Inorganic Chemistry
Year 3

Transition Metal Catalysis

Eighteen Electron Rule

1. Get the number of the group that the metal is in (this will be the number of d electrons)
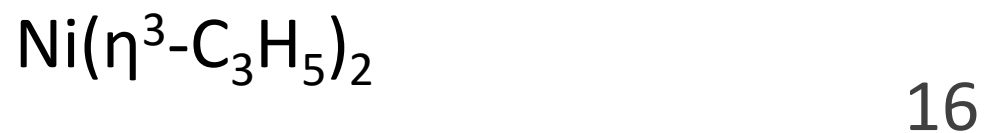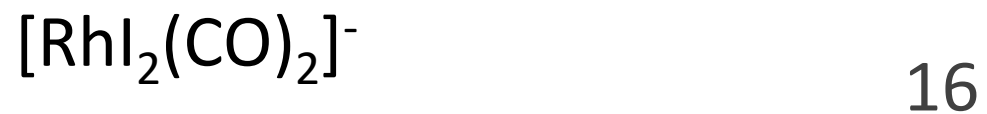
2. Add to this the charge
   1. Negative charge   More electrons   Add to the count
   2. Positive charge   Less electrons   Remove from the count

3. Add the number of donating ligands to the count

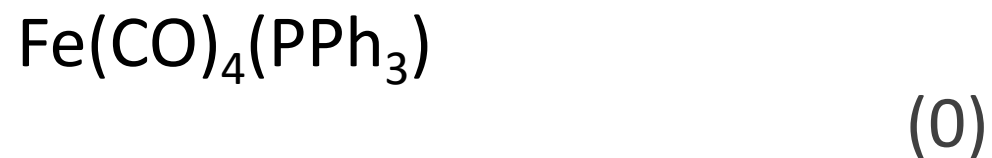A stable complex has a total count of **18**

Eighteen Electron Rule - Test

$Rh(PPh_3)_3Cl$ 16

$HCo(CO)_4$ 18

$[RhI_2(CO)_2]^-$ 16

$Ni(\eta^3\text{-}C_3H_5)_2$ 16

$Fe(CO)_4(PPh_3)$ 18

Oxidation State

1. Start at zero

2. Ignore all formally neutral ligands (ie CO, PPh_3)

3. Add 1 for anionic ligand

4. Positive change, electron removed, add 1

5. Negative charge, electron added, subtract 1

6. Give your result in roman numerals

Revision

Oxidation State - Test

Rh(PPh$_3$)$_3$Cl

(I)

HCo(CO)$_4$

(I)

[RhI$_2$(CO)$_2$]$^-$

(I)

Ni(η^3-C$_3$H$_5$)$_2$

(II)

Fe(CO)$_4$(PPh$_3$)

(0)

Constructing Catalytic Cycles

- Reasonable **18 electron** counts and **coordination numbers**
- Types of reactions
  - Ligand association
  - Ligand dissociation
  - Migration
  - Elimination
  - Oxidative Addition
  - Reductive Elimination
  - Metallacycle formation
  - Transmetallation

Ligand Association / Dissociation

- 18 electron complexes electronically saturated

- Most are co-ordination saturated

- Therefore exchange of ligands require initial dissociation

- The rate of this reaction can be slow

Oxidative Addition / Reductive Elimination

- Complementary process
- Requires two accessible oxidation states of 2 units apart
- Change of co-ordination number is also 2
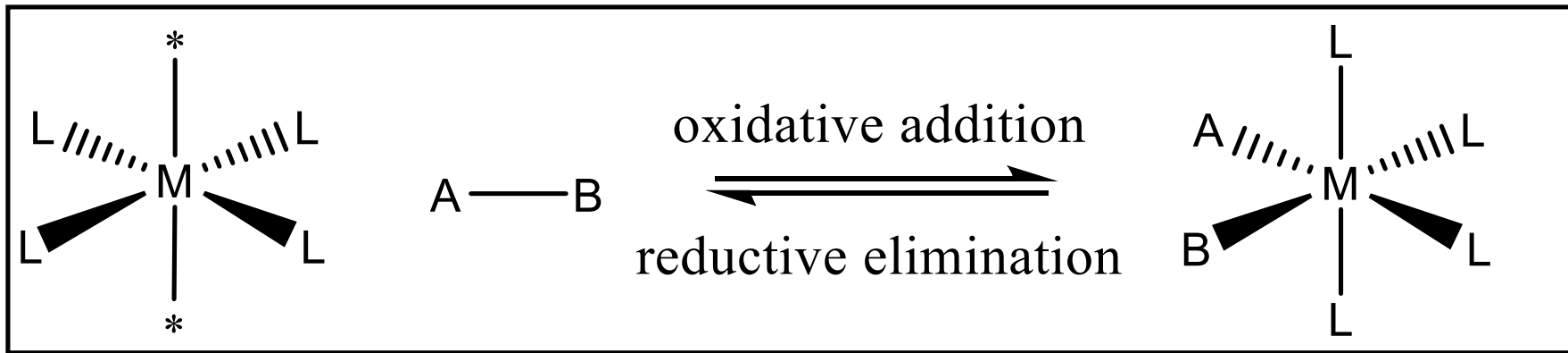
Oxidative Addition

Favoured by:

▶ Low oxidation number

▶ Electron donating ligands

▶ Anionic complexes

▶ Vacant sites

Square planar complexes are ideal for oxidative addition

Types of A – B

H-H

X-X

C-C

H-X

C-X

M-X

Reductive Elimination

- The reverse of oxidative addition

- Takes place in a **cis** sense

- Favoured by the opposite factors:
  - High oxidation state
  - Crowded co-ordination sphere
  - Electron withdrawing ligands
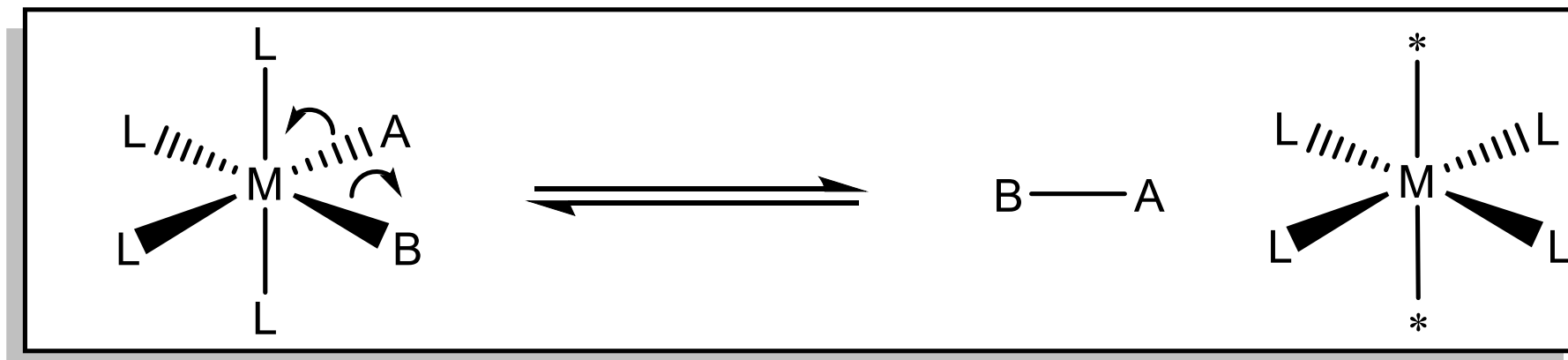
Migration
Alkyl / Hydride
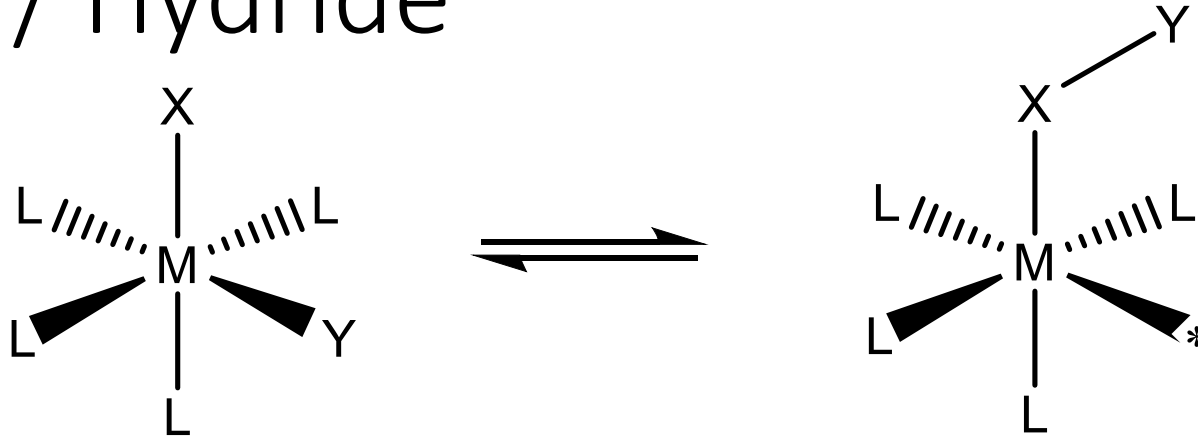
Insertion Reaction

