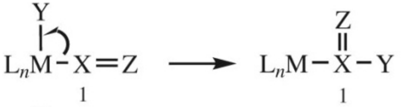
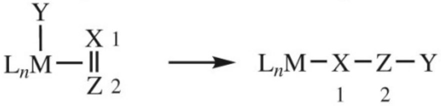
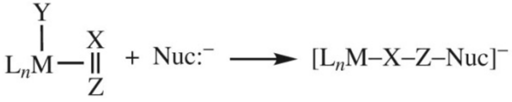
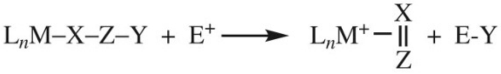
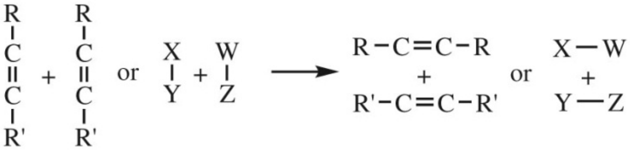
Lecture: Overview of Organometallic Reactions

Chapter 7 Meisler and Spessard

Table 7-1 Common Reactions of Organotransition Metal Complexes

Reaction type	Schematic example	Δ Oxidation state of M	Δ Coordination number of M	Δ e^- count	Text section
Ligand substitution	$L'' + L_nML' \longrightarrow L_nML'' + L'$	0	0	0	**7-1**
Oxidative addition	$L_nM + X\text{-}Y \longrightarrow L_nM(X)(Y)$	+2	+2	+2	**7-2**
Reductive elimination	$L_nM(X)(Y) \longrightarrow L_nM + X{-}Y$	−2	−2	−2	**7-3**
1,1-Insertion[a]	 $L_n\overset{Y}{\overset{\vert}{M}}-\underset{1}{X}=Z \longrightarrow L_nM-\underset{1}{\overset{\overset{Z}{\Vert}}{X}}-Y$	0	−1	−2	**8-1-1**
1,2-Insertion[a]	 $L_n\overset{Y}{\overset{\vert}{M}}-\overset{X\,1}{\underset{Z\,2}{\Vert}} \longrightarrow L_nM-\underset{1}{X}-\underset{2}{Z}-Y$	0	−1	−2	**8-1-1**
Nucleophilic addition[b]	 $L_n\overset{Y}{\overset{\vert}{M}}-\overset{X}{\underset{Z}{\Vert}} + \text{Nuc:}^- \longrightarrow [L_nM\text{–}X\text{–}Z\text{–}\text{Nuc}]^-$	0[c]	0	0	**8-2**
Nucleophilic abstraction[b]	 $L_nM-\overset{\overset{O}{\Vert}}{C}R + \text{Nuc–H} \longrightarrow L_nM\text{–}H + \text{Nuc}-\overset{\overset{O}{\Vert}}{C}R$	0	0	0	**8-3**
Electrophilic addition[b]	$L_nM\text{–}X{=}Z + E^+ \longrightarrow [L_nM{=}X\text{–}Z\text{–}E]^+$	0	0	0	**8-4**
Electrophilic abstraction[b]	 $L_nM\text{–}X\text{–}Z\text{–}Y + E^+ \longrightarrow L_nM^+-\overset{X}{\underset{Z}{\Vert}} + E\text{-}Y$	0	0	0	**8-4**
π- and σ-Bond metathesis[d]	 $\begin{matrix}R\\ \vert\\ C\\ \Vert\\ C\\ \vert\\ R'\end{matrix} + \begin{matrix}R\\ \vert\\ C\\ \Vert\\ C\\ \vert\\ R'\end{matrix}$ or $\begin{matrix}X\\ \vert\\ Y\end{matrix} + \begin{matrix}W\\ \vert\\ Z\end{matrix} \longrightarrow \begin{matrix}R-C{=}C-R\\ +\\ R'-C{=}C-R'\end{matrix}$ or $\begin{matrix}X-W\\ +\\ Y-Z\end{matrix}$				**11-1 and 11-4**

[a] The reverse reaction, called *deinsertion* or elimination, is also possible.

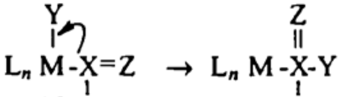
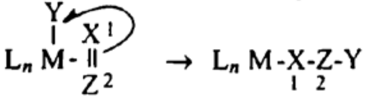
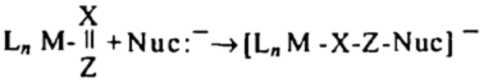
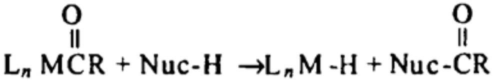
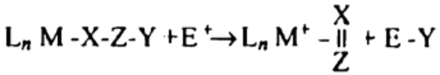
[b] There is no one general reaction; several variations are possible.

[c] Depends upon change in hapticity; e.g., X=Z going from η^3 to η^2 results in a 2 e^- reduction.

[d] Δ oxidation state, coordination number, and e^- count are not applicable here, especially in π-bond metathesis where the metal complex is a catalyst.

Spessard + Miessler

Table 7-1 Common Reactions of Organotransition Metal Complexes

Reaction Type	Schematic Example	ΔOxidation State of M	ΔCoordination Number of M	Δe⁻ Count	Text Section
Ligand substitution	$L_2 + L_n ML_1 \rightarrow L_n ML_2 + L_1$	0	0	0	7-1
Oxidative addition	$L_n M + X\text{-}Y \rightarrow L_n M(X)(Y)$	+2	+2	+2	7-2
Reductive elimination	$L_n M(X)(Y) \rightarrow L_n M + X\text{-}Y$	-2	-2	-2	7-3
1,1-Insertion[a]	 $\overset{Y}{\overset{\vert}{L_n M}}\text{-}\underset{1}{X}{=}Z \rightarrow L_n M\text{-}\overset{Z}{\overset{\Vert}{\underset{1}{X}}}\text{-}Y$	0	-1	-2	8-1-1
1,2-Insertion[a]	 $\overset{Y}{\overset{\vert}{L_n M}}\text{-}\underset{Z^2}{\overset{X^1}{\Vert}} \rightarrow L_n M\text{-}\underset{1}{X}\text{-}\underset{2}{Z}\text{-}Y$	0	-1	-2	8-1-2
Nucleophilic addition[b]	 $L_n M\text{-}\underset{Z}{\overset{X}{\Vert}} + \text{Nuc:}^- \rightarrow [L_n M\text{-}X\text{-}Z\text{-}\text{Nuc}]^-$	0^c	0	0	8-2
Nucleophilic abstraction[b]	 $L_n M\overset{O}{\overset{\Vert}{C}}R + \text{Nuc-H} \rightarrow L_n M\text{-}H + \text{Nuc-}\overset{O}{\overset{\Vert}{C}}R$	0	0	0	8-3
Electrophilic addition[b]	$L_n M\text{-}X{=}Z + E^+ \rightarrow [L_n M{=}X\text{-}Z\text{-}E]^+$	0	0	0	8-4
Electrophilic abstraction[b]	 $L_n M\text{-}X\text{-}Z\text{-}Y + E^+ \rightarrow L_n M^+\text{-}\underset{Z}{\overset{X}{\Vert}} + E\text{-}Y$	0	0	0	8-4

[a] The reverse reaction, called *deinsertion* or *elimination*, is also possible.

[b] There is no one general reaction; several variations are possible.

[c] Depends upon change in hapticity; e.g., X=Z going from η3→η2 results in a 2 e⁻ reduction.

Ligand Substitution Reactions

Associative (A):

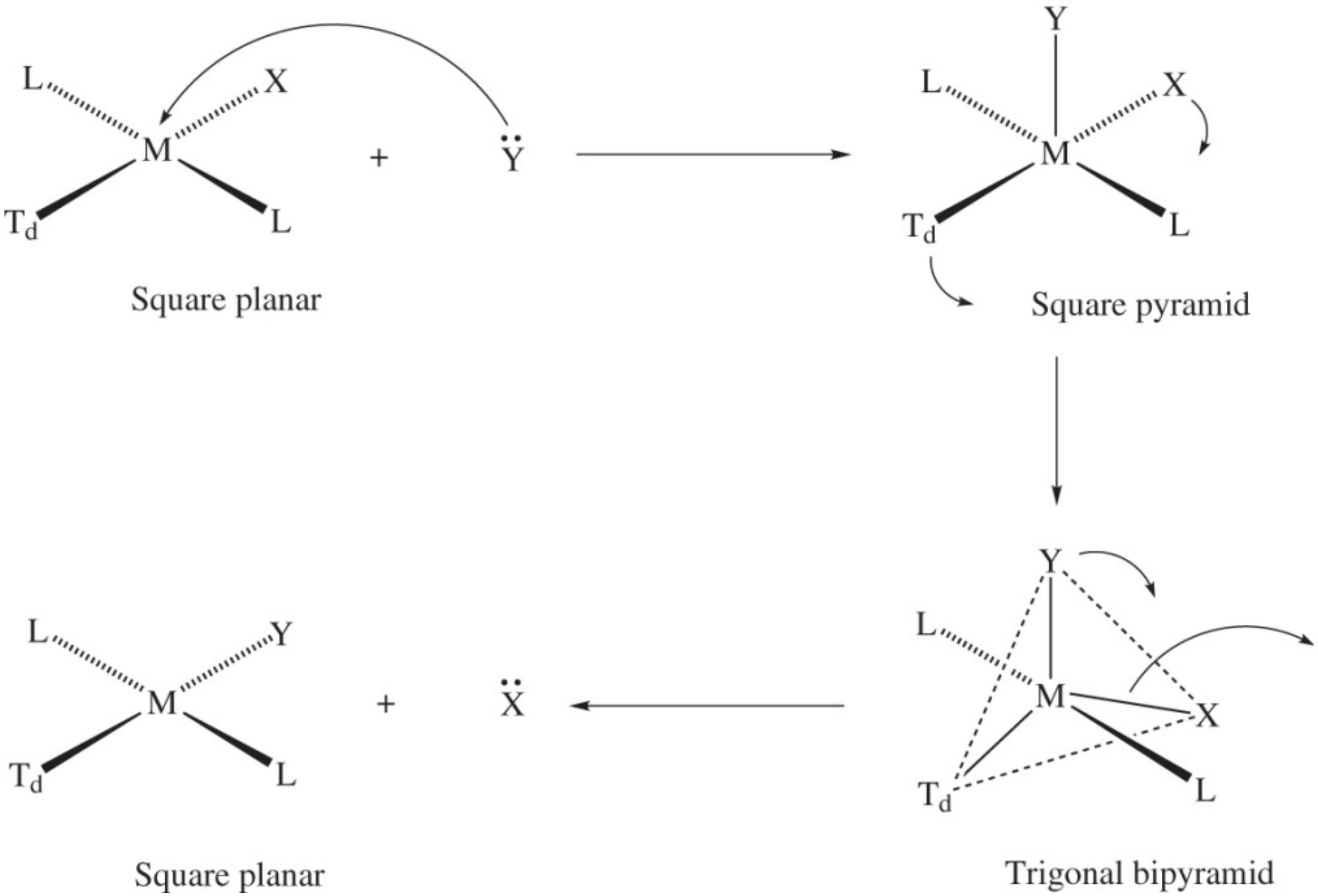
$$L_nML' + L'' \xrightarrow[\text{slow}]{} L_nML'L'' \xrightarrow[\text{fast}]{} L_nML'' + L'$$

