Silicon completes triple crown
First stable compound with a silicon-silicon triple bond is synthesized

STEVE RITTER

Double and triple bonds between two carbon atoms have been standard fare in chemistry for more than a century. And during the past 30 years, clever synthetic strategies have led to alkene and alkyne analogs of all the heavier group 14 elements from silicon to lead—with the exception of a compound containing a silicon-silicon triple bond. Now, the wait for this final member of the alkyne series is over.

Chemistry professor Akira Sekiguchi and coworkers Rei Kinjo and Masaaki Ichinohe of the University of Tsukuba, in Japan, report the synthesis and characterization of the first disilyne [Science, 305, 1755 (2004)]. The team synthesized the compound by using potassium graphite ( KC₈) to reduce a brominated tetrasilane precursor containing extremely bulky groups. The emerald green disilyne crystals are heat stable, but they are air and moisture sensitive. X-ray studies show that the central silicon chain incorporating the triple bond is not linear like in alkynes, but is bent.

"The synthesis of a stable disilyne is a milestone both for silicon chemistry and for multiple-bond chemistry in general," writes chemistry professor emeritus Robert West of the University of Wisconsin, Madison, in an accompanying commentary.

There was a time when many chemists thought that elements below the first row of the periodic table were not capable of forming multiple bonds because of repulsion between electrons of the inner orbitals, West relates. But the discovery in the late 1970s that double-bonded compounds of the heavier elements could be stabilized by bulky substituent groups changed things.

West's group, which prepared the first compound with a silicon-silicon double bond in 1981, was part of a new wave in chemistry that eventually led to the synthesis of doubly bonded compounds for most of the elements in groups 13 to 16.

Sekiguchi spent time in West's group as a postdoc in the mid-1980s working toward the alkyne analogs, and they reported a possible disilyne intermediate. Alkyne analogs of germanium, tin, and lead were finally reported in 2000 and 2002 by chemistry professor Philip P. Power and...
coworkers of the University of California, Davis. But the triple-bonded silicon compound remained elusive, until now.

"This is quite a significant achievement to complete the group 14 series of alkynelike molecules," Power tells C&EN. "The series itself very nicely illustrates how the triple bond weakens on descending the group."

The alkyne analogs have decreasing bond order and increasing lone-pair character going from silicon to lead, Power says. This is observed in the bond angles of the central atoms, which range from the bent disilyne (137°) reported by Sekiguchi’s group to a near right angle for the diplumbyne. The bond order of the silicon compound is about 2.6, while the lead compound effectively has a lead-lead single bond and a lone pair of electrons on each lead atom, Power notes.

The disilyne is very reactive in spite of the steric protection afforded by the bulky substituents, Sekiguchi says. The next step for chemists will be to further explore the chemistry of the alkyne analogs and attempt to synthesize compounds having triple bonds between different atoms.

Chemical & Engineering News
ISSN 0009-2347
Copyright © 2004