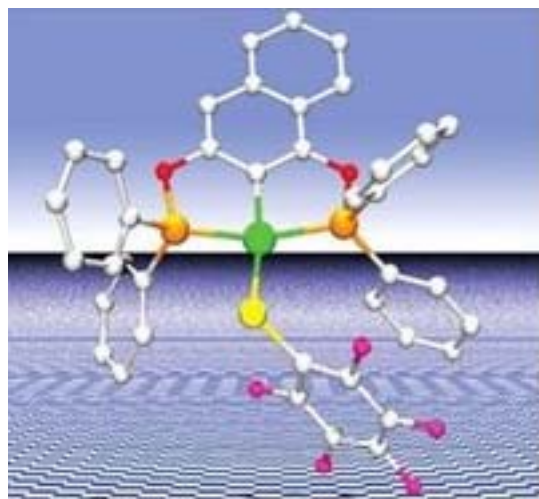


# Synthesis of Pincer Complexes

Yang Zehua

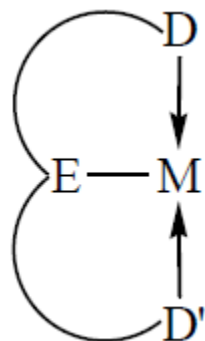
2010.11.13



# Contents

- Introduction
- Synthetic routes of Pincer complexes.
- Demonstration and mechanism of C-H, C-O, and C-C bond activation in pincer synthesis.
- Conclusions

# 1. Introduction



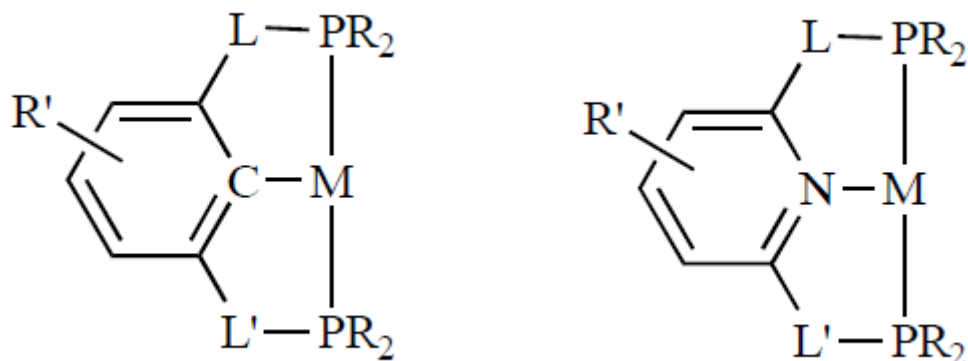
D = donor group: OR, SR, SeR, NR<sub>2</sub>, PR<sub>2</sub>

E = central donor atom: C, N, P

M = metal center

pincer complexes

# Aromatic-based PCP and PNP pincer



L=NH, O, CHR, CH<sub>2</sub>, CH<sub>2</sub>O, C=O(NR)

R=alkyl, aryl, alkoxy, aryloxy, amino

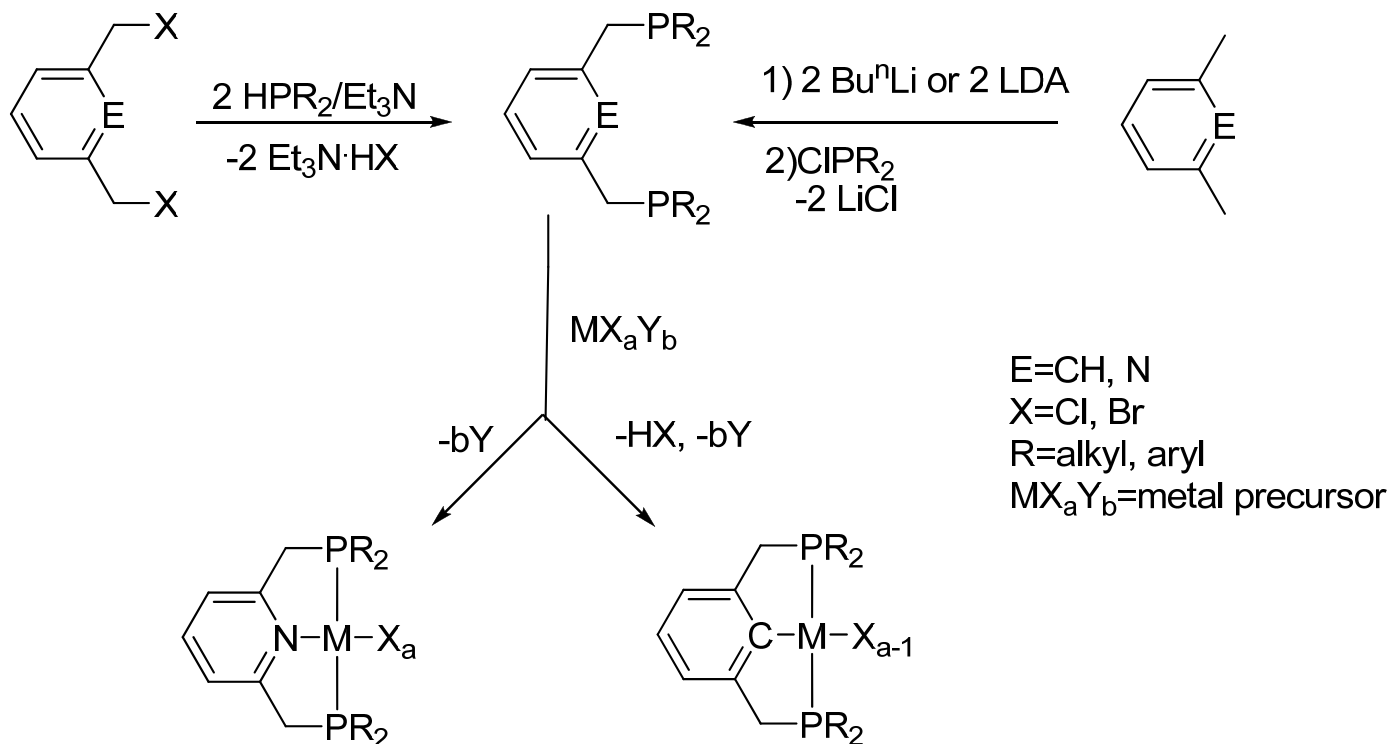
R'= H, electronwithdrawing or electrondonating group

M = Ni, Pd, Pt, Rh, Ir, Fe and Ru

Morales-Morales D .*Current Organic Synthesis*, **2009**, 6,169.

# 2.Synthesis of Pincer complexes

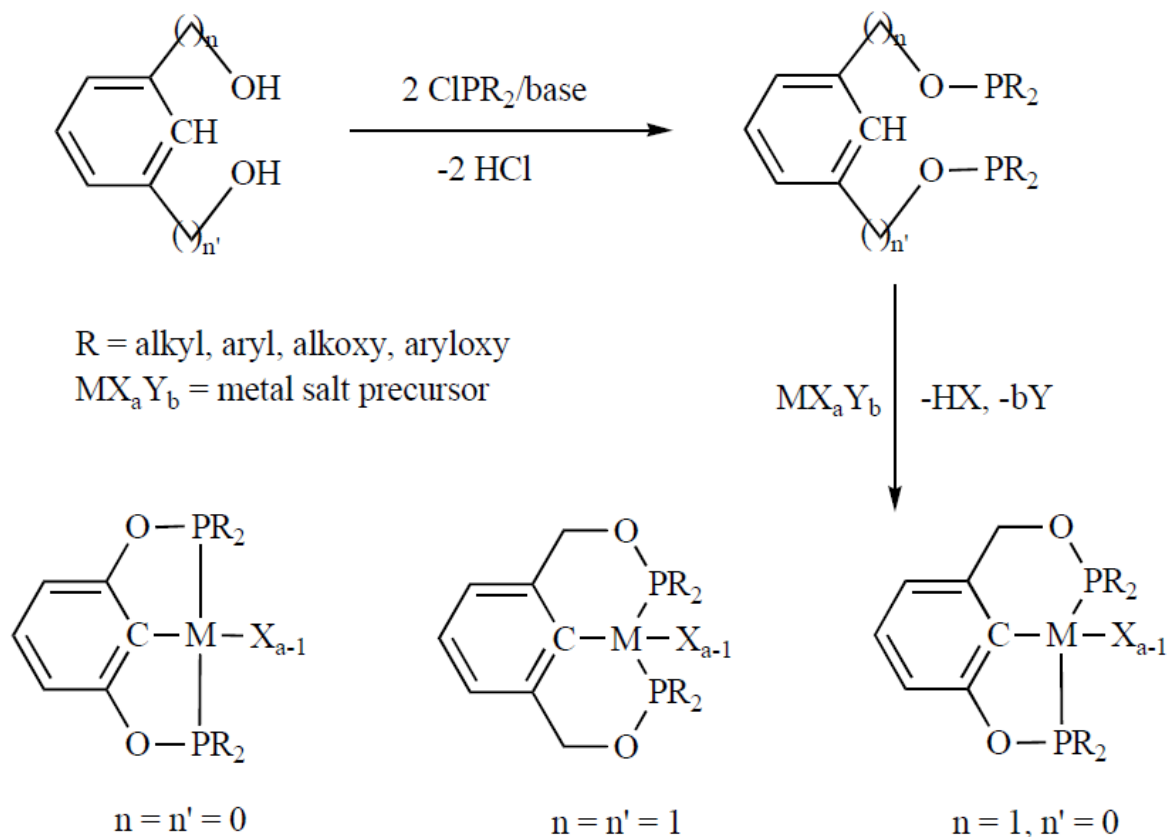
## 2.1 Phosphine Derivatives



Milstein, D. *Organometallics* **2002**, 21, 812.

