

Molecule of the Month

A Stable Dibismuthene – A Compound with a Bi-Bi Double Bond

V Chandrasekhar



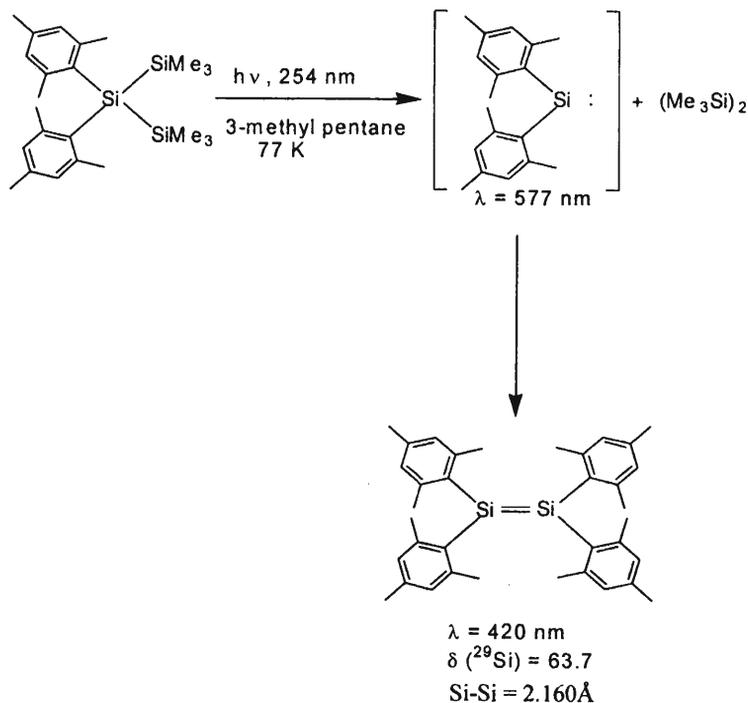
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One of the hallmarks of carbon is its ability to form multiple bonds to itself or to other elements (particularly to O, N or S). This feature is arguably one of the most important reasons for the richness and diversity of organic chemistry and has stimulated inorganic and organometallic chemists to find out if analogous compounds involving other main group elements can be prepared. This is in spite of suggestions from chemists like Grant Urry that the most effective chemistry of silicon arises from the *differences* with the chemistry of carbon compounds rather than with the similarities and his chiding of silicon chemists to *avoid milking the horse and riding the cow* in attempting to adapt the success of organic chemistry in the study of organosilicon compounds. Nevertheless chemists persisted with a sense of doggedness to try and mimic organic molecules with non-carbon elements. The year 1981 marks a watershed in the efforts to prepare and stabilise multiply bonded compounds of heavy main group elements. In this single year stable compounds such as $R_2Si=SiR_2$, $R_2Si=CR'_2$, $RP=PR$ were prepared, structurally characterised and studied.

This flurry of activity began with the success of Robert West at the University of Wisconsin, Madison, USA in isolating and characterising the first disilene containing a silicon-silicon double bond. His strategy involved a kinetic stabilisation of the reactive double bonded system. He reasoned that the reactivity of the double bond in $R_2Si=SiR_2$ can be arrested by having a protective umbrella in the form of sterically encumbered substituents on the silicon atoms (*Box 1*). Using this strategy several stable disilenes and other compounds with a double bond between heavier group 14 to group 16 elements, such as $R_2E=ER_2$ [$E=Ge, Sn$], $RE=ER$ [$E=P, As$] have now been prepared. It would be of interest to readers to note that the first example of a

Box 1

Robert West, a student of Eugene Rochow, the father of modern organosilicon chemistry, was interested in the matrix isolation of divalent silicon species, the silane diyls or silylenes. He found that photolysis of the trisilane, $\text{Mes}_2\text{Si}(\text{SiMe}_3)_2$ in 3-methyl pentane at 77 K led to the formation of an intensely blue coloured silylene, $[\text{Mes}_2\text{Si} \cdot]$. Raising the temperature led to the formation of a yellow solution from which the first disilene was isolated.

