 | 2.02 | |

1.4. Electron count for Z-type ligands

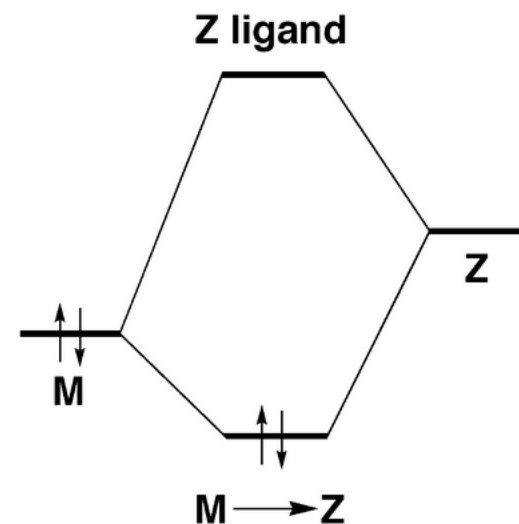
- d^n configuration, $L = 0$, $X = -1$, $Z = -2$.
- Electron counting $L = +2$, $X = +1$, $Z = 0$.



both electrons
provided by ligand
(**dative covalent bond**)



one electron each provided
by ligand and by metal
(**normal covalent bond**)

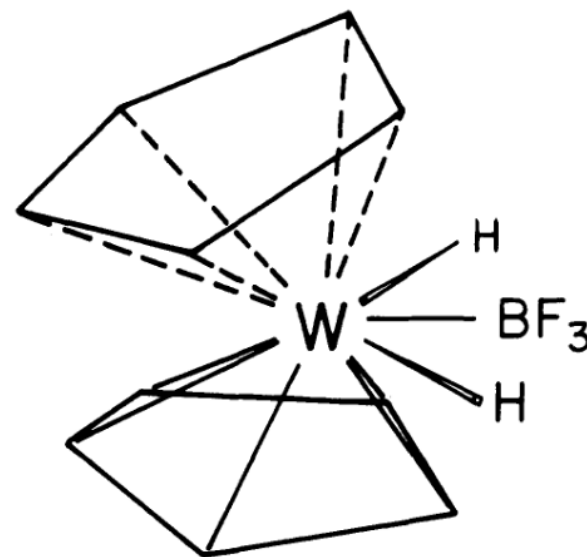


both electrons
provided by metal
(**dative covalent bond**)

2. Metal complexes

- 2.1. Historical view

In 1963 Shriver reported a metal-boron dative complex $[\text{Cp}_2\text{WH}_2(\text{BF}_3)]$.



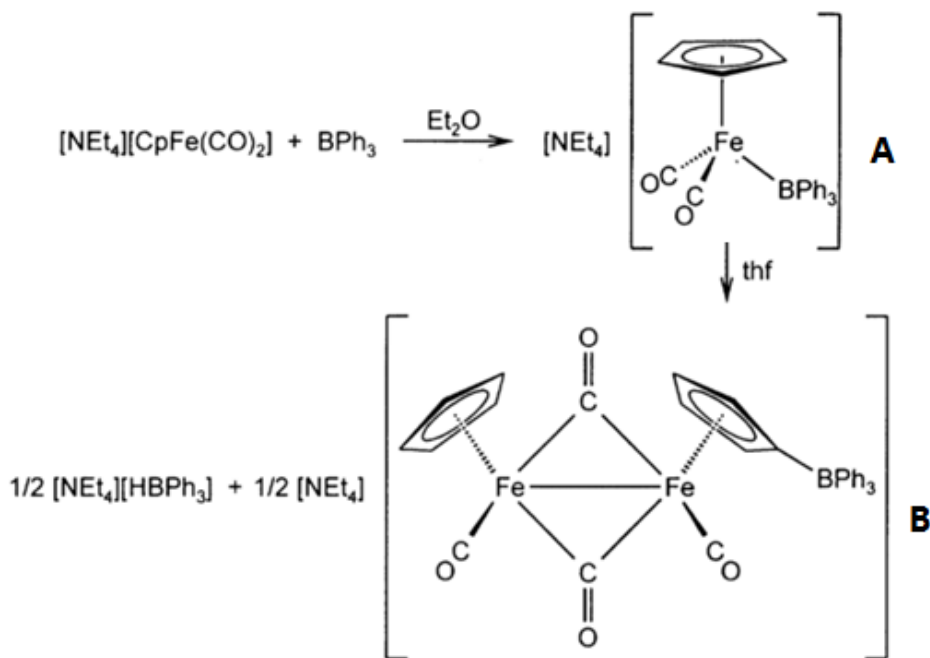
Shriver, D.F. *J. Am. Chem. Soc.* **1963**, 85, 3509

Shriver, D.F. *Acc. Chem. Res.* **1970**, 3, 231

2. Metal complexes

- 2.1. Historical view

In 1979, Hughes reported the complex that contains a metal boron dative bond.

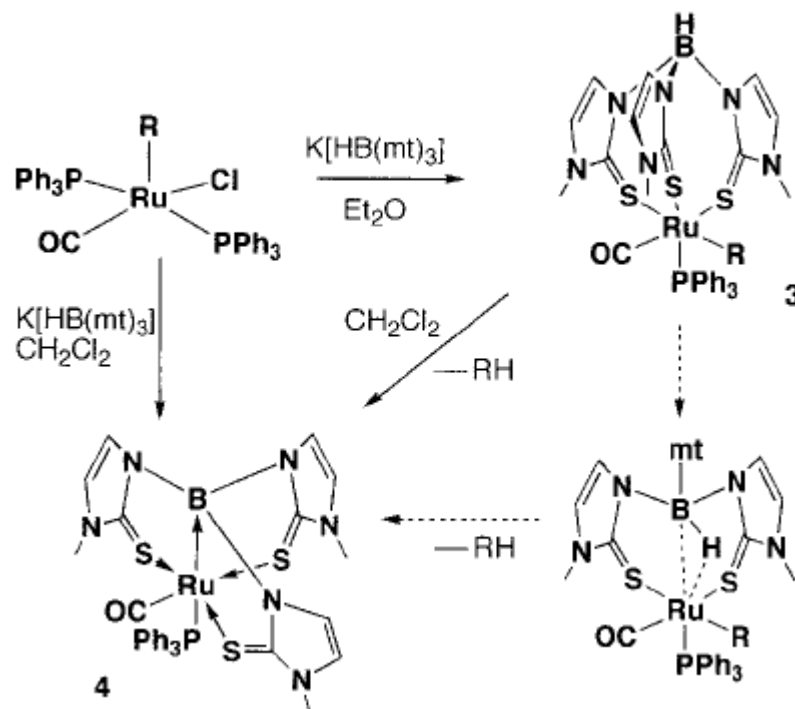


Burlitch, J.M. *et al Inorg. Chem.* **1979**, 18, 1702.

2. Metal complexes

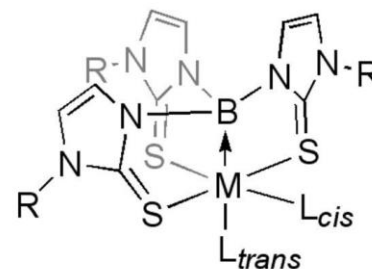
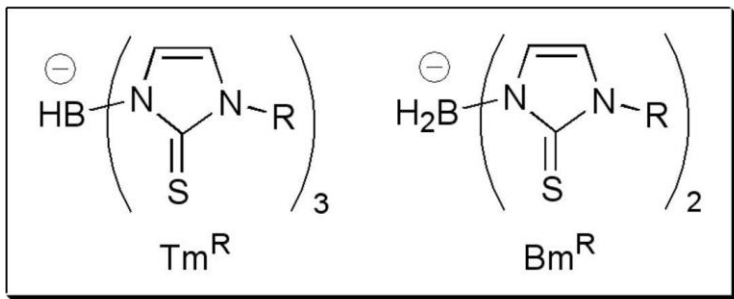
- 2.1. Historical view

Until 1999, Hill's group reported the first metal-borane complex.



Hill, A.F. *et al* *Angew. Chem. Int. Ed.* **1999**, 38, 2759.

2. Metal complexes



$[(\kappa^3\text{-Tm}^t\text{Bu})\text{Fe}(\text{CH}_2\text{SiMe}_3)]$

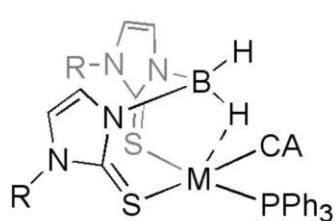
$[\text{MCl}(\text{R}')(\text{CA})(\text{PPh}_3)_2]$

| M | A | R' | M | R | L _{cis} | L _{trans} | |
|---|---|----|-------------|----|------------------|--------------------|-------------------|
| | | | 2.1a | Fe | <i>t</i> Bu | CO | CO |
| | | | 2.1b | Ru | Me | CO | PPh ₃ |
| | | | 2.1c | Ru | Me | CO | CO |
| | | | 2.1d | Ru | Me | CO | CN <i>t</i> Bu |
| | | | 2.1e | Ru | Me | CO | CNXyl |
| | | | 2.1f | Ru | Me | CO | CNMe _s |
| | | | 2.1g | Ru | Me | CS | PPh ₃ |
| | | | 2.1h | Os | Me | CO | PPh ₃ |

Reaction conditions: (i) excess CO; (ii) K[Tm^{Me}], CH₂Cl₂; (iii) Na[Tm^{Me}]; (iv) Na[Tm^{Me}]; (v) PPh₃; (vi) excess CO; (vii) CNTBu; (viii) CNXyl; (ix) CNMe_s.

(i) excess CO; (ii) K[Tm^{Me}], CH₂Cl₂; (iii) Na[Tm^{Me}]; (iv) Na[Tm^{Me}]; (v) PPh₃; (vi) excess CO; (vii) CNTBu; (viii) CNXyl; (ix) CNMe_s.

2. Metal complexes



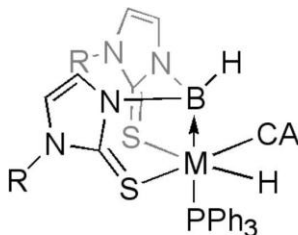
| | M | A | R |
|--------------|----|---|----|
| 2.2a | Rh | O | Me |
| 2.2b* | Rh | S | Me |
| 2.2c* | Ir | O | Me |

↑
i



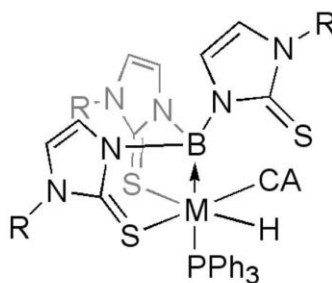
| M | A |
|----|---|
| Rh | O |
| Rh | S |
| Ir | O |

→
ii



| | M | A | R |
|--------------|----|---|----|
| 2.3a* | Rh | O | Me |
| 2.3b* | Rh | S | Me |
| 2.3c | Ir | O | Me |

