

Lecture 9

Inorganic chemistry

Previous lecture

Reactions of Ferrocene
Oxidative addition
Reductive elimination
Migratory Insertion

β -hydrogen elimination

σ -bond metathesis

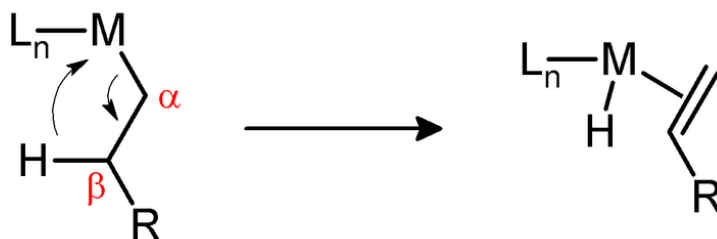
Homogeneous catalysis: industrial
applications

β -Hydride elimination

Beta-hydride elimination is a reaction in which an alkyl group having a β hydrogen, σ bonded to a metal centre is converted into the corresponding **metal-bonded hydride** and a π bonded **alkene**.

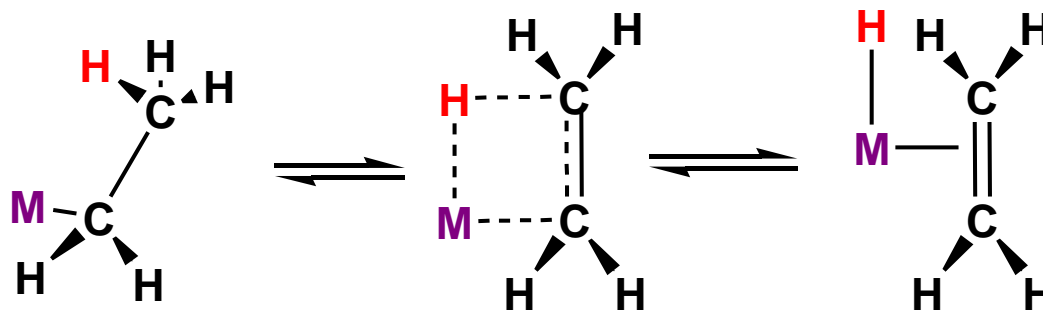
The alkyl must have hydrogens on the beta carbon. For instance butyl groups can undergo this reaction but methyl groups cannot.

The **metal complex must have an empty (or vacant) site** cis to the alkyl group for this reaction to occur.



No change in the formal oxidation state of the metal

mechanism

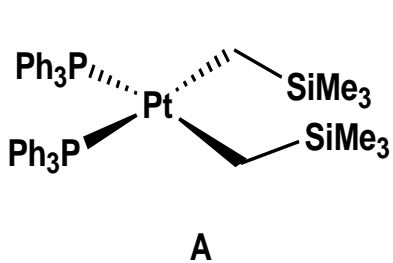


Can either be a vital step in a reaction or an unwanted side reaction

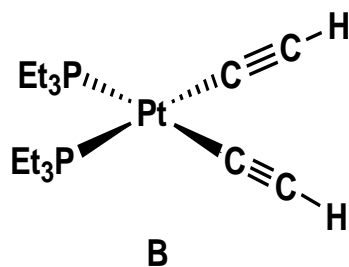
β -hydrogen elimination does not happen when

- (1) the alkyl has no β -hydrogen (as in PhCH_2 , Me_3CCH_2 , Me_3SiCH_2)
- (ii) the β -hydrogen on the alkyl is unable to approach the metal (as in $\text{C}\equiv\text{CH}$), therefore the $\text{M}-\text{C}-\text{C}-\text{H}$ unit cannot become coplanar

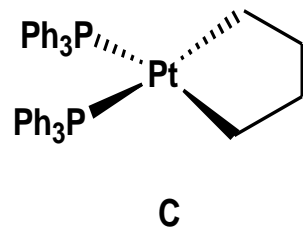
Select the most **unstable** platinum σ complex from the given list. Justify your answer



