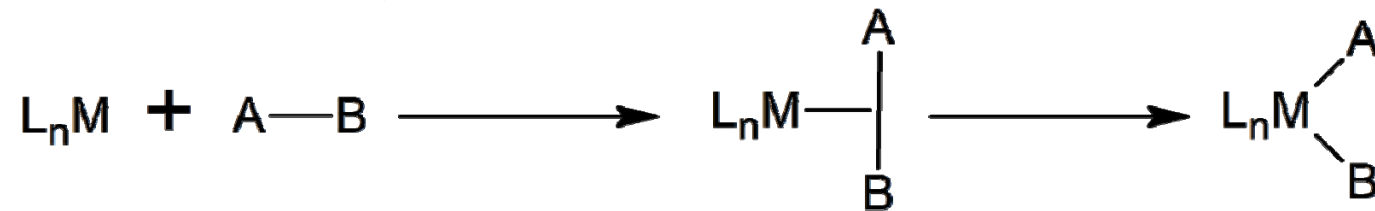


Oxidative Addition

Most Common Type:



Few other type of oxidative addition reactions are also known

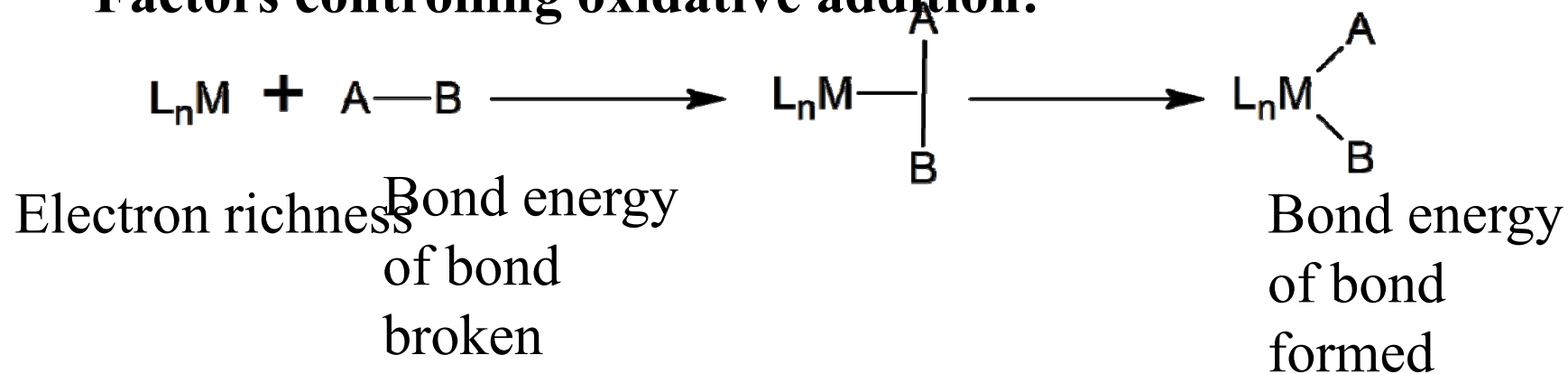
- a) Addition of electrophiles
- b) Addition of unsaturated compounds
- c) Addition of binuclear compounds

Oxidative Addition

Requirement:

- a) Availability of higher oxidation states.
- b) Availability of vacant sites

Factors controlling oxidative addition:



Oxidative Addition

What bonds can be oxidatively added:

X-X H₂, Cl₂, Br₂, I₂, RS-SR, RO-OR

C-C Ph₃C-CPh₃, NC-CN, Ph-CN

C-X CH₃-I, Ph-I, CH₂Cl₂, CCl₄, R-COCl, R-O-R, R-S-R

H-X HCl, HBr, HI, RO-H, RS-H, R₂N-H, R₂P-H, R₂B-H

M-X Ph₃PAu-Cl, ClHg-Cl, R₃Sn-Cl, R₃Si-Cl, Ph₂B-X

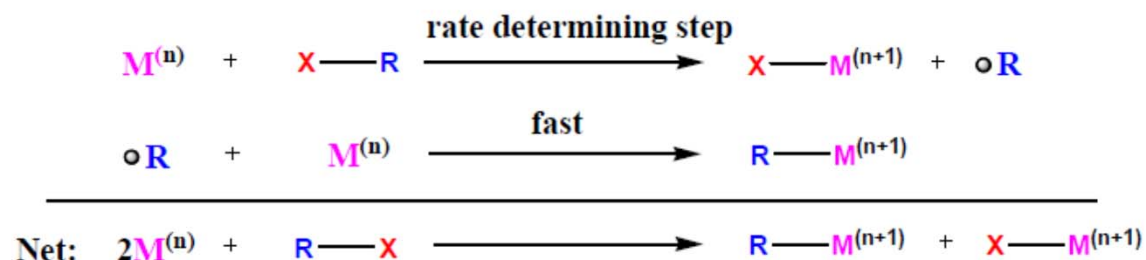
Oxidative Addition

Mechanism:

- a) Concerted mechanism
- b) Non concerted mechanism
 - i) S_N2
 - ii) radical
 - iii) ionic

One-electron Mechanisms for Oxidative Addition

1. Atom Abstraction and combination of the Resulting Radical with a Second Metal



This is not a chain-mechanism!

Characteristics :

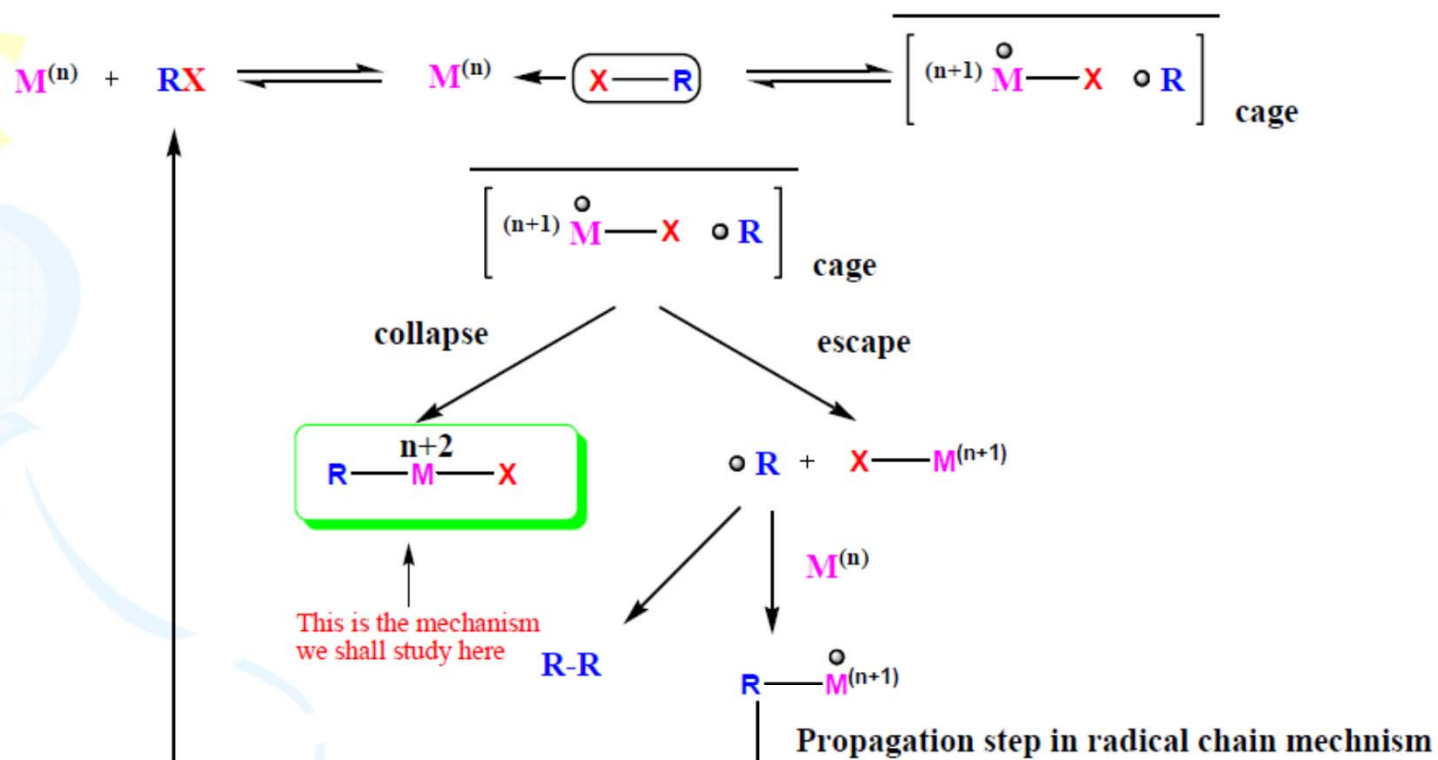
- (a) 2:1 stoichiometry
- (b) Racemization of carbon
- (c) rate = $k[M][RX]$
- (d) Reaction sequence reverse of S_N2
 $3^\circ > 2^\circ > 1^\circ > Me$

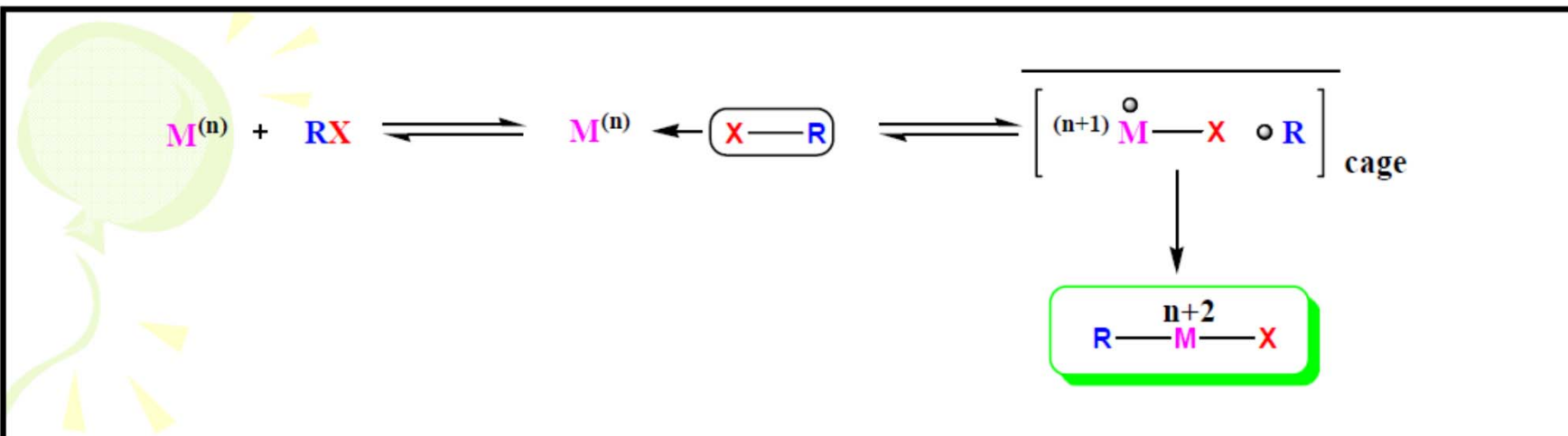
- (e) Reaction sequence with respect to X



Thus R-OTs reacts fast in S_N2 , slow in Radical mechanism

2. Inner-sphere Electron transfer/Caged Radical-Pair Mechanism General :





Characteristics :

(a) The products are very **similar to those of a S_N2 reaction**

(b) The reactivity order is



(this order is determined by thermodynamics)

Note: in S_N2 R-OTs most reactive

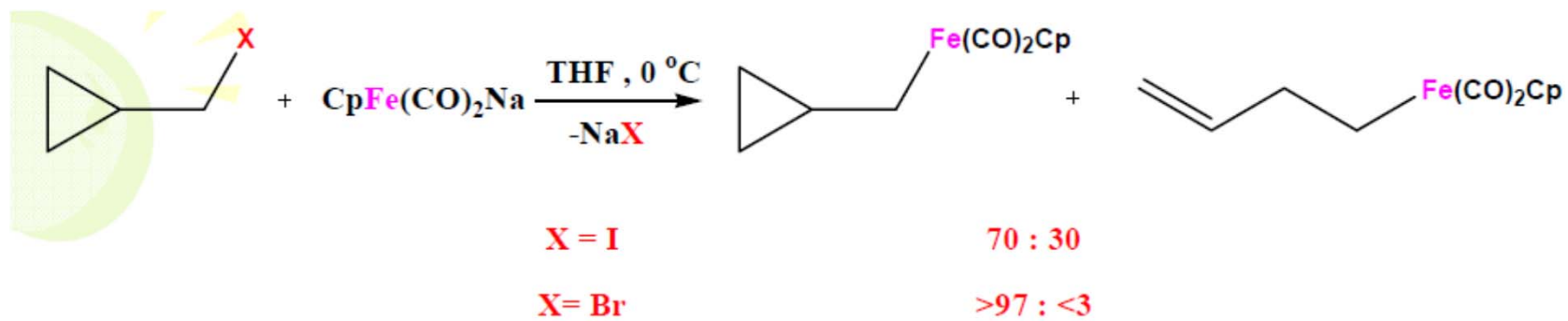


(this order is determined by the relative order of the radicals)

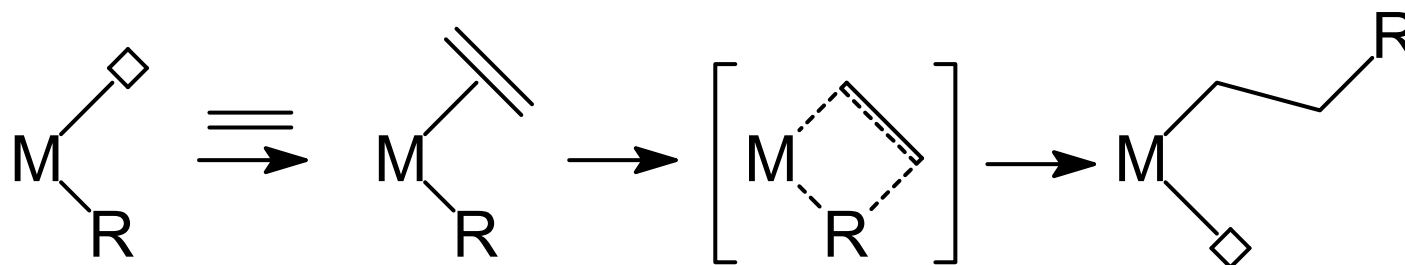
This order is opposite to S_N2 mechanism

(c) This pathway requires a **coordinatively unsaturated metal** capable of undergoing a formal two-electron oxidation

(d) **ArOH does not work as an inhibitor**



Standard Cossee mechanism



Why do olefins polymerise?

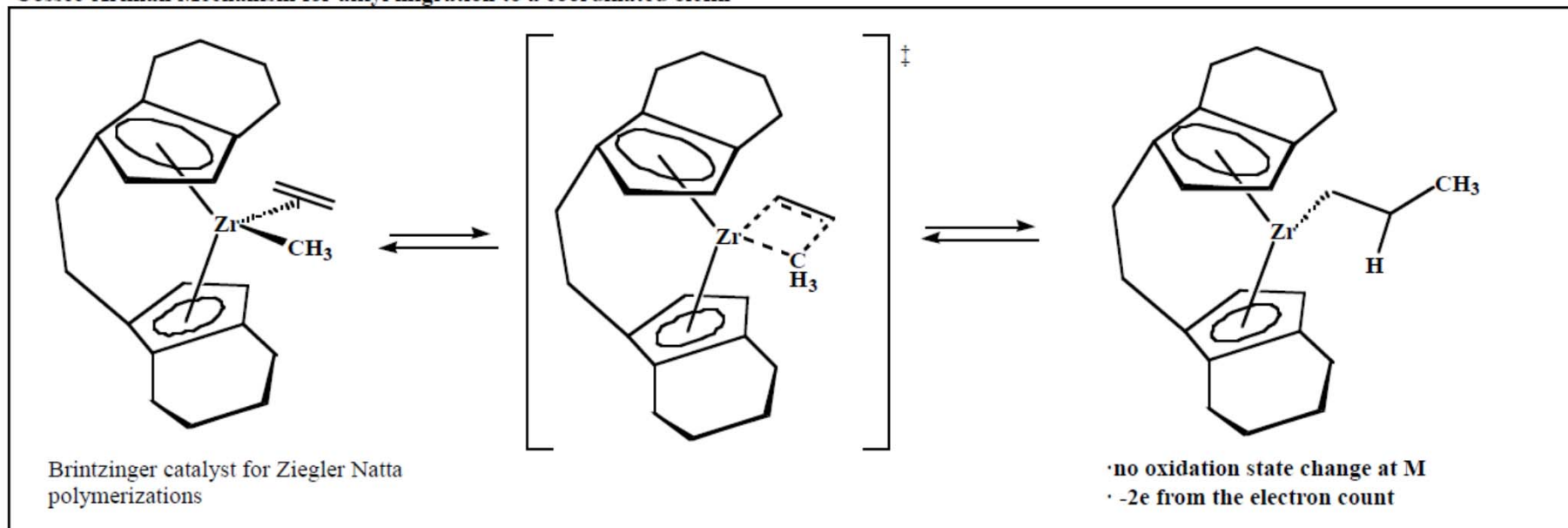
Driving force: conversion of a p-bond into a s-bond

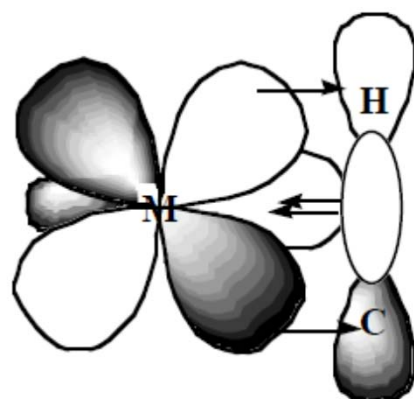
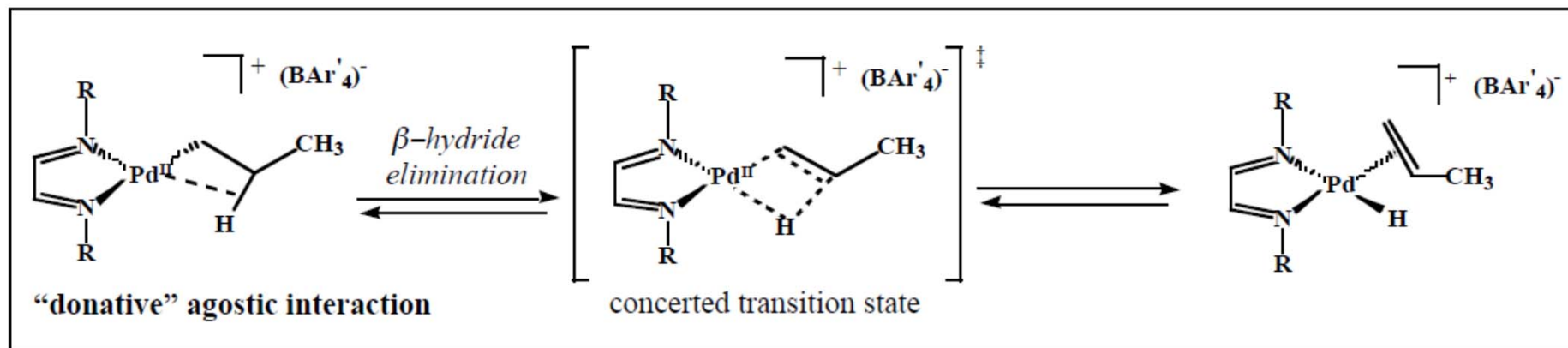
One C=C bond: 150 kcal/mol

Two C-C bonds: $2 \times 85 = 170$ kcal/mol

**Energy release: about 20 kcal per mole of monomer
(independent of mechanism)**

Cossee-Arlman Mechanism for alkyl migration to a coordinated olefin



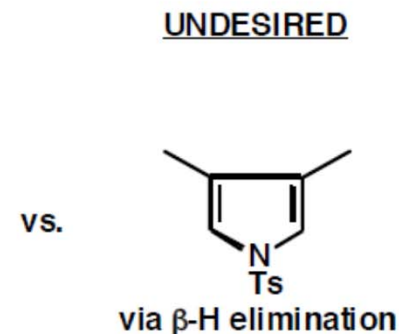
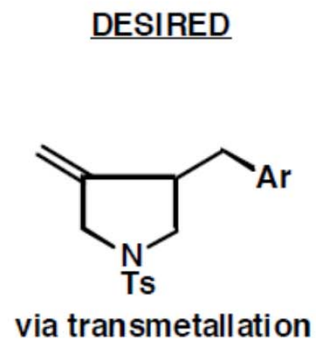
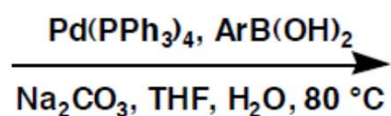
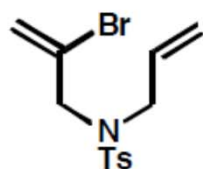


σ -complex

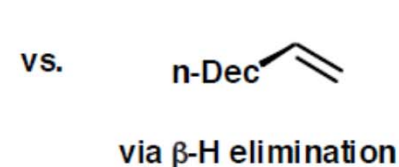
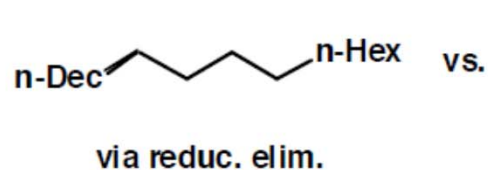
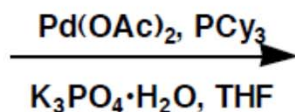
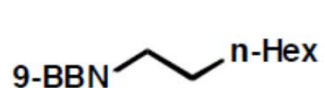
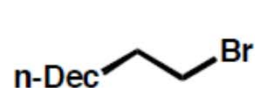
$\sigma\text{-donation} \gg$
 $\pi\text{-backbonding}$

The success of many transition metal mediated reactions relies on the suppression of β -hydride elimination

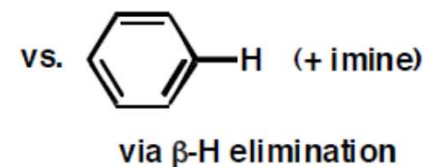
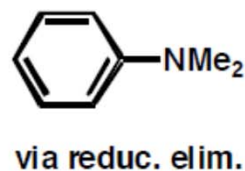
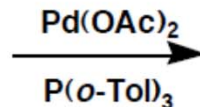
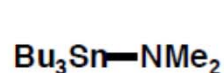
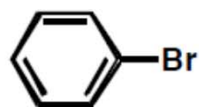
Cascade cyclization-coupling reactions



Formation of sp^3 carbon centers via coupling reactions

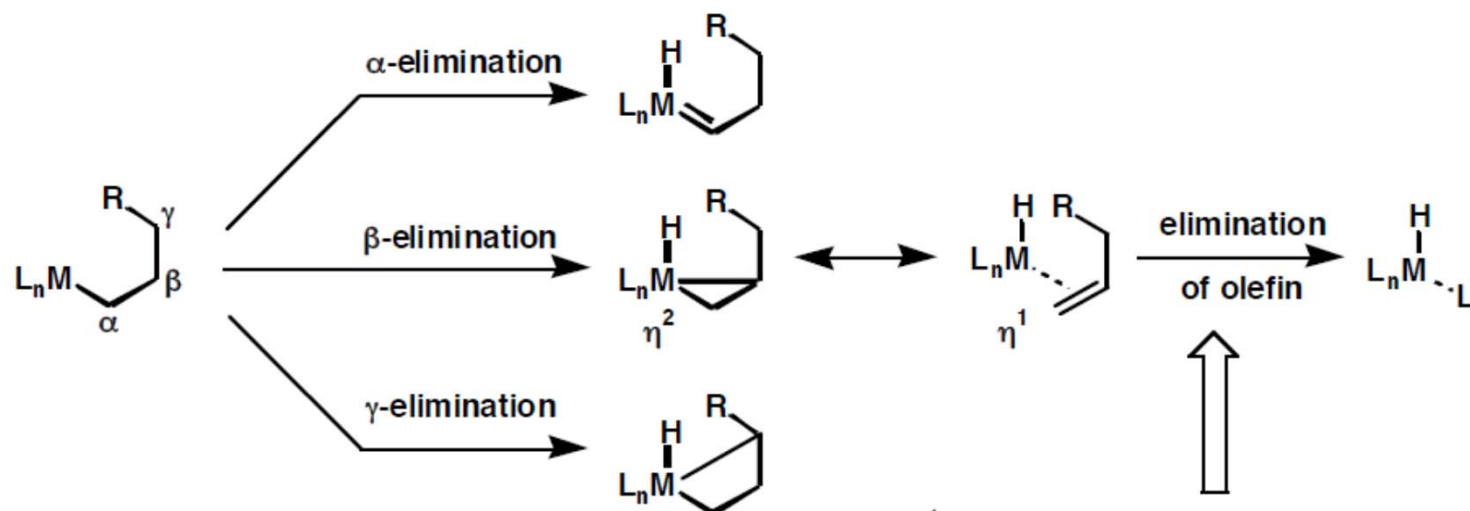


Amination of aryl halides



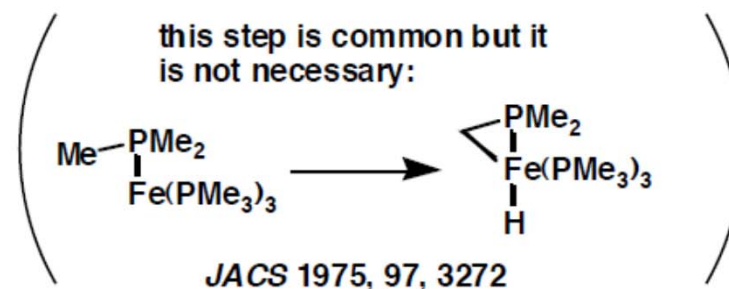
Hydride elimination reactions

- β -hydride elimination is only one type of hydride elimination reaction



- β -hydride elimination was the first well-defined low-energy pathway leading to the cleavage of metal-carbon bonds

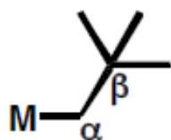
- β -hydride elimination is the most important mechanism for metal alkyl decomposition and metal-catalyzed isomerization



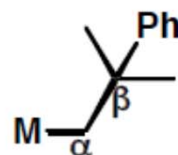
Structural requirements for β -hydride elimination

- metal alkyl complex must have β -hydrogens

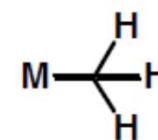
the following complexes are stable to β -hydride elimination



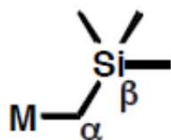
neopentyl



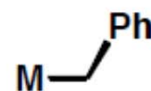
neophyl



methyl



"silyl-neopentyl"



phenyl



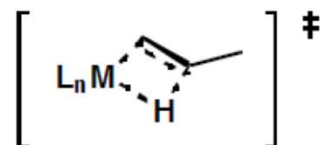
alkynyl

Steric requirements for β -hydride elimination

- resulting olefin product must be a stable structure

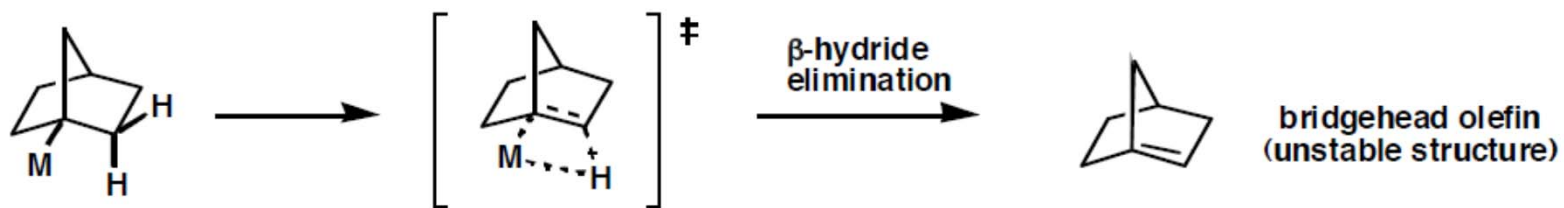
similarly,

- M-C-C-H unit must be able to adopt a roughly co-planar conformation, to accommodate the 4-centered concerted planar transition state:



JACS 1973, 95, 4491
JACS 1976, 98, 6521

example 1



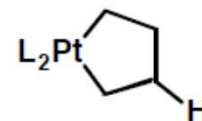
norbornyl metal alkyl is stable to β -hydride elimination because

- it is difficult for the M-C-C-H unit to adopt a planar conformation
- the resulting product contains a bridgehead olefin

example 2

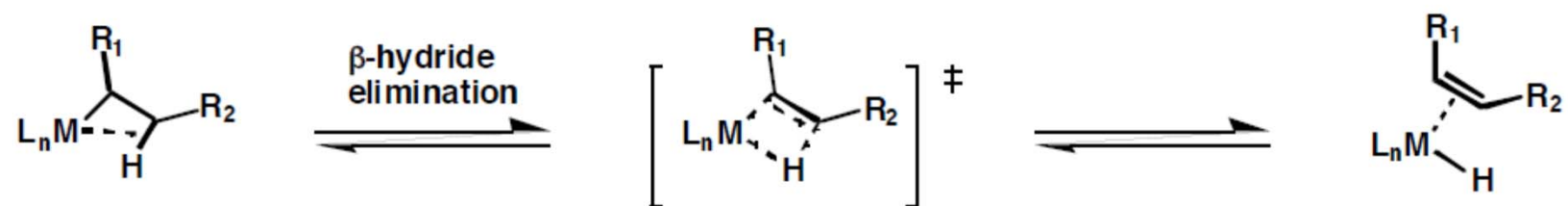
β -hydride elimination of L_2Pt is 10^4 times slower than that of

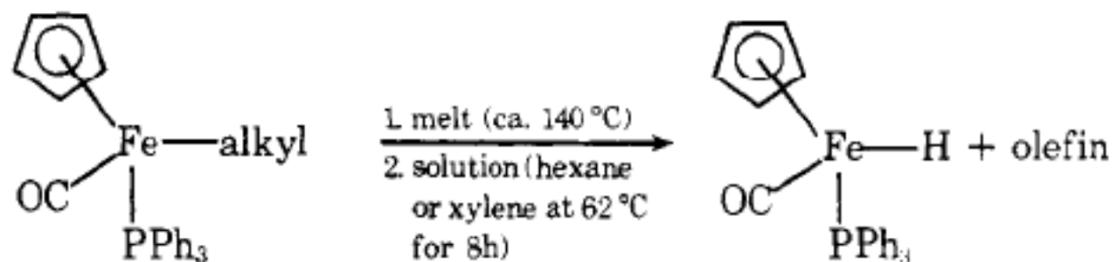
because of the difficulty of forcing the M-C-C-H unit to be planar in



JACS 1976, 98, 6521

The effect of the the alkyl ligand electronics on β -hydride elimination





alkyl = (a) ethyl
 (b) *n*-butyl
 (c) *sec*-butyl
 (d) isobutyl

olefin = (a) ethylene
 (b,c) butenes
 (d) 2-methylpropene

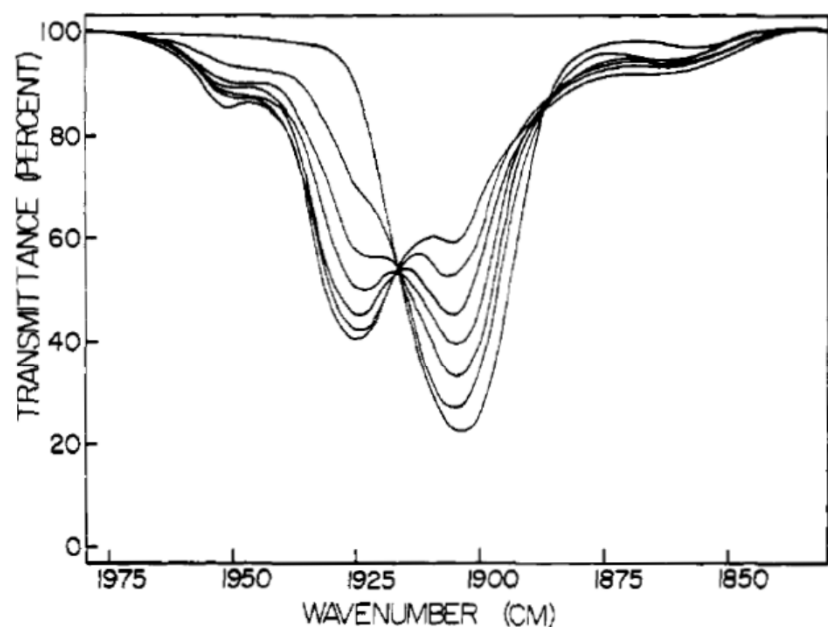


Figure 4. Change of infrared $\nu(\text{CO})$ with time for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(n\text{-butyl})$ in xylene solution of 61.2° . The peak at 1906 cm^{-1} is starting material and the peak at 1925 is $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$.

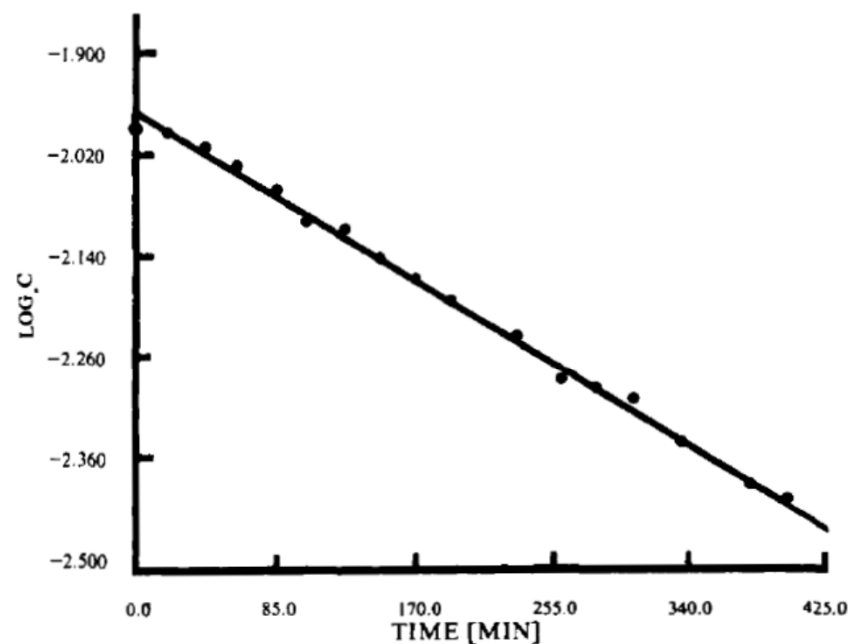
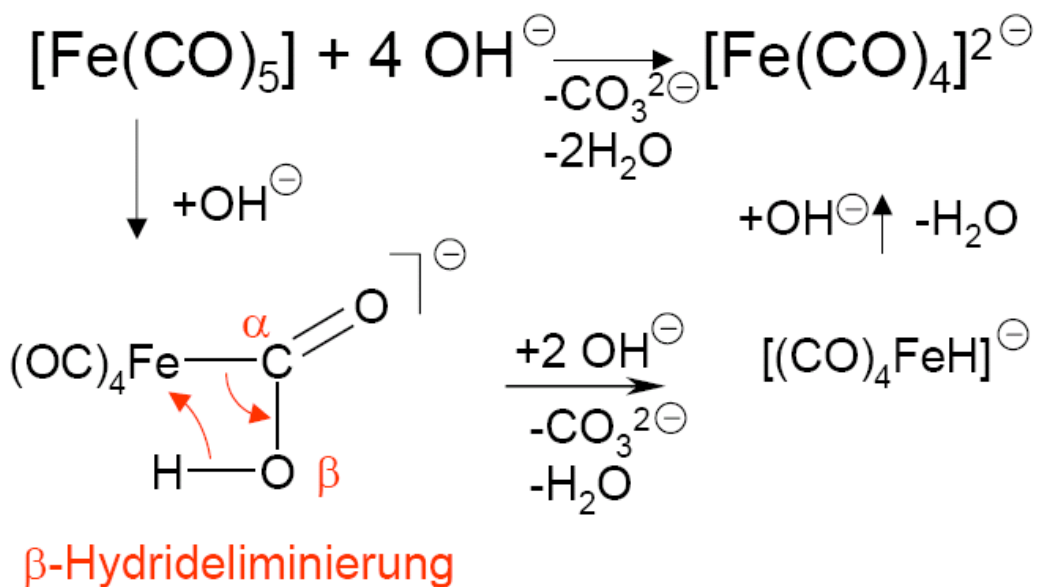


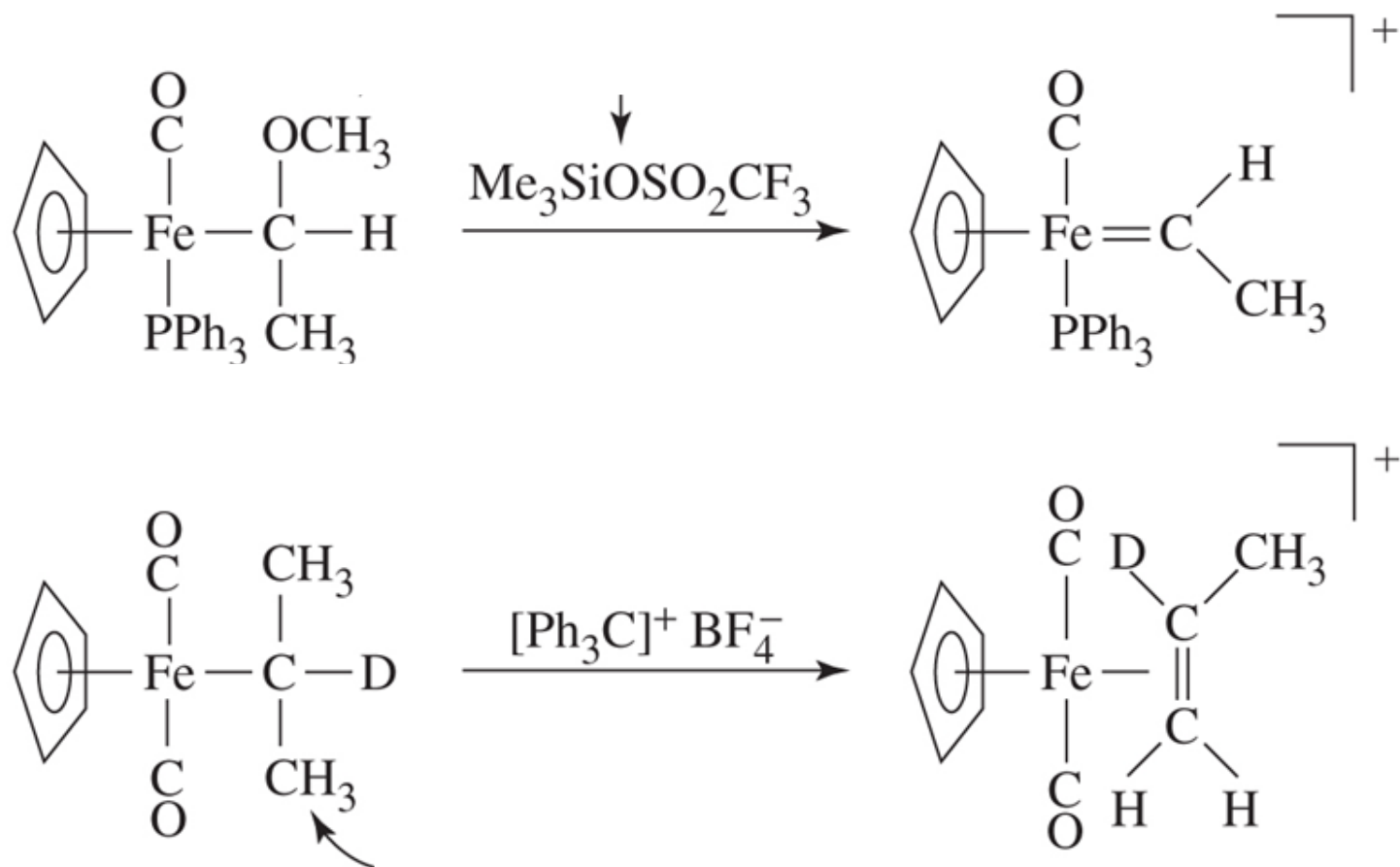
Figure 5. First-order rate plot of the decomposition of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(n\text{-butyl})$ in xylene at 61.2°C .

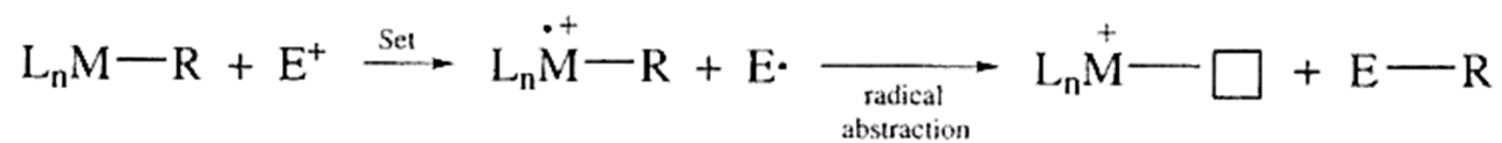
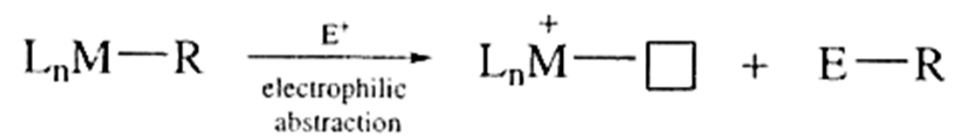
Hieber'sche Basenreaktion

Redoxprozess:
CO-Ligand wird oxidiert,
M wird reduziert.

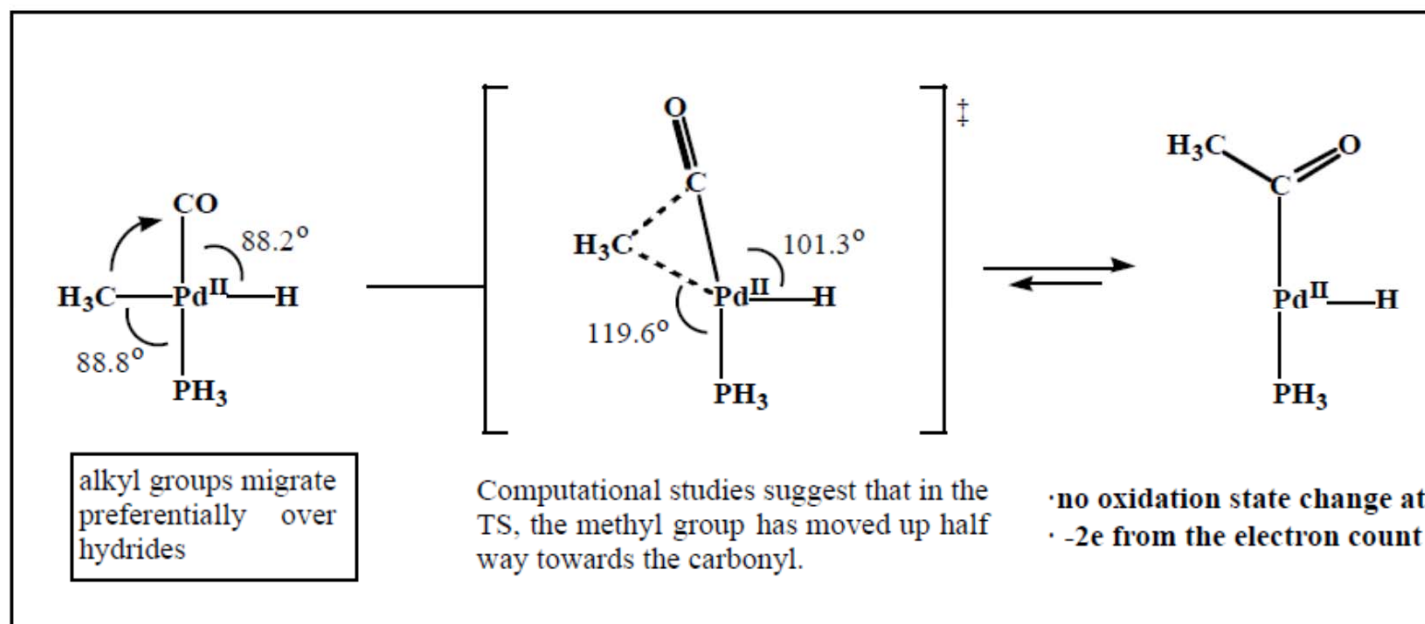


Abstraction = eliminations with no change in metal coordination number



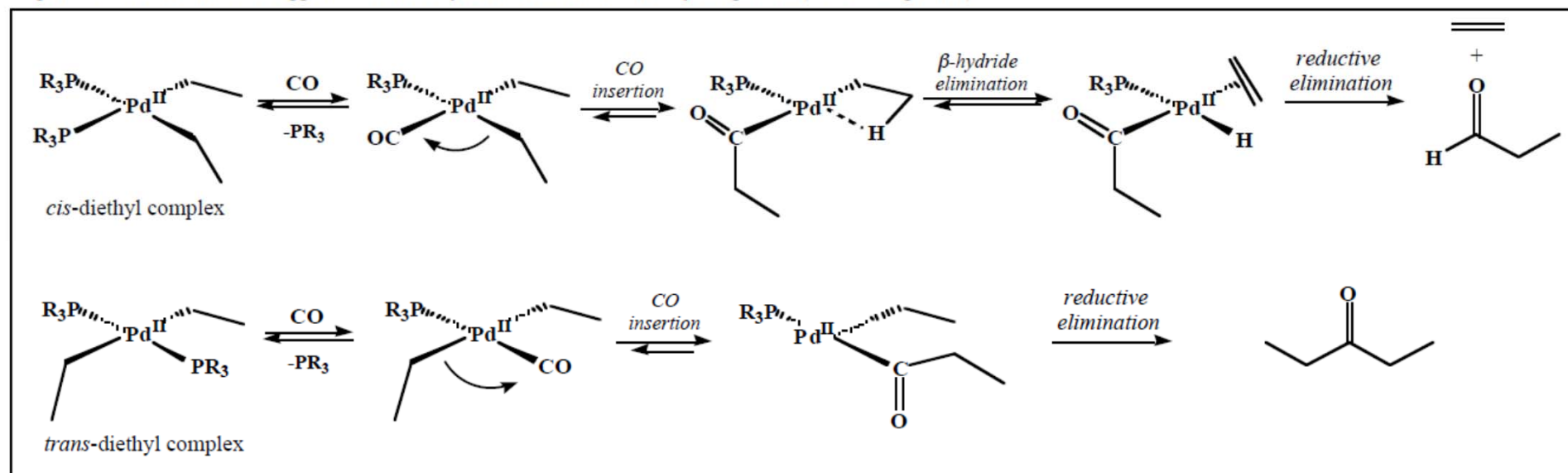


Mechanism for CO insertion : *via* alkyl migration to coordinated CO

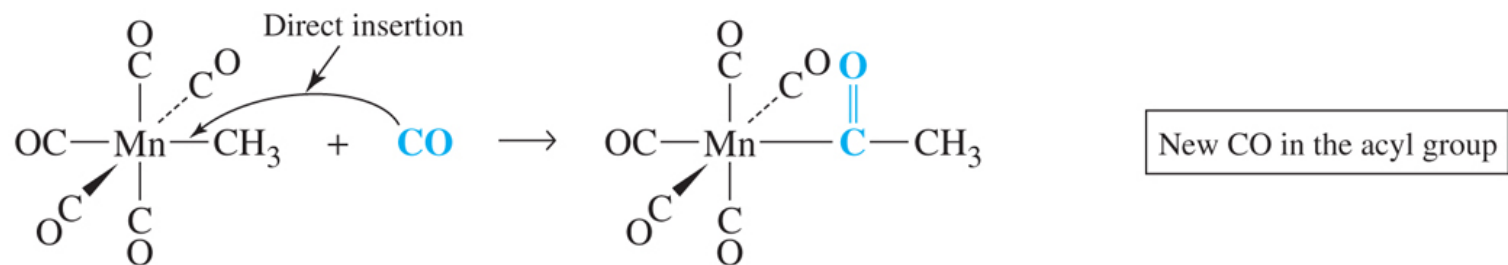


Morokuma *JACS* 1986 (108) 6136.

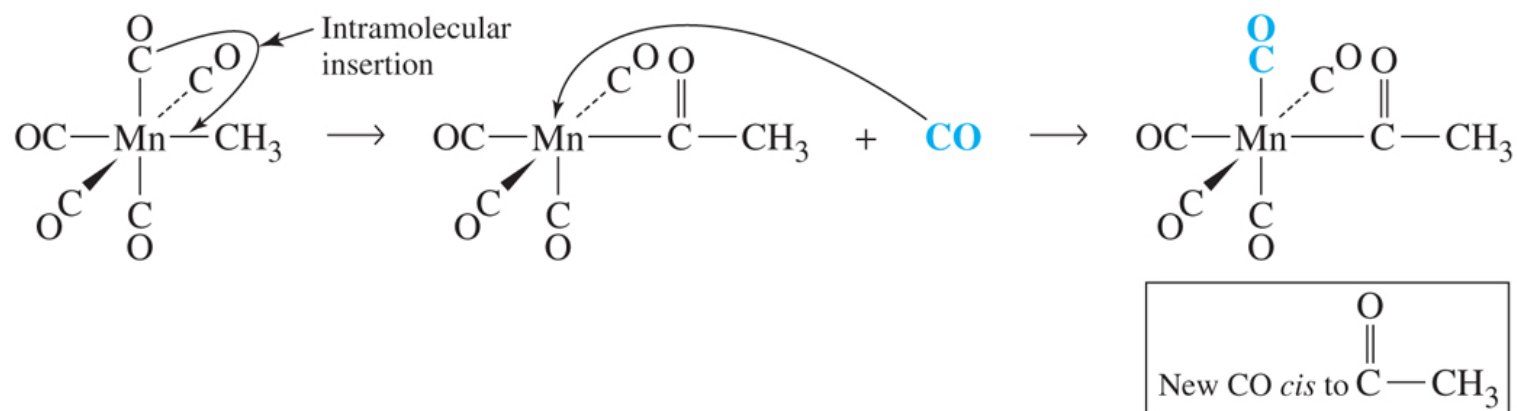
Experimental evidence also suggests that carbonyl insertion occurs *via* alkyl migration (not CO migration)



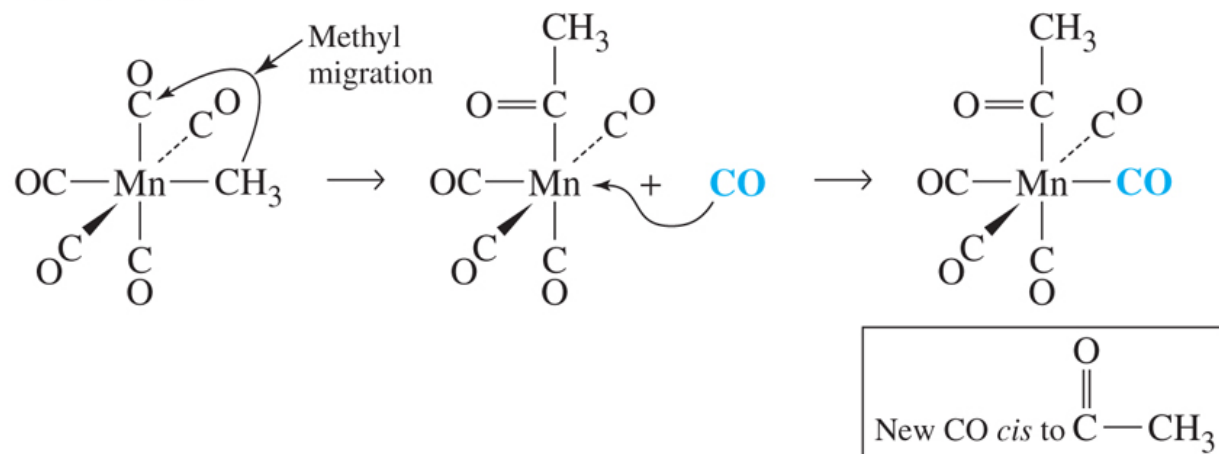
Mechanism 1



Mechanism 2



Mechanism 3



c) Experimental Evidence

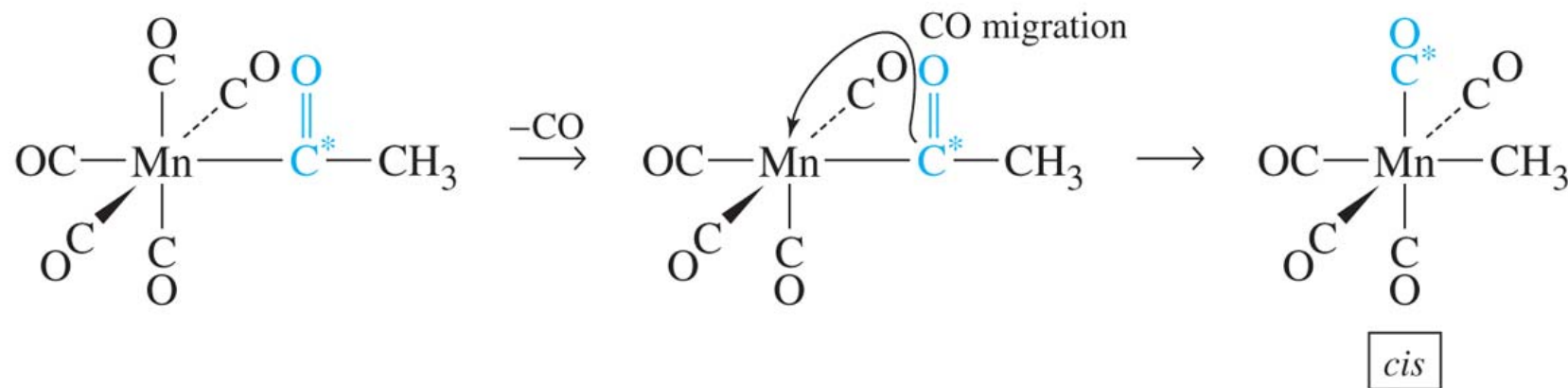
» Free ^{13}CO + complex gives no labeled acyl product

This rules out mechanism #1, CO insertion

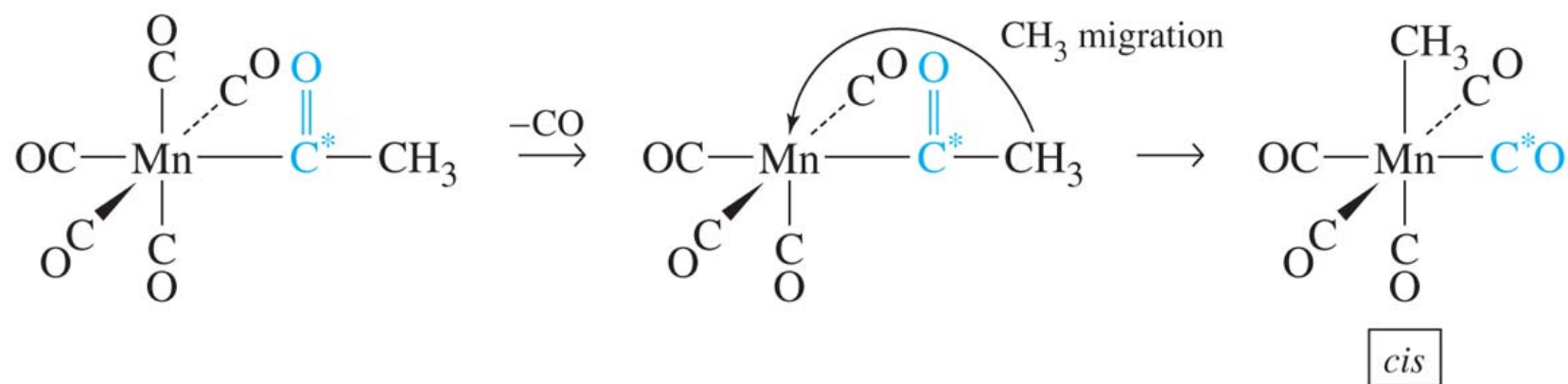
ii. Reverse reaction gives 100% *cis* ^{13}CO and R