Dissociative (D):

$$L_nML' \underset{\text{slow}}{\rightleftharpoons} L_nM + L' \xrightarrow[\text{fast}]{L''} L_nML''$$

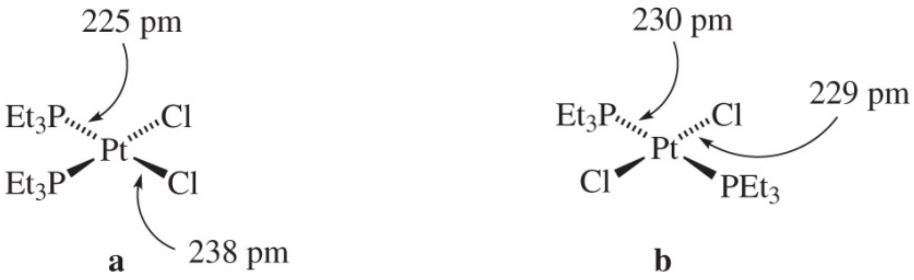
Illustration from page 178

Associative Process for Ligand Substitution in Square Planar Complex



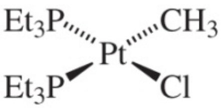
Question: What properties of T_d, X, Y facilitate this reaction??

Thermodynamic Trans Influence



ν (Pt-P) = 442 and 427 cm^{-1}
ν (Pt-Cl) = 303 and 281 cm^{-1}
J (Pt-P) = 3520 Hz

ν (Pt-P) = 415 cm^{-1}
ν (Pt-Cl) = 341 cm^{-1}
J (Pt-P) = 2400 Hz



c

J (Pt-P, PEt$_3$ *trans* to CH$_3$) = 1719 Hz
J (Pt-P, PEt$_3$ *trans* to Cl) = 4179 Hz

Figure 7-1 Spectral and Structural Characteristics of Pt(II) Complexes

Kinetic Trans Effect

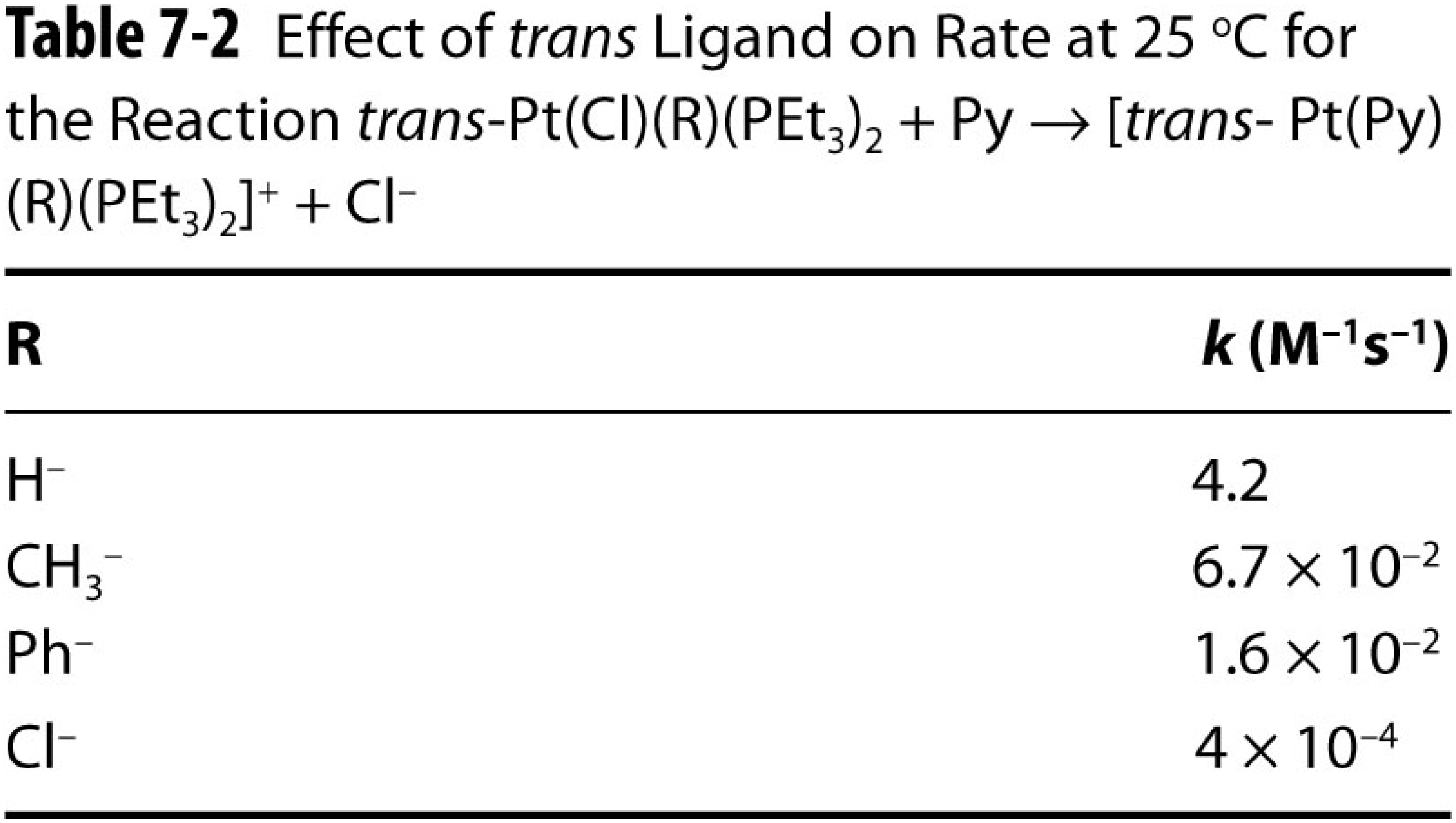
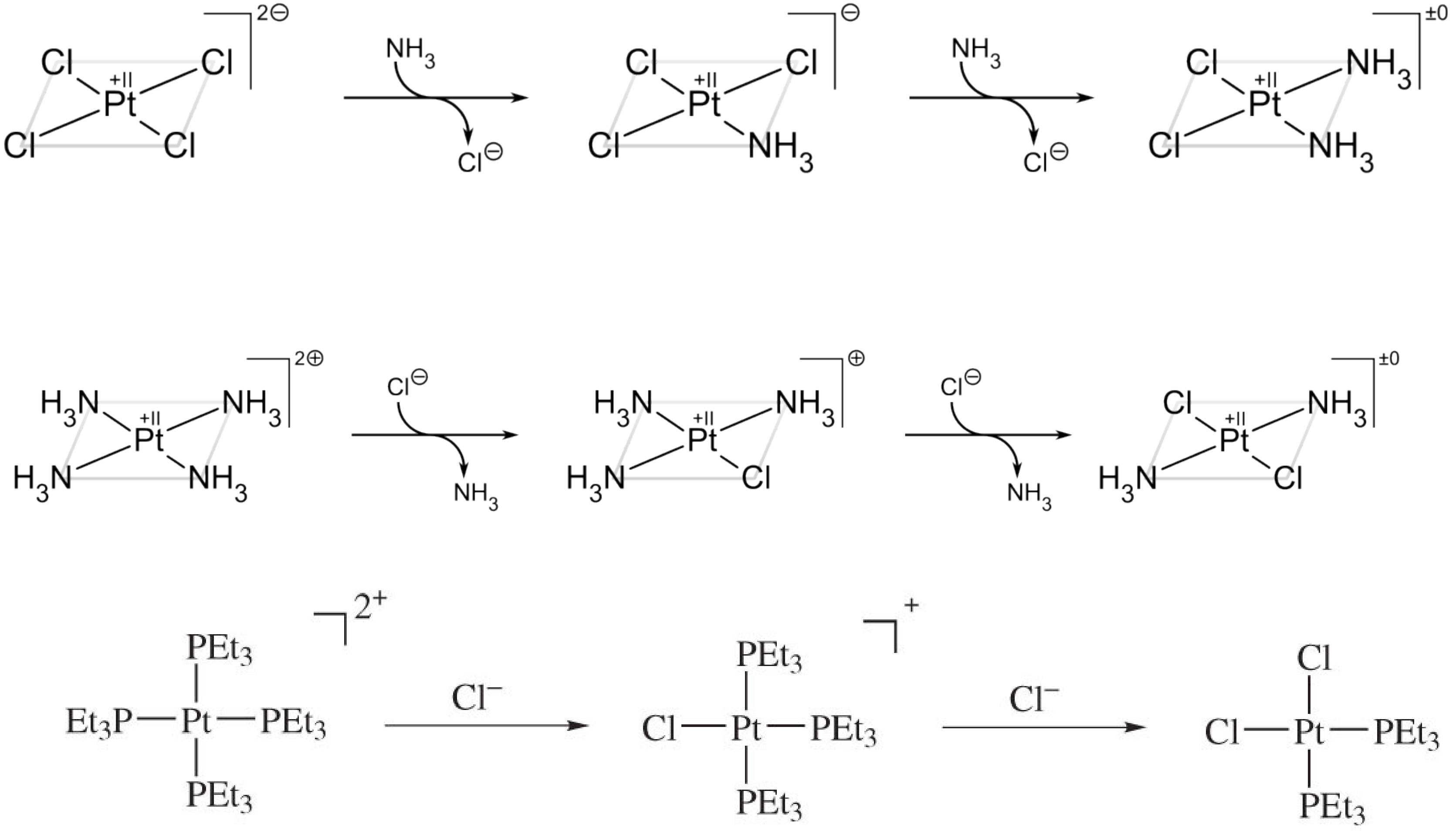


