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cal cation $[1]^+[\text{GaCl}_4]^-$, which indicates that **1** may readily undergo one-electron oxidations, just like basic amines. However, the steric bulk of the carbene ligands impedes the ability of **1** to attack electrophiles using its boron lone pair (although this difficulty could be addressed by further tuning the steric and electronic properties of the carbene ligands). It is rare for three-coordinate boron centers to attack electrophiles, but such reactivity has been reported for boryllithium (see compound **C** in the figure) (11).

Structural studies allow an assessment of the relative contributions of the two major resonance structures (different arrangements of the valence electrons that approximate the bonding). The boron atom of **1** assumes a trigonal planar geometry. The B–C bond distances (~ 1.52 Å) in **1**, similar to those (1.55 Å, average) in compound **B** (10), is between the B–C single-bond distance of carbene-stabilized BH_3 (1.585 ± 0.004 Å) (10) and the B=C double-bond distances (1.31 to 1.42 Å) of methyleneborane derivatives (12). The resonance contribution of **1b** is considerable and is reflected in the B–C bond distances in **1** being somewhat shorter than the

typical B–C single-bond distances. However, both the one-electron oxidation and the protonation of the boron center of **1** indicate the electron-rich nature of the boron center and favor **1a** as the predominant formulation, where boron is in the formal oxidation state of +1 instead of +3. Thus, the strong electrophilicity of cyclic (alkyl)(amino)carbenes—their π -acceptor strength—is critical for delocalizing and stabilizing the lone pair of electrons of the H–B: unit in **1**.

Recently, a series of highly reactive parent molecules have also been stabilized with carbenes, including analogs of methylene ($:\text{CH}_2$) bearing heavier atoms [$:\text{SiH}_2$ (13), $:\text{GeH}_2$ (14), and $:\text{SnH}_2$ (14)] and phosphinidene (PH) (15). Notably, the heavier parent methylene triad was stabilized by accepting an electron pair from the carbene ligand while simultaneously donating its electron pair to a Lewis acid species. Carbene stabilization of heavier group 13 analogs of H–B: (i.e., H–Al:, H–Ga:, and H–In:) should also be expected.

Carbene stabilization of a parent borylene by Kinjo *et al.* is a remarkable breakthrough. This strategy may also be feasible for the synthesis of other borylene derivatives. Carbene-

stabilized borylenes, as Lewis bases, may react with transition metal complexes to produce novel transition metal–borylene chemistry. Is it now possible to stabilize a borylene using only one carbene ligand? Such borylenes—with the central boron atoms having six valence electrons, one lone pair of electrons, and one vacant p orbital—may be considered boron analogs of carbenes.

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CHEMISTRY

H₂O in a Desert of Carbon Atoms

Alan L. Balch

Water is a crucial component of our world (1). The properties of water that allow waves to wash upon our sandy beaches are dependent upon the interactions between multiple water molecules (2). These interactions involve water's dipole moment and its ability to weakly associate with neighboring molecules through hydrogen bonding. In order to understand these interactions at the fundamental level, chemists have been finding routes to isolate and probe small, well-defined clusters of water molecules. On page 613 of this issue, Kurotobi and Murata report the formation of a molecular container compound that can isolate an individual water molecule and trap it inside a carbon cage of the most abundant fullerene, C_{60} (3). That molecular container compound is $\text{H}_2\text{O}@C_{60}$ (see the figure).

Most carbon allotropes, which include naturally occurring graphite and diamond, as well as carbon nanotubes and graphene, exist

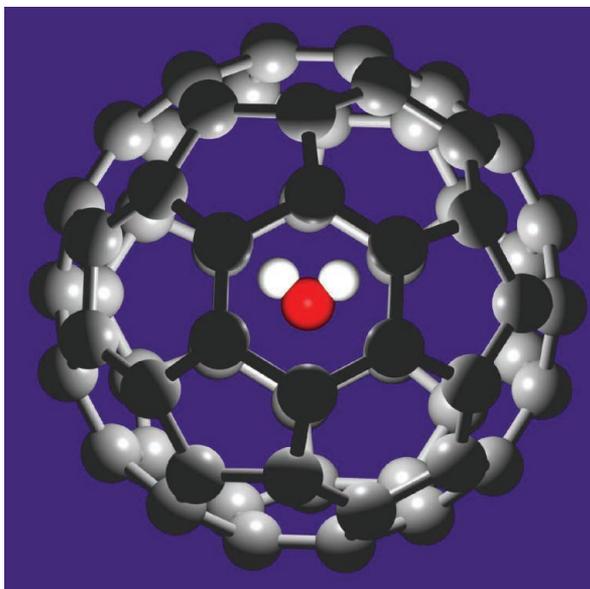
as solids that contain extended networks of carbon atoms (4). Fullerenes, which are also carbon allotropes, are molecular in nature, come in a variety of sizes (C_{60} , C_{70} , C_{90} , and

A chemical process has been developed to trap a single water molecule within a cage of carbon atoms.

so on), and dissolve in various solvents. Thus, C_{60} is soluble in many nonpolar solvents, like benzene and carbon disulfide, where it produces violet- or brown-colored solutions. But

C_{60} is virtually insoluble in water, and considerable effort has been expended to alter its outer surface in order to make the cage water-soluble for biological studies and biomedical applications. Consequently, there is a fundamental incompatibility between the polar water molecule and the highly symmetrical, nonpolar C_{60} that

Isolated and trapped. The structure of the molecular container compound $\text{H}_2\text{O}@C_{60}$ drawn from the crystallographic coordinates. The gray spheres are the 60 carbon atoms of the fullerene. The red sphere is the oxygen atom, and the white spheres are hydrogen atoms. The dipole of the water molecule is aligned vertically.