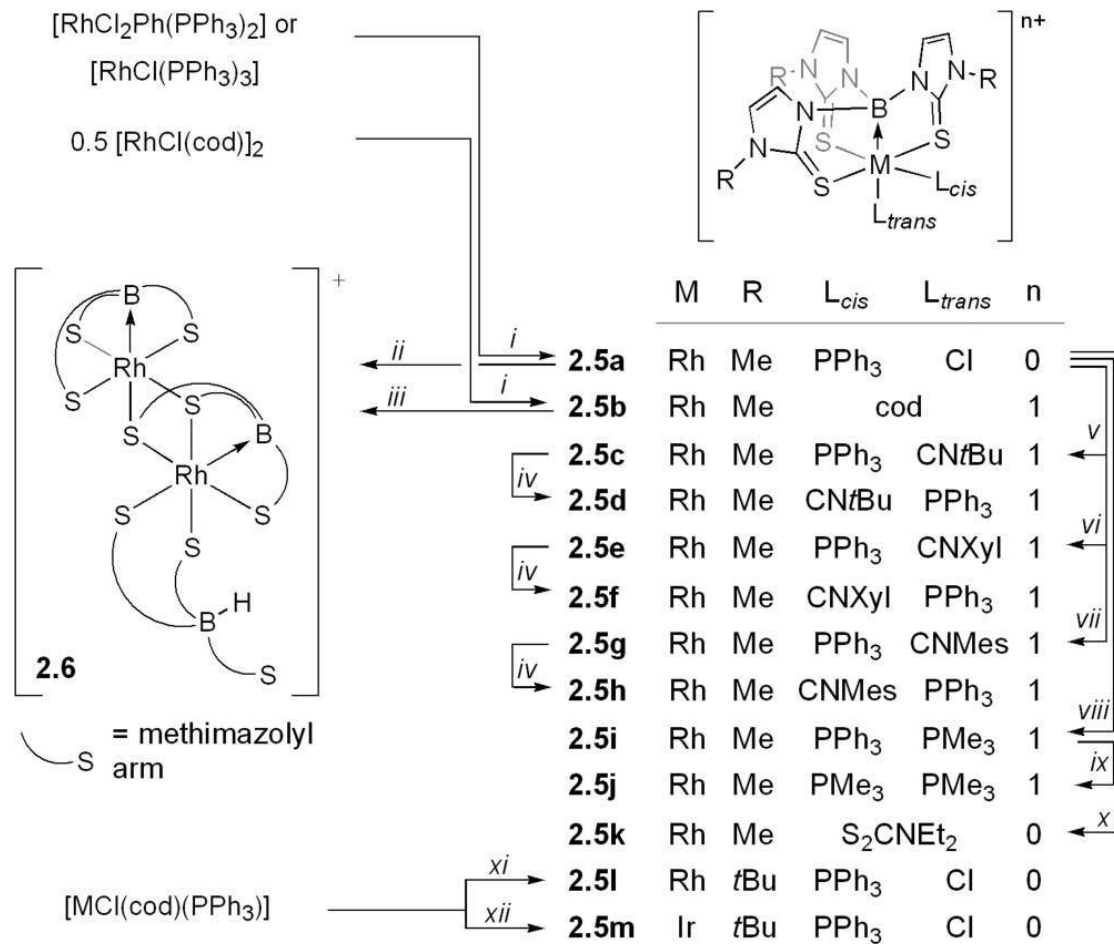
→
iii



| | M | A | R |
|-------------|----|---|-------------|
| 2.4a | Ir | O | Me |
| 2.4b | Ir | O | <i>t</i> Bu |
| 2.4c | Ir | O | Ph |

(i) Na[Bm^{Me}]; (ii) room temperature; (iii) Na[Tm^{Me}]/K[Tm^{*t*Bu}]/Tl[Tm^{*t*Bu}]/Li[Tm^{Ph}]. An asterisk denotes complexes that were detected but not isolated.

2. Metal complexes



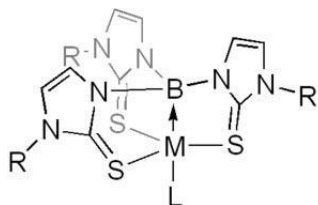
(i) $\text{Na}[\text{Tm}^{\text{Me}}]$; (ii) room temperature; (iii) $\text{Na}[\text{Tm}^{\text{Me}}]$; (iv) refluxing $\text{CH}_2\text{Cl}_2/\text{ethanol}$ (20:1);
 (v) CN*t*Bu; (vi) CNXyl; (vii) CN*Mes*; (viii) PMe_3 ; (ix) excess PMe_3 , refluxing
 $\text{CH}_2\text{Cl}_2/\text{THF}$ (10:1); (x) $\text{Na}[\text{S}_2\text{CNEt}_2]$; (xi) M) Rh, $\text{K}[\text{Tm}^{\text{tBu}}]$; (xii) M) Ir, $\text{K}[\text{Tm}^{\text{tBu}}]$

Braunschweig, H. *et al Chem. Rev.* **2010**, *110*, 3924.

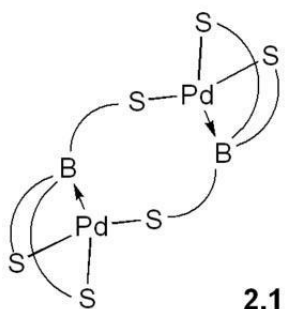
2. Metal complexes



ii ↓



| | M | R | L | |
|-----------------------|----|-------------|------------------|---------------|
| $[\text{NiCl}_2]$ → i | Ni | <i>t</i> Bu | Cl | iv v vi |
| | Ni | <i>t</i> Bu | OAc | |
| | Ni | <i>t</i> Bu | SCN | |
| | Ni | <i>t</i> Bu | N ₃ | |
| iii → | Pd | <i>t</i> Bu | PMe ₃ | |
| | Pt | Me | PPh ₃ | |



2.11

— S —
= methimazolyl arm

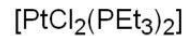
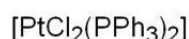
(i) K[Tm^{*t*Bu}]; (ii) K[Tm^{*t*Bu}]; (iii) PMe₃; (iv) Tl[OAc]; (v) K[SCN]; (vi) Na[N₃]; (vii) DBU; (viii) HCl; (ix) Na[Tm^{Me}]; (x) Na[Tm^{Me}]; (xi) room temperature; (xii) Cl₂; (xiii) Br₂; (xiv) I₂; (xv) MeI.

iii →

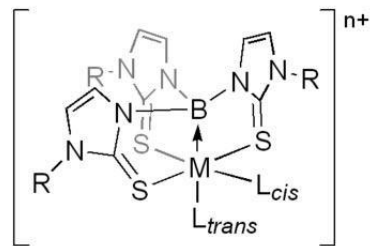
viii

vii

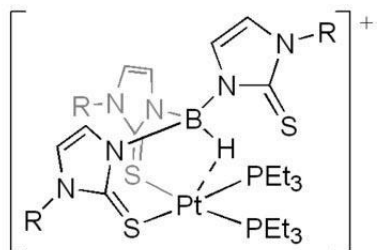
ix



x ↓



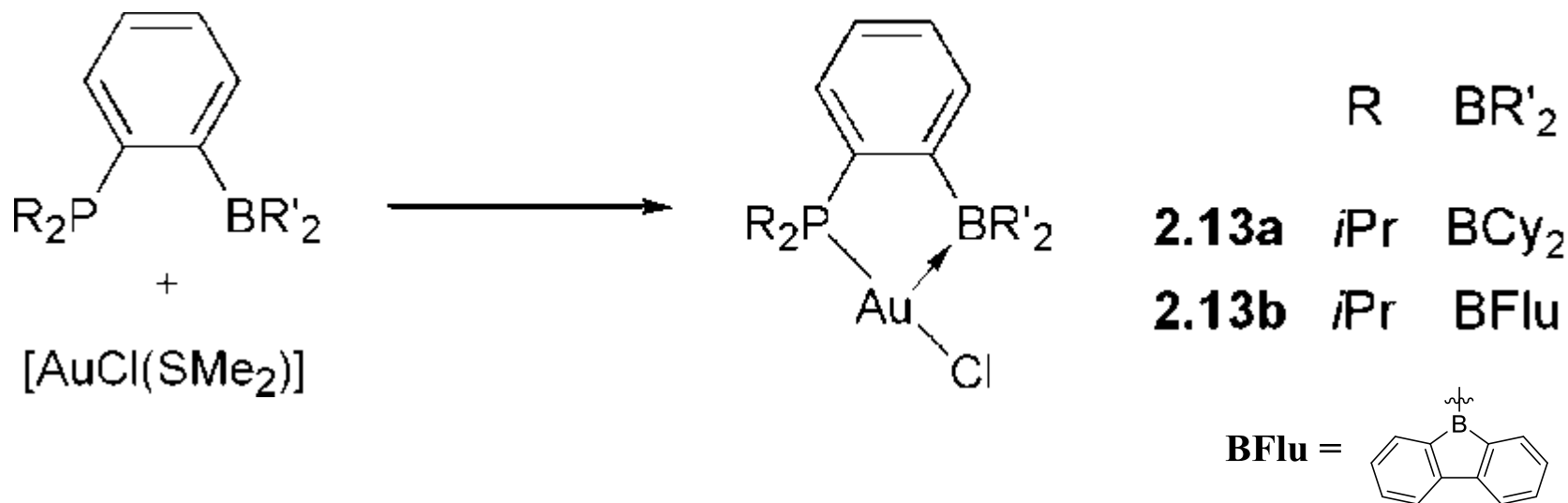
| | M | R | L _{cis} | L _{trans} | n | |
|--------|----|----|------------------|--------------------|---|--------------------------|
| viii → | Pt | Me | H | PPh ₃ | 1 | xii xiii xiv xv |
| vii → | Pt | Me | Cl | Cl | 0 | |
| | Pt | Me | Br | Br | 0 | |
| | Pt | Me | I | I | 0 | |
| | Pt | Me | Me | I | 0 | |
| xi → | Pt | Me | H | PEt ₃ | 1 | |



2.12

Chemical Reviews **2010**, *110*, 3924.

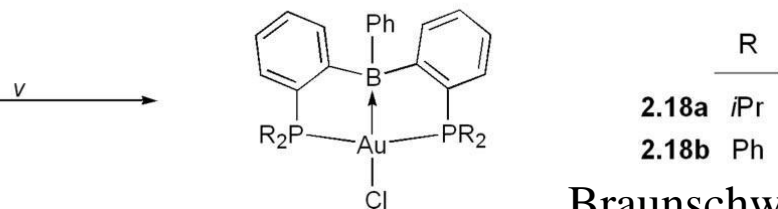
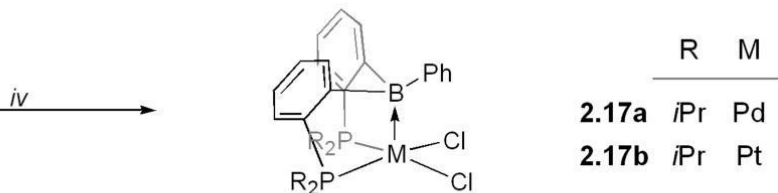
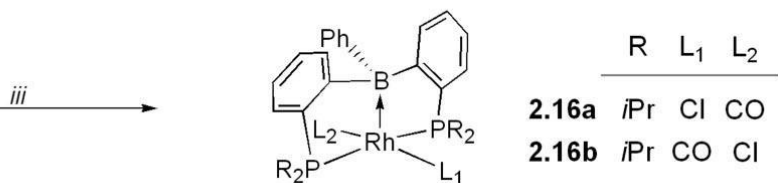
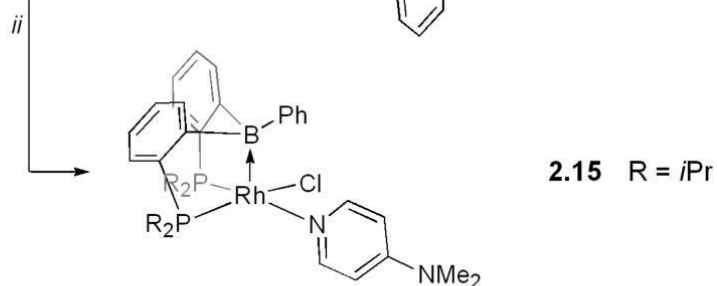
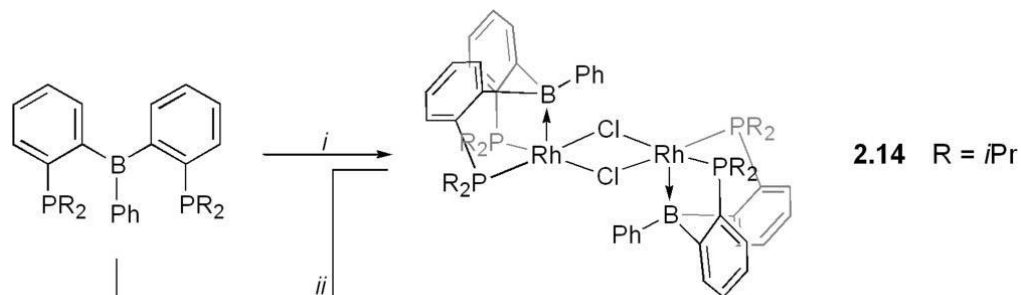
2. Metal complexes



| | ¹¹ B NMR | | Au-B bond distance |
|--------------|---------------------|----------|--------------------|
| | Ligand | Complex | |
| 2.13a | 75.6 ppm | 80.1 ppm | 2.90 |
| 2.13b | 64.5 ppm | 55.2 ppm | 2.663(8) |