Table 7-2 Effect of *trans* Ligand on Rate at 25 °C for the Reaction *trans*-$Pt(Cl)(R)(PEt_3)_2 + Py \rightarrow$ [*trans*- $Pt(Py)(R)(PEt_3)_2]^+ + Cl^-$

R	***k*** **($M^{-1}s^{-1}$)**
H^-	4.2
CH_3^-	6.7×10^{-2}
Ph^-	1.6×10^{-2}
Cl^-	4×10^{-4}

Trans Effect: Applications in Synthesis



(weak) F^-, HO^-, H_2O <NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^-, $SC(NH_2)_2$, Ph^- < SO_3^{2-}< PR_3 < AsR_3, SR_2, H_3C^- < H^-, NO, CO, NC^-, C_2H_4 (strong)

Trans Effect and Influence: Reaction Profiles

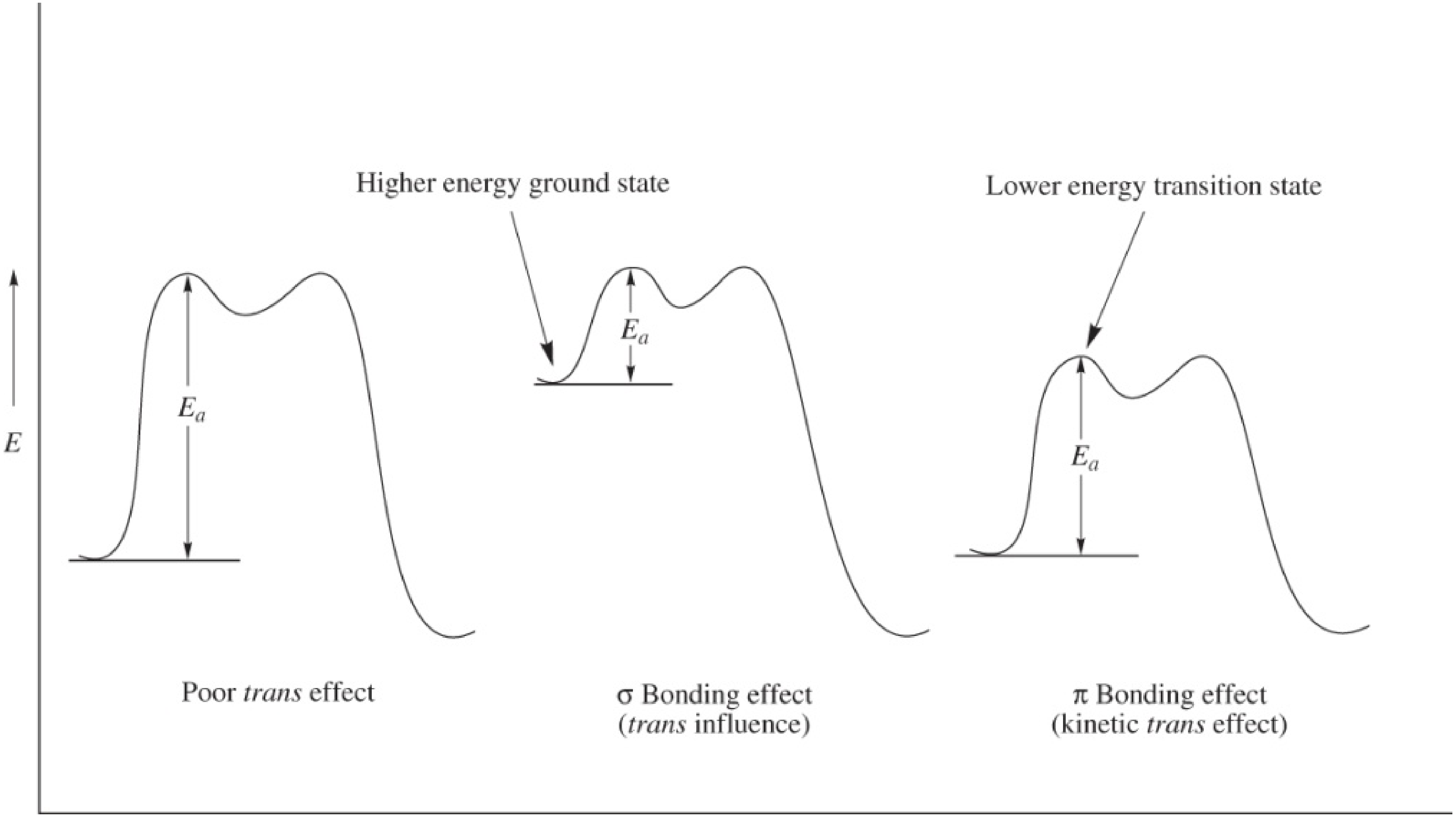
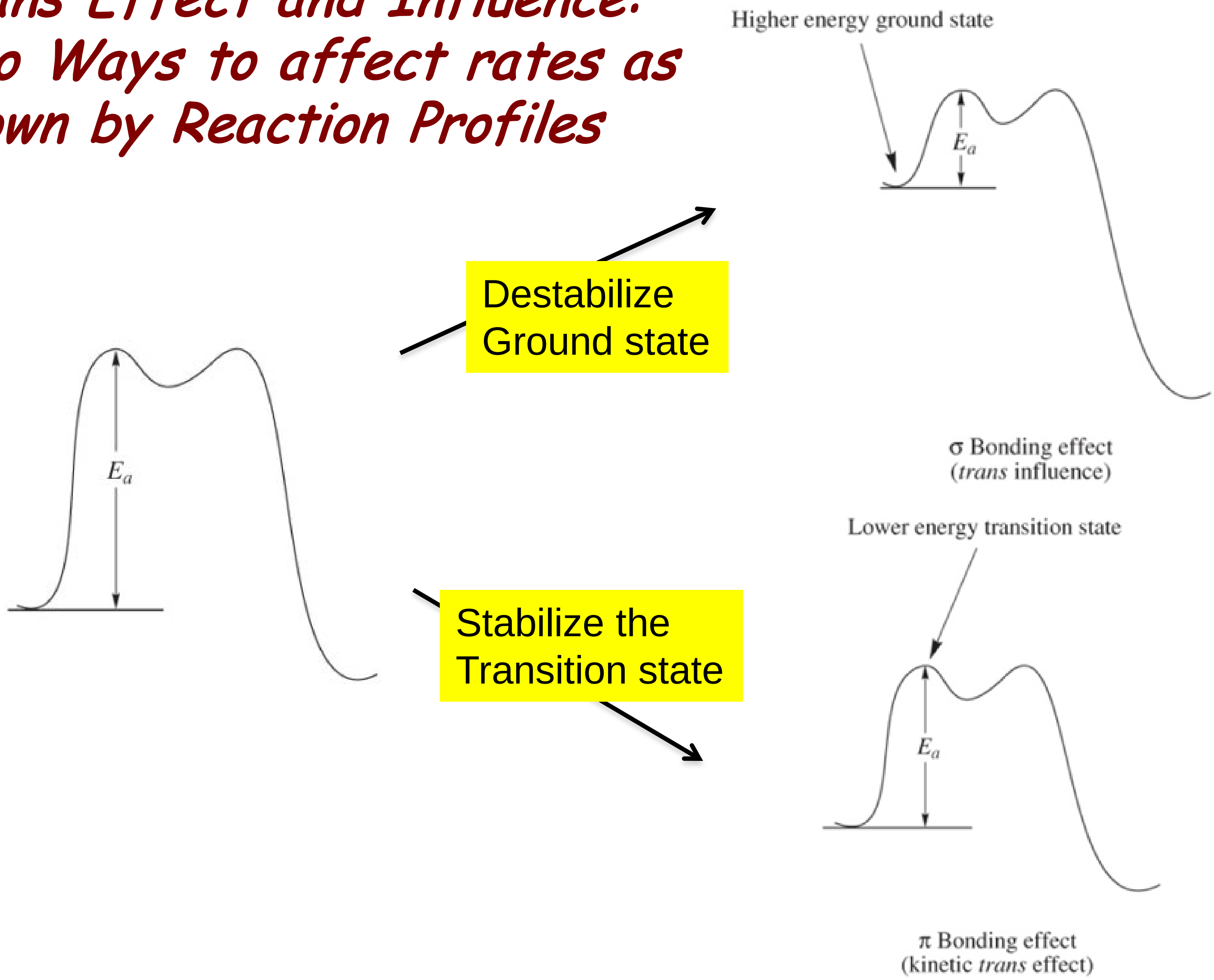


Figure 7-2 Activation Energy and the *trans* Effect The depth of the energy curve for the intermediate and the relative heights of the two maxima will vary with the specific reactants.

Trans Effect and Influence: Two Ways to affect rates as shown by Reaction Profiles



