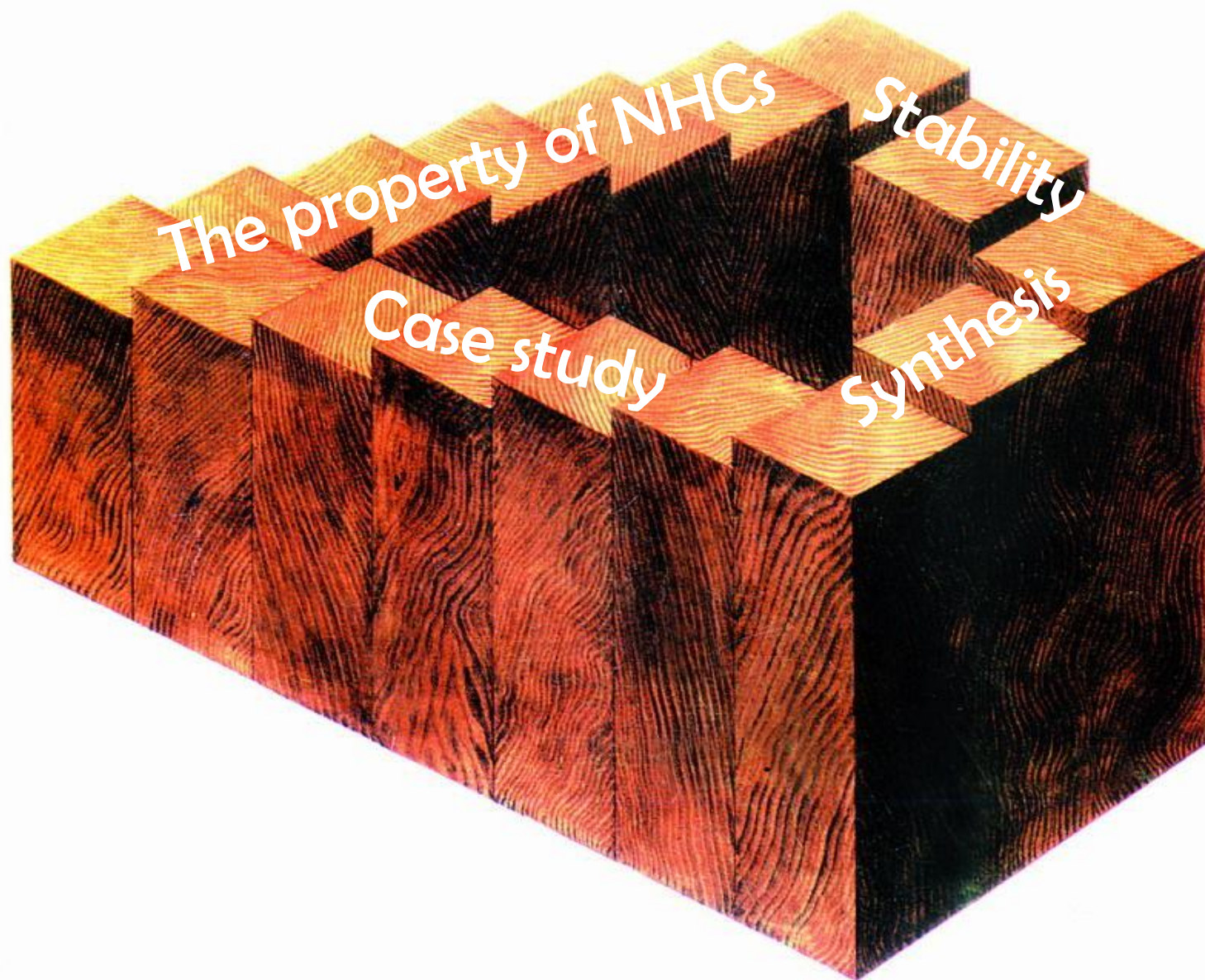


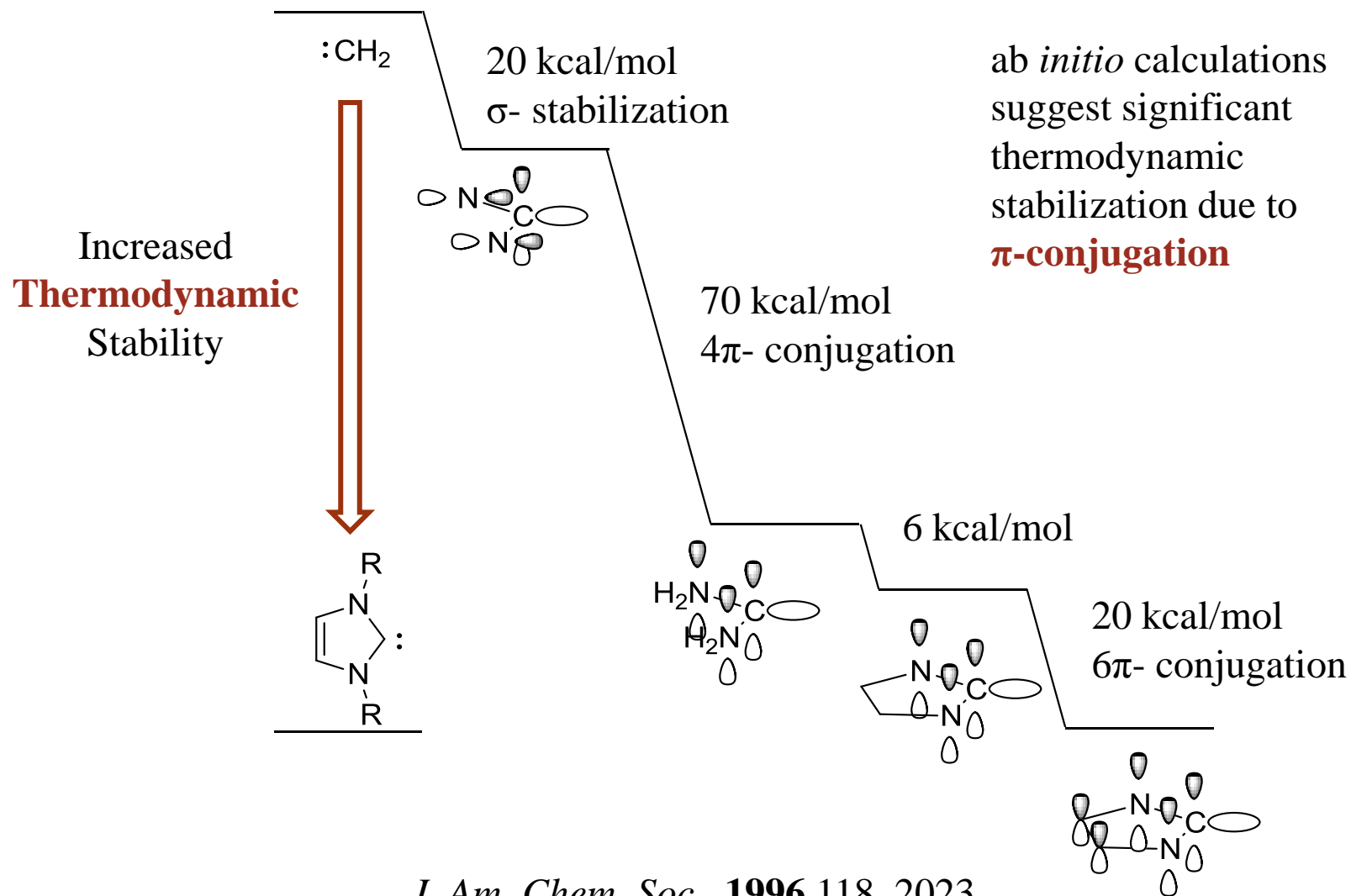
LITERATURE REPORT

Reporter: He Zhiqi
Supervisor: Prof. Yong Huang
2012.11.19

NHCs in Organometallic chemistry



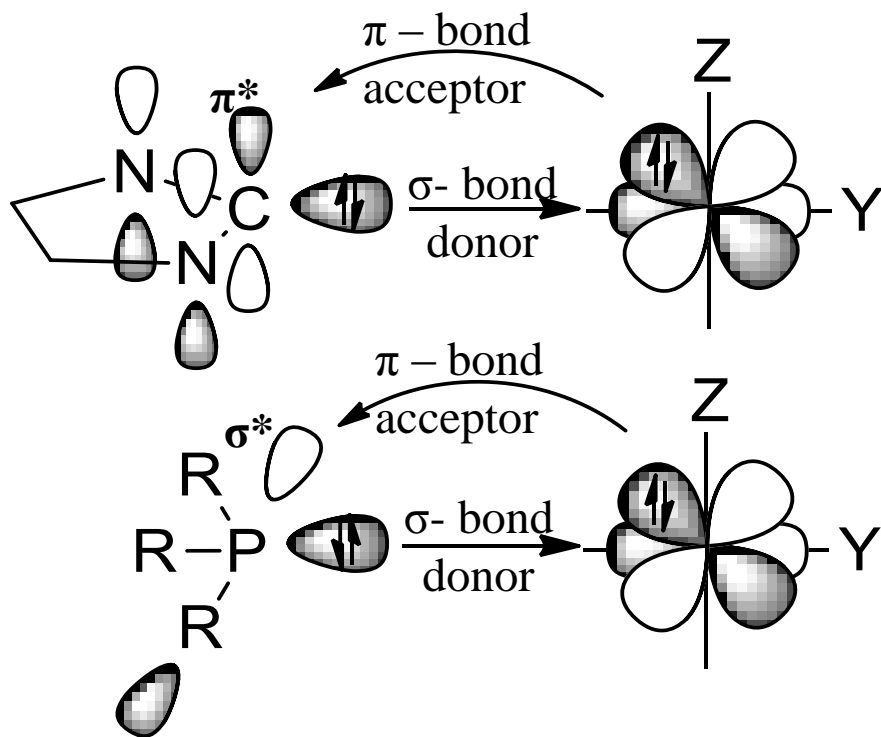
Stability of NHCs



J. Am. Chem. Soc., **1996**, 118, 2023

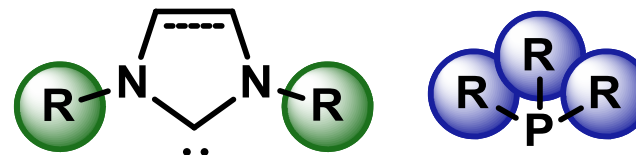
Phosphine Mimics

Electronic property



Steric property

Change R group to vary steric size



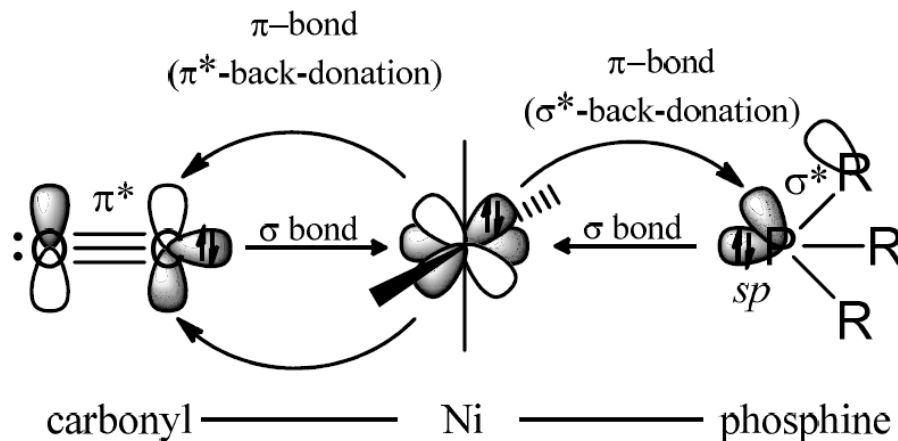
But they are quite different!!!

**Phosphorus
Ligand (L)**

