



University of Lucknow | Centenary Year
लखनऊ विश्वविद्यालय | शताब्दी वर्ष



Applications of Inorganic and Organometallic Compounds

▶ **Stoichiometric Applications**

▶ **Catalytic applications**

- reactions involving hydrogen
- reactions involving carbon monoxide
- reactions involving unsaturated hydrocarbons
- other reactions

▶ **Environmental and Biological Applications**

▶ **Applications in Materials Science**

Organometallic Chemistry



Sir Edward Frankland

(18 January 1825 – 9 August 1899)

(born in Lancaster, England)

“When, on July 28, 1848, Edward Frankland then a 23-year-old faculty member of Queenwood College in Hampshire, England, filled a thick-walled glass tube with finely granulated zinc and ethyl iodide and then sealed it, he did not realize that he had set up the reaction that would produce the first main-group organometallic compounds, ethylzinc iodide and diethylzinc..”

“Frankland devoted only some 15 years of his career to organometallic chemistry.”

D. Seyferth, Organometallics, 20 (2001) 2940-2955.

General Periodic Trends of Organometallic Compounds



Group 1: except lithium, ionic compounds

Li, Be, Mg, B, Al: covalent and multi centre (*e.g.*, 2e-3C) bonds

Group 2-11: M-C bond : σ - bond (*e.g.*, B-CH₃)
 π - bond ((*e.g.*, (CO)₅Cr=CH₂)
 δ -bond ([R₄Re \equiv ReR₄]²⁻)
 η -bond (*e.g.*, Cp₂Fe)

Lanthanides: M-C bond predominantly ionic

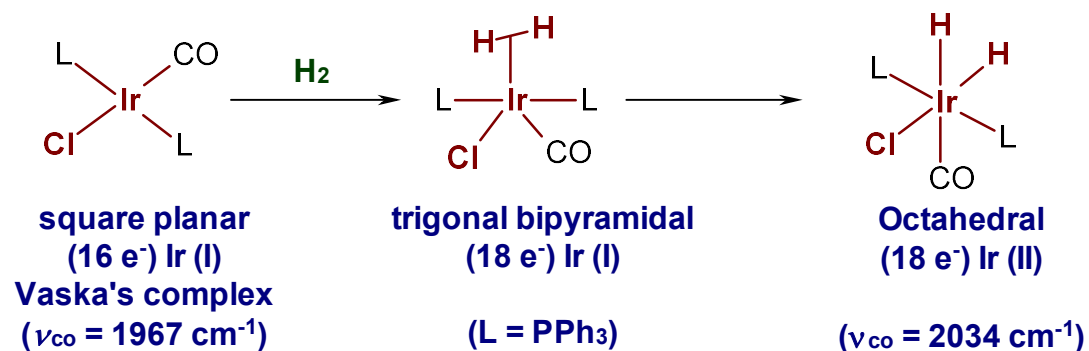
Actinides: M-C bond predominantly covalent

Group 12-16: mainly M-C σ bonds

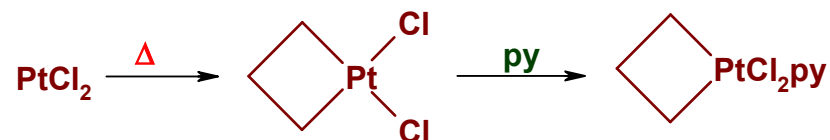
Reaction patterns of transition metal complexes

- Oxidative addition and reductive elimination reactions
- Insertion
- Transmetallation
- Elimination of α - and β - hydrogen
- Nucleophilic attack on ligands coordinated transition metals

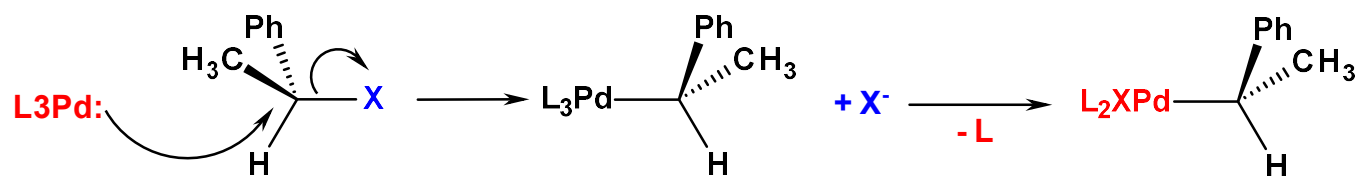
Oxidative additions and reductive elimination reactions



Oxidative addition of other molecules : O₂, D₂, HCl, C₂F₄, I₂, Cl₂



**S_N² Reaction : Found in polarized substrates
such as alkyl, acyl and benzyl halides**



Radical mechanism



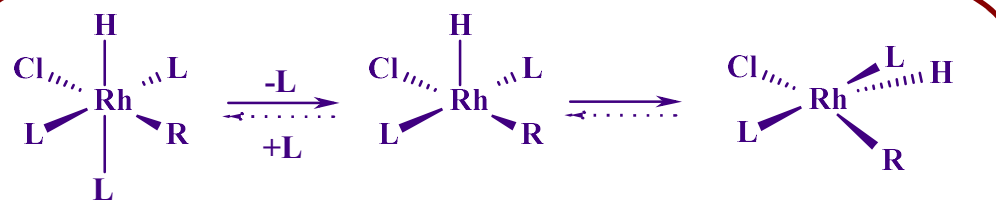
Ionic mechanism



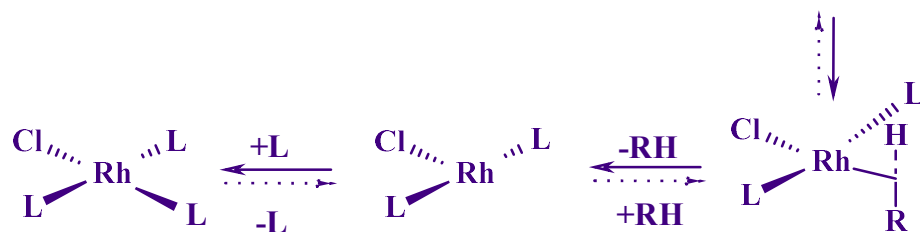
16 e⁻ d⁸ square planar

16 e⁻ d⁸ square planar

Reductive elimination

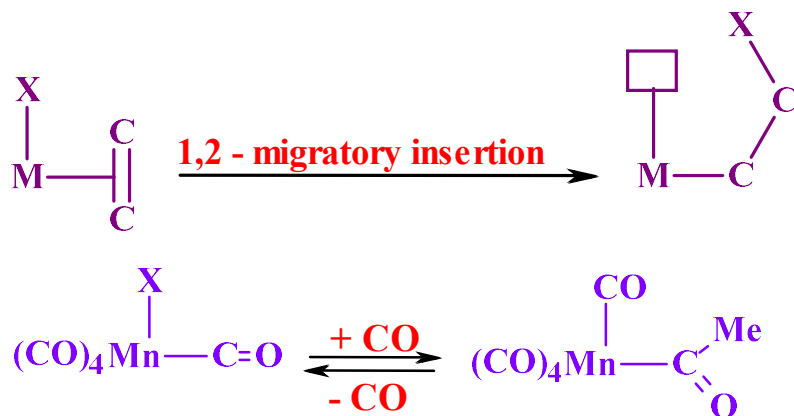


Y-shaped distorted TBP

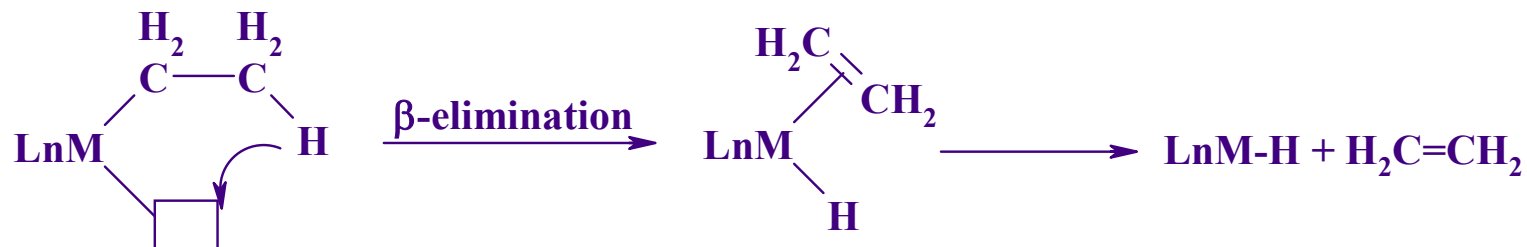
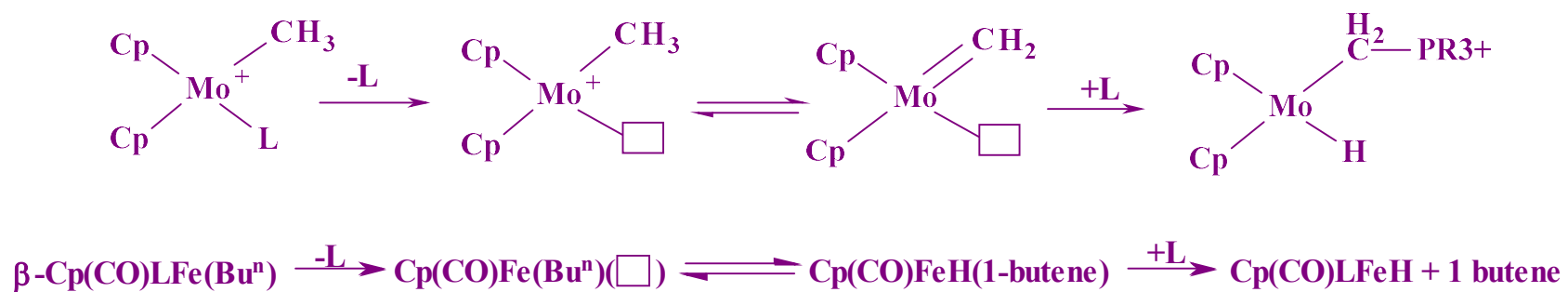