Both mechanism #2 and mechanism #3 are consistent with this result

Mechanism 2



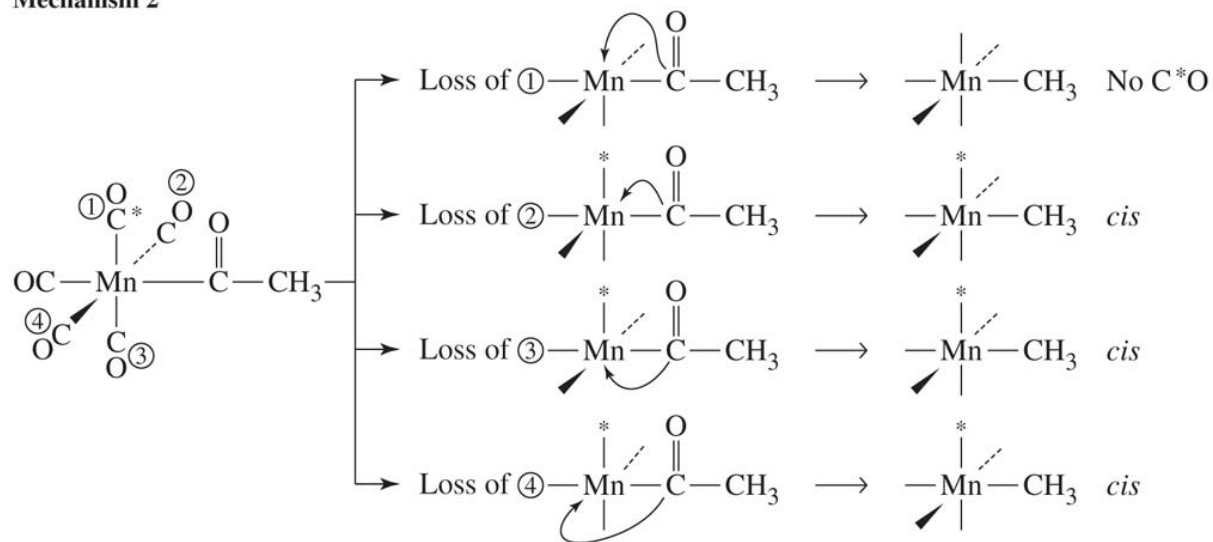
Mechanism 3



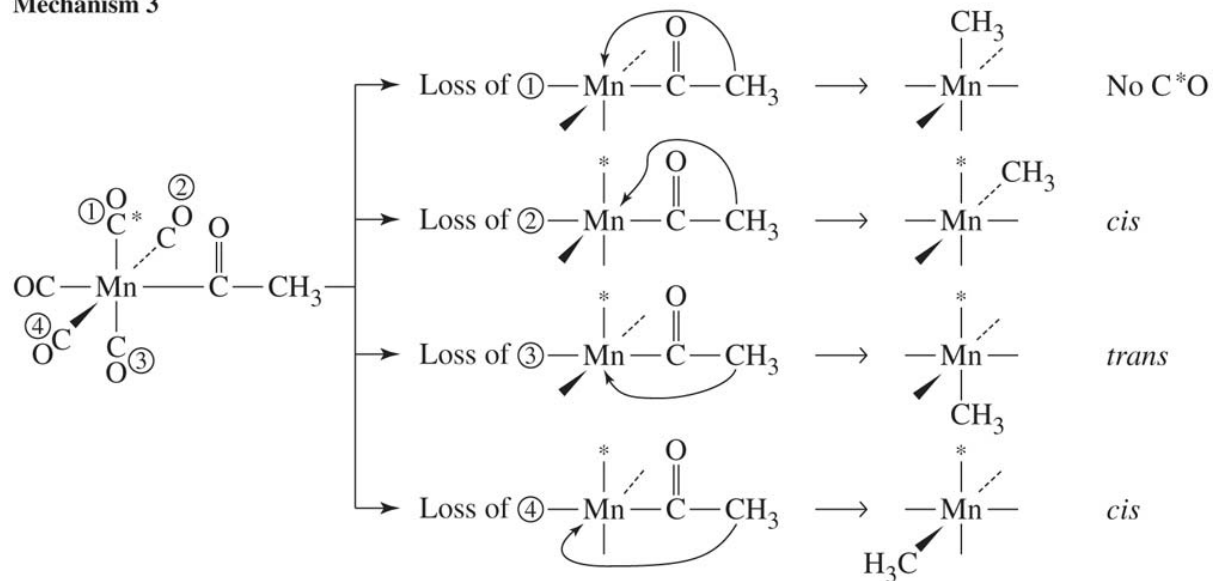
iii. Reverse reaction with ^{13}CO *cis* to acyl group gives 2:1 *cis:trans* product

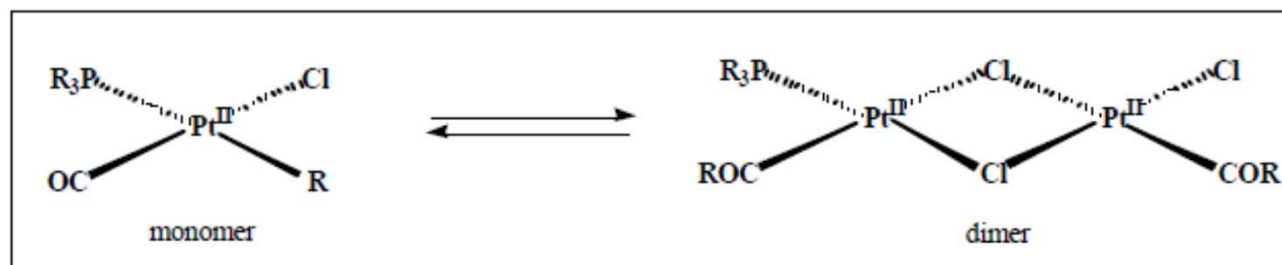
Only Mechanism #3 Alkyl Migration is consistent with this data

Mechanism 2



Mechanism 3





(no dimer observed) $\left\{ \text{---} \text{C} \equiv \text{C} \text{---} \text{Ph} \right\} < \left\{ \text{---} \text{C} \equiv \text{C} \text{---} \text{Me} \right\} < \text{CH}_2\text{Ph} < \text{Me} < \text{Ph} < \text{Et}$

Anderson *Acc. Chem. Res.* **1984** (17) 67.

Electron donating substituents on aryl R groups promote migrations whereas electron withdrawing substituents inhibit them.

R	Monomer	Dimer
	0%	100%
	12%	88%
	24%	76%
	46%	54%
	73%	27%
	100%	0%

Cross *J. Chem. Soc., Dalton Trans.* **1981**, 2317.

Initiation of carbonyl insertion:

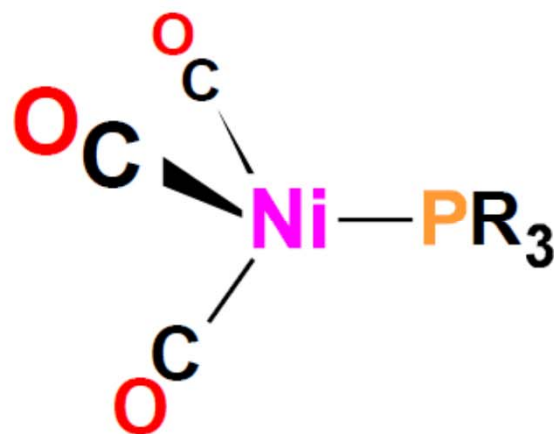
- a) Lewis acids
- b) Oxidation

Phosphine Ligands

Electronics:

Lowest CO stretching frequency:

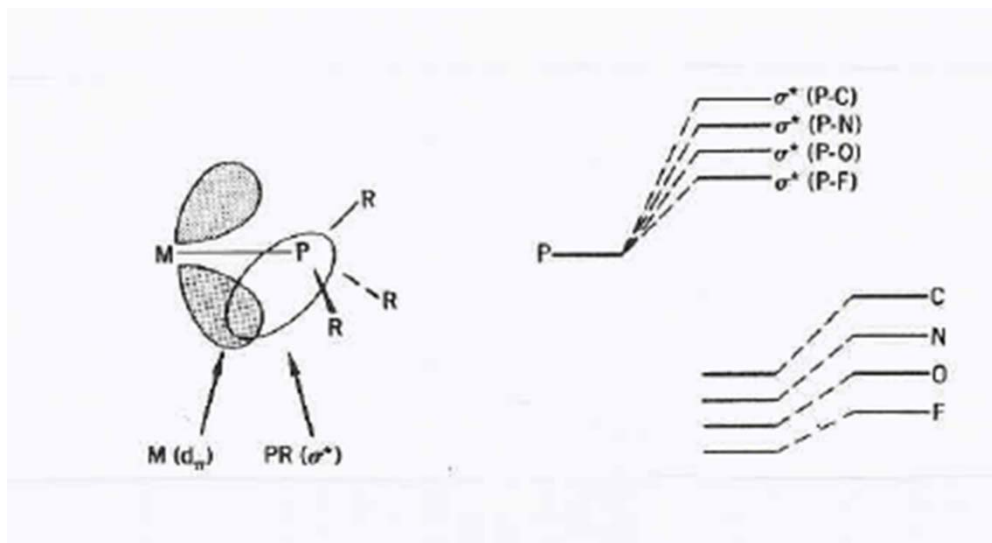
most donating phosphine



Highest CO stretching frequency:

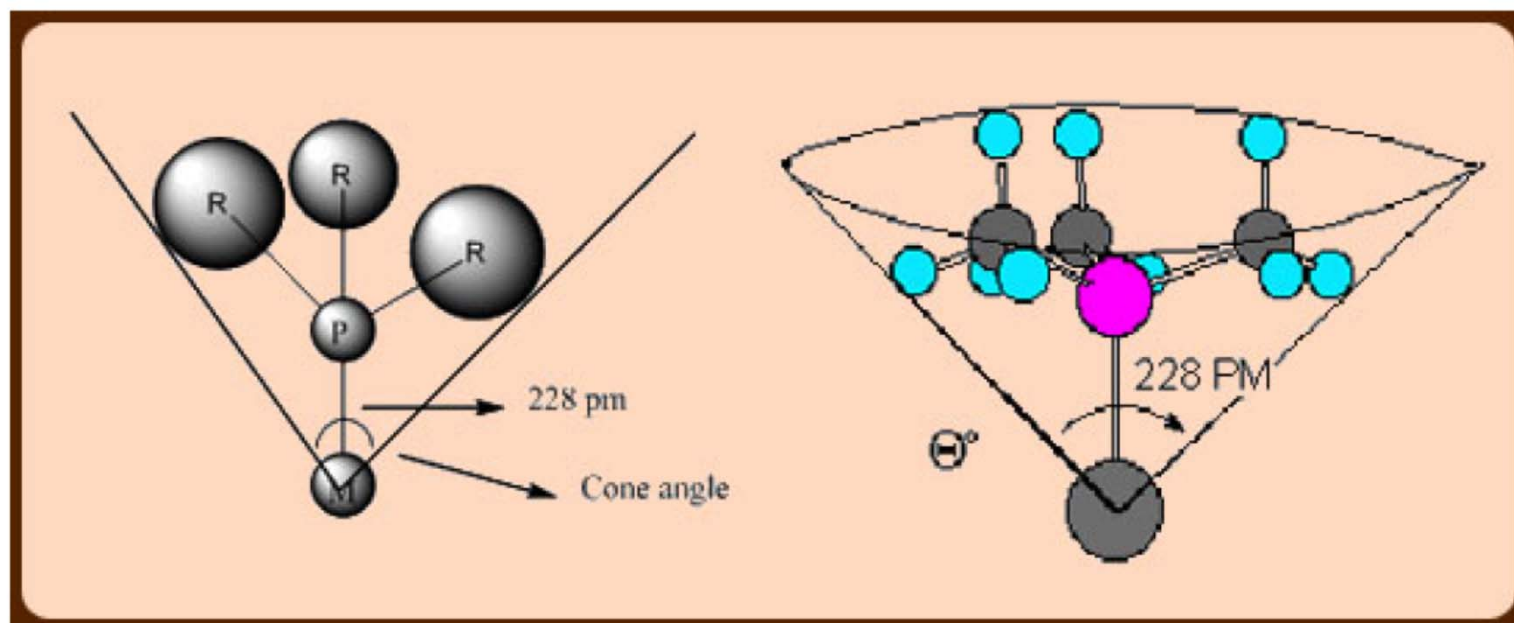
least donating phosphine

(best π -acceptor)

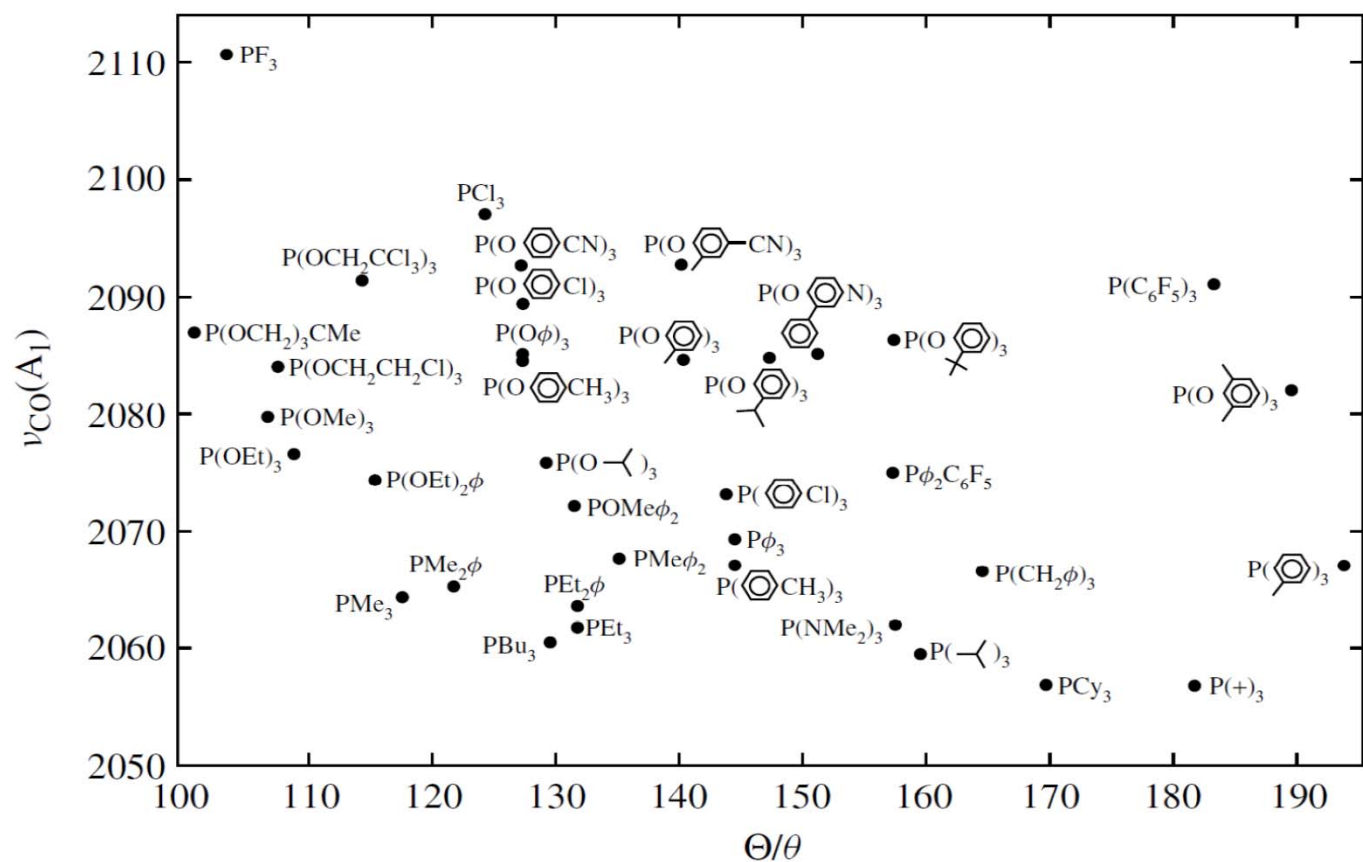
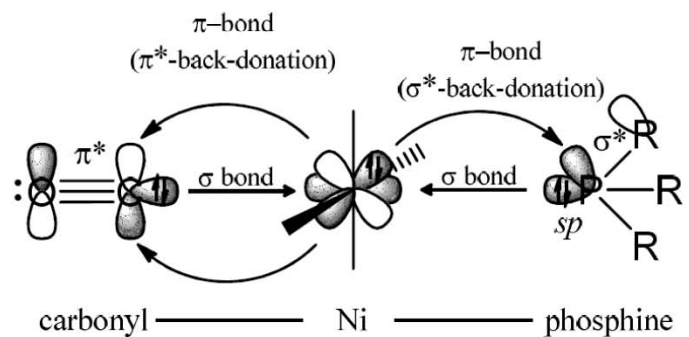


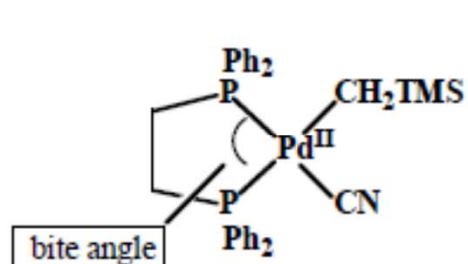
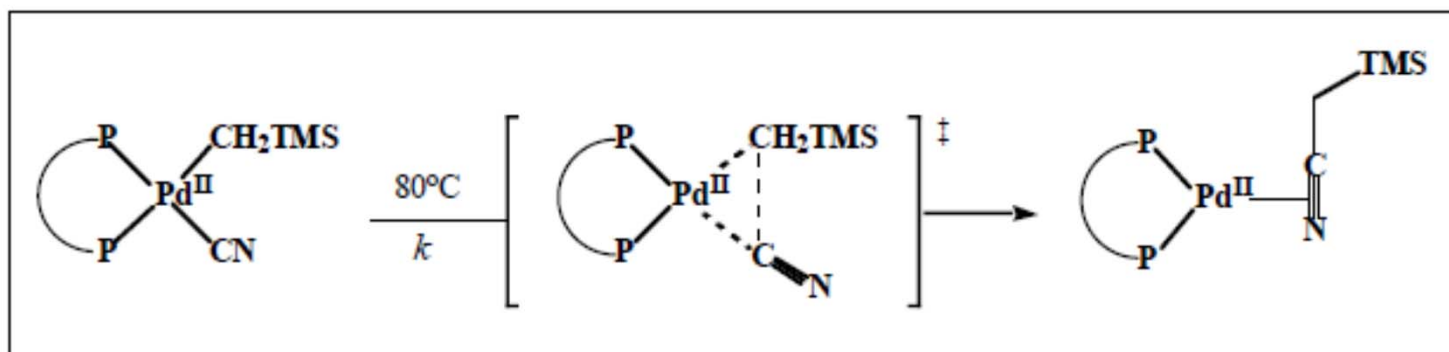
Phosphine Ligands

Sterics:

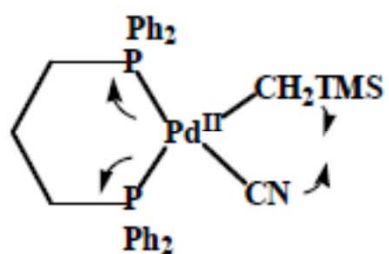


Tolman Plot of Electronic Parameter and Cone Angle

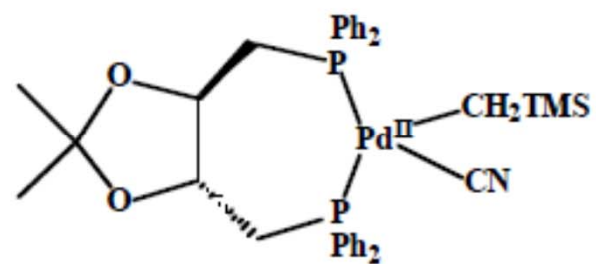




bite angle: 85°
 $k = 2.1 \times 10^{-6}$

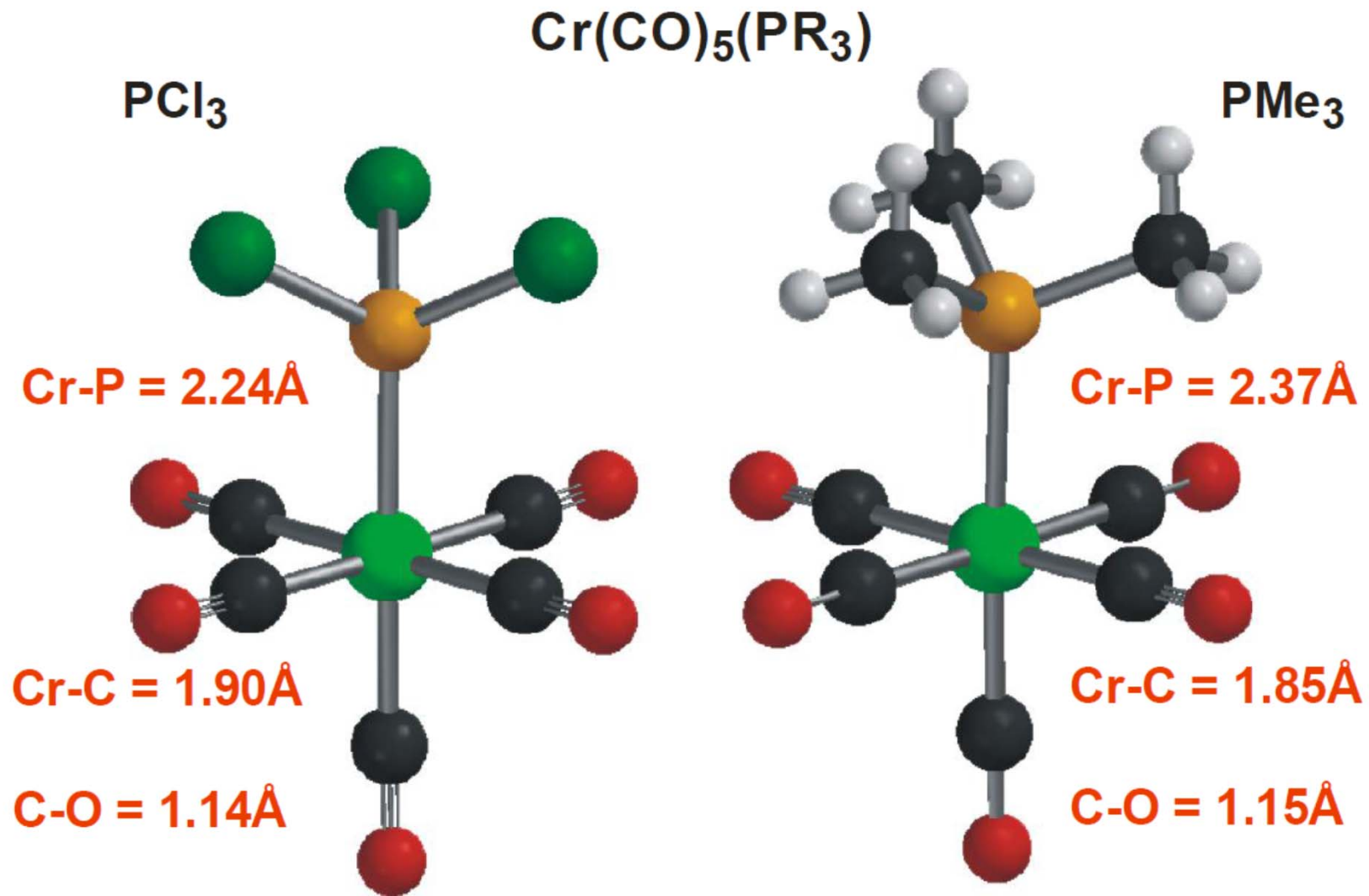


bite angle: 90°
 $k = 5.0 \times 10^{-5}$



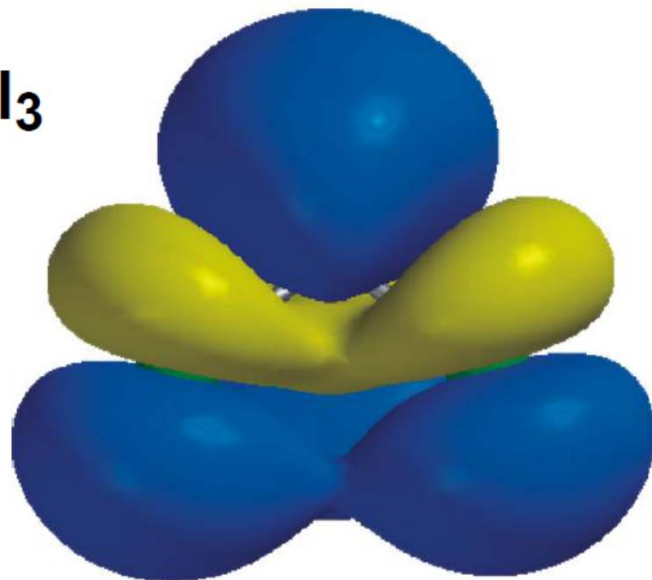
bite angle: 100°
 $k = 1.0 \times 10^{-2}$

Bond length vs Bond strength



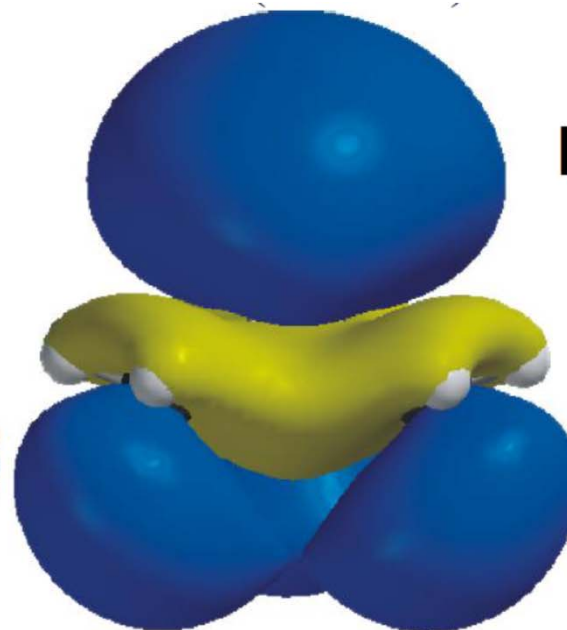
Bond length vs Bond strength

PCl_3



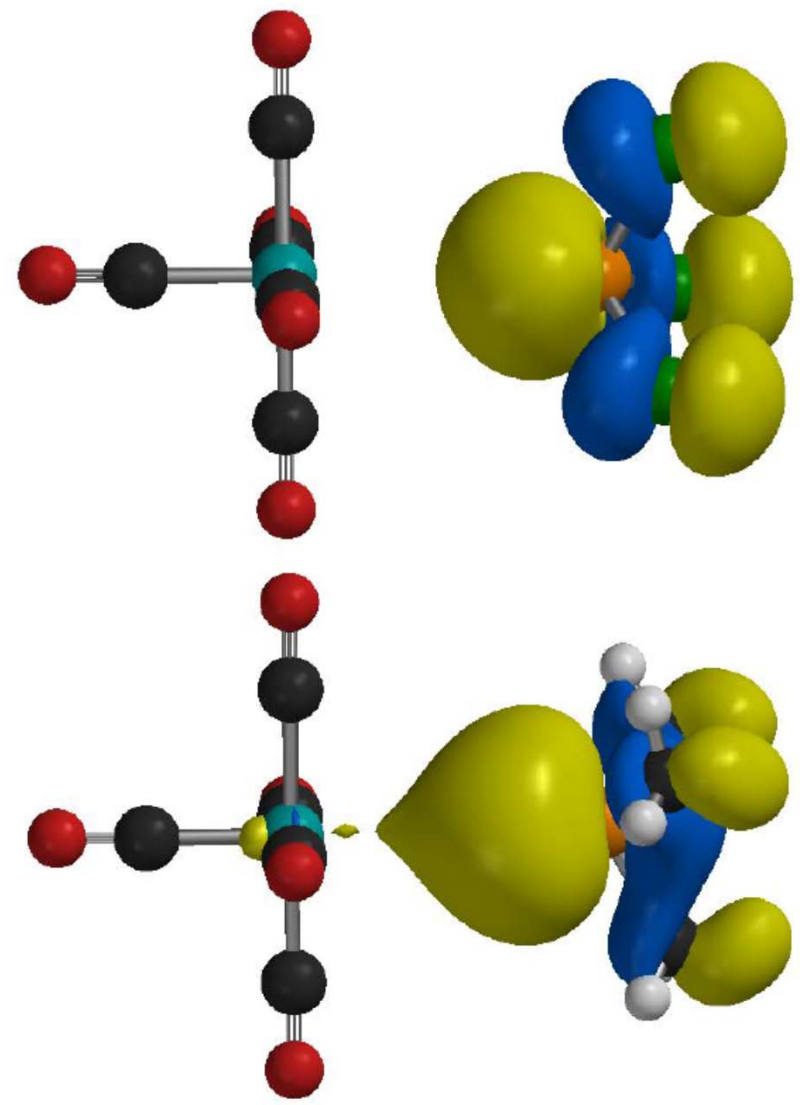
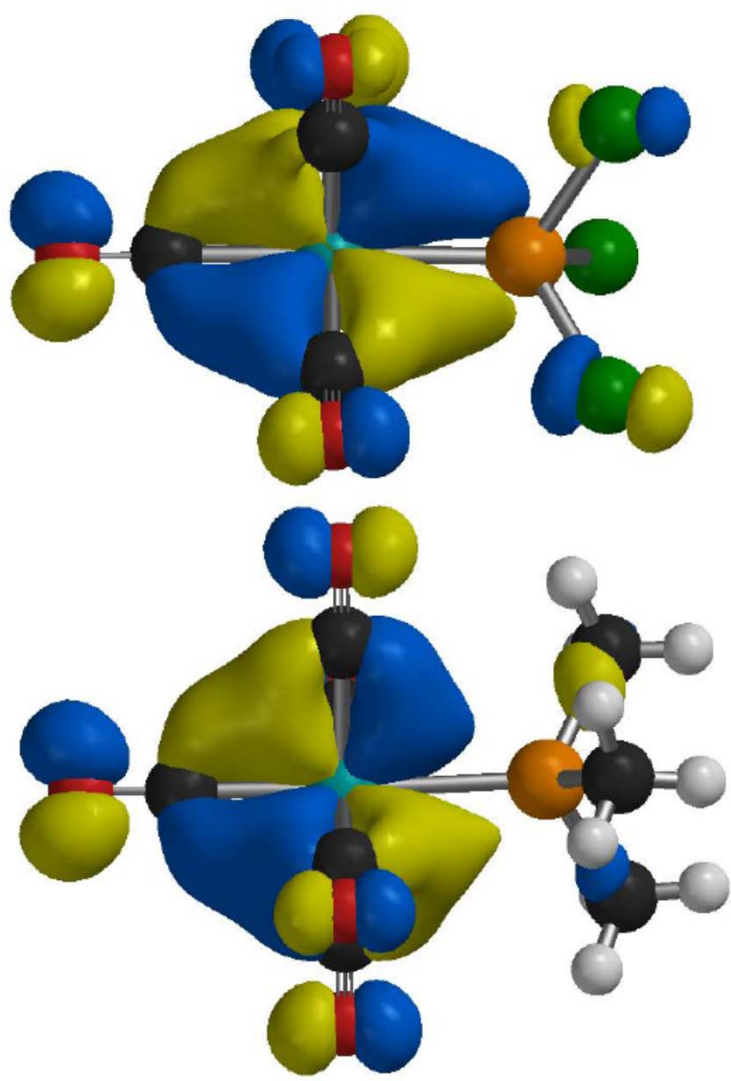
HOMO energy = -8.36 eV

