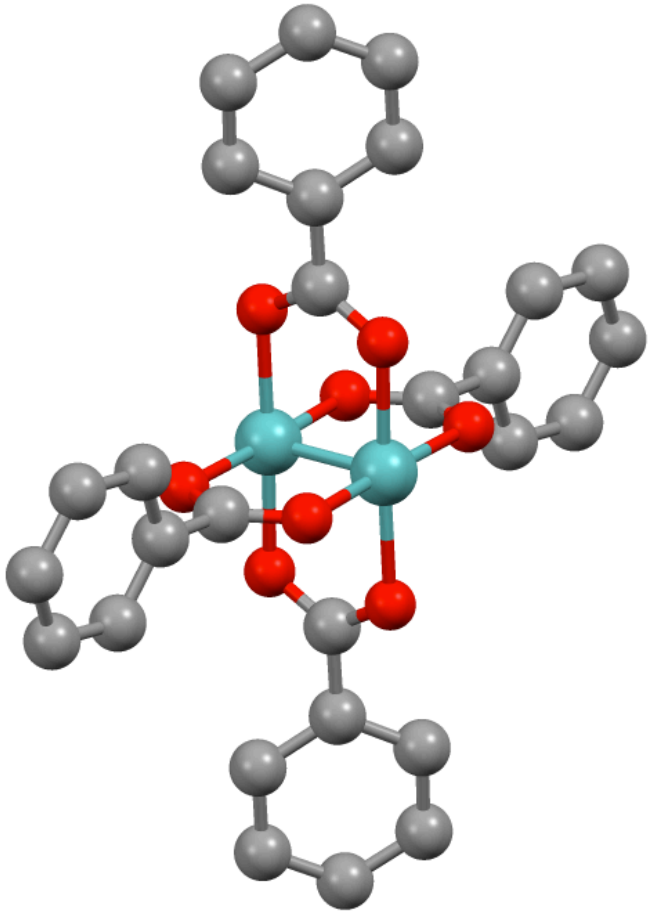
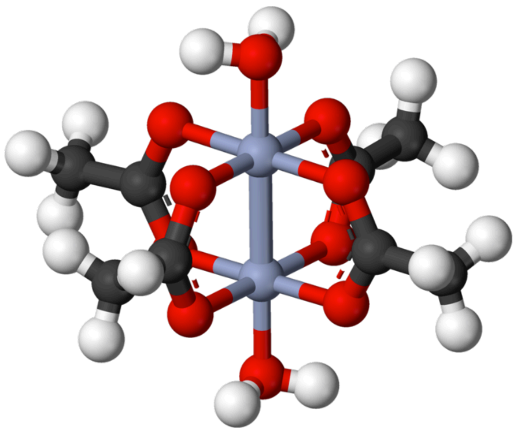
A Brief Survey on Synthesis and Catalytic Reactivity of Metal-Metal Bond Complexes



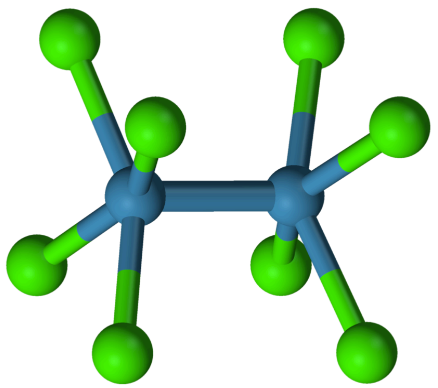
Chi “Chip” Le
MacMillan Research Group
Group Meeting Presentation
April 6th, 2017

Synthesis and Catalytic Reactivity of Metal-Metal Bond Complexes

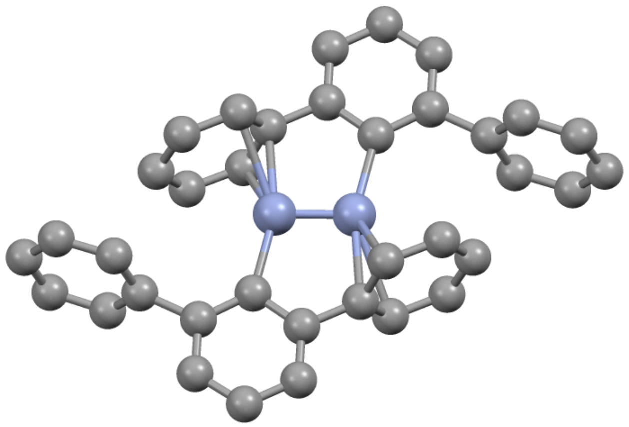
History of the pursuit of the shortest metal-metal bond



$Cr_2(OAc)_4 \bullet 2H_2O$

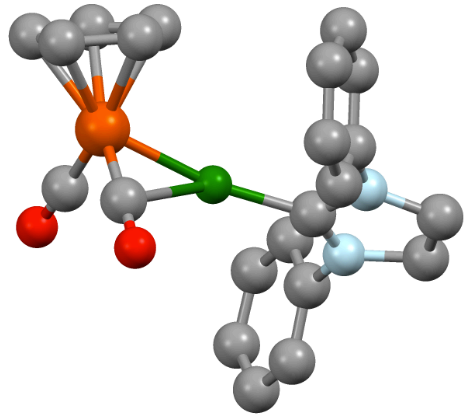


$K_2[Re_2Cl_8]$

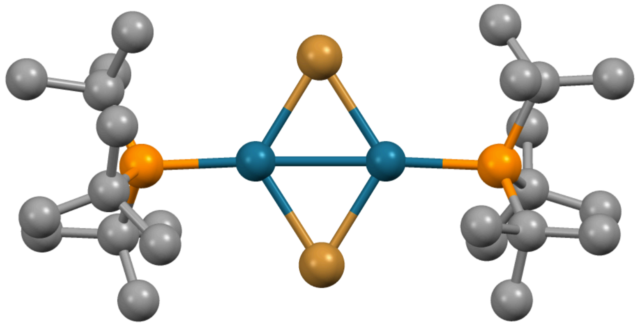


$Cr_2Ar'_2$

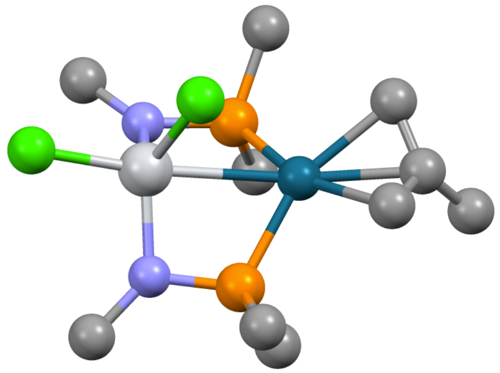
Catalytic reactivity of metal-metal bond complexes



$(NHC)Cu\text{-}FeCp(CO)_2$



$[Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2]$

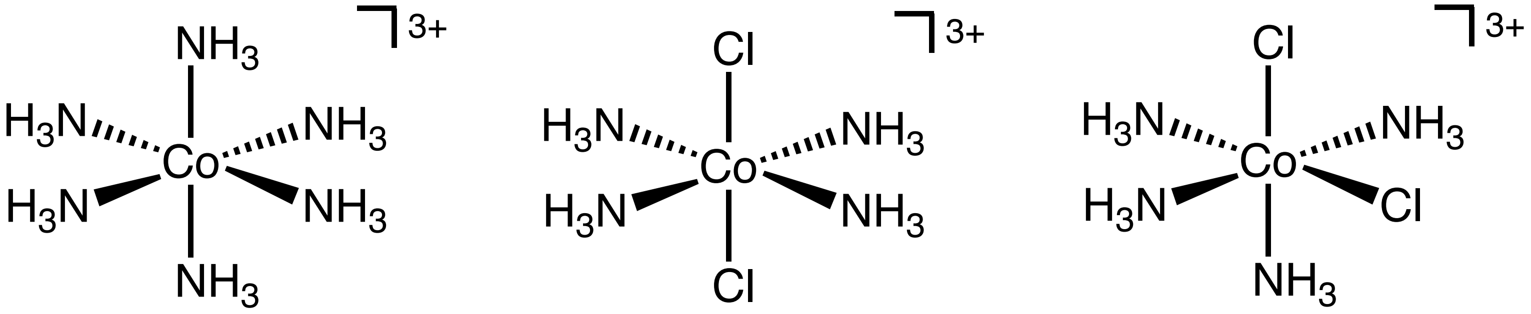


$(\eta^3\text{-methallyl})Pd(PR_3)TiCl_2$

History of the Pursuit of the Shortest Metal-Metal Bond

Alfred Werner

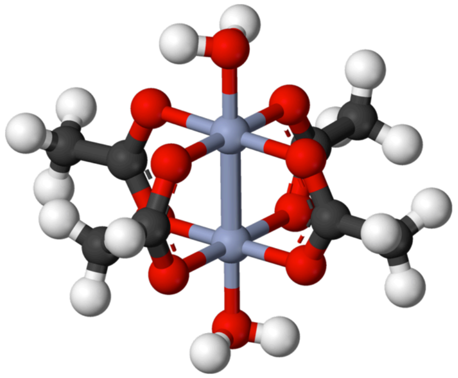
The concept of a single metal ion surrounded by a set of ligands



One-center coordination chemistry (1900)

F. A. Cotton

Multicenter coordination chemistry (1963)



$Cr_2(OAc)_4•2H_2O$

First isolation by Peligot (1844)

⇩

First X-ray by Cotton (1970)

⇩

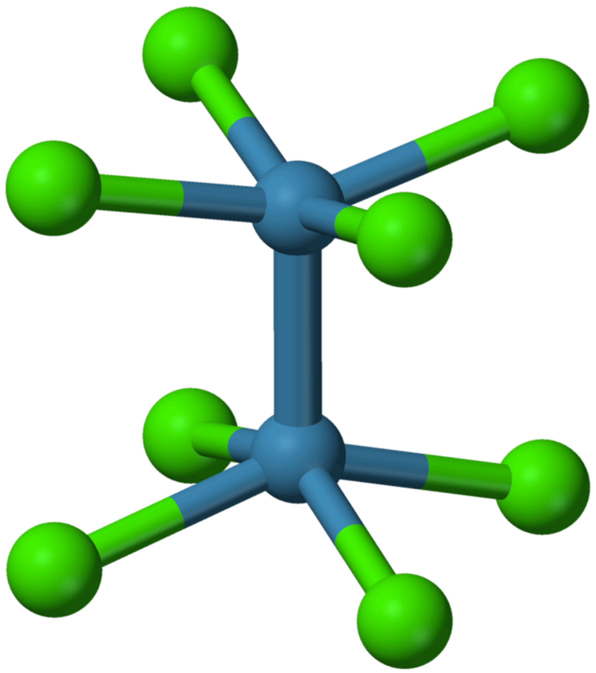
Cr≣Cr ***Quadruple Bond***

History of the Pursuit of the Shortest Metal-Metal Bond

■ Tronev (1952)

■ Cotton (1965)

$$\mathrm{KReO_4} \xrightarrow[\substack{\mathrm{H_2\ (50\ atm)} \\ \mathrm{reflux}}]{\mathrm{HCl\ (conc.)}} \mathrm{K_2[Re_2Cl_8]} \xleftarrow[\substack{\mathrm{H_3PO_2\ (50\%\ aq)} \\ \mathrm{reflux}}]{\mathrm{HCl\ (conc.)}} \mathrm{KReO_4}$$

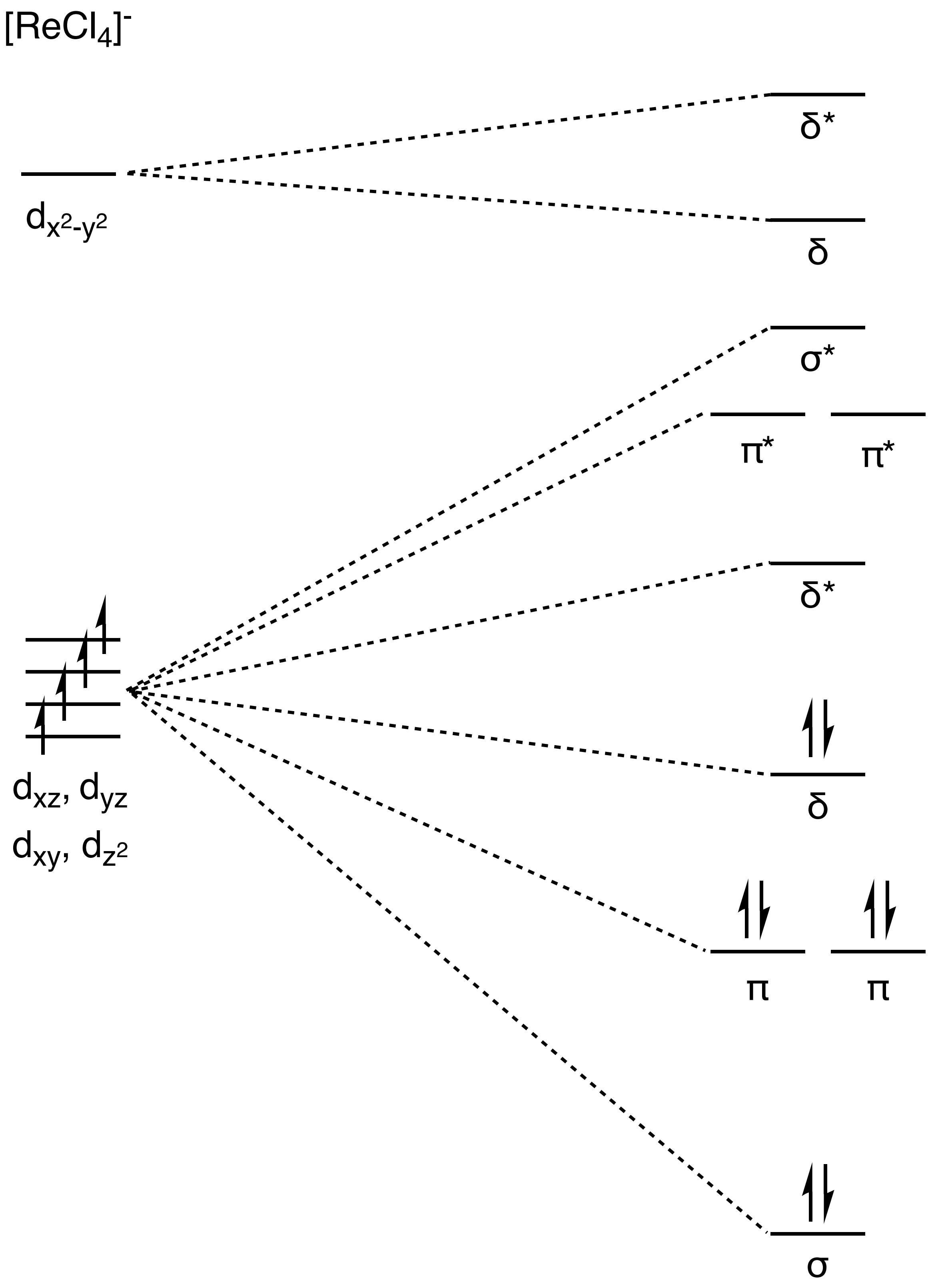


Structure of $[Re_2Cl_8]^{2-}$
as reported by Cotton et al.
(1964 and 1965)

- Re^{3+} diamagnetic compound
- Eclipse conformation of chloride ligands
- Very short Re-Re bond distance of 2.24 Å
- First proposal for a Re≣Re quadruple bond
- Proposed ground state configuration: $\sigma^2\pi^4\delta^2$

Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1965**, *4*, 330.
Cotton, F. A.; Curtis, N. F., Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326.
Cotton, F. A.; Curtis, N. F., Harris, C. B.; Johnson, B. F. G. et al *Science* **1964**, *145*, 1305.
Bondin. S. M.; Tronev, V. G. *Dokl. Akad. Nauk SSSR* **1952**, *86*, 87.
Cotton, F. A.; Murillo, L. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms 3rd edn* (Springer, 2005).

