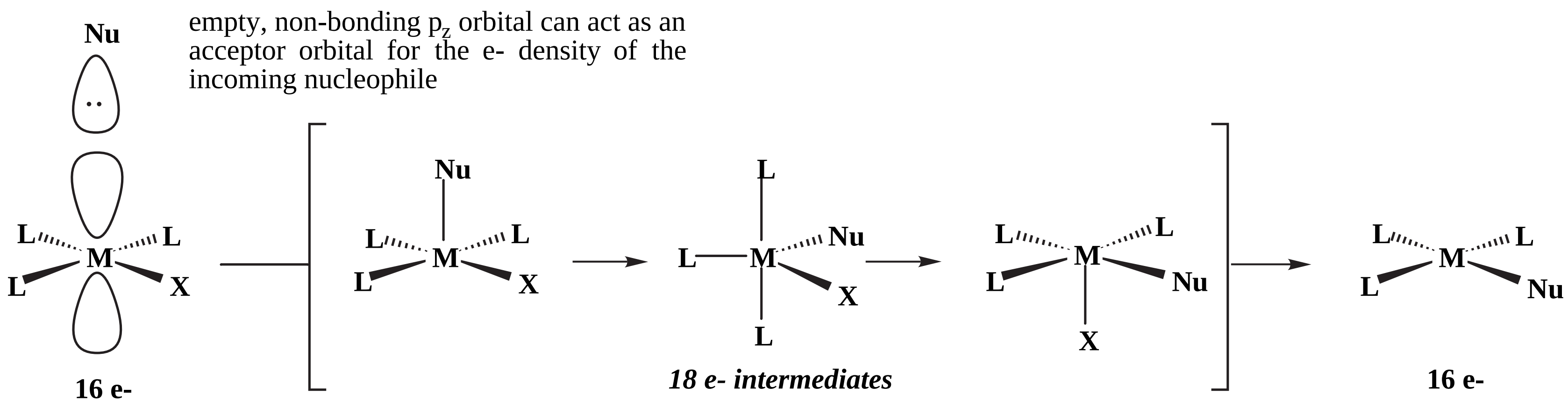
Ligand Exchange Mechanisms

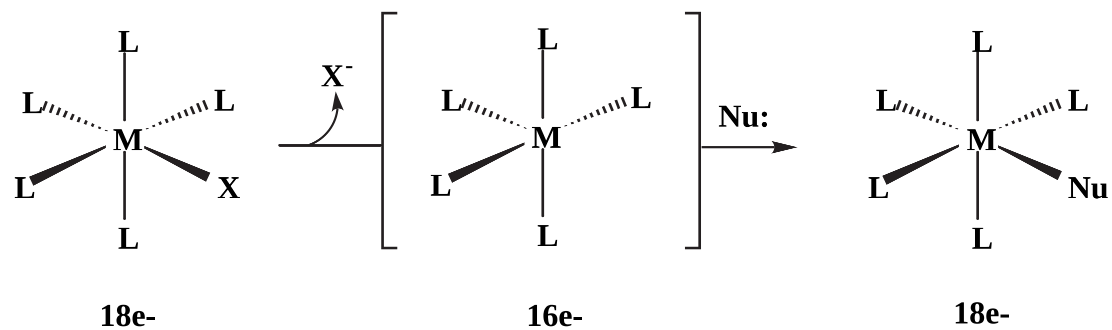
Associative ligand substition: is often called square planar substition because16 e-, d8 square planar complexes generally undergo ligand substitution *via* an associative mechanism (the M-Nu bond is formed before the M-X bond breaks). The intermediate is 18e- and therefore provides a lower energy route to the product than a 14e- intermediate formed *via* dissociative substitution (the M-X bond is fully broken before the M-Nu bond begins to form). Analogous in many ways to S_N2 reactions.



M = Ni(II), Pd(II), Pt(II), Rh(I), Ir(I).

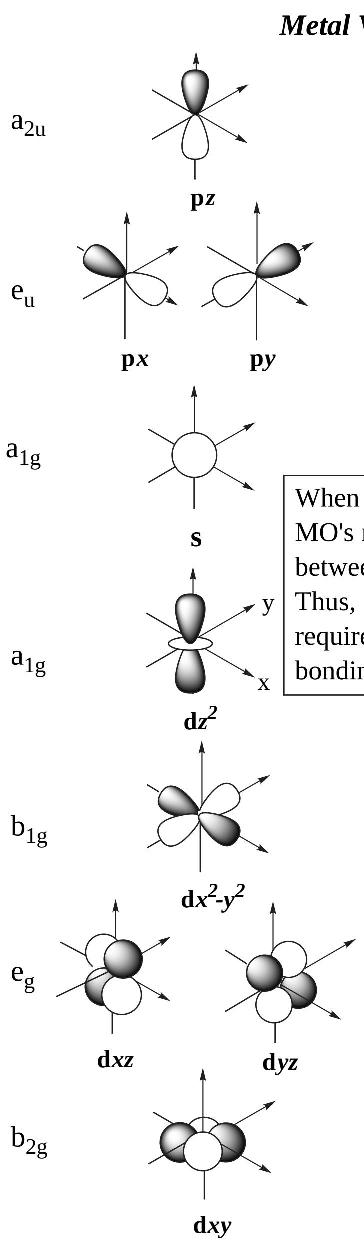
Dissociative ligand substitution is most favored in coordinatively saturated 18e$^-$ complexes (*e.g.* d^{10} tetrahedral, d^6 octahedral). In the dissociative mechanism, the M-X bond is fully broken before the M-Nu bond forms thereby avoiding an energetically unfavorable 20e$^-$ intermediate. Analogous in many ways to S_N1 reactions.

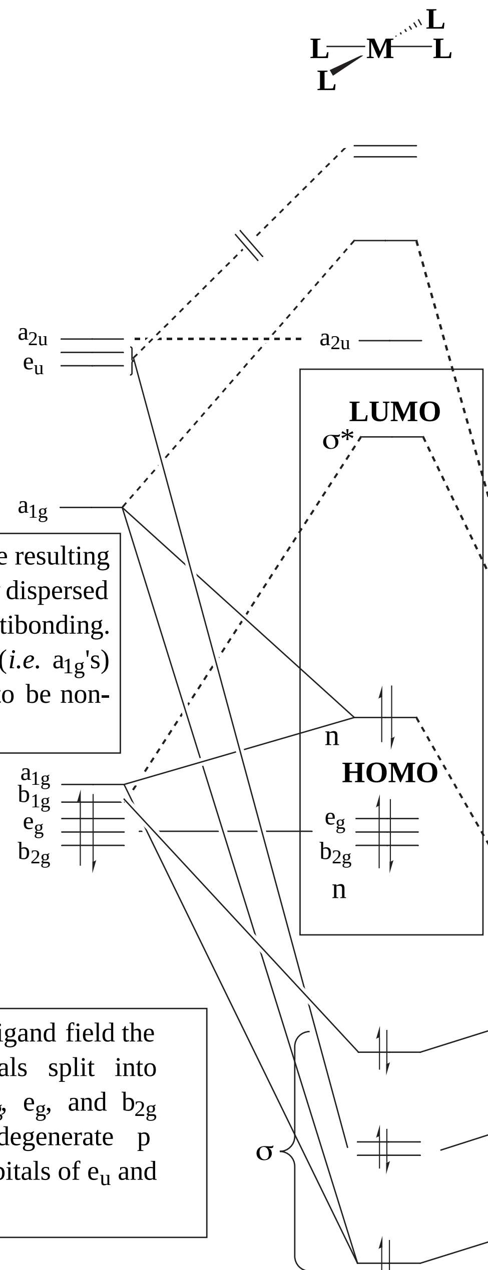
Note that in all ligand substition processes, there is no oxidation state change at the metal center.



M = Ru(II), Co(III), Rh(III), Ir(III)

MO Description of σ bonding in ML_4 square planar

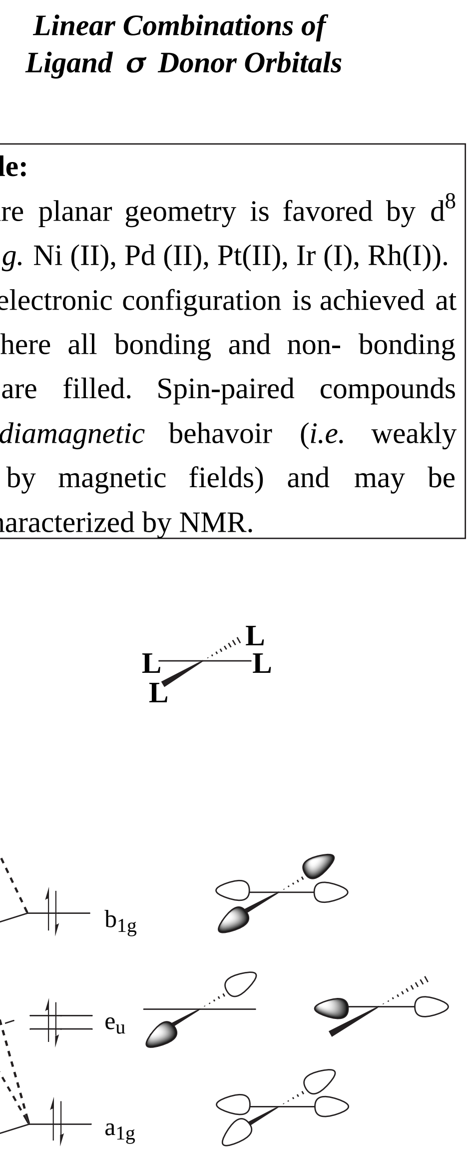




When combining orbitals, the resulting MO's must be symmetrically dispersed between bonding and antibonding. Thus, combining 3 orbitals (*i.e.* a_{1g}'s) requires one of the orbitals to be non-bonding.

In a square planar ligand field the degenerate d orbitals split into orbitals of a_{1g}, b_{1g}, e_g, and b_{2g} symmetries. The degenerate p orbitals split into orbitals of e_u and a_{2u} symmetries.

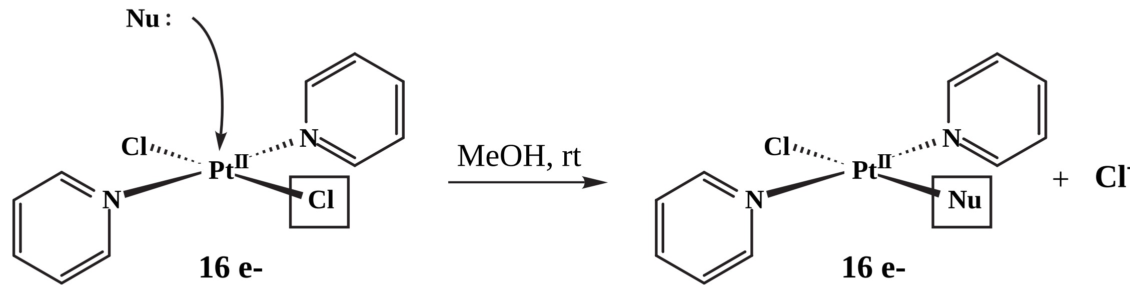
16 e⁻ Rule:
The square planar geometry is favored by d^8 metals (*e.g.* Ni (II), Pd (II), Pt(II), Ir (I), Rh(I)). A stable electronic configuration is achieved at 16 e^-, where all bonding and non- bonding orbitals are filled. Spin-paired compounds display *diamagnetic* behavoir (*i.e.* weakly repelled by magnetic fields) and may be readily characterized by NMR.



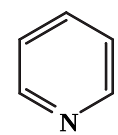
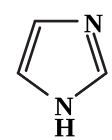
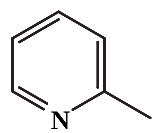
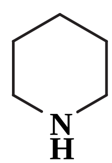
Associative Substitution: the nucleophile

$$\text{Rate} = \frac{-d\,[PtCl_2]}{dt} = k_1[PtCl_2] + k_2[Nu][PtCl_2]$$

k_1: first order rate constant that arises from substition of leaving group by solvent.
k_2: second-order rate constant for bi-molecular attack of Nu on metal complex.

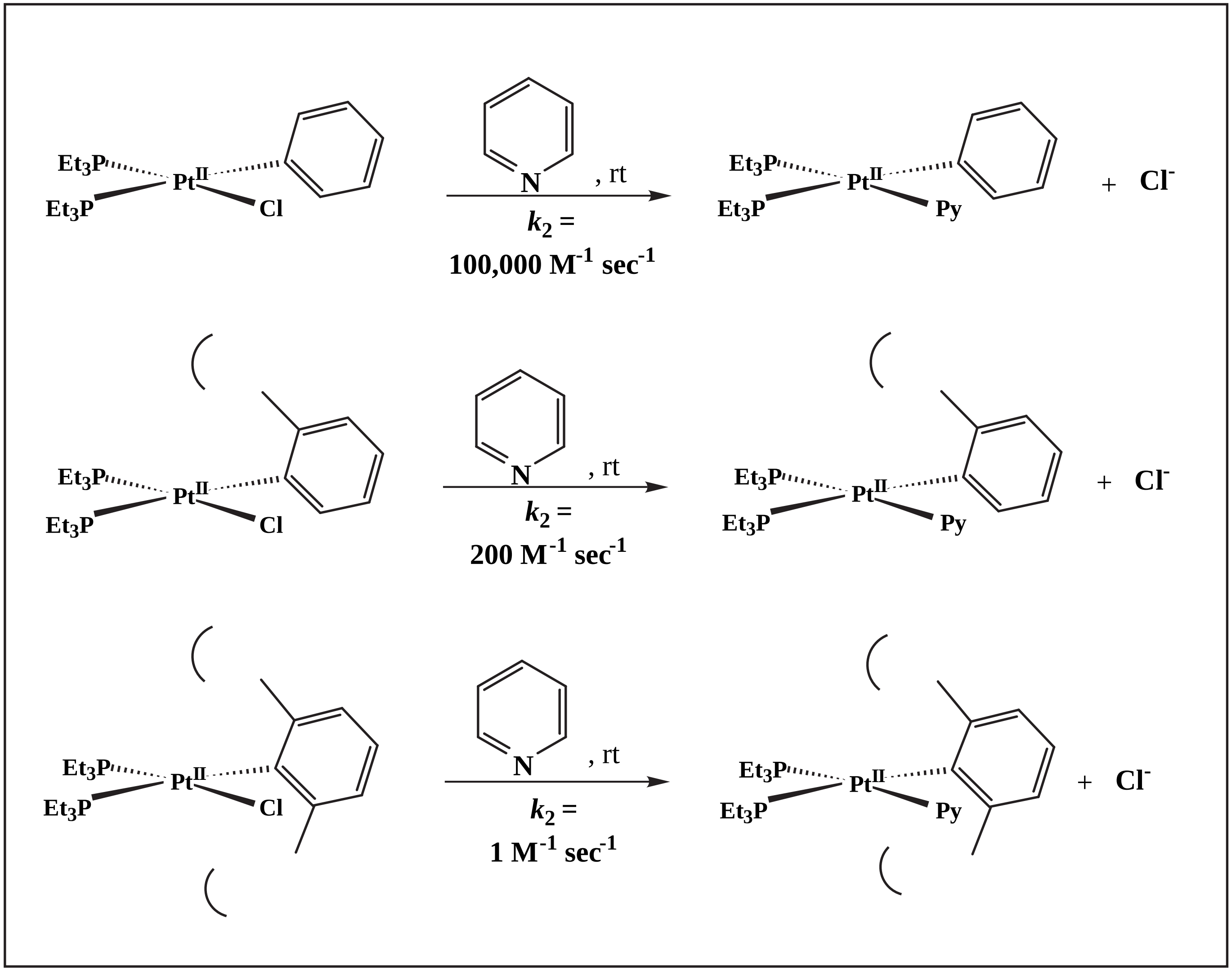


Basicity of the incoming ligand (nucleophile) plays only a minor role in its reactivity for soft metal centers. In general, the softest (*i.e.* most polarizable) nucleophiles react fastest with soft metals like Pt(II) *via* associative substitution. Steric hinderance at the nucleophile (*i.e*. picoline *vs* pyridine) can retard the rate of substition.

Nu	relative rate	Nu	relative rate
MeOH	1		1549
$CH_3CO_2^-$	<100		
CO	<100		
F^-	<158		2754
	158		
CH_3O^-	<250	Br-	15,000
$(Et)_3N$	1175	I-	2.9×10^5
		$C_6H_{11}CN$	2.2×10^6
	1349	$(CH_3O)_3P$	1.7×10^7
		PhS^-	1.5×10^7
		Ph_3P	8.5×10^8
		Et_3P	9.8×10^8
Cl^-	1096		
NH_3	1175		

Associative Substitution: Sterics

Sterically shielding the positions above and below the plane of the square planar complex can lead to significant decreases in the rates of associative substition.

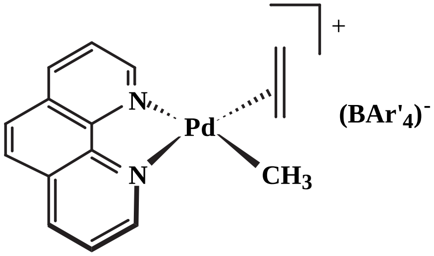


Pearson *J. Chem. Soc.* **1961** 2207.

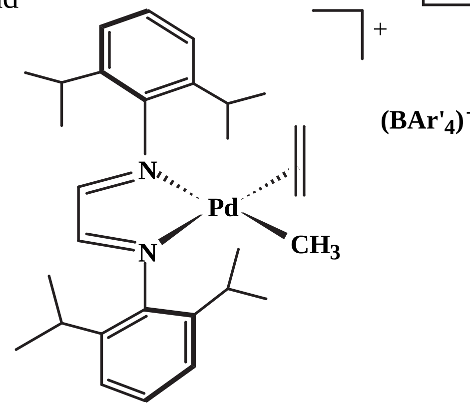
Associative Substitution: Sterics

as the steric bulk of the imine backbone increases, the aryl groups become more rigidly locked perpendicular to the square plane making their ortho substituents more effective at blocking the axial sites above and below the plane.

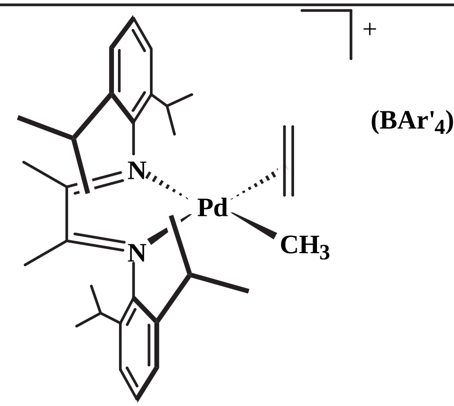
associative second order rate constants for ethylene exchange were examined by ^{1}HNMR in $CDCl_2$ at -85^{o}C



k = too fast to measure even at -100^{o}C.

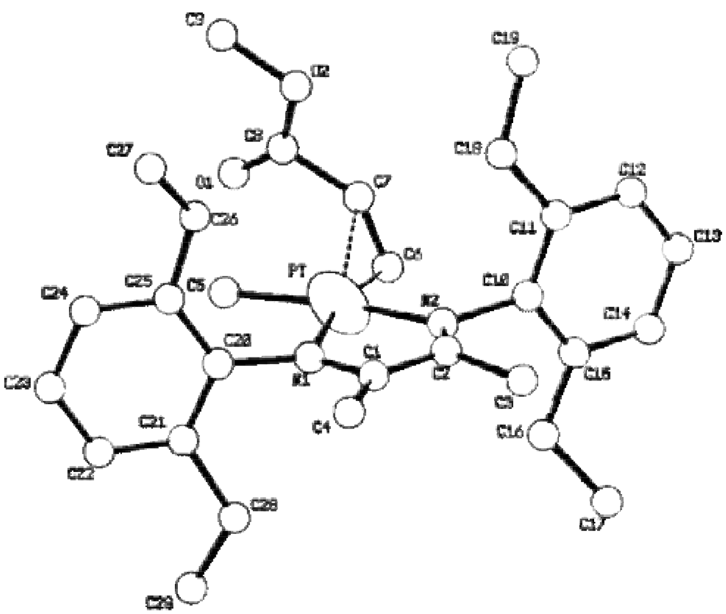


k = 8100 L/mol/sec



k = 45 L/mol/sec

Brookhart *JACS* **1995** (117) 6414.



