ANSTRACT :

The efficiency of an asymmetric organometallic catalyst is determined by the appropriate design of the chiral ligand. The combination of the kinetic robustness of *N*-heterocyclic carbenes with oxazolines as stereodirecting elements appears to be very promising. A novel family of imidazolium salts, where both heterocycles are connected by a (dimethyl)methylene bridge was generated. Reacting various bromide derivatives with imidazoles bearing an oxazoline unit has afforded a family of seven different ligand precursors (60-90% yield). The free carbenes 1-(1-methyl-1-((4*S*)-*iso*-propyl- and *tert*-butyl-4,5-dihydrooxazol-2-yl)ethyl)-3-(di(α-naphtyl)methyl)imidazole-2-ylidene could be isolated by simple deprotonation of the imidazolium salt.

Reaction of an imidazolium salt with the Karstedt catalyst in the presence of potassium tertbutoxide led to the formation of a monodendate trigonal planar Pt(0) complex, which could be oxidised to the bidendate Pt(II) complex by reaction with $CsBr_3$. Subsequent deprotonation of the imidazolium salt and reaction with $[Rh(nbd)Cl]_2$ gave the neutral square-planar Rh(I) complex that is converted into the cationic bidendate complex by bromide abstraction. The methyl substituents on the methylene bridge proved to provide more stability to complexes towards air and to enhance the chelating capacity of the ligand in solution. At the same time, the limit of the chelating capacity of the ligands previously developed in the group, where both heterocycles are directly connected, was emphasised by the generation of the Cu(I) complexes, which crystallised as dimer and coordination oligomers.

The cationic analogues of the rhodium complexes were tested in the catalytic asymmetric hydrosilylation of ketones and afforded different activities and selectivities. The commonly accepted Ojima mechanism not accounting for some of the experimental observations, a comprehensive theoretical investigation of the catalysis mechanism *via* DFT calculations was carried out. Three viable mechanistic pathways could be established. They all involve a first oxidative addition step and differ in the mode of insertion of the ketone, either into the Rh-Si bond (Ojima mechanism), into the Si-H bond (Chan mechanism) or *via* the formation of a silylene intermediate (new mechanistic pathway). The latter is energetically favoured with regard to the postulated ones, by respectively 55 $kJ.mol^{-1}$ (Ojima mechanism) and 120 $kJ.mol^{-1}$ (Chan mechanism). Being only accessible when a dihydrosilane is used, this explains the observed rate enhancement when secondary silanes are used instead of tertiary silanes. Moreover, it accounts for the inverse kinetic isotope effect.