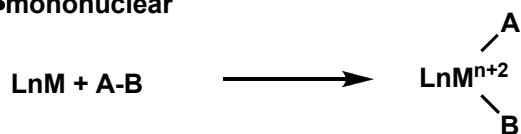


Chapter 6: Oxidative Addition of Nonpolar Reagents

6.1. General

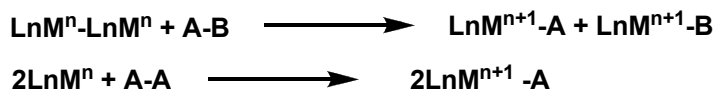
•mononuclear



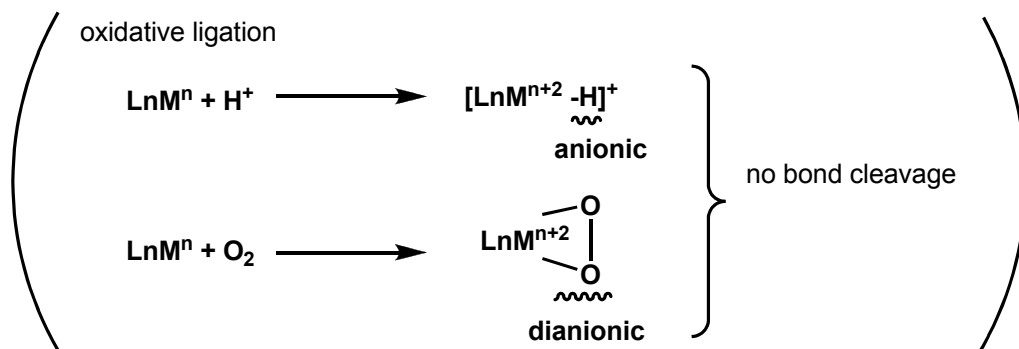
Metal: two electron oxidation

cf. Grignard reagent formation
Carbene insertion

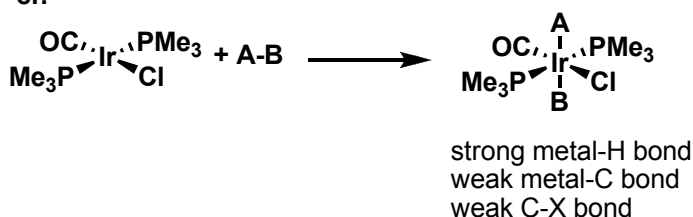
•dinuclear



Metal: one electron oxidation $\times 2$



A-B bond < M-A bond + M-B bond
cf.



A-B	ΔH kcal/mol	ΔG kcal/mol
H-H	-15	-6
CH ₃ -H	-2	+3
CH ₃ -CH ₃	-4	+6
CH ₃ -I	-35	-25

* estimated values

Qualitative trends for oxidative addition

- metal center : electron rich ————— electron poor
 oxi. add. : fast ————— slow
 (red. elim. : slow ————— fast)
 (partial positive charge at the metal during the process)

- Less hindered metal centers are favorable.
 (increased steric hindrance after an oxi. add.)

(red. elim. : More hindered metal centers are favorable)

- for nonpolar reagents { Requires a site of unsaturation.
less than 16e at the metal center

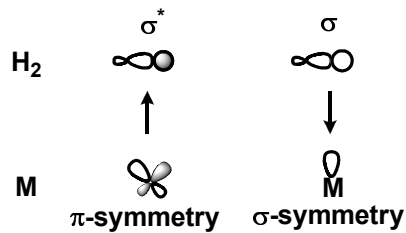
- Rate of ligand dissociation affects the overall rate.

slower		faster
bidentate		monodentate
strongly bound monodentate		weakly bound monodentate