CO ν , cm^{-1}

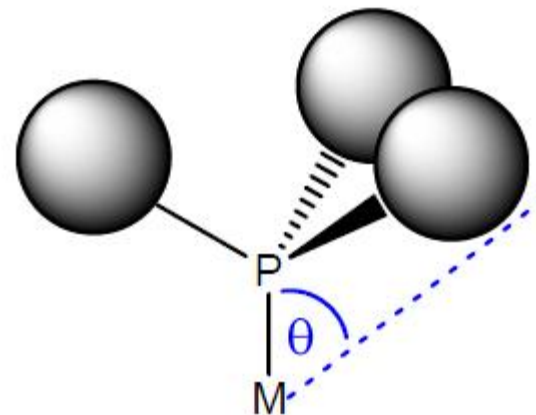
P(<i>t</i> -Bu) ₃	2056
PCy ₃	
P(<i>i</i> -Pr) ₃	2059
P(NMe ₂) ₃	2062
PMe ₃	2064
PPhMe ₂	2065
PBz ₃	2066
PPh ₂ Me	2067
PPh ₃	2069
PPh ₂ (OEt)	2072
P(<i>p</i> -C ₆ H ₄ Cl) ₃	2073
PPh(OEt) ₂	2074
P(OEt) ₃	2077
PH ₃	2083
PCl ₃	2097
PF ₃	2111

Tolman Electronic Parameter



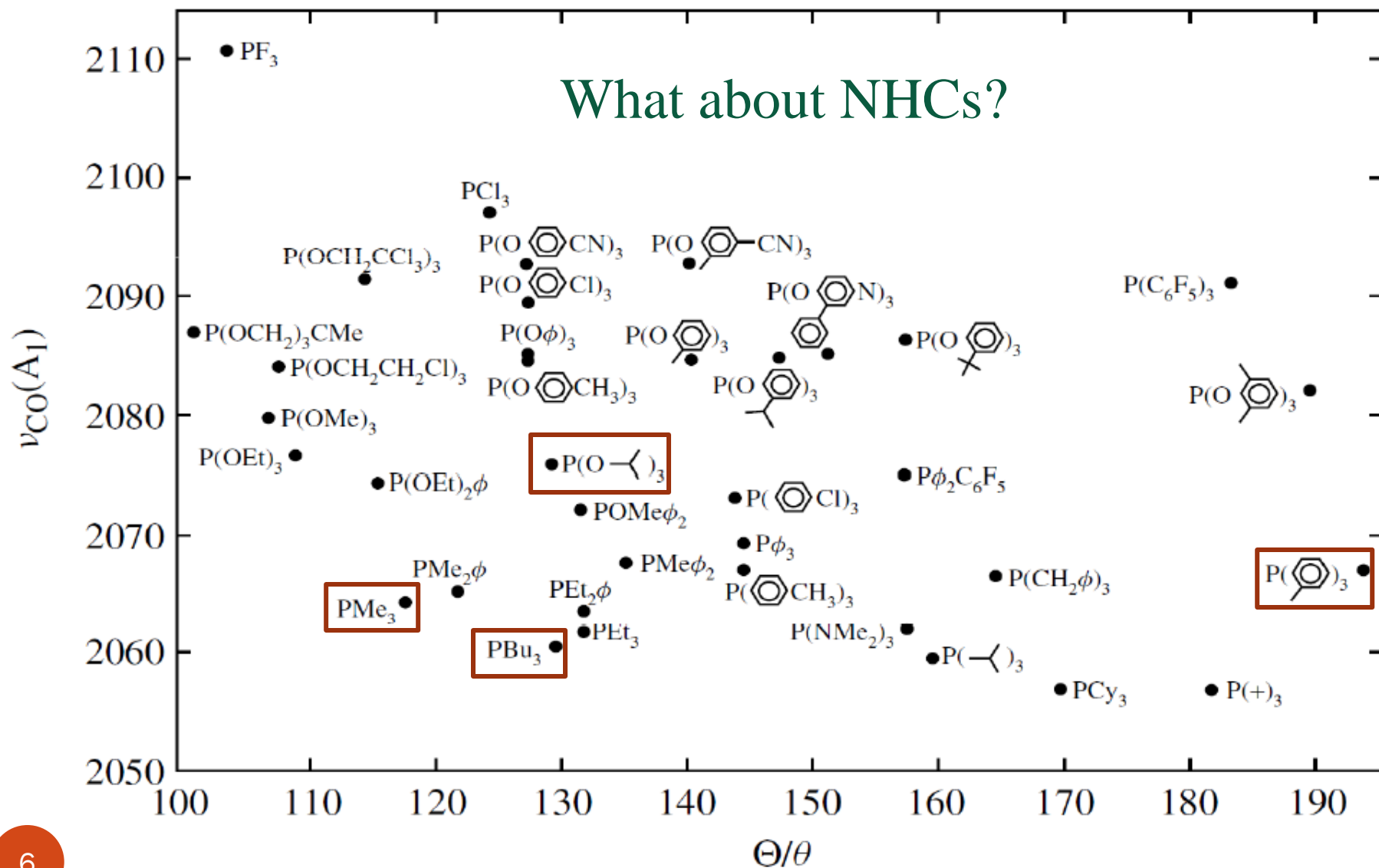
CO stretching frequencies measured for Ni(CO)₃L
where L are PR₃ ligands of different σ -donor abilities.
[$\nu(\text{CO}) = 2143 \text{ cm}^{-1}$]