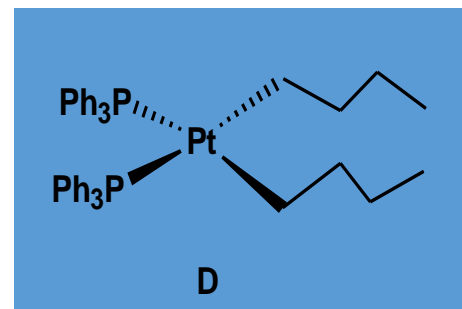
No β -H



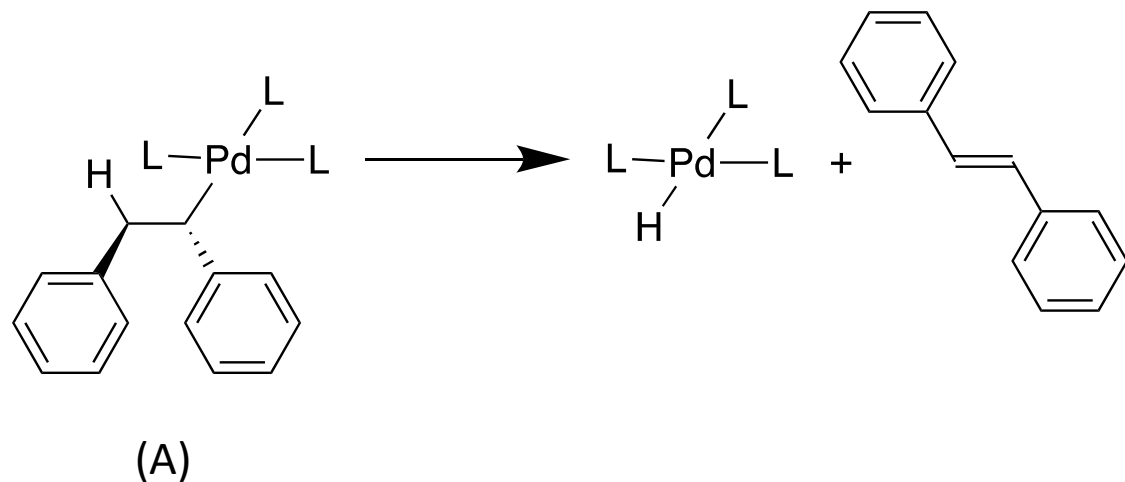
β -H unable to approach M coplanar



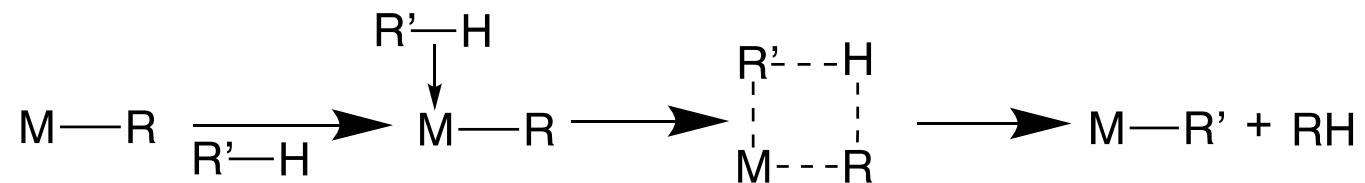
MCCH unit will not be



Predict the stability of compound A?



σ -bond metathesis

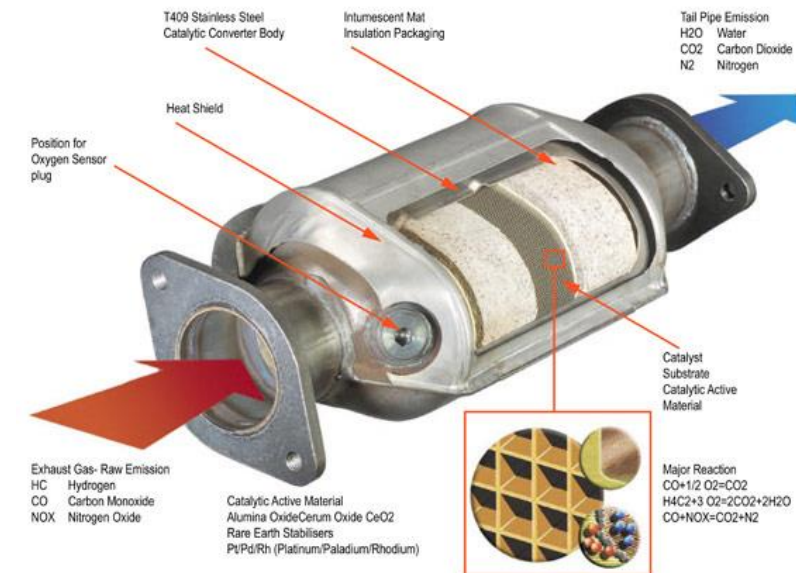
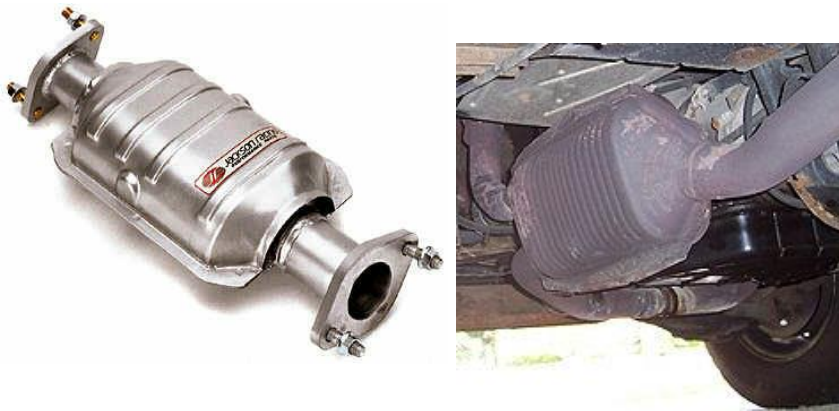


A σ -bond metathesis reaction is a concerted process that sometimes occurs when oxidative addition cannot take place.

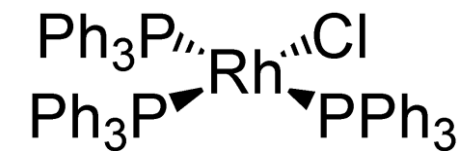
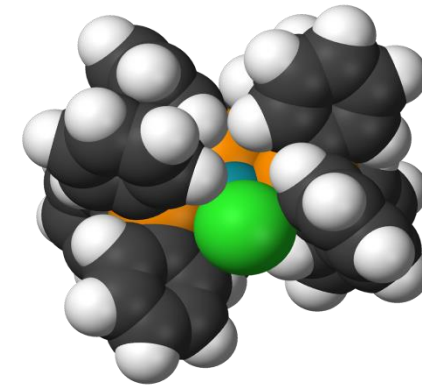
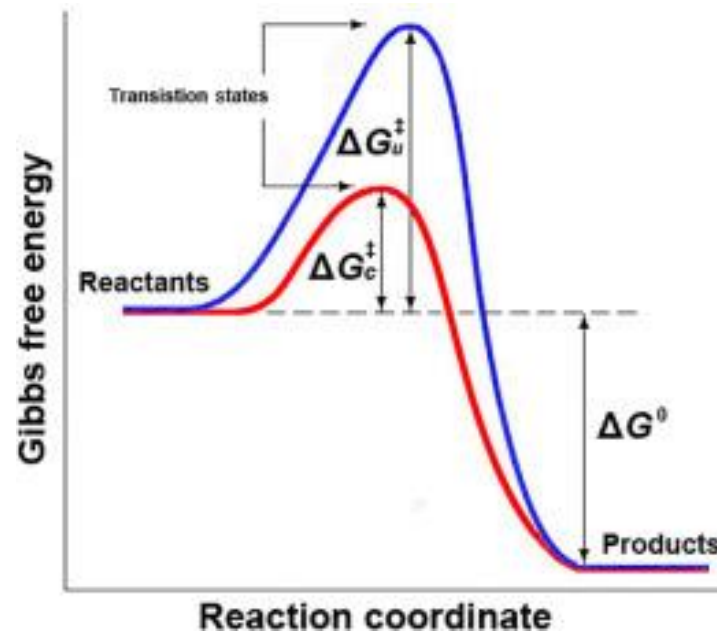
Homogeneous catalysis: industrial applications

Homogeneous catalysis using organometallic Catalysts

A catalyst typically increases the reaction rates by lowering the activation energy by opening up pathways with lower Gibbs free energies of activation (G).