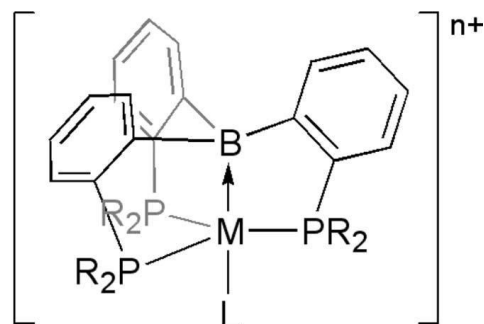
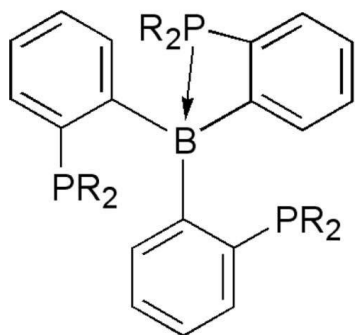
Bontemps, S. *et al* *J. Am. Chem. Soc.* **2006**, 128, 12056.

2. Metal complexes



- (i) $[\text{RhCl}(\text{NBD})]_2$ (0.5 equiv);
 (ii) DMAP;
 (iii) $[\text{RhCl}(\text{CO})_2]_2$ (0.5 equiv);
 (iv) $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$);
 (v) $[\text{AuCl}(\text{SMe}_2)]$.

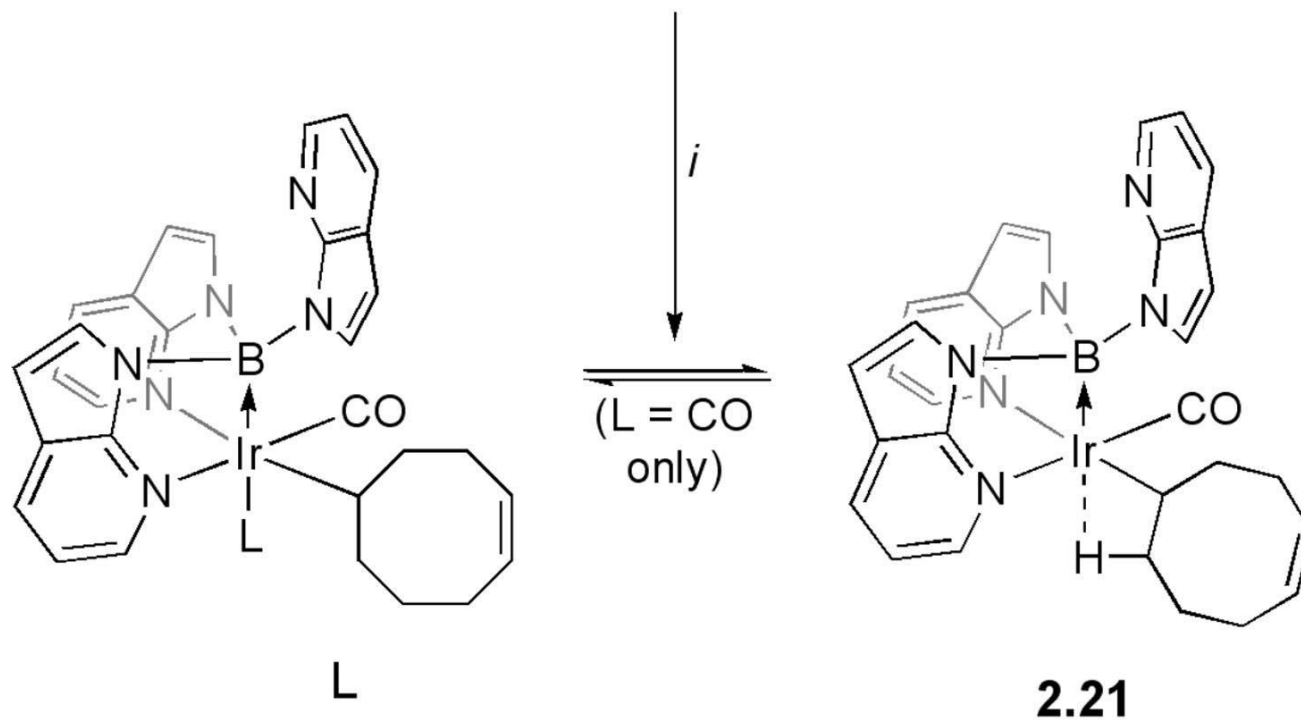
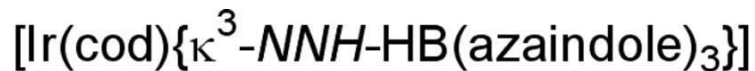
2. Metal complexes



| | M | R | L | n | |
|--------------|--------------|----|-------------|----|---|
| <i>i</i> → | 2.19a | Ni | <i>i</i> Pr | - | 0 |
| <i>ii</i> → | 2.19b | Pd | <i>i</i> Pr | - | 0 |
| <i>iii</i> → | 2.19c | Pt | <i>i</i> Pr | - | 0 |
| <i>iv</i> → | 2.19d | Cu | <i>i</i> Pr | Cl | 0 |
| <i>v</i> → | 2.19e | Ag | <i>i</i> Pr | Cl | 0 |
| <i>vi</i> → | 2.19f | Au | <i>i</i> Pr | Cl | 0 |
| <i>vii</i> → | 2.19g | Au | <i>i</i> Pr | - | 1 |

(i) [Ni(cod)₂]; (ii) [Pd(*Pt*Bu₃)₂]; (iii) [Pt(*Pt*Bu₃)₂]; (iv) CuCl; (v) AgCl; (vi) [AuCl(SMe₂)]; (vii) GaCl₃.

2. Metal complexes



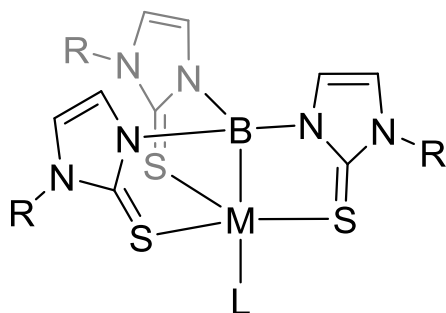
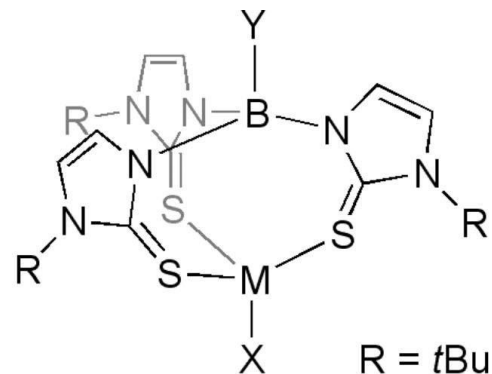
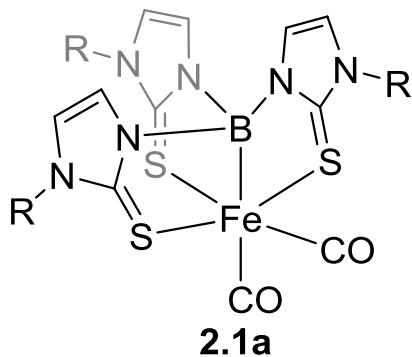
2.20a CO

2.20b CNXyl

2.20c CN*t*Bu

(i) excess CO; (ii) CNXyl; (iii) CN*t*Bu.

2. Metal complexes



| | M | R | L |
|-------------|----|-------------|----------------|
| 2.9a | Ni | <i>t</i> Bu | Cl |
| 2.9c | Ni | <i>t</i> Bu | SCN |
| 2.9d | Ni | <i>t</i> Bu | N ₃ |

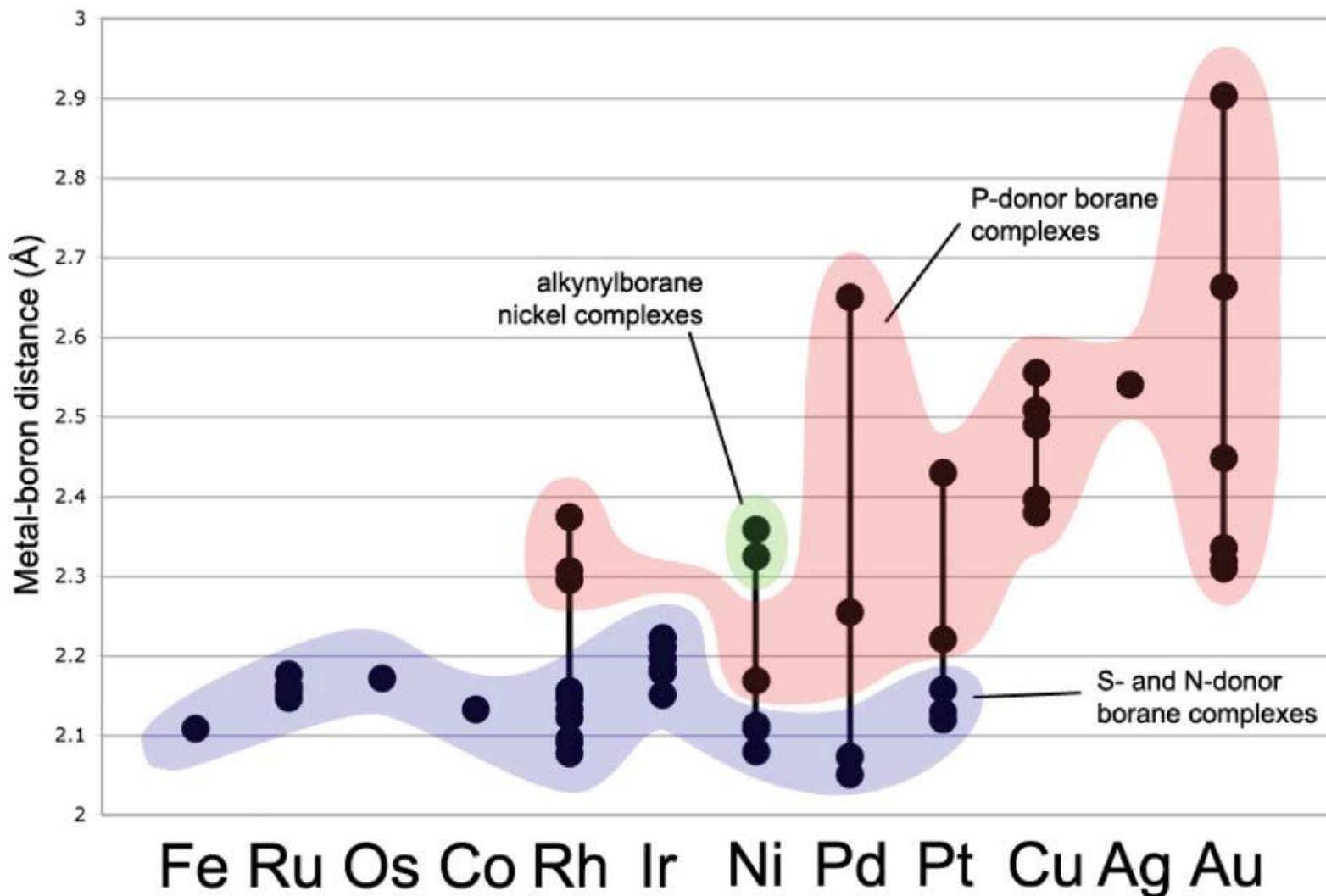
- (i) CHCl₃;
- (ii) CHBr₃;
- (iii) [PhC(O)O]₂;
- (iv) CHCl₃/I₂;
- (v) XeF₂;
- (vi) I₂.

