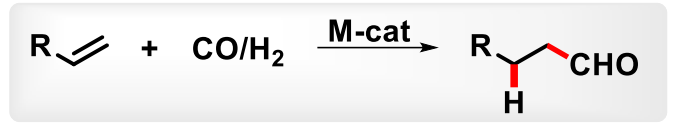
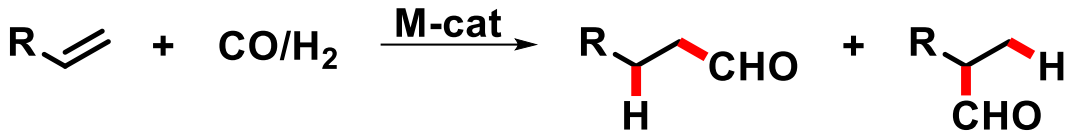
Hydroformylation and related reactions



➢ Hydroformylation

- General scheme



- Catalyst activity

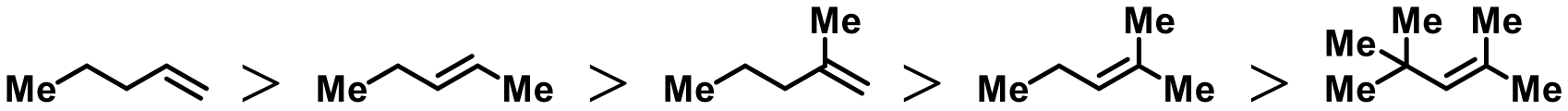
$$HM(CO)_xL_y$$

$$Rh >> Co > Ir, Ru > Os > Pt > Pd >> Fe > Ni$$

- Ligand activity for Rhodium catalysts

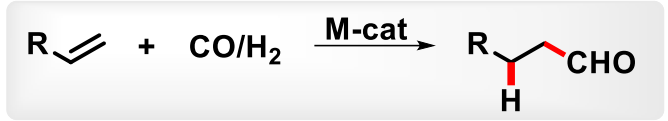
$$Ph_3P >> Ph_3N > Ph_3As, Ph_3Sb > Ph_3Bi$$

