



TÁMOP-4.1.1.F-14/1/KONV-2015-0006

SZTE TTIK, KTCS, 1a) Duális és moduláris
képzésfejlesztés a mesterképzéshez

Fémorganikus kémia 2

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020



MAGYARORSZÁG
KORMÁNYA

Európai Unió
Európai Szociális
Alap



BEFEKTETÉS A JÖVŐBE

A leggyakrabban előforduló fémek a szerves kémiában

Group	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIIIB (8, 9, and 10)			1A (11)
Number of valence electrons	4	5	6	7	8	9	10	11
3d	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
4d	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
5d	Hf	Ta	W	Re	Os	Ir	Pt	Au

haptoszáma: a ligandum atomjainak száma a fém-ligandum kötésben



η^1



η^2



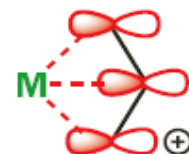
η^1

σ allyl

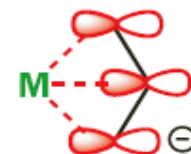


η^3

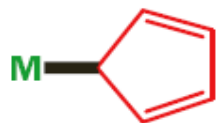
π allyl



allyl cation
complex



allyl anion
complex



η^1

σ complex



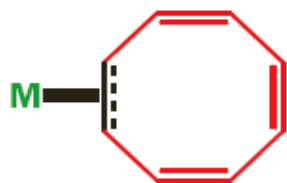
η^3

π complex

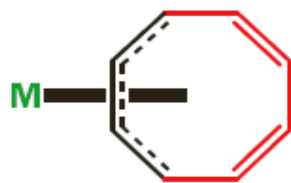


η^5

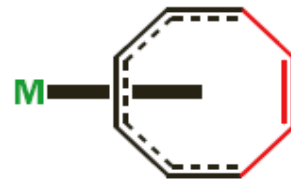
π complex



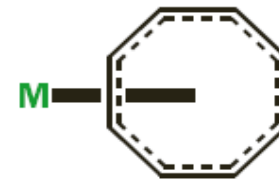
η^2



η^4



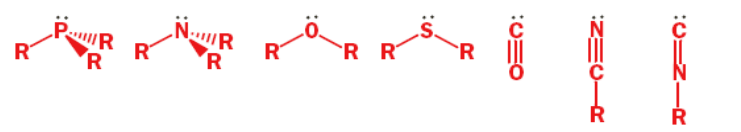
η^6



η^8

A leggyakrabban előforduló ligandumok és alaptulajdonságaik

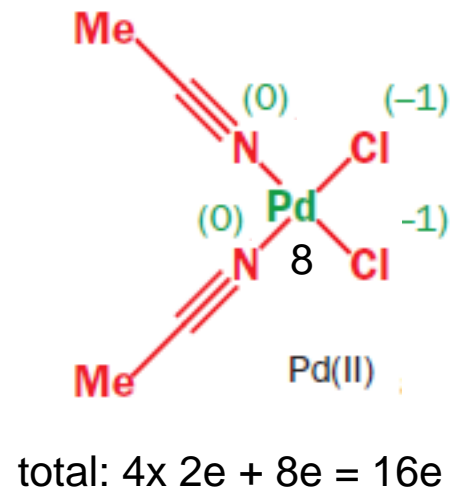
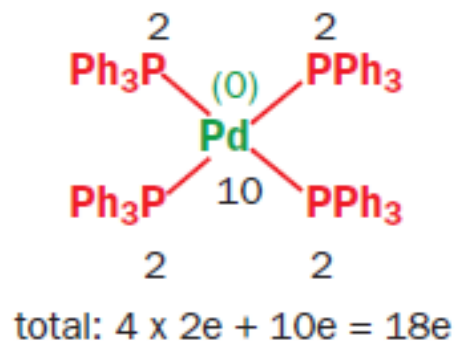
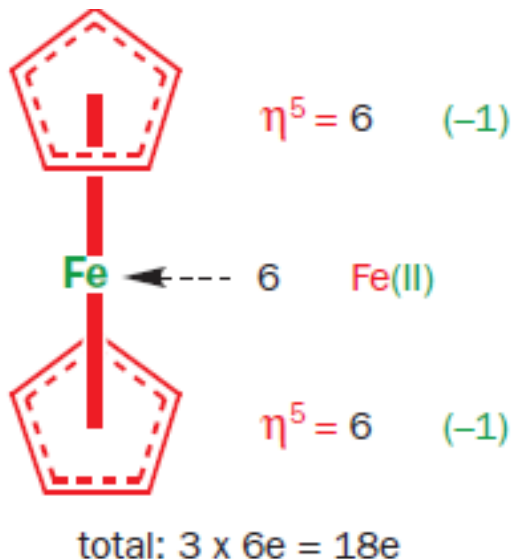
Ligand characteristics

	Formal charge	Electrons donated	
anionic ligands			
Cl^{\ominus} Br^{\ominus} I^{\ominus} CN^{\ominus} OR^{\ominus} H^{\ominus} alkyl^{\ominus}	-1	2	
neutral σ-donor ligands			
	0	2	
unsaturated σ- or π-donor ligands	Hapto number	Formal charge	Electrons donated
aryl, σ -allyl	η^1	-1	2
olefins	η^2	0	2
π -allyl cation	η^3	+1	2
π -allyl anion	η^3	-1	4
diene—conjugated	η^4	0	4
dienyls, cyclopentadienyls (anions)	η^5	-1	6
arenes, trienes	η^6	0	6
trienyls, cycloheptatrienyls (anions)	η^7	-1	8
cyclooctatetraene	η^8	0	8
carbene, nitrene, oxo	η^1	0	2

A fém (formális) oxidációs száma a komplexben

Figyelembe veendő tényezők:

- (1) a ligandum elektronpárt vagy elektronpárokat ad (donál) a fémnek
- (2) a ligandumnak lehet (negatív) töltése
- (3) a komplex kifelé semleges
- (4) A fém 0. oxidációs állapotban annyi elektront tartalmaz, amilyen oszlopban van a periódusos rendszerben

