
Low-Valent Tungsten Redox Catalysis Enables Controlled Isomerization and Carbonylative Functionalization of Alkenes

Nat. Chem. 2022, 14, 632–639, DOI: 10.1038/s41557-022-00951-y.

Tungsten-Catalyzed Alkene Isomerization/ Hydrocarbonylative Cyclization

![Reaction Profile Diagram]

Selected examples:
- 79% yield, dr = 3:1
- 40% yield
- 76% yield
- 65% yield
- 93% yield
- 82% yield
- 85% yield, dr > 20:1
- 65% yield, dr > 20:1

Proposed reaction profile:

Mechanistic experiments:
- 88% yield, >98% D retention
- 90% D

**Significance:** A tungsten-catalyzed isomerization of terminal alkenes to unactivated internal positions followed by subsequent hydrocarbonylation with CO is reported. This work addresses common challenges associated with the regioselectivity of tandem alkene isomerization/functionalization reactions.

**Comment:** Experimental and DFT studies were carried out to elucidate the mechanism. Key to this transformation is the six- to seven-coordinate geometry changes present in the W(0)/W(II) redox cycle and the presence of a conformationally flexible directing group that allows for isomerization to take place.

**Key words**
tungsten catalysis
alkene functionalization
hydrocarbonylation
redox catalysis

**SYNFACTS Contributors:** Mark Lautens, Alexa Torelli

Synfacts 2022, 18(09), 0977 Published online: 18.08.2022
DOI: 10.1055/s-0041-1738683; Reg-No.: L10122SF