

# Reações de acoplamento C-C e ativação C-H

*QFL5835-6 Catálise: uma visão integrada*

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# Prêmio Nobel de Química 2010

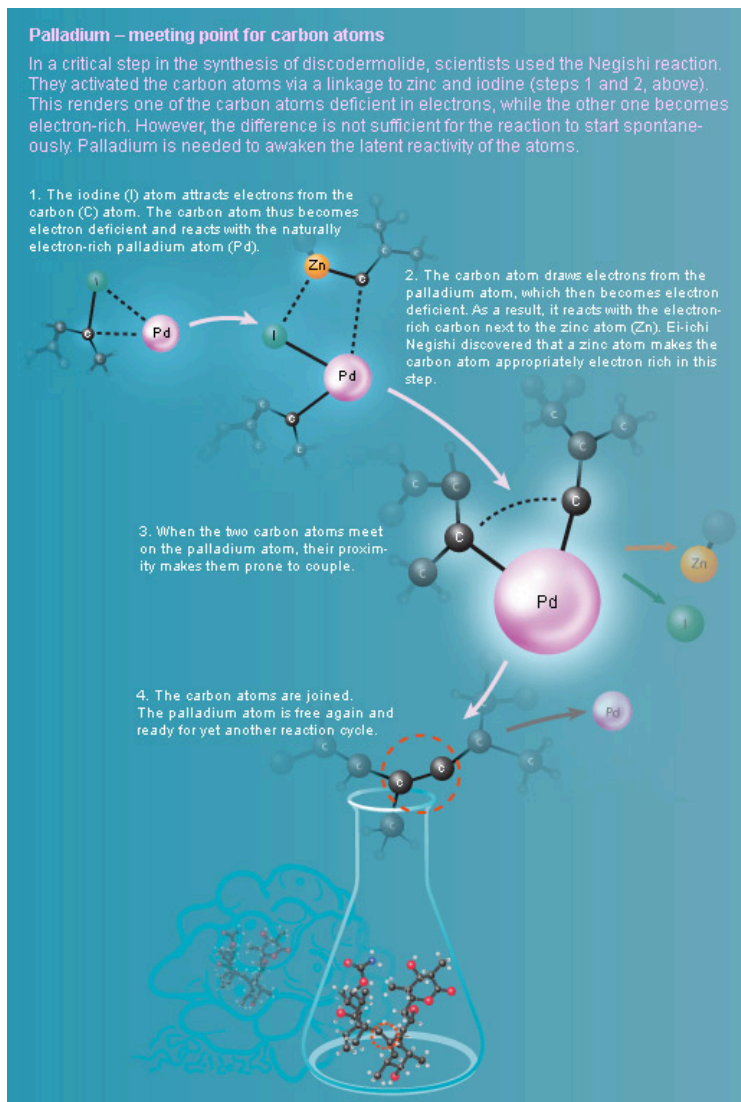


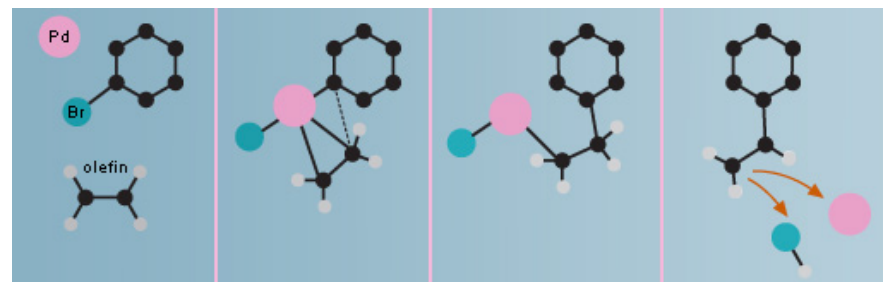
Photo: U. Montan  
Richard F. Heck



Photo: U. Montan  
Ei-ichi Negishi

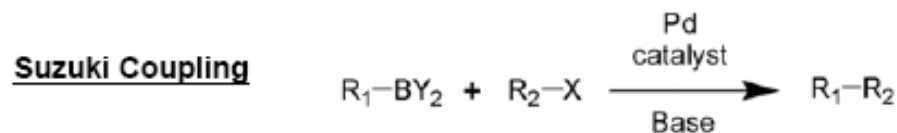
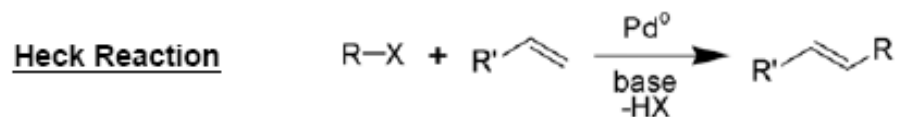