- Rate of the alkene hydroformylation

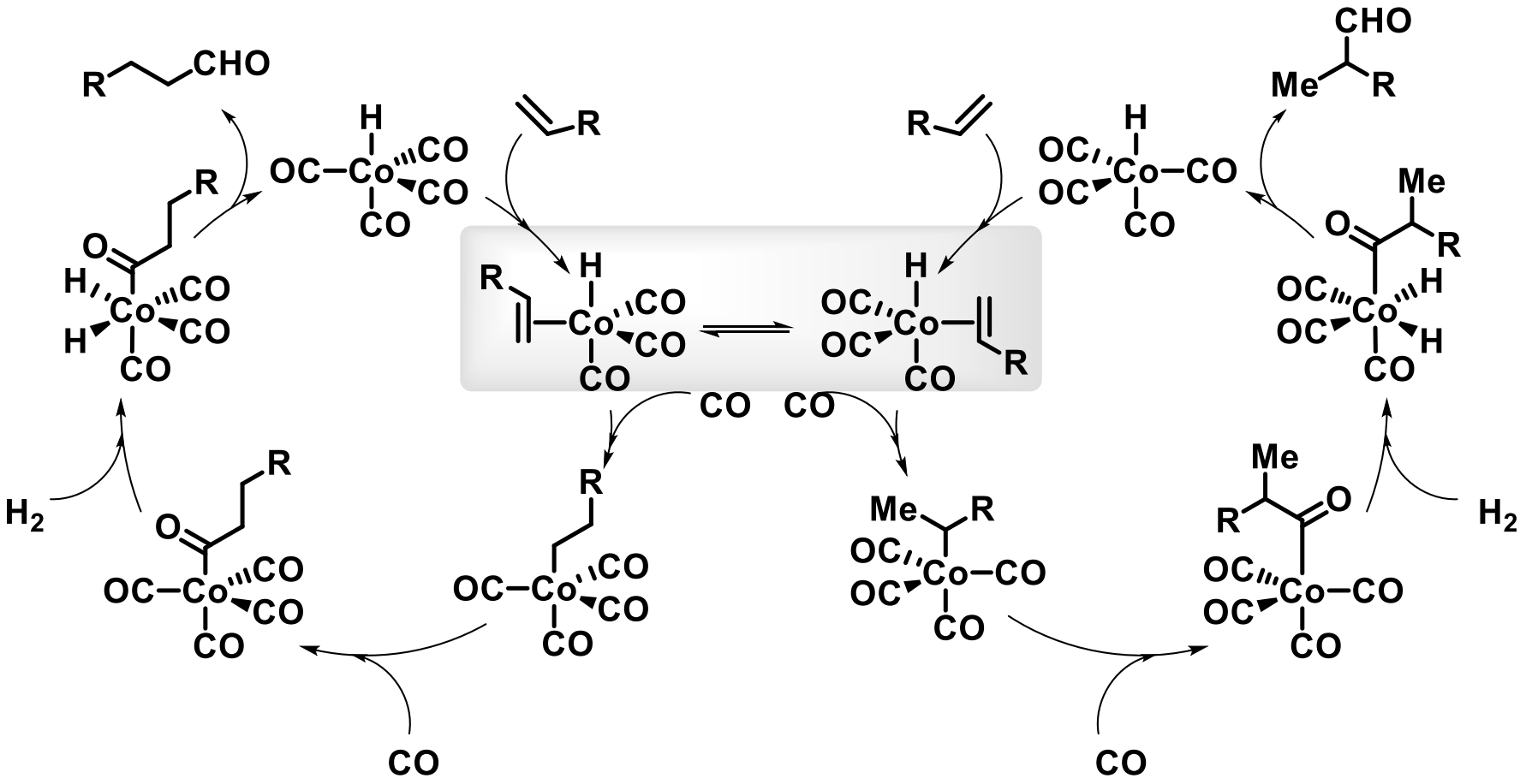


Hydroformylation and related reactions

➢ Hydroformylation

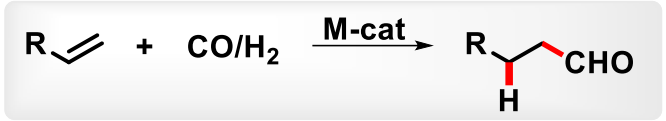


- **Widely accepted mechanism for $HCo(CO)_4$ catalyzed hydroformylation**

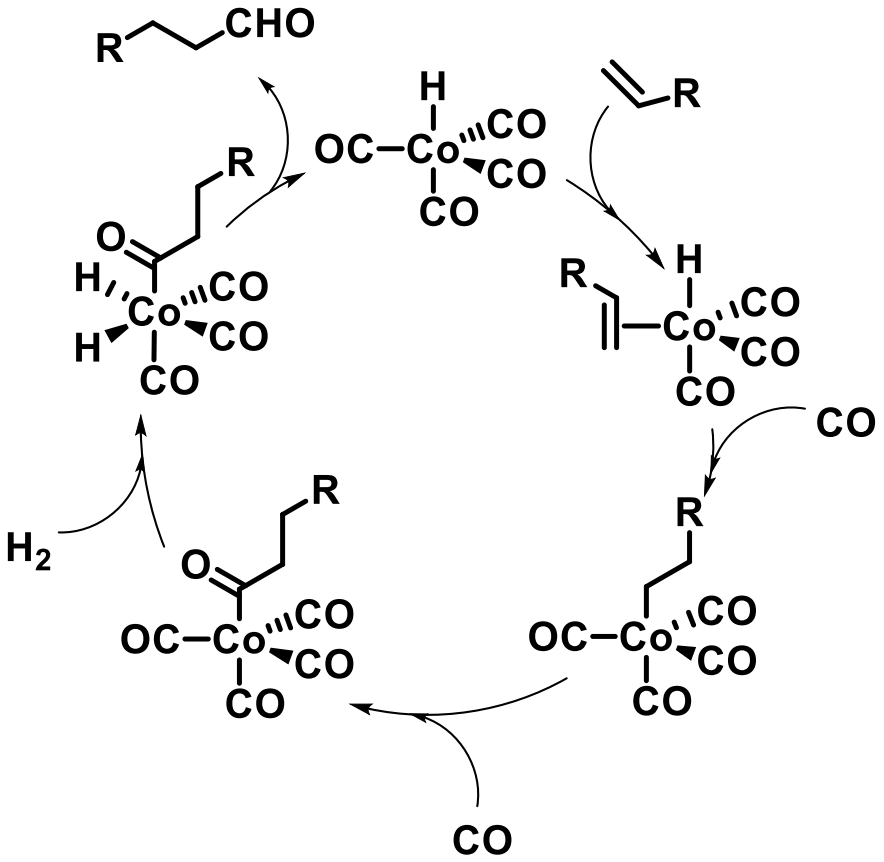


Hydroformylation and related reactions

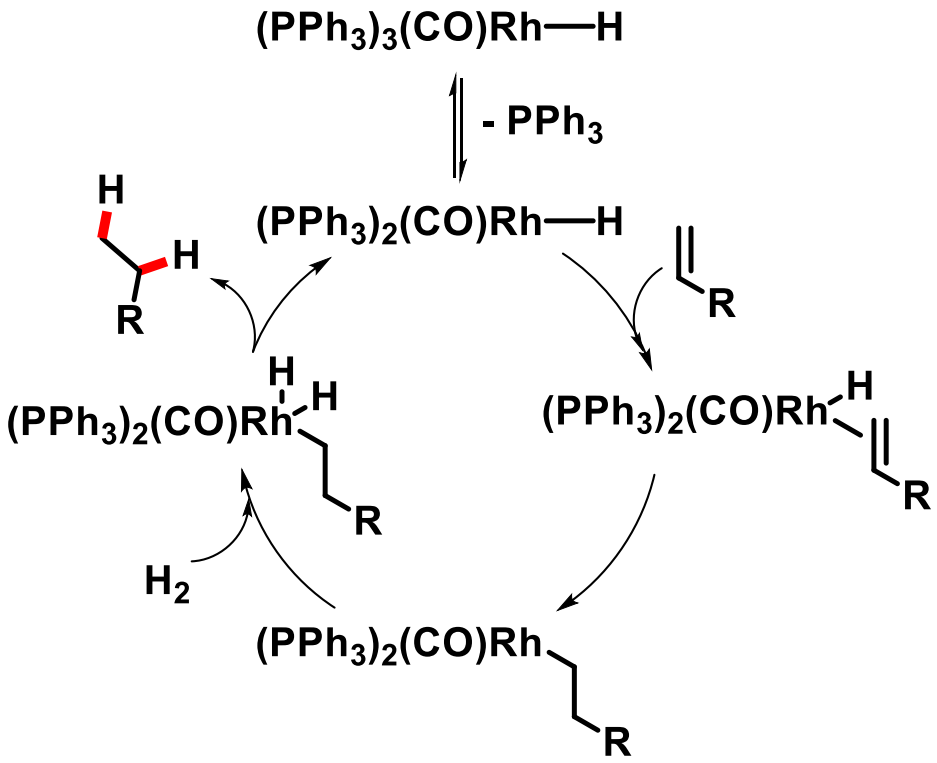
➢ Hydroformylation



- **Mechanism of hydroformylation by [Co(H)CO]**



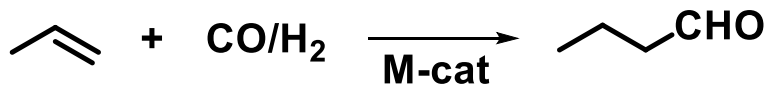
- **Mechanism of hydrogenation by [Rh(H)CO]**

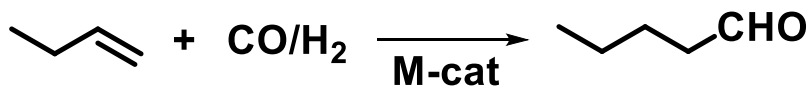


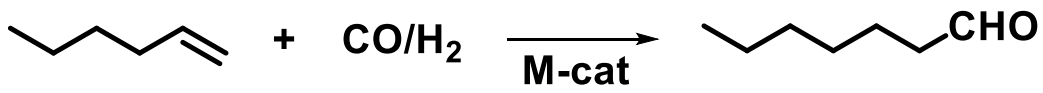
Hydroformylation and related reactions

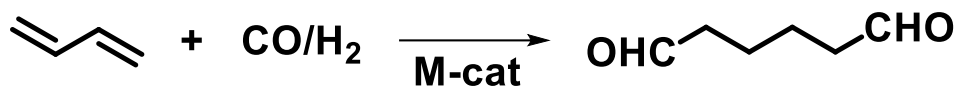
➢ Hydroformylation

- **Industrial production of aldehydes (BASF, Oxea, Eastman, Dow Chemical)**

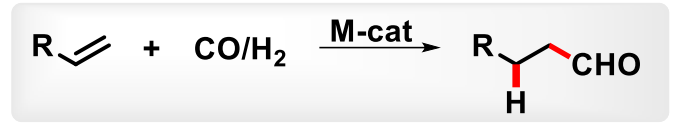






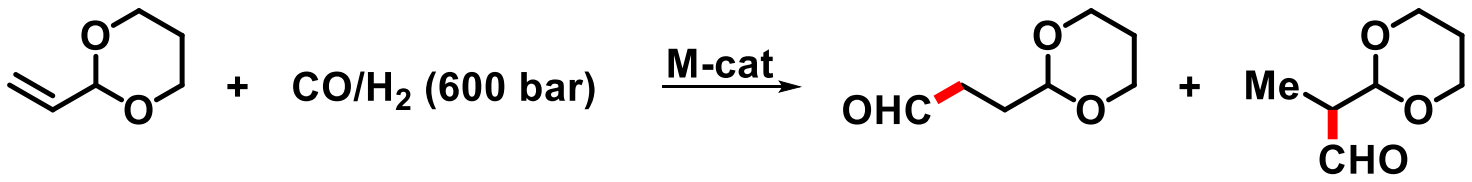


Hydroformylation and related reactions



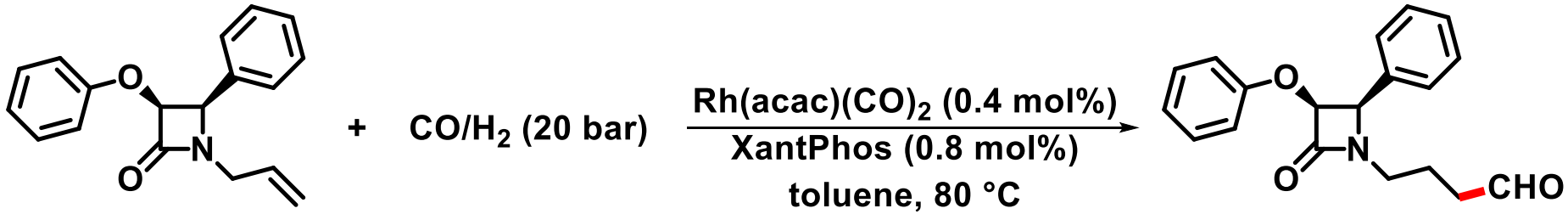
➢ Hydroformylation

- **Selected examples of hydroformylation reaction**



Rh-cat, CO/H_2 (600 bar), 100 °C 25 :75
Rh-PPh_3, CO/H_2 (20 bar), 140 °C 70:30

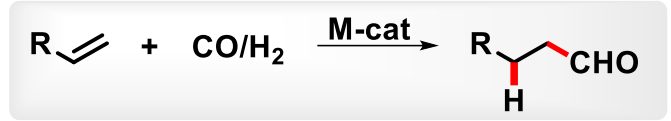
German Patent DE 2111116, **1972**; U.S. Patent 4017550, **1977**



79%
(89:11 selectivity)

