EDITORIAL

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Organometallic chemistry and catalysis†

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At Dalton Discussion No. 6, held in York in September 2003, papers were presented on the uses of organometallic chemistry in bond activation, materials, modelling catalytic intermediates, enzymes and catalysis. In addition, new techniques for studying organometallic reactions were described.

Imagine Sir Edward Frankland's excitement (and alarm) when he opened a glass tube, in which he had heated zinc and methyl iodide, and a flame 12 ft long shot out![1] He had become the first person to make a metal alkyl bond (in diethyl zinc), although Zeise[2] had made his famous salt, now known to contain ethene, nearly 20 years before, thus making him the founder of organometallic chemistry. What Frankland did not know, however, was that nature had been at it for millions of years since one form of vitamin B_{12} (methylcobalamin) contains a Co–Me bond. Schützenberger ($[PtCl_2(CO)_2]$)[3] and Mond ($Ni(CO)_4$)[4] were the first to produce metal complexes containing carbon monoxide, or so everyone thought until it became apparent that nature also got to that one first and not just in carbonmonoxyhaemoglobin. Hydrogenases contain CO (and CN^-) attached to iron[5] and their active site structure and chemistry[5,6] formed the basis of one of the fascinating sessions in Dalton Discussion No. 6 held in York in September 2003. Not only are there still many answers to be obtained concerning the fine details of the active site of all iron and Fe/Ni hydrogenases,[5] but their electrochemical activation[6] provides exciting challenges for modern organometallic chemists as do the design of structural[7] and functional[8] models. These enzymes probably involve hydride or dihydrogen complexes and may even acquire a role in the hydrogen economy.

Dalton Discussions are conferences of a rather different kind. The scene is set by a Keynote Lecturer in each session and this is followed by very short (5 min) presentations with the emphasis on discussion (15 min). Since all the delegates have had the opportunity to read the full papers beforehand, they are well informed and the discussion is very lively. DD6 in York was set up to take a snap-shot of various topical areas in organometallic chemistry and catalysis—to see how it has developed from those early days of Mond and Frankland and to see where the new challenges lie.

Major advances have been made, especially in our understanding of structure and mechanism in organometallic chemistry, so that we can predict a great deal of what will happen or rationalise the unexpected by experiment underpinned with high quality theoretical calculations. Some of the newer techniques were highlighted at the meeting such as infrared spectroscopy on intermediates with picosecond lifetimes[9] and diffusion measurement by NMR.[10] It is now possible to monitor smaller changes in an IR spectrum on a picosecond spectrometer than on most conventional FTIR instruments.[9] One of the most important problems that has now been addressed is the longstanding issue of the structure of $Fe(CO)_4$ in solution and how it can switch spin state by coordinating a solvent molecule such as xenon or an alkane. A hallmark of this Dalton Discussion was the smooth melding of theory and experiment[11–14] in individual contributions, but also from the floor (O. Eisenstein, Montpellier made some especially important interventions). The question of crossing from one spin-manifold to the next was a no-go area for theory until recently but is now accessible, so the $Fe(CO)_4$ problem can be addressed by theory in addition to experiment.[14]

The meeting started with a fine session on the activation of bonds. C–H activation is particularly topical because of the potential for making chemicals from saturated hydrocarbons; attempts to model the final step in the production of methanol form oxidation of methane were described here.[15] The degree of control over which C–H bond is metallated where there are many choices within a molecule was especially impressive, as was the rationalisation of this control.[11,12,16–18] The selectivity can occur because of the metal—α C–H to give carbenes or β C–H to alkene hydrides—or the orientation of the moiety to be activated (C–H between 2 N atoms or next to only one in the same ligand), which can in turn be affected by interactions with remote groups, counterions or by the site available on the metal for attack. The role of ion-pairs is proving much more significant than previously realised, a change from bromide to hexafluoroantimonate can cause a switch in products.[16] Ion-pairing may sometimes be detected directly by NMR spectroscopy; alternatively, it may be revealed by diffusion measurements.[10,16] C–H bonds of aromatics with fluorine substituents are stronger than other aromatic C–H bonds—ironically their increased strength stabilises the C–H activation product and reduces the activation barrier to form it.[12] C–H bonds can migrate backwards and forwards to give a plethora of bonding modes for the C-based fragments, particularly elegant examples[17] may be found at iridium interconverting metal carbenes, alkyls, alkenes and hydrides, many of which could be on the same metal at the same time. These types of molecule give great insight into the likely intermediates in catalytic cycles and should allow the rational design of new catalysts with very high selectivity and reactivity. The interconversions between the various fragments often involve agostic interactions in which intact C–H bonds bind to the metal.[16] It is now possible to design systems where α-agostic interactions are preferred to β-agostic interactions or even one where a cyclopropyl group forms a C–C agostic bond.[11]