Destabilize Ground state

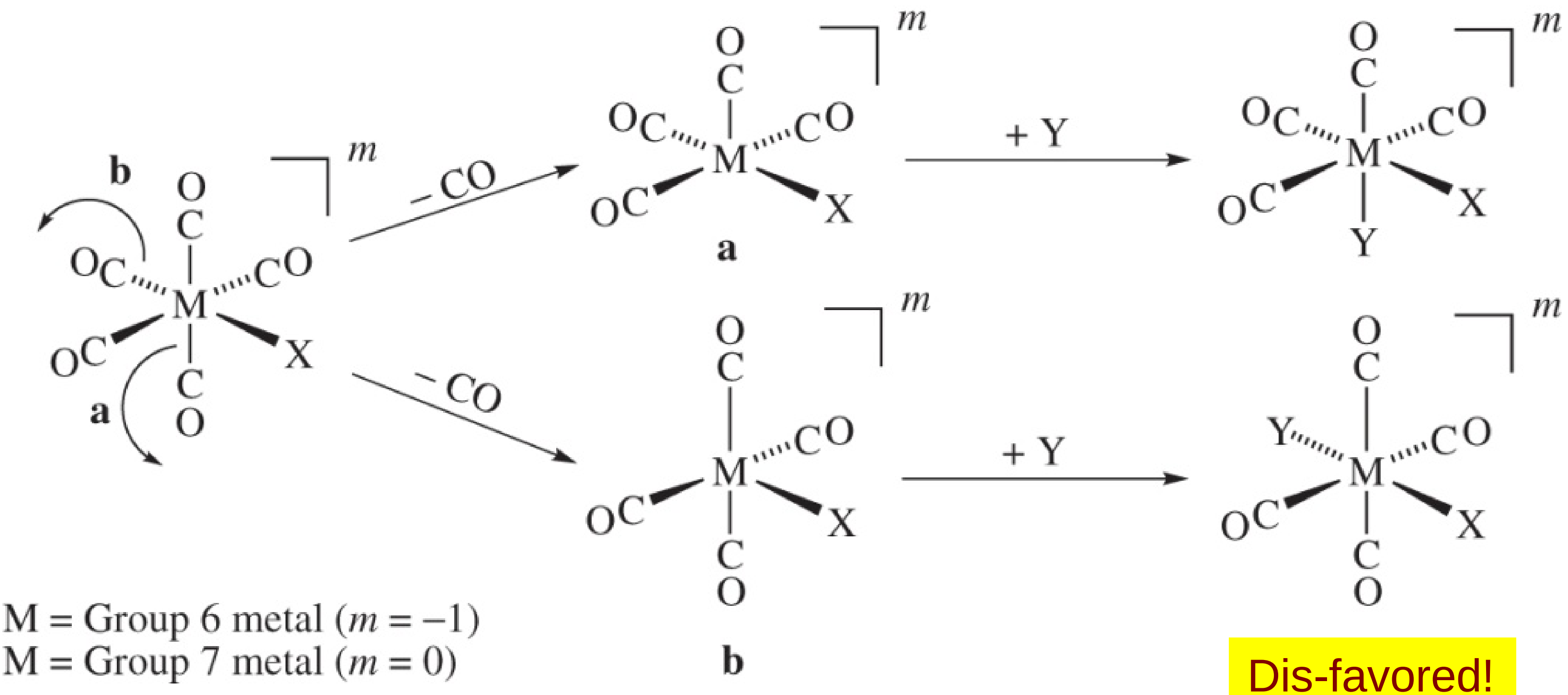
Stabilize the Transition state

σ Bonding effect
(*trans* influence)

π Bonding effect
(kinetic *trans* effect)

Figure 7-5 Intermediates in the Dissociative Substitution of $M(CO)_5X$ Complexes: cis-labilizing effect of X ligands

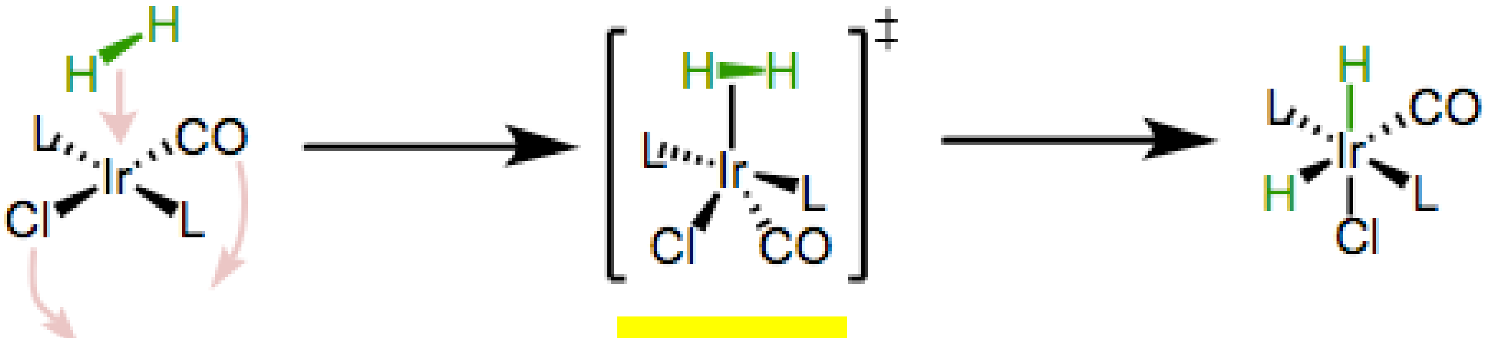
Favored!



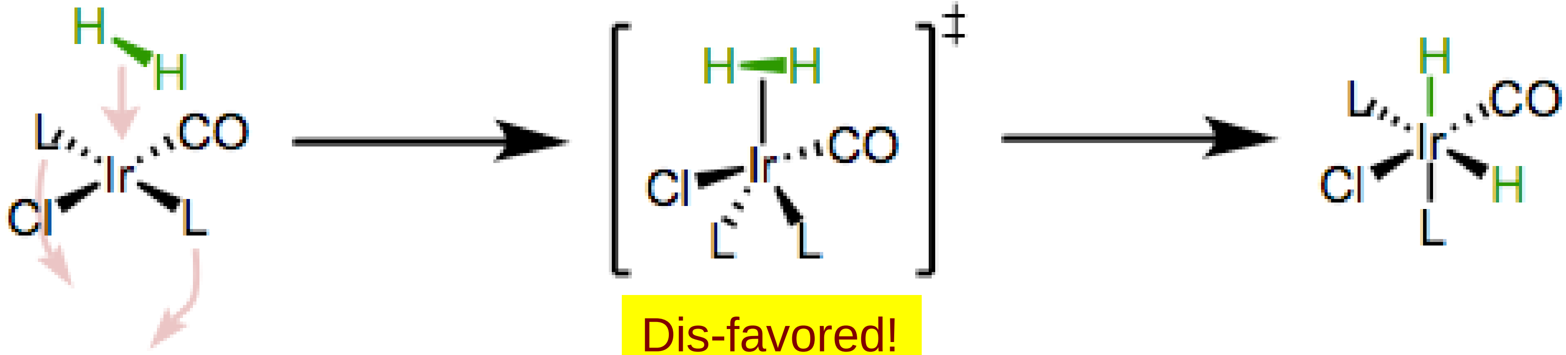
M = Group 6 metal ($m = -1$)
M = Group 7 metal ($m = 0$)

Dis-favored!

The importance of the transition state in H_2 oxidative addition



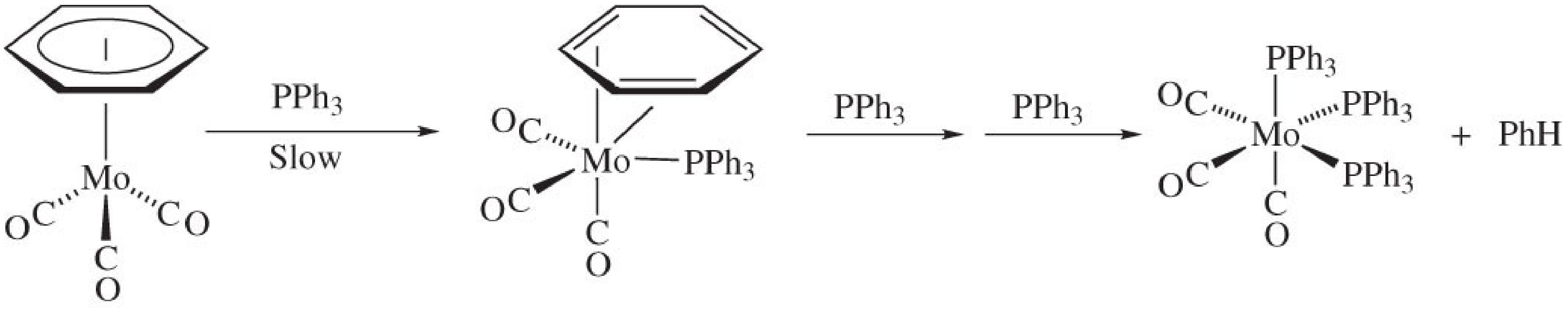
Favored!

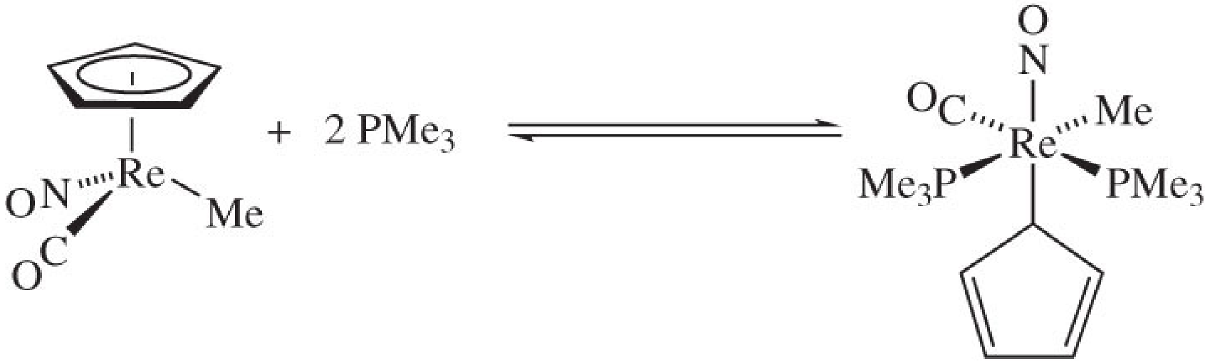


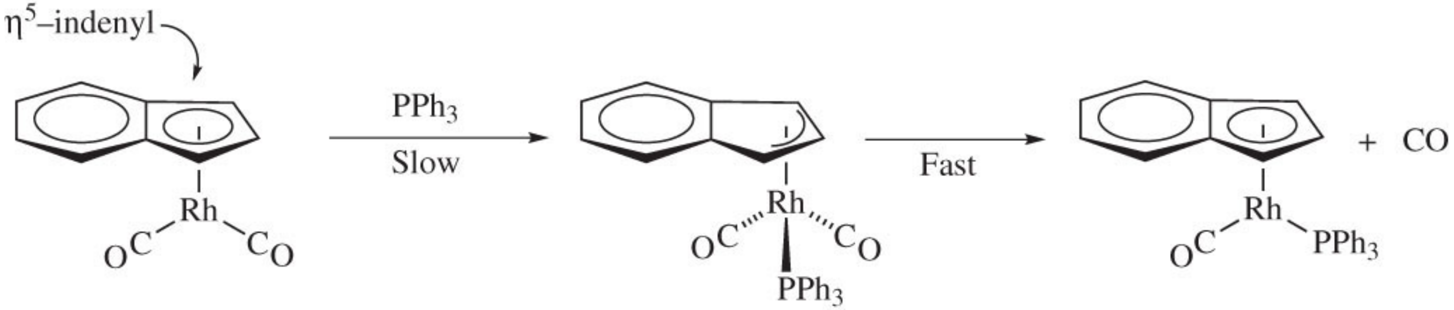
Dis-favored!

What are the factors that favor the cis vs. trans-$L_2Ir(CO)(Cl)(H)_2$ isomers?

