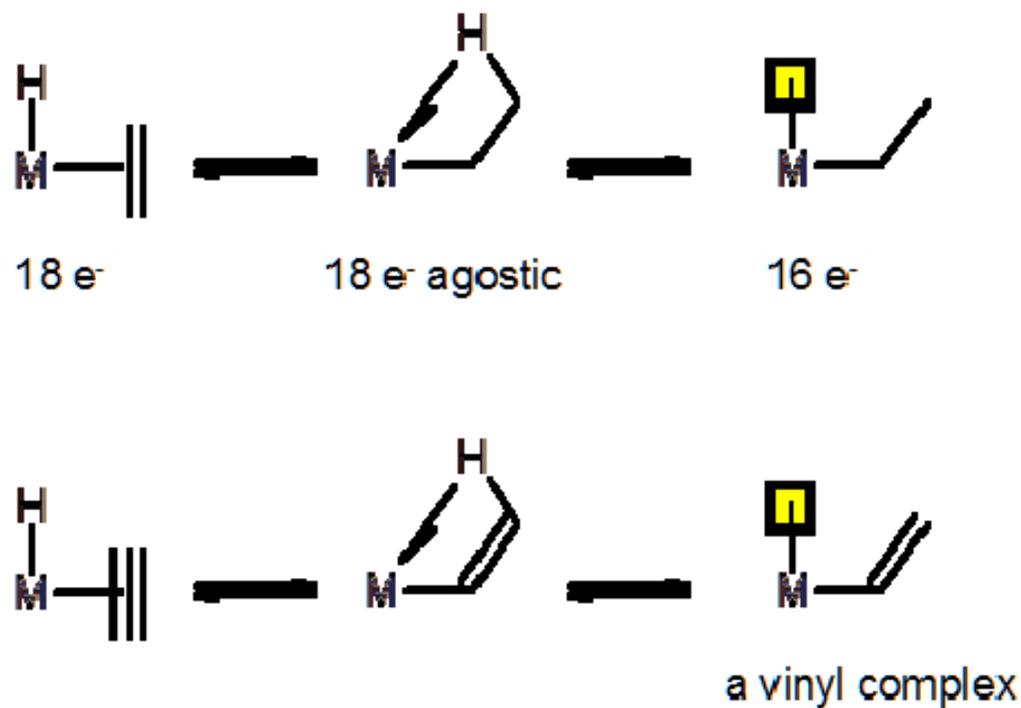


1,2-insertion / de-insertion

1,2-insertion because **M** ends up bound to the atom in position 1 (**X**) while **Y** ends up bound to the atom in position 2 (**Z**)



a) alkene and alkyne insertion into M-H bonds



insertion is slightly exothermic:



bonds broken

M-H	60 kcal/mol
π -C=C	64
	124

bonds formed

M-C	35 kcal/mol
C-H	98
	133

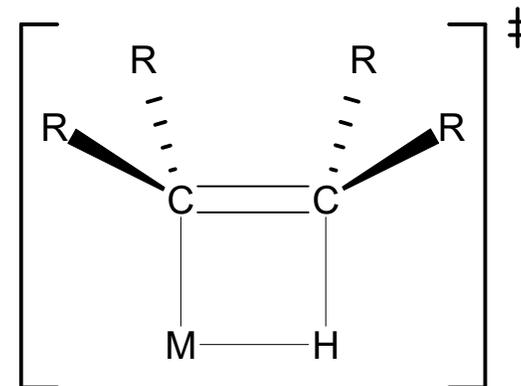
therefore ΔH° is ca. -9 kcal/mol but ΔS° is **negative**

Factors favouring insertion (disfavouring β -H elimination):

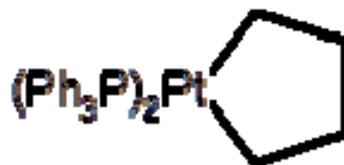
- no β -H available
- unstable alkene product (egs. C=Si, Bredt's rule)
- coordinatively saturated (18 e⁻): no vacant site for agostic H
- d^0 metal centre: no electron density to donate into C-H σ^*
- inability to achieve a coplanar transition state

So, what is the mechanism? Generally agreed that migratory insertion is operative

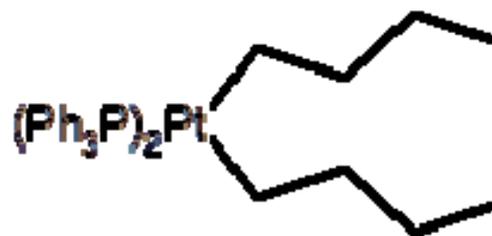
insertion (and elimination) go by a **planar 4-centre transition state**:



thus, alkyls that cannot easily achieve **coplanarity** of the M-C and β C-H bond, do not eliminate rapidly:

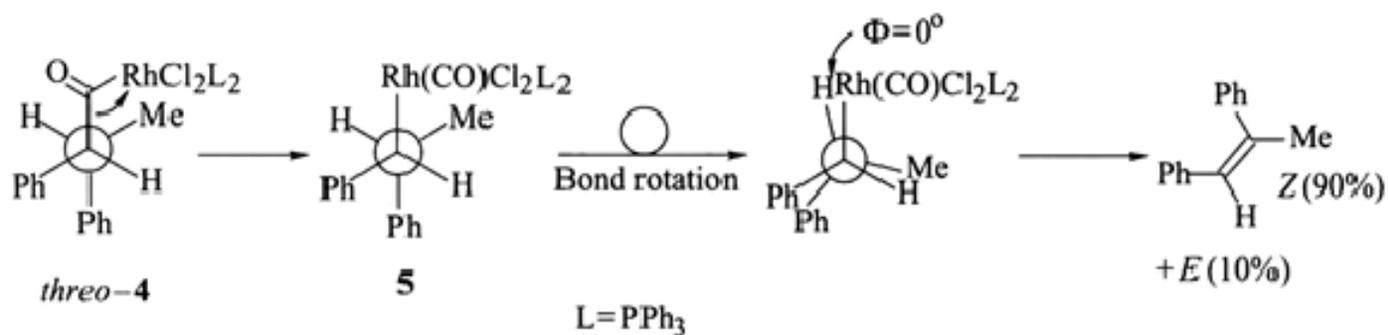


rel. elimination rate
1

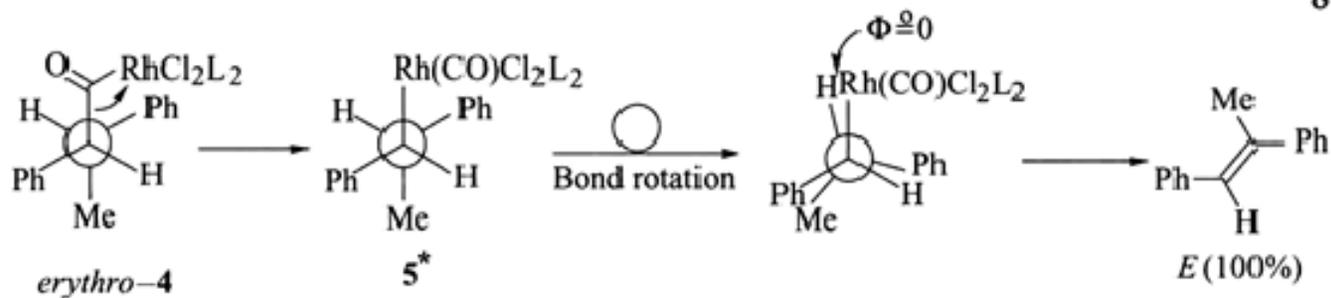


10,000

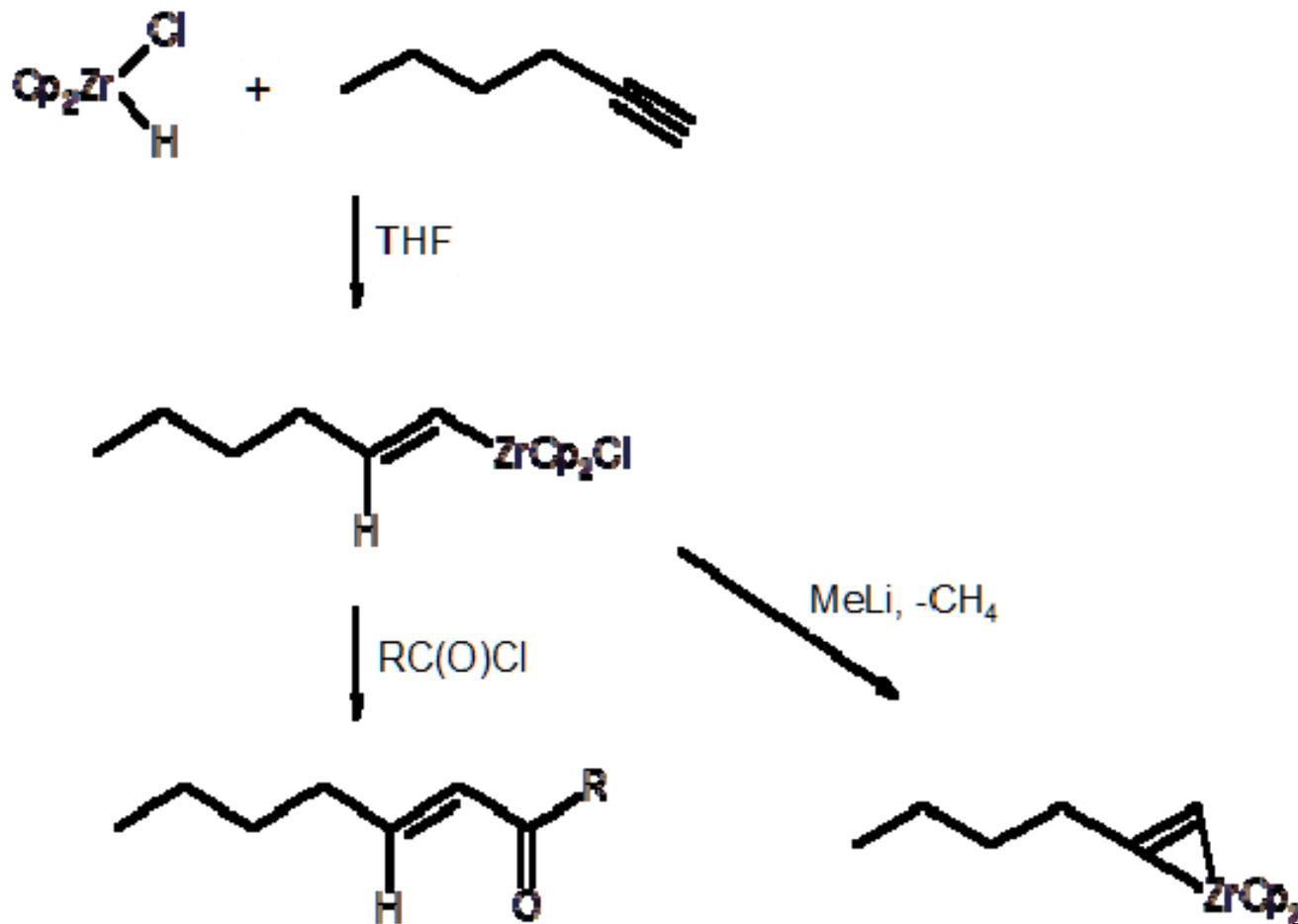
The coplanar, 4-centre transition state implies **syn elimination and insertion**. This requirement therefore dictates the stereochemistry of the alkene product obtained.



8.11



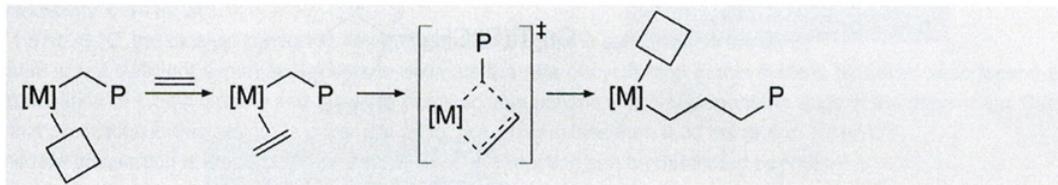
