Transition metal organometallic complexes play a key role in the synthesis of pharmaceuticals and agrochemicals. Indeed, the use of catalysts based on elements such as tungsten, ruthenium and palladium for carbon-carbon and carbon-heteroatom bond formation has had a transformative role in synthetic chemistry. This project will capitalise on some remarkably recent results which show how highly reactive cumulene intermediates may be utilised in synthetic chemistry providing facile access to complex substrates. A key advantage of the methodology is that we may take symmetrical substrates with two identical functional groups and selectively react one. Underpinning the synthetic methodology is the ability of transition metal compounds to stabilise high energy forms of well-known organic groups. As shown in Scheme 1, alkynes have a high energy tautomer called a vinylidene. In the absence of a metal complex the vinylidene is 197 kJ mol\(^{-1}\) higher in energy however metal complexes may stabilise the vinylidene tautomer. However, there exists an even higher energy form of the diyne, 1, a cumulene which lies at 210 kJ mol\(^{-1}\) higher in energy than the parent alkyne.

In collaboration with Professor Paul Low (University of Western Australia, Perth) we have recently discovered a metal complex which is able to selectively exploit the unique reactivity of the cumulene form of this diyne. Specifically, we have found that the ruthenium complex \([2]\) is able to mediate the conversion of 1 to 3 in a highly selective manner (Scheme 2). This corresponds to a net Markovnikov hydrochlorination of the alkyne and, vitally, only one of the two alkyne reacts. This project aims to exploit these remarkable findings

The project will involve (1) the synthesis of new organometallic complexes containing cumulene ligands to confirm their role in this chemistry; (2) the development of the catalytic reaction to explore the range of different nucleophilic reagents that can be induced to reaction with the cumulene and (3) development of new catalysts which will be based on simple, easy to prepare and sustainable metal/ligand combinations.

This project will involve training in synthetic inorganic and organic chemistry, multi-nuclear NMR spectroscopy, X-ray diffraction techniques and mass spectrometry. Linking the experimental data to theoretical calculations will be an important part of the project, as will an interaction with the Low group in Perth.


Application closing date: 17:00 on 11 January 2017
Interview date: 15 February 2017

Funding source: EPSRC or Department of Chemistry
Funding scheme (if any): DTG/Teaching Studentship
Funding Types: Competition
Eligibility: UK

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