transition state

Insertion Reaction



Elimination Reaction

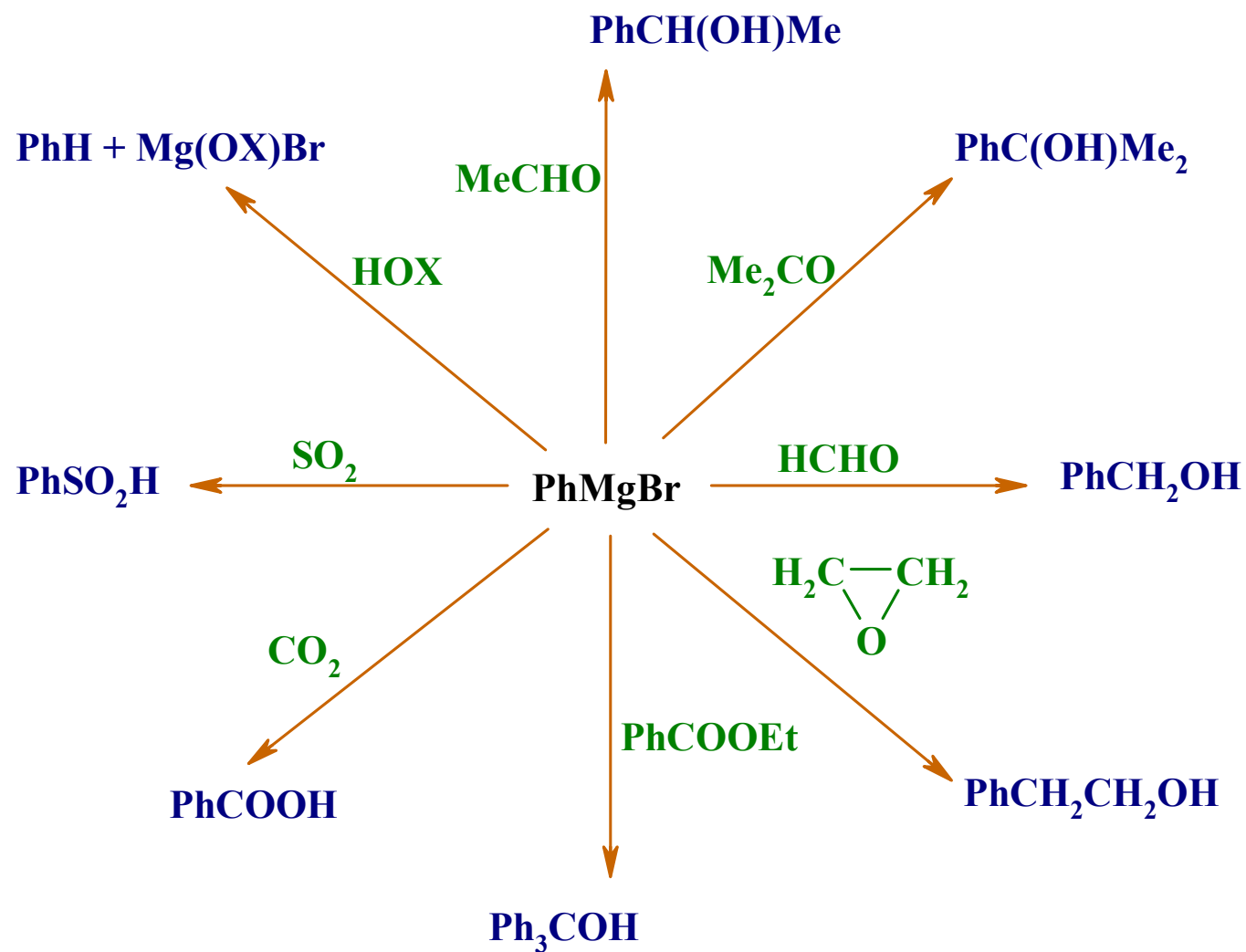


Stoichiometric Applications

Organomagnesium compounds



Victor Grignard
Nobel Prize (1911)



Catalytic Applications

Reactions involving hydrogen

Hydrogenation reactions

Asymmetric hydrogenation reactions

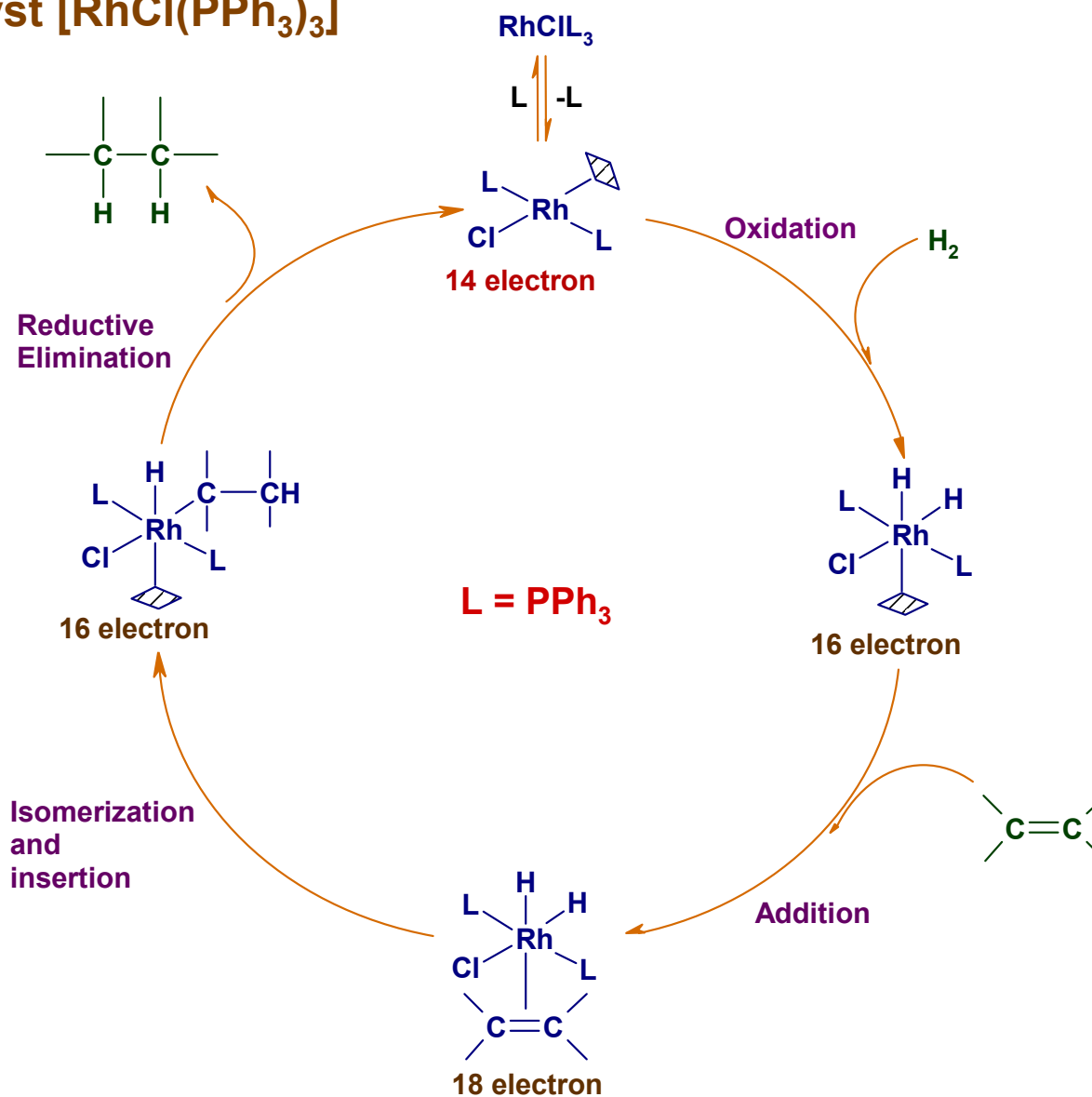
Dehydrogenation reactions

Hydrogenation reactions

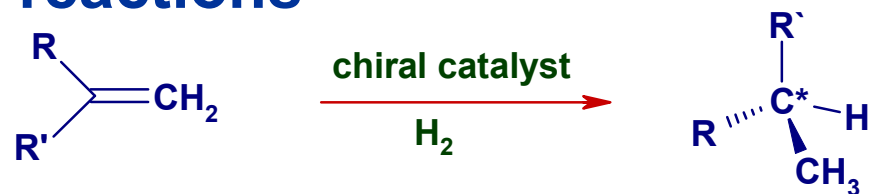
Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$



