Carbon chemistry - 8 electron stable
7 electron reactive
6 electron reactive

Metal chemistry - 18 electron stable
16 electron reactive
14 electron very reactive

But some metals favor 16 Electron: Rhodium
A few metals favor 14e-: Gold
Transition metal reaction mechanisms can be divided into fundamental reaction types.

(page 1012 - 1014 in book)
beta-hydride elimination
Oxidative Addition

R\textsubscript{3}P–Rh–PR\textsubscript{3}

H\textsubscript{2}

Reductive elimination

R\textsubscript{3}P–Rh–H

HCl

Cl\textsubscript{2}

CH\textsubscript{3}Cl
Oxidative Coupling

Reductive Decoupling
How many e⁻?

A 12  B 13  C 14  D 15  E 16  F 17  G 18  H 20
Classify this reaction

A. Ligand Association  B. Ligand Dissociation
C. Ligand Insertion   D. Ligand Deinsertion
E. Oxidative Addition  F. Reductive Elimination
G. Oxidative Coupling  H. Reductive Decoupling
How many e⁻?

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A. Ligand Association  B. Ligand Dissociation
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beta-hydride elimination

Classify this reaction

A. Ligand Association  B. Ligand Dissociation
C. Ligand Insertion   D. Ligand Deinsertion
E. Oxidative Addition F. Reductive Elimination
G. Oxidative Coupling H. Reductive Decoupling
Monsanto Acetic Acid Process

\[ \text{CH}_3\text{OH} + \text{C} \equiv \text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} \]

Rh catalyst

3.75 million tons / year made with this catalyst
(or a related Ir catalyst)

\[ \begin{array}{c}
\text{Rh(1)} \quad 8 \text{ e-} \\
\text{CO} \quad 2 \quad 4 \text{ e-} \\
\text{I}^{-1} \quad 2 \quad 4 \text{ e-} \\
\text{total} \quad 16 \text{ e-}
\end{array} \]

Rh catalyst

+ HI co-catalyst
You can also use Iridium
Write a cyclic mechanism for the above reaction. Give the electron count of each intermediate of the catalytic cycle. Classify each step in your reaction cycle by fundamental reaction type:

Ligand Dissociation or Association, Ligand insertion or deinsertion, oxidative addition or reductive elimination.
Homework Assignment

\[ \text{Homework Assignment} \]

\[ \text{Wilkinson’s catalyst} \]
Organometallic Coupling Reactions used in Organic Synthesis

X = halide or triflate

Heck Reaction
The active catalyst is Pd(0)
Which step is oxidative addition?
Which step is reductive elimination?
Which step is ligand association?
Which step is ligand insertion?
Which step is ligand deinsertion?
What is the “expected” product?

Actual product

Syn addition and Syn elimination
Suzuki Reaction

vinyl or aryl halide or triflate

vinyl or aryl boronic acid

boric acid
\[
\text{B(OH}_2\text{)} \quad \begin{array}{c}
\text{HBr} \\
\text{1 mol}
\end{array} \\
\text{Pd(OAc)}_2 \quad \text{PPh}_3, \text{NEt}_3
\]
Hydroboration of alkynes

HOD

H2O2, OH−

A
B
C
D
E
F
Hydroboration of alkynes

\[ \text{HB(sia)}_2 \rightarrow \text{HB(sia)}_2 \]

secondary isoamyl HB(sia)_2

9-borabicyclononane 9-BBN
catecholborane
Hydroboration of alkynes

\[
\text{H} + \text{MgBr} \rightarrow \text{Li} + B(OCH}\text{CH}_3)_3
\]

1. B(OCH\text{CH}_3)_3
2. H^+

\[
\text{B(OCH\text{CH}_3)_3} \rightarrow \text{B(OH)}_2
\]

**Example Reactions:**

- **Catecholborane (\text{B(OCH}_3)_3**)
  - + H^+ → \text{B(OH)}_2
  - + Li → \text{B(OH)}_2
Vinyl Triflates

\[
\text{Ketone} \xrightarrow{\text{Tf}_2\text{O}} \text{Vinyl triflate}
\]

\[
\begin{align*}
\text{OTf} & \quad \text{Tf}_2\text{O} \\
\text{HOTf} & \quad \text{HOTf} \\
\end{align*}
\]