Multiple bonds continue to fascinate chemists: Discovery of stable Si≡Si and B=O bonds

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It is well known that the two major allotropic forms of carbon, diamond and graphite, contain sp^3 and sp^2 hybridized carbon atoms, respectively. While the former solid is made up of pure σ-C–C single bonds, multiple bonding with a π-component between adjacent carbon atoms characterizes the bonding in the latter. The molecules formed by carbon are no exception. The homologous series of alkenes and alkynes, for example, contain stable C=C double and C≡C triple bonds, respectively. Likewise, nitrogen has a triple bond whereas oxygen has a double bond in their molecules (N_2 and O_2). Heteroleptic double bonds between carbon and lighter p-block elements such as nitrogen and oxygen (C=N and C=O) have been discovered and used by organic chemists for more than two centuries. It has also been possible to explain the bonding in these molecules on the basis of simple hybridization models and VSEPR theory.

The story of stabilizing multiple bonds involving heavier main group elements is nonetheless different. The development in this area has been beleaguered by several road-blocks and controversies. The most important amongst these is the so-called *double bond rule* (a textbook material) which states that those elements with a principal quantum number equal to or greater than three are not capable of forming multiple bonds because of considerable Pauli repulsion between the electrons of the inner shells. This rule, often quoted in many chemistry textbooks, however collapsed in 1981 with the announcement of successful synthesis of stable and isolable compounds containing Si=Si and Si=C compounds by West and Fink[1] and Brook and co-workers[2].

It is instructive to recall the fact that the early studies on multiple bonding in heavier p-block elements was primarily dominated by spectroscopists and theoretical chemists since most of these systems were either obtained by matrix isolation studies or predicted to be stable and isolable by theoretical calculations. Although a distannene was known from the early 1970s due to the work of Lappert and co-workers[3], it was only after the discovery of stable Si=Si and Si=C bonds in 1981 that synthetic main group chemists have turned their attention towards the search for other homoleptic and heteroleptic double bonds involving heavier p-block elements. In the ensuing years, compounds with P=P, As=As, Sb=Sb, Bi=Bi, Ge=Ge, Sn=Sn, Pb=Pb, Ge=S, Ge=Se, Ge=Te linkages were synthesized and their solid-state structures determined by single crystal X-ray diffraction studies[4].

In addition to the interest in stabilizing the stable homo- and heteroleptic double bonds of p-block elements, a parallel research program was set out in various laboratories to realize the triple bonds in heavier main group. The quest for stable triple bonds arguably revealed that the lighter members of groups 13, 14, and 15 behave considerably different from the heavier ones (e.g. Si vs Ge, Sn and Pb; or Al vs Ga, In and Tl). Hence the sequence of these discoveries suggests that the heavier members have yielded multiple bonds in an easier manner. Thus the homoleptic triple bonds involving germanium, tin, and lead were described a few years back by Power[5]. Similarly, an anionic compound supposedly containing a Ga≡Ga linkage was the source of an intense scientific debate in the late 1990s (ref. 6). Although these compounds involving Ge, Sn, and Pb are assumed to contain a formal homoleptic triple bond, the presence of a pronounced electron density on the central atoms (rather than between them) limits or decreases the bond order, especially when one moves down the group (due to well known inert-pair effect). Strikingly, the experimental and theoretical data generated for the heavier Group 13, 14 and 15 compounds also suggest the lower tendency of the s-electrons to participate in bonding. For these reasons, the synthesis of a stable compound containing a 'real' Si≡Si linkage, where inert pair effect does not come into play, became a compelling objective.

After a series of theoretical calculations on the stability of Si≡Si linkage and several unsuccessful attempts of laboratory synthesis of compounds with a silyne linkage, recently Sekiguchi, Kinjo, and Ichinhoe have finally succeeded in isolating thermally stable RSi≡SiR (R = Si(Pr^i)(CH(SiMe$_3$)$_2$)) (Scheme 1; **A**), which contains a *genuine*

triple bond[7]. The strategy used for the synthesis of this compound is very similar to that reported for other low-valent low-coordinate main group compounds both in terms of the use of a bulky substituent on the central atoms and the reduction of a element halide linkage using an alkali metal. Thus, the reduction of 2,2,3,3-tetrabromo-1,1,4,4-tetrakis[bis(trimethyl-silyl)methyl-1,4-diisopropyltetrasilane [Rsi(Cl)$_2$-Si(Cl)$_2$R] with potassium-graphite (KC$_8$) in dry THF yields extremely air- and moisture sensitive emerald-green crystals of **A**, which does not melt or decompose until 128°C. The ^{29}Si NMR chemical shift of +89.9 ppm for the sp-hybridized silicon atoms bearing the triple bonds in **A** is considerably upfield shifted compared to that of silyl substituted disilenes (140–155 ppm) reported in the literature. A single crystal X-ray diffraction study of **A** revealed a short Si≡Si bond (2.062(1) Å), which is 3.8% shorter than a typical Si=Si bond (2.14 Å) and about 13.5% shorter than a normal Si–Si single bond (2.34 Å). Unlike in alkynes, the bond angle R-Si≡Si is considerably bent (137.44°). A DFT calculation at B3LYP/6-31G(d) level of theory reproduces the X-ray structural parameters and makes useful predictions about the observed UV-vis spectrum of **A**. The origin of emerald-green colour of **A** is believed to be the result of the weak forbidden transition observed at 690 nm in hexane.

