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cases, the absence of (or poorly rendered) phonological representations of speech make voice analysis more difficult.

Social and linguistic realms are biologically intertwined even more broadly in early development. Social processing affects language processing by infants: At 9 months of age, infants learn the sound units and words of a foreign language only through interaction with a live person, not via television (8); infants' learning of vocabulary can be predicted by their ability to utilize social information (such as eye gaze) from others (9); infants' vocalizations in speech advance more rapidly when social information is provided contingently on their utterances (10); infants prefer to look at a person who previously spoke their native language as opposed to a foreign language (11); and brain responses to speech in children with autism are predicted by their social interest in speech (12).

Speech provides a canonical example in which linking the source of the information (Who) and the content of the information (What) adds value. It yields optimal information about the world, its inhabitants, and what they might do next. Infants appear predisposed to learn through the integration of social and linguistic information (13).

The grand challenge is to understand how information in one area of the brain connects to, coheres with, and causes activity in another brain area. Whole-brain imaging technology in the form of functional magnetic resonance imaging, magnetoencephalography, and electroencephalography are allowing us to pose specific questions about brain function in people of all ages, including preverbal infants (14). Studies on people with varying capacities and disabilities will help us understand how brains evolved to link Who and What in an increasingly complex social world.

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CHEMISTRY

Building a Lewis Base with Boron

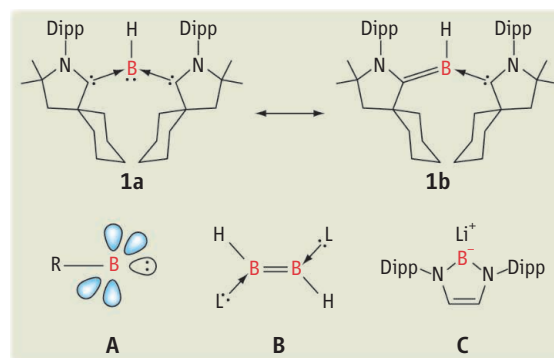
Yuzhong Wang and Gregory H. Robinson

In introductory chemistry courses, acids are defined as substances that increase the concentration of H^+ (or H_3O^+) in solutions (the Arrhenius concept) or act as proton donors (the Brønsted-Lowry concept). The more general Lewis concept defines an acid as a substance that can accept an electron pair and a base as a substance that can donate an electron pair. Compounds with atom centers that are inherently electron-deficient, such as boron or aluminum, readily accept electron pairs. Thus, simple compounds of these elements, such as borane (BH_3) and aluminum chloride ($AlCl_3$), are typically strong Lewis acids. If a monovalent boron center is to bear an electron pair that could be donated as a Lewis base, it would exhaust its own supply of valence electrons and end up with empty orbitals. For example, borylene compounds (such as compound **A** in the figure) (1) would be bases, but they are so reactive that they have only been observed as transient intermediates (2, 3). On page 610 of this issue, Kinjo *et al.* (4) used carbenes to stabilize a borylene (see compound **1** in the figure). This unusual type of base (and analogs yet to be prepared) may open up new avenues in

synthesis and catalysis.

Previous strategies for stabilizing highly reactive borylenes have used transition metals (5), which may provide facile routes to diverse borylenes. The exploration of photochemically or thermally induced borylene transfer

Boron compounds are normally acids, but stable boron bases have been synthesized that may have applications in chemistry involving transition metals.



Boron as a base. Boron compounds normally are acids that accept electron pairs, but Kinjo *et al.* show how to stabilize an electron pair on a boron center so that it forms a base—a borylene compound. The parent borylene **A** ($R = H$) is linear and sp -hybridized, and the lone pair is in an sp orbital. It accepts two electron pairs from two carbenes, yielding a neutral, three-coordinate boron Lewis base **1** (now trigonal planar and sp^2 -hybridized, with the lone pair now in a p orbital). The favored resonance structure **1a** bears a lone pair of electrons at boron. In **1b**, the two valence electrons of boron involves a $B=C$ double bond. Related to **1**, carbene-stabilized neutral diborenes **B** and boryllithium **C** represent other important three-coordinate boron(I) compounds. Dipp, 2,6-diisopropylphenyl; L, N-heterocyclic carbenes; R denotes hydrogen, alkyl, aryl, or halides; boron, red.

reactions represents a remarkable endeavor in this regard (6). The strategy of Kinjo *et al.* for the synthesis of **1** extends the use of carbenes for stabilizing highly reactive main-group species with unusually low oxidation states, such as $H-B=B-H$ (7, 8). Carbene ligands have a lone pair of electrons that can be donated into empty boron orbitals (they are σ -donors), and have empty p orbitals that can help stabilize a lone pair on boron in a p orbital (they are π -acceptors). In this regard, cyclic (alkyl) (amino)carbenes possess stronger σ -donating and π -accepting capabilities than N-heterocyclic carbenes (9). Thus, the potassium graphite reduction of $L:BBr_3$ (where L: denotes N-heterocyclic carbenes) yields carbene-stabilized neutral diborenes (see compound **B** in the figure) (10). Kinjo *et al.* showed that potassium graphite reduction of $L':BBr_3$ [where L': denotes cyclic (alkyl) (amino)carbenes] yields **1**.

Protonation of **1** with trifluoromethane sulfonic acid formed $[1H]^+[CF_3SO_3]^-$ and demonstrated its basicity. Reaction of **1** with gallium trichloride yielded the radi-

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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

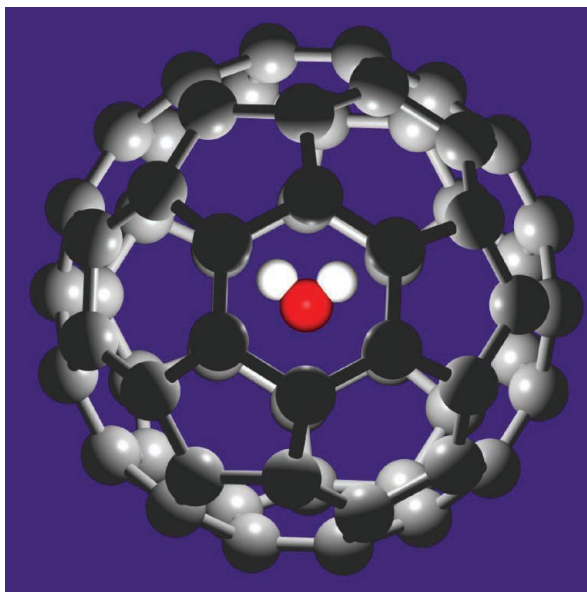
as solids that contain extended networks of carbon atoms (4). Fullerenes, which are also carbon allotropes, are molecular in nature, come in a variety of sizes (C_{60} , C_{70} , C_{90} , and

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.



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