Mechanistic Investigations of "Ligand-Free" Kumada-Tamao-Corriu Cross-Coupling Reactions

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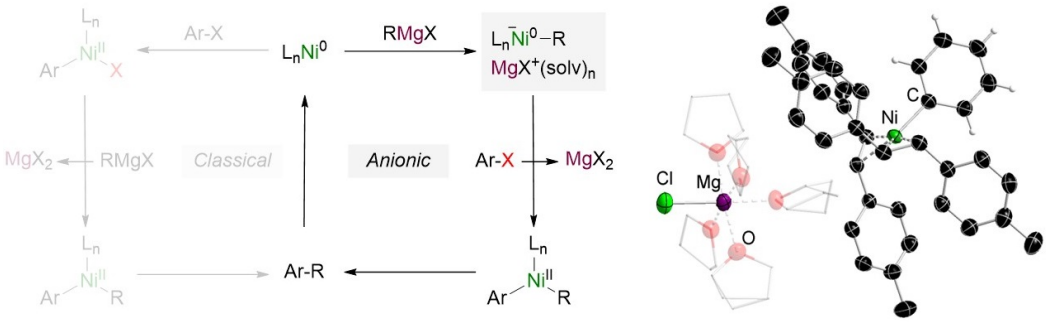
The Kumada-Tamao-Corriu (KTC) cross-coupling reaction was first reported in 1972 and is a powerful synthetic tool to form C–C bonds from Grignard reagents and C(sp^2)–halides using nickel catalysts.[1] Only a few years later, in 1979, Wenkert reported the use of aryl ethers as electrophilic coupling partners in KTC reactions.[2] Since then, the reaction has been further developed and efforts have been directed towards mechanistic understanding.[3] The majority of this research however involves the use of bespoke electron-donating ligands, such as NHCs and phosphines.

In this work, we will focus on mechanistic investigations of the KTC reaction using simple Ni(0)-olefin or Ni(II) catalysts, without the use of auxiliary ligands. Under these "ligand-free" conditions, the reaction instead relies on the formation of electron-rich anionic nickelates,[4] several of which have been isolated and characterised by solution and solid-state techniques. Furthermore, evidence that points towards the importance of bimetallic cooperativity in the Ni-catalysed cross-coupling of aryl ethers will be discussed.[5]



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