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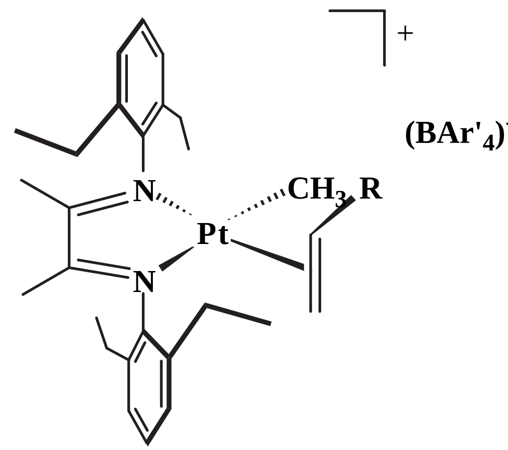
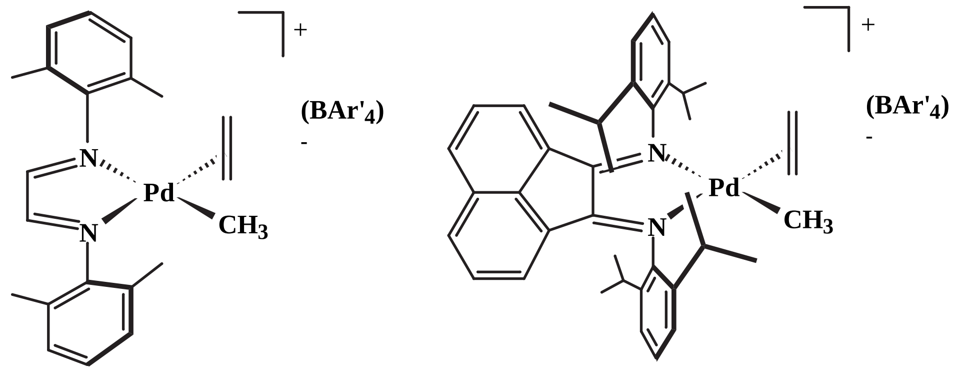
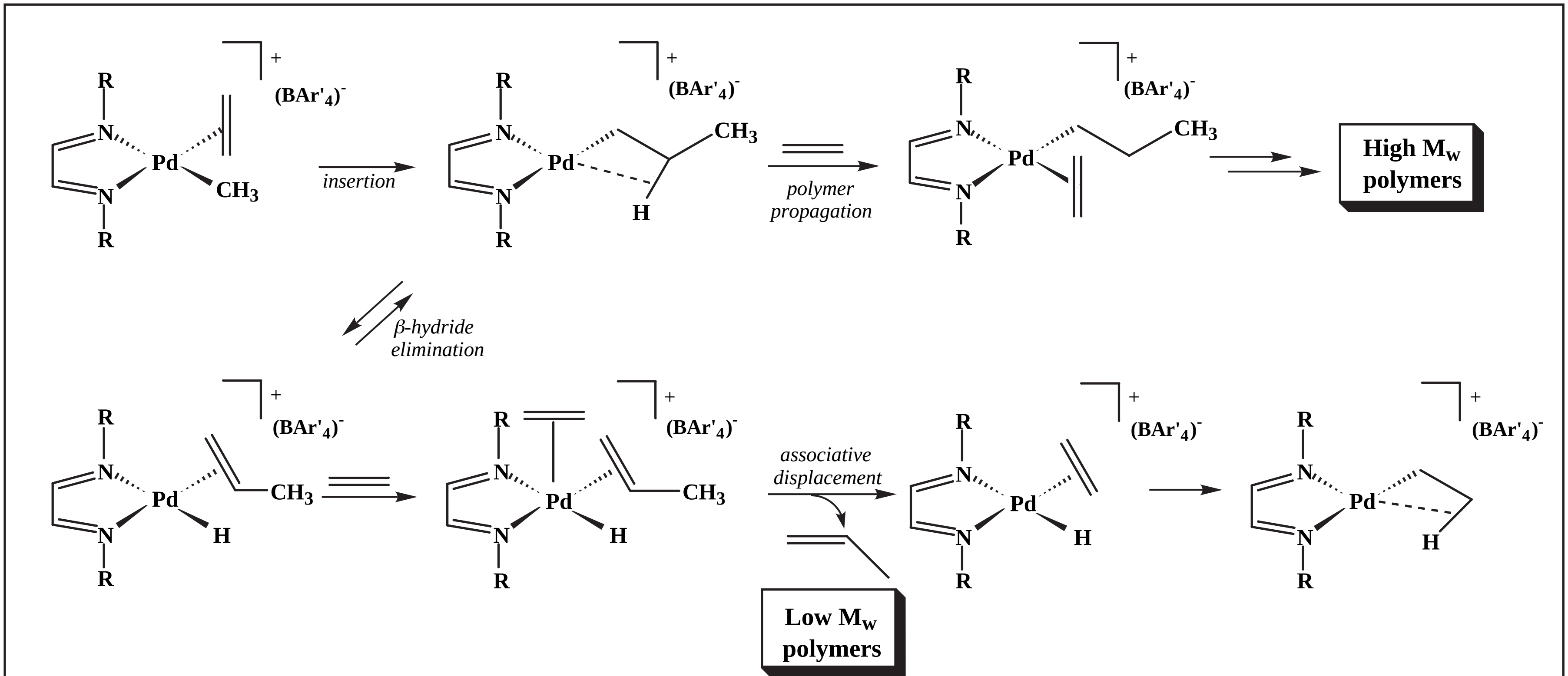


Ruffo *OM* **1998** (17) 2646.

Brookhart Polymerization Catalysts

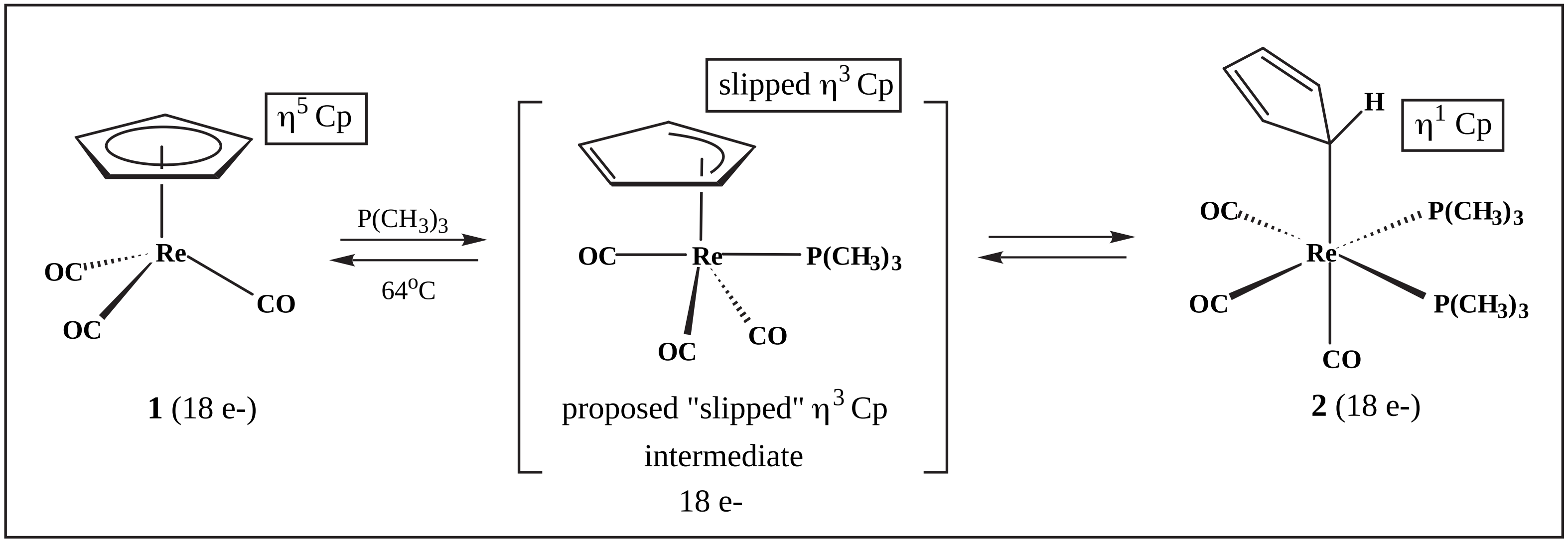


Polymer M_w = 110,000 Polymer M_w = 390,000

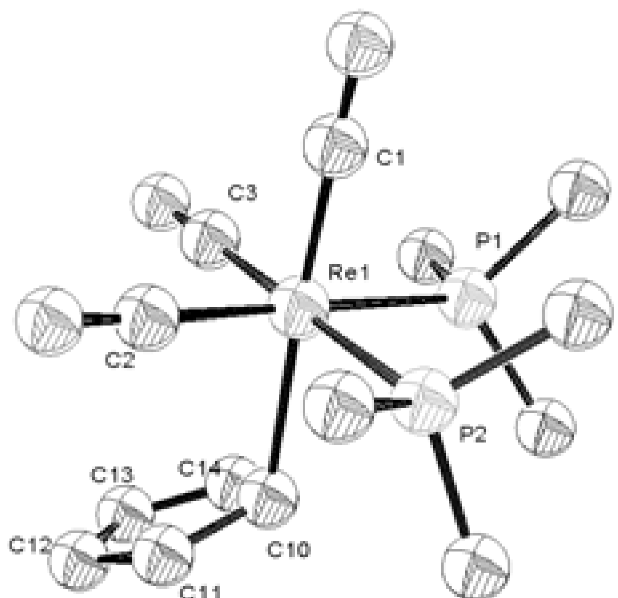


Brookhart *JACS* **1995** (117) 6414.

η^5 to η^1-Cp via Slipped η^3-Cp Intermediate



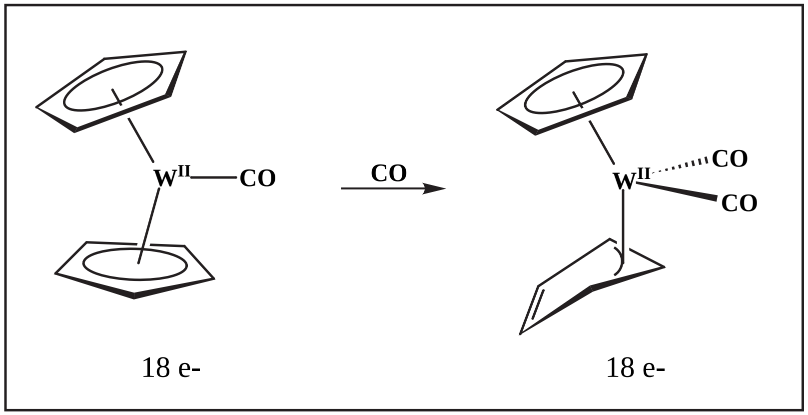
Based on the observation that the rate of reaction of **1** with $P(CH_3)_3$ to form **2** depends on both the concentration of **1** and $P(CH_3)_3$, an associative mechanism was proposed. To account for associative substition at a formally coordinatively and electronically saturated center, the authors propose an η^3 "slipped" Cp intermediate that forms concurrently with phosphine attack.



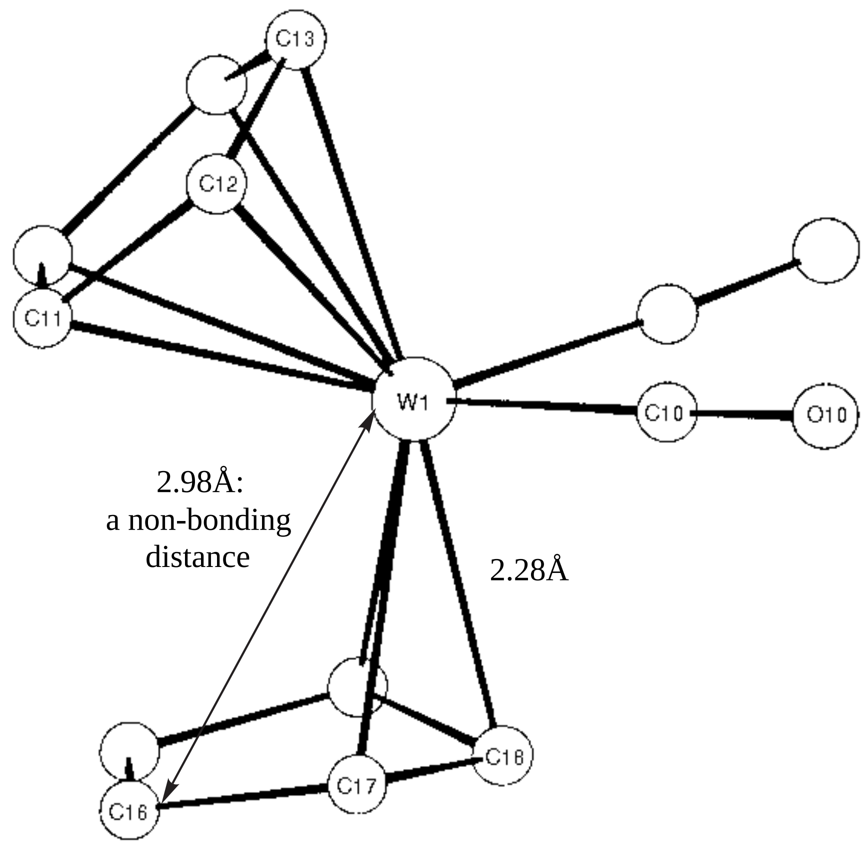
2

Casey *OM* **1983** (2) 535.

η5 to η3 Ring Folding

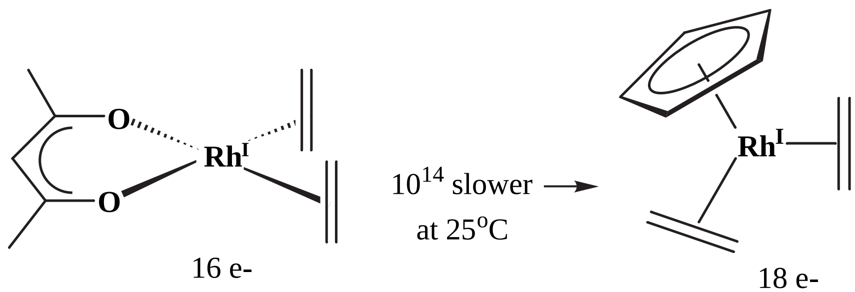


18 e- complexes with cyclopentadienyl, aryl, indenyl ligands may undergo "associative" substitution avoiding an energetically unfavorable 20 e- intermediate *via* ligand rearrangement from η5 to η3 or even η1 (cyclopentadienyl and indenyl). Haptotropic rearrangement may take the form of ring "slippage" where the ring is acentrally bonded to the metal and its aromaticity is disrupted or ring "bending" where the conjugation of the π system is broken.



Huttner J. *Organometallic Chem.* **1978** (145) 329.

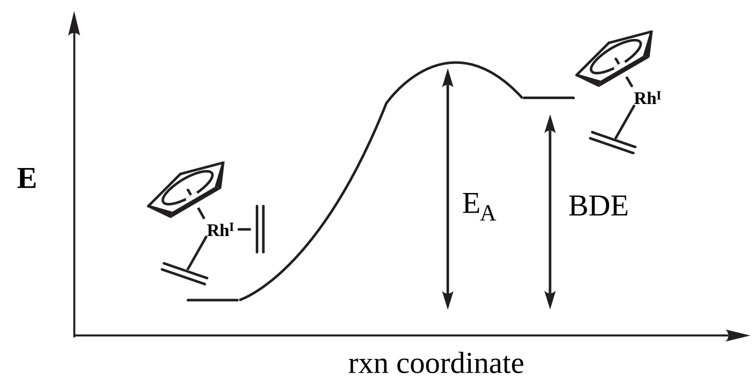
Ligand Exchange: Dissociative Mechanism

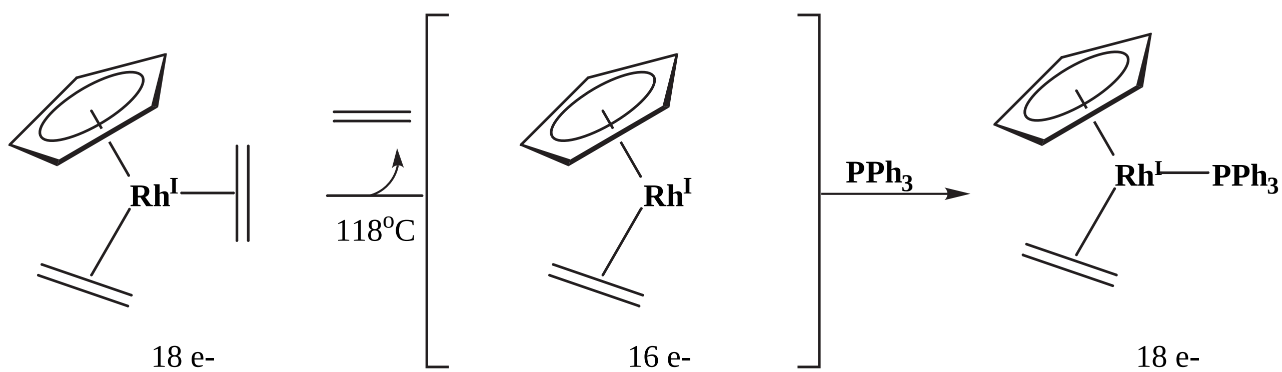


rate of ethylene exchange *via* associative displacement at 25^{o}C is ~ 10^4 sec^{-1}

rate of ethylene exchange *via* dissociative displacement at 25^{o}C is ~ 4 x 10^{-10} sec^{-1}
BDE = 31 kcal/mol

The rate-determining step in a dissociative ligand substition pathway is breaking the M-L bond. Because of the late, product-like transition state for forming the coordinatively unsaturated intermediate in such a process, the M-L BDE is a good approximation of the activation energy(E_A).





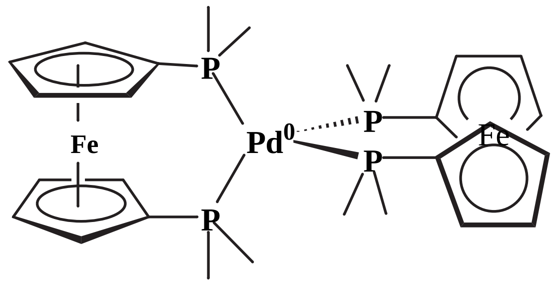
PPh$_3$ (mmol)	*k* x 10^4 sec $^{-1}$
0.20	1.65
1.23	1.73

a 6-fold increase in the concentration of nucleophile does not significantly affect the rxn rate. Results are consistent with a mechanism where the rate-determining step is ethylene dissociation and is not affected by the concentration of the nucleophile.