Brookhart, M. *J. Am. Chem.Soc.* **2004**, 126,1804.

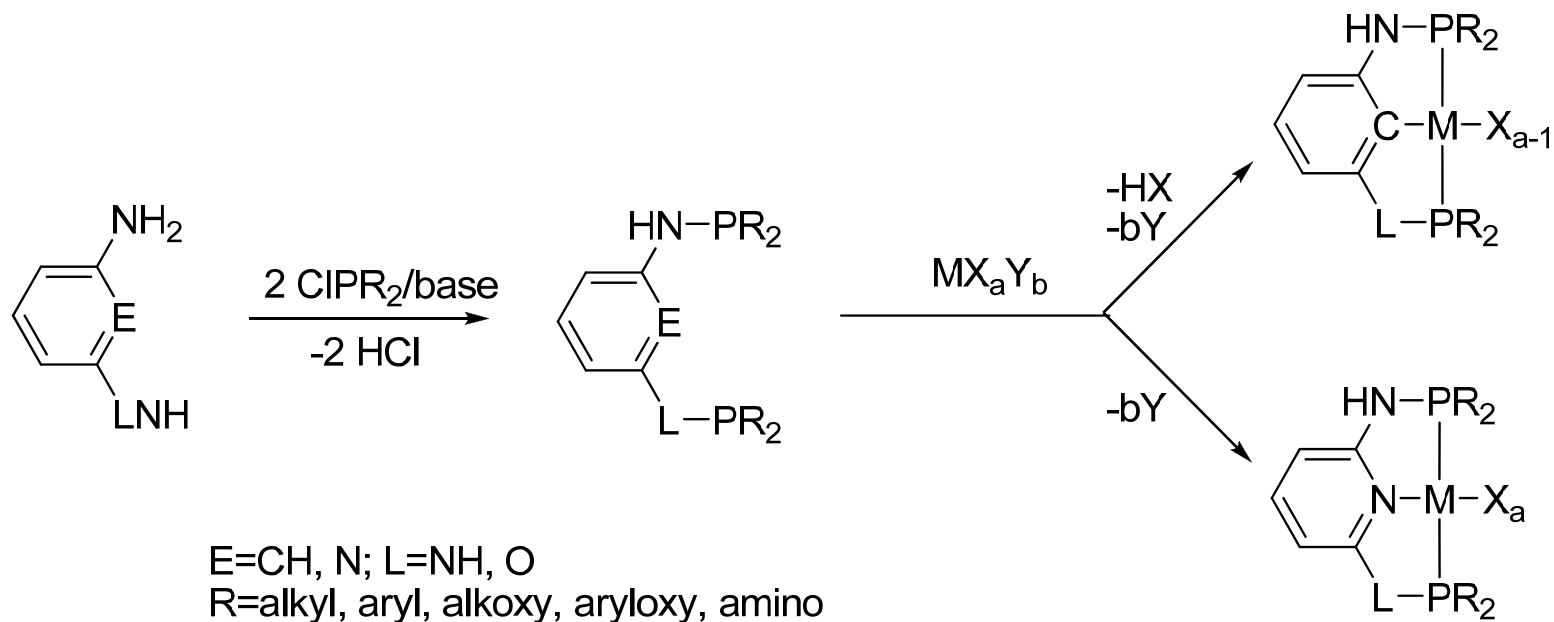
## 2.2 Phosphinite Derivatives



Welch, S. L. *New J. Chem.* **2000**, 24, 745.

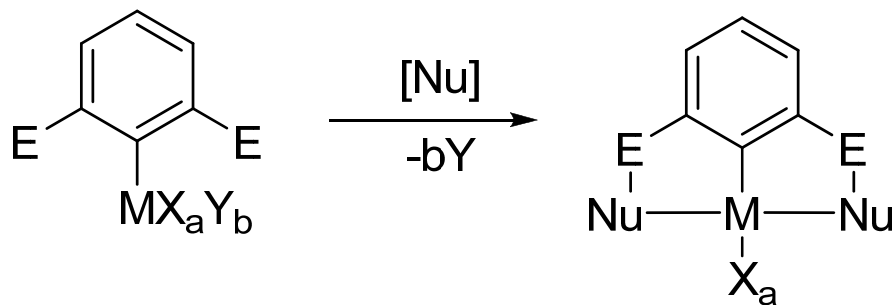
Scully, P. N. *Inorg. Chim. Acta.* **2006**, 359, 1870.

## 2.3 Phosphoramidite

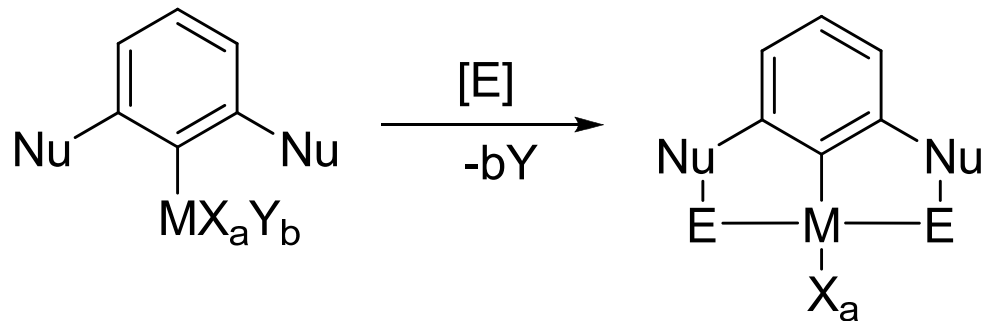


Kirchner, K. *Organometallics*. **2006**, 25, 3817.

## 2.4 Ligand Introduction Routes



Nucleophilic Ligand Introduction Route

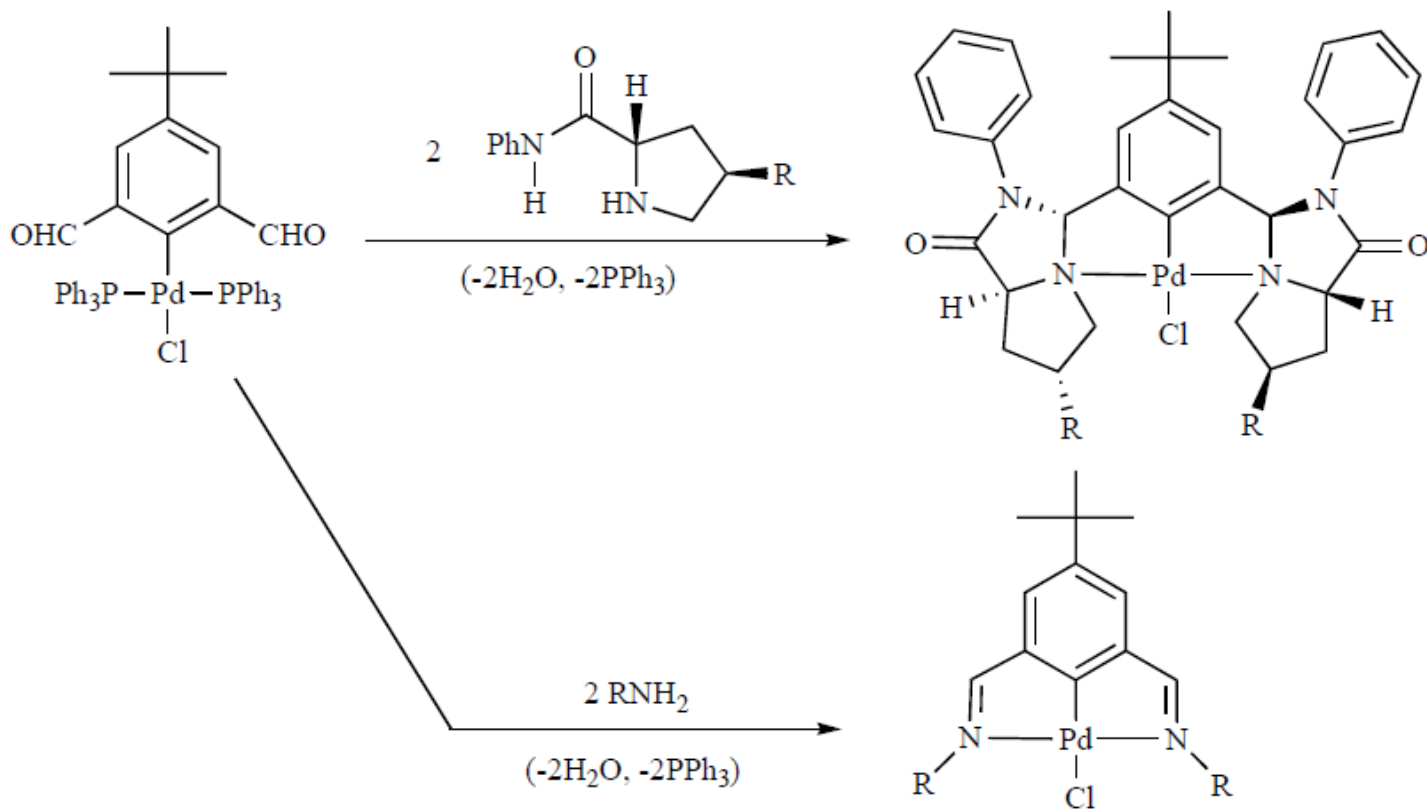


Electrophilic Ligand Introduction Route

Takenaka, K.; Uozumi, Y. *Adv. Synth. Catal.* **2004**, 346, 1693.  
Takenaka, K.; Uozumi, Y. *J. Am. Chem. Soc.* **2005**, 127, 12273.

