Project title: Do we really understand the bonding in transition metal organometallic complexes?
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Transition-metal organometallic complexes play a pivotal role in a wide variety of applications. They are used as catalysts from megaton scales for polymer synthesis to milligram scales for drug discovery in the pharmaceutical industry. In addition, recent work has explored the use of organometallics in materials chemistry (e.g. OLED materials) and in healthcare, as novel therapeutic agents. The importance of organometallic chemistry has been highlighted by the award of several Nobel prizes in the area in recent years. One of the much-lauded advantages of organometallic complexes is the ability to develop structure-activity relationships based on systematic changes to the steric and electronic properties of the ligands. These can in principle be used to inform the design of new metal complexes with advantageous properties for new or existing applications and have been important in the development of important organometallic molecules (e.g. Grubbs’ 2nd generation alkene metathesis catalyst, where the phosphine present in the 1st generation catalyst (PCy3) is substituted for an N-heterocyclic carbene improving its performance significantly).

In order to quantify the effects of changing co-ligands within the coordination sphere of the metal, a number of metrics have been devised, perhaps most famously by Tolman in the 1970s. In these studies a given spectroscopic parameter (such as the stretching frequency of carbonyl ligand) is chosen as a reporting group for these electronic changes at the metal. By recording the IR spectrum, for example, of a series of compounds it is argued that the effects on the electron density at a metal caused by a co-ligand may be evaluated. More modern approaches have focussed on a multi-parameter approach to this problem. However, a common theme is that analytical data from a co-ligand is used as reporter. Therefore, all such methods are, by definition, indirect measures of ligand effects and there are many examples in which the nature of ligand effects may vary depending on the reporter complex used. This suggests that in many cases our understanding of metal-ligand interactions, based on these indirect measures, is not complete.

This project will explore new methods to directly quantify ligand effects in organometallic chemistry, which will not rely on the preparation of reporter complexes, but will involve measurements directly on the metal or ligand of interest. This will involve the preparation of a range of organometallic compounds (e.g. those above), some of which are well-known molecules and some that are at the cutting edge of organometallic chemistry. These will then be probed using advanced spectroscopic methods and computational chemistry.

A student working on this project will be trained in the synthesis of air- and moisture-sensitive compounds, novel NMR spectroscopic methods, advanced X-ray and ultraviolet spectroscopies and, if desired, in high-level computational chemistry methods. The student will attend national and international conferences on organometallic chemistry and will have the opportunity to attend national training events in the above areas.

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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