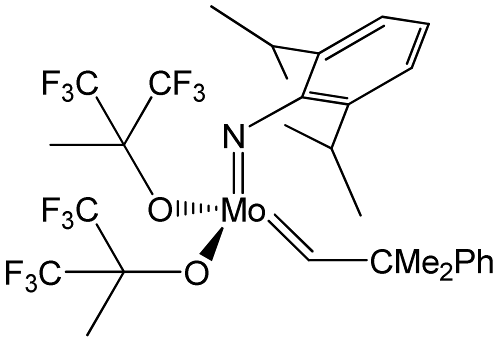
- Both Schrock and Grubbs type alkene metathesis catalysts have a low coordination number CN = 4 (after dissociation of PCy_3 by Grubbs catalyst)
- This allows facile access of the alkene to the central metal centre, where the decisive coordination step occurs.
- Spectator ligands such as imido or oxo functions commonly found in metathesis catalysts promote formation of the metallacyclic intermediates.



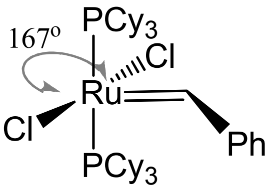
Schrock (1990)

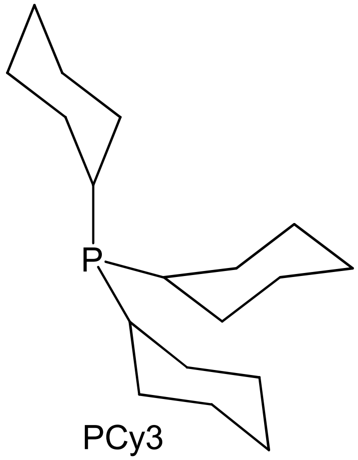
Highly reactive

Poor tolerance of functional groups in substrate

The catalytic activity increases with the electron withdrawing nature of the two alkoxy ligands

Metathesis of tri- and tetra-substituted olefins is possible





PCy3

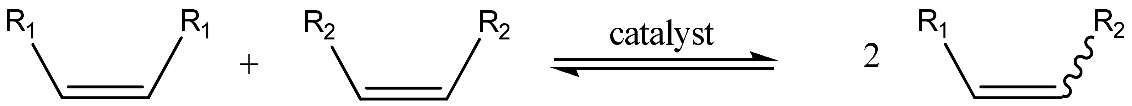
Grubbs (1995)

Tolerance of functional groups in substrate
(CO, OH, NH)

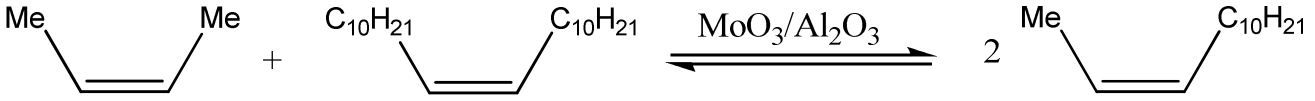
Selectivity towards sterically unhindered olefins and strained olefins

Tri- and tetra-substituted olefins are not attacked

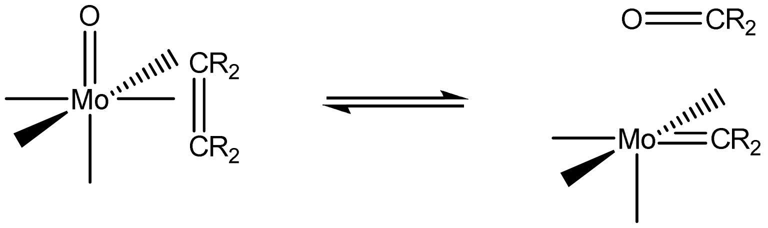
Cross Metathesis (CM)



- Cross metathesis has been used in industry in the form of the Shell higher olefin process (SHOP) since 1977.
- This process is a combination of oligomerization, isomerization, and metathesis steps.
- First, linear C_4 to C_{30+} α-olefin chains are produced from ethylene. Enrichment of the C_8 – C_{18} fraction, which is of interest for application in various productions, is possible by a heterogeneous cross-metathesis reaction.