Ligand Y migrates which enlarges ligand X
Can often be seen as a nucleophilic attack of Y on X

Migrating Ligand Y can be alkyl or halide

X Ligands can be a wide range, CO, CNR, CR_2, C=C, O_2, SO_2

Hydride Migration
Regiochemistry at Alkene
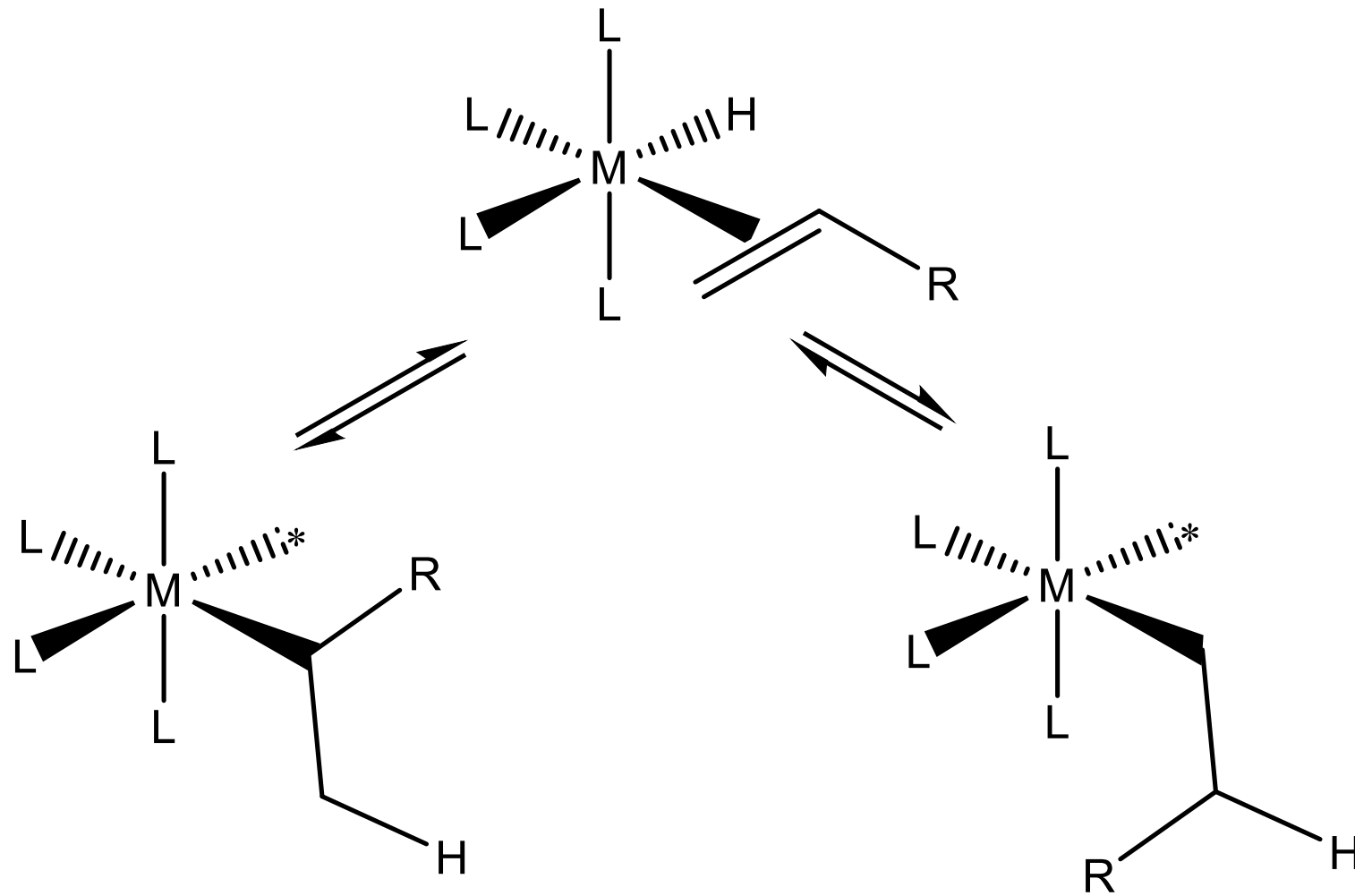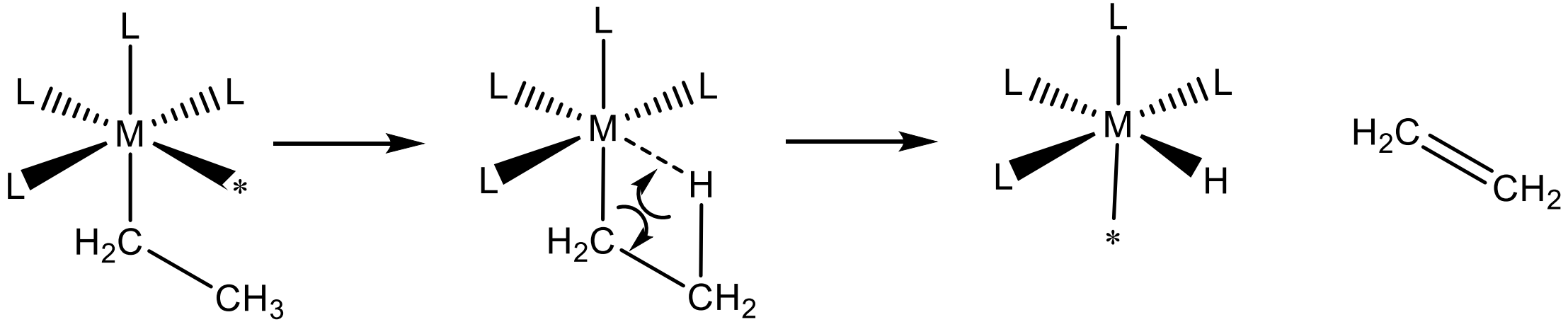
β - elimination

β-elimination

Reverse of hydride migration to an alkene

Coordination number increases during intermediate
Needs a vacant site

M-C-C-H group must be syn coplanar
Must have a beta-hydrogen for beta-elimination to take place

