Some useful reference texts:


Pauson-Khand Reaction

- The reaction can be mediated by a variety of metal complexes. In order to render the reaction catalytic, one must use a high pressure atmosphere of CO.

- The reaction can be accelerated by the addition of various promoters that accelerate the rate of dissociation of CO ligands on metal centers.

- The required alkyn–metal complex does not need to be prepared in situ. The complex can be formed several steps in advance in the context of a synthetic sequence and can even be subjected to silica gel chromatography, but exposure to oxidizing agents will return the starting alkyne.

- The reaction can be performed intramolecularly. Tetrasubstituted alkenes do not react.

- Somewhat incompatible functionalities include halides and vinyl ethers/esters.

- The mechanism has not been fully elucidated.

Proposed mechanism:

Nicholas Reaction

- The reaction can be performed intramolecularly. Tetrasubstituted alkenes do not react.

- Somewhat incompatible functionalities include halides and vinyl ethers/esters.

- The mechanism has not been fully elucidated.
The Chemistry of Cobalt and Iridium

Baran Group Meeting – 30 November 2005
Carlos Guerrero

- $C$, $O$, $N$, and $S$-nucleophiles are all suitable for the Nicholas reaction.
- The reaction can be conducted intramolecularly.
- No allene side products are observed.

Cobalt-Mediated Total Synthesis of (+)-Epoxideictyemene
Schreiber, JACS, 1994, p. 5505.

Homogenous Hydrogenations Using Ir(I)-based Catalysts
The Chemistry of Cobalt and Iridium

Schultz, JOC, 1985, p. 5905.

Crabtree's catalyst

\[
\begin{align*}
\text{Ir} & \quad \begin{array}{c}
\text{P(Cy)}_3 \\
\end{array} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{Me} & \quad \text{N} \\
\text{Me} & \quad \text{N} \\
\end{align*}
\]

5 mol %, Crabtree's catalyst, 1 atm H₂

89%, dr 130:1

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{Me} & \quad \text{N} \\
\text{Me} & \quad \text{N} \\
\end{align*}
\]

5 mol %, Crabtree's catalyst, 1 atm H₂

87%, 41:1

\[
\begin{align*}
\text{Me} & \quad \text{CO}_2\text{Me} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

5 mol %, Crabtree's catalyst, 1 atm H₂

67%, 105:1

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{Me} & \quad \text{N} \\
\end{align*}
\]

5 mol %, Crabtree's catalyst, 1 atm H₂

91%, dr >1000:1


\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{Me} & \quad \text{N} \\
\end{align*}
\]

2.5 mol %, Crabtree's catalyst, 1 atm H₂

>99.9%, dr >99.9%

\[
\begin{align*}
\text{MeO} & \quad \text{N} \\
\end{align*}
\]

2.5 mol %, Crabtree's catalyst, 1 atm H₂

97.7%, dr 96.2%


\[
\begin{align*}
\text{MeO-Biphep} & = \\
\end{align*}
\]

[\text{Ir(COD)Cl}]_2, \text{MeO-Biphep}, I₂, 700 psi, r.t.

99%, 94% ee


\[
\begin{align*}
\text{MeO-Biphep} & = \\
\end{align*}
\]

(-)-galipeine
The Chemistry of Cobalt and Iridium

Baran Group Meeting – 30 November 2005

Carlos Guerrero

Conversion of Alkenes to Enol Silyl Ethers of Acyl Silanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide
Murai, JACS, 1992, p. 9710.

BuO\(\xrightarrow{10 \text{ mmol}}\) 100\% \rightarrow \text{BuO} \xrightarrow{67\%} \text{BuO} \xrightarrow{85\%} \text{Et}_2\text{MeSi} \xrightarrow{\text{OSiEt}_2\text{Me}} \text{SiEt}_2\text{Me}

The mechanism of this transformation has not been elucidated. Mixtures of \(E\) and \(Z\) olefins are produced. The products can be hydrolyzed to give acyl silanes.

Cycloisomerization Reactions

\[
\begin{align*}
\text{O} & \xrightarrow{5 \text{ mol } \% \text{ CpCo(CO)}_2} \text{CO}_2\text{R} \\
\text{H} & \xrightarrow{\text{h}[\text{C}_6\text{H}_6], 0.5 - 2 \text{ h}} \text{CO}_2\text{R}
\end{align*}
\]

ring size:  5  6  7  8
yield:  73\%  81\%  70\%  73\%
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*Baran Group Meeting – 30 November 2005*


![Chemical reaction diagram for the synthesis of a complex molecule.]


Note that the alkyne terminus is incorporated into the new cyclopentene. The terminal alkyne must be subject to the reaction conditions in its protected form.

**Functional Group Interconversions**


Note: this transformation has been demonstrated as shown, but Ru catalysts are superior in this setting.

Yields are high; ynals are viable substrates.
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Baran Group Meeting – 30 November 2005

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1. K$_2$CO$_3$
2. cat. IrH$_5$(i-Pr$_3$P)$_2$

\[
\text{Me} \quad \text{O} \quad \text{\textsuperscript{\neg}C\textsuperscript{\text{-}}\text{Bu}} \quad \text{Bu} \quad \text{O} \quad \text{\textsuperscript{\neg}C\textsuperscript{\text{-}}\text{Pr}}
\]

86% for 2

Possible mechanism:

1. OH
2. cat. IrH$_5$(i-Pr$_3$P)$_2$

\[
\text{Me} \quad \text{O} \quad \text{\textsuperscript{\neg}C\textsuperscript{\text{-}}\text{Bu}} \quad \text{Bu} \quad \text{O}
\]

24—40 h

The \[\text{\textsuperscript{\neg}C\textsuperscript{\text{-}}}\text{unsaturated ketone is also formed as a minor product; propose a mechanism that accounts for both products.}

Synthesis of $N$-Acyl Amino-acids by a Carbonylation Reaction

Wakamatsu, JCS, CC, 1971, p. 1540.

\[
\text{CO, } \text{CO}_2(\text{CO})_8
\]

This isomerization is applicable to ynals, ynones, ynoates, and analogues amides.
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C—H Activation (i.e. C—H O. A.)

C—H activation of tertiary amines

C—H borylation of arenes

\[
\begin{align*}
\text{HB(pin), cat.} & \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 8 h; 73\%} \\
\text{OR} & \quad \text{B}_2\text{(pin)}_2, \quad \text{cat.} \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 8 h; 82\%} \\
\text{HB(pin), cat.} & \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 24 h; 73\%} \\
\text{OR} & \quad \text{B}_2\text{(pin)}_2, \quad \text{cat.} \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 8 h; 81\%} \\
\text{HB(pin), cat.} & \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 2 h; 83\%} \\
\text{OR} & \quad \text{B}_2\text{(pin)}_2, \quad \text{cat.} \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 2 h; 85\%} \\
\text{HB(pin), cat.} & \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 0.5 h; 99\%} \\
\text{OR} & \quad \text{B}_2\text{(pin)}_2, \quad \text{cat.} \quad \frac{1}{2} \text{Ir(OMe)(cod)}_2, \quad \text{dtby, r.t., 0.5 h; 88\%}
\end{align*}
\]