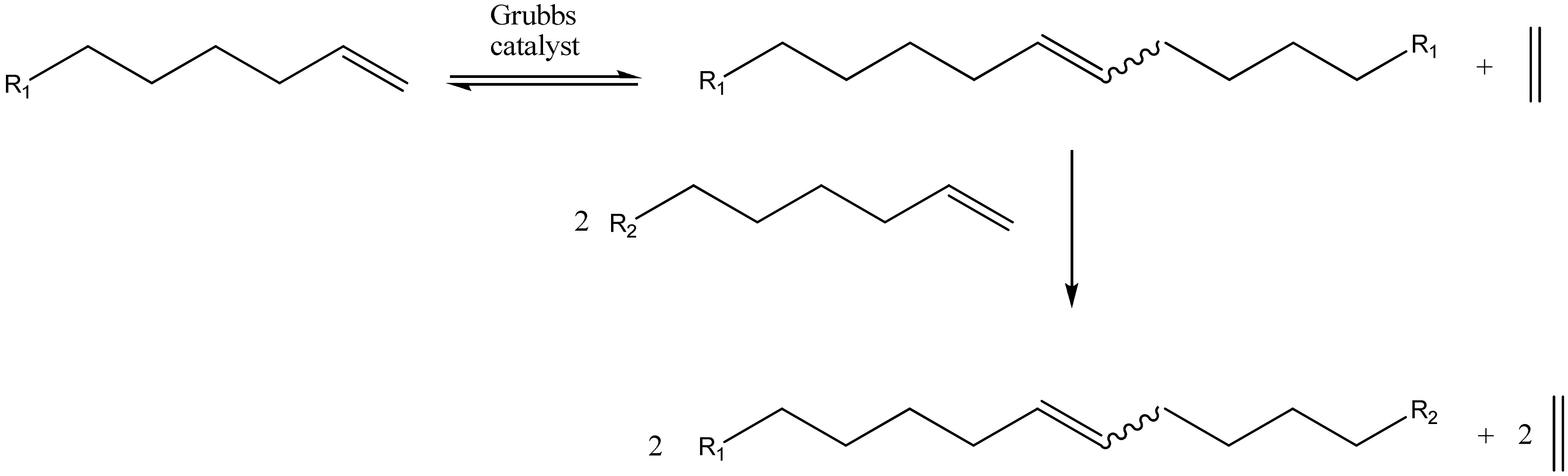
C4 C22 C13



pre-catalyst catalyst

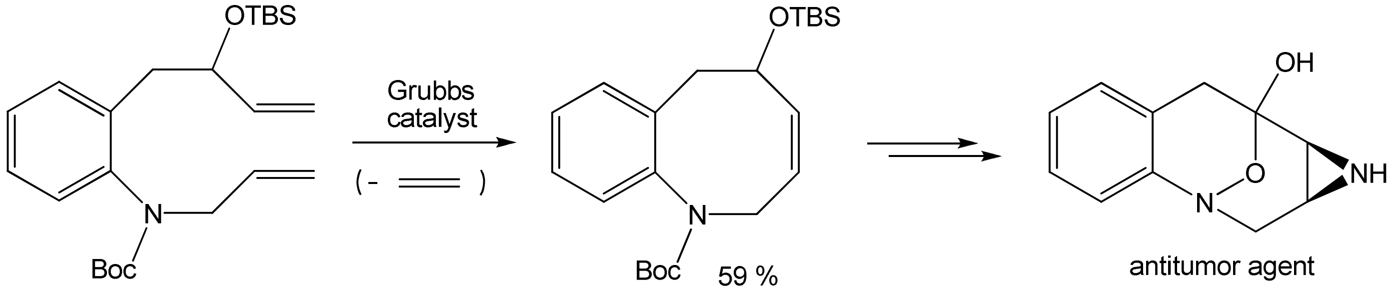
- Cross metathesis has only found limited applications however due to product “branching”.

- Grubbs reported that heterodimers are obtained in high yield when one of the starting olefins first undergoes homodimerization.

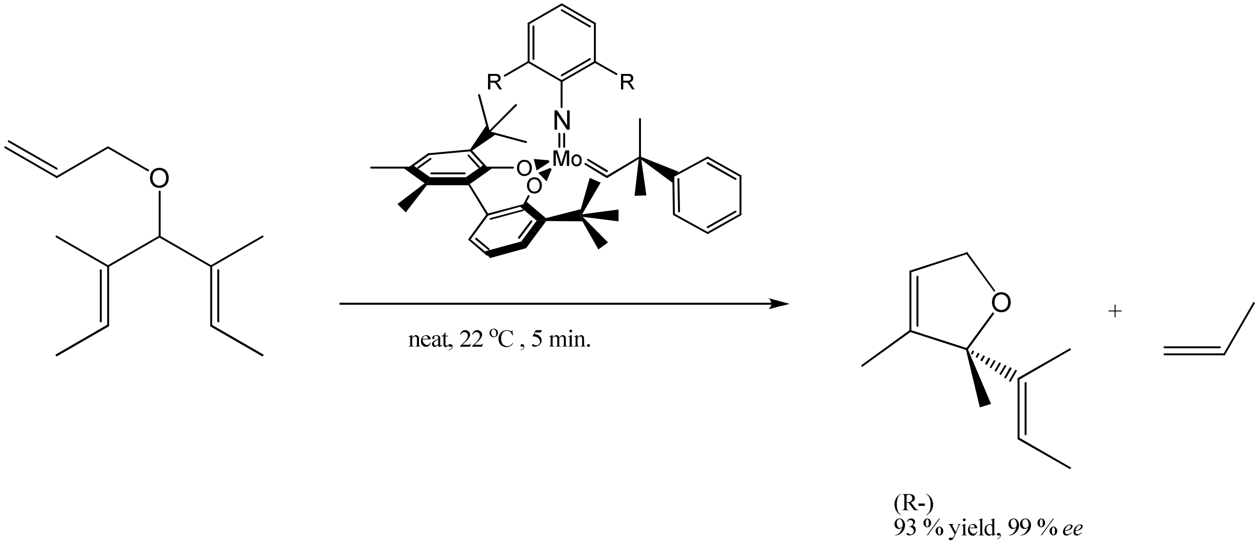


Ring Closing Metathesis (RCM)

- Ring closing metathesis is today considered a standard method in any organic synthesis laboratory (high dilution is required for diffusion controlled RCM to avoid CM).
- Its suitability for the preparation of N-heterocycles has inspired natural product synthesis.

