Homogenous Catalysis

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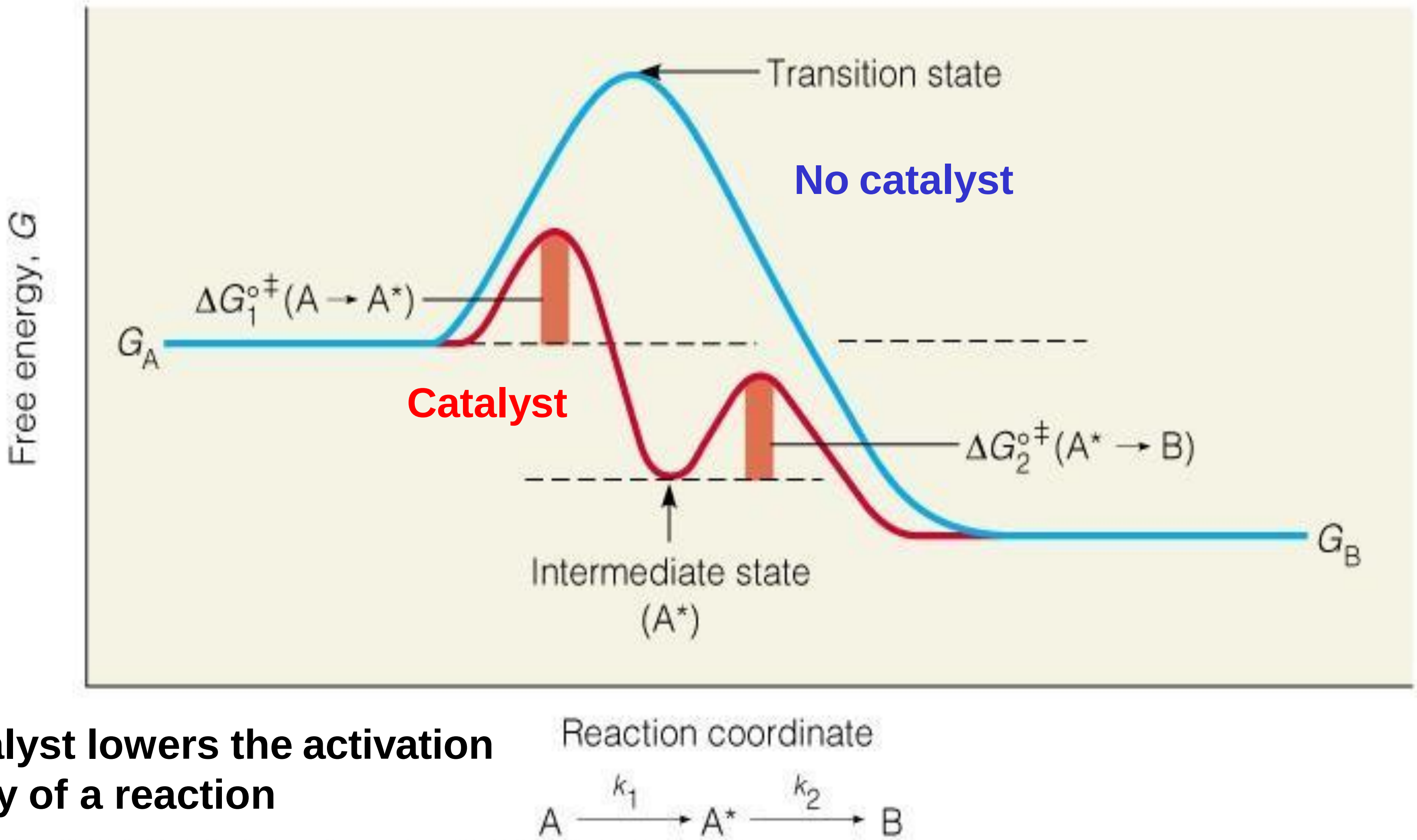
Outline

- Background to Catalysis
- Basic Principles of Homogeneous Catalysis
- Selected Examples

Energy profile of a reaction



A catalyst lowers the activation energy of a reaction

How Does a Catalyst Work?

- Lowering activation energy

- Stabilization of a reactive transition state

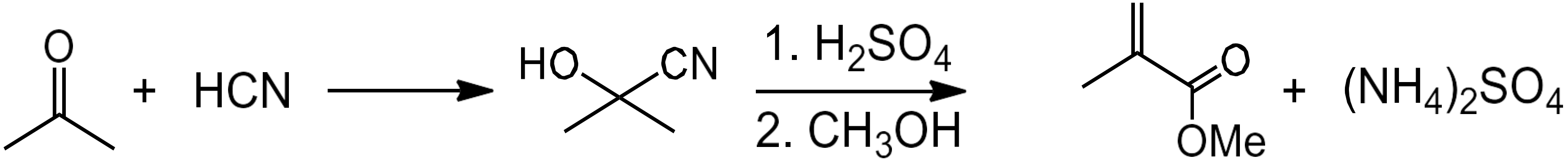
- Bringing reactants together
  - proximity effect
  - orientation effect

- Enabling otherwise inaccessible reaction paths

Advantages of Catalytic Process

Methyl Methacrylate (for Perspex)

Old process: 2.5 kg waste / kg product



Different types of Catalyts

Heterogeneous

- Usually a solid in a different phase from the reactants
- Usually metal or metal oxide

Homogeneous

- In the same phase as the reactants
- Usually a dissolved metal complex

Enzyme (Biological)

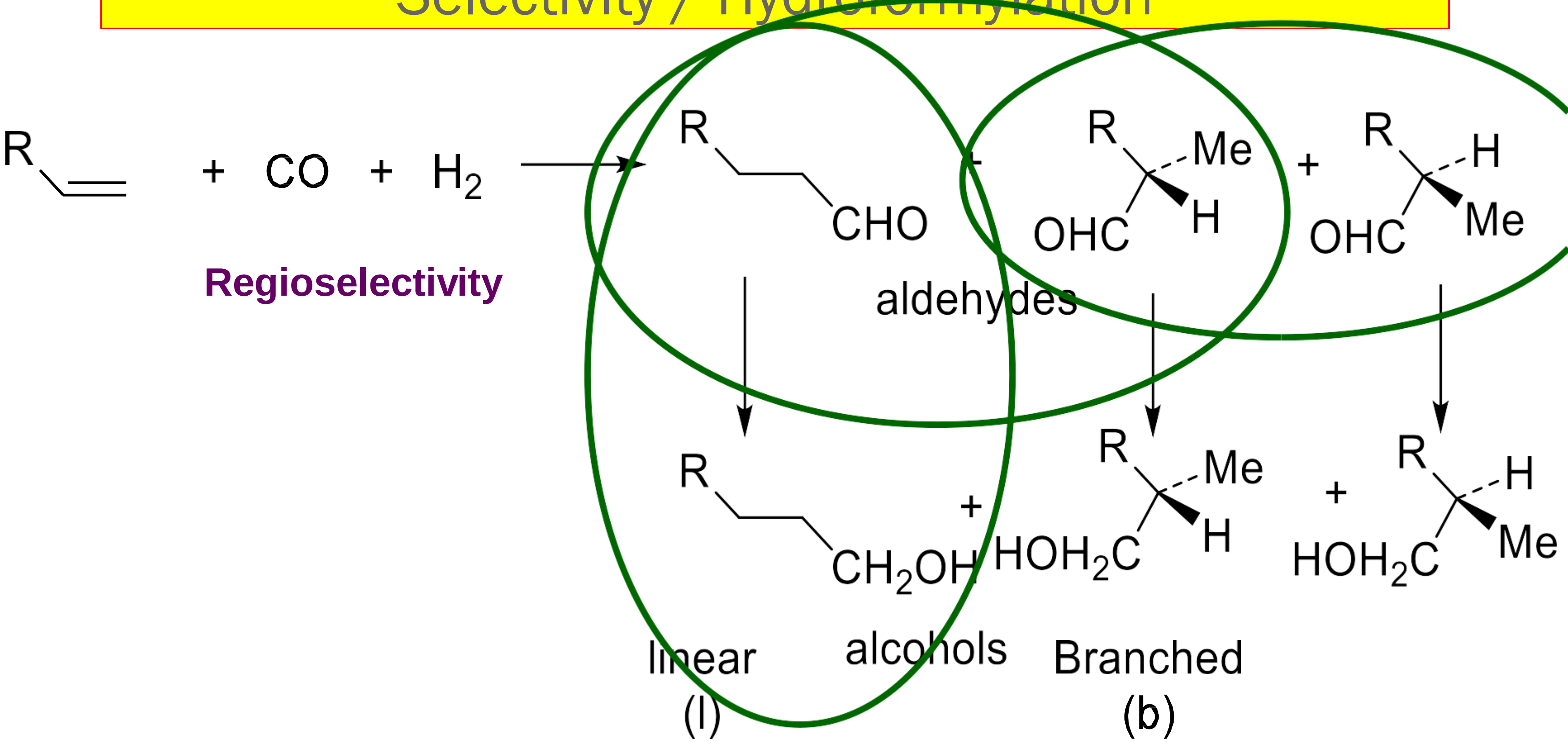
- Usually a complex system in water
- Highly active and selective
- Sometimes rather unstable
- Becoming increasingly popular