History of the Pursuit of the Shortest Metal-Metal Bond



$[ReCl_4]^-$

$d_{x^2-y^2}$

d_{xz}, d_{yz}

d_{xy}, d_{z^2}

δ^*

δ

σ^*

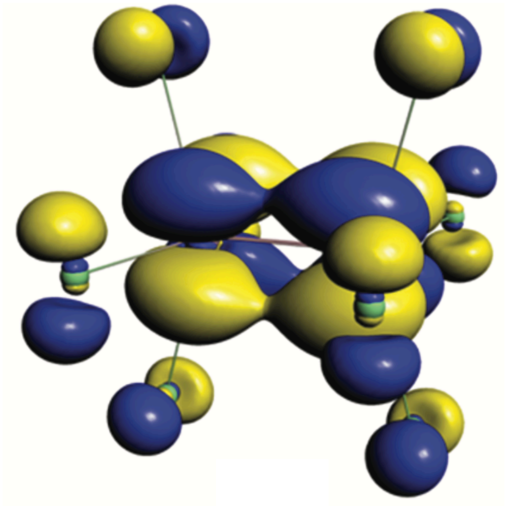
π^* π^*

δ^*

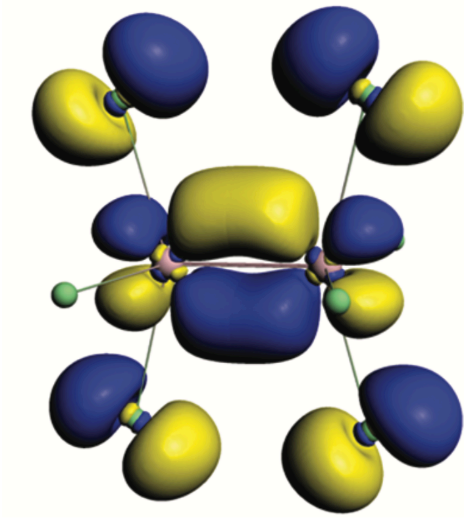
δ

π π

σ

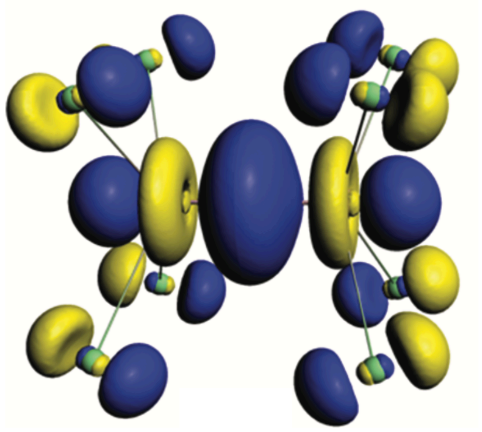


δ ($d_{xy} - d_{xy}$)



π ($d_{xz} - d_{xz}$)

π ($d_{yz} - d_{yz}$)



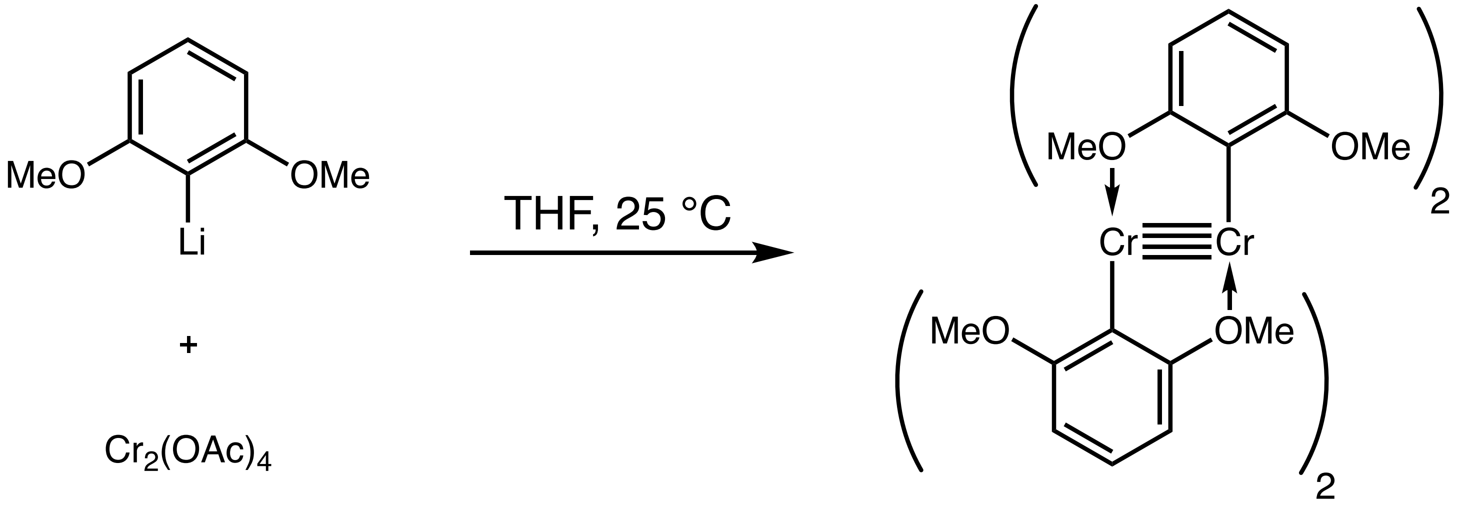
σ ($d_{z^2} - d_{z^2}$)

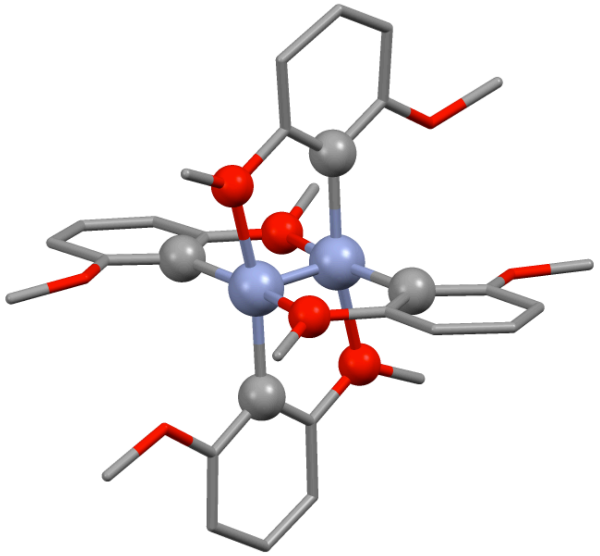
McGrady, J. E. *Molecular Metal-Metal Bonds* (Wiley, 2015).

Blaudeau, J.-P.; Ross, R. B.; Pitzer, R. M.; Mougenot, P.; Bénard, M. J. Phys. Chem. **1994**, *98*, 7123.

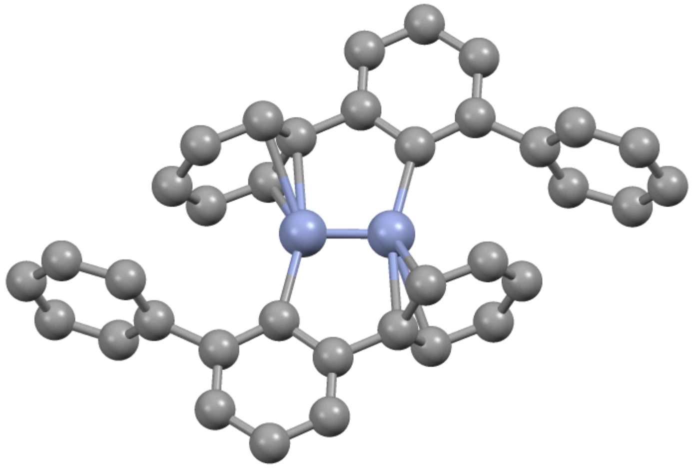
History of the Pursuit of the Shortest Metal-Metal Bond

The shortest metal-metal bond for almost 30 years (Cotton, 1978)

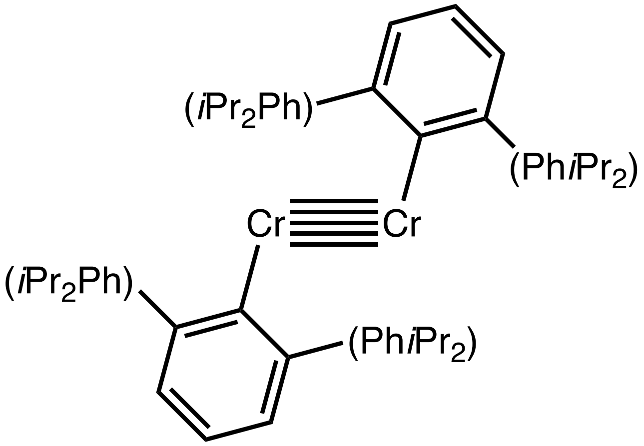




Cr-Cr bond = 1.828 Å



Cr-Cr bond = 1.835 Å



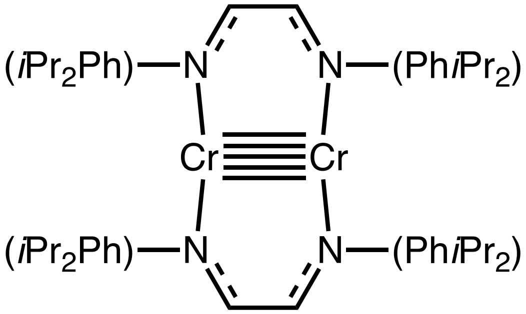
- First quintuple bond ever reported
- Unique *trans*-bent conformation
- Ground state configuration: $\sigma^2\pi^4\delta^4$

Bond length depends more on the ligand framework constraint

Nguyen, T.; Power, P. P. et al *Science* **2005**, *310*, 844.

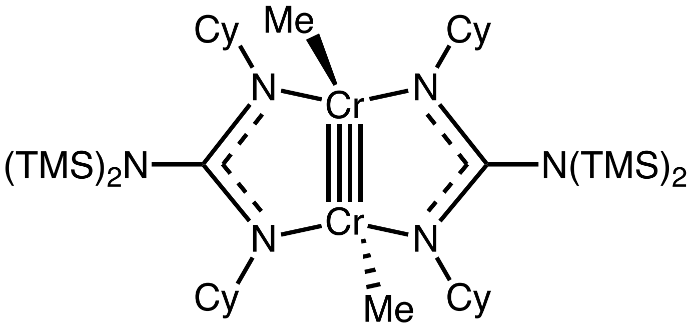
Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084.

History of the Pursuit of the Shortest Metal-Metal Bond



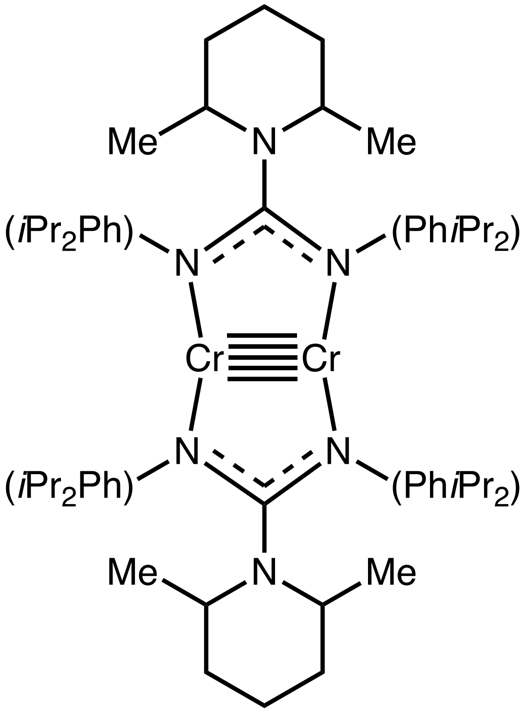
Theopold & Landis (2007)

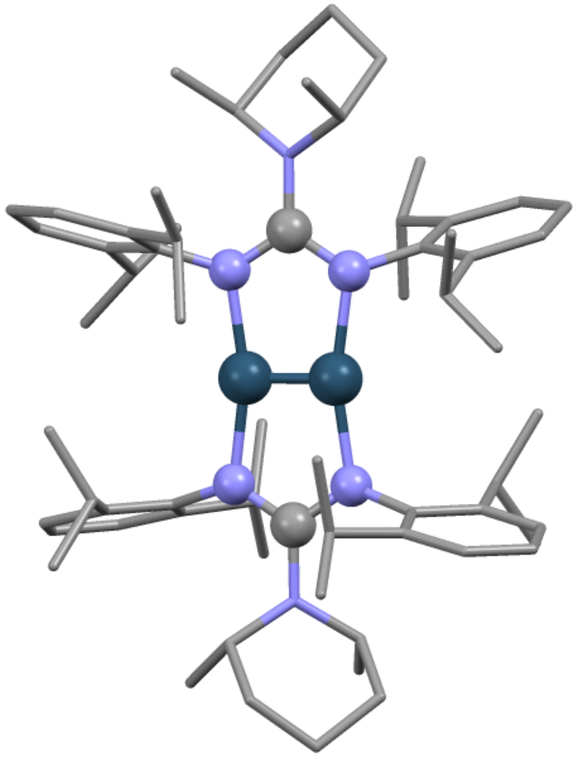
Quintuple Cr-Cr = 1.803 Å



Gambarotta (2008)

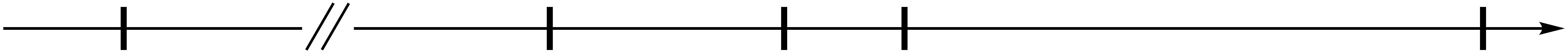
Quadruple Cr-Cr = 1.773 Å





Kempe (2013) *Quintuple Cr-Cr = 1.706 Å*

Shortest metal-metal bond ever reported to date!



