Functionalization of terminal olefins via H migratory insertion /reductive elimination sequence

**Hydrogenation**

$$\text{RCH} \equiv + H - H \rightarrow [\text{RCH} \equiv \text{H} + \text{H} \rightarrow [\text{RCH} \equiv \text{H} + \text{ML}_n \text{H}] \rightarrow \text{RCH} \equiv \text{H} \rightarrow \text{RCH} \equiv \text{H}$$

**Hydroisilylation**

$$\text{RCH} \equiv + H - \text{SiR}_3 \rightarrow [\text{RCH} \equiv \text{H} \rightarrow [\text{RCH} \equiv \text{H} + \text{SiR}_3 \rightarrow \text{RCH} \equiv \text{SiR}_3] \rightarrow \text{RCH} \equiv \text{SiR}_3$$

**Hydrocyanation**

$$\text{RCH} \equiv + H - \text{CN} \rightarrow [\text{RCH} \equiv \text{H} \rightarrow [\text{RCH} \equiv \text{H} + \text{CN} \rightarrow \text{RCH} \equiv \text{CN}] \rightarrow \text{RCH} \equiv \text{CN}$$

**Hydroacylation**

$$\text{RCH} \equiv + H - \text{C} = \text{O} \rightarrow [\text{RCH} \equiv \text{H} \rightarrow [\text{RCH} \equiv \text{H} + \text{C} = \text{O} \rightarrow \text{RCH} \equiv \text{C} = \text{O}] \rightarrow \text{RCH} \equiv \text{C} = \text{O}$$

**Hydroformylation**

$$\text{RCH} \equiv + H - H + \text{O} - \text{C} \rightarrow [\text{RCH} \equiv \text{H} \rightarrow [\text{RCH} \equiv \text{H} + \text{C} = \text{O} \rightarrow \text{RCH} \equiv \text{C} = \text{O} \rightarrow \text{RCH} \equiv \text{C} = \text{O}] \rightarrow \text{RCH} \equiv \text{C} = \text{O}$$
Wilkinson’s Catalyst

**Hydrogenations: OA of H₂**

\[
\text{R} = \overset{\text{cat.}}{\text{Ph₃P}}\overset{(I)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} + \overset{\text{cat.}}{\text{Ph₃P}}\overset{(III)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} \rightarrow \text{R-H}
\]

\[
\text{RX} \rightarrow \text{H₂ (1 atm), benzene, rt, quantitative}
\]

**Hydrosilylations: OA of R₃Si-H**

\[
\text{R} = \overset{\text{cat.}}{\text{Ph₃P}}\overset{(I)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} + \overset{\text{cat.}}{\text{Ph₃P}}\overset{(III)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} \rightarrow \text{R-SiR₃}
\]

**Hydroacylation: OA of RC(\text{"O")-H**

\[
\text{R} = \overset{\text{cat.}}{\text{Ph₃P}}\overset{(I)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} + \overset{\text{cat.}}{\text{Ph₃P}}\overset{(III)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} \rightarrow \text{Ph-N=N-Ph}
\]

**Hydroformylation**

\[
\text{R} = \overset{\text{cat.}}{\text{Ph₃P}}\overset{(I)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} + \overset{\text{cat.}}{\text{Ph₃P}}\overset{(III)}{\text{Rh}}\overset{\text{Cl}}{\text{Cl}} \rightarrow \text{H-O-C}
\]

Rapid PR₃/CO ligand exchange occurs with Wilkinson's catalyst under a CO atmosphere (Rh has a high affinity for CO). CO's are strong π-acids and may serve to disfavor OA of H₂ to generate a Rh(III) dihydride.
**Hydrogenation via σ-bond metatheses: Ru(II) catalysts**

*Wilkinson's Ru catalyst*

Monohydride identified as active catalyst: Formation of Ru(IV) dihydride is prohibitively high in energy.

