[KN6] How Structural Studies May Underpin Enantioselective Catalysis.

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The rational progress in the field of homogeneous catalysis inexorably requires the detailed understanding of the mechanism of the catalytic reaction. This usually could be done by the use of spectroscopic techniques which give us information in the same phase the chemical processes are taking place. However when the catalytic approach searches for the selective preparation of a particular enantiomer, delicate structural interactions become of extraordinary relevance and in these cases X-ray studies – although obtained in the solid state – are of special relevance.

In the last years our group has been working in the area of homogeneous asymmetric catalysis by transition metal complexes. Among the metal-based catalysts, we have been dealing with chiral halfsandwich pseudo-tetrahedral complexes of the type $[M(\eta^n\text{-arene})(L\text{-}L^*)L']^{n+}$ ($M(\eta^5\text{-}C_5Me_5)$, M = Rh, Ir or $M(\eta^6\text{-arene})$, M = Ru, Os), which have been proved to be suitable for both stoichiometric and catalytic studies. The source of chirality is, typically, a homochiral bidentate ligand (L-L*) with C1-symmetry and, in particular, several complexes containing different donor atoms (P-P', N-N', P-N, P-O, OO') have been investigated. It is remarkable that in the resulting complexes the metal itself becomes a stereogenic centre.

In our talk we will try to show how structural studies have been playing a crucial role to establish a clear correspondence between specific structural parameters and chemical and catalytic activity. The behaviour of these half sandwich complexes in asymmetric cycloaddition reactions or asymmetric transfer hydrogenation processes has been analyzed [1-4]. A systematic analysis of their molecular/ crystal structures has been performed; the pertinent intra o intermolecular structural parameters concerning metal bonding, ring puckering of chelate ligands' metallacycles and intramolecular interactions will be discussed.

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