

Organoiron Chemistry

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Baran Group Meeting

9/17/03

Iron

- Hull-Rust Mine in Hibbling, Mn is the largest open pit iron mine in the world
- Iron oxide is produced by every car in New England everyday
- Oxygen is brought to you today by the element iron
- USA used 60 million metric tons of iron ore in 2002

Iron vs. Palladium

- Extensive work has been conducted on Pd chemistry
- Cross coupling reactions are extremely effective but have their disadvantages
 - Ligands needed to create reactive species
 - High cost
 - Reaction times

Iron vs. Palladium

- Cost Difference
 - 6.0 kg of FeCl_3 (97%) = \$85.90
 - 6.0 kg of PdCl_2 (99%) = ?

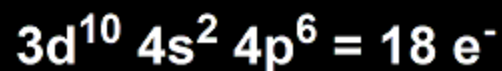
\$69,632.00

The Chemistry

- Fe literature is extensive
- Selected chemistry of Fe (-II), Fe(0), Fe(II), Fe(III) oxidation states

Inorganic Primer

18 e⁻ Rule: Stability is found, but does not require, a full compliment of electrons surrounding the metal center.

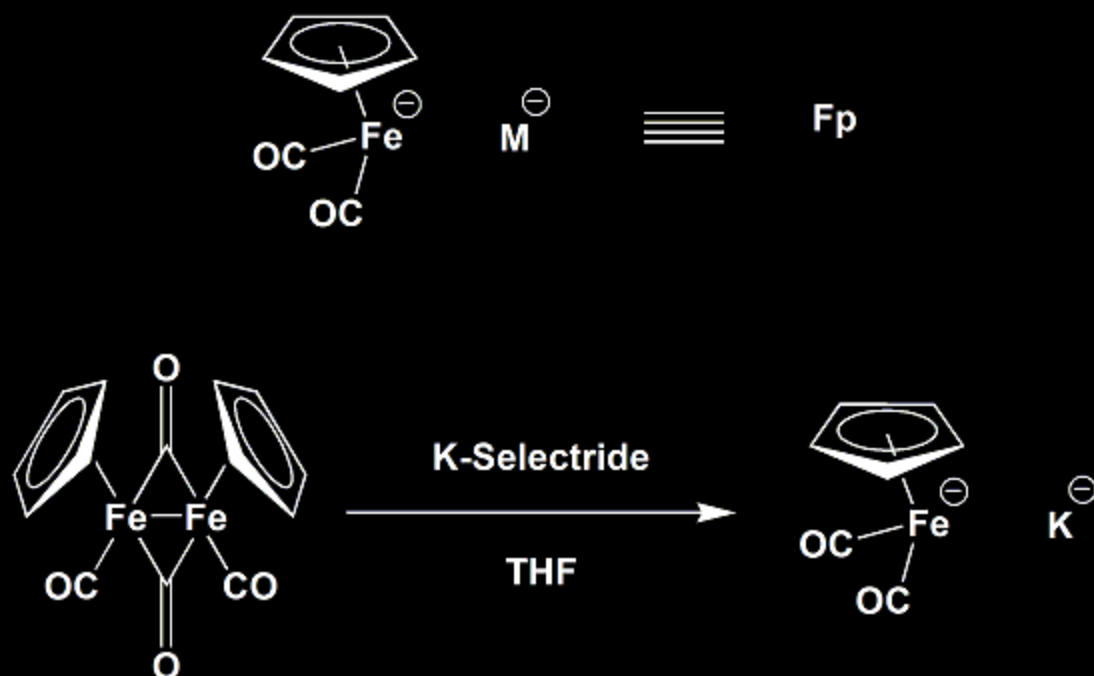


Hund's Rule of Maximum Multiplicity: Lowest energy electron arrangement desired

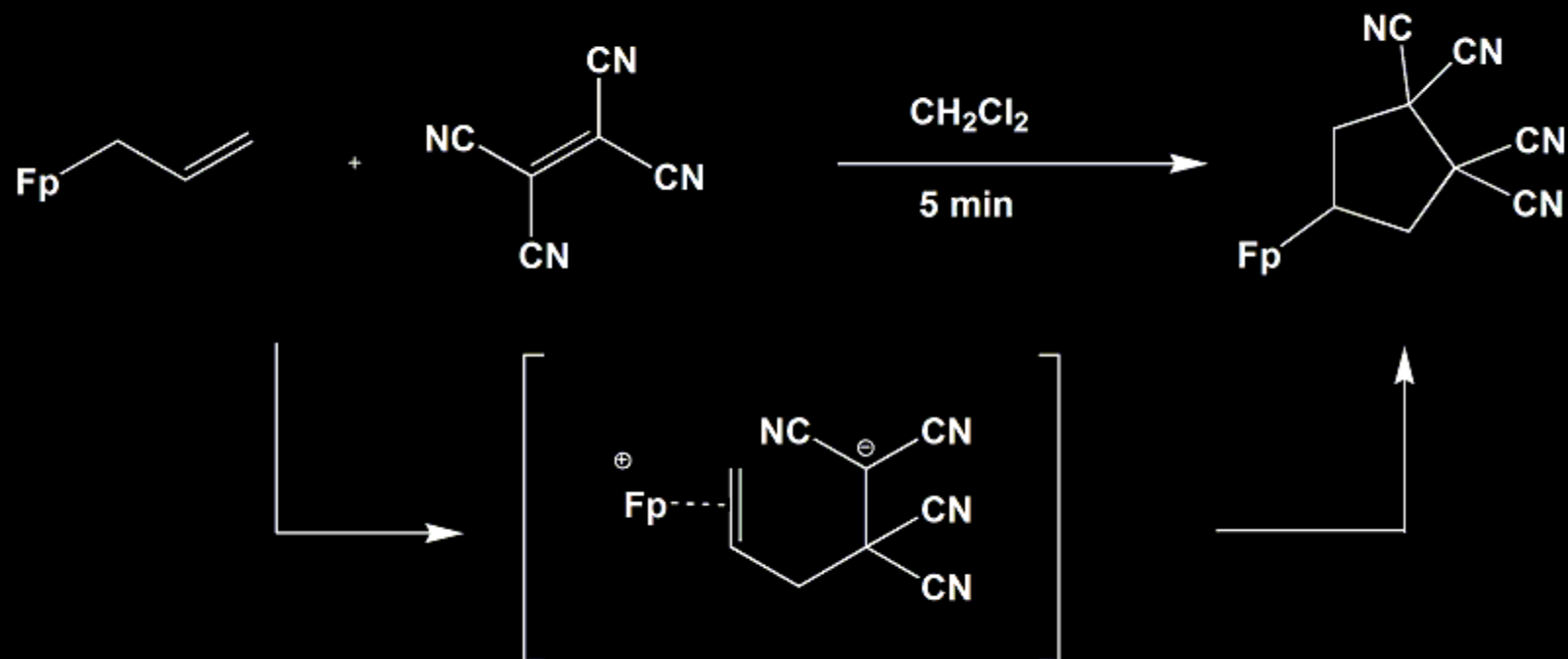
Hapticity

Fe (0) and Fp

Synthesis of Dicarbonyl(cyclopentadienyl)ferrate

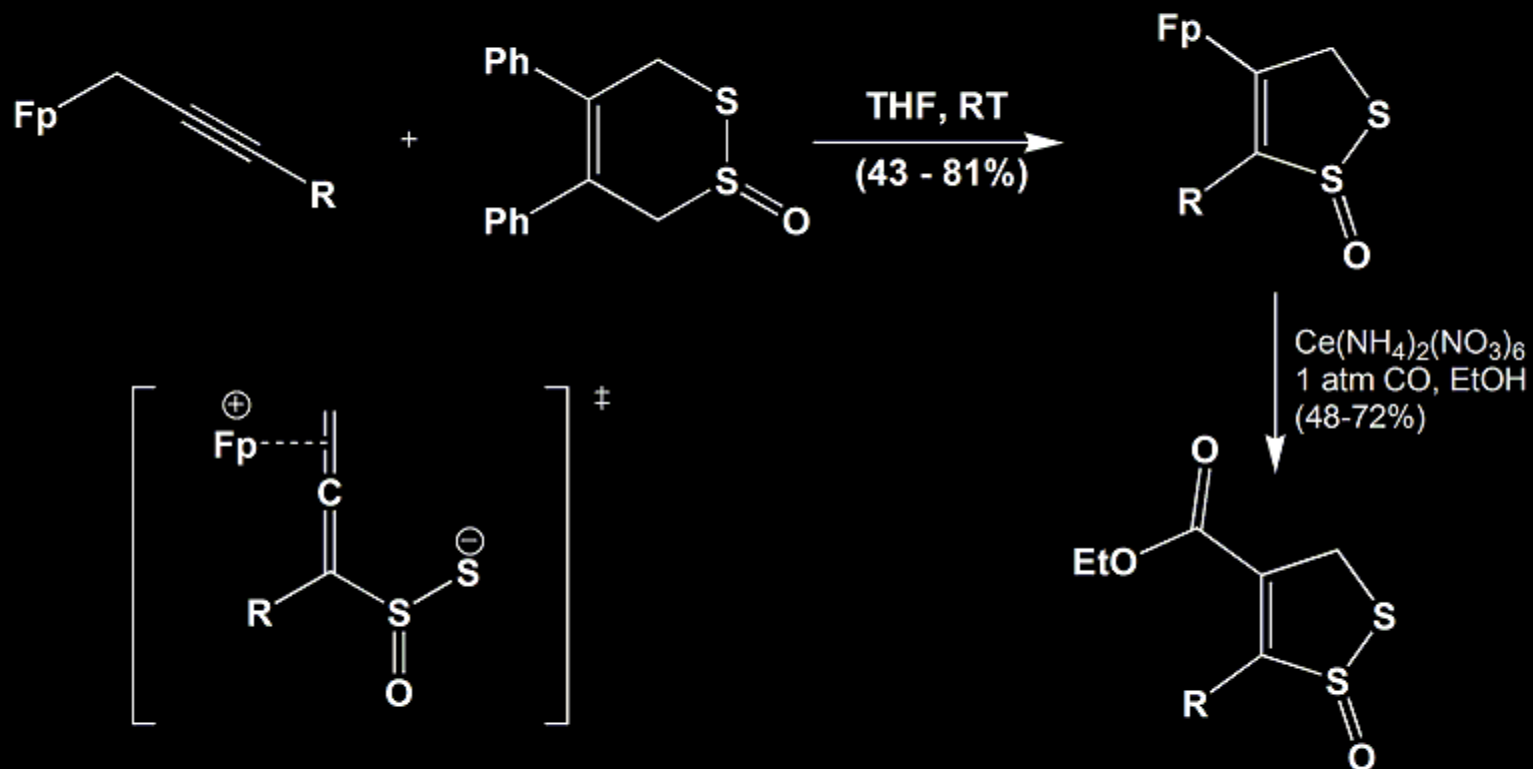


Fe (0) and Fp



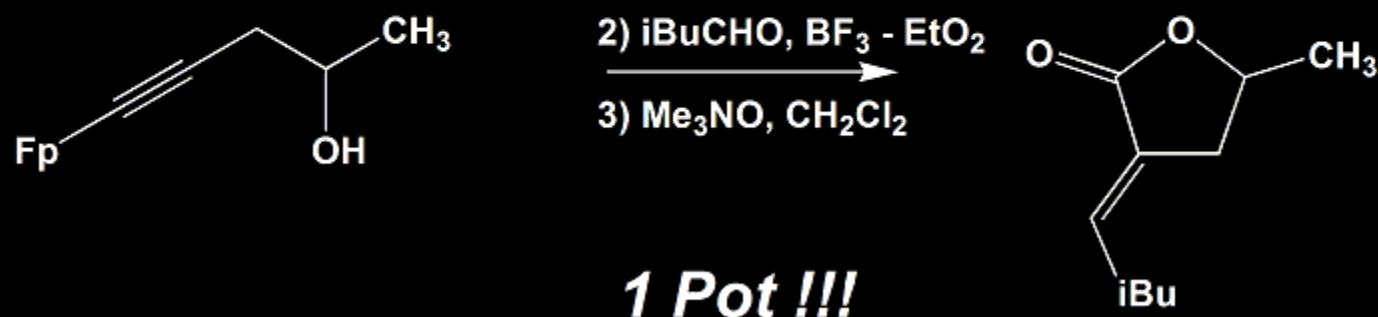
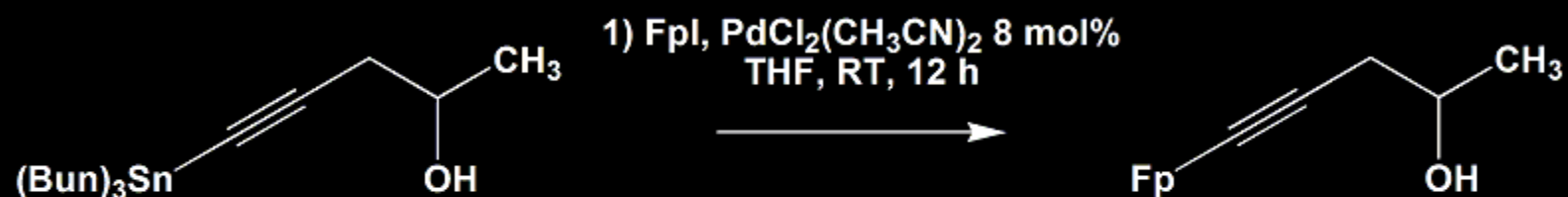
Fe (0) and Fp

