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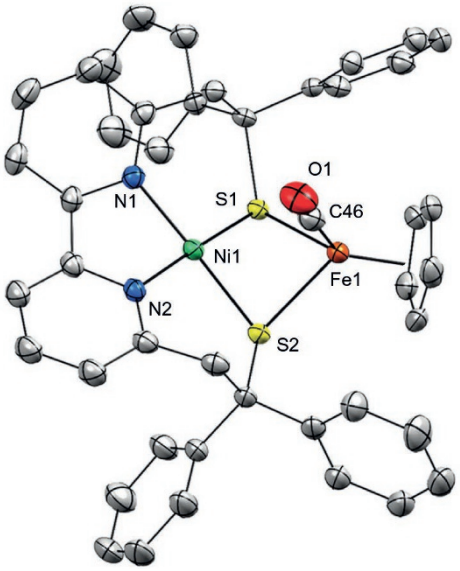
IN BRIEF

HOMOGENEOUS CATALYSIS

Synthetic models close in on enzymes



Adapted from Brazzolotto, D. et al. (2016), Macmillan Publishers Limited

Living systems interconvert protons, electrons and dihydrogen by expressing diiron and/or nickel–iron hydrogenases. The latter are the more robust enzymes, and we hope to mimic their chemistry in synthetic electrocatalysts — small molecules that may ultimately find use in fuel cells. The native mechanism is difficult to replicate because, of the iron and nickel centres in the active site, it is nickel that is postulated to bind protons and dihydrogen. Yet, in synthetic chemistry, it is not nickel but iron that more commonly binds these substrates. A team led by Carole Duboc and Vincent Artero sought to remedy this by preparing a nickel–iron complex in which nickel is bound to a non-innocent bipyridine, which can receive one electron and make bonding to nickel a more attractive prospect for an incoming proton.

Writing in *Nature Chemistry*, the team describes the chemistry of the bipyridine nickel–iron catalyst that, relative to most other nickel–iron hydrogenase models, evolves hydrogen quickly at mild potentials. Although the catalyst is inferior to the enzymes, its mechanism is thought to involve nickel–hydride intermediates — reactive species that are absent in the catalytic cycle of other synthetic catalysts. When bonded to a reduced bipyridine ligand, the nickel site is apparently basic enough to sustain protonation. However, the iron centre cannot be ruled out as a site of protonation, and ensuring the regioselectivity of this reaction remains an important overarching theme in hydrogenase modelling.

David Schilter

ORIGINAL ARTICLE Brazzolotto, D. et al. Nickel-centred proton reduction catalysis in a model of [NiFe] hydrogenase. *Nat. Chem.* **8**, 1054–1060 (2016)