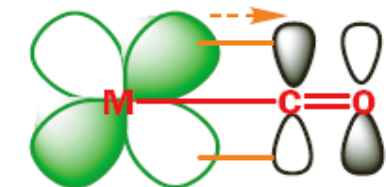


Fém-ligandum kötési módok

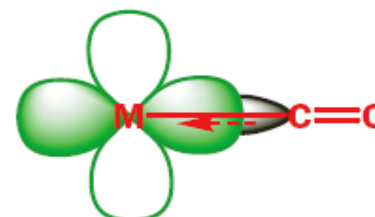
π -donation from metal to ligand



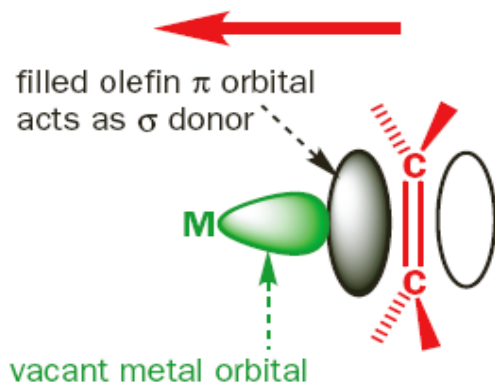
σ -donation from ligand to metal



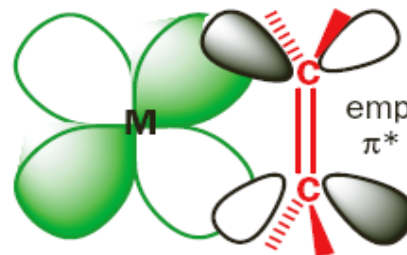
filled d orbital empty π^* on ligand



empty d orbital filled sp on ligand

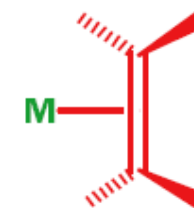


filled metal d orbitals



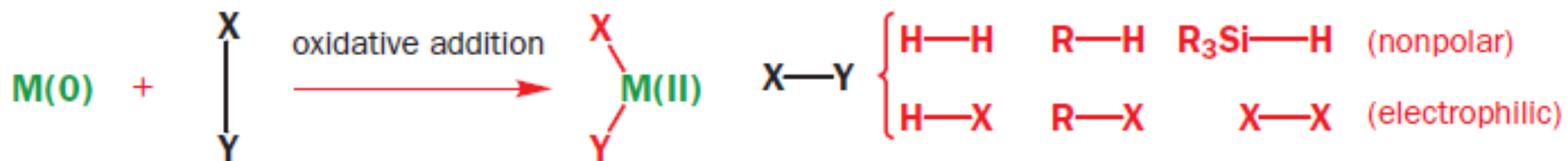
empty olefin π^* orbitals

\equiv

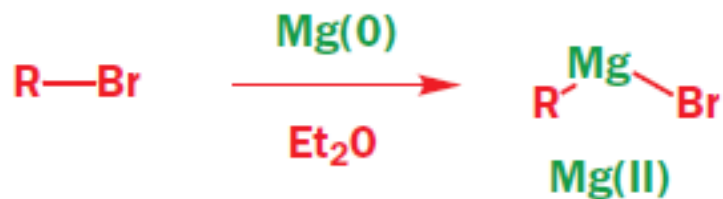


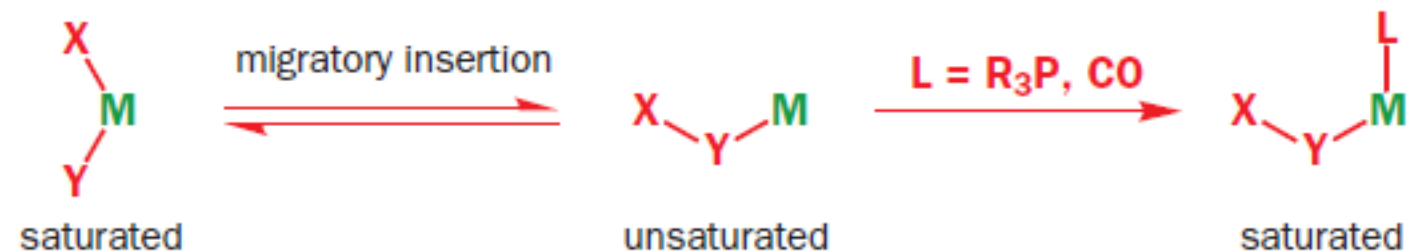
perpendicular π complex

Alapreakciók



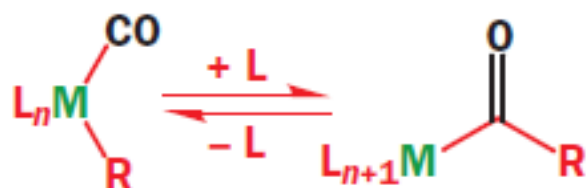
introduces new organic ligands on to metal



