Introduction

Métal de transition = métal qui a une orbitale d partiellement remplie

Comptage des e^- d : Ti^0 d^4 Ti^{+IV} d^0
Pt^0 d^{10} Pt^{+II} d^8

<u>Règle des 18 e⁻</u>

Pour ML_n :
Une configuration électronique stable sera atteinte si toutes les orbitales moléculaires liantes et non liantes sont remplies.

Comment compter les e⁻ ?

Formalisme ionique

1. Déconnecter tous les ligands selon le formalisme suivant :

$M-CO \equiv M^0 \quad :CO$

$M-Cl \equiv M^+ \quad :Cl^-$

$M-CH_3 \equiv M^+ \quad :CH_3^-$

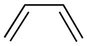
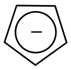
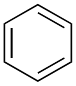
$M{=}O \equiv M^{++} \quad ::O^{2-}$

2. Placer la charge du complexe sur le métal
3. Compter les e⁻ d restant sur le métal
4. Compter les e⁻ donnés par les ligands (tous les e⁻)

$\Longrightarrow$ donne le nombre d'électrons d pour le complexe

Si la règle des 18 e⁻ est atteinte, le complexe est dit "coordinativement saturé".
Si la règle des 18 e⁻ n'est pas atteinte, le complexe est dit "coordinativement non saturé".

Ligands courants

	compté comme	nb. e^- donnés
X	X^-	2
alkyl	R^-	2
H	H^-	2
R_3P	$R_3P:$	2
R_2S	$R_2S:$	2
CO	$:CO$	2
alcène	$=$	2
allyl		4
diène		4
$(C_5H_5)^-$, Cp		6
benzène		6