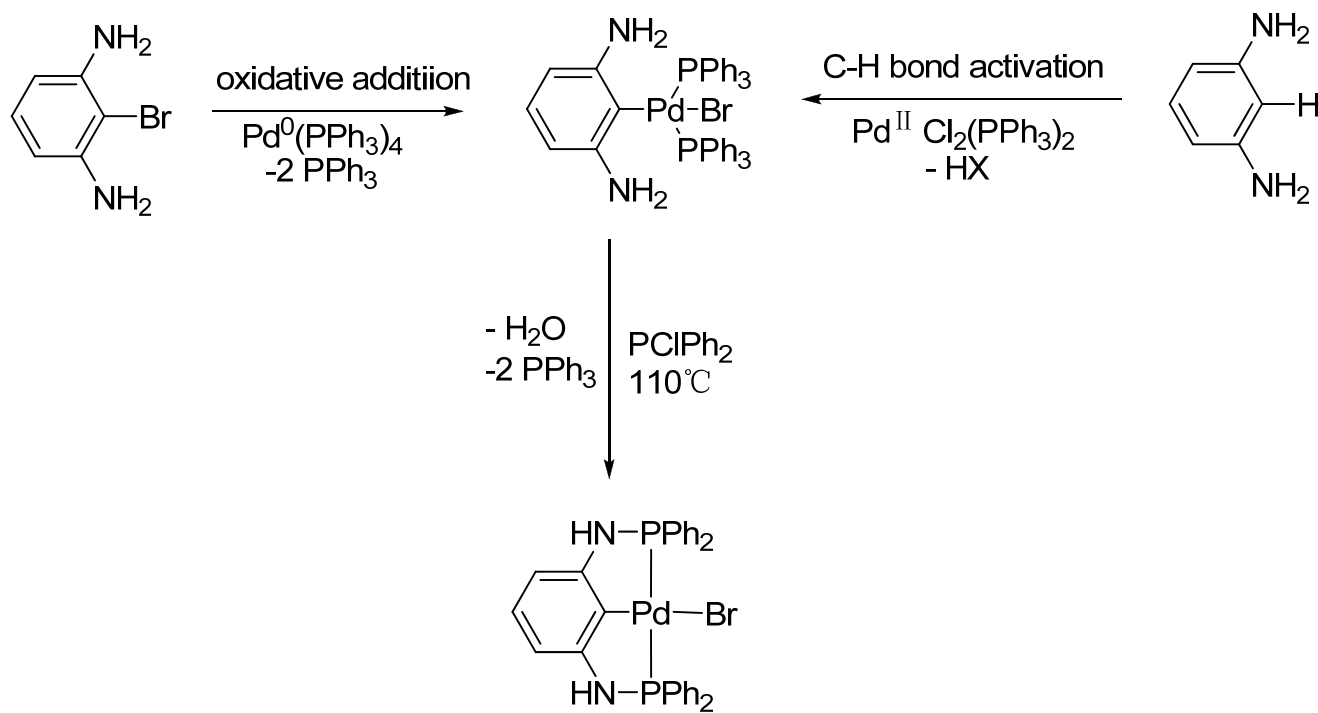


# Nucleophilic Ligand Introduction Demonstration



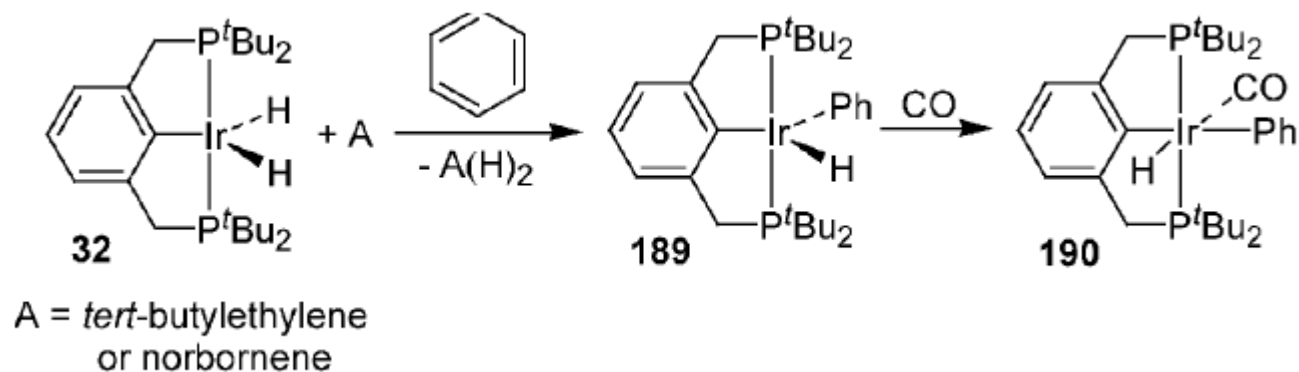
Takenaka, K.; Uozumi, Y. *Org. Lett.* **2004**, 6, 1833.

# Electrophilic Ligand Introduction Demonstration



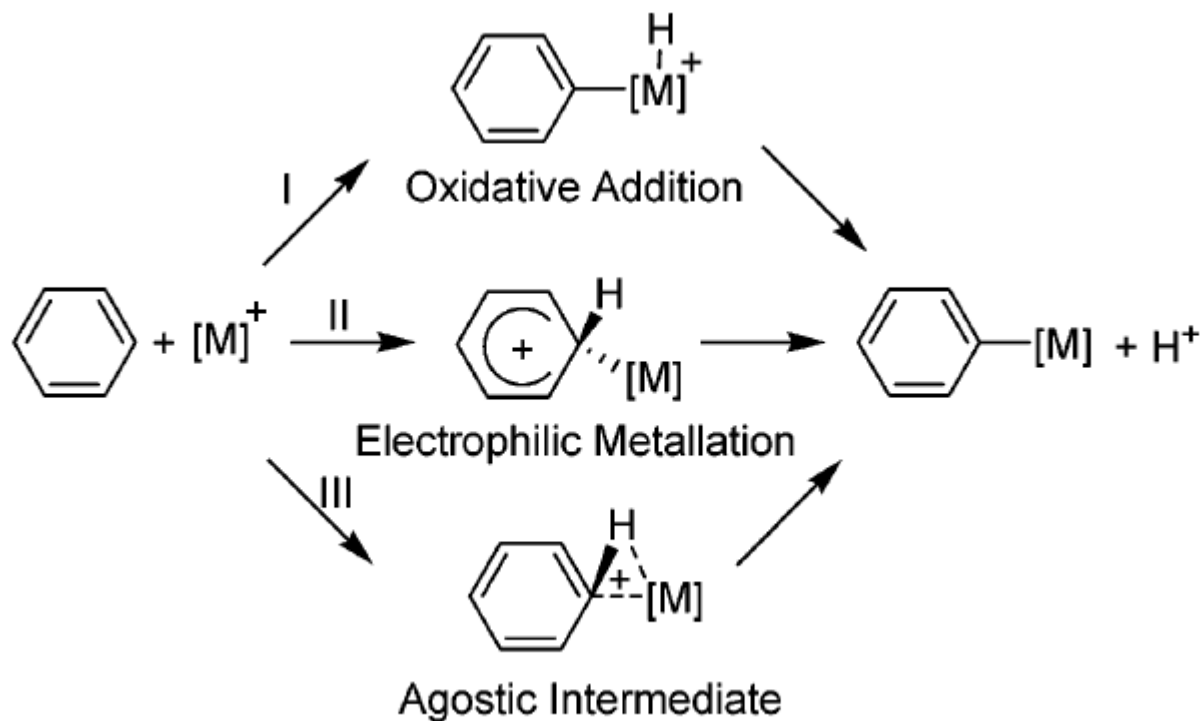
Kimura, T.; Uozumi, Y. *Organometallics*. **2006**, 25, 4883.

### 3. Demonstration and mechanism of C-H, C-O, and C-C bond activation



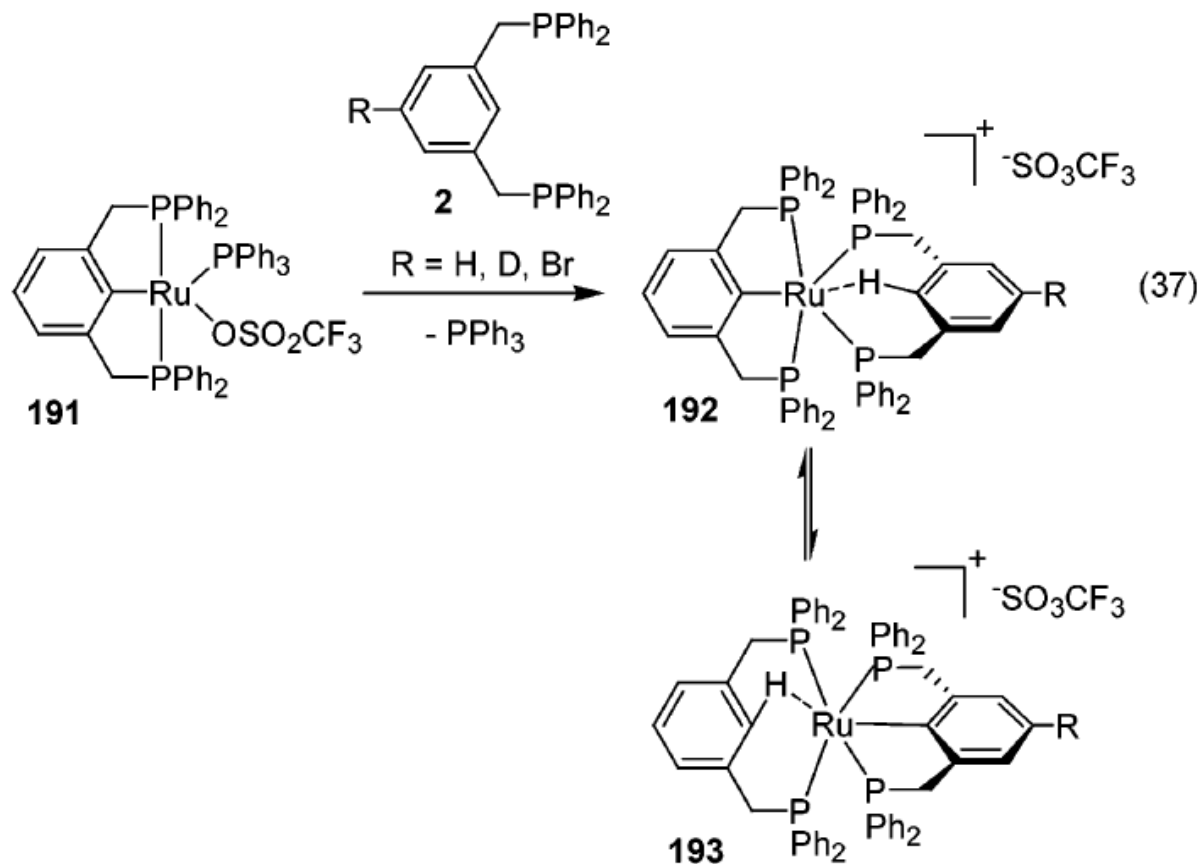
Kanzelberger, M.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, 122, 11017.

