MAX-PLANCK-INSTITUT
FÜR KOLLOID- UND
GRENZFLÄCHENFORSCHUNG

OLEFIN METATHESIS

[HARTIWG CH. 21]

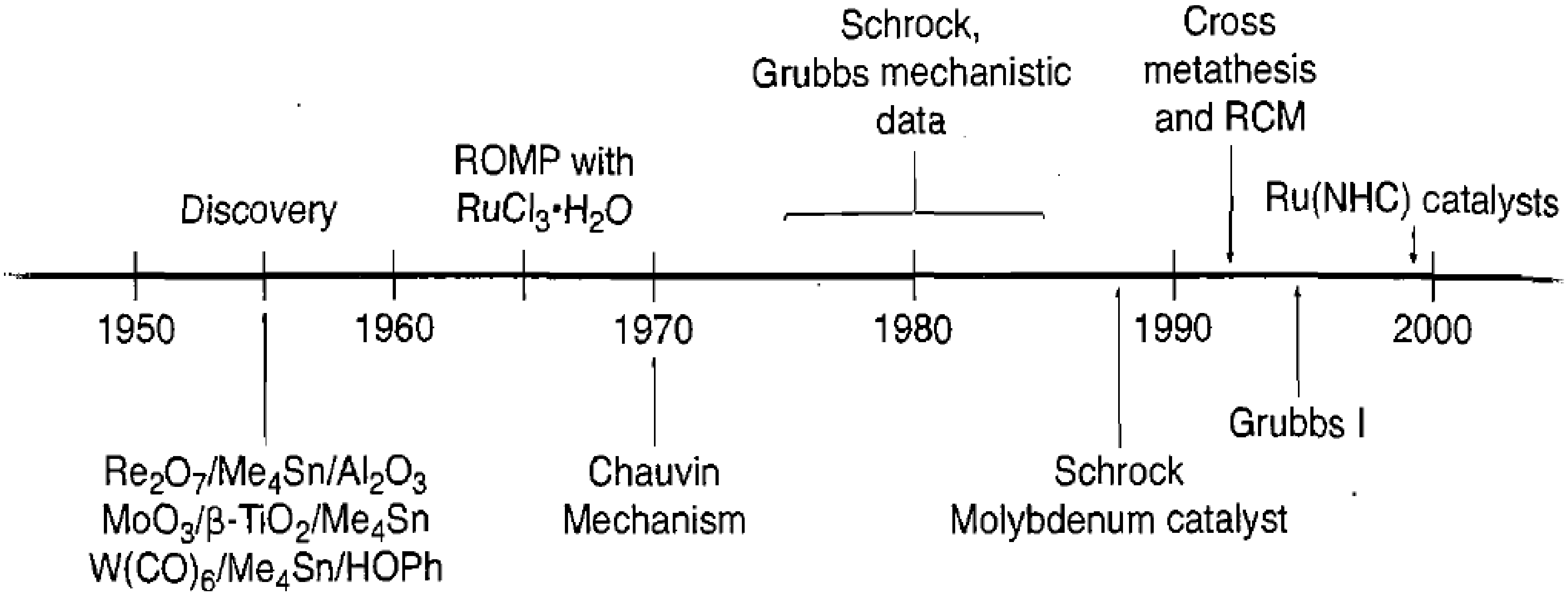
Dr. Dario Cambié

Max Planck Institute of Colloids and Interfaces

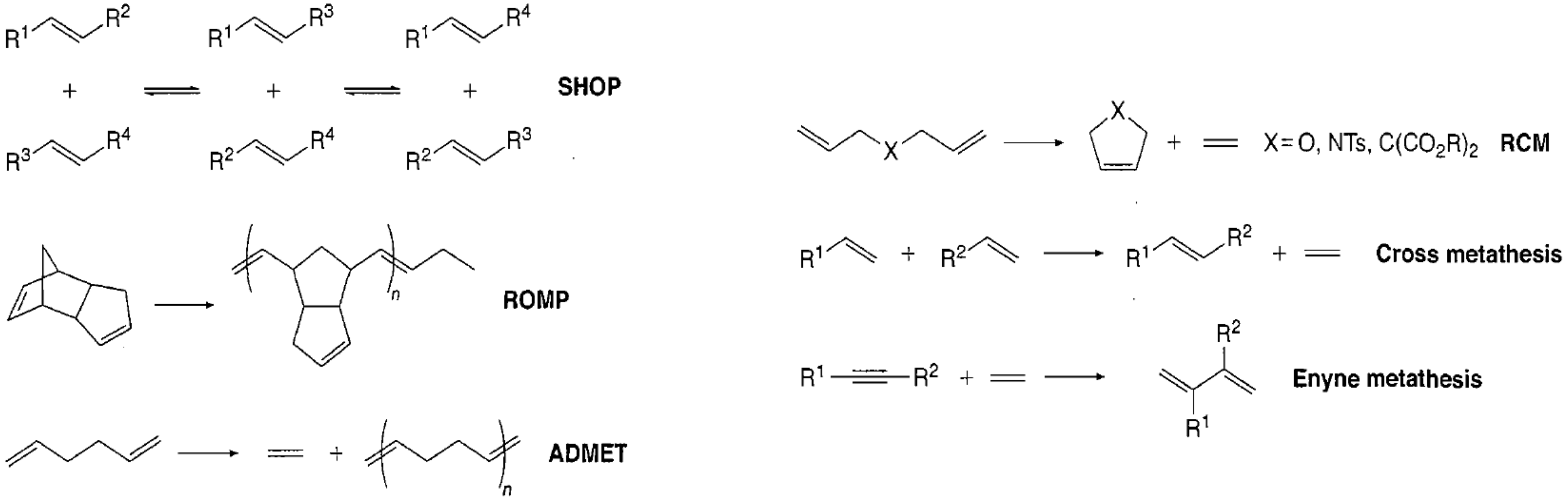
Biomolecular Systems

Dario.Cambie@mpikg.mpg.de

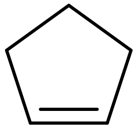
8.1 METATHESIS OVERVIEW



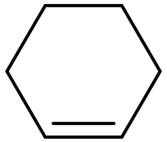
8.1.1 SYNTHETICALLY IMPORTANT METATHESIS TYPES