Heterogeneous

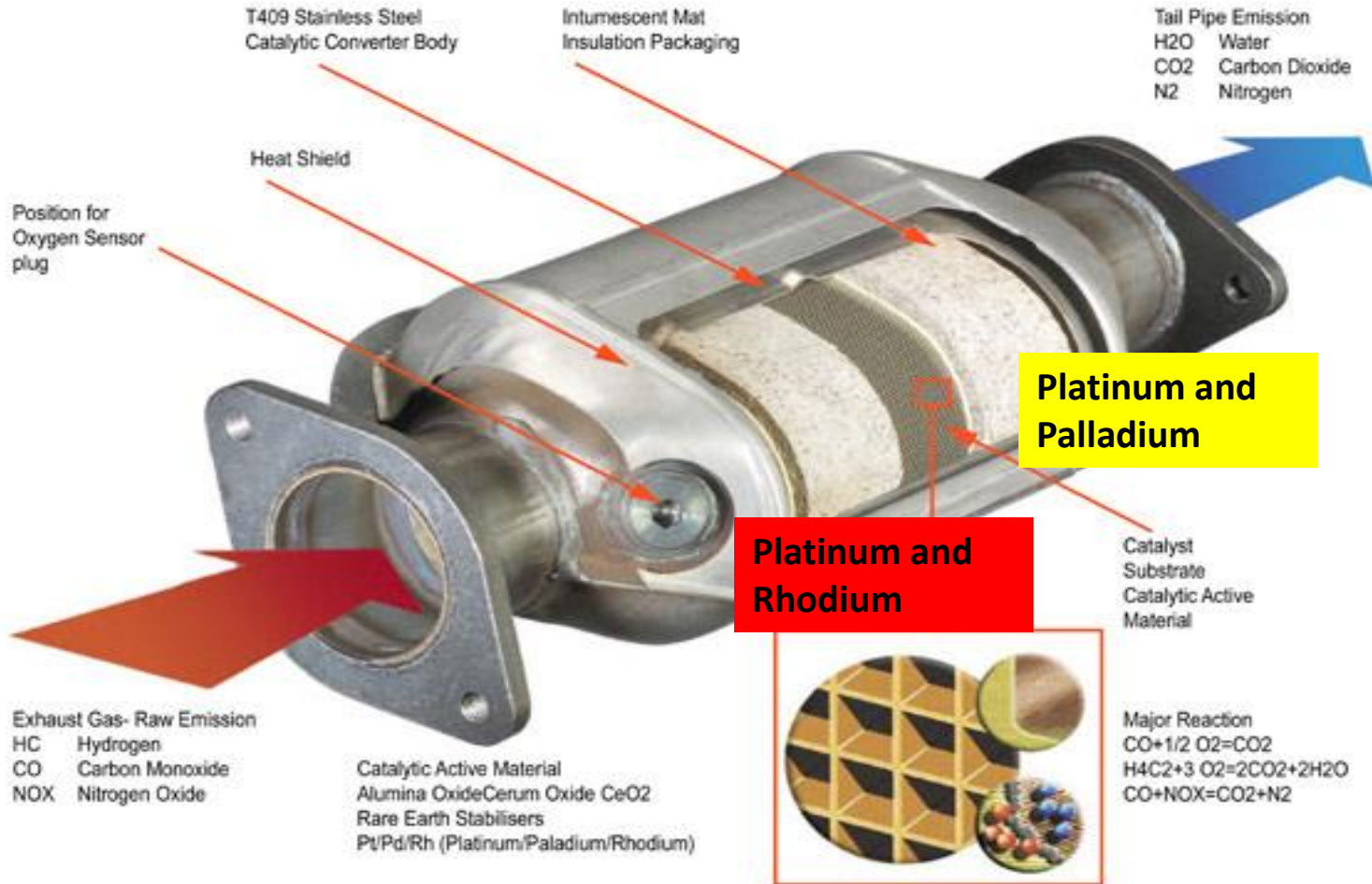


Homogeneous

Homogeneous versus Heterogeneous Catalysis

<i>Parameter</i>	<i>Heterogeneous</i>	<i>Homogeneous</i>
Phase	Gas/solid	Usually liquid/ or solid soluble in the reactants
Required temperature	High	Low (less than 250°C)
Product selectivity	Less (often mixtures)	More
Catalyst recycling	Simple and cost effective	Expensive and complex
Reaction mechanism	Poorly understood	Reasonably well understood
Product separation from catalyst	Easy	Elaborate and sometimes problematic
Fine tuning of catalyst	Difficult	Easy

Heterogeneous Catalyst- Catalytic Converter of a Car



Chemistry at the molecular level – Poorly understood

Home assignment : See Youtube video 'Catalysis'

Turnover Number and Turnover frequency

- The turnover number is defined as the absolute number of passes through the catalytic cycle before the catalyst becomes deactivated. **A large TON (e.g., 10^6 – 10^{10}) indicates a stable, very long-lived catalyst.** The TON can be calculated by dividing the amount of reactant (moles) by the amount of catalyst (moles):

$$\text{TON} = \frac{\text{Number of moles (equivalents) of reactant}}{\text{Number of moles (equivalents) of catalyst}}$$

