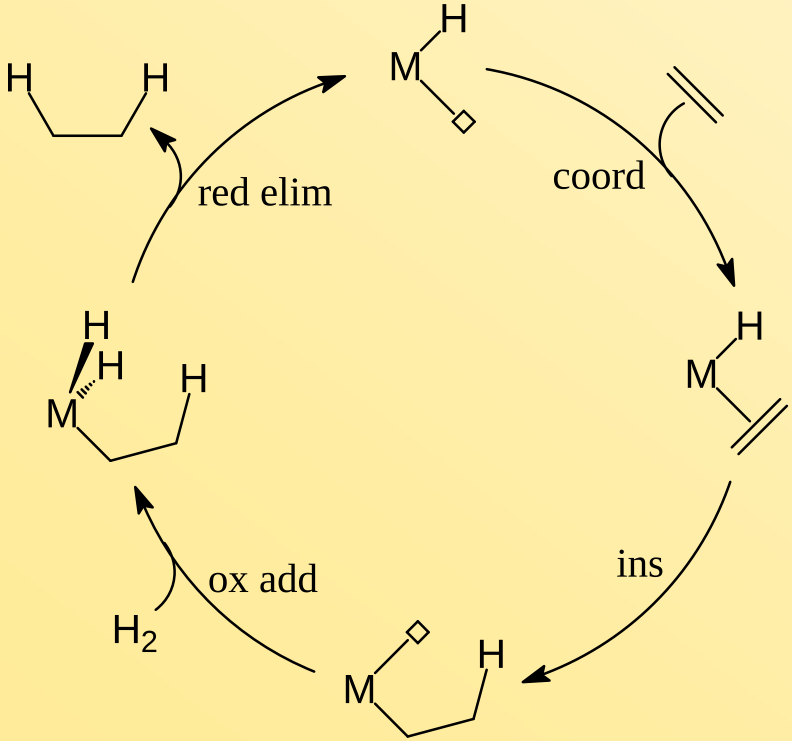
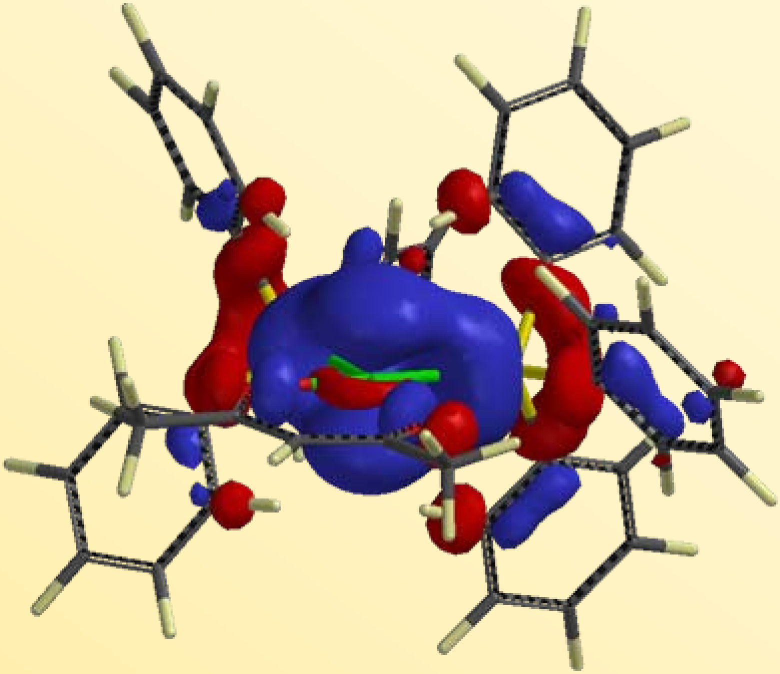
Oxidative Addition and Reductive Elimination





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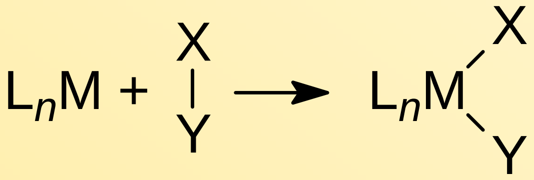
Oxidative Addition

Basic reaction:



The new M-X and M-Y bonds are formed using:

- the electron pair of the X-Y bond
- one metal-centered lone pair

The metal goes up in oxidation state (+2)

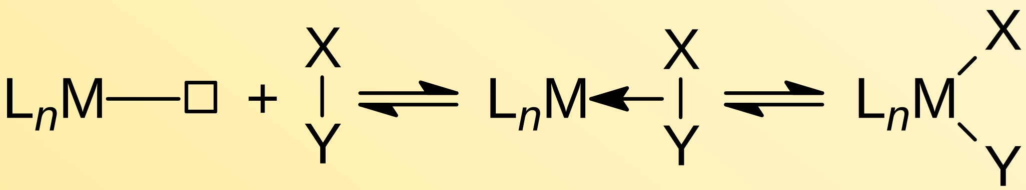
X-Y formally gets reduced to X^-, Y^-

Common for transition metals, rare for main-group metals

One reaction, multiple mechanisms

Concerted addition, mostly with non-polar X-Y bonds

- H_2, silanes, alkanes, O_2, ...
- Arene C-H bonds more reactive than alkane C-H bonds (!)