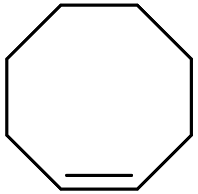
8.1.2 RING-STRAIN IN ROMP



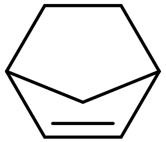
6.5
kcal/mol



0
kcal/mol

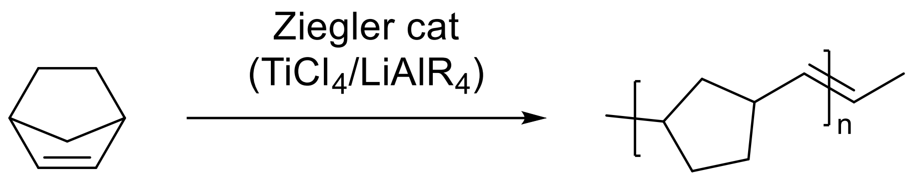


9.6
kcal/mol

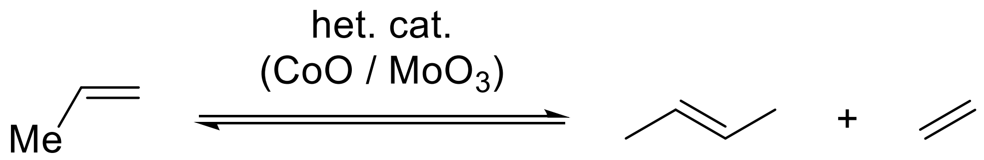


15
kcal/mol

8.2 HISTORY AND MECHANISM



DuPont, *JACS* **1960** 82, 2337. DOI:10.1021/ja01494a057

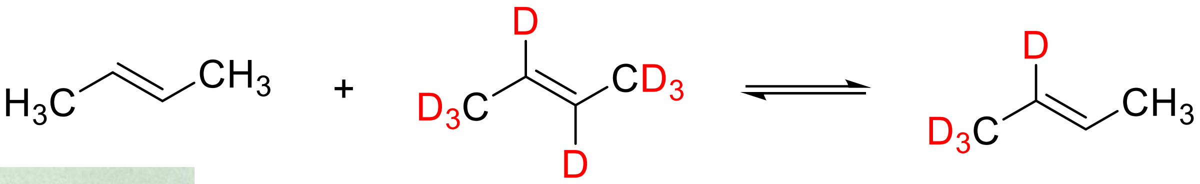


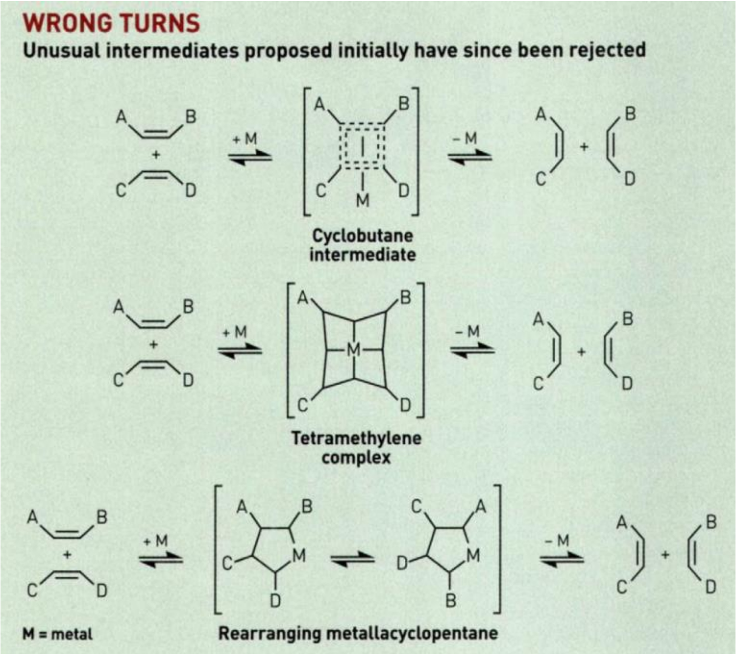
(Phillipps triolefin process)