Photo: U. Montan  
Akira Suzuki



Reação de Heck

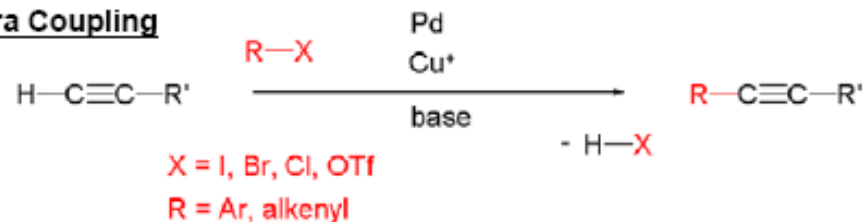
# Reações de acoplamento cruzado C-C



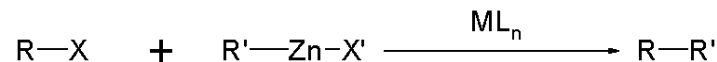
**Stille Coupling**



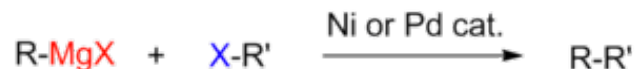
**Sonogashira Coupling**

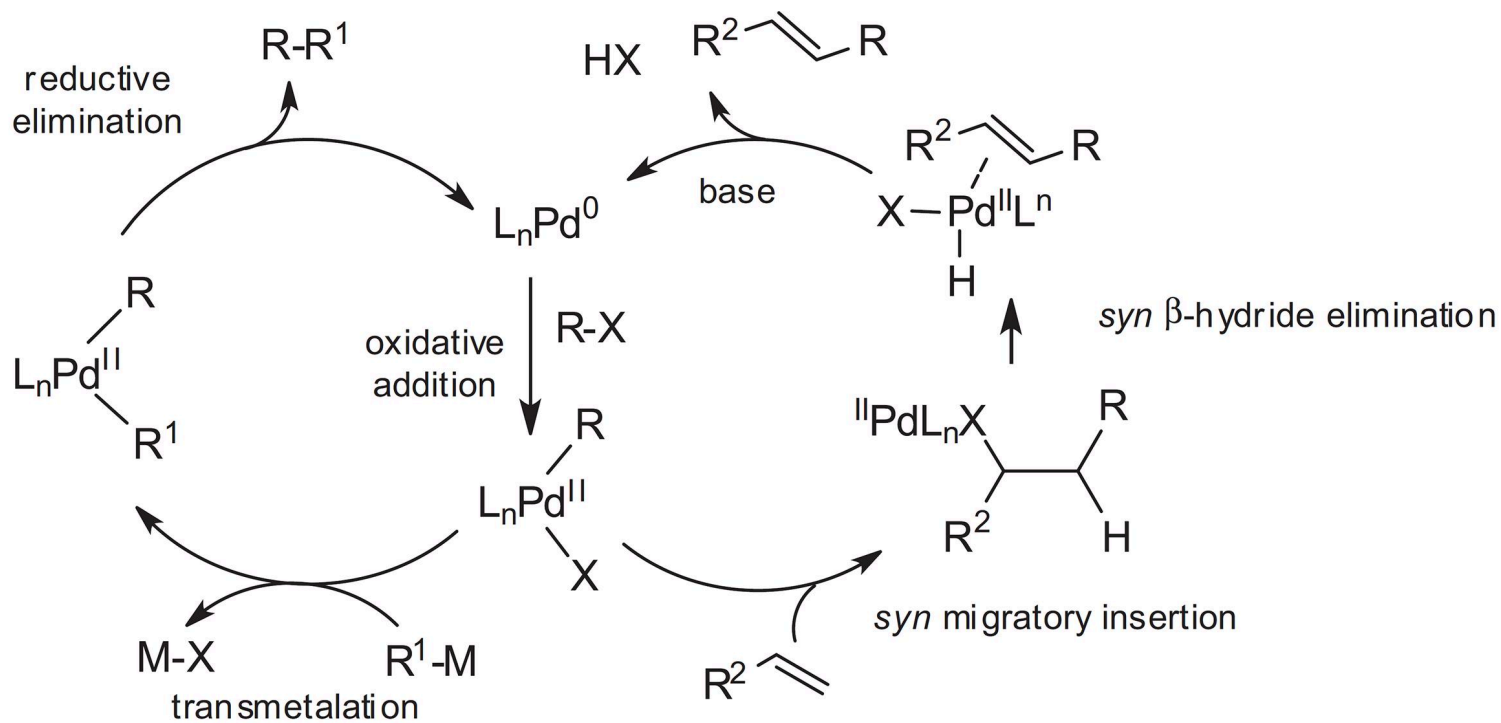


**Negishi Reaction**



**Kumada-Corriu**





Negishi ( $M = ZnR$ )

Suzuki-Miyaura [ $M = B(OH)_2$  or  $B(OR)_2$ ]

