Synthesis, Structure and Applications as Ligands of Carbene-Stabilized Phosphorus (III)-Centered Cations \([\text{LR}_2\text{P}]^+\), \([\text{L}_2\text{RP}]^{2+}\) and \([\text{L}_3\text{P}]^{3+}\)

Manuel Alcarazo, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr/D

Cyclopropenylidene-stabilized \([\text{LR}_2\text{P}]^+\), \([\text{L}_2\text{RP}]^{2+}\) and \([\text{L}_3\text{P}]^{3+}\) cations have been synthesized by reaction between 1-chloro-2,3-bis(dialkylamino) cyclopropenium salts with different phosphorus sources. In addition, the structural characterization of such entities has been carried out. Consistent with the X-ray data, density functional calculations indicate that all these P-centered cations, despite of their moderate to high positive charges, still feature a non-bonding electron pair on the P atom (HOMO) and, depending of the total charge, a low-lying LUMO. These properties render \([\text{LR}_2\text{P}]^+\) as strong \(\sigma\)-donor ligands while \([\text{L}_2\text{RP}]^{2+}\) are moderate \(\pi\)-acceptors. Interestingly, \([\text{L}_3\text{P}]^{3+}\) cations are still able to coordinate metal fragments displaying very poor \(\sigma\)-donor but excellent \(\pi\)-acceptor properties.\(^{[i]}\)

Encouraged by their electronic properties we have tested the potential of these compounds in catalysis and prepared a set of gold, rhodium and platinum complexes in which these salts were used as ligands. The practical utility of such coordination compounds in catalysis has been demonstrated in several mechanistically diverse transformations and will be presented. Additionally, taking advantage of the saline nature of our ligands, the recycling possibilities of the catalysts thereof derived have been also explored.