Phillips Petroleum, *I+EC Product R&D* **1964** 3, 170. DOI: 10.1021/i360011a002

8.2.1 EARLY MECHANISTIC DEBATE

Key observation:





Calderon *JACS* **1968** 90, 4133. DOI: 10.1021/ja01017a039

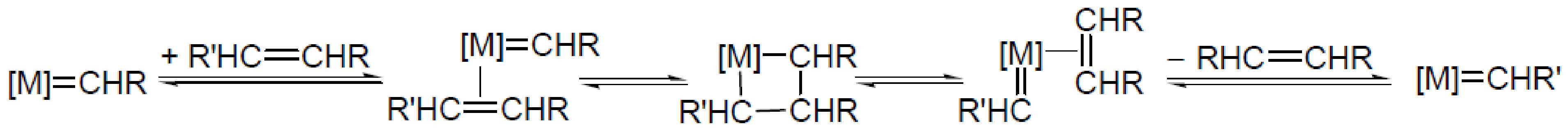
Lewandos Petitt *JACS* **1971** 93, 7087. DOI: 10.1021/ja00754a067

Grubbs *JACS* **1972** 94, 2538. DOI: 10.1021/ja00762a073

C&EN 2002, 80, 51. DOI: 10.1021/cen-v080n051.p029

8.2.2 CHAUVIN MECHANISM

Key insight: metal carbene (alkylidene) intermediate



4' **4** **5** **6** **6'**

Yet: no known metal-carbenes can catalyze the reaction!

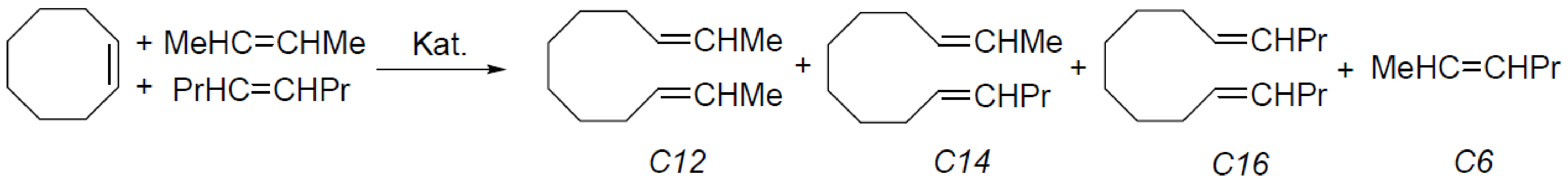
Independently co-proposed (?)

Casey *JACS* **1974** 96, 7808. DOI: 10.1021/ja00832a032

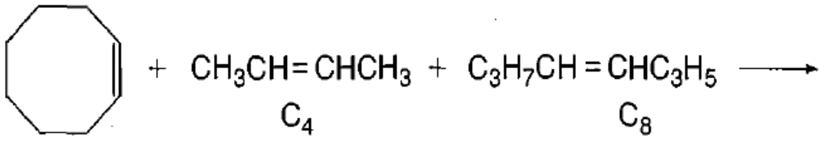
Katz *JACS* **1975** 97, 1592. DOI: 10.1021/ja00839a063 (C12/14/16 experiment)

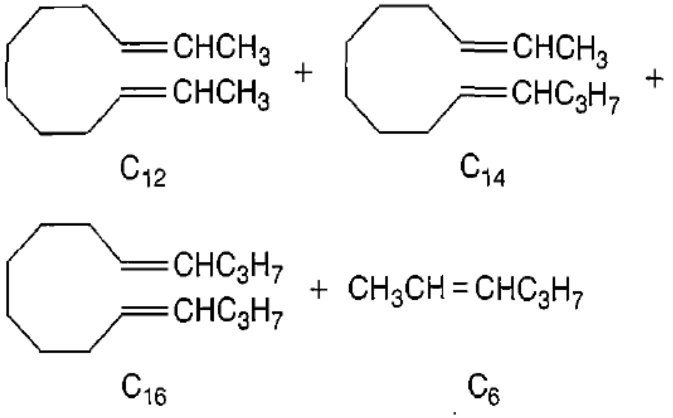
Chauvin, *Die Makromolekulare Chemie* **1971**, 141, 161. DOI: c93th8 (Original mech. proposal)
Chauvin, *ACIE* **2006** 45, 3740. DOI: 10.1002/anie.200601234 (Nobel Lecture)

8.2.2 CHAUVIN MECHANISM – KEY EXPERIMENT



A





If a "pairwise" mechanism occurs, then only C_{12} and C_{16} products are formed at the beginning of the reaction.