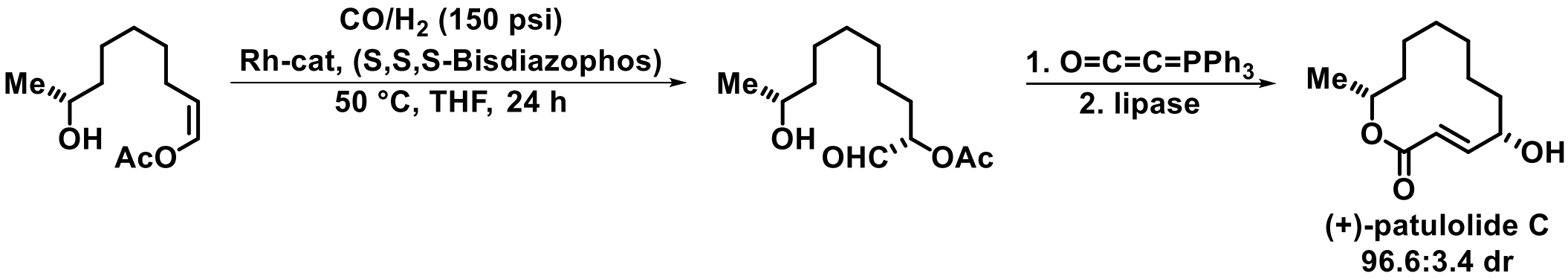
New. J. Chem. **2010**, *34*, 1079

Hydroformylation and related reactions



➢ Hydroformylation

- **Asymmetric hydroformylation**



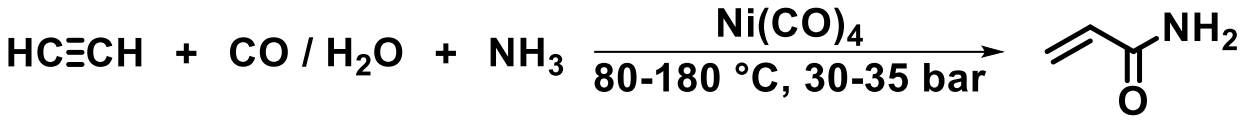
(+)-patulolide C
96.6:3.4 dr

Org. Lett. **2012**, *14*, 1180

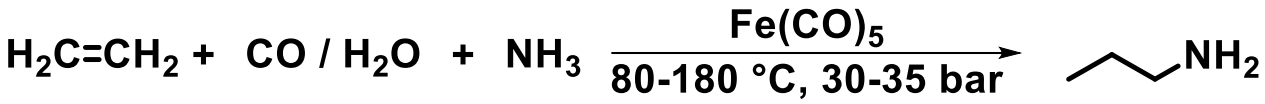
Hydroformylation and related reactions

➢ Hydroaminomethylation

- **Early examples**



Experientia **1949**, *5*, 93

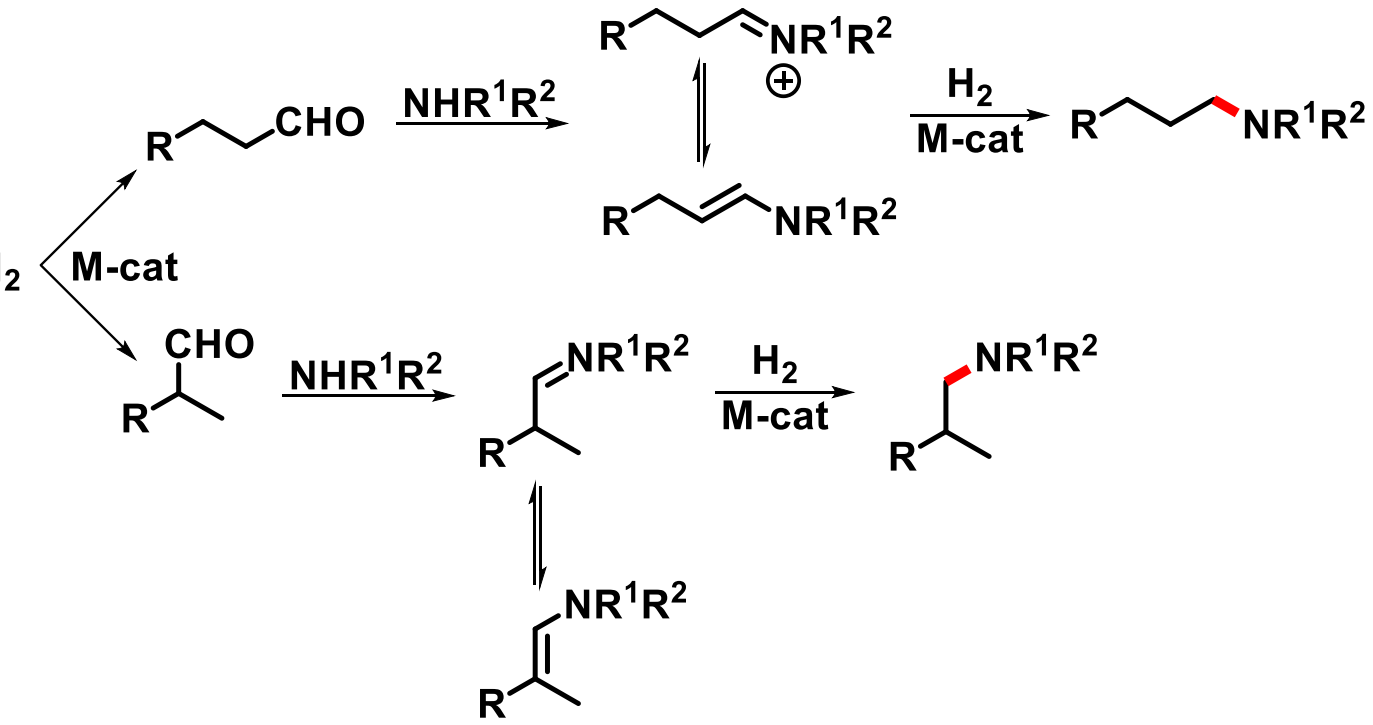


Reppe, W. Patent demand 839 800 (to I.G. Farben, May 5, 1943), then to BASF (July 8, 1949) 1943, allowed on May 26 **1952**