Heterocycles

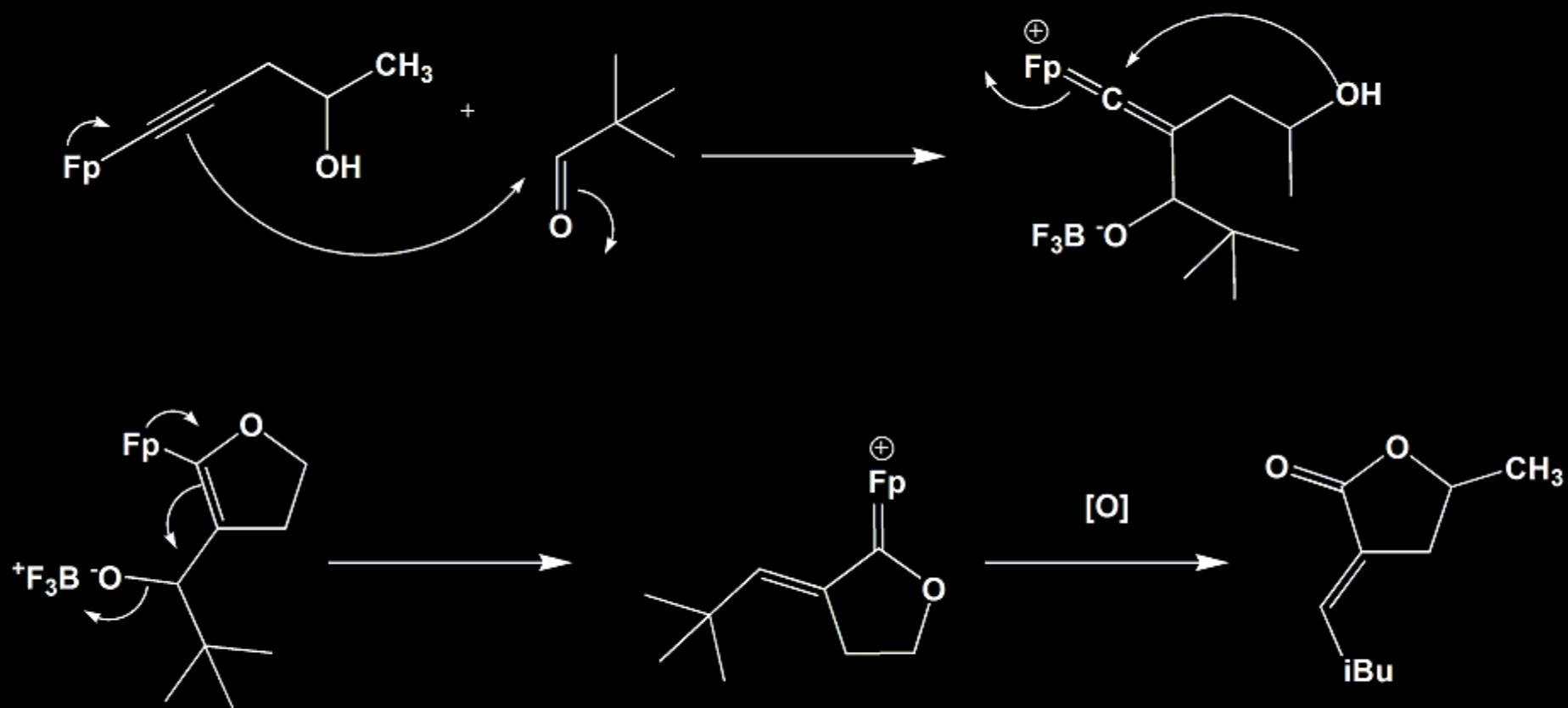


Fe (0) and Fp

Heterocycles: Lactones and Lactams

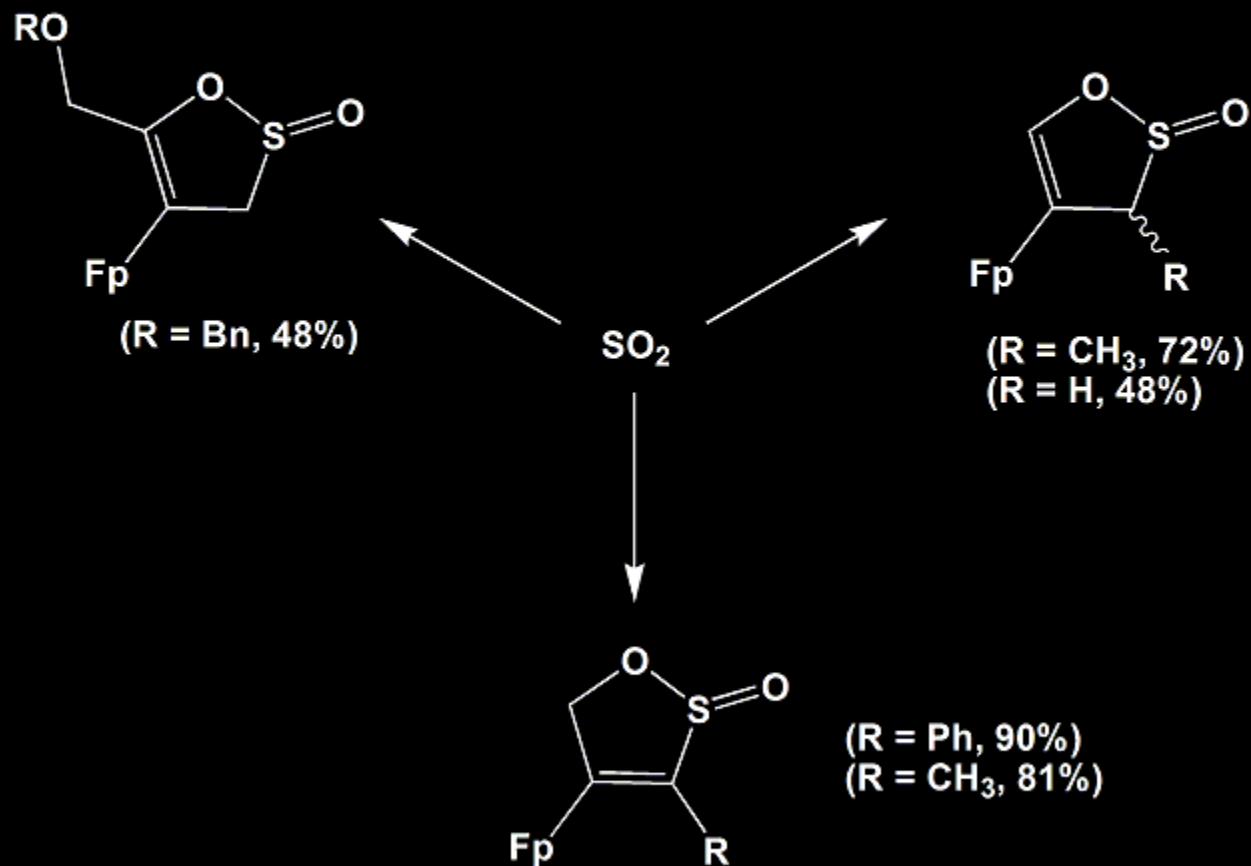


Fe (0) and Fp



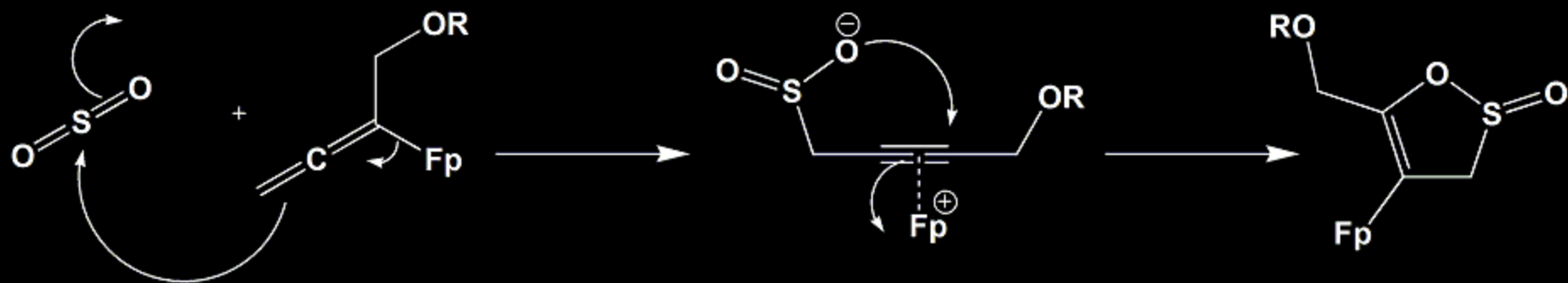
Fe (0) and Fp