# 3.1 Aryl C-H and C-C Agostic Complexes



Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

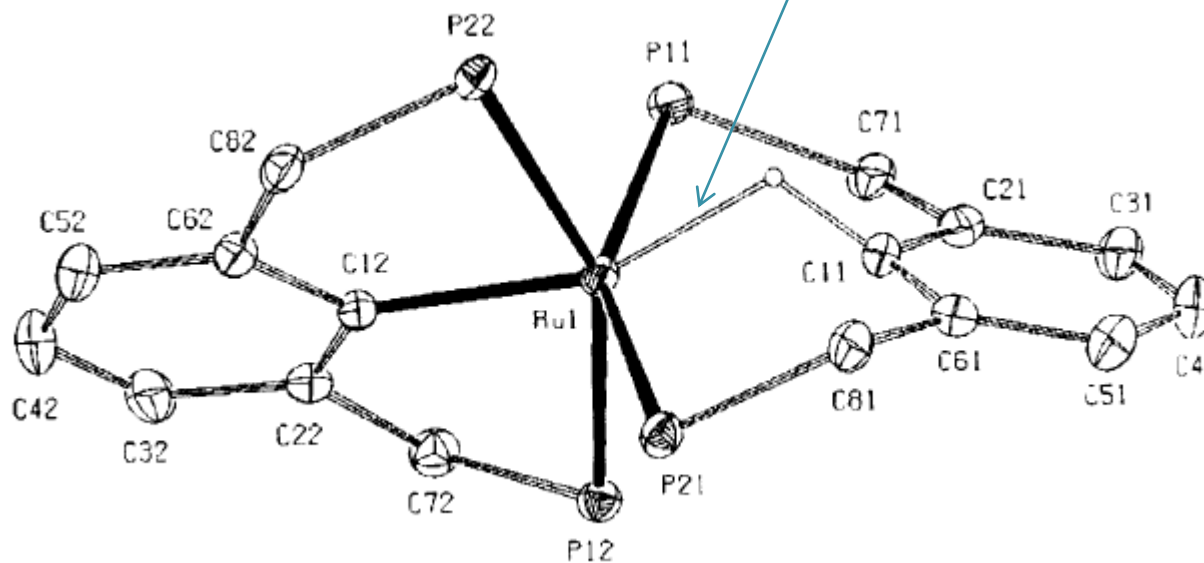
# Demonstration 1



Dani, P.; van Koten, G. *Organometallics*. 2000, 19, 5287.

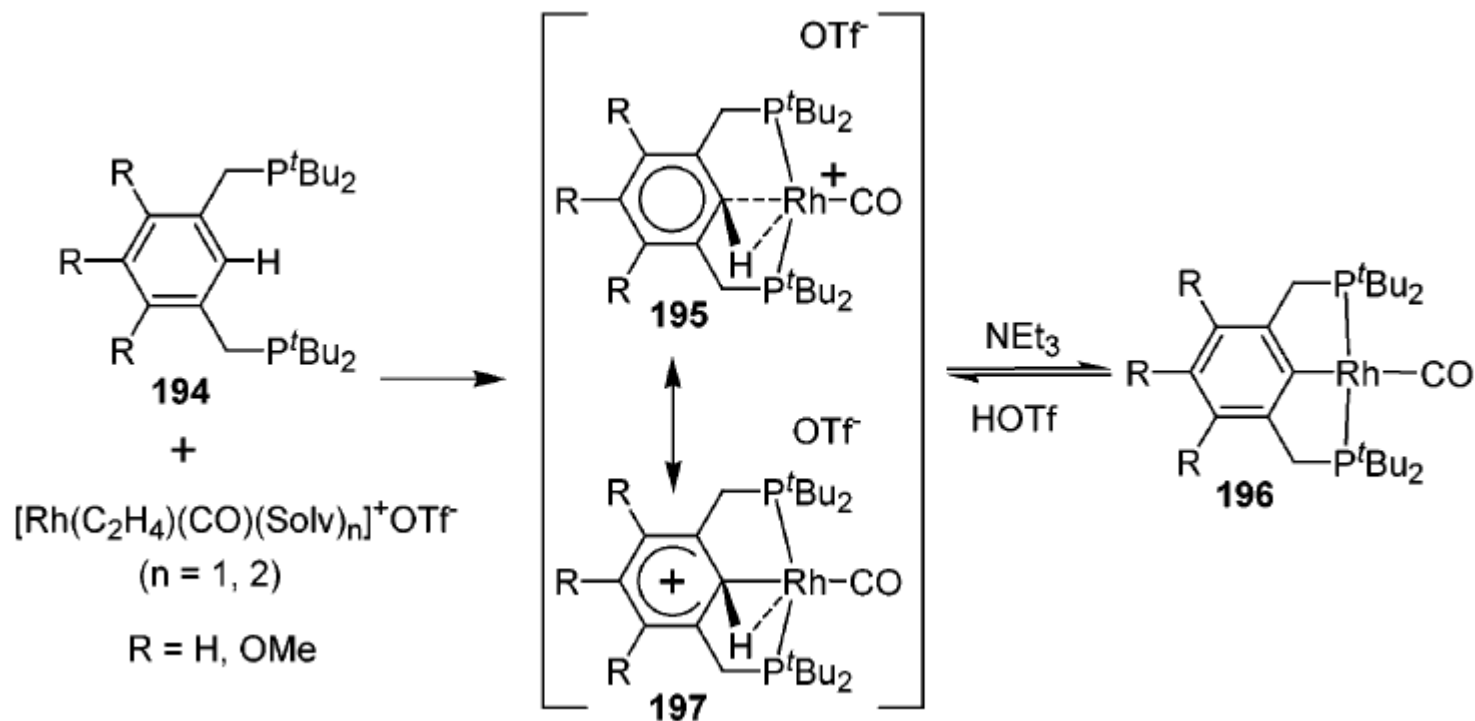
# ORTEP Drawing of C-H...Ru

C-H: 1.15 Å, Rh...H: 1.76 Å  
Compare  
C<sub>6</sub>H<sub>5</sub>-H: 1.101 Å, Ru-H: 1.52 Å



Dani, P.; van Koten, G. *Organometallics*. **2000**, *19*, 5287.

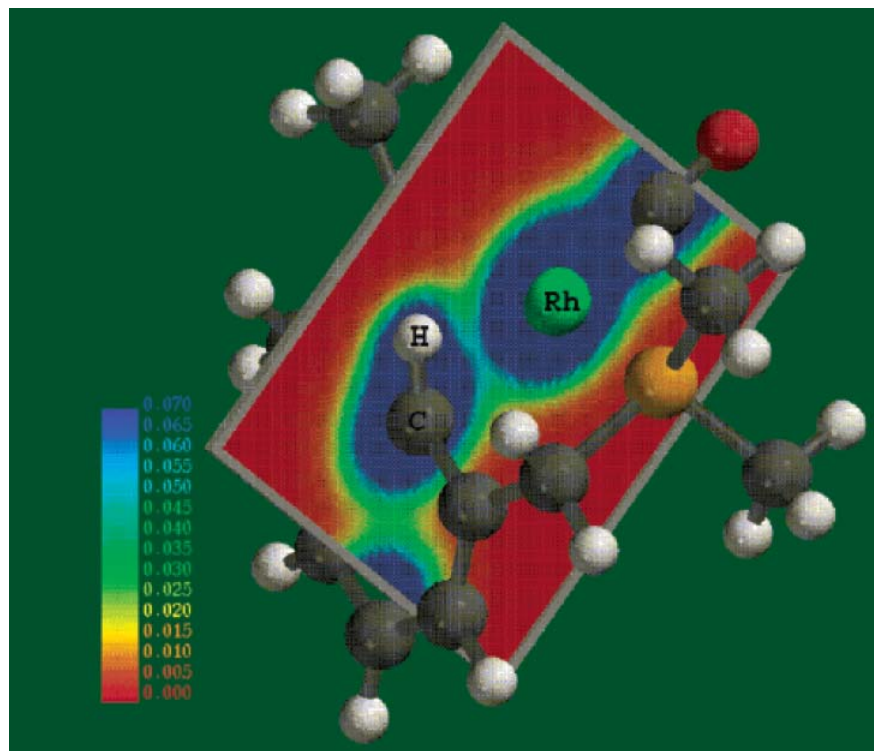
## Demonstration 2



Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.



