A catalyst may be defined by two important criteria related to its stability and efficiency. Name both of these criteria and describe how they are defined with respect to stability or efficiency.

A catalyst may be defined by its *Turnover Number (TN)*. Each time the complete catalyst cycle occurs, we consider one catalytic turnover to have been completed. The more stable the catalyst the greater the turnover number the more product is formed. The *lifetime of the catalyst* before deactivation or decomposition is therefore quantified using the turnover number.

$$\boldsymbol{Turnover\ Number\ (TN) = \frac{moles\ of\ product\ formed}{moles\ of\ catalyst}}$$

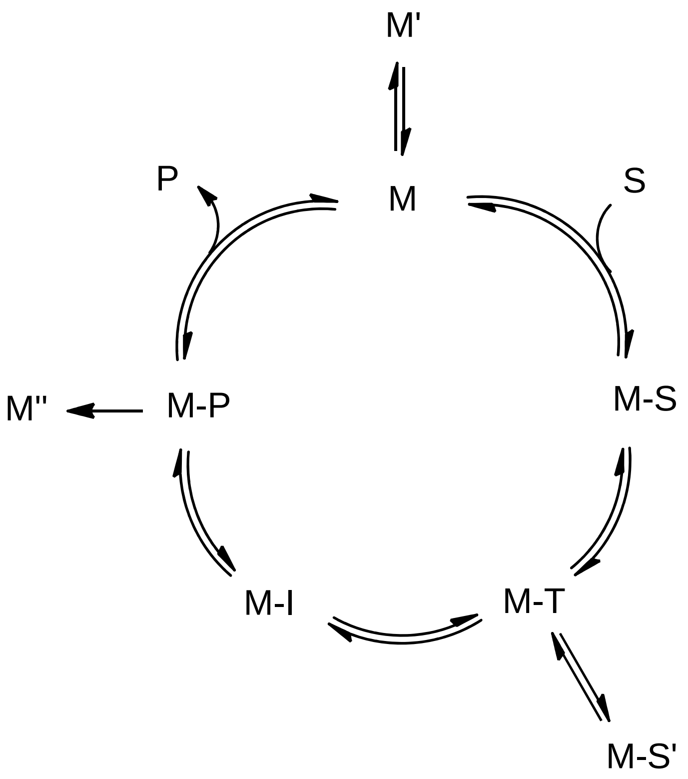
The catalytic rate, i.e. efficiency, can be conveniently given in terms of the Turnover Frequency *(TOF)* measured in turnovers per unit time (often per hour). The greater the turnover frequency the more efficient the catalyst is the quicker the product is formed.

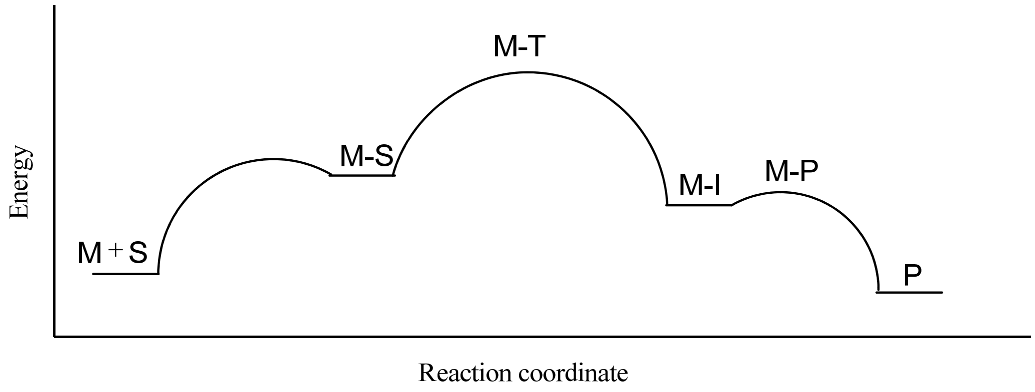
$$\boldsymbol{Turnover\ Frequency\ (TOF) = \frac{moles\ of\ product\ formed}{hour}}$$

It should be noted that efficiency does not necessarily equal stability. The best catalysts will of course be highly stable and kinetically favorable. Some catalysts, however, work extremely fast but will decompose after just a few cycles (high turnover frequency + low turnover number). On the other hand, some catalysts are extremely stable but very slow (high turnover number + low turnover frequency).

Draw a generic catalytic cycle scheme including the species listed below. Using the same species, draw a generic free energy diagram describing transformation of substrate to product. Describe the impact of a catalyst on the overall reaction kinetics, thermodynamics and equilibrium.

- ***a) Catalyst precursor (M')***
- ***b) Active catalyst (M)***
- ***c) Substrate (S)***
- ***d) Catalyst-substrate complex (M-S)***
- ***e) Transition state (M-T)***
- ***f) Intermediate (M-I)***
- ***g) Off loop species (M-S')***
- ***h) Deactivation product (M'')***





A catalysts typically reduces the activation energy required along the reaction coordinate (transitin state and intermediate formation) thus allowing for more favorable kinetics towards product formation. The catalyst only increases the rate of a process but *does not alter its position of equilibrium*, which is decided by the relative thermodynamic stabilities of substrate and products (not the transition states or intermediates along the reaction coordinate).

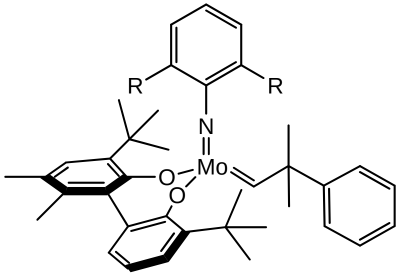
***N*-Heterocyclic carbenes – true or false:**

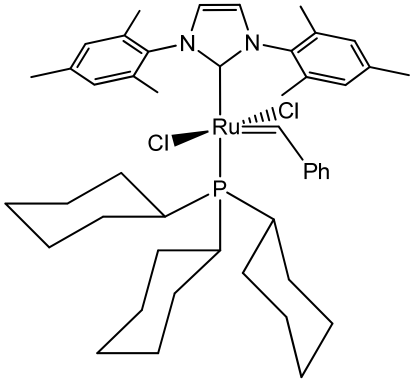
1) ***are prone to electrophilic attack*** *– False.*
2) ***are prone to nucleophilic attack*** *- False (although they are Fischer type carbenes the empty p-orbital is stabilized by the N lone pairs precluding nucleophilic attack).*
3) ***are σ-basic*** *– True. NHC's are very electron rich donors.*
4) ***are π-acidic*** *– False (as the empty p orbital is stabilized by the N lone pairs it does not require back donation from the metal)*
5) ***have steric and electronic influence on catalysis*** *– True.*
6) ***have electronic influence only*** *– False (rarely however the N substituents have no steric effect)*
7) ***are Fischer type carbenes*** *– True.*

Discuss the pros and cons of NHC's wrt catalysis in comparison to the phosphine class of ligands.

Similar to phosphine ligands NHCs are *electronically* and sterically tunable. The nature of the R groups at N1 and N3 have little influence on the electronic properties of the ligand however are very important for imparting steric control in a catalyst. Also, like phosphines they are *very good* σ*-donors* and promote a wide variety of catalytic reactions. Unlike phosphines t*he thermodynamic instability of free NHCs strongly disfavours dissociation, however, reductive elimination can occur with liberation of the imidazolium salt in the presence of an appropriate "cis" elimination partner.*

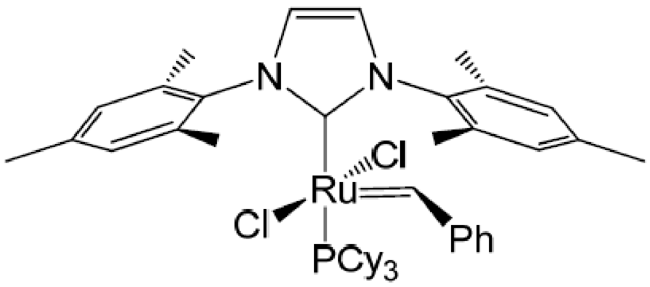
What are the contrasting traits of Schrock and Grubb's metathesis catalysts (2 examples are given below)?