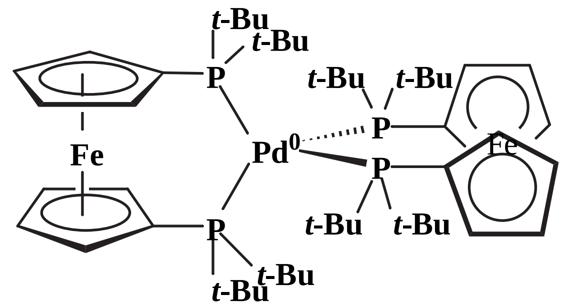
$$\boxed{\text{rate} = \frac{-d\,[LRh(C_2H_4)_2]}{dt} = k_1\,[LRh(C_2H_4)_2]}$$

Cramer *JACS* **1972** (94) 5681.

Ligand dissociation: sterics

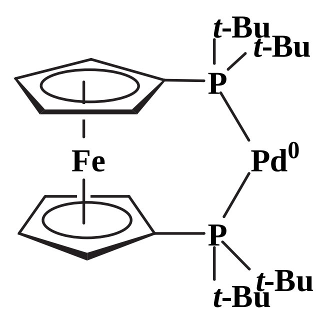


"ineffective catalyst"



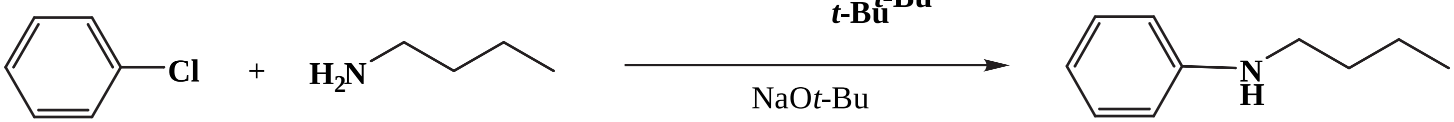
catalyst "resting state"

+L ⇌ dissociative **-L**



catalytically active species

The steric bulk of the bidentate phosphine ligand is thought to weaken the Pd-P bond, thereby favoring ligand dissociation required to form the catalytically active species.



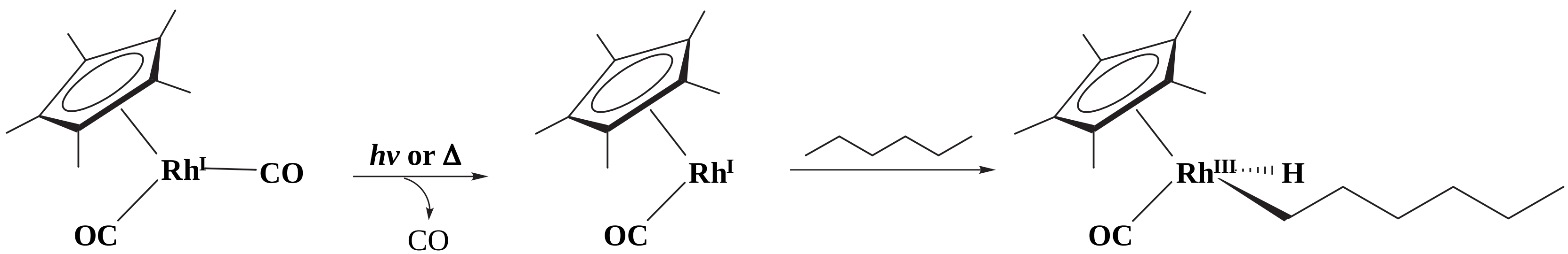
also aryl Br, I, OTs

also aniline, piperidine

Hartwig *JACS* **1998** (120) 7369.

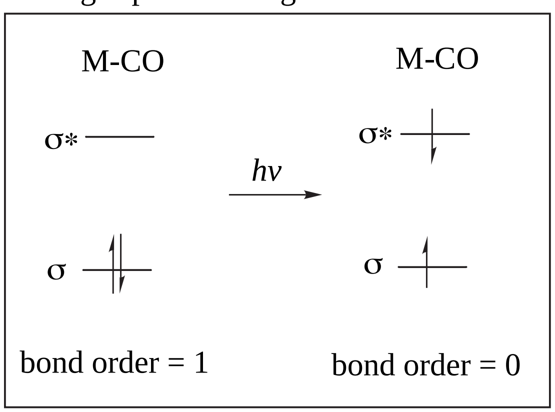
Ligand dissociation: Δ or *hv*

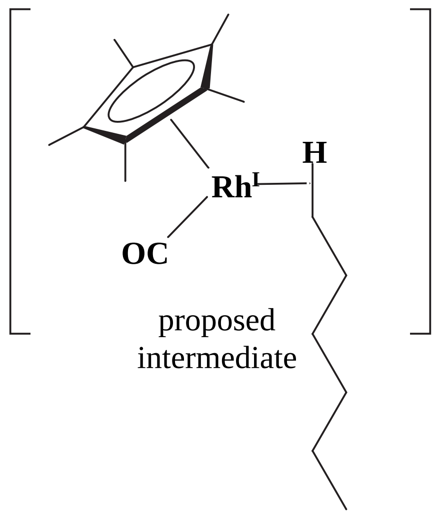
coordinatively and electronically unsaturated complexes capable of oxidatively adding into unactivated C-H bonds.



18 e- 16 e- 18 e-

Light-promoted ligand dissociation

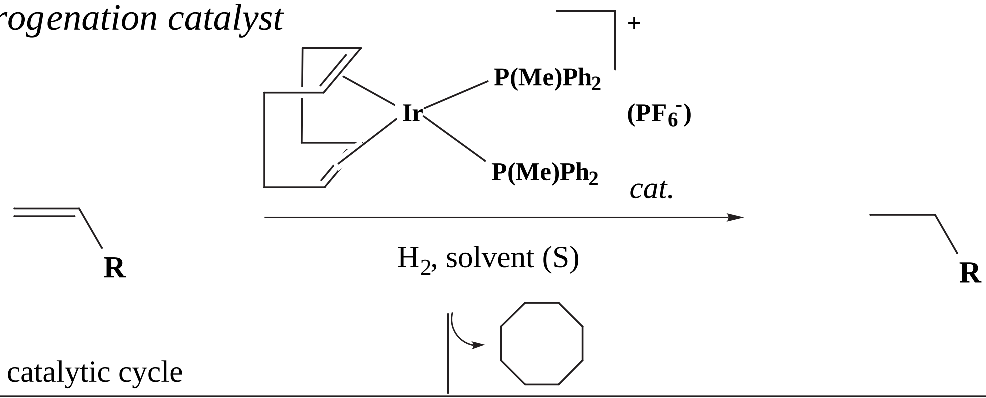




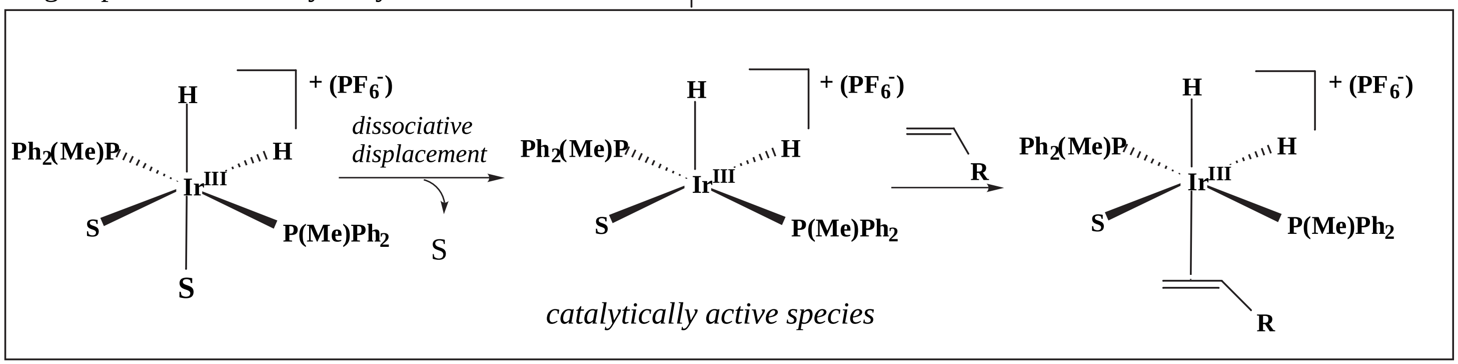
Bergman *JACS* **1994** (116) 9585.

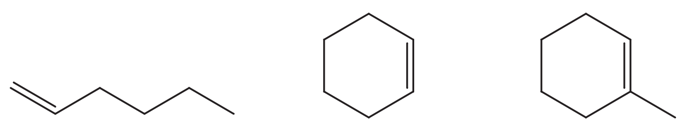
Ligand dissociation:weakly coordinating solvents

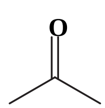
First generation Crabtree hydrogenation catalyst



A glimpse into the catalytic cycle



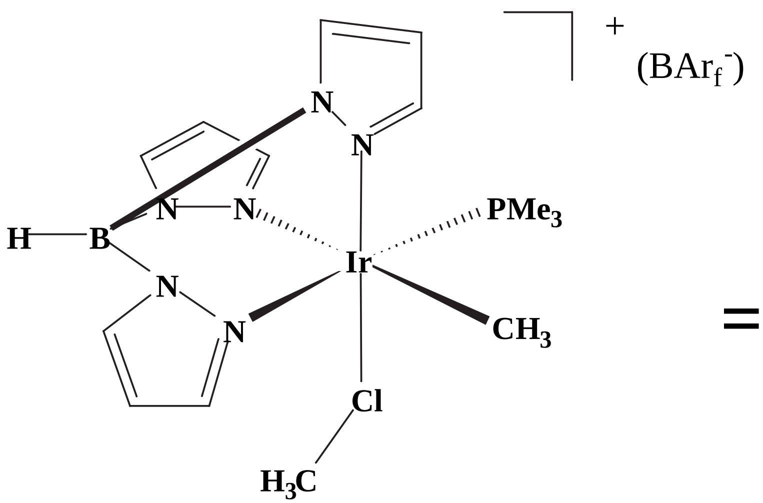


Solvent (S)	**Turnover Frequency (TOF)**		
	~10	0	0
CH_2Cl_2	5100	3800	1900

TOF = mol reduced substrate/mol catalyst/h

Crabtree *Acc Chem Res* **1979** (12) 331.

Non-coordinating solvents: "no such thing"



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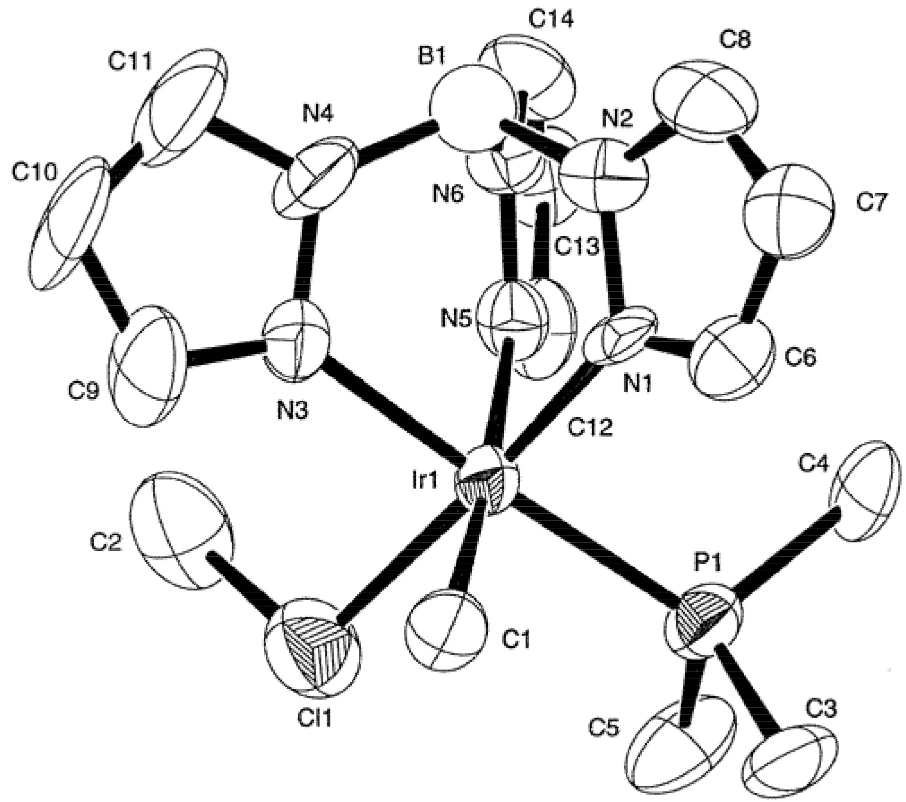


The first isolated chloromethane-metal complex. There are also similar complexes formed with CH_2Cl_2, and Cl_3CH that have been characterized by NMR.

Bergman *JACS* **2001** (123) 11508.

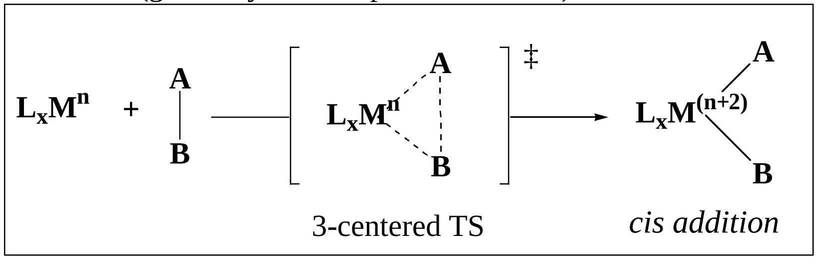
Oxidative Addition/Reductive Elimination

·**Oxidative Addition (OA)**: metal mediated breaking of a substrate σ-bond and formation of 1or 2 new M-L σ bonds. OA requires removal of 2 electrons from the metal's d electron count. This is reflected in a two unit increase in the metal's oxidation state. The formation of 1 or 2 new M-L σ bonds is accompanied by an increase in the metal's coordination number by 1 or 2 units respectively. The latter results in a 2 unit increase in the electron count of the metal complex (*e.g.*16 e^- to 18 e^-). Currently, OA of low valent, electron rich metals to polar substrates is the best way to form M-C σ bonds within the context of a catalytic cycle. *The term oxidative addition confers no information about the mechanism of the reaction.*

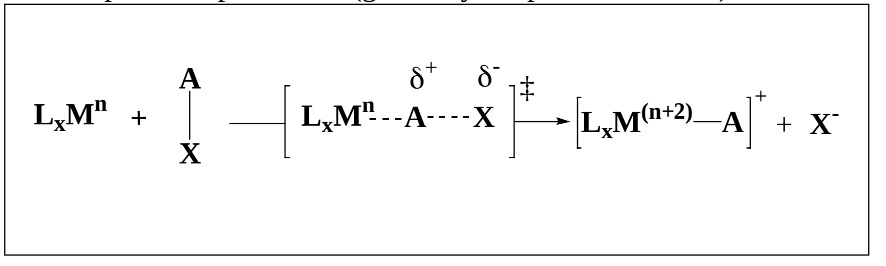
Reductive elimination (RE): microscopic reverse of oxidative addition where two M-L σ bonds are broken to form one substrate σ bond. RE results in the addition of two electrons into the metal d electron count. This is reflected in a two unit decrease in the metal's oxidation state. The breaking of 2 M-L σ bonds is accompanied by a decrease in the metal's coordination number by 2 units. The result is a 2 unit decrease in the electron count of the metal complex (*e.g.* 18e- to 16 e-). The two M-L σ bonds undergoing reductive elimination must be oriented *cis* to each other. Currently, RE is the most common way to form C-C bonds *via* transition metal complexes.

General OA Mechanisms:

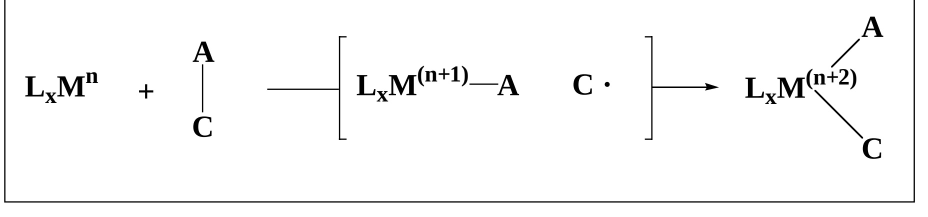
Concerted (generally for non-polar substrates)



Nucleophilic displacement (generally for polar substrates)



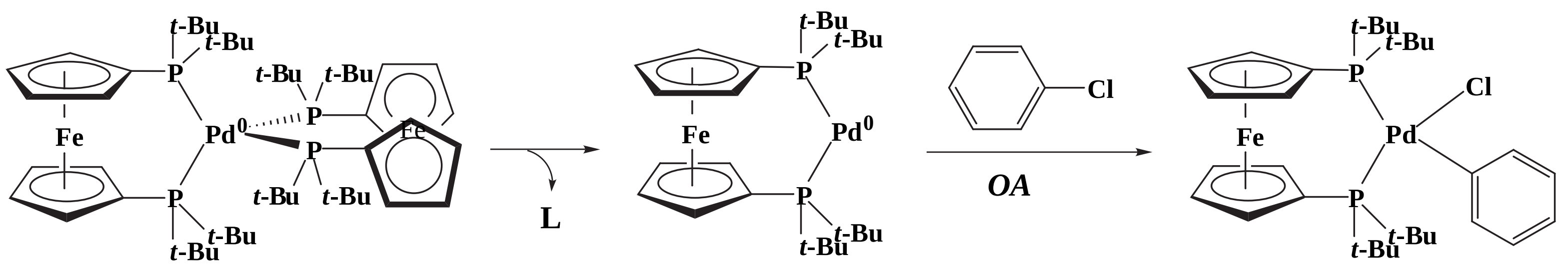
Radical (both non-polar and polar)



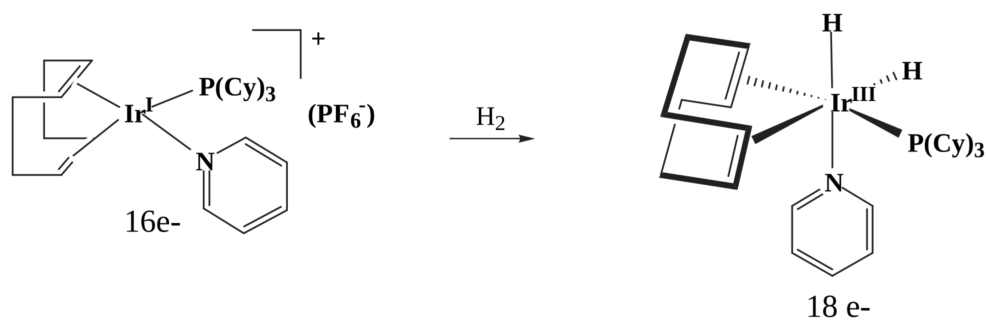
Oxidative Addition

Metal Complex: electron rich metals in low oxidation states, with strong donor ligands and a site of coordinative unsaturation.

d^{10}, tetrahedral, 18 e^- --> d^{10}, ML_2, 14e^- --> d^8, ML_4, square planar, 16e^- (*e.g.* Ni^0, Pd^0, Pt^0)

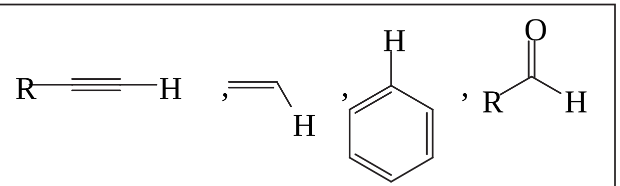


d^8, ML_4, square planar, 16 e^- --> d^6, ML_6, octahedral, 18e^- (*e.g.* Rh^I, Ir^I)

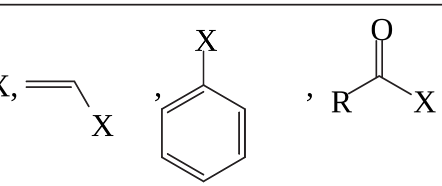


Substrates: two groups segregated into non-polar and polar. Currently, the most facile way to form C-M σ bonds is with polar substrates (*e.g.* alkyl, aryl, and vinyl halides).