This assumes a yield of the product of 100%, which is most often not the case. To calculate the true number of turnovers, the yield obtained needs to be taken into account. For example, if 10 mol of reactant and 2.5 mol of catalyst are used, then the TON becomes, $\text{TON} = 10/4 = 4$

If the yield of the product is 94%, then the actual number of turnovers is

$$\text{Actual TON} = 4 \times 0.94 = 3.76$$

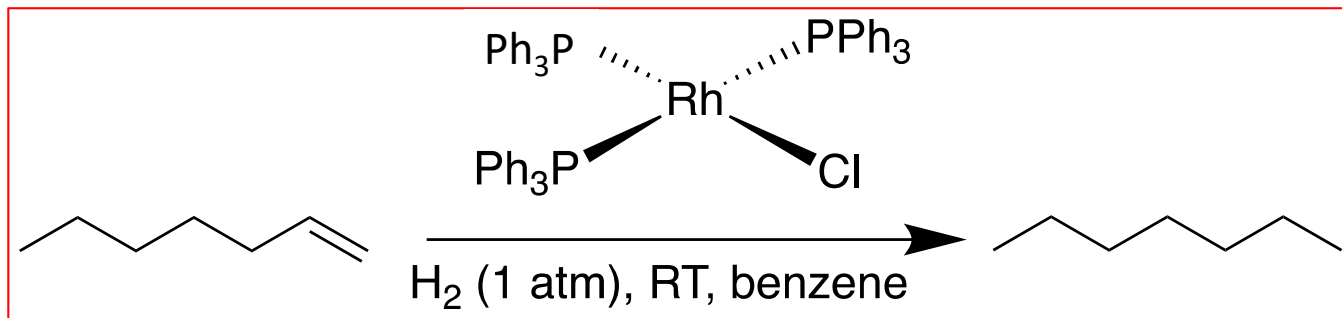
- Turnover frequency is defined as the number of passes through the catalytic cycle per unit time (typically seconds, minutes or hours). This number is usually determined by dividing the TON by the time required to produce the given amount of product. **A higher TOF indicates better efficiency for the catalyst.** The units are just time^{-1}

However, as with the TON, the actual yield of the product also needs to be taken into account. Continuing the example above, if the reaction in question was run for 7 h to obtain the 94% yield, the TOF is

$$\text{TON} = \frac{3.76 \text{ turnovers}}{7\text{h}} = 0.54 \text{ h}^{-1}$$

In general, industrial chemists are interested in both TON and turnover frequency (TOF).

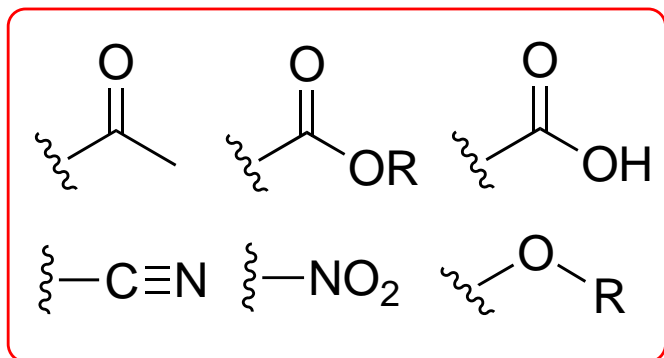
Wilkinson's Catalyst



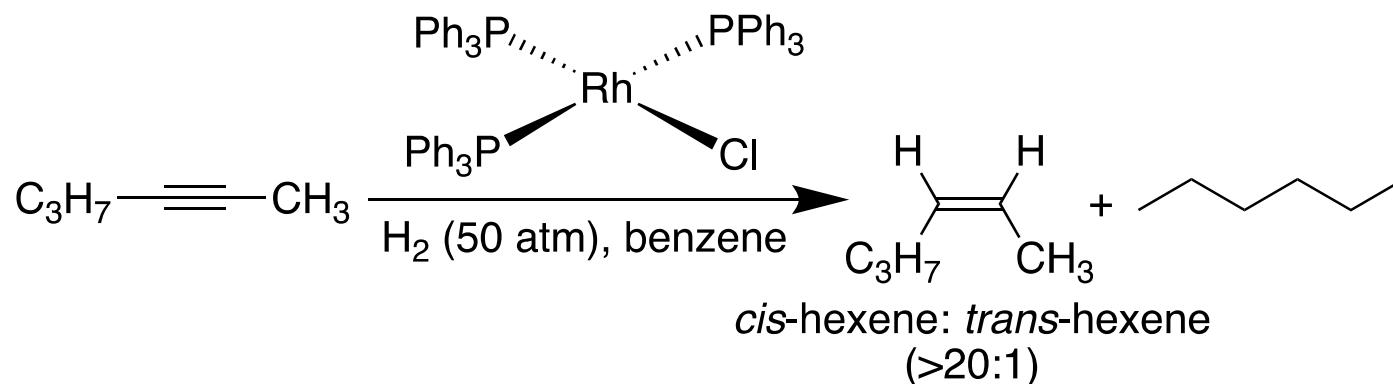
Wilkinson's catalyst: The first example of an effective and rapid homogeneous catalyst for hydrogenation of alkenes, **active at room temperature and atmospheric pressure.**

Square planar 16 electron d^8 complex $(\text{Ph}_3\text{P})_3\text{RhCl}$

Discovered by G Wilkinson as well as by R Coffey almost at the same time (1964–65)