World Catalyts market $ 9 billion

Heterogeneous vs Homogeneous Catalysis

Heterogeneous	**Homogeneous**
Solid metal or metal oxide	Metal complex
Solvent not required	Solvent required (usually)
Thermally robust	Thermally sensitive
Only surface atoms available	All metal centres available
Selectivity can be poor	Selectivity can be tuned
Difficult to study while operating	In situ spectroscopy
Easy separation from products	Difficult product separation
Some processes only heterogeneous $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$ Exhaust catalyst	Some processes only homogeneous $MeOH + CO \longrightarrow MeCO_2H$ Hydroformylation of alkenes

Selectivity / Hydroformylation



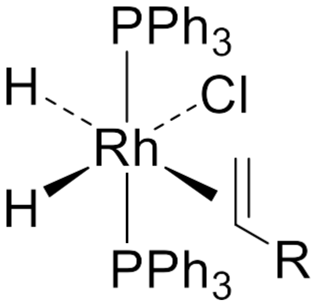
Regioselectivity

Chemoselectivity

Enantioselectivity

Counting electrons

- Determine the oxidation state of the metal and hence the number of d electrons.
- Add 2 for each ligand (note that benzene coordinates through the 3 double bonds so gives 6).
- Add electrons for overall negative charges, subtract electrons for overall positive charges.

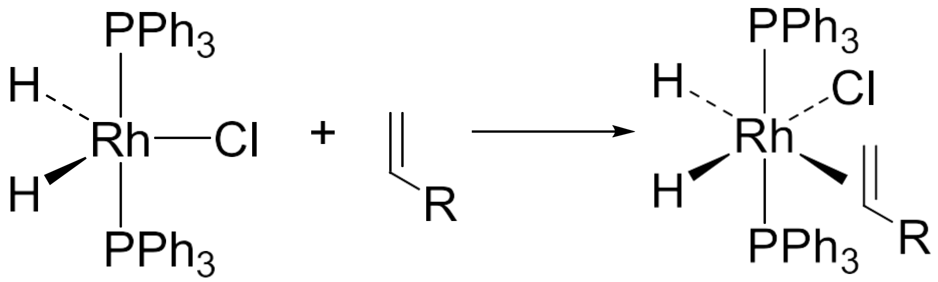


Rh^{III} $4d^6$	6 e
6 x 2e ligands	12 e
Total	18 e

Reactions in catalytic cycles

Coordination

- Need a vacant site (often 14 or 16 e intermediate)

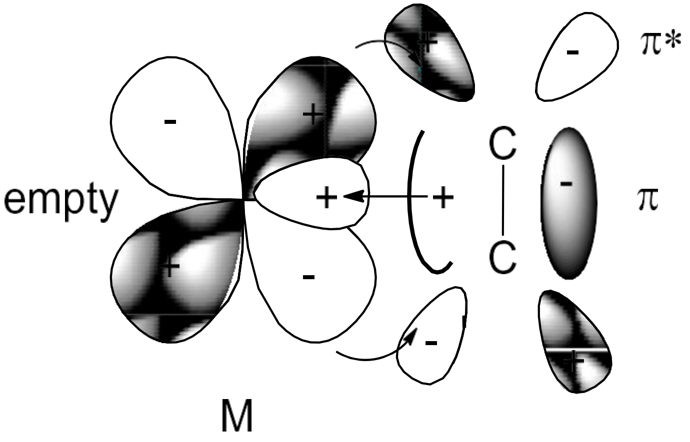


Rh^{III} $4d^6$	6 e	
5 2e ligands	10 e	18 e
Total	16 e	

Bonding of alkenes

- **Donation of electron density from π orbital on C=C to an empty s, p or d orbital on the metal**

- **Back donation of electron density from the filled t_{2g} level on the metal to the empty π^* orbital on C=C**

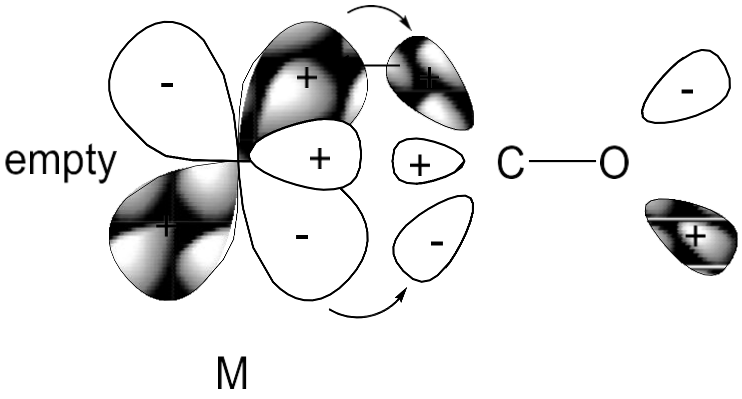


Adds 2 e

Bonding of CO

- **Donation of a lone pair of electrons from the C atom of CO to an empty s, p or d orbital on the metal**

- **Back donation of electron density from the filled t_{2g} level to the empty π^* orbital on CO**



Adds 2 e

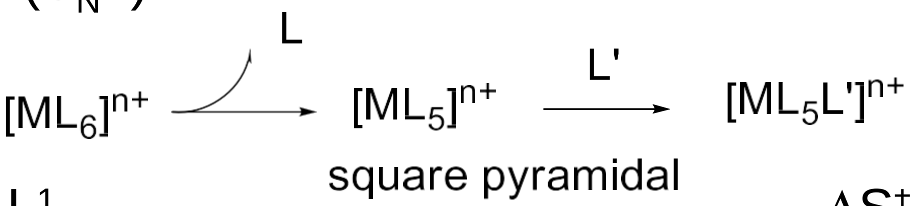
Substitution

Octahedral complexes

Mechanism

$$[ML_6]^{n+} + L' \rightarrow [ML_5L']^{n+} + L$$

1) Dissociative (S_N1)



$$[ML_6]^{n+} \xrightarrow{-L} [ML_5]^{n+} \xrightarrow{L'} [ML_5L']^{n+}$$

square pyramidal

0 order in L'.

$\Delta S^\ddagger$ will be positive

2) Associative (SN2)

$$[ML_6]^{n+} + L' \rightarrow [ML_6L']^{n+} \rightarrow [ML_5L']^{n+} + L$$

7 coordinate

1st order in L'