| | | M | X | Y | |
|-------------|------------|--------------|----|--------------------|--------------------|
| 2.1a | <i>i</i> | 2.23a | Fe | Cl | Cl |
| | <i>ii</i> | 2.23b | Fe | Br | Br |
| | <i>iii</i> | 2.23c | Fe | O ₂ CPh | O ₂ CPh |
| | <i>iv</i> | 2.23d | Fe | I | Cl |
| 2.9a | <i>i</i> | 2.23e | Ni | Cl | Cl |
| | <i>ii</i> | 2.23f | Ni | Br | Br |
| | <i>v</i> | 2.23g | Ni | Cl | F |
| | <i>vi</i> | 2.23h | Ni | I | Cl |
| 2.9c | <i>vi</i> | 2.23i | Ni | I | NCS |
| 2.9d | <i>vi</i> | 2.23j | Ni | I | N ₃ |

Braunschweig, H. *et al Chem. Rev.* **2010**, *110*, 3924.

2. Metal complexes

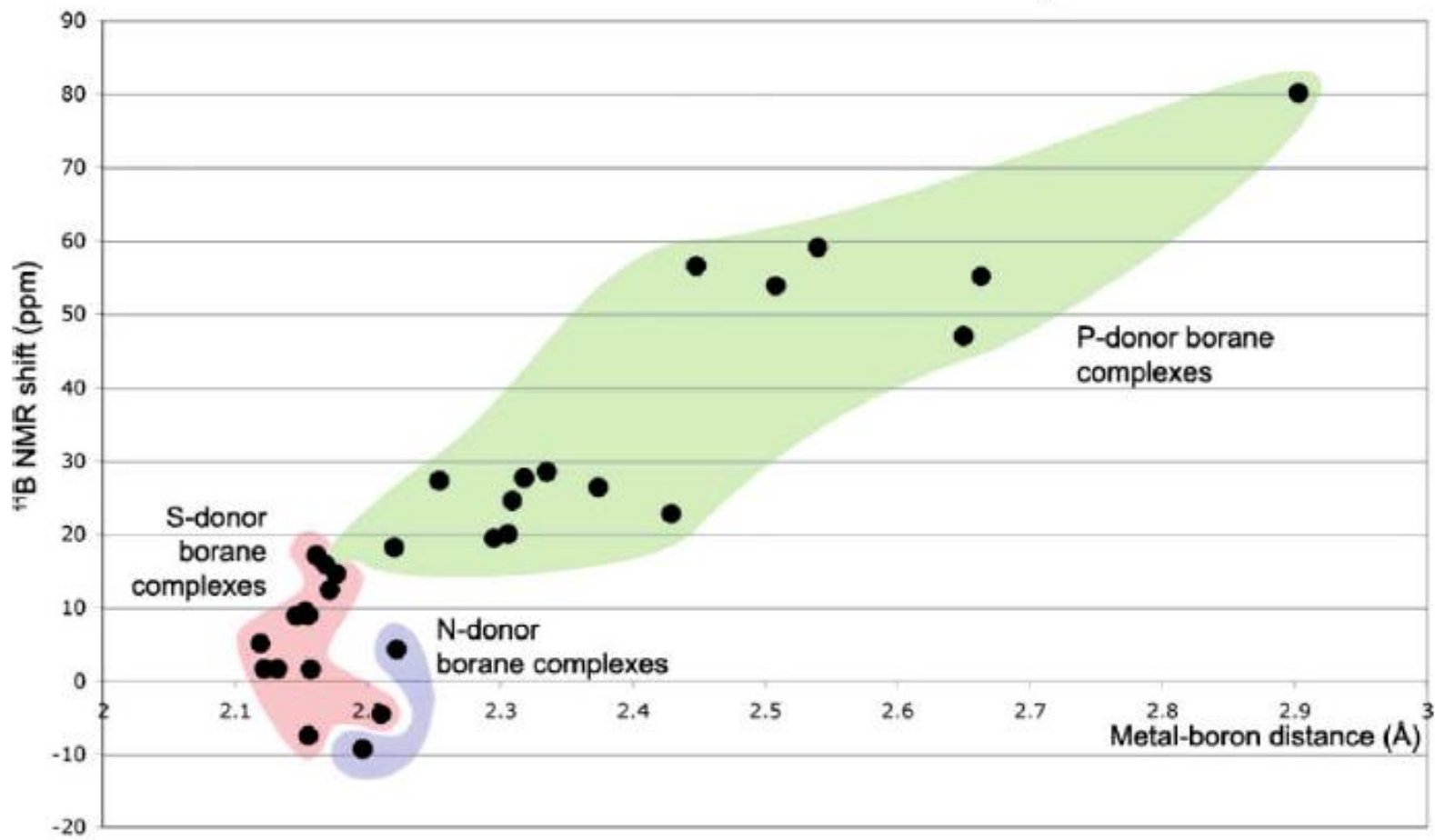
Metal-boron distances in boratrane (borane) complexes



Braunschweig, H.; Dewhurst, R.D. *Dalton Trans.* **2011**, 40, 549.

2. Metal complexes

Metal-boron distance vs. ^{11}B NMR chemical shift in transition metal-borane complexes

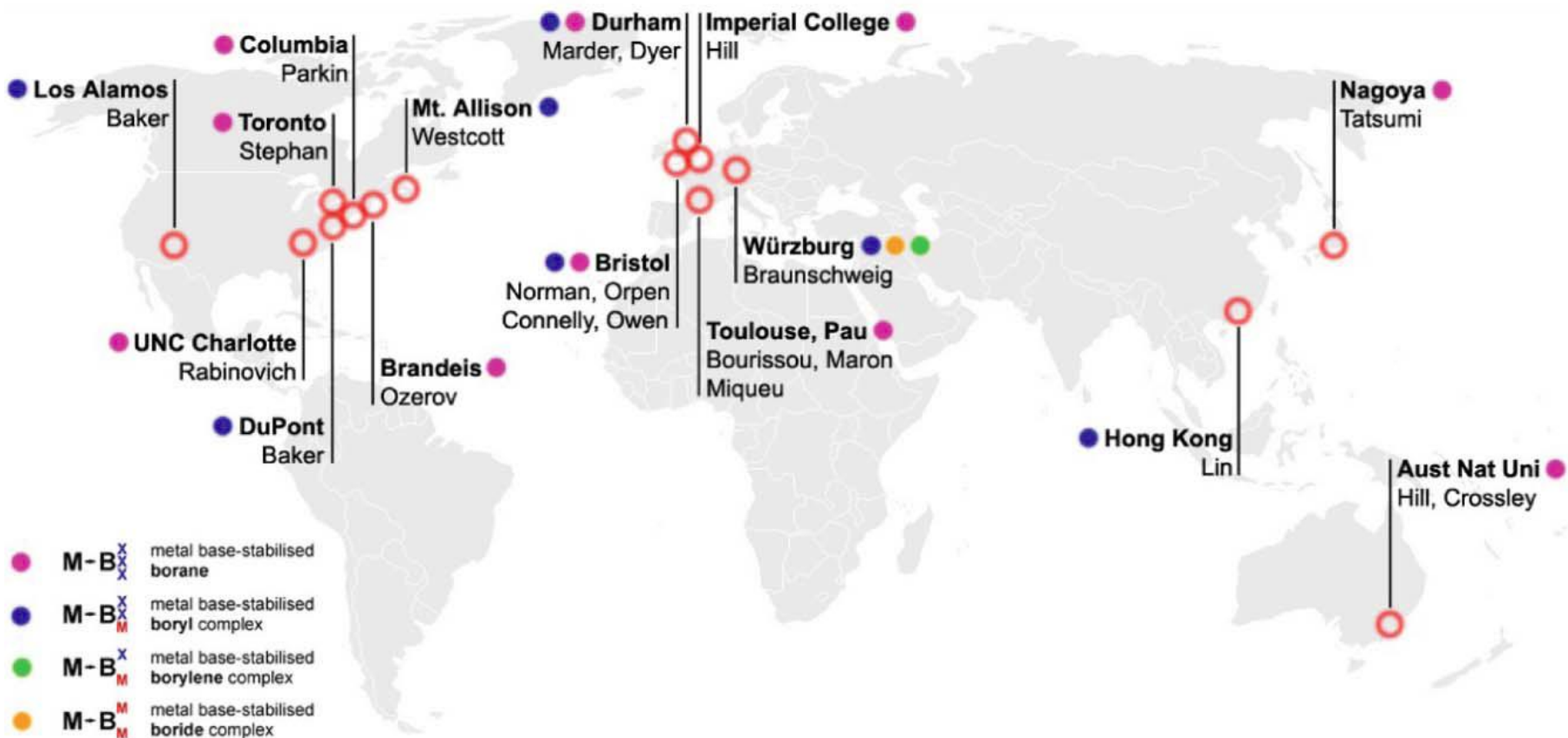


Braunschweig, H.; Dewhurst, R.D. *Dalton Trans.* **2011**, 40, 549.

2. Metal complexes

old

The world of metal-boron dative bonding

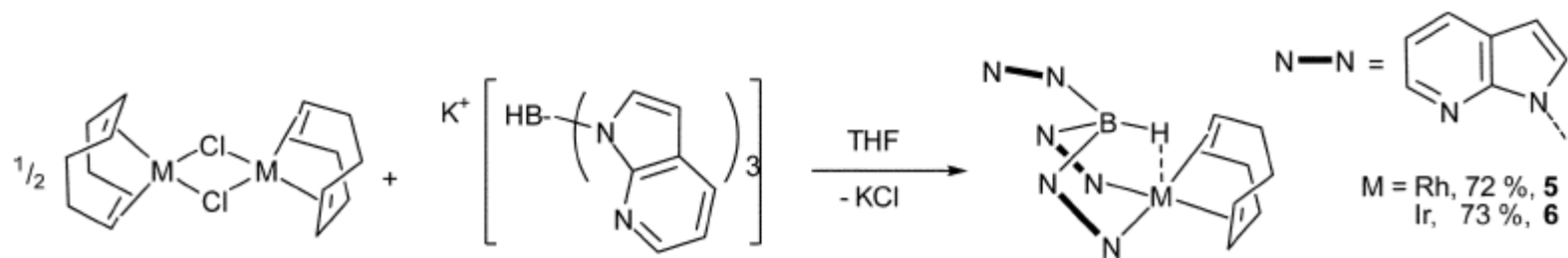


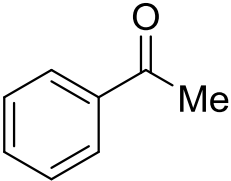
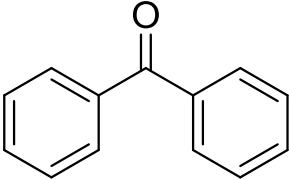
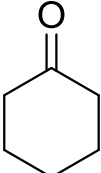
Braunschweig, H.; Dewhurst, R.D. *Dalton Trans.* **2011**, 40, 549.