Exemples

Cp_2ZrHCl

Zr^{+IV}	d^0	0
2 Cp		12
H		2
Cl		2
		16 e^-

Cp_2V

V^{+II}	d^3	3
2 Cp		12
		15 e^-

OsO_4

Os^{+VIII}	d^0	0
4 X O^{2-}		16
		16 e^-

$Fe(CO)_4{}^{2-}$

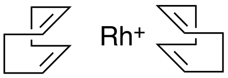
Fe^{-II}	d^{10}	10
4 CO		8
		18 e^-

$Pd(PPh_3)_4$ palladium tetrakistriphénylphosphine

Ph_3P PPh_3
Pd^0
Ph_3P PPh_3

Pd^0	d^{10}	10
4 X PPh_3		8
		18 e^-

$Rh(COD)_2^+$

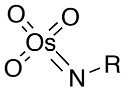


Rh^{+I}	d^8	8
2 X COD		8
		16 e^-

$RhCl(PPh_3)_3$ catalyseur de Wilkinson

Ph_3P PPh_3
Rh^+
Ph_3P Cl^-

Rh^{+I}	d^8	8
3 X PPh_3		6
Cl^-		2
		16 e^-



Os^{+VIII}	d^0	0
3 X O^{2-}		12
N^{2-}		4
		16 e^-

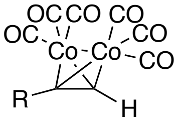
$Pd(PhCN)_2Cl_2$

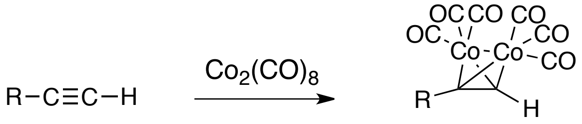
PhCN Cl^-

Pd^{2+}

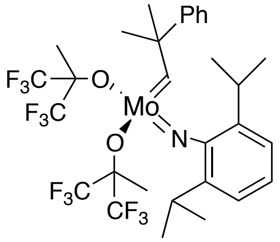
PhCN Cl^-

Pd^{+II}	d^8	8
2 X PhCN		4
2 X Cl^-		4
		16 e^-





Co^0	d^9	9
3 X CO		6
alcyne		2
liaison Co-Co		1
		18 e^-



Mo^{+VI}	d^0	0
2 X RO^-		4
carbène		4
nitrène		4
		12 e^-

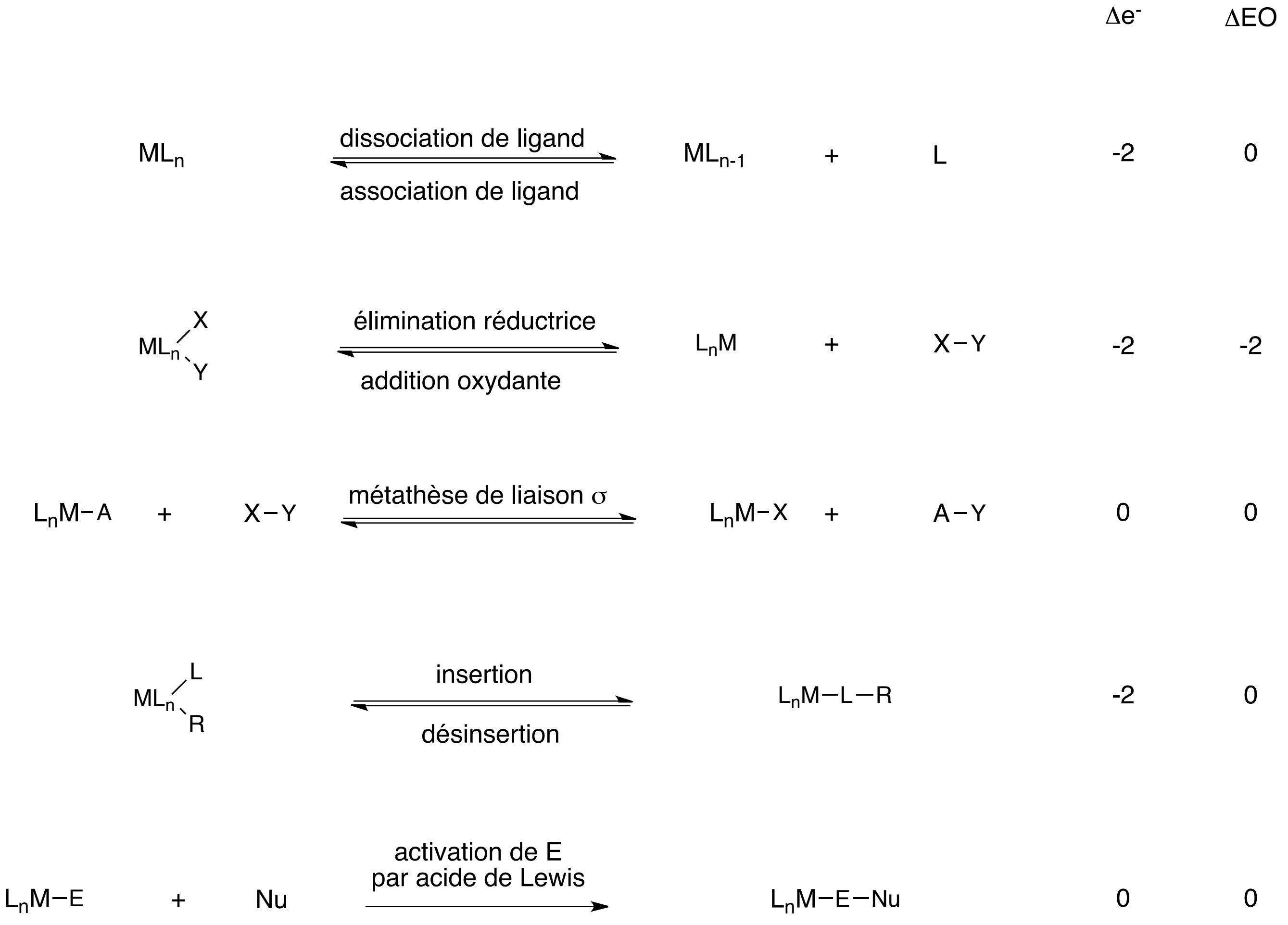
$HMn(CO)_5$

Mn^{+I}	d^6	6
H		2
5 CO		10
		18 e^-

$IrCl(CO)(PPh_3)_2$

Ir^{+I}	d^8	8
Cl		2
CO		2
2 PPh_3		4
		16 e^-

Mécanismes réactionnels



	Δe^-	ΔEO
$ML_n \underset{\text{association de ligand}}{\overset{\text{dissociation de ligand}}{\rightleftharpoons}} ML_{n-1} + L$	-2	0
$ML_n(X)(Y) \underset{\text{addition oxydante}}{\overset{\text{élimination réductrice}}{\rightleftharpoons}} L_nM + X-Y$	-2	-2
$L_nM-A + X-Y \overset{\text{métathèse de liaison }\sigma}{\rightleftharpoons} L_nM-X + A-Y$	0	0
$ML_n(L)(R) \underset{\text{désinsertion}}{\overset{\text{insertion}}{\rightleftharpoons}} L_nM-L-R$	-2	0
$L_nM-E + Nu \xrightarrow{\text{activation de E par acide de Lewis}} L_nM-E-Nu$	0	0