Non-polar substrates: R-H

H_2, R_3Si-H, R_2B-H, RCH_2-H, 

Polar substrates: R-X where X = I, Br, Cl, OTf

H-X, RCH_2-X, 

Transition Metal Oxidation States

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
+8								
+7				○				
+6			○	○	○			
+5		○	○	○	○	○		
+4	●	●	○	○	○	○	○	
+3	○	○	●	○	●	○	○	○
+2	○	○	○	●	○	●	●	●
+1		○	○	○	○	○	○	○

	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
+8					○			
+7				○	○			
+6			●	●	○	○		
+5		●	○	○	○	○		
+4	●	○	○	○	○	○	○	
+3	○	○	○	○	●	●	○	○
+2	○	○	○	○	○	○	●	○
+1		○	○	○	○	○	○	●

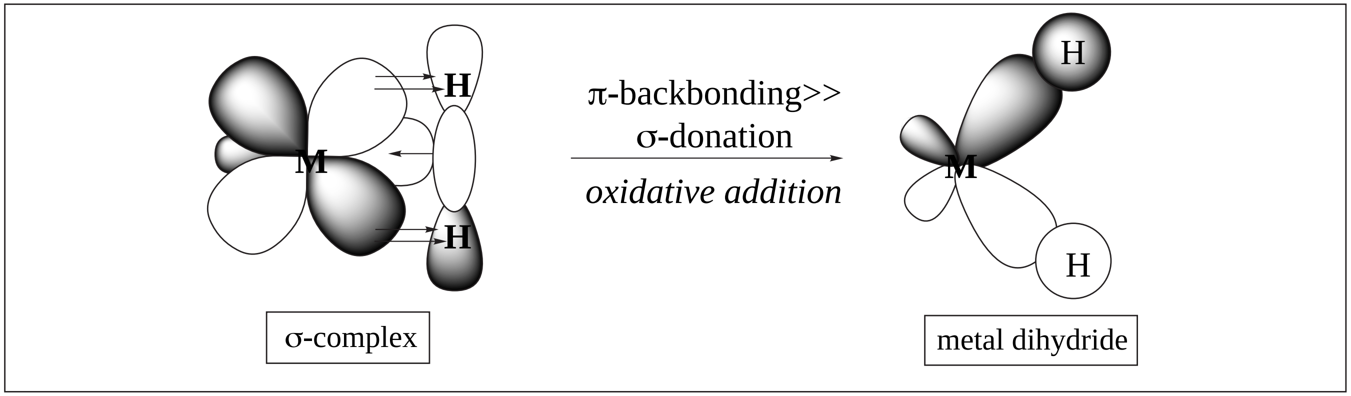
	Hf	Ta	W	Re	Os	Ir	Pt	Au
+8					○			
+7				●	○			
+6			●	○	○	○		
+5		●	○	○	○	○		
+4	●	○	○	○	●	●	●	
+3	○		○	○	○	○	○	●
+2		○	○	○	○	○	○	○
+1		○	○	○	○	○	○	○

○ - Observed positive oxidation state

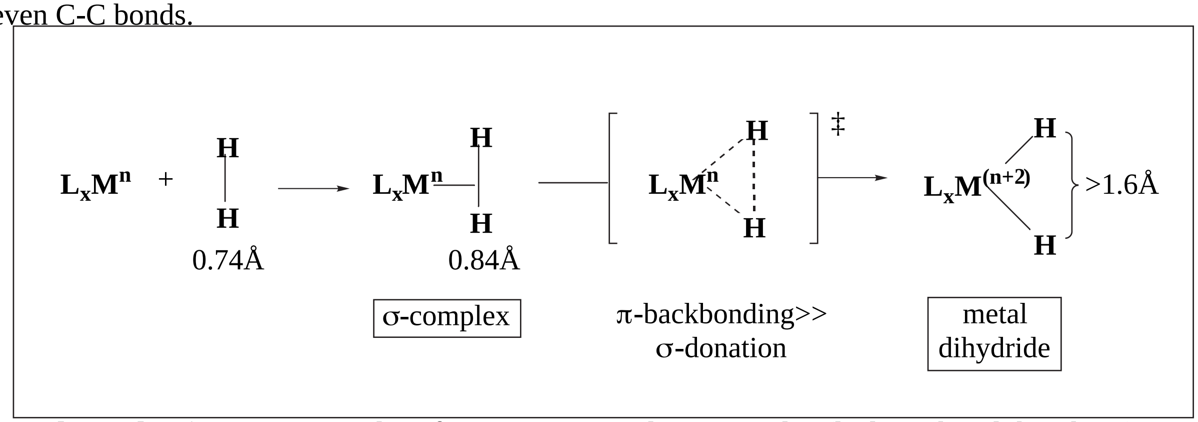
● - Most stable oxidation state (aqueous solution)

Mingos *Essential Trends in Inorganic Chemistry*; Oxford University Press, 1998.

OA: Concerted 3-centered (non-polar substrates)

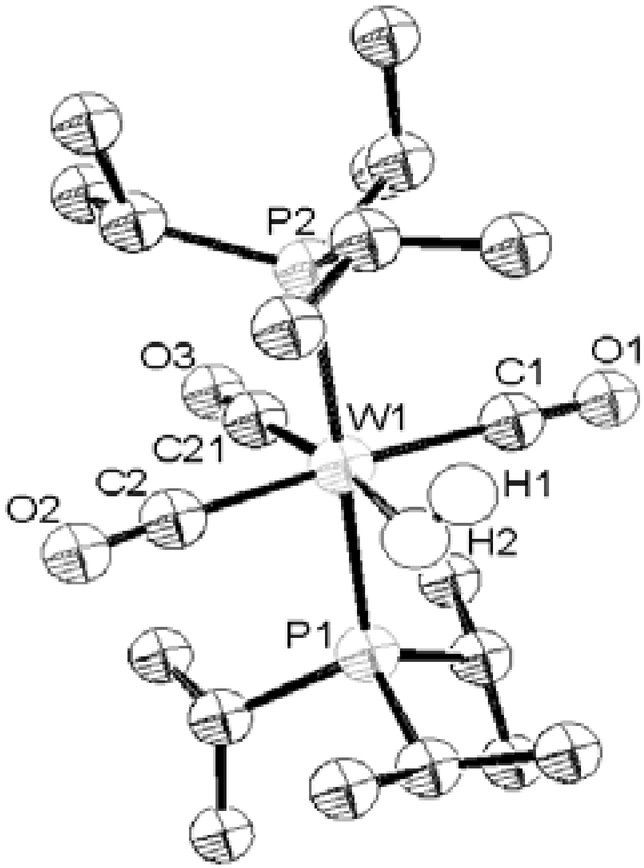


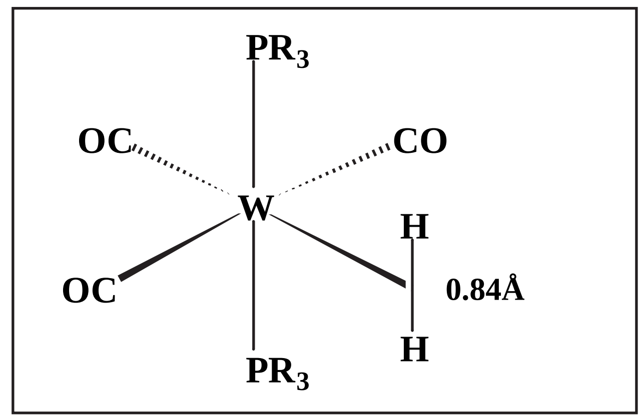
σ-complex: intermolecular binding of a substrate *via* it's σ-bond to a metal complex. σ-complexes are thought to be along the pathway for oxidative addition of non-polar substrates to low valent, e-rich metal complexes. Analogous to the Dewar-Chatt-Duncanson model for olefin metal-bonding, σ-bonding is thought to occur *via* a 2 way donor-acceptor mechanism that involves σ-donation from the bonding σ-electrons of the substrate to empty σ-orbital of the metal and π-backbonding from the metal to the σ* orbitals of the substrate. These bonding principles have been applied to non-polar σ-bonds such as H-H, C-H, Si-H, B-H and even C-C bonds.



Concerted mechanism: σ-complex formation precedes an early (little σ-bond breaking), 3-centered transition state where strong π-backbonding results in oxidative addition of the bound substrate to the metal. The concerted mechanism is thought to operate primarily for non-polar substrates (*i.e.* H-H,C-H, Si-H, B-H) with electron rich, low valent metals. The spectroscopic identification of metal dihydrogen σ-complexes with H-H bond distances stretched between the non-bonding (0.74Å) and dihydride extremes (>1.6Å) provides strong support for this mechanism with H_2.

Dihydrogen σ-complexes

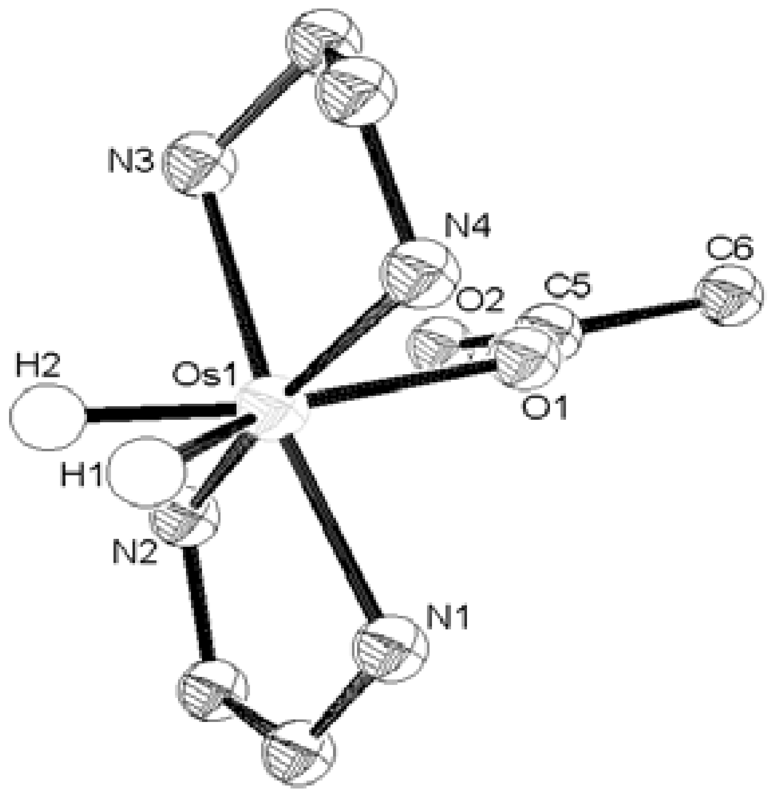


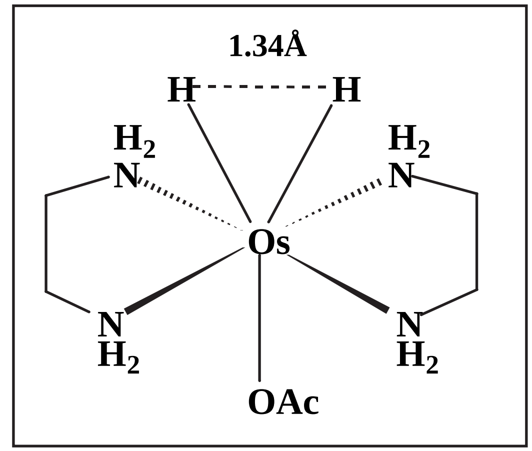


The first stable dihydrogen metal complex was isolated by Kubas. The lengthened H-H bond (0.84Å) is 20% greater than the H-H bond length in free H_2 (0.74Å). This is thought to arise from metal backbonding into the H-H σ* orbital.

Kubas *Acc. Chem. Res.* **1988** (21) 120.

Dihydrogen σ-complexes

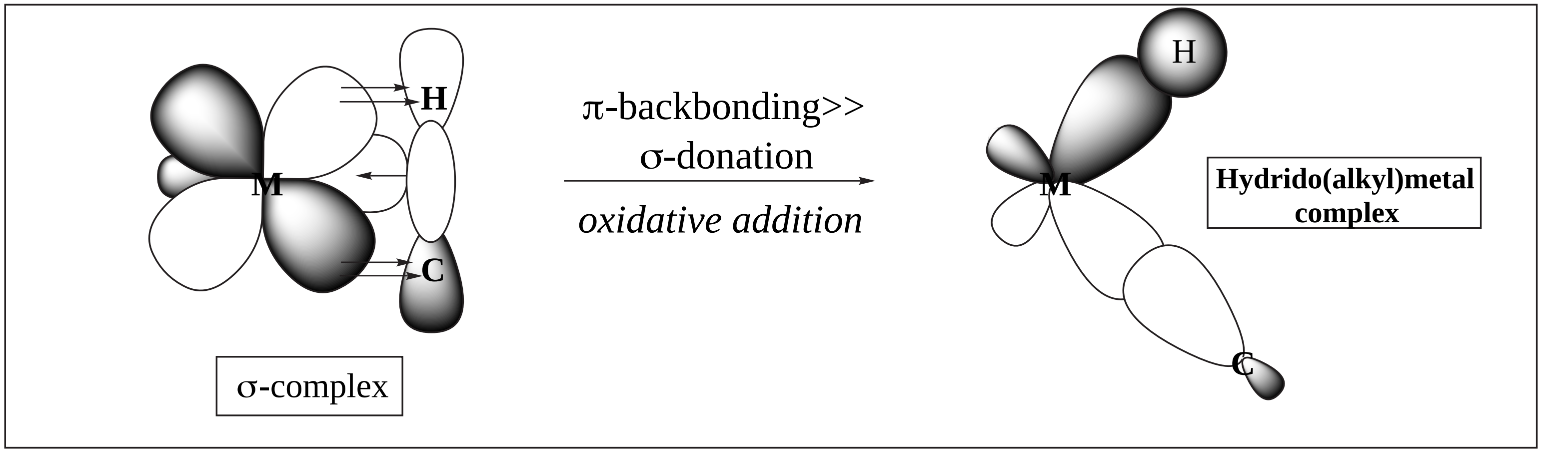




The H-H bond distance is thought to be a measure of the metal's ability to backdonate its electrons. Low oxidation state metal complexes such as $[Os(H_2)(en)_2(OAc)]^+$ with strong σ- and π-donor ligands are very effective π-backbonders as evidenced by the very long H-H bond in their M-H_2 σ-complex.

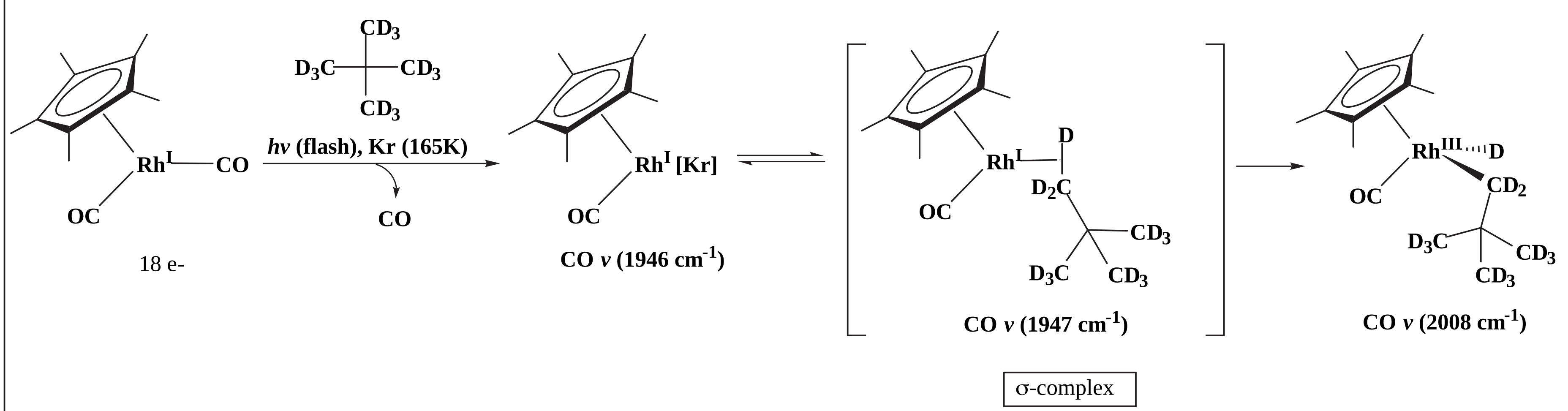
Taube *JACS* **1994**(116) 4352.

sp^{3}C-H OA via σ complex intermediates



regioselectivity: sp^2 C-H > 1^o sp^{3}C-H> 2^o sp^3 C-H >>> 3^o sp^3 C-H. There is both a kinetic and thermodynamic preference to form the least sterically hindered C-M σ bond. Kinetic preference: activation barrier to σ-complex formation is lower for less sterically hindered C-H bonds and bonds with more s character. Thermodynamic preference: stronger C-M bonds are formed (see Structure and Bonding, pg. 32).