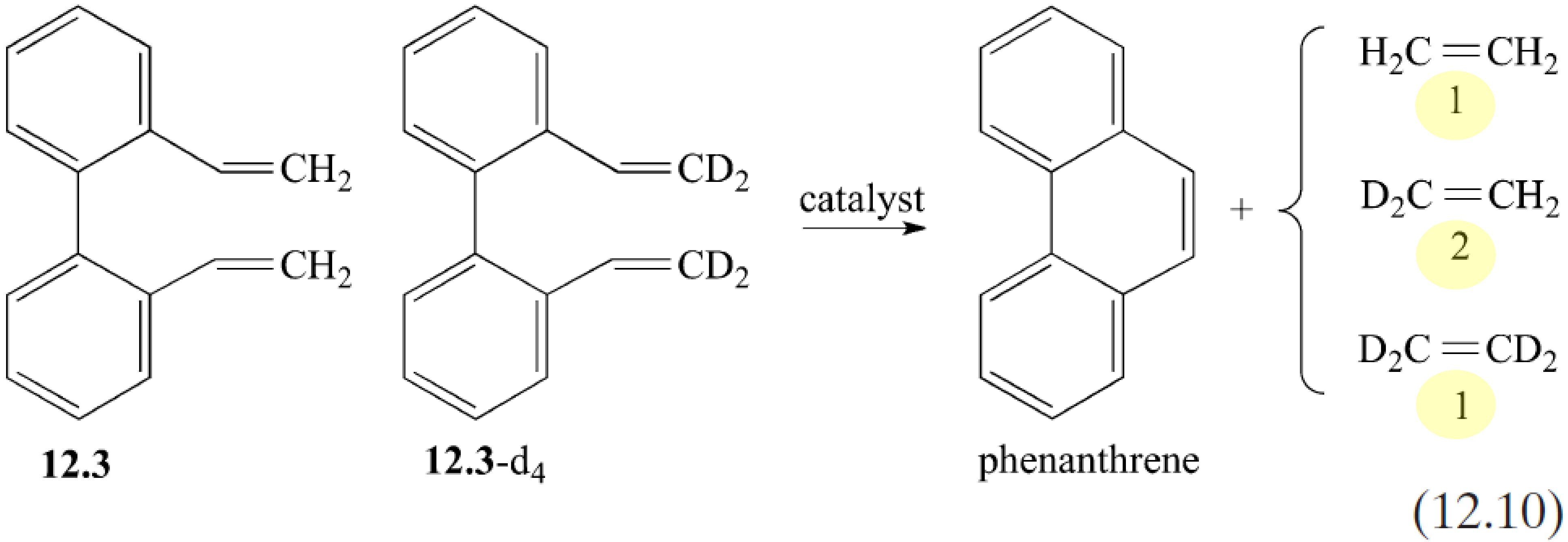
If a "non-pairwise" mechanism occurs, then all products are formed at the beginning of the reaction.

Initial rates:

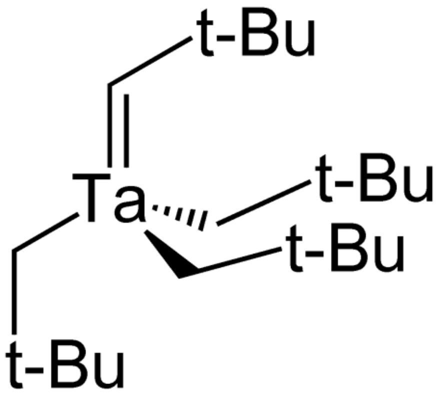
C14/C12 0.7

C14/C16 8.35

8.2.2 CHAUVIN MECHANISM – KEY EXPERIMENT

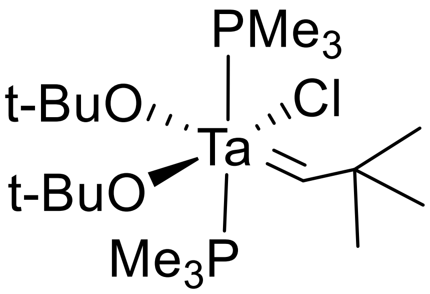


8.3.1 SCHROCK CATALYST DEVELOPMENT



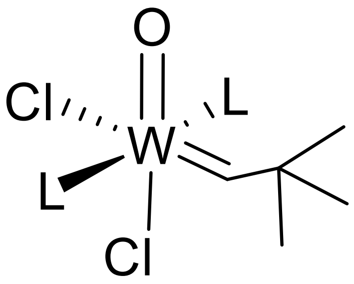
1974

inactive



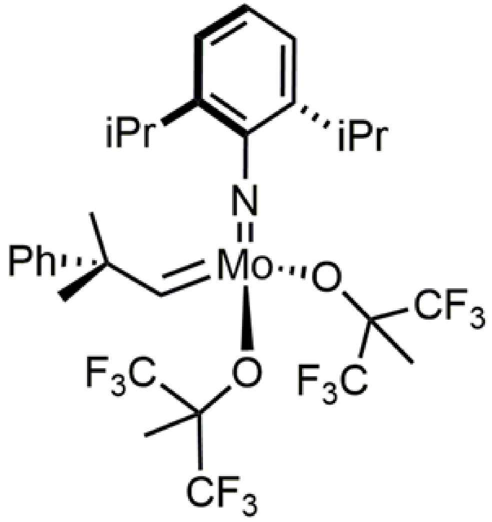
1980

active



1980

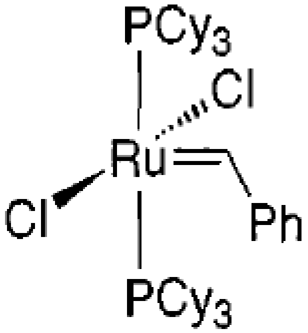
active



1991-1992

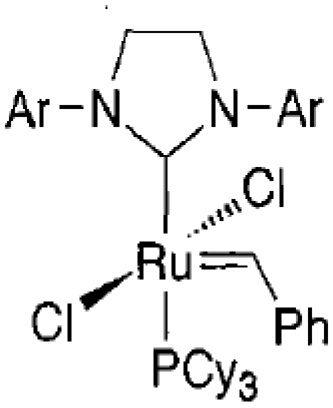
Very active

8.3.2 GRUBBS CATALYST DEVELOPMENT



Grubbs I

1992-1997



Grubbs II

1999

…catalysts for Z-selective metathesis

8.3.2 GRUBBS CATALYST - CHEMOSELECTIVITY

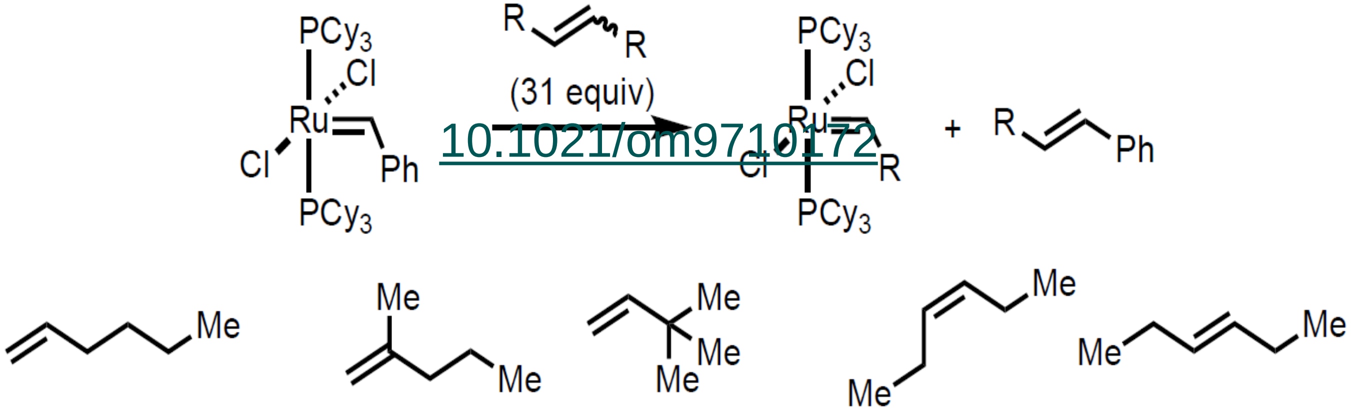
Titanium	Tungsten	Molybdenum	Ruthenium
Acids	Acids	Acids	**Olefins**
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	**Olefins**	Aldehydes
Esters, Amides	**Olefins**	Ketones	Ketones
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