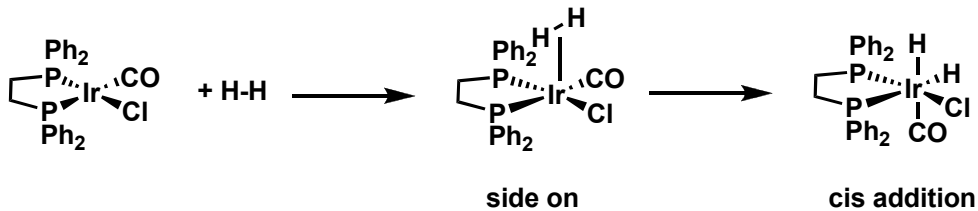
6.2. Oxidative Addition of H₂

single metal center

side on > end on
 cis addition (trans addition is "forbidden")
 "early" transition state



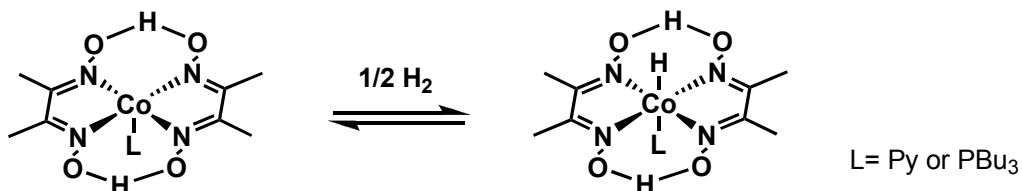
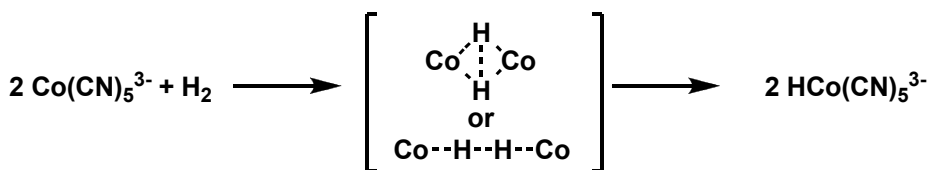
ex.



two metal centers

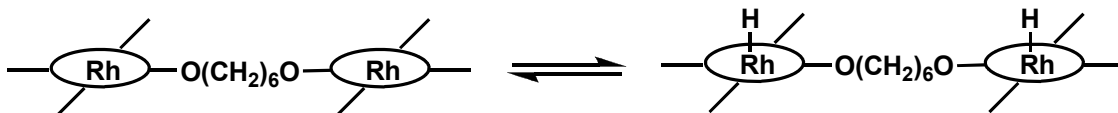
most common with cobalt complex

ex.



$$\text{rate} = k[\text{H}_2][\text{M}]^2$$

The transition state would be formed by combination of H₂ and two metal centers.



Preorganization enhances the rate : 10³ faster than (TMP)Rh

J. Am. Chem. Soc. 1994, 116, 7897.

6.3. Oxidative Addition of Si-H

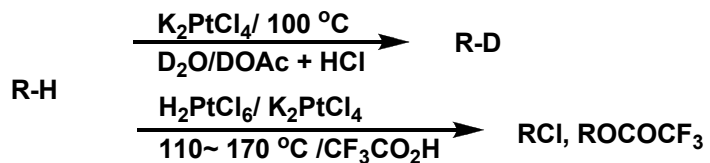
similar mechanism to H₂ oxidative addition
 stereochemistry at Si : retention

6.4. Oxidative Addition of C-H

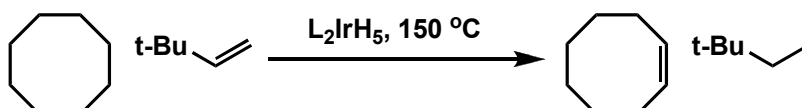
non-radical processes
 via alkane σ -complexes } is the most common