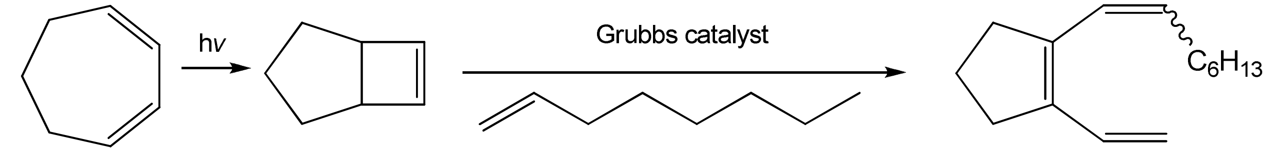


- Assymetric ring closing metathesis (ARCM) has also been developed.

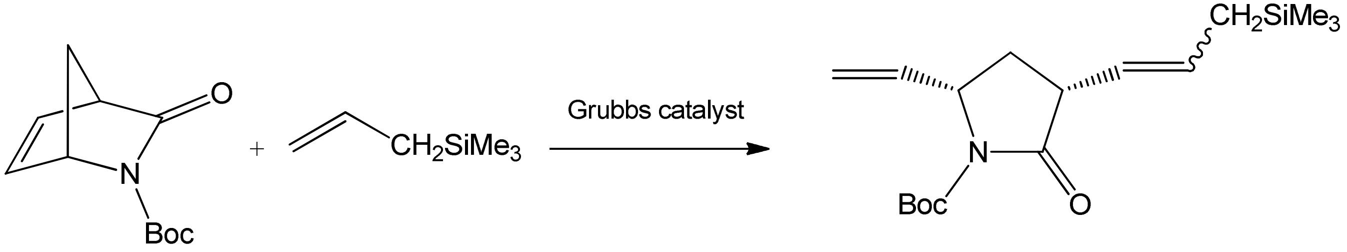


Ring Opening Metathesis (ROM)

- Ring opening metathesis is the reversal of ring closing metathesis.
- ROM is applied as a cross-metathesis in the presence of ethylene and is in principle suitable for the preparation of terminal dienes.
- Ring strain favors ring opening, and thus ROM processes are especially common with norbornenes and coclybutenes.