Geoffrey Wilkinson
Nobel Prize (1973)

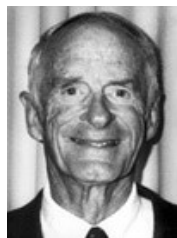


Asymmetric hydrogenation reactions



optically pure product

Nobel Prize 2001

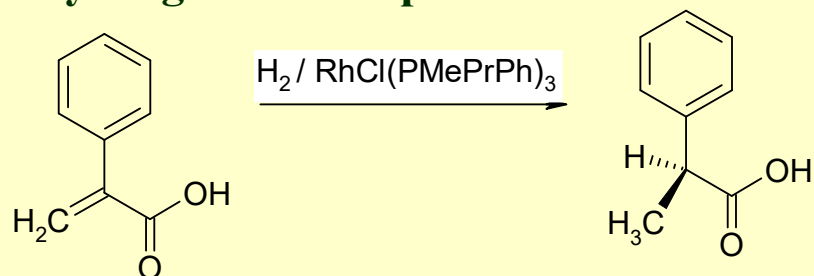


William S. Knowles

25% Nobel Prize

Retired in 1986 from Monsanto company, St. Louis, MO

Hydrogenation of prochiral olefins



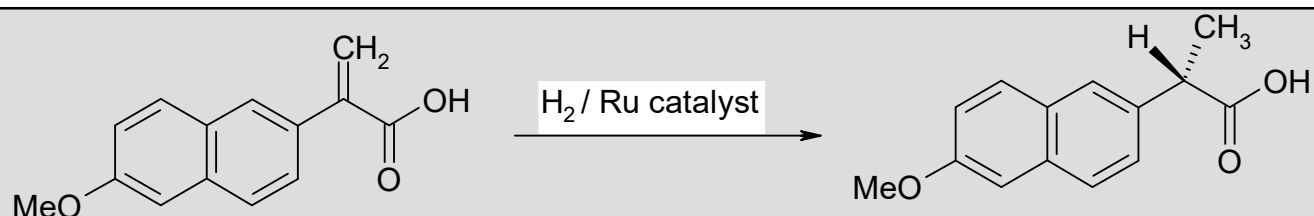
Angew. Chem. Int. Ed., 41(2002) 1999



Ryoji Noyori

25% Nobel Prize

Nagoya University, Japan



S-naprofen (97% ee)

Angew. Chem. Int. Ed., 41(2002) 2008

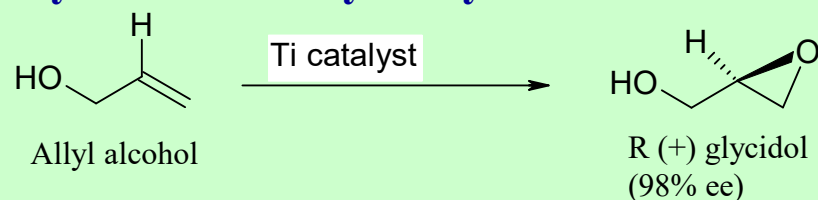


K. Barry Sharpless

50% Nobel Prize

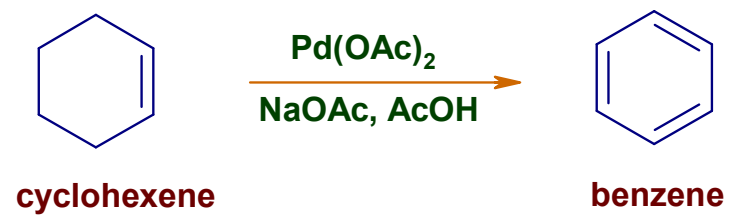
Scripps's Institute, La Jolla, California

Asymmetric epoxidation Asymmetric -dihydroxylation



Angew. Chem. Int. Ed., 41(2002) 2024

Dehydrogenation reactions



Reactions involving carbon monoxide

Fischer-Tropsch synthesis

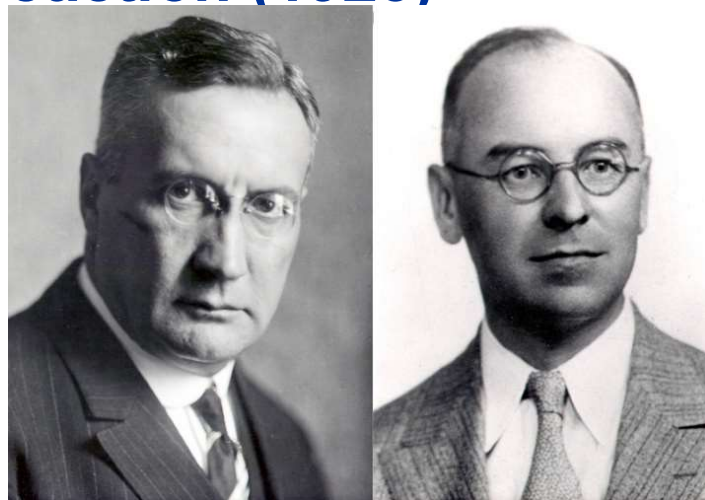
Hydroformylation

Carboxylation

Carbonylation of methanol

Water gas shift reaction

Fischer-Tropsch reaction (1923)



Franz Joseph Emil Fischer (19 March 1877 -1 December 1947) **Hans Tropsch** (7 Oct. 1889- 8 Oct.1935)

Reductive polymerization of CO

most commonly catalyzed by cobalt supported on alumina, silica or titania

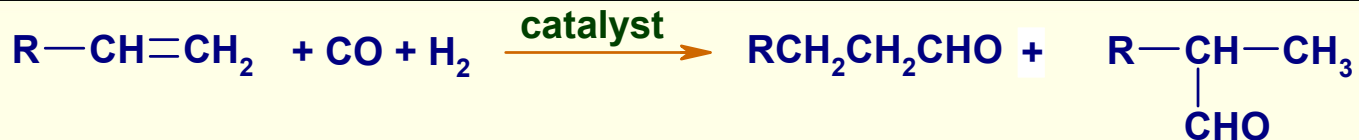


In 1943 Germany produced 585000 tons of products which contained 46% gasoline, 23% diesel oil, 3% lubricating oil and 28% waxes