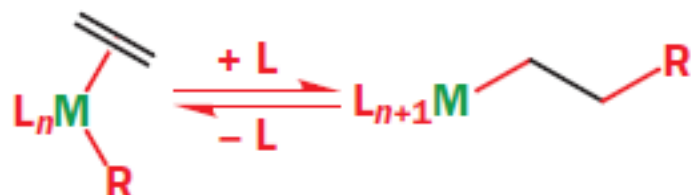


X migrates from M to Y
Y inserts into the M-X bond

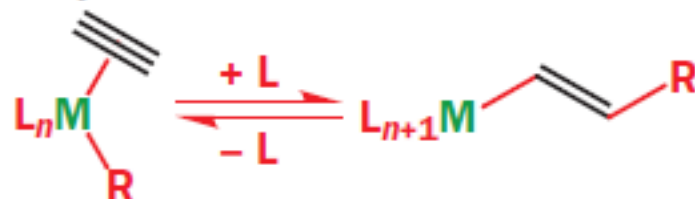
carbonylation



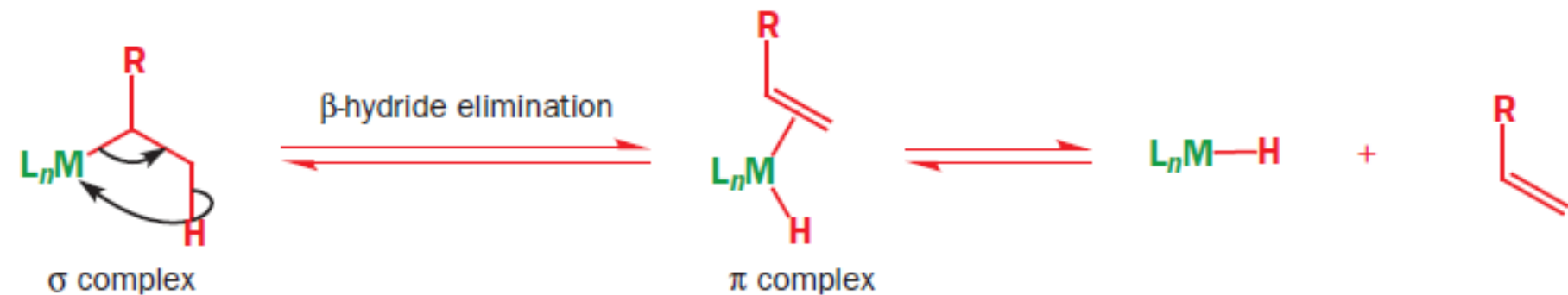
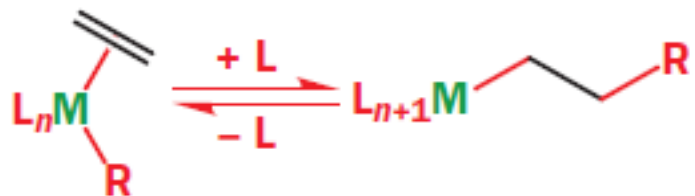
carbometallation or hydrometallation, R = H

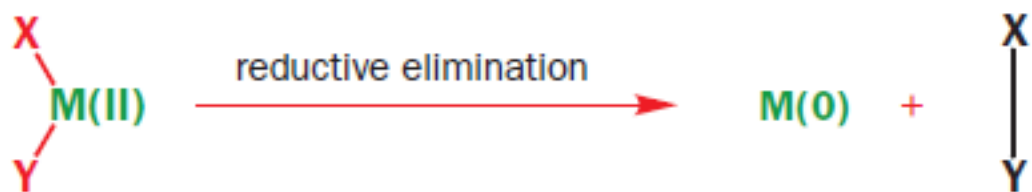


alkyne insertion

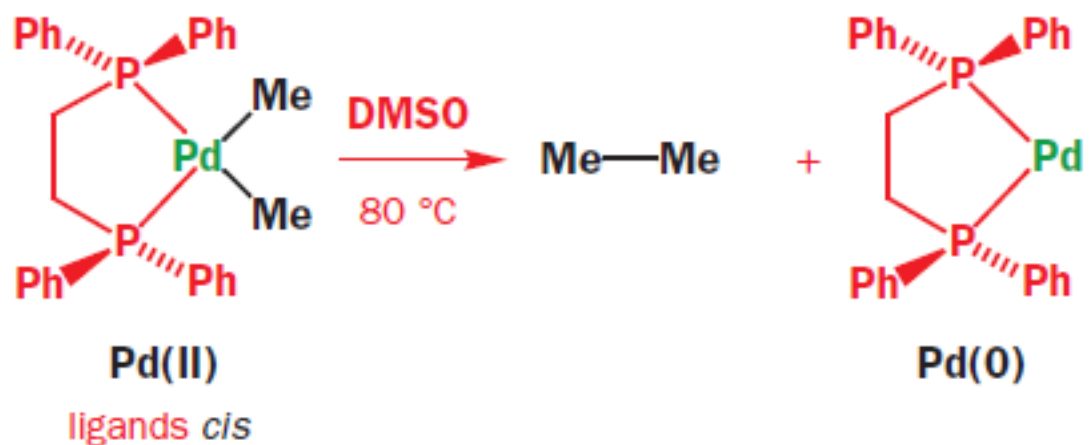


carbometallation or hydrometallation, R = H

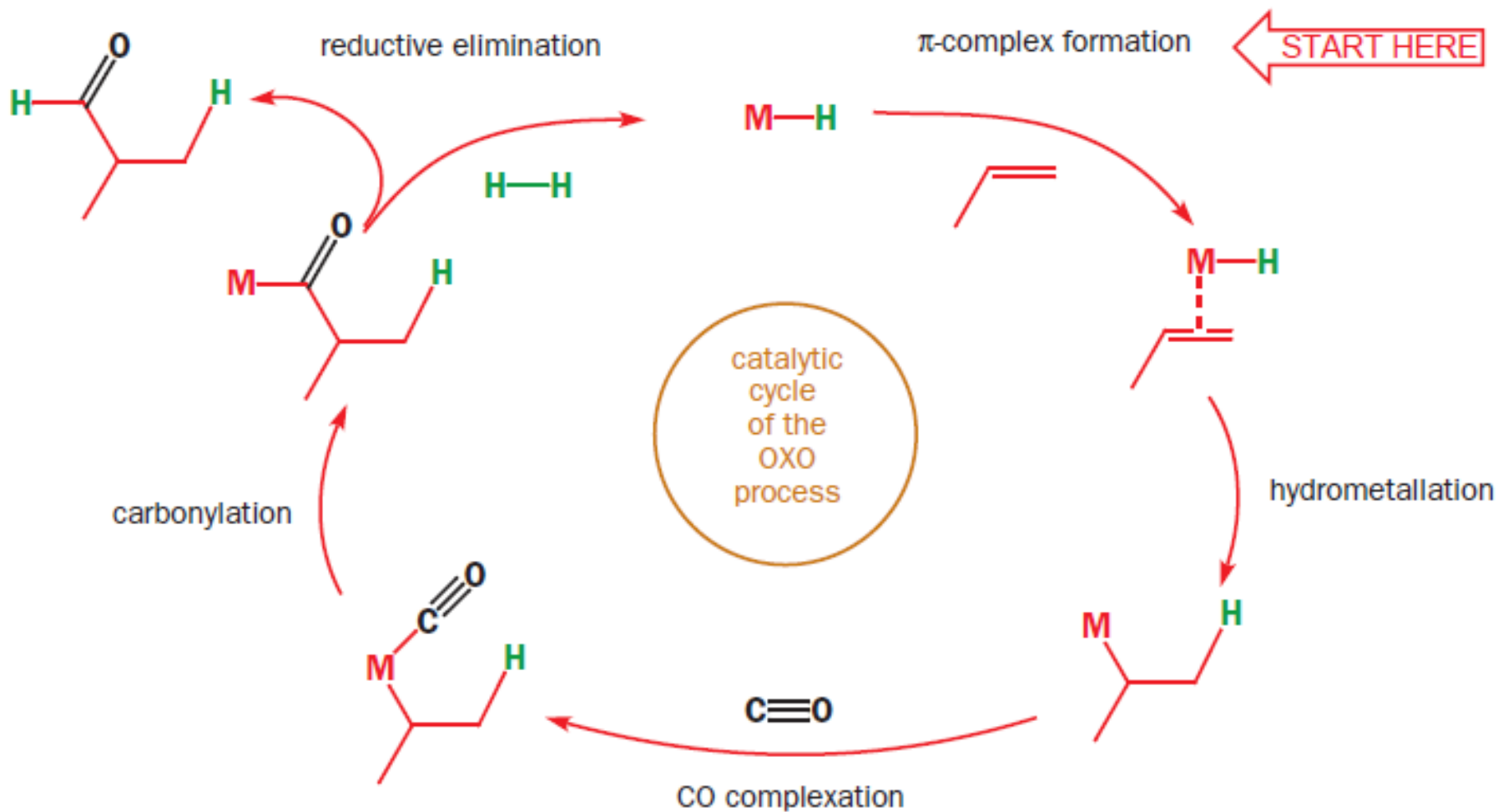
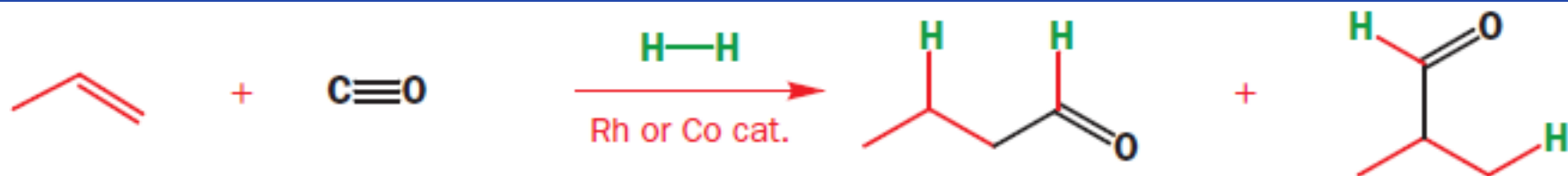