89 % yield
E/Z = 1:3.2

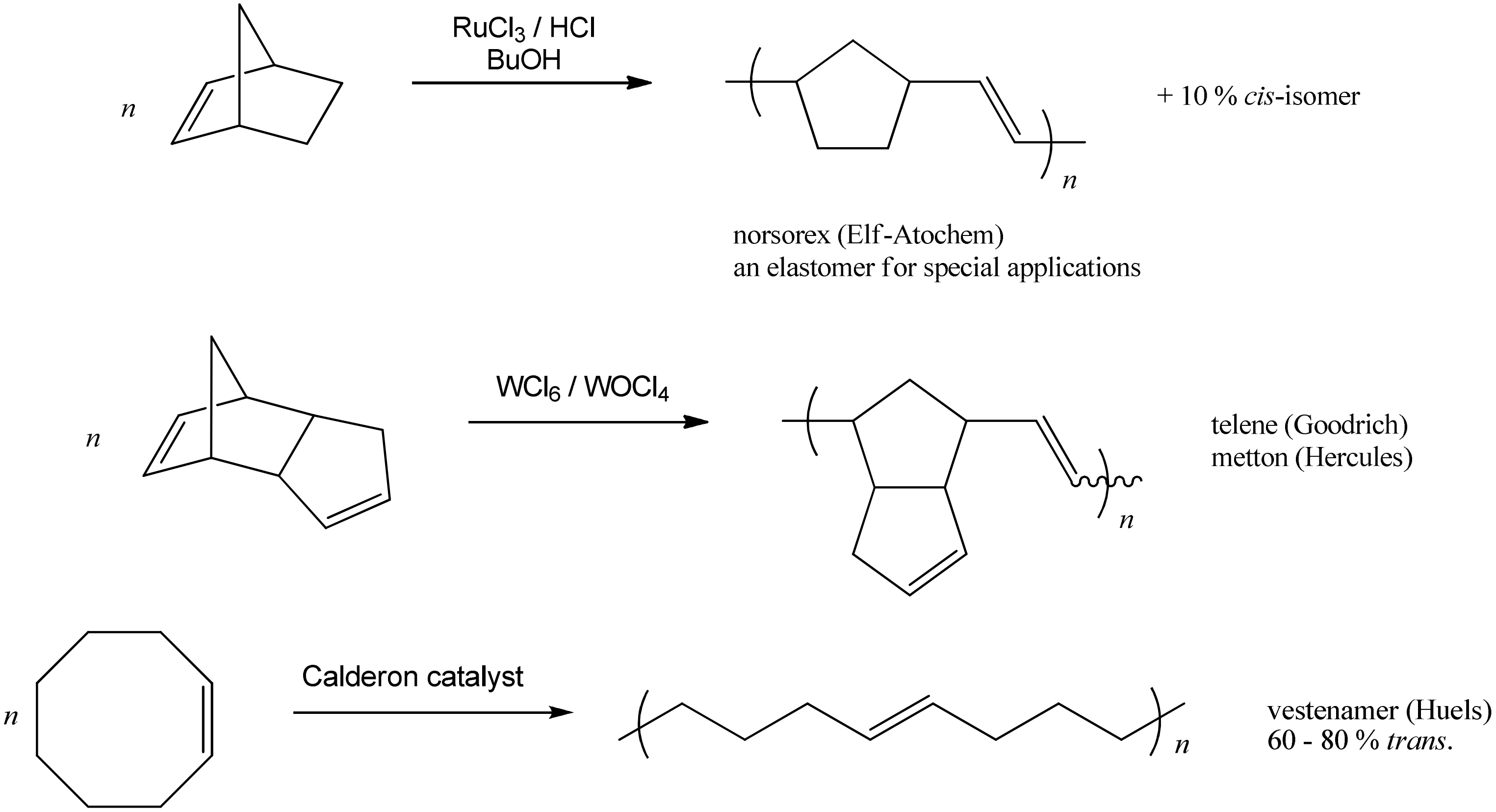


83 % yield
E/Z = 2:1

- High dilution and excess α-alkene largely suppresses the self-metathesis of the cycloalkane.
- Synthetic utility is limited by the formation of different cross-metathesis and self-metathesis products, however, in some cases selectivity can be controlled.

Ring Opening Metathesis Polymerization (ROMP)

- Whereas in ROM the self metathesis is suppressed, this process is desired in ROMP thus the use of open-chain alkene substrates is avoided.
- ROMP has been used industrially since 1976:



+ 10 % *cis*-isomer

norsorex (Elf-Atochem)
an elastomer for special applications

telene (Goodrich)
metton (Hercules)

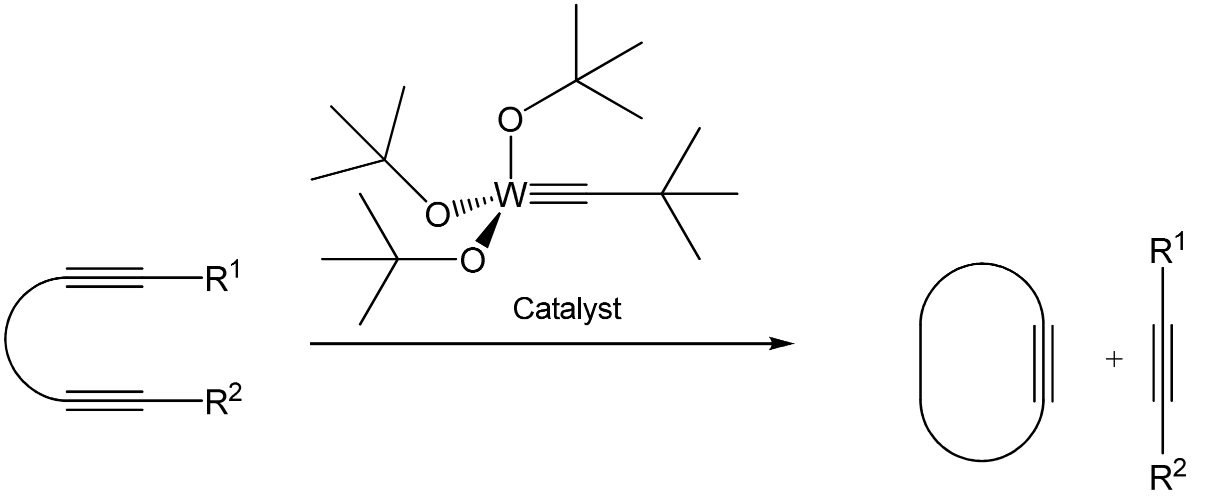
vestenamer (Huels)
60 - 80 % *trans*.

- The C=C bonds allow for cross-linking (vulcanization) following ROMP.

- ROMP processes are unique in that the C=C double bond of the monomer is conserved in the polymer.
- The catalytically active species is fixed to the end of the growing chain (aka living polymer).
- As soon as a certain monomer is consumed, the chain reaction can be continued with a different monomer (**block co-polymerization**).
- A $L_nM{=}CR_2$ unit can be deactivated by a reaction with a carbonyl group to yield a metal oxide allowing narrow molar-mass distributions to be achieved.

