Chemistry of Boron and Silicon Subhalides

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Until recently, the use of high temperatures (>1000°) has held few attractions for the majority of synthetic chemists concerned with compounds stable only under moderate conditions. This situation has begun to change with more widespread use of a simple technique for conducting reactions of gaseous atoms and small molecules which exist at high temperatures with ordinary compounds. The gaseous high-temperature species and the vapor of a compound with which it may react are liberated simultaneously inside a high-vacuum system and condensed together on a surface cooled by liquid nitrogen or other refrigerant. In the vacuum, gas-phase collisions are few and reaction occurs almost entirely in the condensed phase, either at the moment of condensation or when the surface is subsequently warmed.

The scope of this method is considerable.[1] High-temperature species which can be made easily on a scale of a few millimoles up to a mole include atoms of most elements as well as many small molecules, such as carbenoids and radicals, with obvious potential reactivity.

Two main classes of high-temperature species are being studied at Bristol: first, transition-metal atoms, whose reactions with inorganic and organic compounds were initially studied here[2] and are now also being investigated by other groups;[1,3] second, low-valency compounds of boron and silicon, particularly those classed as carbenoids[4]—the boron monohalides, the silicon dihalides, and silicon monoxide. Interest in the boron and silicon compounds, the main topic of this Account, stems from their exceptional reactivity at low temperatures and the range of compounds to which they offer unique synthetic pathways. Some aspects of the chemistry of silicon difluoride were considered in a previous Account,[5] and SiF_2 will be discussed now only in relation to other low-valency species.

Preparation of the Species

The preferred method of making the gaseous subhalides is by reduction of a silicon tetrahalide or a boron trihalide with silicon or boron, respectively, as this uses readily available starting materials. The equilibria

$$Si(s) + SiX_4(g) \rightleftharpoons 2SiX_2(g)$$

$$2B(s) + BX_3(g) \rightleftharpoons 3BX(g)$$
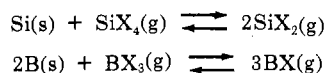
are shifted to the right at high temperatures and low pressures. Thus, at a pressure of 0.1–1.0 Torr, 90% yields of SiF_2, $SiCl_2$, and $SiBr_2$ can be obtained at 1300° and a 90% yield of BF at 1850°. Lower pressures force the equilibria further to the right, but the number of gas–solid collisions is reduced and the practicable rate of formation of the subhalide is less.

Attempts to make SiI_2 under these conditions give mainly iodine because of dissociation of the diiodide to iodine atoms and solid silicon. Boron monochloride is also difficult to make by this method, as the equilibrium is only shifted sufficiently to the right at temperatures above 2000°, perilously close to the melting point of boron. Since there is no satisfactory material for containing molten boron, the monochloride is better made from diboron tetrachloride (see below).

When they are being used as reagents, SiF_2, $SiCl_2$, and BF are prepared in the apparatus shown in Figure 1. The higher halides are passed over hot boron or silicon in an inductively heated graphite tube, and gaseous subhalides, formed at the rate of 20–100 mmol in 1 hr, emerge into a high vacuum ($p < 10^{-4}$ Torr) and condense immediately on the liquid nitrogen cooled walls of the vacuum chamber. A substantial excess of the vapor which is to react with the subhalide is passed into the apparatus simultaneously and condenses on the cold walls. The cocondensate is often highly colored at −196°, but the color fades when the liquid nitrogen is removed and the walls are warmed to room temperature. Excess reactants and volatile products are pumped out of the chamber through a wide-bore pumping line which permits even sparingly volatile compounds to be collected quite quickly.

A different apparatus can be used to prepare silicon difluoride, in which off-gases from a furnace are pumped along a glass tube at low pressure before being condensed at −196°. This is possible because SiF_2 has a lifetime in the gas phase at room temperature of several seconds, probably a thousand times greater than the lifetimes of $SiCl_2$ and BF under comparable conditions. However, as discussed later, silicon difluoride prepared in such an apparatus behaves differently from that made in the apparatus of Figure 1.

Direct reduction with the metalloid is also the best

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(1) P. L. Timms, *Advan. Inorg. Chem. Radiochem.*, 14, 121 (1972).

(2) P. L. Timms, *Chem. Commun.*, 1033 (1969).

(3) J. J. Havel, M. J. McGlinchey, and P. S. Skell, *Accounts Chem. Res.*, 6, 97 (1973).

(4) O. M. Nefedov and M. N. Manakov, *Angew. Chem., Int. Ed. Engl.*, 5, 1021 (1966).

