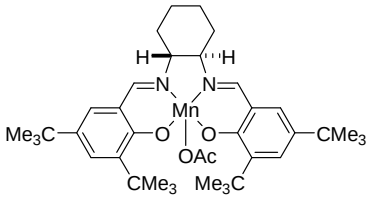
Lecture "Modern Synthetic Methods"

Take-home messages from Week 14

3.4. Metal-mediated redox-processes

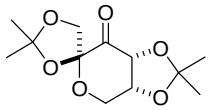
Oxidations:

Jacobsen-Epoxidation:



- Chiral Mn^{III}-salen ligand and NaOCl
- Radical mechanism of oxygen atom transfer
- Works best with *Z*-olefins, trisubstituted olefins require addition of pyridine-*N*-oxides

Shi-Epoxidation:



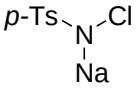
- Organocatalytic epoxidation using a chiral ketone derived from fructose, forming a chiral dioxirane

Dihydroxylation:

- (Chiral) amines catalyze the reaction
- Two competing catalytic cycles, one with low ee
- Biphasic reaction mixture, reoxidation of OsO_3 in the aqueous phase → shutting down of the second cycle
- $(DHQ\mathit{D})_2PHAL$: quini(*di*)ne ligands linked by phtalazine

Aminohydroxylation:

- Formation of $O_3Os{=}NR$
- Terminal oxidant i.e. Chloramine-T:

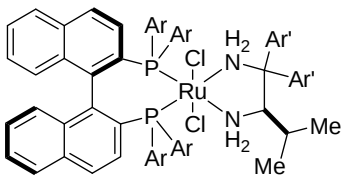


Reductions:

Olefin reduction:

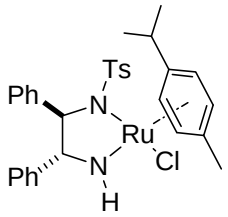
- Rh/Ru complexes with chiral phosphines (e.g. BINAP)

Ketone reduction:



- Corey-Itsuno reduction (with BH_3)
- Noyori reduction of β-keto-esters (with H_2)

Transfer hydrogenation:



- Mechanism related to Oppenauer/Meewein-Ponndorf-Verley
- Equilibrium can be shifted by excess/removal of reagent (isopropanol/acetone)