**Making Homogeneous Catalysts Greener**

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Catalysis is a key process in green chemistry and its importance is highlighted as one of the 12 Principles of Green Chemistry.[1] While many current homogeneous catalysts are effective, they are often far from ideal because they show little or no selectivity and operate in non-benign organic solvents. The overall goal of this proposal is to overcome this problem by attaching specially designed functional elements adjacent to the active sites in selected catalysts. These functional elements will introduce selectivity by providing specially sculpted hydrophobic cavities near the active site that will control which molecules can undergo reaction as well as introducing enantioselectivity to the products formed from prochiral substrates. As an important additional feature, they will also impart water solubility to the catalysts.

To achieve these goals, the functional elements will be synthesised from specially designed cyclic or linear short chain peptides. A considerable amount is known about peptide synthesis and the conformational properties of small peptides. This knowledge will be used to construct the appropriate peptide chains that will impart the required properties to the catalyst, in particular a chiral, hydrophobic cavity adjacent to the active site of the metal and a hydrophilic exterior.[2]

The manganese salen complex known as Jacobsen's catalyst has been selected as a convenient platform for testing the efficacy of the appropriately designed peptide functional elements. Jacobsen's catalyst is a well-known homogeneous catalyst that facilitates the formation of epoxides from alkenes (see Figure 1).[3] It is relatively simple to prepare and functionalise and therefore provides an ideal system for this study. The peptide units will be covalently linked to the saturated linker (as indicated schematically in Figure 2) as this is in very close proximity to the active site. The addition of peptides, or even PEG-resin-bound peptides,[4] will allow an easily constructible chiral cavity within which the metal catalyst can reside. Once the functionalised catalyst has been synthesised, it will be tested for activity and the results fed back into the design of superior versions of the catalyst.

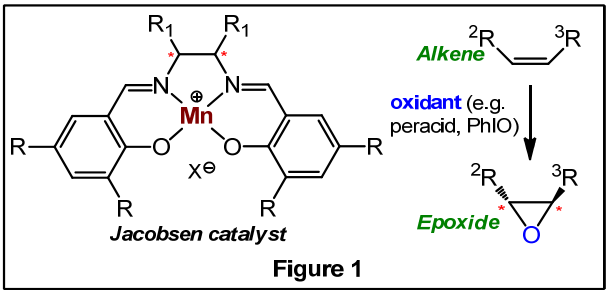

Figure 1

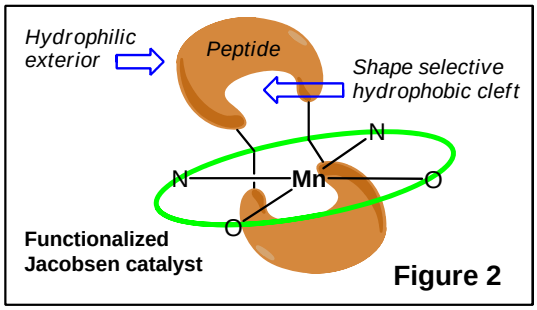

Figure 2

After the design principles of the peptide functional elements have been confirmed for the Jacobsen's catalyst platform, extension to other homogeneous catalyst systems will be investigated. Specific examples will include hydrogenation catalysts and oxidation catalysts.

References


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3. T. Flessner, S. Doye "*N*,*N*′-Bis(3,5-di-t-butylsalicylidene)-1,2-cyclohexanediamino-manganese(III) chloride – the Jacobsen catalyst," *Journal für praktische Chemie*, 1999, *341*, 436-44.
4. K. Worm-Leonhard, M Meldal, *'Green Catalysts: Solid-Phase Peptide Carbene Ligands in Aqueous Transition-Metal Catalysis' European Journal of Organic Chemistry*, 2008, 5244-5253.