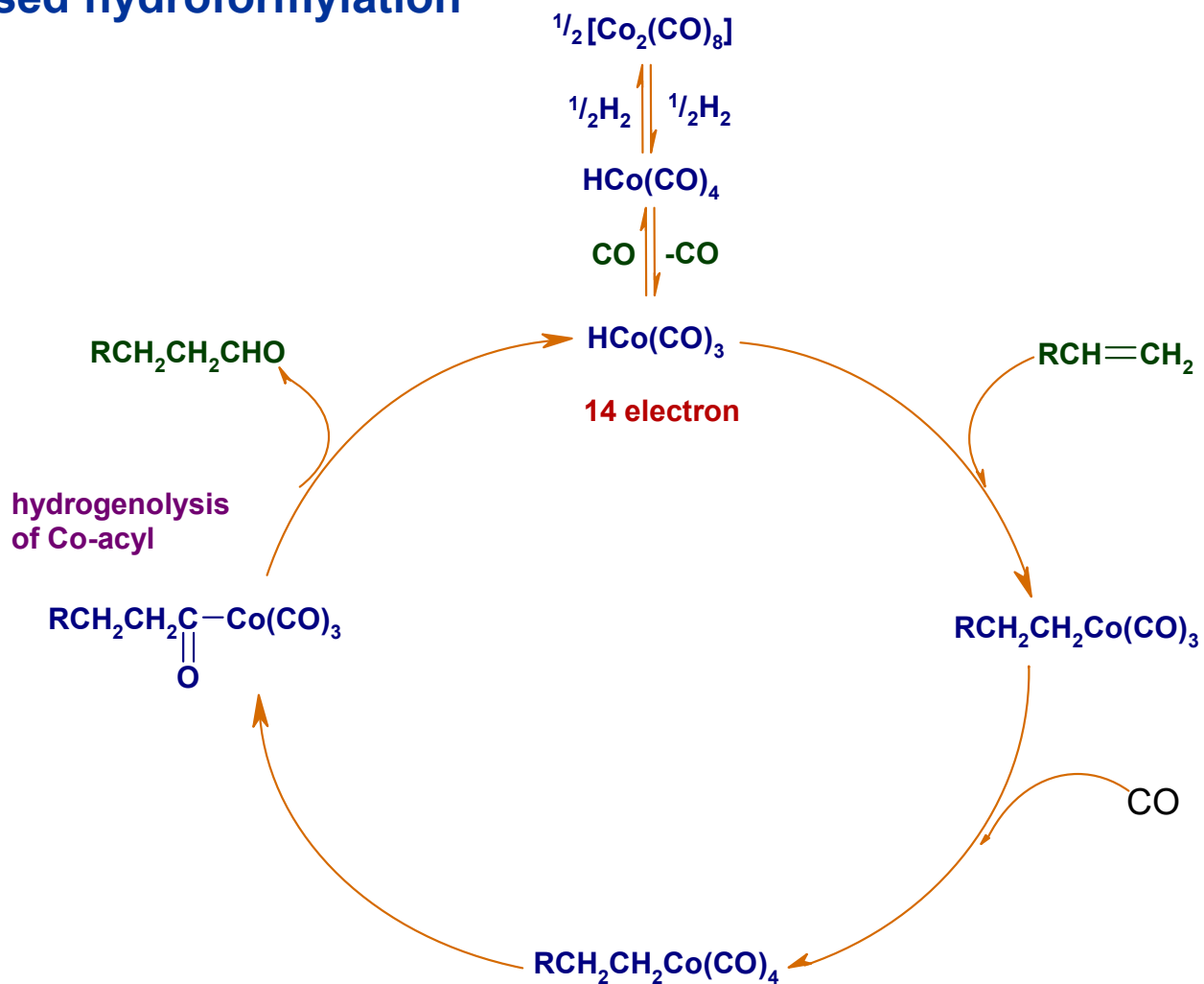
Hydroformylation or 'OXO' reactions

Otto Roelen (1938) – effect of alkene on Fisher-Tropsch reaction

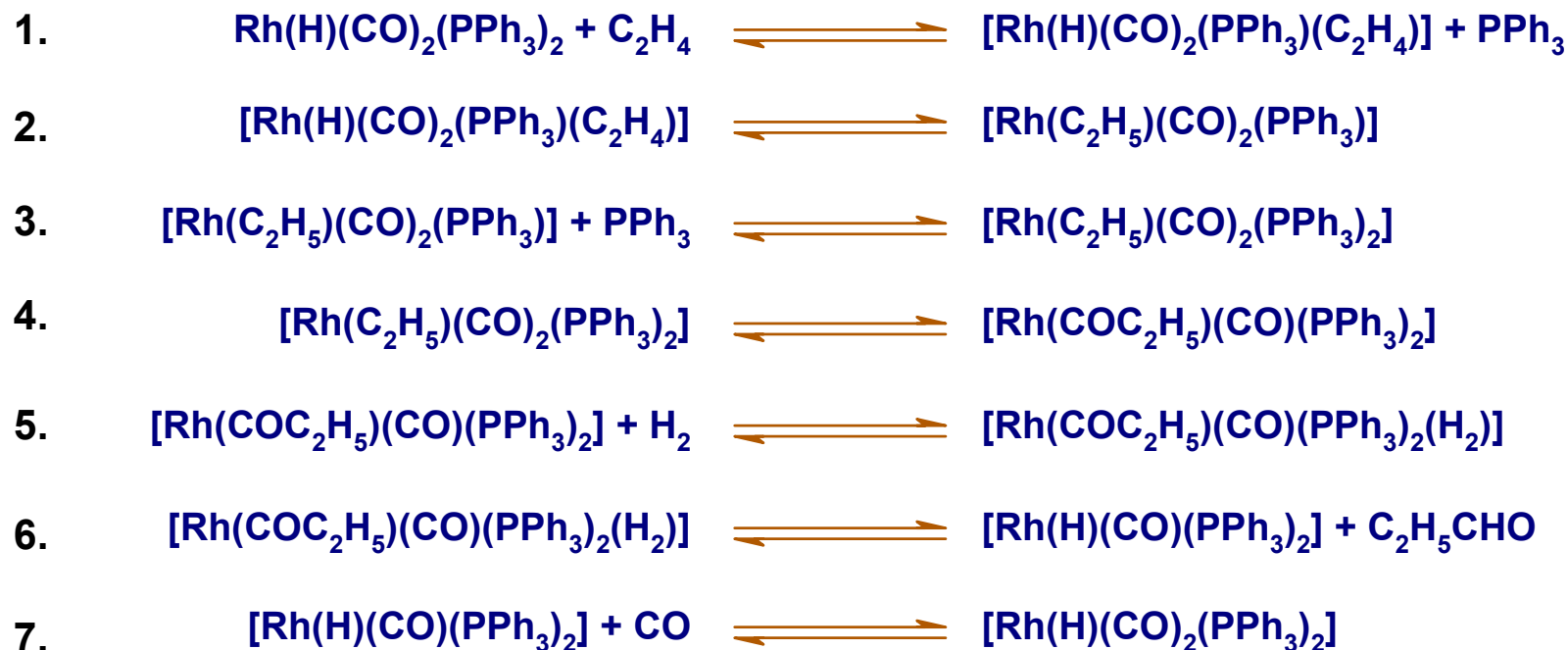
Reaction of an olefin with CO and hydrogen



Cobalt catalysed hydroformylation



Hydroformylation of C₂H₄ by [Rh(H)(CO)₂(PPh₃)₂]



Ligand addition to sixteen electron species – 3&7

Ligand substitution – 1

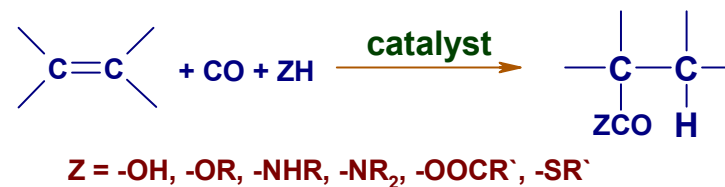
Ligand insertion with in coordination sphere – 2 & 4

Oxidative addition – 5

Reductive elimination - 6

Carboxylation

REPPE (1940) type reaction – used $\text{Ni}(\text{CO})_4$



Carboxylation of olefins in presence of CO and appropriate protic compound

Carbonylation of Methanol



- i) BASF (Germany) (1965) $\text{Co}(\text{OAc})_2/\text{CoI}_2$ 680 atm./ 250°C
- ii) MONSANTO (USA) (1968) $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ~30 atm./ 180°C

Water-gas shift reaction



- i) Find application in CO removal, hydrogen production and adjustment of H₂:CO ratio in synthesis gas.
- ii) Platinum group metal complexes are used as catalyst

Reactions involving unsaturated hydrocarbons

Ziegler Natta Polymerization

Olefin metathesis

Cyclisation and linear oligomerization

Co-dimerization of olefins

Isomerization of alkenes

Hydroboration and Hydrosilylation

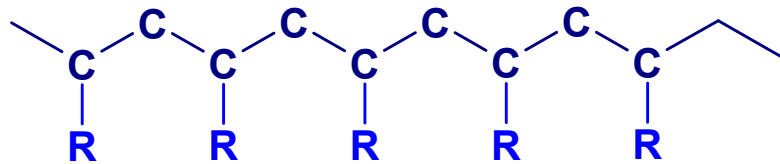
Ziegler Natta Polymerization



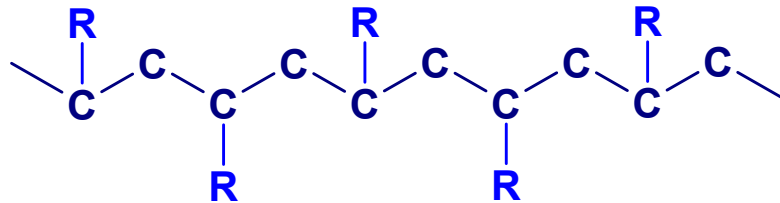
Karl Ziegler **Giulio Natta**
Nobel Prize (1963)

- 2,200,000 tons of polyethylene per year
- 2,900,000 tons of polypropylene per year
- Polymerization of α -olefin by AlR_3 and transition metal compounds.
Reaction is stereospecific.