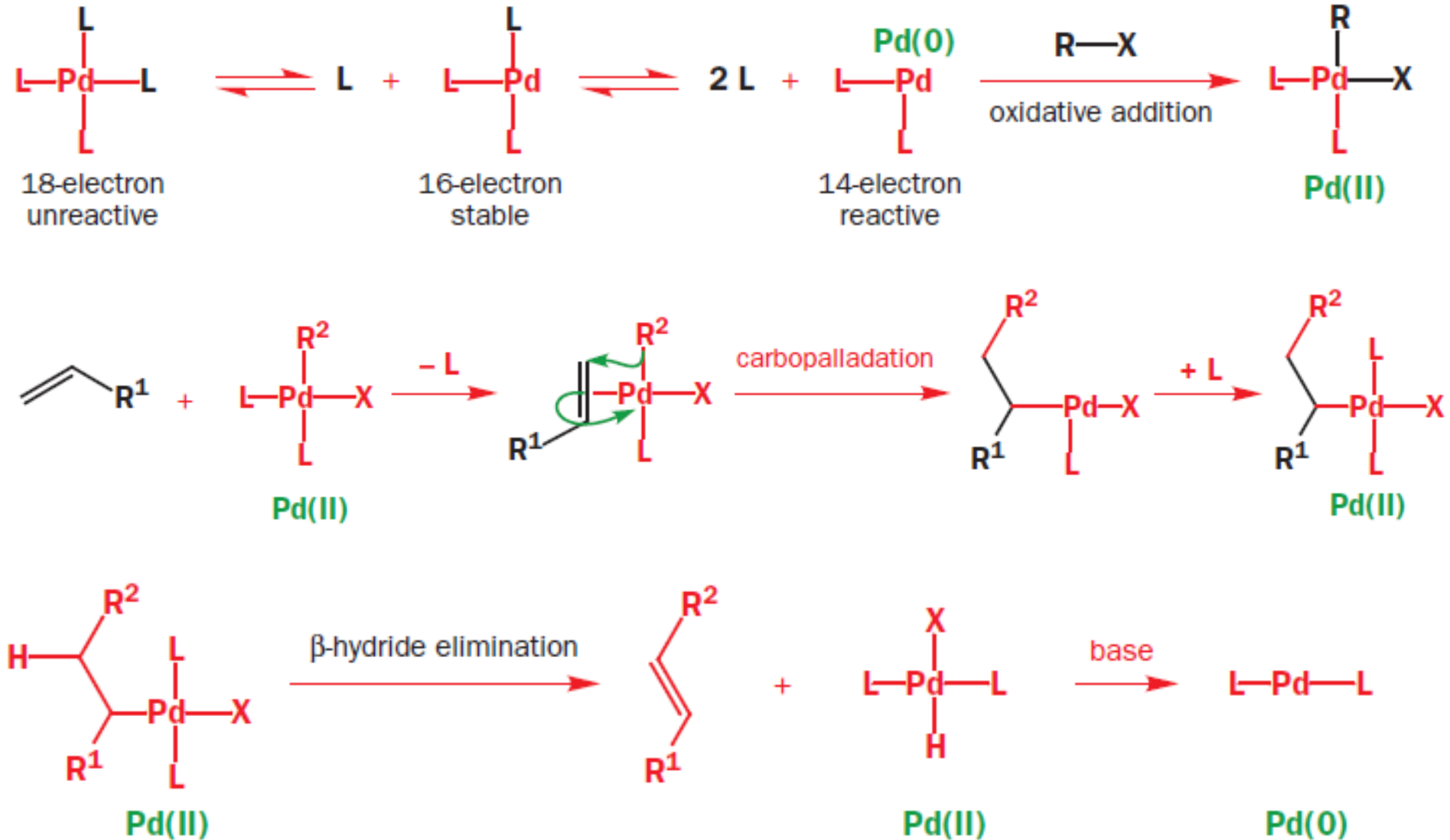
removes organic ligands from metal producing new organic product