# Electron Density Calculation

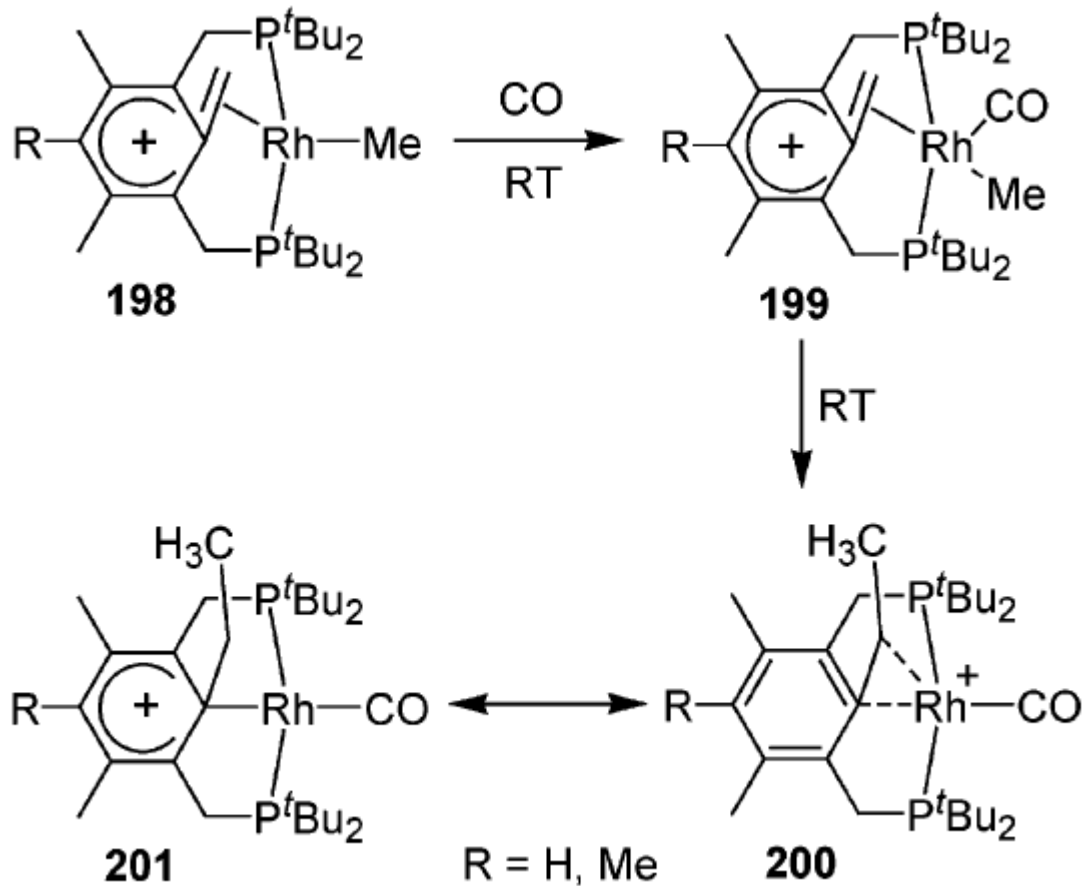


Positive charge locate on the metal center

Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.

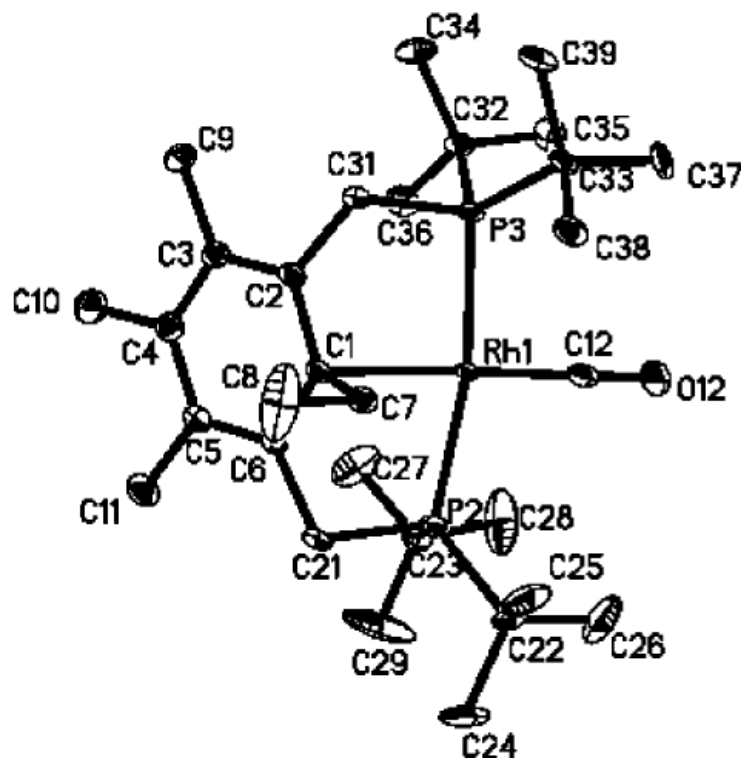


# C-C Agostic Complexes



Vigalok, A.; Milstein, D. *Organometallics*. **1999**, 18, 895.

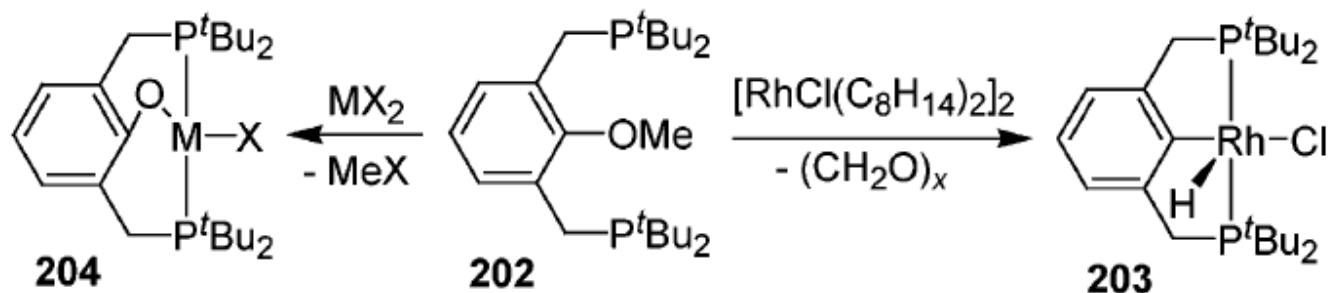
# ORTEP Drawing of C-C...Ru



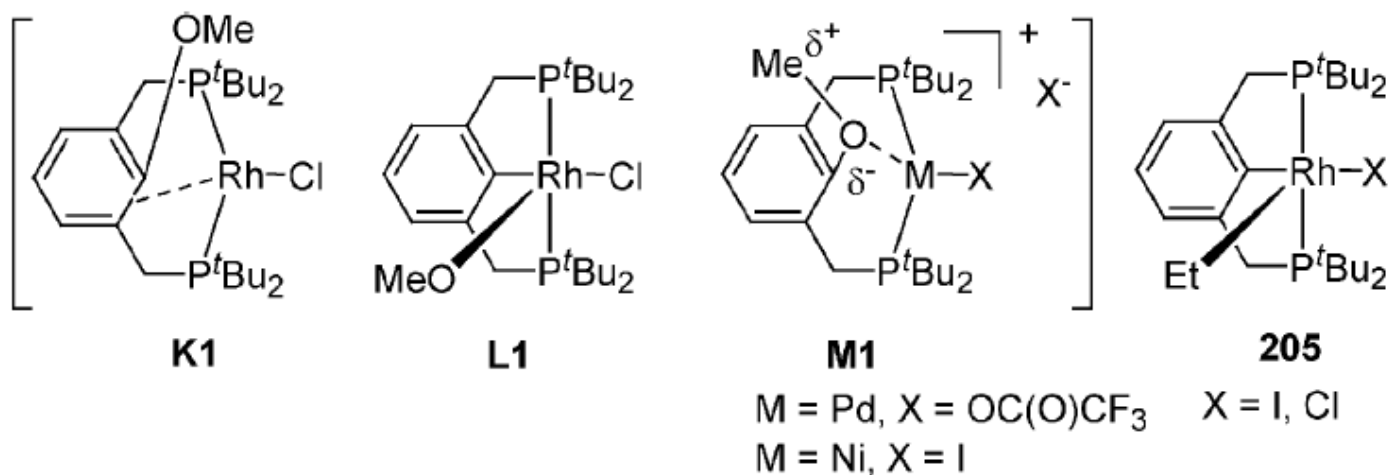
Distance between C-C bond and the Rh center is shorter than the sum of the van der Waals radii of the atoms involved (2.817 Å).

Metal-C<sub>ipso</sub> bond distance of 2.354(3) Å is longer than regular C-Rh *bonds*.

