

functional theory calculations lend a great deal of support for the proposed reaction pathway. They corroborate the fact that the nitride is not accessible via thermolysis, and that its production is exergonic if calculated from a singlet system. Three different reaction pathways for the formation of the observed amide product were investigated to eliminate other possible mechanisms.

Interestingly, the mechanism by which the uranium nitride forms the observed amide product is analogous to that of the C–H activation chemistry performed by Fe=O from cytochrome P450 (Fig. 1b). If the effort in the high-oxidation iron oxide field is any indication, much more energy will need to be spent before a terminal uranium nitride molecule can be bottled. The lessons learned so far is that terminal uranium nitrides are very reactive. Organometallic chemists know a few tricks to circumvent this problem. One that has worked very well for iron nitrides is to choose a suitably protecting supporting ligand^{11,12}. This ligand shields the terminal nitride from unwanted interactions with the solvent or with itself. Although the particular solution always seems obvious in hindsight, the abundance of reports containing failed attempts shows that finding it can seem closer to trial and error than to design. To make matters worse, uranium is very large. And bigger doesn't necessarily mean better, because all the skills learned from transition-

metal chemistry can rarely be applied to uranium because it has a special way (*f*-orbitals, high electrophilicity) of interacting with ligands^{13,14}. The supporting ligand of choice for uranium in the present case, cyclopentadienyl, is as old as organometallic chemistry. Many options are available and the possibilities for reaching the desired target are endless.

Batista, Kiplinger and co-workers present a new avenue for exploring not only the formation of terminal nitrides but of other interesting uranium molecules as well. They still face challenges before their system is thoroughly understood. Clarification of the peculiar effect of the amide ligand present in the starting uranium compound will allow the isolation of other examples. Careful isotopic labelling will aid in supporting the mechanistic hypothesis formulated. Finally, application of the principles learned here to other systems will support not just their work but advance the entire field of uranium organometallic chemistry. In spite of all these challenges, new chemistry has emerged. Although entirely synthetic and remote from biological systems, this chemistry has parallels with some of the most important iron enzymes found in nature. Even though the name of uranium has not caught the attention of poets the same way iron did, enthusiasm for this element is certainly growing. In addition to its importance to

nuclear energy, the uranium nitride described here also showed reactivity highly relevant to catalytic processes. This is no small feat given that the price of uranium competes with that of iron and that new transformations always take chemistry in unforeseeable directions. □

Paula Diaconescu is in the Department of Chemistry and Biochemistry, University of California, Los Angeles 90095, California, USA. e-mail: pld@chem.ucla.edu

References

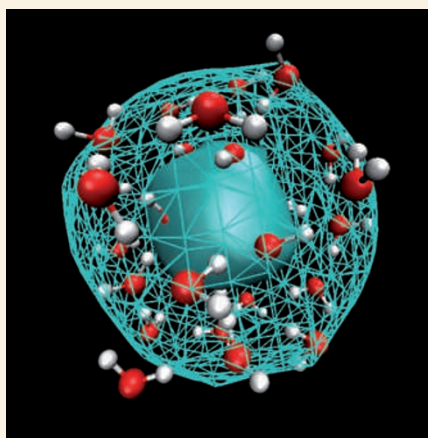
1. Thomson, R. K. *et al. Nature Chem.* **2**, 723–729 (2010).
2. Brennan, J. G. & Andersen, R. A. *J. Am. Chem. Soc.* **107**, 514–516 (1985).
3. Arney, D. S. J. & Burns, C. J. *J. Am. Chem. Soc.* **117**, 9448–9460 (1995).
4. Korobkov, I., Gambarotta, S. & Yap, G. P. A. *Angew. Chem. Int. Ed.* **41**, 3433–3436 (2002).
5. Evans, W. J., Kozimor, S. A. & Ziller, J. W. *Science* **309**, 1835–1838 (2005).
6. Fox, A. R. & Cummins, C. C. *J. Am. Chem. Soc.* **131**, 5716–5717 (2009).
7. Fox, A. R., Arnold, P. L. & Cummins, C. C. *J. Am. Chem. Soc.* **132**, 3250–3251 (2010).
8. Nocton, G., Pecaut, J. & Mazzanti, M. *Angew. Chem. Int. Ed.* **47**, 3040–3042 (2008).
9. Kalina, D. G., Marks, T. J. & Wachter, W. A. *J. Am. Chem. Soc.* **99**, 3877–3879 (1977).
10. Bruno, J. W. *et al. J. Am. Chem. Soc.* **104**, 1860–1869 (1982).
11. Vogel, C. *et al. Angew. Chem. Int. Ed.* **47**, 2681–2684 (2008).
12. Scepianiak, J. J. *et al. J. Am. Chem. Soc.* **130**, 10515–10517 (2008).
13. Kozimor, S. A. *et al. J. Am. Chem. Soc.* **131**, 12125–121367 (2009).
14. Diaconescu, P. L., Arnold, P. L., Baker, T. A., Mendiola, D. J. & Cummins, C. C. *J. Am. Chem. Soc.* **122**, 6108–6109 (2000).

HYDRATED ELECTRONS

Defying cavity

Hydrated electrons — free electrons in aqueous solution — have been well studied for the past half a century, not only because they pose many fundamental questions about solute–solvent interactions, but also because they can occur as a result of ionizing radiation and cause damage to biomolecules such as DNA. Much of the evidence previously reported supports the ‘cavity model’: the idea that a free electron occupies an almost spherical void that excludes water molecules.

Now Ross Larsen, Benjamin Schwartz and William Glover, from the National Renewable Energy Laboratory, UCLA and Stanford University respectively, have used a new model to study the hydrated electron (*Science* **329**, 65–69; 2010). Their results suggest that it inhabits a region that does not exclude water; on the contrary, the hydrated electron



© 2010 AAAS

effectively attracts water molecules. The researchers' model uses a new potential to describe the interactions between water molecules and a free electron. The potential displays features not previously included in simulations of this type, such as a strong

attraction between water's oxygen atoms and the electron.

Inspection of calculated probability distributions for the distance between the hydrogen or oxygen atoms of water and the electron's centre of mass reveal that the electron's charge is spread through a volume that includes, on average, 37 water molecules (pictured) rather than existing in an exclusive cavity. Calculations also show that without the electron the same volume would only contain 30 molecules, indicating that the hydrated electron is attractive. The model agrees well with experimental data from optical absorption spectroscopy and photo-excited state dynamics.

GAVIN ARMSTRONG

The original version of this story first appeared on the Research Highlights section of the *Nature Chemistry* website.