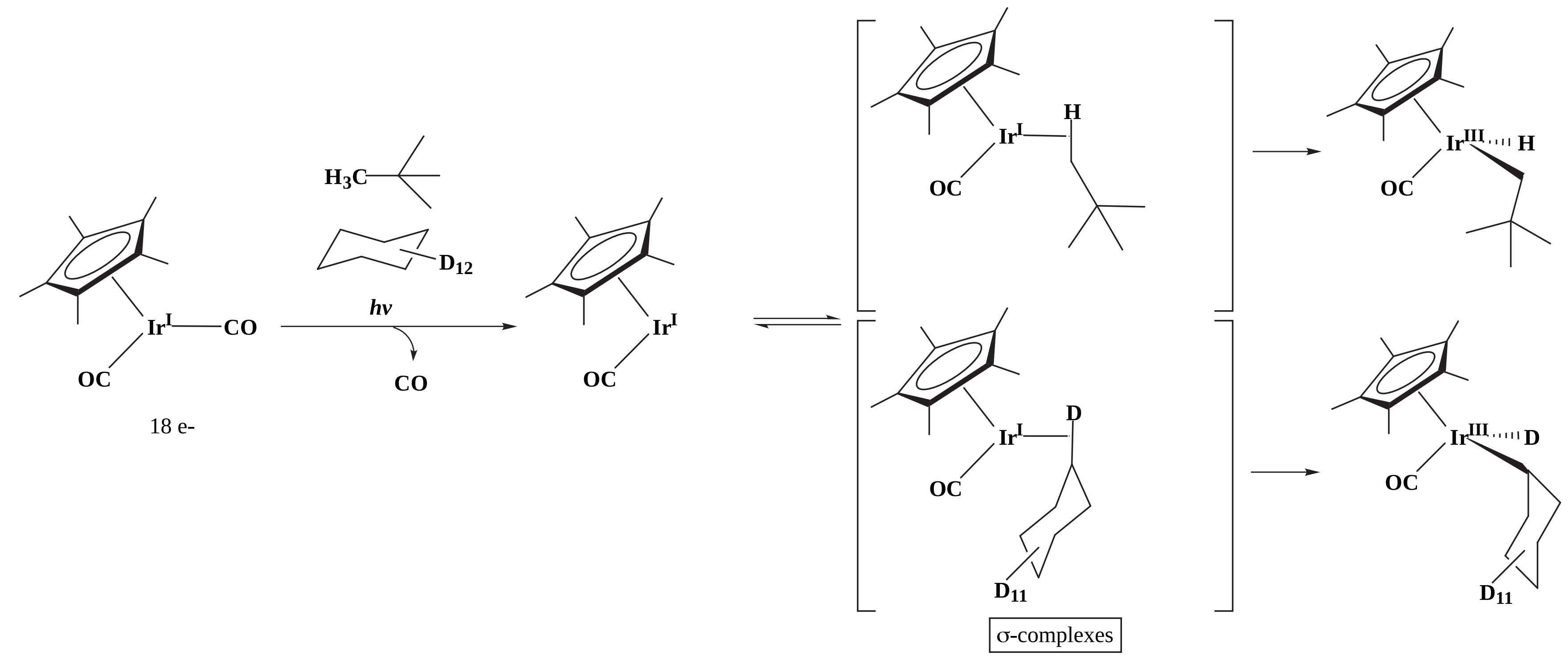
Evidence in support of a σ-complex intermediate:



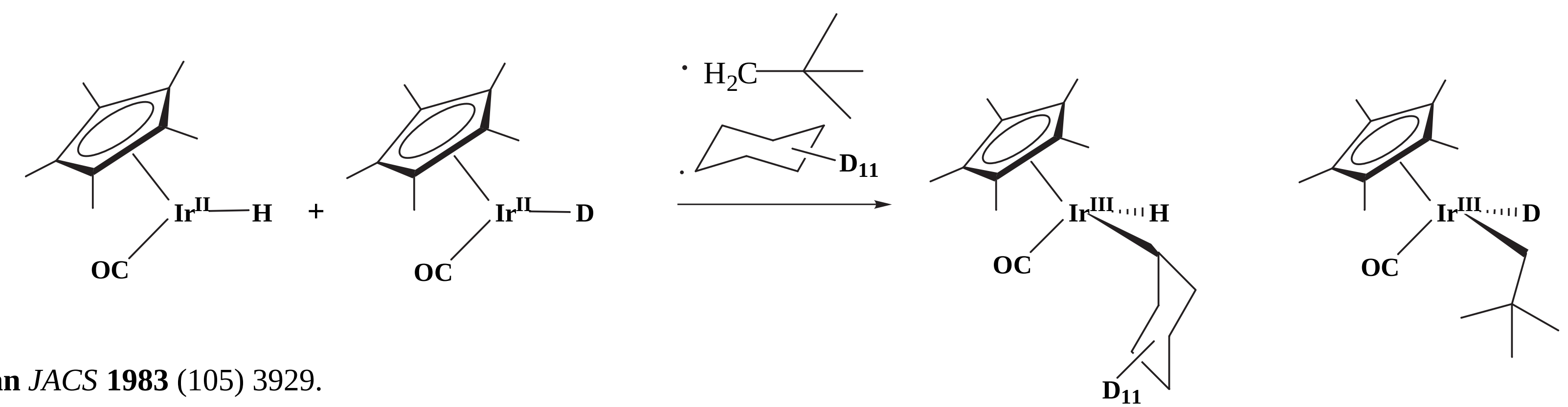
Bergman *JACS* **1994** (116) 9585.

sp^3C-H: concerted vs. radical

crossover experiment: evidence in support of a concerted mechanism.

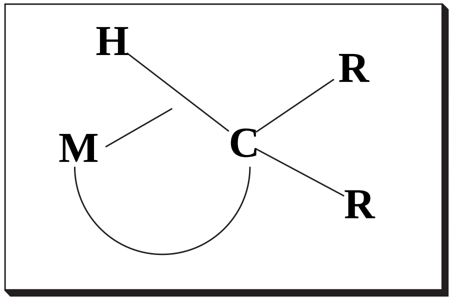


Less than 7% of the crossover products were observed by ^{1}HNMR. This may be indicative of a minor radical pathway.



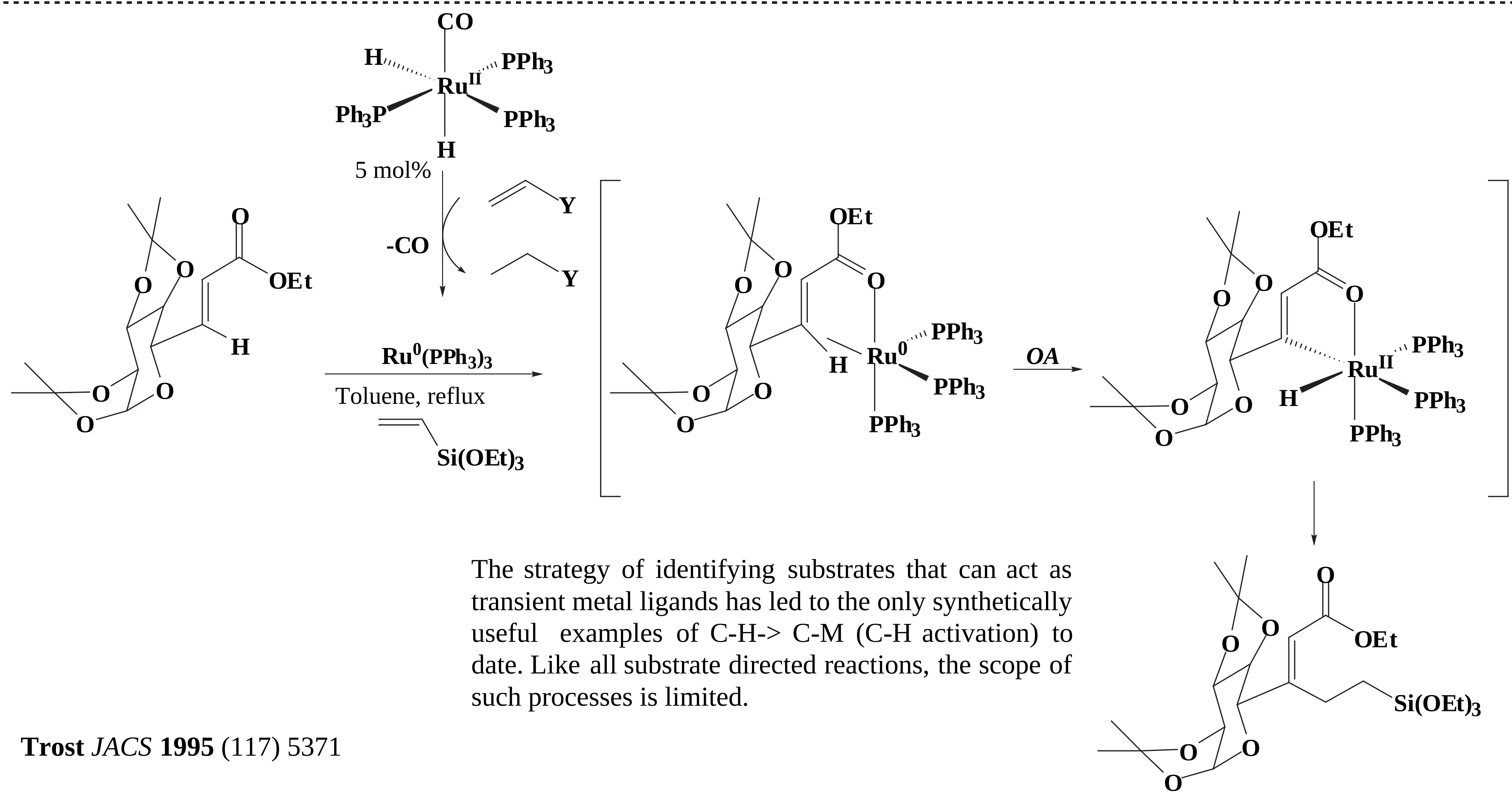
Bergman *JACS* **1983** (105) 3929.

Agostic interactions: intramolecular σ-complex



An agostic interaction is generally defined as an intramolecular σ-complex that forms between a metal and a C-H bond on one of its ligands.

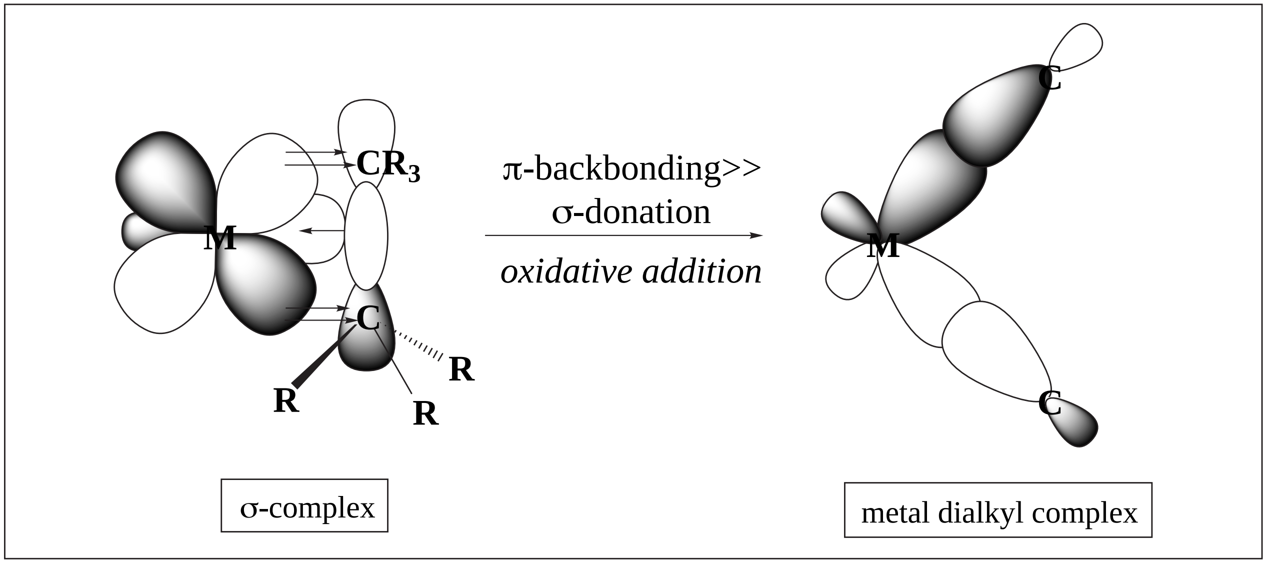
Brookhart *JOMC* **1983** (250) 395



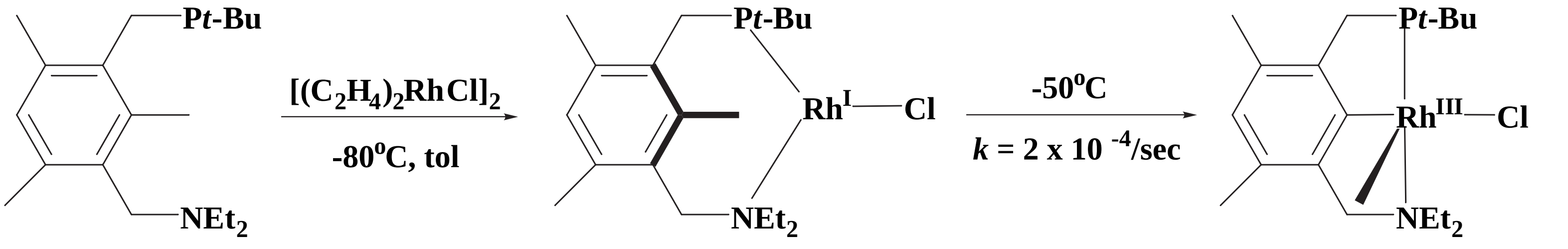
The strategy of identifying substrates that can act as transient metal ligands has led to the only synthetically useful examples of C-H-> C-M (C-H activation) to date. Like all substrate directed reactions, the scope of such processes is limited.

Trost *JACS* **1995** (117) 5371

OA: sp^3C-sp^3C



Even though BDE's of C-C bonds are lower than those of analogous C-H bonds (*e.g.* C_6H_5-CH_3:100 kcal/mol *vs.* C_6H_5-H: 110 kcal/mol), transition metal mediated OA's into C-C bonds are much more rare than those for analogous C-H bonds. Formation of the σ-complex is kinetically disfavored by steric repulsion between the metal complex and the carbon substituents and by the high directionality of the sp3C-sp3C bond that localizes the σ bonding orbital deep between the carbon nuclei. Milstein and coworkers are able to overcome the kinetic barrier by approximating the C-C bond at the metal center.

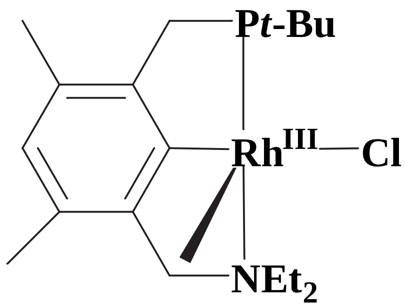


stable @ -80°C
observed by 1H NMR

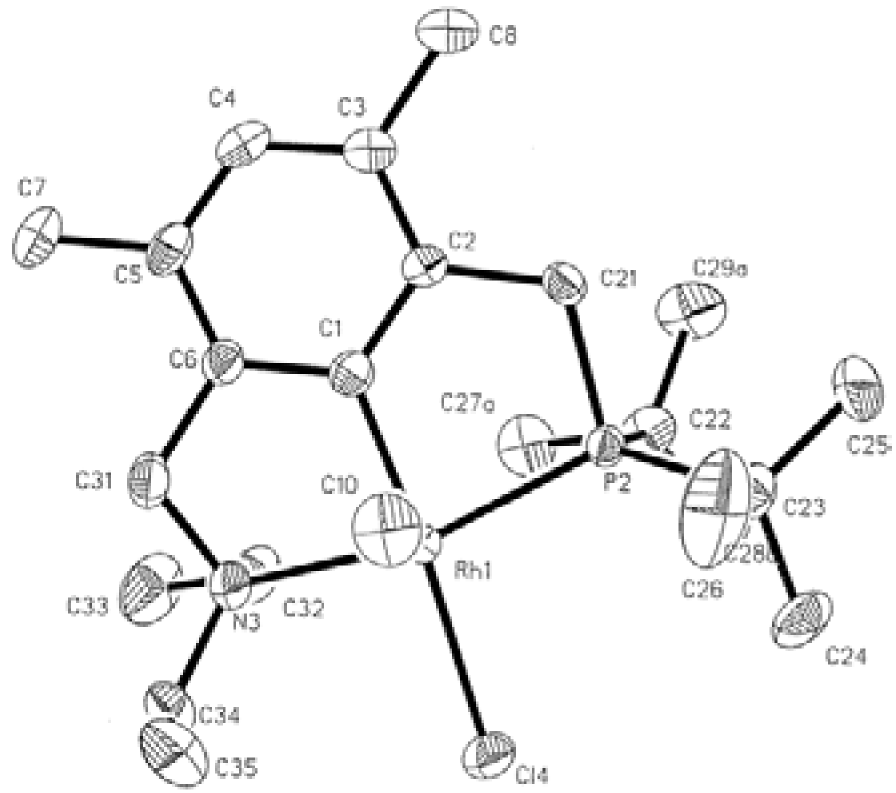
only product observed
(no C-H activation product)

Milstein *JACS* **2000** (122) 9848.

OA: sp^3C-sp^3C

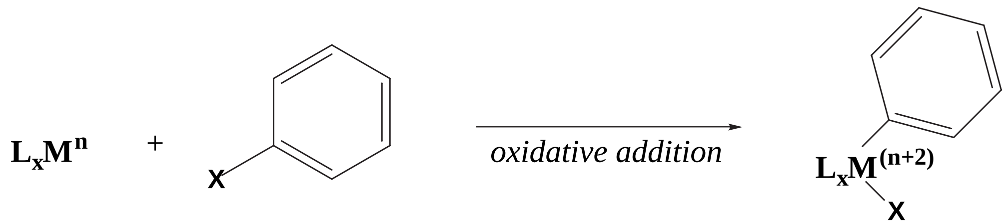


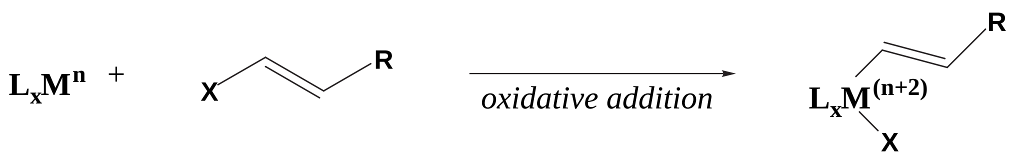
only product observed
(no C-H activation product)



Milstein *OM* **1997** (16)3981.

OA with C_{sp2}-X bonds: aryl and vinyl halides





Note: retention of stereochemistry in OA to vinyl halides

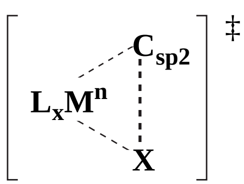
Rate of OA X = I>Br>Cl>>F

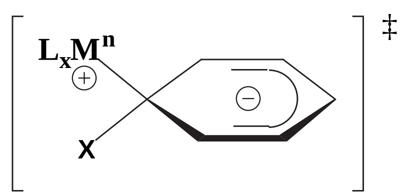
Three main mechanisms to consider for this process:

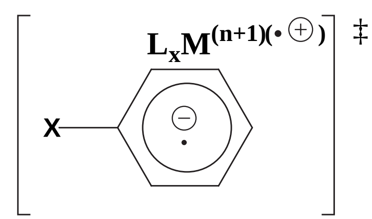
1. Concerted process with unsymmetrical, minimally-charged, 3-centered transition state

2. S_NAr-like with highly charged transition state

3. Single-electron transfer processes with oppositely-charged, radical intermediates



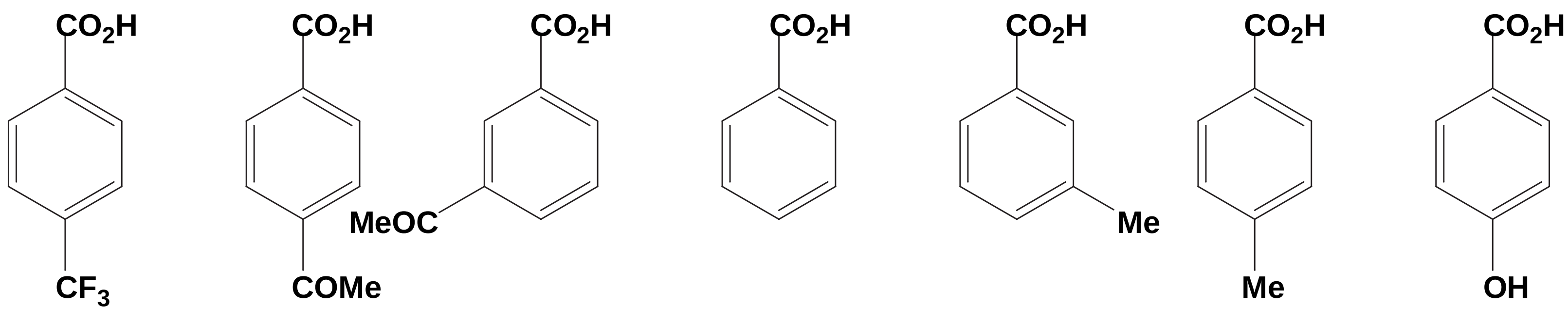




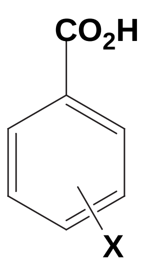
Hammet plots (linear free energy relationships) - a valuable mechanistic probe

See Carey and Sunberg: Part A, 3rd Edition. pp 196-209.