Hydroformylation and related reactions

➢ Hydroaminomethylation

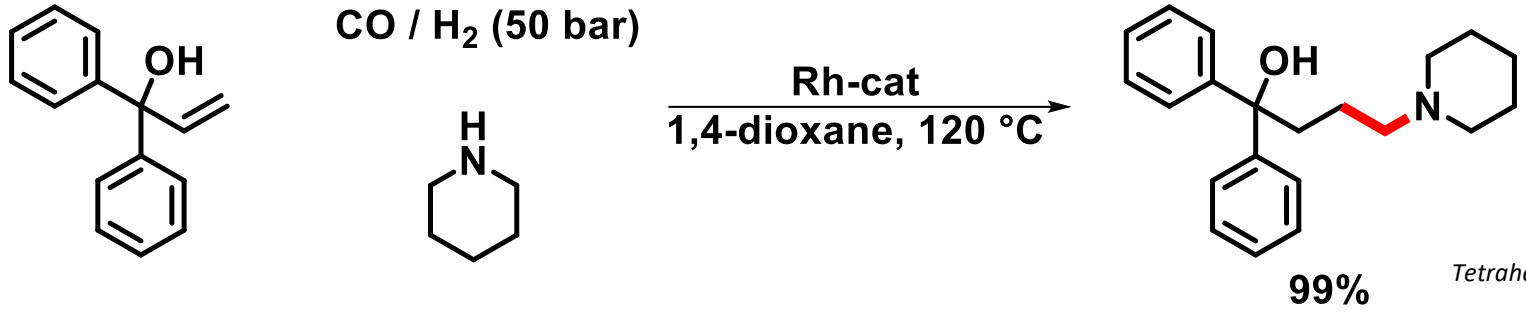
- Mechanistic consideration



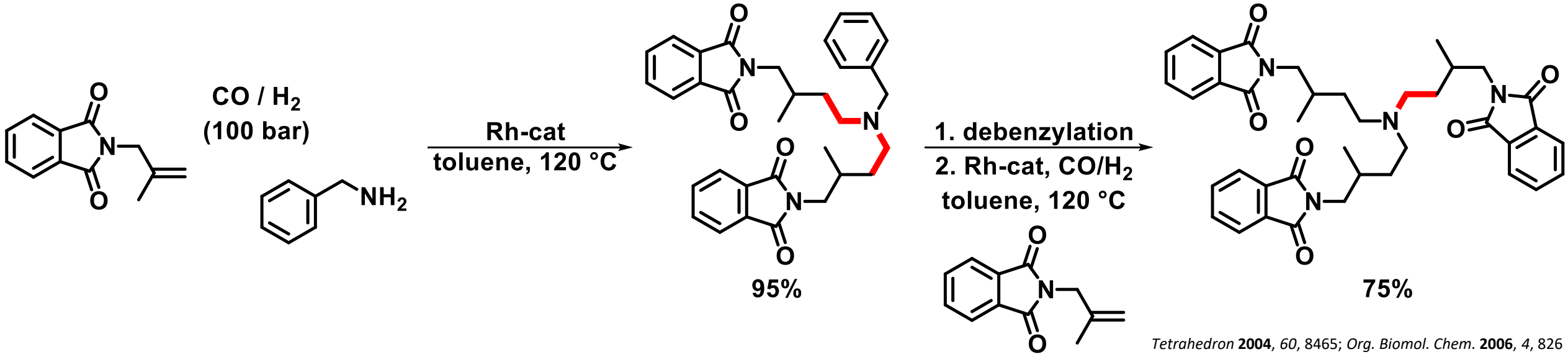
Hydroformylation and related reactions

➢ Hydroaminomethylation

- **Recent examples**



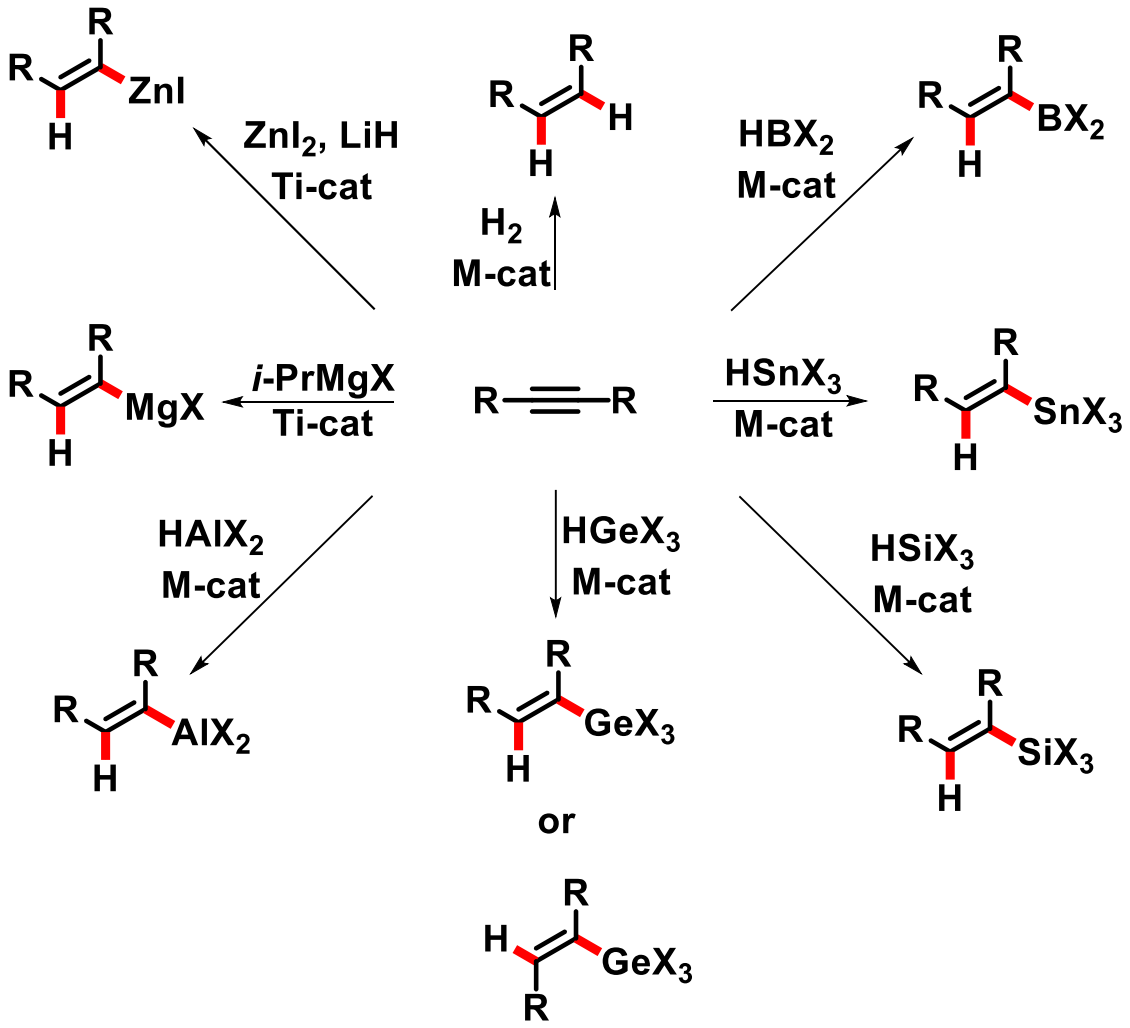
Tetrahedron **2004**, *60*, 11487



Tetrahedron **2004**, *60*, 8465; *Org. Biomol. Chem.* **2006**, *4*, 826

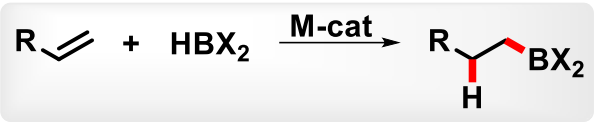
Hydroformylation and related reactions

➢ Transition-metal-catalyzed hydrometallations

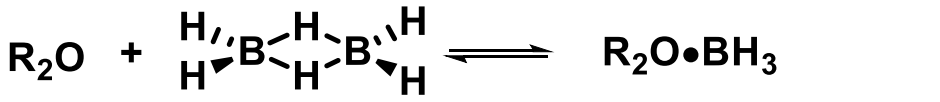


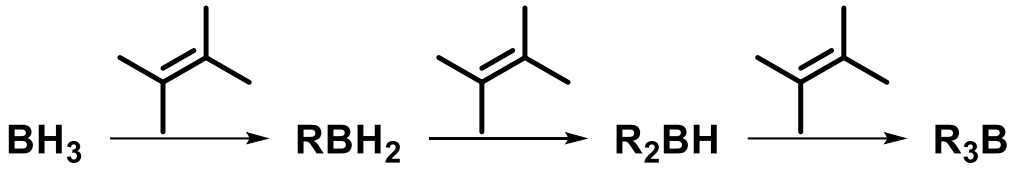
Hydroformylation and related reactions

➢ Transition-metal-catalyzed hydrometallations

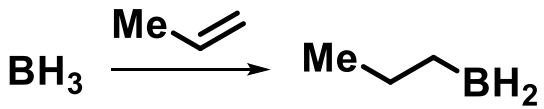


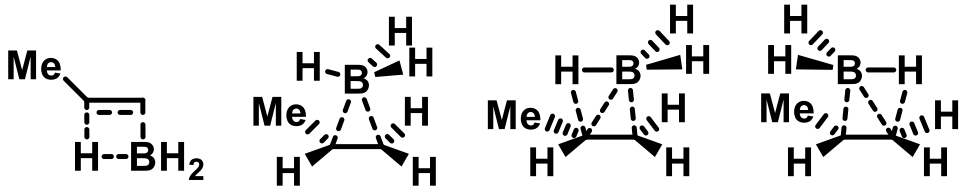
- **Hydroboration**





  - **Proposed transition states for the borane addition to 1-propene**



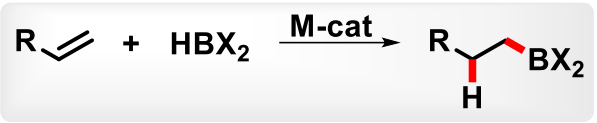


J. Am. Chem. Soc. **2009**, *131*, 3130

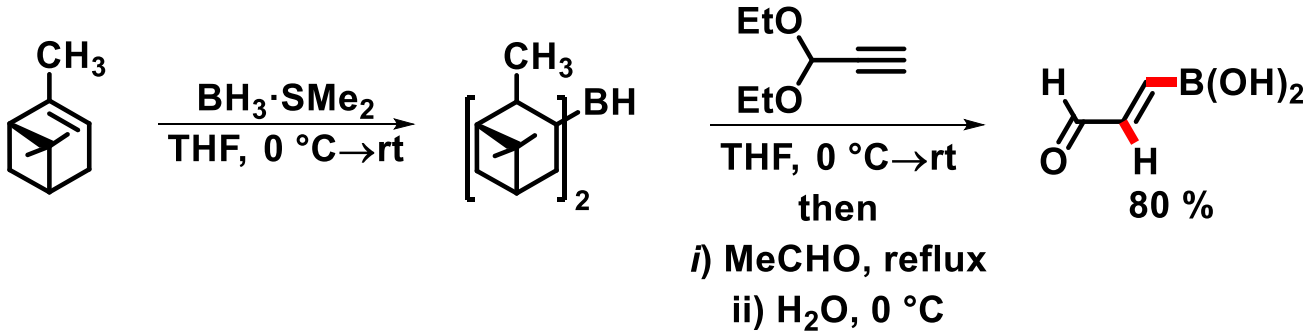
- **Why transition-metal-catalyzed hydroboration?**

Hydroformylation and related reactions

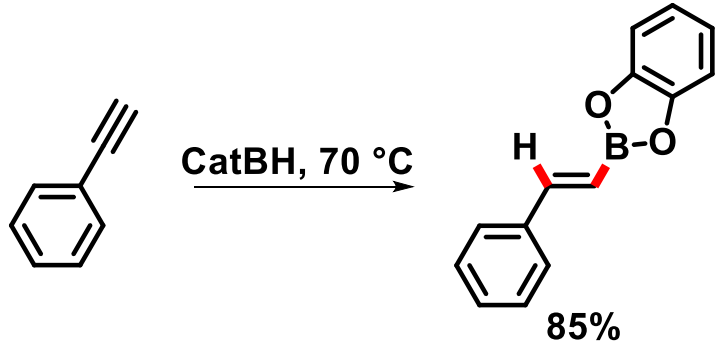
➢ Transition-metal-catalyzed hydrometallations



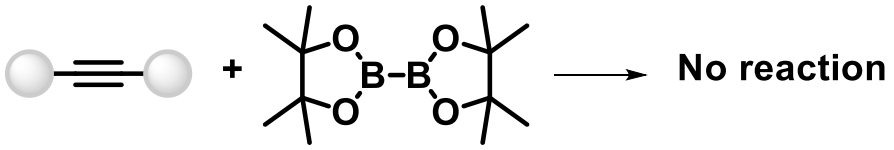
- **Hydroboration**
  - **Why transition-metal-catalyzed hydroboration?**