PMe_3

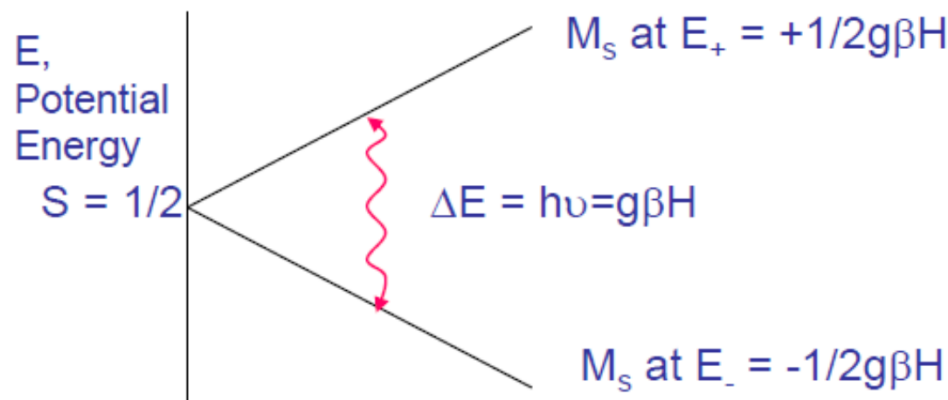


-6.23 eV

Bond length vs Bond strength



EPR = Electron Paramagnetic Resonance
 Can observe systems with $S = 1/2, 3/2, 5/2, \text{ etc}$



H, Magnetic Field

Abs

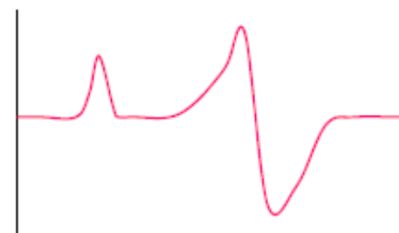
$\frac{dAbs}{dH}$

H

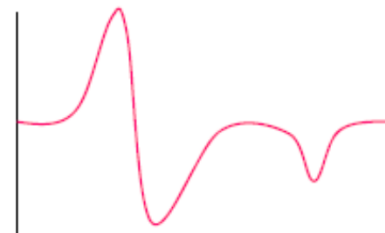
Isotropic Symmetry

Principal g-value
 $g = h\nu/\beta H$ ($g = 2.0023$ for e^-)

Quantified by Integration
 and comparison to
 Cu(II)EDTA standard



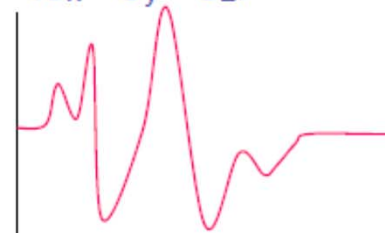
Axial Symmetry ($g_{\parallel} > g_{\perp}$)



Axial Symmetry ($g_{\perp} > g_{\parallel}$)



Rhombic Symmetry
 ($g_x \neq g_y \neq g_z$)



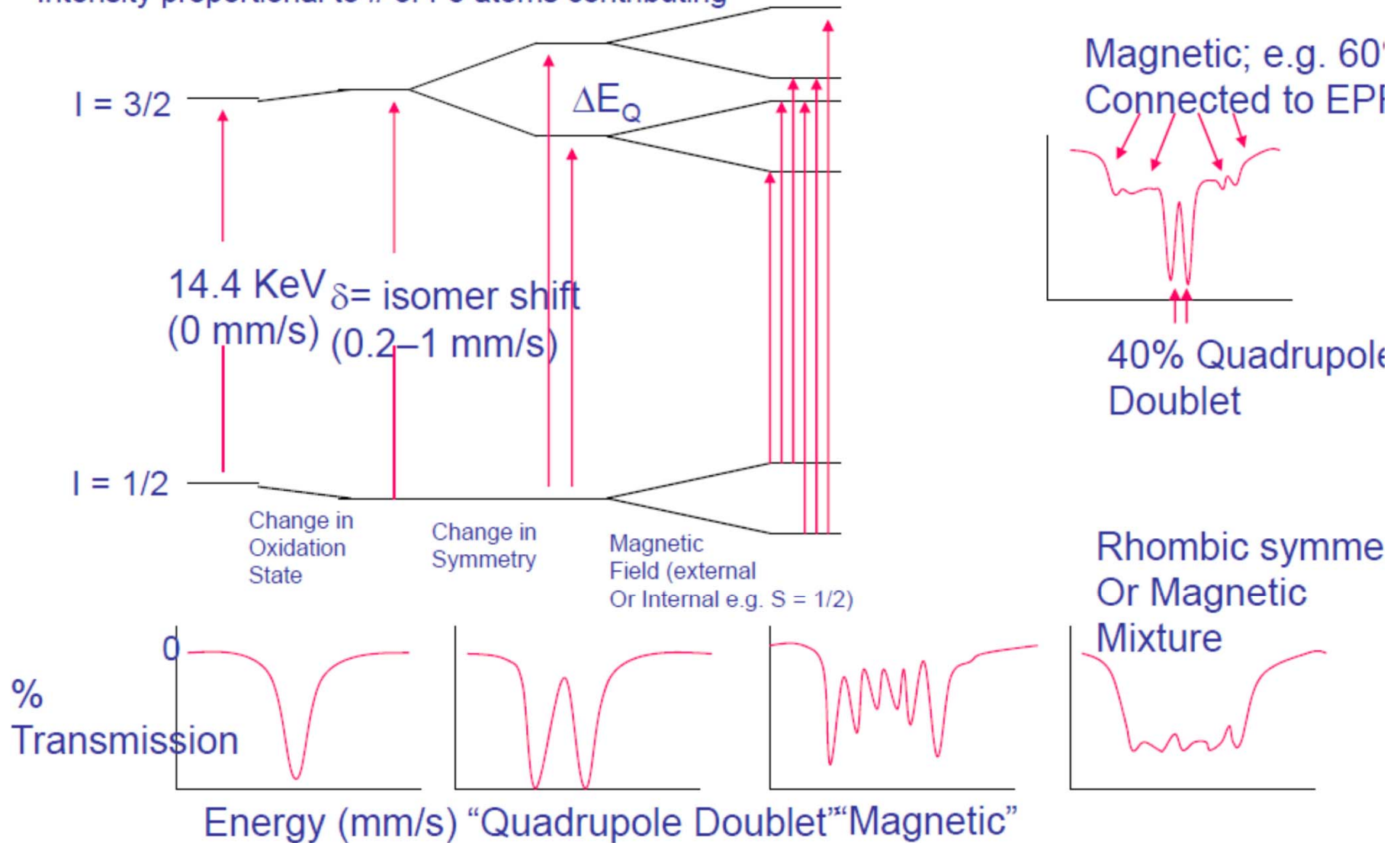
Mixture of Signals

Mössbauer Spectroscopy (Nuclear γ -Ray Resonance)

Useful for ^{57}Fe ($I = 3/2$) Systems

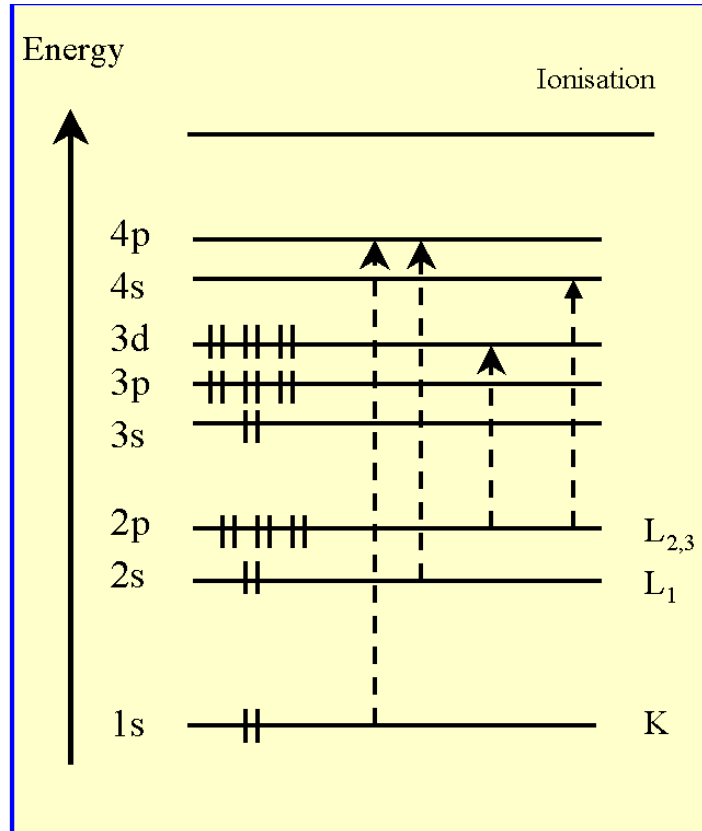
All electronic and magnetic states observed (no "Mössbauer-Silent Fe")

Intensity proportional to # of Fe atoms contributing

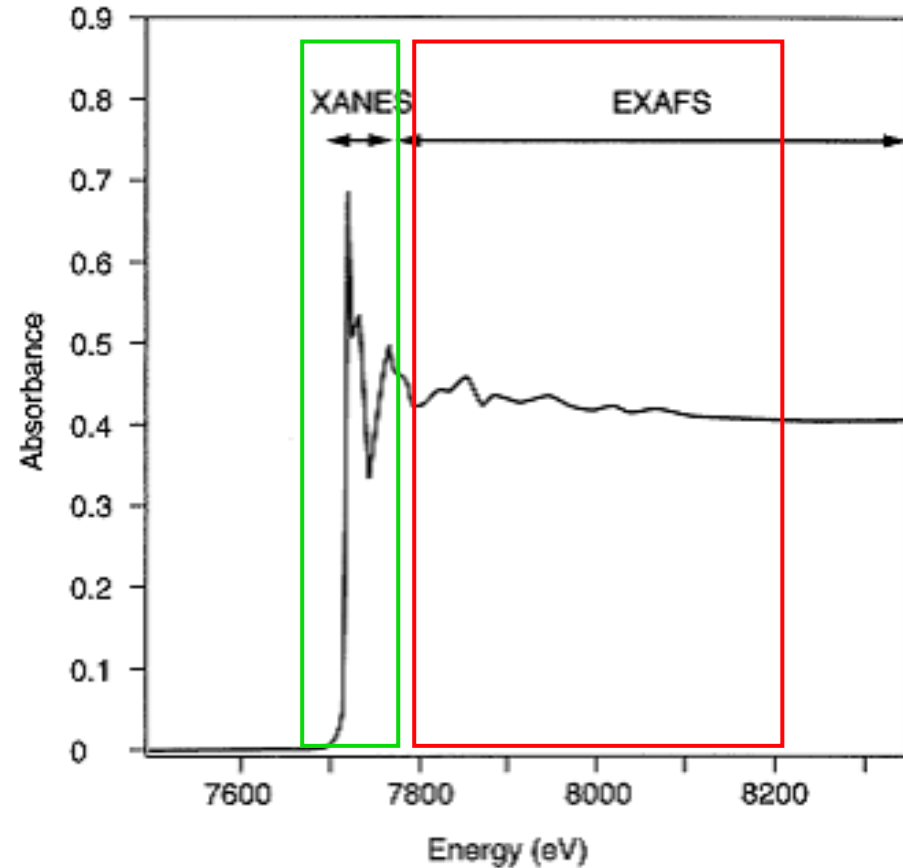


X-RAY ABSORPTION SPECTROSCOPY: XAS, EXAFS, XANES

When an atom is bombarded by X-rays:

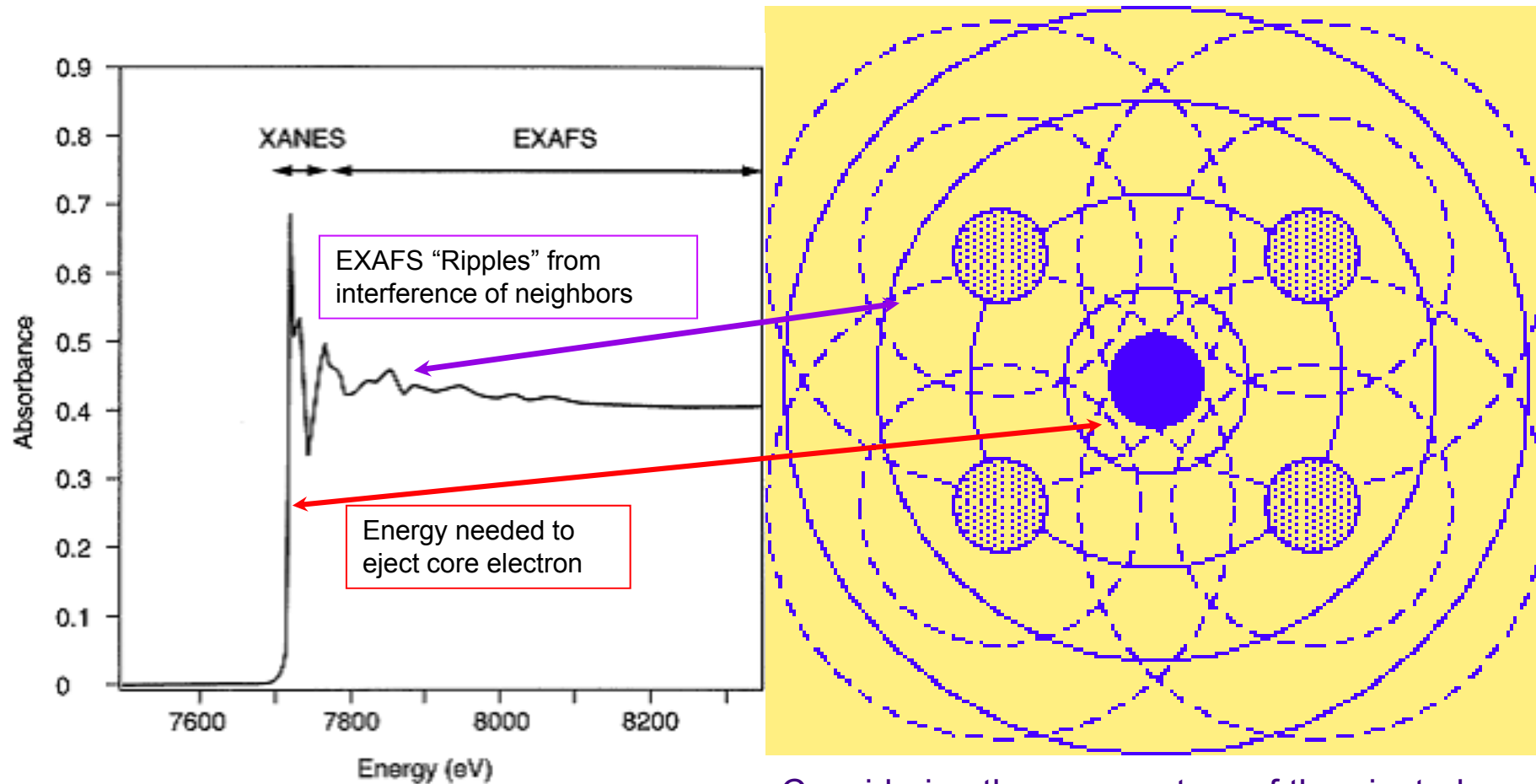


ΔE : 100 meV at 400 eV



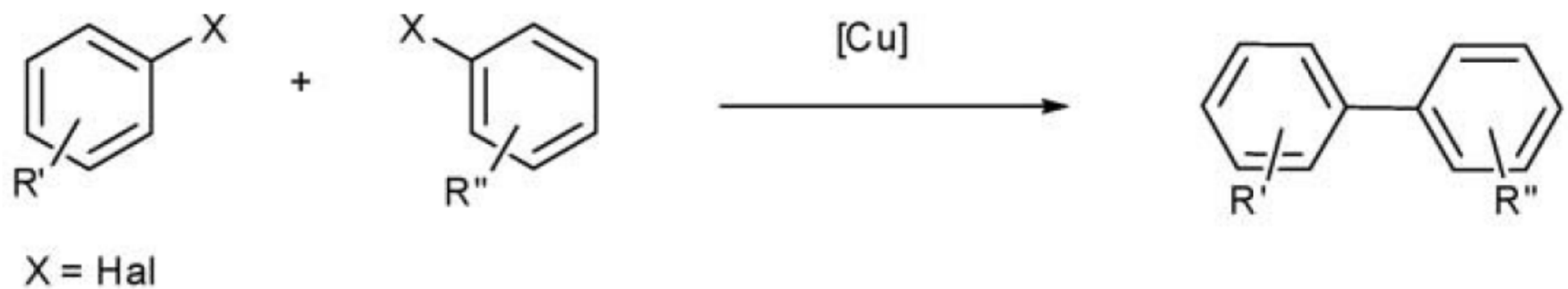
- an electron from a core level is excited to the unoccupied states of the system
- changing the X-ray excitation energy changes the unoccupied state the electron can reach
- **EXAFS**: extended X-ray absorption Fine Structures
- **XANES**: X-ray Absorption Near Edge Structure

When a photoelectron is ejected:

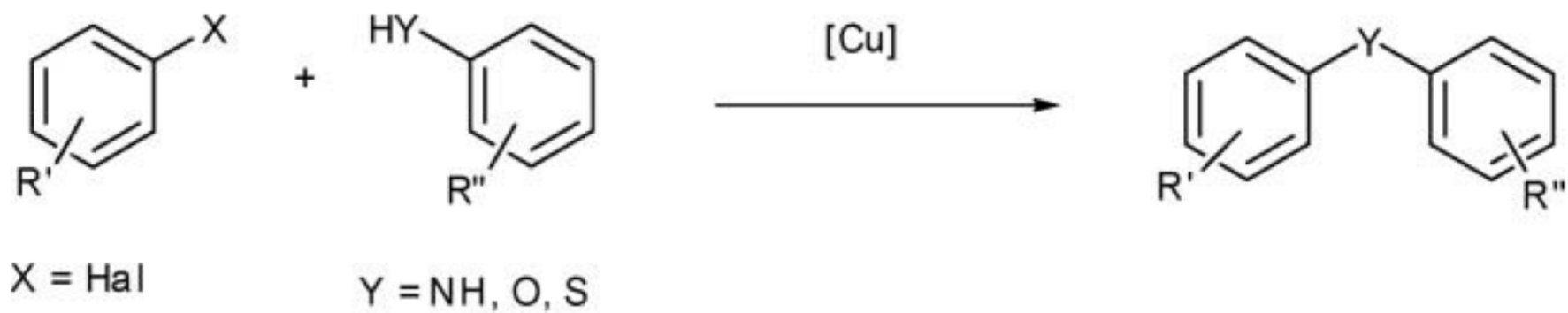


Considering the wave nature of the ejected photoelectron and regarding the atoms as point scatterers a simple picture can be seen in which **the backscattered waves interfere with the forward wave** to produce either peaks or troughs.

RAWDATA <http://www.haverford.edu/chem/Scarrow/EXAFS123/Plotting%20Graphs.htm>
FITTING <http://www.haverford.edu/chem/Scarrow/EXAFS123/FITTING.htm>
REFINING <http://www.haverford.edu/chem/Scarrow/EXAFS123/REFINING.htm>



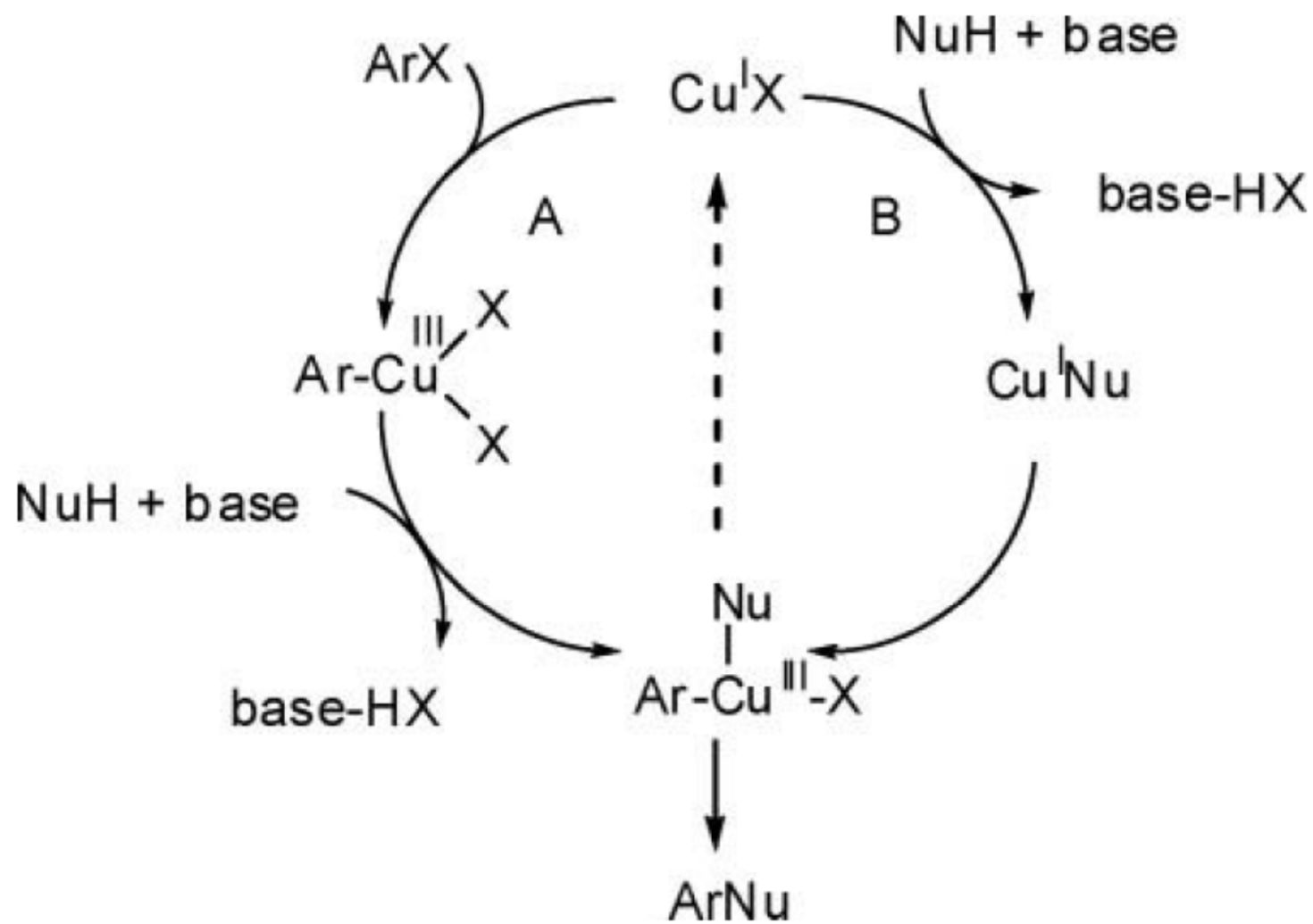
Ullmann Reaction

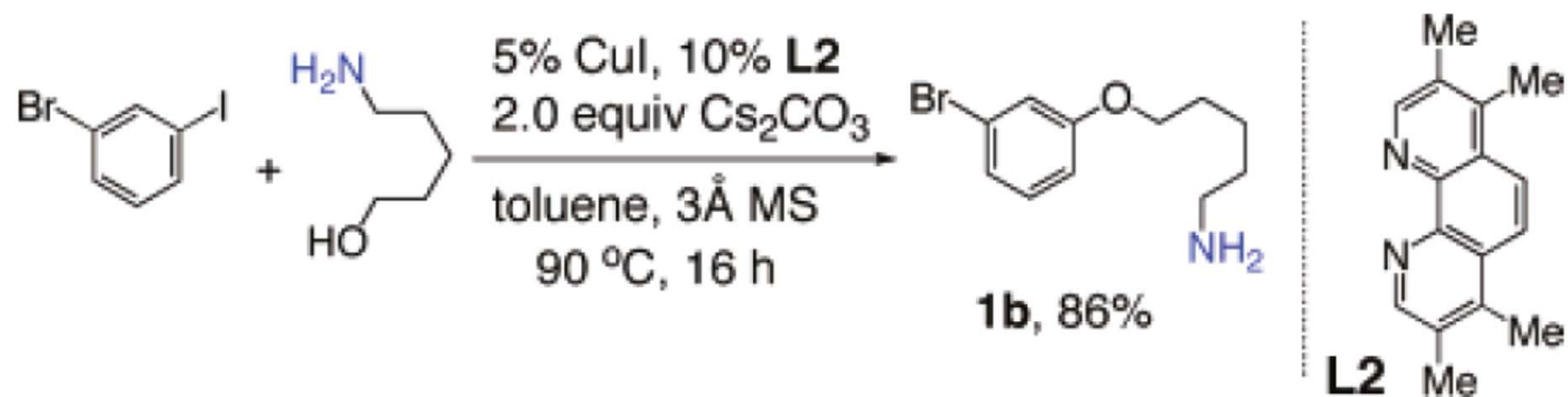
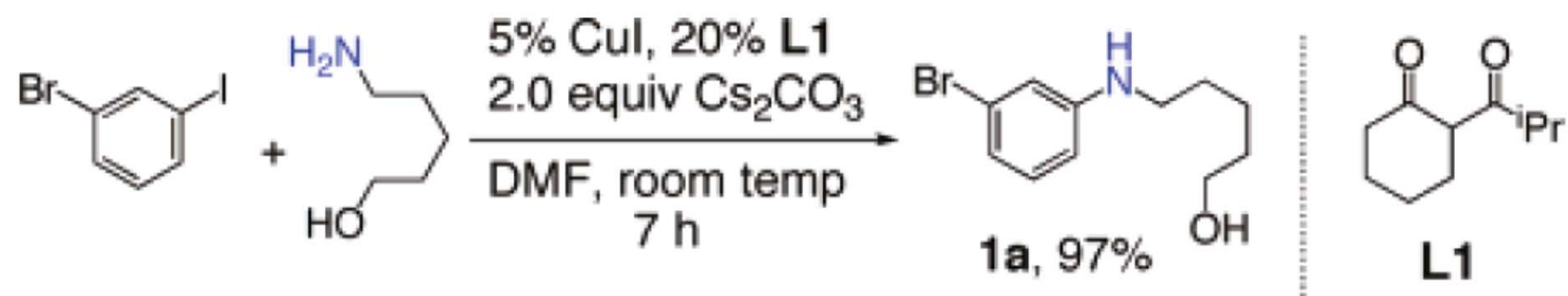