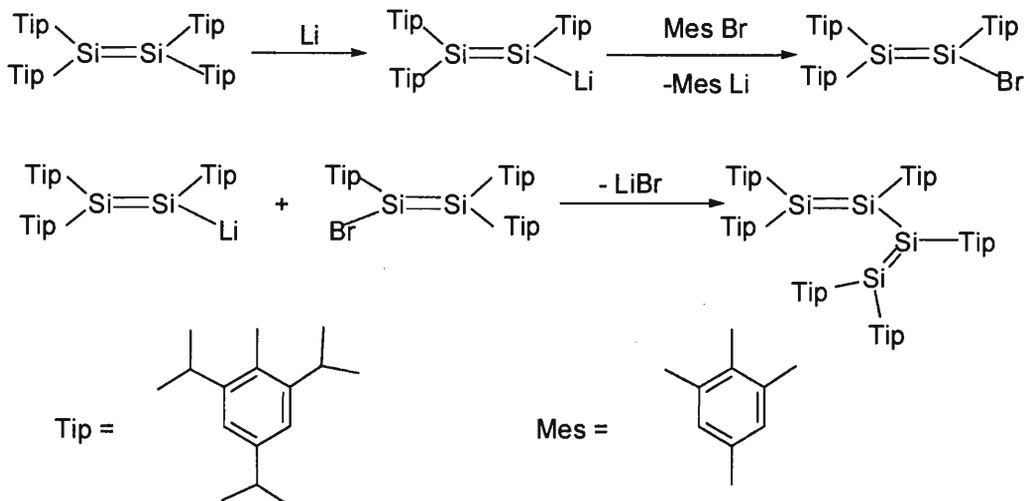


tetrasilabutadiene has also very recently been synthesised and characterised (Box 2).

Although a number of double bonded compounds involving P and As have been isolated the compounds with the heavier elements such as antimony and bismuth could not be prepared. Why should any one be interested in preparing them? One can find an answer to this question perhaps if one paraphrases the mountaineers in the reverse sense and says *because they are not there*. The reason they were not there for a long time is because the protecting groups known were simply not efficient enough. Norihiro Tokitoh and Renzi Okazaki from the University of Tokyo have developed an extremely efficient steric protecting group 2,4,6-tris (bis (trimethylsilyl) methyl) phenyl (Tbt) (Scheme 1). Utilizing this ligand they have prepared several unusual compounds $\text{R}_2\text{E}=\text{X}$ ($\text{E}=\text{Si}, \text{Ge}$; $\text{X}=\text{S}, \text{Se}$) (Scheme 2) and also successfully prepared a silanaphthalene where a silicon atom is present in lieu of a carbon in a naphthalene skeleton. In view of

Box 2

Weidenbruch and coworkers have synthesised the first example of a tetrasilabutadiene, which is stable at room temperature. The synthetic sequence is shown below:



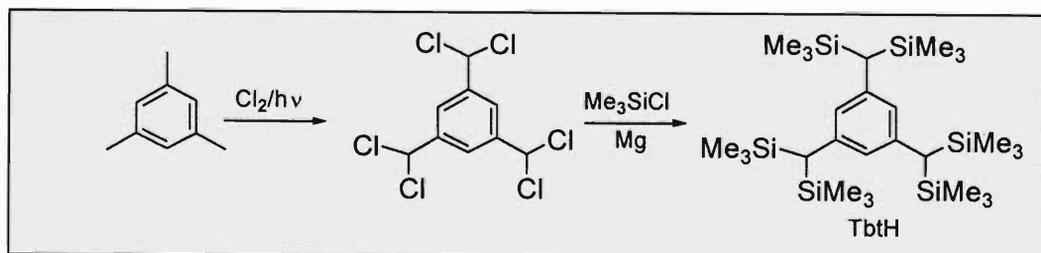
* the silabutadiene is stable upto 267° C.