Associative Ligand Substitution Reactions in 18-electron complexes: Does not use 20-e intermediates







Classic Dissociative Reaction

Dissociative Reactions: rate = $k[M\text{-}CO]^1$

$$cis\text{-}Mo(CO)_4(PR_3)_2 \quad + \quad CO \longrightarrow Mo(CO)_5(PR_3) + PR_3$$

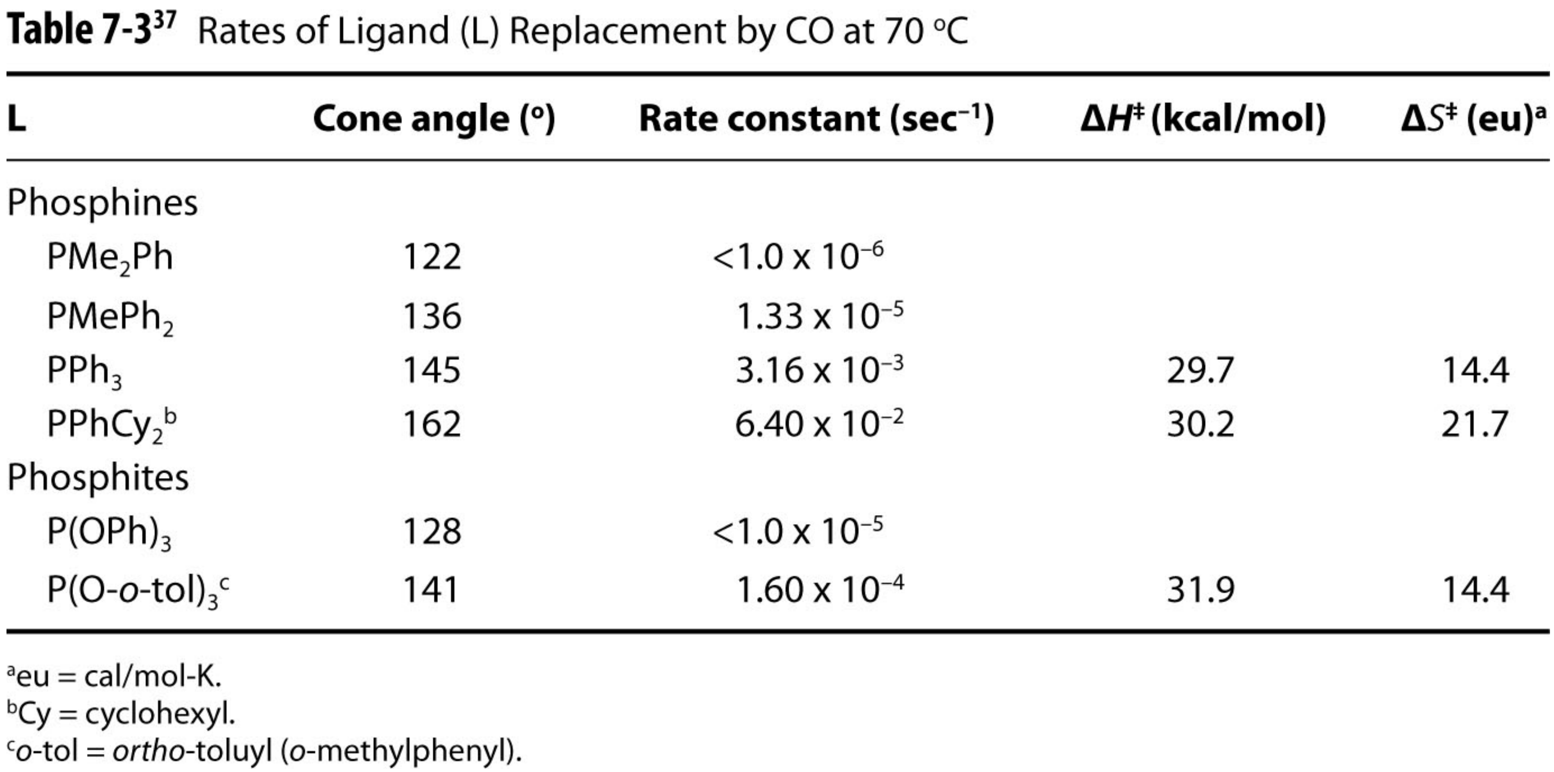


Table 7-3[37] Rates of Ligand (L) Replacement by CO at 70 °C

L	Cone angle (°)	Rate constant (sec^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)[a]
Phosphines				
PMe_2Ph	122	$<1.0 \times 10^{-6}$		
$PMePh_2$	136	1.33×10^{-5}		
PPh_3	145	3.16×10^{-3}	29.7	14.4
$PPhCy_2$[b]	162	6.40×10^{-2}	30.2	21.7
Phosphites				
$P(OPh)_3$	128	$<1.0 \times 10^{-5}$		
$P(O\text{-}o\text{-}tol)_3$[c]	141	1.60×10^{-4}	31.9	14.4

[a] eu = cal/mol-K.

[b] Cy = cyclohexyl.

[c] *o*-tol = *ortho*-toluyl (*o*-methylphenyl).

Competing Dissociative and Interchange-Dissoc. Reaction Pathways

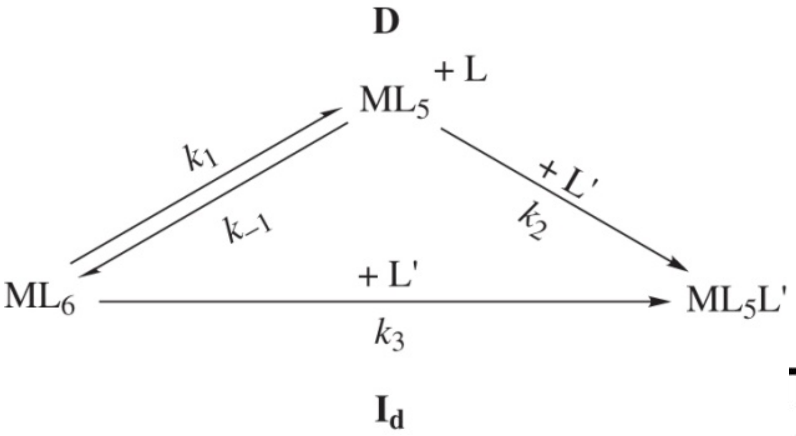


Table 7-4[a] Activation Parameters for Ligand Substitution of $M(CO)_6$ with PBu_3

M	$\Delta H_1^{\ddagger b}$	$\Delta S_1^{\ddagger c}$	$\Delta H_3^{\ddagger}$	$\Delta S_3^{\ddagger}$
Cr	40.2	22	25.5	–15
Mo	31.6	6.7	21.7	–15
W	39.9	14	29.2	–6.9

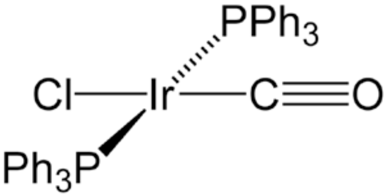
[a] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **1966**, *88*, 3658 and R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **1967**, *6*, 2082.

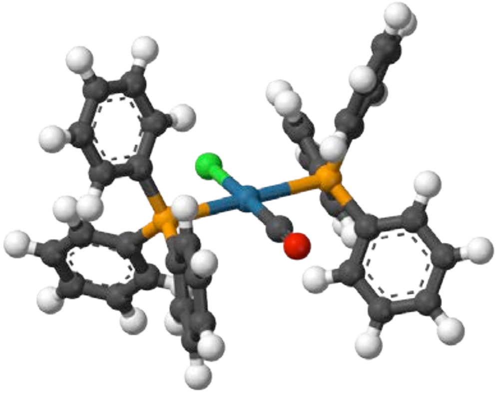
[b] kcal/mol.

[c] Entropy units (eu), cal/mol-K.

Vaska's complex

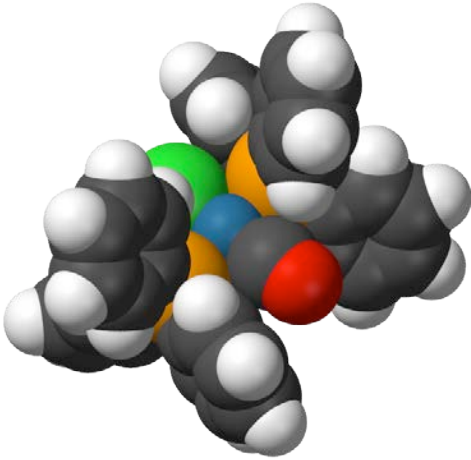
trans-$IrCl(CO)[P(C_6H_5)_3]_2$



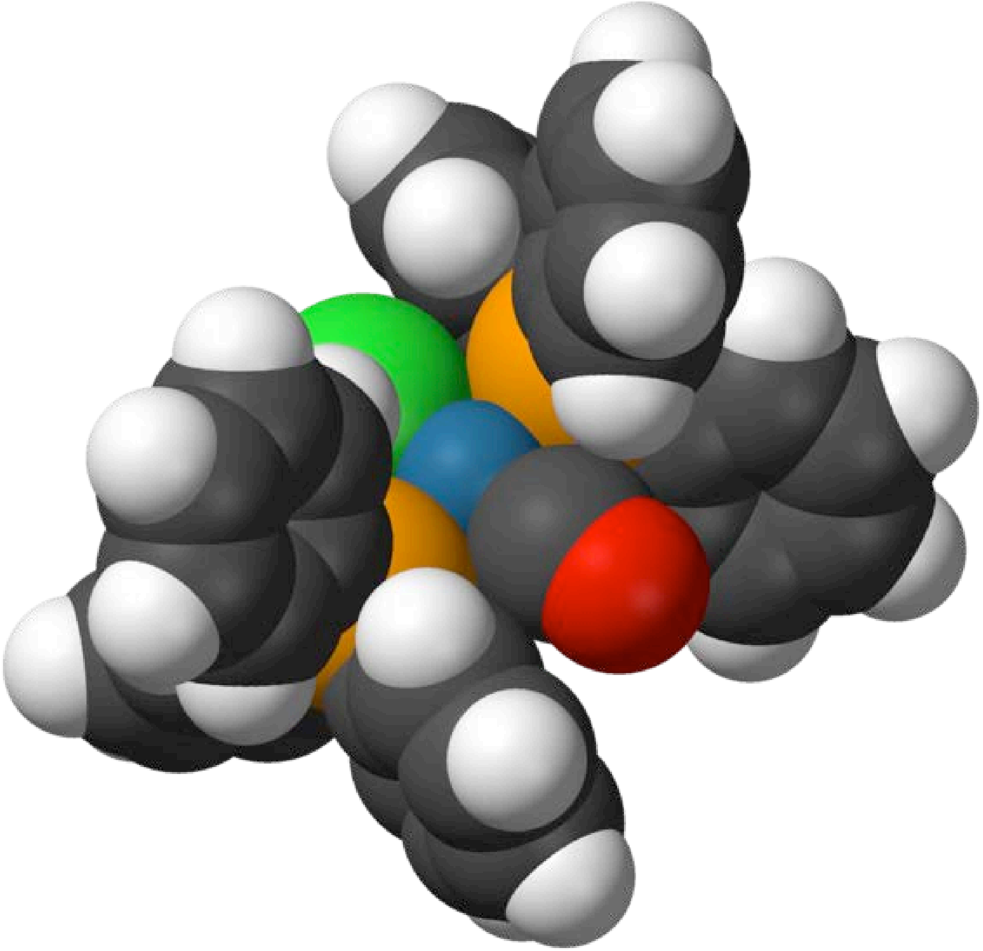


Synthesis might be trans-effect directed: $Ir(PR_3)_4^+$ + ?