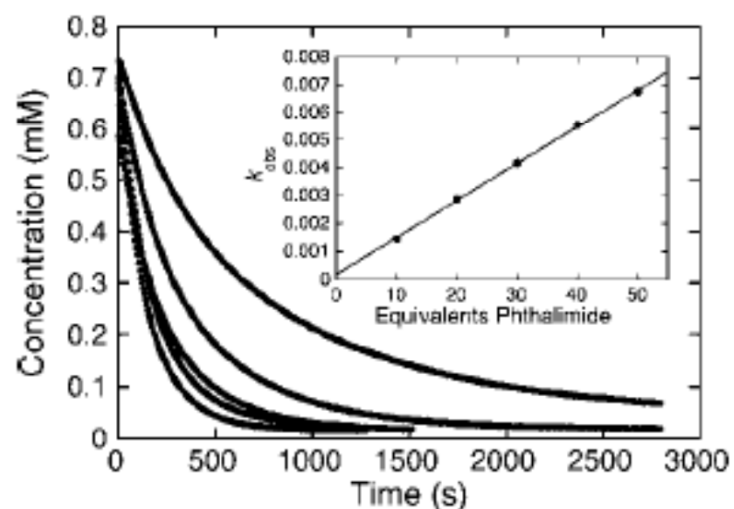
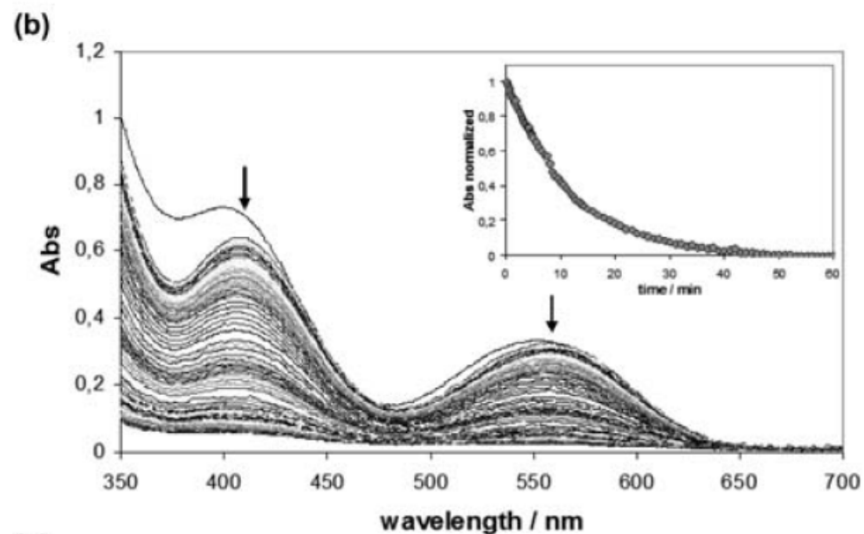
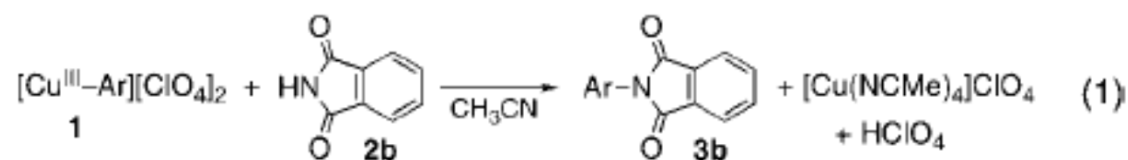
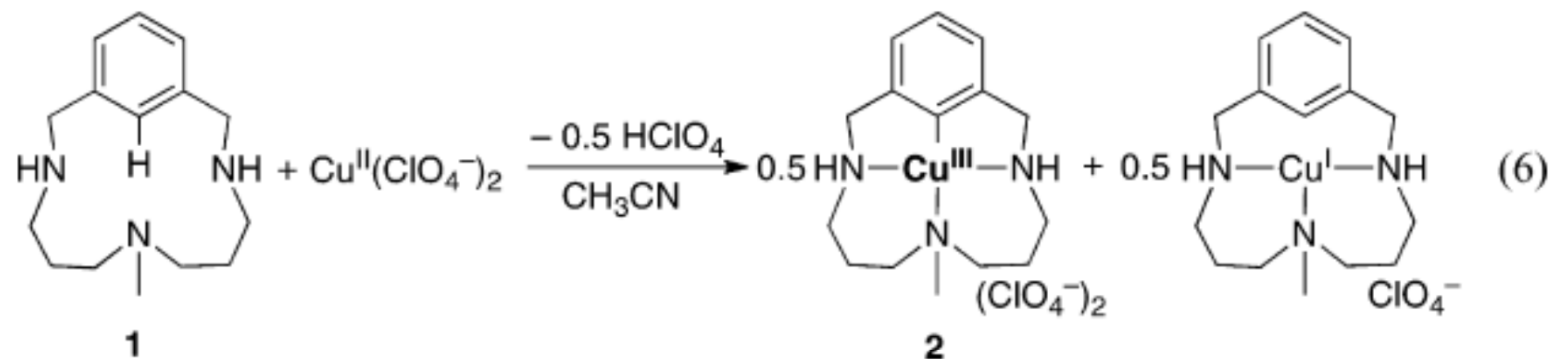
Ullmann Condensation

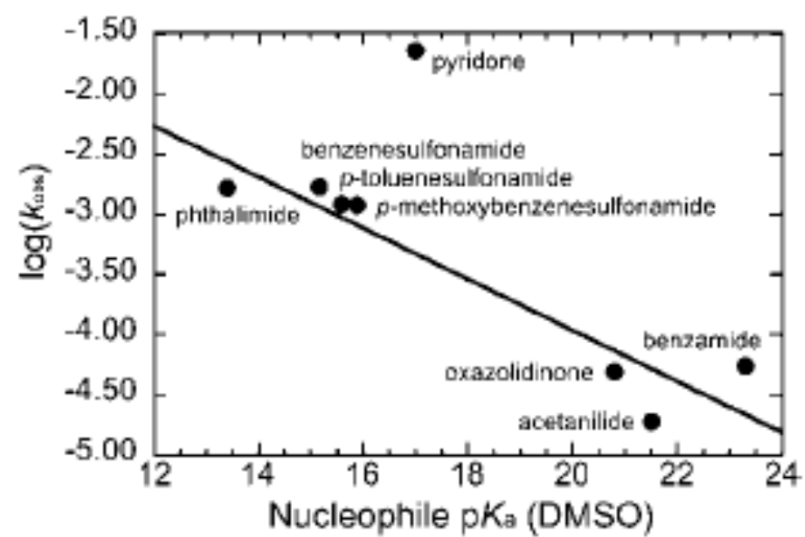
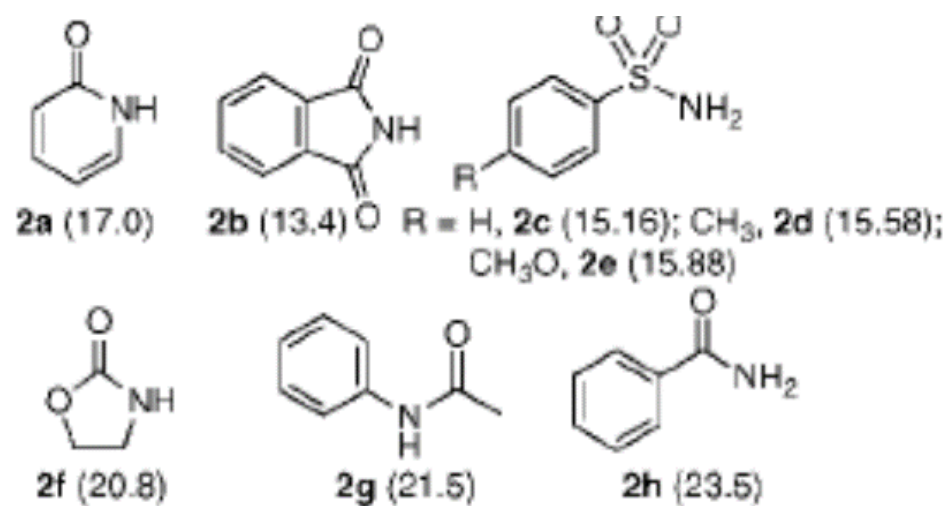
Possible mechanisms:

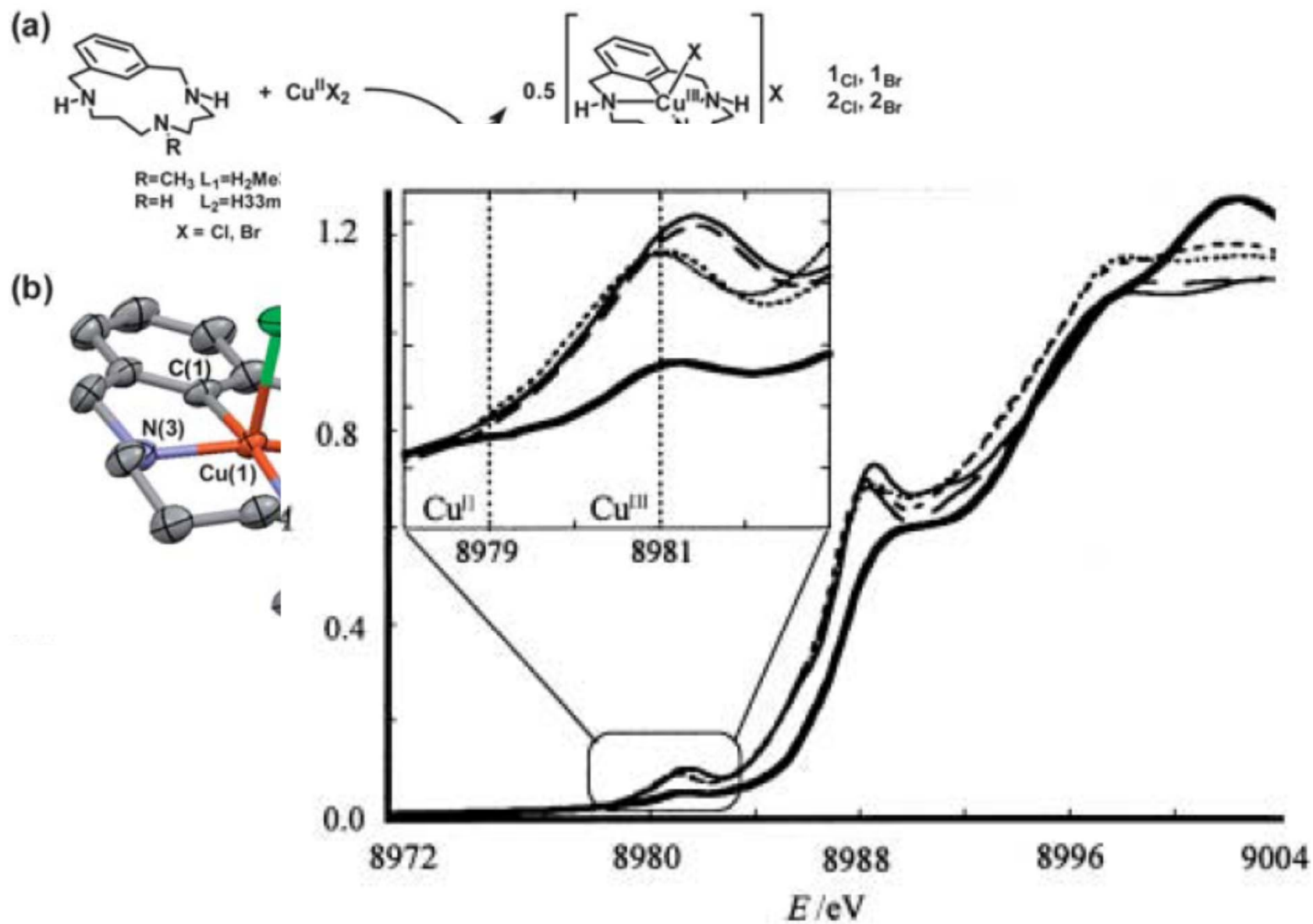
- (1) Oxidative addition of ArX on copper(I) resulting in an intermediate Cu(III) species.
- (2) Aryl radical intermediates, either *via* single electron transfer (SET) or *via* halide atom transfer (AT).
- (3) σ -bond metathesis through a four-centre intermediate.
- (4) π -complexation of copper(I) on ArX.

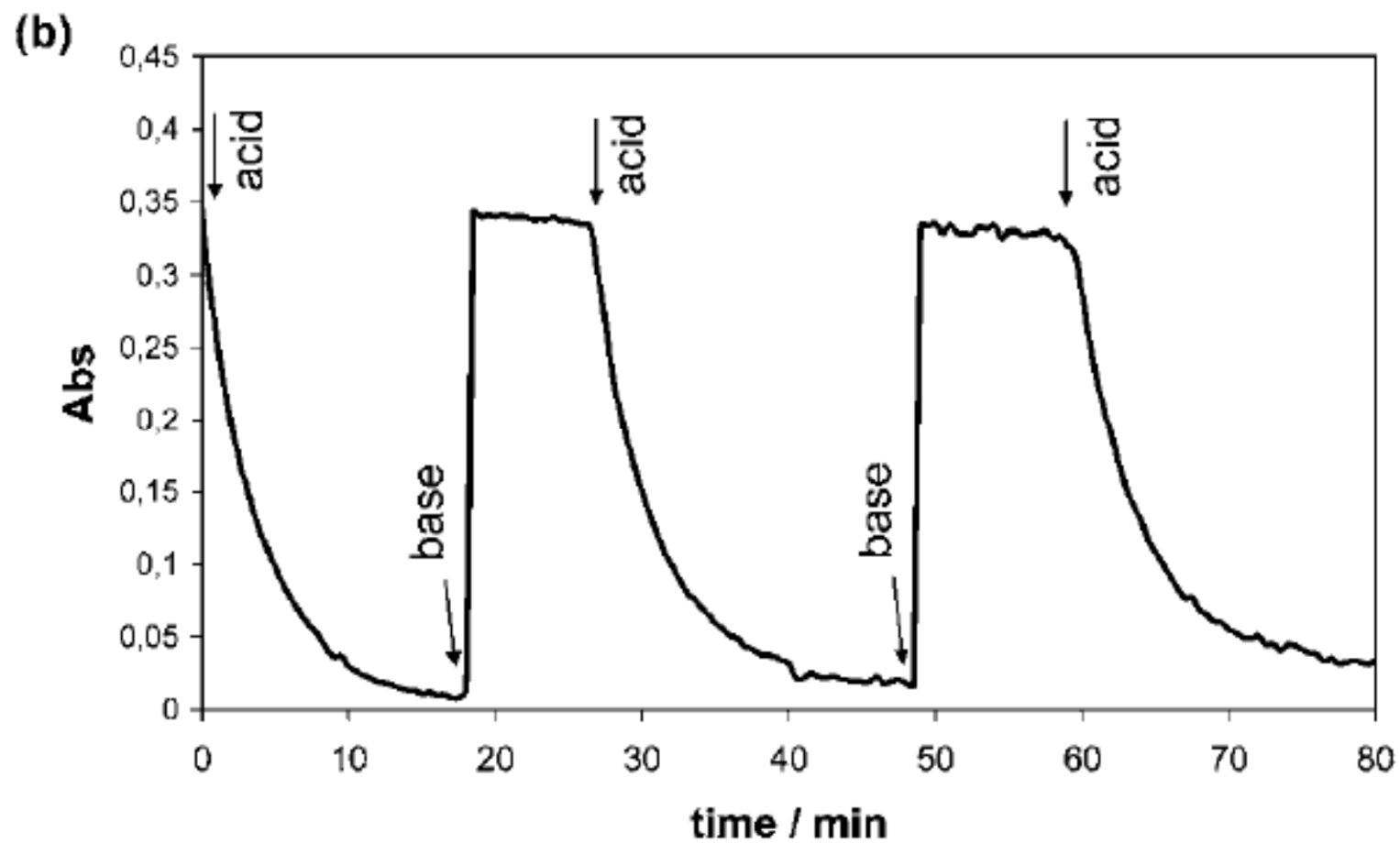
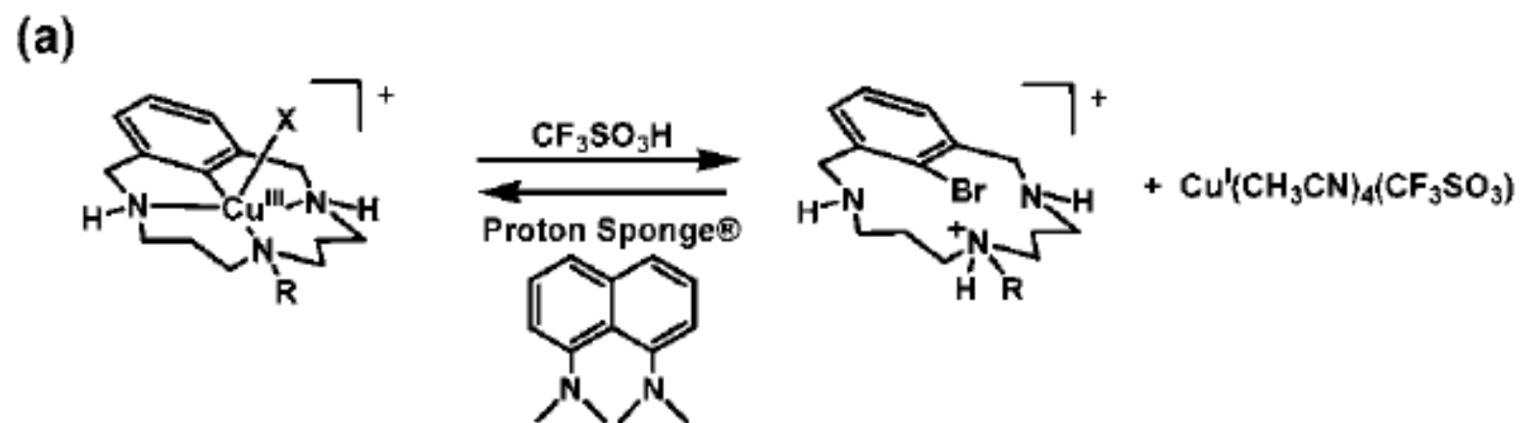


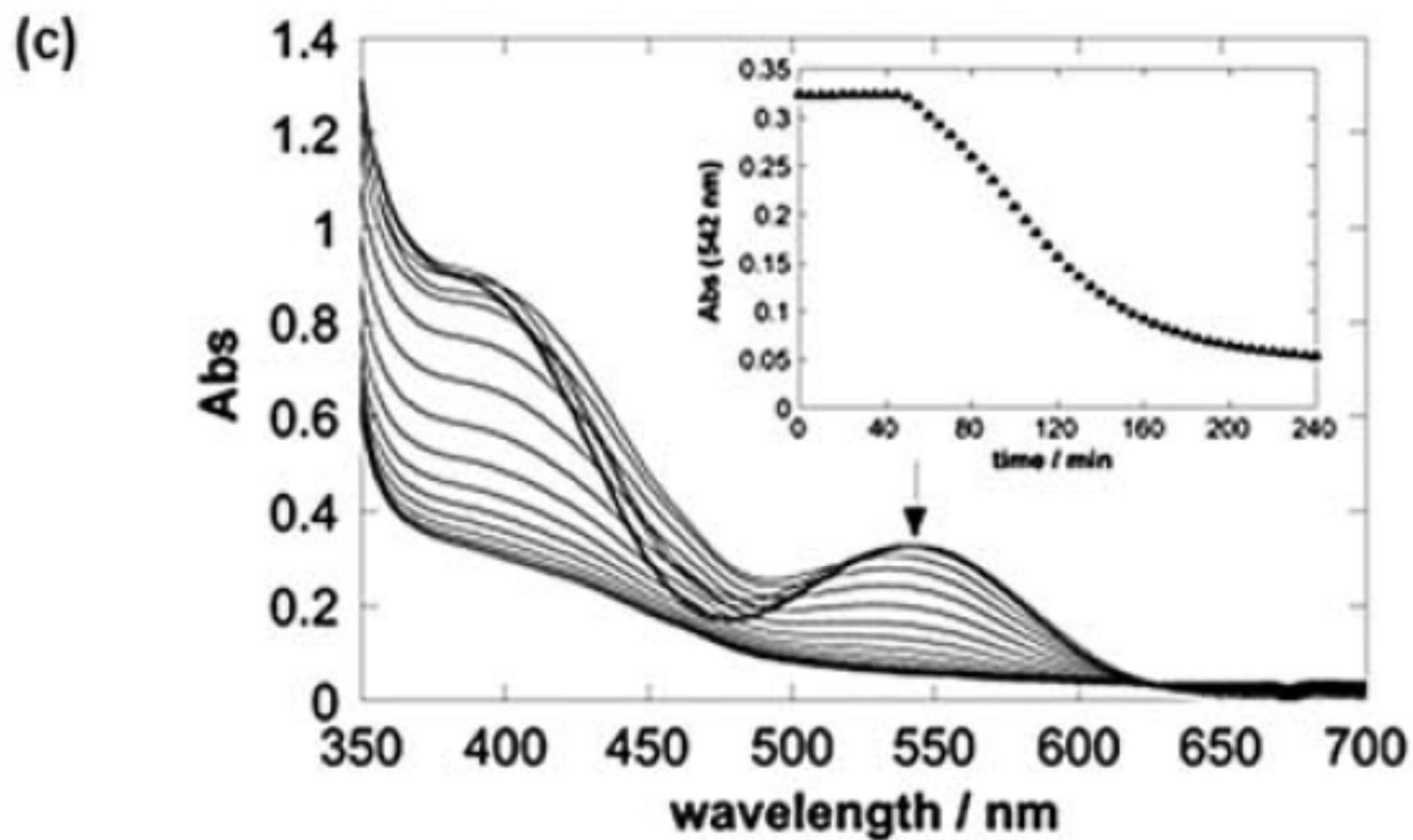
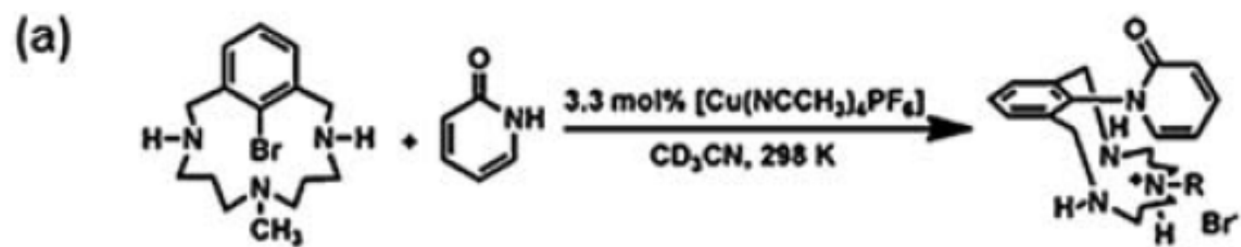




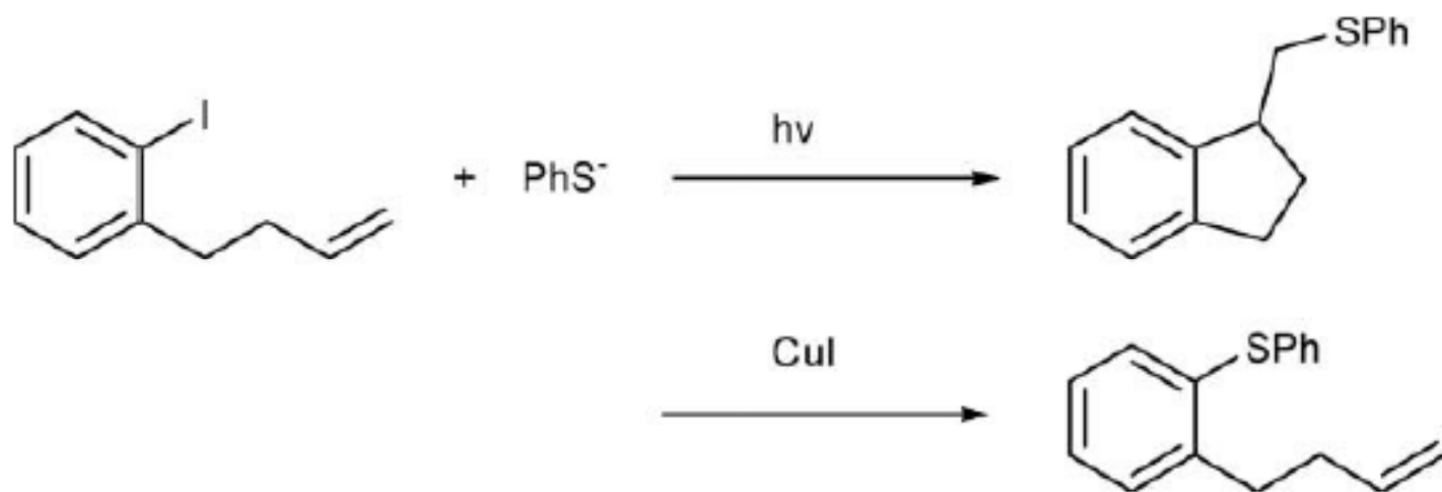


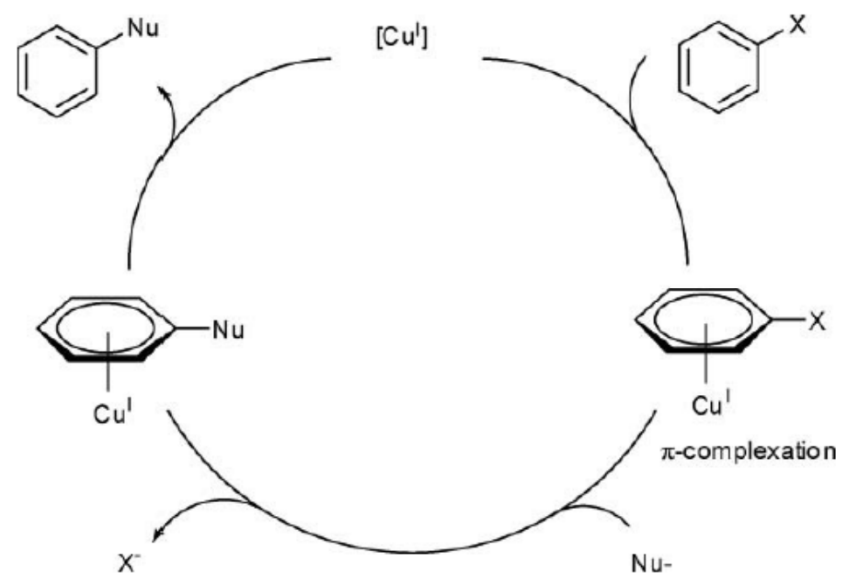
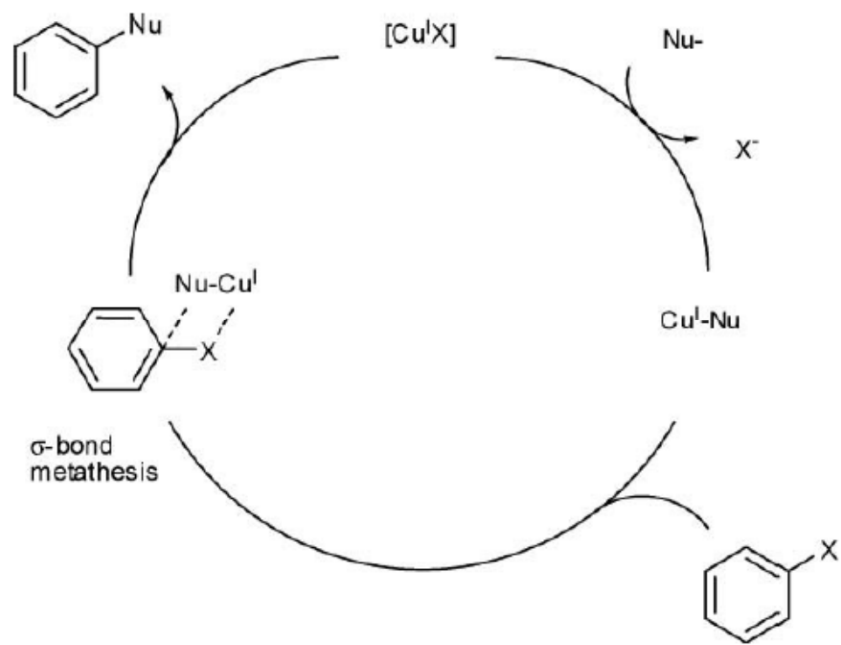