Chem. Eur. J. **2003**, *9*, 466



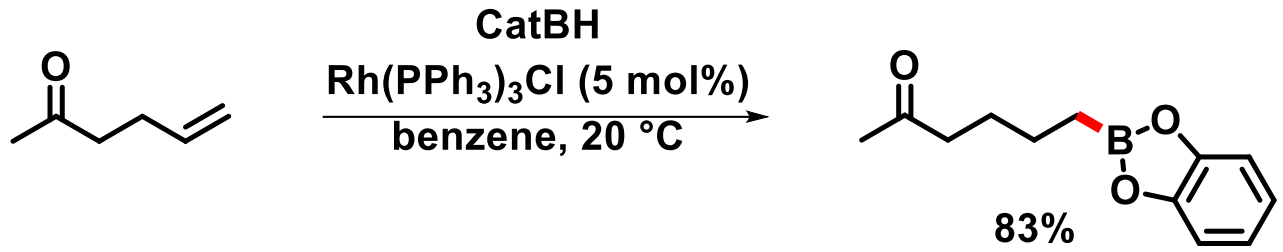
J. Org. Chem. **1975**, *97*, 5249



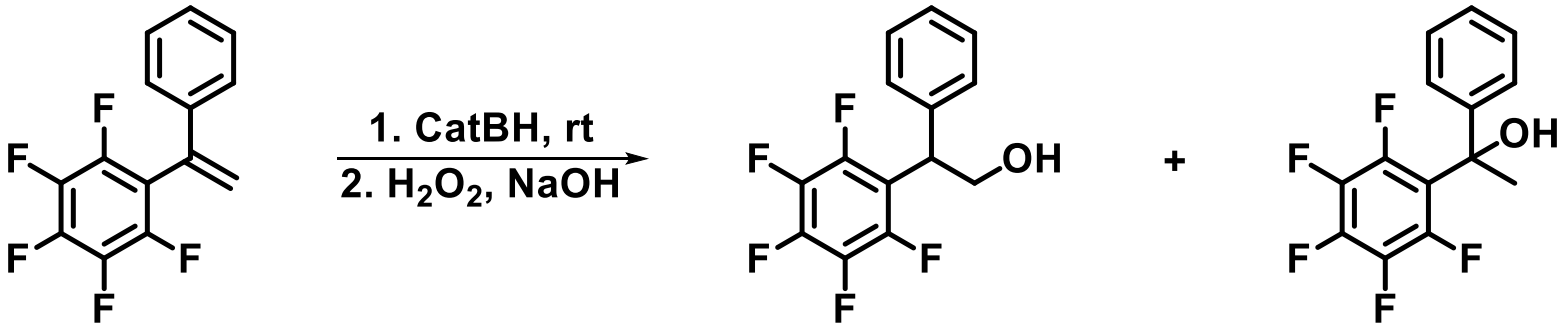
Hydroformylation and related reactions

➢ Transition-metal-catalyzed hydrometallations

- **Transition-metal-catalyzed hydroboration (Cu, Ni, Co, Fe …)**



Angew.Chem. Int. Ed. **1985**, *24*, 878

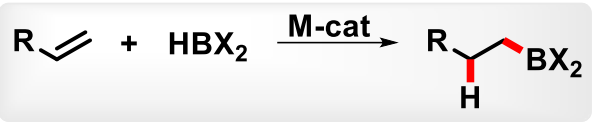


(QUINAP)Rh^+	4 :96
(DPPB)Rh^+	70 : 30

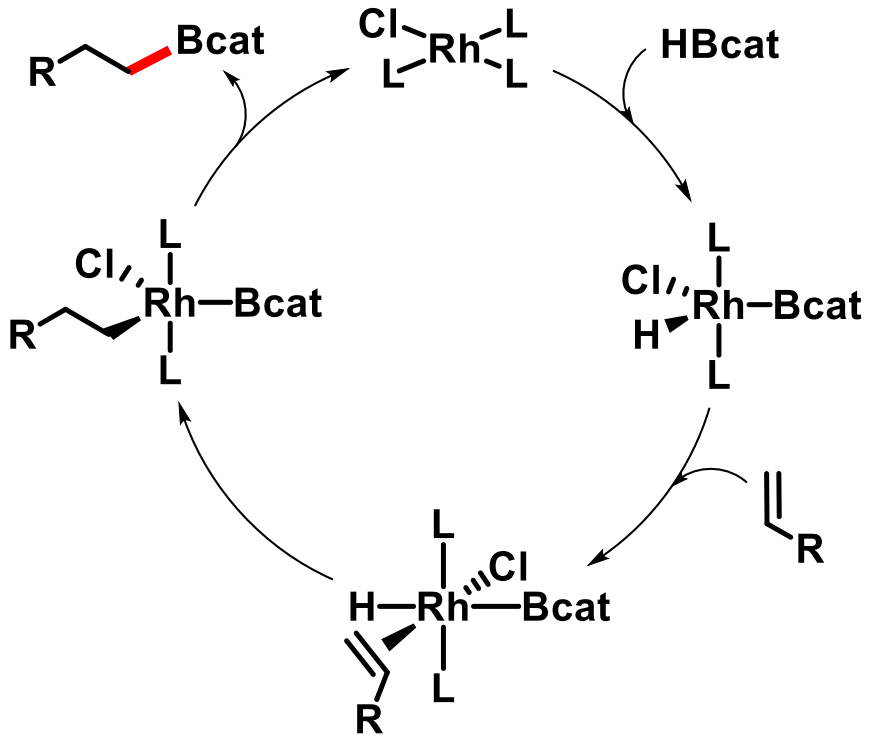
Chem. Commun. **2005**, 5284

Hydroformylation and related reactions

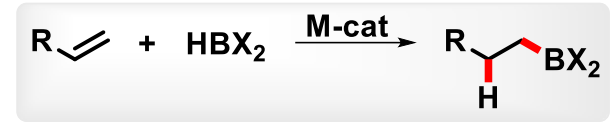
➢ Transition-metal-catalyzed hydrometallations



- **Mechanism of rhodium-catalyzed hydroboration**

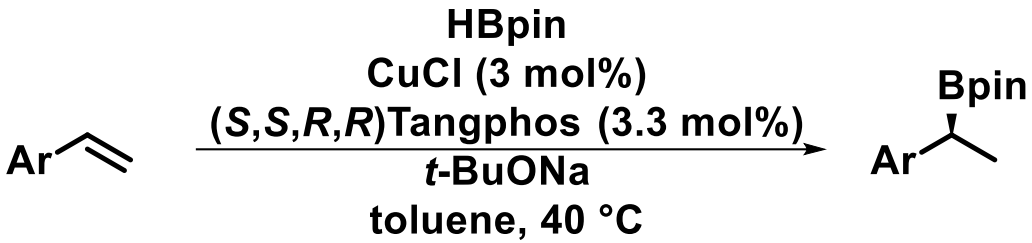


Hydroformylation and related reactions

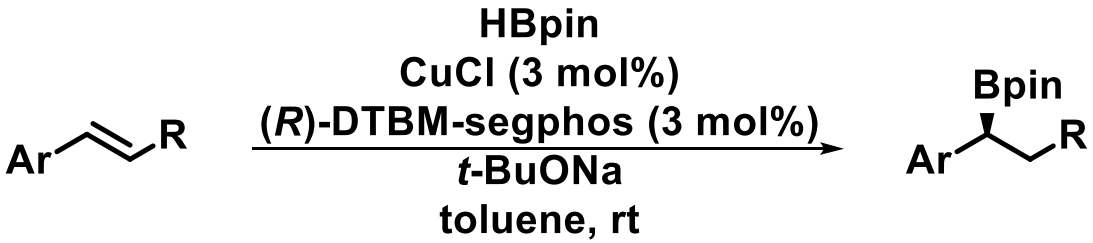


➢ Transition-metal-catalyzed hydrometallations

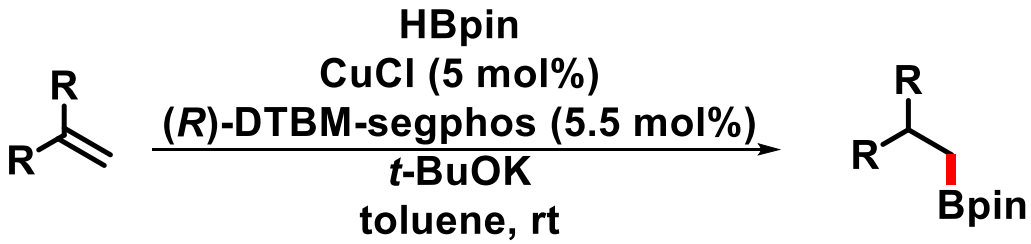
- **Transition-metal-catalyzed hydroboration (Cu, Ni, Co, Fe …)**



Angew. Chem. Int. Ed. **2009**, *48*, 6062



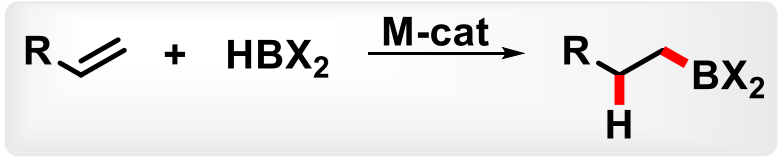
Angew. Chem. Int. Ed. **2013**, *52*, 3989; *Chem. Asian J.* **2011**, *6*, 1967



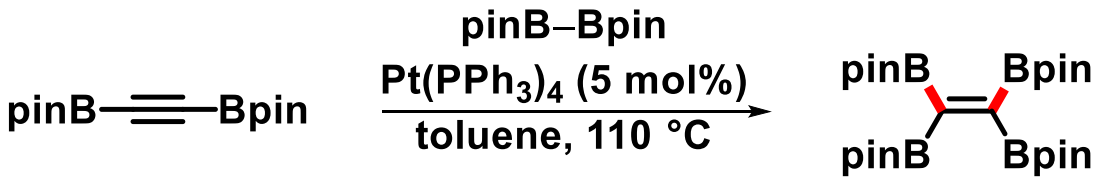
J. Am. Chem. Soc. **2017**, *139*, 13660

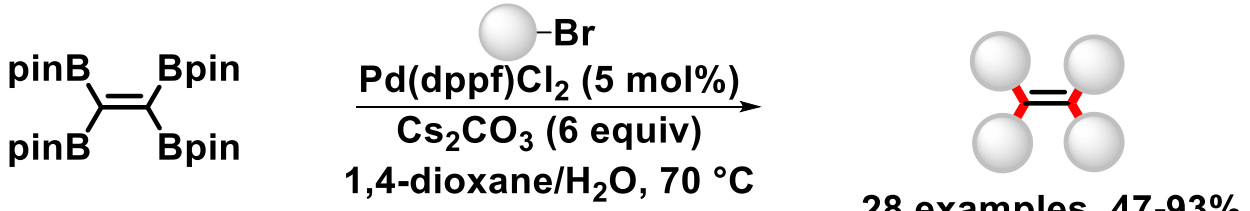
Hydroformylation and related reactions

➢ Transition-metal-catalyzed hydrometallations



- Transition-metal-catalyzed hydroboration (Cu, Ni, Co, Fe …)
  - Lego-based approach to tetrasubstituted alkenes



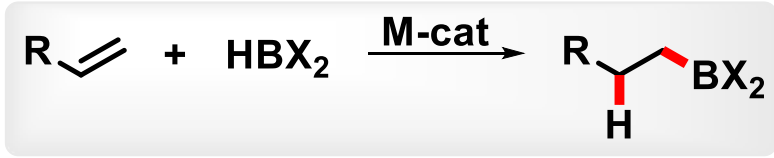


28 examples, 47-93%

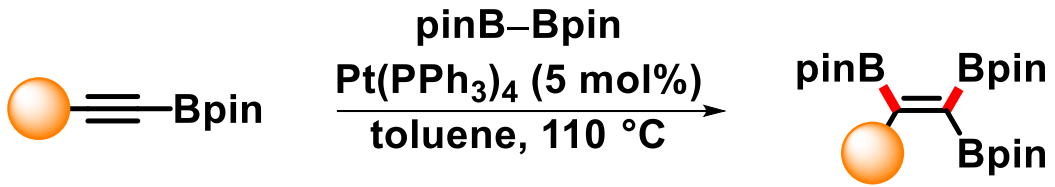
Angew. Chem. Int. Ed. **2020**, *59*, 20090