Reaction Steps
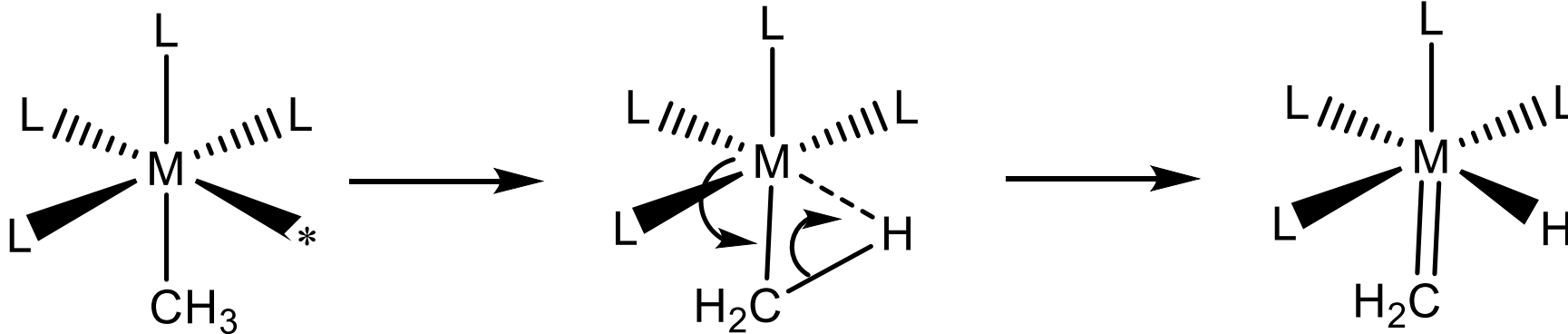
α - elimination

α-elimination

Alpha-elimination is the reverse of hydride migration to an alkylidene (Carbene)

Usually not seen if beta-elimination is possible due to the less favourable transition state

Reaction Steps - Test

Draw a scheme showing beta-hydride elimination from $[Cp_2Ti(n\text{-}Pr)]^+$
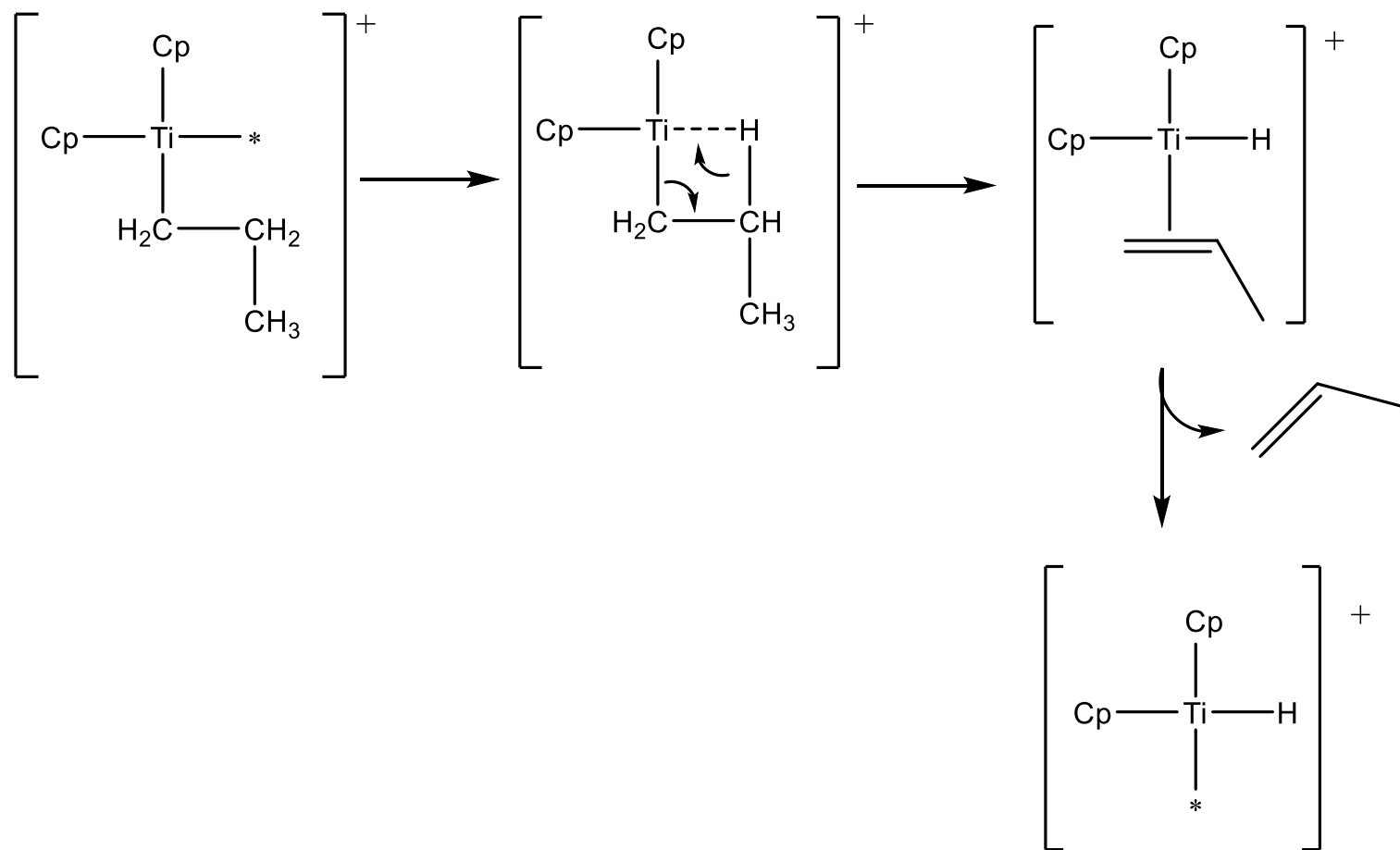
Hydrogenation - Test

Give electrons counts for each of the intermediates.