Cotton (1978)
1.828 Å

Power (2005)
1.835 Å

2007
1.803 Å

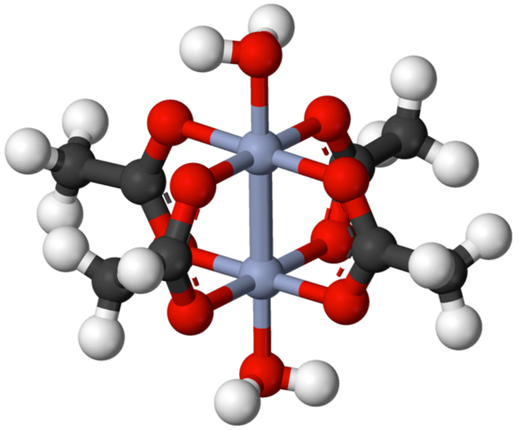
2008
1.773 Å

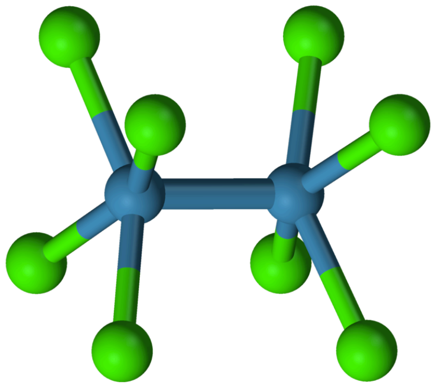
2013

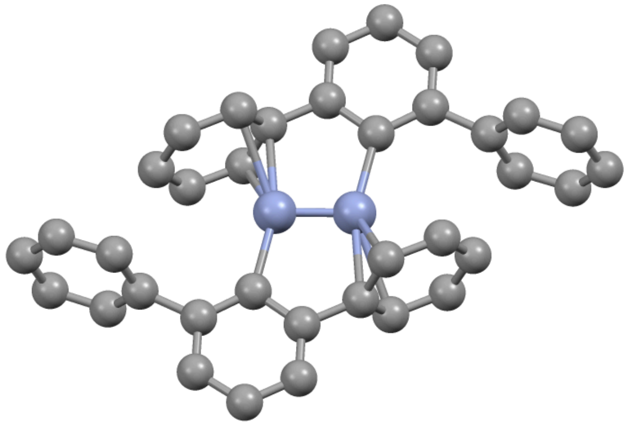
Nair, A, K,; Harisomayajula, N. V. S.; Tsai, Y.-C. *Inorg. Chim. Acta* **2015**, *424*, 51.

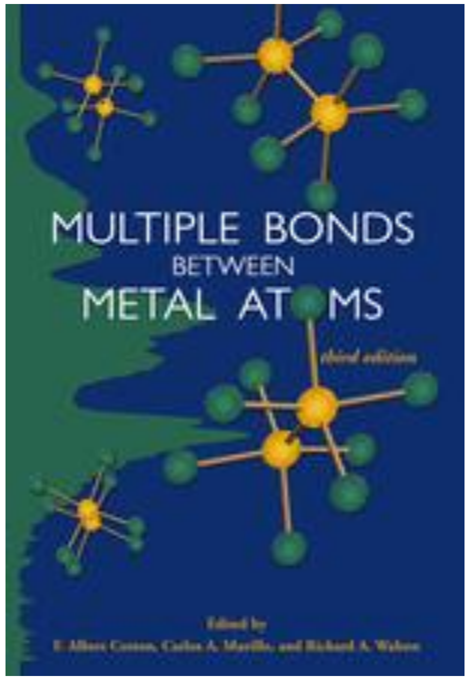
Synthesis and Catalytic Reactivity of Metal-Metal Bond Complexes

History of the pursuit of the shortest metal-metal bond

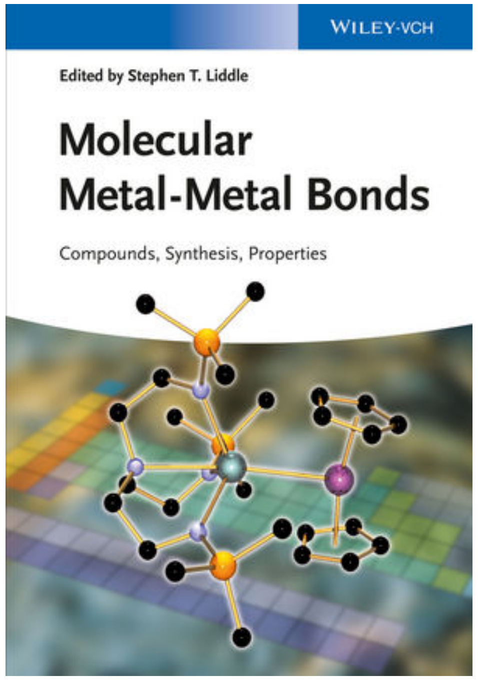

$Cr_2(OAc)_4 \bullet 2H_2O$


$K_2[Re_2Cl_8]$


$Cr_2Ar'_2$



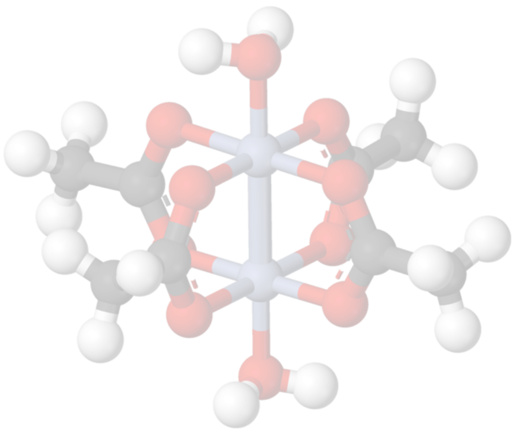
Cotton et al (2005)



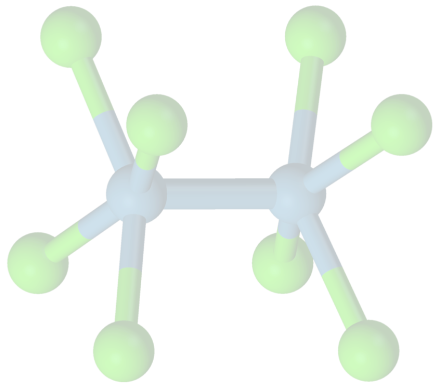
Liddle et al (2015)

Synthesis and Catalytic Reactivity of Metal-Metal Bond Complexes

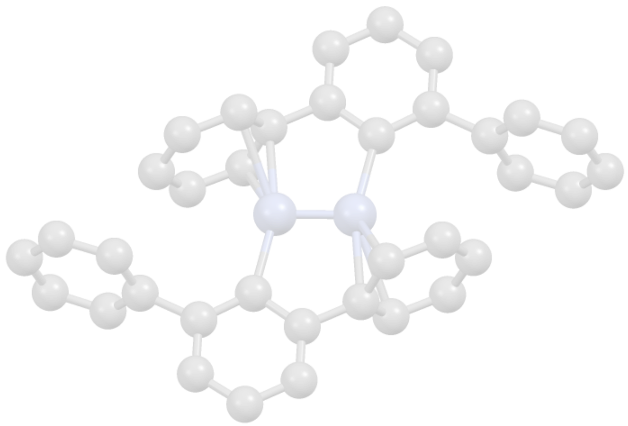
History of the pursuit of the shortest metal-metal bond



$Cr_2(OAc)_4\bullet 2H_2O$

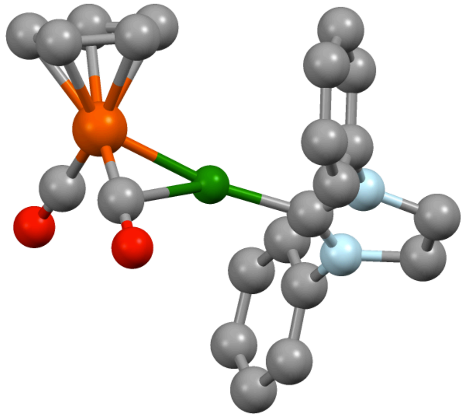


$K_2[Re_2Cl_8]$

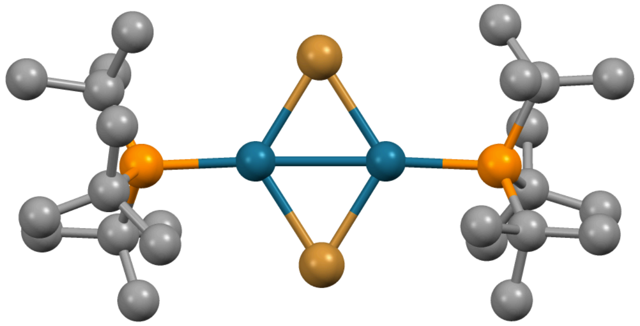


$Cr_2Ar'_2$

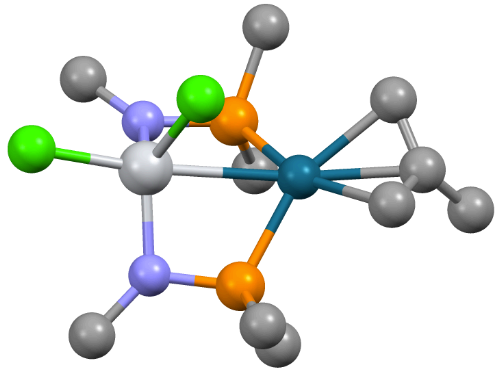
Catalytic reactivity of metal-metal bond complexes



(NHC)Cu-FeCp$(CO)_2$

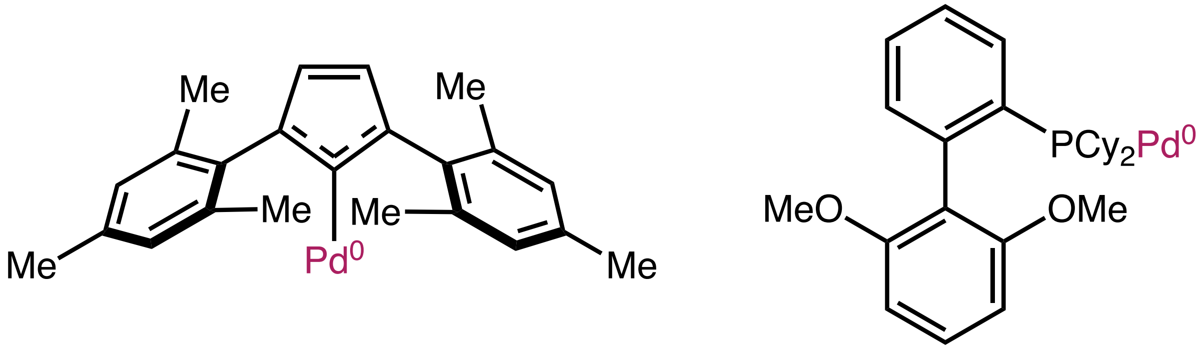


$[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$

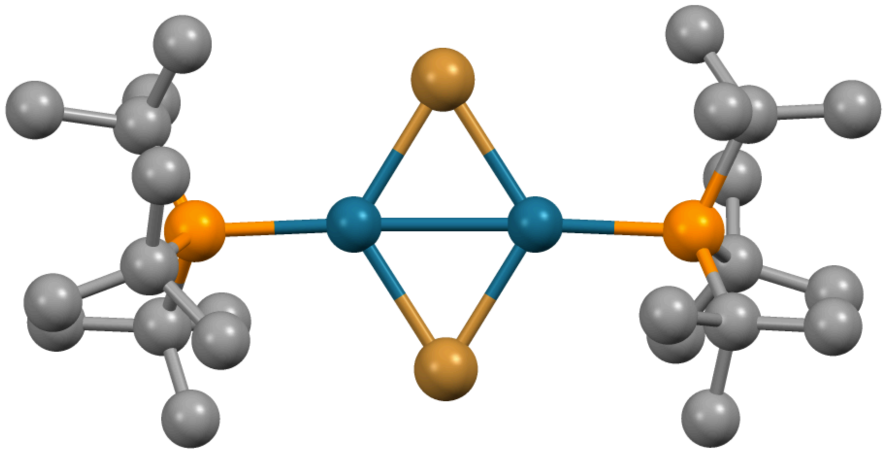


$(\eta^3$-methallyl)Pd$(PR_3)TiCl_2$

Catalytic Reactivity of Metal-Metal Bond Complexes



- Coordinately unsaturated Pd(0) complex
- Highly reactive catalysts for cross coupling
- Maintaining 1:1 M:L is crucial to high reactivity



$Pd_2(\mu\text{-}Br)_2(P\textit{t}\text{-}Bu_3)_2$

First reported by Mingos (1996)

$Pd^0P\textit{t}\text{-}Bu_3$

Highly reactive catalyst for
cross coupling with aryl chlorides

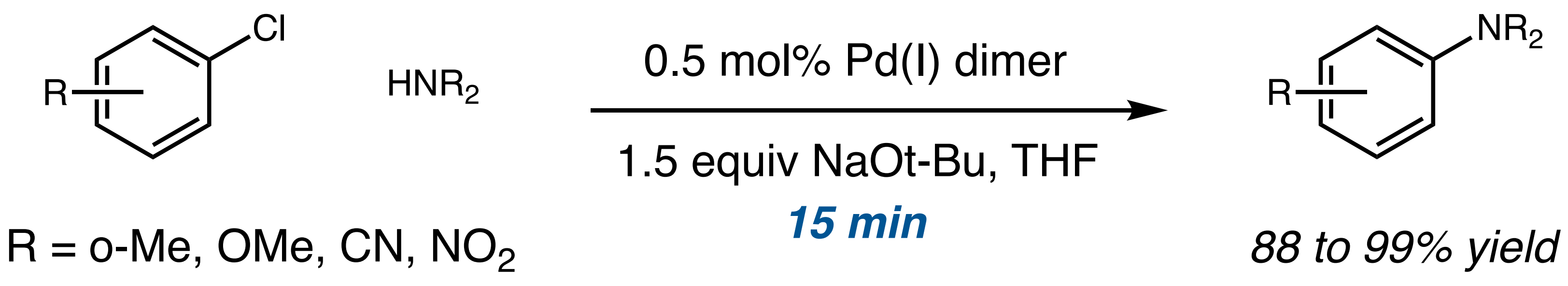
$Pd^0(dba)_2$ / $P\textit{t}\text{-}Bu_3$

Conventional precursor

Pd(I) dimer could serve as air-stable Pd(0) precatalyst

Vilar, R.; Mingos, D. M. P.; Cardin, C. J. *J. Chem. Soc., Dalton Trans.* **1996**, *4314*.