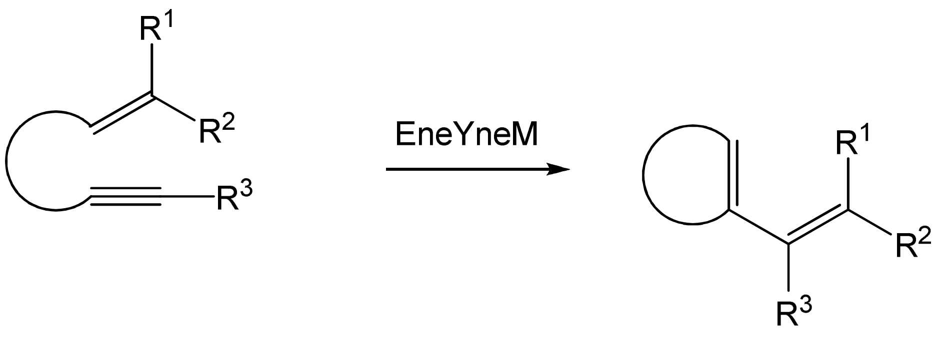
Alkyne Metathesis

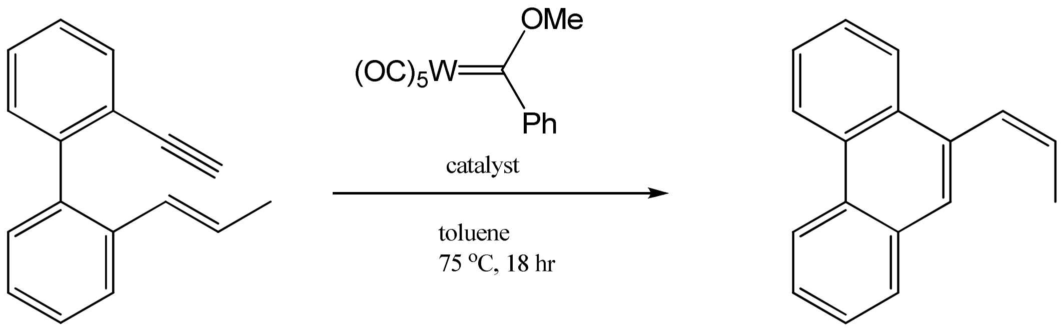
- Metathesis involving C≡C triple bonds can proceed symmetrically (YneYneM) and in the mixed form (EneYneM).
- The ring closing metathesis of two alkynes (YneYneRCM) under high dilution conditions leads to a cycloalkyne and (preferentially) a volatile open alkyne.