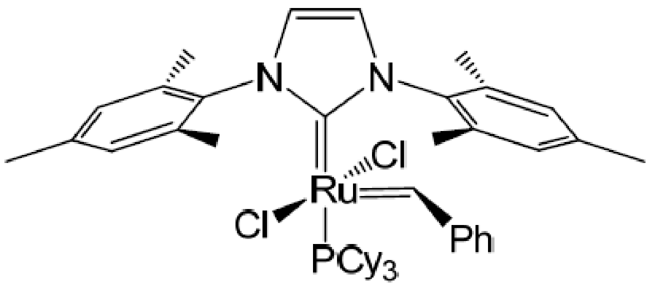


Schrock catalysts are highly reactive, have a poor tolerance for substrate functional groups, show increased TOF with increased ligand electron withdrawing strength, and are active for metathesis of tri- and tetra-substituted olefins. Grubb's catalysts have a higher tolerance of substrate functional groups, are selective towards sterically unhindered olefins and strained olefins and are inefficient towards metathesis of tri- and tetra-substituted olefins.

Which of the following structures represents the true structure of Grubbs catalyst (a) or (b)? Briefly explain why?



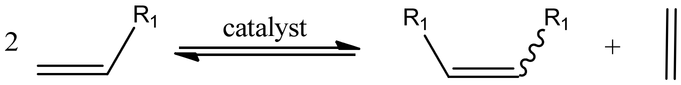
(a)



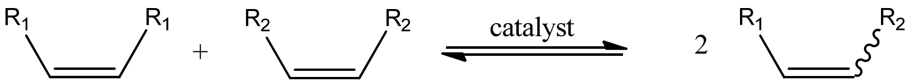
(b)

Structure (a) is a more realistic representation of the true Ru-C bond in Grubb's catalysts. Although they are Fischer type carbenes the empty p-orbital on the sp^2 carbon atom is stabilized by the N lone pairs precluding the need for back donation from the Ru center.

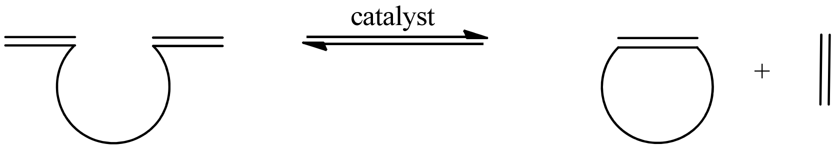
Label each of the following metathesis reactions accordingly an suggest anticipated products.



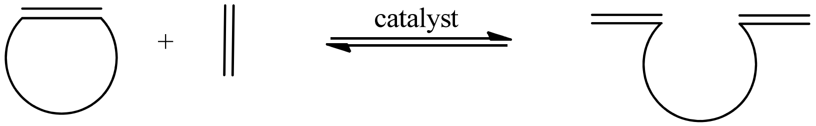
self-metathesis



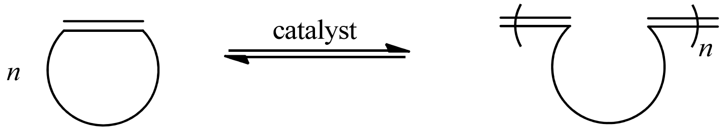
cross-metathesis



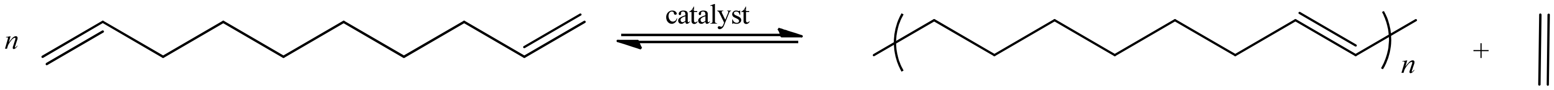
ring closing metathesis



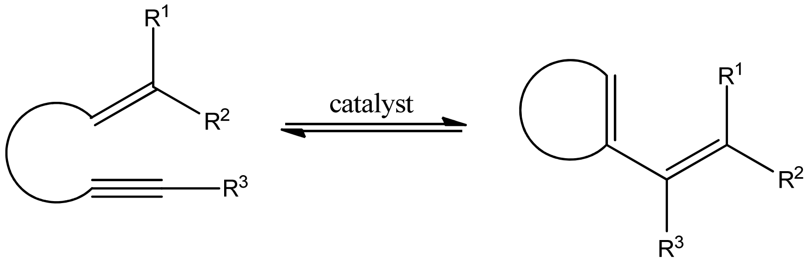
ring opening metathesis



ring opening metathesis polymerization

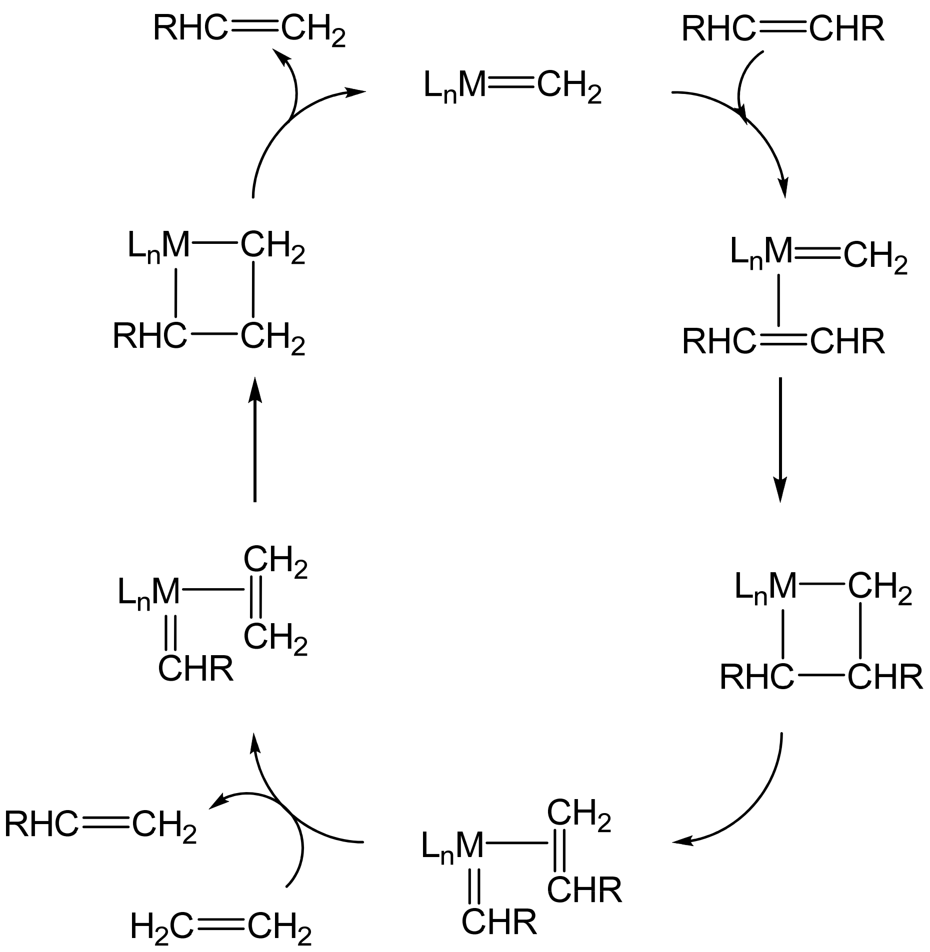


acyclic diene metathesis polymerization



ene-yne metathesis

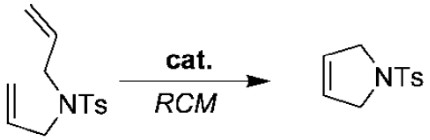
Complete the following metathesis catalytic cycle. What type of metathesis is taking place?