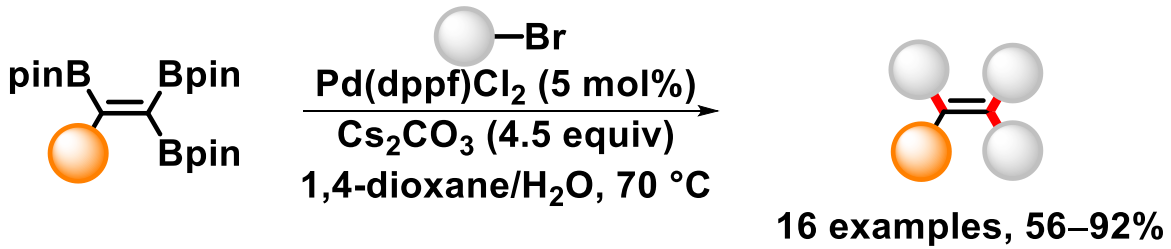
Hydroformylation and related reactions

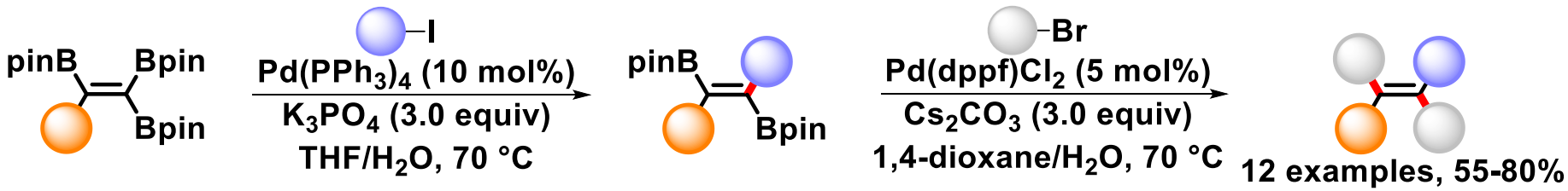
➢ Transition-metal-catalyzed hydrometallations



- Transition-metal-catalyzed hydroboration (Cu, Ni, Co, Fe …)
  - Lego-based approach to tetrasubstituted alkenes

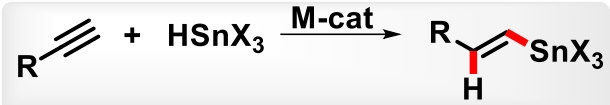






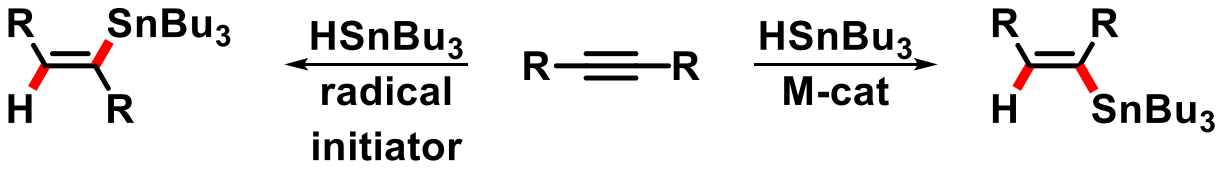
Angew. Chem. Int. Ed. **2009**, *48*, 6062

Hydroformylation and related reactions

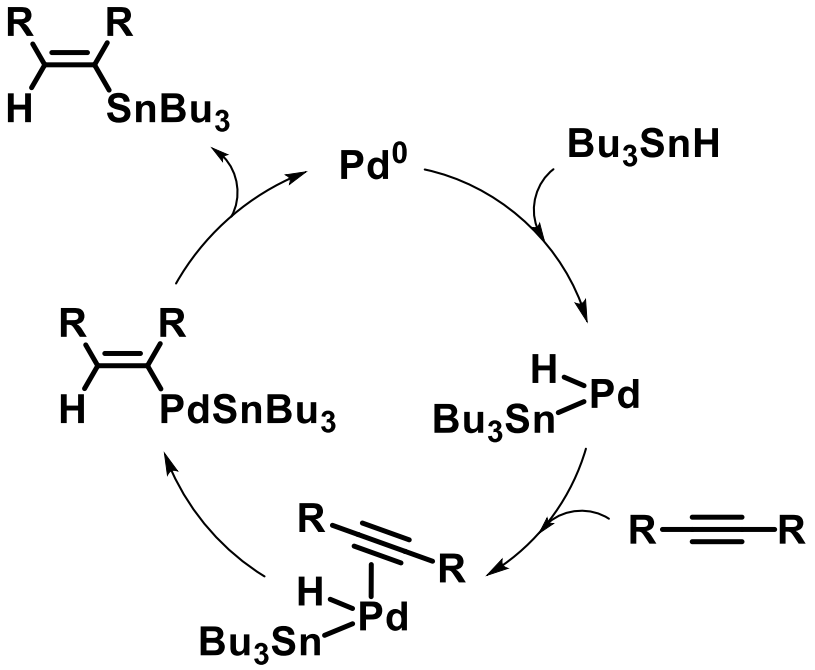


➢ Transition-metal-catalyzed hydrometallations

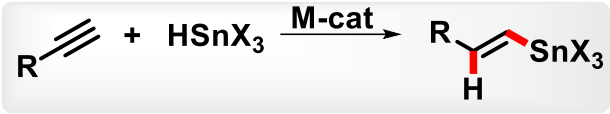
- **Transition-metal-catalyzed hydrostannylation**