early examples

Shilov's early example

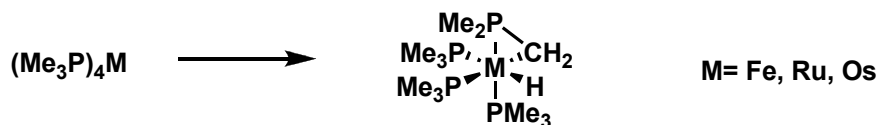
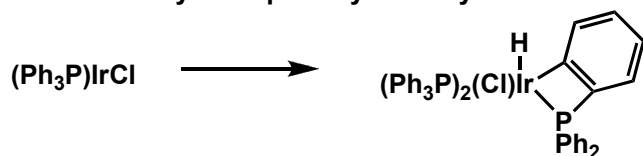


dehydrogenation



intramolecular

general tendency: Ar > primary > methylene



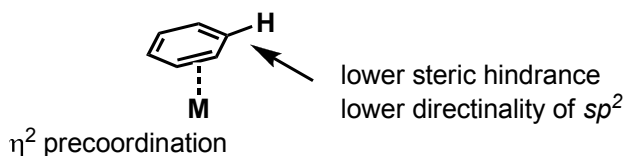
cyclometallation

- deactivation pathway
- can be a stable precursor of active catalyst
- can be a active species (less common) (*J. Am. Chem. Soc.* 2003, 125, 14272.)

intermolecular

arene > alkane (both kinetically and thermodynamically)

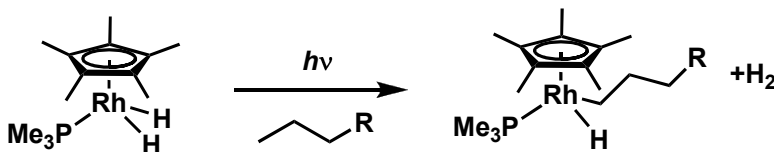
The difference between M-aryl and M-alkyl is larger than H-aryl and H-alkyl.



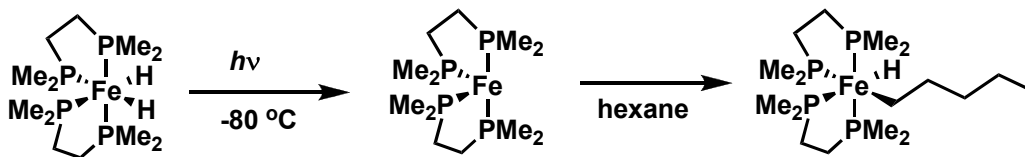
Metal alkyl-hydride complexes are known for group 7-10. (Re, Fe, Rh, Ir, Pt...)

The greater strength of M-C bonds of third-row transition metal makes the oxid. add. common.

Rh and Ir with Cp, anion ligand, PCP-pincer constitute major examples.



Additions to group 8-10 metals with chelating alkylphosphines are known.



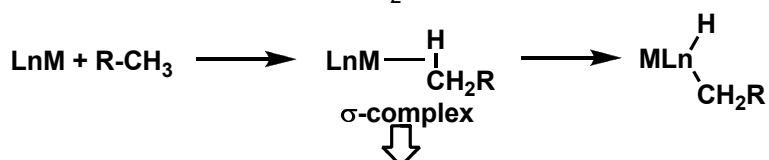
Alkane oxidative addition

- high selectivity at primary C-H (contrast with radical, metal carbene)

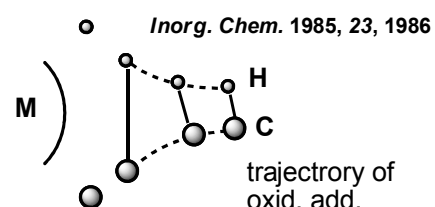


Mechanism

same orbital interaction as H_2



not directly observed but supported by several data



Kinetic selectivity for primary C-H is unclear. (ex. 64 times faster than secondary)

$\text{Cp}^*\text{Ir}(\text{PMe}_3)$: not selective

$\text{Cp}^*\text{Re}(\text{PMe}_3)_2$, $\text{Cp}^*\text{Rh}(\text{PMe}_3)$: highly selective

Methods to generate unsaturated intermediates

photolysis of M-CO or MH_2 ($\text{Cp}^*\text{Ir}(\text{CO})_2$)