## 3.2 Competitive $SP^2$ - $SP^3$ and $SP^3$ - $SP^3$ C-O Bond Activation



$M = \text{Pd}, X = \text{OC}(\text{O})\text{CF}_3$   
 $M = \text{Ni}, X = \text{I}$

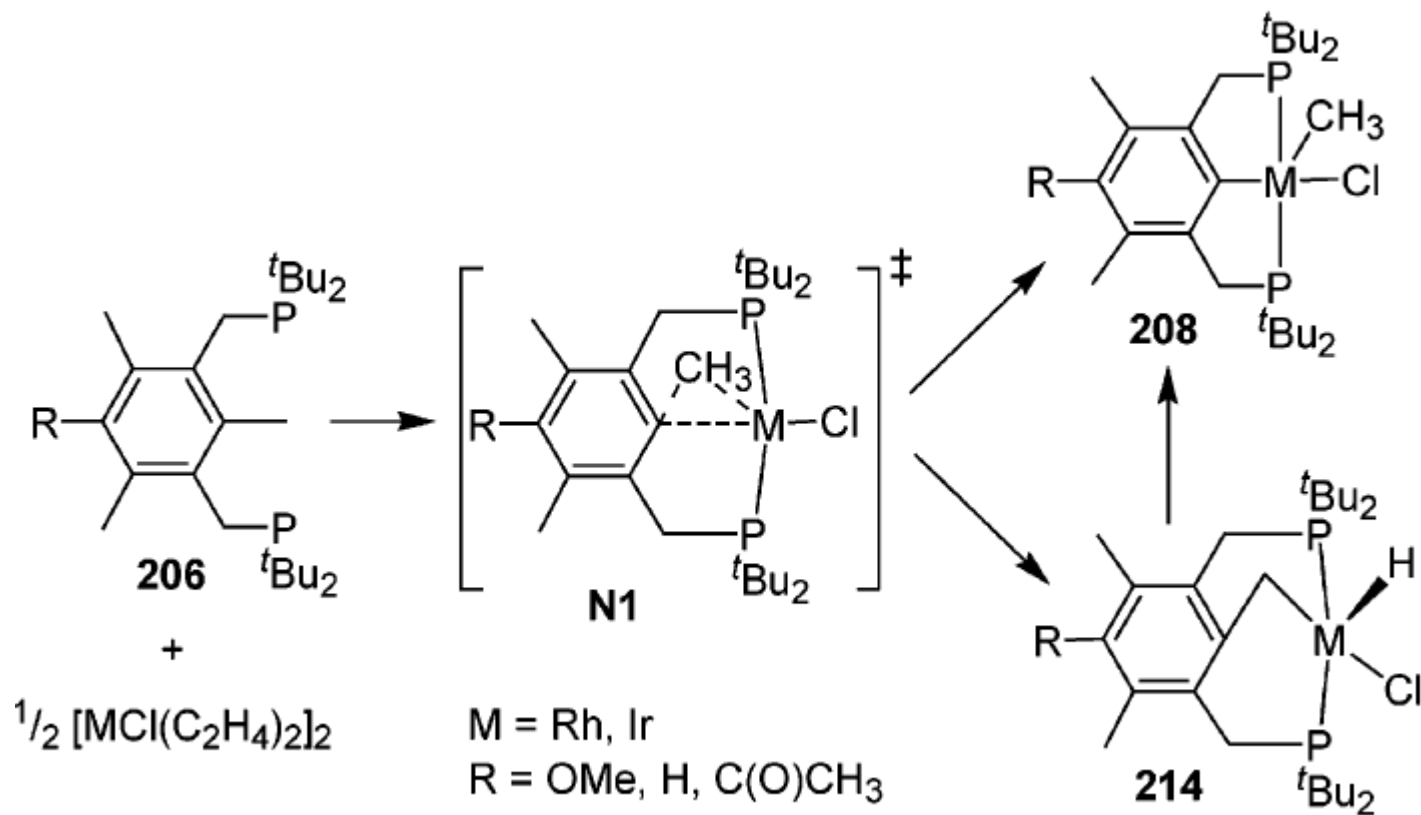


# Conclusion of Competitive C-O Bond Activation

- Aryl-O or alkyl-O bond activation depending on the applied metal complex precursor and the alkoxy group.
- the Rh(I) metal center only activates aryl-O bond, whereas the Pd(II) and Ni(II) systems preferentially activate the alkyl-O single bond.

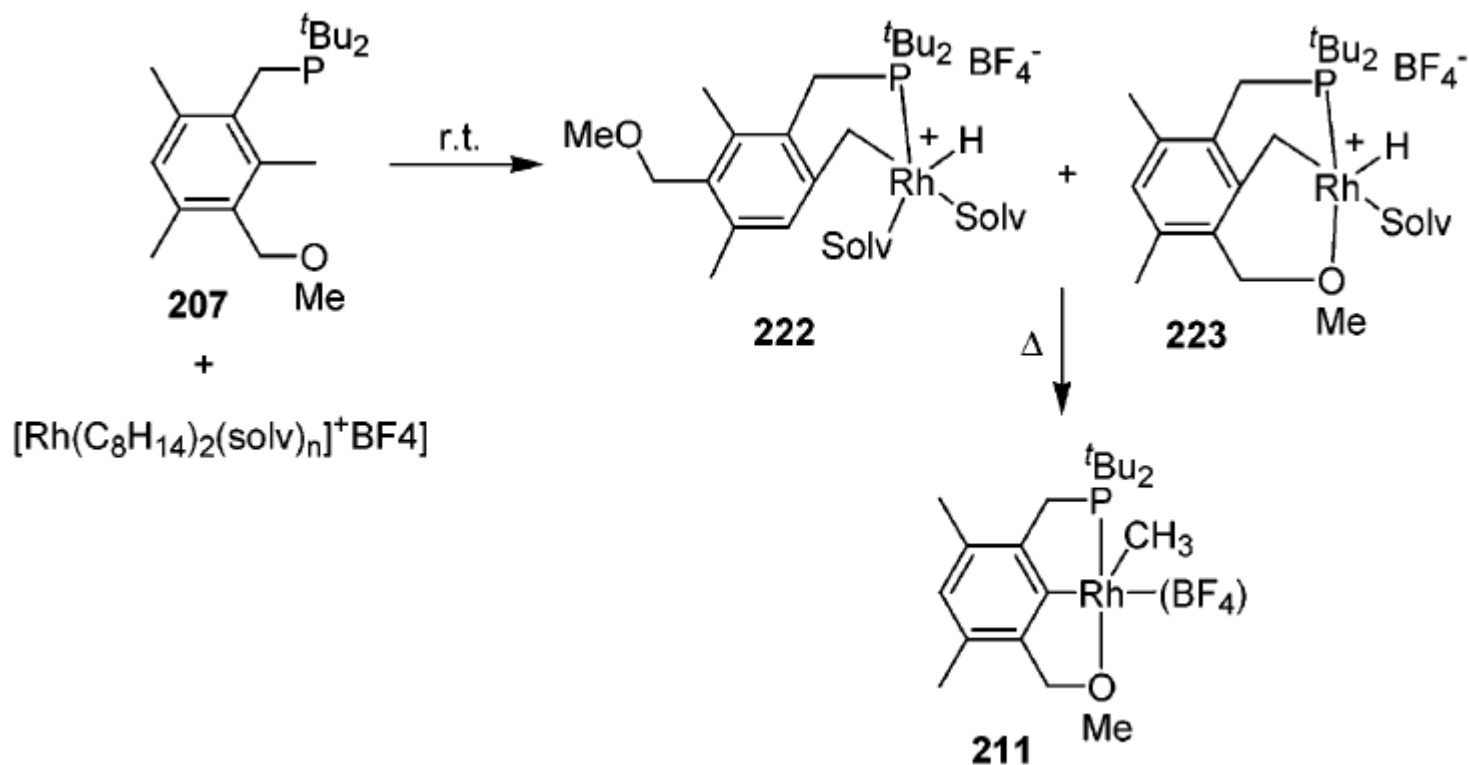
van der Boom M.E., Milstein D. *Chem. Rev.* **2003**, 103, 1759

### 3.3 Selective C-C Bond Activation



Rybtchinski, B; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406.

# Demonstration



Rybtchinski, B; Milstein, D. *J. Am. Chem. Soc.* **2001**, 123,9064.

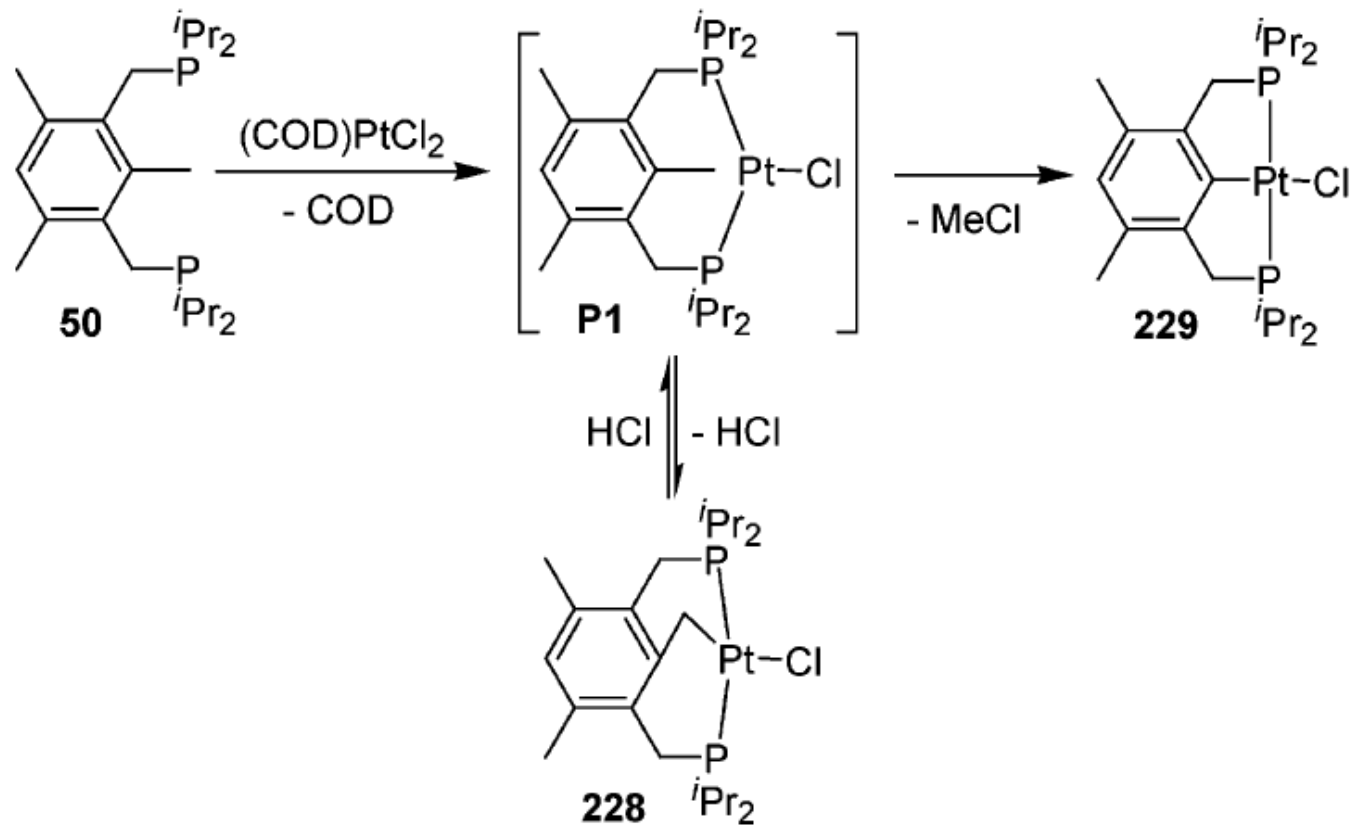
# Compare of C-C and C-H Bound Activation

