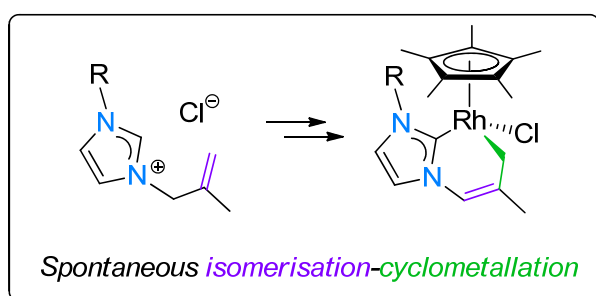


# CYCLOMETALLATED RHODIUM AND IRIIDIUM NHC COMPLEXES IN CATALYSIS

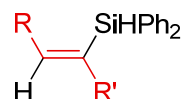
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The synthesis and catalytic activity of a range of iridium- and rhodium-based *N*-heterocyclic carbenes (NHC) complexes will be discussed. The synthesis of the imidazolium salts was done *via* the addition of the relevant alkyl halides to imidazole. Two metal precursors of rhodium,  $[\text{Cp}^*\text{RhCl}_2]_2$ , and iridium,  $[\text{Cp}^*\text{IrCl}_2]_2$ , were synthesised and subsequently applied to the synthesis of the novel complexes *via* a silver transmetallation method. This method required the addition of the relevant imidazolium ligand precursors to silver(I) oxide in the absence of light to form silver-carbene intermediate complexes, followed by the addition of the metal (Ir or Rh) precursor to allow transmetallation to occur. Initial coordination of the NHC is followed by a rare non-aromatic  $\text{C}(\text{sp}^2)\text{-H}$  activation of its alkenyl-tether, leading to a  $\text{C}(\text{sp}^3)\text{-Rh}$  cyclometallated product [1,2]. In light of the reactivity of the alkenyl arm observed in the rhodium complexes, a benzyl substituent was introduced as the second N-substituent of the NHC ligand in order to discern whether there would be competition between aliphatic C-H activation of the alkenyl arm *vs.* the aromatic activation of the benzyl arm. Interestingly, in the iridium case, cyclometallation *via* the benzyl substituent was favoured. All the complexes were applied as pre-catalysts in the hydrogenation reactions with conversions of up to 100% obtained.



Catalytic hydrosilylation



$\beta$ -E isomer (major)

[1] van Vuuren, E.; Malan, F. P.; Landman, M., *Coord. Chem. Rev.*, **2021**, 430, 213731.

[2] van Vuuren, E.; Malan, F. P.; Cordier, W.; Nell, M.; Landman, M., *Organometallics*, **2022**, 41, 187-200.