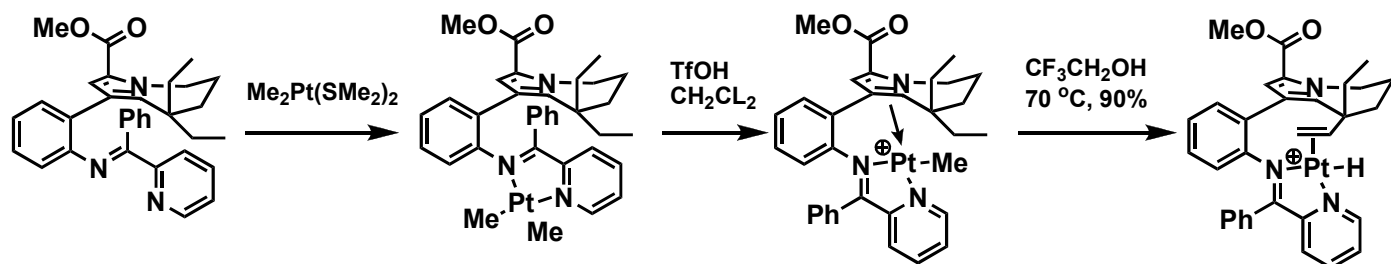
thermolysis of alkyl hydride complex

abstraction of halide (addition of $\text{AgB}(\text{Ar}_f)_4$)

protonation of alkyl complex

Application

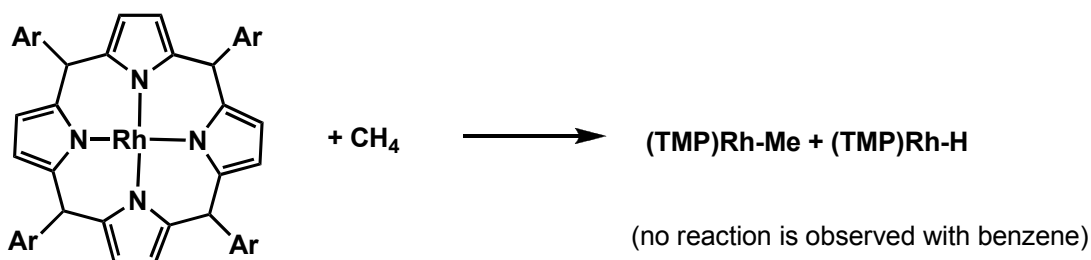
synthesis of rhazinilam



Dinuclear activation of C-H

rare example

process is similar to H_2 oxid. add.



6.5. Other than oxidative addition

d^0 Metals cannot undergo oxidative addition.

σ -Bond metathesis or [2+2] reactions.

σ -bond metathesis

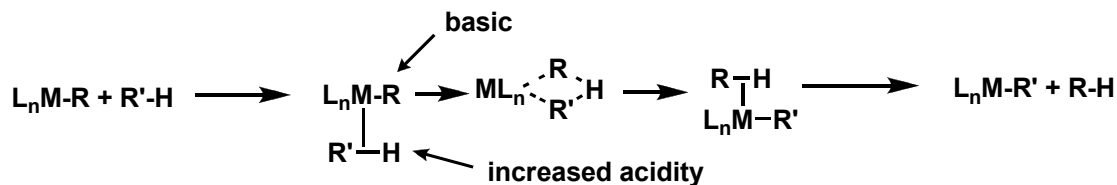


common among d^0 transition metal (lanthanide, actinide, main group compounds)

multi-step sequence

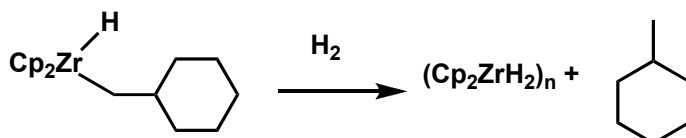
requires a site of unsaturation

The reactivity of σ -bond metathesis of H_2 , C-H, Ar-H parallels the reactivities of oxid. add.