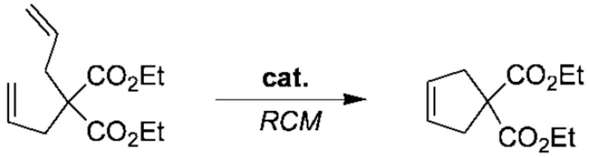
This is a cross metathesis reaction that can be summarized as follows:

$$RHC{=}CHR + H_2C{=}CH_2 \xrightleftharpoons{\text{Cat.}} 2\ RHC{=}CH_2$$

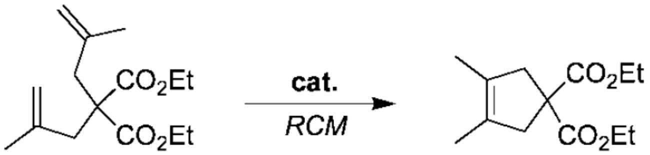
Suggest anticipated products for each of the following Metathesis reactions.
Draw a mechanism for the enyne reaction.



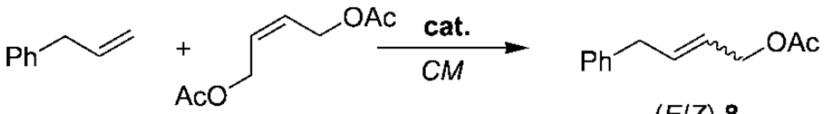
2 **3**



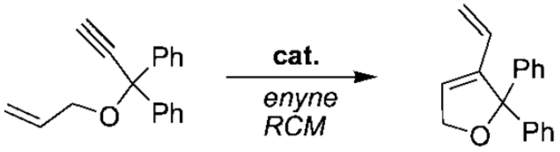
4 **5**



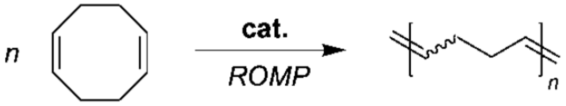
6 **7**



(*E*/*Z*)-**8**



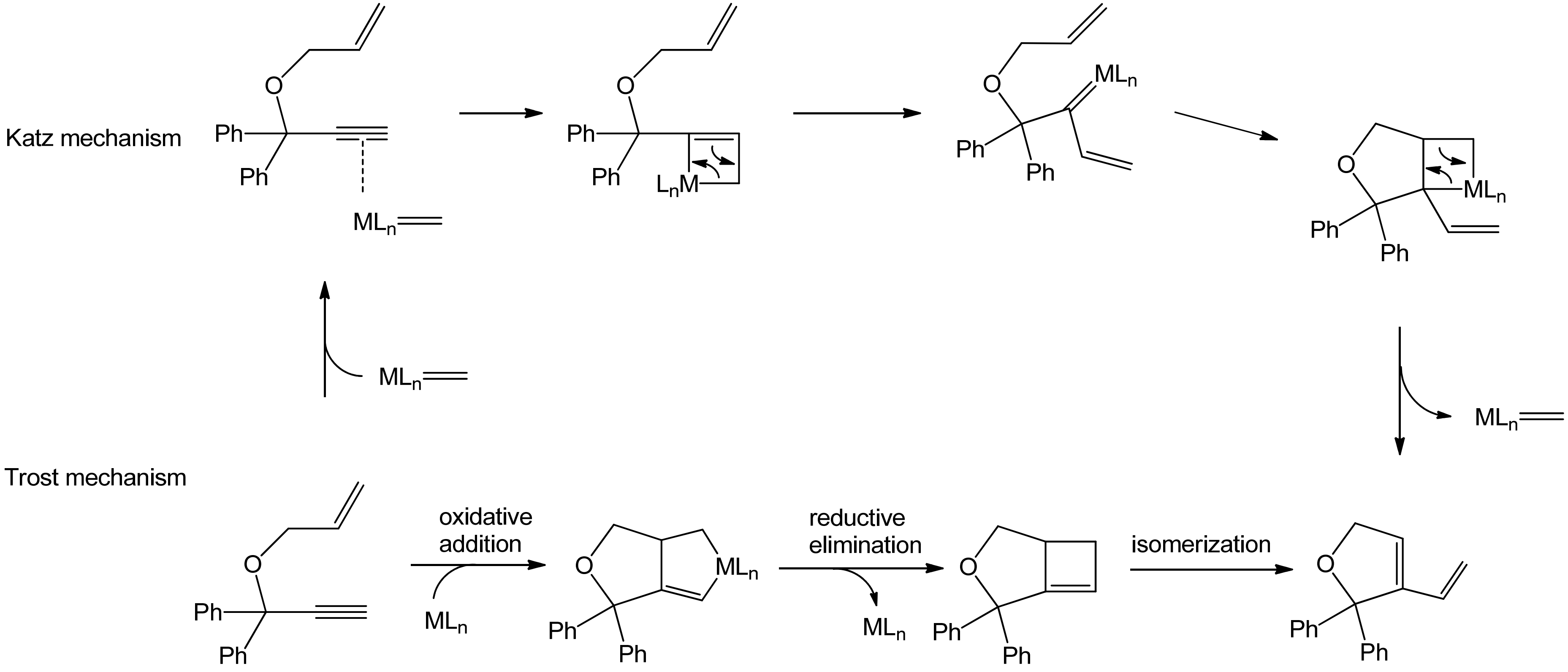
9 **10**



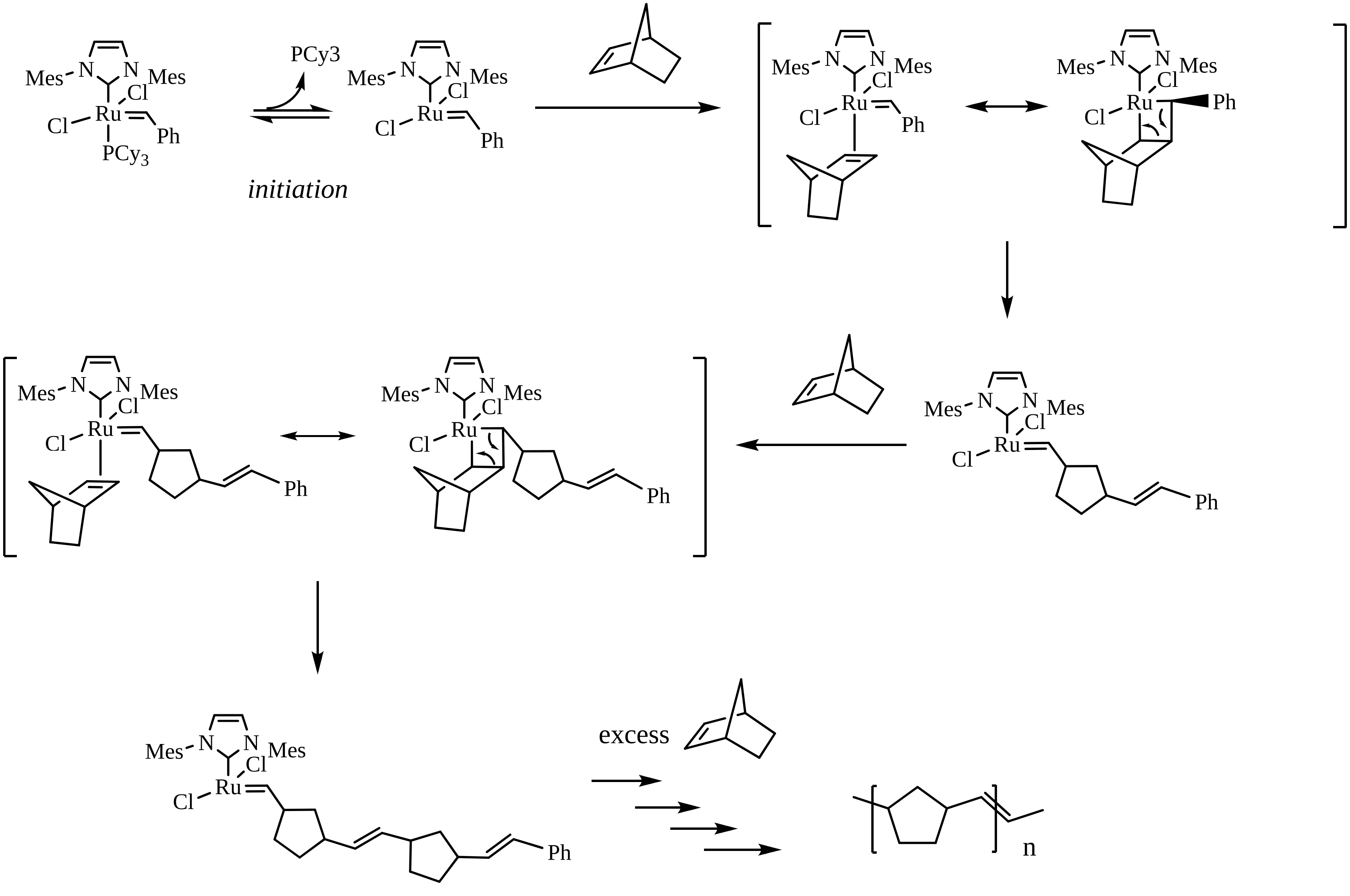
COD

Draw a mechanism for the enyne reaction.

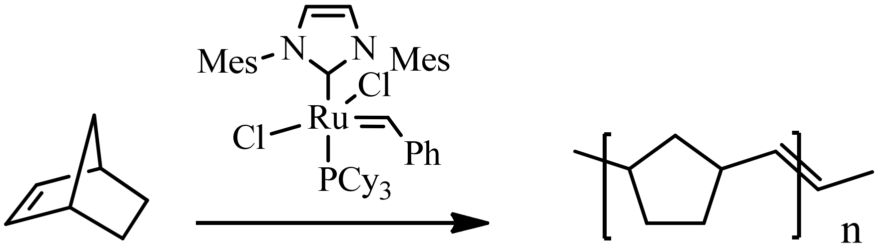