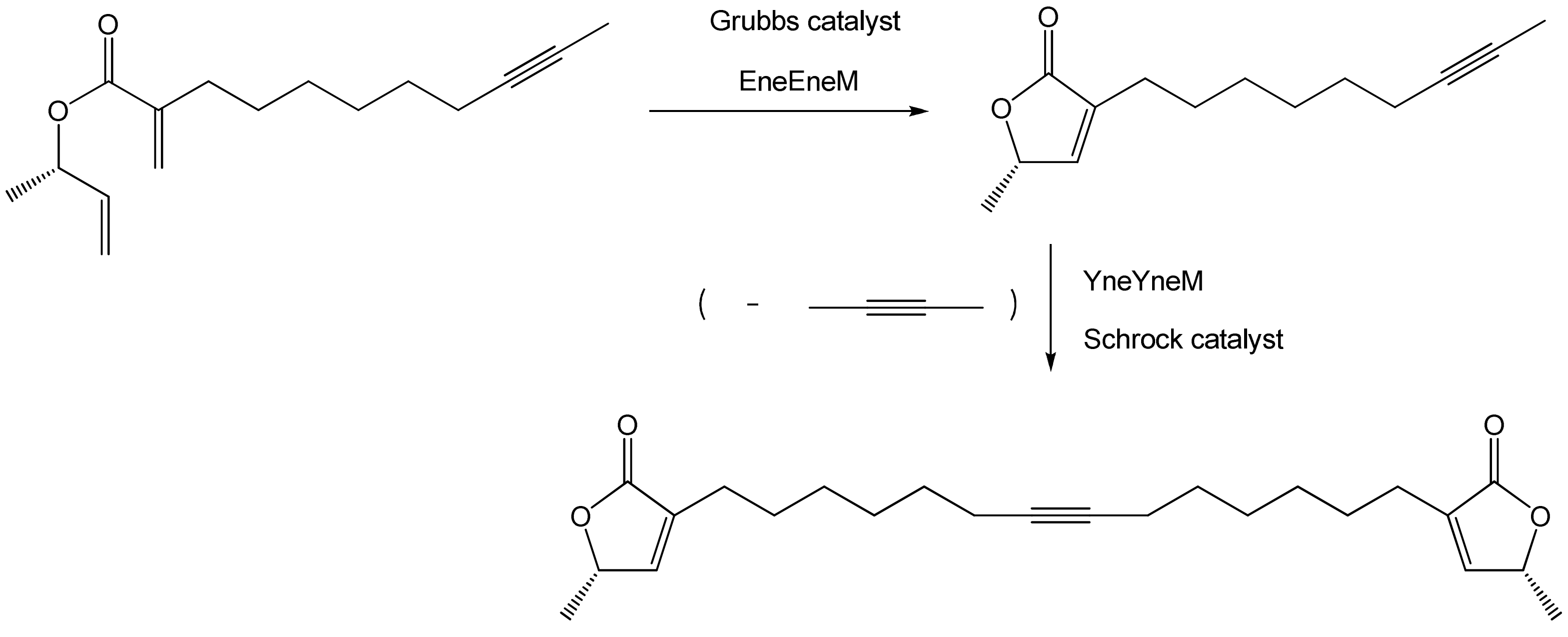
Alkene-Alkyne Metathesis

- Mixed enyne metathesis (EneYneM) have been know to occur

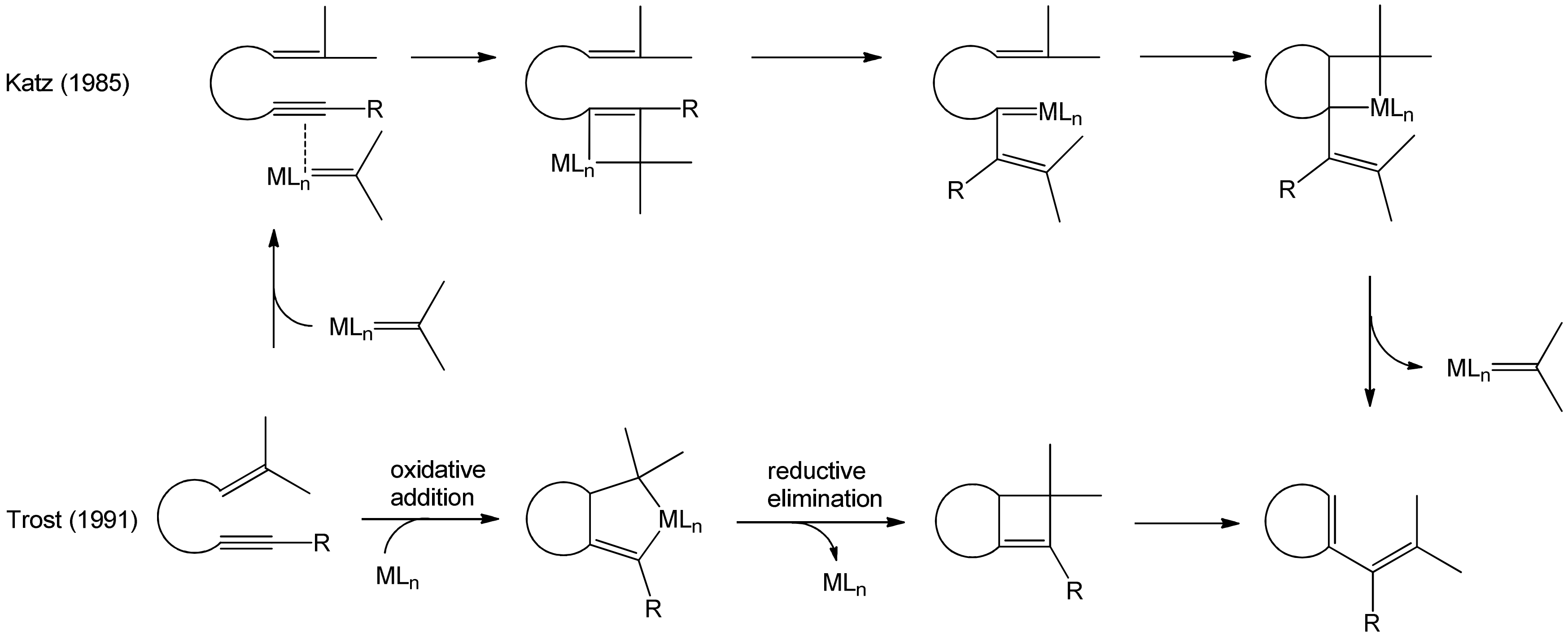




- The presence of C=C double and C≡C triple bonds in the reactants presents two kinds of challenges:
  - ➢ selective metathesis with the formation of only one bond type (EneEneM, YneYneM)
  - ➢ the participation of both structural elements (EneYneM)
- This competition can be controlled by careful choice of catalyst.

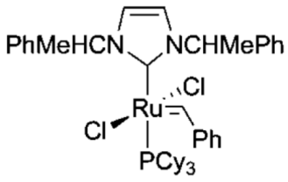


- A special feature of the alkene-alkyne metathesis is its “atom economy” as all carbon atoms remain in the product.
- In addition, a butadiene moiety is formed in the product which is suitable for further functionalization (e.g. Diels-Alder reaction).
- Two mechanisms have been proposed; the reaction pathway being determined by the nature of the substrate and the catalyst.



Modern Grubbs catalysts

- Mindful of the stabilizing effect of NHC ligands, the groups of Nolan, Grubbs, and Fuerstner and Herrmann, independently and almost simultaneously proposed the idea of combining a labile phosphine group for rapid metathesis initiation with a non-labile NHC ligand.
- The **resulting mixed phosphine/NHC complexes proved to be far superior** to the bis(NHC) and bis(phosphine) complexes in overall metathesis activity.



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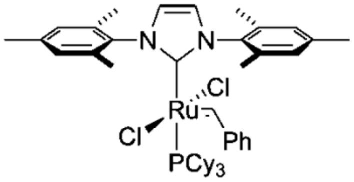
Fürstner and Herrmann, **1999**



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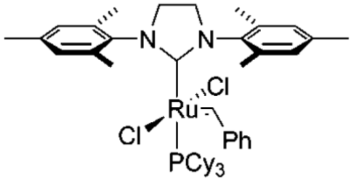
Nolan, Grubbs, **1999**