Schwartz's reagent allows easy (but stoichiometric) functionalization of alkenes and alkynes by single insertion. Note that this is a d^0 metal centre and β -H elimination is not favourable.



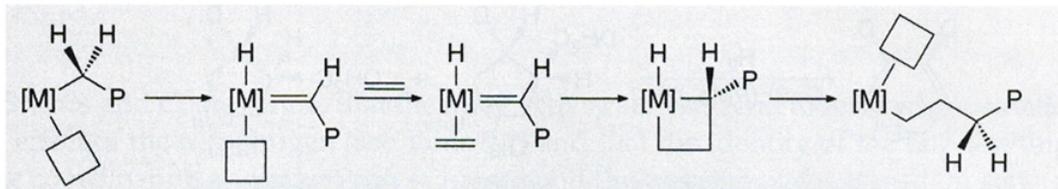
b) alkene insertion into M-C bonds

Mechanism not established with certainty but most evidence suggests the **Cossee-Arlman** option:

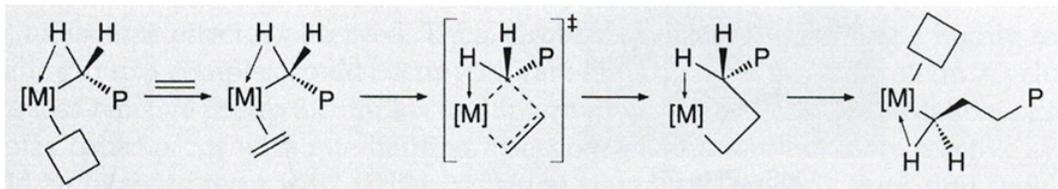
Cossee–Arlman mechanism (direct insertion)