Heterocycles: Cycloaddition to SO₂



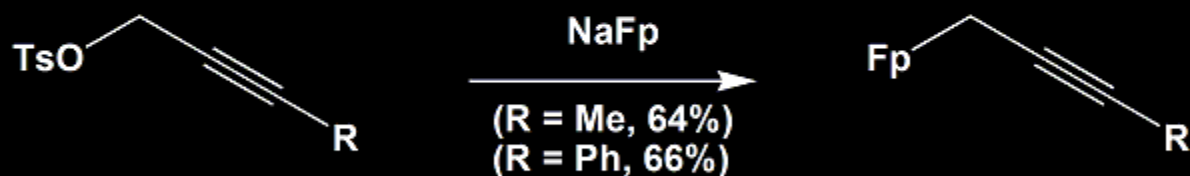
Fe (0) and Fp

Mechanism of SO₂ Addition

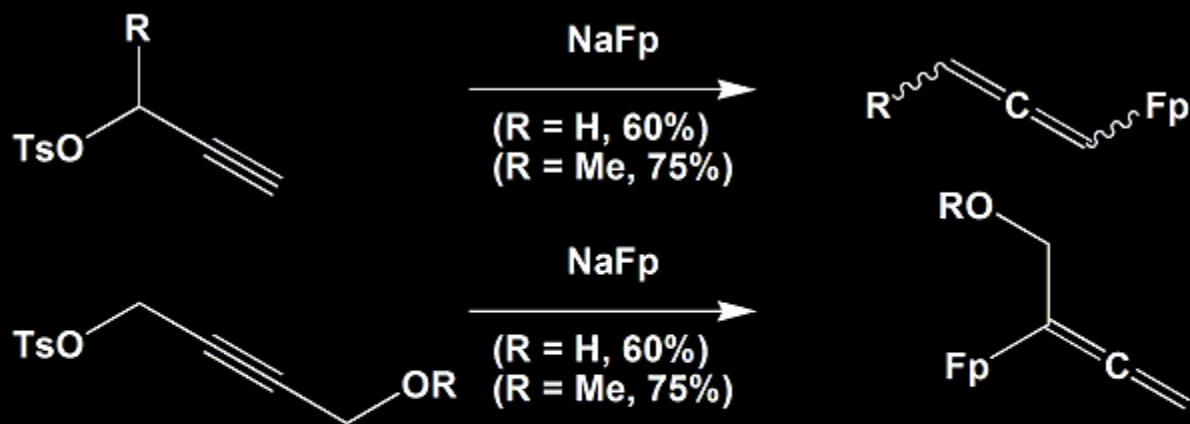


Fe (0) and Fp

Synthesis of α -Fp Alkynes

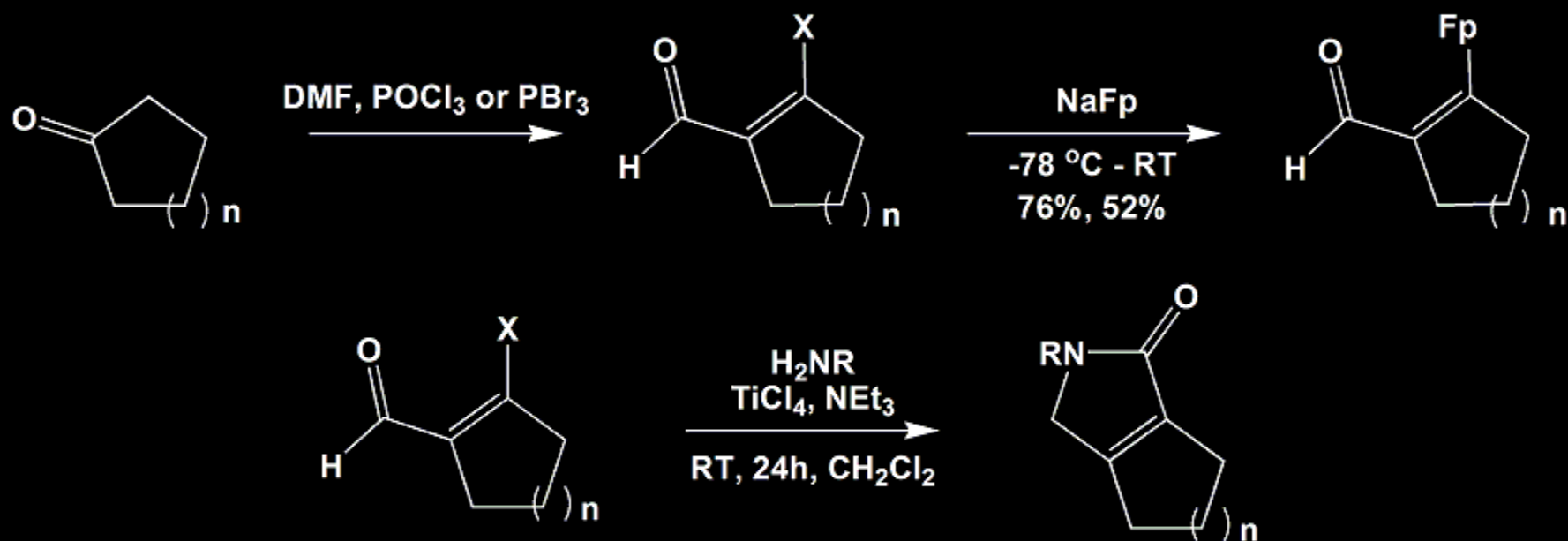