While the details of the study reported for **A**, without any doubt, indicate the presence of a *genuine* triple bond between silicon atoms, the success in the synthesis of **A** should again be attributed to the use of the well-established idea of kinetic stabilization. The bulky Si(Pr^i)(CH(SiMe$_3$)$_2$ substituent on central silicon not only provides the necessary kinetic stability to the Si≡Si linkage by protecting it from decomposition, but also stabilizes it from an electronic point of view (earlier calculations also indicate that a silyl substituent on the triply bonded silicon is preferred over an alkyl or aryl substituent).

The use of a kinetically stabilizing ligand has once again been the central strategy for another important discovery reported a few weeks ago, where a boracycle, [LB=

A

Scheme 1.

B
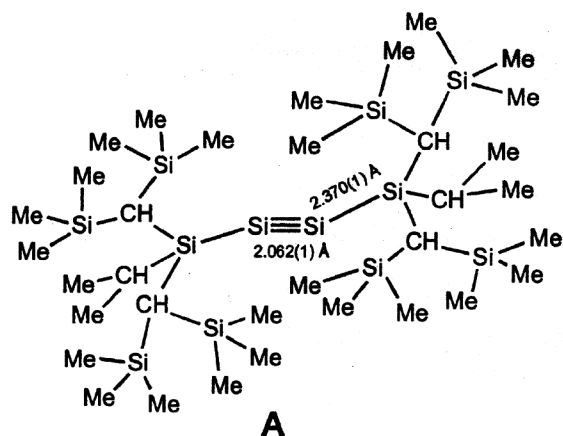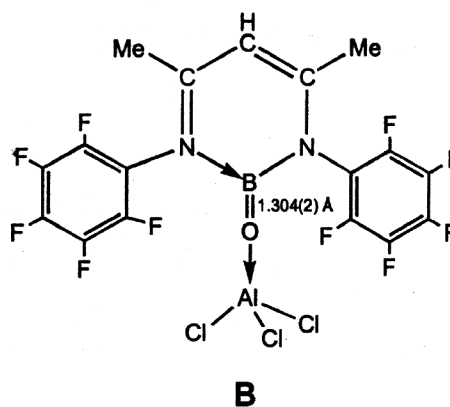
Scheme 2.

O → AlCl$_3$] (L = a chelating β-diketiminate; {HC(CMe)$_2$(NC$_6$F$_5$)}$^-$) (Scheme 2, **B**) with a stable B=O linkage has been characterized in the solid-state by Vidovic et al.[8] The synthesis of this compound is remarkable in the sense that there are no experimental data available for π-bond strengths of homoleptic multiple bonding in Group 13 elements. The attempts to make homo-/heteroleptic multiple bonds in the boron group have been a rather difficult task; stabilization of E=O has been hampered by the oxophilicity of the group 13 compounds which makes the formation of E–O–E linkage more facile than that of E=O.

Vidovic et al.[8] have overcome the problem of stablizing B=O linkage by starting from a chelating monoanionic β-diketiminate ligand (LH) that contains pentafluoro phenyl substituents on the imino nitrogen atoms which bind to the boron atom. The reaction of LH with MeAlCl$_2$ followed by treatment with AlCl$_3$ produces [LBCl][AlCl$_4$] through a methane elimination and exchange-autoionization reaction. The mild hydrolysis of [LBCl][AlCl$_4$] by stoichiometric amount of water in CH$_2$Cl$_2$ produces **B**, which is

formally a AlCl$_3$ adduct of oxoborane [LB=O]. In **B**, the six-membered BN$_2$C$_3$ ring is planar. The B=O bond which is under focus is considerably short (1.304 Å), although it is somewhat difficult to make a clear assessment of the B–O bond order based on the data available at Cambridge Crystallographic Data Centre since there is a pronounced dependence on the stereoelectronic characteristics of the other boron substituents. The DFT calculations carried out on a model boroxane and its AlCl$_3$ adduct are suggestive of the facts that the B=O distance increases only very marginally by adduct formation (by 1.9%; 1.292 vs 1.316 Å) and the double bond character is retained to a large extent.

To summarize, the synthesis of the stable silyne **A**, nearly a quarter century after the discovery of silene R$_2$Si=SiR$_2$, marks a new milestone in the multiple bonding in main group. Studies on the chemical bonding and reactivity of these systems are likely to provide a new chapter in an already rich silicon chemistry. Similarly, due to the use of group 13 compounds in the catalysis (mainly due to their Lewis acidic nature, e.g. methylalumoxane MAO),

the discovery of oxoborane **B** can be considered as a very significant step forward in the area of group 13 multiple bonded systems.

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