- **Mechanism of palladium-catalyzed hydrostannylation**

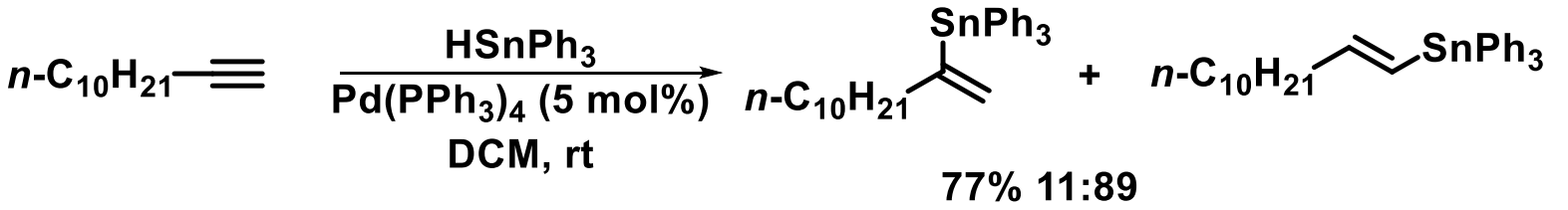


Hydroformylation and related reactions

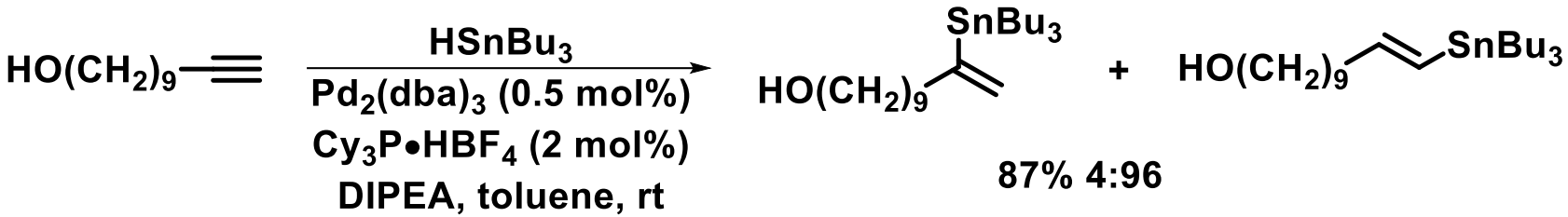


➢ Transition-metal-catalyzed hydrometallations

- **Transition-metal-catalyzed hydrostannylation**

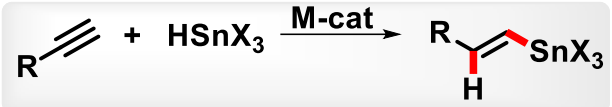


Bull. Chem. Soc. Jpn. **1987**, *60*, 3468



Org. Lett. **2008**, *10*, 861

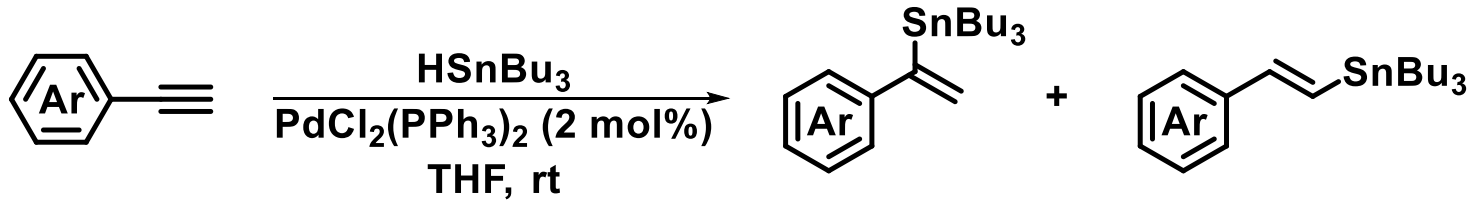
Hydroformylation and related reactions

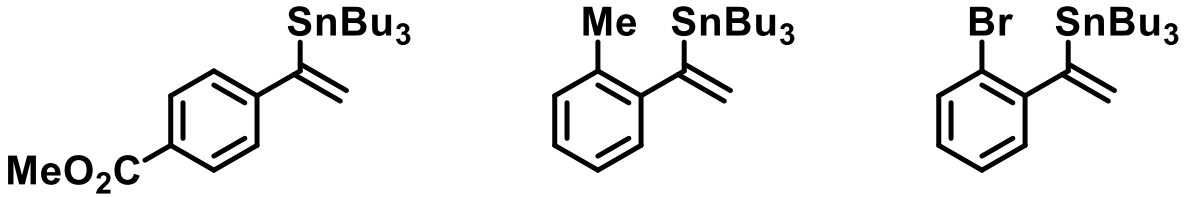


➢ Transition-metal-catalyzed hydrometallations

- **Transition-metal-catalyzed hydrostannylation**

  - **Hydrostannylation of *ortho*-substituted arylacetylenes**





86%
85:15

76%
100:0

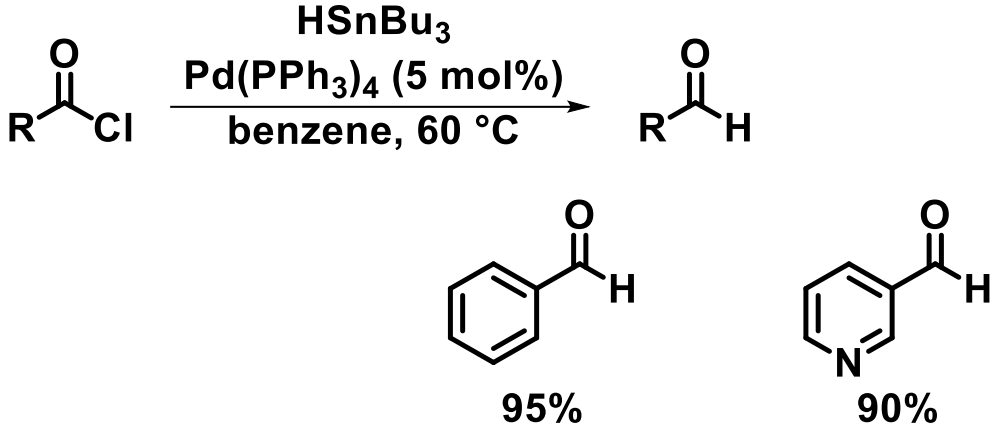
93%
100:0

J. Org. Chem. **2009**, *74*, 1337; *Synlett* **1999**, 246

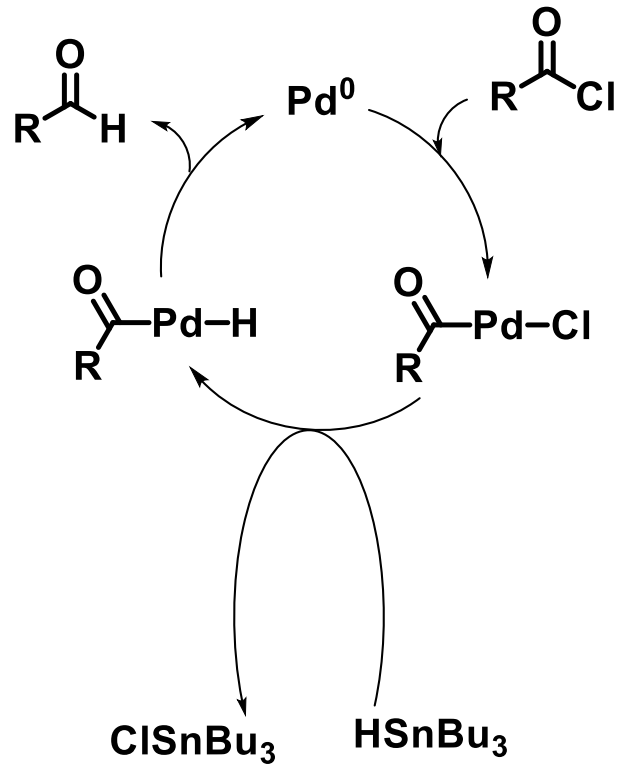
Hydroformylation and related reactions

➢ Transition-metal-catalyzed hydrometallations

- **Transition-metal-catalyzed hydrostannylation**
  - **Other applications of R_3SnH – reduction of acyl chlorides**



✓ **Proposed mechanism**

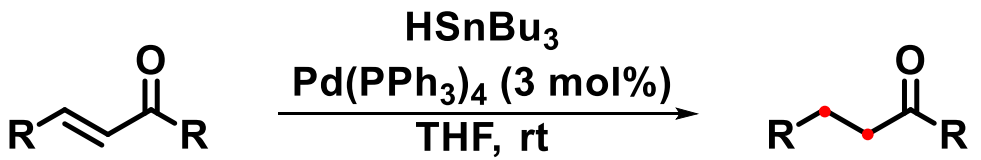


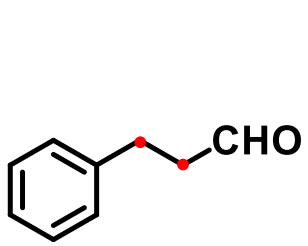
J. Org. Chem. **1981**, *46*, 4439

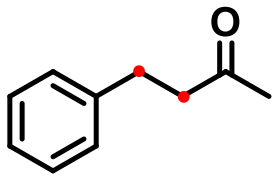
Hydroformylation and related reactions

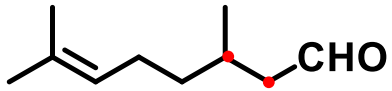
➢ Transition-metal-catalyzed hydrometallations

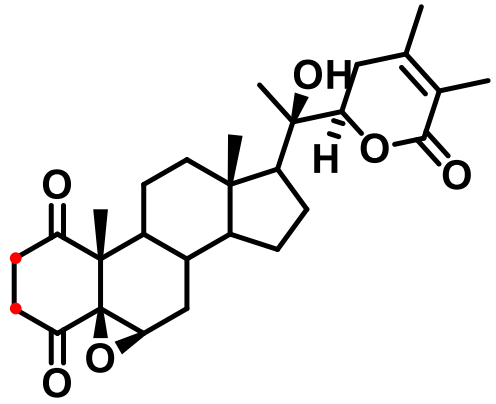
- **Transition-metal-catalyzed hydrostannylation**
  - **Other applications of R_3SnH – reduction of α,β-unsaturated ketones**









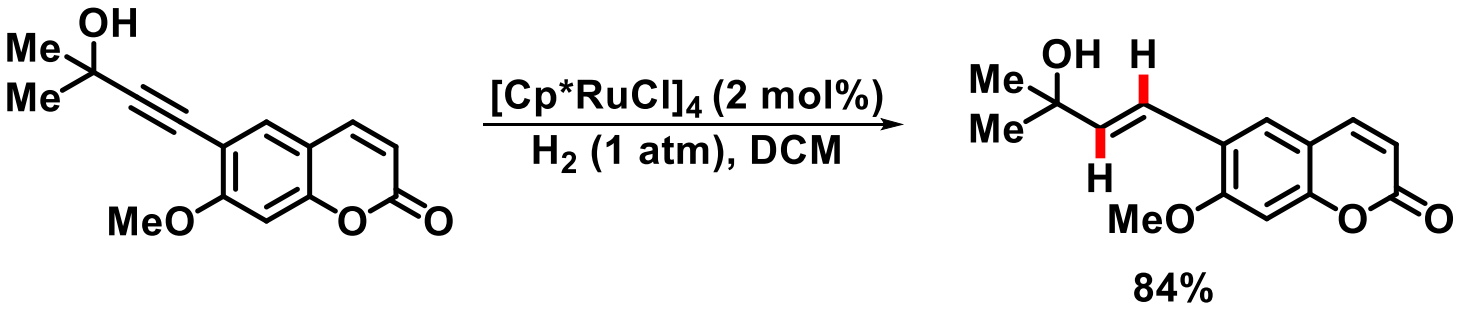


Tetrahedron Lett. **1982**, *23*, 477

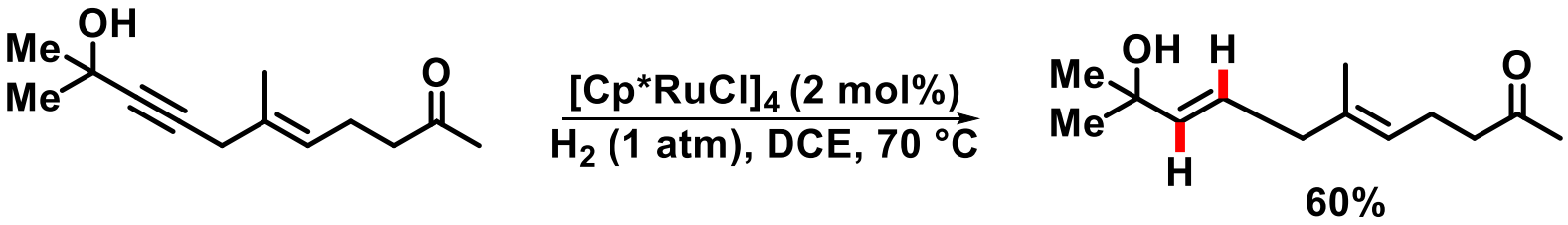
Hydroformylation and related reactions

➢ *Trans* hydrogenation and *trans* hydrometallation

- So far, all reactions of hydrido complexes have been syn additions
  - Selected examples