lower stability than late metals

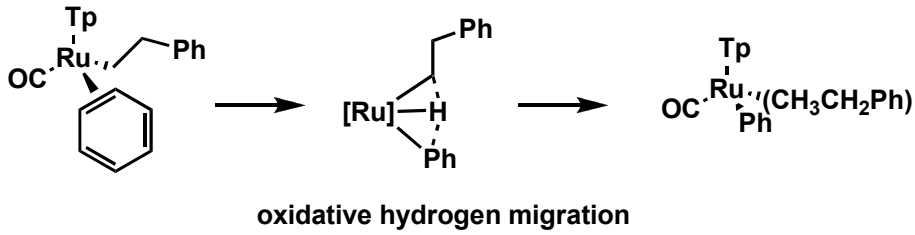
$[\text{CpRu}(\text{dmpe})(\text{H}_2)]^+$: pKa 17.6 in MeCN



Even late transition metals can undergo σ -bond metathesis in some cases.

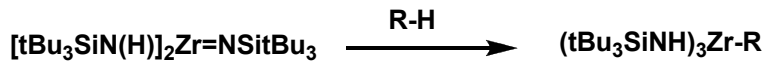
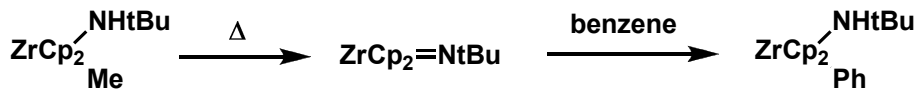
More common with H_2 than C-H heterolytic cleavage.
(Due to higher acidity and stability of dihydrogen complexes.)

The amount of M-H bonding is a one determining factor.



[2+2] additions with M=N or M=C complexes

ex. Ti, Zr, Ta, W

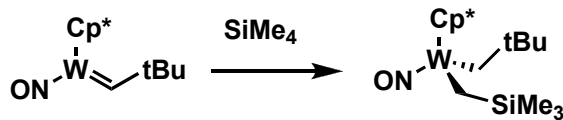


Ti=N complex

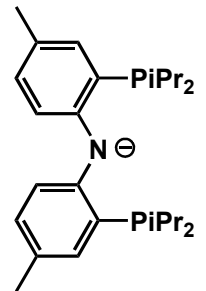
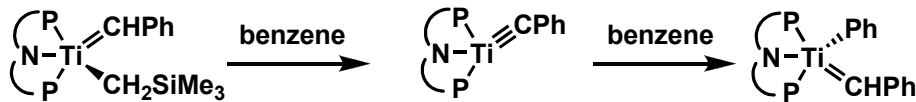
kinetics: primary > secondary
arene > alkane