3. Reaction

- 1. Transfer hydrogenation of ketones
- 2. Hydrogenation of alkenes
- 3. Reduction of nitrogen to ammonia

3. Reactions



| | Run | Complex | Catalyst amount/mol % ^a | Substrate ^b | Conversion (%) ^c | | | TOF ^d |
|---|-----|----------------|------------------------------------|------------------------|-----------------------------|----|-----|------------------|
| | | | | | 1h | 3h | 12h | |
| A:  | 1 | 5 | 0.5 | A | 17 | 45 | 97 | 34 |
| | 2 | 6 | 0.5 | A | 25 | 76 | 98 | 50 |
| | 3 | 5 ^e | 0.5 | A | — | — | 2 | — |
| | 4 | 6 ^e | 0.5 | A | — | — | 2 | — |
| | 5 | 5 | 0.5 | B | 16 | 59 | >99 | 32 |
| B:  | 6 | 6 | 0.5 | B | 12 | 47 | >99 | 24 |
| | 7 | 5 | 0.5 | C | 87 | 99 | >99 | 174 |
| | 8 | 6 | 0.5 | C | 87 | 95 | >99 | 174 |
| | 9 | 5 | 0.1 | C | 85 | 90 | 95 | 850 |
| C:  | 10 | 6 | 0.1 | C | 87 | 94 | >99 | 870 |
| | 11 | 5 | 0.01 | C | 56 | 87 | >99 | 5600 |
| | 12 | 6 | 0.01 | C | 73 | 89 | >99 | 7300 |

^a 6 mL of 0.2 M KOH in *i*-PrOH, 1.2 mmol of substrate, 83 °C. ^b A—acetophenone, B—benzophenone, C—cyclohexanone. ^c Measured by NMR integration. ^d Calculated between 0–1 h. ^e No KOH added.

3. Reactions

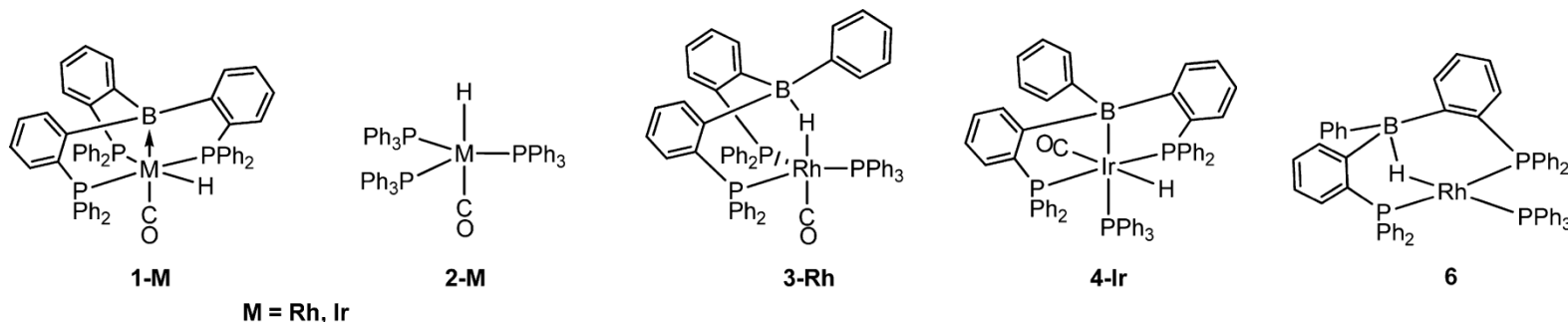
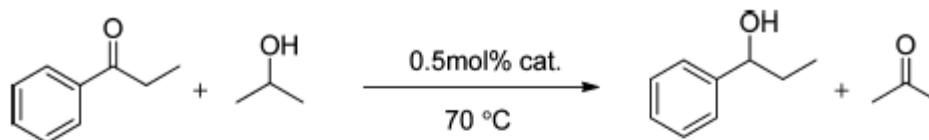


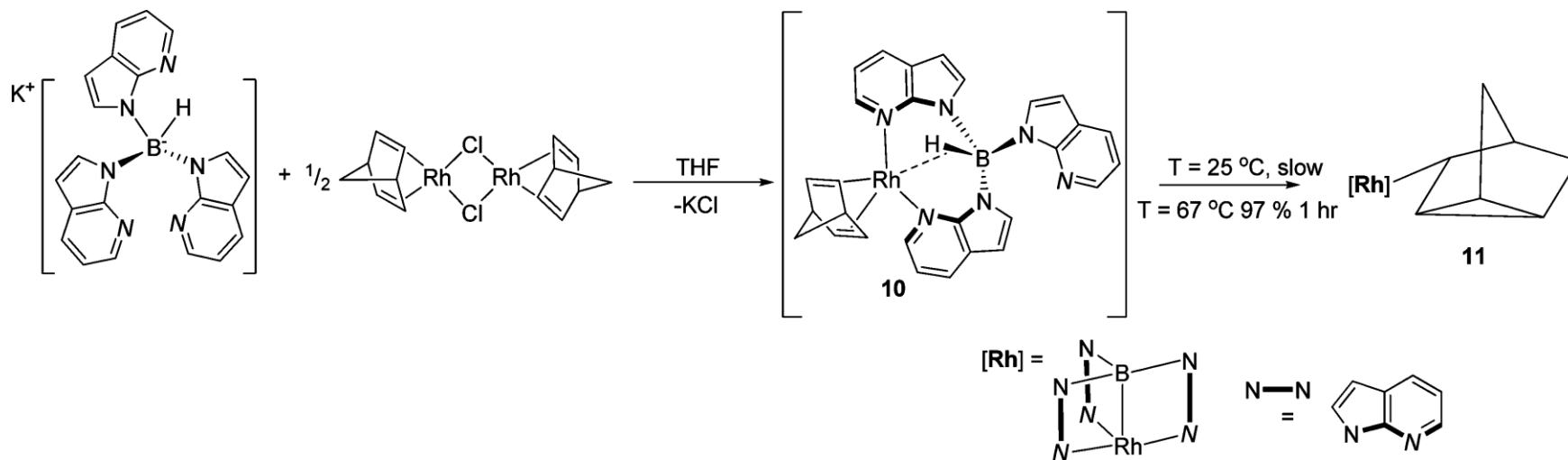
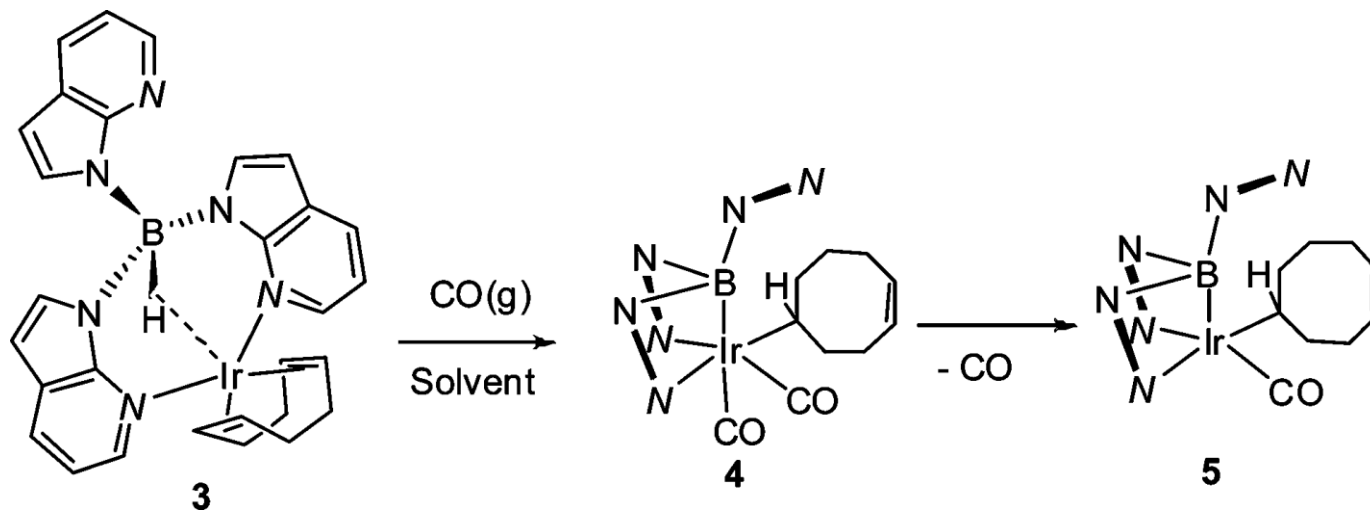
Table 2. Transfer Hydrogenation of Ethyl Phenyl Ketone^a



| entry | cat. | T (°C)/t (h) | yield (%) ^b |
|-------|-------------------|--------------|------------------------|
| 1 | 2-Rh | 70/20 | 29 |
| 2 | 2-Ir | 70/20 | 20 |
| 3 | 3-Rh | 70/20 | 90 |
| 4 | 3-Rh | 70/40 | 99 |
| 5 | 4-Ir | 70/20 | 25 |
| 6 | 1-Rh | 70/20 | 30 |
| 7 | 1-Ir | 70/20 | 0 |
| 8 | 2-Rh ^c | 70/20 | 11 |
| 9 | 6 | 70/20 | 0 |
| 10 | 3-Rh ^d | 70/20 | trace |

^aReaction was carried out with S/C = 200. ^bDetermined by GC analysis. ^c3 equiv of BPh₃ was added. ^d10 equiv of PPh₃ was added.