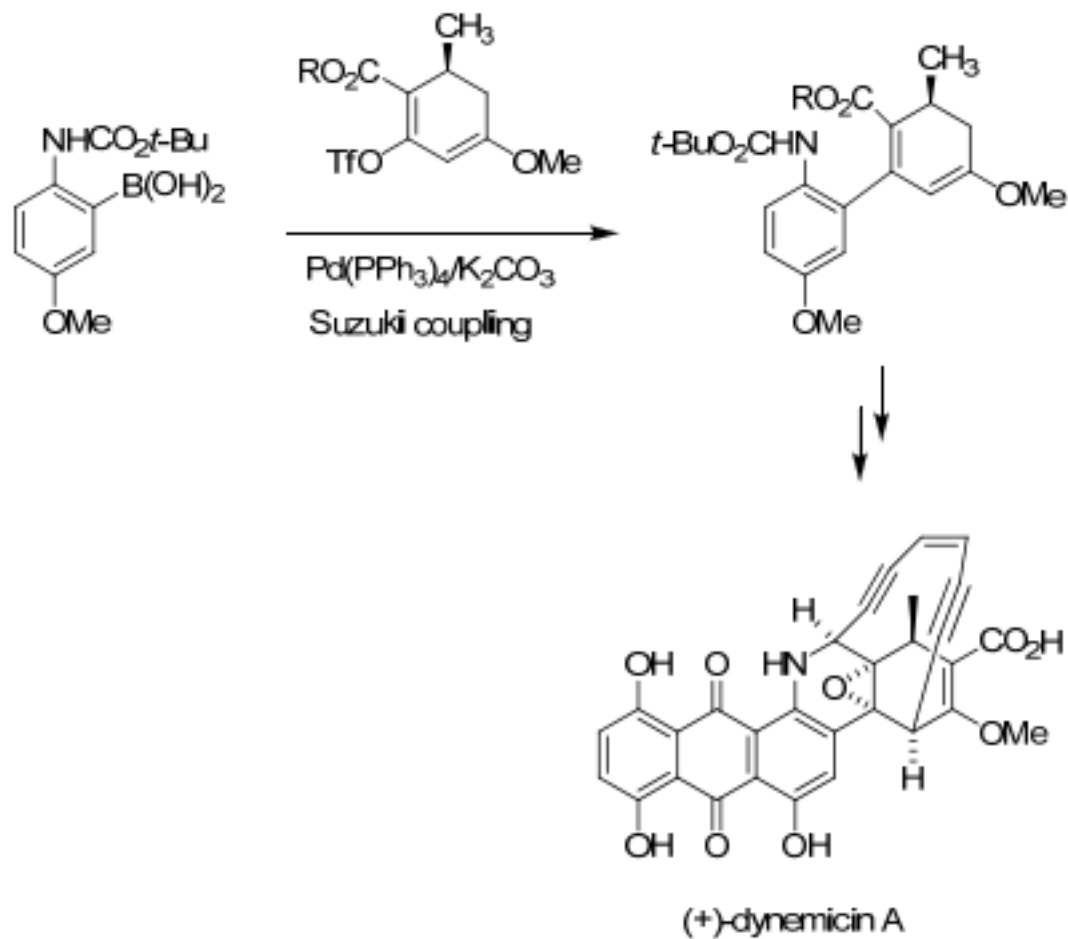
Stille ( $M = SnR_3$ )

Sonogashira ( $M = Cu^I$ )

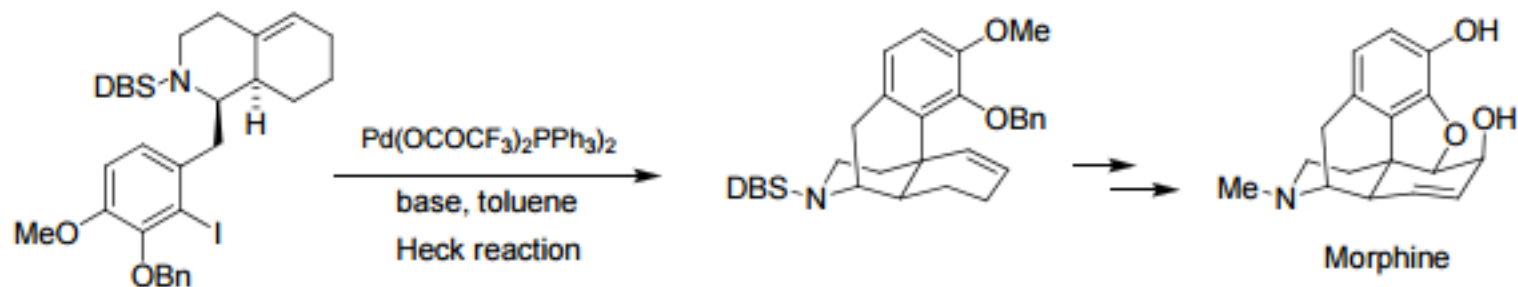
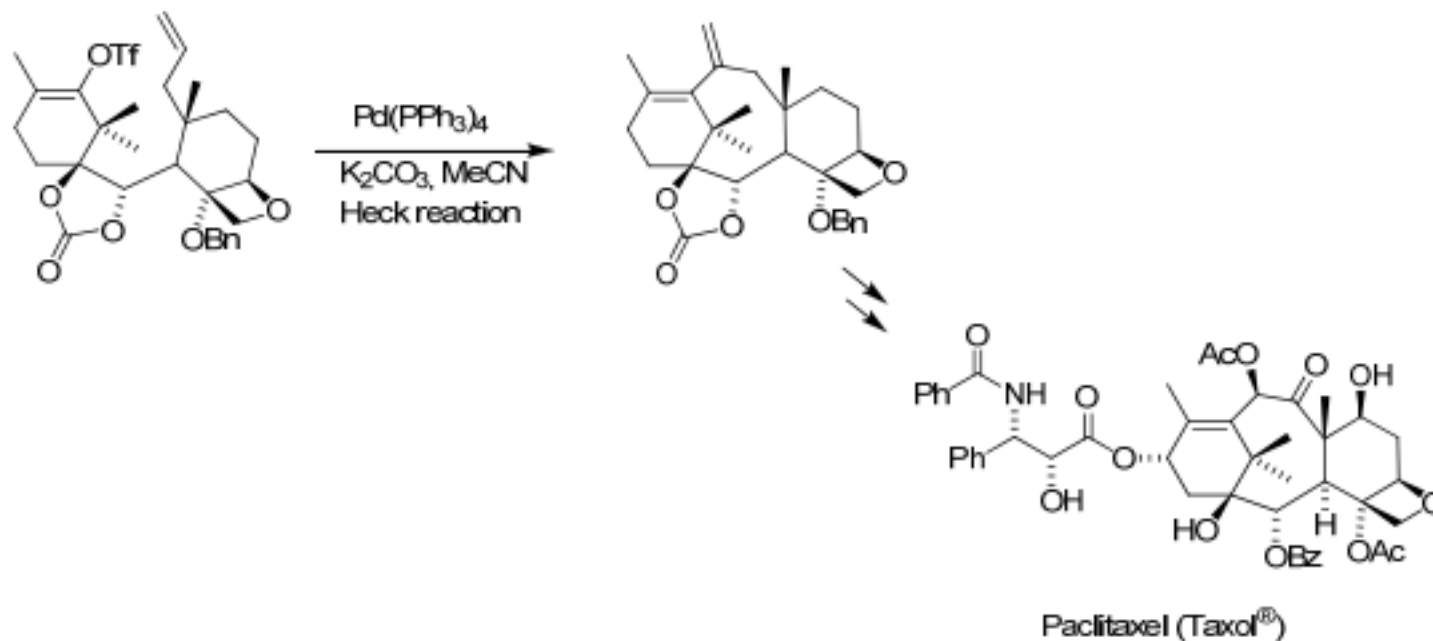
Heck-Mizoroki