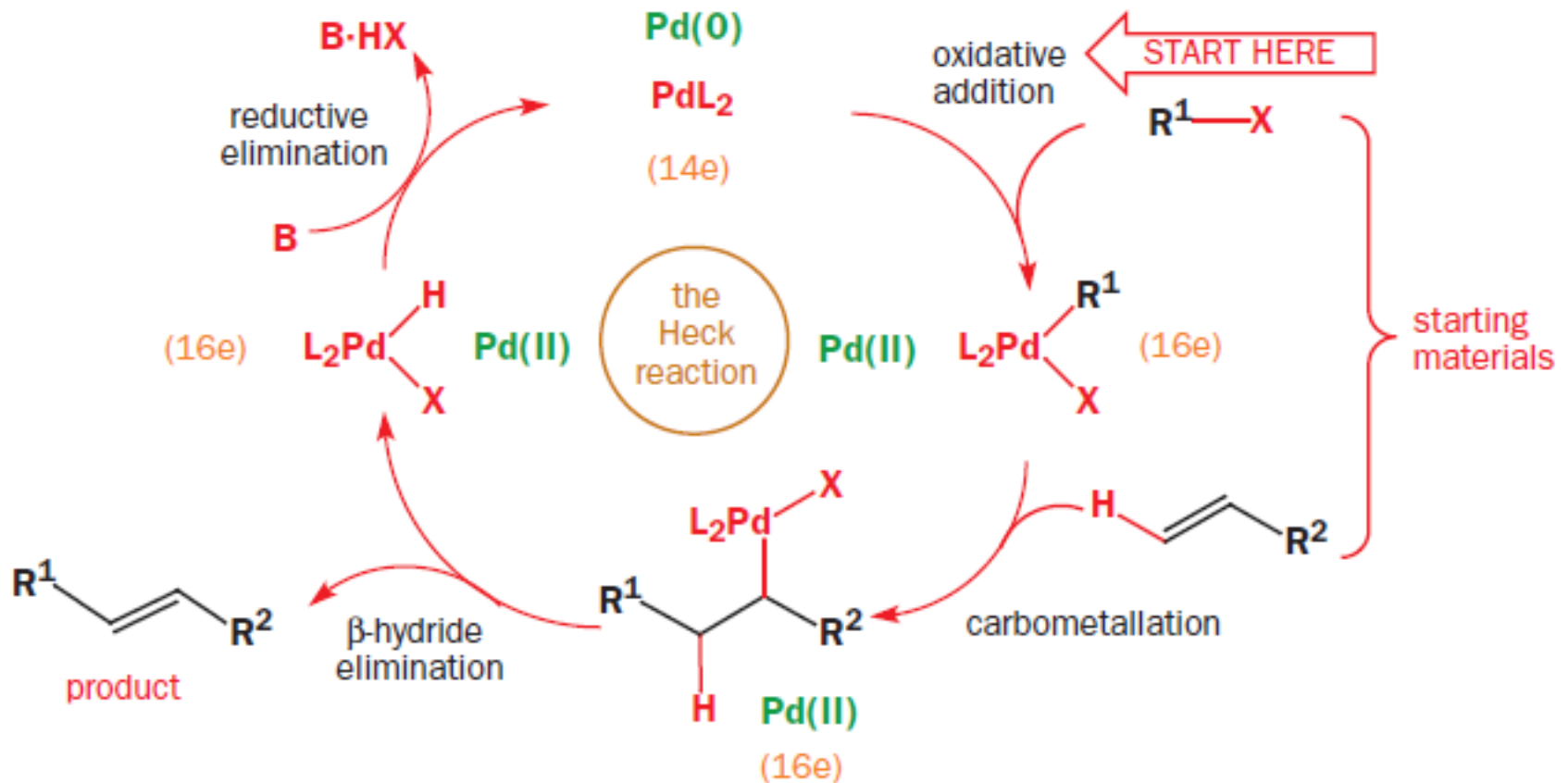
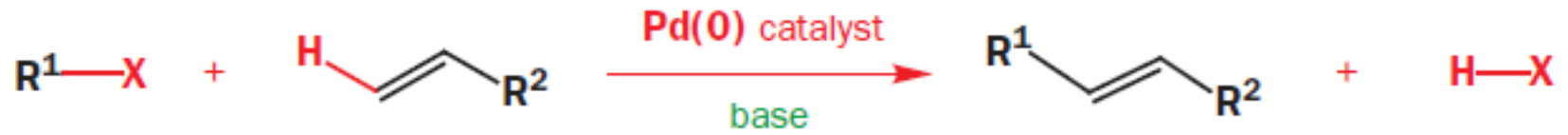
Oxosintézis

