

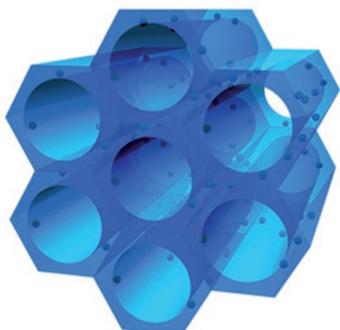
and enables their coordination to transition metals. The three-membered ring carbene — a cyclopropenyl-ylidene moiety bearing amino substituents on the two doubly bonded carbon atoms, and an unshared pair of electrons on the remaining carbon atom — is a stronger  $\sigma$ -donor and a poorer  $\pi$ -acceptor than the carbenes previously investigated.

Several dialkyl and diaryl phosphonium species were stabilized using the cyclopropenyl-based carbene ligand. Despite being cations, they have electron densities that are close to those of phosphines, and they successfully coordinated to gold centres. The resulting gold complexes showed catalytic efficiencies comparable to those of the conventional gold catalysts featuring the corresponding trialkyl or triaryl phosphines, but because the phosphonium adducts are ionic they are likely to be more easily recyclable.

#### MESOPOROUS MATERIALS

### Nothing is impossible

*J. Am. Chem. Soc.* **133**, 5094–5102 (2011)



© 2011 ACS

Chemists like a challenge, in particular the challenge of making compounds or materials that their peers consider ‘impossible’. Examples like outlandish organic structures and unexpected noble gas compounds have been conquered by clever syntheses. Even zeolites, with their large internal voids, were not expected to be stable, but materials with extremely large pore spaces have been made. Current opinion suggests that mesoporous silica materials should be made of  $\text{SiO}_4$  units with four connections, and that having more than 25%  $\text{RSiO}_3$  units — which can only connect to three others — would result in the framework collapsing.

Now, a team led by Geoff Ozin from the University of Toronto have made such an ‘impossible’ material, a mesoporous hydridosilica  $\text{HSiO}_{1.5}$ . They used a surfactant triblock copolymer as a template and the structure was stable after it was removed, even up to a temperature of 300 °C. Above this temperature, the team expected that the

material would densify, but instead the pore walls disproportionate without collapsing. This results in nanocrystalline silicon particles being embedded within the silica walls.

Ozin and colleagues suggest that the unexpected stability of the mesoporous hydridosilica is related to the effects of  $\text{SiOH}\cdots\text{HSi}$  hydrogen bonding and the Si–H groups only having a small steric demand. The embedded nanocrystalline silicon particles are photoluminescent thanks to their nanosize.

#### ATMOSPHERIC CHEMISTRY

### Pathfinders

*Environ. Sci. Technol.* **45**, 2691–2697 (2011)

Although nitrous oxide might be better known to the general public as laughing gas, its environmental effects are no laughing matter: it has a greater potential for global warming than the much-vilified carbon dioxide and also contributes heavily to catalytic ozone depletion. Its formation is mainly attributed to the activity of microbes in soil that feed on ammonium nitrate fertilizers, but the source of 30% of global nitrous oxide is unknown. Now, Vicki Grassian and co-workers from the University of Iowa have uncovered a non-biological source of nitrous oxide in the laboratory whereby it is generated from ammonium nitrate through a light-driven process at a surface; conditions comparable to those of atmospheric aerosols or surface soil.

Grassian and co-workers studied nitrous oxide production using a model  $\text{Al}_2\text{O}_3$  surface coated with ammonium nitrate. Using Fourier transform infrared spectroscopy, they observed nitrous oxide formation when the surface was bathed in light, which increased in a humid atmosphere. The team gained key details about the reaction mechanism by isotopically labelling the surface-coating ammonium groups. Two possible mechanisms were observed: one features the reaction of  $\text{NO}_2$  with  $\text{NH}_2$  and another does not feature ammonium but involves the surface-mediated hydrolysis of  $\text{NO}_2$  groups (formed through the photolysis of nitrates).

The presence of unlabelled nitrogen atoms in nitrous oxide formed in a relatively humid atmosphere implied that its formation did not directly involve the ammonium groups, highlighting the importance of the heterogeneous hydrolysis path and explaining the enhancement seen at increased humidity. Analysis using the Community Multiscale Air Quality model suggests that the formation path studied could account for 1% of the current estimated US national total.

## blogroll

### BOOM

#### Exploding myths and exploding compounds

How do you make a compound with 10 nitrogen atoms in a row, formula  $\text{C}_2\text{H}_2\text{N}_{10}$ ? Carefully, that’s how. After a few blogs and tweets had picked up on a particularly violent TOC graphic in *Inorganic Chemistry* ([dx.doi.org/10.1021/ic200071q](http://dx.doi.org/10.1021/ic200071q)) featuring shattered glass and fractured funnels, Infinitflux featured an interview (<http://go.nature.com/yxrtFs>) with one of the authors, Davin Piercey. Piercey works with Thomas Klapötke at the Ludwigs-Maximilians University in Munich and told readers about his adventures with such violently explosive compounds. Fortunately, safety is taken incredibly seriously in the Klapötke lab with “personal protection equipment for potential shrapnel; Kevlar gloves and arm protectors [...], and basic body armour.” This gear means Piercey is in the lucky position of considering the shrapnel-induced explosion of his remaining product merely “annoying”!

Have you ever wanted to irritate a whole industry? If so, you could take a leaf out of Donald Light and Rebecca Warburton’s publication in *Biosocieties* ([dx.doi.org/10.1057/biosoc.2010.40](http://dx.doi.org/10.1057/biosoc.2010.40)) which suggested that the cost of developing a drug is around \$50 million, rather than the oft-quoted \$800 million. Derek Lowe took issue with this (<http://go.nature.com/scFpcz>) and took apart their article. Lowe feigned surprise that big pharma is in such bad shape: “\$43 million for a drug, you should be able to raise that pretty easily, even in this climate — and then you just stand back as the money gushes into the sky.”

Chembites is a new addition to the chemistry blogosphere and aims to “help undergraduates navigate current chemical literature” (<http://chembites.wordpress.com>). A group of MIT graduate students write the posts, which are short summaries of research articles. As Sidechain Bob says on Transition States “the hardest thing to do as an undergraduate is to read the literature”, so Chembites “distilling it down to be understandable for an undergraduate” may prove very useful (<http://go.nature.com/UB3CNQ>).