Cyclometallation of Amines, Imines and Oxazolines with \([\text{MCl}_2\text{Cp}^*]\)_2 (M = Rh, Ir) and \([\text{RuCl}_2(p\text{-cymene})]\)_2

David L. Davies, Omar Al-Duaij, John Fawcett and David R. Russell
University of Leicester, Leicester, UK LE1 7RH. (dld3@le.ac.uk)

Cyclometallated complexes are well known and have a wide range of applications.\(^1\) Methods for their synthesis often involve alkyl or aryl-halide starting material often with a transmetallation step. Alternatively, cyclometallation may occur by a C-H activation process; this is particularly well-developed in palladium chemistry. Metal catalysed C-H activation followed by C-C bond formation is potentially extremely efficient in terms of atom economy and chemoselectivity and is thus a very desirable transformation from a Green Chemistry point of view.

We have examined the use of \(\text{NaOAc}\) to promote cyclometallation of nitrogen donor ligands to prepare half-sandwich complexes (A or B). Previous routes to arene ruthenium complexes of \(\text{3}\) have used mercury reagents\(^2\) though an improved C-H activation route has been described more recently.\(^3\) Such complexes show interesting reactivity with alkenes\(^4\) and alkynes\(^2,5\) and are relevant to ruthenium mediated alkene-aryl coupling.

We have reacted CN-donor ligands \(\text{1-3}\) with \([\text{RuCl}_2(p\text{-cymene})]\)_2 or \([\text{MCl}_2\text{Cp}^*]\)_2 (M = Rh, Ir) in the presence of \(\text{NaOAc}\). All the substrates were cyclometallated by \([\text{IrCl}_2\text{Cp}^*]\)_2 whilst only imines \(\text{2ab}\) reacted with \([\text{RhCl}_2\text{Cp}^*]\)_2 (M = Rh, Ir) and only the alkyl imines \(\text{2a}\) were cyclometallated by \([\text{RuCl}_2(p\text{-cymene})]\)_2 under these conditions. These cyclometallations occur at room temperature and in high yield but do not occur in the absence of acetate. We will describe the X-ray structures of some of the complexes and discuss the mechanism of the C-H activation.

References