TSRI - CHEM 530
Organometallics

Day 7: Carbenes and other M–C and M–X Multiple Bonds

April 15, 2019

TODAY'S TOPICS

- Fischer carbenes
- Schrock carbenes
- NHCs
- diazo transfer
- carbynes, oxos, and imidos

CHEMIST OF THE DAY

name?
known for?

QUOTE OF THE DAY

"The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.

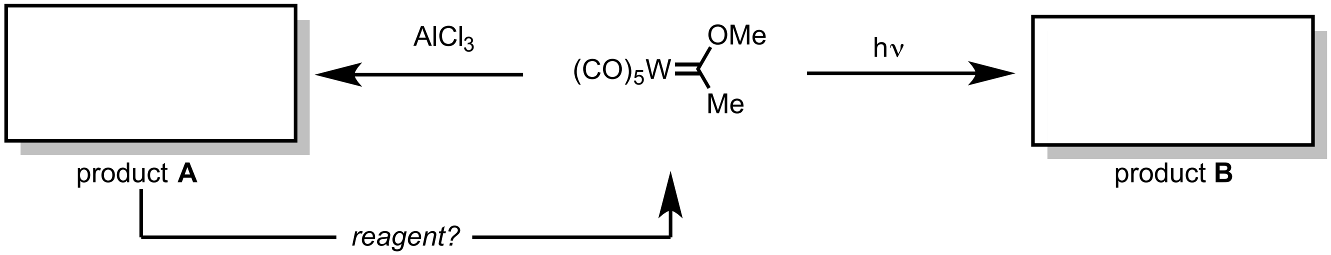
- Sir William Bragg

READING

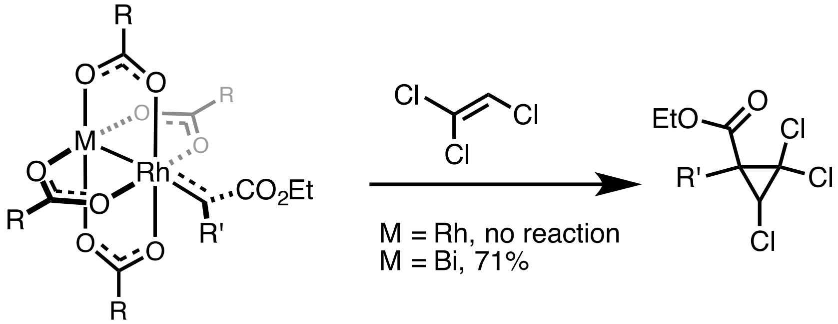
Hartwig: Ch. 13
Crabtree: Ch. 11

PROBLEMS OF THE DAY

#1 When the tungsten–carbene shown below is treated with a Lewis acid (left) or irradiated with light (right), two different products, **A** and **B**, are formed. **Predict the structures of A and B, and push arrows to rationalize both connectivities.** *Bonus:* How can product **A** be recycled back to the starting material?



#2 In an effort to probe the mechanistic nuances of dirhodium(II) catalysts in carbene transfer reactions, several groups have studied variants in which one Rh(II) center is replaced with Bi(II). These complexes only exhibit Lewis acidic behavior at the Rh(II) face, thereby providing a model system in which there is no ambiguity over the nature of distal metal ligation. Lately, there is growing interest in studying hetetobimetallic Rh paddlewheel dimers as catalysts for carbene transfer reactions, including the following example by Neese and Fürstner.



Replacement of rhodium with bismuth leads to a more reactive complex in the cyclopropanation of tetrachloroethylene. **Rationalize this observation.**

#3 Transition-metal–silylene complexes are the silicon analog of transition-metal–carbene complexes.

A. Draw qualitative orbital diagrams for a transition-metal–silylene and contrast it to carbenes. (Do you believe silyene is predominantly singlet or triplet in nature?)

B. Based on your reasoning in Part A, **predict how silylenes, stannylene, and germylenes behave as σ-donors and π-acceptors.**