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Research Interests: Homogeneous Catalysis, Asymmetric Synthesis, Synthetic Methodology, Organometallic and Co-ordination Chemistry.



Our group are interested in developing new catalysts for cleaner organic transformations. This includes new types of catalytic reactions, and developing catalytic chemistry that does not work effectively at present. Solving these difficult problems often involves using skills in several chemical disciplines including organic synthesis, organometallic, mechanistic, supramolecular, co-ordination, and main group chemistry.

### Asymmetric Catalysis

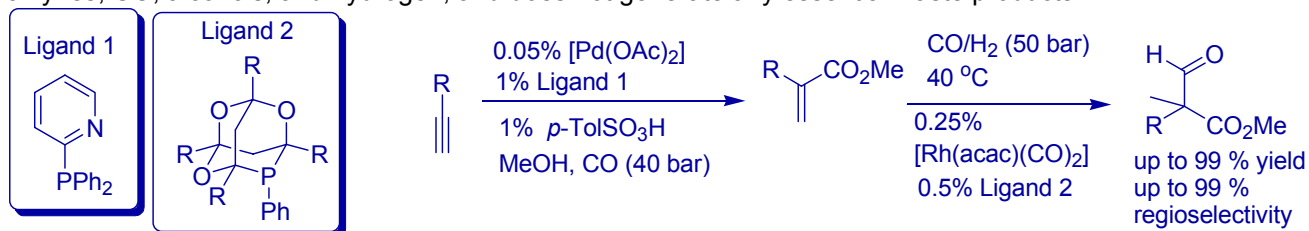
Asymmetric synthesis has developed into one of the most important fields of modern chemistry. The most efficient method to prepare an enantiomerically pure compound is to use a tiny amount of a chiral catalyst to mediate an asymmetric transformation. We are interested in developing new families of chiral catalysts (both metal based, and purely organic catalysts) for a range of metal catalysed asymmetric reactions, including asymmetric hydrogenation, hydroformylation, cross-coupling, Ene, and Michael additions.

### Homogeneous Catalysis in Organic Chemistry

As a general philosophy, the group likes to work on "difficult reactions", and therefore designs catalysts from the bottom up, gaining a greater understanding of factors affecting catalytic activity and reaction mechanisms, prior to designing new catalysts for new / modified /difficult catalytic reactions.

For example, in our work on Pd catalysed cross-coupling of unreactive aryl chlorides using phosphino-amine ligands, we first identified the design requirements within the ligands needed to give very electron rich reactive metal centres, prior to developing catalysts for the Suzuki and Hiyama reactions. More recent work in this area involves researching how catalysts can activate weak nucleophiles towards cross-coupling chemistry, and a mechanistically inspired approach is also being used here.

In ongoing work on hydroformylation in organic synthesis, a considerable search for catalysts yielded a new process for the atom-efficient synthesis of elusive quaternary aldehydes that ultimately comes from the bulk chemicals, alkynes, CO, alcohols, and hydrogen, and does not generate any essential waste products.



The group is supported by EPSRC, Leverhulme Trust, and several industrial companies, and tries to solve synthetic problems of industrial significance. Research group website: <http://chemistry.st-and.ac.uk/staff/mlc/group/Grupo.htm>

### SELECTED RECENT PUBLICATIONS

- Bulky, electron rich hemilabile phosphines in the Suzuki reaction of aryl chlorides. M. L. Clarke, D. J. Cole-Hamilton, and J. D. Woollins, *J. Chem. Soc. Dalton Trans.*, 2001, 2721 and refs therein.
- First microwave accelerated Hiyama couplings: clean cross-coupling of aryl chlorides within minutes. M. L. Clarke, *Adv. Synth. Catal.*, 2005, 347, 303.
- Phenylphosphatrioxa-adamantanes: bulky, robust, electron-poor ligands which give very efficient rhodium(I) hydroformylation catalysts, M. L. Clarke, A. Marr, A. G. Orpen, P. G. Pringle, A. M. Ward, D. A. Zambrano-Williams, *Dalton Trans.*, 2005, 1079.
- Highly regioselective rhodium catalysed hydroformylation of unsaturated esters: the first practical method for quaternary selective carbonylation. M. L. Clarke and G. J. Roff, *Chemistry: A Euro Journal*, 2006, 12, 7978.
- A highly efficient process for regio-selective hydroformylation and hydroaminovinylolation of methyl acrylate, M. L. Clarke and G. J. Roff, *Green Chemistry*, 2007, 9, 792.
- Hydrogenation of aldehydes, ketones, imines, esters and anhydrides catalysed by a ruthenium complex of a chiral tridentate ligand, M. L. Clarke, M. B. Diaz-Venezuela, and A. M. Z. Slawin, *Organometallics*, 2007, 26, 16.
- Self-Assembly of organocatalysts: a new approach to fine-tuning organocatalytic reactions. M. L. Clarke and J. A. Fuentes, *Angew. Chem. Int. Ed.*, 2007, 46, 930.