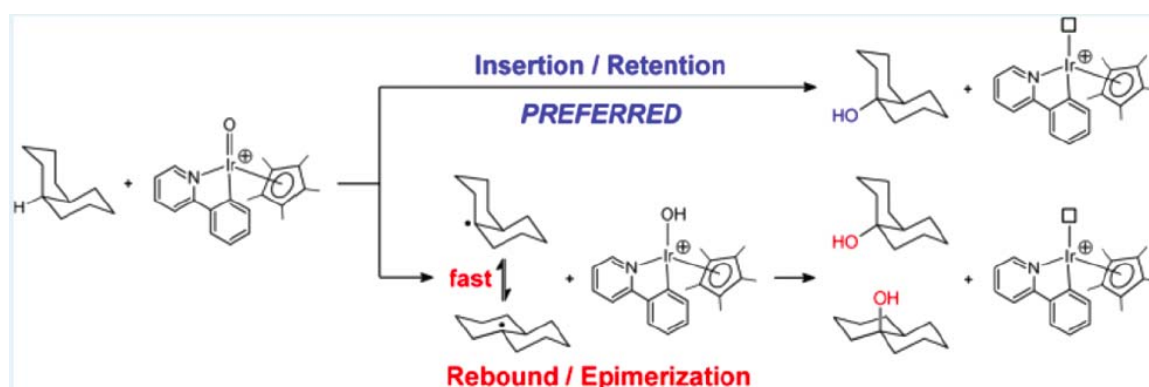


Organometallic Precatalysts for Oxidation of Water and Alkyl CH Bonds

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With primary oxidants Ce(IV) and NaIO₄, precatalysts of the types Cp*Ir(chel)Cl (chel = dipy, 2-pyridylphenyl and related) mediate oxidation of alkyl C-H to C-OH with retention of configuration at carbon. Calculations by David Balcells and Odile Eisenstein suggest a spin state dependence of the pathway (see Figure).¹ For example, cis-decalin is converted to cis-9-decalol. In collaboration with Gary Brudvig, we find that these oxidants, as well as anodic oxidation, lead to water being converted to dioxygen by Cp*Ir(chel)Cl and [Cp*Ir(OH₂)₃]SO₄.² In some cases the catalysis is homogeneous, in others heterogeneous, a distinction that is made from dynamic light scattering and quartz crystal nanobalance measurements.³ In the case of [Cp*Ir(OH₂)₃]SO₄, for example, a blue layer (BL) of electrochromic iridium oxide is deposited on the anode; this is an extremely active water oxidation catalyst.⁴



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