A

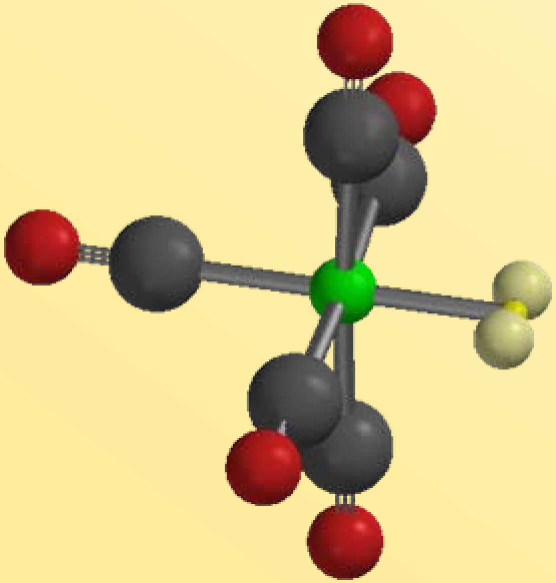
Intermediate ***A*** is a σ-complex.

Reaction may stop here if metal-centered lone pairs are not readily available.

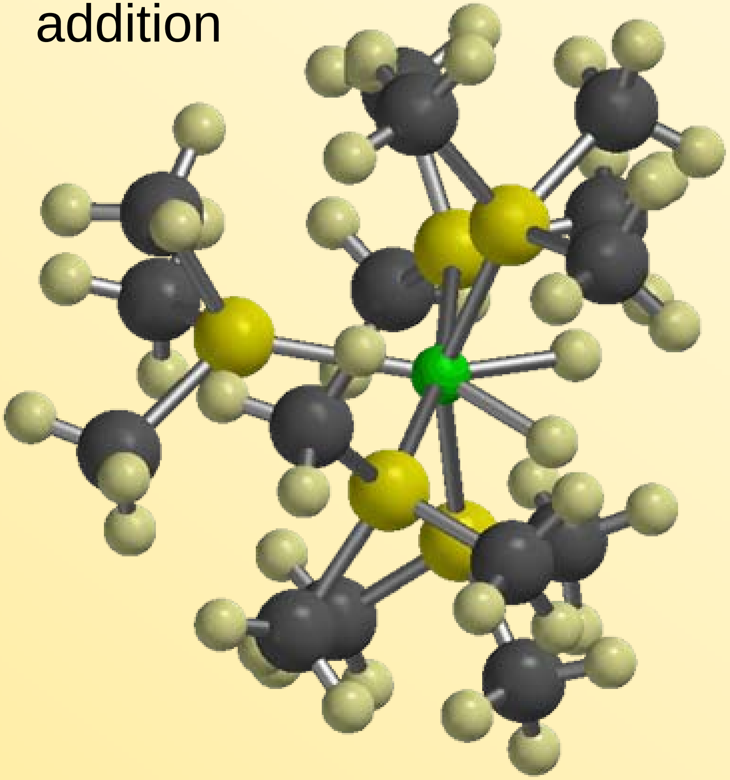
Final product expected to have *cis* X,Y groups.

Concerted addition, "arrested"

$Cr(CO)_5$: coordinatively unsaturated, but metal-centered lone pairs not very available: σ-complex



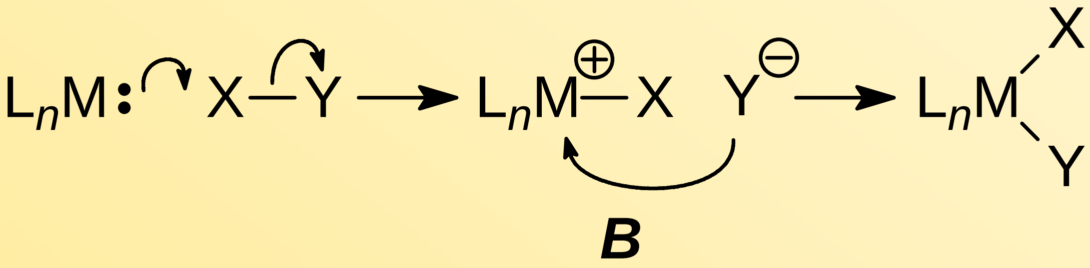
$Cr(PMe_3)_5$: phosphines are better donors, weaker acceptors: full oxidative addition



One reaction, multiple mechanisms

Stepwise addition, with polar X-Y bonds

- HX, R_3SnX, acyl and allyl halides, ...
- low-valent, electron-rich metal fragment (Ir^{I}, $Pd^{(0)}$, ...)



Metal initially acts as ***nucleophile***.

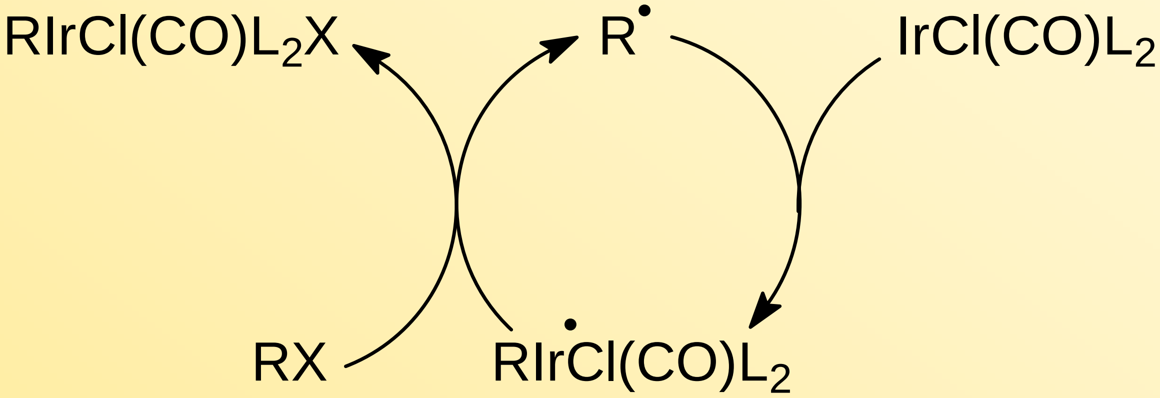
- Coordinative unsaturation less important.