$\Delta S^\ddagger$ negative

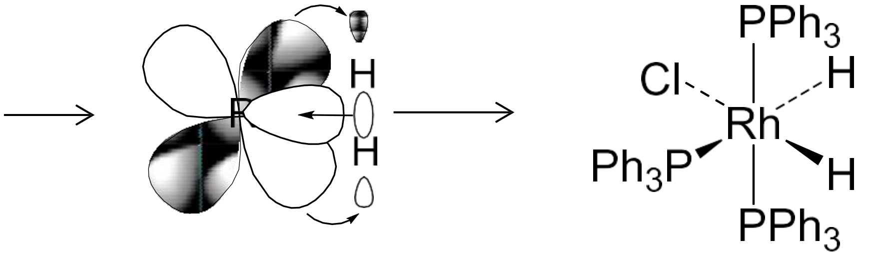
3) Hybrid mechanisms

No change in e count

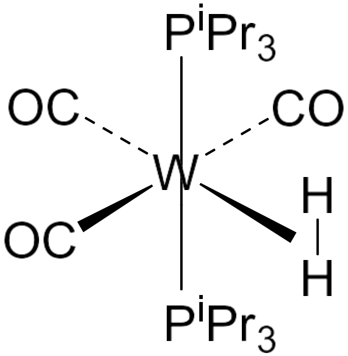
Oxidative Addition

Concerted addition

$[RhCl(PPh_3)_3]$ + H_2



Rh^I 16 e



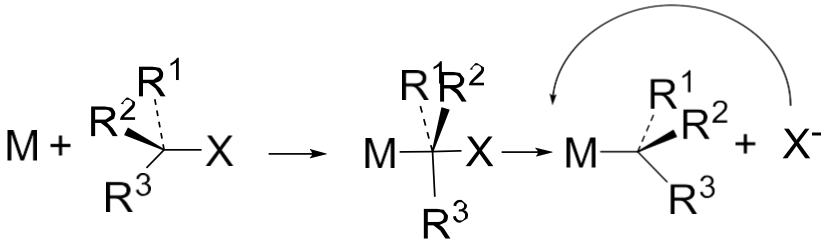
Rh^{III} 18 e

Adds 2 e

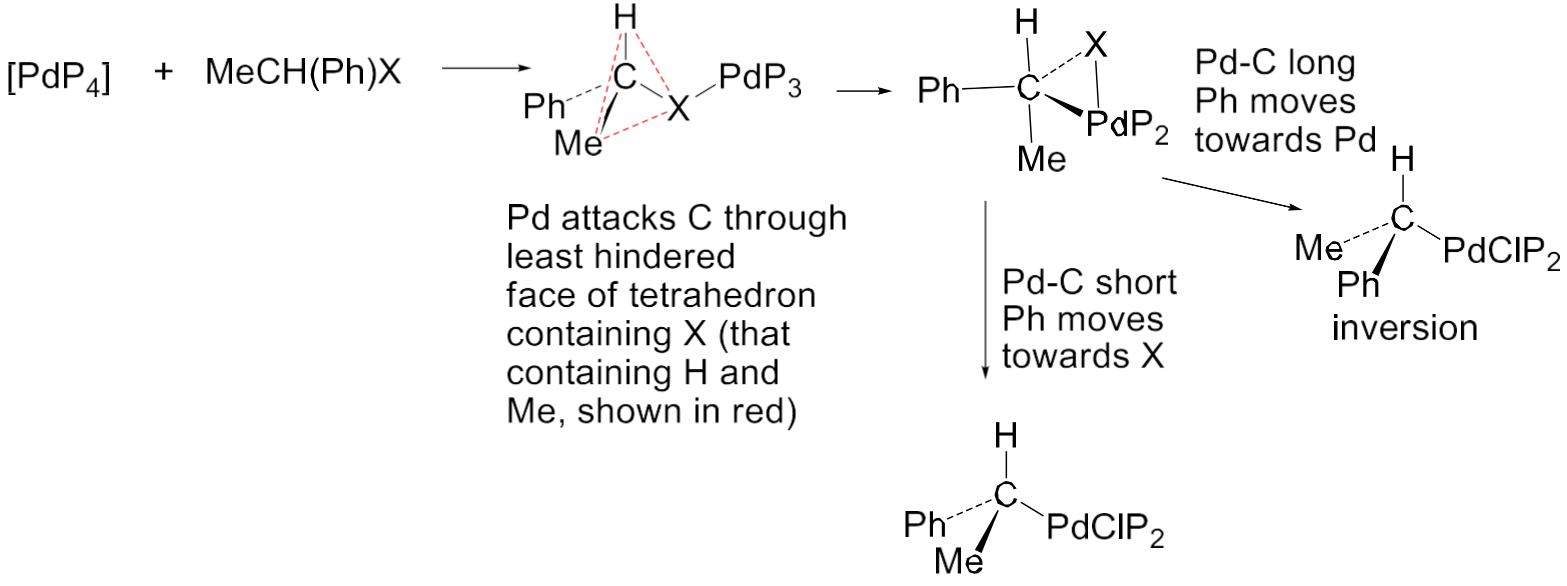
Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J., *J. Am. Chem. Soc.*, 1984, 106, 451

Alkyl halides – S_n2

Should give inversion of configuration



Trans **addition usually goes by this mechanism**



Pd attacks C through least hindered face of tetrahedron containing X (that containing H and Me, shown in red)

Pd-C long
Ph moves
towards Pd

inversion

Pd-C short
Ph moves
towards X

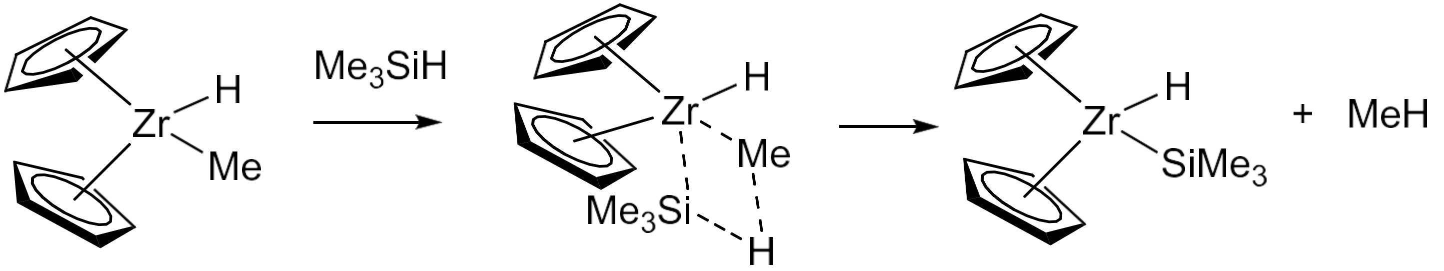
Retention of configuration

If both pathways have similar energy partial racemisation will occur

J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.* 1977, **10**, 434

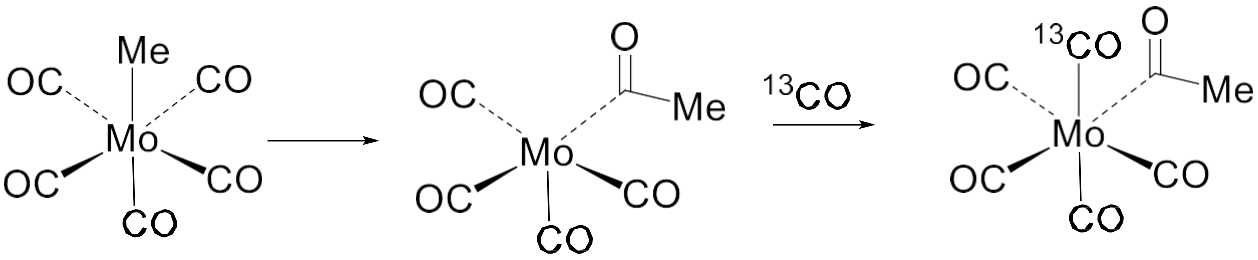
σ–bond metathesis

Occurs when metal is in highest oxidation state (d^0) and oxidative addition is not possible



No change in e count

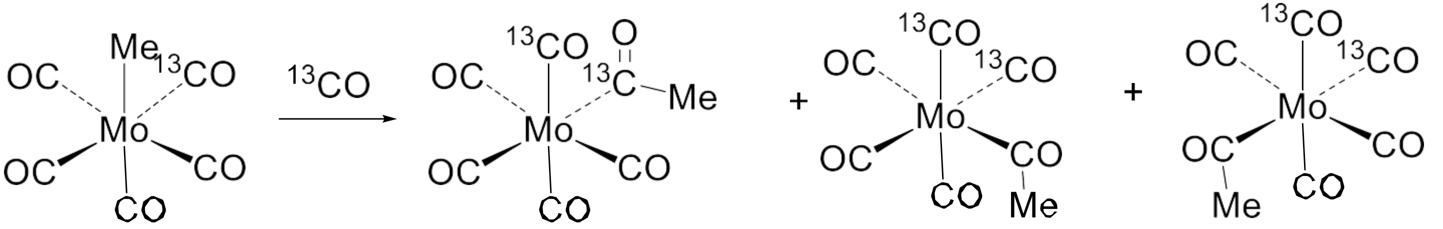
Migratory insertion



- **Incoming ligand does not insert**
- **Incoming ligand ends up *cis* to the acyl**
- **Me and CO involved in migration are mutually *cis***

Removes 2 e

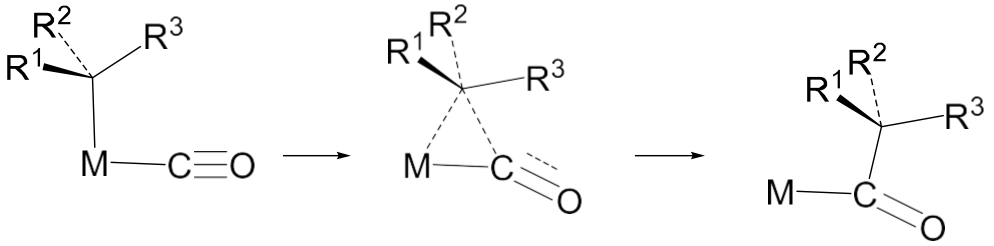
Which moves?