- The Katz or Trost mechanism is sufficient.



Below is an example of a ROMP reaction catalyzed by Grubbs catalyst. Complete the mechanism by including the missing intermediate steps during propogation of chain growth [It is ok to us L_3Ru for shorthand if you wish].



Below is an example of a ROMP reaction catalyzed by Grubbs catalyst.
Draw a complete mechanism for this reaction.

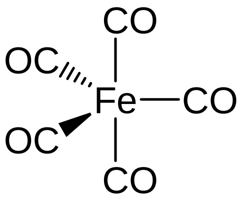


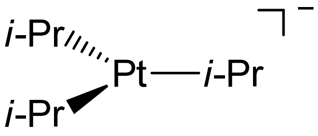
See previous slide.

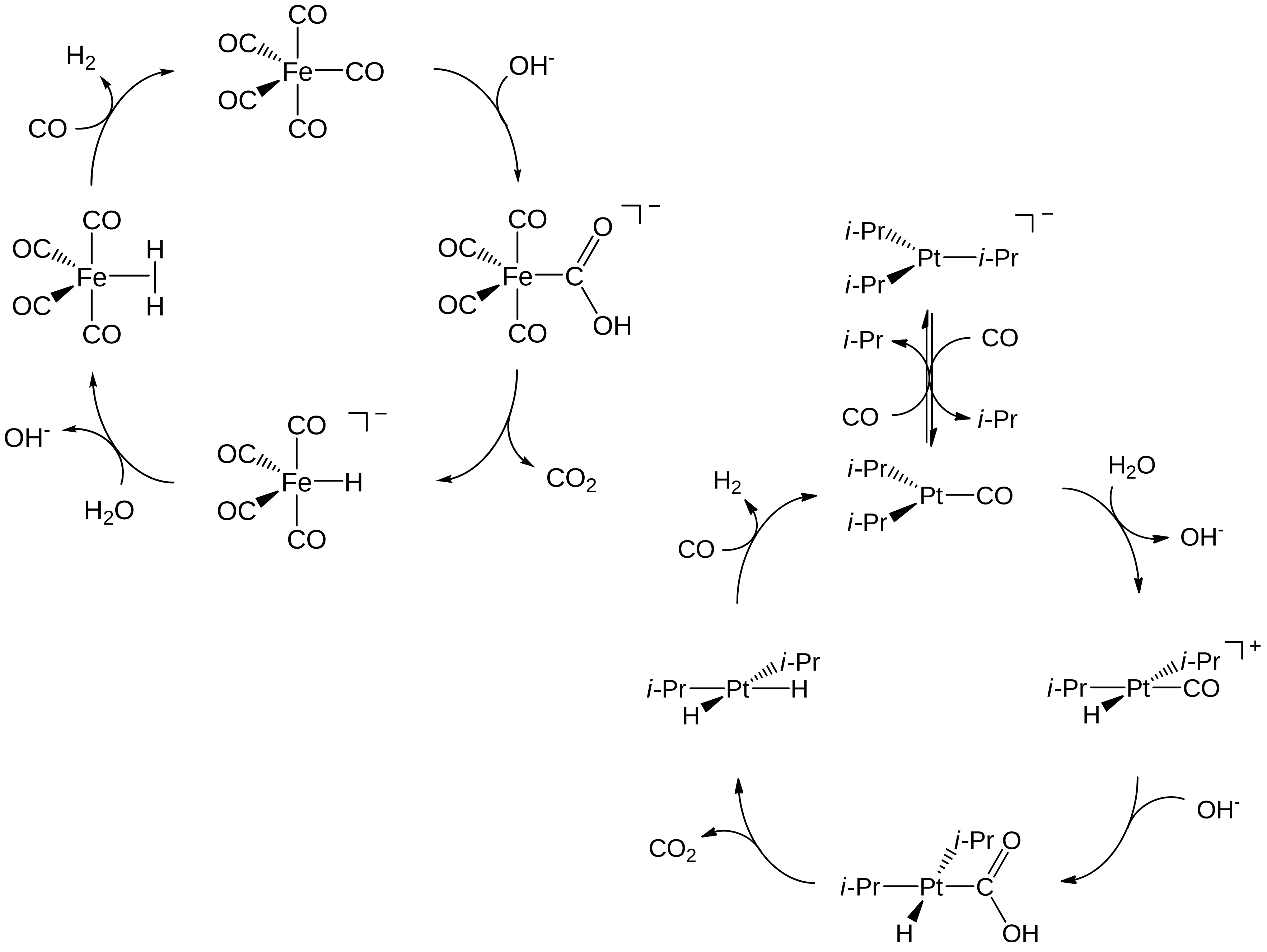
Name the reaction below.
Suggest at least two catalysts that are know to perform this reaction.
Write a catalytic cycle for one of these reactions.