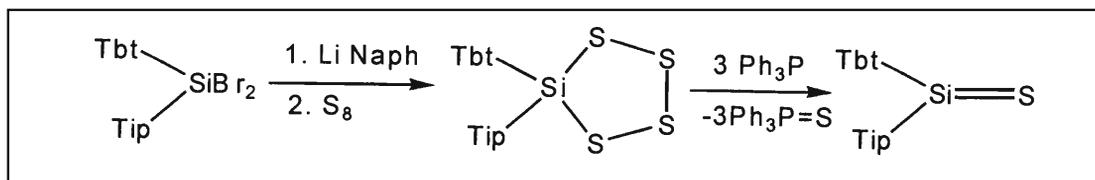
* It adopts a *s-cis* conformation with a dihedral angle of 51° between the planes of the planar Si=Si bonds.

* UV spectra show a 100 nm bathochromic (red) shift in comparison to the isolated disilenes.

these successes the Tokyo group planned the scaling of the synthetic summit using the Tbt protecting group. They succeeded in stabilizing the first dibismuthene (and also the first distibene) by a three step synthetic strategy (*Scheme 3*). First, bismuth trichloride was reacted with TbtLi to afford TbtBiCl₂. This was treated with Li₂Se to give a six-membered ring, a triselenatri-bismuthane. The next step, which is the key in the synthesis, is the deselenization from the six-membered Bi-Se inorganic ring. This is accomplished by the reaction with P(NMe₂)₃. As is well

Scheme 1.

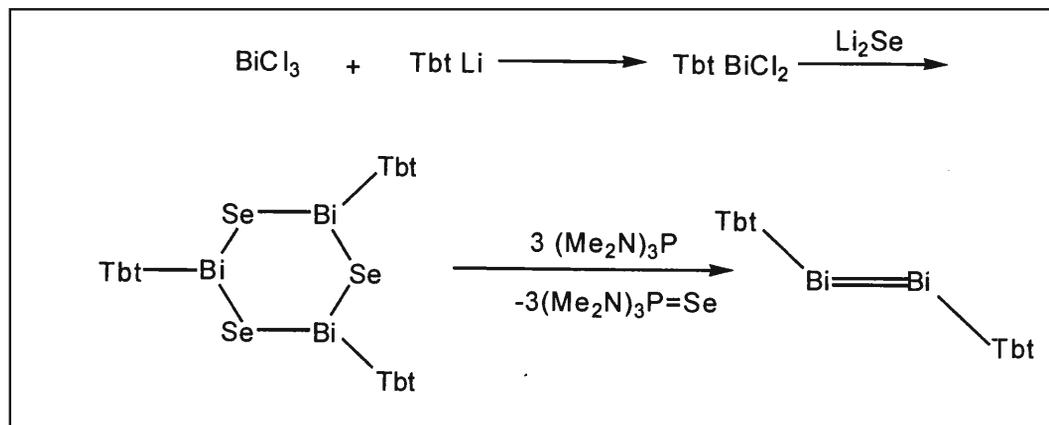



Scheme 2.

known, P (III) compounds tend to readily oxidise to P(V) derivatives. In this instance Se is abstracted by phosphine to generate insitu $[R\text{Bi}]$ which dimerises to the double bonded bismuthene $R\text{Bi}=\text{Bi}R$. How do we know that this compound contains a true double bond? One looks at several things. First, of course, is the length of the bond present between the two bismuth atoms. As is well known in carbon compounds the bond length decreases on going from a single bonded derivative to a double bonded one. This trend continues in silicon and other compounds also (Box 3). In dibismuthene the bond length is $2.8206(8)\text{\AA}$. This value is about 6% shorter than the Bi-Bi single bond length of $2.990(2)\text{\AA}$ found in $\text{Ph}_2\text{Bi}-\text{BiPh}_2$. Theoretical calculations have been performed on the hypothetical molecules, $\text{H}_2\text{Bi}-\text{BiH}_2$ (3.009\AA) and $\text{HBi}=\text{BiH}$ (2.795\AA). The bond angles around carbon in $\text{R}_2\text{C}=\text{CR}_2$ are 120° . This is because of the sp^2 hybridisation at carbon. In dibismuthene the Bi-Bi-C bond angle is 100.5° . This suggests that Bi prefers to maintain the $(6s)^2(6p)^3$ valence electron configuration and perhaps utilises only the three orthogonal p orbitals for σ as well as π bonding. This observation is also consistent with the well-known inert-pair effect.