Ratio 1 **A** 2 **B** 1 **C**

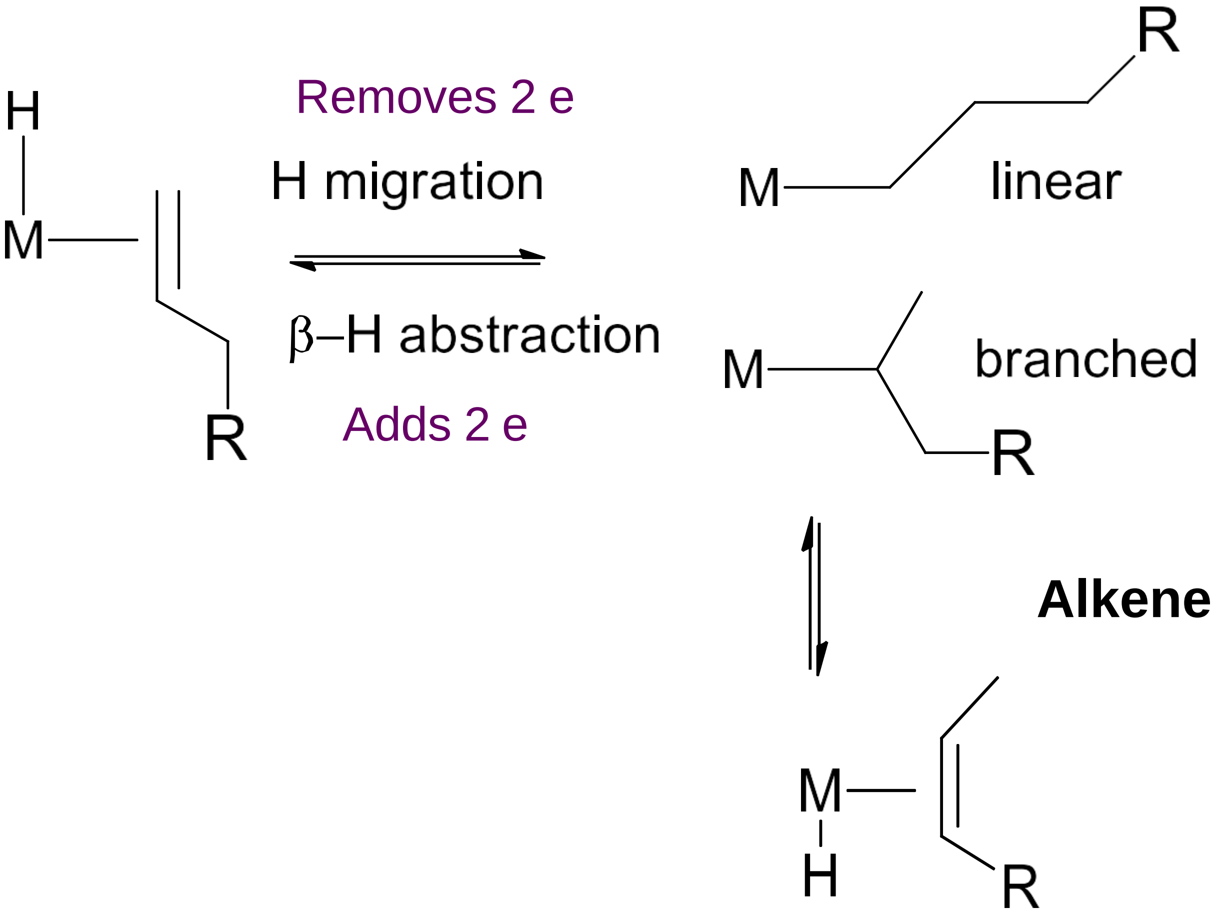
Me must move.

