

DIATOMIC SILICON

MAIN-GROUP CHEMISTRY: Carbene-stabilized Si(0) compound could spark new wave of silicon chemistry

A STABLE COMPOUND that contains a silicon-silicon double bond and at the same time has a lone pair of electrons residing on each silicon atom has been prepared by a team of chemists at the University of Georgia (*Science* 2008, 321, 1069).

These attributes are usually equated with extreme instability in a molecule. But Yuzhong Wang, Gregory H. Robinson, and coworkers tamed the L:Si=Si:L species by using an N-heterocyclic carbene as a bulky ligand (L:).

The silicon atoms are in the formal oxidation state of zero in the molecule, which is exceedingly rare for a compound incorporating a main-group element such as silicon. The zero oxidation state is a phenomenon usually reserved for naturally occurring elemental allotropes (such as diamond), pure metals, and metals in certain types of transition-metal complexes.

Inorganic chemists who have learned about L:Si=Si:L say that the Si₂ unit can be thought of as an allotrope of silicon, and as such it could broadly expand the boundaries of silicon chemistry.

To make the diatomic Si(0) species, the Georgia researchers first coordinated an N-heterocyclic carbene to silicon tetrachloride to

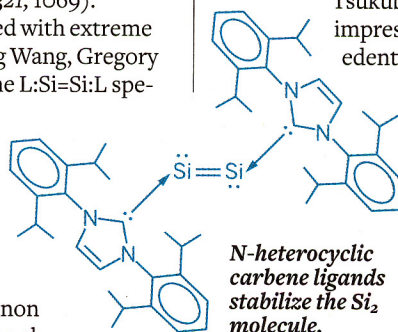
form the Si(IV) compound L:SiCl₄. The chemists treated this compound with a strong reducing agent (potassium graphite, KC₈) in tetrahydrofuran at room temperature to make L:Si=Si:L, which they isolated in crystalline form. Previously, the naked Si₂ molecule without ligands could only be examined spectroscopically in the gas phase or in an argon matrix at very low temperature.

The carbene-stabilized Si₂ molecule “represents a major advance in low-valent, low-coordinate main-group chemistry,” comments inorganic chemist Alan H. Cowley of the University of Texas, Austin. Organosilicon specialist Akira Sekiguchi of the University of Tsukuba, in Japan, agrees, adding that “the impressive finding opens up new, unprecedented possibilities in organometallic chemistry.”

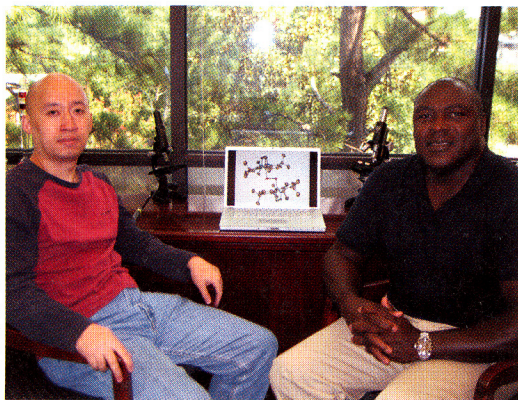
The experimental results on L:Si=Si:L are supported by computational studies carried out by Robinson’s chemistry department colleagues. Among the key findings is that the carbene ligands don’t withdraw electron density from the silicon atoms, but rather they donate electrons to help stabilize the nonbonding electron

pair on each silicon atom. Similar behavior is normally found in transition metals when ligands donate electron pairs into the metal’s empty orbitals. In effect, silicon in L:Si=Si:L is behaving like a transition metal.

As a result, L:Si=Si:L and other potential molecules like it “are not just academic curiosities,” explain C. Adam Dyker and Guy Bertrand of the University of California, Riverside, in a commentary that accompanies the Georgia team’s *Science* paper. The carbene-stabilized Si(0) compounds should exhibit much greater solubility than the standard silicon allotropes, Dyker and Bertrand note. This property might permit the silicon compound to undergo chemical transformations not otherwise possible, similar to the way soluble metal(0) complexes can mediate homogeneous rather than heterogeneous catalysis. —STEVE RITTER



Wang (left) and Robinson pose with a model of L:Si=Si:L.



COURTESY OF GREG ROBINSON

REGULATION Food & Drug Administration reaffirms bisphenol A safety

Current levels of exposure to bisphenol A (BPA) from canned food linings and polycarbonate plastic bottles are too low to cause health effects in humans, including infants, according to a draft assessment FDA released on Aug. 15. The report comes after months of debate over the use of the estrogenic chemical in food-contact products such as baby bottles and infant formula cans.

FDA previously deemed BPA safe in products that come in contact with food

and beverages, but because of health concerns raised last spring by Health Canada and the National Toxicology Program, the agency agreed to revisit its position (*C&EN*, June 2, page 36).

Industry groups welcomed the news and applauded FDA for focusing on the science and not changing its stance. But environmental groups were quick to point out flaws in the agency’s analysis.

The Environmental Working Group (EWG), a nonprofit group that has been

pushing for a ban on BPA in children’s products for years, claimed that FDA ignored hundreds of studies that show toxic effects of BPA at low levels. FDA relied on outdated, industry-funded studies that “do not adequately address the impacts of early life exposure to the developing brain, behavior, and the reproductive system,” EWG said in a written statement.

FDA plans to hold a public meeting to discuss its BPA draft assessment on Sept. 16. —BRITT ERICKSON