3. Reactions



3. Reactions

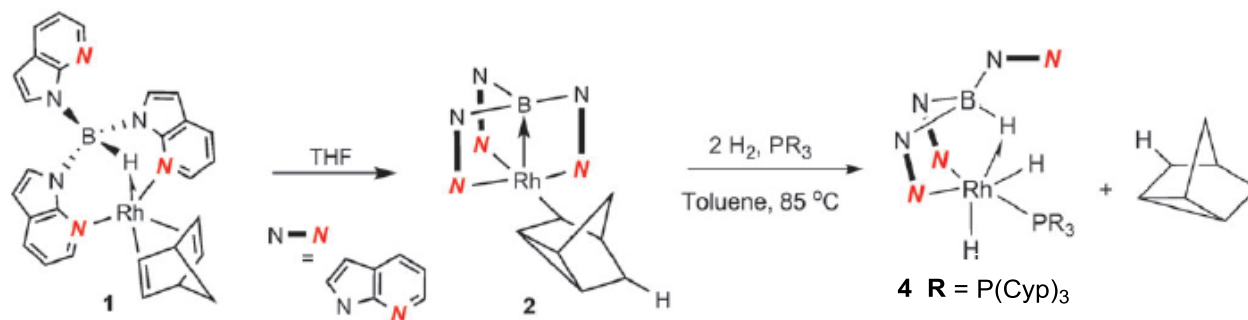


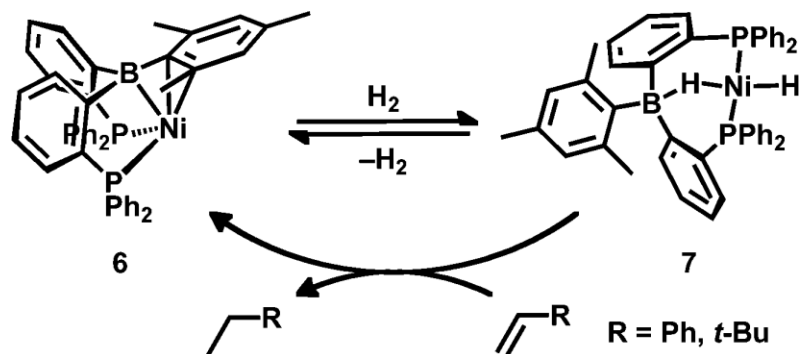
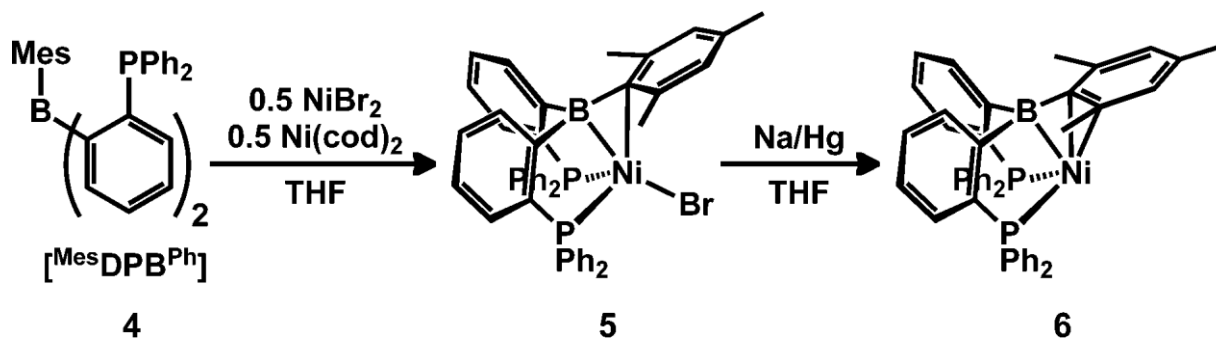
Table 1 Hydrogenation of olefins using complexes **2** and **4**^a

| Complex | Cat. loading (mol%) | Substrate | Conversion ^d (%) |
|----------|---------------------|-------------|-----------------------------|
| 2 | 1.0 ^b | Styrene | >99 |
| 2 | 0.1 ^c | Styrene | 85 |
| 4 | 0.1 ^c | Styrene | 50 |
| 2 | 1.0 ^b | Cyclooctene | >99 |
| 2 | 0.1 ^c | Cyclooctene | 43 |
| 4 | 0.1 ^c | Cyclooctene | 7 |

^a 2.5 bar H₂, 85 °C. ^b 2 mmol of olefin, 0.02 mmol of **2** or **4**, C₆D₆ (2 mL). ^c 7 mmol of olefin, 0.007 mmol of **2** or **4**, C₆D₆ (1 mL).

^d Conversion measured by NMR integration relative to internal standard after 18 h.

3. Reactions



1 mol% catalyst, 1 atm H_2 ,
room temperature, 99% yield

■ ACKNOWLEDGMENTS

This work was supported by the NSF Center for Chemical Innovation: Powering the Planet grant CHE-0802907, and by the Gordon and Betty Moore Foundation. We thank Professor Greg Fu for a helpful suggestion.

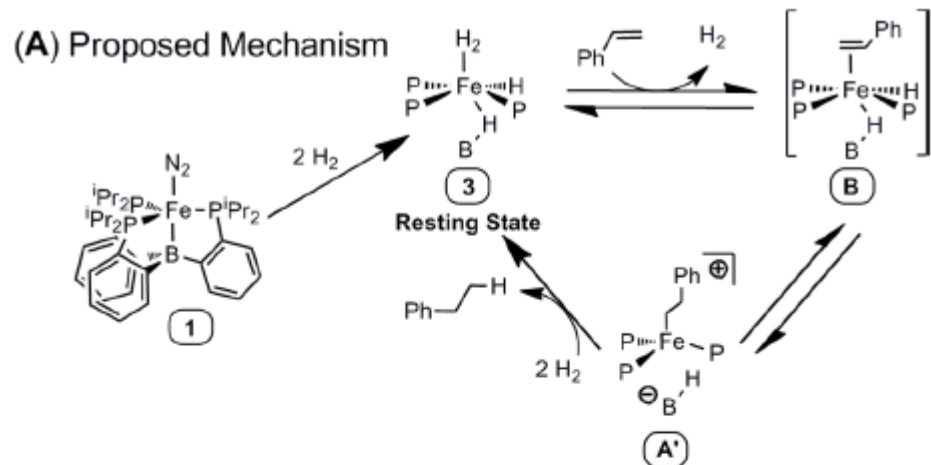
Harman, W.H.; Peters, J.C. *J. Am. Chem. Soc.* **2012**, *134*, 5080.

3. Reactions

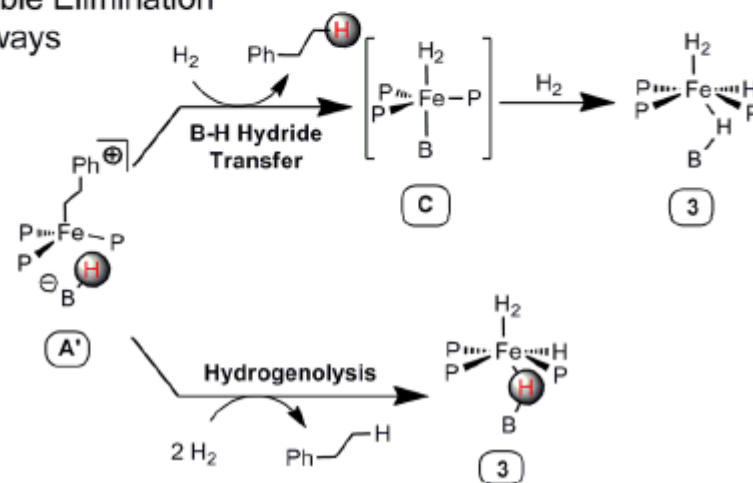
Table 1. Catalytic Hydrogenations by **1** with H₂^a

| precatalyst | substrate | product | TOF (h ⁻¹) ^d |
|-------------|------------------------------|--------------|-------------------------------------|
| 1 | ethylene ^b | ethane | 15 |
| 1 | styrene ^b | ethylbenzene | 0.27 |
| 1 | phenylacetylene ^c | ethylbenzene | 0.16 |

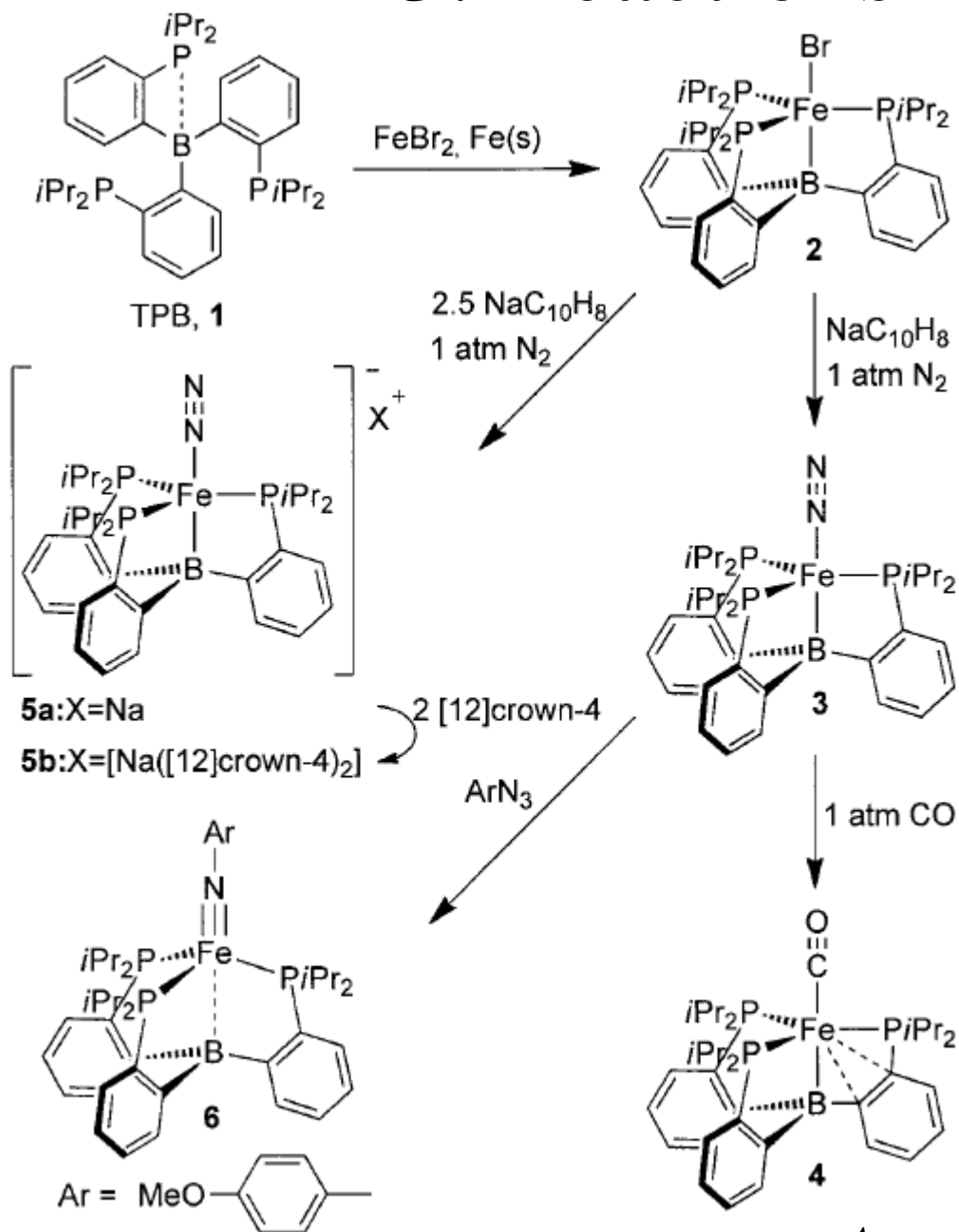
^aConditions: Room temperature, 0.01 M **1**, 1 atm H₂, and 0.01 M ferrocene as an internal integration standard in d₆-benzene. ^b0.3 M substrate. ^c0.29 M substrate. ^dAs determined by ¹H NMR spectroscopy at >95% product.