thermodynamics: primary > secondary
aryl complex > alkyl complex

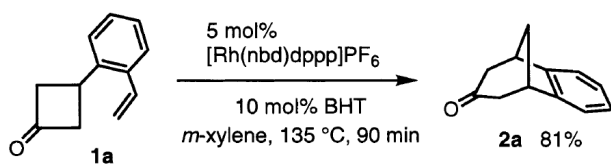
carbene complex



alkylidyne complex

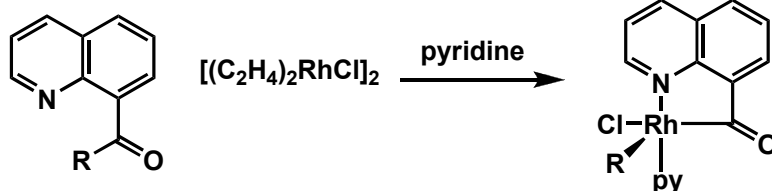


6.6. Oxidative Addition of C-C strained ring system

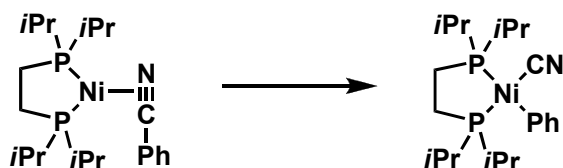


J. Am. Chem. Soc. 2002, 124, 13976

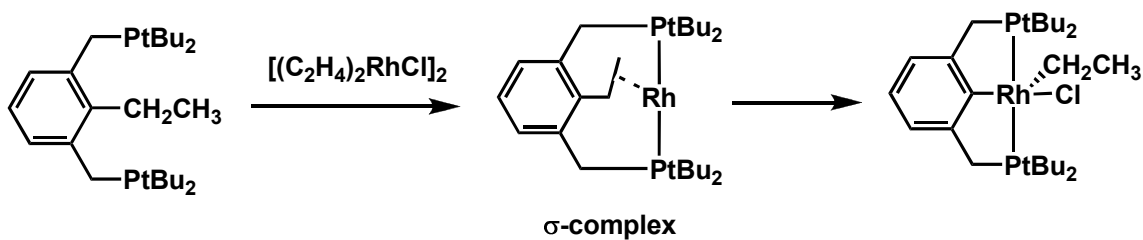
ligating group



exception: aryl nitrile

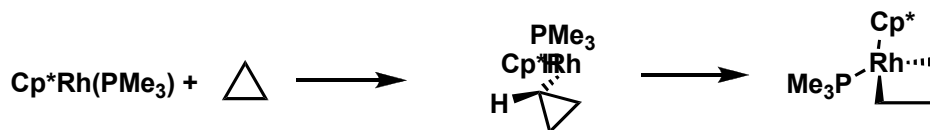


PCP pincer complex



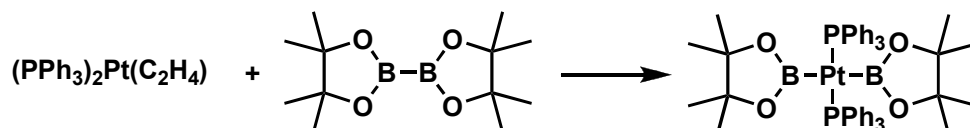
M-C(sp^2) has higher stability than M-C(sp^3).

relative rate of C-H or C-C insertion depends on substrates and complex



6.7. Oxidative Addition of E-E

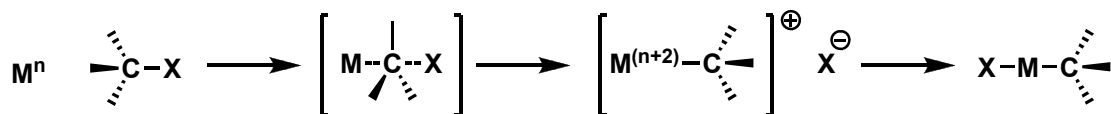
Oxidative addition to Si-Si, B-B, Si-B, Sn-B is easier.



Chapter 7: Oxidative Addition of Polar Reagents

7.1. S_N2 Pathways

Metal acts as a nucleophile.

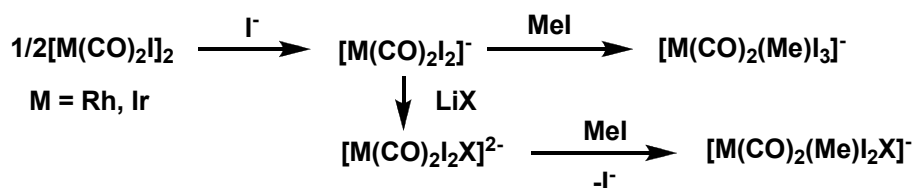


- faster reaction in more polar solvents
- inversion
- kinetics are second order
- relative rate: Me > 1° > 2° >> 3° ; I > Br > Cl >> F



Na₂Fe[CO]₄ : d¹⁰ "supernucleophile"
It can react with neopentyl chloride.

Precoordination of an anion to a neutral metal can accelerate the oxid. add.
(The origin of the effect was unclear...)