Heck-Matsuda (with  $[L_nPd^{II}R]^+$  after oxidative addition)

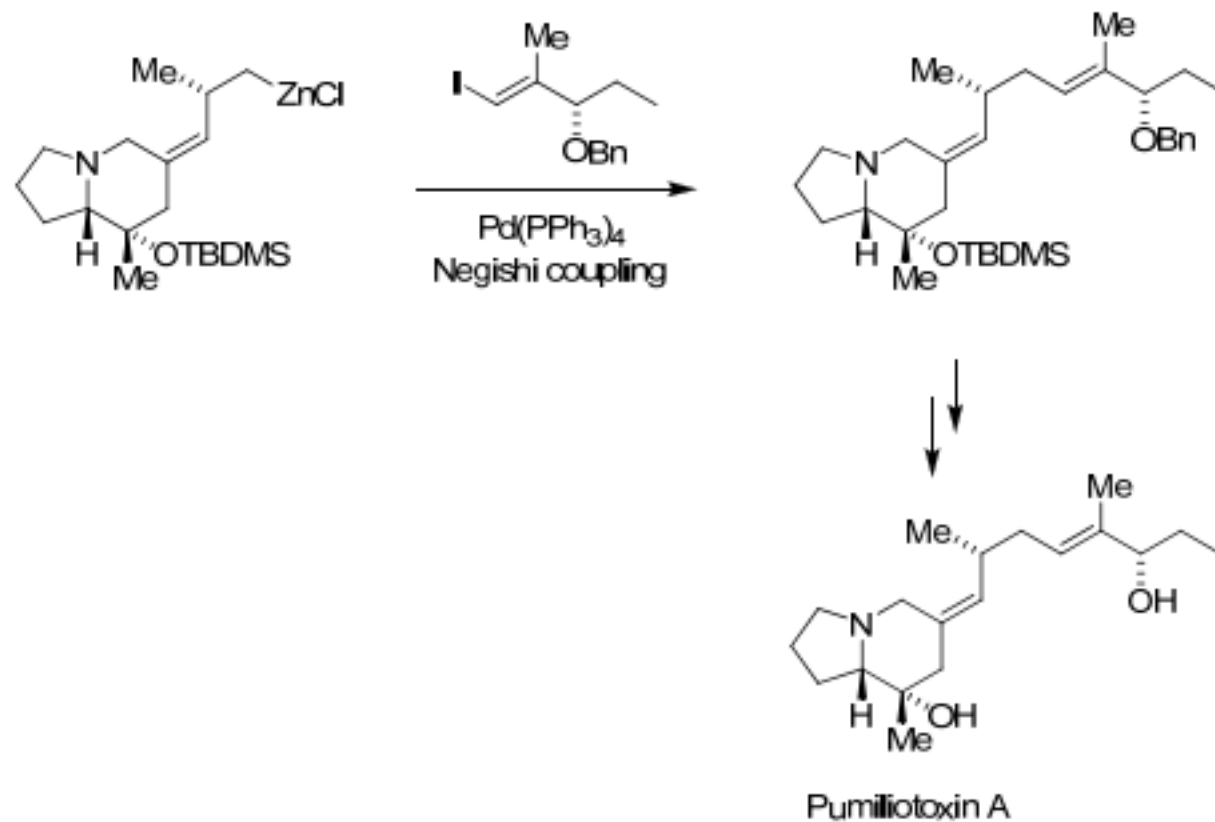
# Reações de acoplamento cruzado C-C



# Reações de acoplamento cruzado C-C



# Reações de acoplamento cruzado C-C



# Prêmio Nobel de Química 2005



Photo: U. Montan  
Yves Chauvin



Photo: R. Paz  
Robert H. Grubbs



Photo: L.B. Hetherington  
Richard R. Schrock

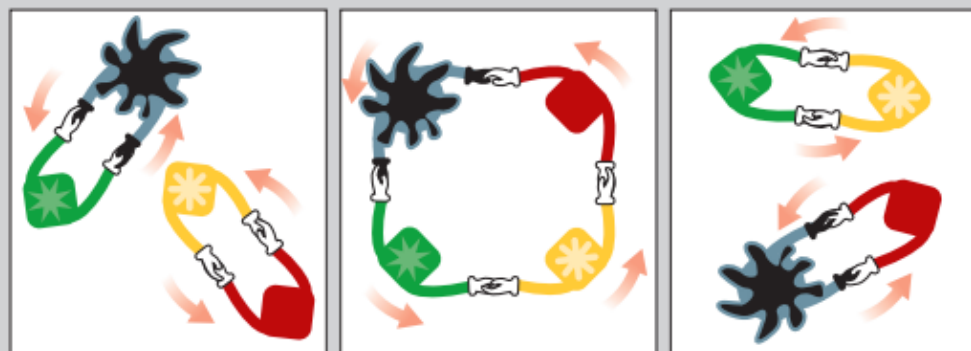
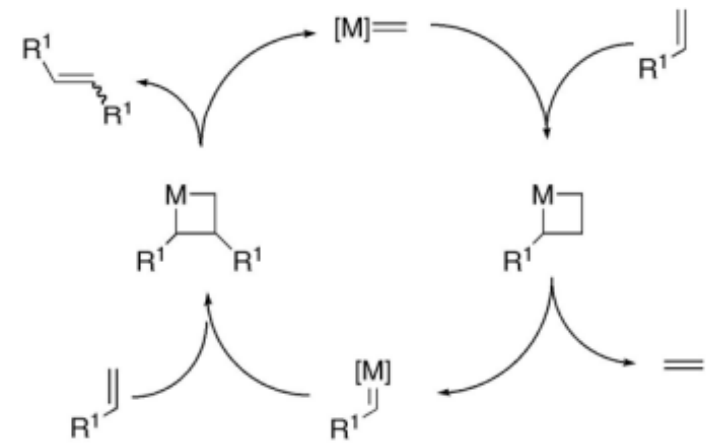
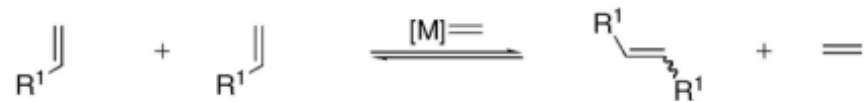
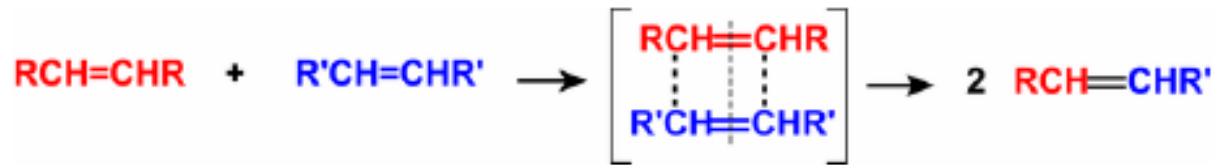


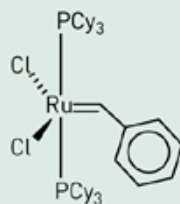
Figure 4. Chauvin's mechanism described above can be viewed as a dance in which the "catalyst pair" and the "alkene pair" dance round and change partners with one another. The metal and its partner hold hands with both hands and when they meet the "alkene pair" (a dancing pair consisting of two alkylides) the two pairs unite in a ring dance. After a while they let go of each other's hands, leave their old partners and dance on with their new ones. The new "catalyst pair" is now ready to catch another dancing "alkene pair" for a new ring dance or, in other words, to continue acting as a catalyst in metathesis.



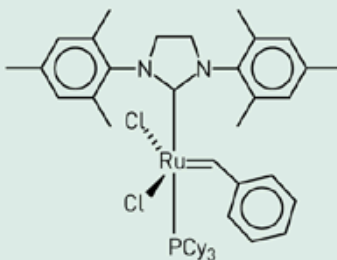
# Reações de metátese de olefinas



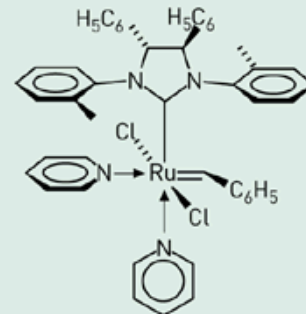
# Metátese de olefinas – alguns catalisadores