1	NA
2	12
3	14
4	16
5	14
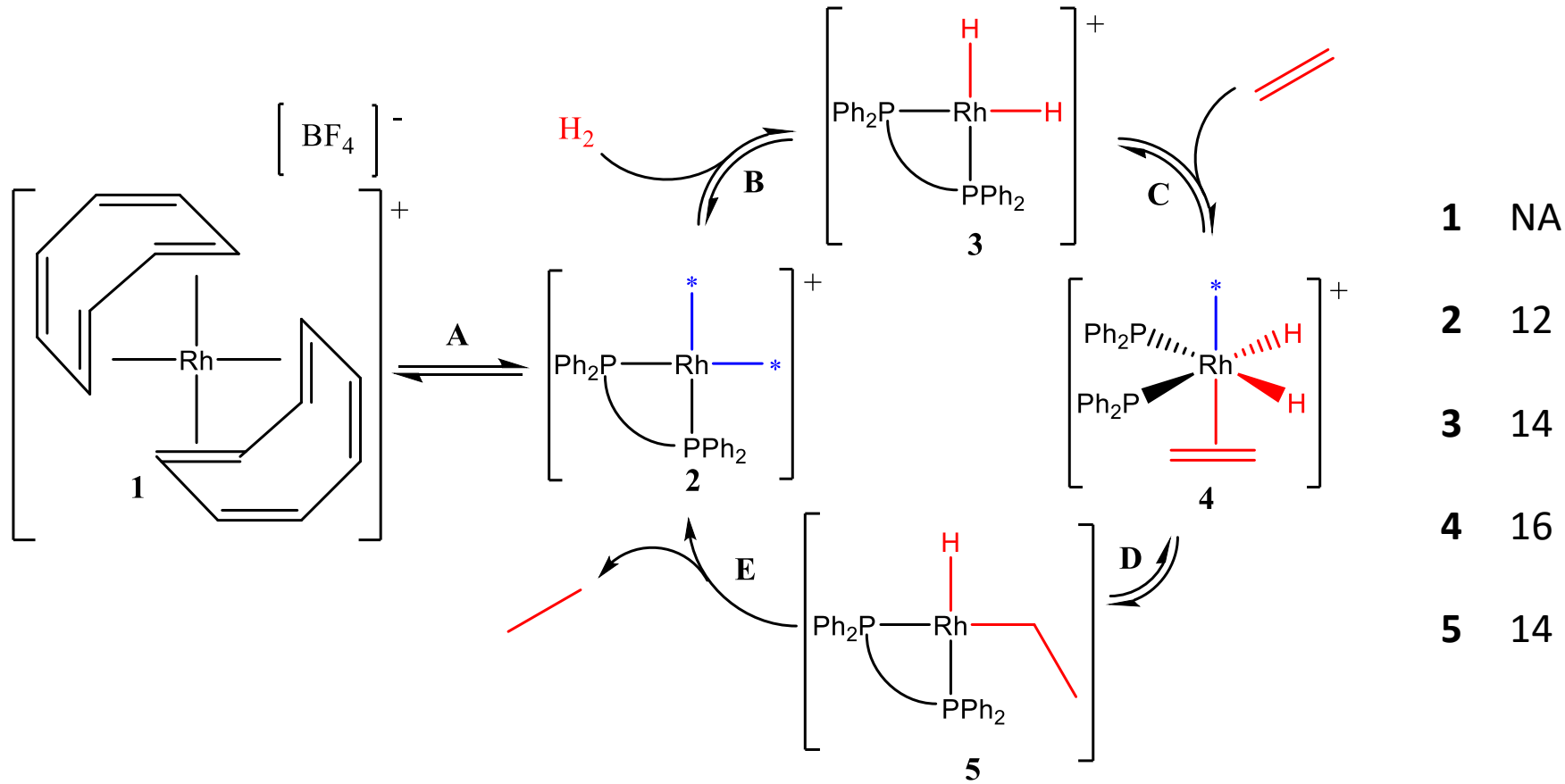
Hydrogenation - Test

State the oxidation state of the metal centre in each of the intermediates
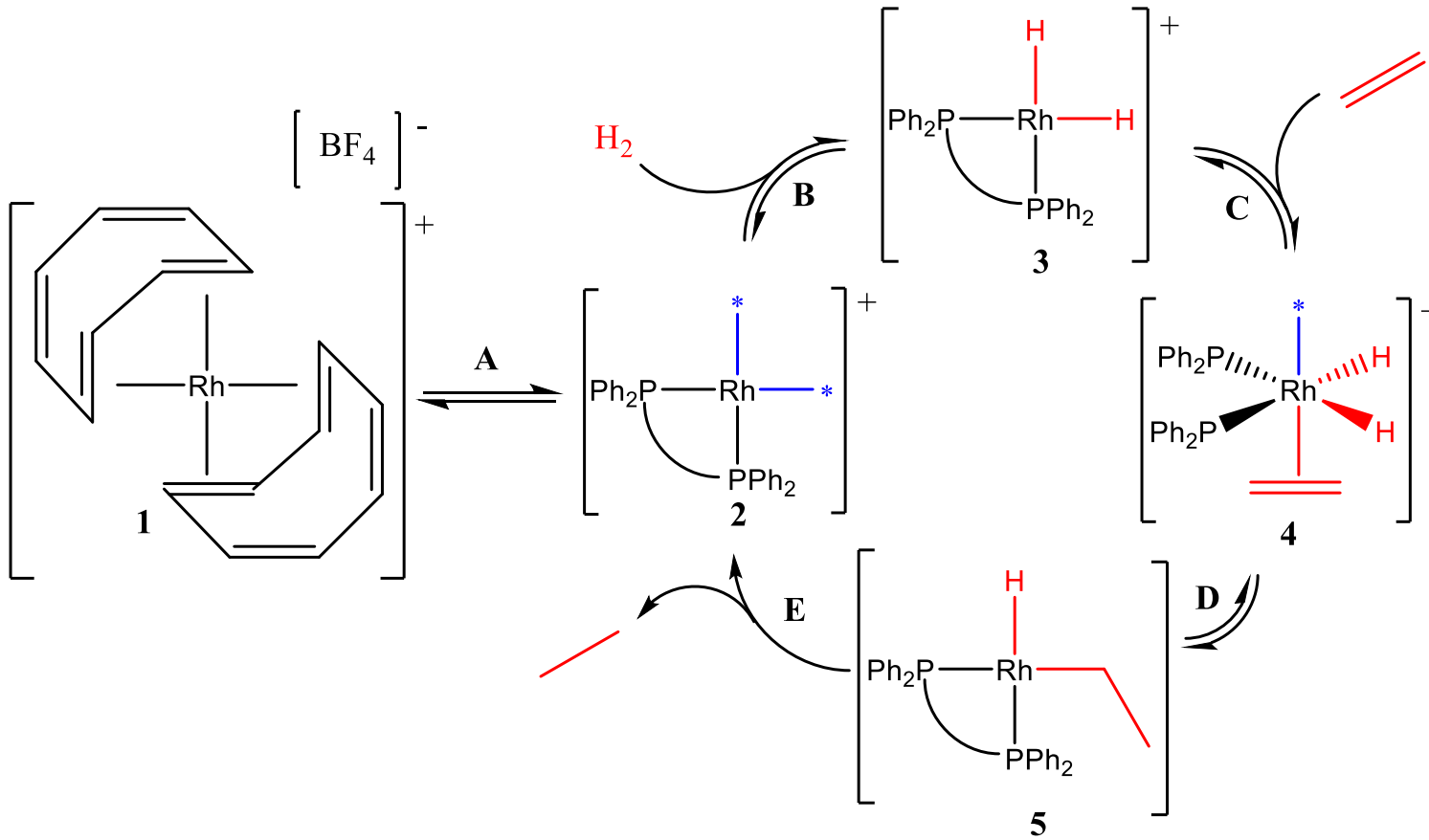
1	NA	NA
2	12	(I)
3	14	(III)
4	16	(III)
5	14	(III)

Hydrogenation - Test

Name each of the reaction steps in the catalytic cycle.
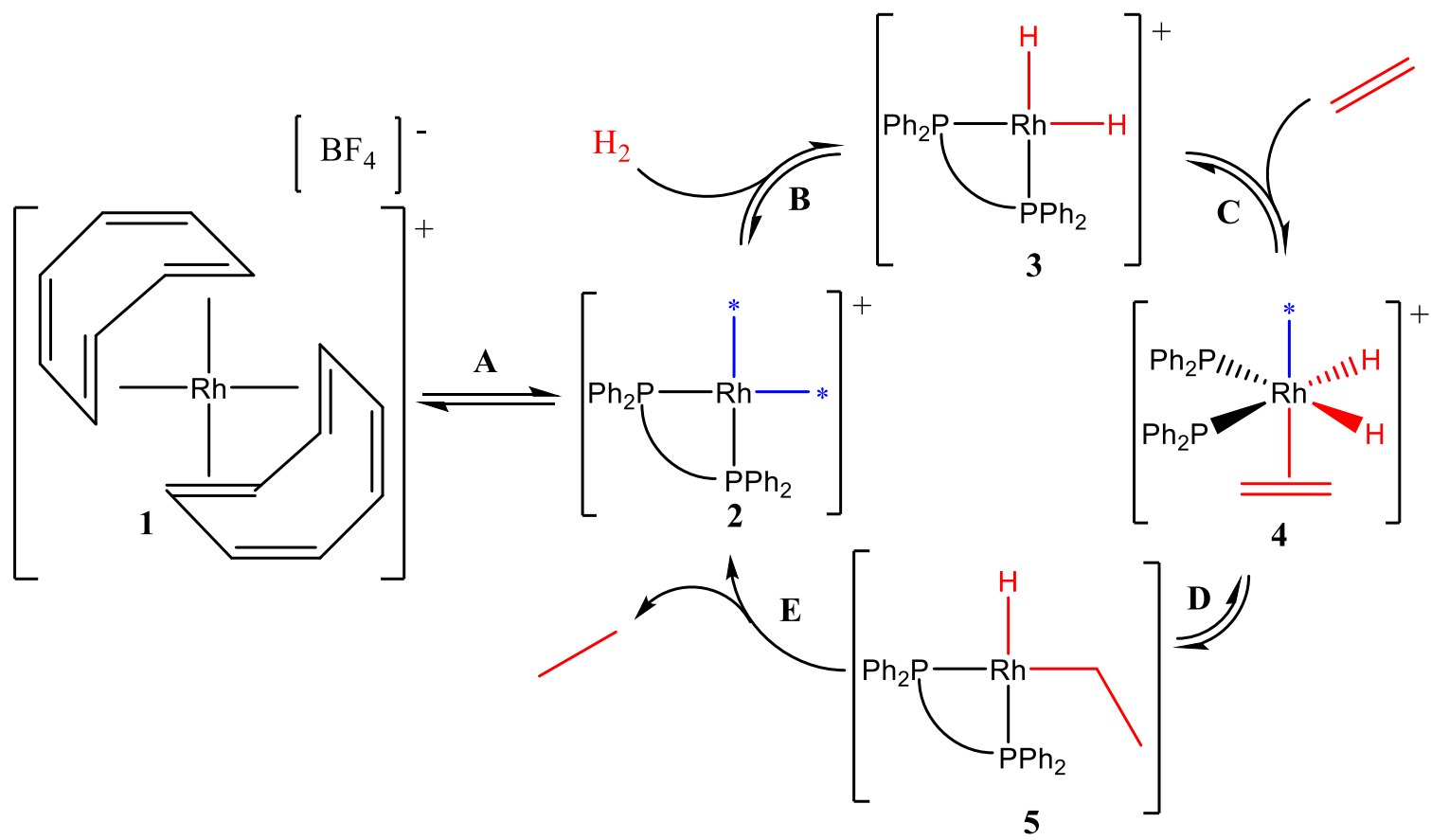
A   Dis/Associaton Ligand Exchange

