chemical shift of the ^{13}C peak depends on its location in the core — either at an olefinic, cyclopropyl or bridgehead position — and plotting these values against their intensities generates a pattern that reflects the presence of different amounts of bullvalene isomers in any given sample. Adding an analyte alters the population distribution and leads to a different pattern. If other parameters such as solvent and temperature remain unchanged, the new pattern is characteristic of the particular analyte.

Different patterns were generated for C_{60}, a pyrrolidinone-substituted C_{60}, and C_{70}, demonstrating that related fullerene structures could be distinguished using this approach. A control study using a bullvalene derivative lacking the porphyrin recognition elements gave the same patterns, regardless of which fullerene analyte was present.   *SC*

REACTION DYNAMICS
Roaming recognized
Science **335**, 1075–1078 (2012)

Transition-state theory has given chemists the framework with which to understand and explain most chemical reactions. Sometimes, however, incongruous experimental results can force chemists to consider other more exotic possibilities. In the past decade, details have emerged of a new mechanism for photodissociation reactions in which an atom, on attempting to break its bond with a small molecule, does not have enough energy to escape. It 'roams' around the remaining fragment before reacting with it further and abstracting another atom to form the final products.

Previously, such reactions were observed to occur on the electronic ground-state potential-energy surface and were always accompanied by a competing reaction pathway that followed a more standard route: that is, through a traditional transition state. Now, Simon North of Texas A&M University and co-workers — studying the photo-dissociation of NO_3 to NO and O_2 — have observed roaming on the excited-state surface and have shown that there is no route that proceeds via a standard transition state. The reaction was previously understood to occur through two pathways, one of which was shown by North in 2011 to involve roaming in the ground state and one of which, until now, remained uncharacterized. Previous calculations, however, have suggested that this route involved roaming on the excited-state surface.

To confirm this theoretical prediction, North and co-workers looked for signs that the reaction products came from two different electronic surfaces. Such a signature was predicted (using *ab initio* calculations)

to be visible in the orbital symmetry of the NO products and was later observed using ion imaging.   *GA*

ASYMMETRIC HYDROGENATION
Cobalt competes
J. Am. Chem. Soc. **134**, 4561–4564 (2012)
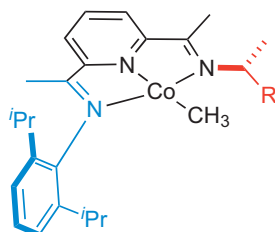
Asymmetric hydrogenation of alkenes is arguably the most successful method for the production of single enantiomer products from prochiral starting materials. The majority of catalysts for these reactions, however, are based on precious metals such as ruthenium, rhodium or iridium. Furthermore, many of these reactions reported so far require the presence of coordinative groups in the substrates to 'lock' the conformation of the intermediate and ensure high selectivity. Now, Paul Chirik and co-workers from Princeton University have reported a series of cobalt complexes that can catalyse the highly enantioselective hydrogenation of unfunctionalized alkenes.

Non-precious metal catalysts for asymmetric hydrogenation have been described previously, but these have had problems with poor selectivity or activity. Chirik and co-workers, among others, have reported highly active cobalt and iron catalysts based on coordination of tridentate bis(imino)pyridine ligands — but so far these ligands have involved symmetric systems not suitable for asymmetric catalysis. In the present work, a redesign of the ligand allows incorporation of a single chiral amine. Initially a series of methyl-substituted catalysts were targeted, but the route Chirik and co-workers used for the synthesis also led to the formation of cyclometallated complexes.

The methylated complexes catalysed the hydrogenation of a series of styrene derivatives with generally good selectivities and activities. The cyclometallated compounds, however, although poor as precatalysts for the standard substrates, were found to be useful for hydrogenation of one very unhindered substrate where the methylated catalyst had performed badly. This intriguing pattern of reactivity will help to inform the design of future catalysts.   *SD*

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey, Anne Pichon and Neil Withers.

blogroll

Arnie and artemisinin
A chemist who wants to terminate malaria and a calculation to have at your fingertips.

"Malaria. I hate this parasite. I want to kill it." Imagine these words spoken in a voice similar to Arnold Schwarzenegger's and you'll understand why they nearly made Karl Collins fall off his chair, as he explained in a post at A Retrosynthetic Life (http://go.nature.com/AHSHxv). Of course, it wasn't Arnie speaking, but Peter Seeberger of the Max Planck Institute, who discussed his efficient and cheap route to making artemisinin. Seeberger's development means that "artemisinin factories the size of large cardboard boxes can be made for £10,000". Overall, the cost of producing this potent antimalarial could fall to "10% of what it is today" — this might go some way to explain why Seeberger's next appointments were with the UN and the Gates Foundation. Collins explains more about Seeberger's career in his blogpost and you can read the *Angewandte Chemie* paper that reports the continuous flow synthesis via http://doi.org/c55rks.

"By the time you finish this sentence, your fingernails will have grown one nanometre." If you read that sentence with some scepticism, you're not alone. Zen Faulkes, who blogs at Neurodojo, asked "Is that accurate?" (http://go.nature.com/IInVym). To start with, his students did some guesstimations, 'Fermi problem' style, that showed it might be true, but like any good scientist, Faulkes wanted data. So he measured the growth rate of his fingernails using callipers accurate to 0.01 mm. After five or six measurements on ten fingers he arrived at an average fingernail growth rate of 0.92 nm per second! But wait — Faulkes went a step further and discovered it took him about 3.77 seconds to read that sentence, so his fingernails would have grown a whopping 3.47 nm. Interested readers may like to tackle the problem posed in the comments: How many moles of β-keratin are deposited onto the nail per second?