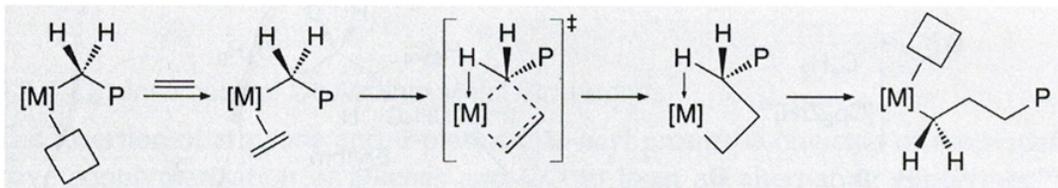
Green–Rooney mechanism (hydride shift)



Modified Green–Rooney mechanism (ground and transition state α -agostic interaction)



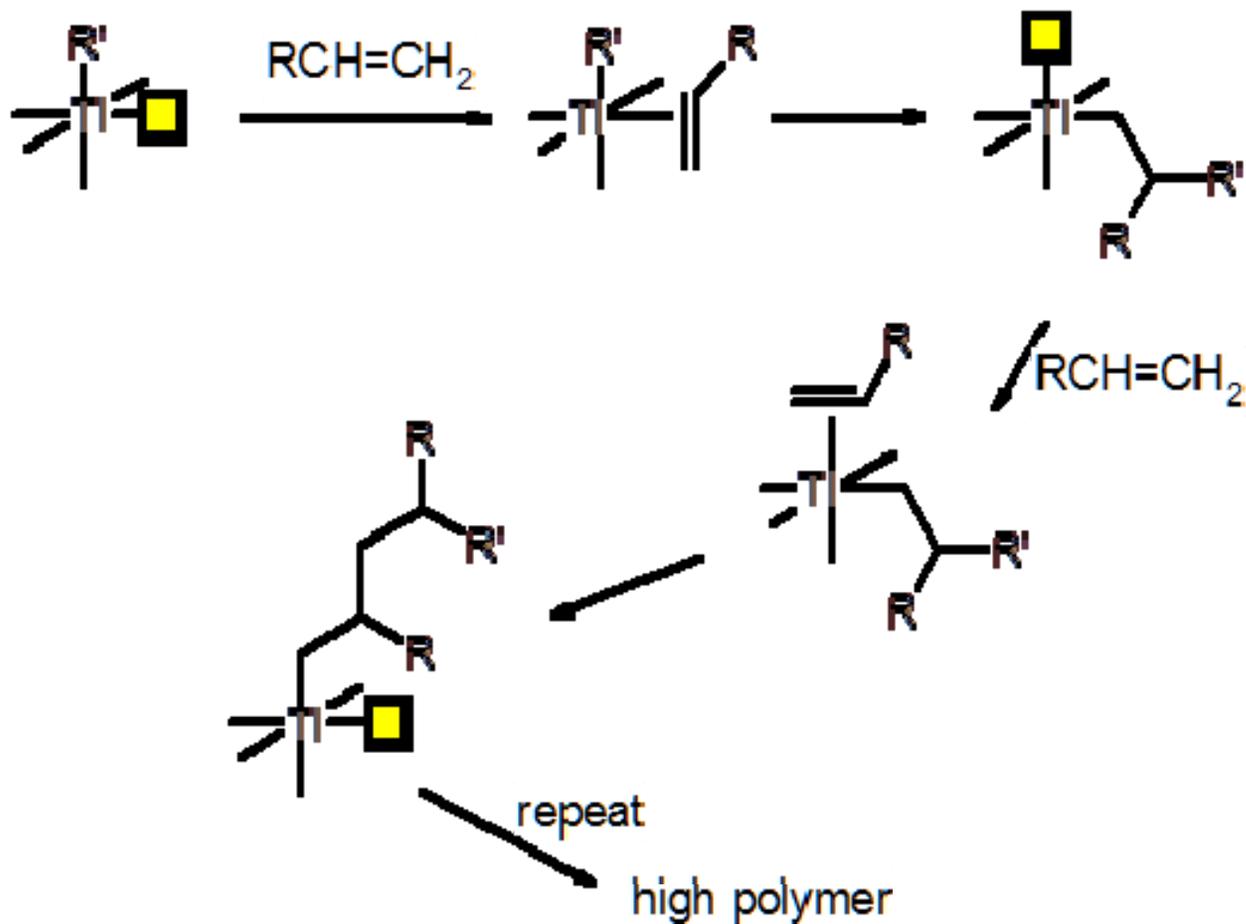
Transition state α -agostic mechanism



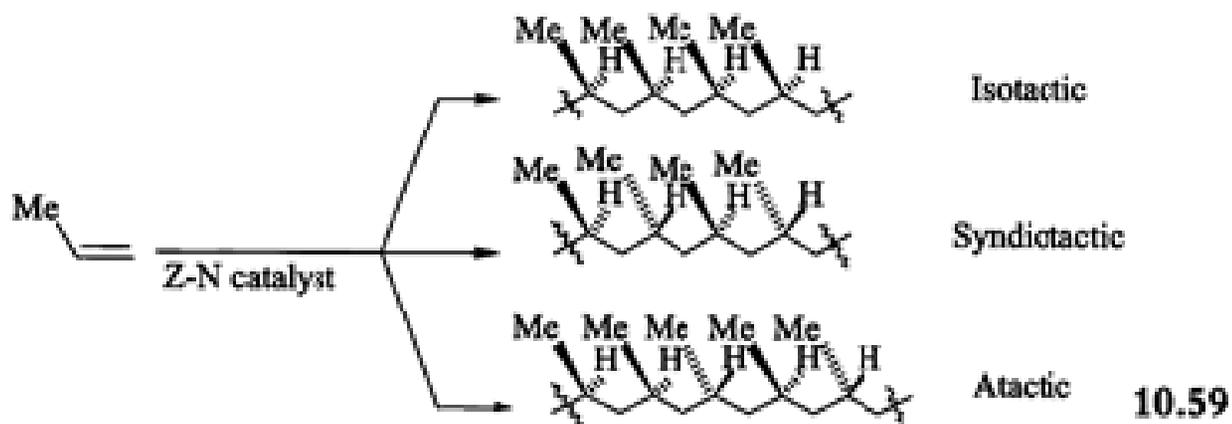
From Hartwig: Organotransition Metal Chemistry