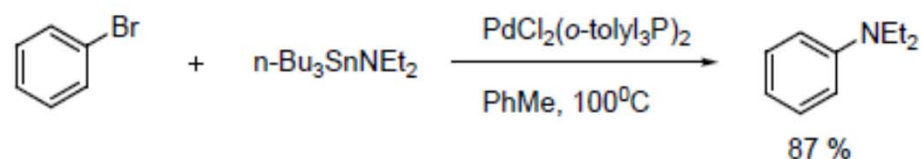
Radical clock test



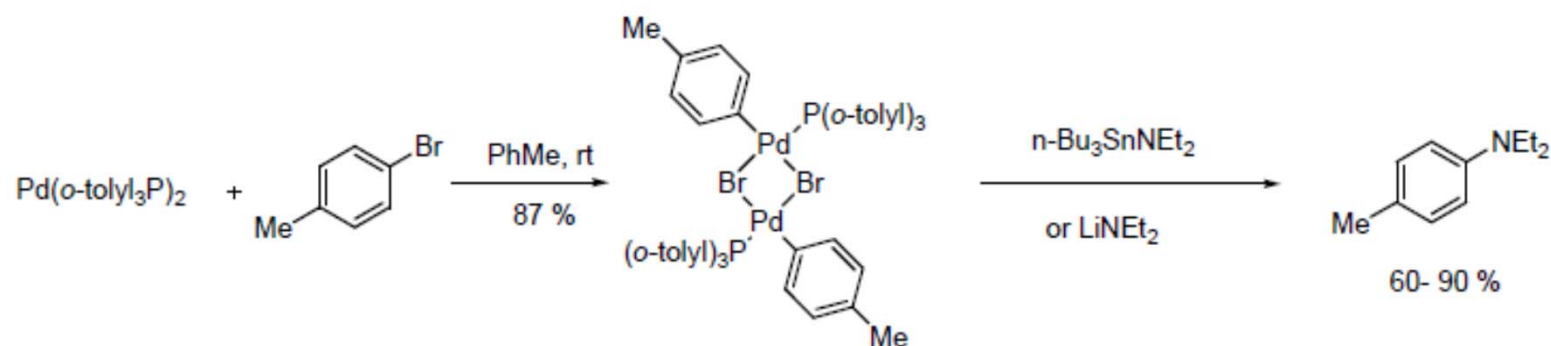


Pd-Catalyzed Amination- Tin

Initial Report- Kosugi, 1983

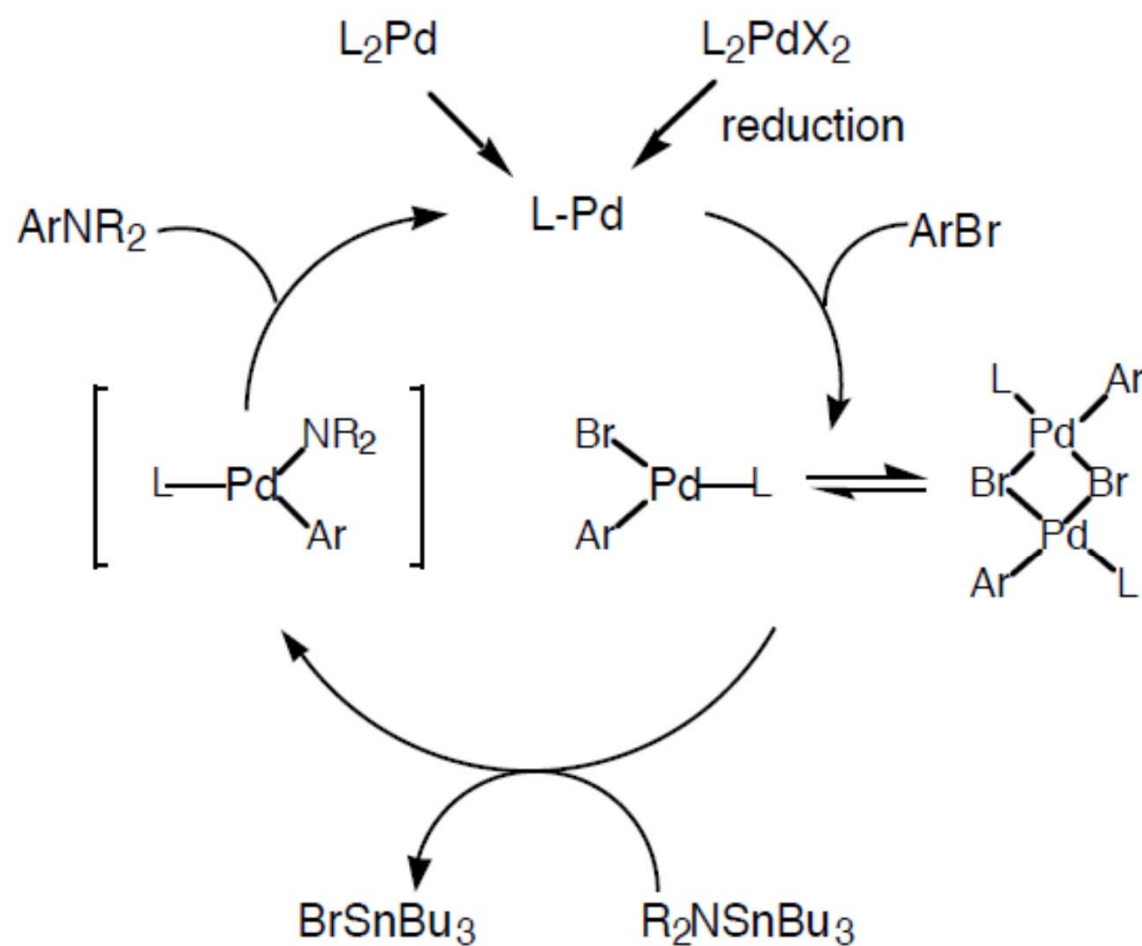


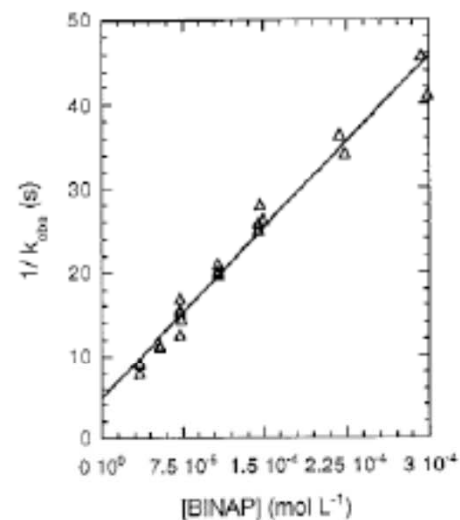
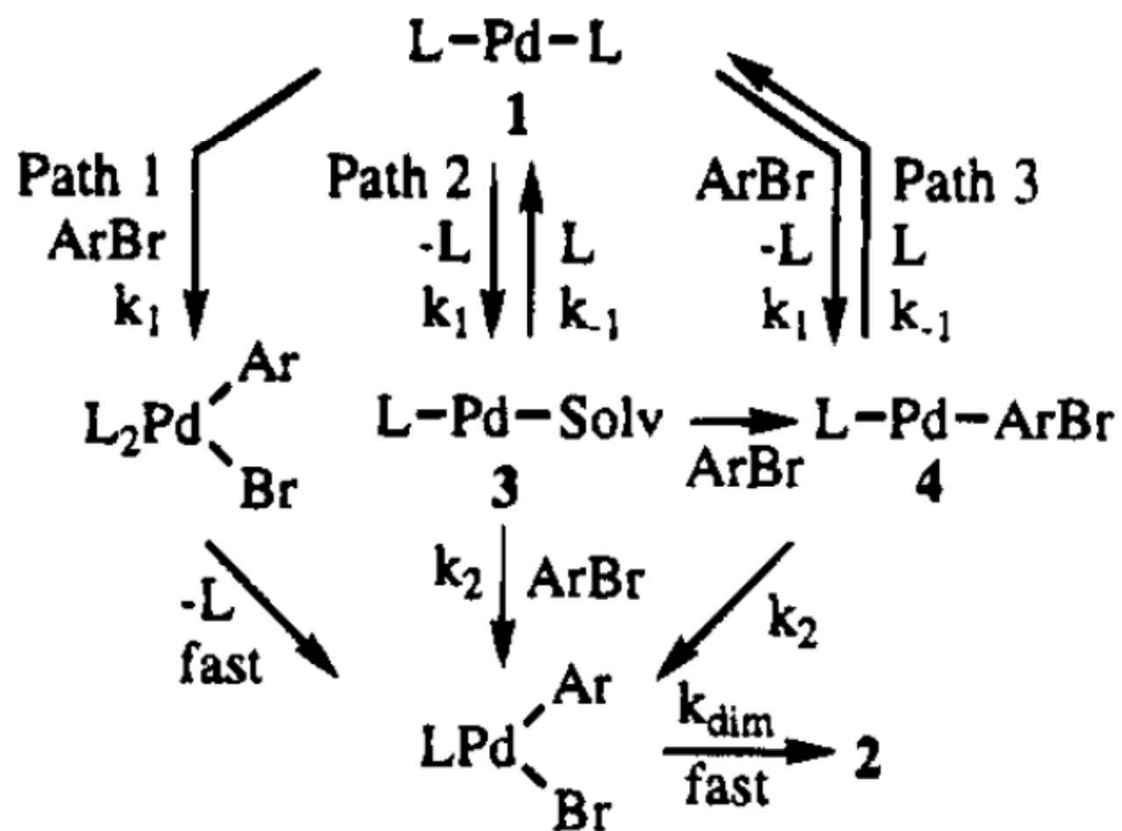
Hartwig, 1994



Tin mediated cross-couplings were rarely used due to poor substrate scope and toxicity

Proposed Catalytic Cycle



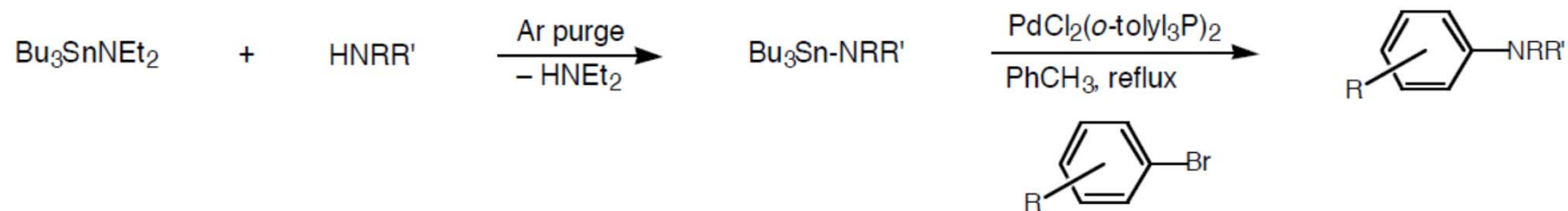


-1st order in ligand

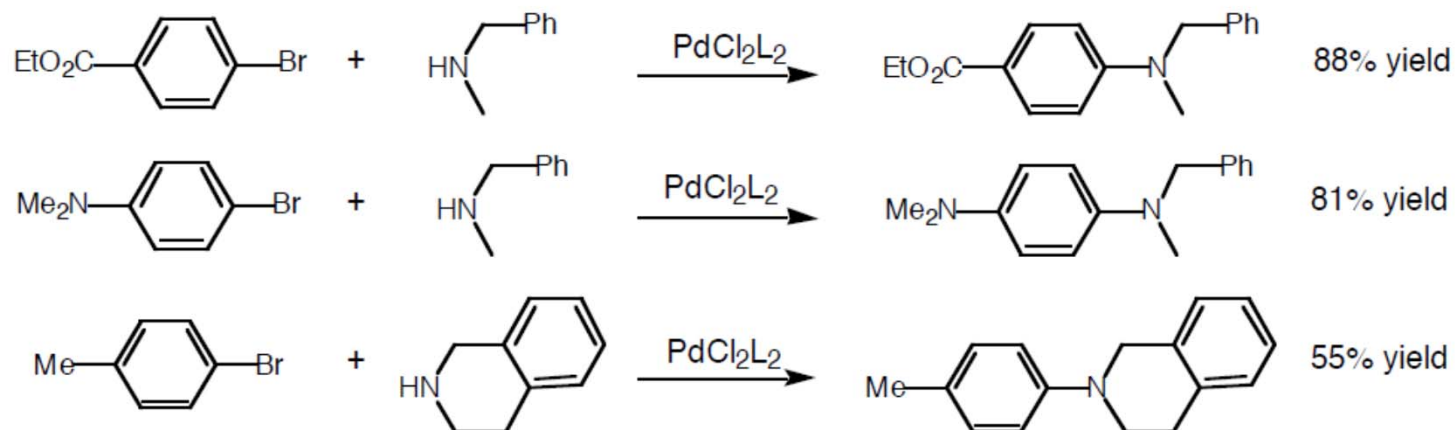
solvent	rate (x10 ⁻⁵ s ⁻¹)
PhH	9.9
THF	7.3
PhMe	8.1

Buchwald Enters the Field

- ◆ Three months after Hartwig's paper is submitted, Buchwald submits the following work, beginning an ongoing trend of independent, overlapping research
- ◆ Buchwald expands the scope of the reaction by generating tin amines *in situ*

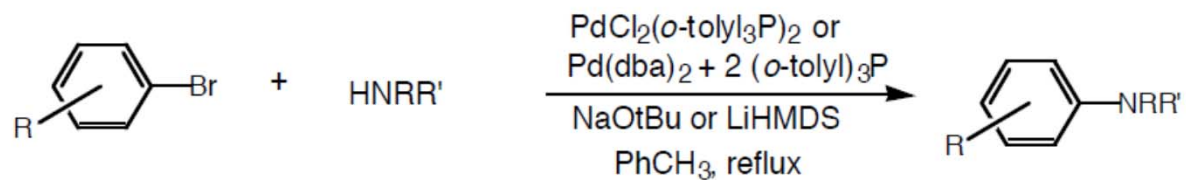


- ◆ Use of tin reagents is still required, but a large variety of amines are made available through transmetalation
- ◆ Reaction still restricted to aryl bromides
- ◆ Only secondary amines and primary anilines can be used
- ◆ *o*-substituted aryls not reported
- ◆ Catalyst loadings of less than 2% are typical, most reactions run 24 h

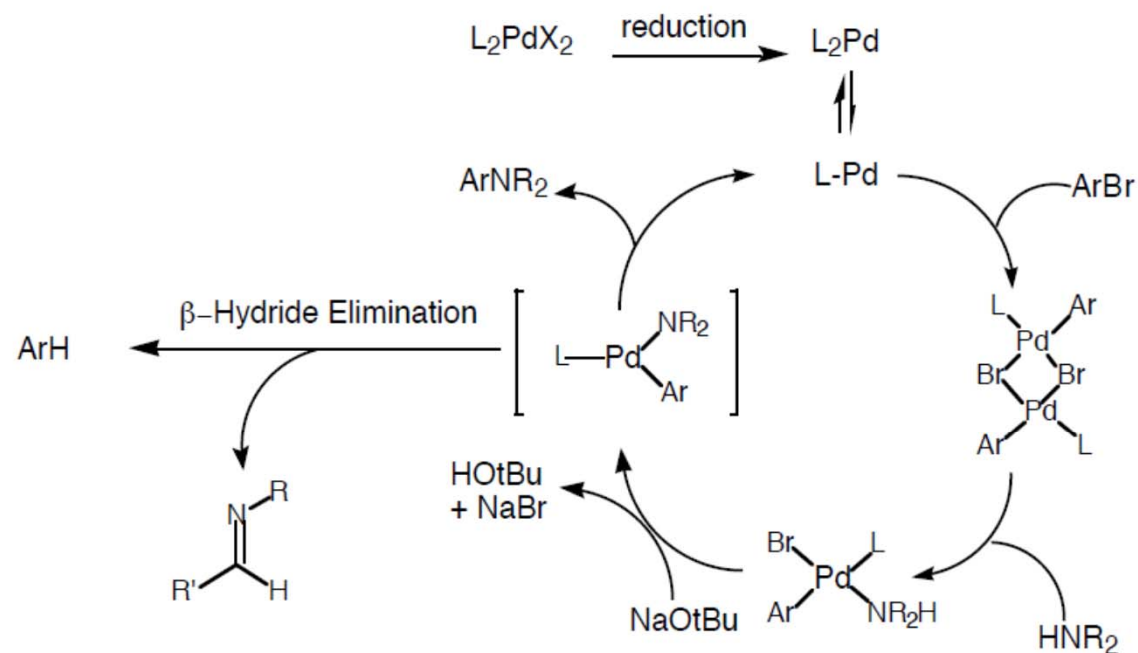


Tin-Free Catalysis

- ◆ Once again in quick succession, Buchwald and Hartwig publish methods for tin-free aryl-amine couplings

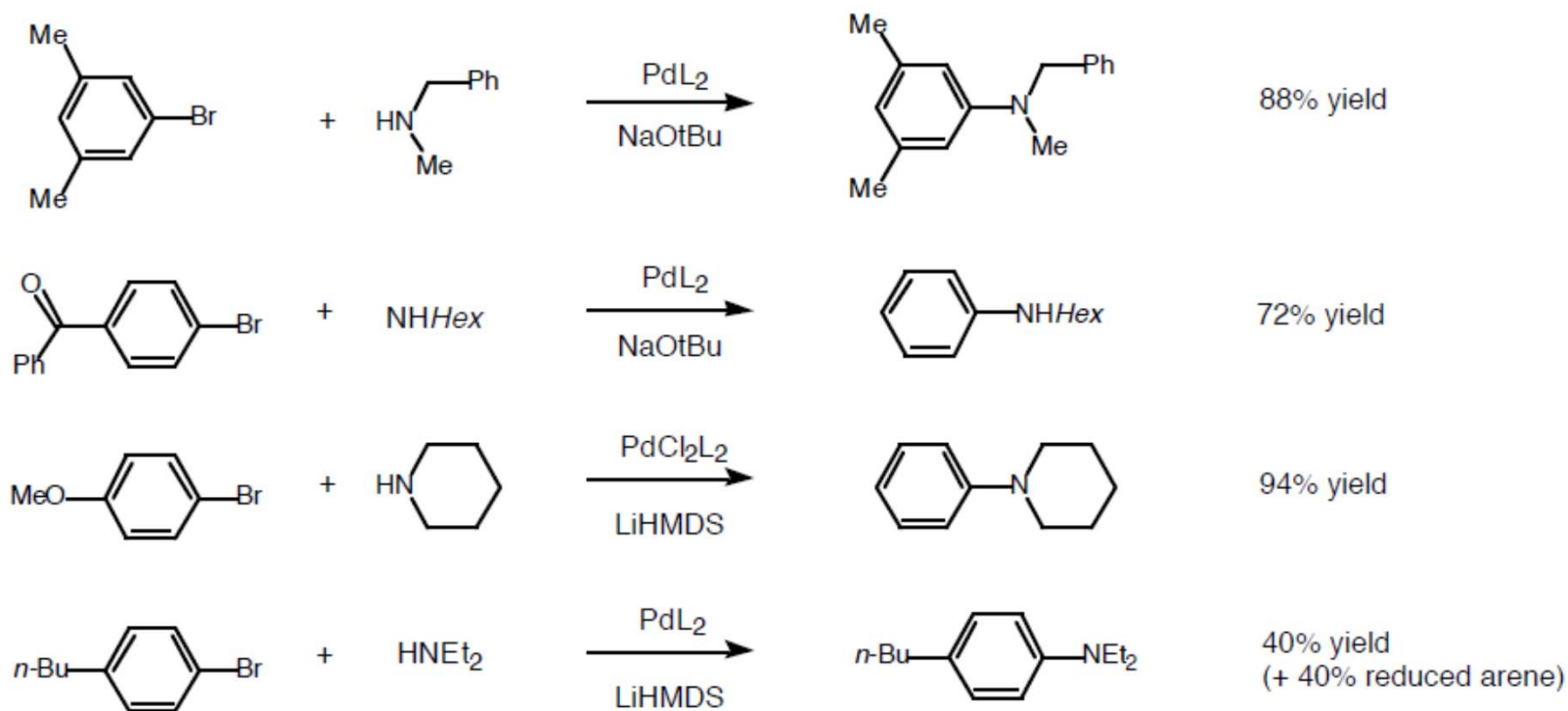


- ◆ A new catalytic cycle is proposed in which the base deprotonates Pd-amine complexes
- ◆ Pd(0) shown to be resting state of catalyst, so oxidative addition is now the rate-limiting step



Expansion of Scope

◆ The new conditions allow for greater substrate scope

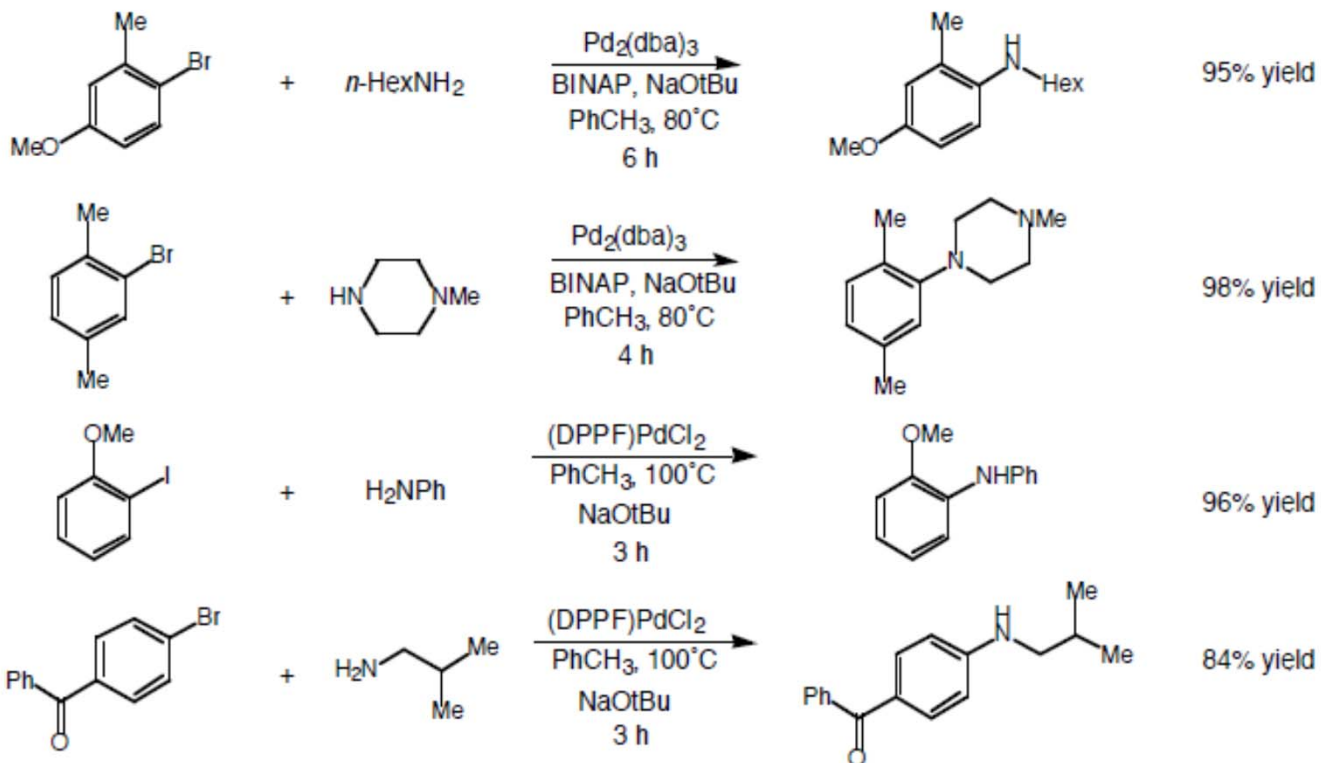


L = (o-tolyl)₃P

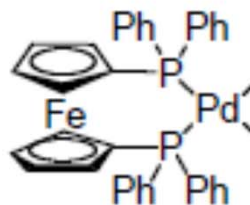
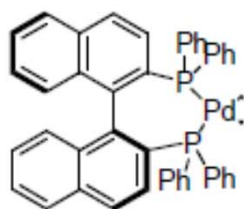
- ◆ Primary amines can be coupled with electron-withdrawing aryl halides
- ◆ Cyclic secondary amines and alkyl anilines are good substrates
- ◆ Most acyclic secondary alkyl amines are problematic with electron-rich or neutral aryl halides

Bidentate Ligands: A Dramatic Advance

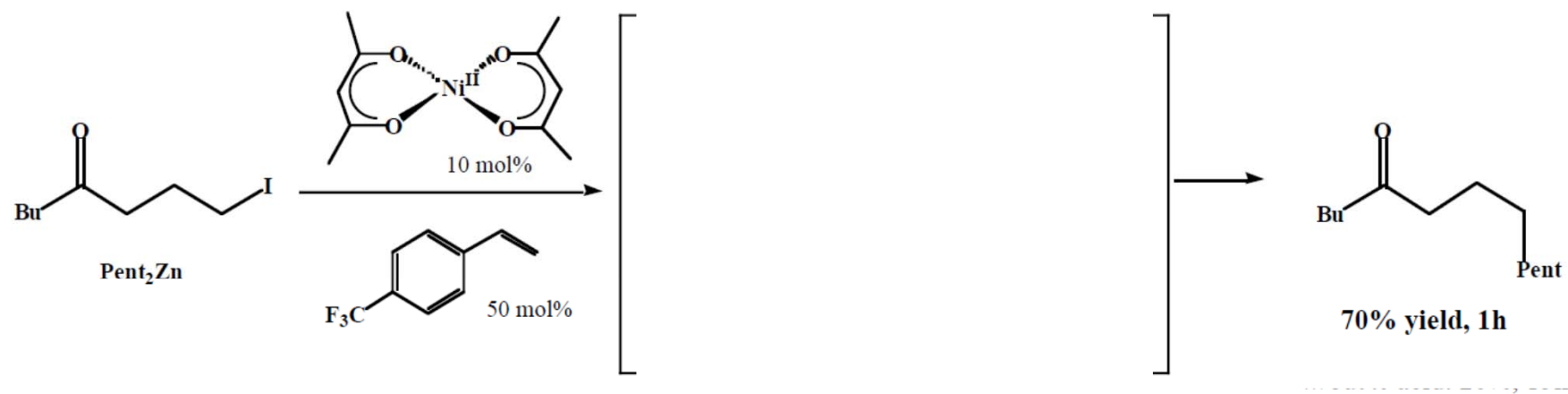
- ◆ In back-to-back communications, Buchwald and Hartwig report vast improvements in scope and yield by use of bidentate phosphine ligands
- ◆ Catalyst loadings are typically 0.5-1.0 mol%, and reactions are typically faster



Wolfe, J.; Wagaw, S.; Buchwald, S. *J. Am. Chem. Soc.*, **1996**, *118*, 7215
 Driver, M.; Hartwig, J. *J. Am. Chem. Soc.*, **1996**, *118*, 7217