Recall the effect of e- withdrawing groups and e- donating groups on the acidity of benzoic acid resulting from stabilization and destabilization of the carboxylate anion, respectively:



pKa	3.66	3.72	3.83	4.19	4.25	4.33	4.57



Define:

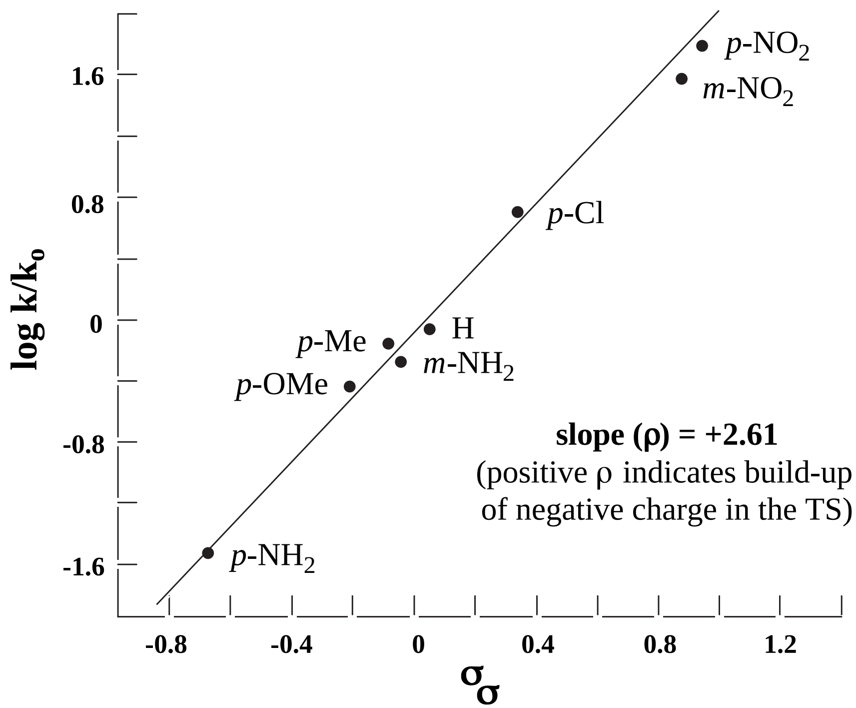
$$\sigma = pKa_H - pKa_X$$

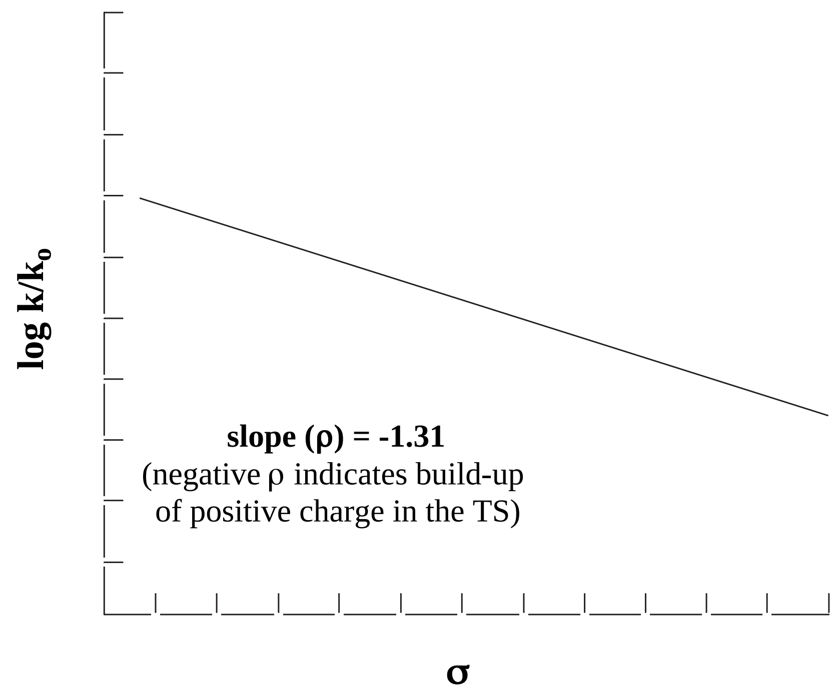
Substituent group	σ_{meta}	σ_{para}
CF_3	0.46	0.53
COMe	0.36	0.47
Cl	0.37	0.24
H	0	0 (by definition)
OMe	0.10	-0.12
Me	-0.06	-0.14
OH	0.13	-0.38

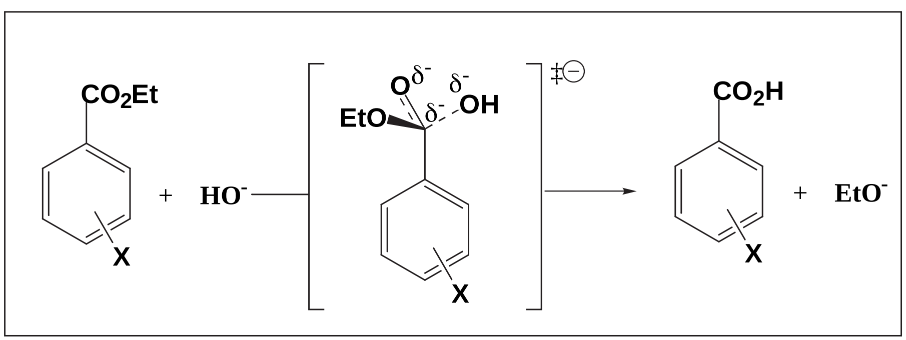
Because these same substituents can often similarly stabilize or destabilize polar transtition states for reactions involving aryl substrates, a linear relationship can exist between σ and reaction rate for such processes. This type of ***"linear free energy relationship"*** can lend valuable insight into the charge characteristics of the transition state for various reactions.

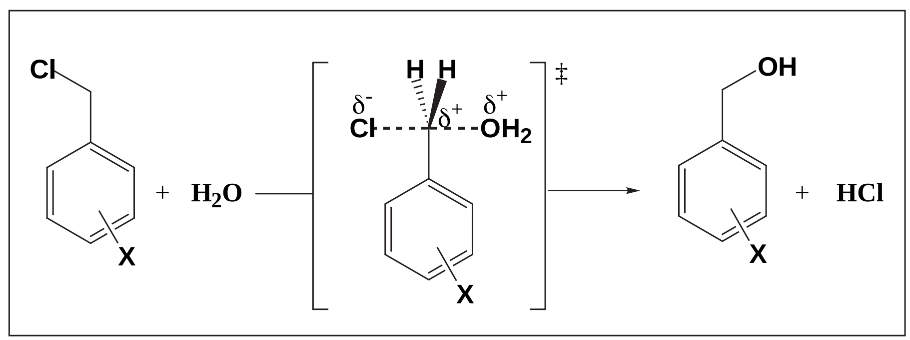
Hammet plots (linear free energy relationships) - a valuable mechanistic probe

See Carey and Sunberg: Part A, 3rd Edition. pp 196-209.

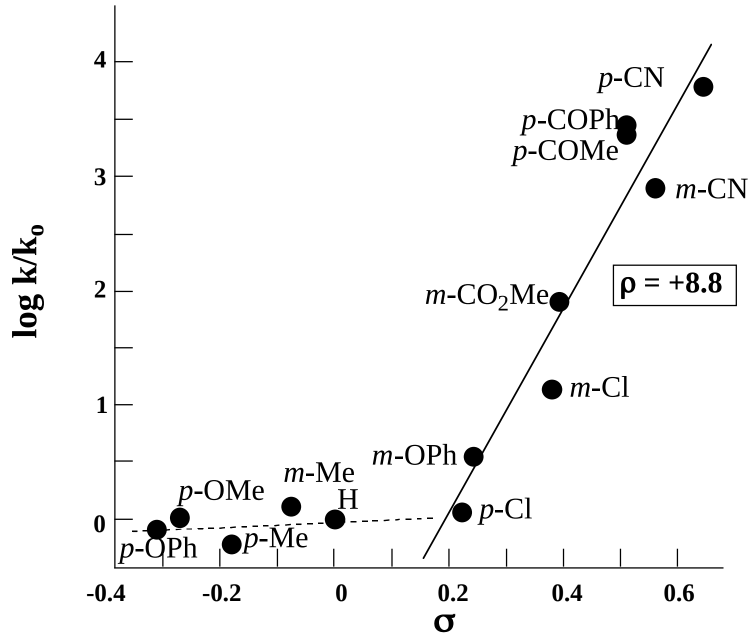


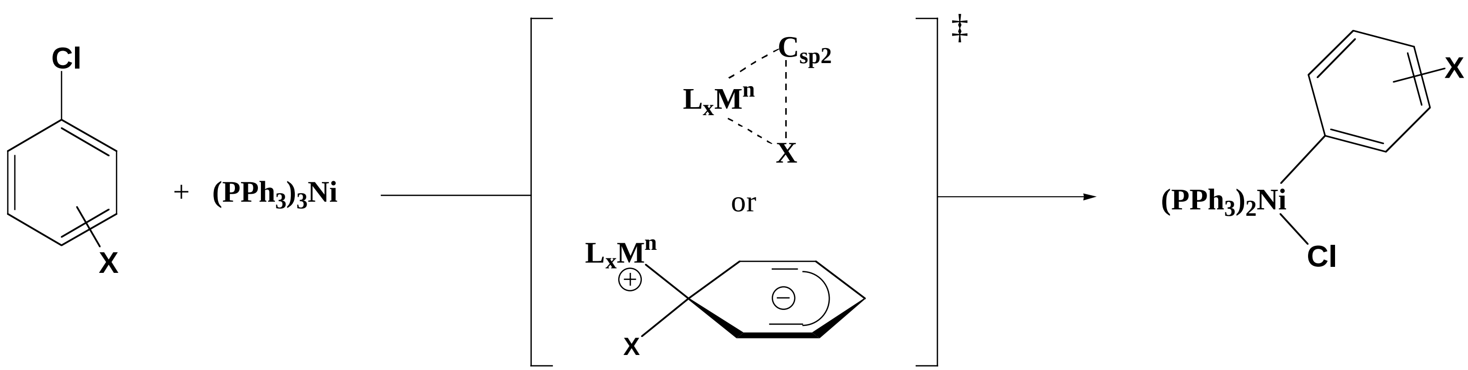






Oxidative addition of aryl chlorides to tris(triphenylphosphine)nickel(0)

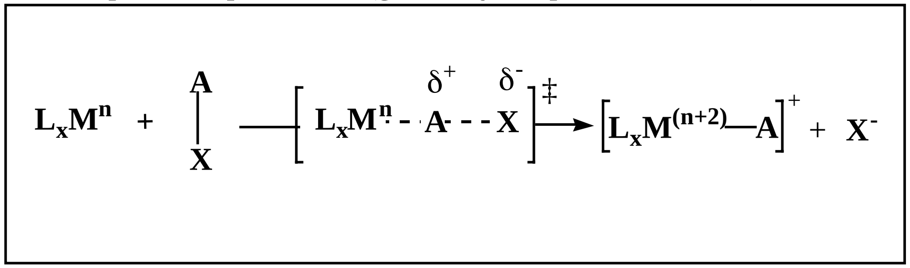




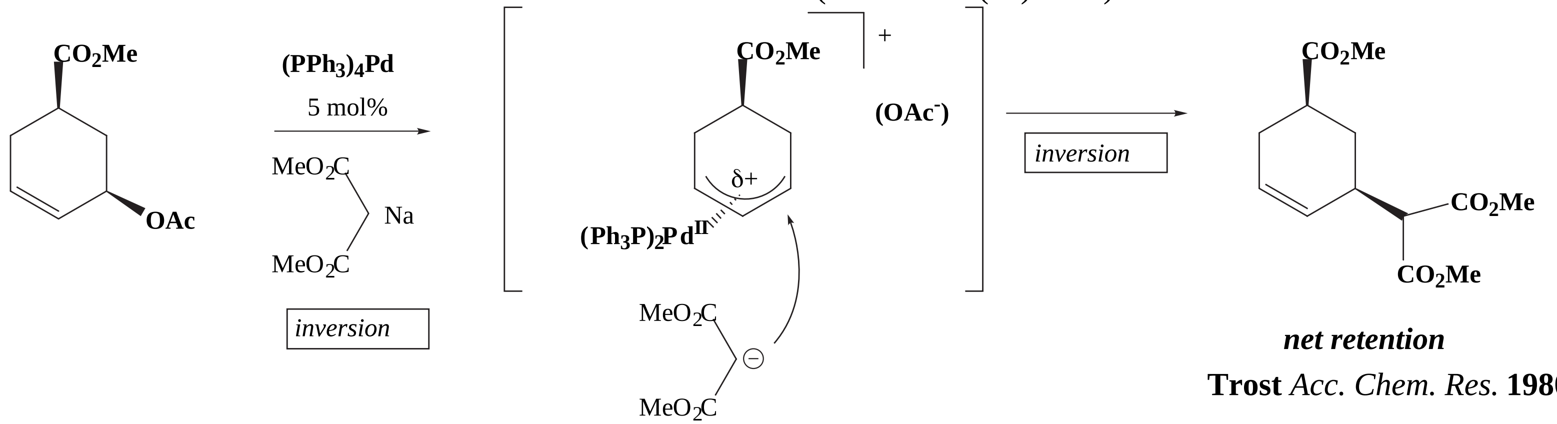
Foa and Cassar *J. Chem. Soc Dalton* **1975** 2572.

OA: C_{sp3}-X:alkyl, allyl, and benzyl halides

Nucleophilic displacement (generally for polar substrates)

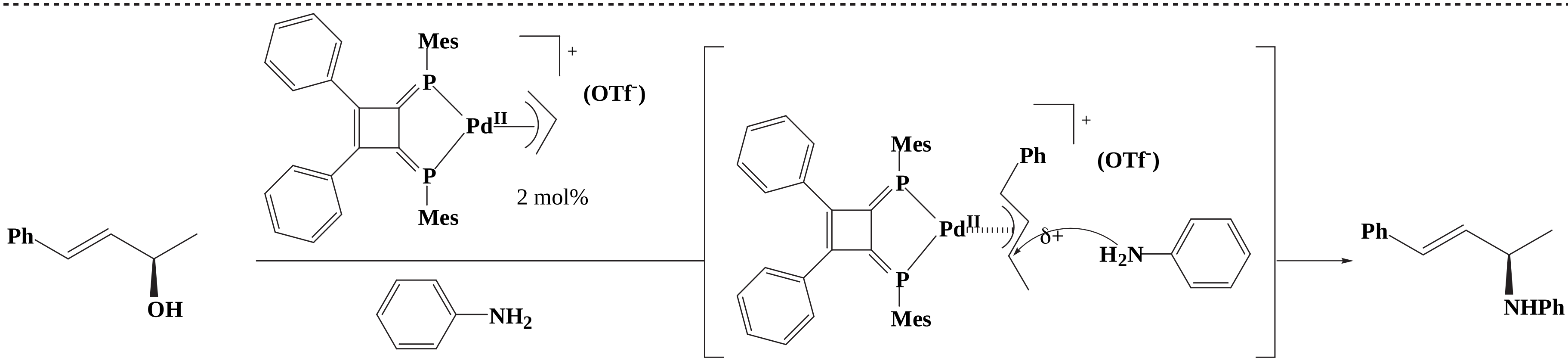


" Stereochemistry is the single most valuable type of mechanistic evidence in reactions that make or break bonds to tetrahedral carbon." G.M. Whitesides (*JACS* **1974** (96) 2814).



net retention

Trost *Acc. Chem. Res.* **1980** (13) 385.



Ozawa *JACS* **2002** (124) 10968.

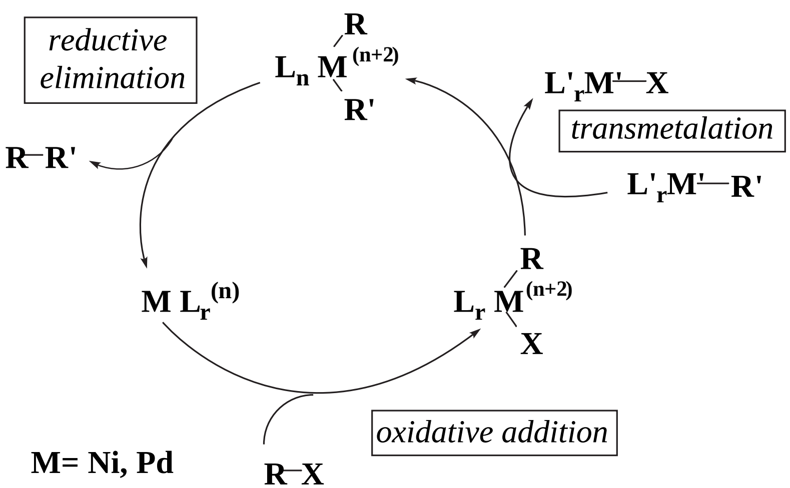
Transmetalation: Definition and Utility

Definition: the transfer of an organic group from one metal center to another. The process involves *no formal change in oxidation state* for either metal.

$$L'_nM'{-}R' + L_nM{-}X \xrightleftharpoons[]{} L'_nM'{-}X + L_nM{-}R$$

Transmetalation

Transmetalation is often a reversible process, with the equilibrium favoring the more ionic M-X bond. Subsequent reactivity of one L_nM-R species can drive the equilibrium in one direction. This is often exploited in cross-coupling reactions, where a transmetalated intermediate undergoes a reductive elimination to generate a new organic product. Subsequent oxidative additions generates a new substrate for transmetalation



Commonly used transmetalation reagents and their associated cross-coupling reaction

$$R\text{-}M^1 + X\text{-}M^2 \rightarrow X\text{-}M^1 + R\text{-}M^2$$

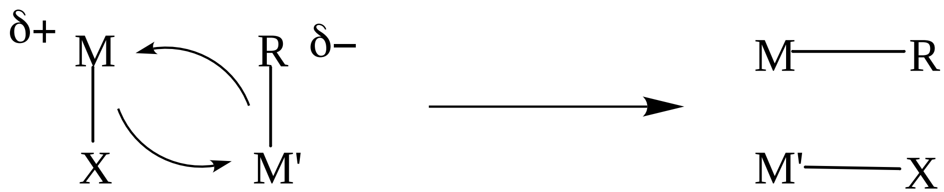
M^2 is typically group 10

Reagent	R	X-coupling reaction
LiR, MgXR	vinyl, aryl, allyl, alkyl	Kumada
$RZrClCp_2$	vinyl, alkyl	
RZnCl	vinyl, aryl, alkyl	Negishi
$RCuL_n$	alkynyl, aryl	e.g. Sonagashira
$RSnR'_3$	vinyl, aryl, alkynl	Stille
$RB(OR')_2$	vinyl, aryl	Suzuki
R-9BBN	alkyl	Suzuki-Miyaura
$RSiR'_3$	aryl, vinyl ,alkyl	Hiyama
AlR_2, AlX_2	alkyl	

In general the rates of transmetalation of R follow the order :alkynyl> aryl,vinyl>alkyl

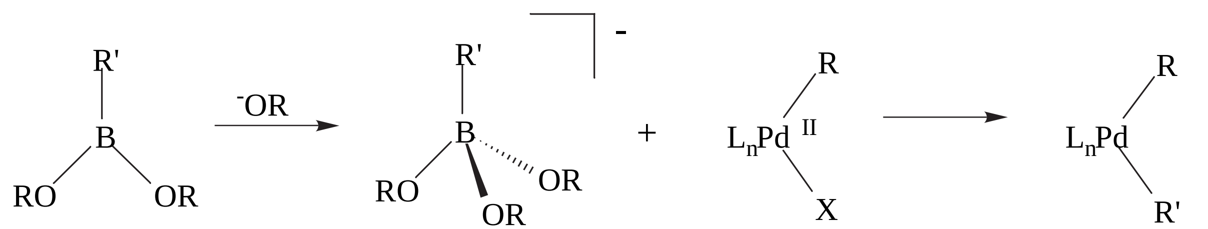
Transmetalation: Mechanism

The mechanism for transmetalation is the least-studied of the basic reaction steps. In a simple picture, the metal accepting the R group is the electrophile and the M-R bond being transferred is the nucleophile. M-R bond formation may or may not be simultaneous with M'-X bond formation, depending on the nature of X and the actual complexes involved.