Scheme 9.9

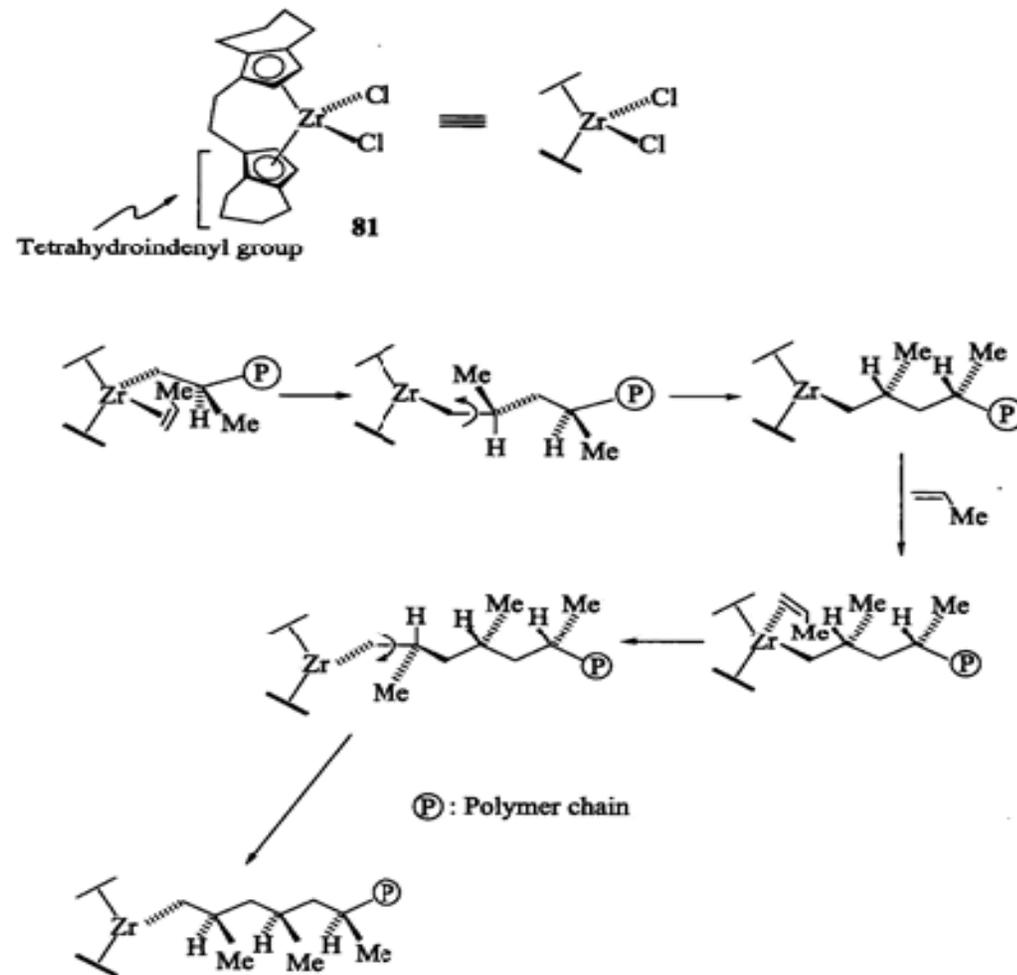
Ziegler-Natta polymerization of alkenes (*a heterogeneous reaction*) is the classic example of this reaction:



- *Homogeneous* versions of the Z-N reaction using Cp_2ZrR^+ as the catalysts are used industrially
- *Stereochemical* control is possible by careful design of the catalyst structure.