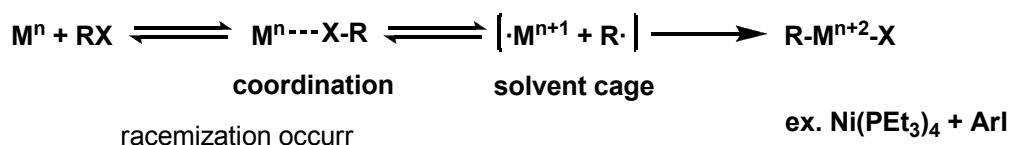


7.2. Radical Pathway

- weaker and more-hindered electrophiles
- coordinatively saturated metal centers
- metal complexes which are prone to undergo one-electron oxidation (most common with first low metals)

(aryl sulfonates : non-radical pathway)

Inner-Sphere Electron Transfer



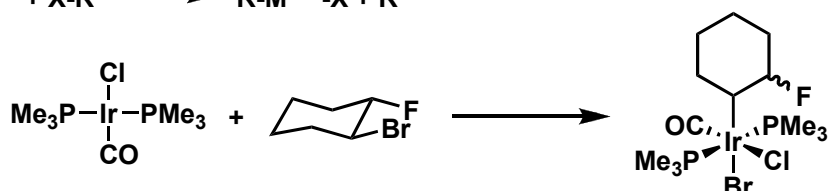
Radical Chain Pathway

require coordinatively unsaturated metal center
initiator: trace impurities, trace O₂, light induced radical etc.

initiation

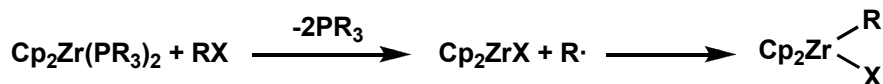
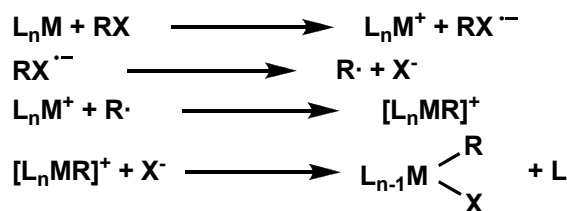


propagation



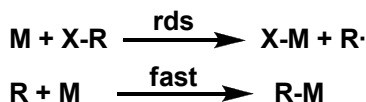
Outer-Sphere Electron Transfer

metal: coordinatively saturated
 electrophile: susceptible to electron transfer
 sterically hindered
 weak C-X bond

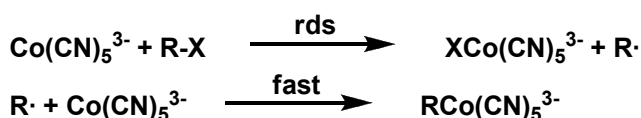


Atom Abstraction and Combination of the Resulting Radical with a Second Metal

facile one-electron oxidation
 slow two-electron oxidation
 generates the two products



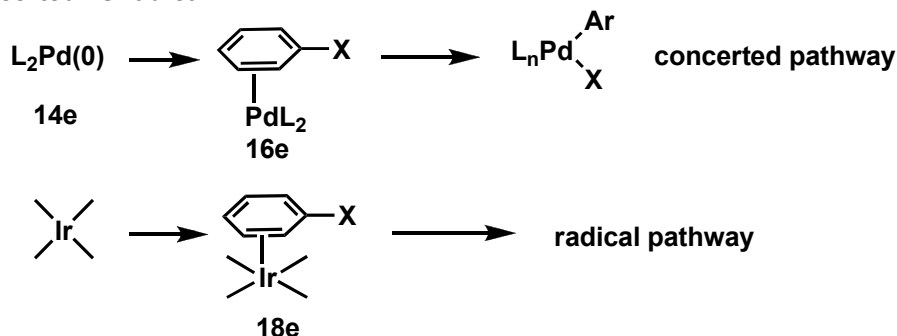
Ligand: the bulkier the slower
 Electrophile: RI > RBr >> RCl