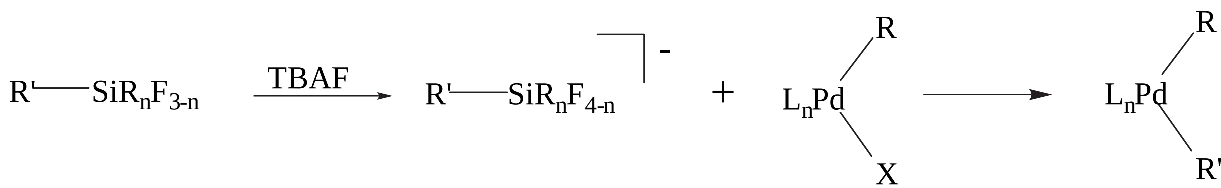
With this model, increasing the nucleophilicity of R by altering the ligands on M' and increasing the electrophilicity of M through its ligands will facilitate the transmetalation step. For weakly nucleophilic transmetalation reagents, an added nucleophile or base often facilitates the transmetalation.

Transmetalation with the Suzuki coupling often requires added base



Suzuki *Chem. Rev.* **1995** (95) 2457.

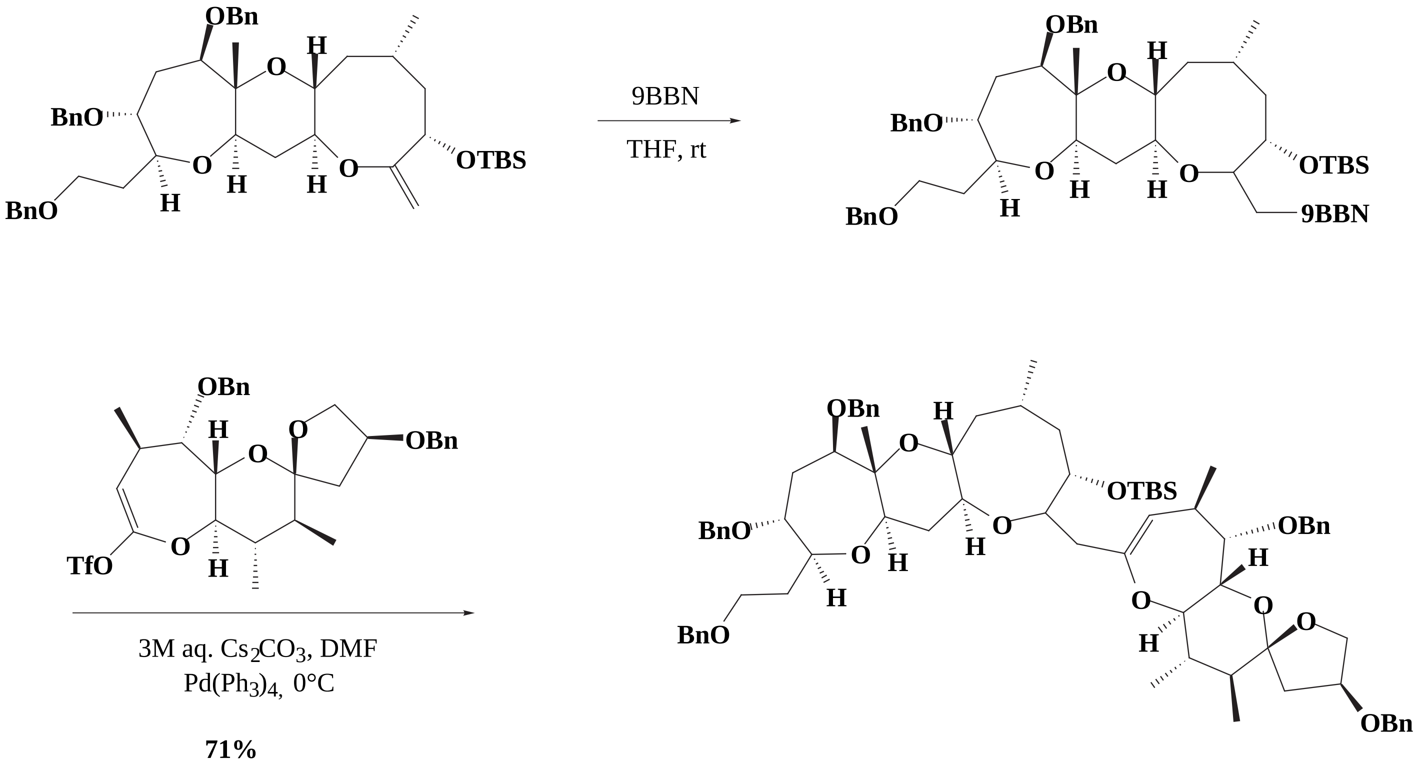
F⁻ is thought to activate the organosilicon reagent for transmetalation *via* formation of a nucleophilic pentavalent silicate in a Hiyama coupling



Hiyama *Tet. Lett.* **1990** (31) 2719.

Transmetalation with advanced intermediates

Suzuki-Miyaura



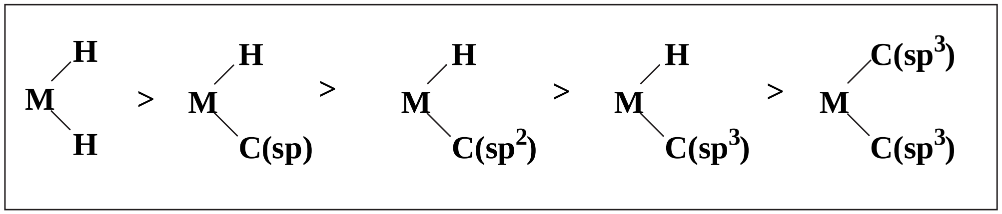
Synthetic studies on Ciguatoxin

Takakura *ACIEE*, **2001** (*40*) 1090

Reductive Elimination

Reductive elimination is a key transformation in transition metal mediated catalysis, often representing the product forming step in a catalytic cycle.

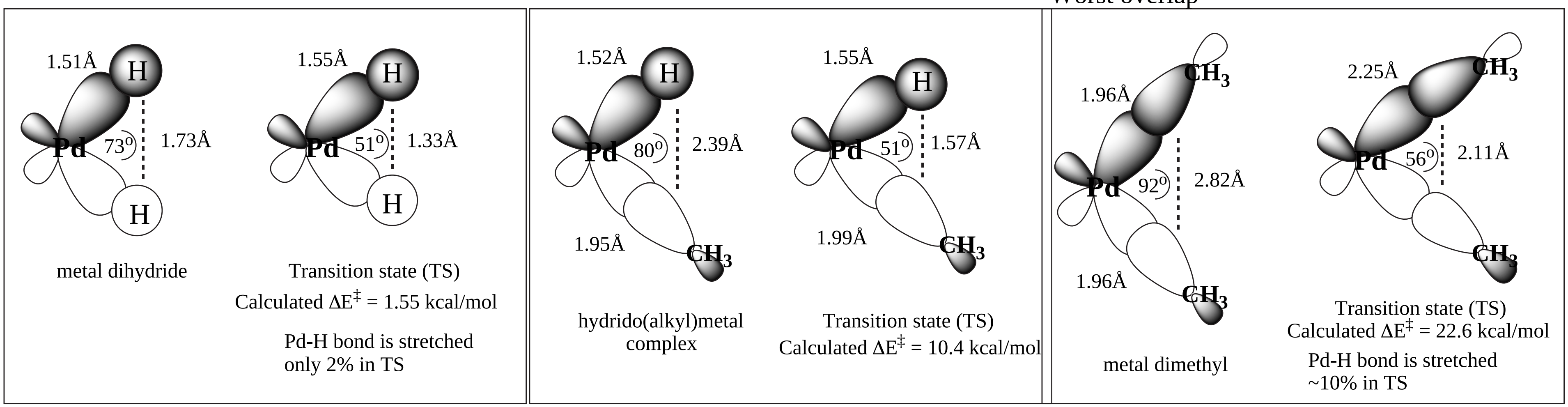
General trend for reductive elimination from d^8 square planar complexes:



Orbitals with more s character are less directional and lead to better overlap in the transition state for reductive elimination (RE). Note: *cis* orientation of the ligands is required for RE to occur.

Best overlap

Worst overlap



metal dihydride

Transition state (TS)
Calculated $\Delta E^{\ddagger}$ = 1.55 kcal/mol

Pd-H bond is stretched only 2% in TS

hydrido(alkyl)metal complex

Transition state (TS)
Calculated $\Delta E^{\ddagger}$ = 10.4 kcal/mol

metal dimethyl

Transition state (TS)
Calculated $\Delta E^{\ddagger}$ = 22.6 kcal/mol

Pd-H bond is stretched ~10% in TS

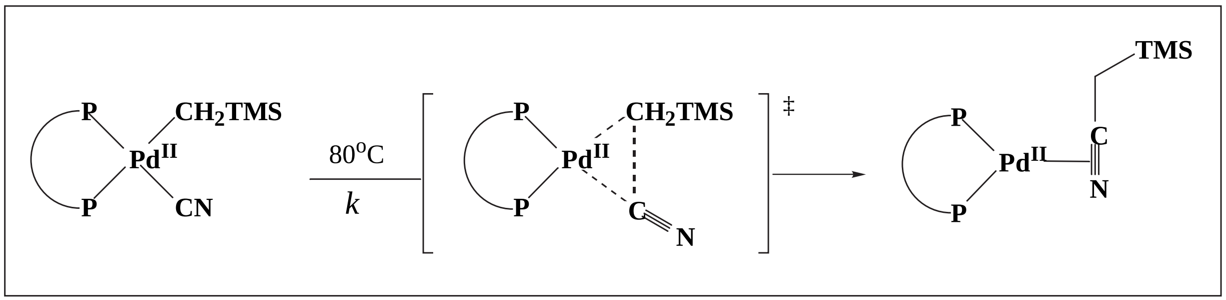
Goddard *JACS* **1984** (106) 8321.
Dedieu *Chem. Rev.* **2000** 543.

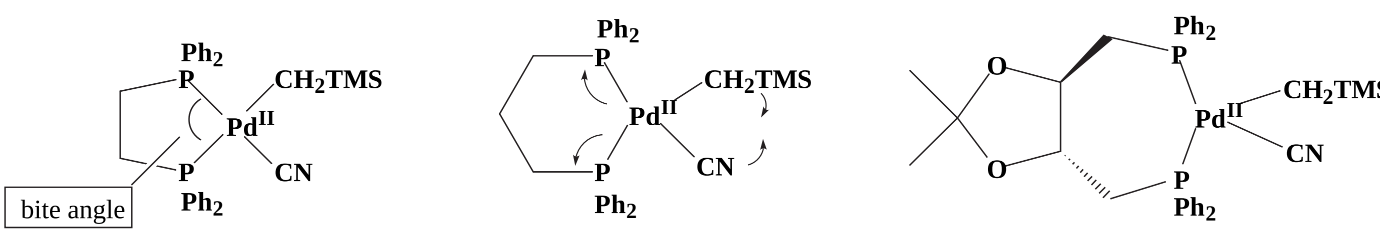
· Computational studies suggest that the spherical symmetry of the s orbitals of H allows the simultaneous breaking of the M-L σ bonds while making the new σ bond of the product.

RE: Bite Angle Effects

RE can be promoted by:

· **Increasing the bite angle of the ligand**
· Increasing electrophilicity of metal center (*e.g.* π-acids)
· Ligand dissociation





bite angle: 85° $k = 2.1 \times 10^{-6}$ | bite angle: 90° $k = 5.0 \times 10^{-5}$ | bite angle: 100° $k = 1.0 \times 10^{-2}$

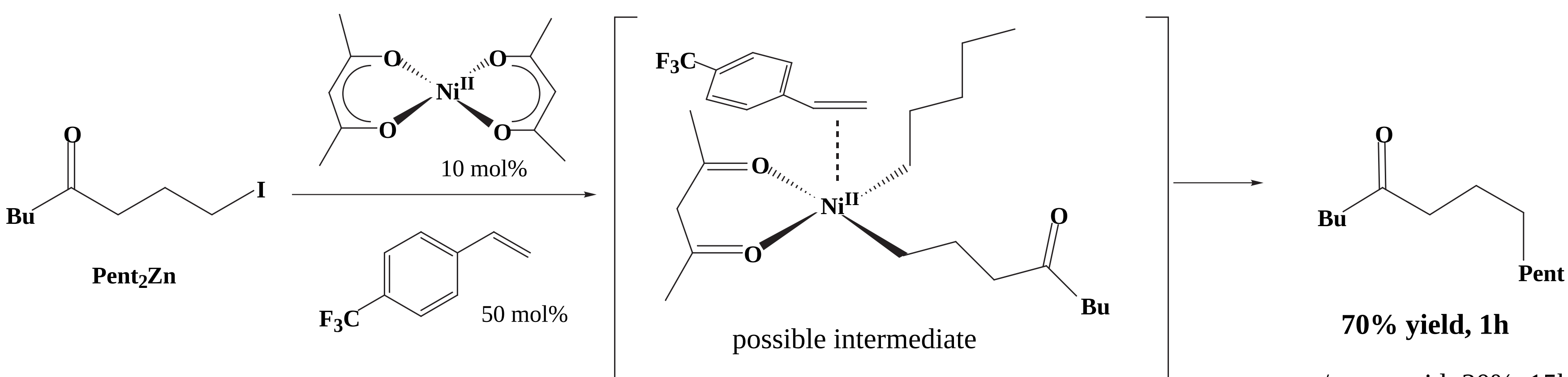
Large bite angles of diphosphines have been shown to enhance the rates of reductive elimination from square planar complexes presumably by bringing the two departing ligands closer together.

Moloy *JACS* **1998** (120) 8527.

RE: π-Acid Effects

RE can be promoted by:

· Increasing the bite angle of the ligand
· **Increasing electrophilicity of metal center (*e.g.* π-acids)**
· Ligand dissociation



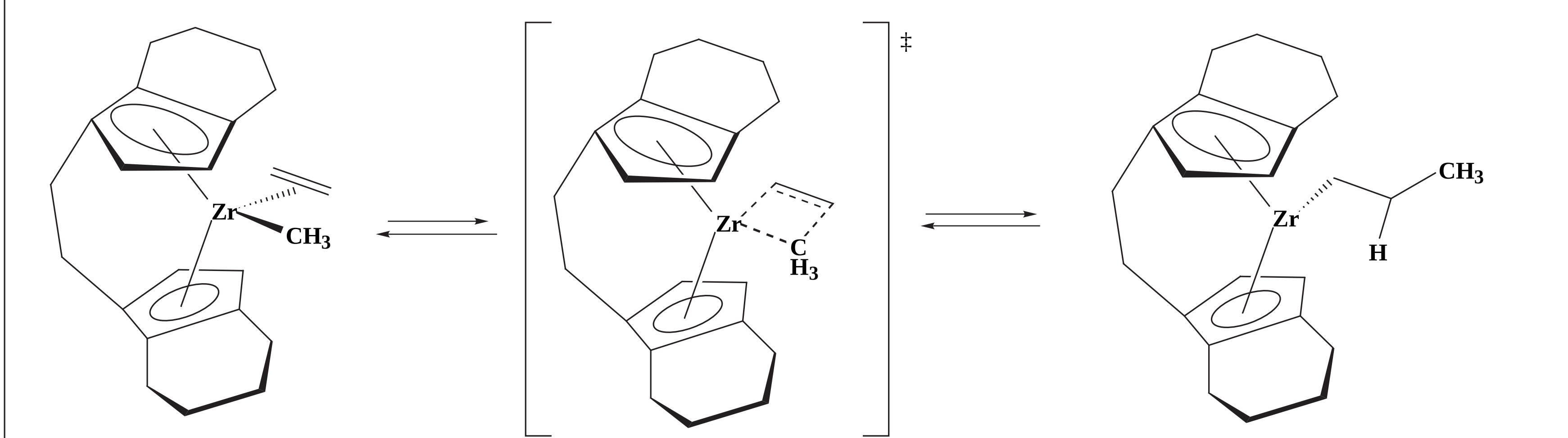
70% yield, 1h

w/out π-acid: 20%, 15h

Knochel *ACIEE* **1998** (37) 2387.

Migratory Insertion/De-insertion: Alkyl, H

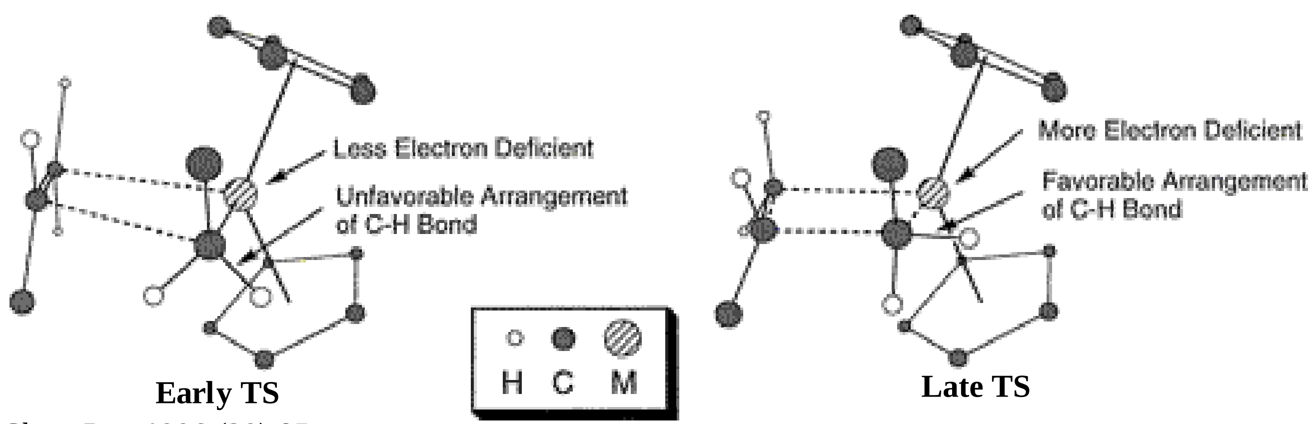
Cossee-Arlman Mechanism for alkyl migration to a coordinated olefin



Brintzinger catalyst for Ziegler Natta polymerizations

- no oxidation state change at M
- -2e from the electron count

The π-bonding electrons of the olefin are used in σ-bond formation with a M-alkyl σ*. Formation of the new C-C and M-C σ bonds are thought to occur simultaneously with breaking of the π-bond and alkyl-M σ bond through a 4-centered concerted transition state. Migratory insertion of a hydride into a coordinated olefin (the microscopic reverse of β-hydride elimination) is thought to procede *via* the same mechanism. For metal alkyls, the equilibrium lies to the right, whereas for metal hydrides it lies to the left.