entry	ligand	precursor	solvent	kinetic products	thermodynamic product
1	PCN (52)	neutral	benzene	C-C	C-C
2	PCN (52)	neutral	toluene	C-C	C-C
3	PCN (52)	neutral	3-fluorotoluene	C-C	C-C
4	PCP (206)	neutral	benzene	C-H;C-C	C-C
5	PCP (206)	neutral	THF	C-H;C-C	C-C
6	PCP (206)	cationic	THF	C-H;C-C	C-C
7	PCP (206)	cationic	MeCN	C-H	C-H
8	PCO (207)	cationic	THF	C-H	C-C
9	PCO (207)	cationic	acetone	C-H	C-C
10	PCO (207)	cationic	MeOH	C-H	C-C
11	PC (213)	cationic	MeOH	C-H	C-H

van der Boom M. E., Milstein D.J. *Chem. Rev.* **2003**, *103*, 1759



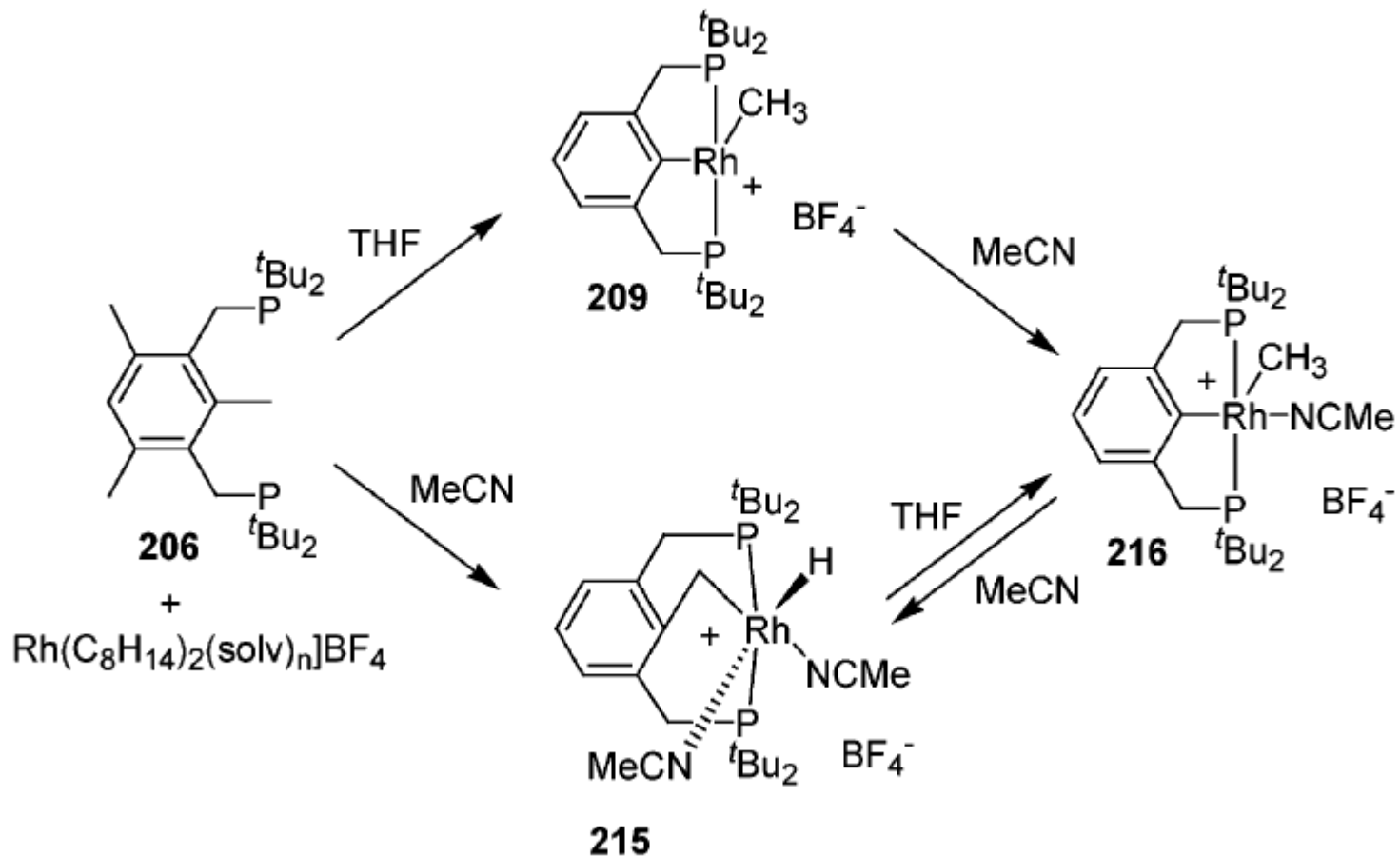
# Special Case



Van der Boom, M. E; Milstein, D. *Inorg. Chem.* **2006**,45, 7068.