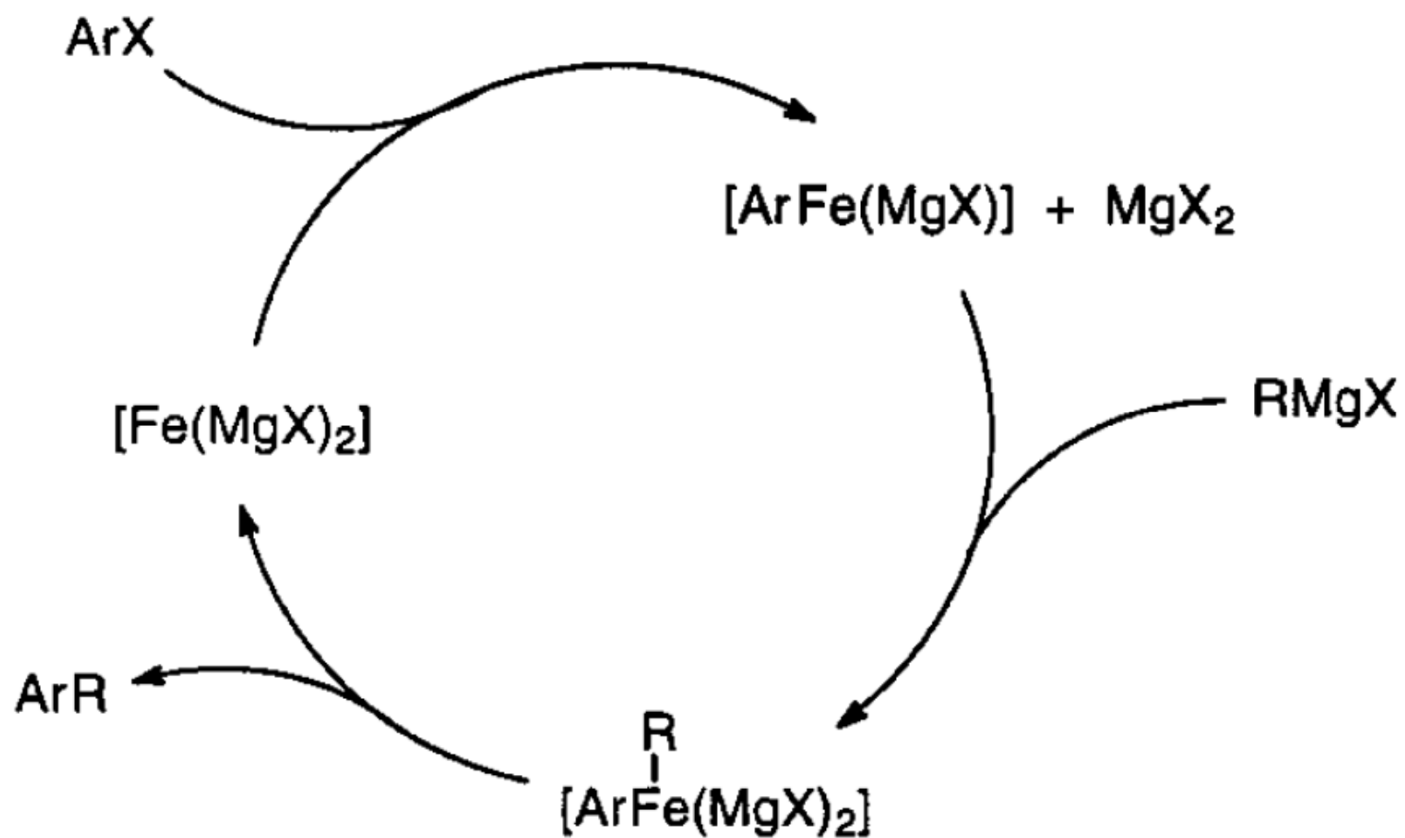


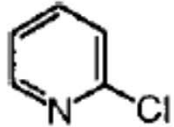
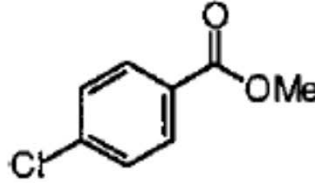


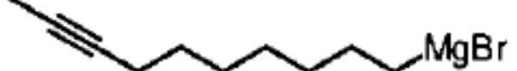
Alkyl-Alkyl coupling



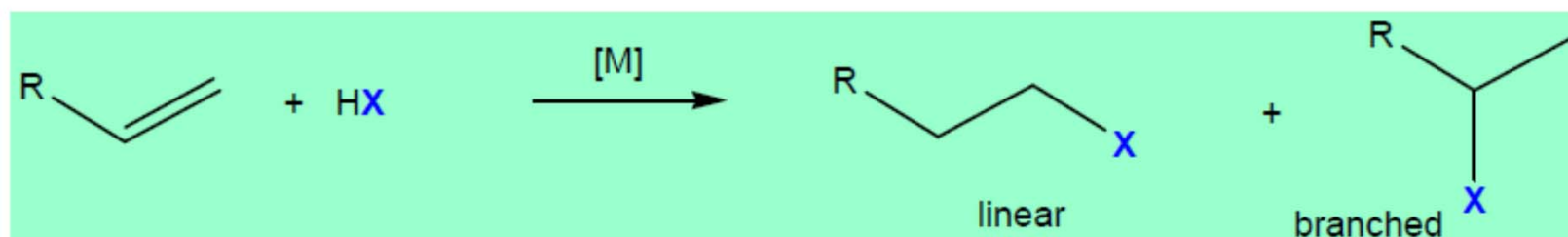
Knochel *ACIEE* 1998 (37) 2387.

Iron-mediated Cross Coupling

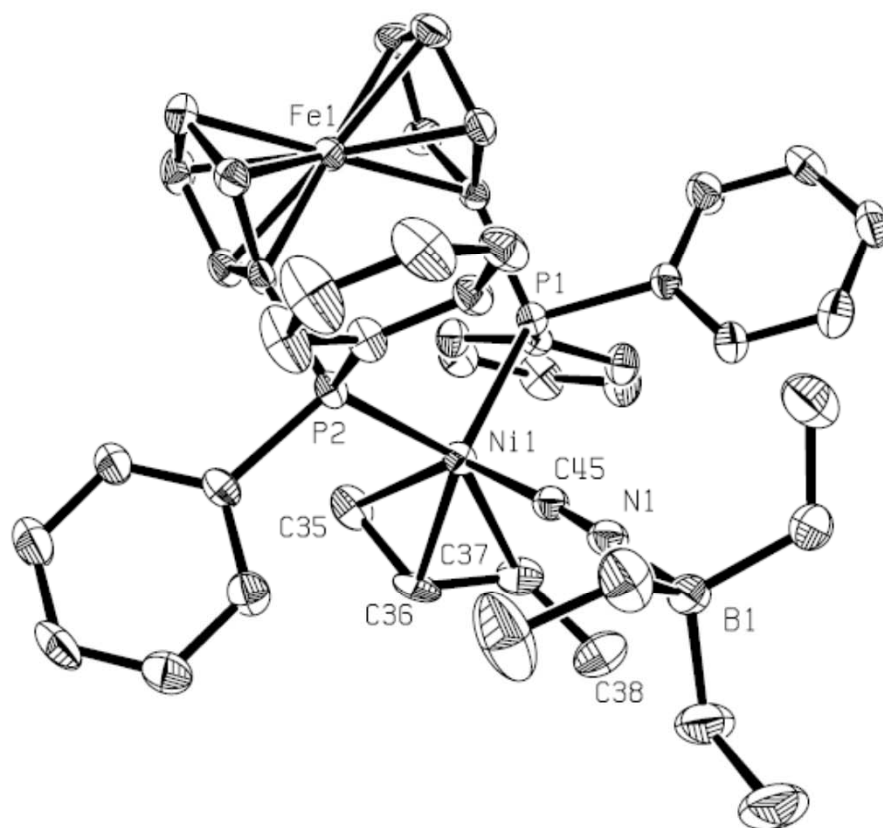
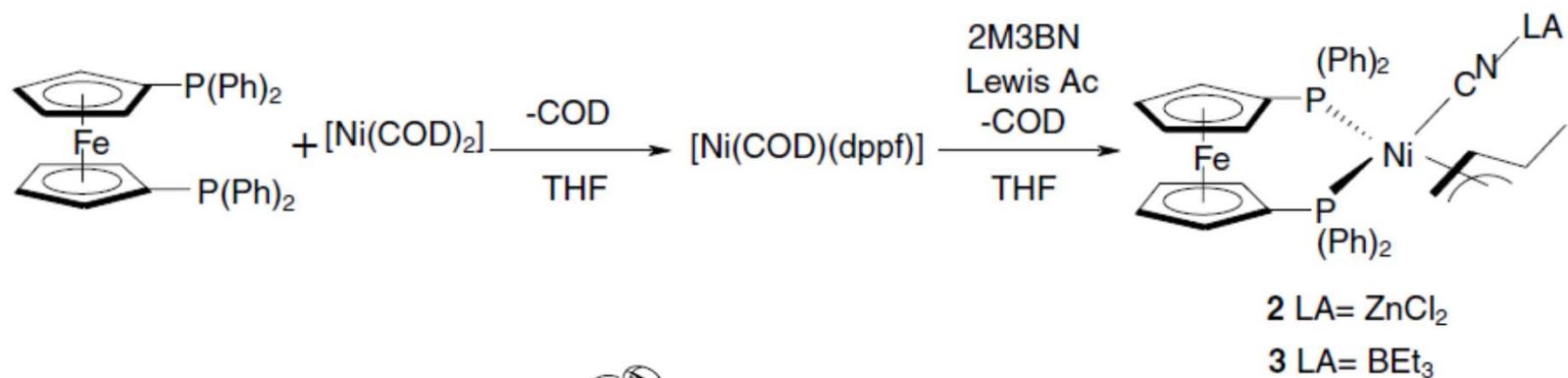


Entry	ArCl	RM	Fe salt [5 %]	ArR [%] ^[b]
1		<i>n</i> -C ₆ H ₁₃ MgBr	[Fe(acac) ₂]	90
2		<i>n</i> -C ₆ H ₁₃ MgBr	[Fe(acac) ₃]	91
3		<i>n</i> -C ₆ H ₁₃ MgBr	FeCl ₃	88
4		<i>n</i> -C ₆ H ₁₃ MgBr	[Fe(salen)Cl]	96
5		C ₂ H ₅ MgBr	[Fe(acac) ₃]	> 95
6		<i>n</i> -C ₆ H ₁₃ MgBr	[Fe(acac) ₃]	> 95
7		<i>n</i> -C ₆ H ₁₃ MgBr	FeCl ₂	> 95
8		<i>n</i> -C ₁₄ H ₂₉ MgBr	[Fe(acac) ₃]	> 95
9		<i>i</i> -C ₃ H ₇ MgBr	[Fe(salen)Cl]	59
10			[Fe(acac) ₃]	91 ^[c]
11			[Fe(acac) ₃]	88 ^[c]
12			[Fe(acac) ₃]	85 ^[c]
13		H ₂ C=CHMgBr	[Fe(acac) ₃]	0
14		H ₂ C=CHCH ₂ MgBr	[Fe(acac) ₃]	0
15		C ₆ H ₅ MgBr	[Fe(acac) ₃]	28
16		Et ₃ ZnMgBr	[Fe(acac) ₃]	93
17		<i>n</i> -C ₄ H ₉ Li	[Fe(acac) ₃]	0

Hydrofunctionalization of Olefins



X = CN, hydrocyanation
 SiR(R')(R''), hydrosilylation
 BR₂, hydroboration (mostly, dialkoxy-/diaryloxiboranes)
 N(R)R', hydroamination



Hydrosilylierung

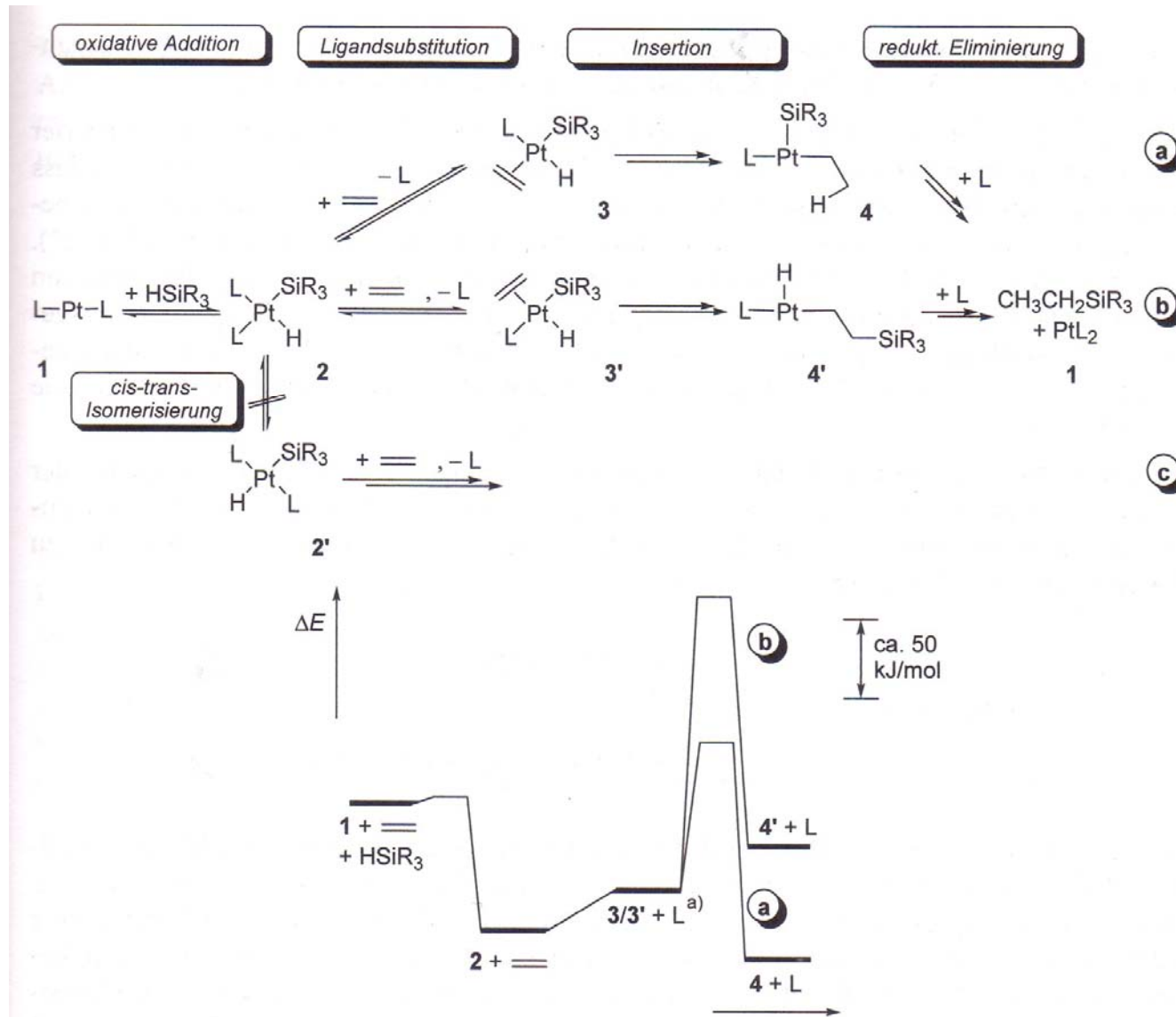
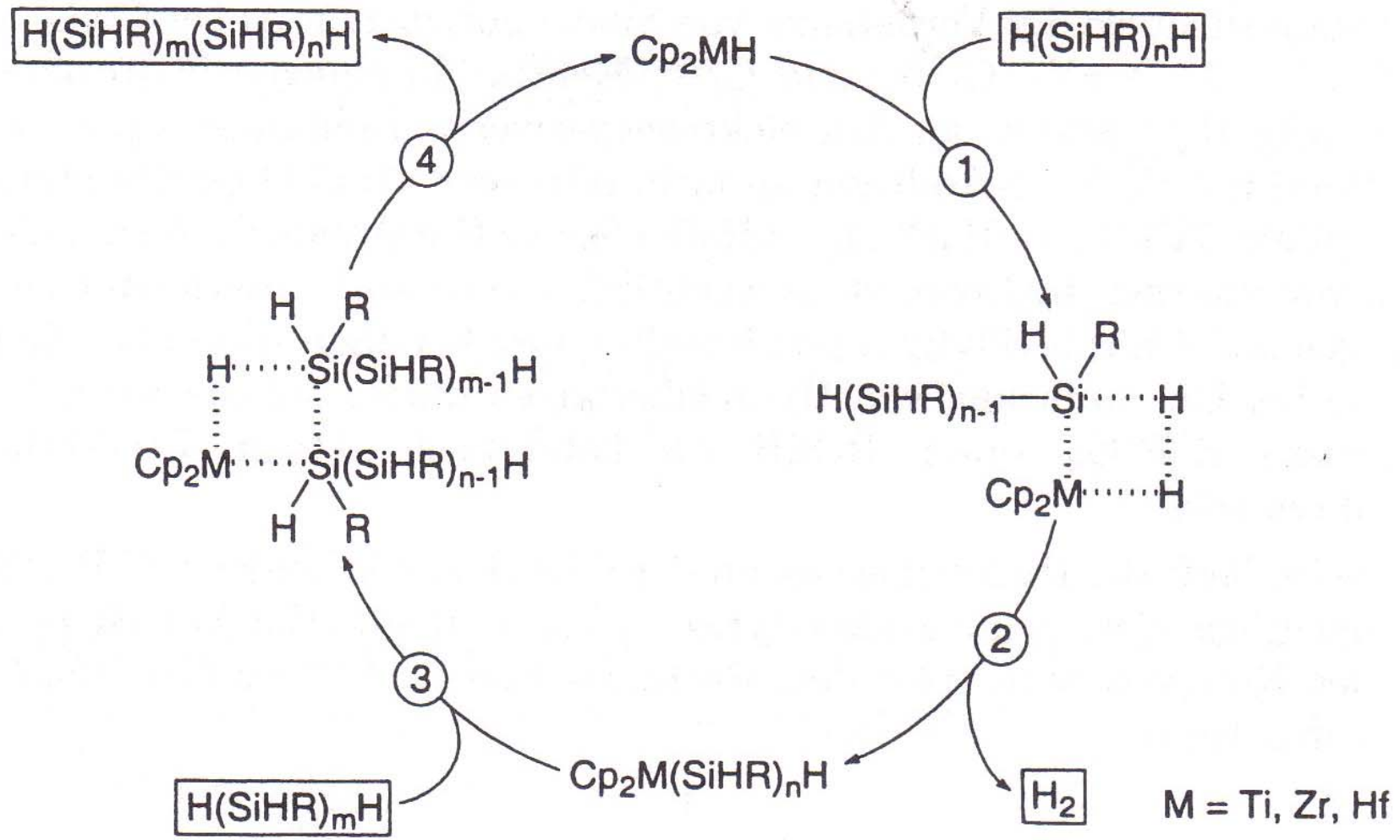


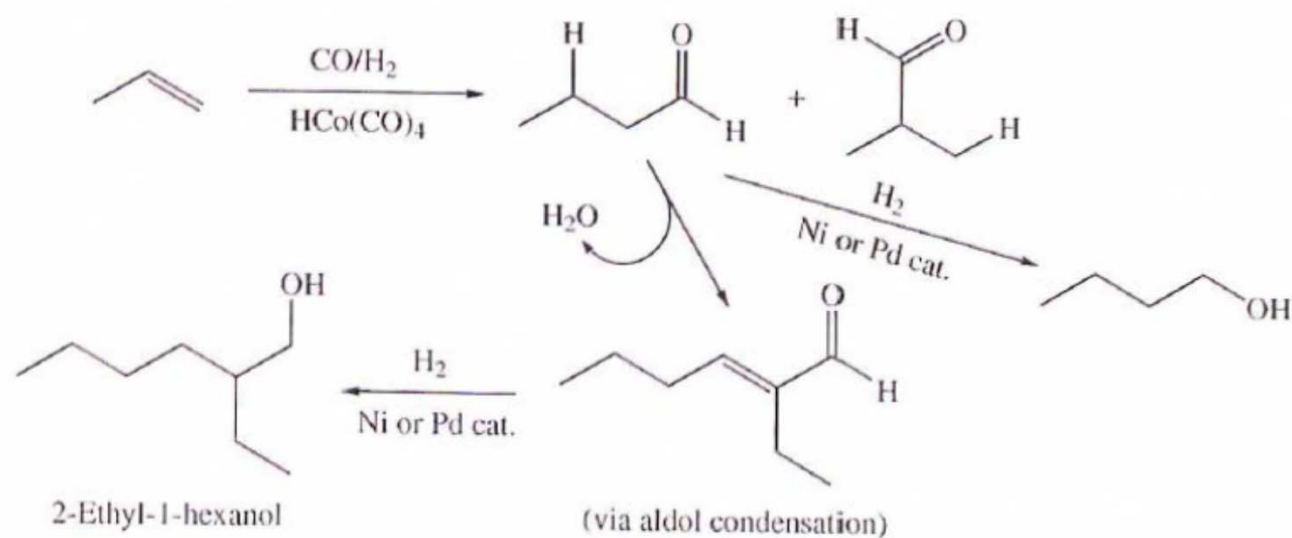
Abbildung 12.5. Zum Mechanismus der Addition von HSiR_3 ($\text{R} = \text{H}, \text{Me}, \text{Cl}$) an Ethen katalysiert durch PtL_2 ($\text{L} = \text{PH}_3$). Die angegebenen Energien beziehen sich auf $\text{R} = \text{H}$; entsprechendes gilt für $\text{R} = \text{Me}, \text{Cl}$ (adaptiert und gekürzt nach Sakaki 1999). a) Der Energieunterschied von **3** und **3'** ist marginal.



Dehydrosilylkupplung

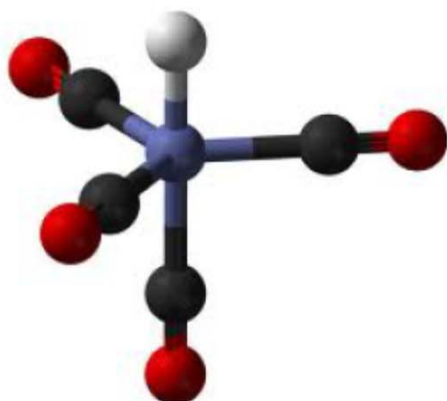
- **What is hydroformylation?**

- produces aldehyde from alkene via
- addition of a CO and H₂ to a alkene

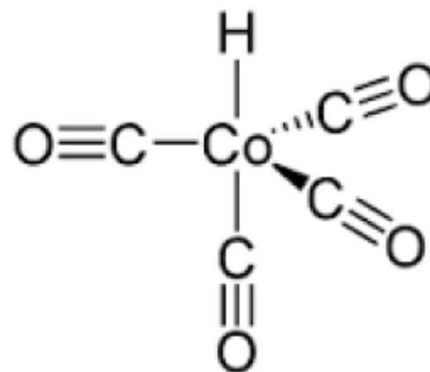


"Organometallic Chemistry", Spessard and Miessler

Cobalt Catalyst: $\text{HCo}(\text{CO})_4$



$\text{HCo}(\text{CO})_4$

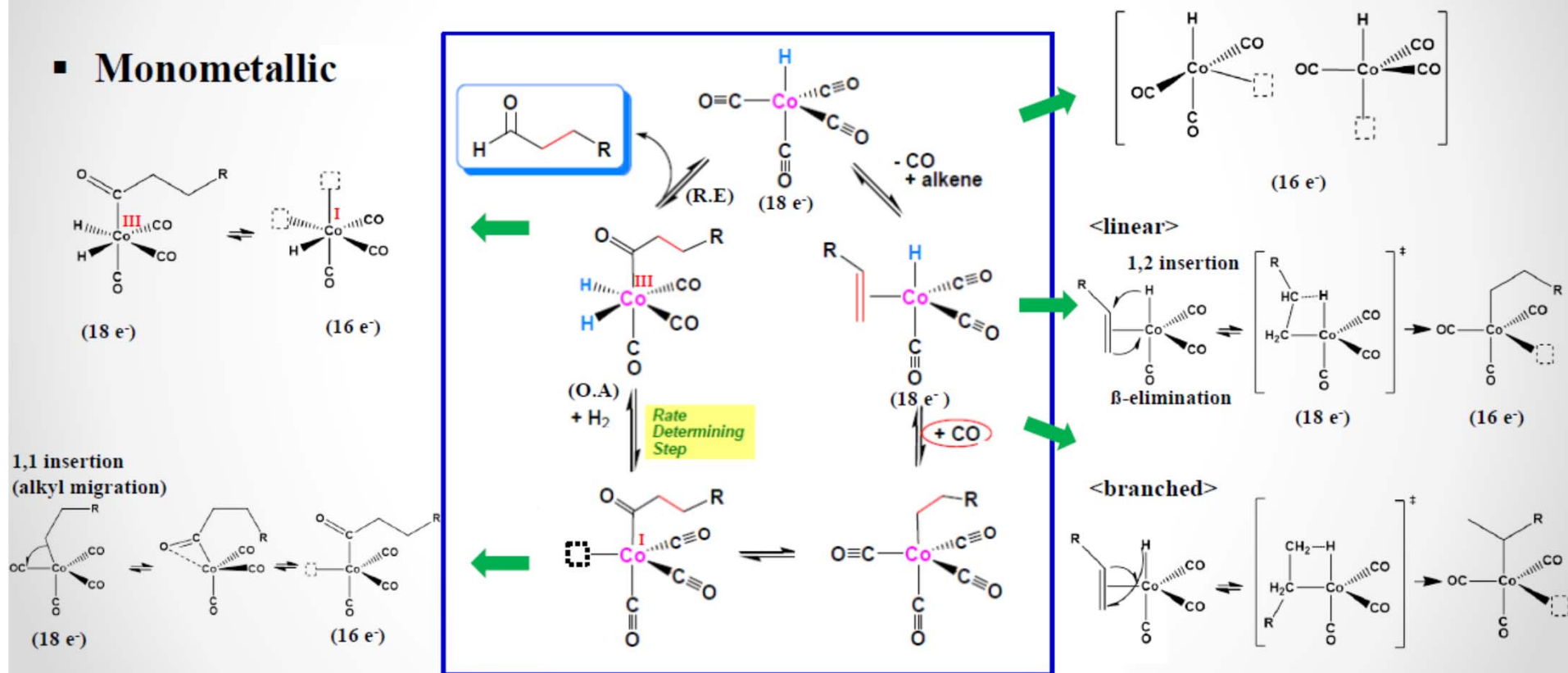


- oldest homogeneous catalysis process still in use
- total H_2/CO (ratio= 1:1) pressures of 200- 300 bar and 110- 180 °C
- ratio of linear to branched aldehyde: ca. 4 to 1
- decomposed to metallic Co at high temperature and low CO pressure

● *Otto Roelen at Ruhrchemie in Germany in 1938*

Hydroformylation Mechanism

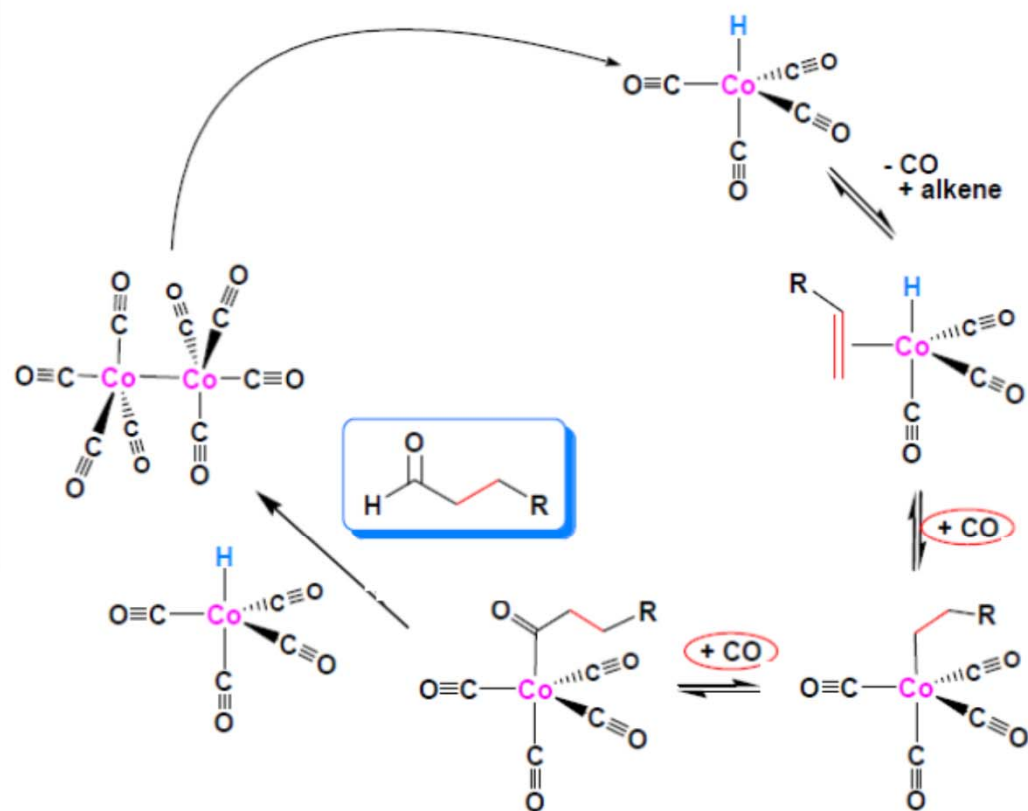
Monometallic



R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, 1961, 83, 4023 ● 8

Hydroformylation Mechanism

- Bimetallic



R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, 1961, 83, 4023

Cobalt Catalyst

- **Kinetics**

$$\frac{d(\text{aldehyde})}{dt} = k[\text{alkene}][\text{Co}][\text{H}_2][\text{CO}]^{-1}$$