↑ Increasing Reactivity

Grubbs, *Acc Chem Res* **2001** 34, 18. DOI: 10.1021/ar000114f

POD #1

For the reaction below, **order the olefins from most to least reactive.**

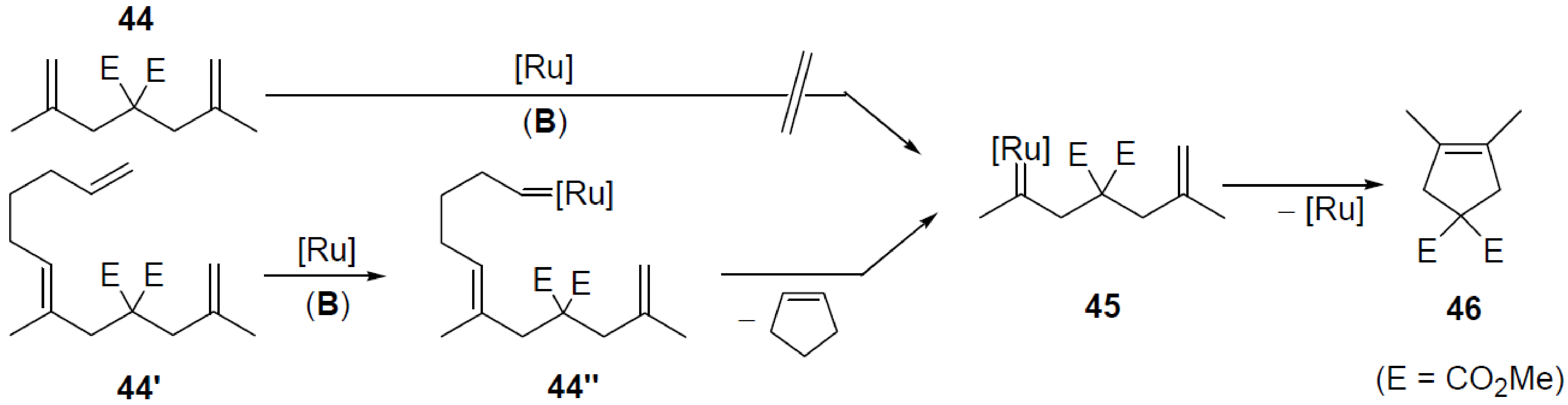


10.1021/om9710172

A	B	C	D	E
1	**5**	**4**	**2**	**3**

Grubbs, *Organometallics* **1998** 17, 2484**.** DOI: 10.1021/om9710172

8.3.3 RELAY RCM

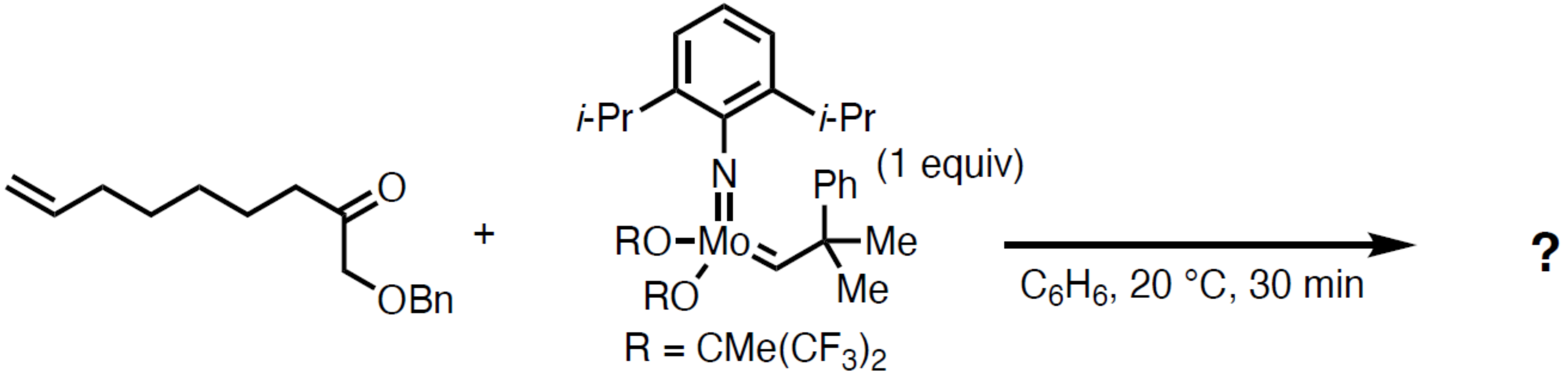


POD #2

Consider the reaction below by Fu and Grubbs using the Schrock catalyst.

a. Provide the oxidation state, d-electron count, and overall electron count of the Mo complex

b. Predict the product and propose a plausible mechanism.



Fu and Grubbs *JACS* **1993**, *115*, 3800. DOI: 10.1021/ja00062a066

8.4.1 CROSS METATHESIS – SELECTIVITY RULES

Type 1 – rapid homodimerization

Type 2 – slow homodimerization

Type 3 – no homodimerization

Type 4 – olefin insert to CM, but do not deactivate the cat (spectator)

Reaction between Type 1 -> Statistical CM

Reaction between two olefin of the same type (not 1) -> non-selective CM

Reaction between olefins of two different types (especially 1 + 2/3) -> **selective CM**

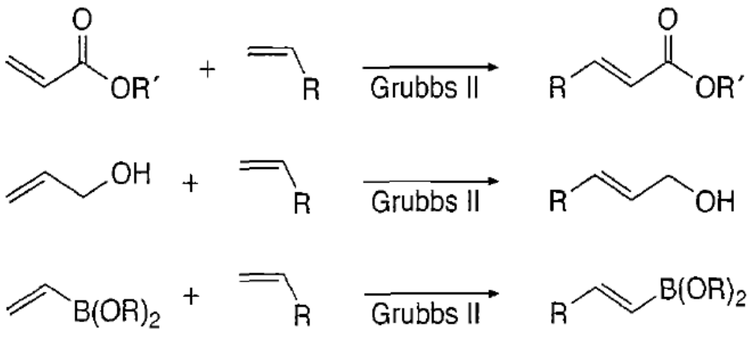
8.4.1 CROSS METATHESIS – SELECTIVITY RULES

Table 2.15 Model for selectivity in CM, expanded to include cyclometallated Z-selective metathesis catalysts. Adapted with permission from Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360. © 2003 American Chemical Society.