1. Dissociation/association de ligands

$$ML_n \underset{\text{association de ligand}}{\overset{\text{dissociation de ligand}}{\rightleftharpoons}} ML_{n-1} \quad + \quad :L$$

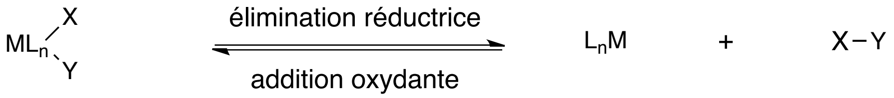
$$X\text{-}ML_n \underset{\text{association de ligand}}{\overset{\text{dissociation de ligand}}{\rightleftharpoons}} ML_n \quad + \quad :X$$

Exemple

$$Pd(PPh_3)_4 \rightleftharpoons Pd(PPh_3)_3 \ + \ PPh_3 \rightleftharpoons Pd(PPh_3)_2 \ + \ PPh_3$$

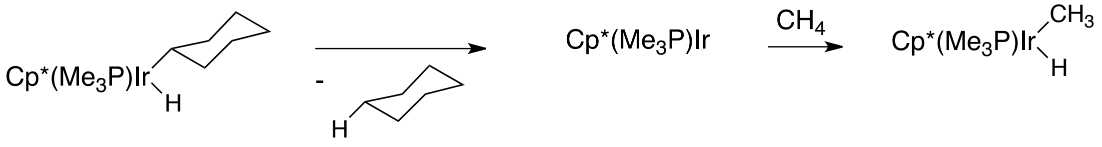
Pd(0), 18 e$^-$ Pd(0), 16 e$^-$ Pd(0), 14 e$^-$

2. Addition oxydante/élimination réductrice



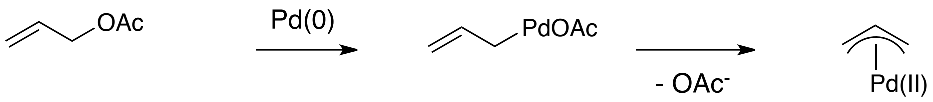
$$ML_n(X)(Y) \underset{\text{addition oxydante}}{\overset{\text{élimination réductrice}}{\rightleftharpoons}} L_nM \quad + \quad X-Y$$

Exemple



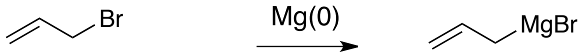
Ir(III), 18 e$^-$ Ir(I), 16 e$^-$ Ir(III), 18 e$^-$

Bergman 84JACS7272



Pd(0) Pd(II) Pd(II)

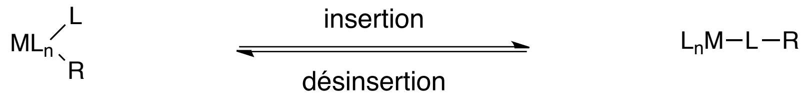
Tsuji-Trost



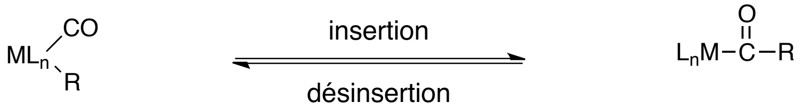
Mg(0) Mg(II)

Grignard

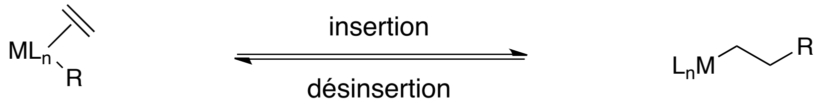
3. Insertion migratoire/déinsertion



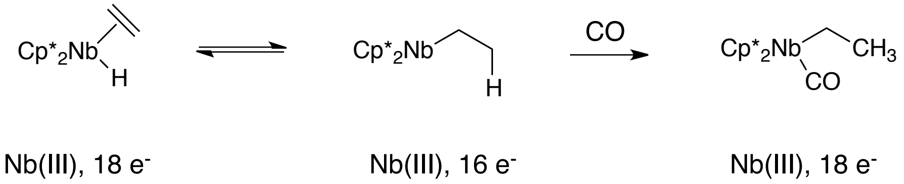
L = CO



L = alcène

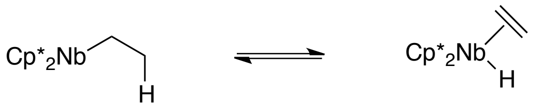


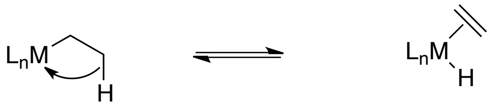
Exemple



Bercaw 85JACS2670

Avec R = H, déinsertion appelée *élimination de β-H*

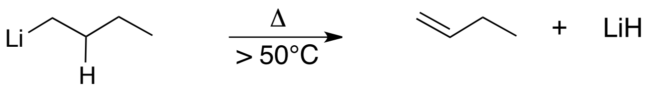




Conditions :