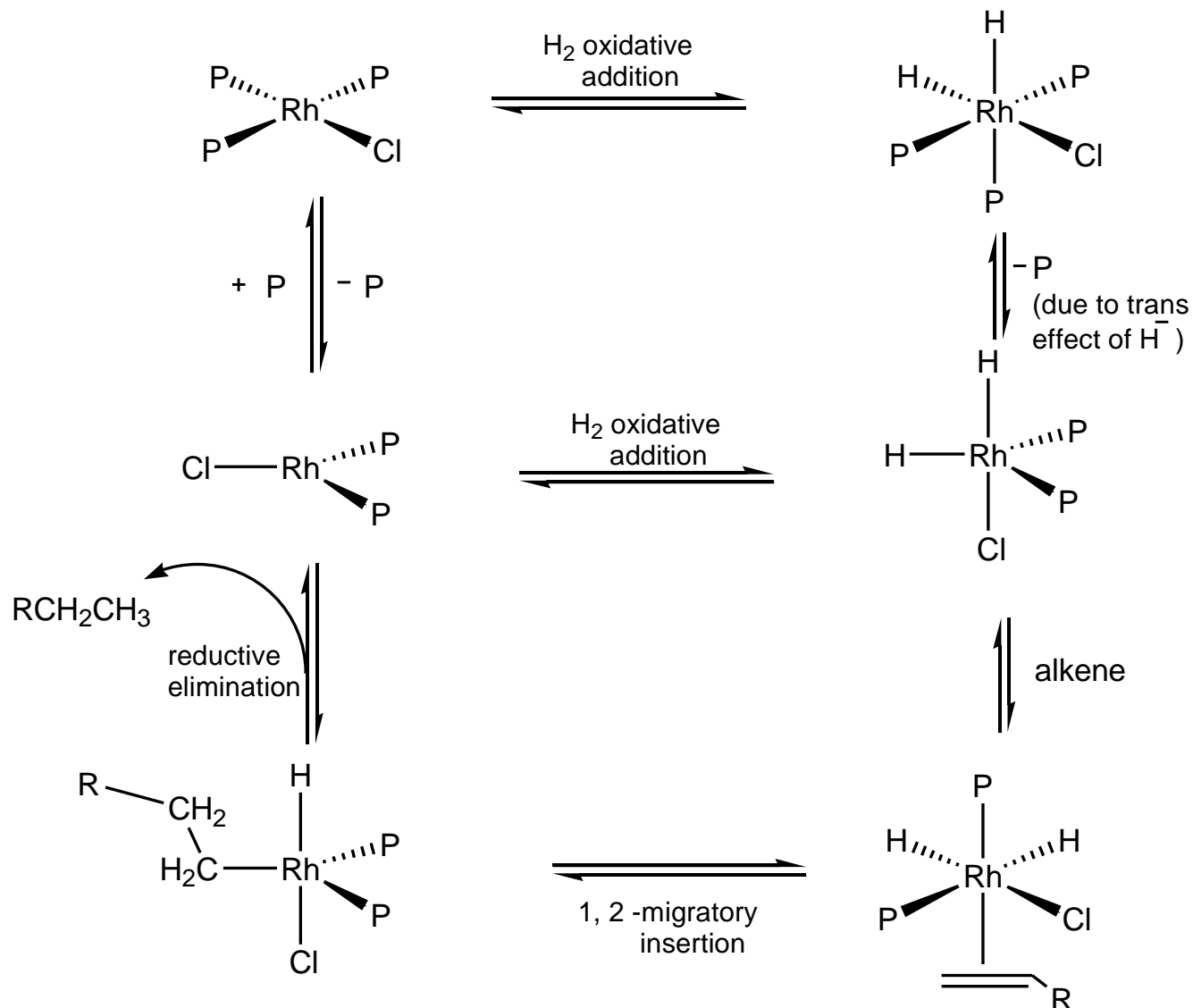


➤ These functional groups remain unaffected during hydrogenation reaction catalyzed by Wilkinson's catalyst.



➤ Wilkinson hydrogenation reaction is stereospecific.

Catalytic cycle for hydrogenation

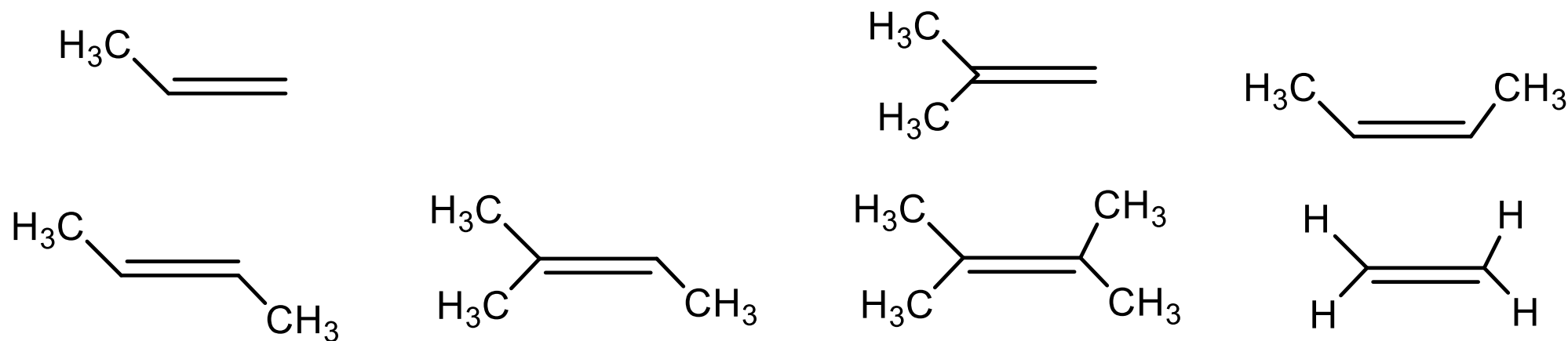


Kinetic studies have shown that the dissociation of PPh_3 from the distorted square planar complex $\text{RhCl}(\text{PPh}_3)_3$ in benzene occurs only to a very small extent ($k = 2.3 \times 10^{-7} \text{ M}$ at 25°C), and under an atmosphere of H_2 , a solution of $\text{RhCl}(\text{PPh}_3)_3$ becomes yellow as a result of the oxidative addition of H_2 to give *cis*- $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$.