(B) Possible Elimination Pathways



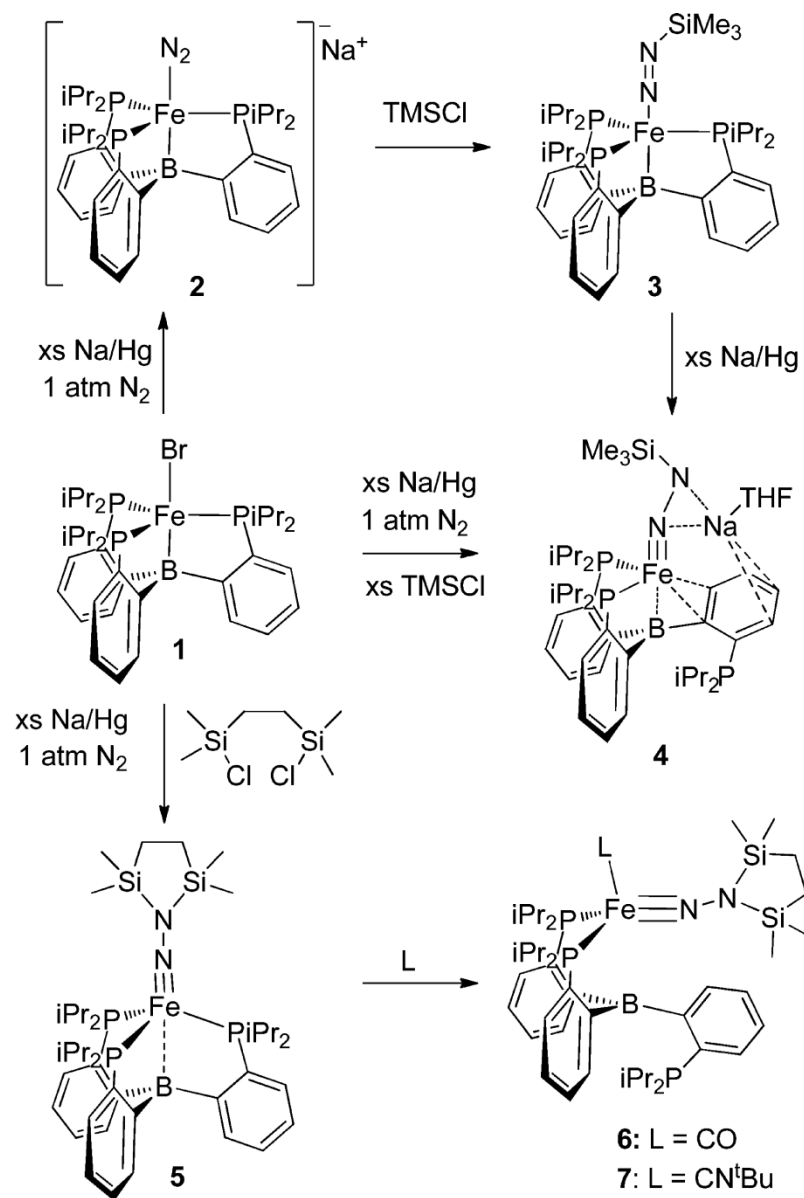
3. Reactions



Moret, M.E.; Peters, J.C.

Angew. Chem. Int. Ed. **2011**, *50*, 2063.

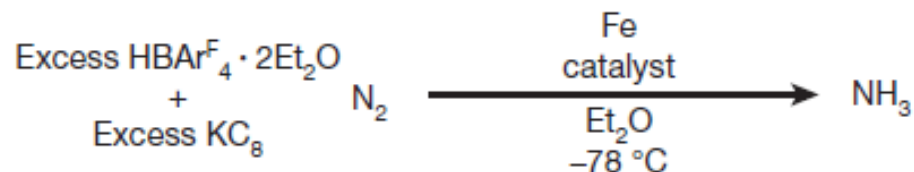
3. Reactions



Moret, M.E.; Peters, J.C. *J. Am. Chem. Soc.* **2011**, *133*, 18118.

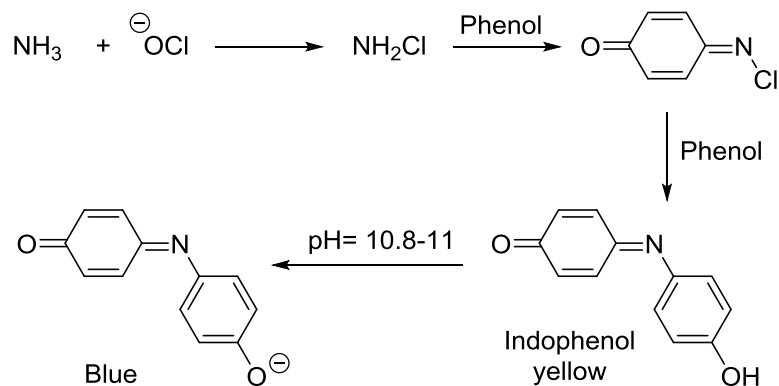
3. Reactions

Table 1 | Ammonia generation from N₂ mediated by Fe precursors

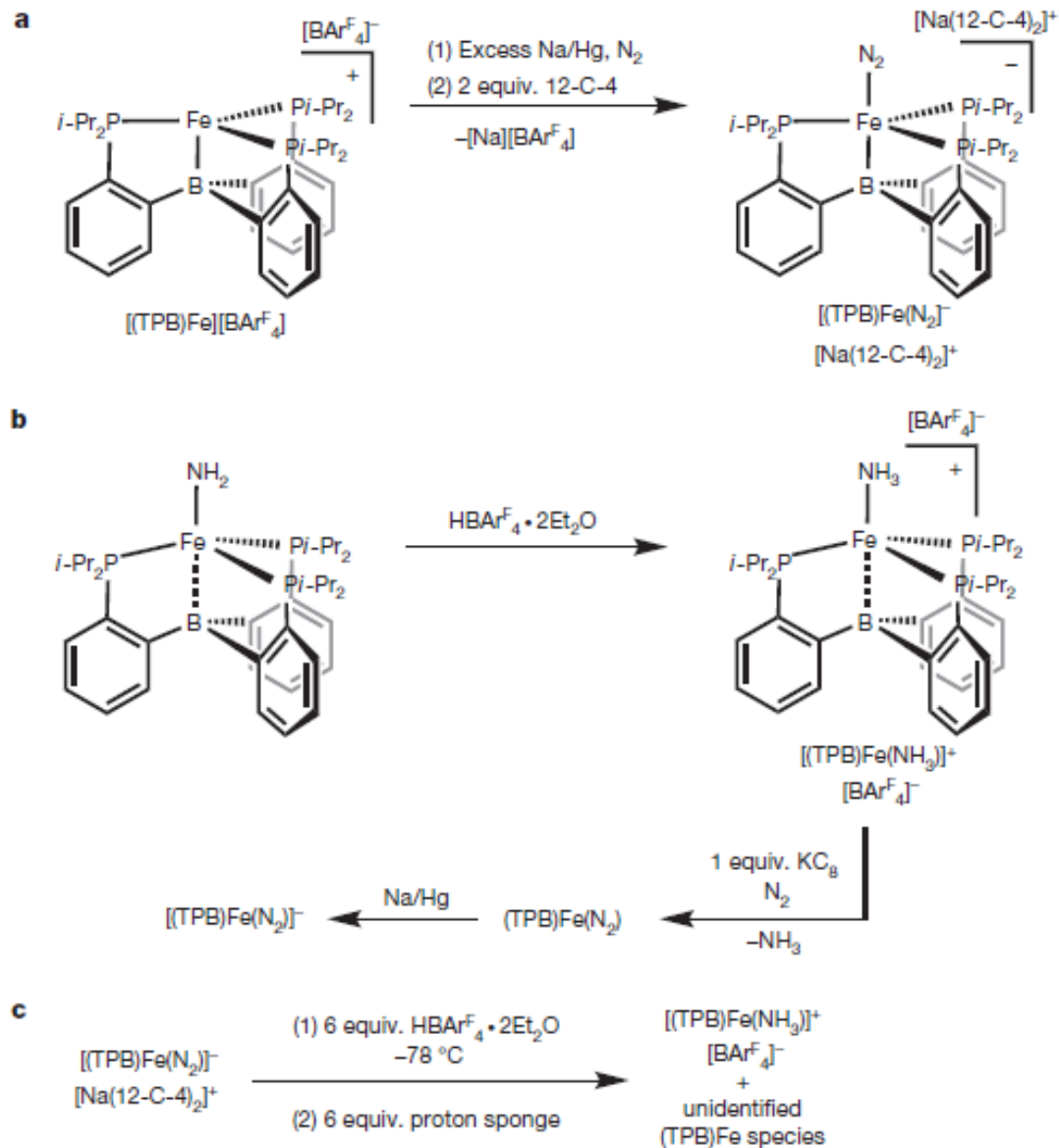


Using standard catalytic conditions as described in the text

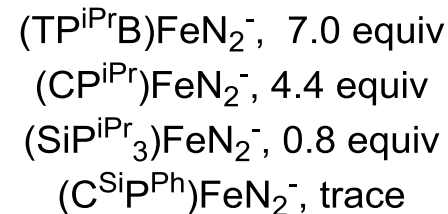
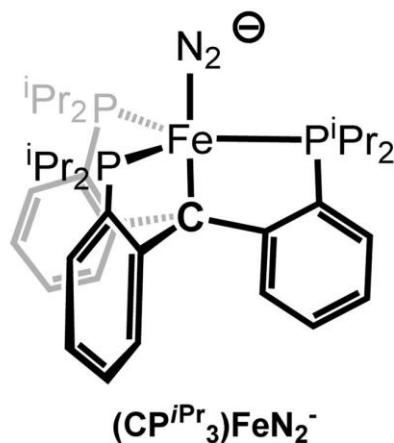
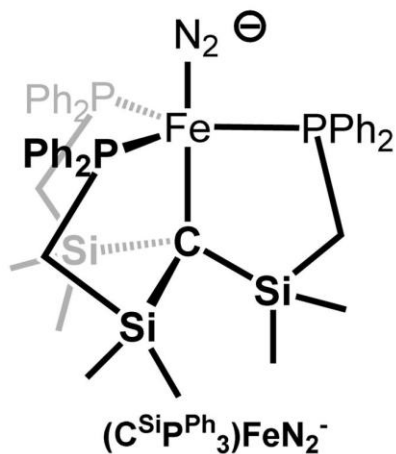
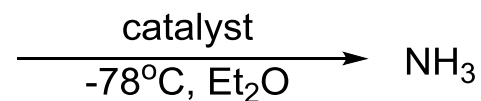
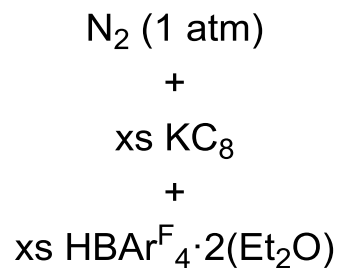
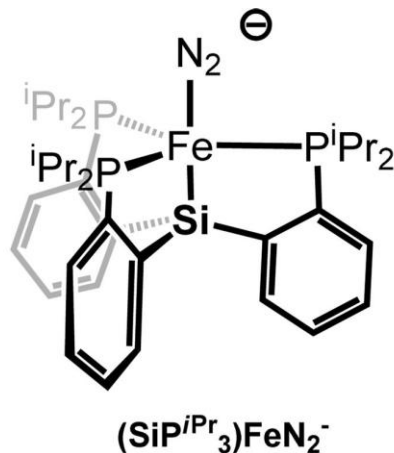
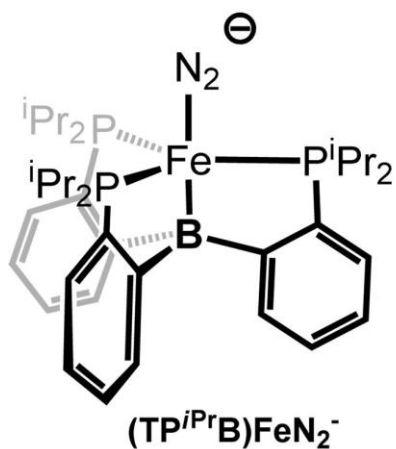
| Entry | Fe precursor | NH ₃ equiv./Fe† |
|-------|---|----------------------------|
| 1 | [(TPB)Fe(N ₂)] [Na(12-crown-4) ₂] | 7.0 ± 1‡ |
| 2 | [(TPB)Fe][BAR ^F ₄] | 6.2 |
| 3 | [(SiP ^{i-Pr} ₃)Fe(N ₂)] [Na(12-crown-4) ₂] | 0.7 |
| 4 | (TPB)(μ-H)Fe(N ₂)(H) | 0.5 |
| 5 | FeCl ₂ · 1.5THF | <0.1 |
| 6 | FeCl ₃ | <0.1 |
| 7 | Cp ₂ Fe | <0.2 |
| 8 | Fe(CO) ₅ | <0.1 |
| 9 | None | <0.1 |



3. Reactions



3. Reactions



4. Brief summary

- 1. This field is re-established in 1999.
- 2. The metal complexes with late TM are reported.
- 3. To my knowledge there are three type catalytic reactions: transfer hydrogenation of ketones, hydrogenation of alkenes and alkynes, and reduction of nitrogen to ammonia.