B   Oxidative Addition

C   Alkene Binding

D   Hydride Migration

E   Reductive Elimination

Addition to Alkene

Phosphine Ligands

- The phosphine ligand is one of the best ligands for hydrogenation
- Good two electron donor with steric tuning of coordination sphere and metal accessibility by changing the phosphine substituents (pi-acidity and tolman cone angle)
- Fast turnover needs
  - Bulky group favours dissociation
  - Good donors favour oxidative addition

Alkene Polymerisatic

Ziegler Catalyst

TiCl$_4$

Activated by AlEt$_3$

Mild Conditions

Controlled process: Yields HIGH DENSITY linear polymer

TACTICITY

ISOTATIC

SYNDIOTATIC
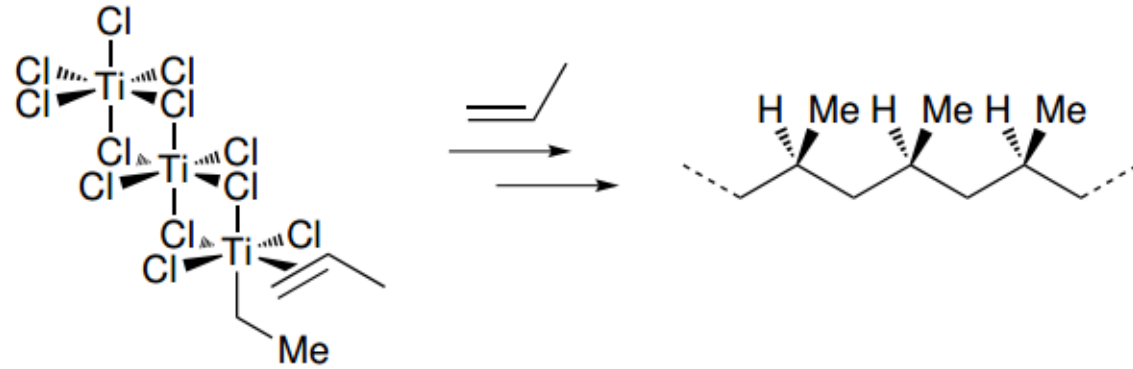
ATATIC

Prochiral propene monomer is bound with the same enantioface in both sites: isotatic polypropene results
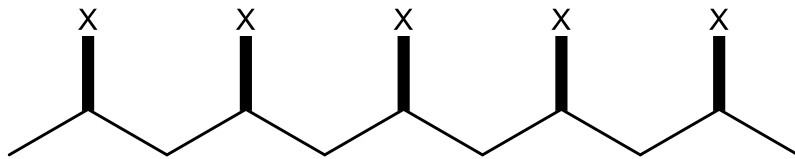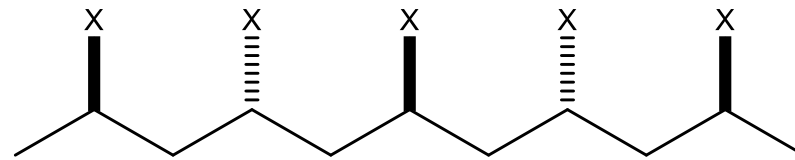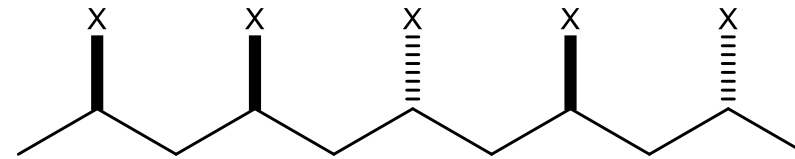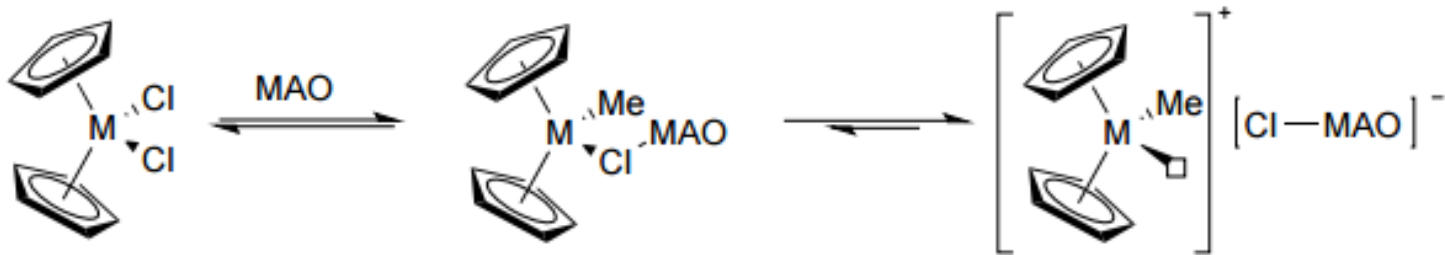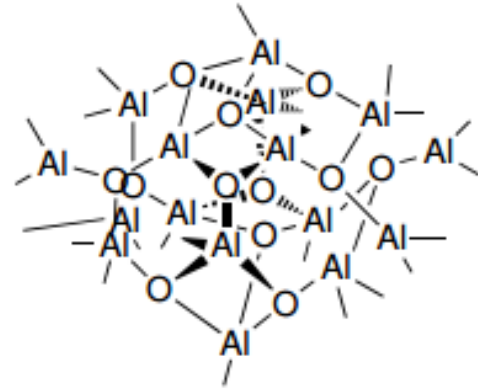
Cossee-Arlman Mechanism
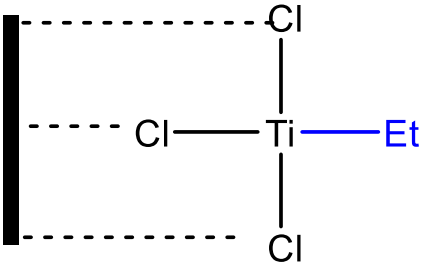
Metallocene Mechanism

MAO
Methylaluminoxane
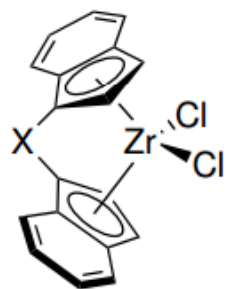
Hydrolysis of AlMe$_3$ gives MAO [-Al(Me)-O-]n

Co-Catalysts and Activators
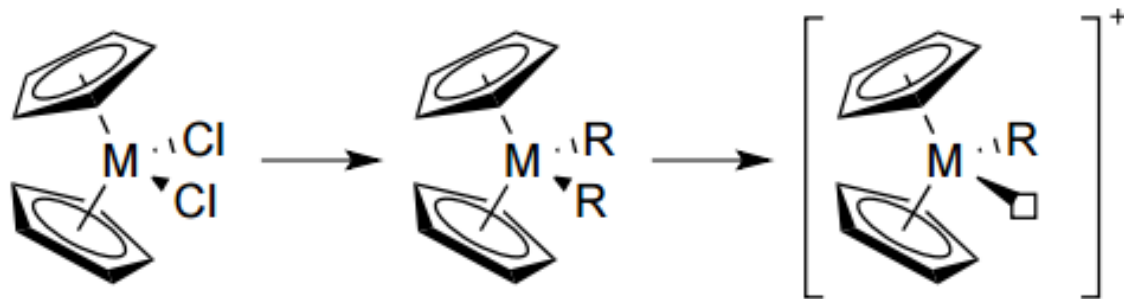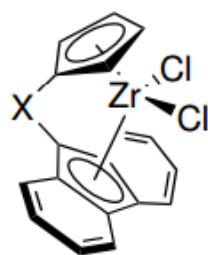

