CpRu-Catalyzed Pyridine Dearomatization Through Double Carbene Insertions

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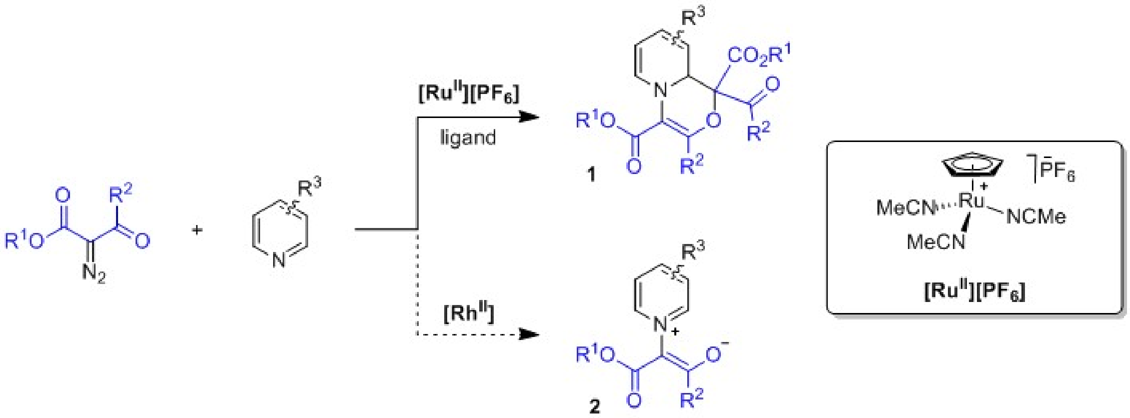
CpRu complexes are interesting alternatives to copper and dirhodium species for the metal-catalyzed decomposition of diazo compounds.[1] In this context, it has been shown that combinations of $[CpRu(CH_3CN)_3][PF_6]$ and diimine ligands react catalytically with α-diazo-β-ketoesters and allow subsequent condensation, OH and 1,3-CH insertion reactions.[2] Recently, using this catalytic combination, new dioxene motifs were synthetized by enantiospecific *syn* -opening of epoxides.[3]

In a new development that uses electron-poor pyridines and quinolines as substrates, the direct formation of original oxazine moieties **1** is described. Reactions proceed by tandem (double) additions of carbenes and a dearomatization of the azaaromatics. Such a process occurs primarily *via* ruthenium cyclopentadienyle catalysis since, under Rh(II)-mediated reactions, pyridinium ylides **2** are the major adducts.[4] Mechanistic insights will be also presented.



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