If CO moves cannot get C



Retention of configuration

Hydride migration and *β*-hydrogen abstraction



Removes 2 e

H migration

β–H abstraction

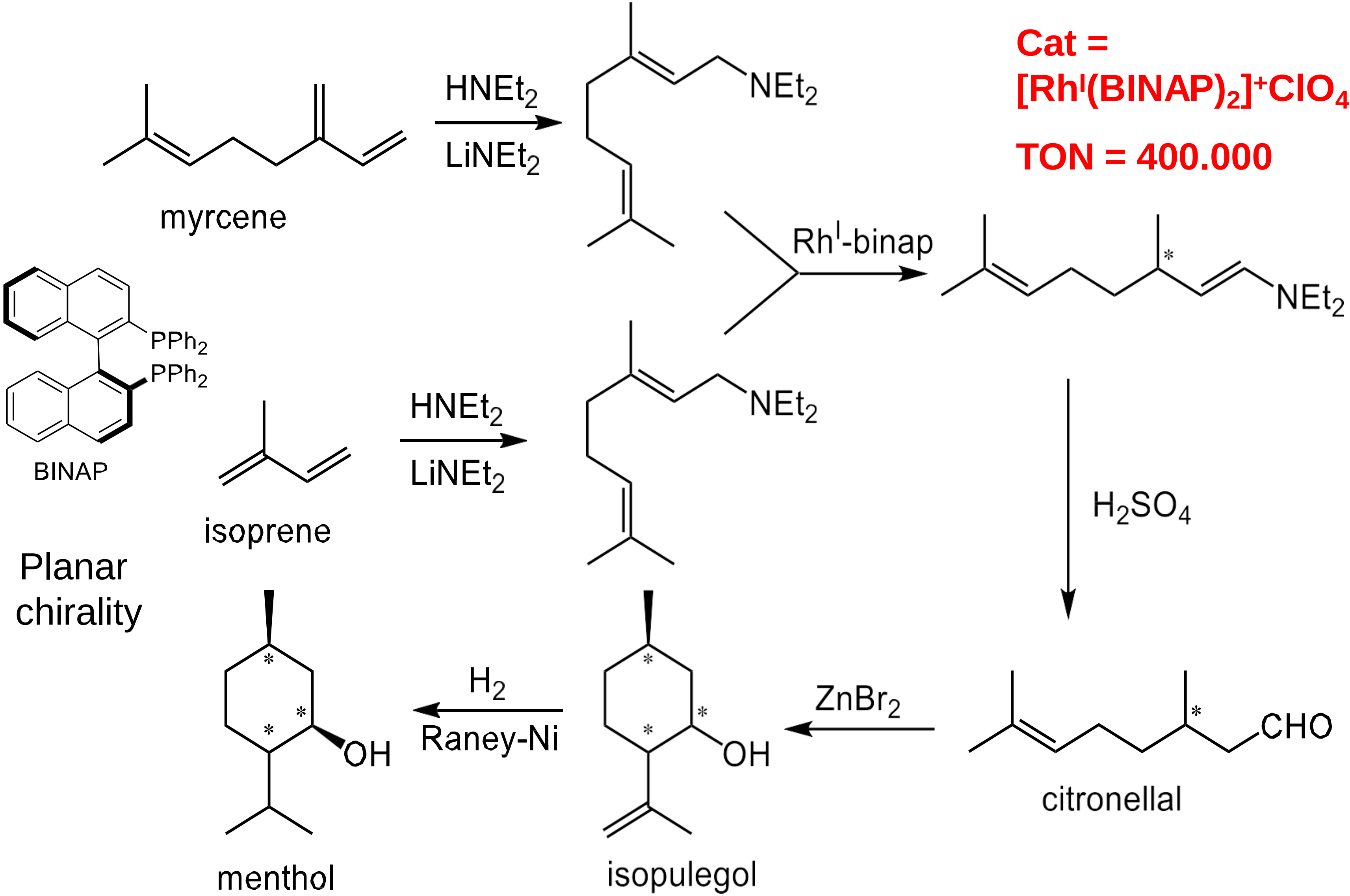
Adds 2 e

linear

branched

Alkene isomerisation

Takasago Menthol Synthesis



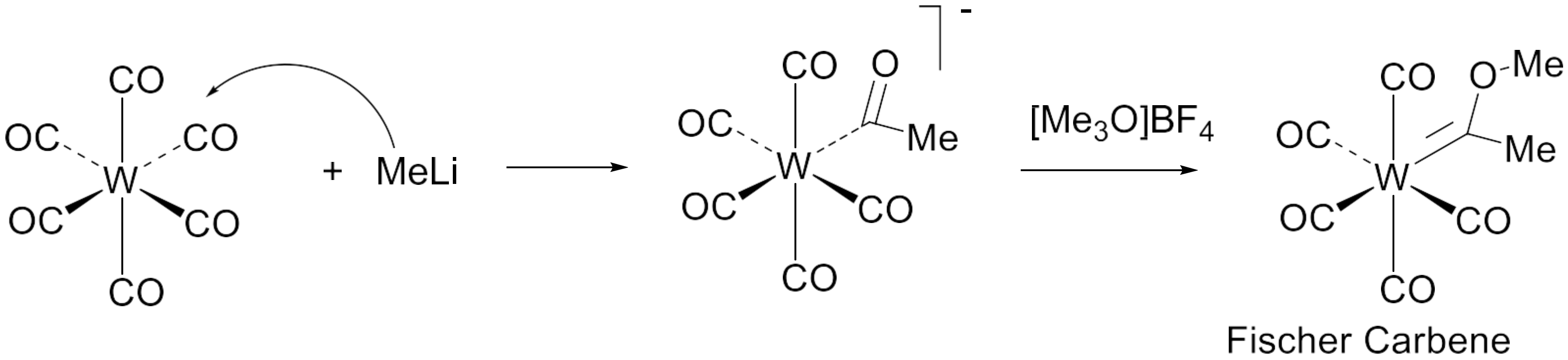
Cat =
$[Rh^{I}(BINAP)_2]^{+}ClO_4^{-}$

TON = 400.000

Planar chirality

K. Tani, T. Yamagata, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya. A. Miyashita, R. Noyori and S. Otsuka, *J. Am. Chem. Soc.*, 1984, **106**, 5208

Attack on Coordinated ligands



Nucleophilic **Electrophilic**

E. O. Fischer and co-workers

No change in e count

The Wacker Process

$$[PdCl_4]^{2-} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 4\,Cl^- + 2\,H^+$$

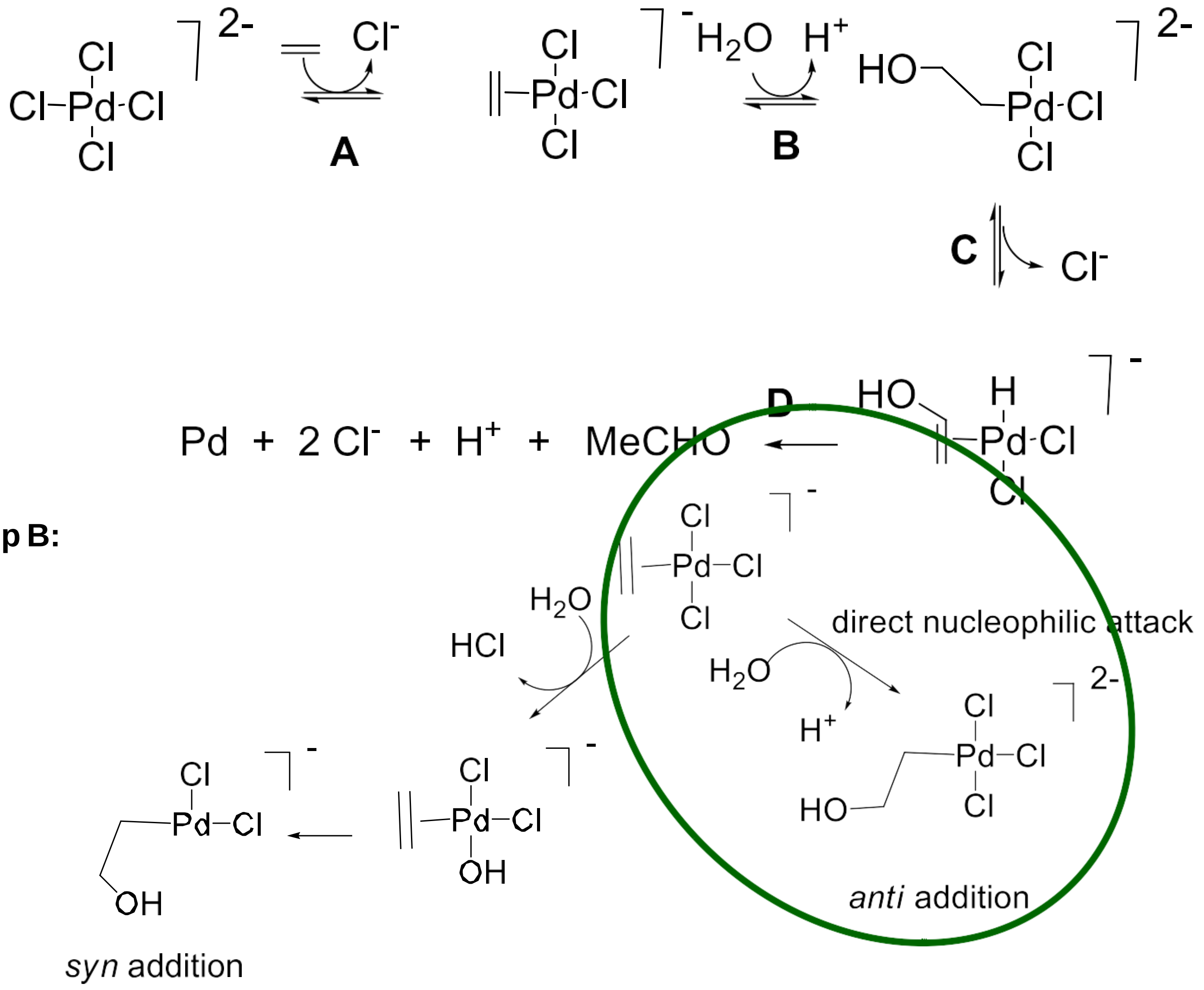
$$Pd + 2\,Cu^{2+} + 4Cl^- \rightarrow [PdCl_4]^{2-} + 2\,Cu^+$$

$$2\,Cu^+ + \tfrac{1}{2}\,O_2 + 2\,H^+ \rightarrow Cu^{2+} + H_2O$$

$$C_2H_4 + \tfrac{1}{2}\,O_2 \rightarrow CH_3CHO$$

1970’s 2 M tonnes per year - decreasing

Mechanism



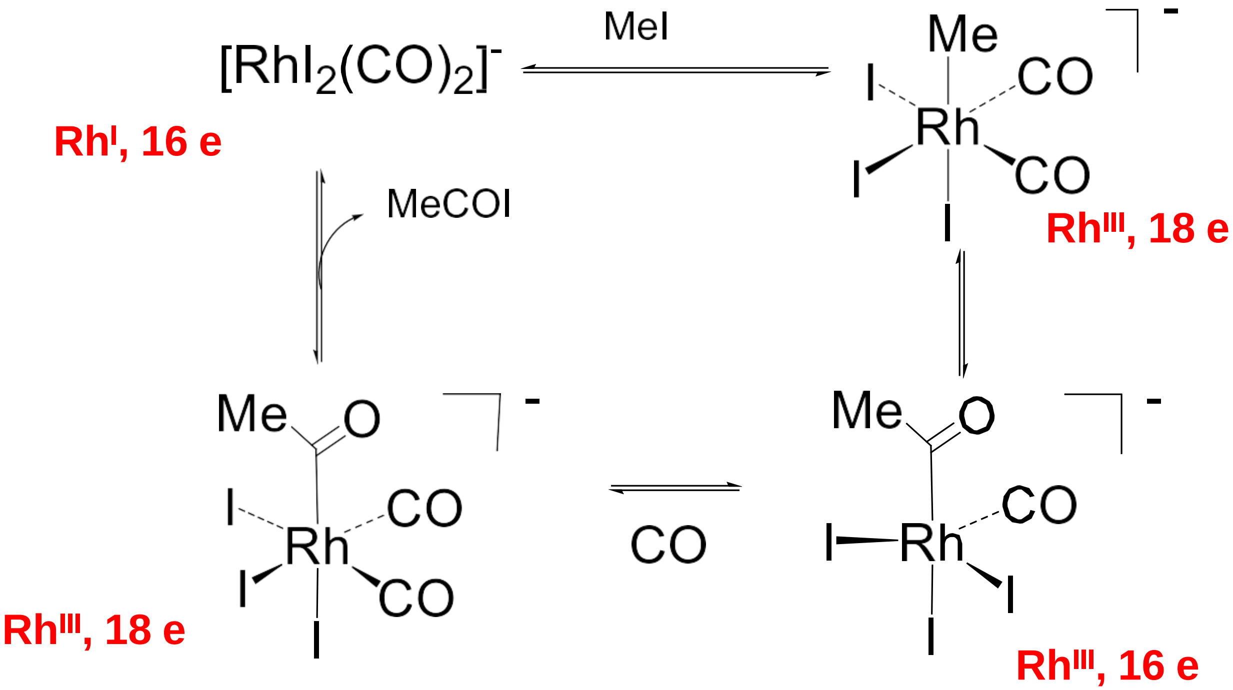
Step B:

Unit steps in Catalytic reactions

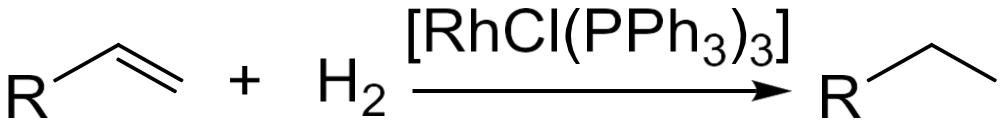
		Change in No of electrons
Introduction of substrates onto metal centre		
- Simple Coordination		+2
- Substitution		0
- Oxidative Addition		+2
- Sigma bond metathesis		0
Reactions between substrates in coordination sphere.		
- Migratory insertion		-2
- Attack of Nucleophiles onto coordinated ligands		0
- β-H abstraction		+2
Releasing substrates from Metal Centre.		
- Decoordination	**Reverse of introduction**	-2
- Substitution		0
- Reductive Elimination		-2
- Sigma bond metathesis		0

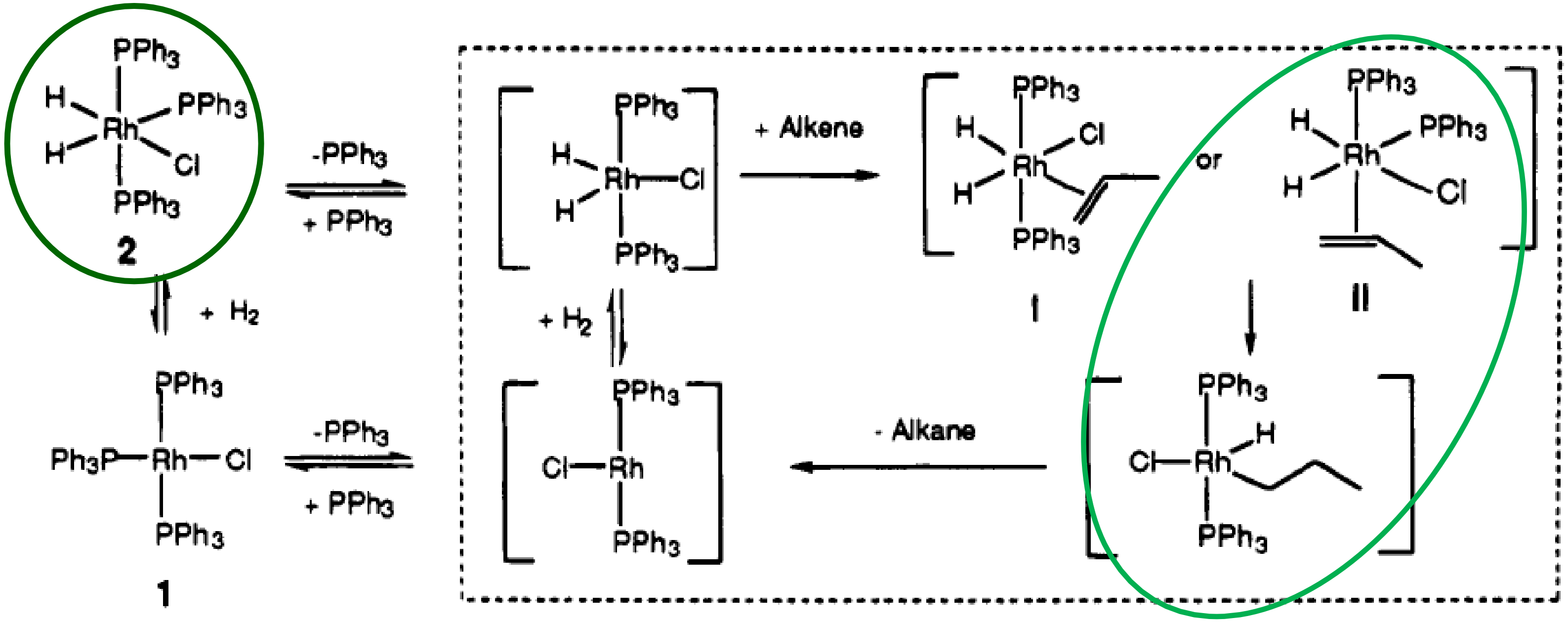
16/18 e Rule

- Catalytic cycles often proceed through a variety of intermediates alternating between 16 and 18 electrons



Catalytic hydrogenation (Wilkinson's catalyst)





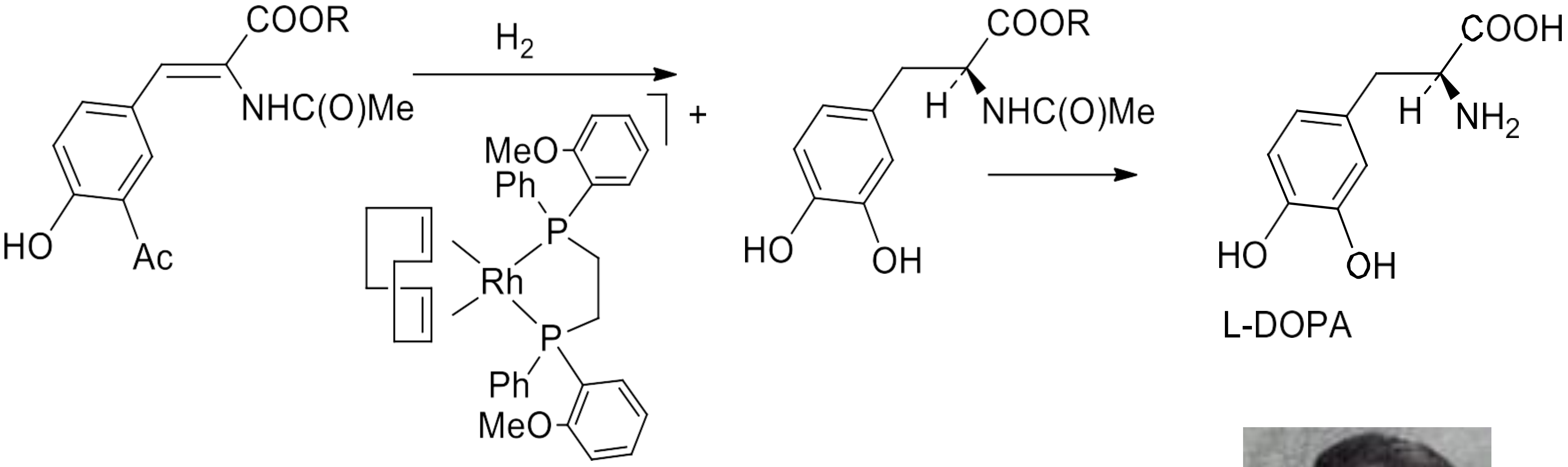
By ^{31}P and ^{1}H NMR spectroscopy see only compound 2 , a resting state outside the catalytic cycle – no information about cycle

Kinetics suggest H migration onto alkene is rate determining

Parahydrogen allows detection of II

Duckett et al, *J. Am. Chem. Soc,* 1994, **116,** 10548

Asymmetric hydrogenation



W. S. Knowles
Nobel Prize, 2001

W.S. Knowles and M.J. Sabacky, *Chem. Commun.,* 1968, 481

Ketone hydrogenation

Rhodium based catalysts are usually of very low activity unless very electron rich (e. g. [$RhH(CO)(PEt_3)_3$] for aldehyde hydrogenation, J. K. MacDougall et al, *J. Chem Soc. Dalton Trans.*, 1996, 1161)