*Noyori's Ru catalyst*

Possible monohydride hydrogenation mechanisms (Hydrogenations, pg. 156).

- **σ-bond metathesis**
  - no oxidation state change

- **Base-promoted heterolytic cleavage**

- **Protonolysis**
Rate of migratory insertion into olefin: $M-H > > M-C$

The difference of 10.3 kcal/mol in the free energy of activation of ethyl vs hydride migratory insertion into ethylene in these systems corresponds to a rate ratio of $k_{HMI}/k_{ELMI}$ of $10^7-10^8$. The effect is thought to be kinetic in nature.

**Rationalization:** Better overlap is possible because of non-directionality of the H orbital.

Note: at the TS of olefin insertion, both $\sigma$M-H to $\pi^*$C=C back-donation and $\pi$C=C to $\sigma^*$ M-H donation are necessary for bond exchange.

**Trigonal-bipyramidal structure**
**Regioselectivity of hydrometallation**

**Aliphatic terminal olefins:** For aliphatic terminal olefins, there is both a strong thermodynamic preference to form the sterically less hindered M-C bond.

Structure & Bonding, pg. 32: As seen for C-H σ bonding, there is a general trend towards weaker M-C σ bonds with increased substitution.

If an equilibration mechanism exists, M-alkyls will isomerize to the least sterically hindered 1o product. For more examples of this see: Hydroformylation, pg. 205 and 206.

**Conjugated terminal olefins:** For conjugated olefins, hydride insertion results in formation of the 2o M-C which can be stabilized as a delocalized η3-intermediate.

**Hydroformylation, pg. 192, 194, 195; Hydrocyanation, pg. 232.**

**Ligand Effects?** Hayashi’s observed hydrosilylation regioselectivities with aliphatic terminal olefins cannot be rationalized using our models (Hydrosilylation, pg. 189).
Unsolved problem: intermolecular silylformylation of terminal olefins

Desired silylformylation product:

\[
\begin{align*}
\text{R} & \quad \text{catalyst}^* \quad \text{CO, } \text{R}_3\text{Si-H} \\
\text{SiR}_3 & \quad \text{OH} \\
\text{H} & \quad \text{O}
\end{align*}
\]

Tamao oxidation
acetate aldol equivalent
polyacetate polyol

Observed silylformylation product:

\[
\begin{align*}
\text{C}_4\text{H}_9 & \quad \text{Co}_2\text{(CO)}_8 \quad (0.7 \text{ mol}%) \\
\text{HSiEt}_2\text{Me} & \quad (1 \text{ eq), CO} \\
\text{benzene, 140}^\circ \text{C, 20h} \\
\text{mj. product linear}
\end{align*}
\]

Route of the problem? One hypothesis is that hydrometalation of terminal olefins with Co-H occurs at a faster rate than silylmetalation with Co-SiR₃. The overall result is the hydroformylated aldehyde product which can further react with Co-SiR₃ (recall Si is oxophilic) to give the silylenol ether. See Silylformylation, pg. 211.

Silylenol ether formation regenerates the Co-H species.
**Unsolved problem: direct hydroacylation of terminal olefins**

**Desired hydroacylation product**

\[
\text{R}^\prime \quad \text{H} \quad + \quad \text{R} \quad \text{Catalyst} \quad \rightarrow \quad \text{R} \quad \text{O} \quad \text{R}^\prime
\]

direct route to di-substituted ketones from unactivated precursors

Observed intermolecularly: decarbonylation

\[
\text{C}_4\text{H}_9\text{O} + \quad \rightarrow \quad \text{Ph}_3\text{P} \quad \text{Rh} \quad \text{PPh}_3 \quad \text{Cl} \quad \text{CHCl}_3 \quad \rightarrow \quad \text{Ph}_3\text{P} \quad \text{Rh} \quad \text{CO} + \quad \text{C}_2\text{H}_12
\]

Route of the problem? One hypothesis is as follows: The catalyst must have three "open" and adjacent coordination sites for the acyl, hydride, and olefin moieties to effect successful hydroacylation. Upon oxidative addition of the aldehyde to give the hydridoacyl metal species, intramolecular binding of the acyl alkyl substituent to the syn open site competes effectively with intermolecular olefin binding and results in decarbonylation.
Functionalization of terminal alkynes via migratory insertion / reductive elimination sequence?