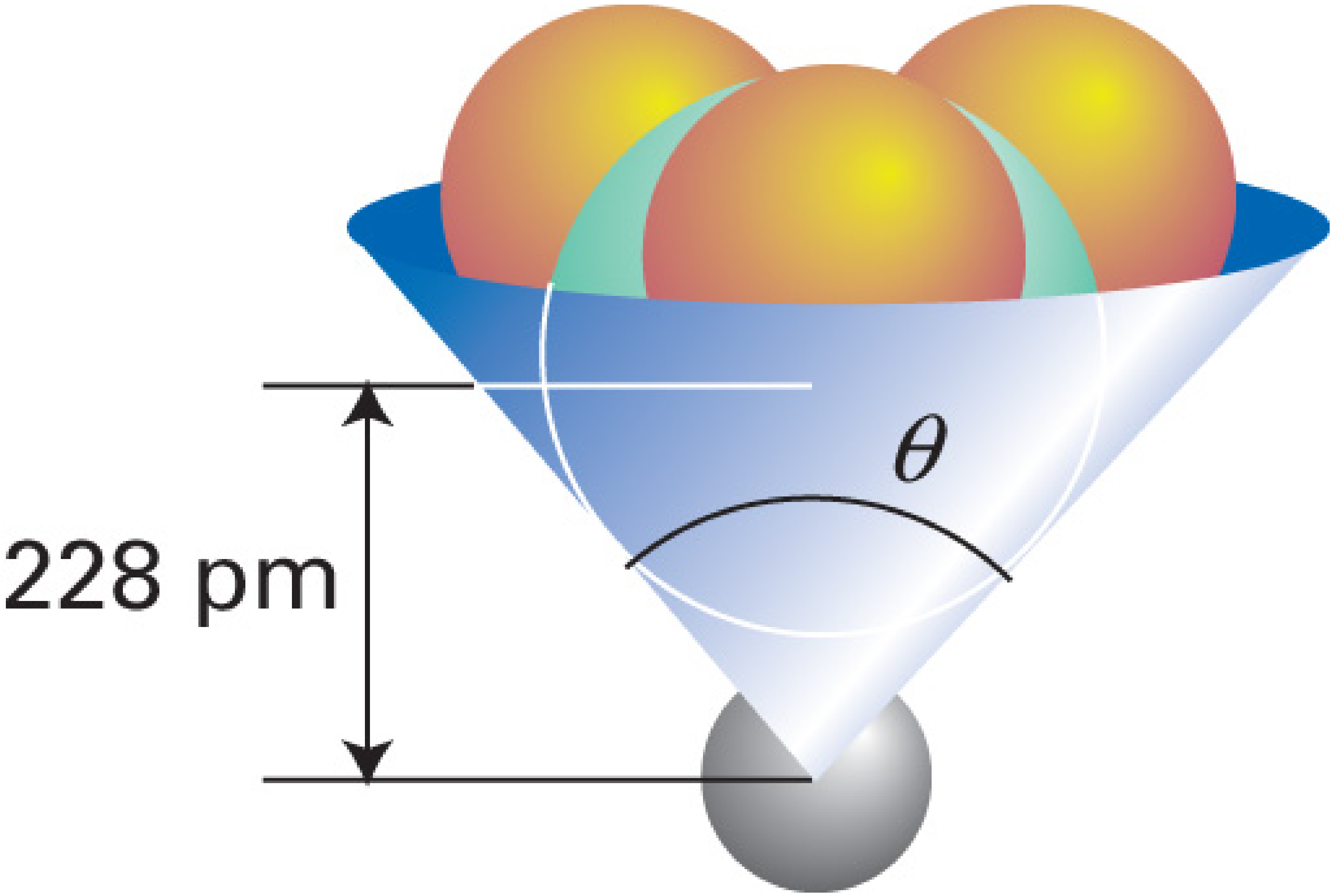
Problems: PPh_3 ligand is too large; CONE ANGLE = 145°



Space-filling model of Vaska's Complex



Inorganic Chemistry Chapter 1: Figure 21.12



Inorganic Chemistry Chapter 1: Table 21.7

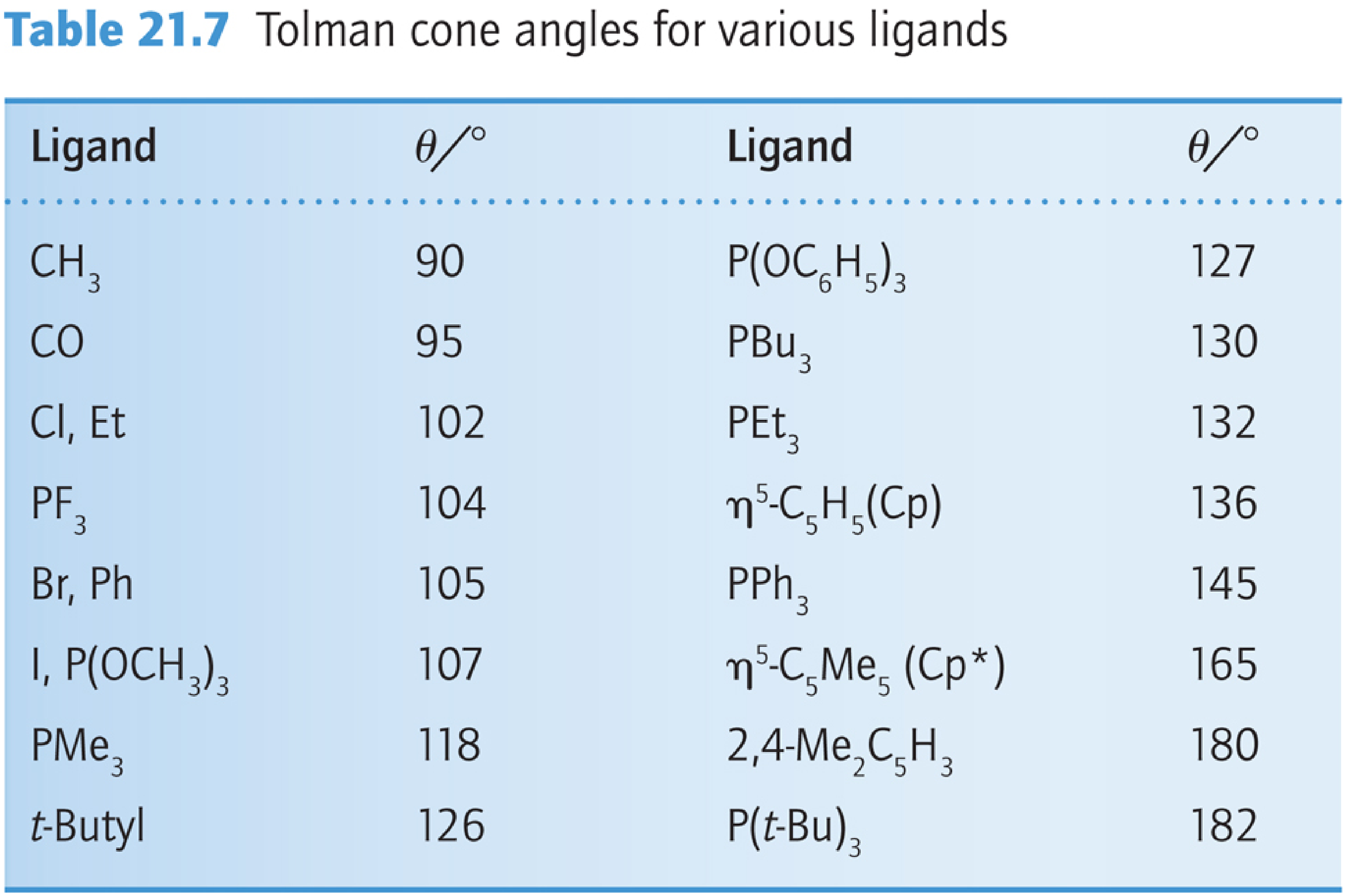
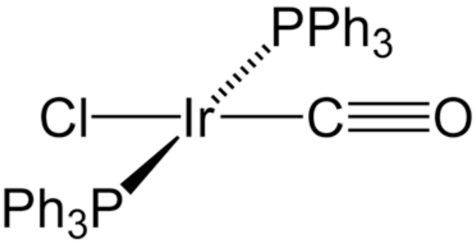


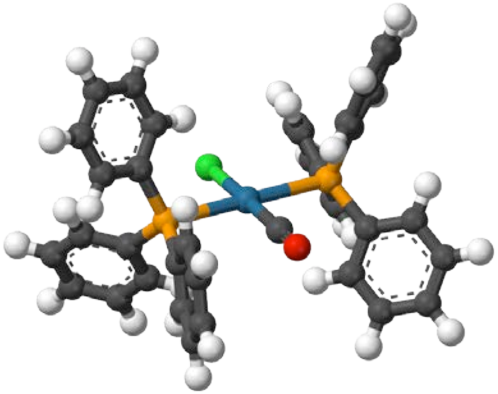
Table 21.7 Tolman cone angles for various ligands

Ligand	$\theta/°$	Ligand	$\theta/°$
CH_3	90	$P(OC_6H_5)_3$	127
CO	95	PBu_3	130
Cl, Et	102	PEt_3	132
PF_3	104	η^5-C_5H_5(Cp)	136
Br, Ph	105	PPh_3	145
I, $P(OCH_3)_3$	107	η^5-C_5Me_5 (Cp*)	165
PMe_3	118	2,4-$Me_2C_5H_3$	180
t-Butyl	126	P(*t*-Bu)$_3$	182

Vaska's complex

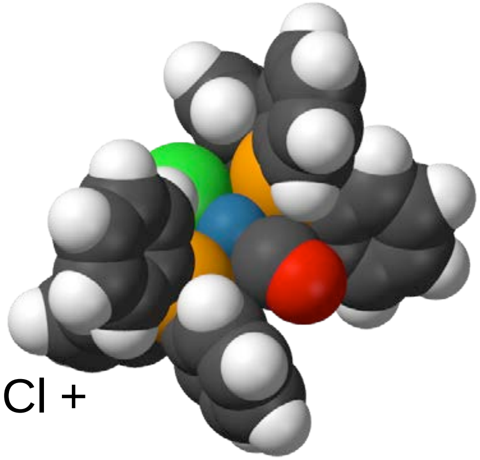
trans-$IrCl(CO)[P(C_6H_5)_3]_2$





Synthesis might be trans-effect directed: $Ir(PR_3)_4^+$ + ?