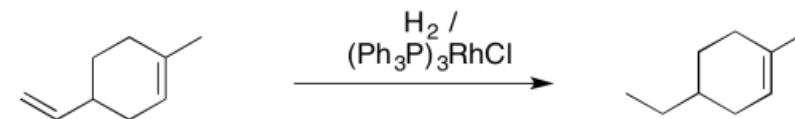
The trans effect is the labilization (making unstable) of ligands that are trans to certain other ligands.

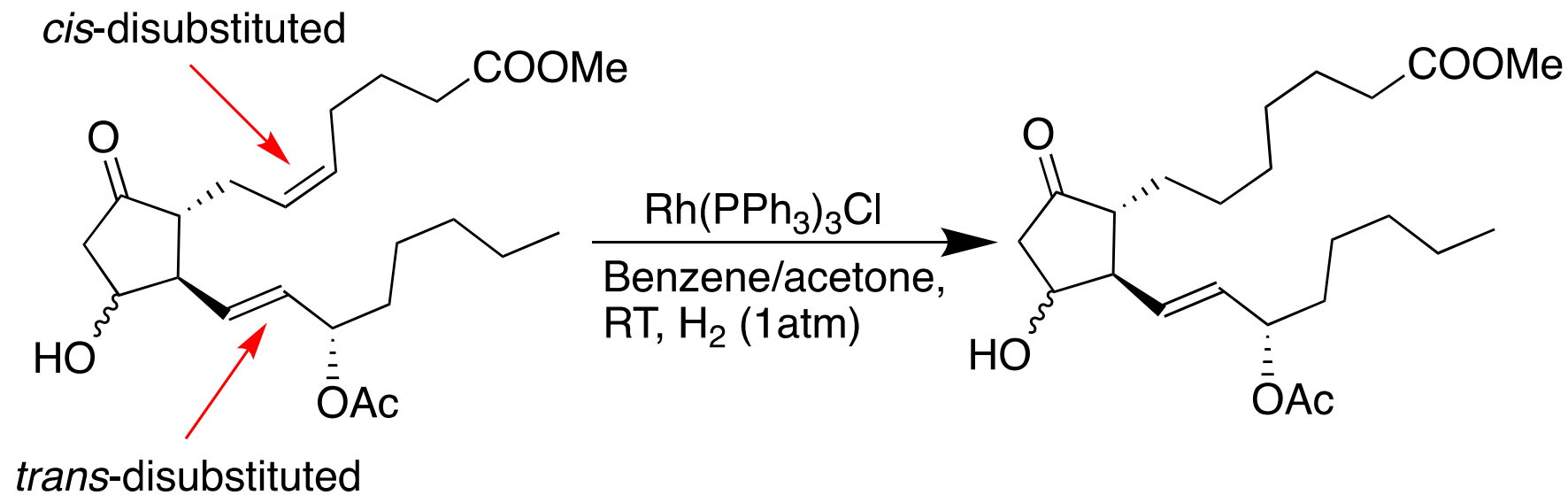
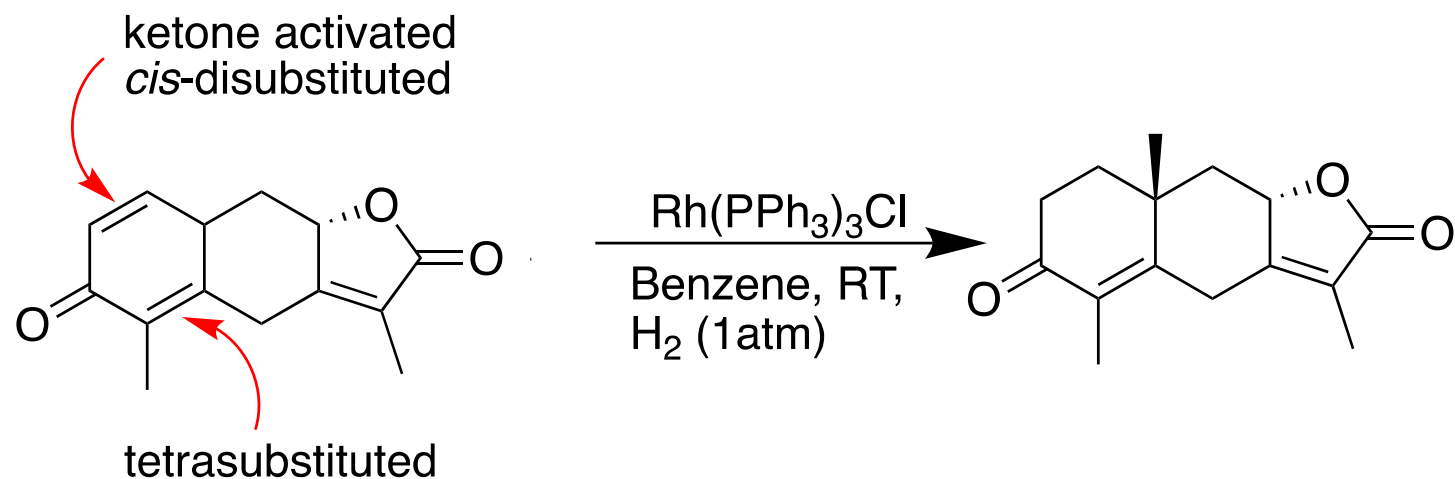


Find out the relative reactivity of the following alkenes for the homogenous catalytic hydrogenation with Wilkinson's catalyst



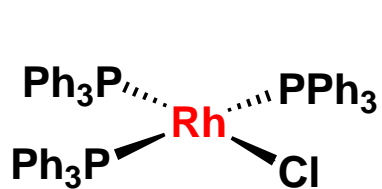
- Cis alkenes undergo hydrogenation more readily than trans alkenes
- Internal and branched alkenes undergo hydrogenation more slowly than terminal ones
- Strongly coordinating alkene such as ethylene binds preferentially Rh so that the resulting complex is stable and does not participate in the catalytic cycle.