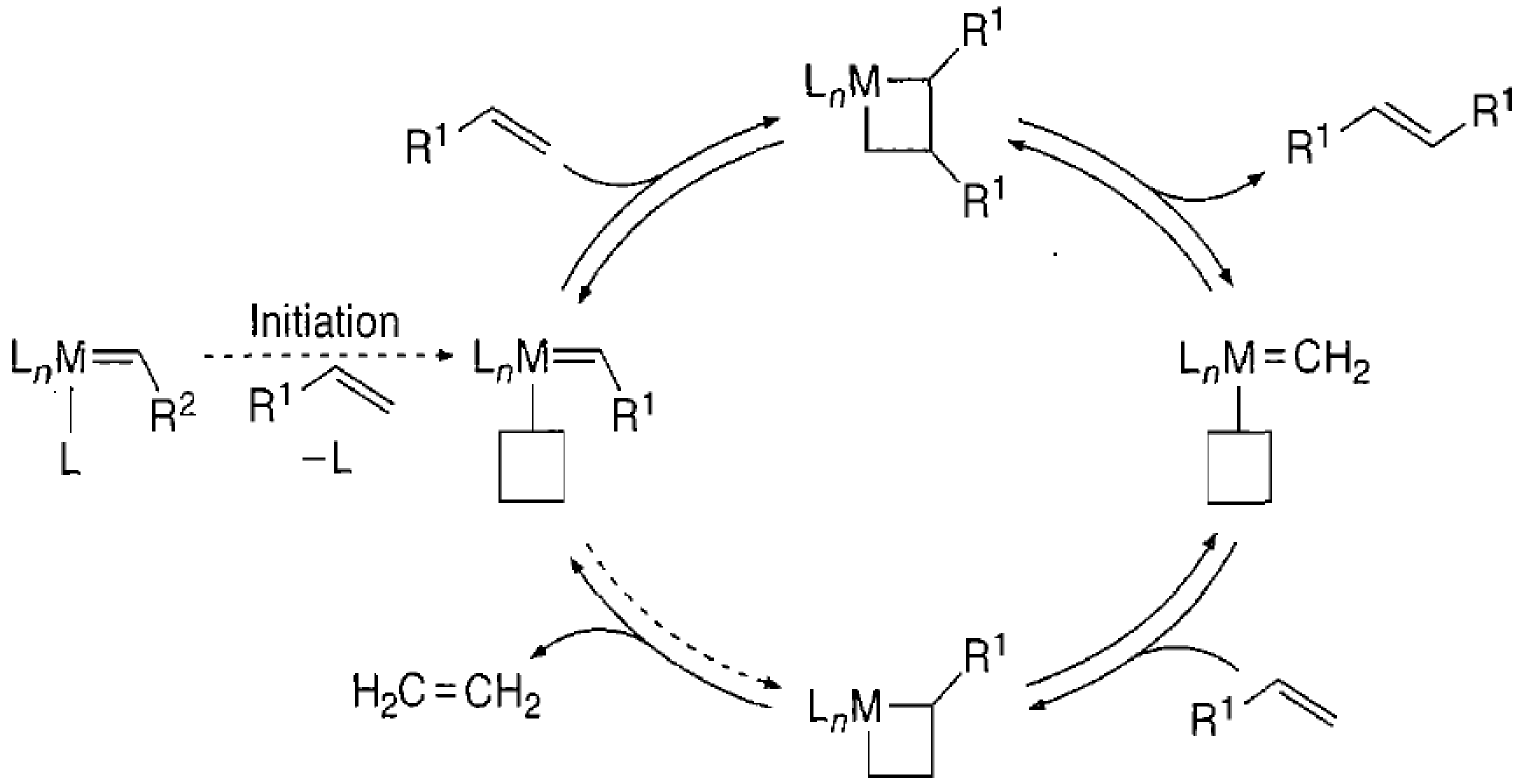
Catalyst	Grubbs I	Grubbs II		Grubbs Z
Type I (fast homodimerization)	• terminal olefins • allyl silanes • 1° allylic alcohols • 1° allylic ethers • 1° allylic esters • allyl boronates • allyl halides	• terminal olefins • 1° allylic alcohols • 1° allylic esters • allyl boronates • allyl halides • styrenes (no large ortho sub.)	• allyl phosphonates • allyl silanes • allyl phosphine oxides • allyl sulfides • protected allyl amines	• terminal olefins • allyl silanes • 1° allylic ethers • allyl anilines • allyl boronates
Type II (slow homodimerization)	• styrene • 2° allylic alcohols • vinyl dioxolanes • vinyl boronates • vinyl cycolpentane	• styrenes (large ortho sub.) • acrylates / acrylic acid • acrylamides • acrolein • vinyl ketones	• unprotected 3° allylic alcohols • 2° allylic alcohols • vinyl epoxides • perfluoro-alkane olefins	• vinyl dioxolanes • vinyl boronates • vinyl epoxides • vinyl cyclopentane • protected 1° allyl amines
Type III (no homodimerization)	• vinyl siloxanes	• 1,1-disub. olefins • non-bulky trisub. olefins • vinyl phosphonates	• phenyl vinyl sulfone • 4° allylic C olefins • protected 3° allylic amines	
Type IV (spectators to CM)	• 1,1-disub. olefins • disub. α,β-unsaturated carbonyls • 4° allylic C olefins • perfluoro-alkane olefins • protected 3° allylic amines	• vinyl nitro olefins • trisubstituted allyl alcohols, protected		• 1,1-disub. olefins • 4° allylic C olefins