- le C en β du M porte un H
- conformation coplanaire au niveau de M-C-C-H -> le H sera proche de M
- site de coordination vacant sur le métal

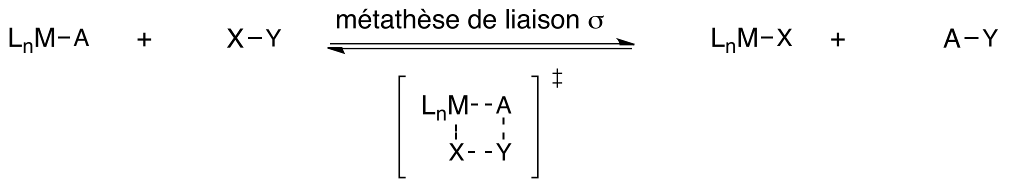
- réaction plus rapide pour des métaux avec orbitales d que pour les métaux des familles a



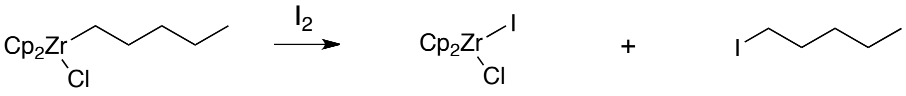
Ziegler 50Liebigs179

4. Réactions à 4 centres

4.1. Métathèse de liaison sigma

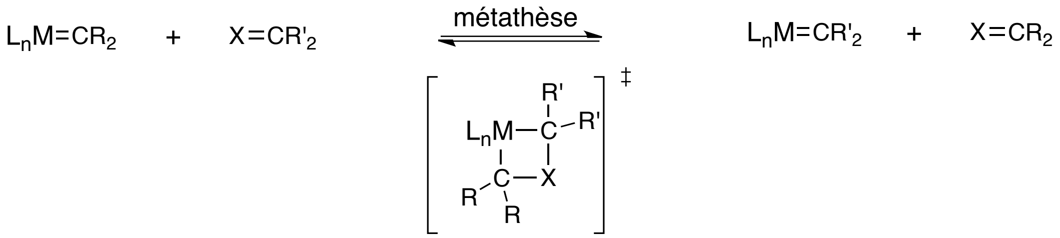


Exemple

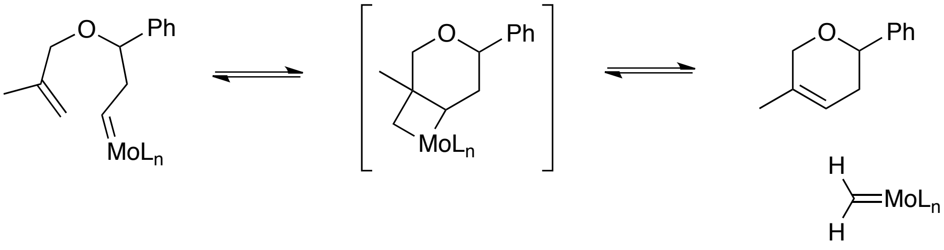


Zr(IV), 16 e$^-$ Zr(IV), 16 e$^-$ Schwartz 75JACS3851

4.2. Métathèse d'oléfines

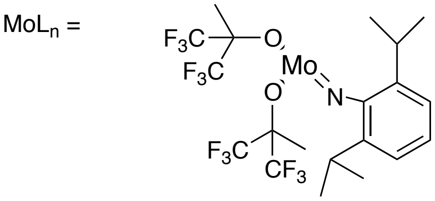


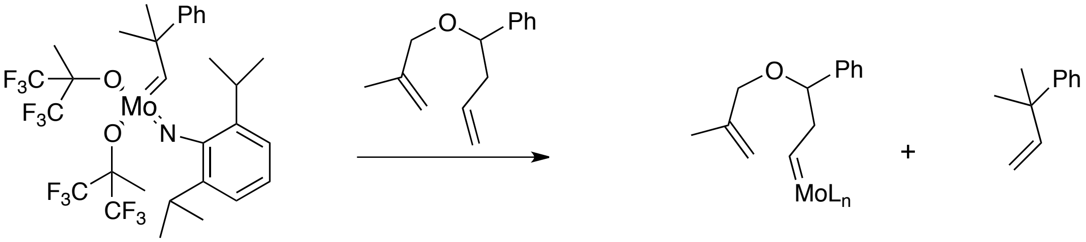
Exemple



Mo(VI), 12 e$^-$ Mo(VI), 12 e$^-$ Mo(VI), 12 e$^-$

Grubbs 92JACS7324





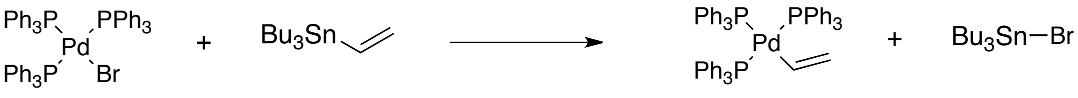
1ère étape du cycle catalytique de RCM

5. Transmétallation

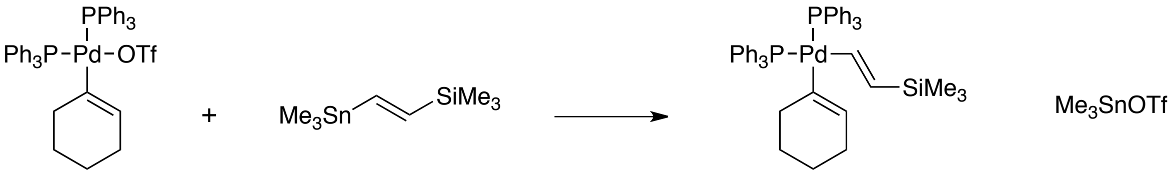
