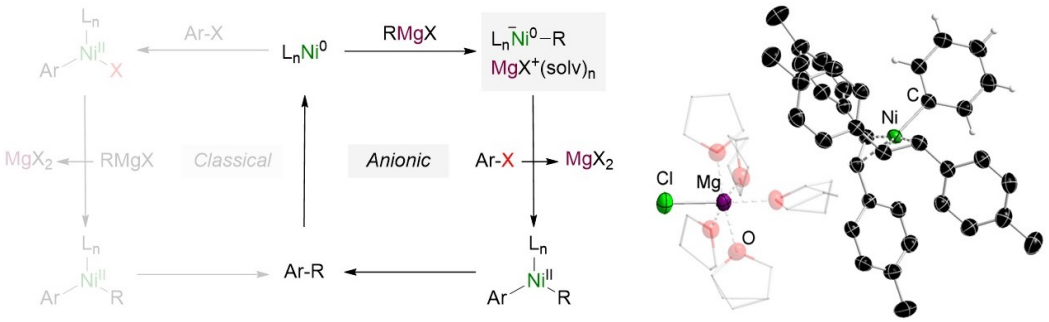
Mechanistic Investigations of "Ligand-Free" Kumada-Tamao-Corriu Cross-Coupling Reactions

L. Vedani[1], A. M. Borys[1], E. Hevia[1]*

[1]Universität Bern, Departement für Chemie, Biochemie und Pharmazie

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]



[1] a) K. Tamao, K. Sumitani, M. Kumada. *J. Am. Chem. Soc.,* **1972**, 94, 12, 4374–4376, b) J. P. Masse, R. J. P. Corriu. *J. Chem. Soc., Chem. Commun.*, **1972**, 144a-144a
[2] E. L. Michelotti, C. S. Swindell, E. Wenkert. *J. Am. Chem. Soc.,* **1979**, 101, 8, 2246–2247
[3] J. B. Diccianni, T. Diao. *Trends in Chem.,* **2019**, 1, 9, 830–844
[4] A. M. Borys, E. Hevia. *Angew. Chem. Int. Ed.,* **2021**, *60*, 24659–24667
[5] L. Vedani, A. M. Borys, E. Hevia. *In preparation*