- **Olefin type depends on cat!**

CM examples:

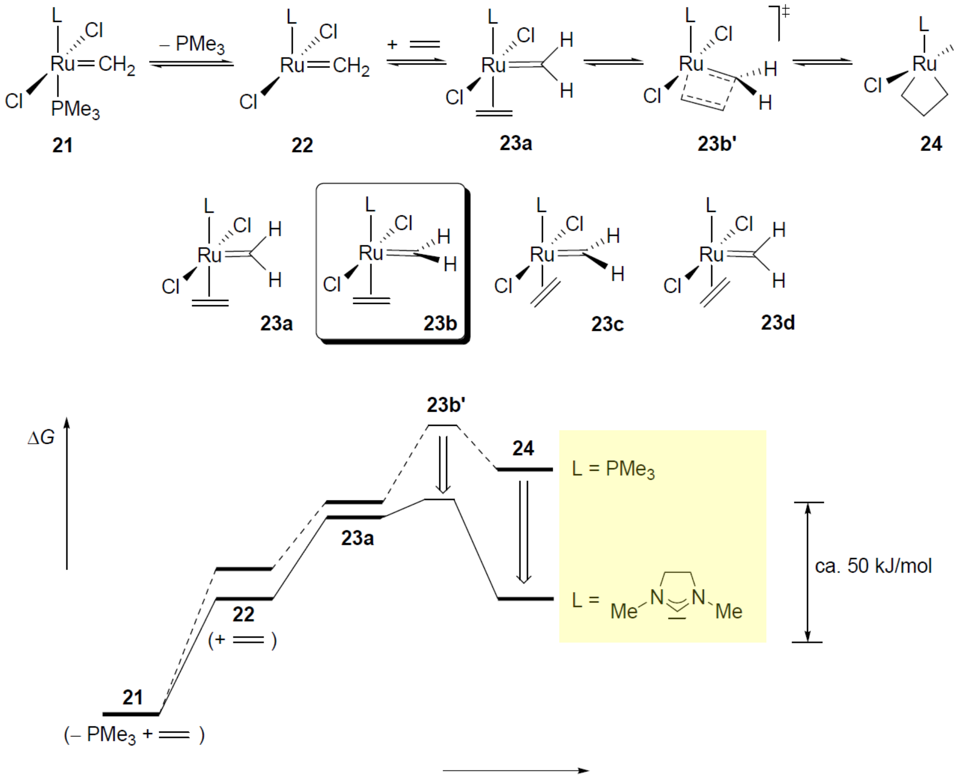


8.5 MECHANISM



Grubbs *JACS* **2001** 123 6543. DOI: 10.1021/ja010624k

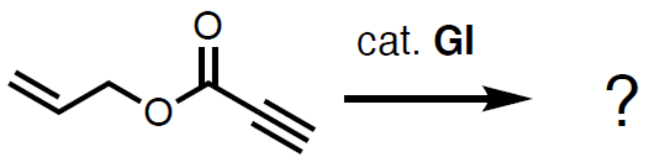
8.5.1 GRUBBS-1 VS. GRUBBS-2

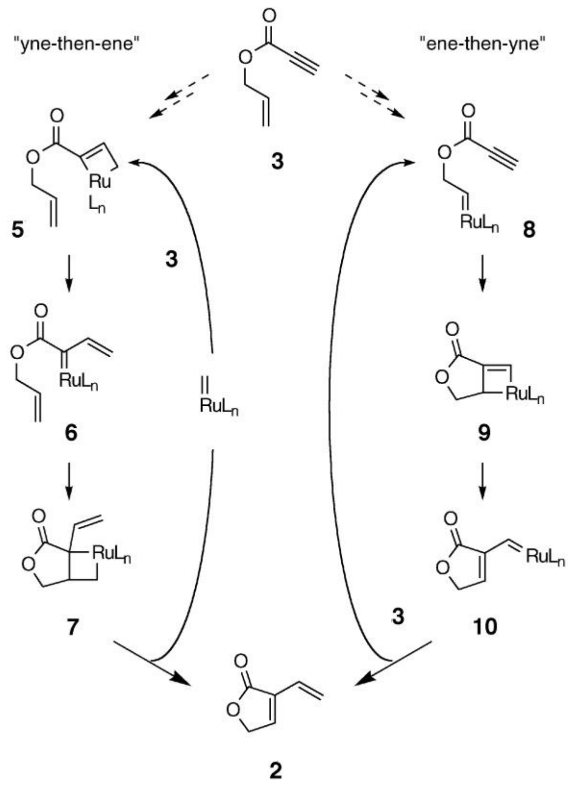


- Top is G1
- Bottom is G2

POD #3

For the reaction below, predict the product and **draw out two or more possible mechanism and propose experiments to disambiguate among them.**





OL **1999** 1 277. DOI: 10.1021/ol9905912