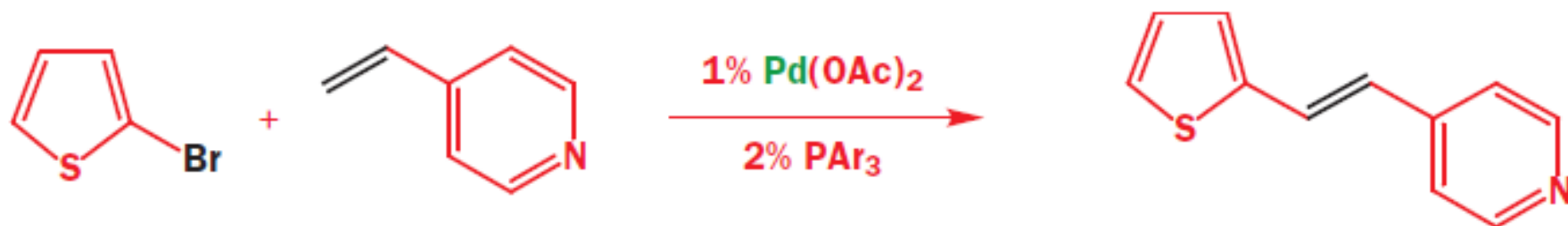


A Pd-komplexek tipikus reakciósora



A Heck-reakció

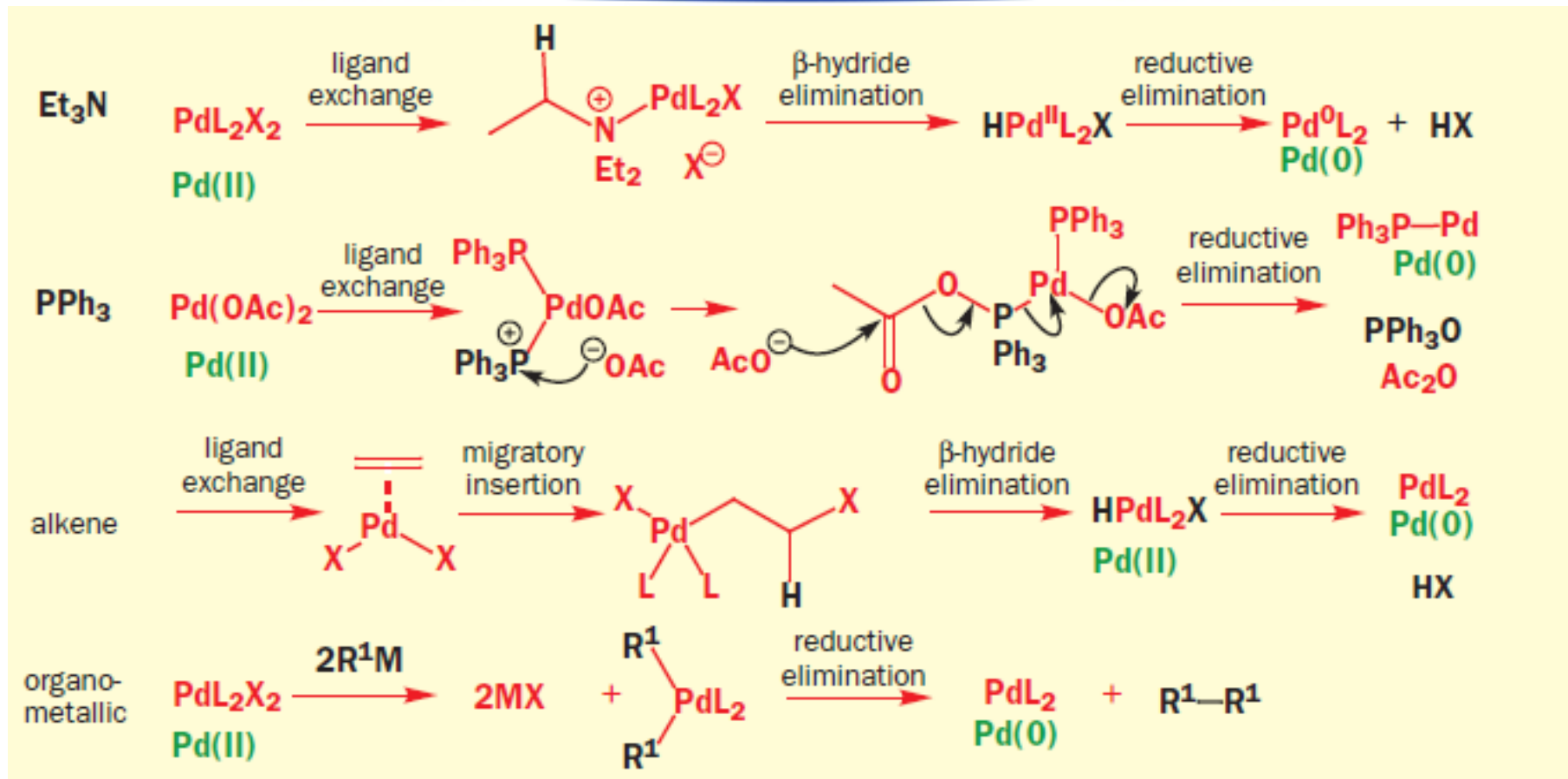




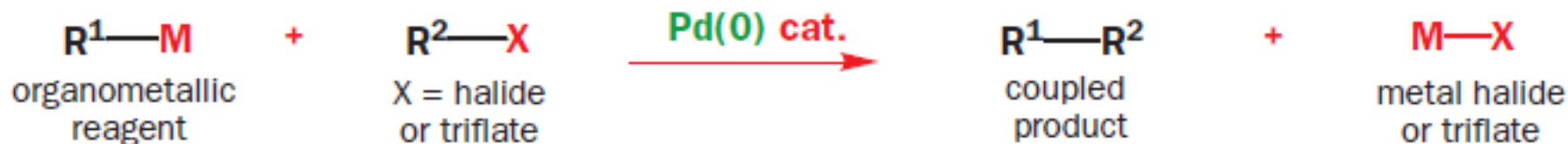
Lehetséges szubsztrátok: aril-, heteroaril-, vinil- és benzilhaloidok és triflátok; egyébként β -hidrid elimináció történik.

A reakció nem érzékeny funkciós csoportok jelenlétére és arra sem, hogy a szubsztrát tartalmaz-e elektronszívó vagy elektronküldő csoporto(ka)t.

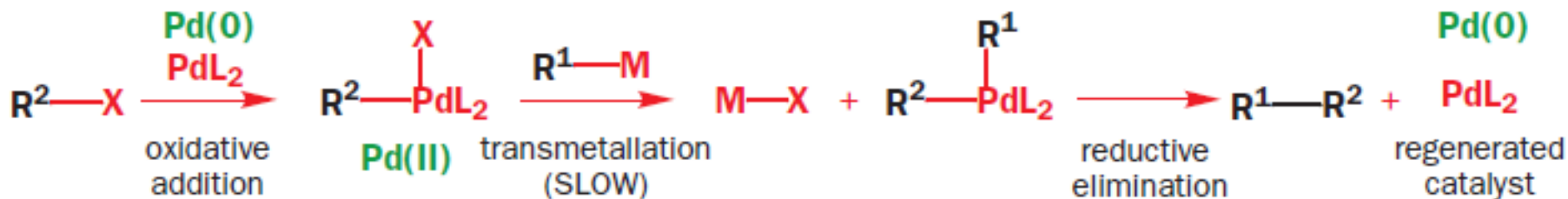
A Pd(0)-katalizátor (in situ) előállítása



Keresztkapcsolási reakciók



így megy:

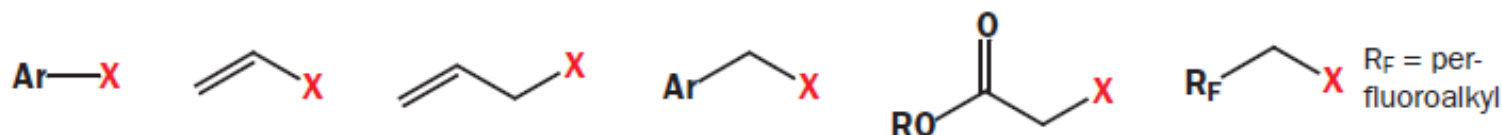


$\text{R}^1\text{—M}$ $\text{R}^1 =$ almost anything including examples with β H

$\text{M} = \text{MgX, ZnX, Cu, SnR}_3, \text{SiR}_3/\text{TASF, ZrCp}_2\text{Cl, AlMe}_2, \text{B(OR)}_2$

