Initial Stages in the Rhodium(III)-Catalyzed C-H Bond Activation of Primary Alcohols in Aqueous Solution

The mechanism of the catalytic H/H exchange in primary alcohol substrates derived from aldopentoses, promoted by a macrocyclic rhodium(III) complex, has been shown to occur by a reversible redox reaction that gives aldehyde and a rhodium hydride complex. Hydride exchange in the latter complex promotes the introduction of solvent hydrogen in the primary alcohol formed by the reverse reaction. The hydride complex has been crystallographically characterized as a trifluoromethanesulfonate salt that contains the trans-[Rh(cycb)(H)(OH2)](2+) (cycb = rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) cation. The hydride complex is stable for extended periods of time in acidic solution in the absence of oxidants. In basic solutions a series of base-catalyzed reactions take place to yield ultimately the same mixture of [Rh(cycb)(OH)(2)](+) isomers as produced by base hydrolysis of the trans-[Rh(cycb)(Cl)(2)](+) complex.