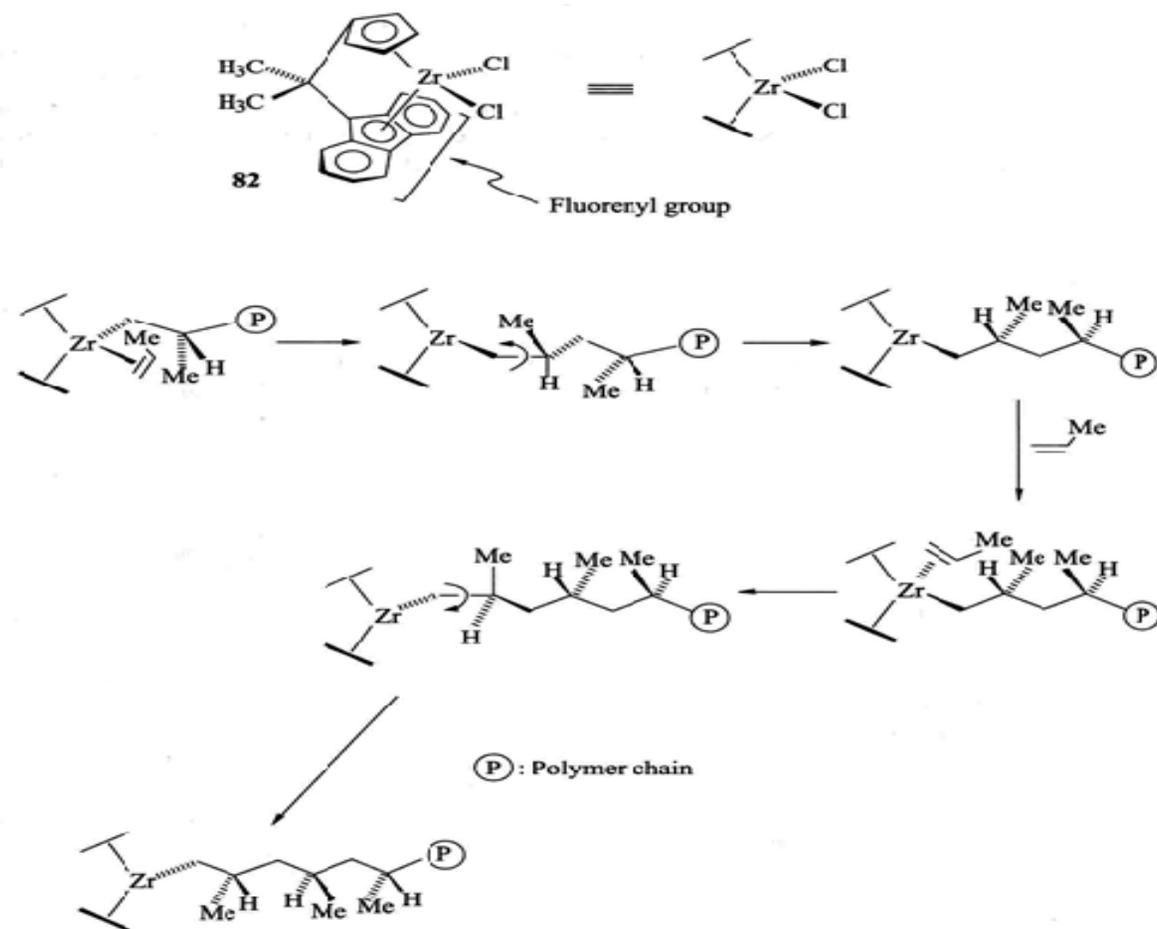
Isotactic
polypropylene



Scheme 10.17
A Mechanism for Isotactic Polymerization

From Spessard and Meissler

Syndiotactic polypropylene

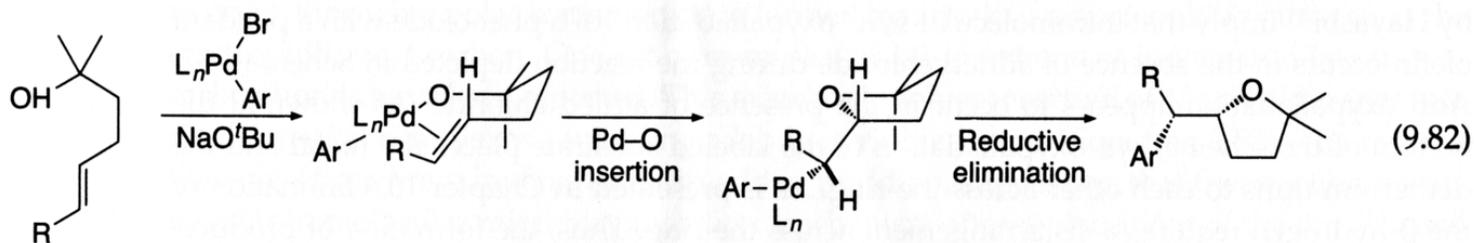


Scheme 10.18
Mechanism for Syndiotactic Polymerization

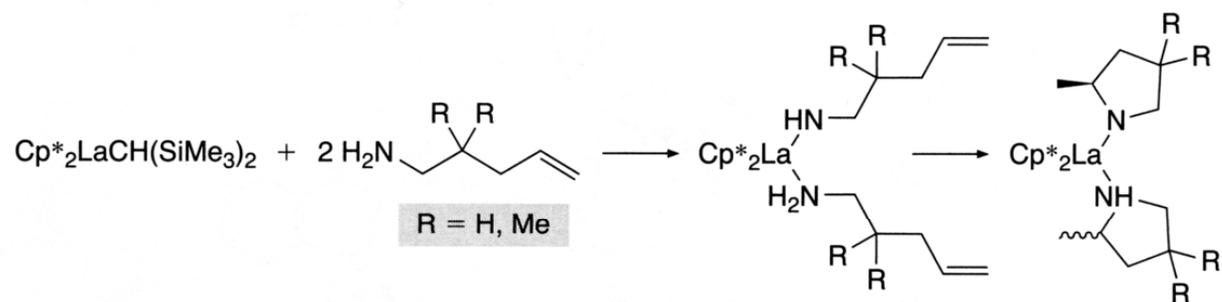