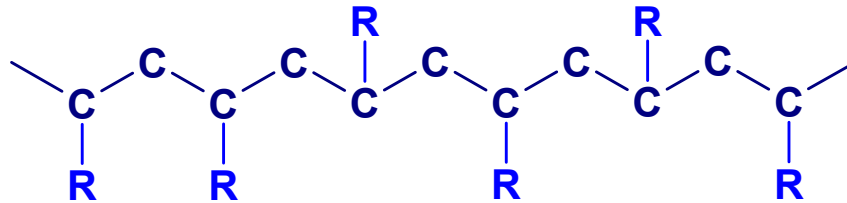
isotactic



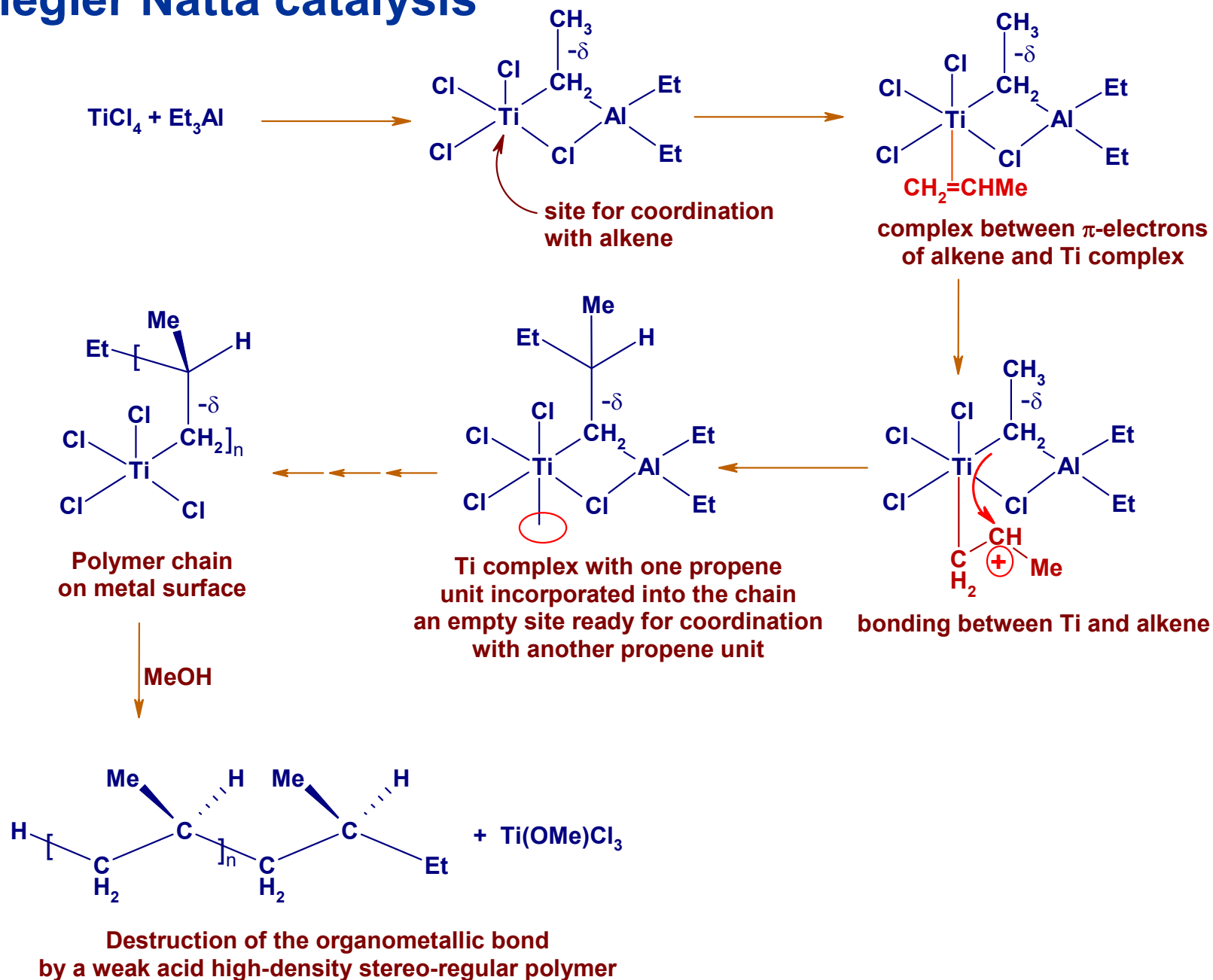
syndiotactic



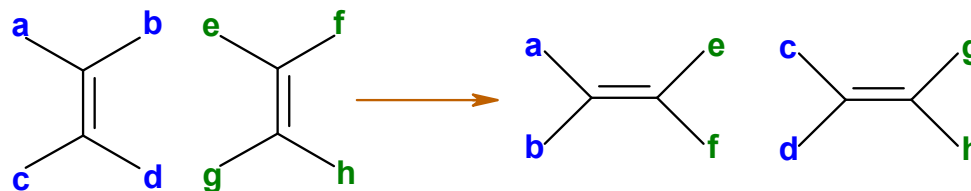
actactic



Ziegler Natta catalysis



Olefin Metathesis

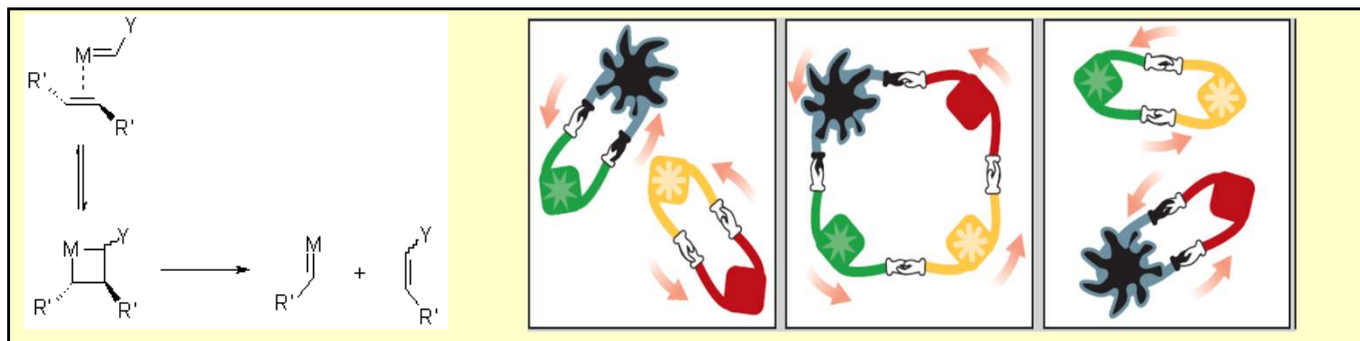


Nobel Prize 2005



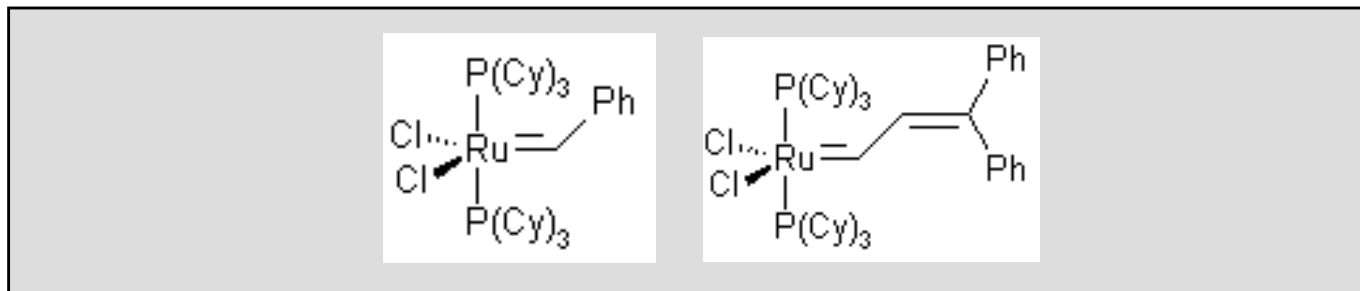
Yves Chauvin

Institut Français du Pétrole
Rueil-Malmaison, France



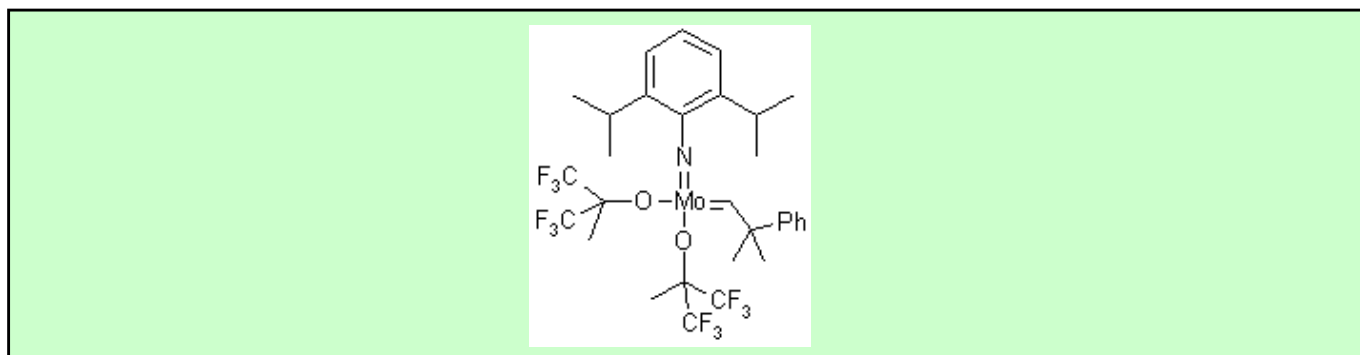
Robert H. Grubbs

California Institute of Technology
(Caltech), Pasadena, CA, USA