Synthesis of Fp Allenes and 1,1-Alkoxy-Fp Allenes



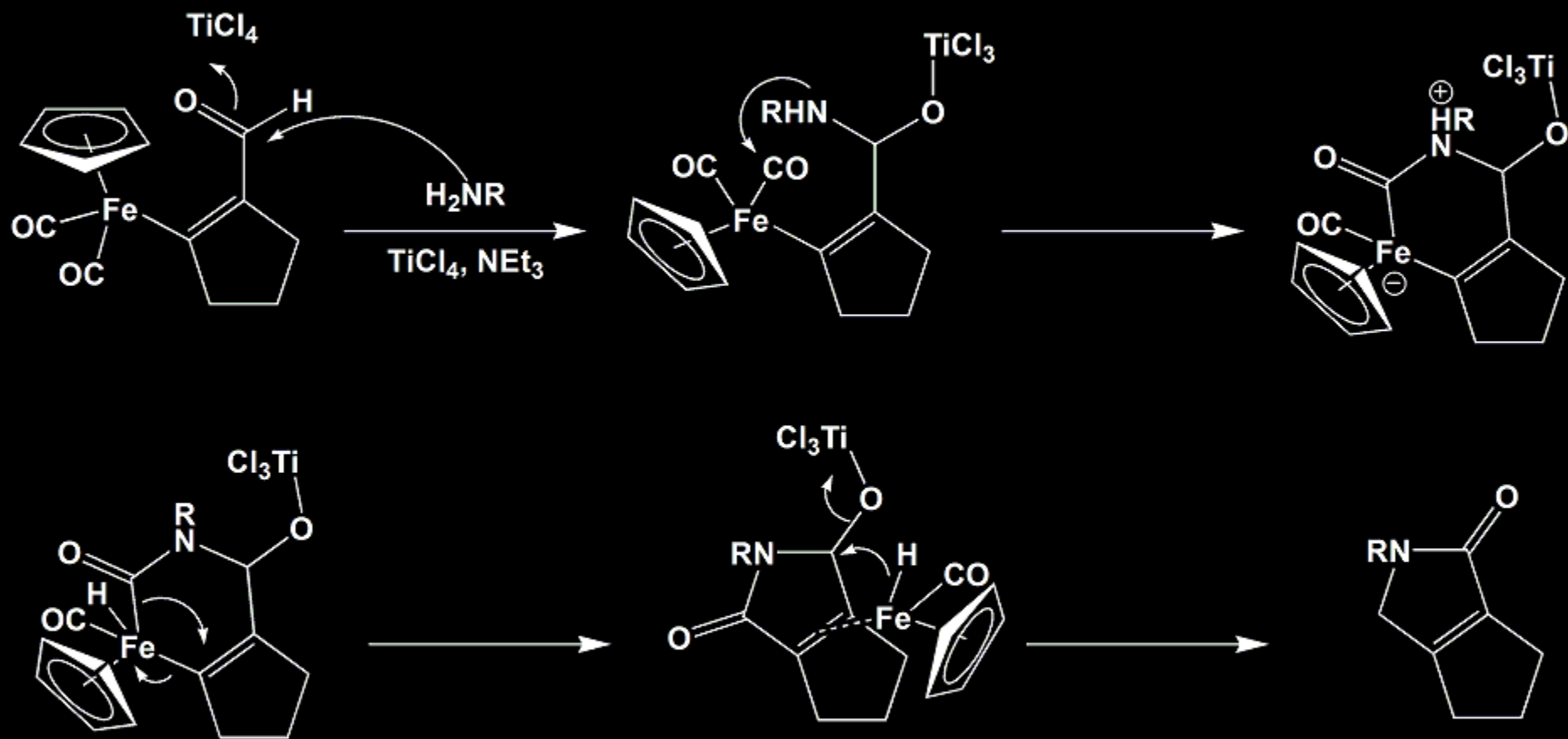
Fe (0) and Fp

Heterocycles: Lactones and Lactams



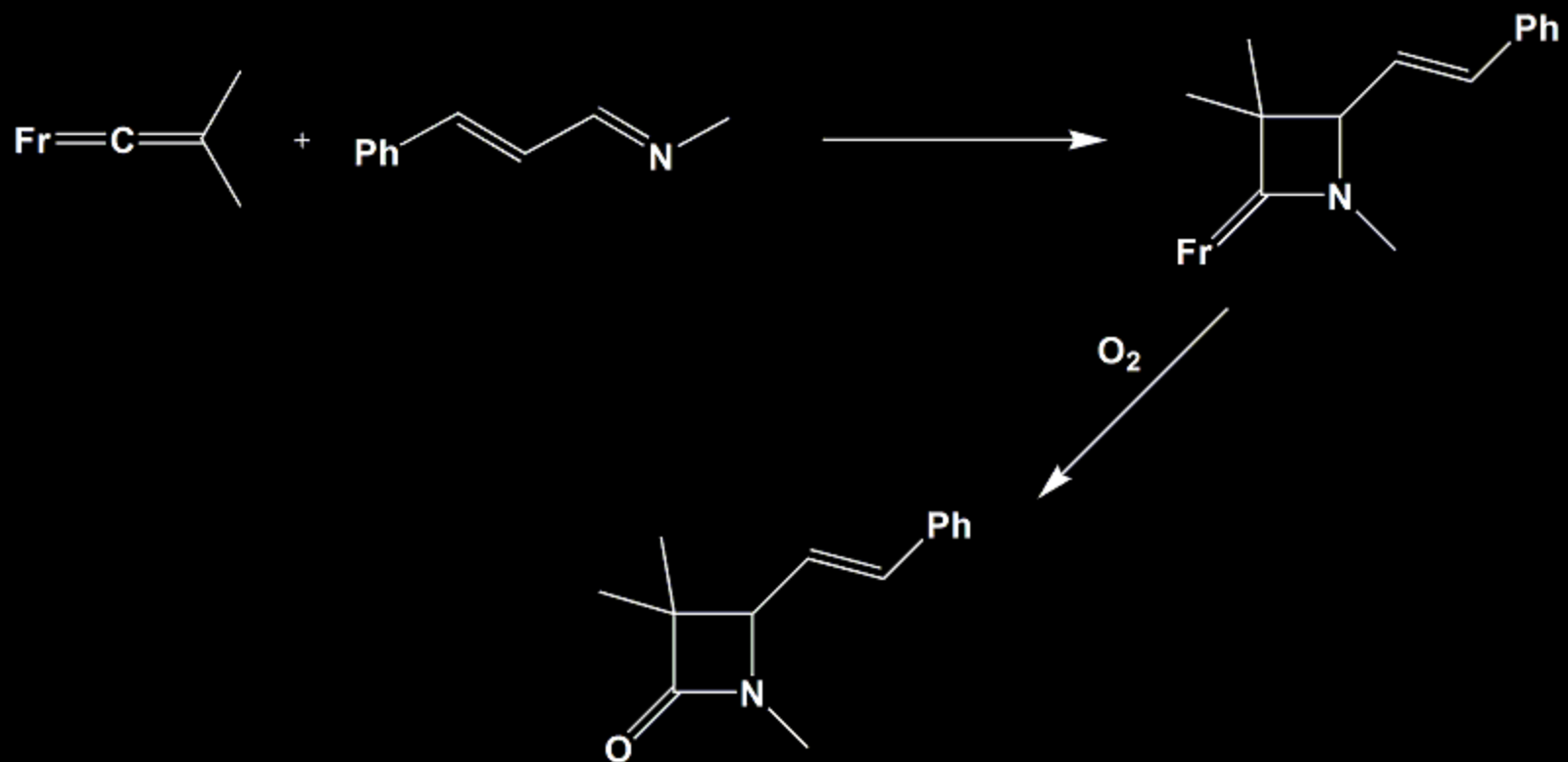
n = 2, 3
R = C₆H₁₁, 56%
R = (S)-CH(CH₃)Ph, 61%