**Hydrogenation**

\[ R\equiv + H-H \leftrightarrow \begin{bmatrix} H \\ LnM-H \equiv R \end{bmatrix} \xrightarrow{MI} \begin{bmatrix} R-H \equiv MLn \end{bmatrix} \xrightarrow{RE} \begin{bmatrix} R-H \equiv H \end{bmatrix} + \begin{bmatrix} H-H \end{bmatrix} \]

**Silylformylation**

\[ R\equiv + H-SiR_3 + CO \leftrightarrow \begin{bmatrix} CO \\ LnM-SiR_3 \equiv R \end{bmatrix} \xrightarrow{MI} \begin{bmatrix} CO \\ LnM-SiR_3 \end{bmatrix} \xrightarrow{MI} \begin{bmatrix} H-O \equiv L_n(SiR_3)M \end{bmatrix} \xrightarrow{RE} \begin{bmatrix} R-O \equiv SiR_3 \end{bmatrix} \]

**Hydroacylation**

\[ R\equiv + H-O^\equiv \xrightarrow{\text{masked}} \begin{bmatrix} R' \end{bmatrix} \xrightarrow{MI} \begin{bmatrix} R' \equiv MLn \end{bmatrix} \xrightarrow{RE} \begin{bmatrix} R'\equiv O \end{bmatrix} \]
Unsolved problem: hydroformylation of terminal alkynes

**Desired hydroformylation product:**

\[
\begin{align*}
R- & \quad \text{catalyst}^* \quad \text{CO, H}_2 \\
\text{(E)-}\alpha,\beta-\text{unsaturated aldehydes}
\end{align*}
\]

Route of the problem: Acetylenes form stable metallocyclopropane/propene complexes that resist hydroformylation under mild conditions.

\[
R\equiv\equiv R' + 2\text{CO} \quad \rightarrow \quad \text{(OC)}_3\text{Co-Co(CO)}_3
\]

Under forcing conditions of high CO/H\textsubscript{2} pressure and high temperatures, terminal acetylenes are converted to fully saturated linear aldehydes.

\[
R\equiv\equiv H \quad \xrightarrow{\text{Ph}_3\text{P-Rh}^{(4)} \text{PPPh}_3 \text{H}_2/\text{CO} (1:1, 100 \text{ atm}), 80^\circ\text{C}, 24 \text{ hrs, 73\% conversion}} \quad \rightarrow \quad \text{CHO}
\]

possible intermediate (never observed)
Silylformylation of alkynes

Terminal alkynes:

terminal sp C is selectively silylated

\[
\text{Me} \equiv \equiv \text{H} \quad \xrightarrow{\text{Rh}_4(\text{CO})_{12} (1 \text{ mol}) \quad \text{Me}_2\text{PhSiH} (1 \text{ eq}) \quad \text{NET}_3 (1 \text{ eq}), \text{CO} (29 \text{ atm}) \quad 2\text{h}, \text{100}^\circ\text{C}}\quad \text{Me} \equiv \equiv \text{SiMe}_2\text{Ph} \quad \text{OHC} \quad 99\% \text{ yield} \quad Z:E \ (80:20)
\]

Z-isomer is the kinetic product. E-isomer arises from isomerization under the carbonylation conditions.

There is no mechanism to regenerate Rh-H once it has been consumed in a cycle. Unlike the silylformylation of alkenes, the product of aldehyde silylmetalation has no \(\beta\)-hydrogen available for elimination.