Ionic intermediate (***B***).

Final geometry (*cis* or *trans*) not easy to predict.

One reaction, multiple mechanisms

Radical addition has been observed but is relatively rare



$RIrCl(CO)L_2X$

$R^\bullet$

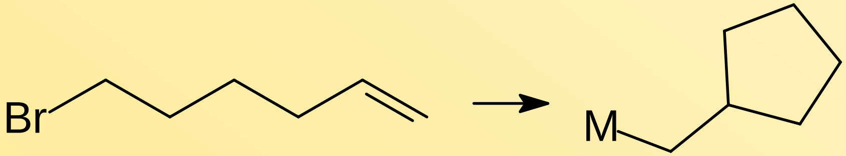
$IrCl(CO)L_2$

RX

$R\overset{\bullet}{Ir}Cl(CO)L_2$

Tests:

- Formation R-R
- CIDNP
- Radical clocks:



One reaction, many applications

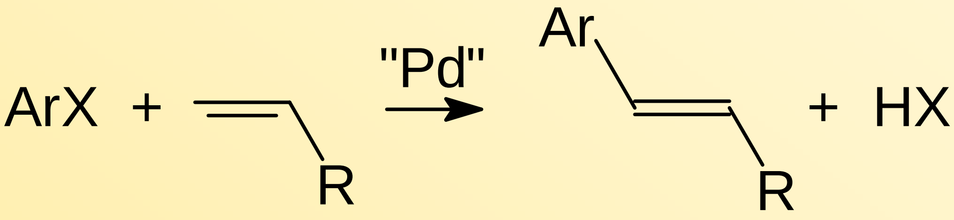
- Oxidative addition is a key step in many transition-metal catalyzed reactions
  - Main exception: olefin polymerization
- The easy of addition (or elimination) can be tuned by the electronic and steric properties of the ancillary ligands
- The most common applications involve:

a) Late transition metals (platinum metals)

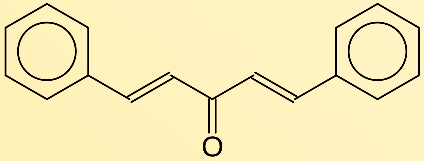
b) C-X, H-H or Si-H bonds

Many are not too sensitive to O_2 and H_2O
and are now routinely used in organic synthesis.

The Heck reaction



- Pd often added in the form of $Pd_2(dba)_3$.



dba, not quite an innocent ligand

- Usually with phosphine ligands.
- Typical ***catalyst loading***: 1-5%.

  But there are examples with turnovers of 10^6 or more

- Heterogenous Pd precursors can also be used

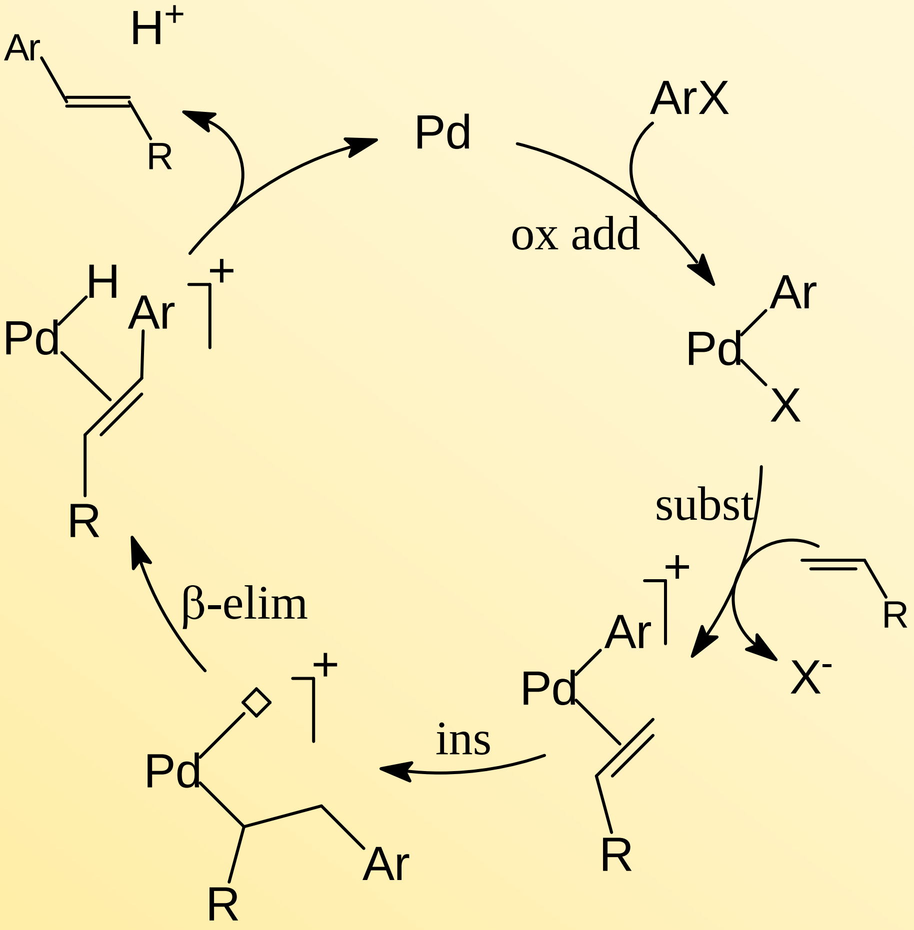
  But the reaction itself happens in solution

The Heck reaction

- For most systems, we don't know the coordination environment of Pd during catalysis.

