Experimental and Theoretical Mechanistic Investigation of the Iridium-Catalyzed Dehydrogenative Decarbonylation of Primary Alcohols

The mechanism for the iridium-BINAP catalyzed dehydrogenative decarbonylation of primary alcohols with the liberation of molecular hydrogen and carbon monoxide was studied experimentally and computationally. The reaction takes place by tandem catalysis through two catalytic cycles involving dehydrogenation of the alcohol and decarbonylation of the resulting aldehyde. The square planar complex IrCl(CO)(rac-BINAP) was isolated from the reaction between [Ir(cod)Cl](2), rac-BINAP, and benzyl alcohol. The complex was catalytically active and applied in the study of the individual steps in the catalytic cycles. One carbon monoxide ligand was shown to remain coordinated to iridium throughout the reaction, and release of carbon monoxide was suggested to occur from a dicarbonyl complex. IrH2Cl(CO)(rac-BINAP) was also synthesized and detected in the dehydrogenation of benzyl alcohol. In the same experiment, IrHCl2(CO)(rac-BINAP) was detected from the release of HCl in the dehydrogenation and subsequent reaction with IrCl(CO)(rac-BINAP). This indicated a substitution of chloride with the alcohol to form a square planar iridium alkoxo complex that could undergo a beta-hydride elimination. A KIE of 1.0 was determined for the decarbonylation and 1.42 for the overall reaction. Electron rich benzyl alcohols were converted faster than electron poor alcohols, but no electronic effect was found when comparing aldehydes of different electronic character. The lack of electronic and kinetic isotope effects implies a rate-determining phosphine dissociation for the decarbonylation of aldehydes.