Department of Chemistry, University of California, Davis, CA 95616, USA. E-mail: albalch@ucdavis.edu

needs to be overcome if a water molecule is to be placed inside the fullerene. Additionally, the water molecule needs to enter the closed fullerene cage.

To encapsulate the water molecule, Kurotobi and Murata began with an intact C_{60} molecule. Through a series of chemical reactions, they opened a hole in its surface without removing any of the 60 carbon atoms. This strategy had been used before for the insertion of molecular hydrogen into C_{60} to form $H_2@C_{60}$ (5). However, in order to accommodate the greater size of H_2O relative to H_2 , a larger hole needed to be cut into the fullerene. Kurotobi and Murata generated an opening that was ringed with oxygen atoms, whose presence allowed strong hydrogen bonding. Thus, the opening in the fullerene created an environment that could attract water molecules. Nevertheless, elevated pressure and temperature were needed to force a water molecule into the inside of the opened C_{60} container. Once the water molecule entered the cavity, a new set of chemical transformations was used to close the hole. An intact C_{60} cage emerged with the water molecule mechanically trapped inside.

The resulting molecule, $H_2O@C_{60}$, is a remarkable combination of a polar molecule encapsulated into a highly symmetric and nonpolar cage. Generally, the polarity of a molecule is associated with its external shape. The bent water molecule is polar, whereas the linear carbon disulfide and the highly symmetric C_{60} are not. Calculations by Kurotobi and Murata suggest that the polarity of $H_2O@C_{60}$ is nearly the same as that of H_2O . Earlier computations at lesser levels of sophistication suggested that the polarity of $H_2O@C_{60}$ would be lower than that of water (6–8). An experimental determination of the dipole moment of $H_2O@C_{60}$ would clarify this issue, but the different chromatographic behavior of C_{60} and $H_2O@C_{60}$ certainly points to a difference in their polarity.

Trapping a guest molecule inside a suitable host molecular container like a fullerene is a fascinating area of supramolecular chemistry. Other notable successes in this area using nonfullerene hosts include the stabilization of otherwise unobservable guest molecules such as the elusive cyclobutadiene, C_4H_4 (9), and lowering the reactivity of a chemically energetic molecule like P_4 (10). Fullerenes themselves can act either as guests or as hosts. As guests, fullerene cages may be found on the inside of carbon nanotubes where nano-peapods are formed (11). However, fullerenes are best known as hosts, which can encapsulate a variety of different entities to form endohedral fullerenes such as $H_2O@C_{60}$.

These endohedral fullerenes may be conveniently divided into two groups: those with neutral molecules or atoms inside and those with electropositive metals inside. In the latter category, there is appreciable transfer of electrons from the metal to the carbon cage, which becomes anionic (12). In these cases, the metal ions strongly interact with the carbon cages, determine the size and shape of the cage that traps the metal, and alter the chemical reactivity of the external surface of the molecule (13). In contrast, when neutral molecules or atoms are present inside fullerene cages, the interactions between guest and host are rather modest. Thus, spectroscopic studies by nuclear magnetic resonance show that both H_2 and H_2O are free to move about inside the C_{60} cage. Future work will determine the extent of the effects of the internal water molecule on the reactivity of the carbon cage of $H_2O@C_{60}$, but interesting developments are anticipated.

The formation of $H_2O@C_{60}$ represents an extreme in ongoing efforts that are examining the properties of small clusters of water molecules. Suitable molecular containers have been prepared that can contain assemblies of 4 to 45 water molecules (14, 15). Related studies have constructed a series of “molecular apple peels” from oligomers of aromatic amides that fold helically and can encapsulate one or two water molecules (16). How-

ever, these containers provide sites where the enclosed water molecules can undergo hydrogen bonding, a feature denied the water molecule in $H_2O@C_{60}$. Thus, $H_2O@C_{60}$ is a remarkable molecule, a molecular container compound in which water cannot undergo conventional hydrogen bonding, but where it conveys an apparently sizable dipole moment onto a nearly isotropic fullerene cage.

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CELL BIOLOGY

A Cellular Roadmap for the Plant Kingdom

Christian R. Landry

Mapping the *Arabidopsis* protein interactome helps show that plant pathogens target highly connected proteins.

One can learn a lot from an urban subway network just by looking at its map. It illustrates crossroads that must be under high surveillance, for example, because a disruption at these central stations can affect the entire system. The map also reflects the city's history, with old lines running through the urban center and recent ones along the periphery. In recent years, researchers have worked to draw analogous maps for cellular networks. These maps link

proteins that physically interact and reflect how cells organize biochemical and biophysical processes and convey molecular signals. Attempts to develop entire protein interaction maps (interactomes), however, have been limited to bacteria, unicellular fungi, and a few animals. Now, two studies in this issue, by the *Arabidopsis* Interactome Mapping Consortium (1) on page 601 and Mukhtar *et al.* (2) on page 596, add a flowering plant to the list. They report on the interactome of *Arabidopsis thaliana* and show how pathogens may exploit protein interactions to manipulate a plant's cellular machinery.

A. thaliana is an annual that is a major model organism for basic and applied

Institut de Biologie Intégrative et des Systèmes (IBIS), Département de Biologie and Regroupement stratégique sur la fonction, la structure et l'ingénierie des protéines (PROTEO), Université Laval, Québec, Québec, G1V 0A6, Canada. E-mail: christian.landry@bio.ulaval.ca