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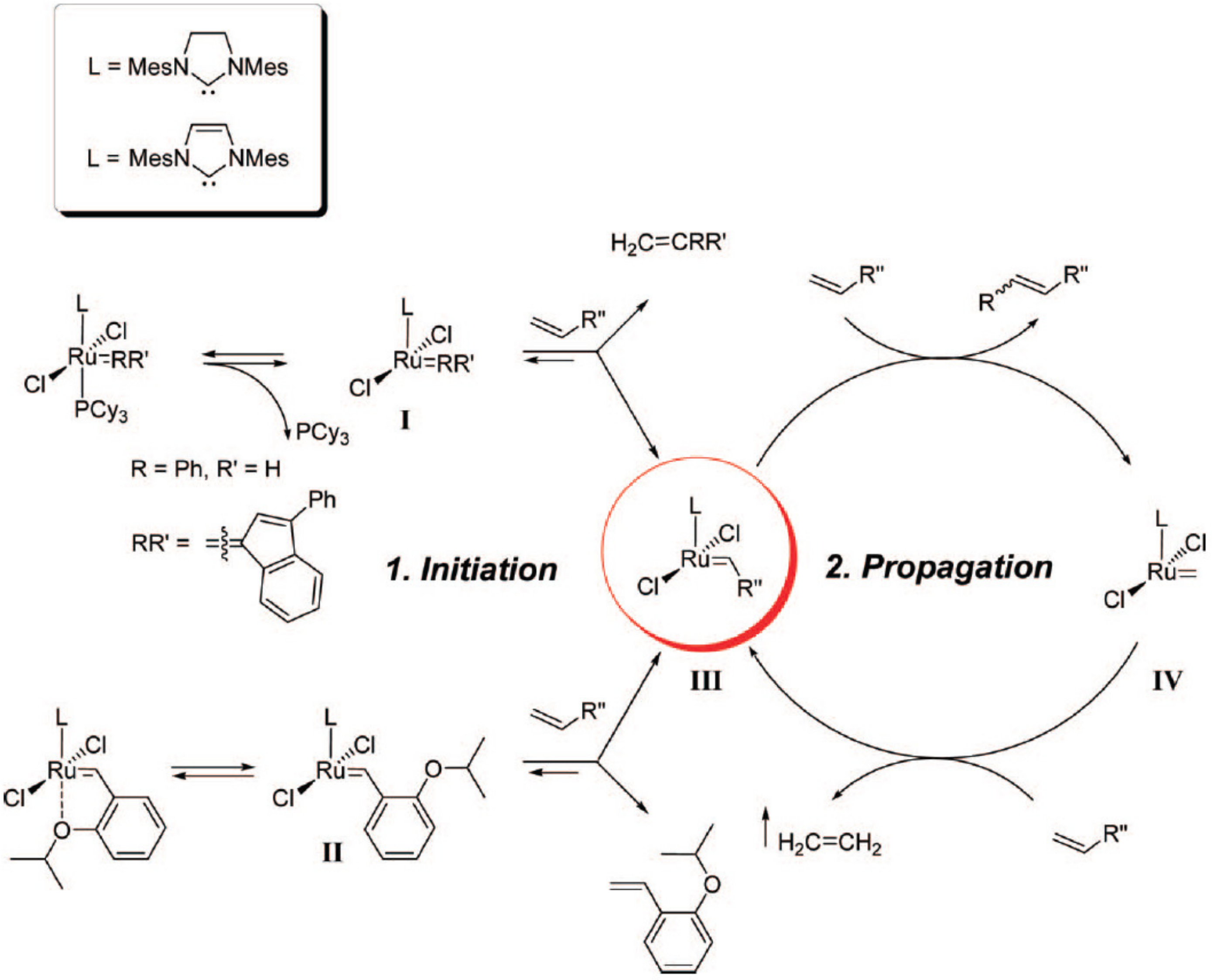
Grubbs, **1999**

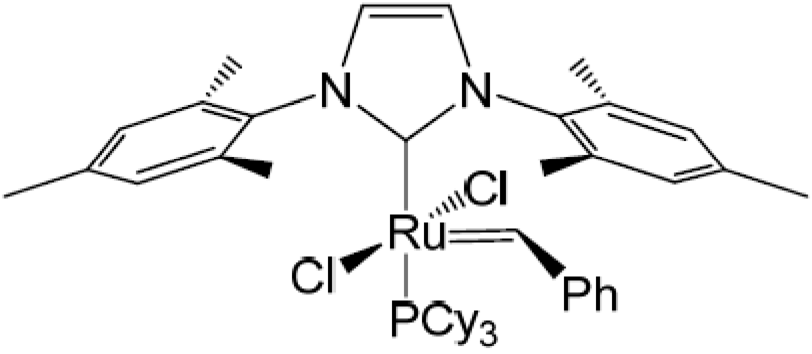
Mechanism of Metathesis Catalyzed by Common Ru Precatalysts



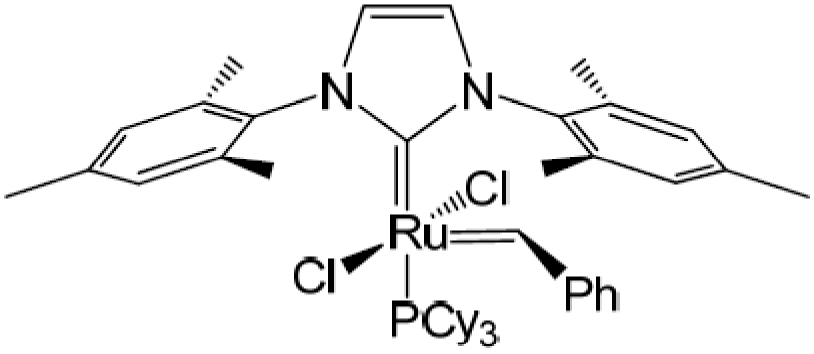
N-Heterocyclic carbenes, true or false;

i) are prone to electrophillic attack when complexed
ii) are prone to nucleophilic attack when complexed
iii) are σ-basic
iv) are π-acidic
v) have steric and electronic influence on catalysis
vi) have electronic influence only
vii) are Fischer type carbenes

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

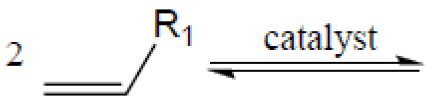


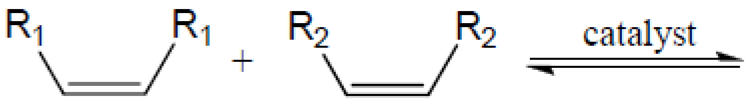
(a)