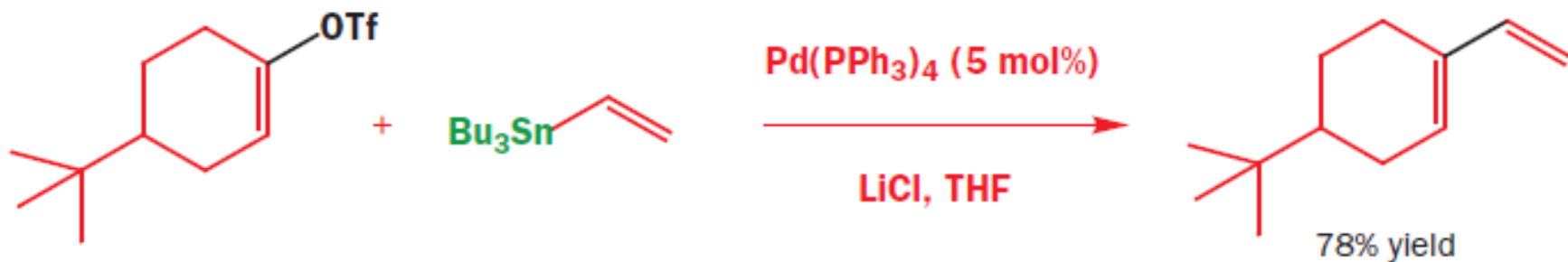
$\text{R}^2\text{—X}$ R^2 must not have β Hs that can eliminate

$\text{X} = \text{I, Br, (Cl), OTf, OPO(OR)}_2$

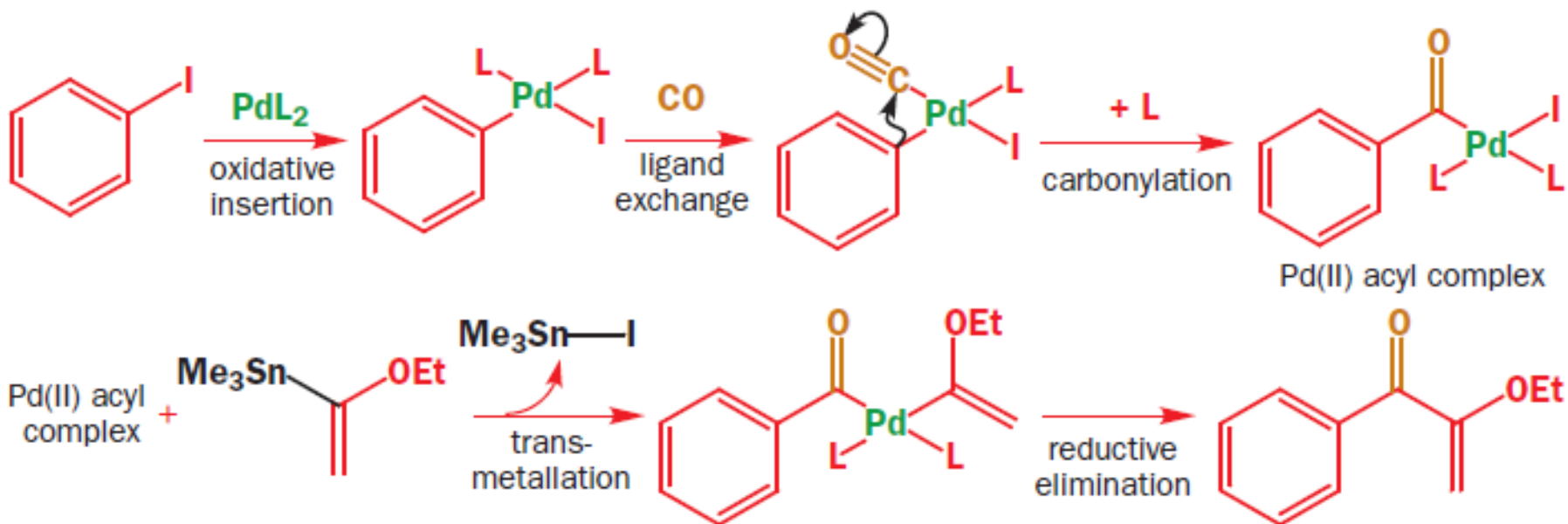


Stille-kapcsolás

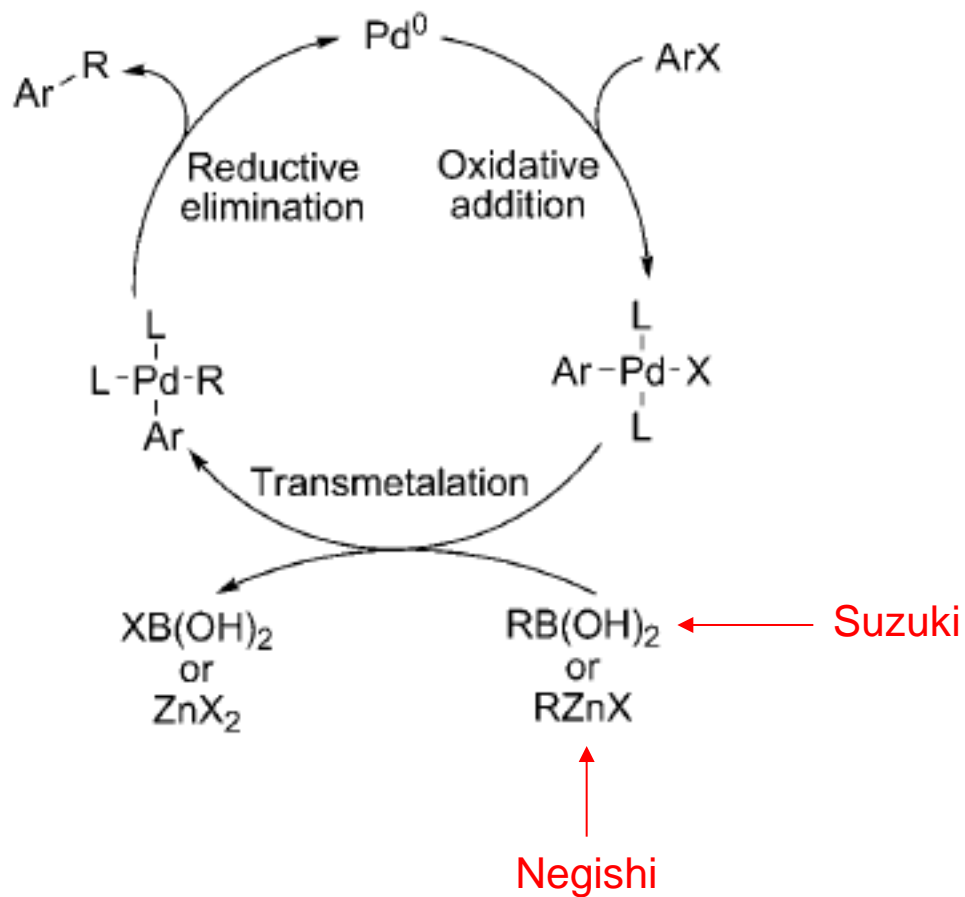
a reakció lényege (egy példán keresztül)