Problems: PPh_3 ligand is too large; CONE ANGLE = 145°



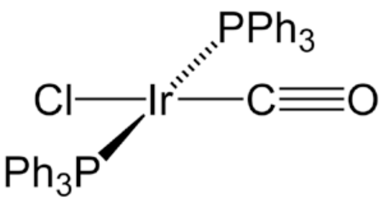
Alternate way:

$IrCl_3(H_2O)_3 + 3\ P(C_6H_5)_3 + HCON(CH_3)_2 + C_6H_5NH_2 \longrightarrow$

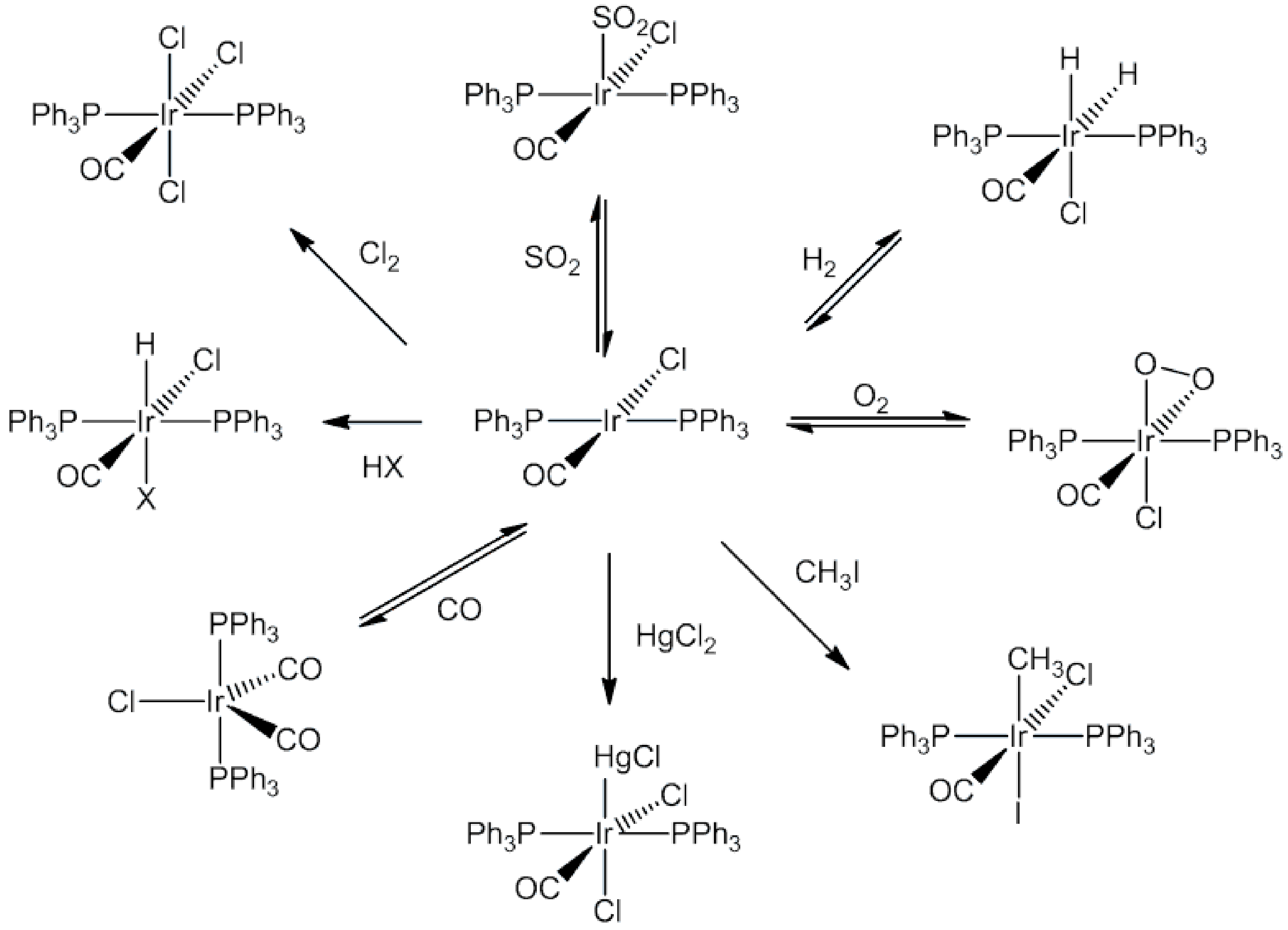
$IrCl(CO)[P(C_6H_5)_3]_2 + [(CH_3)_2NH_2]Cl + OP(C_6H_5)_3 + [C_6H_5NH_3]Cl + 2\ H_2O$

Why 3 PPh_3?

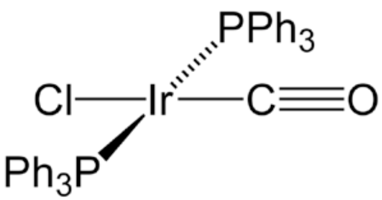
Vaska's complex trans-$IrCl(CO)[P(C_6H_5)_3]_2$



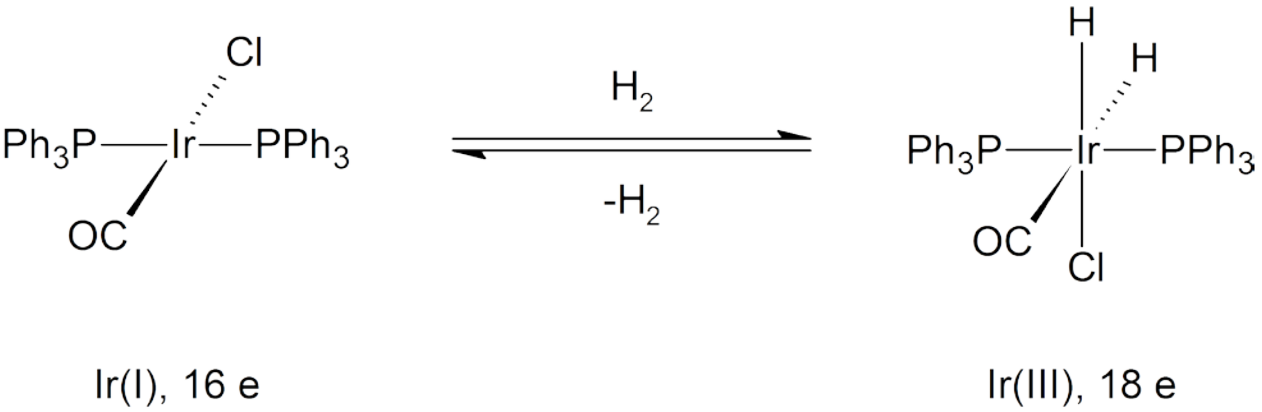
Vaska's complex helped provide the conceptual framework for homogeneous catalysis.

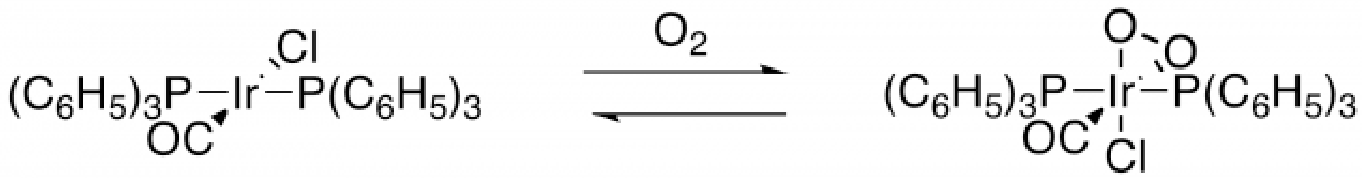


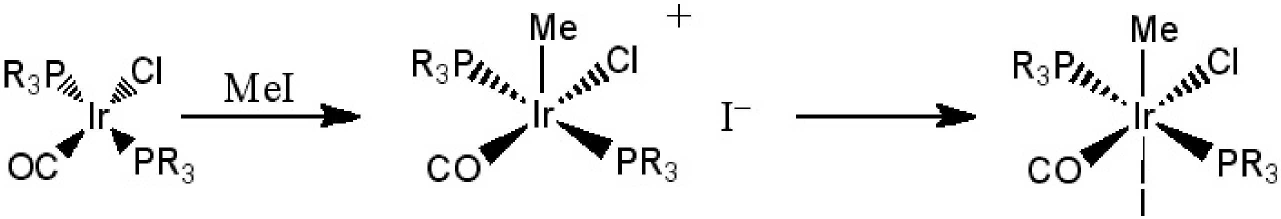
Vaska's complex trans-$IrCl(CO)[P(C_6H_5)_3]_2$



Vaska's complex helped provide the conceptual framework for homogeneous catalysis.