Catalytic Reactivity of Metal-Metal Bond Complexes



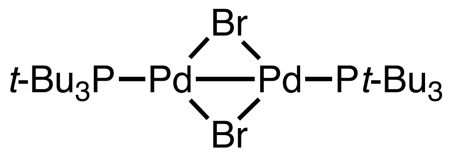
0.5 mol% Pd(I) dimer

1.5 equiv NaOt-Bu, THF

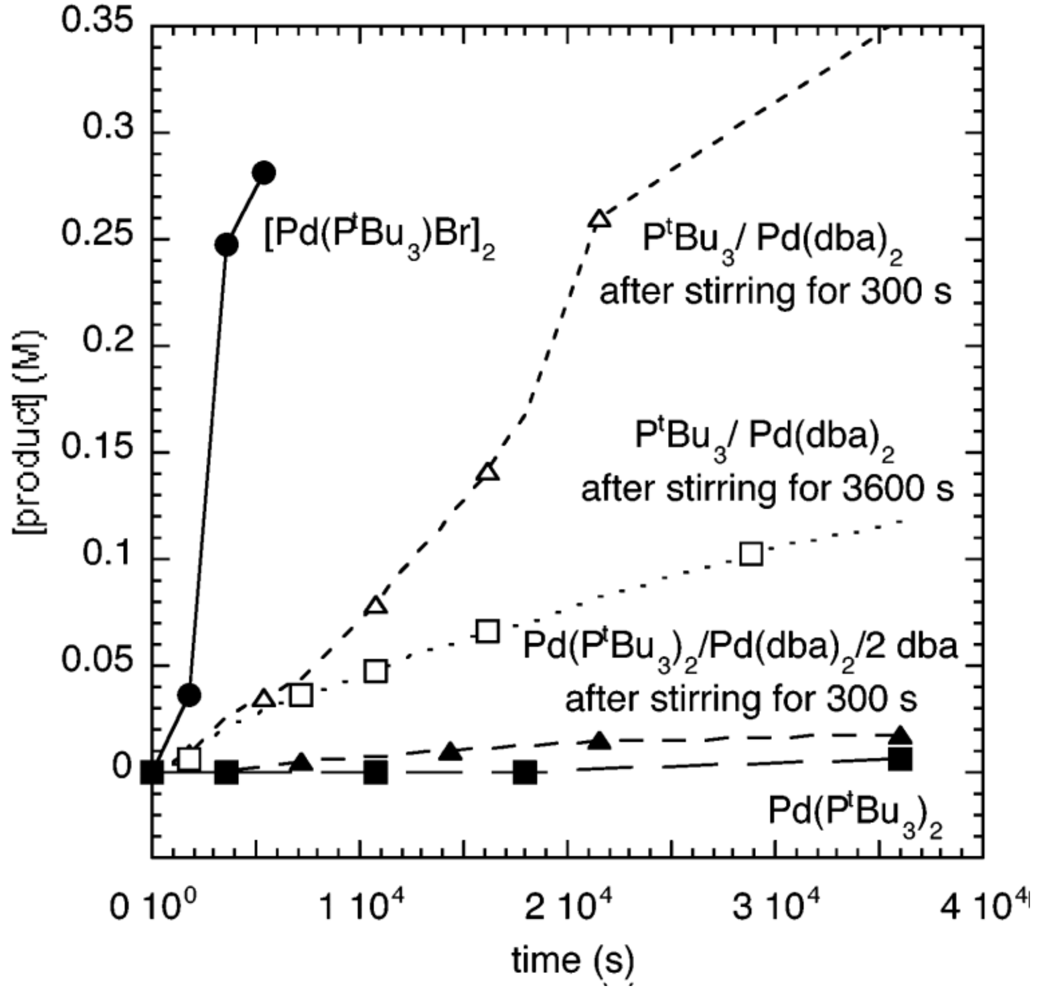
15 min

R = o-Me, OMe, CN, NO$_2$

88 to 99% yield



Pd(I) dimer



Rate studies on the amination of 3-bromothiophene with different Pd^{0}PtBu$_3$ sources

Pd(I) dimer → Pd^{0}P*t*-Bu$_3$

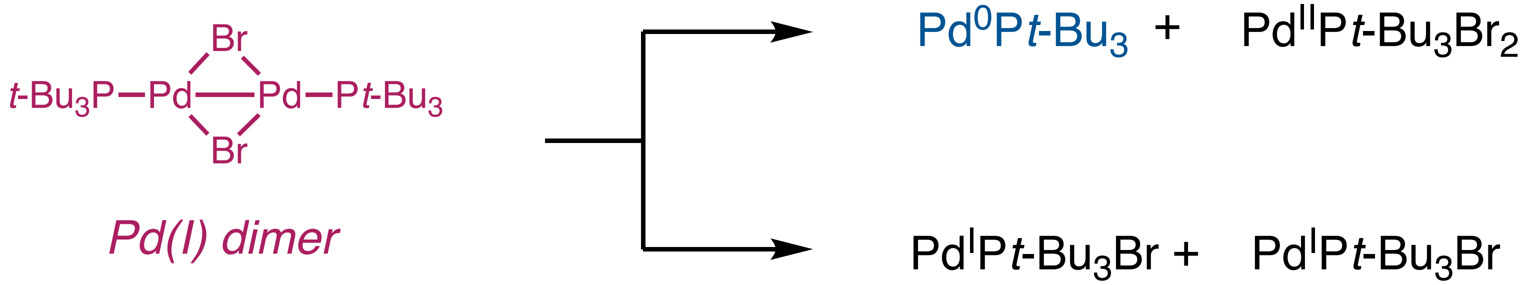
- *Rapid release of active monoligated Pd(0)*
- *Disproportionation, dissociation or reduction?*

- *What is the mode of activation to access Pd(0)?*
- *What about a bimetallic catalysis scenario?*

Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861.

Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 4746.

Catalytic Reactivity of Metal-Metal Bond Complexes



Pd(I) dimer

$Pd^{0}Pt\text{-}Bu_3$ + $Pd^{II}Pt\text{-}Bu_3Br_2$

Disproportionation

$Pd^{I}Pt\text{-}Bu_3Br$ + $Pd^{I}Pt\text{-}Bu_3Br$

Dissociation

$Pd^{0}(Pt\text{-}Bu_3)_2 \longrightarrow Pd^{0}Pt\text{-}Bu_3 + Pt\text{-}Bu_3$ ΔG = 27.2 kcal/mol (DFT)

Often considered the rate-limiting step in Pd(dba) / Pt-Bu$_3$ protocols

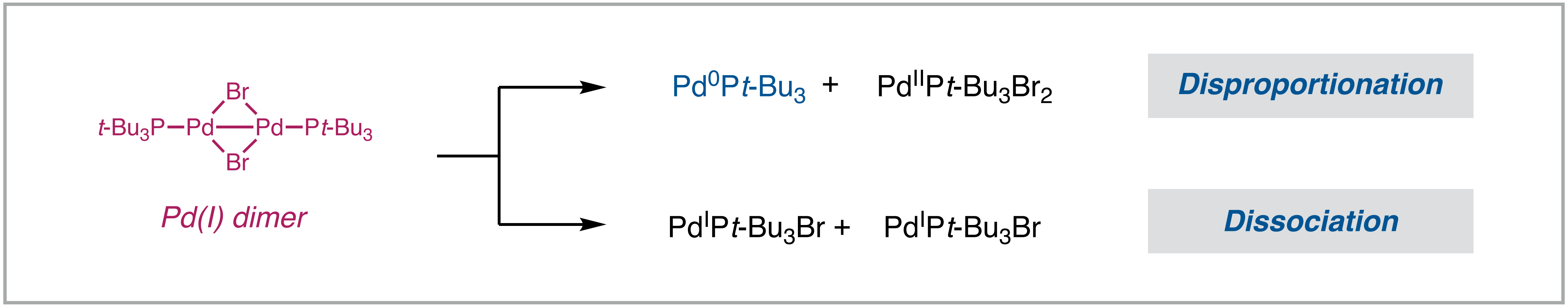
Since rate Pd(I) dimer is more reactive, disproportionation should be more favorable

Pd(I) dimer $\longrightarrow Pd^{0}Pt\text{-}Bu_3 + Pd^{II}Pt\text{-}Bu_3Br_2$ ΔG = 38.1 kcal/mol (DFT)

The general assumption that Pd(I) dimer directly disproportionate to Pd(0) in solution seems unlikely

Proutiere, F.; Aufiero, M.; Schoenebeck, F. *J. Am. Chem. Soc.* **2012**, *134*, 606.

Catalytic Reactivity of Metal-Metal Bond Complexes



Pd(I) dimer

$Pd^0Pt\text{-}Bu_3$ + $Pd^{II}Pt\text{-}Bu_3Br_2$ **Disproportionation**

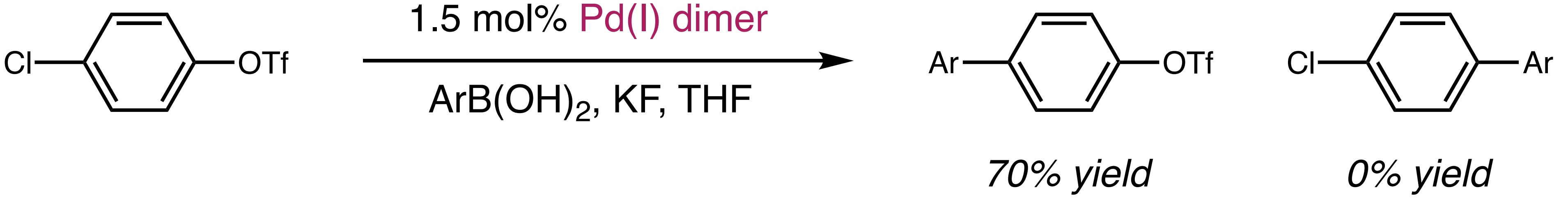
$Pd^IPt\text{-}Bu_3Br$ + $Pd^IPt\text{-}Bu_3Br$ **Dissociation**

Pd(I) dimer $\longrightarrow$ $Pd^IPt\text{-}Bu_3Br$ + $Pd^IPt\text{-}Bu_3Br$ $\Delta G = 24.8$ kcal/mol (DFT)

DFT calculation suggests Pd(0) and Pd(I) should have different selectivity toward Ar-X oxidative addition

$Pd^0Pt\text{-}Bu_3$ ⇒ ArCl oxidative addition is favored by 9.8 kcal/mol (DFT)

$Pd^IPt\text{-}Bu_3Br$ ⇒ ArOTf oxidative addition is favored by 8.4 kcal/mol (DFT)



1.5 mol% Pd(I) dimer

$ArB(OH)_2$, KF, THF

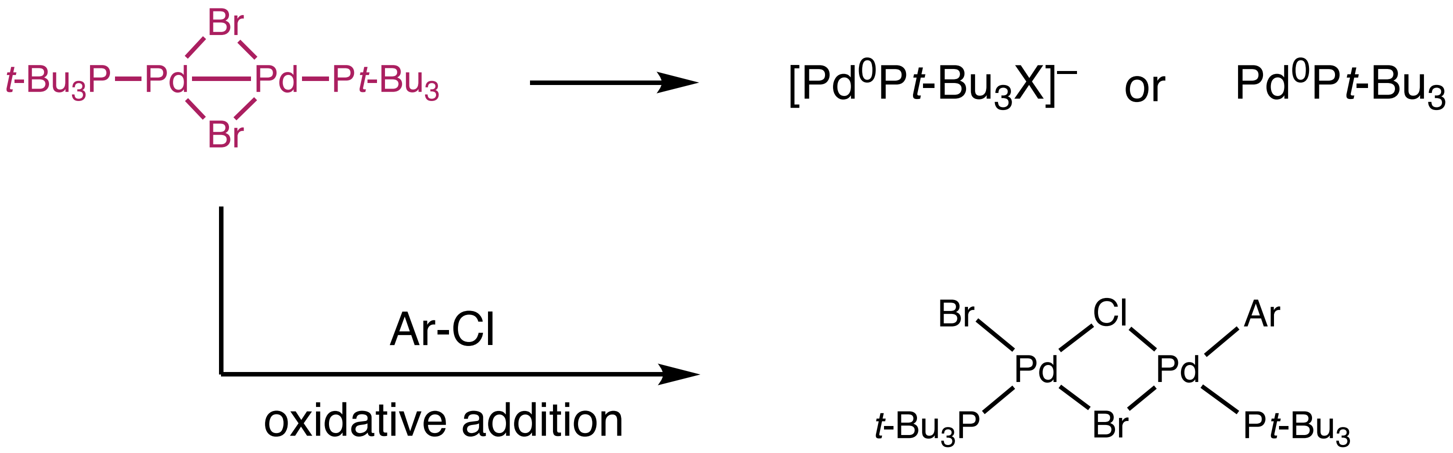
70% yield

0% yield

Dissociation pathway is unlikely

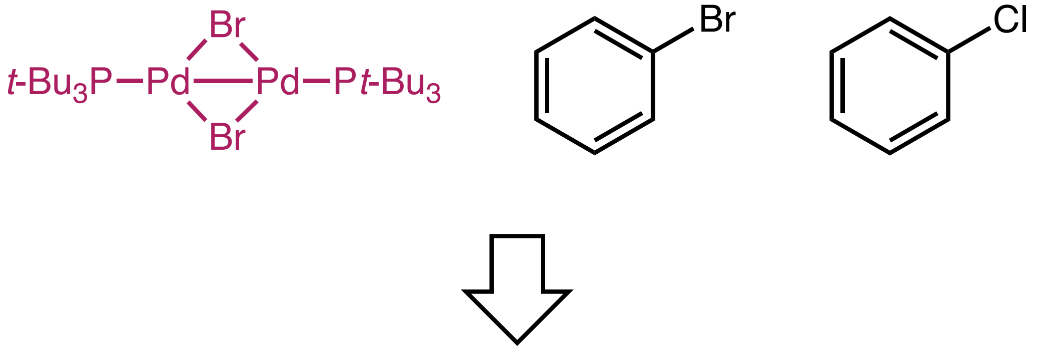
Proutiere, F.; Aufiero, M.; Schoenebeck, F. *J. Am. Chem. Soc.* **2012**, *134*, 606.

Catalytic Reactivity of Metal-Metal Bond Complexes



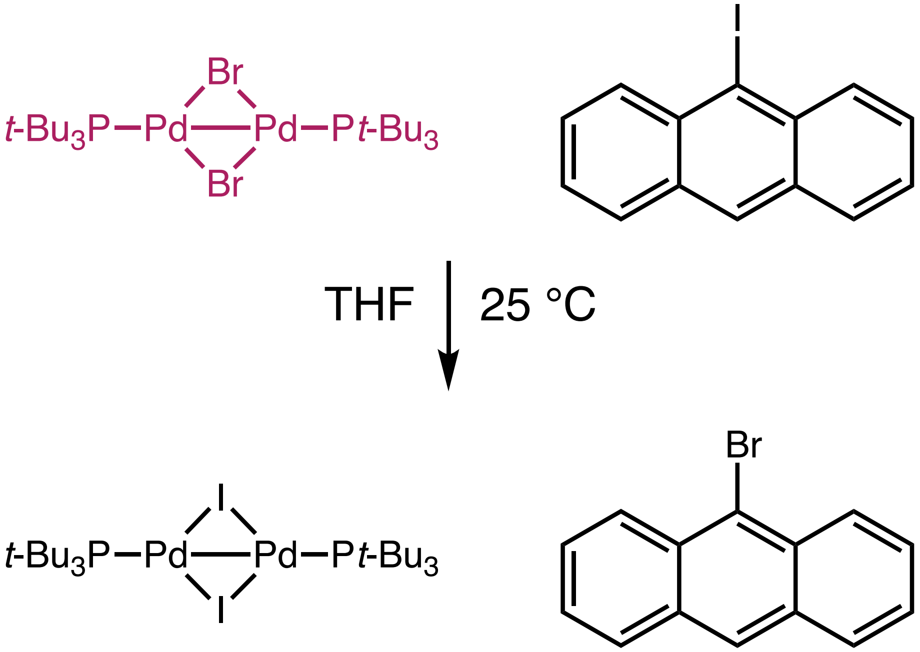
Studies of reduction pathway have not been reported

Is Bimetallic Catalysis Possible with Pd(I) Dimer?



