Design and delineation in homogeneous catalysis – John Brown

In efforts to develop catalytic asymmetric synthesis, we have been concerned with the structural features associated with chelating ligands, and how the recognition process leading to selectivity arises. The CDS databases provide a wealth of information that assists the process and indeed can function positively at every stage. Recently we have been engaged in providing a full conformational analysis of phosphinamines, and the information in the database reveals that apparently similar ligands with the same atom connectivity may possess very different chelate geometries. What is more striking is the fact that the variations seem to correlate with catalytic efficiency – relatively flat geometries seem to be good for ketone hydrosilylation and relatively puckered species are good for alkene hydroboration.

A second area of impact of the CDS database on our work is the analysis of the geometry of coordinated ligands and the way this impinges on catalysis. For example, alkenes in the Heck reaction may give rise to alternative products thought bond forming steps of alternate regiochemistry. Interestingly, coordinated alkenes are not symmetrically disposed with respect to the plane of coordination – when orthogonal to a square plane distortions can arise that shift the centroid of the double bond away to bring the best sigma-bonding carbon closer to the plane. This has been demonstrated by a series of X-ray structures of alkene rhodium complexes, by DFT calculations, and by a search of the Cambridge Structural Database that demonstrates the general trend. The advantage of this approach is that a sufficient number of structures are contained in the database and the retrieval of relevant information using the facilities provided by the CDS is rapid and simple. An example based on the geometry of monosubstituted alkenes is shown.