Thanks!

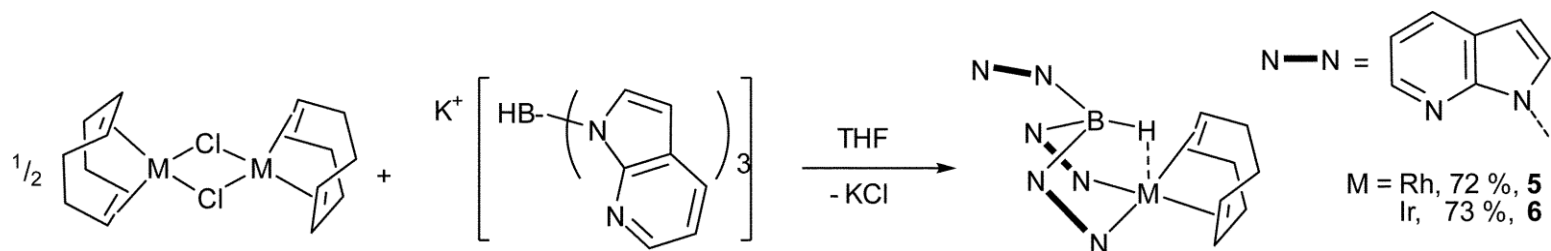
- Be NMR-tube-philic!



Question time!

Question 1

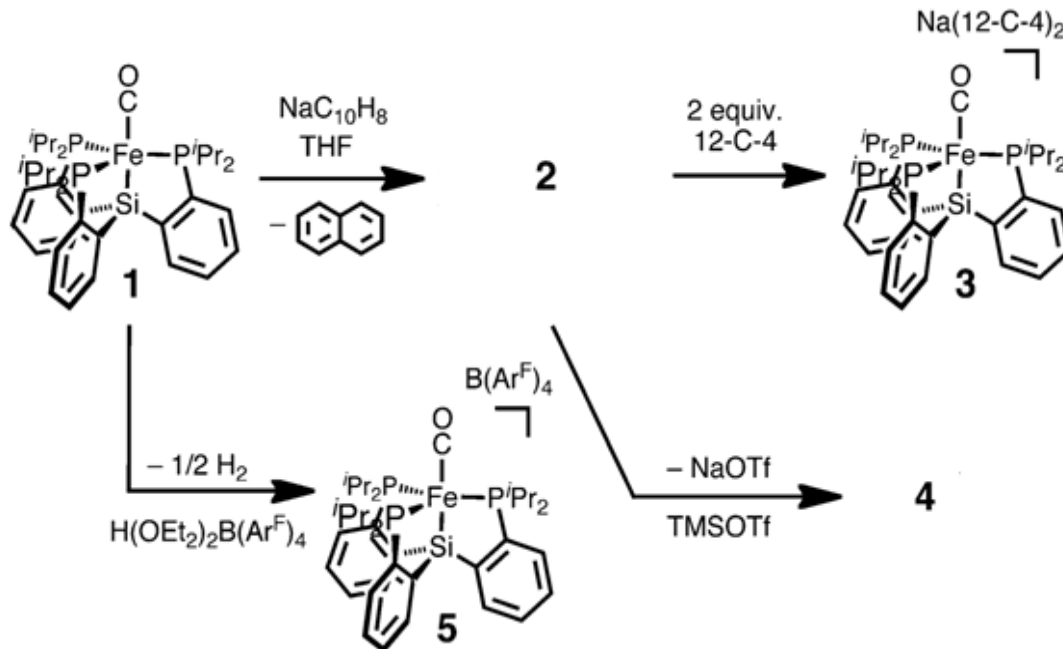
Propose a mechanism for the hydrogenation of ketone with complex **5**:



Question time!

Question 2

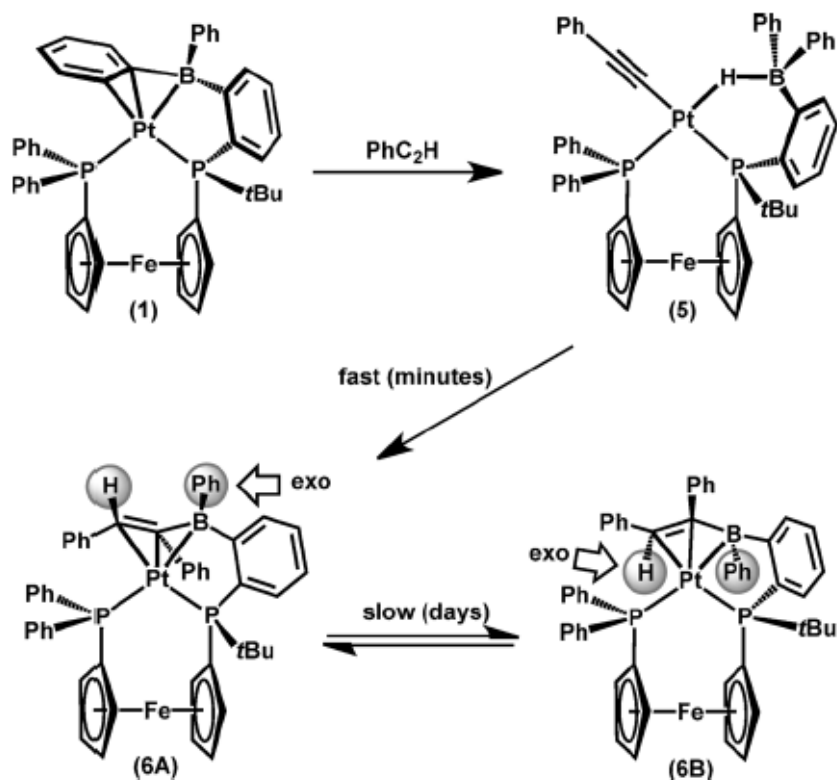
Silicon can also be a Lewis acid, and it has similar effect as boron when coordinate to metal. Complete the following transformation:



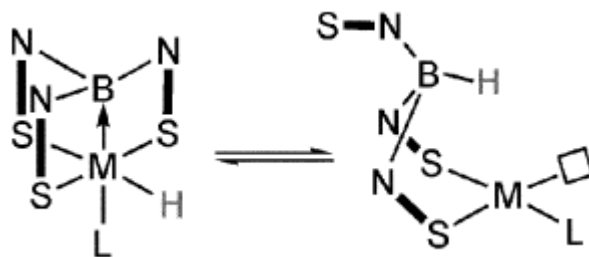
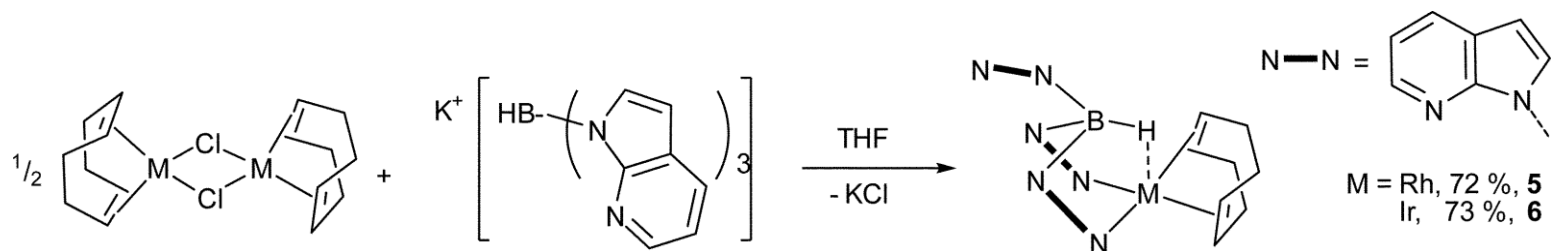
Question time!

Question 3

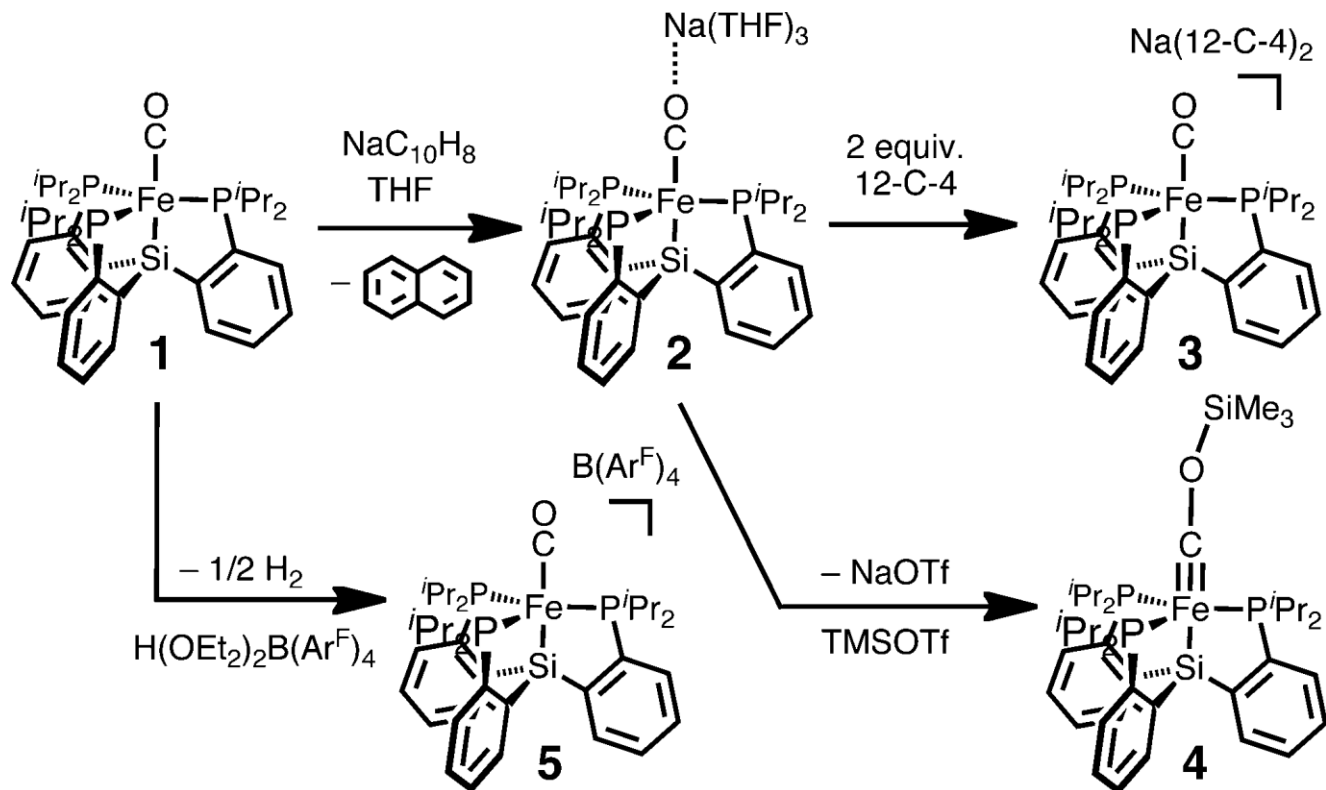
Propose a possible mechanism for the transformation of **5** to **6A**.



Question 1



Question 2



Question 3