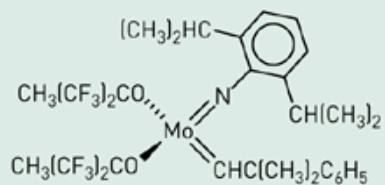
**Grubbs catalyst**



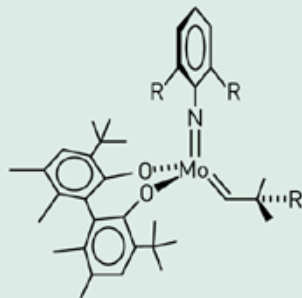
**Grubbs second-generation catalyst**



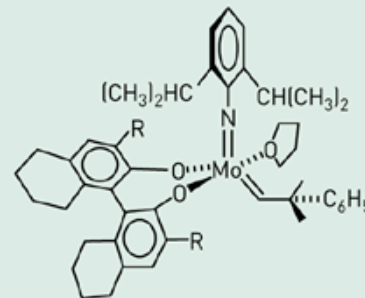
**Grubbs chiral ruthenium catalyst**



**Schrock catalyst**



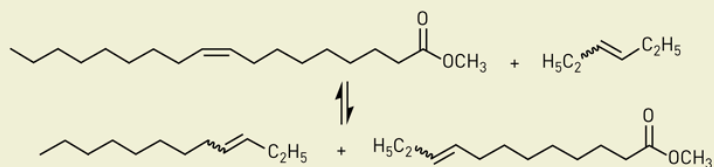
**Schrock-Hoveyda chiral molybdenum catalysts**



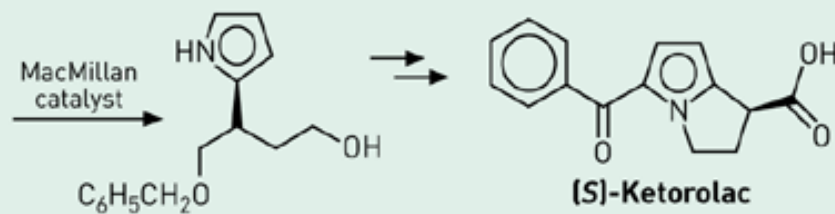
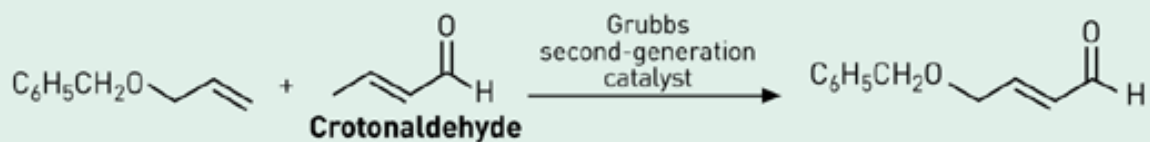
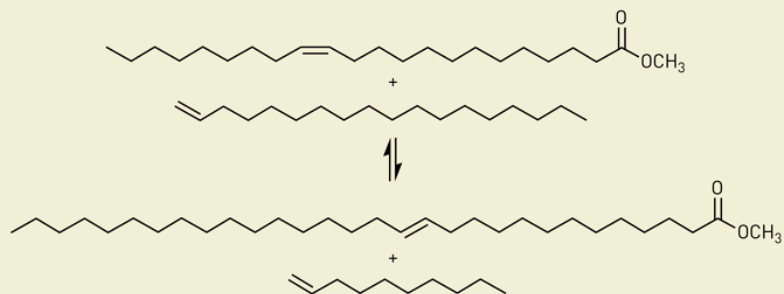
Cy = cyclohexyl

# Metátese cruzada de olefinas - aplicação

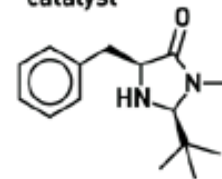
Cross-metathesis can be used to shorten unsaturated fatty acid esters ...



... or to extend them



**MacMillan catalyst**



# Metátese de olefinas - tipos

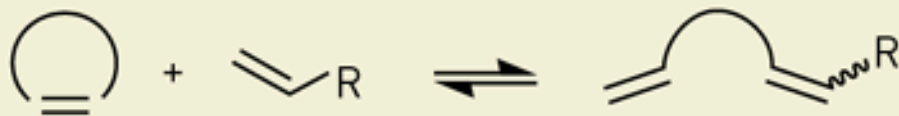
Cross-metathesis



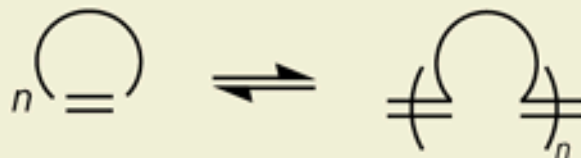
Ring-closing metathesis



Ring-opening metathesis



Ring-opening metathesis polymerization



Acyclic diene metathesis polymerization



# Ativação C-H

Refere-se a qualquer etapa de reação em que o catalisador cliva uma ligação carbono-hidrogênio