Roles:

- To scavenge Lewis basic and Brønsted acidic impurities
- To alkylate the metal centre
- To generate a cationic metal alkyl
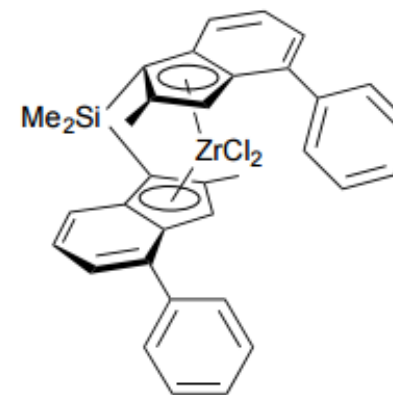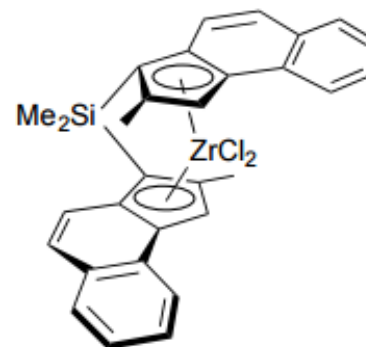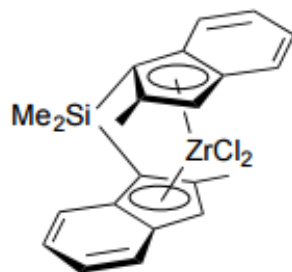- To provide a very weakly co-ordinating counterion

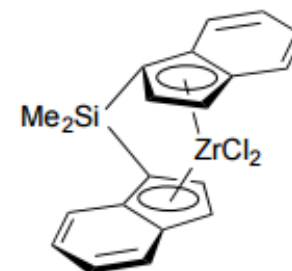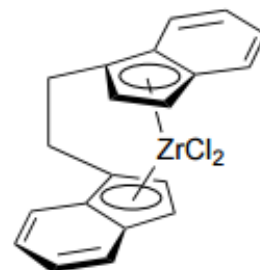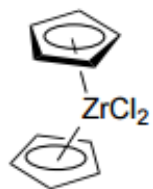# Ligand Symmetry and Tacticity

C_2 symmetric: isotactic PP

C_s symmetric: syndiotactic PP

The last system can form more than 50 000 C−C bonds per second!

Alkene Polymerisation Catalysts

Essential Features:

- Electron Deficiency
- Vacant coordination site adjacent to the growing polymer chain
- Steric protection at the metal centre to prevent beta-hydride elimination
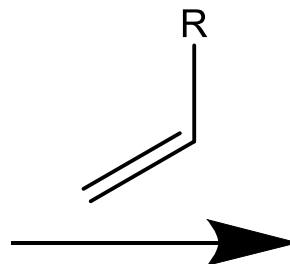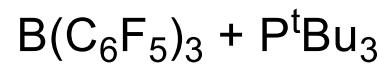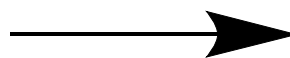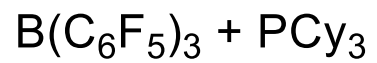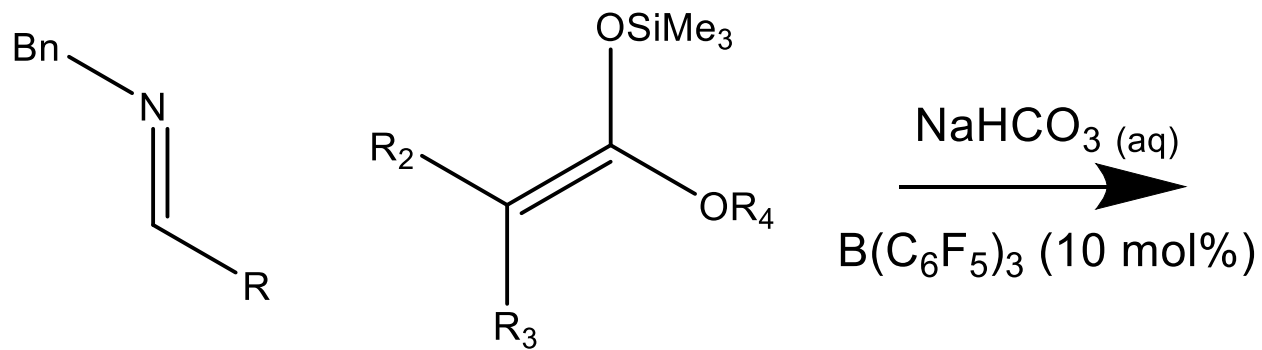
Cations and Anions

Cationic complexes

- ► Prevent dimerisation
- ► Increase M−C bond strength
- ► Suppress β-H elimination
- ► Increase electrophilicity and thus alkene binding

Weak anions

- ► Support cationic complexes
- ► Leave free sites on metal
- ► Do not degrade under reaction conditions

Give products for the following reactions with a brief explanation why:

$$Bn-N=CH-R \quad + \quad \underset{R_3}{\overset{OSiMe_3}{\underset{|}{R_2-C=C-OR_4}}} \quad \xrightarrow[\quad B(C_6F_5)_3 \ (10 \ mol\%) \quad]{NaHCO_{3 \ (aq)}}$$

$$B(C_6F_5)_3 + PCy_3 \qquad \longrightarrow$$

$$B(C_6F_5)_3 + P^tBu_3 \qquad \xrightarrow{\qquad}$$

Give products for the following reactions with a brief explanation why:
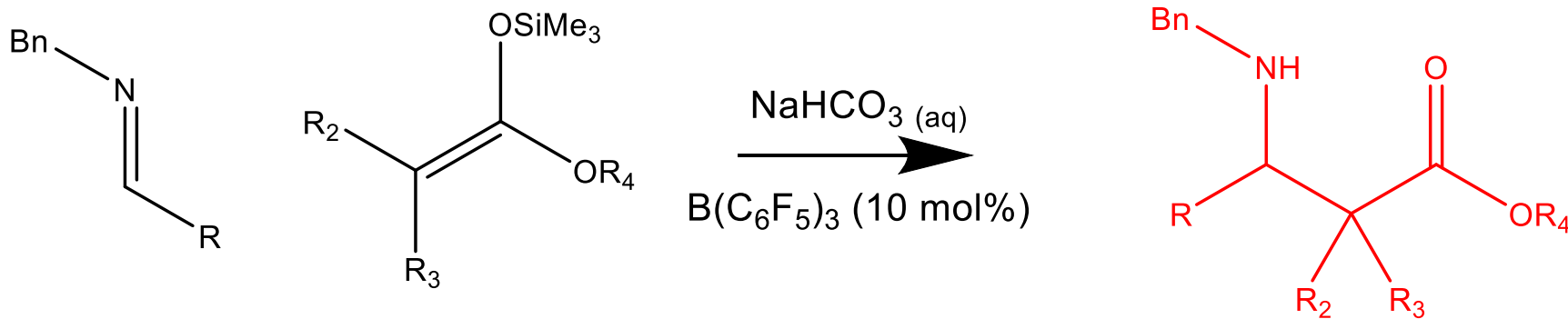
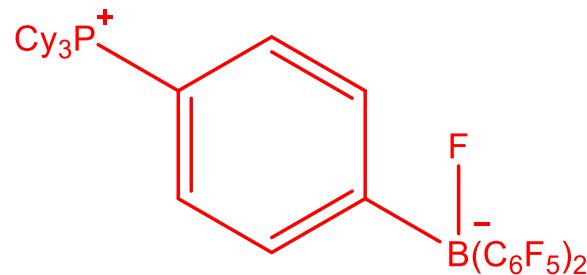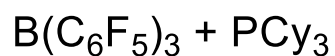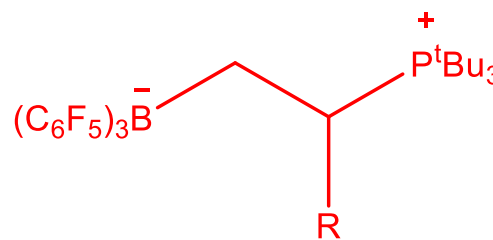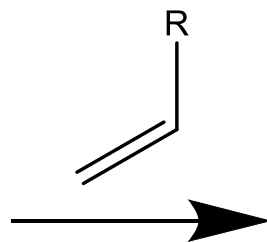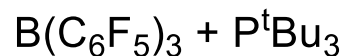Catalyses aldol type reaction by coordinating nitrogen.