84%

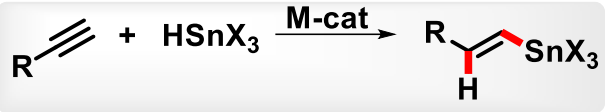


60%

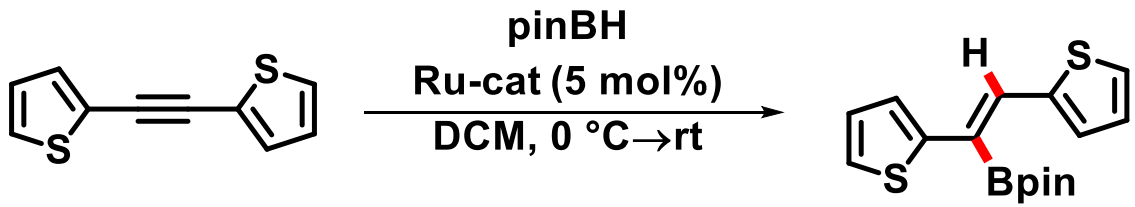
J. Am. Chem. Soc. **2018**, *140*, 3156

Hydroformylation and related reactions

➢ *Trans* hydrogenation and *trans* hydrometallation

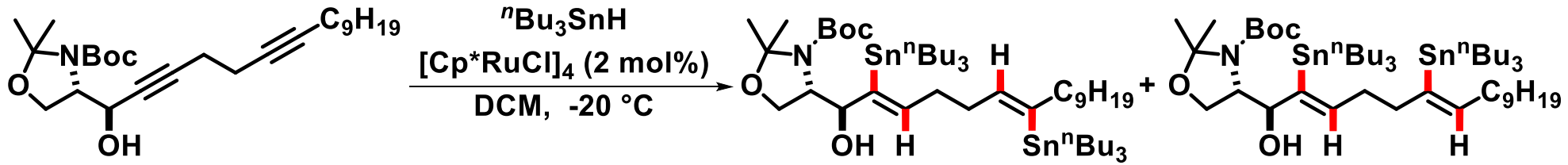


- **Selected examples**



72%
***E*:*Z* 84:16**

Angew. Chem. Int. Ed. **2013**, *52*, 14050



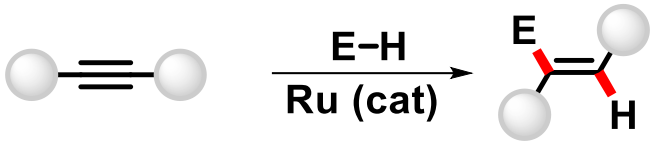
84%
***Z*/*Z*:*Z*/*E* >20:1**

Chem. - Eur. J. **2018**, *24*, 9667

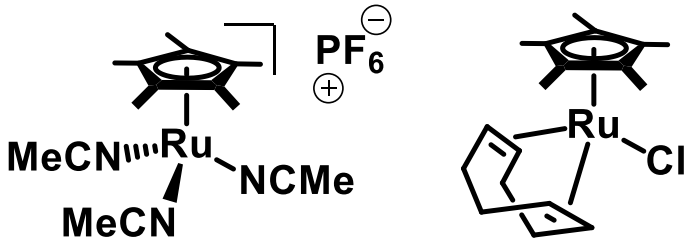
Hydroformylation and related reactions

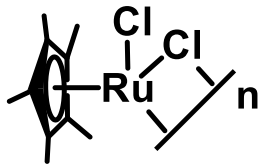
➢ *Trans* hydrogenation and *trans* hydrometallation

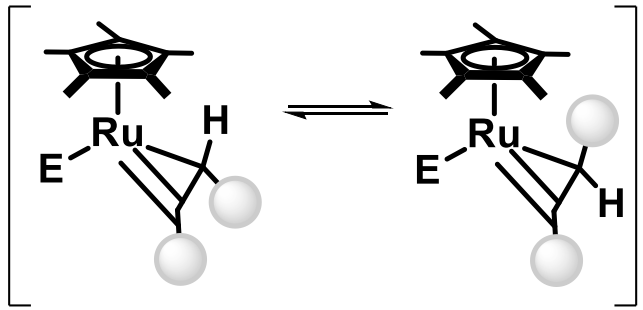
- **Different mechanism**



Ru precatalyst

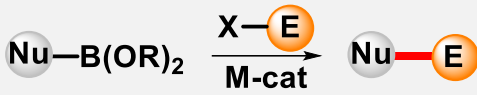




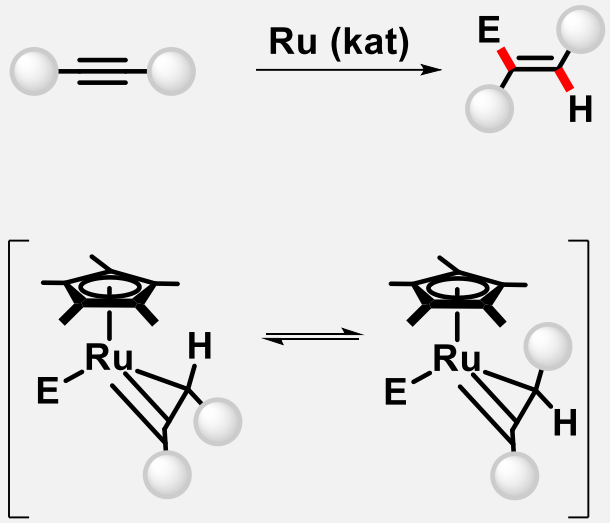


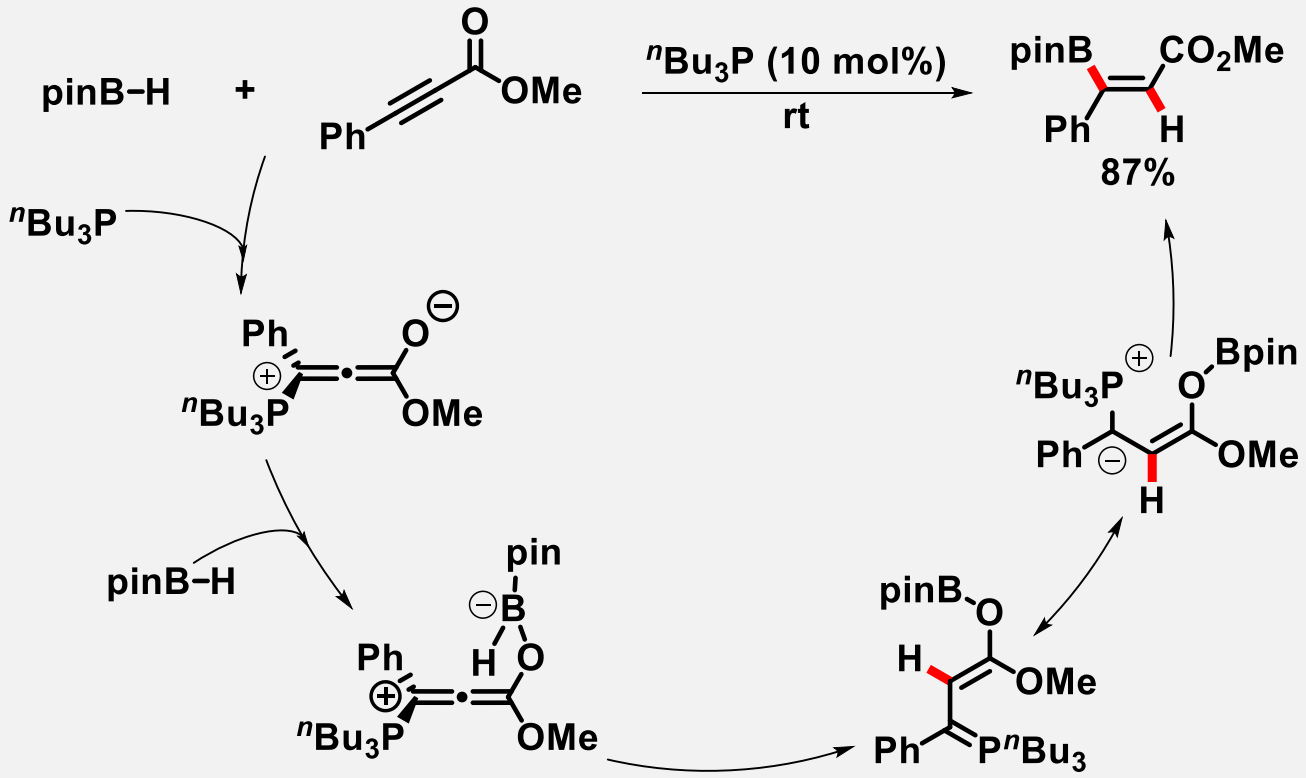
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ Suzuki Reaction (Suzuki–Miyaura reaction)



- Synthesis of boronic acids or boronic acid esters
  - Anti hydroboration (suitable for vinylboronic acids)





J. Org. Chem. **2018**, *83*, 10436