Pd(I) dimer remains intact, zero reactivity

Bimetallic catalysis is not operative for aryl chloride/bromide coupling



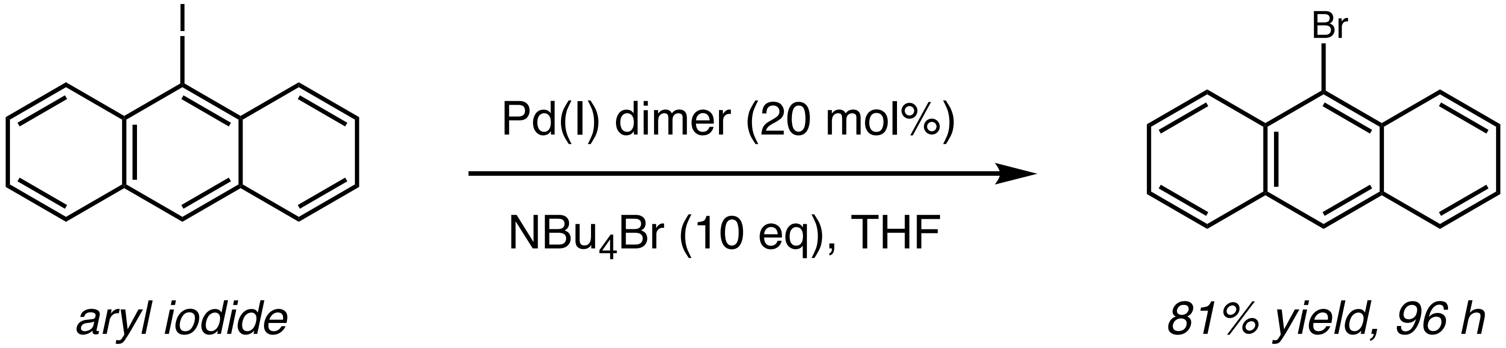
Bimetallic O.A. and R.E.?

Bonney, K. J.; Proutiere, F.; Schoenebeck, F. *Chem. Sci.* **2013**, *4*, 4434.

Proutiere, F.; Aufiero, M.; Schoenebeck, F. *J. Am. Chem. Soc.* **2012**, *134*, 606.

Seechurn, C. C. C. J.; Sperger, T.; Scrase, T. G.; Schoenebeck, F.; Colacot, T. J. *J. Am. Chem. Soc.* **2017**, *ASAP.*

Catalytic Reactivity of Metal-Metal Bond Complexes

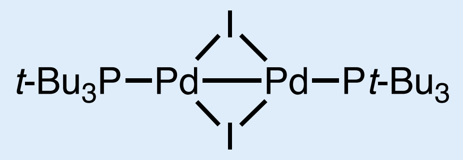


aryl iodide

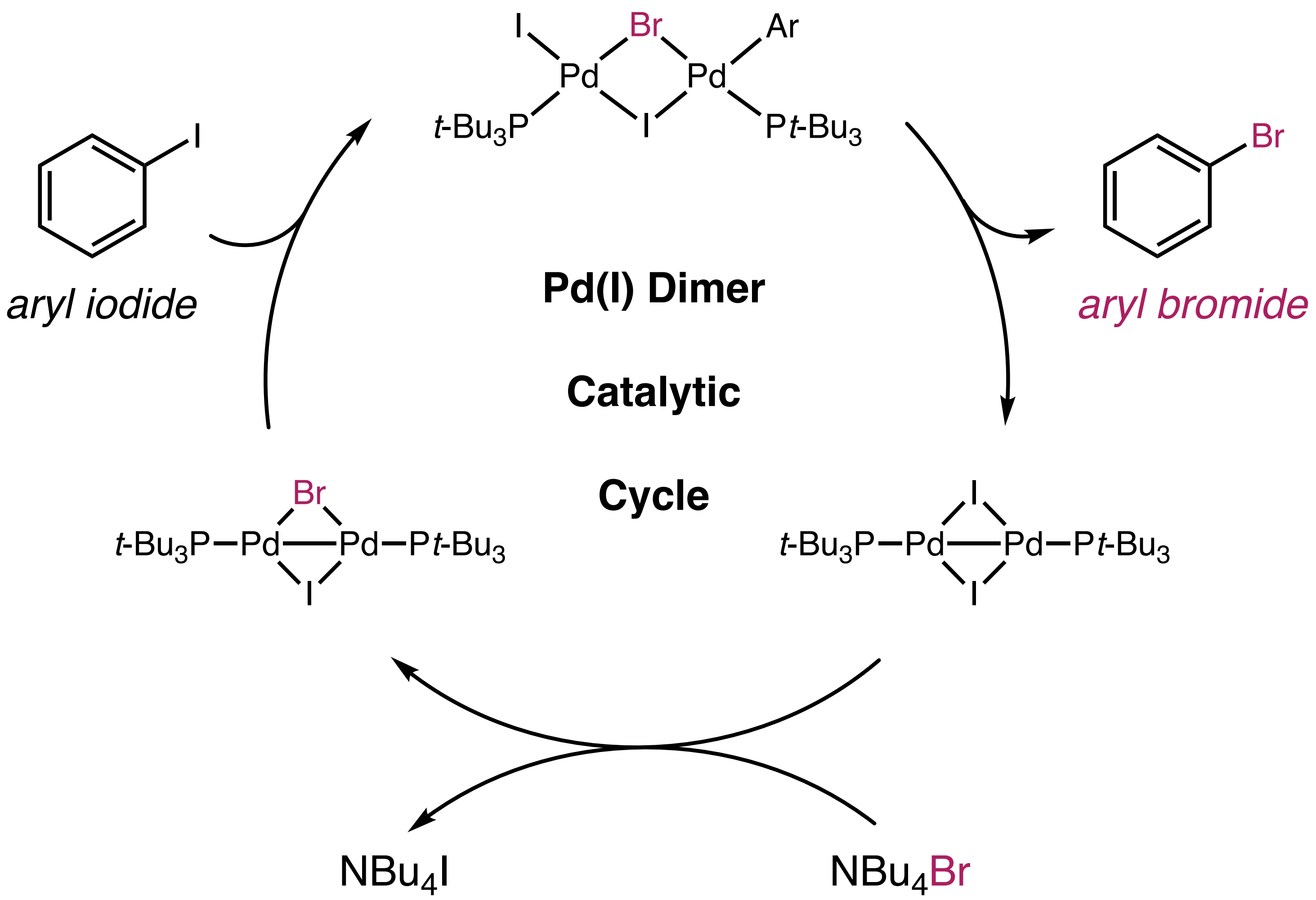
Pd(I) dimer (20 mol%)

NBu_4Br (10 eq), THF

81% yield, 96 h



Pd(I) dimer



aryl iodide

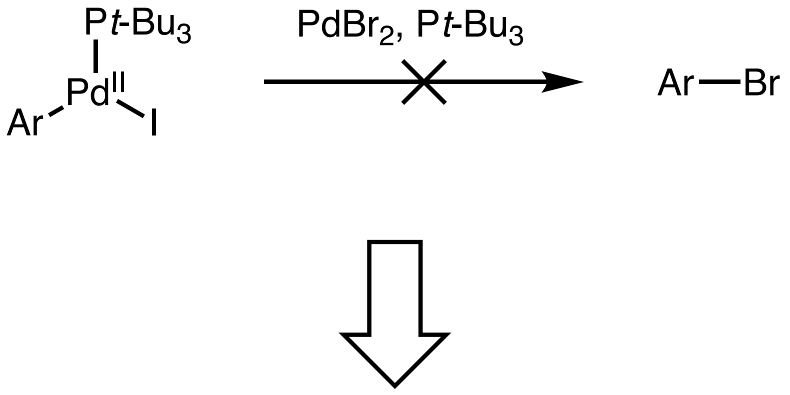
aryl bromide

Pd(I) Dimer

Catalytic

Cycle

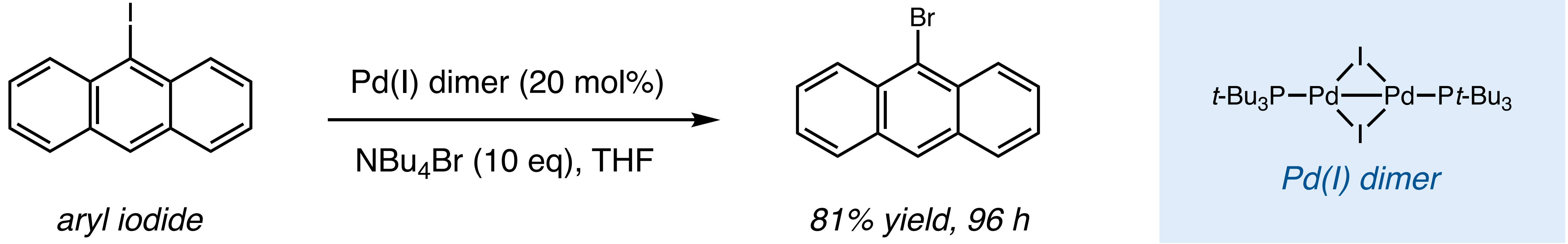
Single Pd(II) does not readily undergo reductive elimination



Formation of Pd-Pd bond lowers the activation barrier for R.E.

Bonney, K. J.; Proutiere, F.; Schoenebeck, F. *Chem. Sci.* **2013**, *4*, 4434.

Catalytic Reactivity of Metal-Metal Bond Complexes



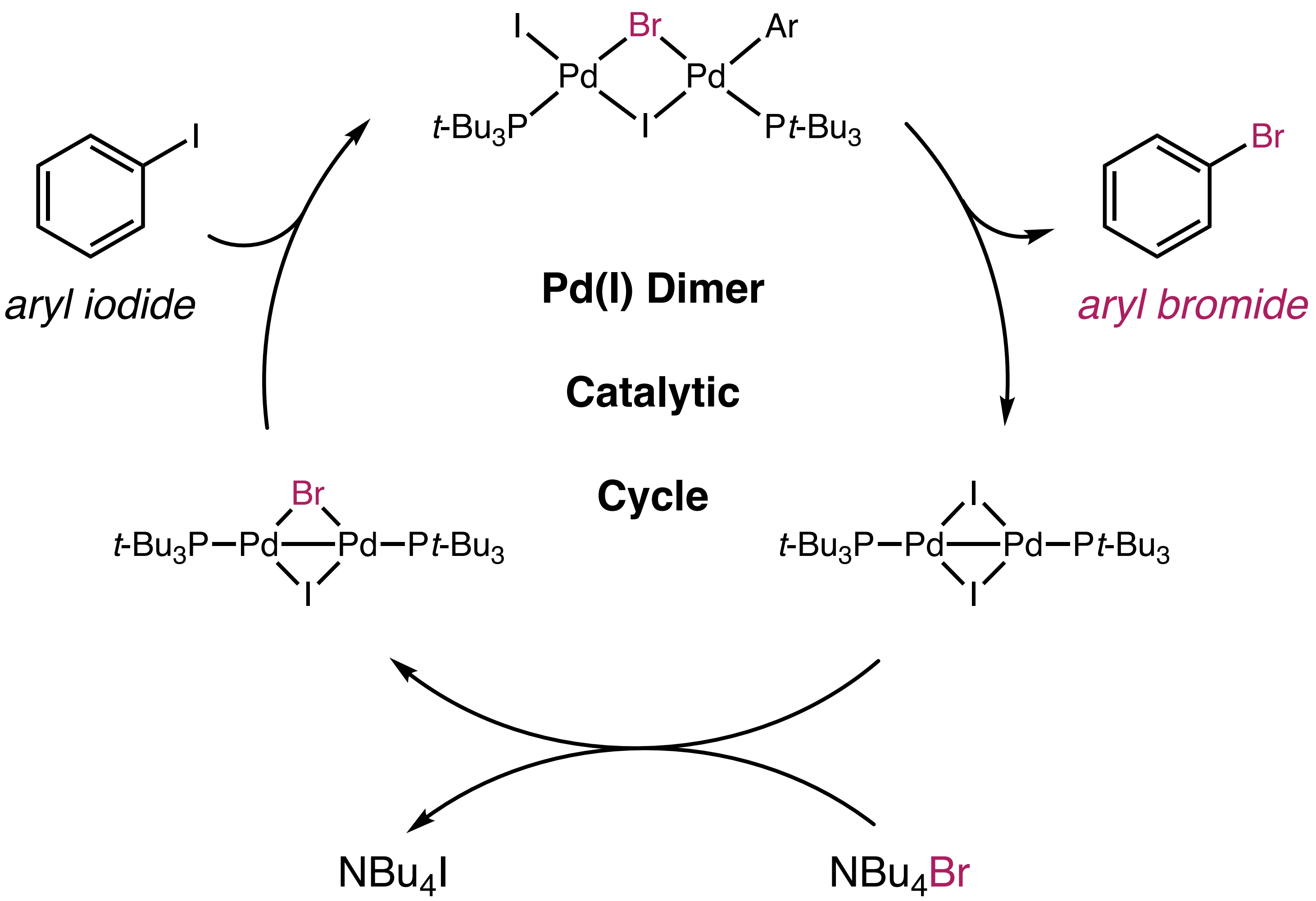
Pd(I) dimer (20 mol%)

NBu$_4$Br (10 eq), THF

aryl iodide

81% yield, 96 h

Pd(I) dimer



aryl iodide

Pd(I) Dimer

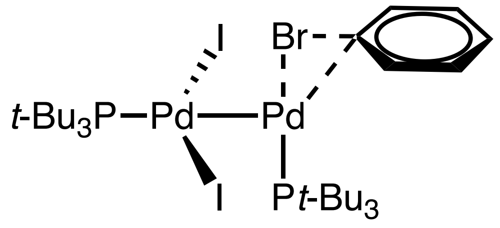
Catalytic

Cycle

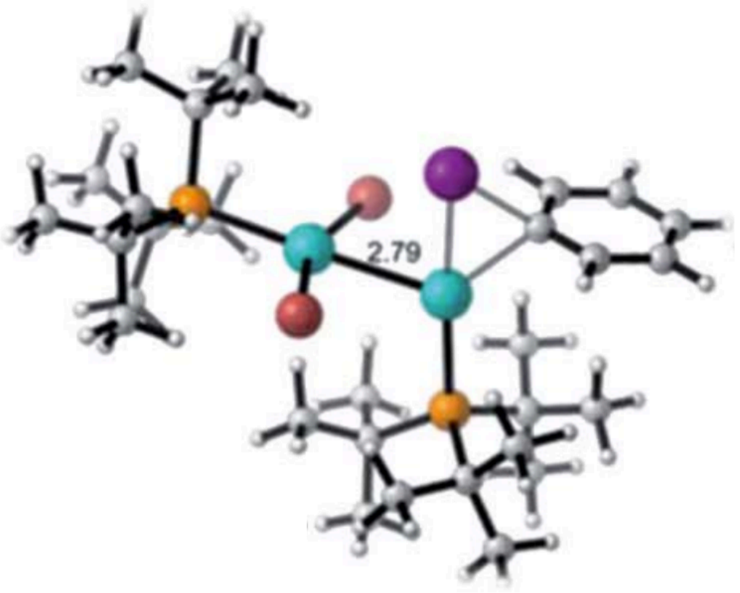
aryl bromide

NBu$_4$I

NBu$_4$Br

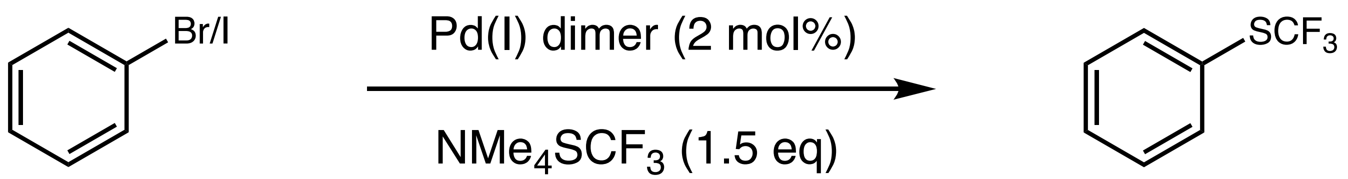


TS for O.A. and R.E.