Moderate size ions
-cant form direct adduct
-can form reactant zwitterion

Bulky size ions
-cant form direct adduct
-cant form reactant zwitterion
- Frustrated lewis pair activates substrates

Use knowledge of electronegativity to predict products for the following reactions:

^{n}BuLi + BH$_3$ →

^{n}BuLi + NH$_3$ →

^{n}BuLi + H$_3$NBH$_3$ →
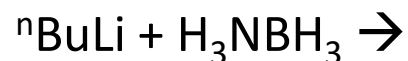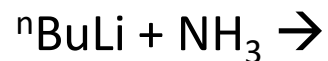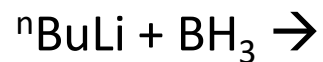
Phosphorus hydrogen bonds (P-H) are **very weakly polarised**. Is dehydrocoupling observed in H$_3$B-P(Ph)H$_2$?
If so:
- Why?
- Would you expect homo- or hetero- dehydrocoupling?
- Would you expect it to be fast or slow?

Give an example of a reagent that could catalyse this dehydrocoupling. How does it work?

a) Use knowledge of electronegativity to predict products for the following reactions:

^{n}BuLi + BH$_3$ → [Li]$^+$ [B(^{n}Bu)H$_3$]$^-$

^{n}BuLi + NH$_3$ → BuH + LiNH$_2$

^{n}BuLi + H$_3$NBH$_3$ → [Li]$^+$ [H$_2$NBH$_3$]$^-$

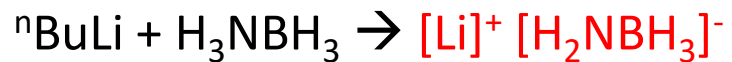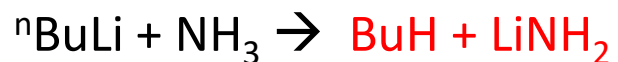b)i) Phosphorus hydrogen bonds (P-H) are **very weakly polarised**. Does it undergo dehydrocoupling in H$_3$B-P(Ph)H$_2$? If so, why, and would you expect homo- or hetero- dehydrocoupling? Would you expect it to be fast or slow?

Yes. Borane pulls electron density through molecule making P-H acidic. Undergoes **hetero**dehydrocoupling to form polymer. Expect slow.

ii) Give an example of a reagent that could catalyse this dehydrocoupling. How does it work?
B(Ar$_F$)$_3$ - displaces a borane in substrate molecule to form (Ar$_F$)$_3$B-PPhH$_2$. Stronger LA hence catalyses reaction. B(Ar$_F$)$_3$ needs to dissociate from product continue polymerisation.
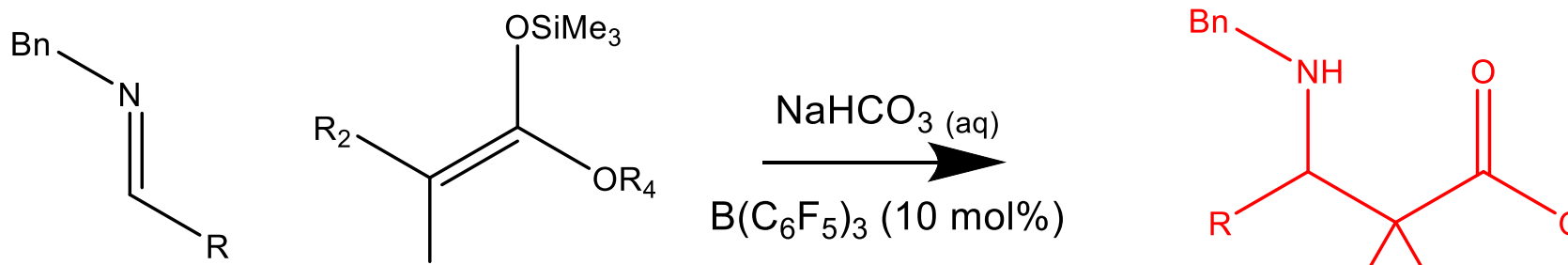
Ethylsilane and diethylstannane go through slightly different dehydrocoupling mechanisms when catalysed by group IV mettalocenes such as zirconocene hydrochloride.

Give catalytic cycles for both substrates. What are the differences?