7.3. Concerted Oxidative Addition

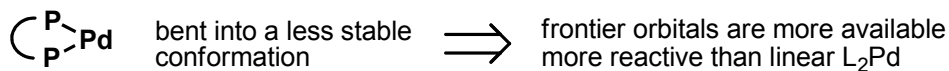
oxid. add. to ArX

concerted vs radical



palladium complex

typically occurs to a 14-electron complex



highly bulky phosphine ligands: via LPd (12e) or associative mechanism to L_2Pd (14e)

bite angle

small bite angle

faster at the step of C-X cleavage
 less hindered (slower dissociation of ligands)



large bite angle ligands

faster overall multistep oxid. add. process

alkyl vs aryl phosphines

Alkyl phosphines are more reactive due to the higher electron donating nature. (related carbenes also have high reactivity)

reaction rate of R-X: I > OTf > Br > Cl \approx OTs

(but depend on the identity of the metal center)

Added anion can influence the rate of oxid. add. by forming anionic complex.

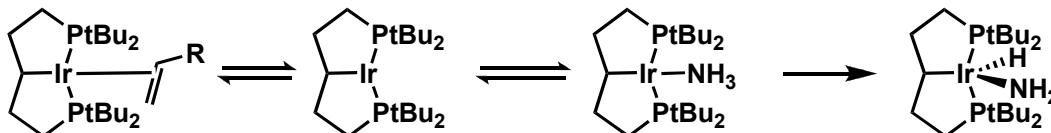
Oxidative Addition of Reagents with H-X Bonds of Medium Polarity

via three-centered transition state or protonation of a basic metal center

protonation pathway

with hindered trialkyl phosphine or mixed alkyl arel phosphine ligands

three-centered transition state

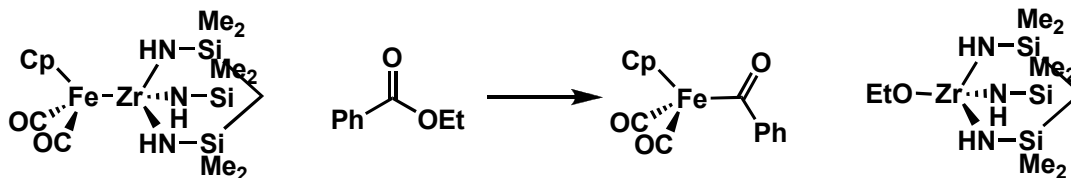
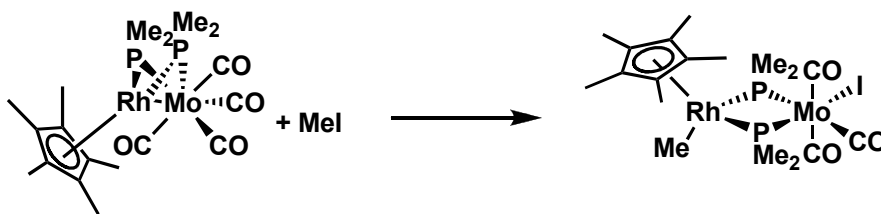


P-H and S-H bonds are more favorable substrate than N-H and O-H.
(weaker X-H bonds, more acidic, stronger M-S, M-P bond)

Oxid. add. of aniline is more common than alkyl amines due to the acidity.

7.4. Dinuclear Oxidative Additions of Electrophilic A-B

Both homodinuclear and heterodinuclear complexes are known.
Mechanism are closely related to those of mononuclear complexes.



early-late heterobimetallic

Summary

MeI : $\text{S}_{\text{N}}2$ pathway

higher alkyl : radical pathway (coordinatively saturated : outer-sphere electron transfer
coordinatively unsaturated: inner-sphere electron transfer)

ArX : Many radical pathways are known, but Pd(0) tends to undergo concerted pathway.

HX : Three-centered transition state is more common.