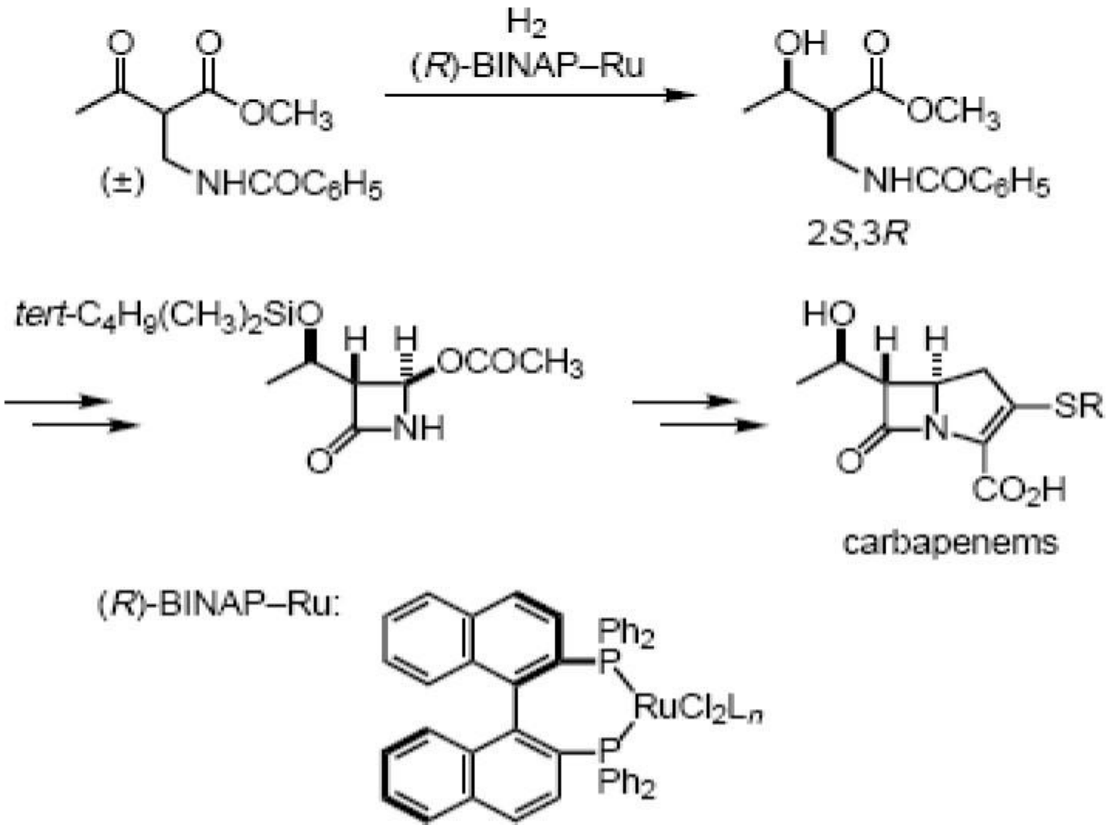
Ruthenium based catalysts are preferred

Asymmetric Catalysis by Architectural and Functional Molecular Engineering:
Practical Chemo and Enantioselective Synthesis of Ketones

R. Noyori
Nobel Prize, 2001

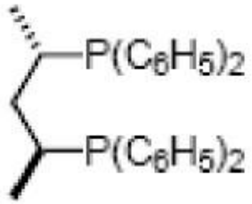
R. Noyori and T. Ohkuma *Angew..Chem.Int. Edi.* 2001,**40,** 40-73.

Hydrogenation of activated ketones

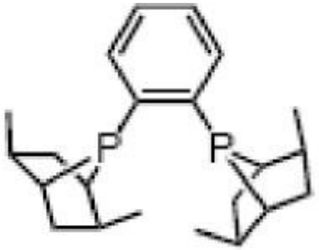


R. Noyori and T. Ohkuma *Angew..Chem.Int. Edi.* 2001,**40,** 40-

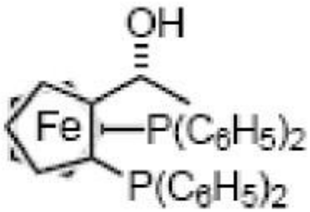
Ligands for asymmetric ketone hydrogenation