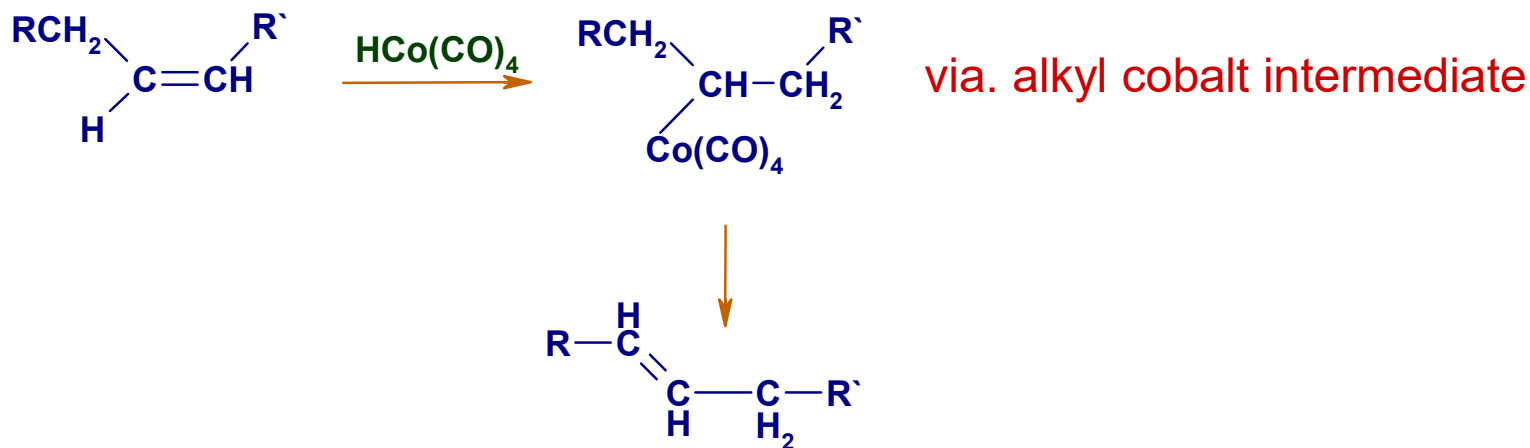
Richard R. Schrock

Massachusetts Institute of
Technology (MIT)
Cambridge, MA, USA

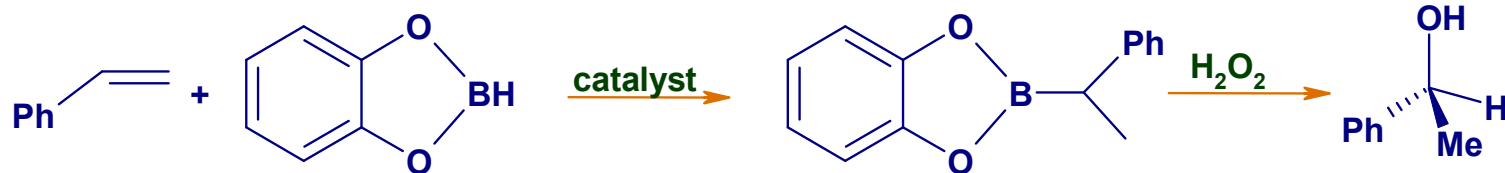


Isomerization of alkenes

Transition metal compounds bring about double bond migration in hydrocarbons

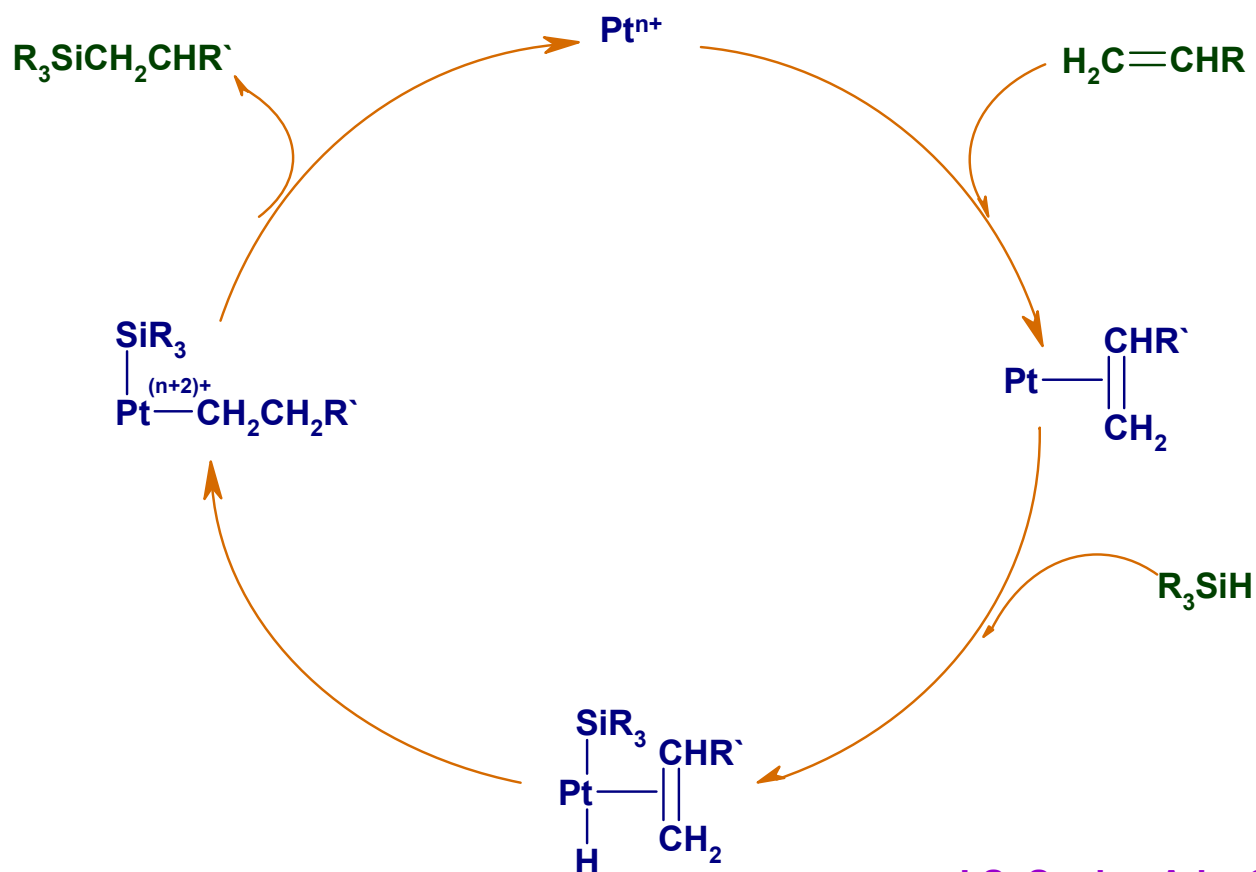


Hydroboration



Herbert C. Brown
Nobel Prize (1979)

Hydrosilylation



J.S. Speier, *Adv. Organomet. Chem.*, 17 (1979) 407

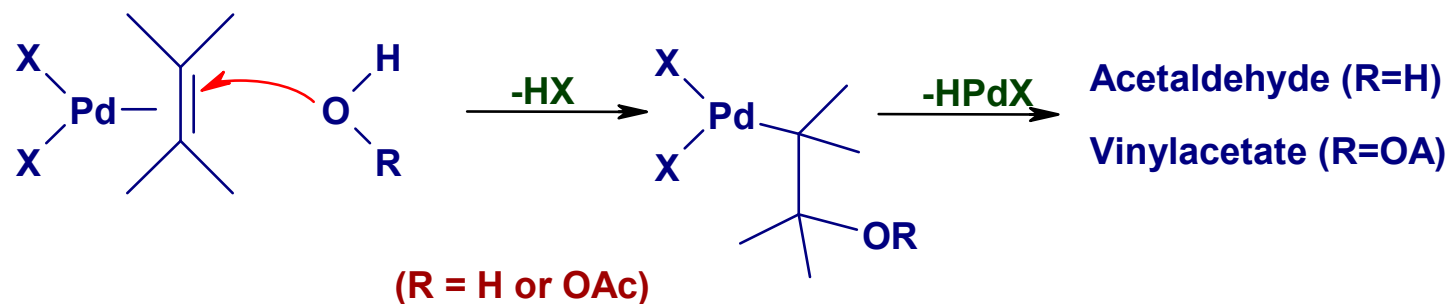
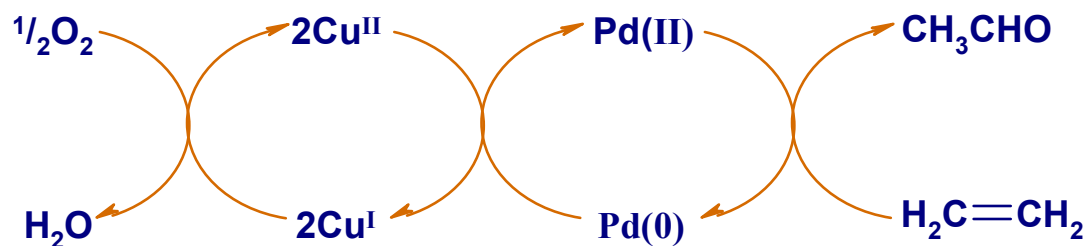
Other reactions