- At best, we can detect one or more ***resting states***.

- The dramatic effects of ligand variation show that ***at least one ligand*** is bound to Pd for ***at least part of*** the cycle.



The Heck reaction

- Works well with aryl iodides, bromides
- Slow with chlorides
- Hardly any activity with acetates etc
- Challenges for "green chemistry"

- Pt is ineffective
  - Probably gets "stuck" somewhere in the cycle

Suzuki and Stille coupling

$$RX + ArB(OH)_2 \xrightarrow{\text{"Pd"}} RAr + XB(OH)_2$$

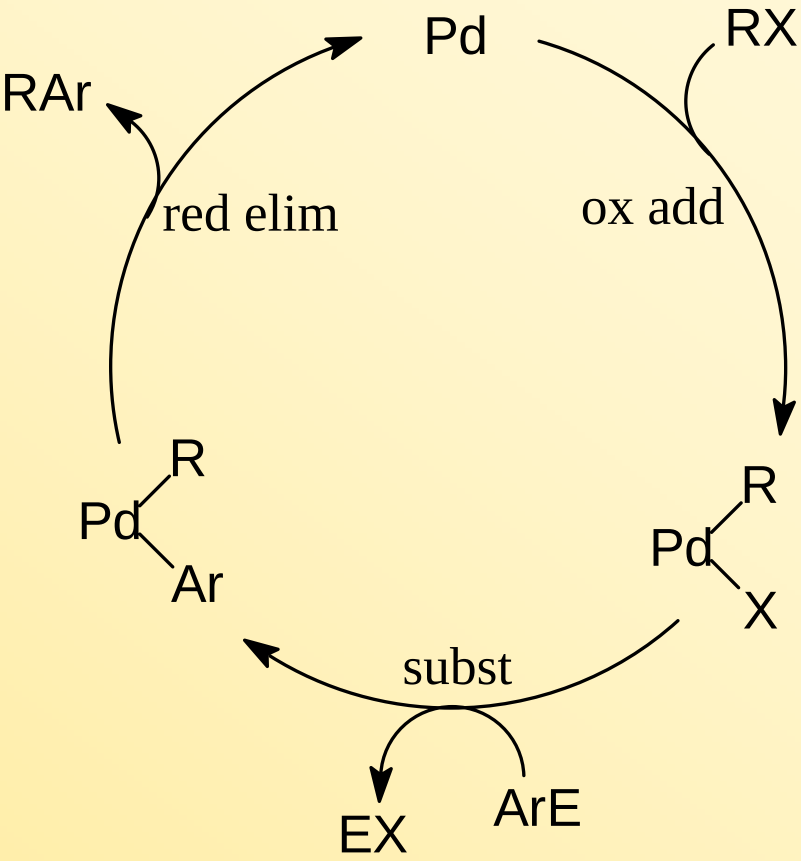
$$RX + ArSnR'_3 \xrightarrow{\text{"Pd"}} RAr + XSnR'_3$$

R = aryl or vinyl

- Glorified Wurtz coupling
- Many variations, mainly in the choice of electrophile
  - Instead of $B(OH)_2$ or $SnMe_3$, also MgCl, ZnBr, etc
- The Suzuki and Stille variations use convenient, air-stable starting materials

Suzuki and Stille coupling

- The oxidative addition and reductive elimination steps have been studied extensively.
- Much less is known about the mechanism of the substitution step.
  - The literature mentions "open" (3-center) and "closed" (4-center) mechanisms
- This may well be different for different electrophiles.



Reductive elimination

Rate depends strongly on types of groups to be eliminated.

Usually easy for:

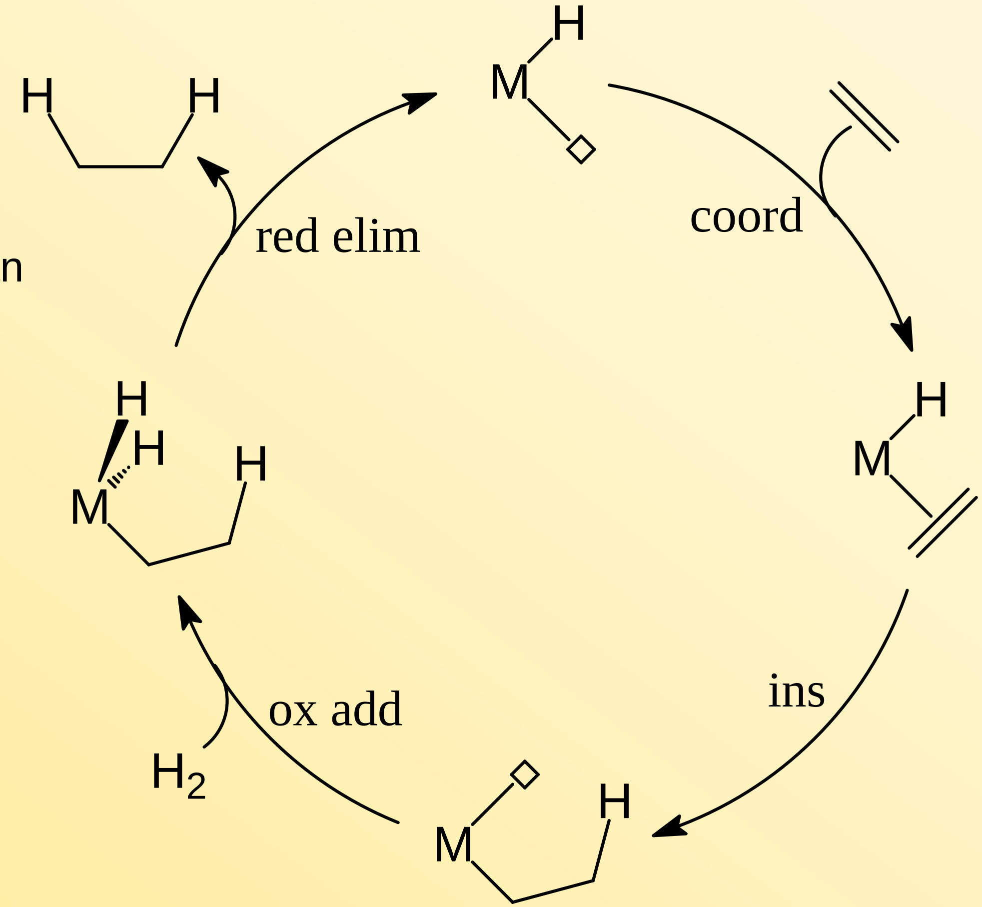
- H + alkyl / aryl / acyl
  - H 1s orbital shape, c.f. insertion
- alkyl + acyl
  - participation of acyl π-system
- SiR_3 + alkyl etc

Often slow for:

- alkoxide + alkyl
- halide + alkyl
  - thermodynamic reasons?

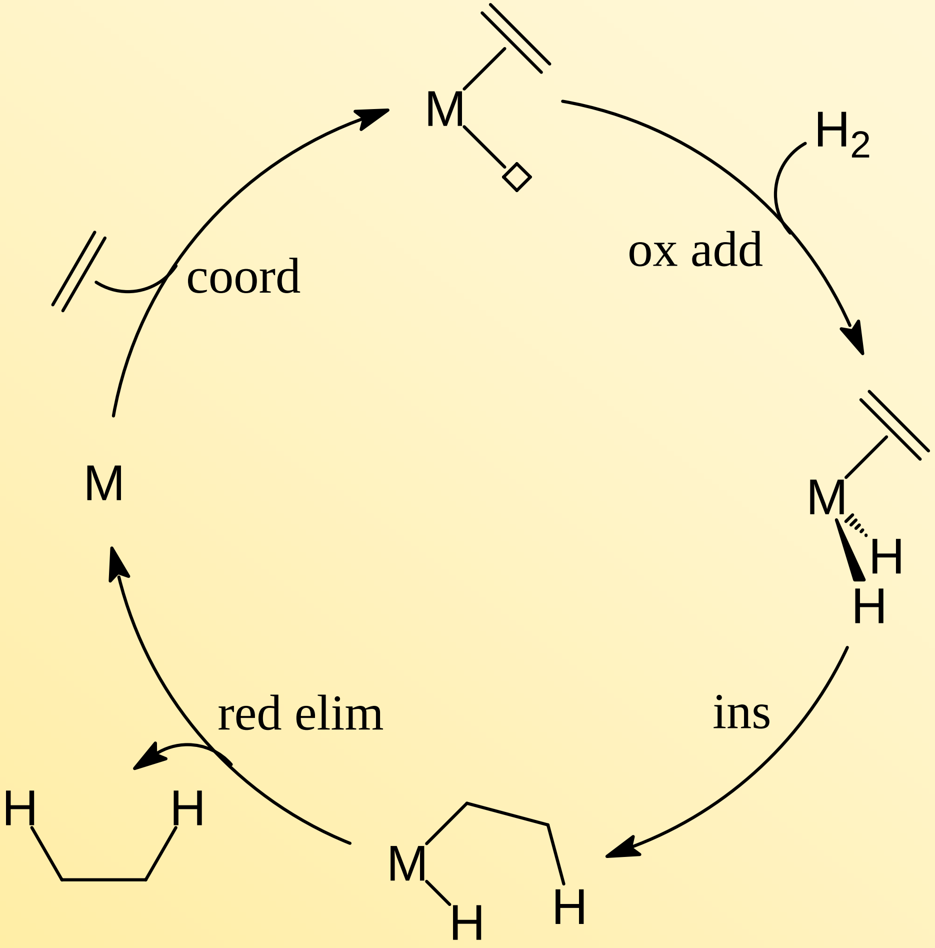
Catalytic olefin hydrogenation (1)

- Usually with platinum metals.
  - e.g. Wilkinson's catalyst
- Many chiral variations available.
  - enantioselectivity mechanism can be very subtle
- For achiral hydrogenation, heterogeneous catalysts ("Pd black") are often a good alternative.
- Extremely high turnovers possible.
- For early transition metals, σ-bond metathesis instead of oxidative addition.



