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

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**Tungsten-Catalyzed Alkene Isomerization/ Hydrocarbonylative Cyclization**

**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.

**Proposed reaction profile:**

**Mechanistic experiments:**

**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

- 90% D retention
- >98% D retention

- 88% yield
- 85% yield, dr > 20:1
- 90% D