Tolman's cone angle

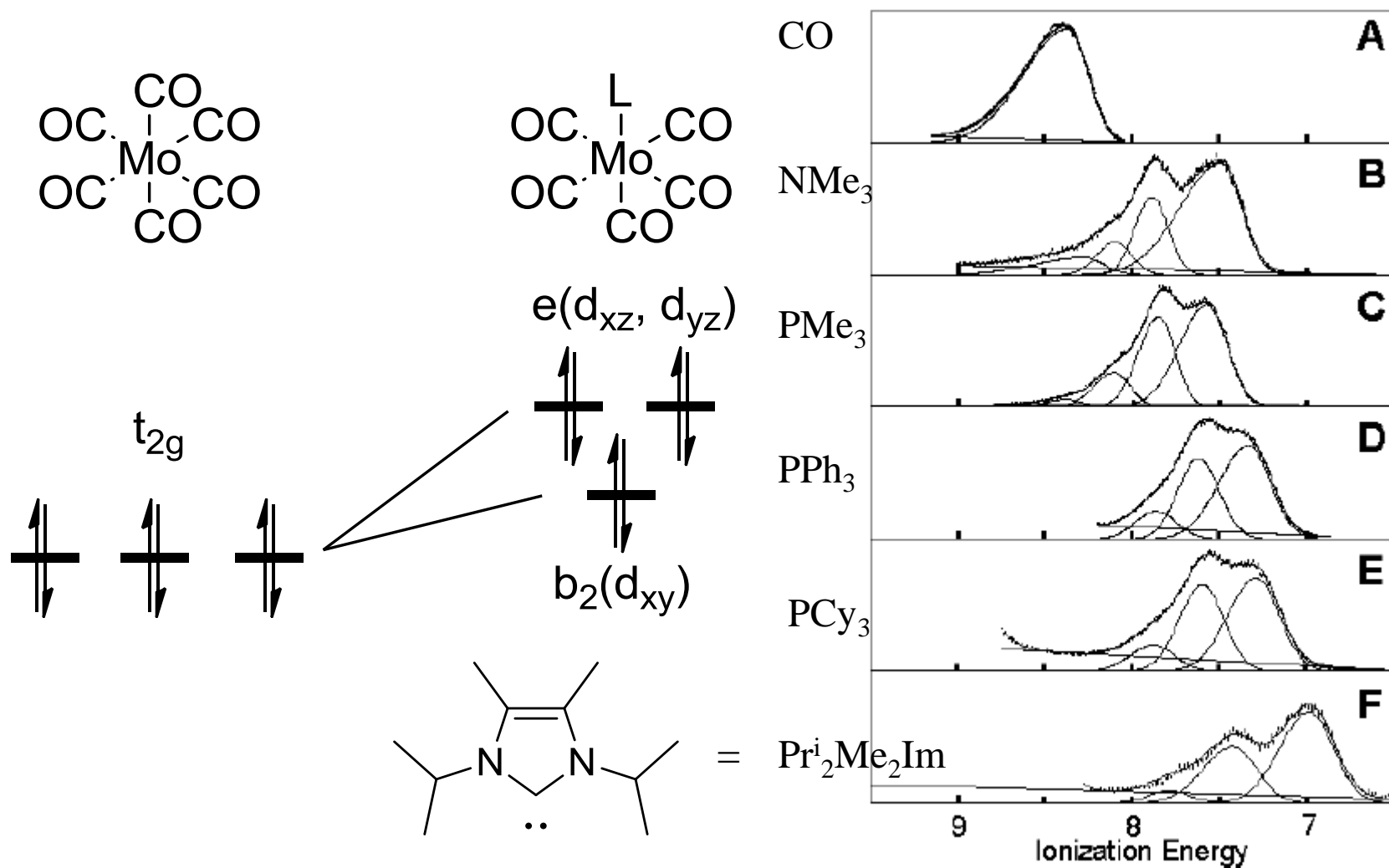


Chem. Rev., 1977,77, 313

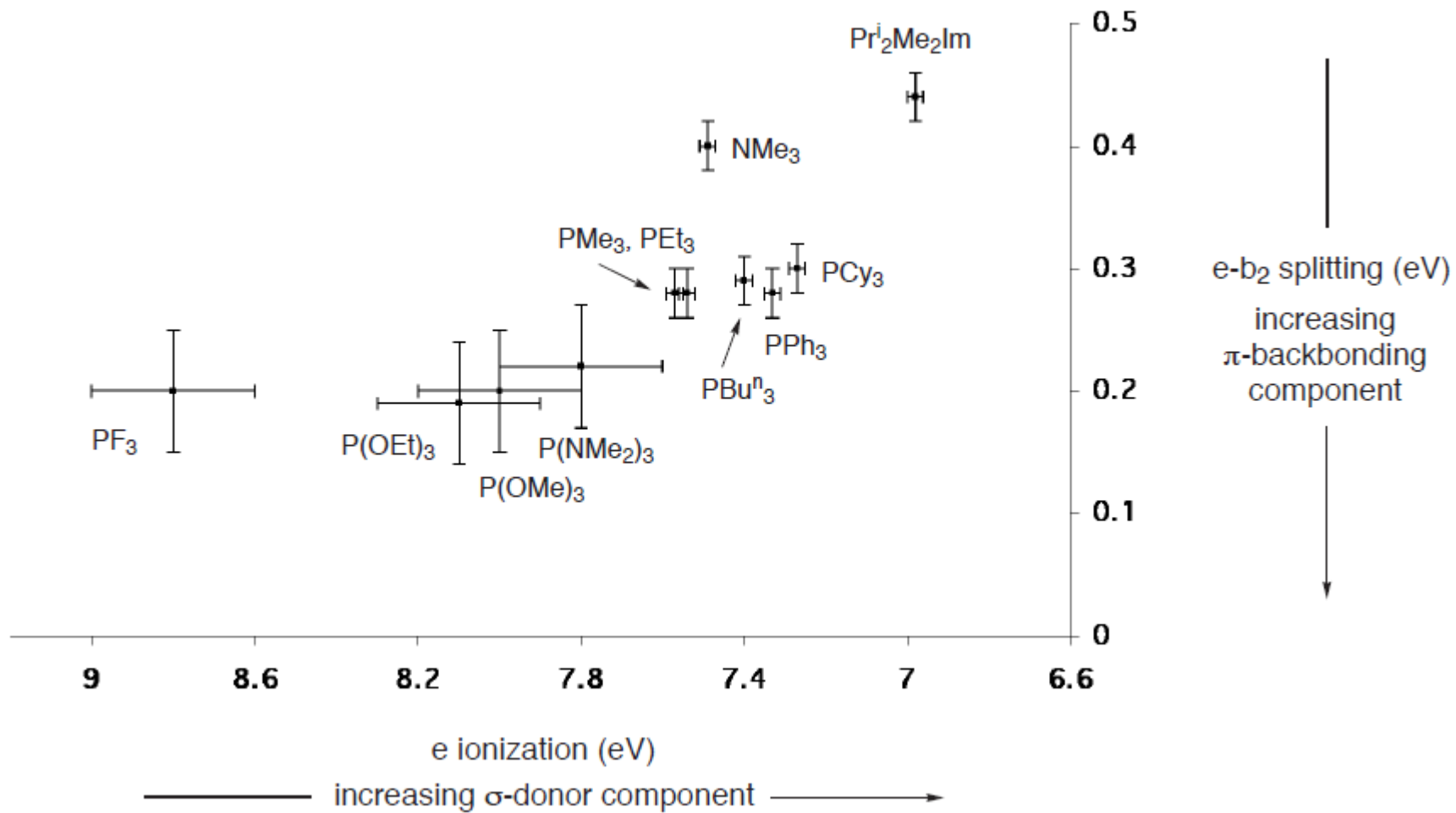
Tolman Plot of Electronic Parameter and Cone Angle



Different electronic property between PR_3 and NHCs

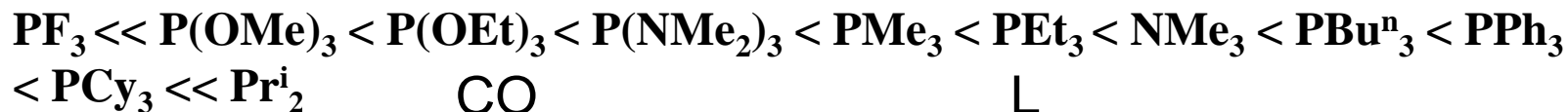


Trnka Tina Maria, Dissertation (Ph.D.) *Caltech*, 2003

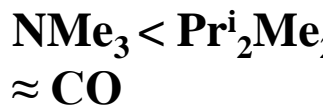
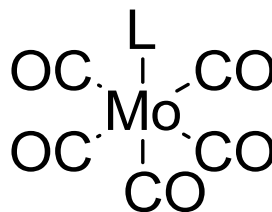
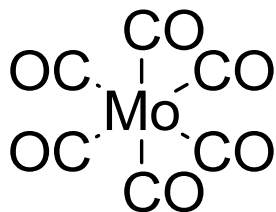


The σ - donor and π -acceptor order of different ligands

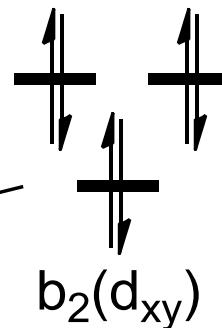
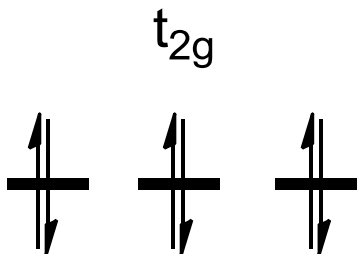
The σ - donor order:



The π -acceptor



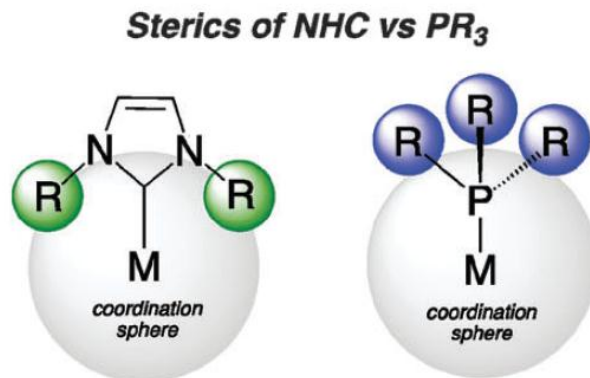
cis to L. The primary
variance in backbonding
ligand. Because C



terminal and the e is the
highest energy orbital
for phosphine or carbene
ligands. Interaction with its four

interactions with carbonyl is stabilized to higher ionization energy compared to the two orbitals comprising the e set. For the complexes in this study, the energy separation between the e and b_2

The steric difference of NHCs and PR_3



Overall:

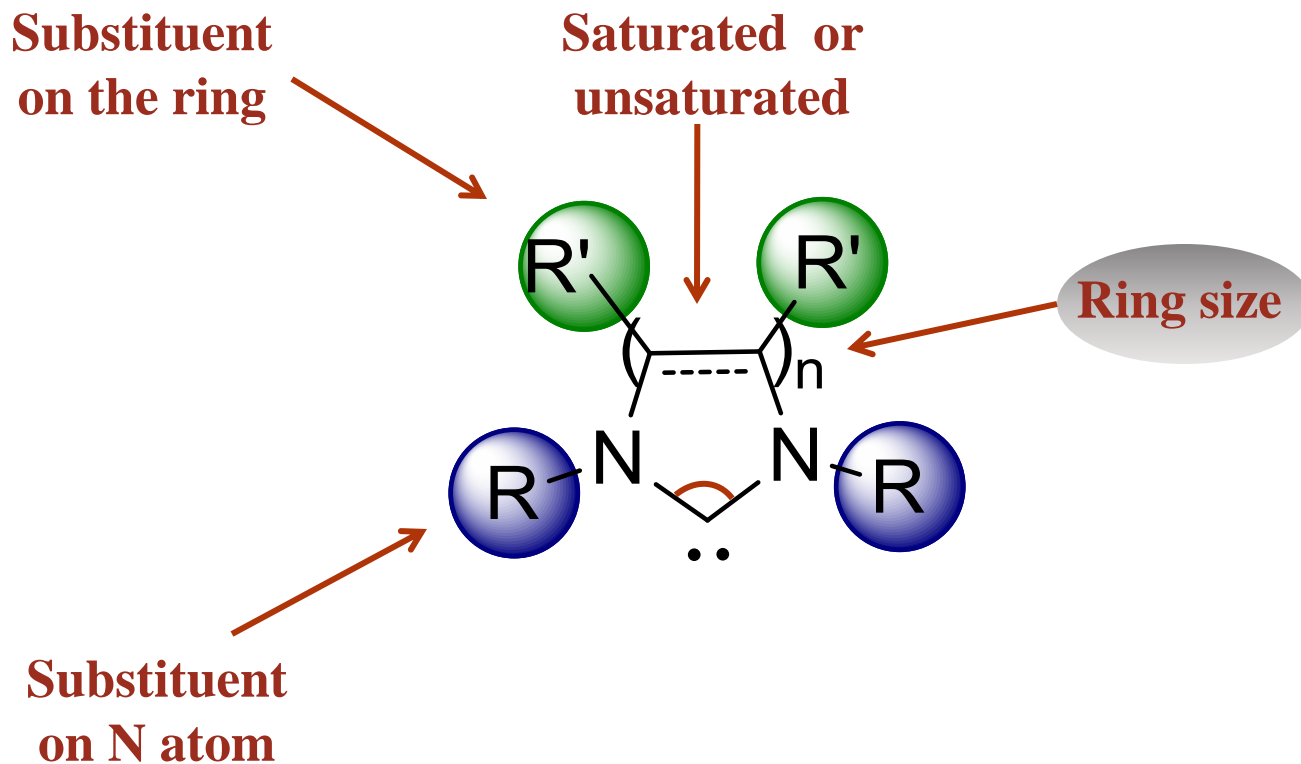
Electron property:

NHCs are stronger σ - donor but weaker π -acceptor ligands than phosphine ligands.

Steric property:

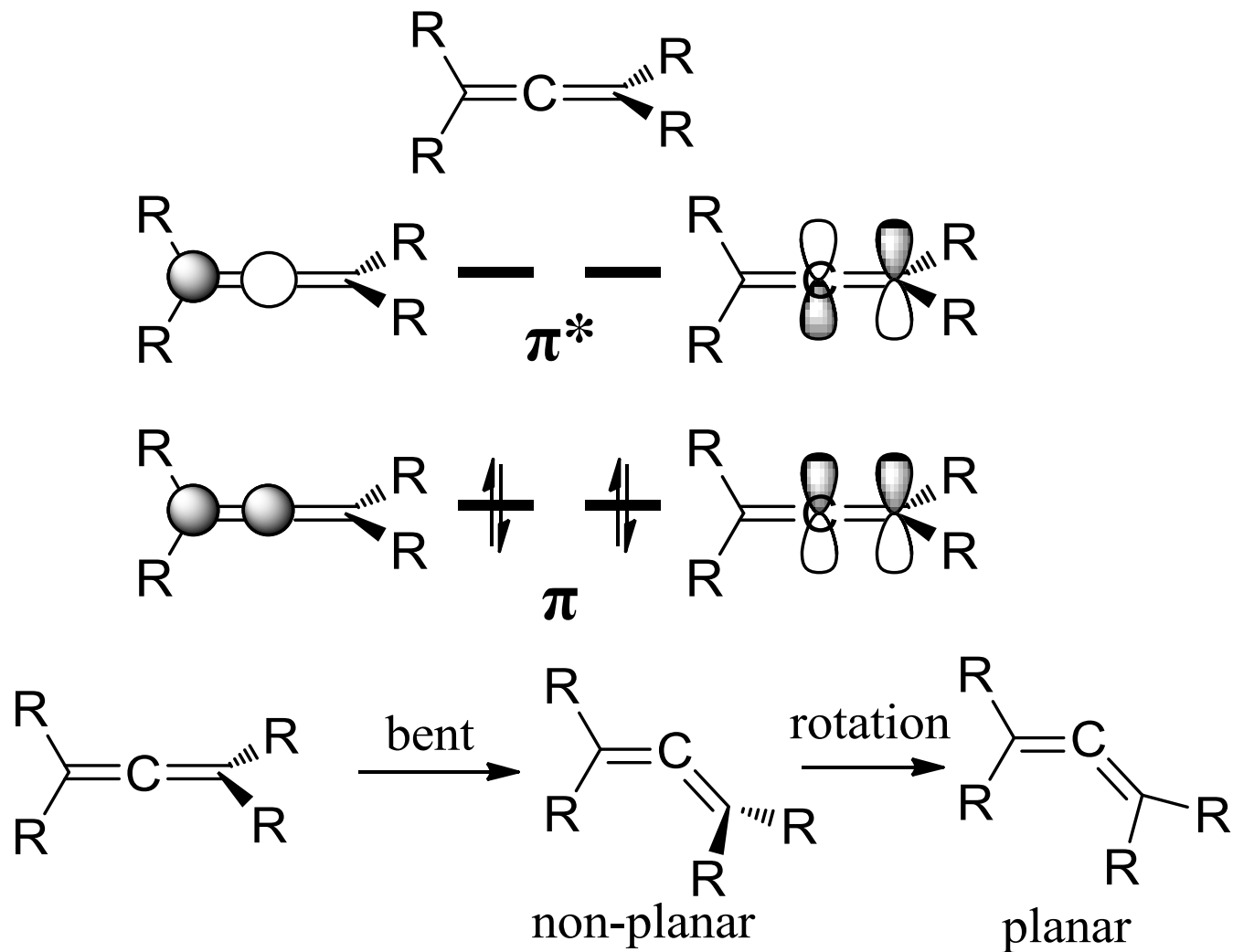
R group can play a significant role in the metals reactivity and potential catalysis.