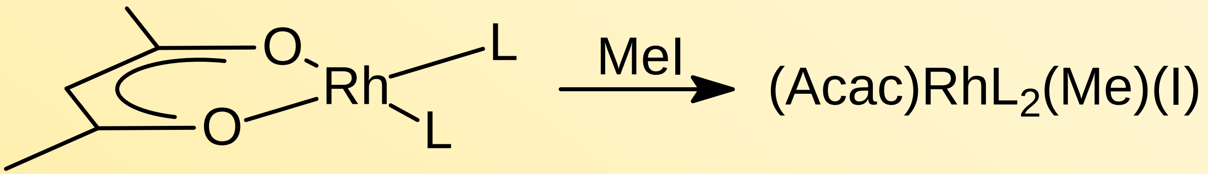
Catalytic olefin hydrogenation (2)

- Alternative mechanism for metals not forming a "stable" hydride.
- Requires oxidative addition, not observed for early transition metals.
- Distinguish between mechanisms using H_2/D_2 mixtures or PHIP.

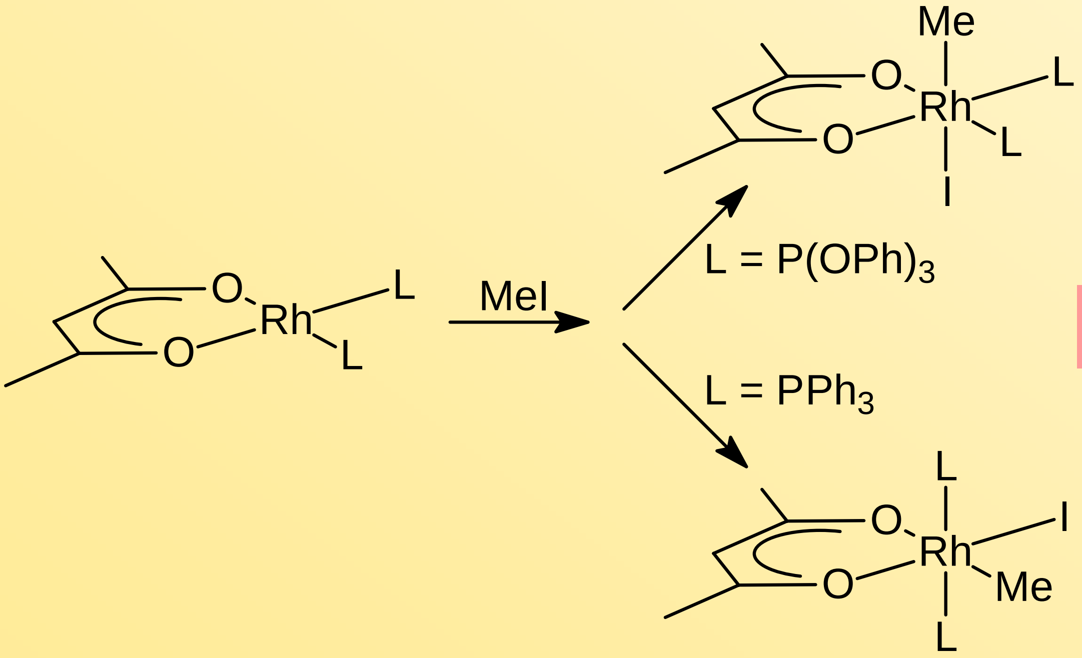


Oxidative addition of MeI to (Acac)RhL$_2$

Shestakova et al, *J. Organomet. Chem.* **2004**, *689*, 1930



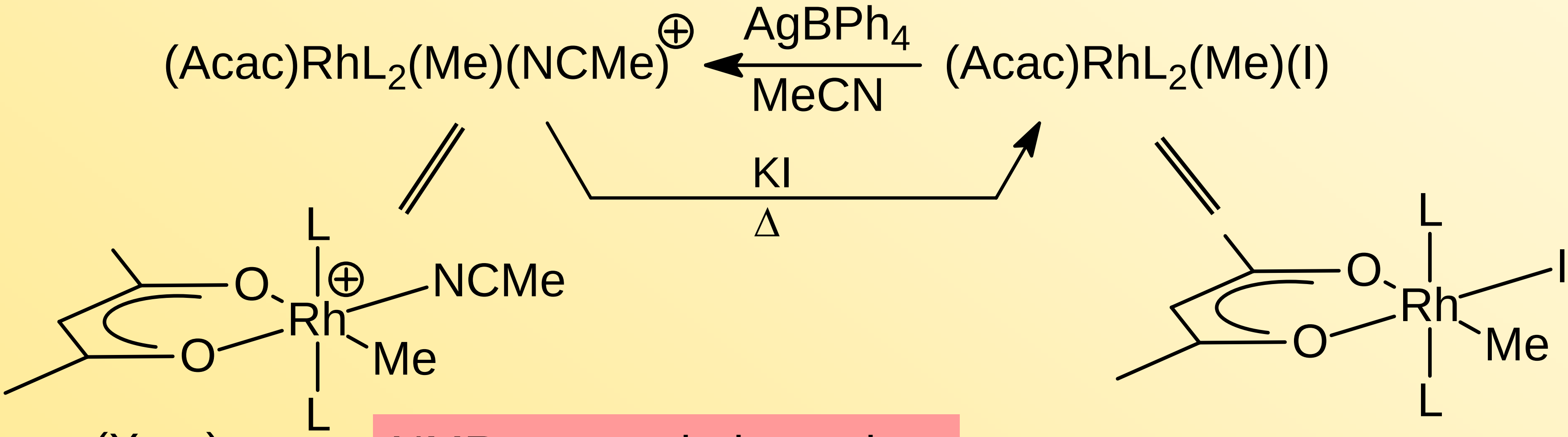
Generally thought to involve nucleophilic attack of the Rh lone pair on MeI (ionic mechanism).