egy részletes mechanizmus

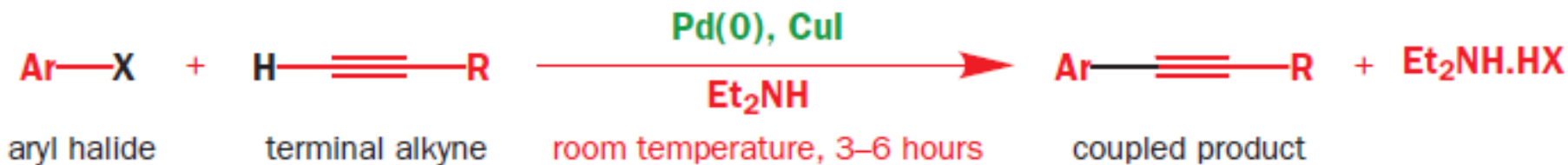


Suzuki- és Negishi-kapcsolás

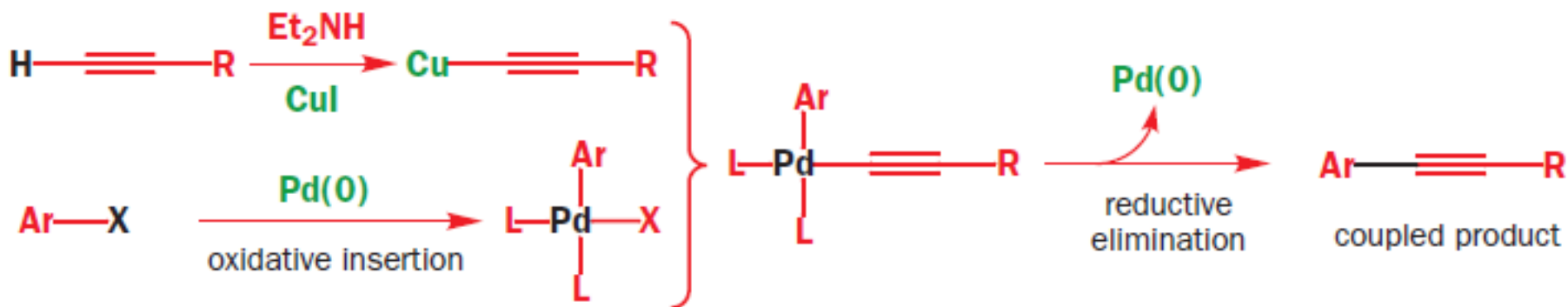


Sonogashira-kapcsolás

a reakció lényege (egy példán keresztül)

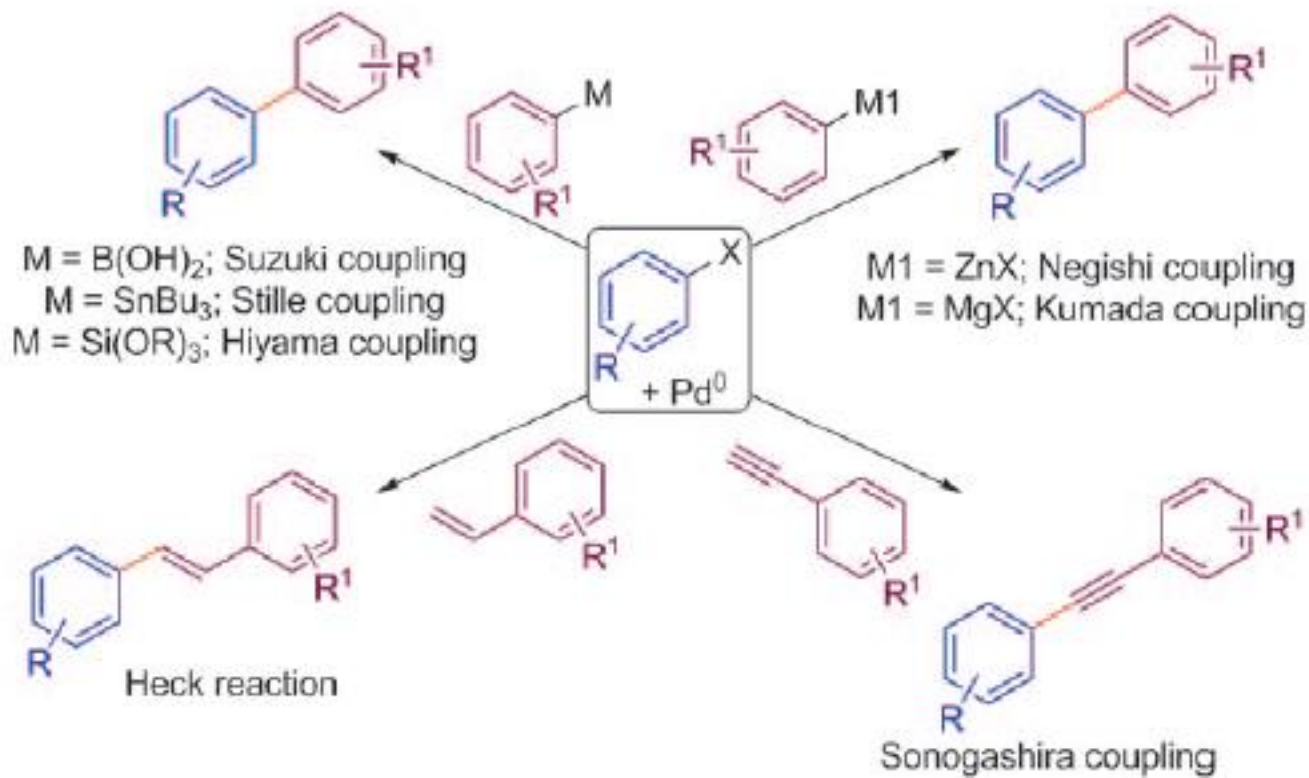


egy részletes mechanizmus



általában Pd(II)-vegyületet használunk (pl. bis(trifenilfoszfin)palladium(II) kloridot), amely in situ koordinatívan telítetlen, így azután nagyon reaktív Pd(0)-vá redukálódik.

Pd-katalizálta keresztkapcsolási reakciók – összefoglaló



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