(5) J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 4, 145 (1971).
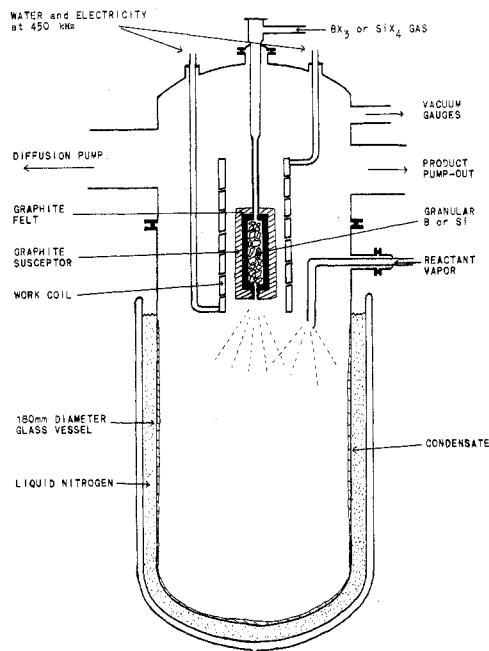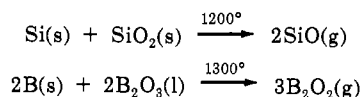
Figure 1. Apparatus for the formation of subhalides at high temperature.

method of making gaseous silicon and boron suboxides. For these reactions between condensed phases,

$$Si(s) + SiO_2(s) \xrightarrow{1200°} 2SiO(g)$$

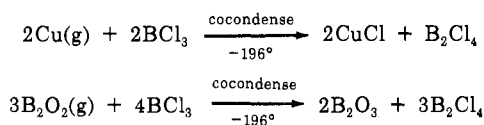$$2B(s) + 2B_2O_3(l) \xrightarrow{1300°} 3B_2O_2(g)$$

an apparatus is used in which the gaseous suboxide sprays upward from a resistance-heated open crucible mounted near the bottom of a cooled vacuum chamber and condenses on the walls along with any other vapor passed into the chamber.[6] It should be noted that "boron monoxide," O=B—B=O, is not a carbenoid, although it is a fairly reactive molecule at low temperatures.

An alternative synthesis of the silicon and boron subhalides is flash thermolysis of a catenated compound of type Si_2X_6 or B_2X_4, e.g., decomposition of hexafluorodisilane.[7] The method is generally less

$$Si_2F_6 \xrightarrow[\text{1 Torr}]{700°} SiF_2 + SiF_4$$
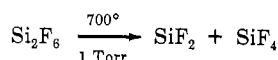
attractive than reduction with the metalloid because the catenated compounds are often not readily available and because the subhalide can only be obtained 50% pure. Nevertheless, the method has to be used for making boron monochloride. Fortunately, diboron tetrachloride is now easily made from reactions involving condensation of high temperature species, which can be represented by
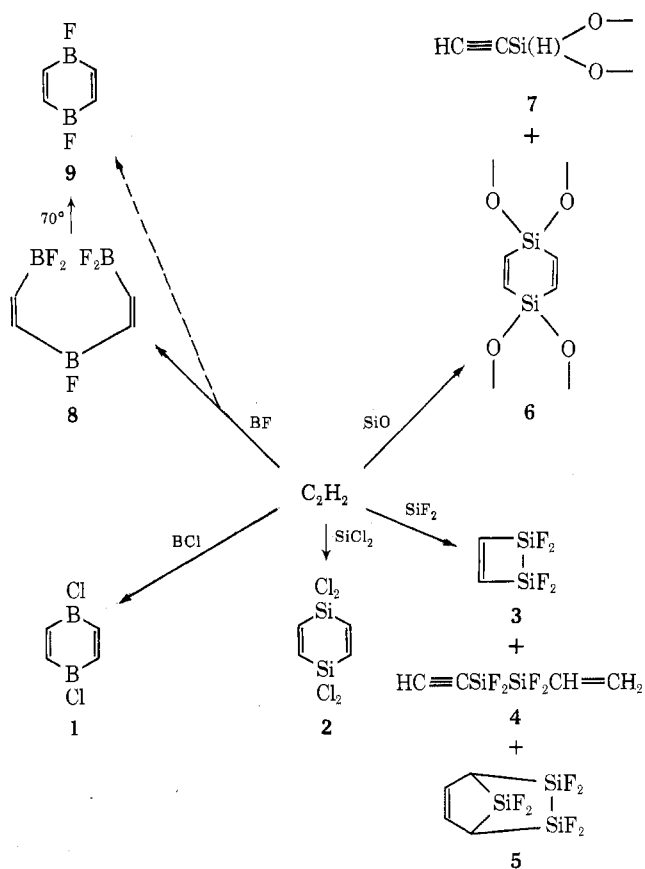
$$2Cu(g) + 2BCl_3 \xrightarrow[-196°]{\text{cocondense}} 2CuCl + B_2Cl_4$$

