Abstract: The use of N-heterocyclic carbenes to modify homogeneous metal catalysts is widespread since the high metal–NHC bond strength renders high oxidative and chemical stability to NHC–ligated metal complexes. Despite this fact, the use of NHCs to modify metal surfaces has received little attention until recently. We will describe the use of NHC ligands to stabilize metal surfaces, including Au(111), Cu(111), Pt(111) and other metals. Films prepared by the deposition of NHCs show molecular ordering on the surface and remarkable stability. The impact of NHCs on the chemistry of nanoclusters will also be discussed, including the preparation of chiral NHC-stabilized Au nanoclusters. We will also describe advances in cross-coupling chemistry the preparation of complex chiral molecules of interest to the pharmaceutical industry. This will include the ability to cross-couple seemingly identical boron substituents with different electrophiles, taking advantage of inherent differences in transmetallation behaviour. The development of novel electrophiles for Suzuki-Miyaura cross coupling chemistry particularly sulfones as electrophiles for alkyl cross-coupling reactions will also be described.