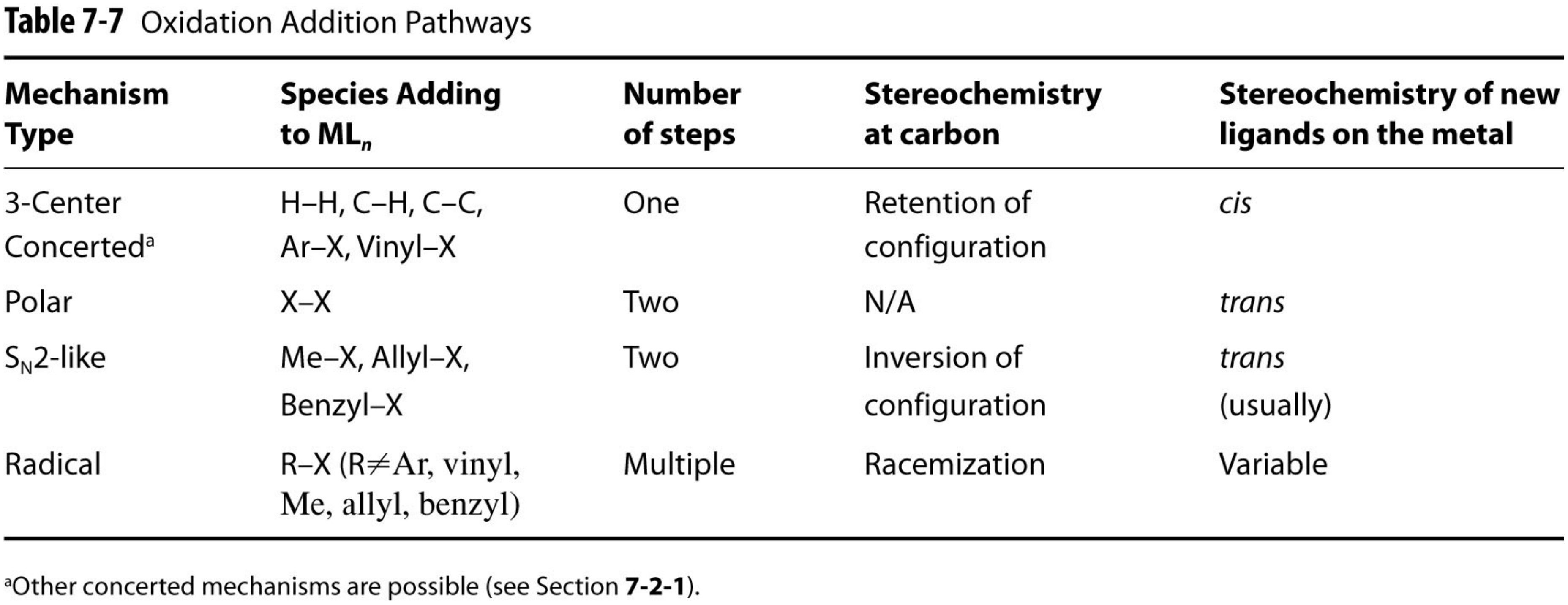
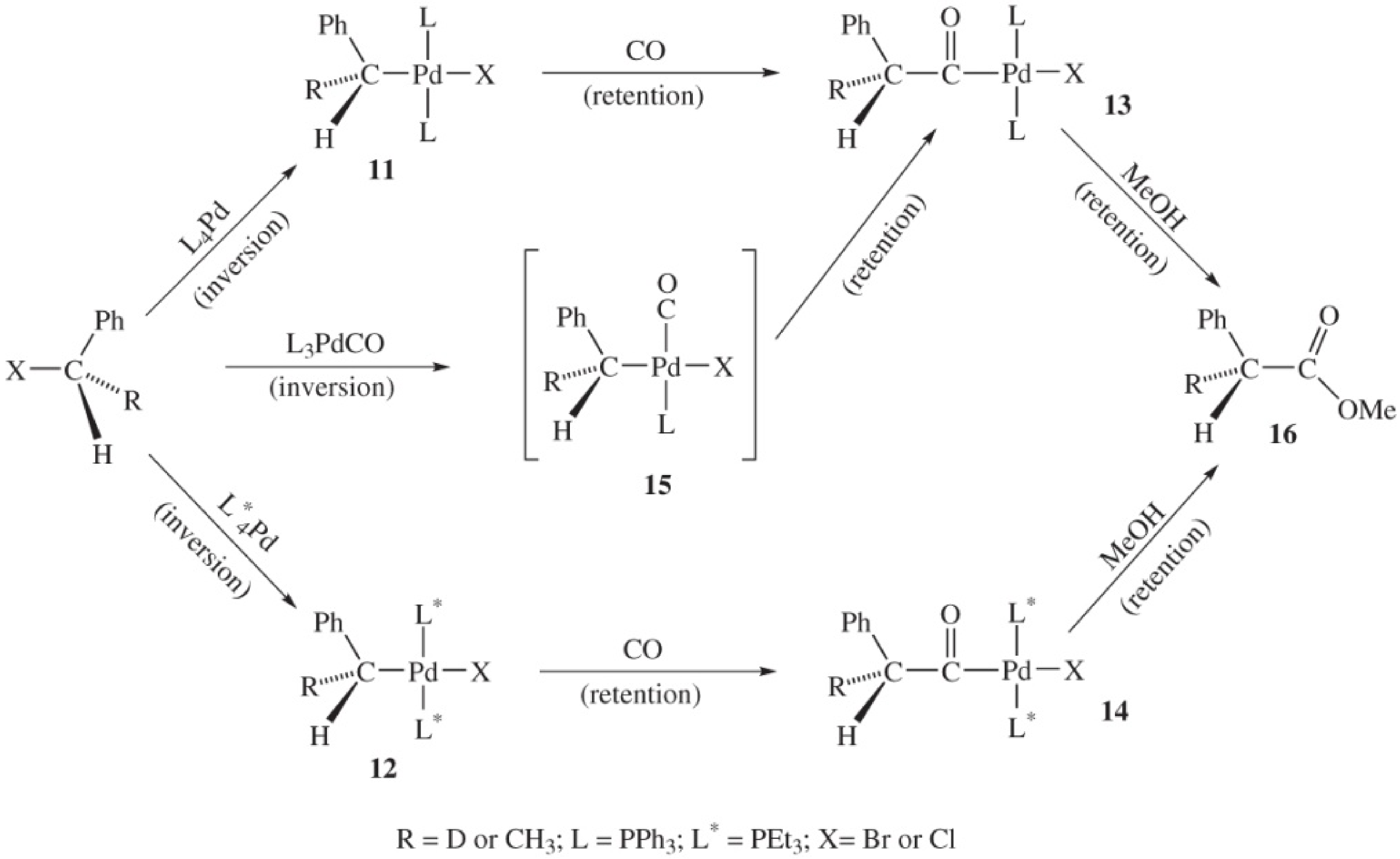


Table 7-7 Oxidation Addition Pathways

Mechanism Type	**Species Adding to ML$_n$**	**Number of steps**	**Stereochemistry at carbon**	**Stereochemistry of new ligands on the metal**
3-Center Concerted[a]	H–H, C–H, C–C, Ar–X, Vinyl–X	One	Retention of configuration	*cis*
Polar	X–X	Two	N/A	*trans*
S_N2-like	Me–X, Allyl–X, Benzyl–X	Two	Inversion of configuration	*trans* (usually)
Radical	R–X (R≠Ar, vinyl, Me, allyl, benzyl)	Multiple	Racemization	Variable

[a] Other concerted mechanisms are possible (see Section **7-2-1**).

John Stille: Oxidative Addition to Pd° Complexes



R = D or CH_3; L = PPh_3; L* = PEt_3; X= Br or Cl

Scheme 7.7 Stereospecific Reactions of Palladium Complexes

Basic Transformations in Organometallic Chemistry

1. ligand substitution

$$L_nM^q\text{-}L \rightleftharpoons [L_nM^q] + L \qquad \text{dissociative}$$

$$L_nM^q\text{-}L + L' \rightleftharpoons L_nM^q\text{-}L' + L \qquad \text{associative}$$

2. external attack at ligands by nucleophiles and electrophiles

$$L_nM^{q/q\text{-}2}{=}X + \ddot{N}u^- \rightleftharpoons L_n\ddot{M}^{q\text{-}2}{-}X{-}Nu]^-$$

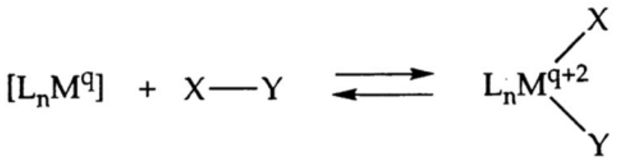
(X = CO, CNR, CR_2, *etc.*; $Nu^- = R^-, OR^-$, *etc;*)

$$L_nM^q{=}X + E^+ \rightleftharpoons L_nM^q{-}X{-}E]^+$$

(X = olefin, acetylene, oxo, *etc*; $E^+ = H^+, R^+$, *etc*)

$$L_nM^q{-}R + \ddot{N}u^- \rightleftharpoons [L_n\ddot{M}^{q\text{-}2}]^- + RNu$$

3. oxidative addition/reductive elimination * (X-Y = H_2, R-H, H-Cl, R-Br, *etc*)



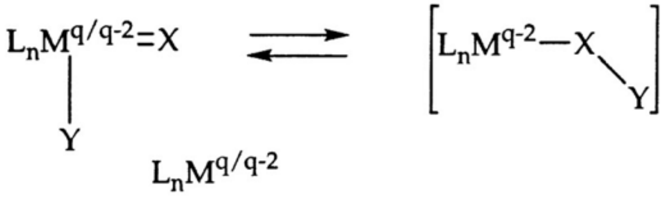
$$[L_nM^q] + X{-}Y \rightleftharpoons L_nM^{q+2}(X)(Y)$$

(*involves change in electron count and valency at metal of 2)

J.E. Ber

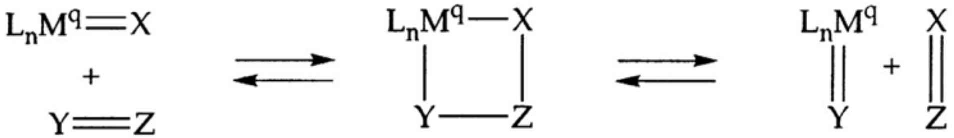
Basic Transformations in Organometallic Chemistry

4. α migratory insertion/elimination (X = CO, CNR, CR_2, NR, O; Y = H, R, OR, *etc*)



5. β migratory insertion/elimination (X = H, R; Y = Z = olefin, ketone, *etc*)

6. reversible 2+2 addition (X = CR_2, NR, O; Y=Z = olefin, ketone, *etc*)



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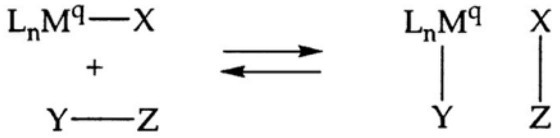
Basic Transformations in Organometallic Chemistry

7. σ bond metathesis (X,Y = H, R; Z = H)



8. "1,2 addition/elimination" (X = O, NR, CR_2; Y-Z = RO-H, H_2, R-H)