Fe (0) and Fp



Fe (II) and Fr

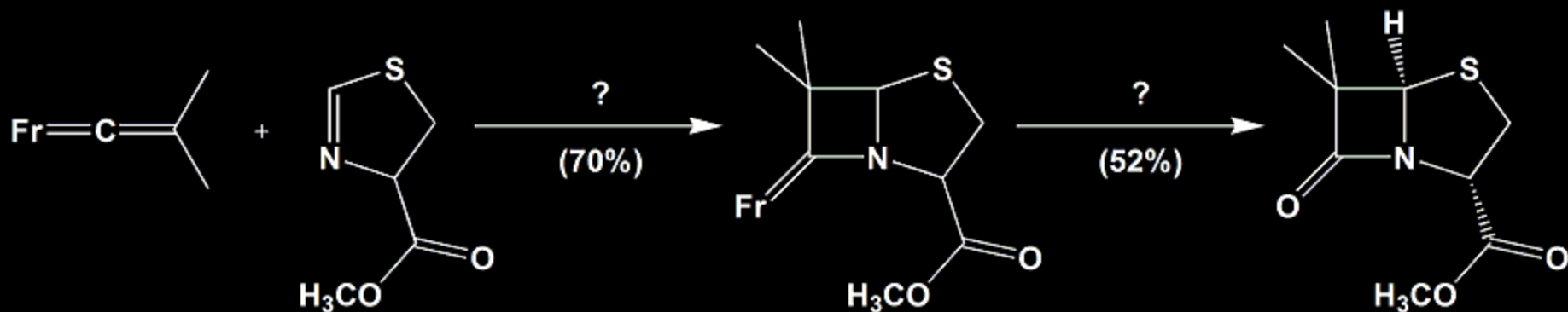
Heterocycles



$\text{Fr} = (\text{Ph}_3\text{P})(\text{Cp})(\text{OC})\text{Fe}^+$

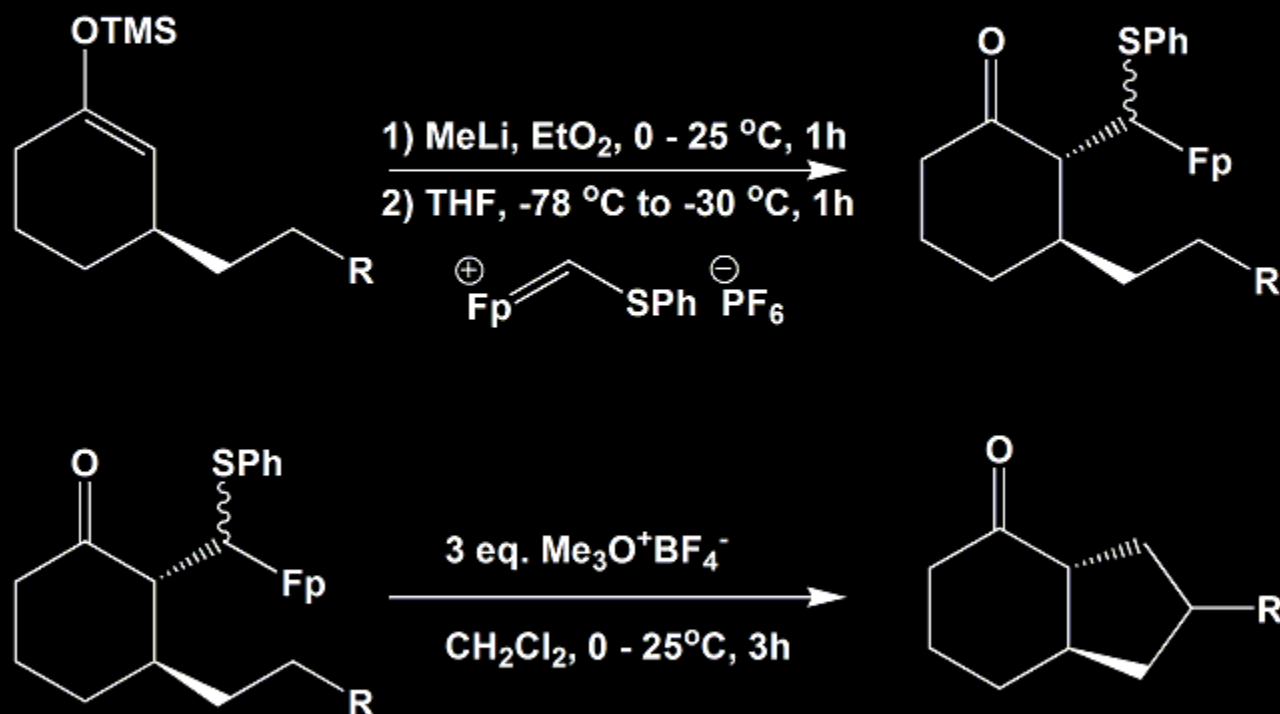
Fe (II) and Fr

Heterocycles

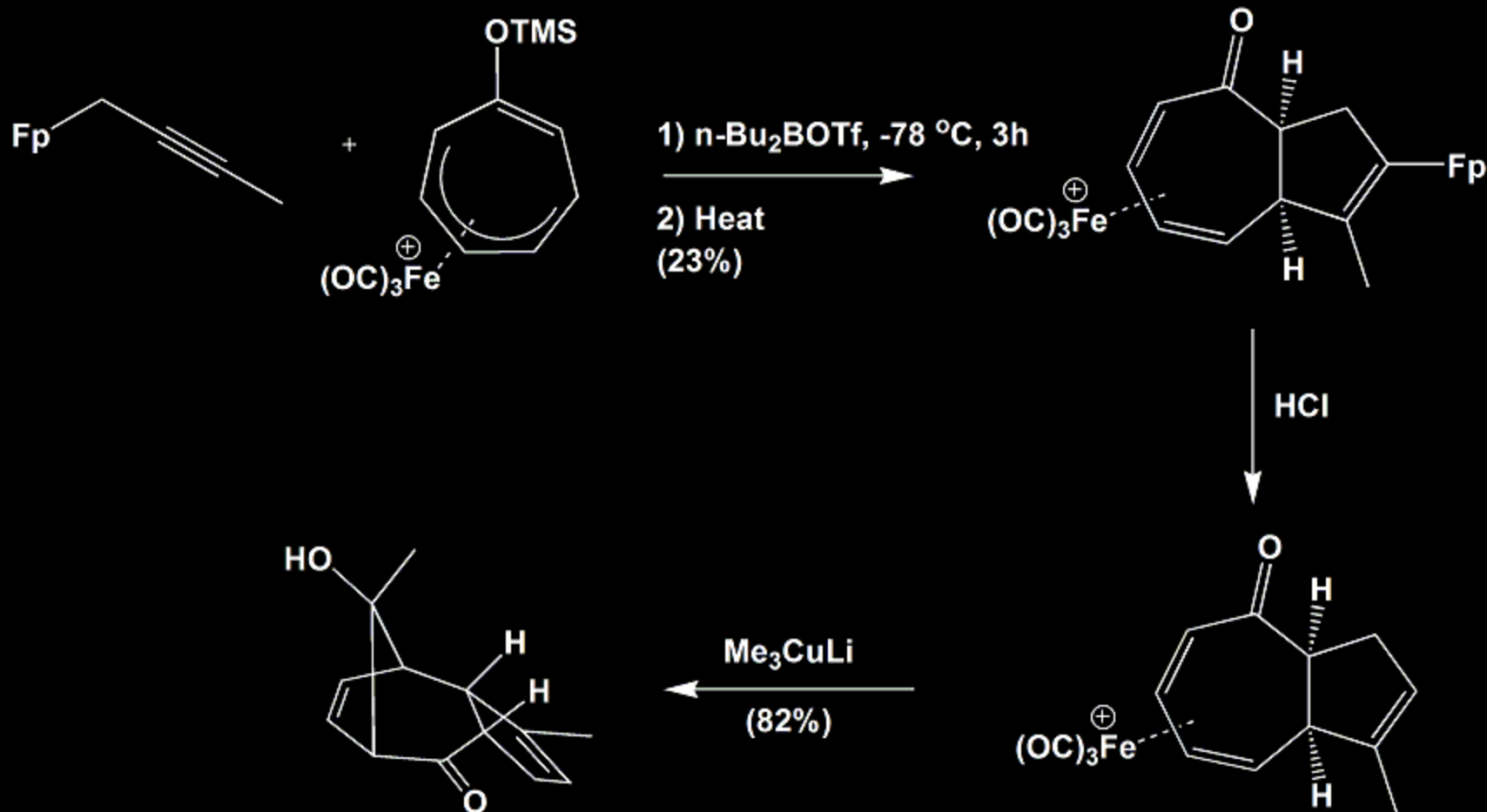


Fe (0) and Fp

C-H Bond Insertion: Cationic Carbenes

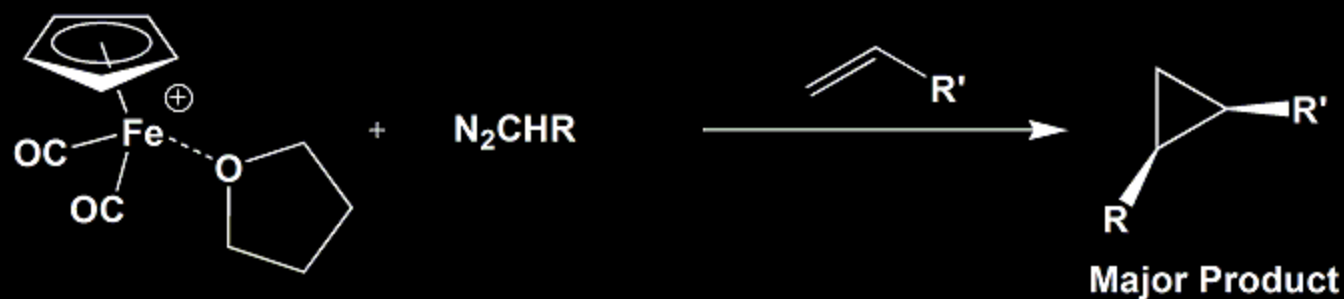


Fe (II), Fe(0), Fo and Fp



Fe (0) and Fp

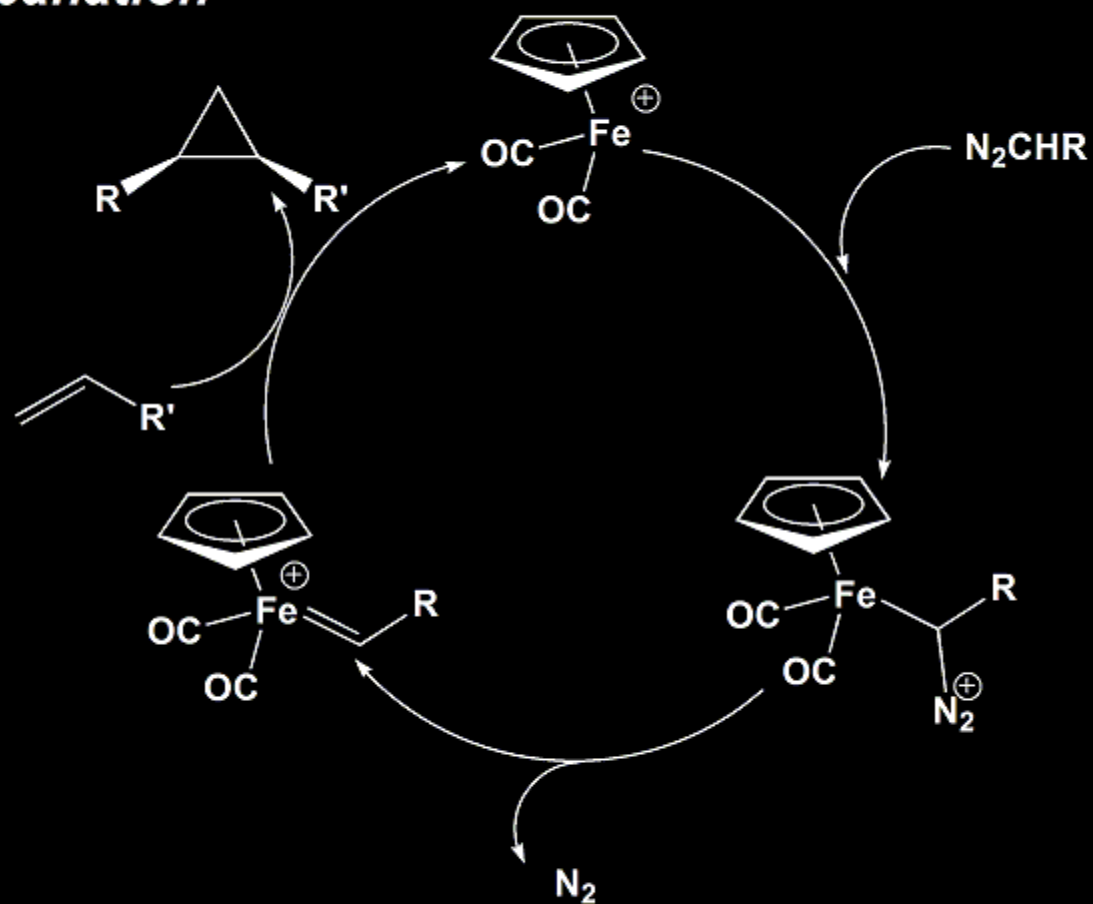
Cyclopropanation