The C–F bond has resisted activation for many years, but many examples of its activation are now being discovered using early,[19] middle[20] or late[20] transition metals. Once again, high level theory is being used to great effect in aiding our understanding of how these very stable molecules can be activated. P–H[21] and Si–H[22] bond activation was also discussed. The very elegant molecules containing a silane ligand bridging two

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ruthenium centres while maintaining intact Si–H bonds were particularly remarkable—once again a theoretical interpretation was at the ready.[22]

New materials with controlled and unusual properties will be enormously important in the future. Organometallic chemistry has played a major part in catalysing the formation of new polymeric materials. Much finer control is now possible and it was pleasing to see that Frankland's diethyl zinc still has a role to play in its reactions with chiral aminoalcohols to give complexes which, after reaction with small amounts of ethanol, give highly active and enantioselective catalysts for the copolymerisation of CO_2 and epoxides.[23] This formed part of an elegant study on the enantioselective formation of chiral polyepoxides, esters and carbonates,[23] which was complemented by a discussion of new catalysts for atom transfer radical polymerisation. The metal-based radical initiator helps give precise control over the microstructure and molecular weight distribution in these radical polymerisations that are notoriously difficult to control.[24]

Much less attention has been paid to polymers which contain heteroatoms in the backbone, but the work on cyclic borazines and polyphosphinoboranes is beginning to produce new materials. The ring opening of ansa ferrocenes with Si and other bridging groups is already producing fascinating materials with striking optical properties.[25] Chemie douce methods (templating with lamella phases of surfactants) have produced very interesting mesoporous silicates, but real advances are now being made in the synthesis of other mesoporous oxides, tantalum being highlighted at this meeting.[26] Filling the pores with fullerenes or reduced early transition metals provides materials with very high solid state conductivities or hydrogen storage capacity (up to 9%),[26] perhaps offering another contribution to the hydrogen economy.

Homogeneous catalysis continues to be a major driver for research in organometallic chemistry. New catalysts for unusual reactions such as the hydrothiolation of alkynes[27] are important, whilst researchers are always striving for extended lifetimes, very high activities and selectivities with cheap substrates and easy recyclability. Catalyst precursors capable of exceeding 50 million turnovers for Suzuki coupling using cheap but difficult substrates such as 4-chloroanisole were described[28]—elegant ligand design is essential for long lifetimes, even though the ligand is believed to be lost during the catalyst activation process. The degree of aggregation of the (probably) Pd(0) active species is open to debate, but the rates, although high, still have some way to go to catch up the 50,000 turnovers per second possible using hydrogenase enzymes as electrocatalysts.[6] New sol–gel solids, in which catalysts with the metal–ligand interaction stabilised by chelation are attached to the gel through polyethylene glycol spacers, offer a new and promising approach to low-leaching heterogenised catalysts.[29]

In two days of lively presentations and animated discussion, it became clear that organometallic chemistry is alive and well. It has a strong future in biology, materials, synthesis and catalysis. We are extremely well equipped with techniques to probe these exciting and fascinating molecules. With the advent of combined molecular mechanics and DFT calculations, high level theory can now be applied to much more complex molecules so that the interplay between steric and electronic effects can effectively be untangled at last.

It was refreshing to see that the excitement felt by Frankland is still very much alive in modern organometallic chemists and the 75 posters † stimulated very lively discussion on a wide range of topics.

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