What's going on ?

Model complexes for cationic intermediates

- Independent synthesis of a cationic ***trans*** complex:



(Xray)

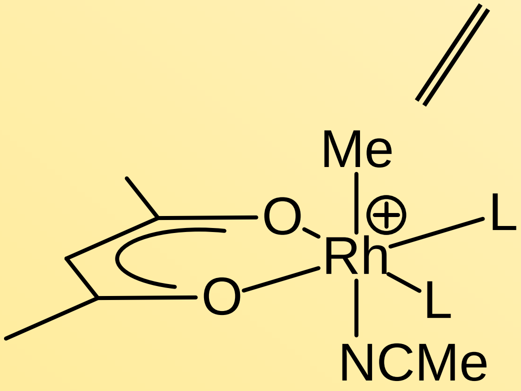
(1)

NMR spectra independent of temperature

Model complexes for cationic intermediates

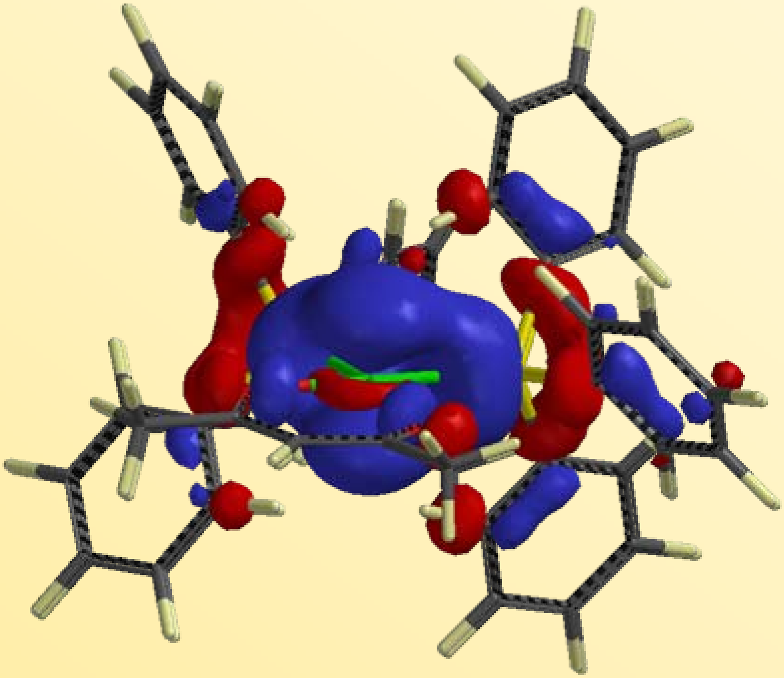
- Trapping (?) of an ionic intermediate

$$(Acac)RhL_2(Me)(NCMe)^{\oplus} \xleftarrow[\text{MeCN}]{\text{MeI, NaBPh}_4} (Acac)RhL_2$$



(Xray) ***(2)***

NMR spectra
temperature-dependent



VT-NMR of (2)