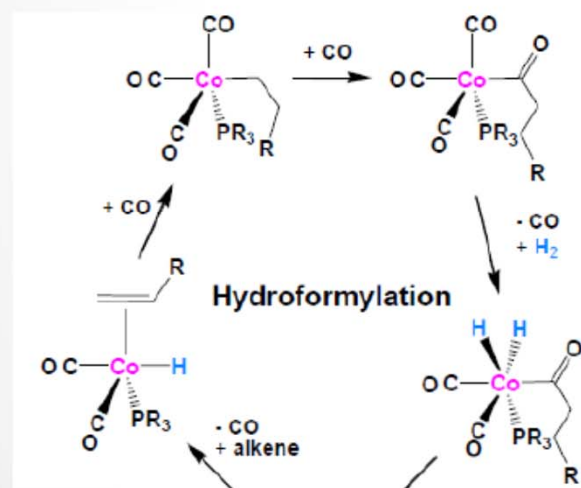
- inversely proportional to CO concentration because CO dissociation from the coordinatively saturated 18e⁻ species is required
- using a 1:1 ratio of H₂/CO, the reaction rate is independent of pressure
- HCo(CO)₄ is only stable under certain minimum CO partial pressures at a given temperature
-
- CO pressure ↑ → reaction rate ↓ & high ratio of linear to branched product
- CO pressure ↓ → reaction rate ↑ & branched alkyl ↑ (reverse β-elimination)

Cobalt Phosphine-Modified Catalyst

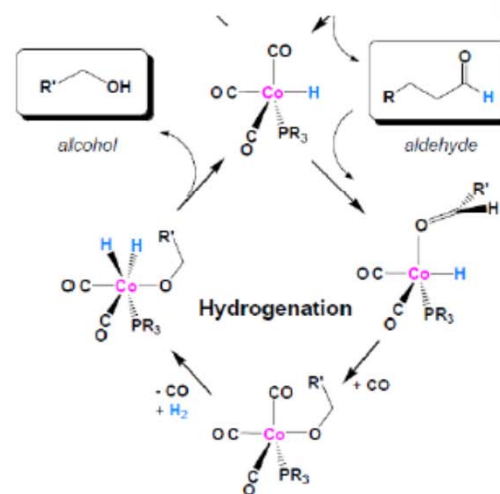
- The addition of PR_3 ligands cause a dramatic change in rate and regioselectivity due to electronic and steric effect of substitution of PR_3

➤ Electronic effect of PR_3 :

- stronger Co-CO bond (do not decompose) → less CO pressure
- stronger Co-CO bond → less active than $\text{HCo}(\text{CO})_4$ → 5- 10 times slower
- hydridic characteristic of hydride → increase the hydrogenation capability



at 100- 180 °C
and 50- 100 bar
5- 10 slower



Two stage of
hydroformylation
and hydrogenation
combined into one
step

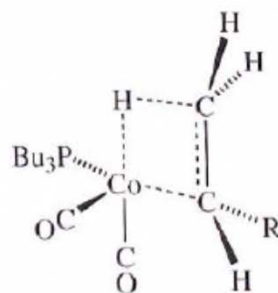
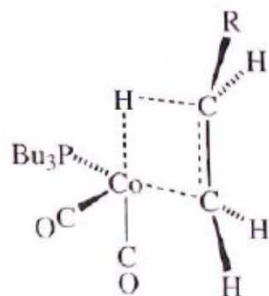
L. H. Slaugh and R. D. Mullineaux, *J. Organometal. Chem.*, 1968, 13, 469.

Cobalt Phosphine-Modified Catalyst

- The addition of PR_3 ligands causes a dramatic change in rate and regioselectivity due to electronic and steric effect of substitution of PR_3

➤ **Steric effect of PR_3 :**

- Bulky PR_3 group influences the insertion direction of alkene to Co complex and geometry of intermediate (favors Anti-Markovnikov; Hydrogen transferred to carbon with bulkier R group)



Linear: Branched = 9: 1

L. H. Slaugh and R. D. Mullineaux, *J. Organometal. Chem.*, 1968, 13, 469.

Cobalt Phosphine-Modified Catalyst

- Relationship between steric effect and regio-selectivity

Table 1. Hydroformylation of 1-hexene using $\text{Co}_2(\text{CO})_8/2\text{P}$ as catalyst precursor. 160°C , 70 atm, 1.2:1 H_2/CO

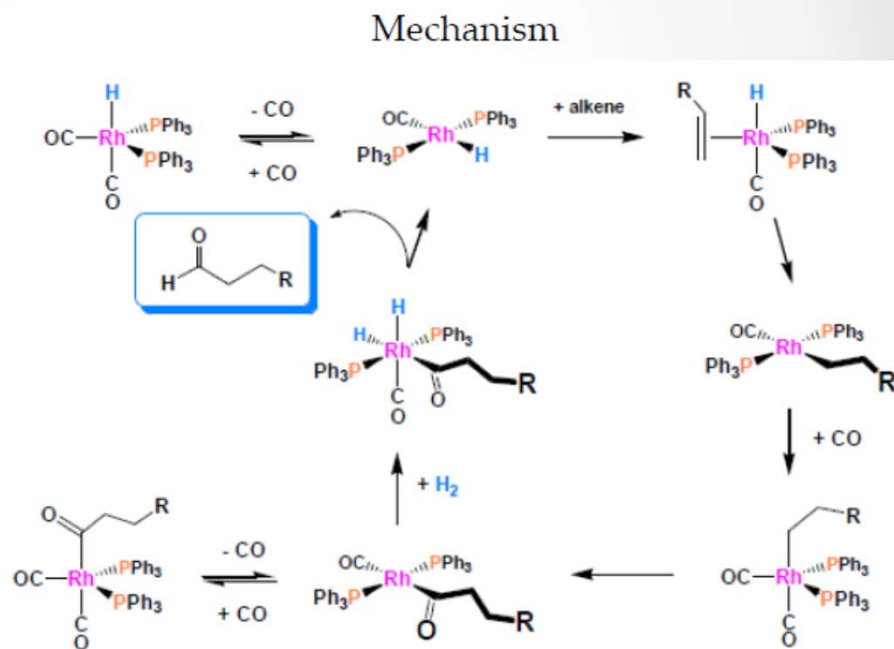
PR_3	pK_a	Tolman ν (cm^{-1})	Cone Angle $^\circ$	$k_r \times 10^3$ (min^{-1})	% Linear Prod	Aldehyde to alcohol
$\text{P}(i\text{-Pr})_3$	9.4	2059.2	160	2.8	85.0	--
PEt_3	8.7	2061.7	132	2.7	89.6	0.9
PPr_3	8.6	2060.9	132	3.1	89.5	1.0
PBu_3	8.4	2060.3	136	3.3	89.6	1.1
PEt_2Ph	6.3	2063.7	136	5.5	84.6	2.2
PEtPh_2	4.9	2066.7	140	8.8	71.7	4.3
PPh_3	2.7	2068.9	145	14.1	62.4	11.7

➔ Steric and electronic effect of substitution of PR_3 affects the linear to branched ratio

Rhodium Catalyst

- *Advantage of Rh catalyst over Co catalyst:*

- Rh complex 100-1000 more active than Co complex
- at ambient condition (15-25 bar, 80-120 °C)
- energy saving process
- linear to branched ratios as high as 15 to 1



Rhodium Catalyst

- Selective catalyst with the substitution of PR_3 ligands
- Rate determining steps are not fully understood

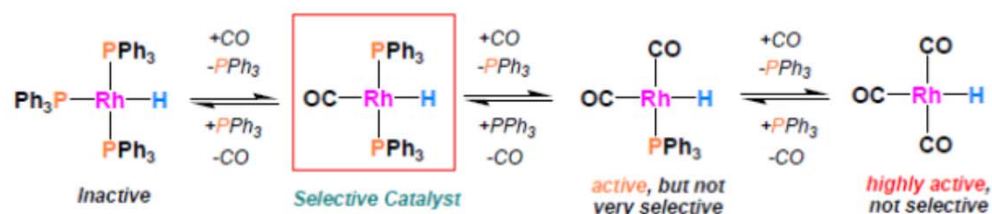
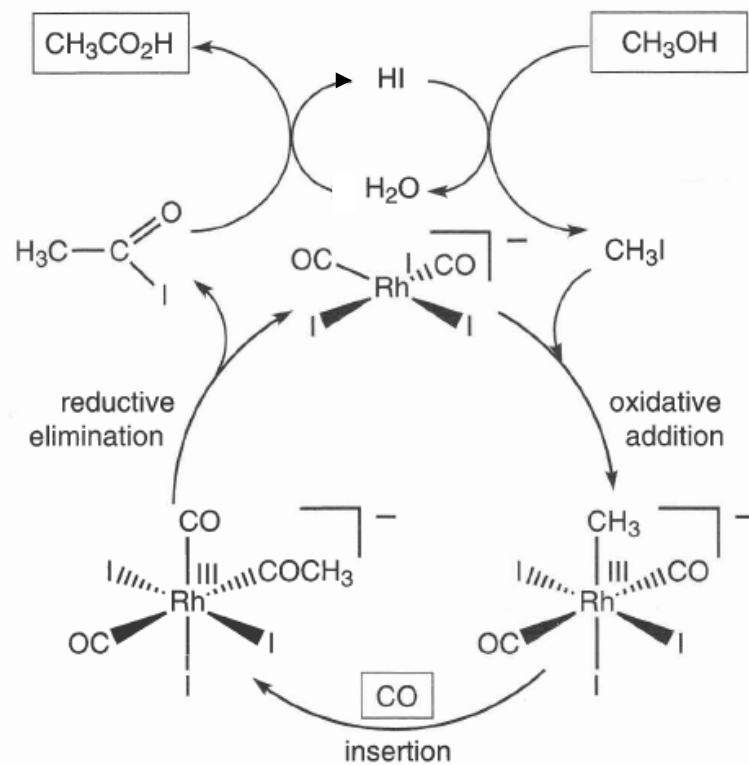


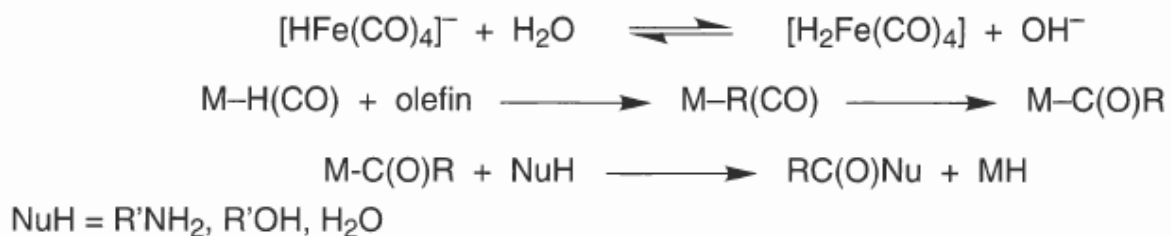
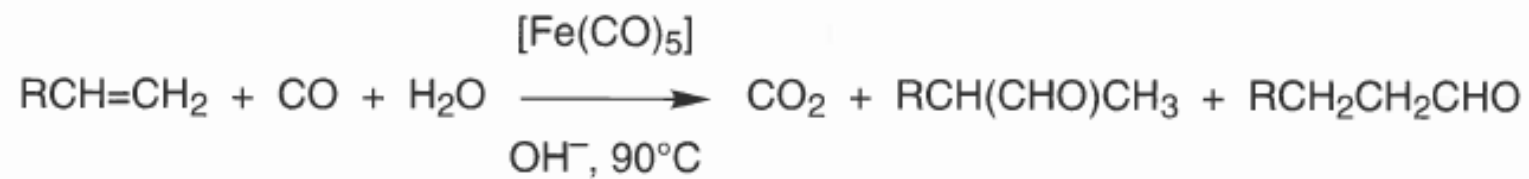
Table 2. Rate constants and Regioselectivities for the Hydroformylation of 1-Hexene using $\text{Rh}(\text{acac})(\text{CO})_2$ with Different PPh_3 Concentrations. Reaction Conditions: 90 psig (6.2 bar), 1:1 H_2/CO , 90° C.

[Rh] (mM)	[PPh ₃] (M)	PPh ₃ /Rh ratio	k_{obs} (min ⁻¹ mM Rh ⁻¹)	l:b ratio
0.5	0.41	820	0.032	11
1	0.82	820	0.016	17



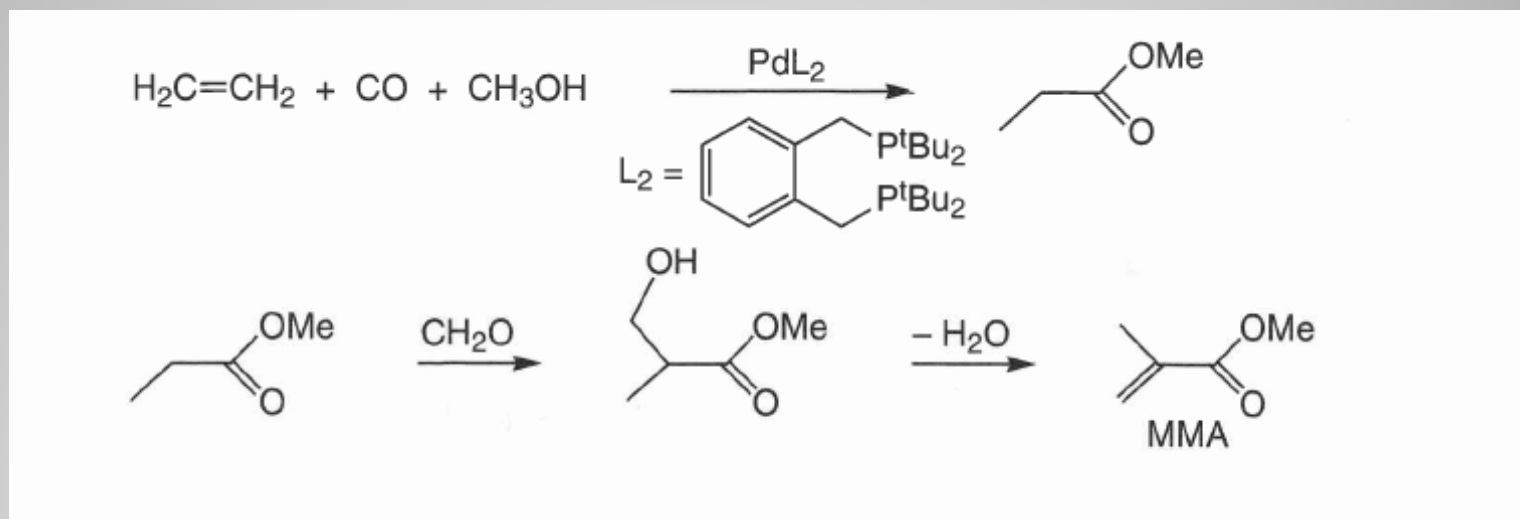
Mechanism of methanol carbonylation involving double catalysis: Rh^{I} and HI

MONSANTO PROCESS



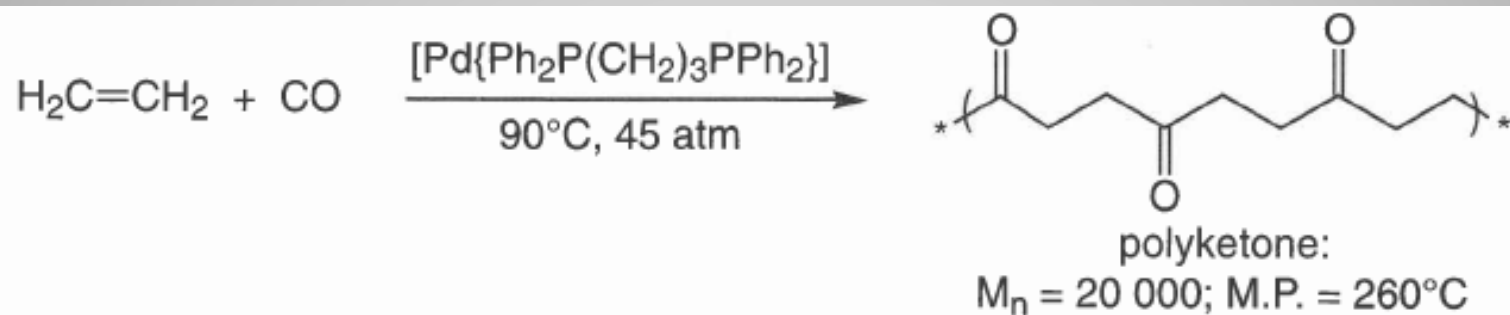
CARBONYLATION OF ALKENES/ALKYNES : REPPE RXN

Production of methyl methacrylate (MMA) – an intermediate for the polymer synthesis of plexiglass.



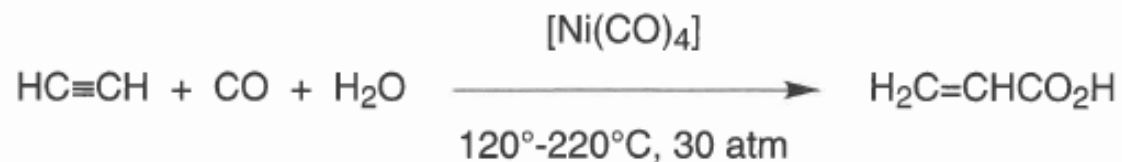
CARBONYLATION ALKENES AND ALKYNES

Synthesis of polyketones: In the absence of methanol

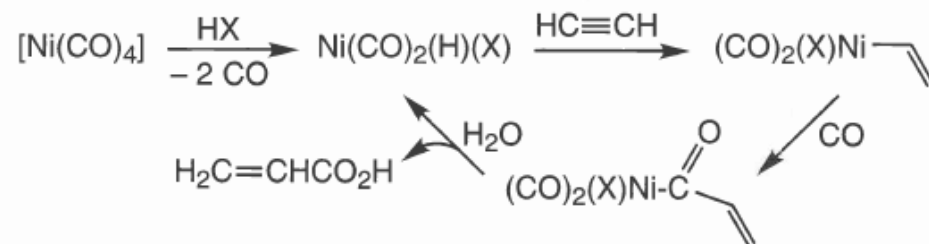


CARBONYLATION OF ALKENES AND ALKYNES

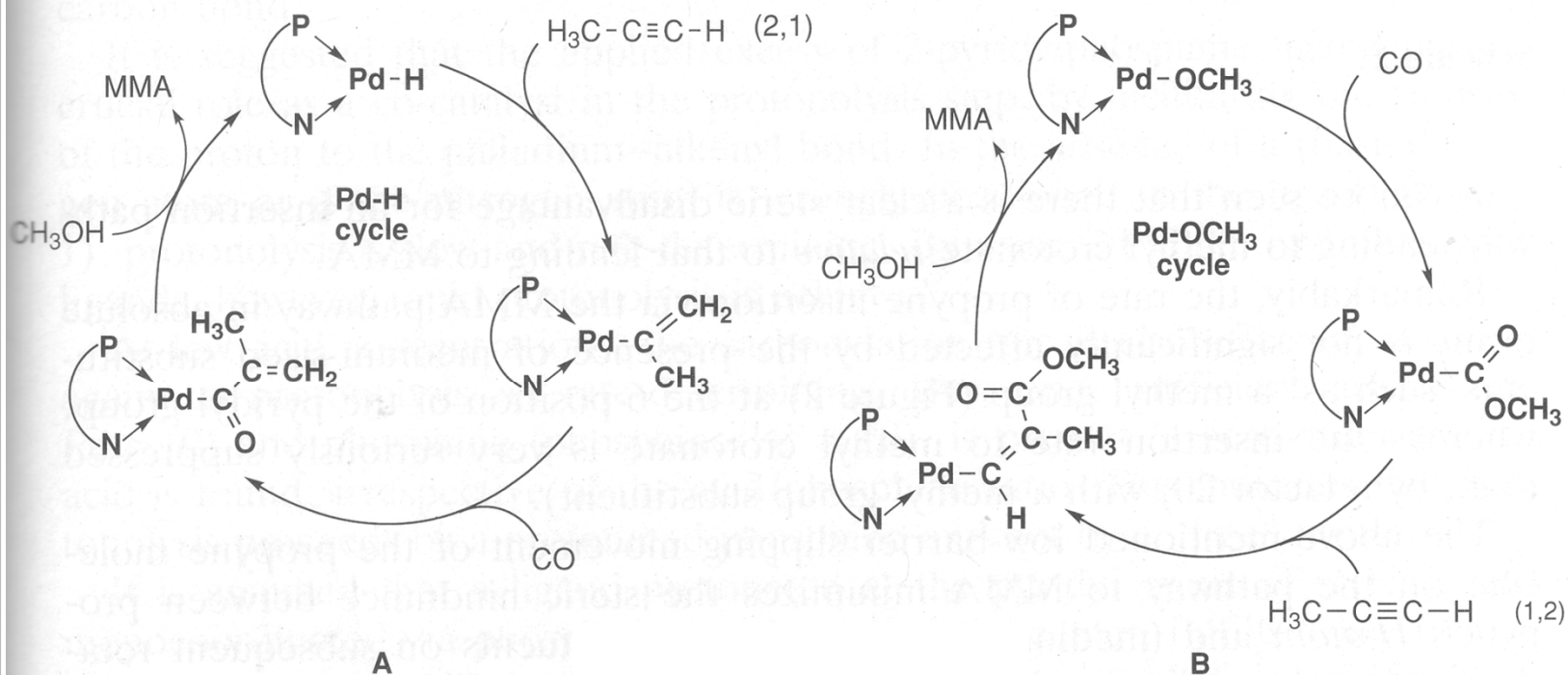
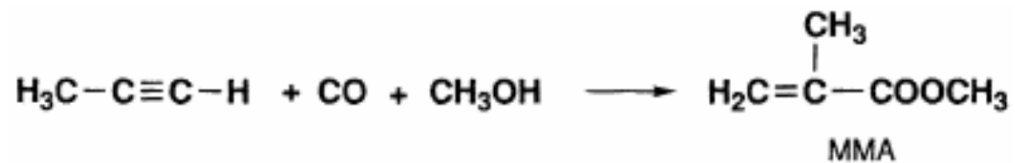
Industrial application of the Reppe reaction using alkynes: Acrylic acid synthesis.



Mechanism:



CARBONYLATION OF ALKENES AND ALKYNES



Scheme 1. The two possible cycles for the formation of methyl methacrylate.

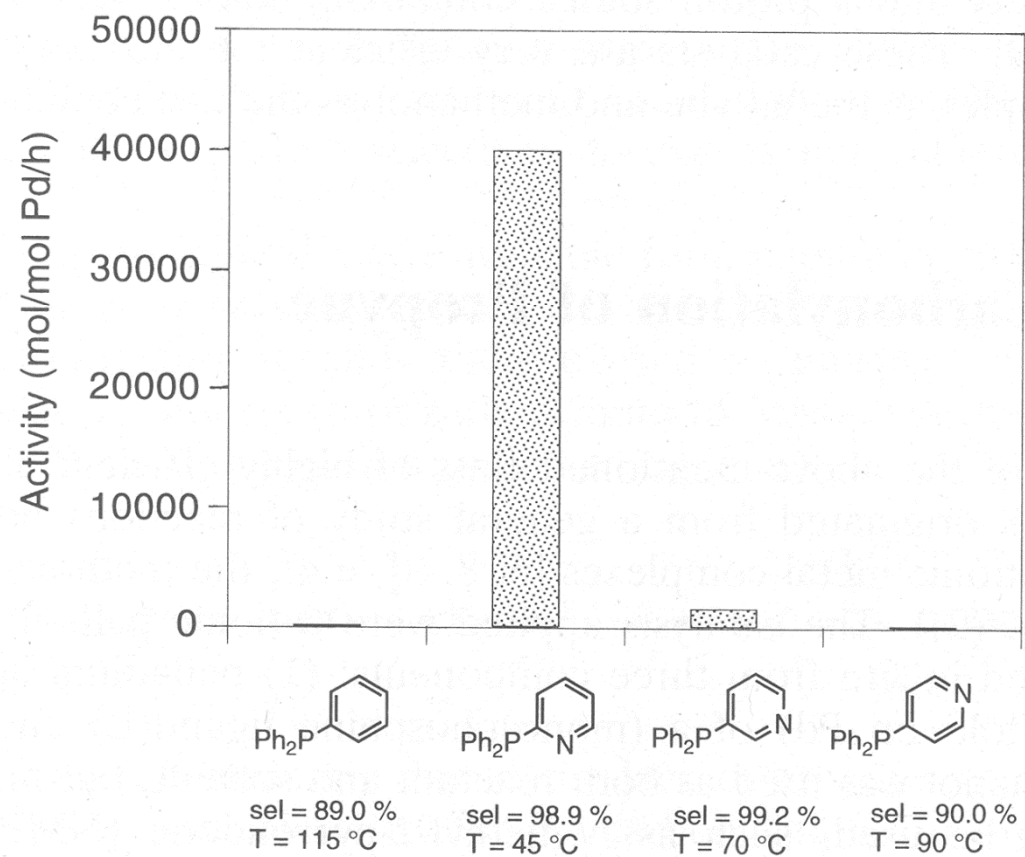
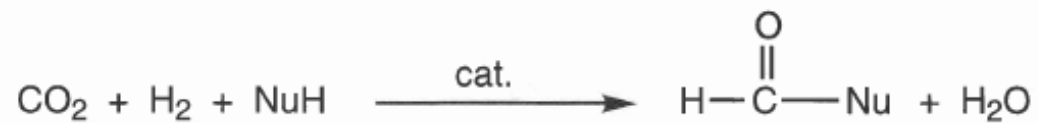
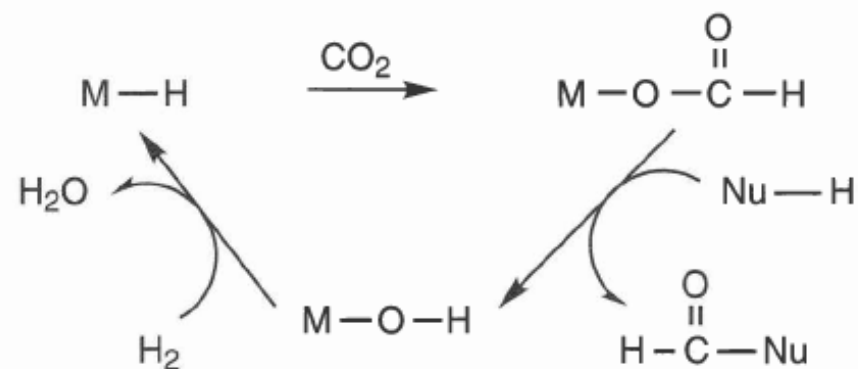


Figure 1. Effect of ligand structure. sel = selectivity.



Nu = RO : 160°C, 100-200 bar, cat. : [Ni(dppe)₂]

Nu = NMe₂ : 100-125°C, 60-120 bar, cat. : [Co(dppe)₂H]



Proposed mechanism for the catalytic carboxylation of alcohols and dialkylamines

CARBOXYLATION