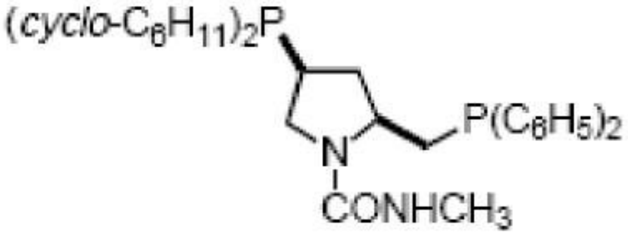
(*S*,*S*)-BDPP



(*R*,*S*,*R*,*S*)-Me-PennPhos

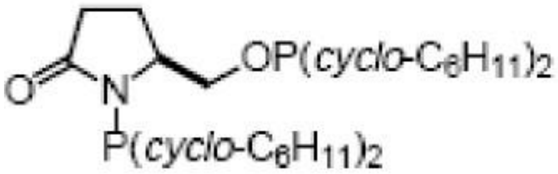


(*R*,*S*)-BPPFOH

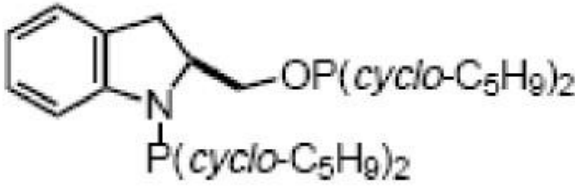


(2*S*,4*S*)-MCCPM

Non-classical ligands



(*S*)-Cy,Cy-OxoProNOP



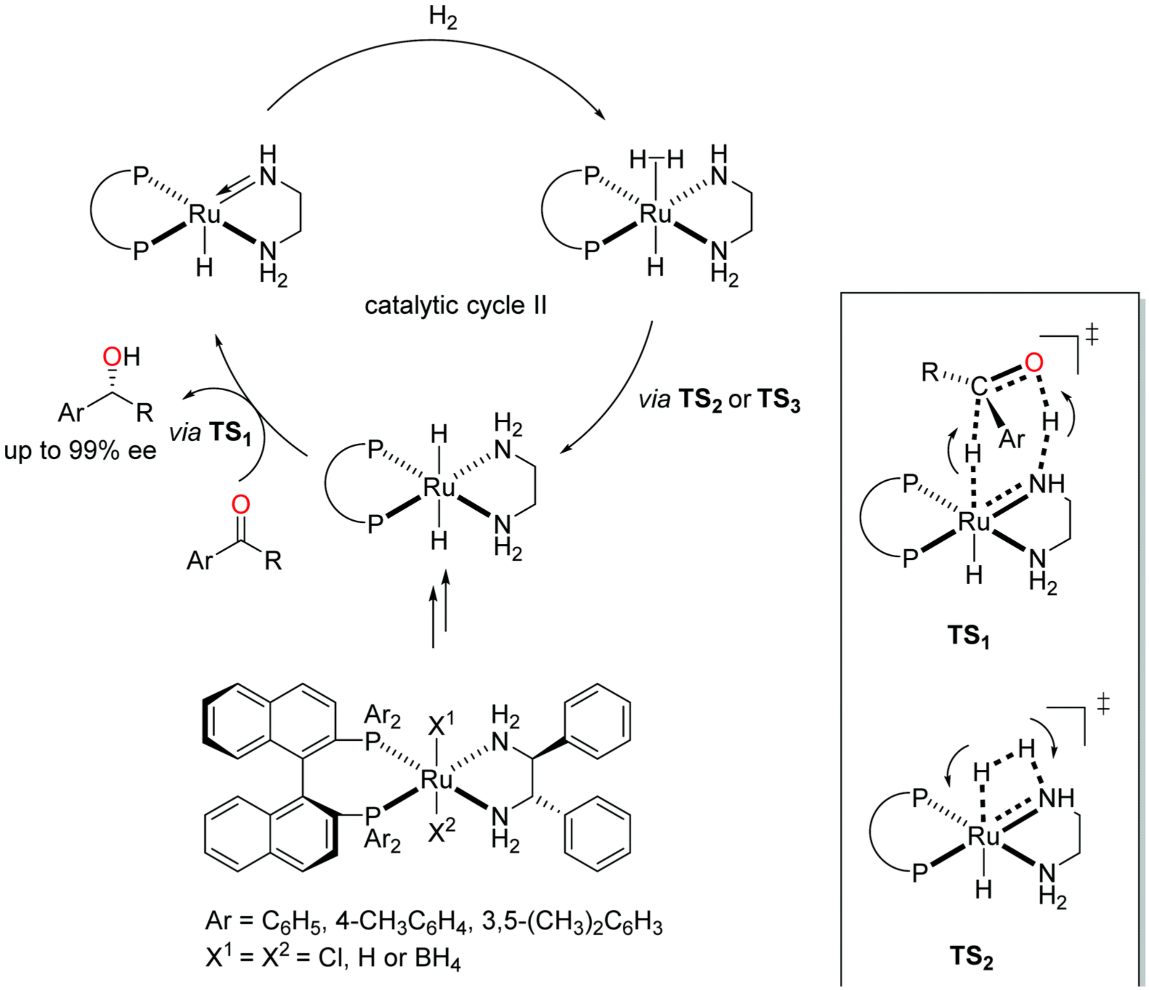
(*S*)-Cp,Cp-IndoNOP

R. Noyori and T. Ohkuma *Angew..Chem.Int. Edi.* 2001,**40,** 40-73.

Outer sphere mechanism

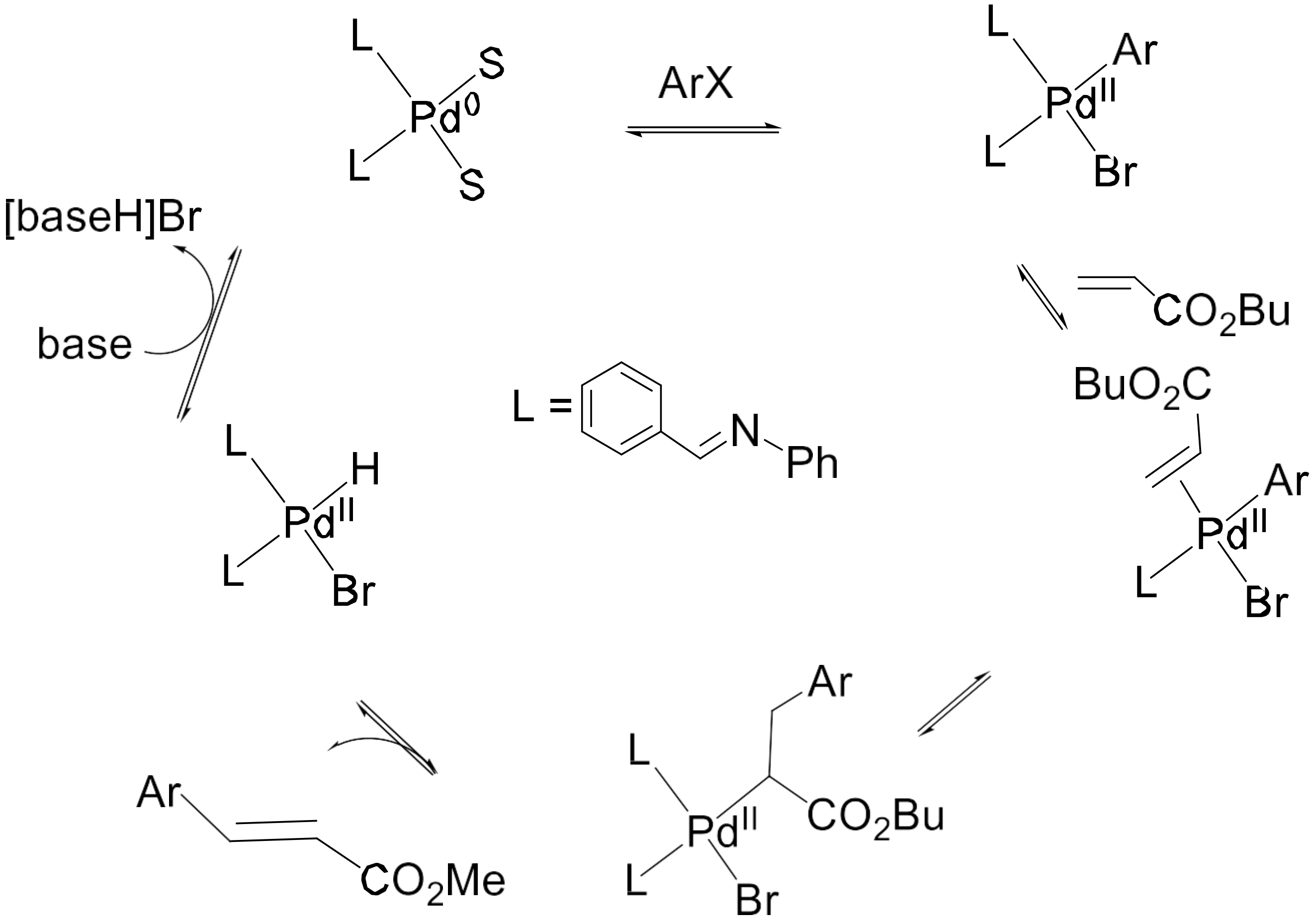
Addition of H⁺ and H⁻

Substrate does not bind to the metal



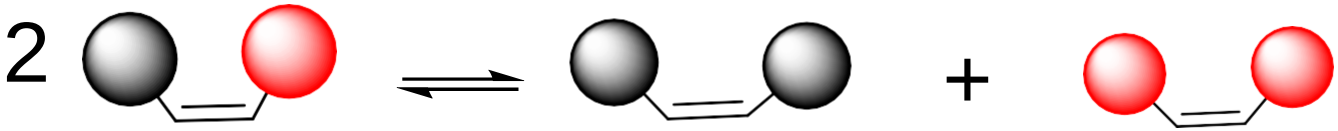
P.A. Dub and J. C. Gordon, *Dalton Trans.*, 2016,**45**, 6756

Heck Coupling Mechanism



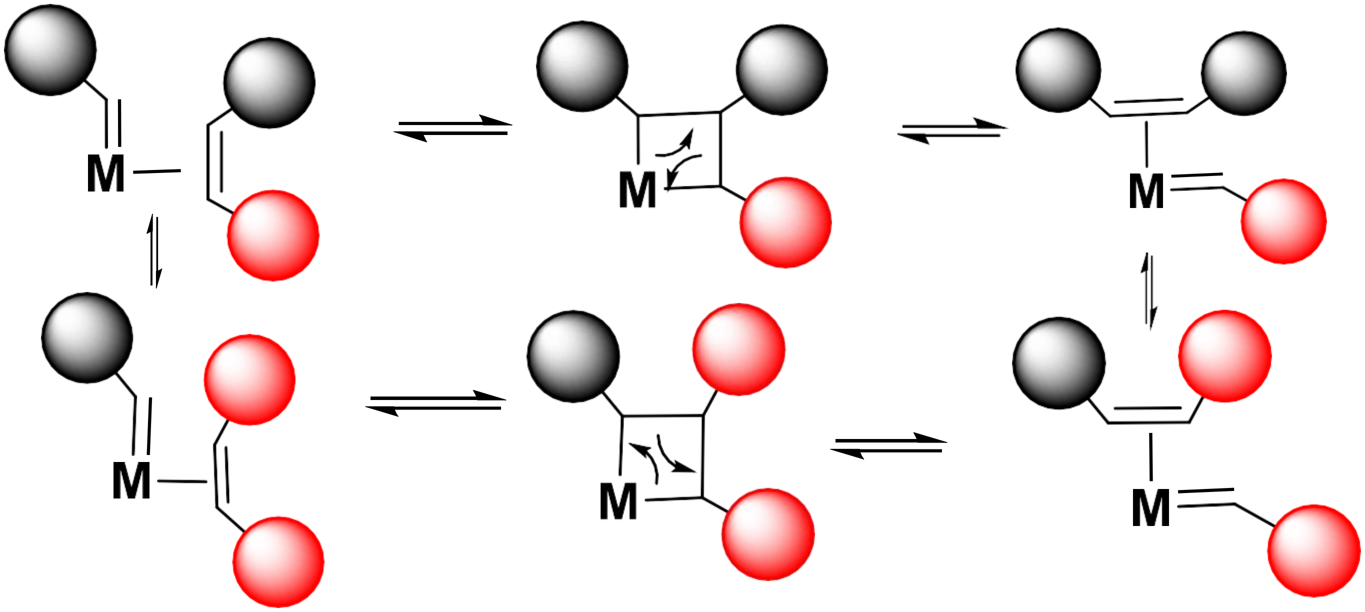
Blackmond and coworkers, *Angew Chem. Int. Ed*. 2005, **44**, 4302; *J. Am. Chem. Soc*. 2001, **123**, 1848

Alkene Metathesis



Cross-Metathesis

metathesis: from Greek
***meta*, change; *tithenai*, place**



Thank you