Bonney, K. J.; Proutiere, F.; Schoenebeck, F. *Chem. Sci.* **2013**, *4*, 4434.

Catalytic Reactivity of Metal-Metal Bond Complexes

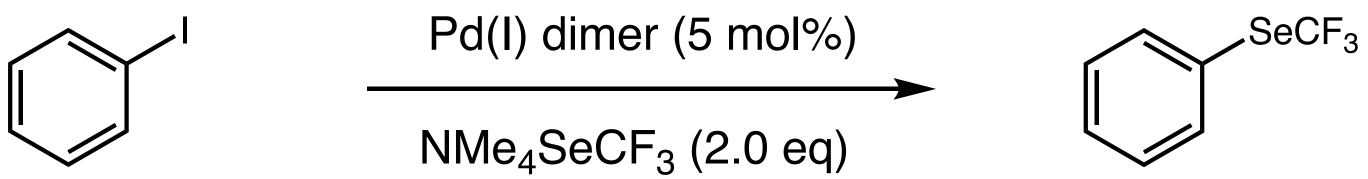


Pd(I) dimer (2 mol%)

NMe_4SCF_3 (1.5 eq)

27 examples

65 to 99% yield

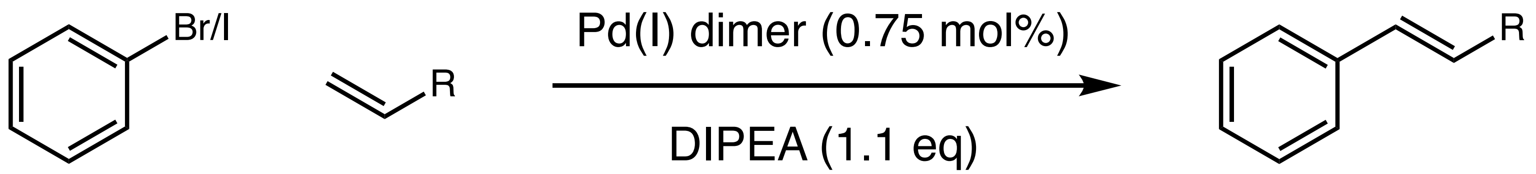


Pd(I) dimer (5 mol%)

NMe_4SeCF_3 (2.0 eq)

20 examples

62 to 99% yield



Pd(I) dimer (0.75 mol%)

DIPEA (1.1 eq)

20 examples

46 to 99% yield

Pd(I) dimer can serve as an air-stable, reusable catalyst with enhanced reactivity

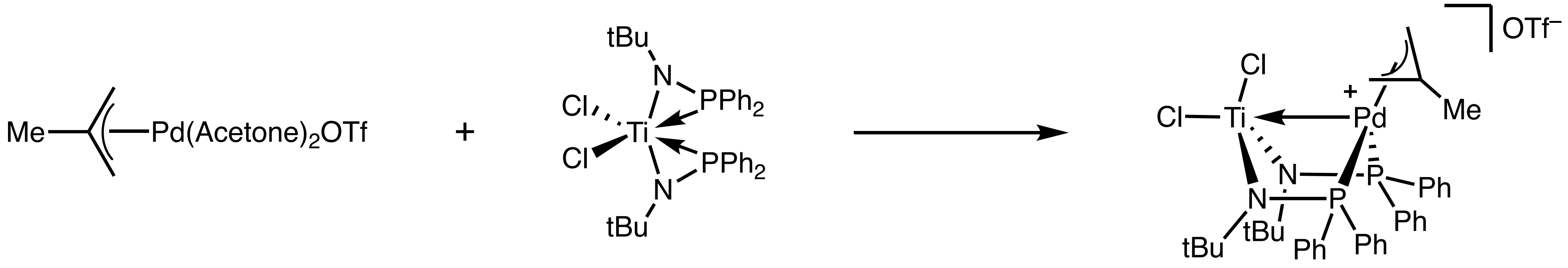
Sperger, T.; Stierner, C. K.; Schoenebeck, F. *Synthesis* **2017**, *49*, 115.

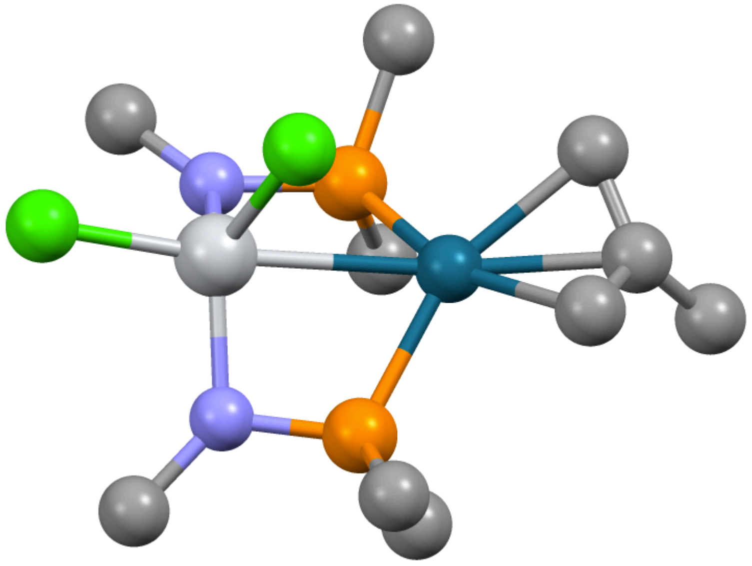
Yin, G.; Kalvet, I.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2015**, *54*, 6809.

Aufiero, M.; Sperger, T.; Tsang, A. S.-K.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2015**, *54*, 10322.

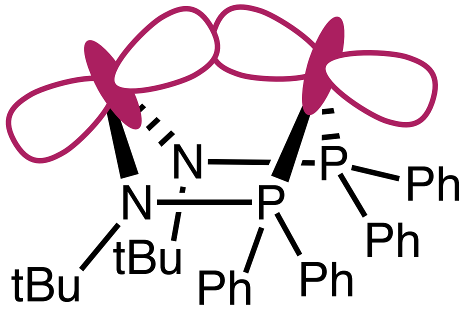
Catalytic Reactivity of Metal-Metal Bond Complexes

First synthesis of heterobimetallic Pd–Ti complex (Nagashima, 2009)



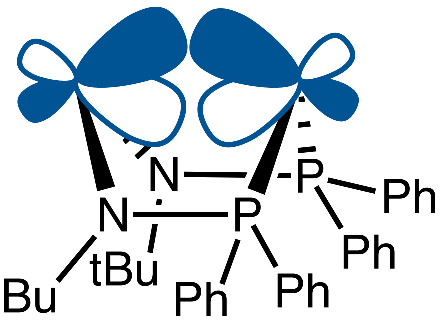


$(\eta^3\text{-methallyl})Pd(PR_3)TiCl_2$



HOMO-1

d_{z^2}–d_{z^2}



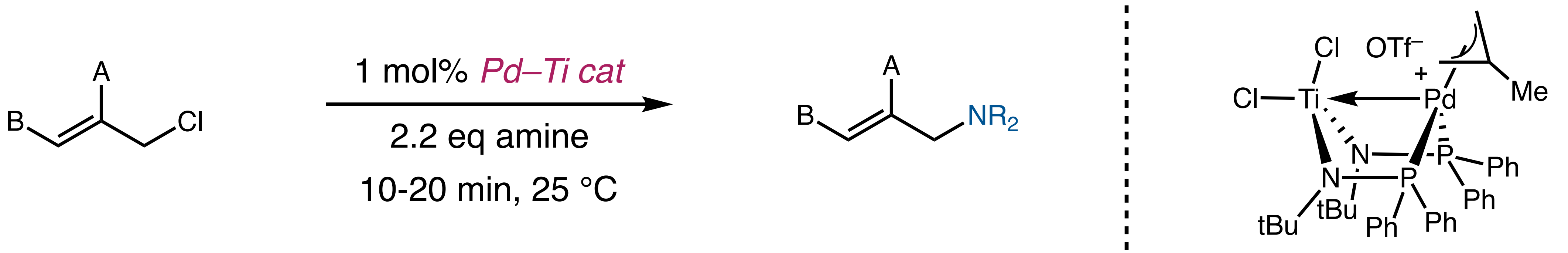
HOMO

d_{yz}–d_{yz}

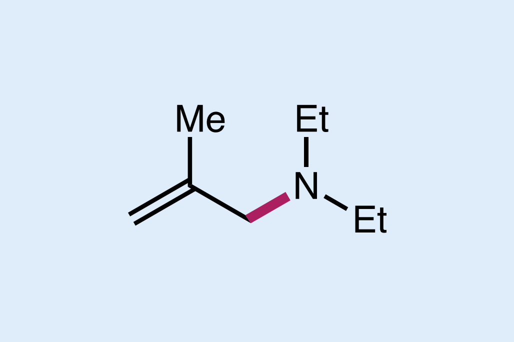
Strong interaction between Pd and Ti centers

Tsutsumi, H.; Sunada, Y.; Shiota, Y.; Yoshizawa, K.; Nagashima, H. *Organometallics* **2009**, *28*, 1988.

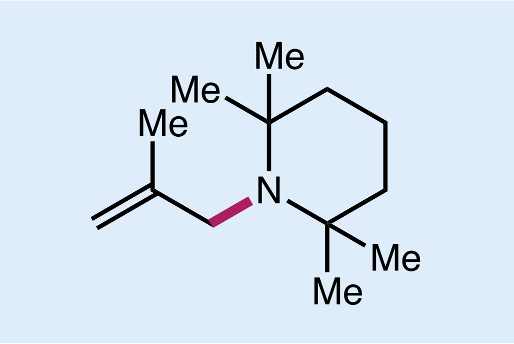
Catalytic Reactivity of Metal-Metal Bond Complexes



Bimetallic Pd–Ti exhibits enhanced catalytic reactivity towards allylic amination



Pd–Ti cat	*>99% yield, 1 min*
Pd(dppe)(η^3-allyl)	45% yield, 6 h
Pd(PPh_3)$_2$(η^3-allyl)	>99% yield, 1 min

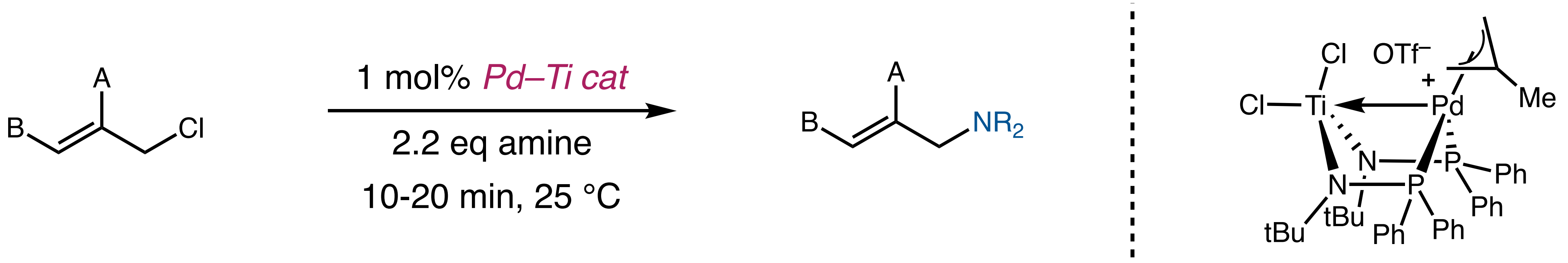


Pd–Ti cat	*>99% yield, 20 min*
Pd(dppe)(η^3-allyl)	<5% yield, 24 h
Pd(PPh_3)$_2$(η^3-allyl)	trace yield, 24 h

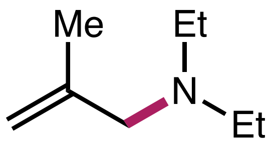
Walker, W. K.; Kay, B. M.; Ess, D. H.; Michaelis, D. J. et al *J. Am. Chem. Soc.* **2015**, *137*, 7371.

Walker, W. K.; Anderson, D. L.; Stokes, R. W.; Smith, S. J.; Michaelis, D. J. *Org. Lett.* **2015**, *17*, 752.

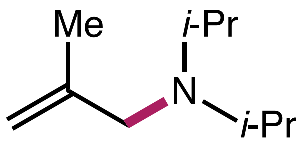
Catalytic Reactivity of Metal-Metal Bond Complexes



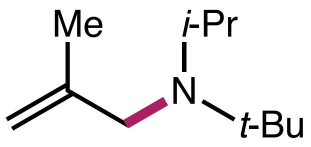
Bimetallic Pd–Ti exhibits enhanced catalytic reactivity towards allylic amination