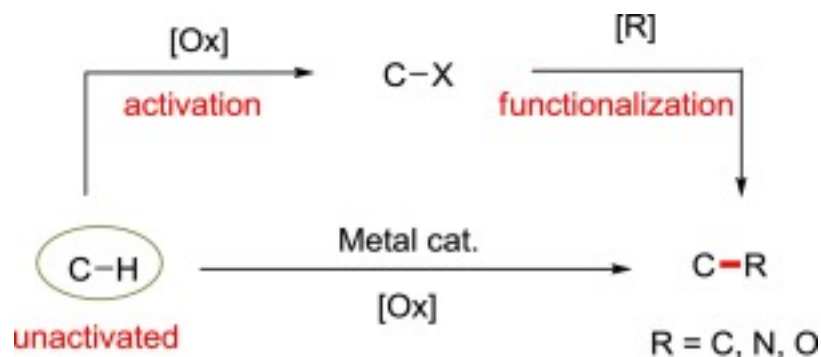
Uma ligação C-H isolada numa molécula tem uma reatividade muito baixa devido à grande barreira cinética associada à clivagem da ligação C-H e à natureza apolar desta ligação. Por esta razão, a reatividade seletiva desse grupo não-funcional está sob estudo desde várias décadas e ainda é considerada como o Santo Graal na química.

**Table 1**  
Bond dissociation energies and  $pK_a$  values of selected hydrocarbon C—H bonds.

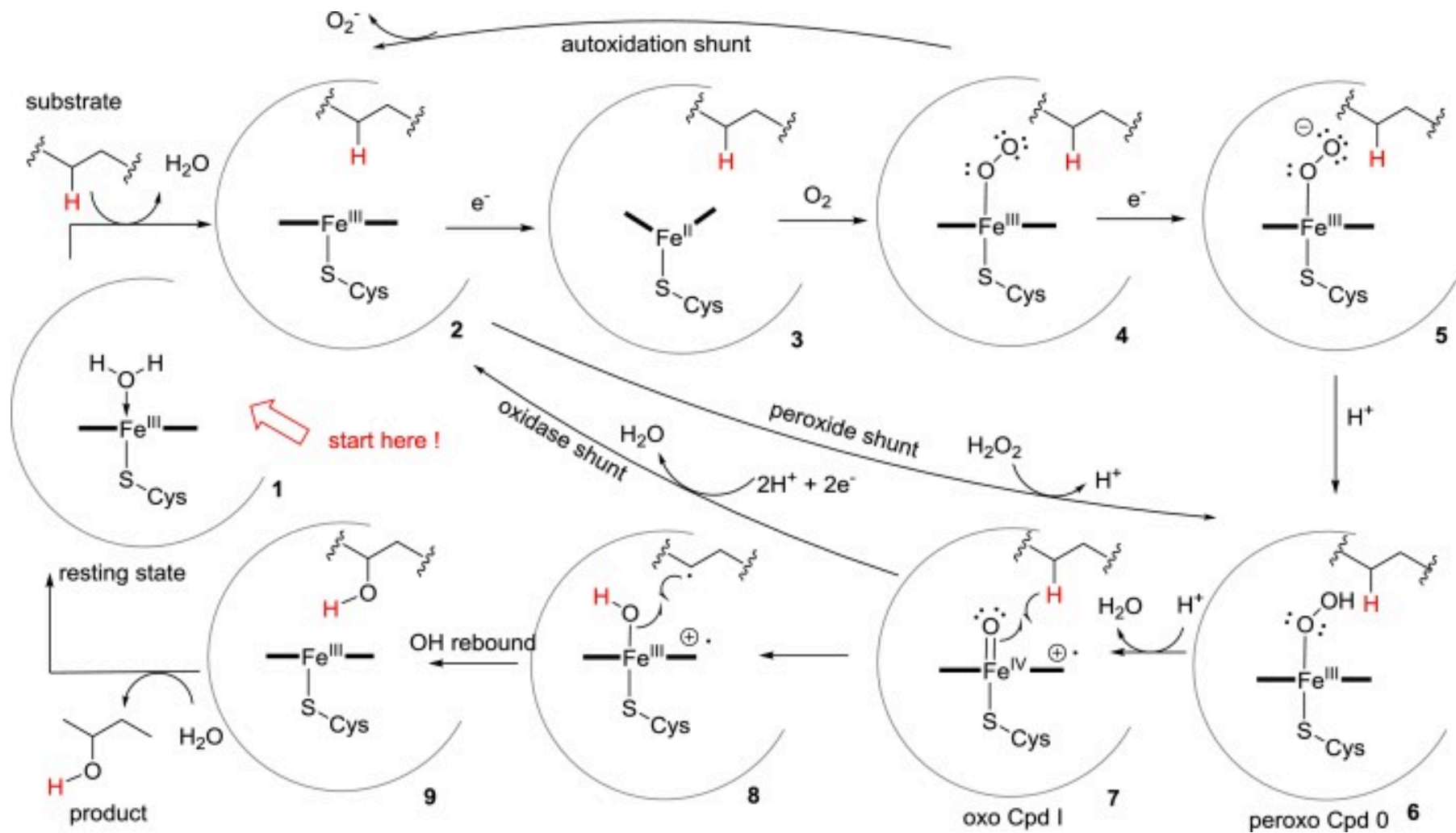
Type of C—H	C(sp)	C(sp <sup>2</sup> ) <sub>arom</sub>	C(sp <sup>2</sup> ) <sub>vinyl</sub>	C(sp <sup>3</sup> ) <sub>1°</sub>	C(sp <sup>3</sup> ) <sub>2°</sub>	C(sp <sup>3</sup> ) <sub>3°</sub>	C(sp <sup>3</sup> ) <sub>allylic</sub>
structure							
BDE (kJ/mol)	552.2	473.0	460.2	410.8	397.9	389.9	361.1
$pK_a$	~25	43	44	~50	~50	~50	43

# Ativação C-H

A química de ativação / funcionalização C-H catalisada por metais permite a construção econômica e original de ligações C-C, bem como ligações C-O e C-N, a partir de hidrocarbonetos (ou fragmentos de hidrocarbonetos) sem a necessidade de etapas de oxidação não catalíticas anteriores.

