difficult to oxidize with high enantioselectivity. One such class of substrates are the α-alkyl styrenes, which have continually proven to be challenging when compared with the more amenable monosubstituted or β-disubstituted versions. Miquel Costas and co-workers at the Universitat de Girona have now developed a catalytic system that can carry out epoxidation reactions with good results over a range of styrenes, including α-alkyl-substituted.

The group had previously shown that a non-heme iron catalyst could activate hydrogen peroxide for asymmetric epoxidations. One interesting insight was the effect played by co-ligands, with both chiral and achiral carboxylic acids having a significant effect on yield and stereoselectivity. The team reasoned that this could allow them to easily tailor the catalytic system by using the same metal complex combined with various chiral acid additives, with amino acids an obvious starting point. Thus, in this work they employed a range of *N*-protected amino acids as co-ligands, and observed good enantioselectivities for the epoxidation of *cis*-β-methylstyrene. The absolute stereochemistry of the products was controlled by the iron complex rather than the amino acid — indeed only minor match/mismatch effects were observed when the enantiomeric form of the iron catalyst was switched. An exception to this was an imide-protected *iso*-leucine, which gave different yields and enantioselectivities depending on the chirality of the iron complex, implying that the co-ligand was intimately involved in the active site. Costas and co-workers then carried out the screening of other substrates using this catalyst/co-ligand combination.

Most notably, this combination outperformed other variants in the epoxidation of α-alkylstyrenes. Selectivities were moderate for α-metylstyrenes, but were impressive when the α-methyl was replaced with other alkyl groups. Substrates with primary, secondary or tertiary groups were epoxidised with enantiomeric excesses generally greater than 80% and reaching 97% — an impressive result considering the limited range of methodologies capable of dealing with this class of substrates. *EB*

SUBPORPHYRINS

Hydride enters the ring

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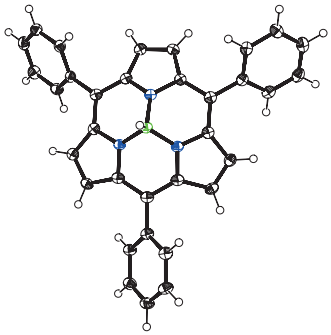
Subporphyrins are the smaller cousins of porphyrin macrocycles. They consist of three pyrrole moieties — rather than four as in their better-known counterparts — linked by methine carbons and adopt a bowl-shaped structure that typically features a boron atom, with an axial ligand, in its central



cavity. The axial ligand can be exchanged, and although methoxide, hydroxide, fluoride and phenyl-substituted boron-based subporphyrins are known, preparing hydrides has proven difficult. Now, in a collaboration between Yonsei University and Kyoto University, Dongho Kim, Atsuhiro Osuka and co-workers have synthesized subporphyrinato boron(III) hydrides by reduction of their methoxide counterparts.

Using a Lewis acid was key to the successful synthesis — other reducing agents proved either non- or too reactive — and suggested a mechanism in which the acid facilitates the exchange of the methoxy group. Three derivatives were produced whose methine carbons were decorated with phenyl (pictured), methoxyphenyl and bromophenyl pendant groups, respectively. X-ray crystallography of all three subporphyrins showed that they all adopt similar bowl shapes, pointing to an sp^3 hybridized central boron that bears an axial hydride ligand. Characterization by mass spectrometry, ^{1}H- and ^{11}B-NMR spectroscopy, and infrared spectroscopy of the phenyl-decorated compound also indicated the presence of a boron hydride moiety. Furthermore, its absorption and fluorescence emissions, and redox potentials, were consistent with those expected for the hydride compound as determined from comparisons with other subporphyrins and calculations using density functional theory. The infrared stretching frequencies and crystallographic bond distances pointed to a slightly weaker B–H bond than that of ammonia borane.

The chemical reactivity of the phenyl-decorated subporphyrin also concurs with that of a hydridic compound. It produced hydrogen gas on reaction with water and hydrochloric acid, and was able to reduce an aromatic aldehyde and an aromatic imine in the presence of a Lewis acid catalyst. Those hydroboration reactions likely involved a borenium cation, and produced subporphyrin derivatives featuring axial B–O and B–N groups, respectively. *AP*

Written by Enda Bergin, Stephen Davey, Claire Hansell and Anne Pichon.

blogroll

Coding chemistry

Why the rise of the machines is a good thing for chemistry.

No matter your research interests, I'll bet you depend more on computers — databases, scripts, templates, macros, electronic laboratory notebooks, sketching tools, machine learning — than ever before. Luckily, the chemblogosphere has you covered.

First of all, Mark Wolf, blogging at Magic Acid, wants to help you build a grad-school dream machine — capable of mapping 3D changes in battery electrodes — for less than US$1,000 (http://go.nature.com/9wNC9y). Need to learn a programming language? Then take a look at Chemistry Apprentice, who has laid out a nice (and free!) path (http://go.nature.com/4g38n8) to learn JavaScript and Python using online resources.

Next, Martin Stoermer, of the aptly-named Chemistry and Computers blog, opines (http://go.nature.com/LYXepL) on indexing open-access chemistry data. He desires a model similar to that set by physics (with arXiv) or biomedical research (with PubMed). Meanwhile, Egon Willighagen at Chem-bla-ics, makes budding programmers aware (http://go.nature.com/KzcR2U) of the Royal Society of Chemistry's efforts to promote open science. They are providing access to their databases in exchange for Wikipedia contributions.

Finally, there was a lively debate (http://go.nature.com/Q1GfCW) at In the Pipeline over some seemingly odd structures from a molecular dynamics paper published in *Nature Chemistry*. Derek took issue with an extra methylene group and a potentially unstable hemiaminal before the lead author of the study quickly confirmed in the comments that they were simply drawing errors. The discussion continued, however, with academic heavyweights Henry Rzepa and Peter Murray-Rust chiming in, calling for reforms against what they consider to be outmoded publishing customs in the Internet age (http://go.nature.com/ZN2Atf).

Written by See Arr Oh, who blogs at http://justlikecooking.blogspot.com