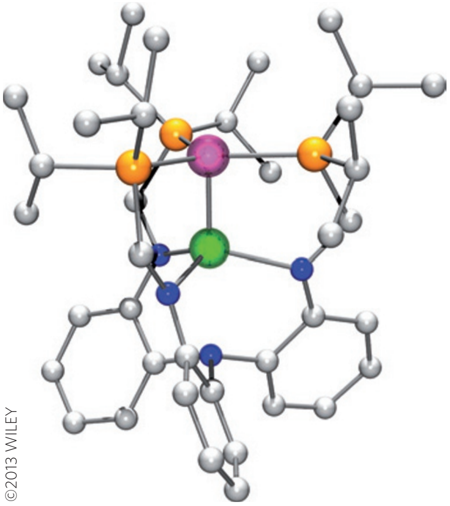

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This is because the bonding orbitals (based on the metal's *d* orbitals) become larger as you move down the periodic table making overlap, and thus bonding interactions, more favourable. Thus the majority of compounds with metal–metal multiple bonds made so far involve at least one of the larger second- and third-row metals.

Now, a team of researchers led by Laura Gagliardi and Connie Lu from the University of Minnesota have isolated, for the first time, complexes that have multiple bonds between the first-row transition metals iron and chromium. They used a dinucleating heptadentate P,N-ligand to stabilize the metal–metal bonds, and in two of the complexes studied they observed effective bond orders of 2.21 and 2.30. As a consequence of being bonded first-row metals, the compounds contain ultra-short metal–metal bonds of 1.94 Å and 1.97 Å; the shortest metal–metal bonds of all heterobimetallic species made in terms of absolute distance.

Isolating these complexes as crystals allowed the team to look carefully at the nature of bonding between the metals. Analysis of the solids by Mössbauer spectroscopy showed unusually large quadrupole splitting of >5 mm s^{-1}, indicating that the metal centres were in a particularly unusual ligand environment. Quadrupole splitting is a feature of all γ-ray spectroscopy (such as Mössbauer), and occurs when nuclei that have a spin quantum number greater than ½ find themselves in an external electric field gradient (EFG), which splits the spin state in two and produces a doublet in the spectrum. This can be measured to determine the strength of the EFG, which tells us more about the chemical environment around the metal nucleus. The unusually high quadrupole splitting in these compounds indicates that the EFG was particularly strong and most likely caused by the placement of a hard nitride ligand near a low-spin iron centre. *RD*

HOMOGENEOUS CATALYSIS

A reforming process

Nature **495,** 85–89 (2013)

The problems associated with the storage and transport of hydrogen prevent the widespread adoption of hydrogen-based fuel cells. One proposed solution is to use a carrier liquid from which hydrogen can be generated as and when it is needed. Methanol has been proposed as one such carrier; however, hydrogen is typically generated from methanol by reforming with steam — a process that requires temperatures in excess of 200 °C and pressures of 25–50 bar. These conditions limit the efficiency of the process and make it unsuitable as the hydrogen source for portable fuel cells.

Now, a team led by Matthias Beller at the University of Rostock in Germany have developed an efficient homogeneous catalyst that dehydrogenates methanol at low temperature. The active catalyst is formed from an octahedral ruthenium complex by removing a labile chloride ligand and converts methanol to three H_2 molecules and carbon dioxide. In a series of steps, the alcohol is first oxidized to formaldehyde, then formic acid, before finally being converted to carbon dioxide. One equivalent of hydrogen gas is liberated at each stage representing the complete conversion of all available hydrogen in methanol. The additional hydrogen atoms required are supplied by water or a hydroxide base and the catalytic process is capable of generating H_2 at temperatures as low as 72 °C.

Catalysts with a metal-on-metal-oxide-support structure have been used for methanol reforming before, however, this is the first organometallic dehydrogenation catalyst defined at a molecular level that can liberate more than one molecule of hydrogen for each molecule of methanol converted. The catalyst is tolerant of a range of methanol–water mixtures, is stable for over 350,000 catalytic cycles and retains high activity over several weeks. The process produced hydrogen and carbon dioxide with only very low levels of CO and CH_4, which is important if the H_2 is to be subsequently used in a fuel cell. *RJ*

Written by Gavin Armstrong, Stephen Davey, Ruth Doherty and Russell Johnson.

blogroll

Chemistry in crowds

Are bloggers the new peer reviewers?

Back in January a chemistry blog with a difference popped into being. Blog Syn (http://blog-syn.blogspot.com) is more than the usual opinion, analysis and amusing Twitter memes (try Magdeline Lum's account of #dangerous5 for a good version of that; http://go.nature.com/Y2SRd3). Instead, this new blog has the laudable aim of using crowdsourcing to reproduce chemists' published results.

The third reaction tackled by Blog Syn, with posts in February (http://go.nature.com/wcWiCd) and March (http://go.nature.com/2YYESa), is from a 2002 *J. Am. Chem. Soc.* paper from K. C. Nicolaou's group. There ensues an interesting series of failures, genuinely helpful dialogue with some of the authors (including Phil Baran and Tamsyn Montagnon) and finally the missing factor is found: water!

Writing at Grand CENtral, Fredrik von Kieseritzky nicely summed up (http://go.nature.com/e1gdLJ) why there is a place for Blog Syn, as he laments the decline in the quality of methods sections of papers and calls for journals to promote experimental procedures from supporting information back into the main text. Moreover, in the wake of Blog Syn's early success some interesting arguments arose about (pseudo)anonymity in blogging. The point being that Baran's comments can be easily attributed to him but most of the contributors to Blog Syn remain pseudonymous. Points for and against anonymity were discussed by von Kieseritzky and also Rich Apodaca at Depth-First (http://go.nature.com/RtKgIq).

Baran's encounter with Blog Syn may have made him reconsider his feelings towards bloggers; his lab now hosts The Open Flask (http://openflask.blogspot.com). Nevertheless his opening post does start with a quote from one of his colleagues about blogs: "Never before have so many people with so little to say said so much to so few...".

Written by Mark Lorch, who blogs at http://www.chemistry-blog.com