Nickel N-Heterocyclic Carbene Chemistry: C–H Activation Reactions and Catalysis

This presentation describes recent advances in the chemistry and the catalytic reactions of half-sandwich nickel complexes that bear N-heterocyclic carbenes (NHCs) as ligands. The syntheses and structures of neutral and cationic complexes of general formula \([\text{CpNi(NHC)}X] \ X = \text{Cp, Cp*, X = Cl, I and [CpNi(NHC)]+} \ (S = \text{CH} 3 \text{CN, acetone})\), respectively, will be discussed. The talk will then focus on three facets of this research:

1) The use of these complexes as catalysts for the Miyaura-Suzuki coupling of aryl halides.
2) The base assisted C–H activation reactions of \(\alpha\)-C-H bonds of ketones and of nitriles that are carried out by these complexes.
   - Intramolecular C–H activation of the \(\alpha\)-C-H bonds of nitriles, that are attached to the NHC ligand as a side-arm, leads to new nickelacycles; acetone undergoes a remarkable double C-H activation reaction.
3) The recent use of Ni-NHC half-sandwich complexes as catalysts for the hydrosilylation of aldehydes and ketones (via probable CpNi(NHC) hydride intermediates) and for ketone arylation reactions.

Recent representative publications:
- Facile displacement of \(\eta_5\) \(\rightarrow\) cyclopentadienyl ligand from half \(\rightarrow\) sandwich alkyl,NHC \(\rightarrow\) nickel complexes: an original route to robust cis-\(\rightarrow\) C,\(\rightarrow\) nickel square planar complexes. Chem. Commun., 2013, 49, 6424. 