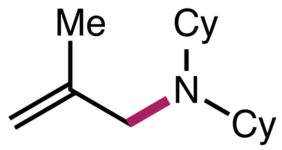
>99% yield



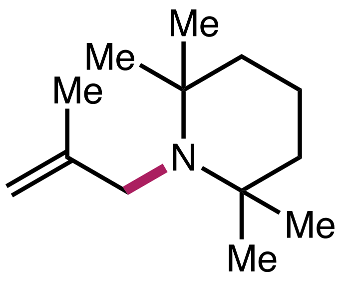
72% yield



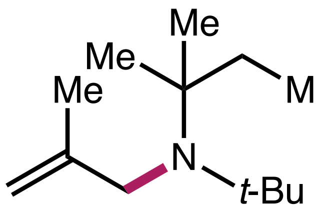
98% yield



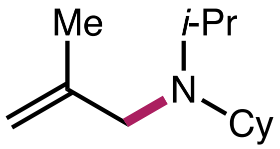
>99% yield



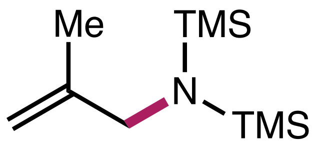
>99% yield



<5% yield



82% yield



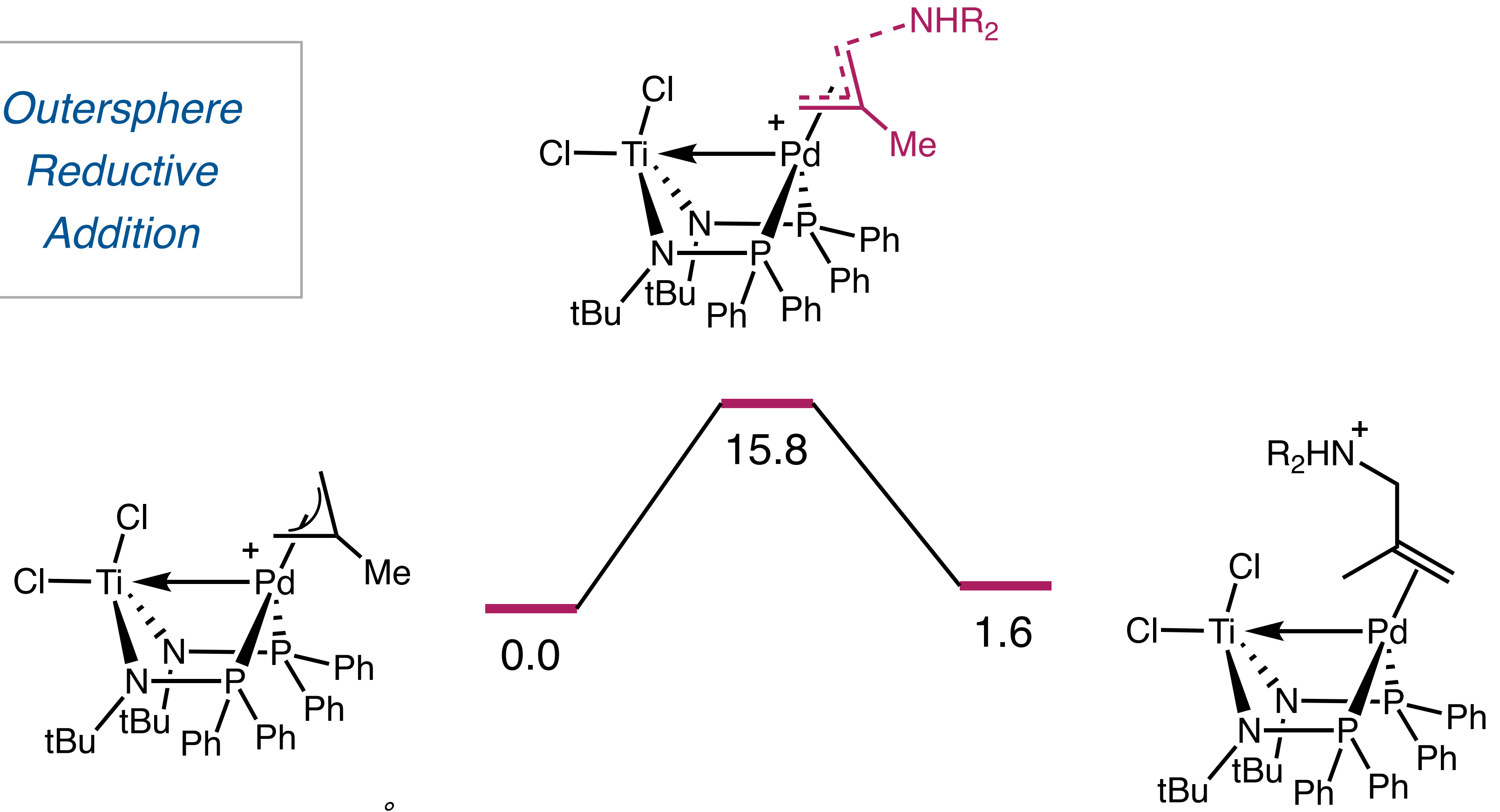
>99% yield

Walker, W. K.; Kay, B. M.; Ess, D. H.; Michaelis, D. J. et al *J. Am. Chem. Soc.* **2015**, *137*, 7371.

Walker, W. K.; Anderson, D. L.; Stokes, R. W.; Smith, S. J.; Michaelis, D. J. *Org. Lett.* **2015**, *17*, 752.

Catalytic Reactivity of Metal-Metal Bond Complexes

Outersphere Reductive Addition

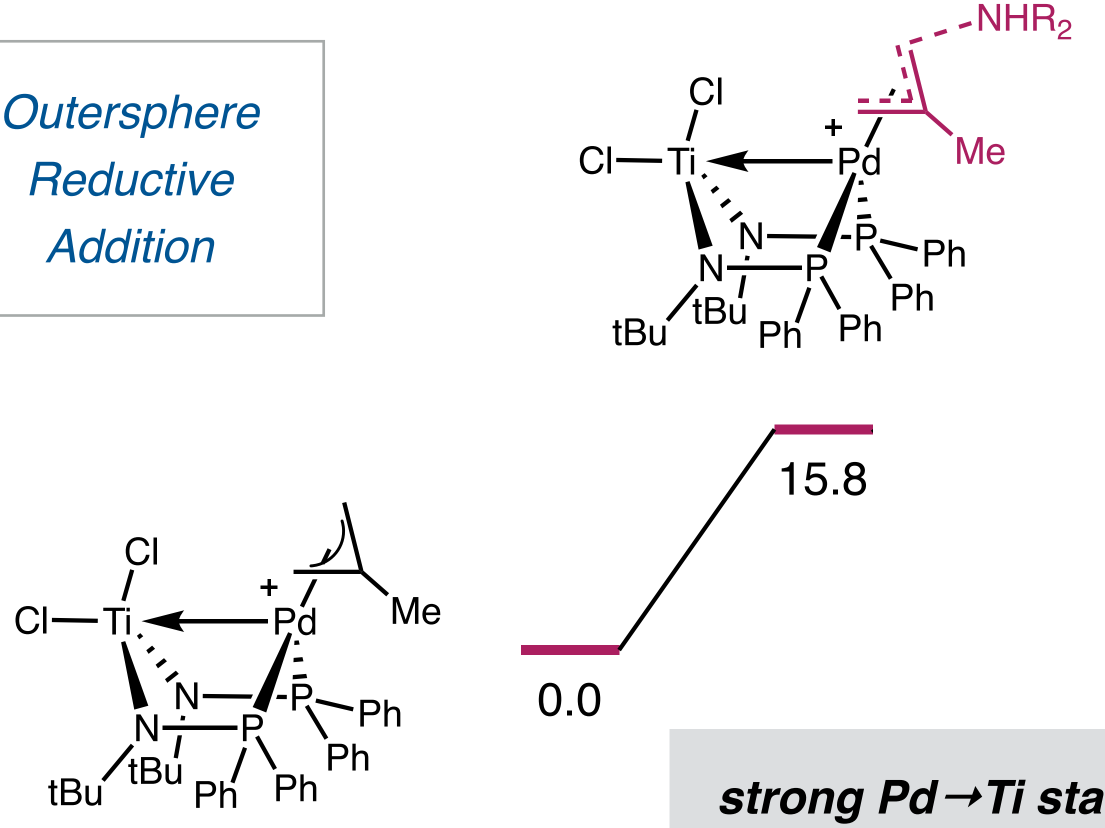


Pd–Ti bond: 2.88 Å

Walker, W. K.; Kay, B. M.; Ess, D. H.; Michaelis, D. J. et al *J. Am. Chem. Soc.* **2015**, *137*, 7371.

Catalytic Reactivity of Metal-Metal Bond Complexes

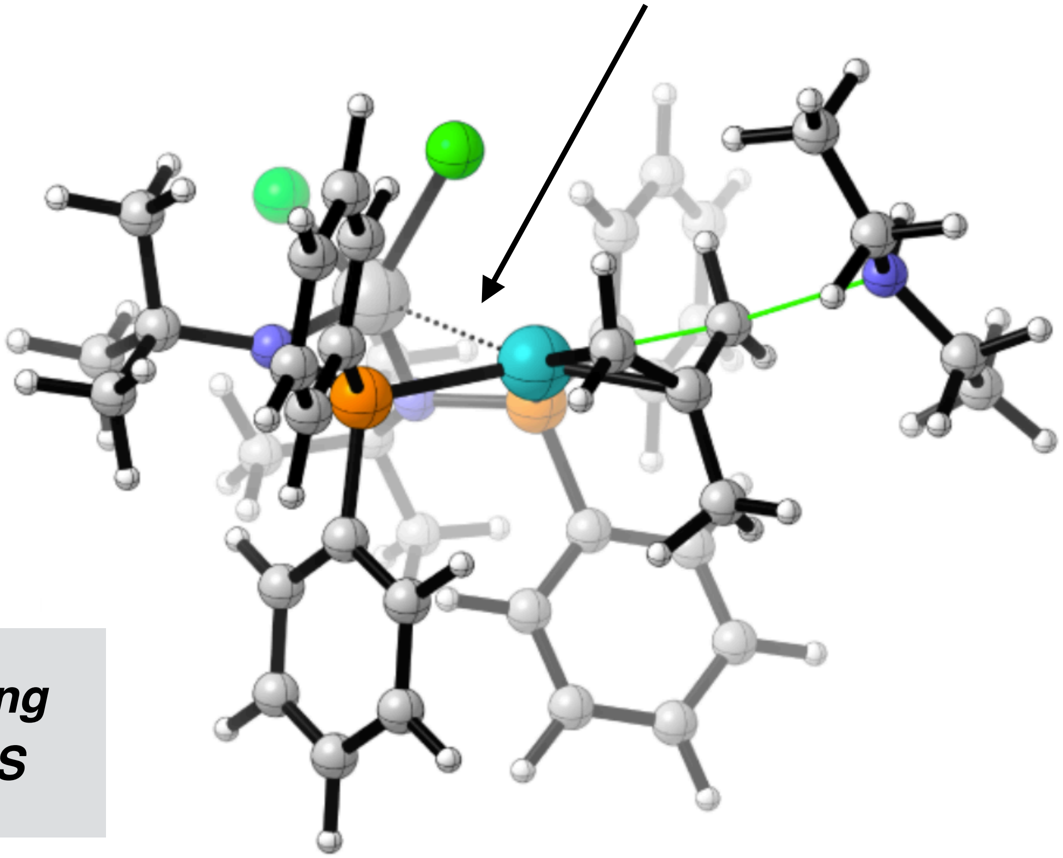
Outersphere Reductive Addition



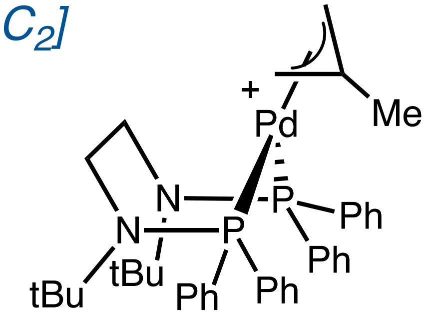
Pd–Ti bond: 2.88 Å

strong Pd→Ti stabilizing interaction through TS

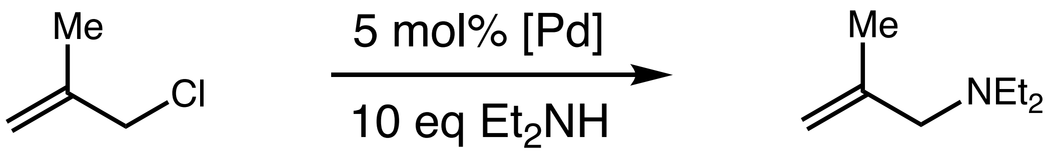
DFT Calculated TS with Pd–Ti bond: 2.77 Å



[Pd-C$_2$]



- *Similar P-Pd-P bite angle*
- *Boat conformation (X-ray)*
- *ΔG‡ = 23.8 kcal/mol (DFT)*

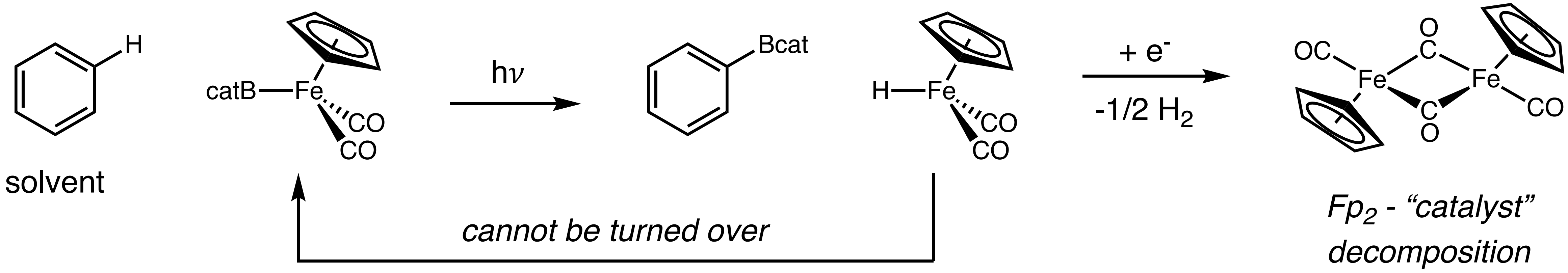


[Pd-Ti] catalyst	>99% yield, 1 min
[Pd-C$_2$] catalyst	51% yield, 3 h

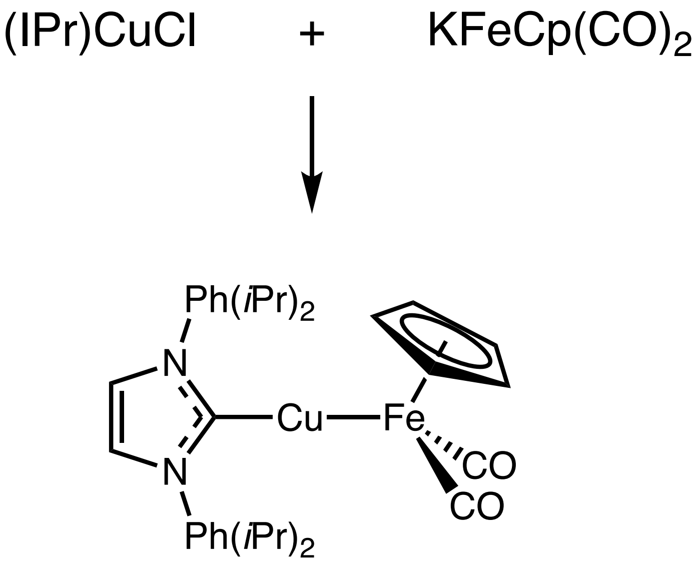
Walker, W. K.; Kay, B. M.; Ess, D. H.; Michaelis, D. J. et al *J. Am. Chem. Soc.* **2015**, *137*, 7371.

Catalytic Reactivity of Metal-Metal Bond Complexes

Initial discovery of stoichiometric C-H Borylation (Hartwig, 1995)



Fp_2 - “catalyst” decomposition



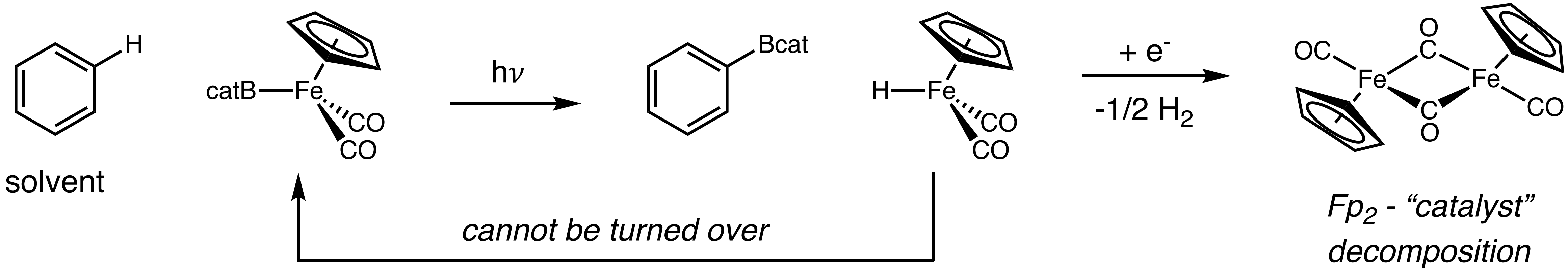
(IPr)Cu-Fp

Mazzacano, T. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2013**, *135*, 17258.

Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357.

