

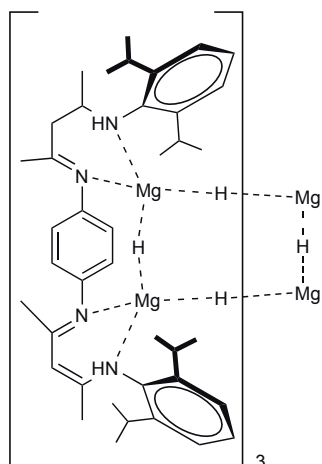
(where the phosphorus atom behaves as a nucleophile) but also as an unexpected source of hydrides (where a hydrogen atom acts as the binding site). Phosphination and reduction occurred under kinetic and thermodynamic control, respectively.

This dual reactivity was further confirmed by theoretical calculations that suggested that both reaction pathways go through transition states involving six-membered rings. The P–B–H and C–O–Li moieties adopt two transition states, depending on their relative orientations, so that the carbonyl is closer to either the phosphorus or hydrogen atoms. This reactivity may prove useful in future for asymmetric phosphination steps.

HYDROGEN STORAGE

Stability through rigidity

Angew. Chem. Int. Ed. **50**, 4156–4160 (2011)



For hydrogen to be widely used as a sustainable and non-polluting fuel, a way to store and release it is needed. For use as a vehicle fuel, the storage medium must be as lightweight as possible. Magnesium hydride (MgH_2) has been suggested as the basis for such an application because it has a relatively high level of hydrogen by weight (7.7 wt%) and can reversibly store and release it. The high stability of MgH_2 , however, renders it difficult for widespread use: a temperature of 300 °C is required. Reducing the particle size improves this and efforts are now focused on a bottom-up approach to make molecular clusters of magnesium and hydrogen.

Now, Sjoerd Harder and colleagues from the Universities of Groningen and Duisburg-Essen have created a cluster with eight magnesium atoms and ten hydride ions. Furthermore, each cluster releases five molecules of hydrogen on heating to only 200 °C. The $[\text{Mg}_8\text{H}_{10}]^+$ core is stabilized by three bulky tetradentate bridged

bis(β -diketiminate) ligands. Each ligand binds to a Mg–H–Mg moiety and the three together act like an inverse crown ether to trap a central $\text{Mg}_2\text{H}_7^{3-}$ unit.

The ligand framework is so rigid that no exchange of bridging hydride ions is seen on the NMR timescale. The cluster is very thermally stable in a toluene solution, with no decomposition seen after being heated at 180 °C for two days. Removing the hydrogen was possible under vacuum at 200 °C, which is the first observation of hydride ions converting to hydrogen molecules in a magnesium hydride complex.

POLYMER SYNTHESIS

ATRP at the flick of a switch

Science **332**, 81–84 (2011)

Radical polymerization, in which polymers grow through their repeated chain reaction with monomers at radical centres, has become one of the most important synthetic techniques in polymer chemistry. One of the principal breakthroughs in the field was the development of atom transfer radical polymerization (ATRP), which reduces the probability of inevitable radical termination reactions — in which two active chains couple together — and therefore enables the synthesis of polymers with controlled molecular weights and narrow weight distributions.

Now Krzysztof Matyjaszewski of Carnegie Mellon University and colleagues from the California Institute of Technology, and the University of Padova, have developed a method whereby ATRP can be switched on or off by the application of an electrochemical potential. The key to ATRP is keeping the concentration of propagating radical species low, reducing their chances of meeting. This is ensured by taking advantage of the equilibrium between the active species and a dormant counterpart that temporarily flickers into life to add a number of monomers, and then falls dormant again. This process effectively reduces the concentration of the propagating species.

The equilibrium is mediated by a transition metal redox couple, one of which activates the propagating species and the other deactivates it. Matyjaszewski and colleagues have now shown that it is possible to control the equilibrium and thus the overall ATRP process by applying an electrochemical potential that, depending on its magnitude, can either reduce the deactivating transition metal species or oxidize the activating species. The technique was demonstrated to give exceptional control over the polymerization of methyl acrylate in acetonitrile with molecular weight increasing linearly with conversion whereas molecular weight distributions decreased.

blogroll

Dear chemists...

Embracing rational irrationality and a 200th birthday celebration.

“When we hear ‘chemicals’ we think death, harm, cancer, birth defects, danger, pain, poison, pollution, hazardous waste, Love Canal, Bhopal. Oh, joy!” This was part of a letter addressed to ‘chemists’ from ‘the public’ to celebrate the International Year of Chemistry, written ironically by David Ropeik as part of his guest blog for *Scientific American* (<http://go.nature.com/CY8moU>). Ropeik’s point, if bluntly made, was that chemists need to address the fact that the public has real fears about their exposure to ‘chemicals’. Whether or not those fears are entirely rational, he argues, chemists should embrace them as part of a wider dialogue if they are to get the public to appreciate the benefits of chemistry.

Quite a few people on Twitter thought Ropeik was at best guilty of ignoring his own advice by successfully alienating the community he was trying to advise. But KJHaxton on *Endless Possibilities* (<http://www.possibilitiesendless.com/?p=673>) was able to see past the “chemist bash centred on the notion that [the IYC] exists solely to convince the generally ignorant public [...] that chemistry is in fact a Very Good Thing.” Haxton concludes that the IYC “is about far more than overcoming so-called chemophobia, let’s not allow one blog post to make it so.” Neil Gussman on *The Chemical Heritage blog* (<http://go.nature.com/535uQ6>) took the advice on board: “[chemistry needs] the reality check Ropeik provided: the most powerful tools do the most damage when misused.”

And finally...showing chemistry in a more positive light, Google used the 200th anniversary of Robert Bunsen’s birth to create a great ‘doodle’ of the eponymous burner that brightened everyone’s day. Of course, there was more to Bunsen than just a burner, as we were quick to point out on the *Sceptical Chymist* (<http://go.nature.com/qce4S9>), and Michelle Francl even showed us the link between Bunsen and quantum mechanics at the *Culture of Chemistry* (<http://go.nature.com/2ASgqQ>).