The property of different NHCs

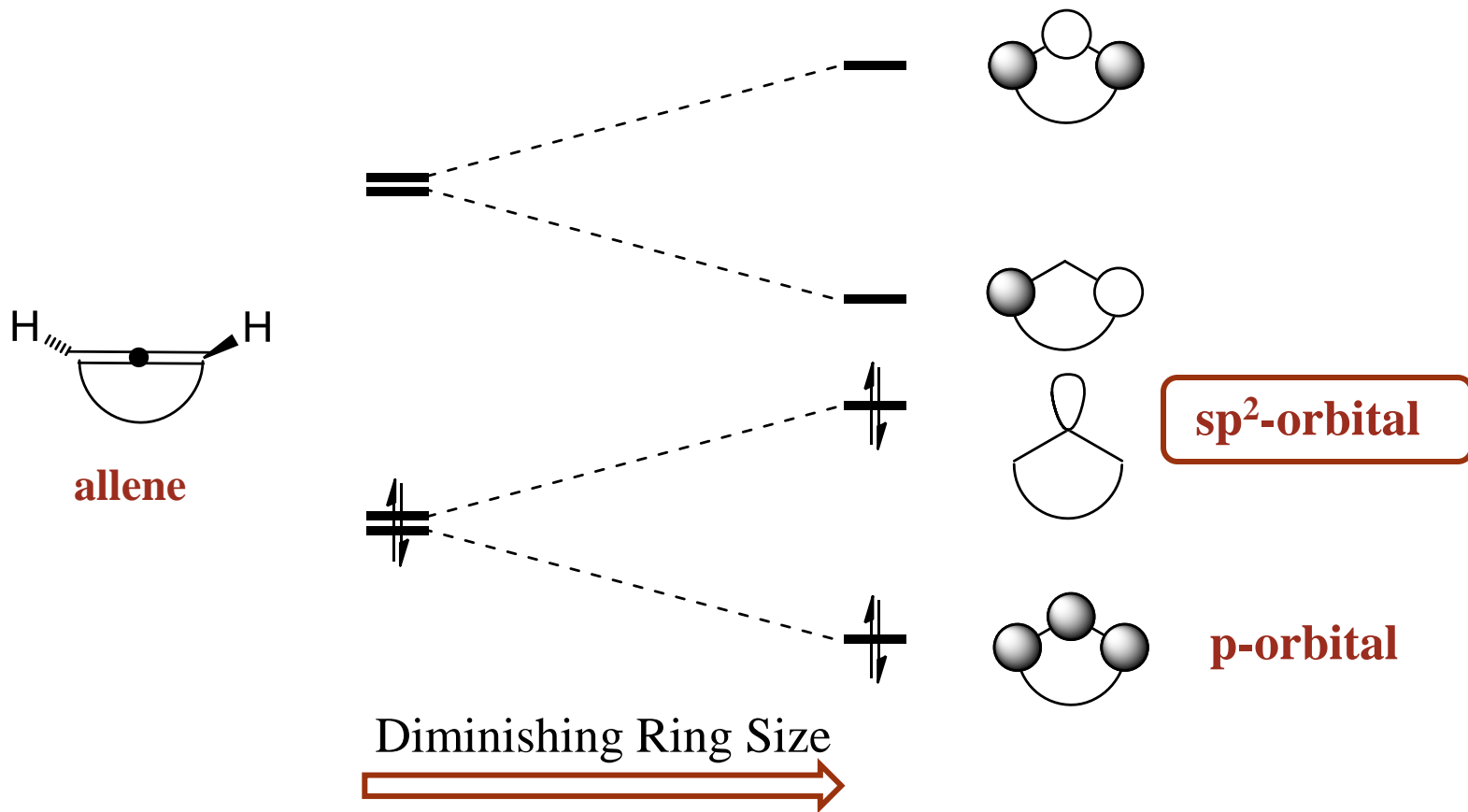


Ring size

Brief recall of Yu's lesson

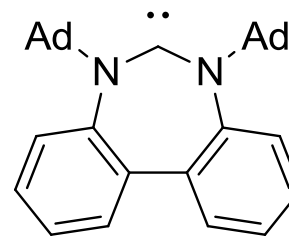
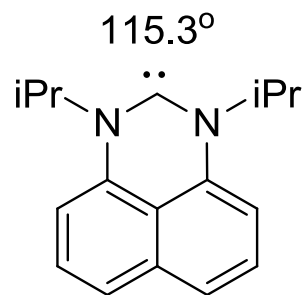
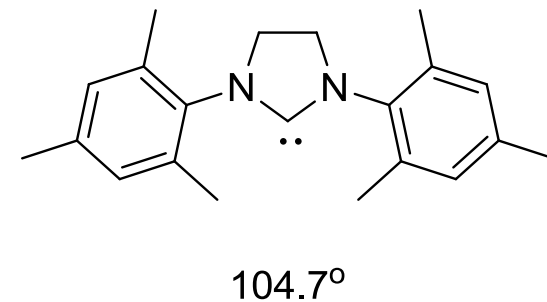
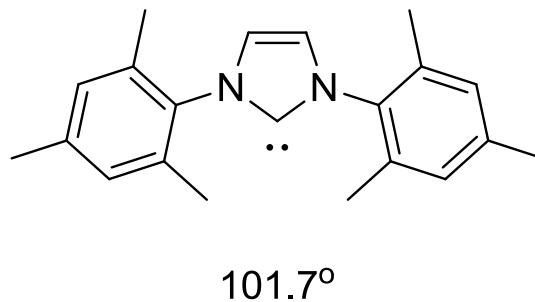
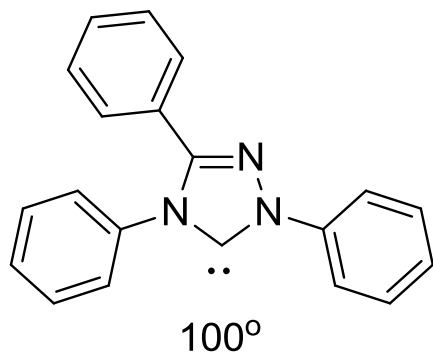


Orbital of bent planar allene



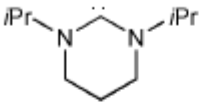
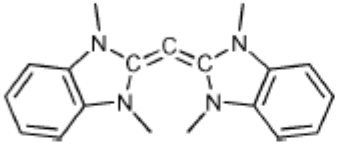
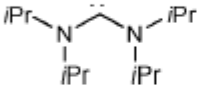
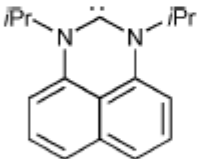
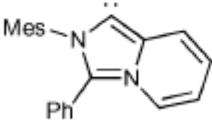
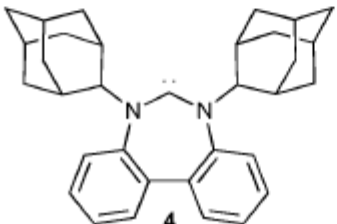
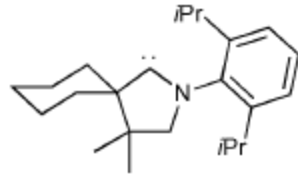
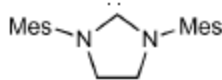
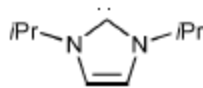
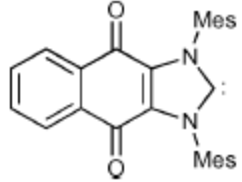
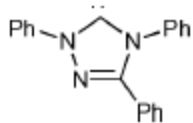
Chem. Rev. **1989**, 89, 1111

Angle of N-C-N

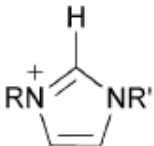
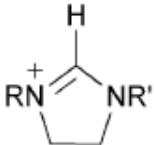
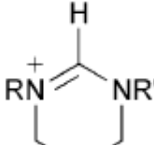
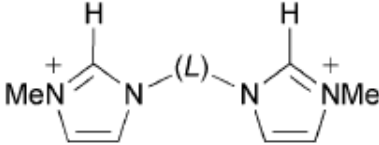


J. Am. Chem. Soc. **1995**, 117, 11207;
Angew. Chem. Int. Ed. **2005**, 44, 5269
Dalton Trans., **2009**, 2284

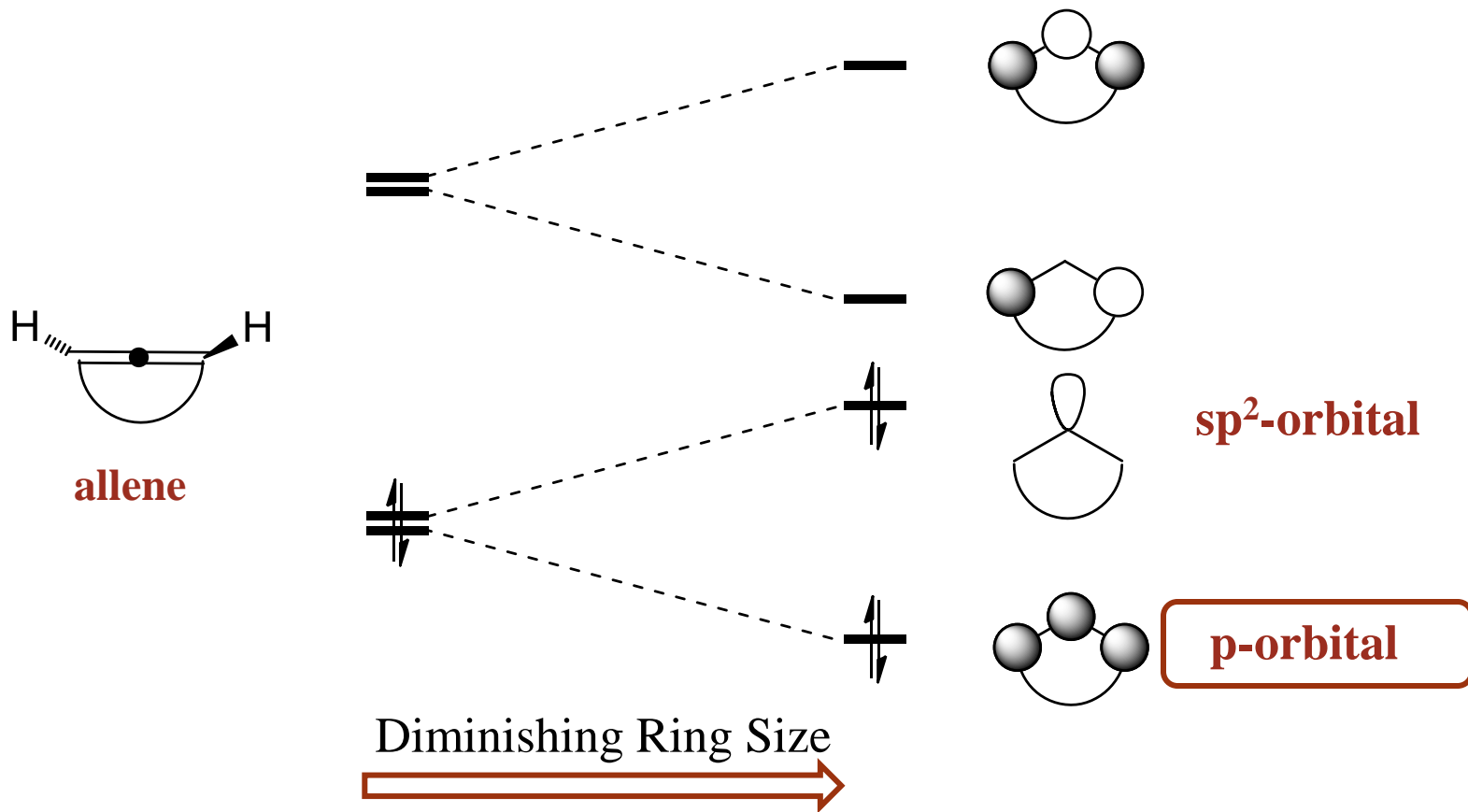
Table 1 Average CO stretching frequencies (ν_{ave}) of various (carbene)Rh(CO)₂Cl complexes