$$H_2O + CO \xrightleftharpoons{\text{catalyst}} H_2 + CO_2$$

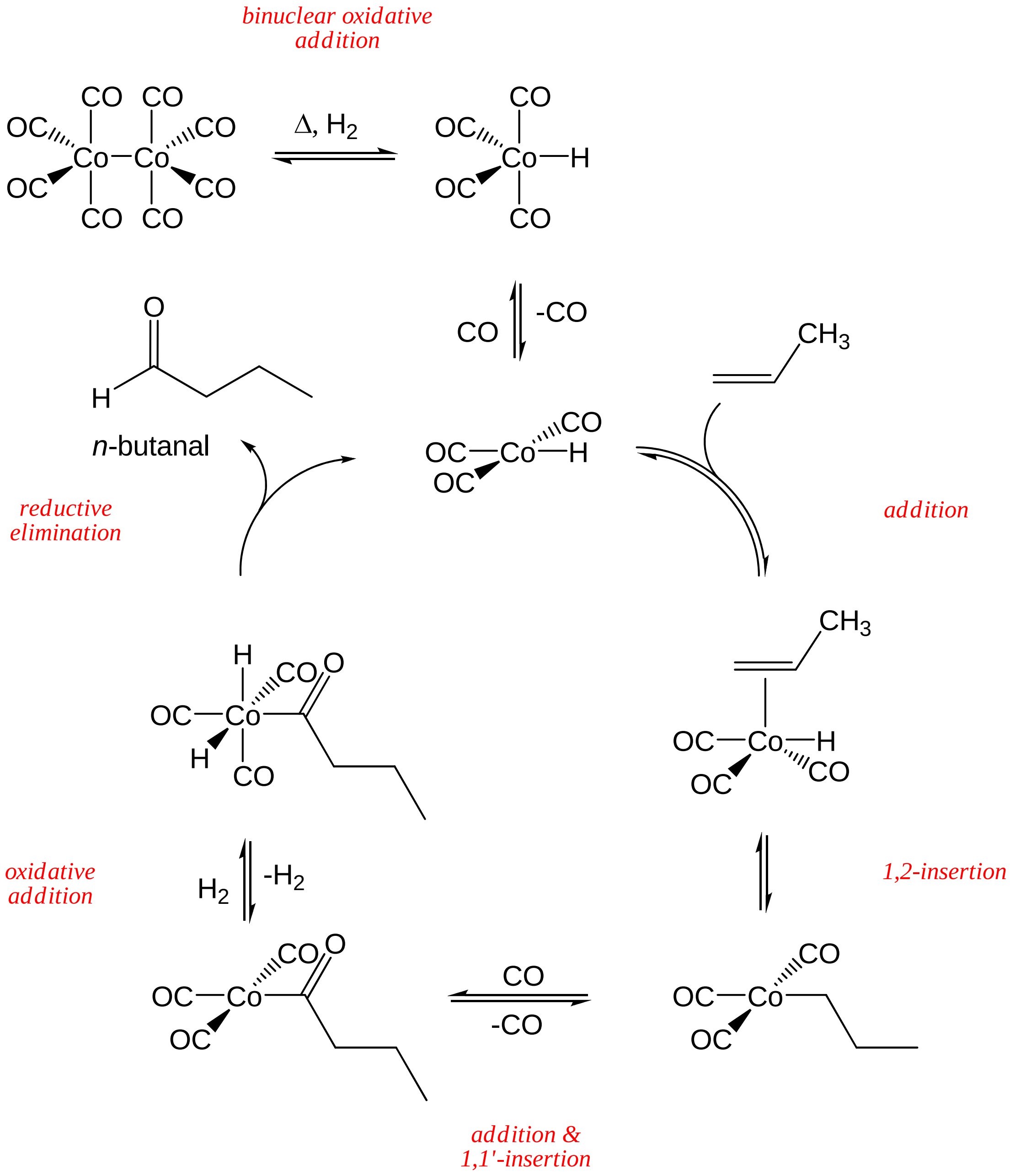
Water-gas shift reaction.