$$L_nM{-}X \quad + \quad M'{-}R \longrightarrow L_nM{-}R \quad + \quad M'{-}X$$

X = groupe partant (halogénure, triflate)
M' + d'habitude un métal de famille a

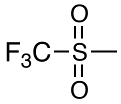
Exemple



Stille 86ACIEE508



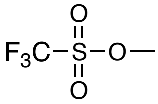
Tf— ≡



$F_3C{-}SO_2{-}$

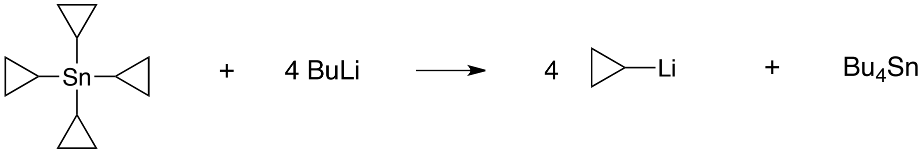
triflyle (trifluorométhanesulfonyl)

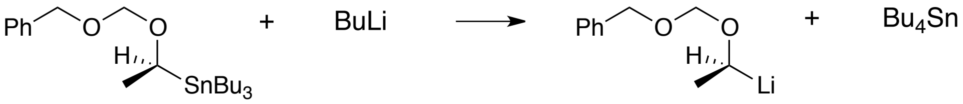
TfO— ≡



$F_3C{-}SO_2{-}O{-}$

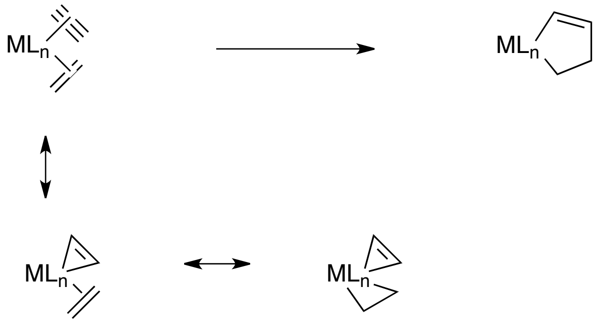
triflate (trifluorométhanesulfonate)





McGarvey 82JOC5421

6. Couplage oxydatif



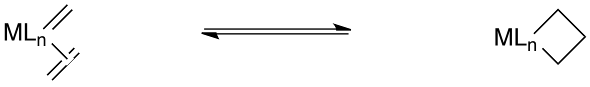
Buchwald 88CR1047

Exemple

métalacyclopentane

Ni(0), 16 e$^-$
d^{10}

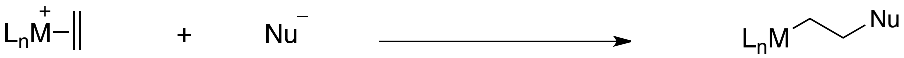
Ni(II), 16 e$^-$
d^8



métalacyclobutane

(intermédiaire dans métathèse)

7. Activation d'un électrophile vis-à-vis d'une attaque nucléophile



Hegedus COS vol. 4, chap. 3.1
Semmelhack COS vol. 4, chap. 2.4