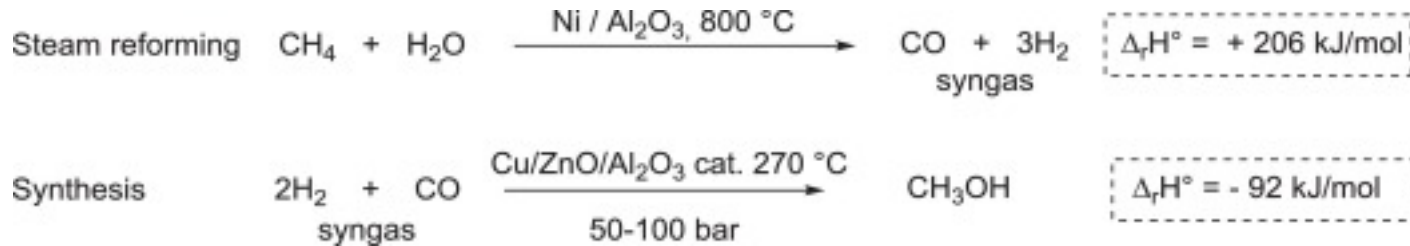


# Ciclo catalítico da citocromo P450

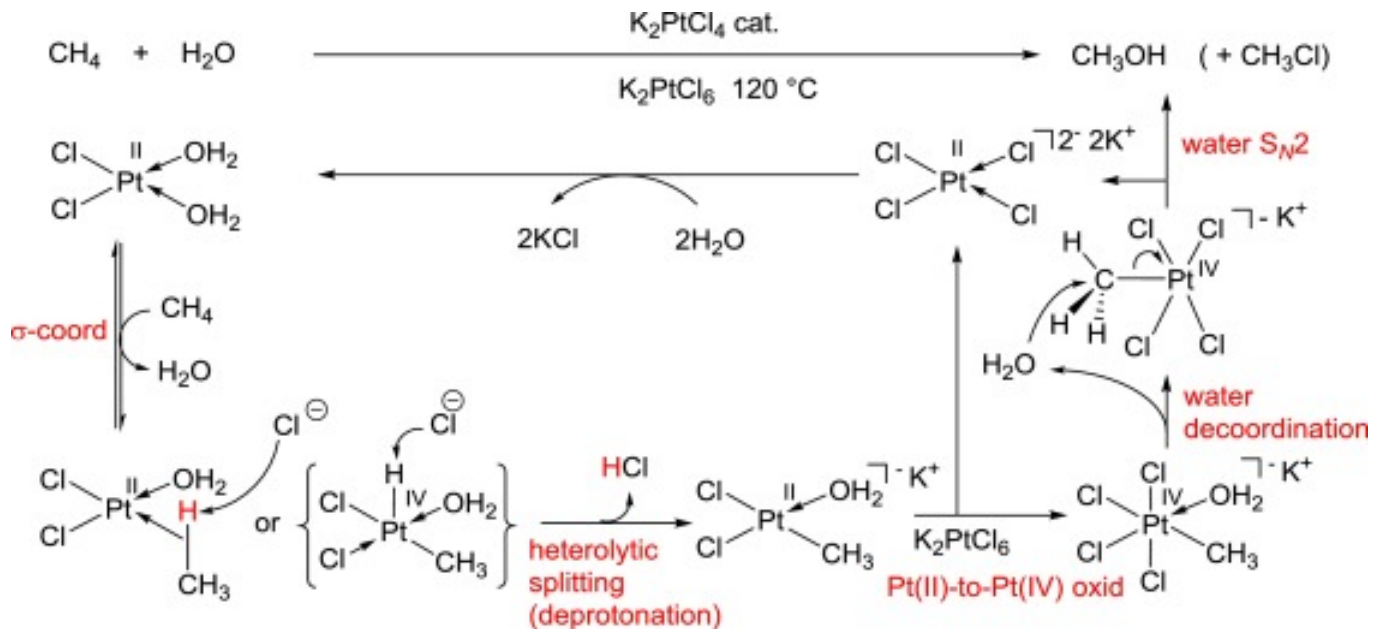


# Síntese de metanol

Catálise heterogênea: Processo industrial ICI (Imperial Chemical Industries), Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, 50–100 bar e ~270 °C



Catálise homogênea – reação de Shilov (1972)







# Trabalho da semana

Temas a escolher para apresentação na próxima aula

- Bioinspired C-H bond activation
- C-C cross coupling: alternativas ao uso de base