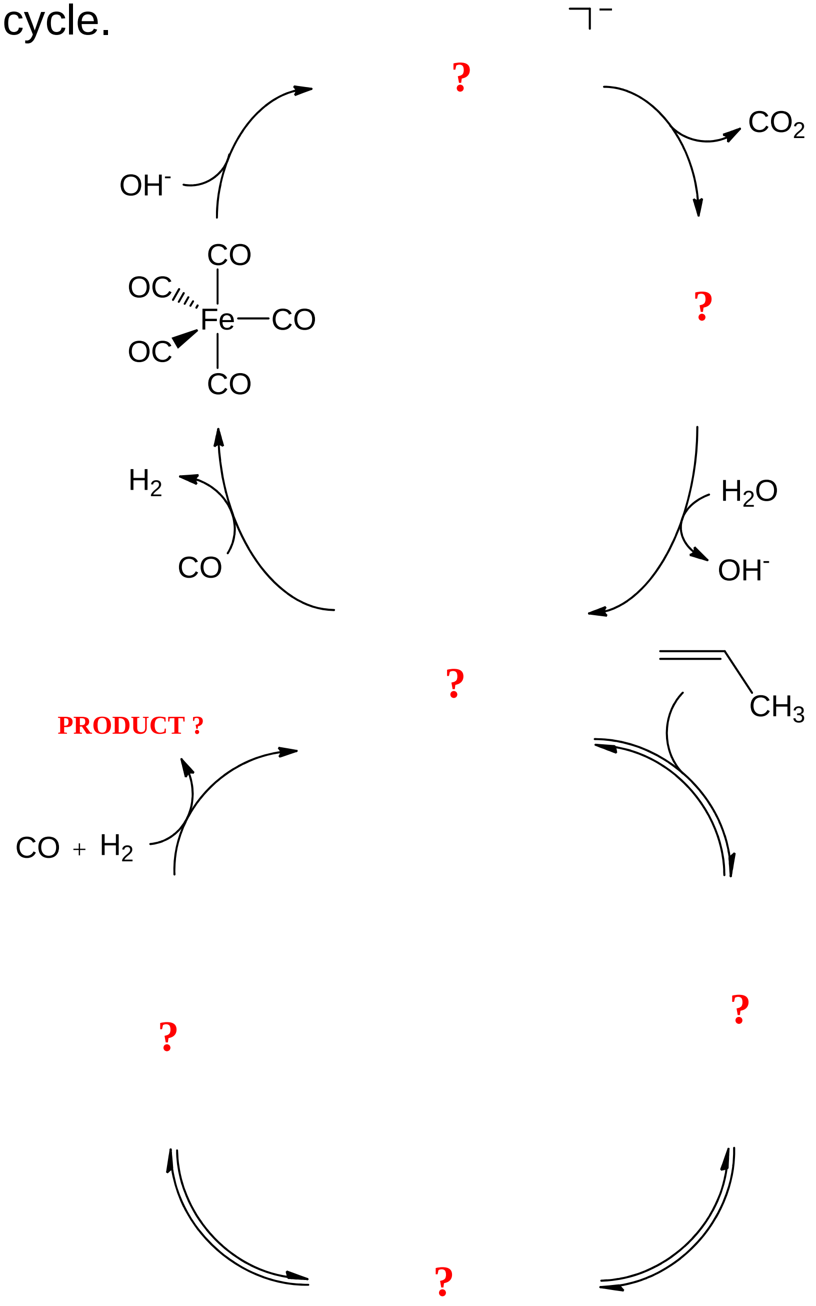


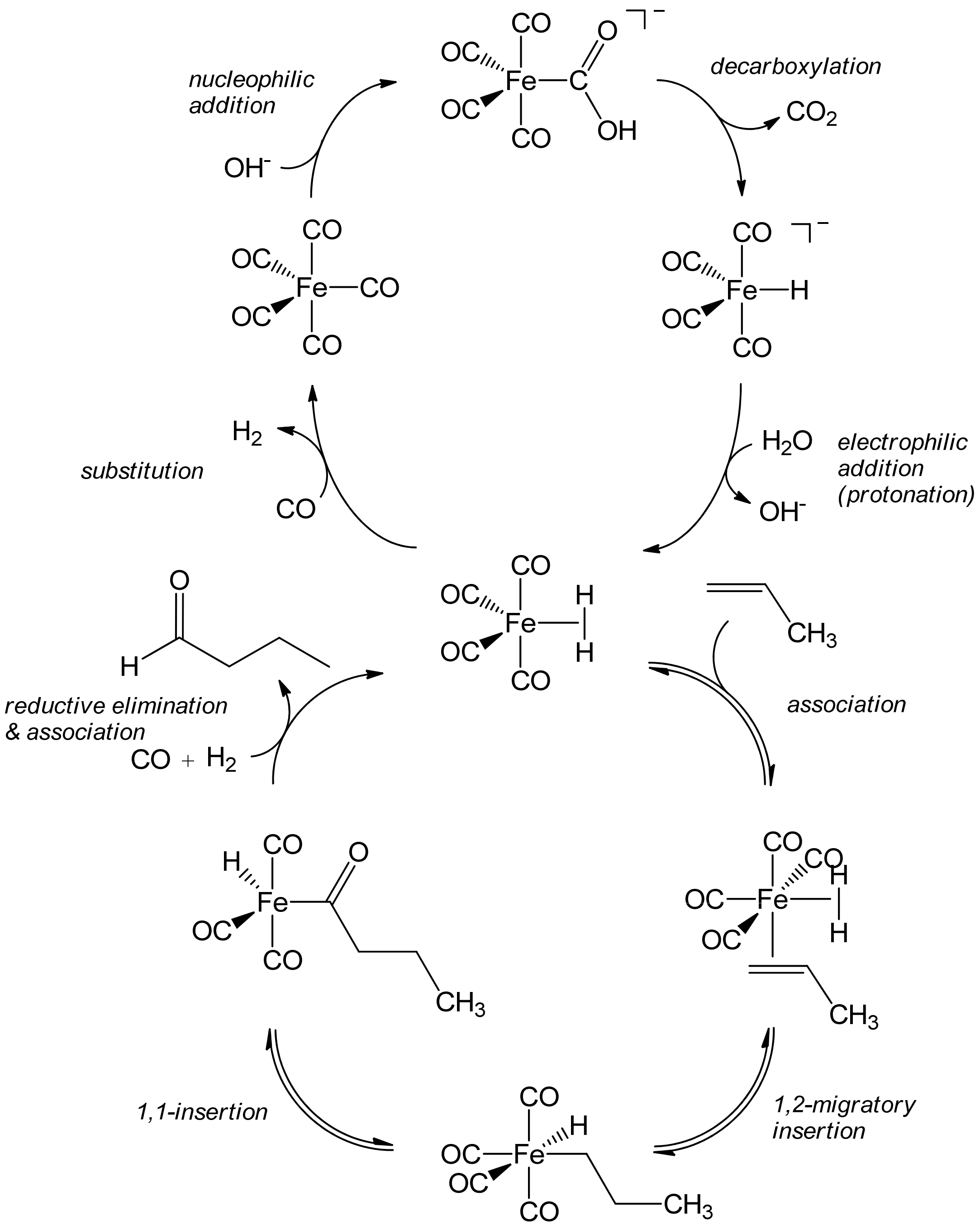

H2
CO
OC
Fe
CO
OH-
CO
OC
Fe
H
H
CO
O
C
OH
OH-
H2O
CO
OC
Fe
H
CO2
i-Pr
Pt
i-Pr
i-Pr
CO
i-Pr
CO
i-Pr
H2
H2O
i-Pr
Pt
CO
OH-
CO
i-Pr
Pt
H
i-Pr
i-Pr
Pt
CO
H
+
OH-
CO2
i-Pr
Pt
C
O
OH
H

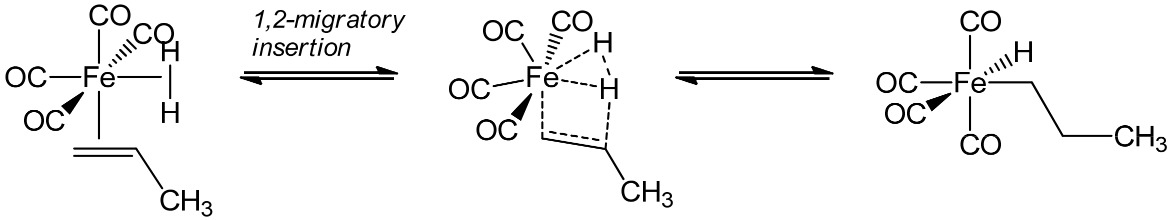
Name the class of reaction below an draw a catalytic cycle to describe product formation.



Name the class of reaction below and complete the cycle.
Name rxn type fore each step of the cycle.
Describe any important transition states not
explicitly included in the cycle.



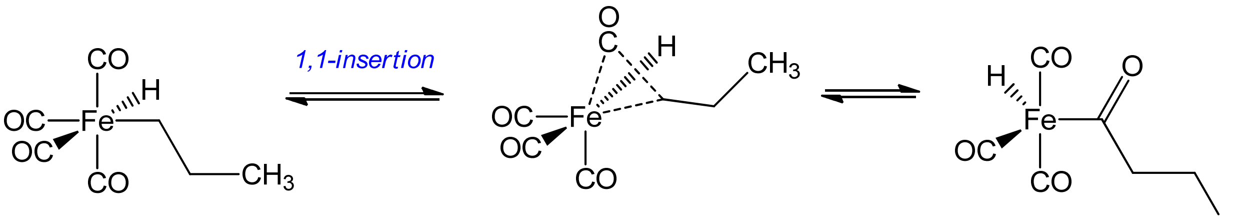

nucleophilic addition
OH-
decarboxylation
CO2
H2O
electrophilic addition (protonation)
OH-
substitution
H2
CO
association
reductive elimination & association
CO + H2
1,1-insertion
1,2-migratory insertion
Fe
CO
OC
OH
H
CH3



transition state

CN = 6 *(octahedral)*
OS = 0
#d e^{-} = 8
VE = 20

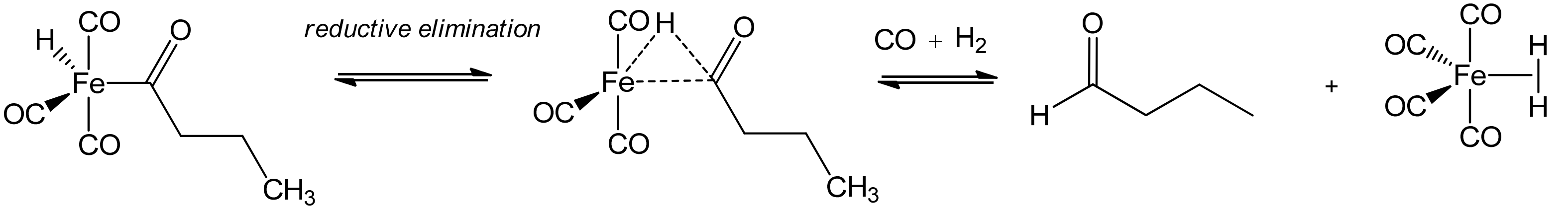
CN = 6 *(trigonal bipyramidal)*
OS = +2
#d e^{-} = 6
VE = 18