- ▶ **Wacker process**
- ▶ **Carbon-carbon and carbon-hetero atom bond formation**
- ▶ **Dinitrogen complexes (nitrogen fixation)**
- ▶ **Oxidation with transition metal dioxygen and peroxy complexes**
- ▶ **CO₂ activation**
- ▶ **SO₂ complexes**
- ▶ **CH activation**
- ▶ **Epoxidation reactions with ROOH**

Wacker process

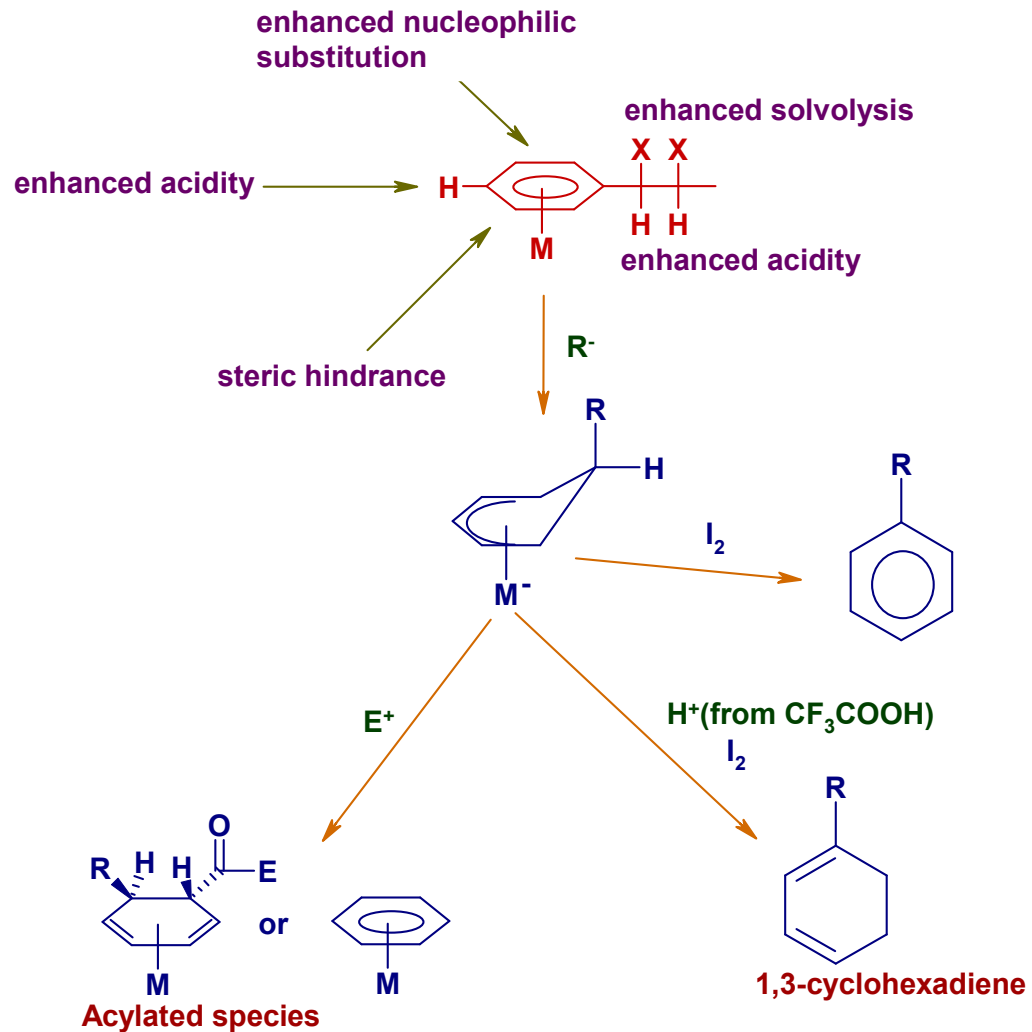
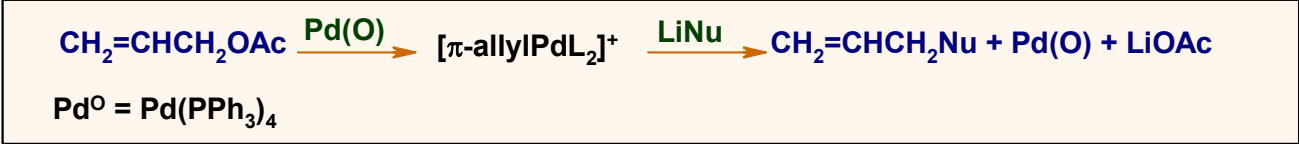


- F.C. Philips, Am. Chem. J., 16 (1894) 255
- S.C. Ogburn Jr. and W.C. Brastow, JACS, 55 (1933) 1307



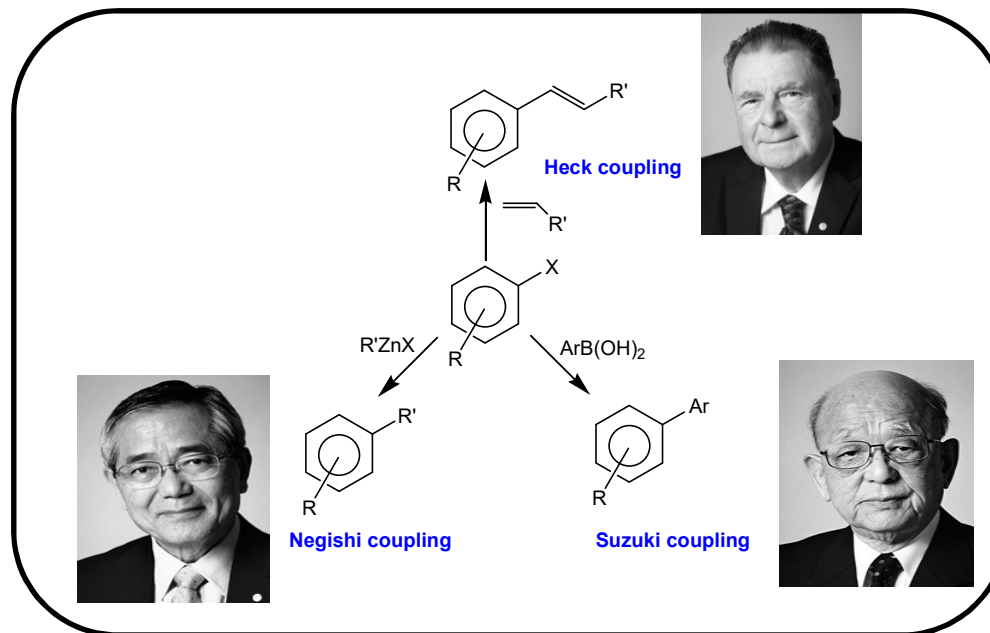
- J. Smidt et.al., Angew. Chem., 71 (1959) 176
- J. Smidt et.al., Angew. Chem., 74 (1962) 93

Nucleophilic attack on ligands coordinated transition metals



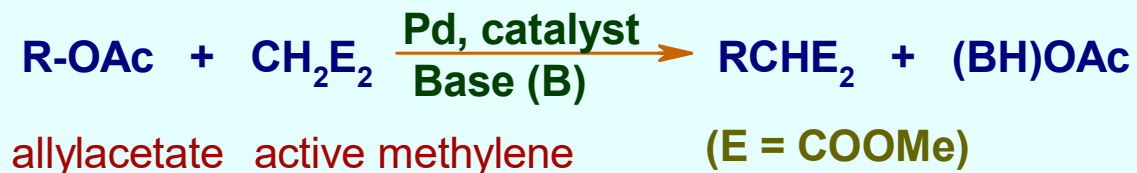
Carbon-carbon and carbon-hetero atom bond formation