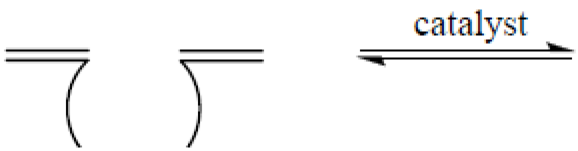


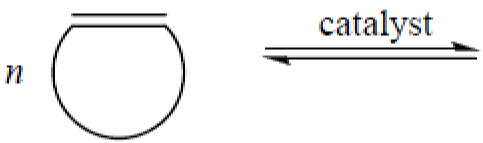
(b)

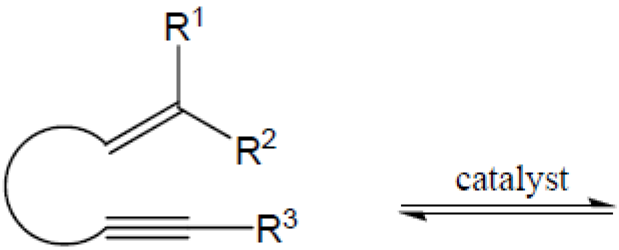
Label each of the following metathesis reactions accordingly an suggest anticipated products.



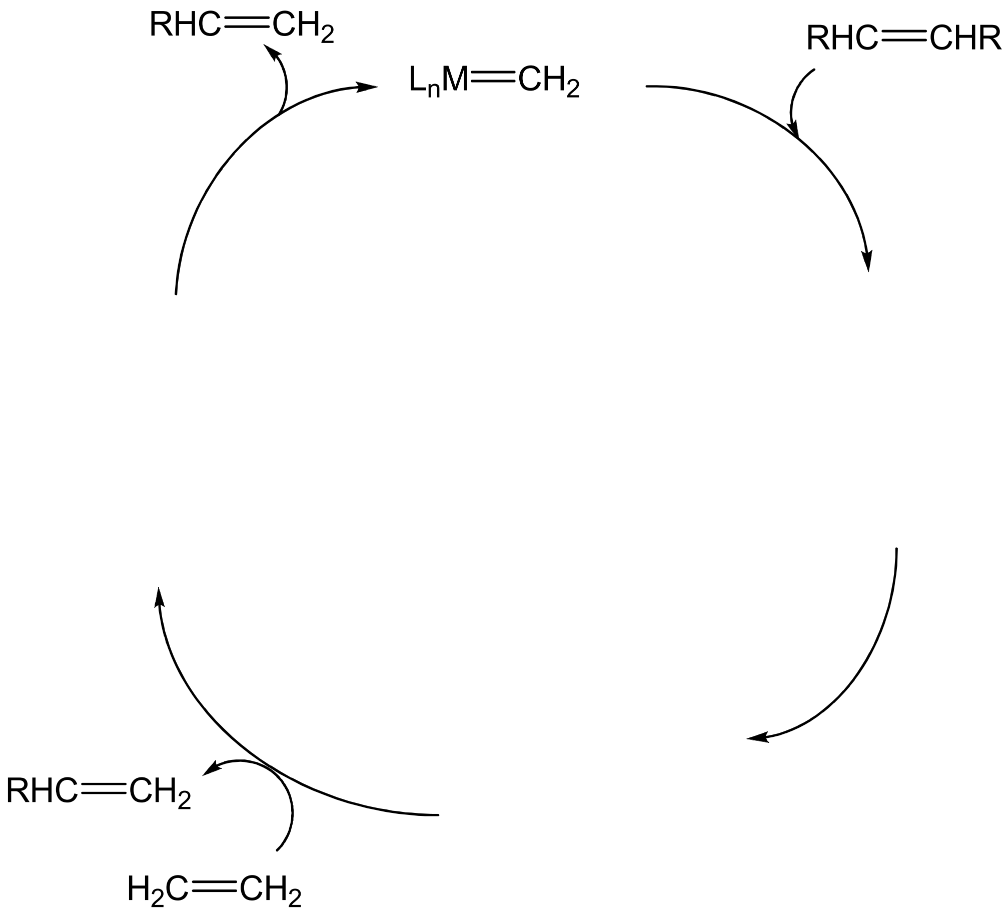




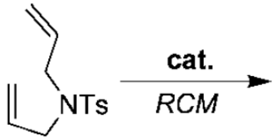




Complete the following metathesis catalytic cycle. What type of metathesis is taking place?



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



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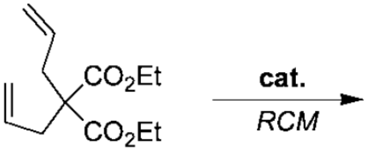

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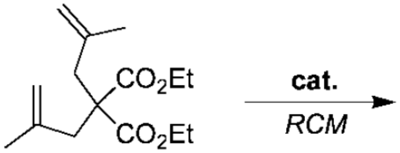

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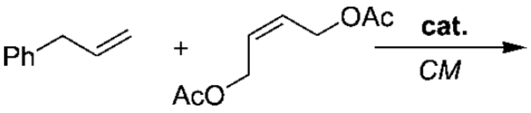

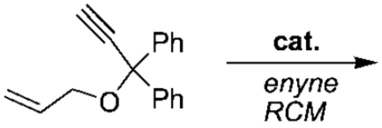

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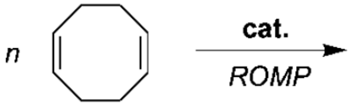

COD

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].