$^{31}P\{^1H\}$ NMR

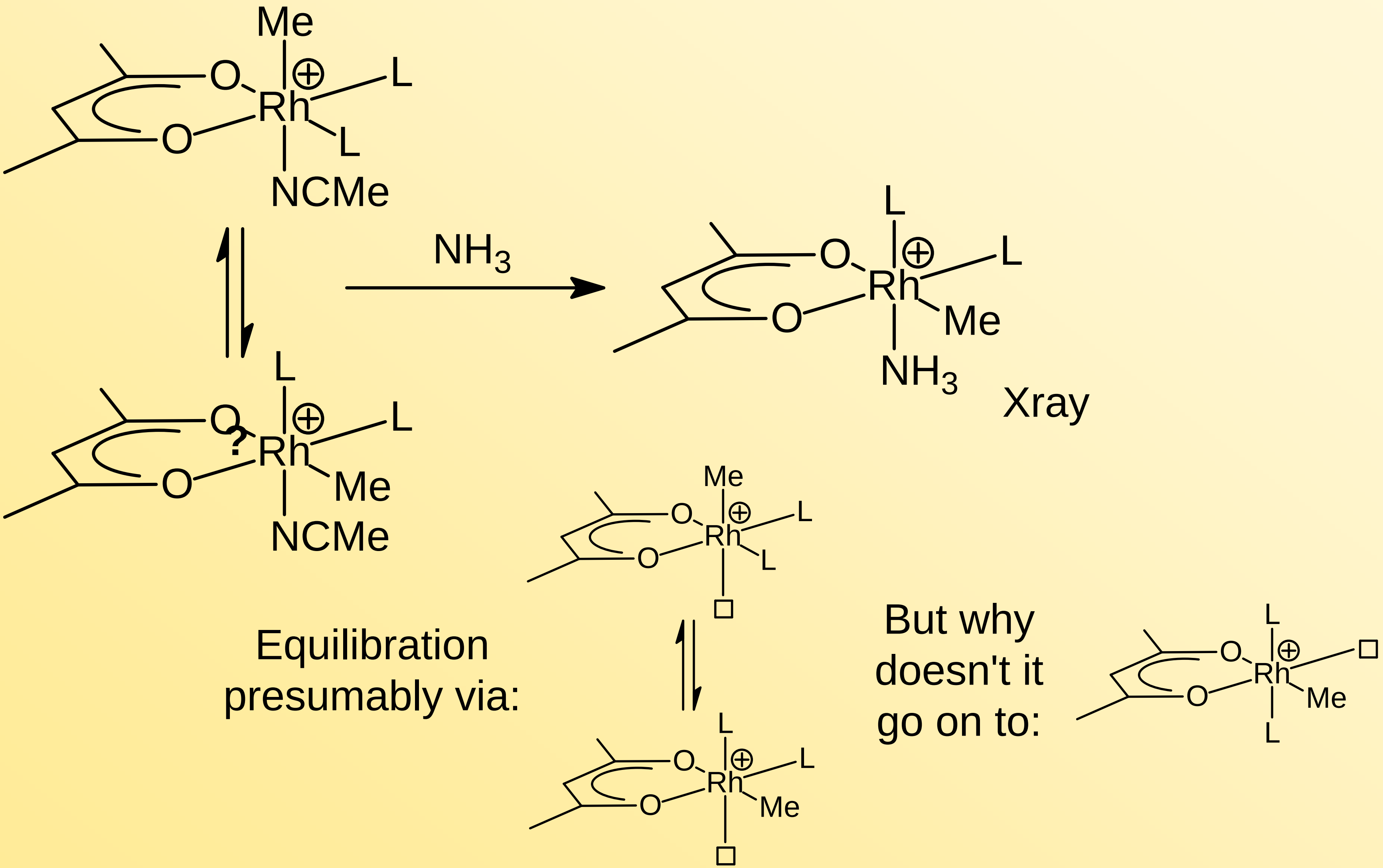
At RT: 1 broadened doublet at 29.8 ppm

At -50°C: sharp, intense doublet at 29.7 ppm; two much less intense "***dd***" at 27.3, 23.6 ppm

Equilibrium between a symmetric and an asymmetric species, ***neither*** of which is ***(1)*** ! The symmetric one probably corresponds to the X-ray structure.

The benzoylacetonate complex shows similar behaviour, but now at low T ***both*** species have inequivalent P atoms.

Reaction of (2) with NH_3

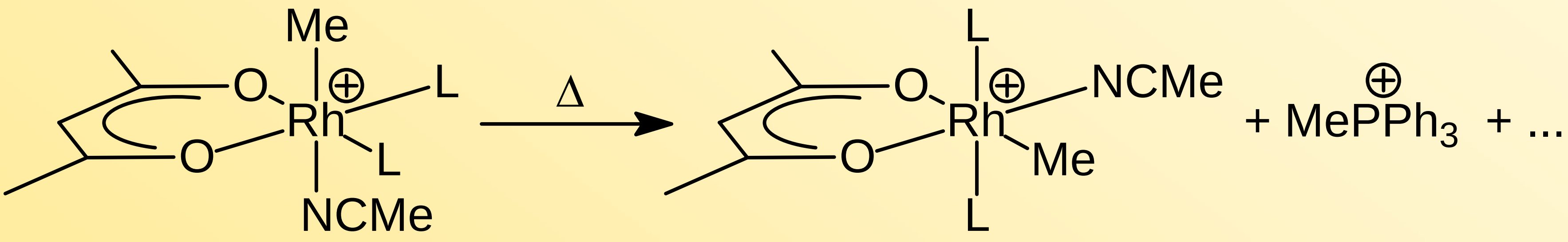


Xray

Equilibration presumably via:

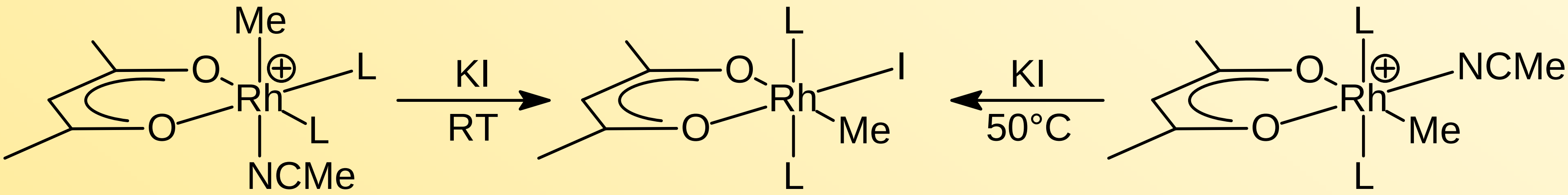
But why doesn't it go on to:

Heating of (2)



(2) **(1)**

Reaction with iodide



(2) **(1)**

Rate difference caused by *trans* effect of Me group in ***(2)*** ?

Conclusions ?

- Oxidative addition ***probably*** begins with attack of Rh d_{z2} at Me group of MeI leading to an ionic ***cis*** intermediate.

- The initial ionic product can be trapped, but would otherwise react further to the neutral ***trans*** final product.

- The ionic ***cis*** acetonitrile complex is labile at RT, equilibrates rapidly between ***two isomeric cis forms***, but will only go to the ***trans*** product at higher temperature.

- It seems ***likely*** that the ***trans*** ionic complex is thermodynamically favoured, but the key experiment to prove that is not reported.