transition state

CN = 6 *(octahedral)*
OS = +2
#d e^{-} = 6
VE = 18

CN = 5 *(trigonal bipyramidal)*
OS = +2
#d e^{-} = 6
VE = 16

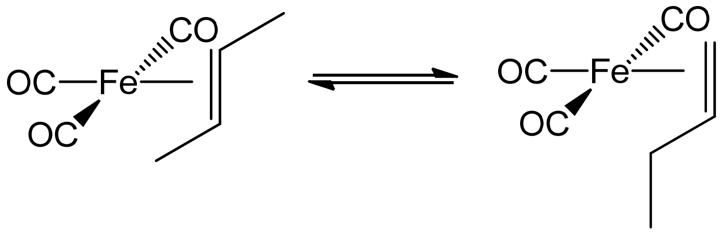


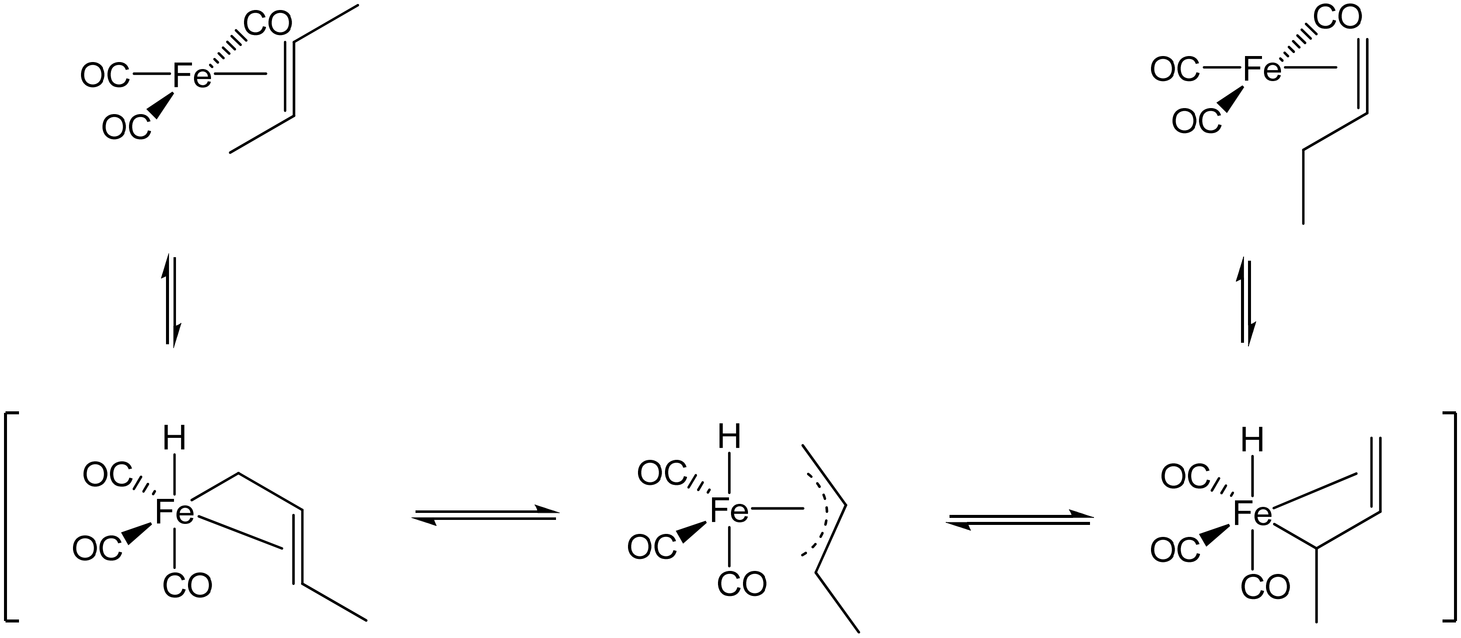
transition state

CN = 5 *(trigonal bipyramidal)*
OS = +2
#d e^{-} = 6
VE = 16

CN = 5 *(trigonal bipyramidal)*
OS = 0
#d e^{-} = 8
VE = 18

Draw a mechanism for the following isomerization.





Mechanisms to study:

Metathesis (generic + Grubbs ROMP)

Alkene Hydrogenation

- oxidative addition
- H_2 activation

Water-gas shift reaction

Alkene hydroformylation (Oxo + Reppe)

Monsanto acetic acid process

Wacker oxidation

Cross-coupling (generic)

Kumada

Negishi

Stille

Miyaura

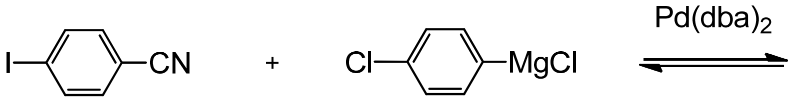
Suzuki

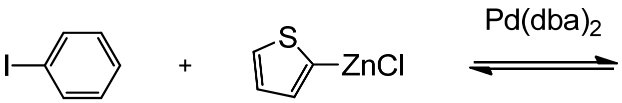
Sonogashira

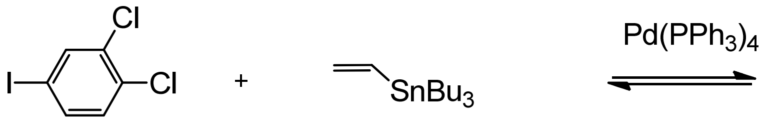
Buchwald-Hartwig

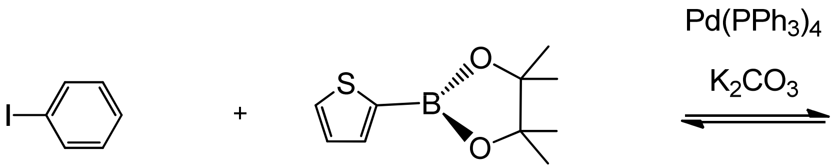
Mozoriki-Heck

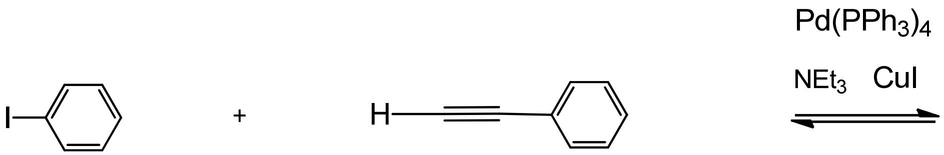
- *Name the class of reaction.*
- *Always identify complete and balanced chemical reaction if not given.*
- *Draw full cycle, or complete the cycle if given portions.*
- *Follow oxidation states, coordination numbers, geometry, total electron count (18 VE rule).*
- *Name rxn. type fore each step of the cycle.*
- *Describe any important transition states not explicitly included in the cycle.*
- *Be prepared to draw any metal-ligand (metal-substrate) bonding interactions.*