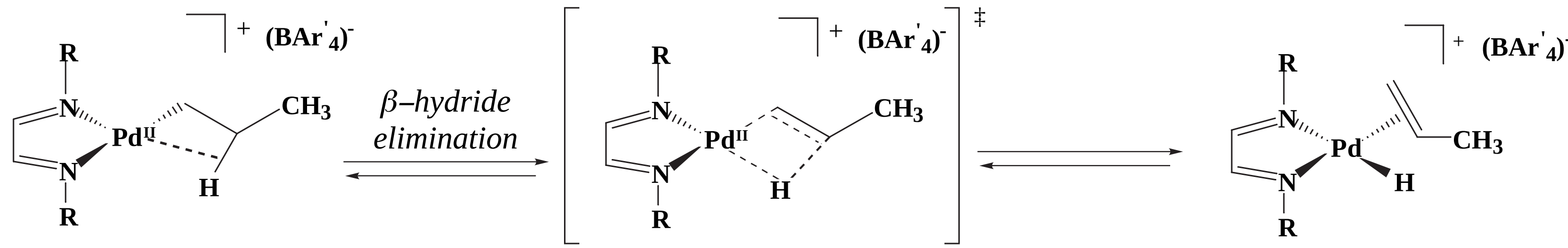


Early TS **Late TS**

Grubbs and Coates *Acc. Chem Res.* **1996** (29) 85.

β-Hydride Elimination

A significant decomposition pathway for metal alkyls is β-hydride elimination which converts a metal alkyl into a hydrido metal alkene complex.

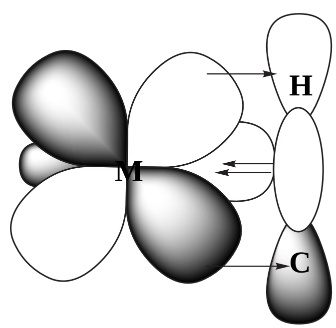


"donative" agostic interaction

concerted transition state

β-hydride elimination can occur when:

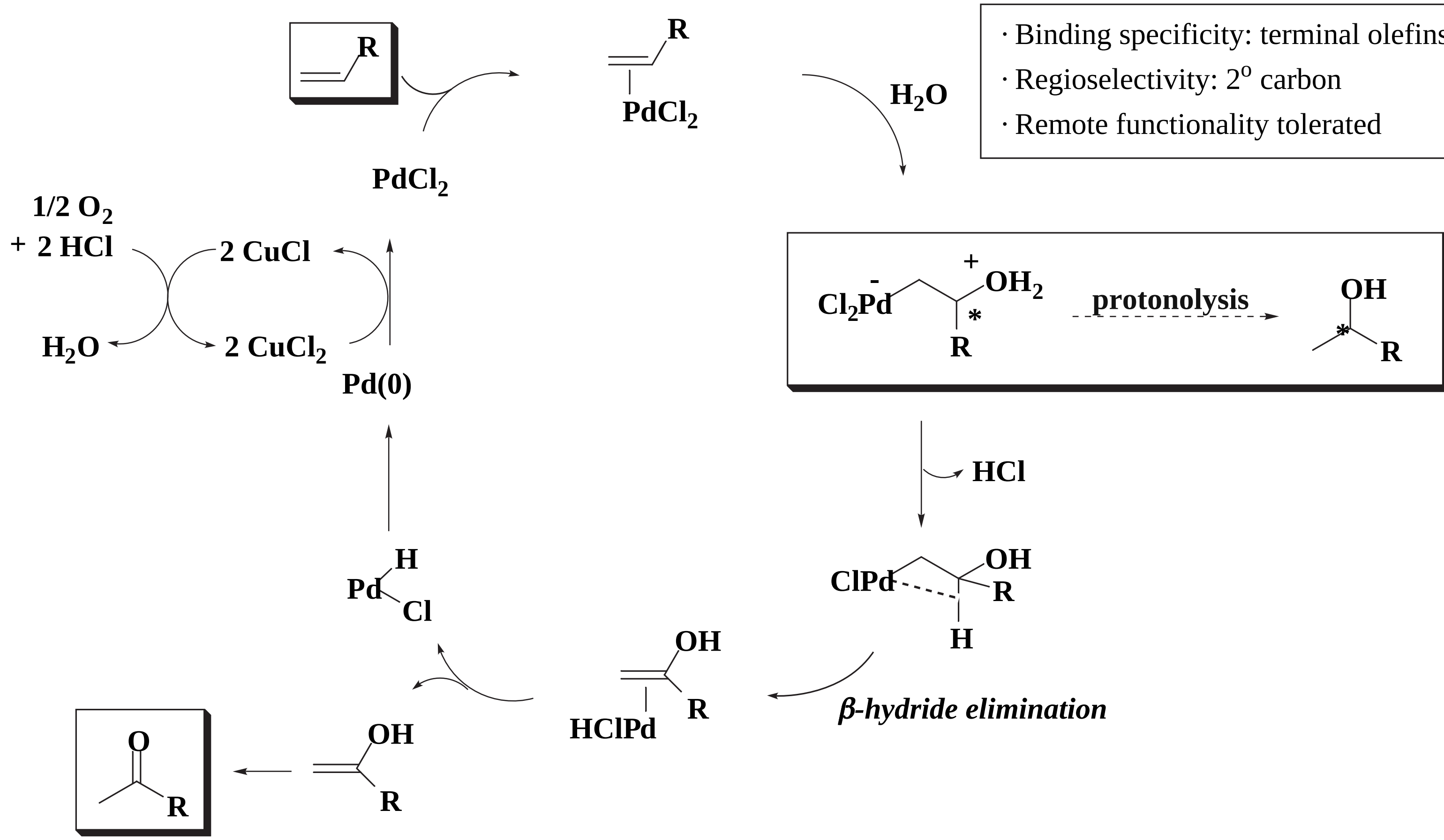
· *cis* to the alkyl group there exists is a site of coordinative unsaturation on the metal which corresponds to a site of electronic unsaturation (empty metal orbital).
· the M-C-C-H unit can take up a coplanar conformation which brings the β-hydrogen in close enough proximity to the metal to form an agostic interaction.
· the metal is electrophilic resulting in an agostic interaction that is primarily electron donative in nature (*i.e.* σ-donation>>π-backbonding).



σ-donation >> π-backbonding

σ-complex

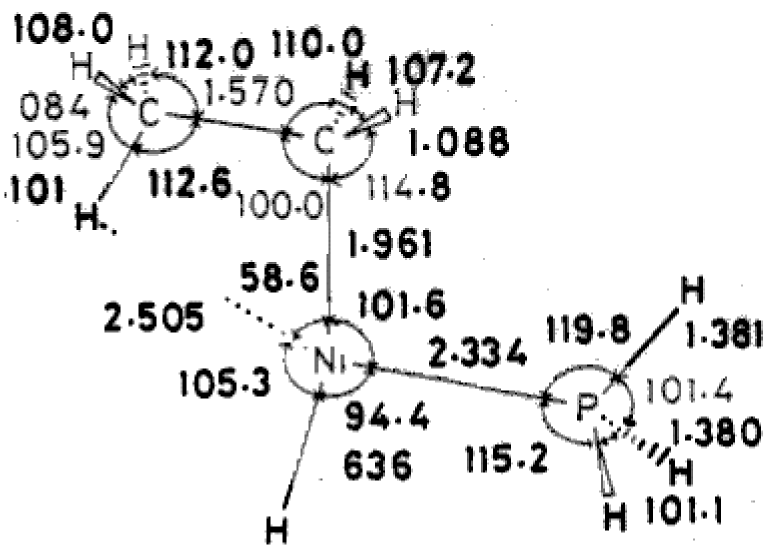
Wacker Oxidation

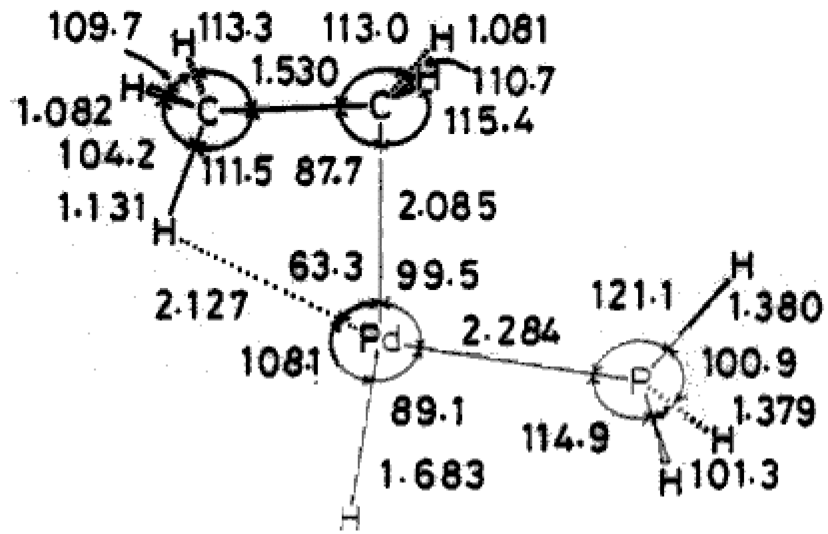


· Binding specificity: terminal olefins
· Regioselectivity: 2^o carbon
· Remote functionality tolerated

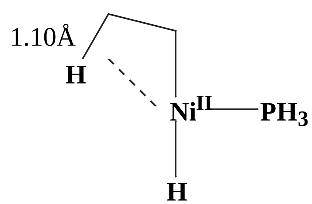
Commericial production of acetaldehyde

β-Hydride Elimination



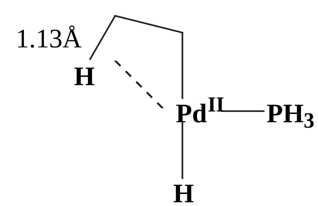


Computational studies suggest that the higher energy of the Ni(II) vacant d orbital (0.1069 hartree) with respect to that of the analogous Pd(II) complex (0.0505 hartree) results in a weaker donative agostic interaction with the βCH σ bond. The energetically optimized geometries of the agostic complexes show a greater lengthening of the βC-H bond in the Pd(II) complex than in the Ni(II) complex, indicative of greater σ-donation in the former. These computational results are consistent the experimentally observed greater stability of Ni alkyls towards β-hydride elimination that Pd alkyls and can be rationalized based on the greater electronegativity of Pd(II) vs Ni(II) as reflected in their respective second ionization potentials.



second ionization potential
Ni(II): 18.15 eV

recall: sp^3 C-H is 1.09Å

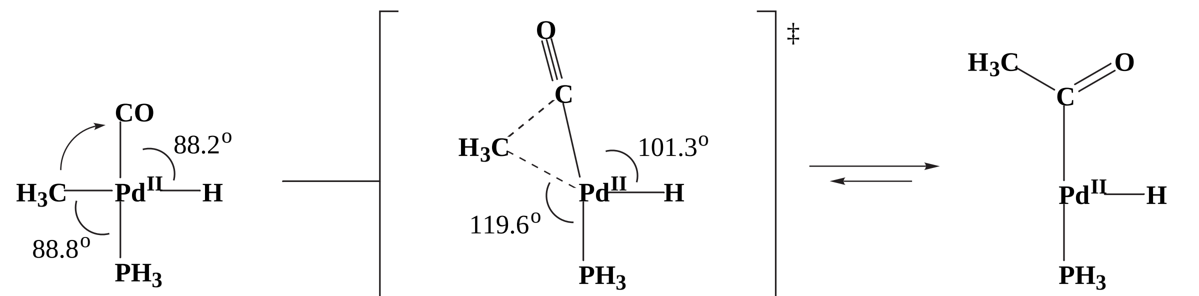


second ionization potential
Pd(II): 19.9 eV

Morokuma *JACS* **1985** (107) 7109.

Migratory Insertion/De-insertion: CO

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



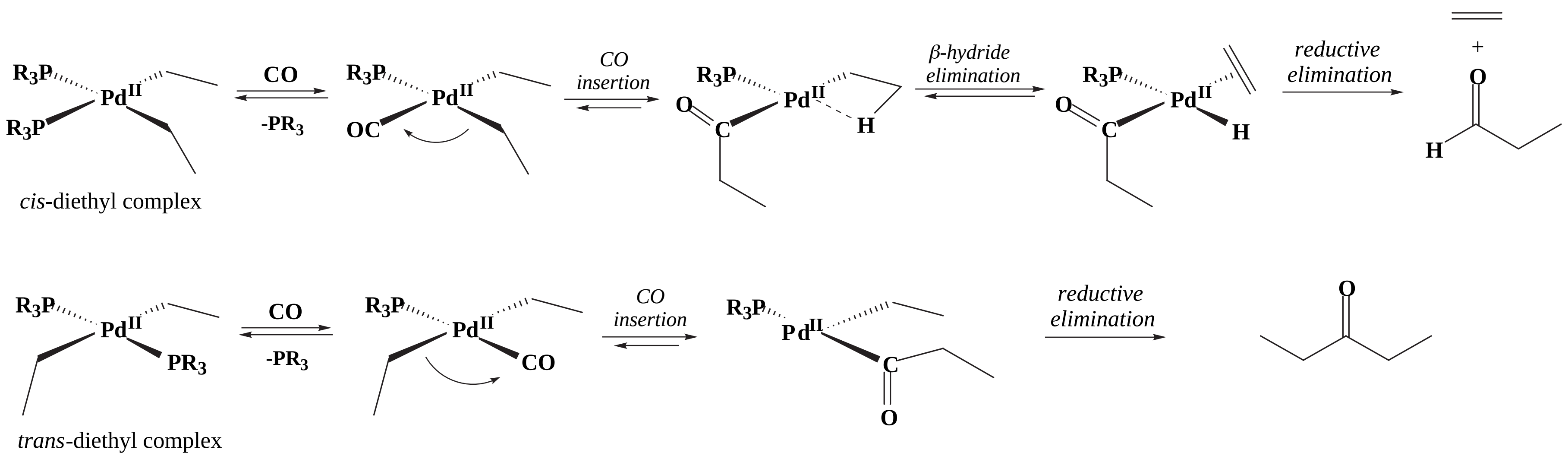
alkyl groups migrate preferentially over hydrides

Computational studies suggest that in the TS, the methyl group has moved up half way towards the carbonyl.

·no oxidation state change at M
· -2e from the electron count

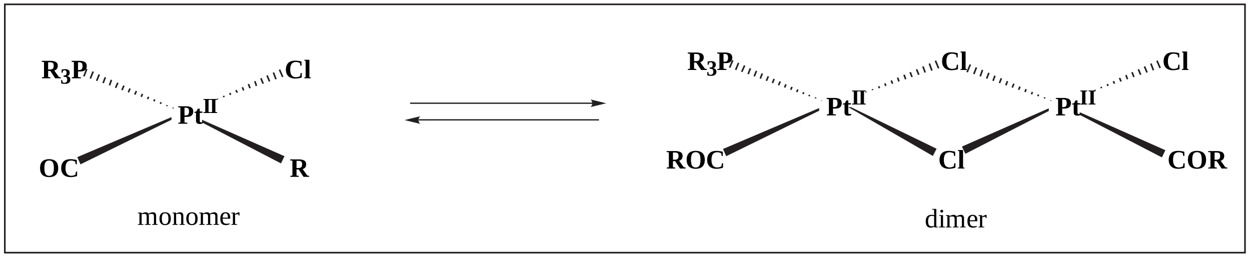
Morokuma *JACS* **1986** (108) 6136.

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



Yamamoto *Chem. Lett.* **1981** 289.

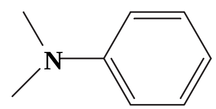
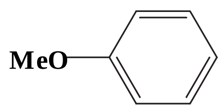
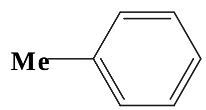
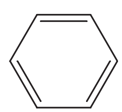
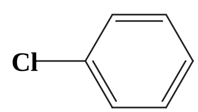
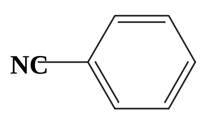
Migratory Insertion/De-insertion: CO



(no dimer observed) $-C\equiv C-$Ph < $-C\equiv C-$Me < CH_2Ph < Me < Ph < Et

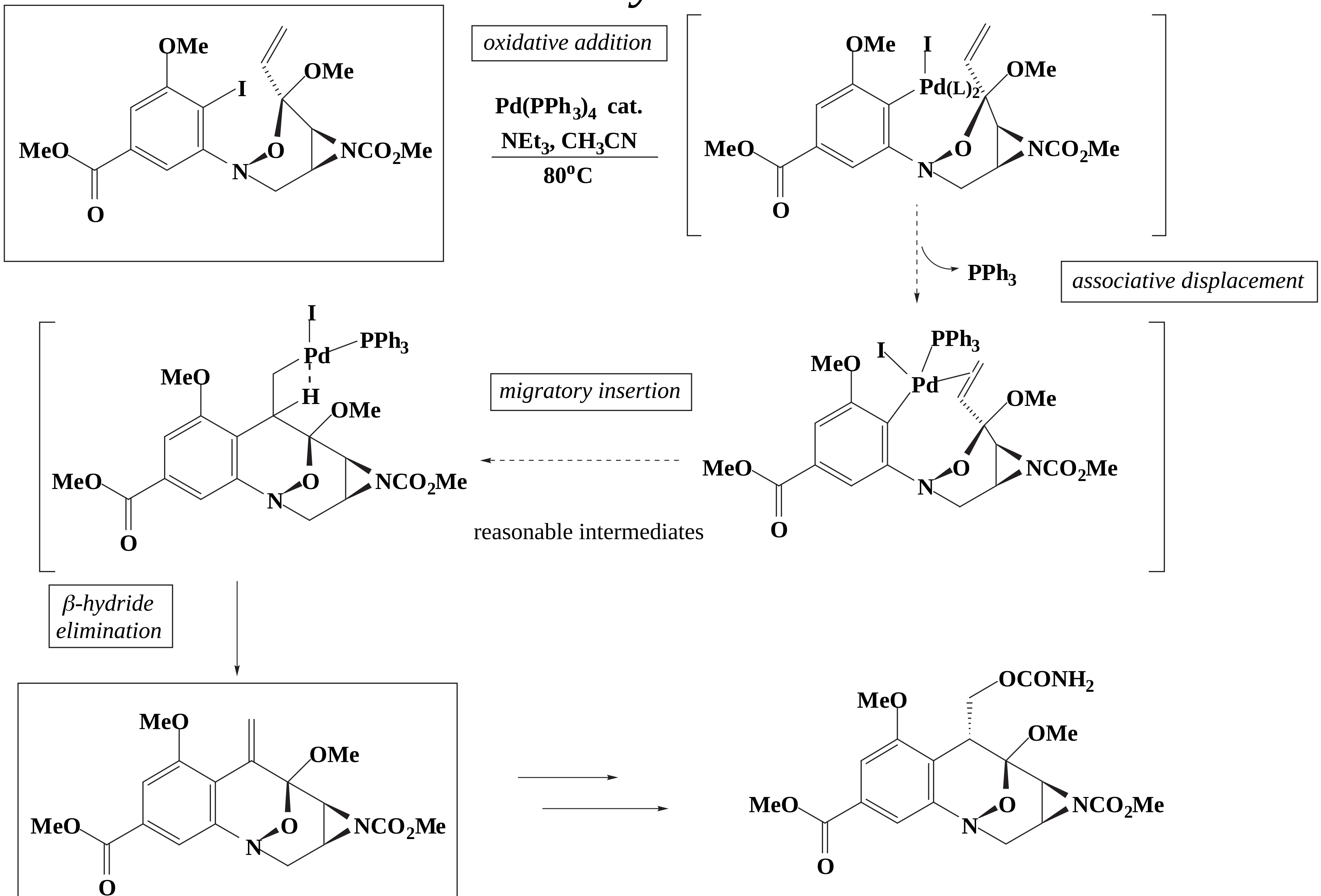
Anderson *Acc. Chem. Res.* **1984** (17) 67.

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.

Heck Arylation



(±)-FR-900482

Danishefsky *JACS* **1993 (**115) 6094.