C-C coupling reactions
Nobel Prize in Chemistry 2010

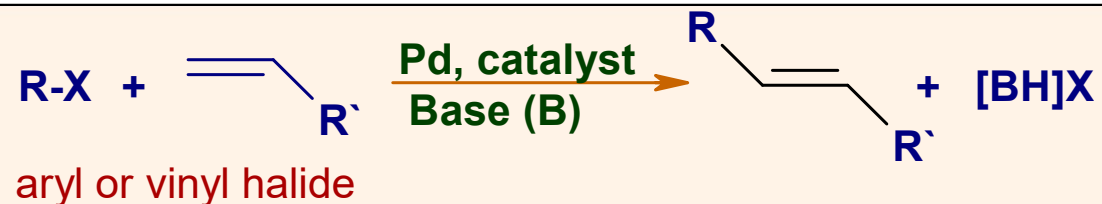


C-C Coupling reaction

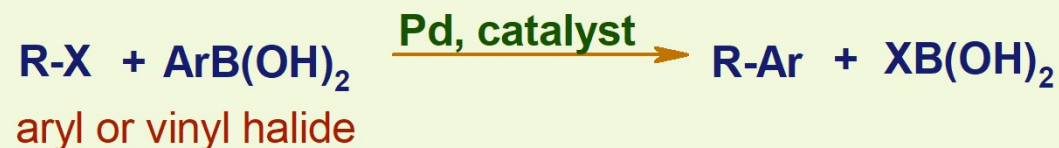
Tsuji-Trost reaction



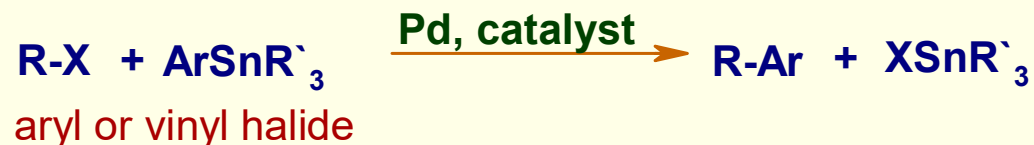
Mizoroki-Heck reaction



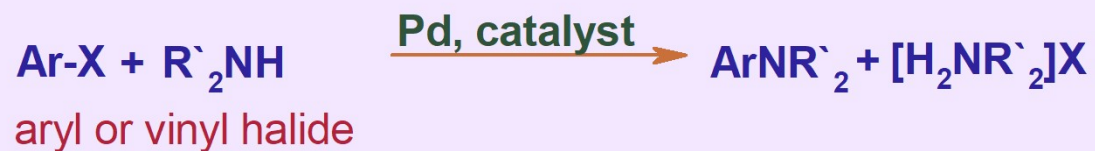
Miyaura-Suzuki reaction



Stille coupling



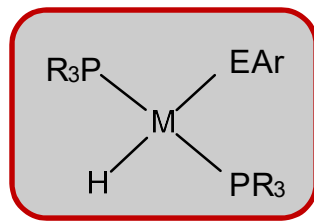
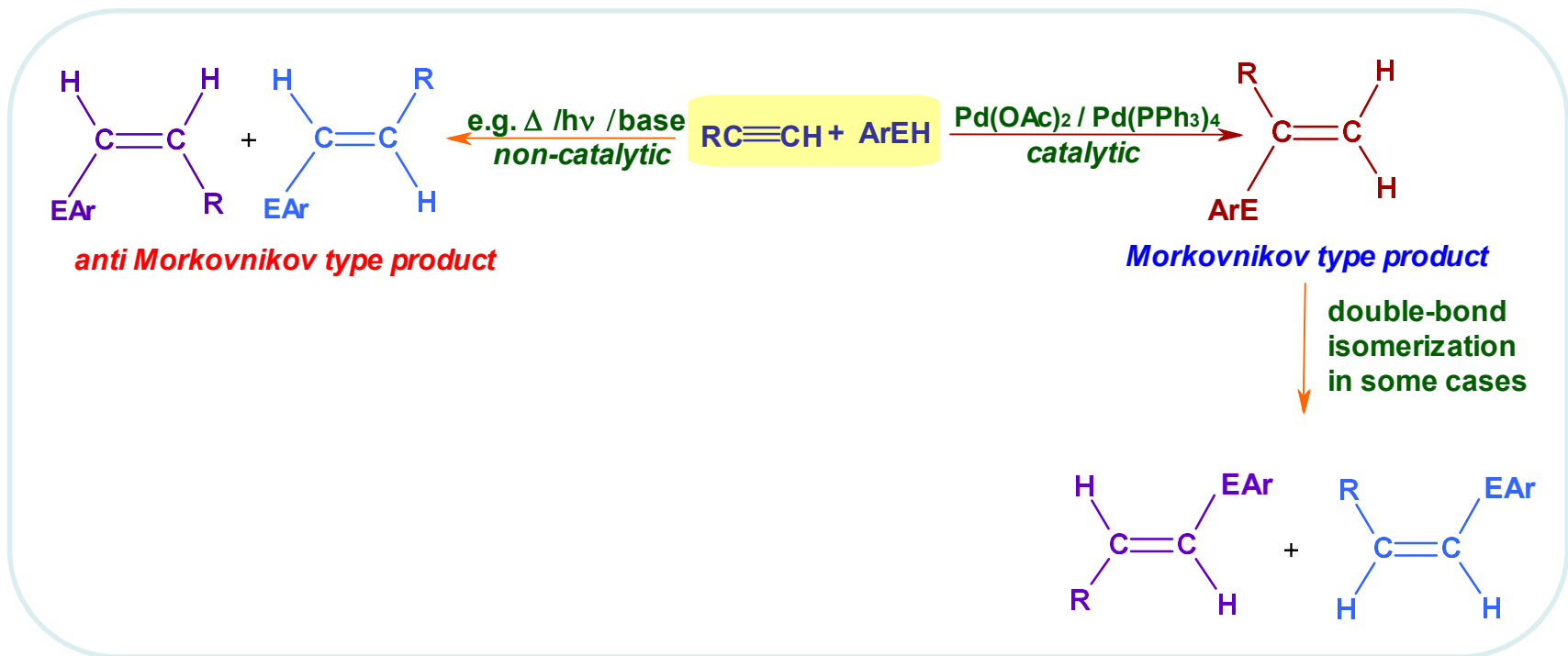
Butchwald-Hartwig amination



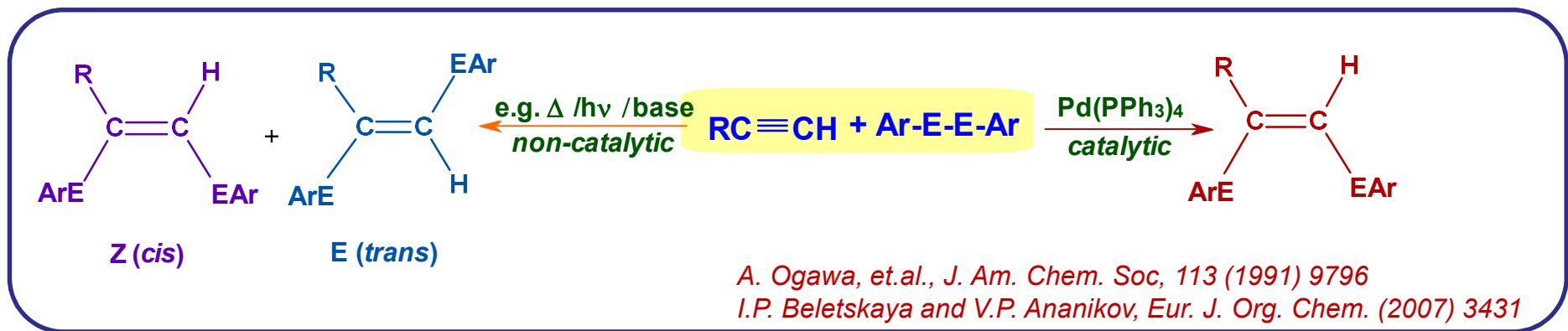
Carbon-hetero atom bond formation

C-B	C-C	C-N	C-O
	C-Si	C-P	C-S
	C-Ge		C-Se
	C-Sn		C-Te



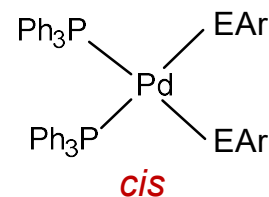


Key intermediate



- Arylchalenides showed good reactivity as against dialkyldichalcogenides
- Only low valent palladium complexes, (e.g. Pd(PPh₃)₄) showed activity while Pd(II) (e.g. PdCl₂(PPh₃)₂, Pd(OAc)₂, PdCl₂(PhCN)₂) complexes are inactive

- Active intermediate



(*trans* derivatives are inert)