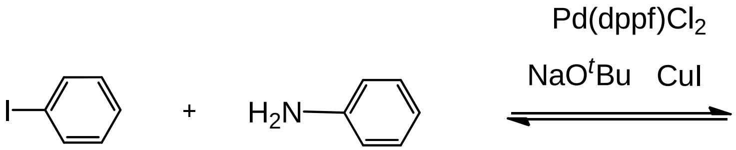

I
CN
+
Cl
MgCl
Pd(dba)$_2$

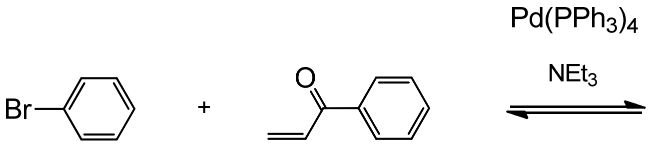

I
+
S
ZnCl
Pd(dba)$_2$


Cl
I
Cl
+
SnBu$_3$
Pd(PPh$_3$)$_4$

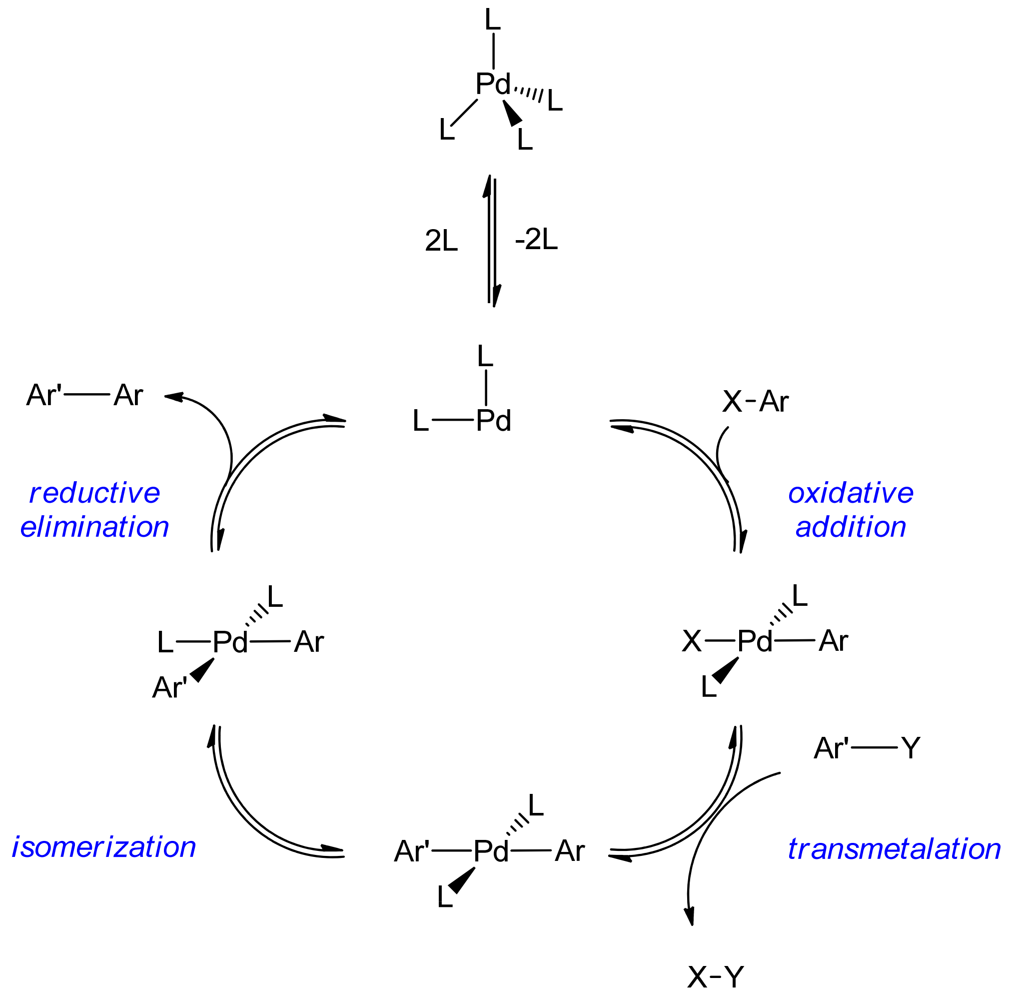

I
+
S
B
O
O
Pd(PPh3)4
K2CO3


I
+
H
Pd(PPh3)4
NEt3 CuI

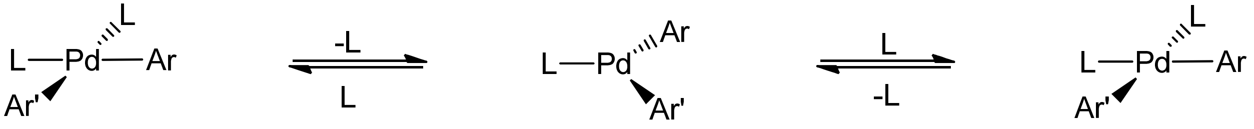

I
+
H2N
Pd(dppf)Cl2
NaOtBu CuI


Br
+
O
Pd(PPh3)4
NEt3

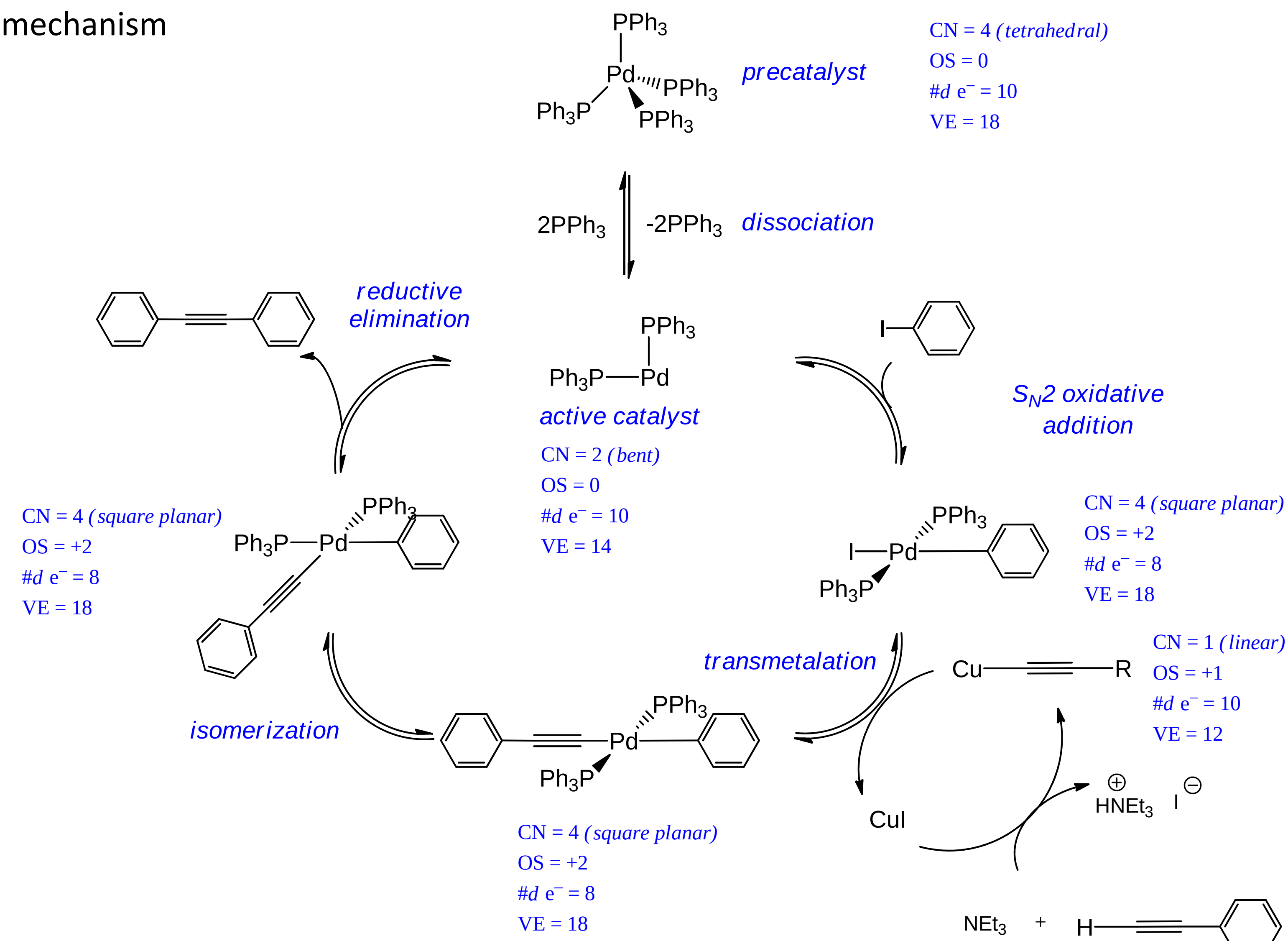
- Generic Pd(0) catalyzed bisaryl cross coupling reaction



plausible cis-trans isomerization mechanism



- Example mechanism



CN = 4 *(tetrahedral)*
OS = 0
#d e$^-$ = 10
VE = 18

CN = 2 *(bent)*
OS = 0
#d e$^-$ = 10
VE = 14

CN = 4 *(square planar)*
OS = +2
#d e$^-$ = 8
VE = 18

CN = 4 *(square planar)*
OS = +2
#d e$^-$ = 8
VE = 18

CN = 1 *(linear)*
OS = +1
#d e$^-$ = 10
VE = 12

CN = 4 *(square planar)*
OS = +2
#d e$^-$ = 8
VE = 18

S_N2 oxidative addition