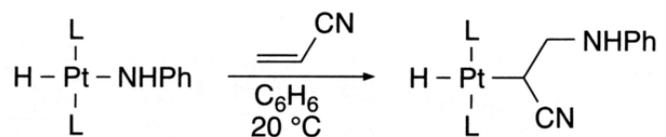
c) alkene insertion into Metal-E bonds (E = O, N, Si)

Insertions into M-O bonds are rare, but known:

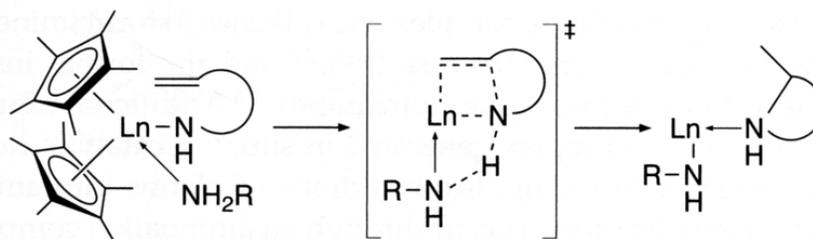
WHY?



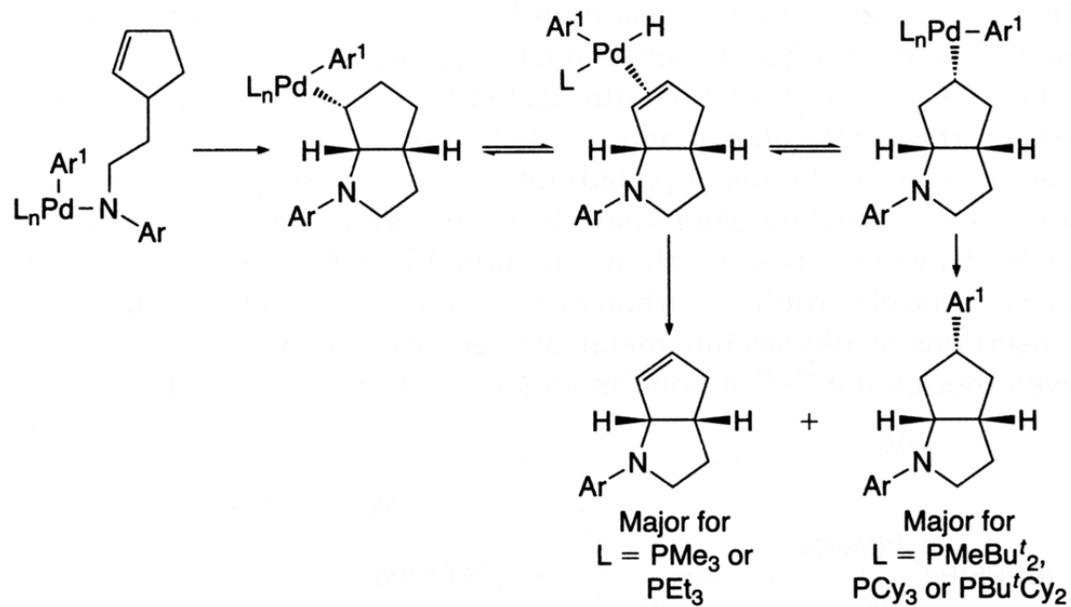
Hydroamination: insertion into amido M-N bonds