Ethylsilane
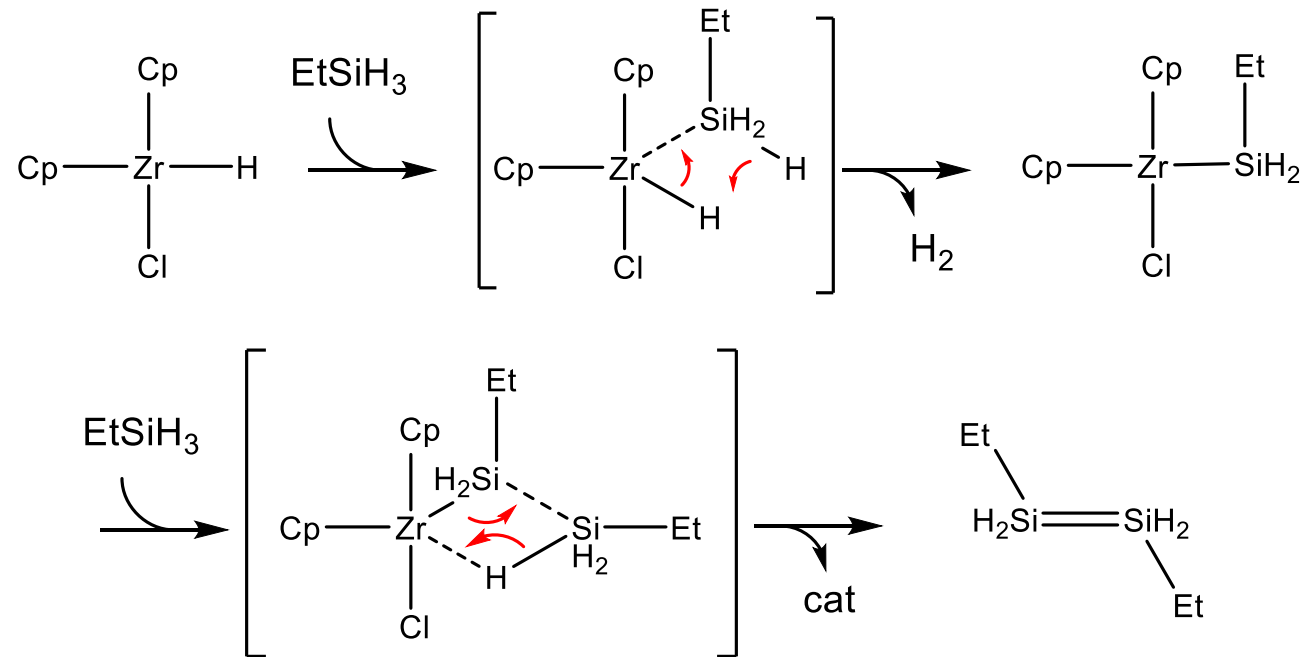
Diethylstannane
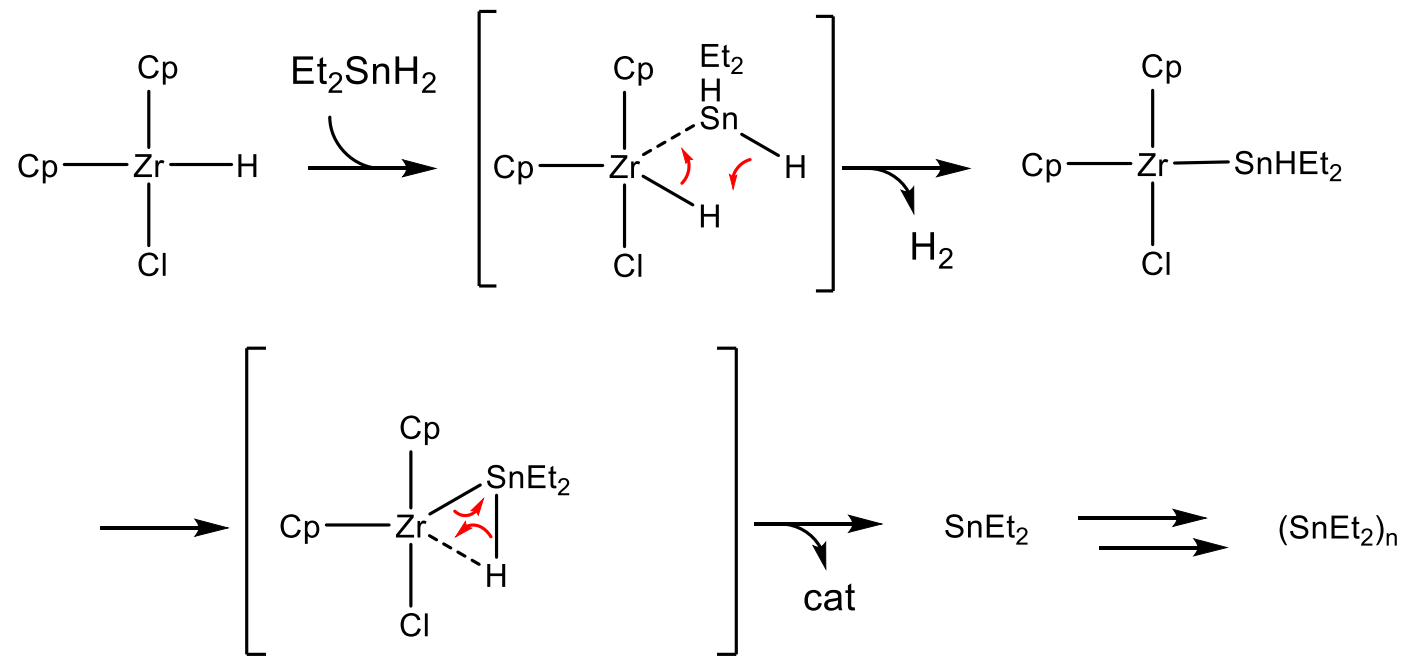
Show how the following reagents are a precursor for a very highly active polymerisation catalyst. Show intermediates.

$ZrCp_2Me_2$
$[CPh_3]^+ [B(C_6F_5)_4]^-$
Low Temp CD_2Cl_2

What tacticity is the following *very short* polypropylene chain? What spectroscopic technique would you use to determine this and why? How many different peaks would you observe?
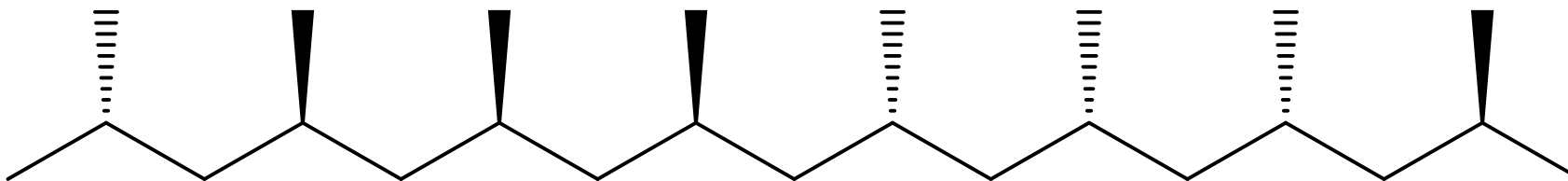
i)
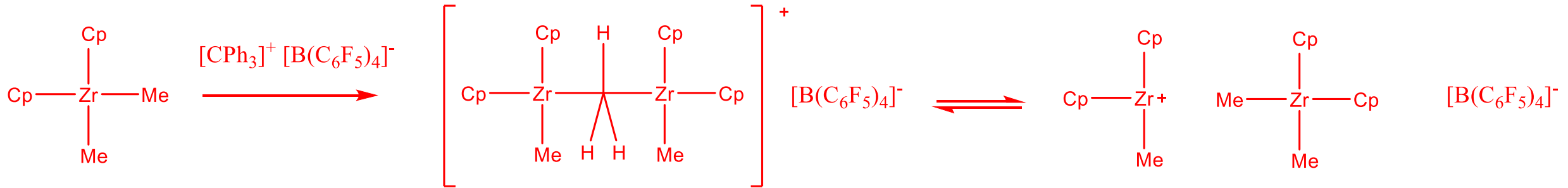
ii)

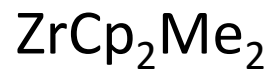What tacticity is the following *very short* polypropylene chain? What spectroscopic technique would you use to determine this and why? How many different peaks would you observe?

r   m   m   r   m   m   r

rmmr
mmrm
mrmm
rmmr

Atactic (Random)

See two peaks in ^{13}C NMR as some pentads replicated

What are the different types of errors in a polymer chain?

Catalysts either work with an *enantiomorphic site control* or a *chain end control* 'algorithm' when an error is processed in the polymer chain.
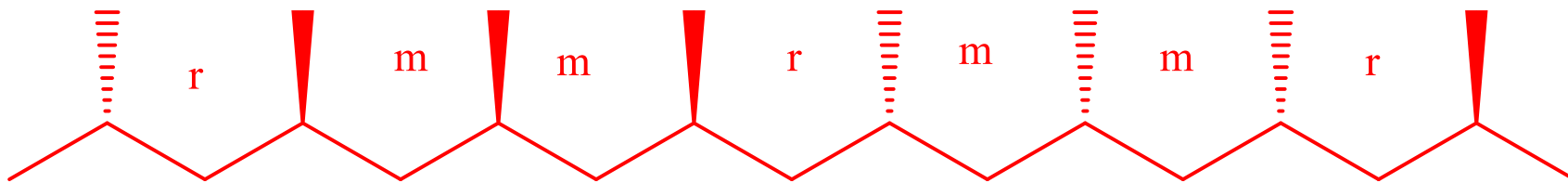
- What is the difference between *site control* and *chain end control*?
- Give an example of a catalyst that exhibits *site control* and an example of a catalyst that exhibits *chain end control*.
- How could you use a spectroscopic method to tell the difference?

What are the different types of errors in a polymer chain?

Isolated Stereo Error (wrong configuration processed)

Isolated Regio Error (wrong end of alkyl migration so integrate a **blank** methylene group)

Catalysts either work with an *enantiomorphic site control* or a *chain end control* 'algorithm' when an error is processed in the polymer chain.

- What is the difference between *site control* and *chain end control*?

Site control – Wrong stereochemistry processed, next chain fixed to normal stereochemistry and proceeds as normal (SSSSSS**RSSSSSS**)

Chain end control – Wrong stereochemistry processed then continues with inverted stereochemistry (SSSSSS**RRRRRR**)

- Give an example of a catalyst that exhibits *site control* and an example of a catalyst that exhibits *chain end control*.

SC – C_2 or C_s ligands

CE – Cp_2TiCl_2 at low temp, Zeigler Nata ('$TiCl_4$')

- How could you use a spectroscopic method to tell the difference?

SC – mmrr, mrrm   NO mmrm

CE – mmrm   NO mmrr, mrrm