Suggested Reading

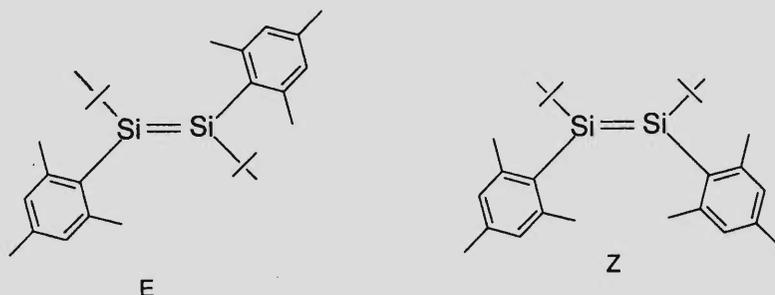
- [1] R West, *Angew. Chem. Int. Edn. Engl.*, 26, 1201, 1987.
- [2] T Muller, *Angew. Chem. Int. Edn. Engl.*, 37, 68, 1998.
- [3] N Tokitoh, Y Arai, R Okazaki, S Nagase, *Science*, 277, 78, 1997.
- [4] N Tokitoh, Y Arai, T Sasamori, R Okazaki, S Nagase, H Uekusa, Y Ohashi, *J. Am. Chem. Soc.*, 120, 433, 1998.

Scheme 3.


Box 3. Comparison of Olefins, Disilenes and Dibismuthene

1. On going from C-C to C=C, from Si-Si to Si=Si and from Bi-Bi to Bi=Bi there is a shortening of bond length. The extent of shortening is about 6-8%. In contrast to olefins, disilenes and dibismuthene deviate from planarity.

2. In olefins the barrier to rotation around the C=C bond is quite high. Therefore E (trans) and Z (cis) isomers where possible can be isolated separately. In disilenes the barrier to rotation around Si=Si is about 70% as large as that for comparable alkenes. Consequently although the E and Z isomers can be isolated individually they undergo slow thermal isomerization from Z to E. The situation with dibismuthene is not yet known.



3. In contrast to most olefins disilenes are yellow or orange with electronic absorption being in the visible region between 400 and 470 nm. In dibismuthene this is further red shifted.

4. The ^{29}Si resonances are strongly deshielded and the $^1J(\text{Si-Si})$ coupling constant is nearly twice as large in Si=Si systems in comparison with Si-Si. These trends are similar to what are observed in the ^{13}C NMR of alkenes.

What other support is present for the double bond? Dibismuthene is purple in colour and shows electronic transitions characteristic of a double bond viz., a $n \rightarrow \pi^*$ transition (660 nm; ϵ 100) and a $\pi \rightarrow \pi^*$ transition (525 nm; ϵ 4000). Lastly the Bi-Bi stretching frequency of 134 cm^{-1} observed for dibismuthene is 31 cm^{-1} higher than that observed for $\text{Ph}_2\text{Bi-BiPh}_2$.

The synthesis of dibismuthene and several other fascinating molecules on the way shows how synthetic chemistry involving main group elements has come of age. The next summits to be conquered are those compounds *that are still not there*—hexasilabenzene, silaalkynes ... and so on and hopefully their conquest is just round the corner.

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