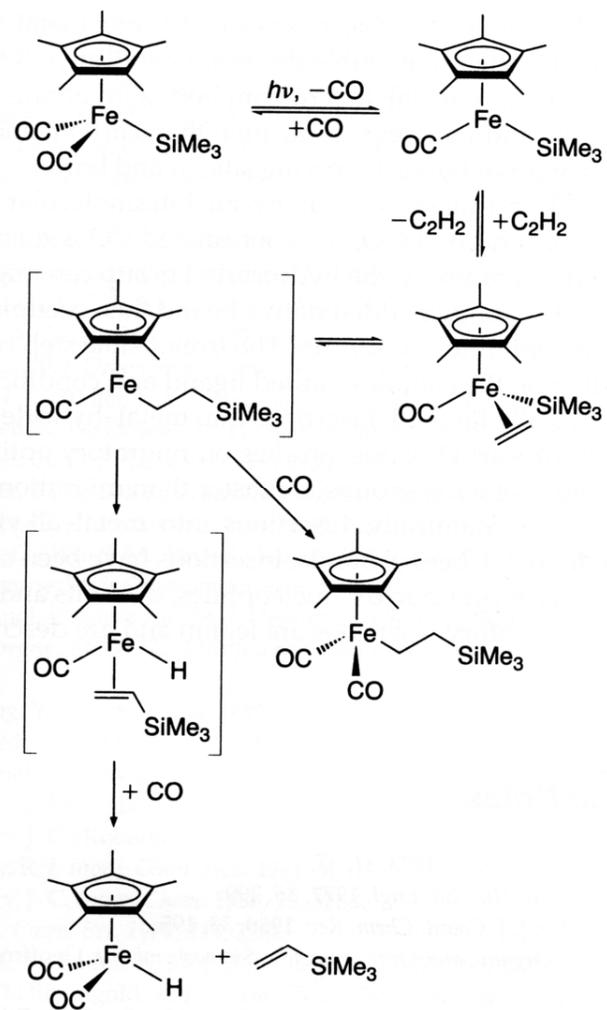
via



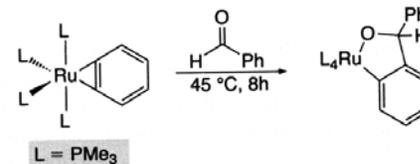
Hydroamination at a late TM centre: competing β -H elimination and reductive elimination



Insertion of alkene into a M-Si bond is a key step in hydrosilylation (aka hydrosilylation)

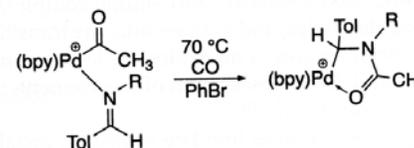
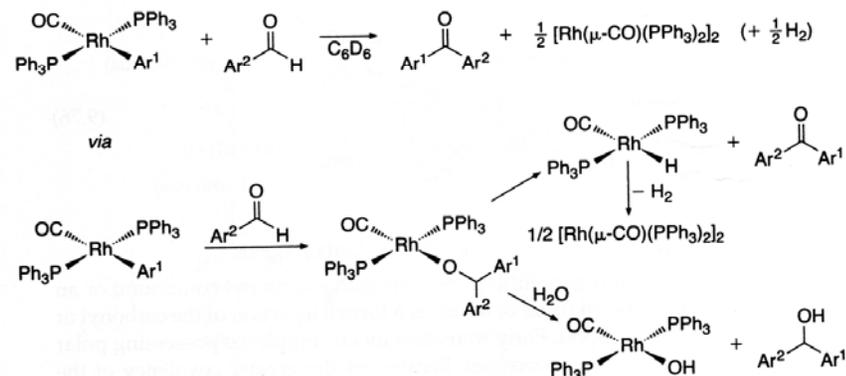
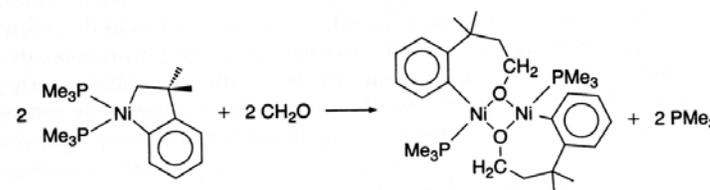


d) Insertion of other multiple bonds into the M-C bond



Most common examples:

- Aldehydes (ketones less so)
- Imines



CO₂ insertion: virtually **all** metal alkyls will do this