20- 80% yields with 50/1 to all cis product

Fe (0) and Fp

Cyclopropanation



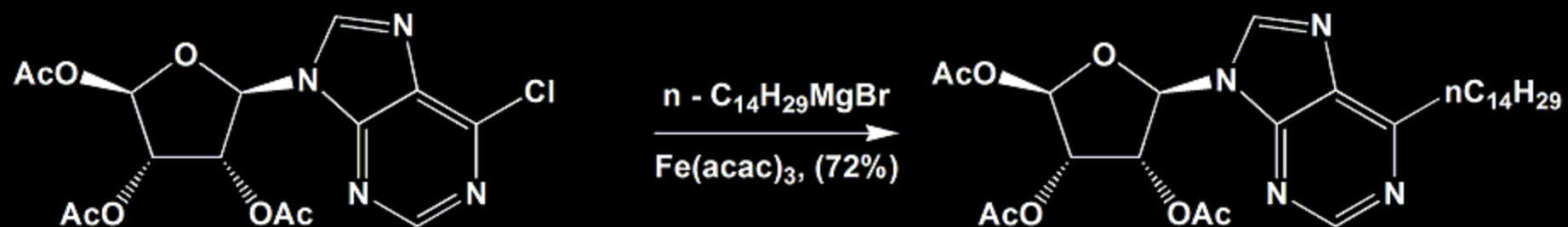
Fe (-II)

Iron Catalyzed Cross Coupling



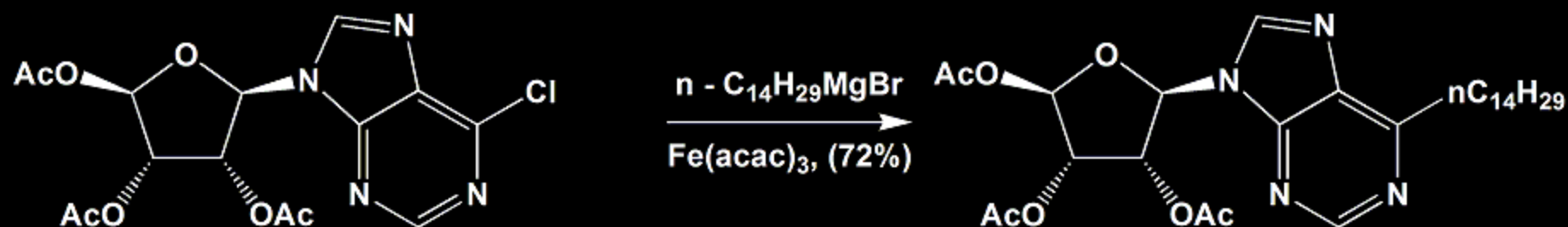
Fe (-II)

Amazing Iron Catalyzed Cross Coupling



Fe (-II)

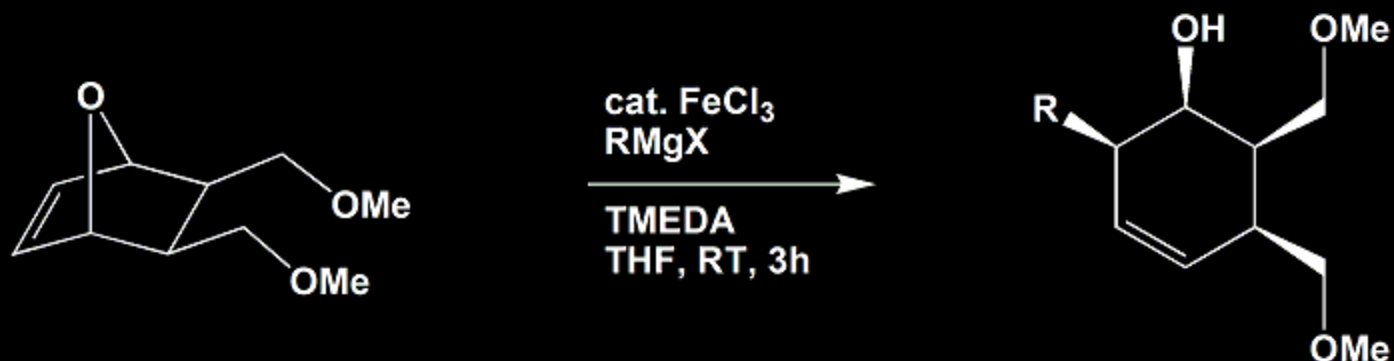
Amazing Iron Catalyzed Cross Coupling



NO Acyl Addition

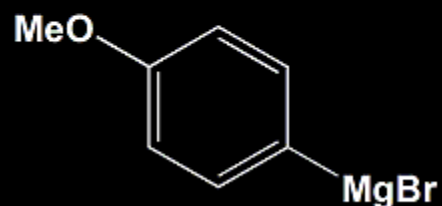
Fe (III)

Stereoselective Ring Opening

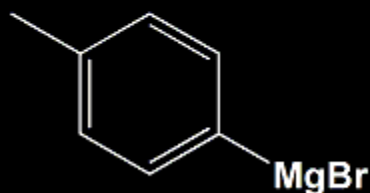


Fe (III)

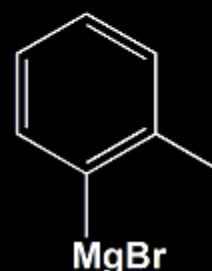
Stereoselective Ring Opening: Grignards



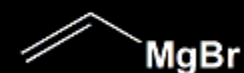
3h, (69%)



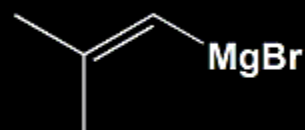
5h, (72%)



1h, (75%)



13h, (41%)



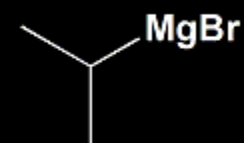
5h, (40%)



1h, (24%)

n C₁₄H₂₉MgBr

1h, (54%)



1h, (92%)

Summary

Fe-alkene, allene, alkyne chemistry

Fe is cheap with respect to Pd

18 e⁻ Rule

Hapticity

Simplicity of Use

Fe keeps you alive