Entry	Carbene	ν_{ave}/cm^{-1}
1		2012
2		2014
3		2020
4		2029
5		2032
6		2033
7		2036
8		2038
9		2041
10		2042
11		2049

pKa of azolium ion

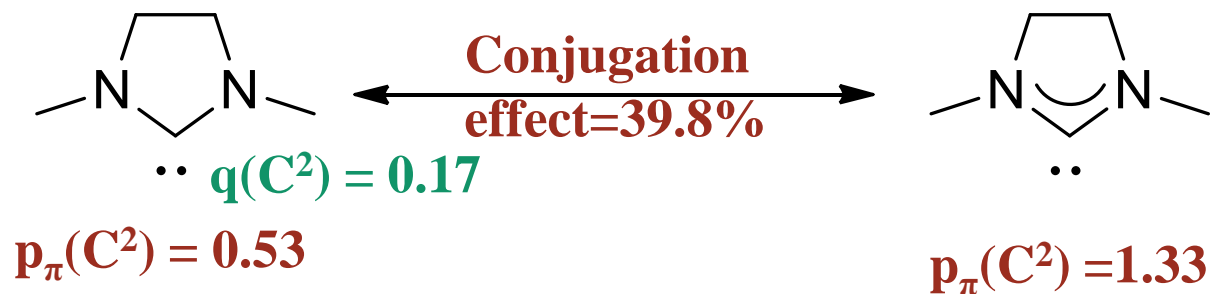
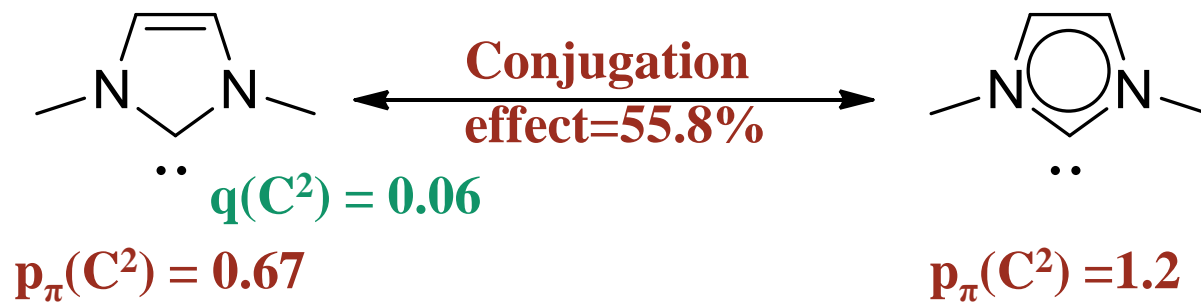
Azolium ion		Counterion, X ⁻	$k_{\text{DO}}^a/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{HO}}/\text{M}^{-1} \text{s}^{-1}$	pK _a ^b
 1H ⁺	a: R = R' = 4-chlorophenyl	Cl ⁻	3.92×10^5	1.63×10^5	19.8
	b: R = R' = 4-methoxyphenyl	Cl ⁻	4.80×10^4	2.00×10^4	20.7
	c: R = R' = 2,4,6-trimethylphenyl	Cl ⁻	4.08×10^4	1.70×10^4	20.8
	d: R = R' = 2,6-di(<i>i</i> -propyl)phenyl	Cl ⁻	2.00×10^4	8.33×10^3	21.1
	e: R = ethyl, R' = methyl	Cl ⁻	2.29×10^2	9.54×10^1	23.0 ^f
	f: R = <i>n</i> butyl, R' = methyl	PF ₆ ⁻	1.07×10^2	4.42×10^1	23.3
	g: R = <i>n</i> hexyl, R' = methyl	PF ₆ ⁻	1.03×10^2	4.25×10^1	23.4
	h: R = <i>no</i> ctyl, R' = methyl	Br ⁻	1.04×10^2	4.29×10^1	23.4
	i: R = R' = <i>t</i> -butyl	Cl ⁻	1.69	7.04×10^{-1}	25.2
	j: R = R' = adamantyl	Cl ⁻	1.07	4.46×10^{-1}	25.4
 2H ⁺	b: R = R' = 4-methoxyphenyl	Cl ⁻	4.26×10^4	1.77×10^4	20.7
	c: R = R' = 2,4,6-trimethylphenyl	Cl ⁻	1.19×10^4	4.96×10^3	21.3
	d: R = R' = 2,6-di(<i>i</i> -propyl)phenyl	Cl ⁻	8.37×10^3	3.49×10^3	21.5
 3H ⁺	k: R = R' = ethyl	PF ₆ ⁻	3.48×10^{-3}	1.45×10^{-3}	27.8
	l: R = R' = <i>i</i> -propyl	PF ₆ ⁻	1.48×10^{-3}	6.15×10^{-4}	28.2
 4H ⁺	m: L = CH ₂	I ⁻	2.98×10^{5d}	1.24×10^5	19.9
	n: L = (CH ₂) ₂	I ⁻	$5.87 \times 10^{3d,e}$	2.45×10^3	21.6
	o: L = (CH ₂) ₃	I ⁻	1.30×10^{3d}	5.40×10^2	22.3
	p: L = phenyl	I ⁻	2.03×10^{5d}	8.44×10^4	20.1

Orbital of bent planar allene



Chem. Rev. **1989**, 89, 1111

Conjugation effect of imidazole and imidazoline

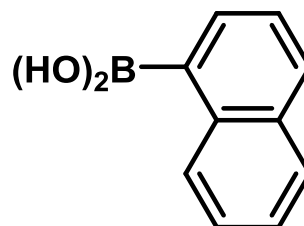
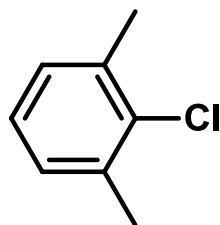
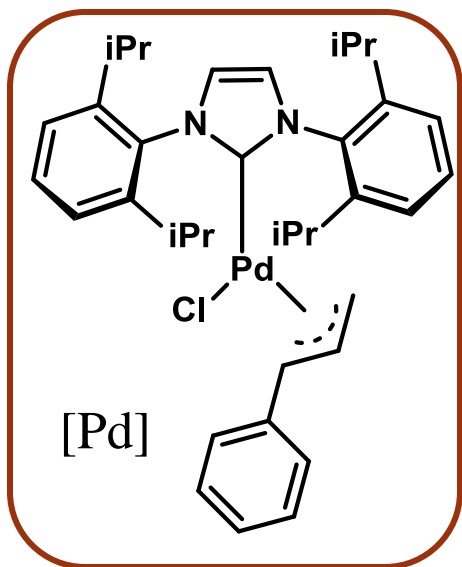
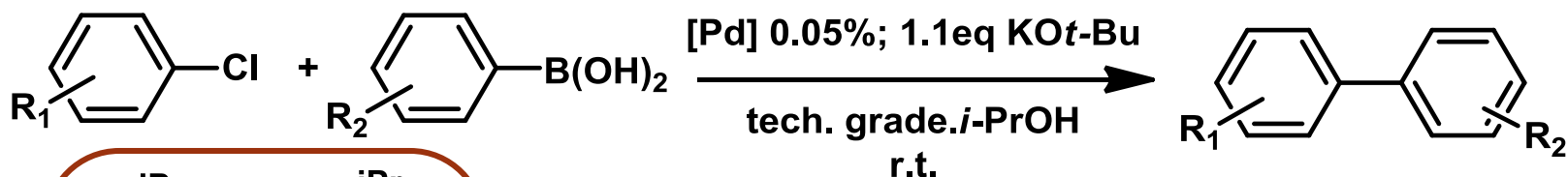


J. Am. Chem. Soc. **1996**, 118, 2039

Case Study

1. Cross coupling reaction

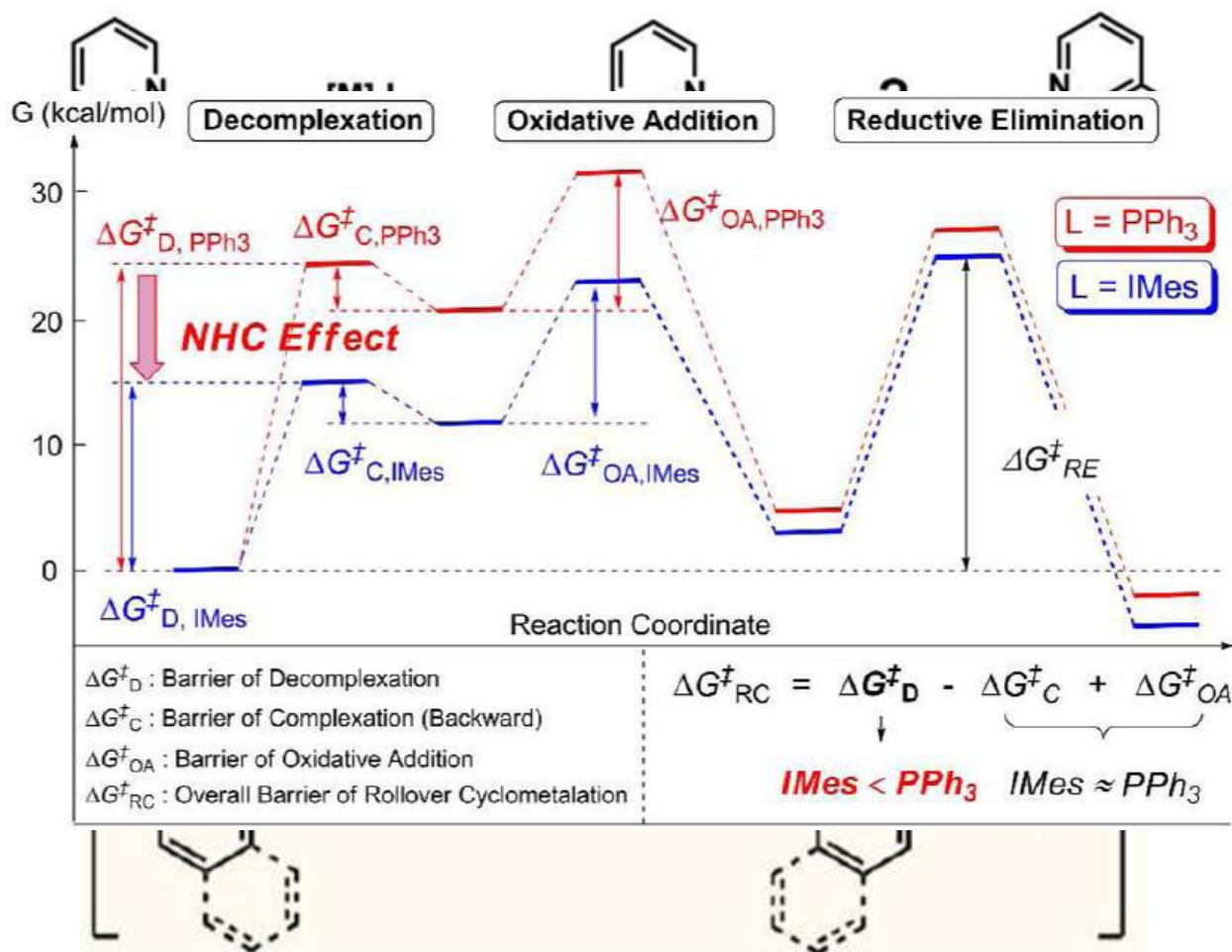
----Suzuki, Negishi, Kumada, Stille, Hiyama, Sonogashira, Heck, Buchwald—Hartwig
Coupling Reaction