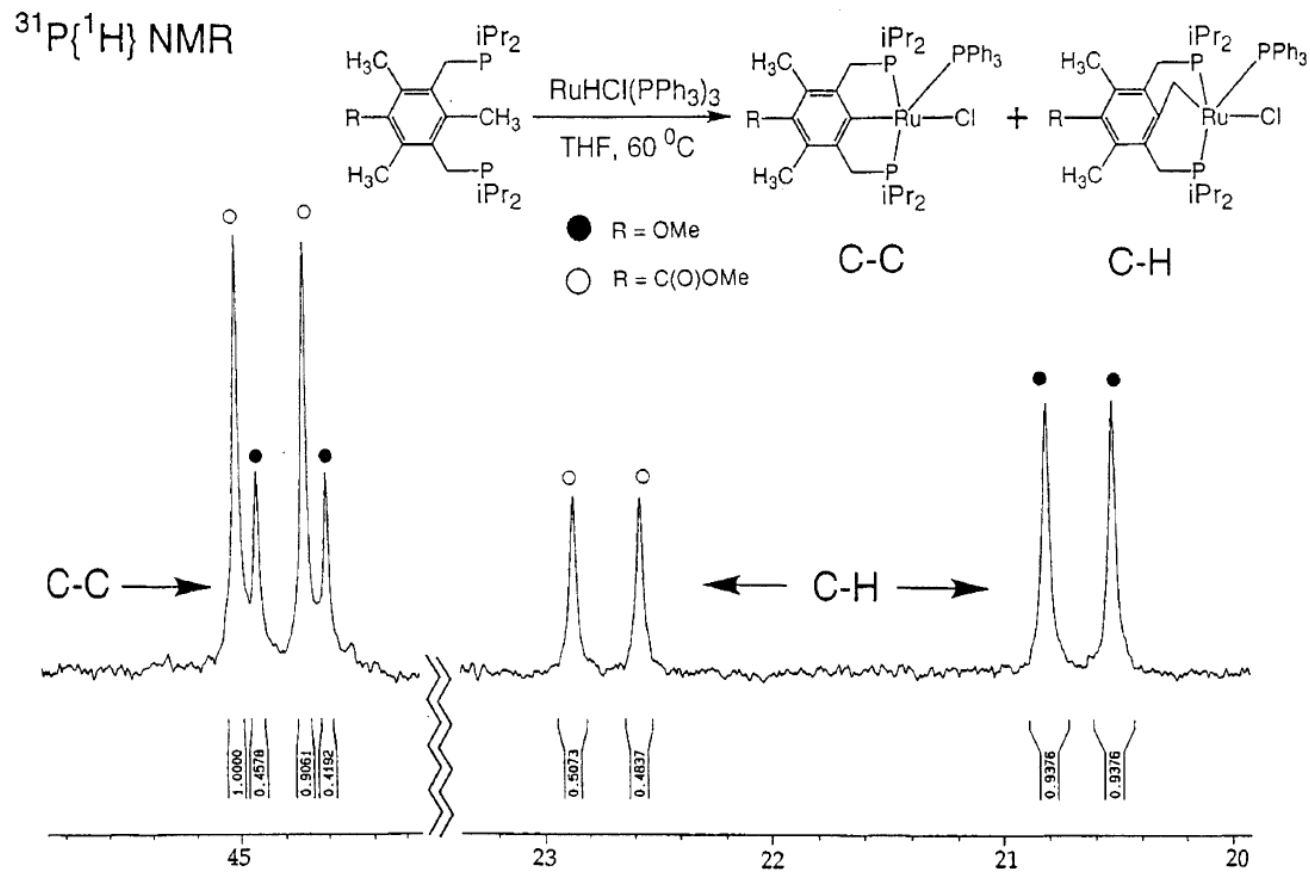


# Solvent Effect



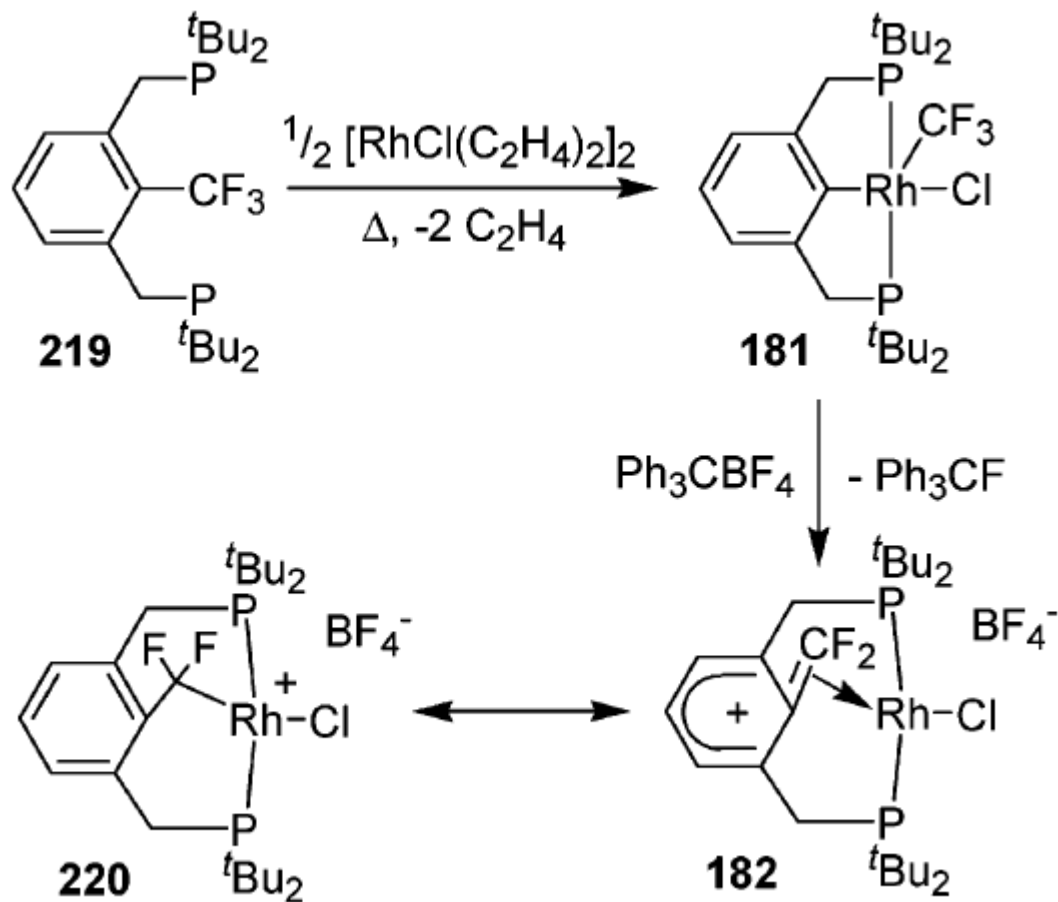
Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528

# Substituent Effect



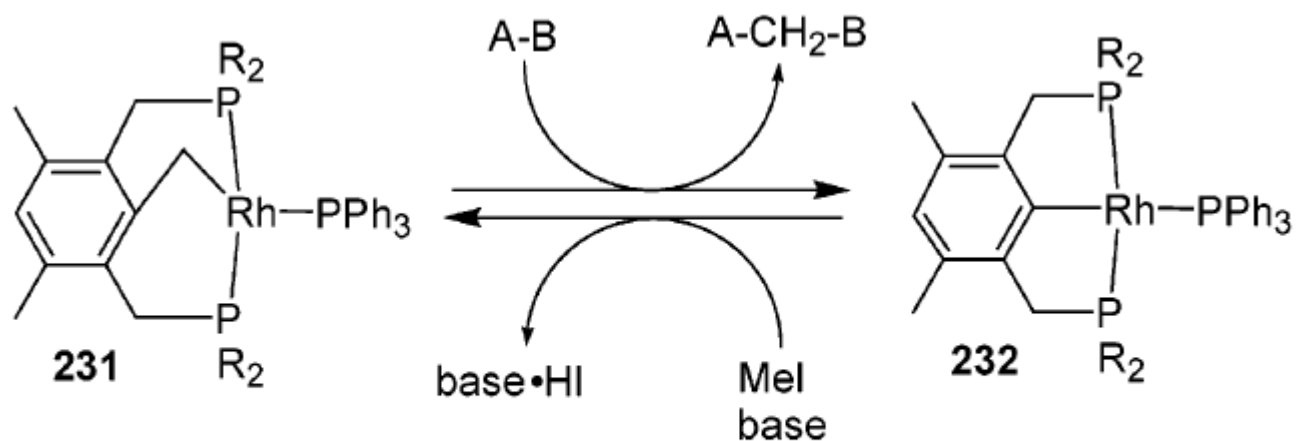
Regis, R. M Milstein, D. *Organometallics* . 2001, 20, 1719.

# Competitive C-F and C-C Bond Activation



van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652

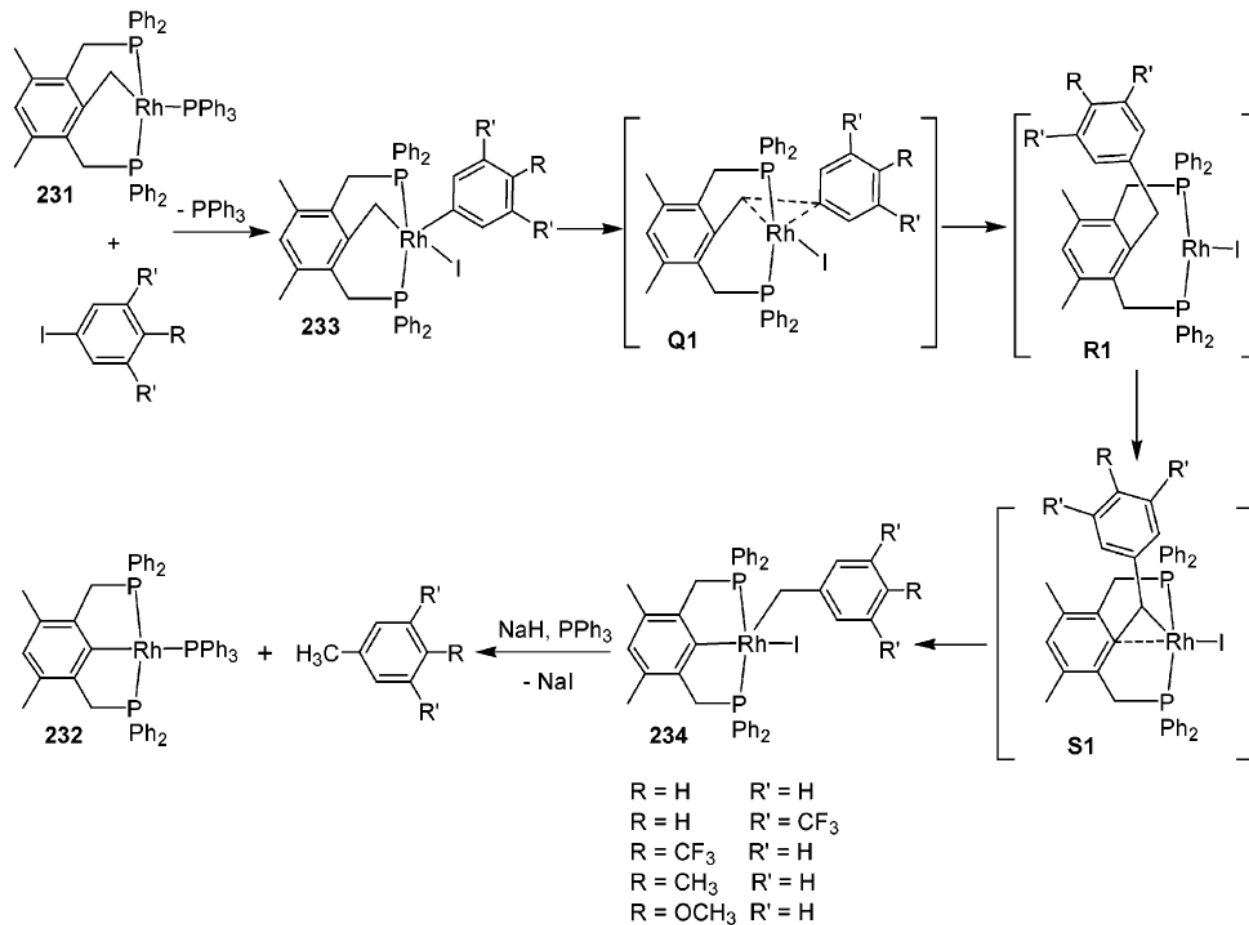
# Methylene Transfer to Incoming Reagents



A = H, B = H, SiOEt<sub>3</sub>, SiPh, Ph; A = B = (MeO)<sub>3</sub>Si  
R = Ph, <sup>i</sup>Pr

Gozin, M ; Milstein, D. *Nature*. **1994**, 370, 42.

# Methylene Transfer Mechanism



Cohen, R; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 7723.

## Conclusions

- Pincers are synthesized in two routes: Metal introduction route and Ligand introduction route.
- In most Ligands, C-H bond activation is kinetically favored, whereas C-C bond activation is thermodynamically preferred.
- Design of a highly efficient enantioselective PCP complexes is still a highly desirable target.



**Thanks !**