Bäckvall's Dynamic Kinetic Resolution

Significance: In 1997, Bäckvall and co-workers presented a ruthenium(II)-catalyzed racemization of secondary alcohols coupled with enzymatic kinetic resolution to form the corresponding acetates in high yields and enantiomeric excesses. This protocol's advantage over common kinetic resolution is a theoretical yield of the enantiomerically enriched acetates of 100%. A monomeric ruthenium complex later introduced is able to racemize alcohols in under 10 min at room temperature with a low catalyst loading of 0.5 mol% (Angew. Chem. Int. Ed. 2004, 43, 6535). This catalyst is still the benchmark for the racemization of secondary alcohols.

Comment: Bäckvall's dynamic kinetic resolution (DKR) is the first example of a dual catalytic system combining transition-metal and enzyme catalysis. From a mechanistic point of view, a slippage of the Cp ring from η⁵- to η³-coordination to form a free coordination site was initially assumed in the racemization process, but computations as well as mechanistic experiments strongly suggest a CO dissociation mechanism (Acc. Chem. Res. 2013, 46, 2545).