Catalytic Reactivity of Metal-Metal Bond Complexes

Initial discovery of stoichiometric C-H Borylation (Hartwig, 1995)

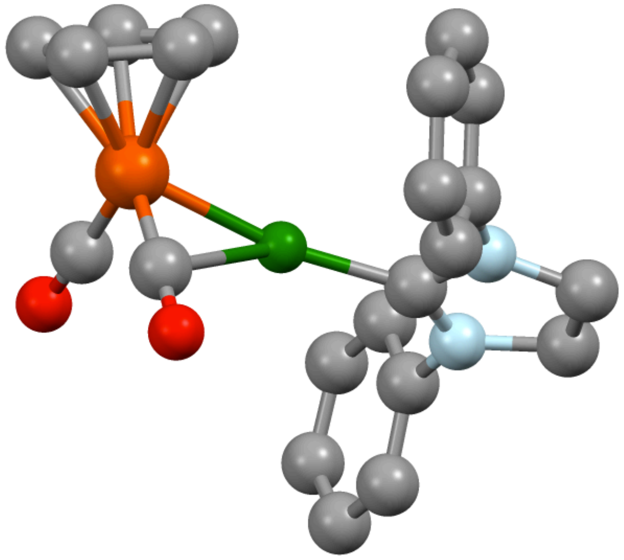


solvent

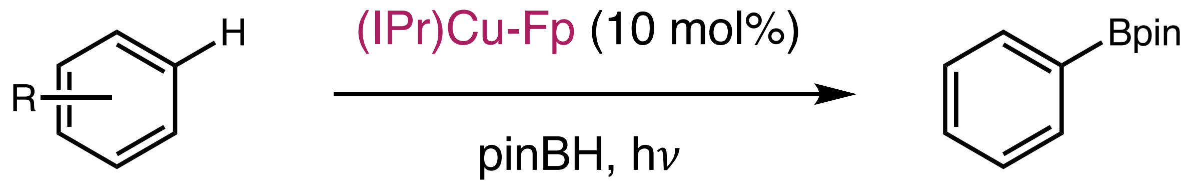
cannot be turned over

Fp$_2$ - "catalyst" decomposition

Catalytic C-H borylation via Fe-Cu cooperative catalysis (Mankad, 2013)



(IPr)Cu-Fp



solvent

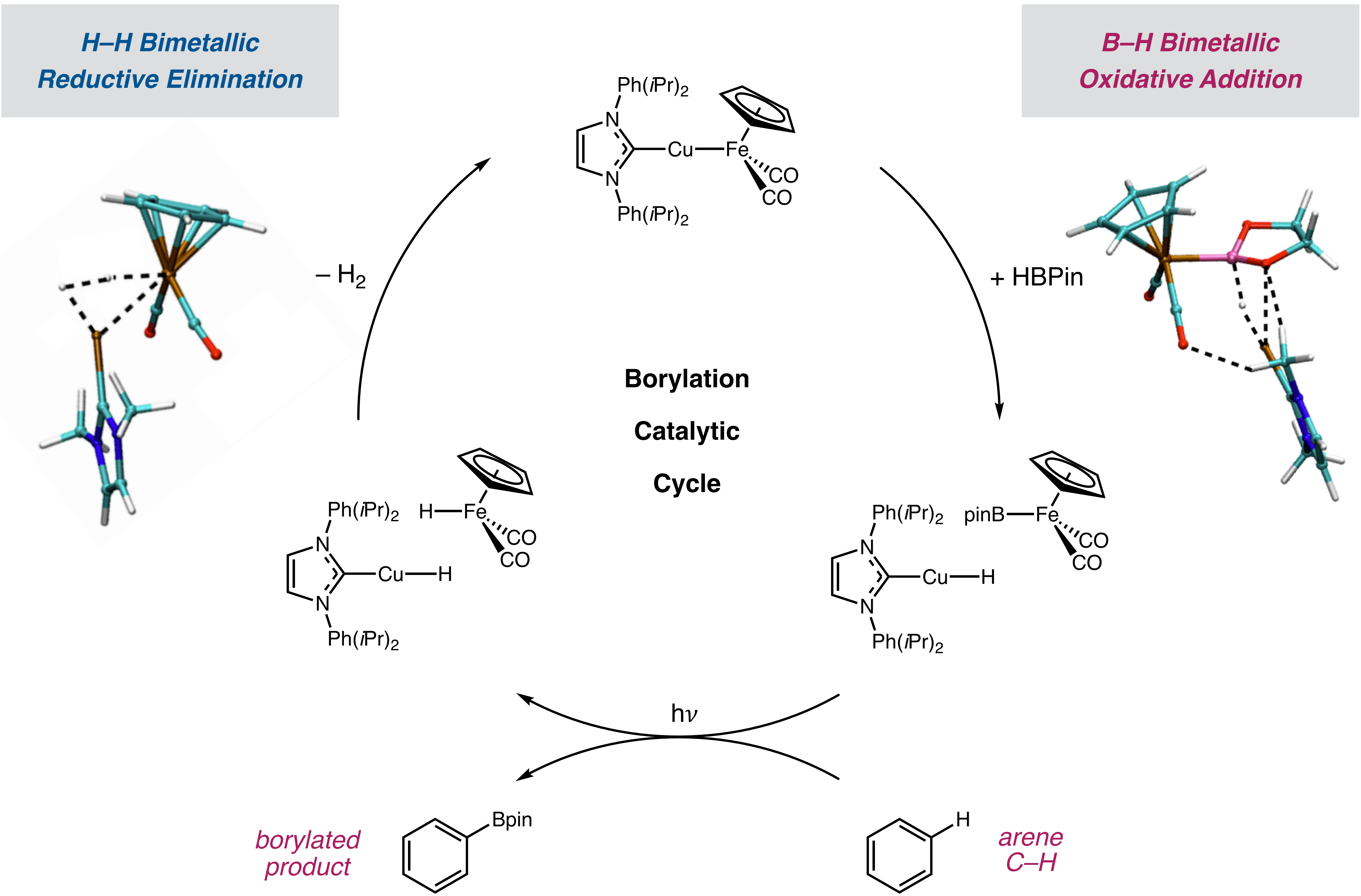
71% yield

Mechanism features a bimetallic oxidative addition and a bimetallic reductive elimination

Mazzacano, T. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2013**, *135*, 17258.

Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357.

Catalytic Reactivity of Metal-Metal Bond Complexes



H–H Bimetallic Reductive Elimination

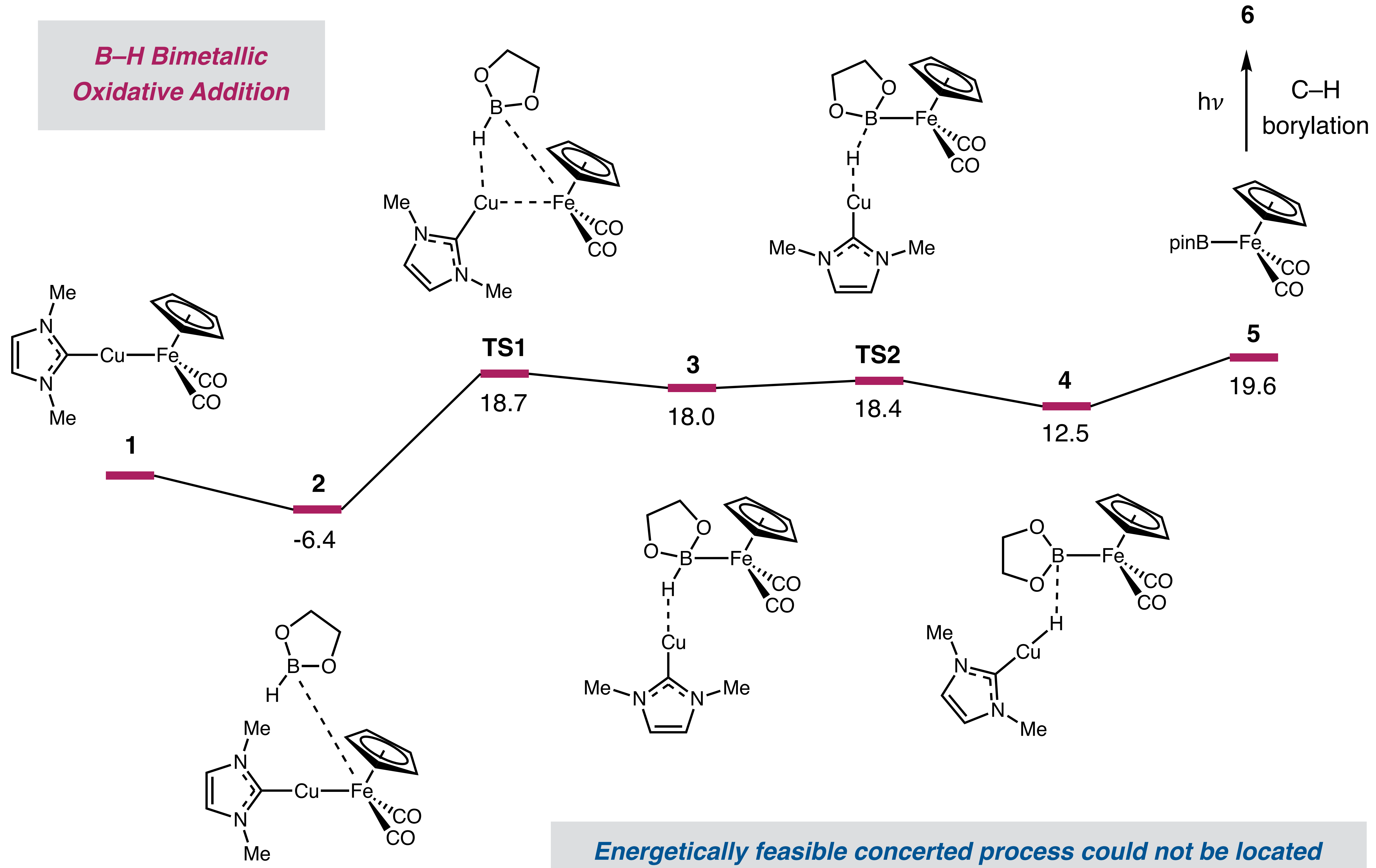
B–H Bimetallic Oxidative Addition

Borylation Catalytic Cycle

Mazzacano, T. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2013**, *135*, 17258.

Catalytic Reactivity of Metal-Metal Bond Complexes

B–H Bimetallic Oxidative Addition

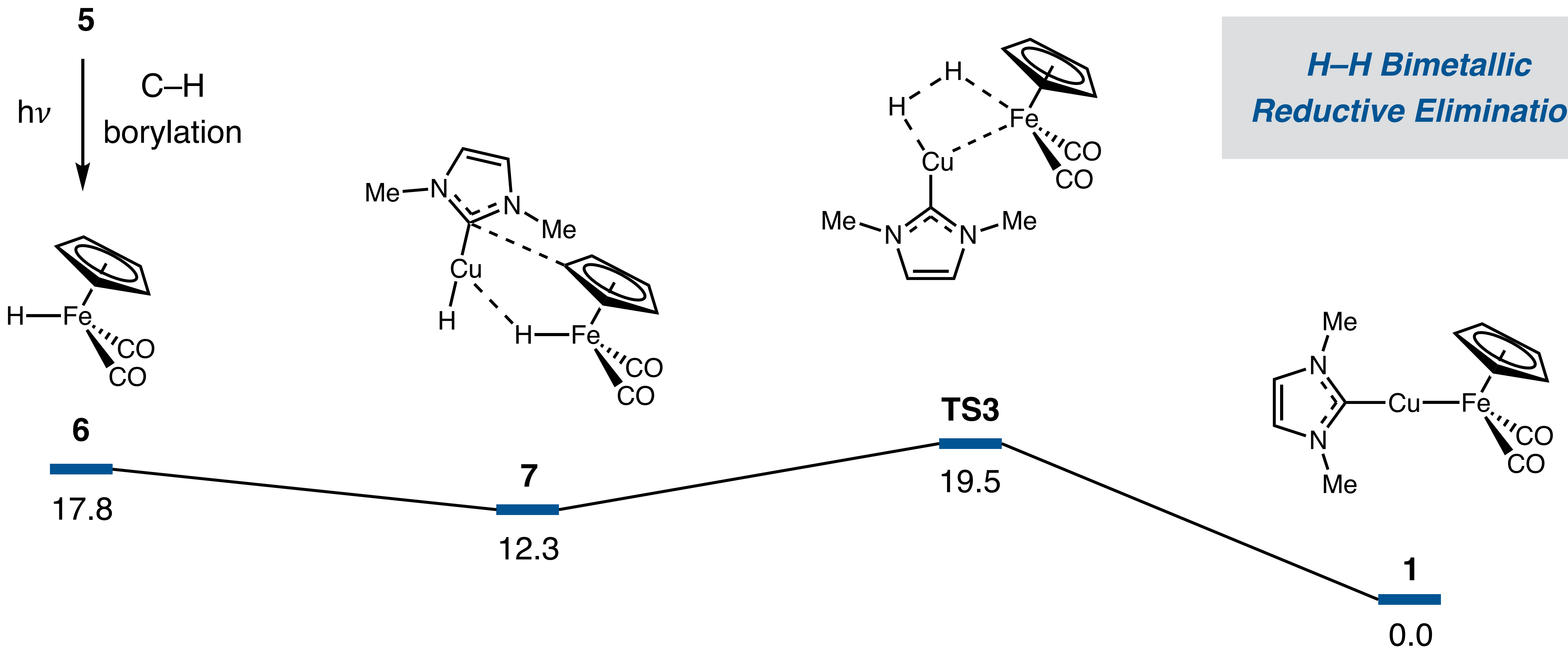


Energetically feasible concerted process could not be located

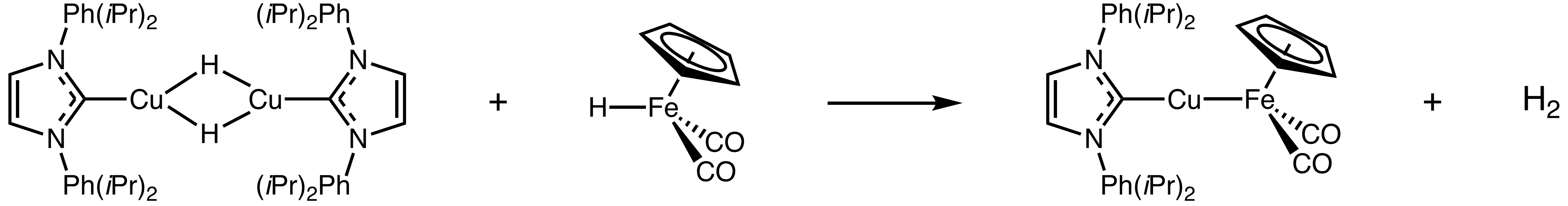
Parmelee, S. R.; Mazzacano, T. J.; Zhu, Y.; Mankad, N. P.; Keith, J. A. *ACS. Catat.* **2015**, *5*, 3689.

Catalytic Reactivity of Metal-Metal Bond Complexes

H–H Bimetallic Reductive Elimination



Regeneration of active catalyst via bimetallic R.E. was confirmed experimentally



Parmelee, S. R.; Mazzacano, T. J.; Zhu, Y.; Mankad, N. P.; Keith, J. A. *ACS. Catat.* **2015**, *5*, 3689.