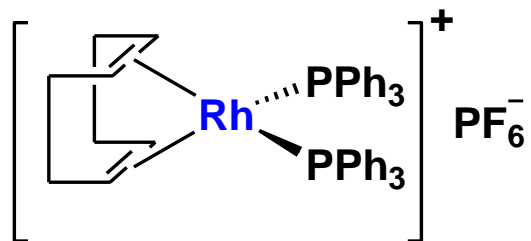


Pd/C, H_2

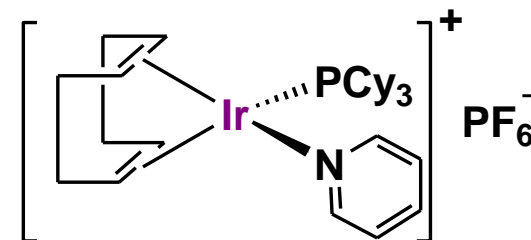
Fine tuning of a catalyst: hydrogenation catalysts which are more efficient than Wilkinsons catalyst





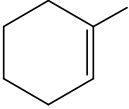
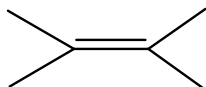
Wilkinson's catalyst



Schrock-Osborn's catalyst

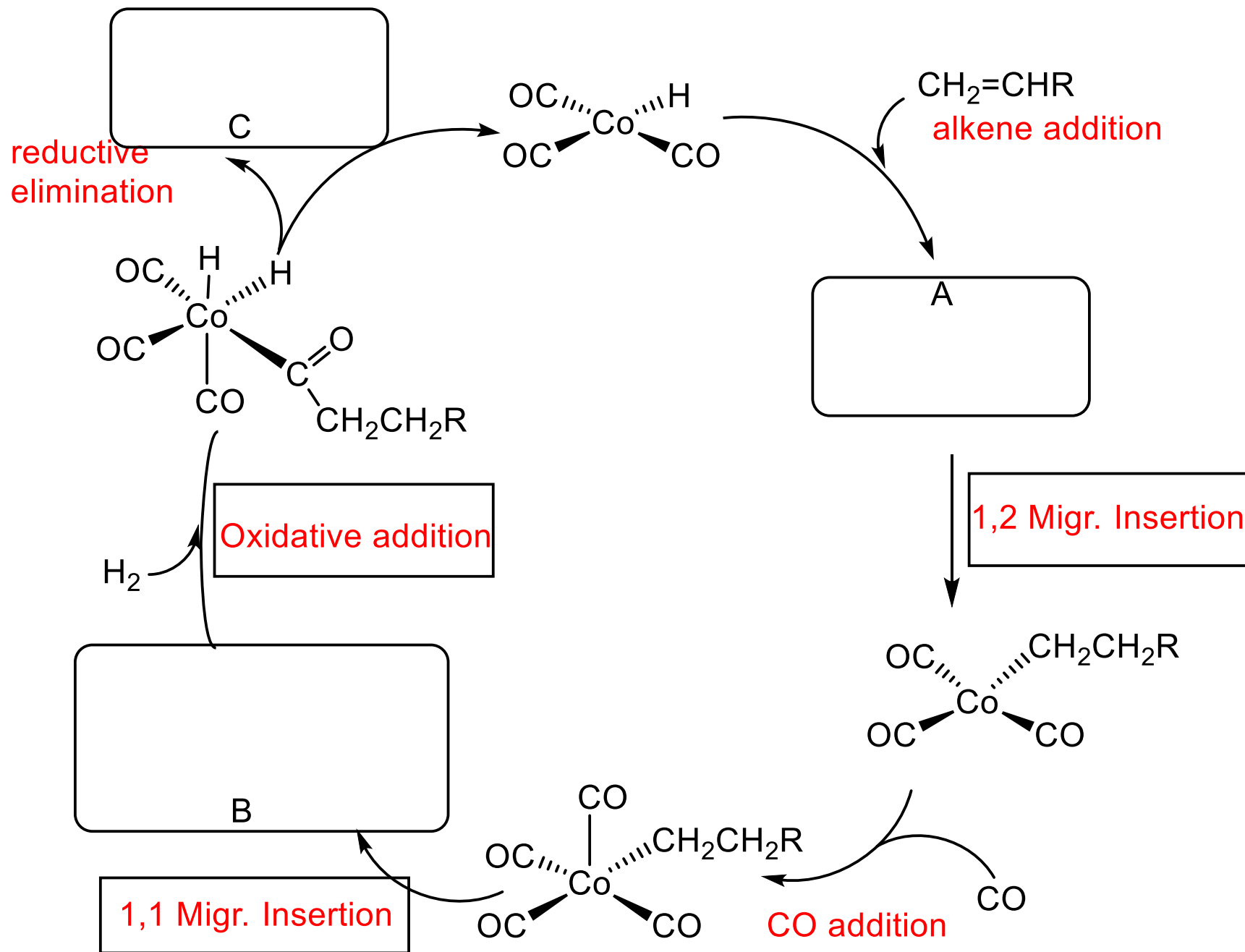


Crabtree's catalyst

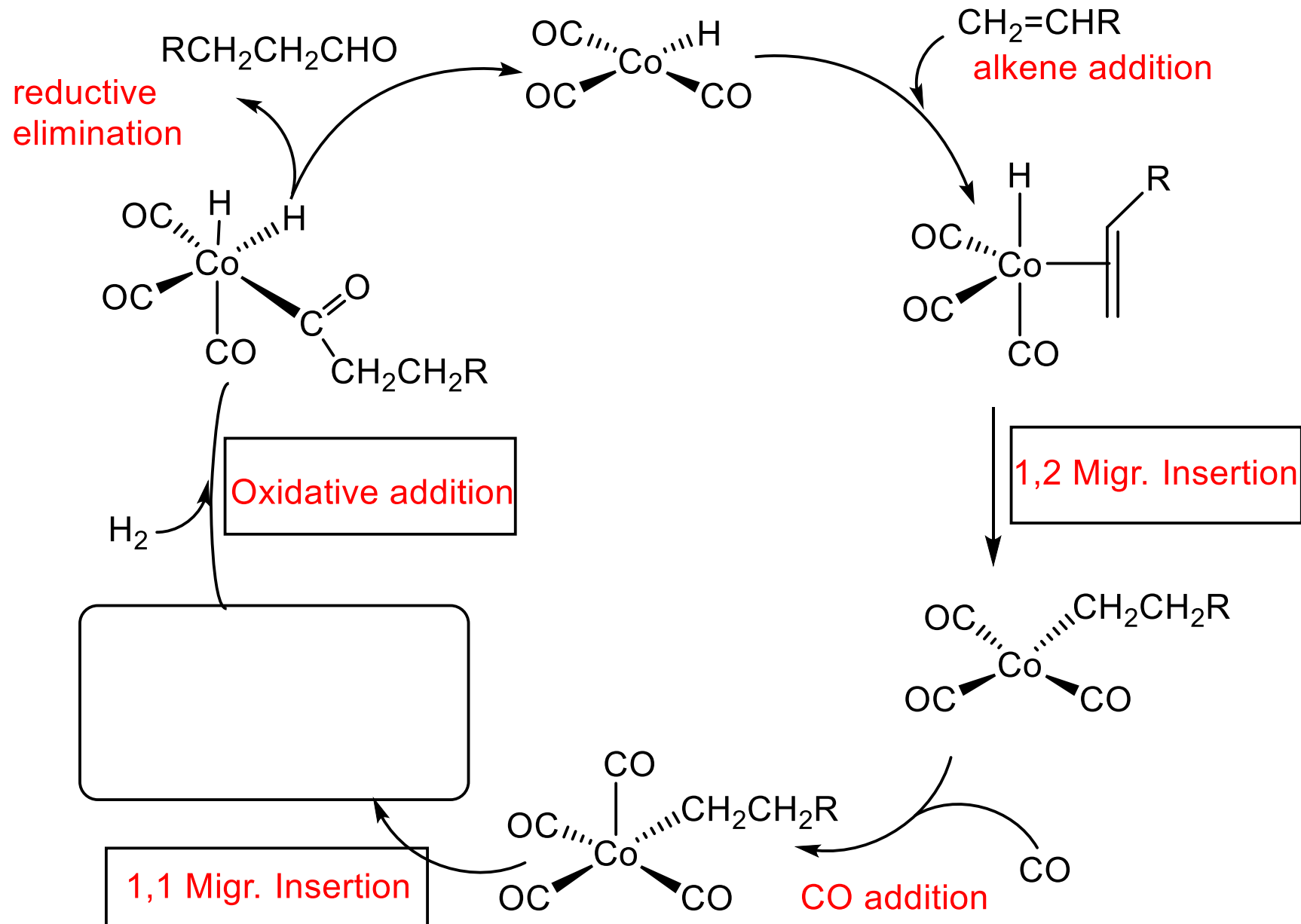
Catalyst 25°C, 1 atm H ₂	Turnover frequency (TOF) in h ⁻¹ for hydrogenation of alkenes			
				
Wilkinson's catalyst	650	700	13	NA
Schrock–Osborn catalyst	4000	10	NA	NA
Crabtree's catalyst	6400	4500	3800	4000

The cationic metal center is relatively more electrophilic than neutral metal center and thus favours alkene coordination.

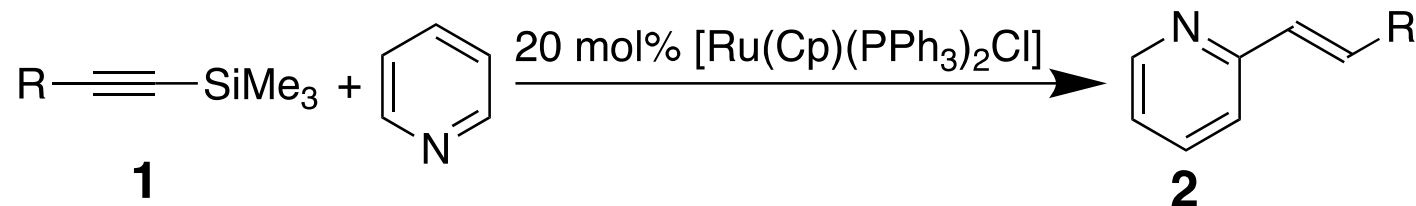
Problem solving- fill in the blanks



Problem solving- fill in the blanks



The following data was obtained for the alkenylation of pyridine with alkynyl silanes. Determine which substituent (R) gives the best TON and TOF for the compounds when the R groups are varied.



Entry	1 R =	Time (h)	Product	Yield (%)
1	Ph (1a)	7	2a	87
2	P-Me-C ₆ H ₄ (1b)	9	2b	92
3	N-C ₅ H ₁₁ (1c)	6	2c	90
4	1-cyclohexenyl	11	2d	75

20 mol% of the catalyst used, which means $1/(20/100) = 5$

Entry 1. TON = $5 \times 0.87 = 4.35$; TOF = $4.35/7 = 0.62 \text{ h}^{-1}$

Entry 2. TON = $5 \times 0.92 = 4.6$; TOF = $4.60/9 = 0.51 \text{ h}^{-1}$

Entry 3. TON = $5 \times 0.90 = 4.5$; TOF = $4.50/6 = 0.75 \text{ h}^{-1}$

Entry 4. TON = $5 \times 0.75 = 4.5$; TOF = $3.75/11 = 0.34 \text{ h}^{-1}$

Best TON is obtained for entry 2 and the best TOF is obtained for entry 3.