	T	Yield
0.05%; r.t.	15h	94%
50 ppm; 80°C	3h	93%

Chem. Soc. Rev., **2011**,40, 5151

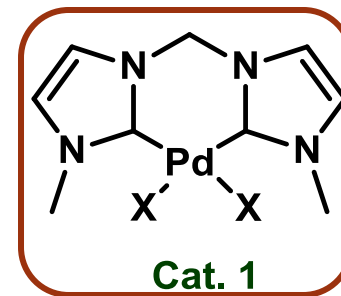
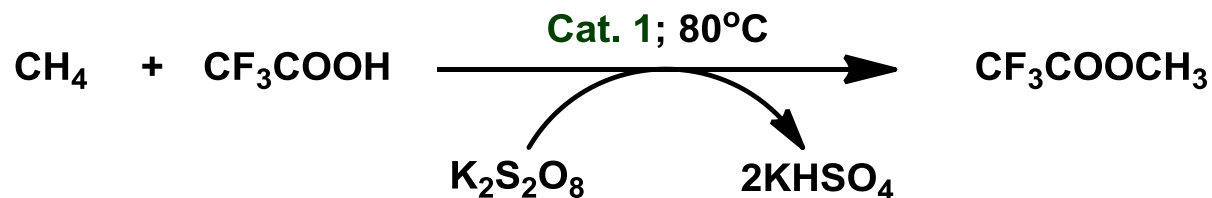
2. Chang's work



J. Am. Chem. Soc., 2012,134, 17778

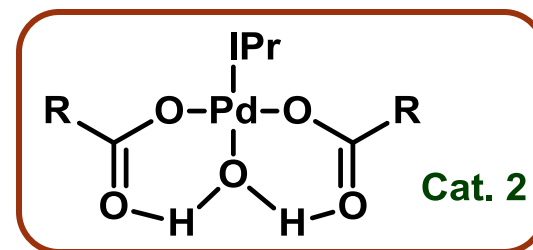
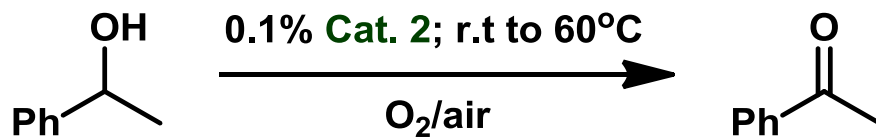
3. Oxidation chemistry

Oxidation of Methane:



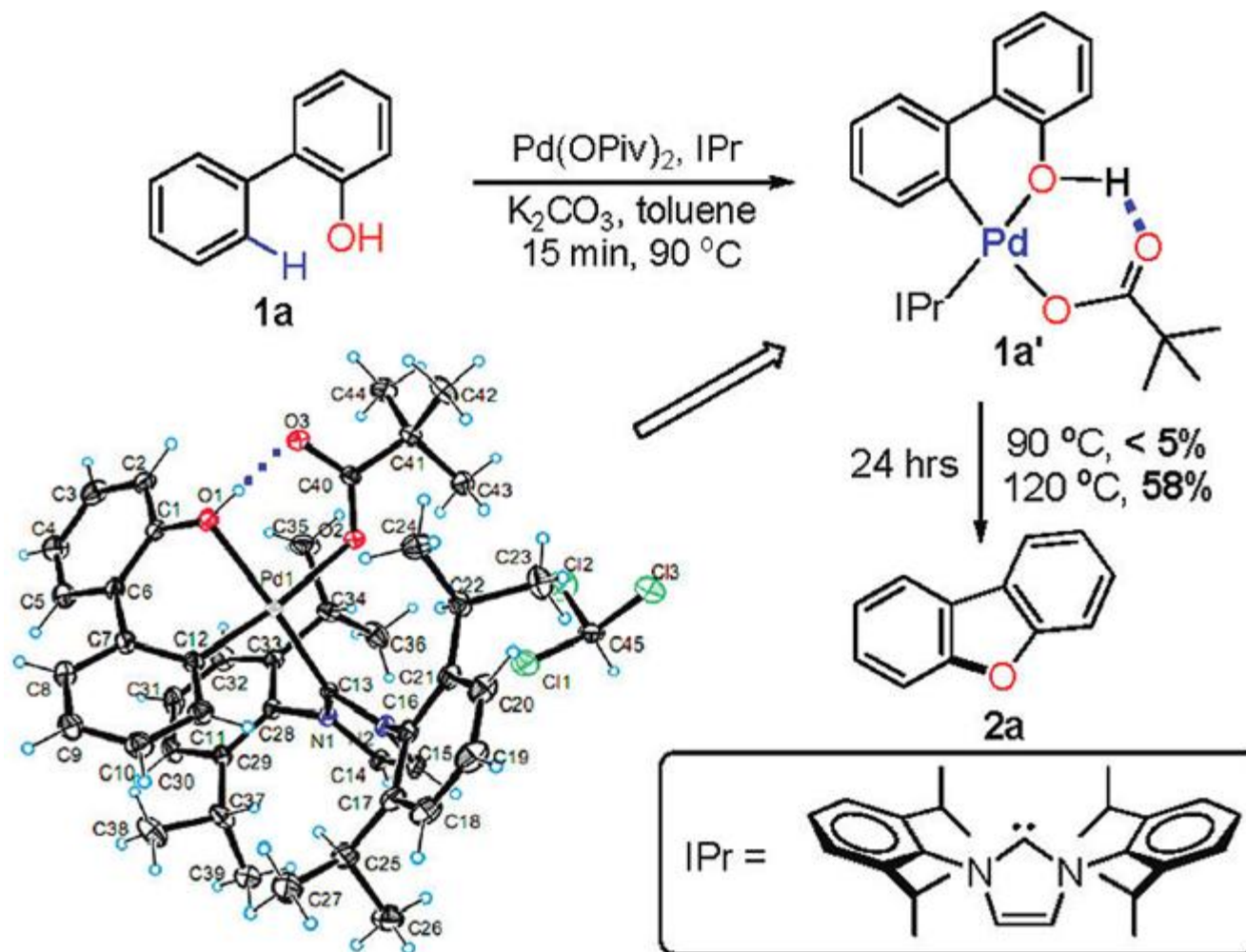
Angew. Chem. Int. Ed. **2002**, 41, 1745

Aerobic Alcohol Oxidation:



J. Org. Chem. **2005**, 70, 3343

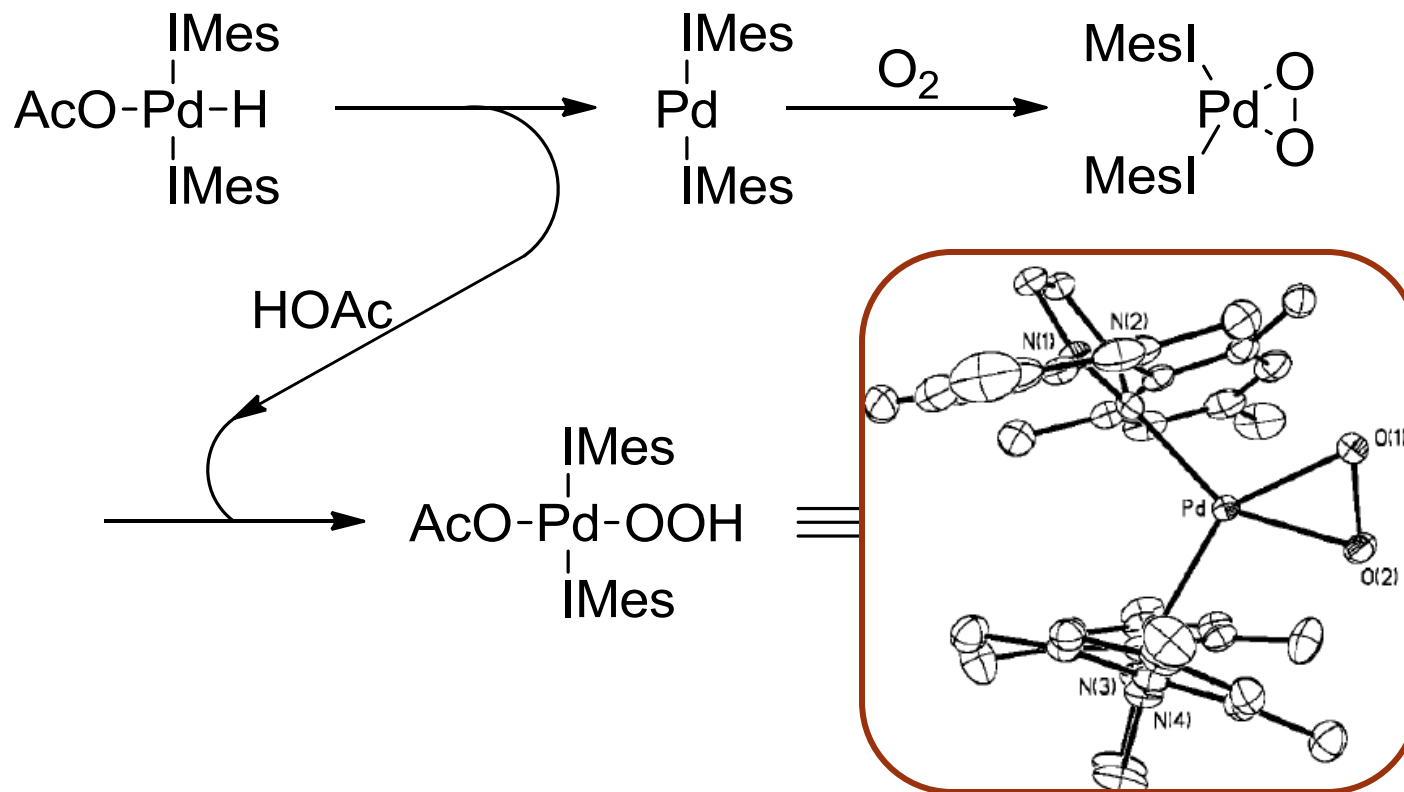
Aerobic C-H activation:



J. Am. Chem. Soc., **2011**, 133, 9250

Pd oxidation reaction:

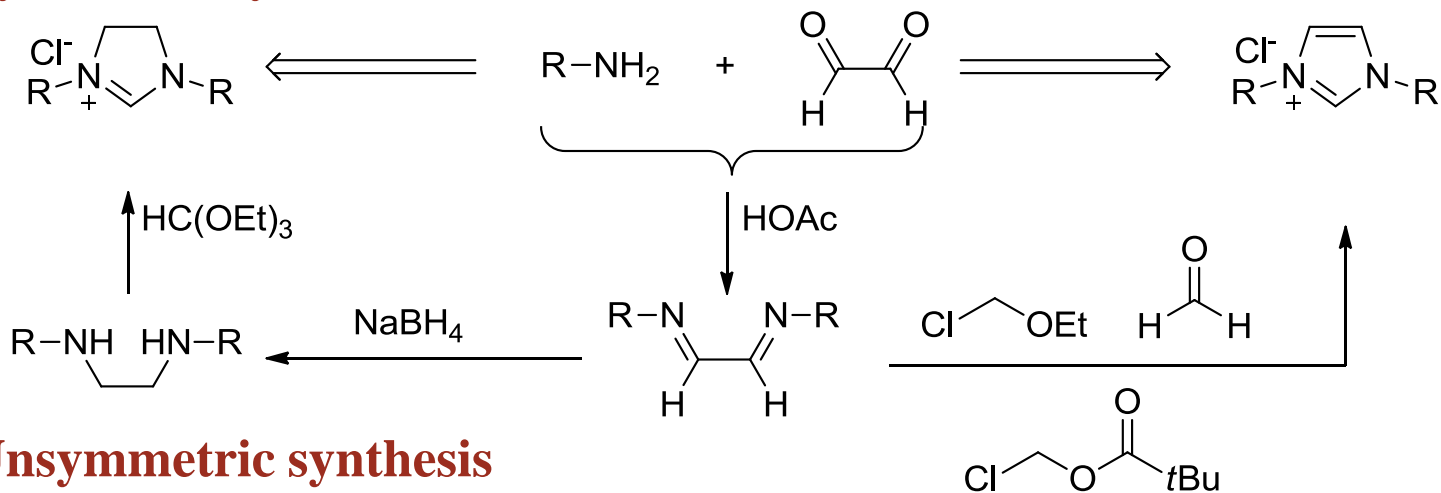
----Shannon S. Stahl has studied a lot



J. Am. Chem. Soc., **2004**, 126, 10212; *Angew. Chem. Int. Ed.* **2006**, 45, 2904; *J. Am. Chem. Soc.*, **2007**, 129, 4410; *Angew. Chem. Int. Ed.* **2007**, 46, 601; *J. Am. Chem. Soc.*, **2008**, 130, 5753

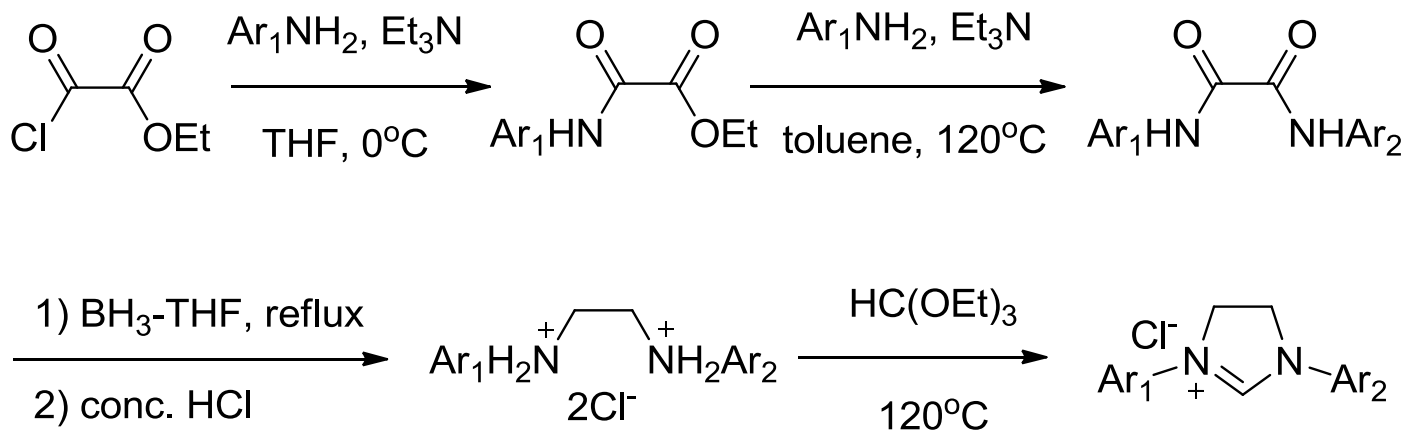
Synthesis

1. Symmetric synthesis



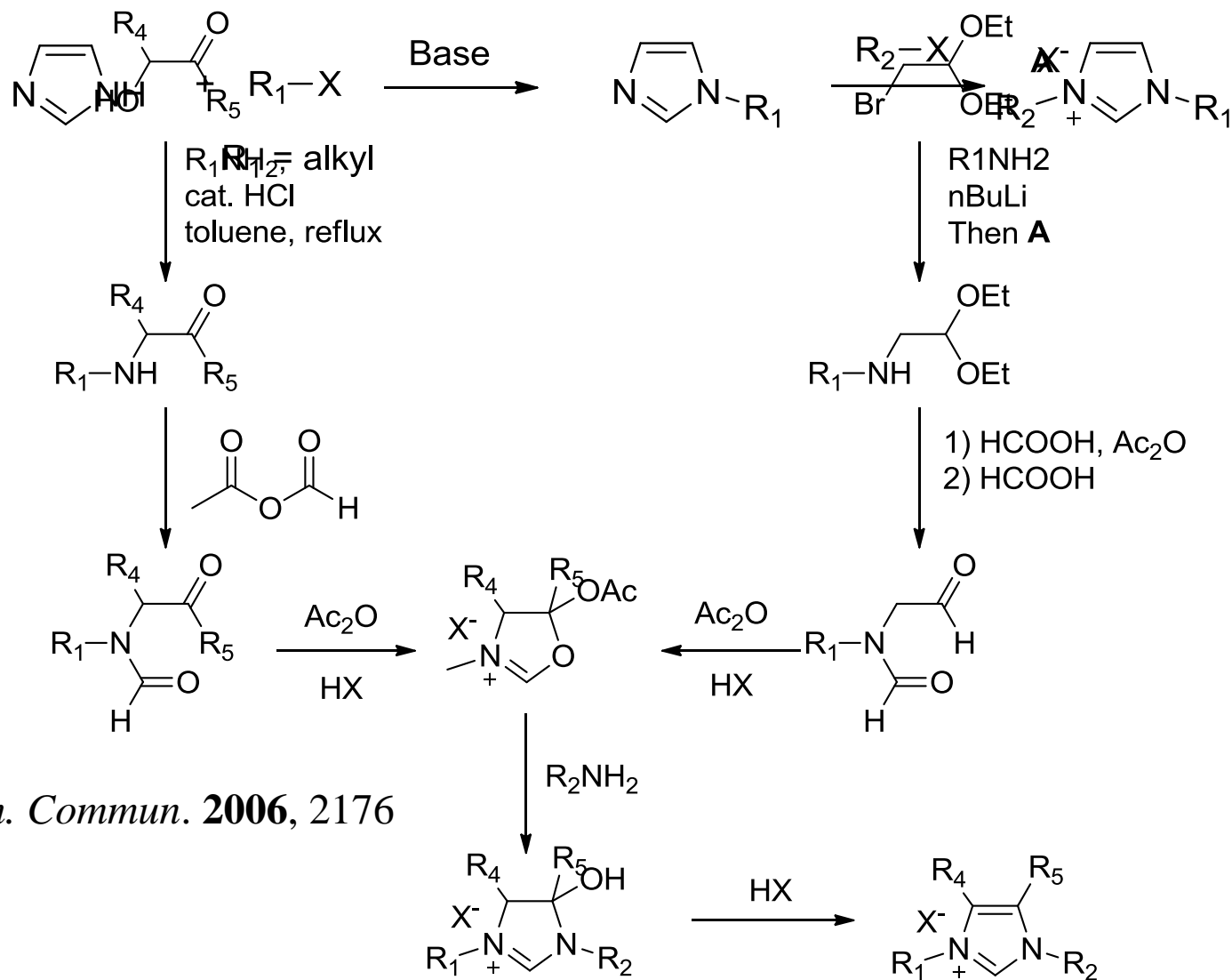
2. Unsymymmetric synthesis

a. Unsymmetric synthesis of imidazolidinium salts



2. Unsymmetric synthesis

b. Unsymmetric synthesis of imidazolium salts



Chem. Commun. **2006**, 2176

Summary

a. We have compared the difference between PR3 and different NHCs, show the similar but different chemistry, and introduce the synthesis of NHCs

b. There are still many things that we can do according to it's property.

**Thanks for Your
Attention!**