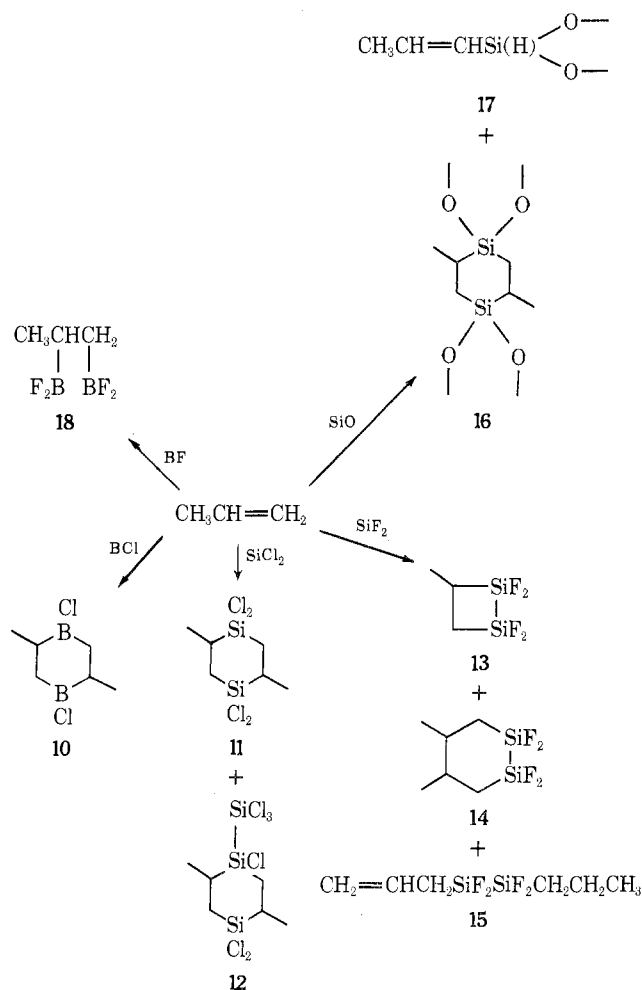$$3B_2O_2(g) + 4BCl_3 \xrightarrow[-196°]{\text{cocondense}} 2B_2O_3 + 3B_2Cl_4$$

(6) E. T. Schaschel, D. N. Gray, and P. L. Timms, *J. Organometal. Chem.*, **35**, 69 (1972).

(7) M. Schmeisser and K. P. Ehlers, *Angew. Chem.*, **76**, 281 (1962).

The reaction with copper vapor is well suited for making B_2Cl_4 on a 100-mmol scale.[8]

Boron monochloride is prepared by passing B_2Cl_4 vapor through a short length of narrow bore quartz tubing heated to 1100° mounted inside a vacuum chamber like that in Figure 1. Two reactions occur in the tube: a heterogeneous cracking of B_2Cl_4 to BCl_3 and solid boron which coats (and may block) the inside of the tube, and cracking to BCl and BCl_3 which depends mainly on collisions between gas molecules. Very low pressures favor the former mechanism, but at an optimum pressure of a few Torr about 50% of the B_2Cl_4 is cracked by the latter mechanism. In this way, 10–20 mmol of BCl can be formed in 1 hr.

Reactions of the Species with Unsaturated Organic Compounds

Like carbenes and other carbenoids, the boron and silicon high-temperature species react readily with alkenes and alkynes, and this a good way of making organometalloid compounds. As the reactions occur on condensation at −196°, it is sometimes possible to isolate and characterize products unstable at room temperature. Schemes I and II show the compounds obtained by reacting the carbenoid species with acetylene and propene. The choice of propene and not ethylene in these reactions was for an experimental reason. Ethylene is so volatile that its vapor pressure at −196° is sufficient to spoil the high vacuum required to use BF, BCl, $SiCl_2$, and SiO as reagents.

Scheme I

(8) P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 830 (1972).

Scheme II

$CH_3CH=CHSi(H)$⟨O—, O—⟩

17

+

(structure 16)

16

CH_3CHCH_2 | F_2B BF_2

18

SiO

BF

$CH_3CH=CH_2$

BCl |SiCl₂   SiF₂

(structure 10: Cl-B ring with B-Cl)

10

(structure 11)

11

+

$SiCl_3$ | $SiCl$ | (structure 12)

12

(structure 13: SiF₂-SiF₂ ring)

13

+

(structure 14: SiF₂, SiF₂)

**14**

+

$CH_2=CHCH_2SiF_2SiF_2CH_2CH_2CH_3$

15

Boron monochloride and silicon dichloride react in a model way. They both give high yields of the 1,4-metalloid-substituted cyclohexadienes 1 and 2 with acetylene, and the corresponding cyclohexane derivatives 10 and 11 with propene. These products are presumed to be formed *via* unstable cyclopropene and cyclopropane derivatives which immediately dimerize, *e.g.*

$HC{\equiv}CH$ + BCl → [HC=CH, B, Cl] → 1
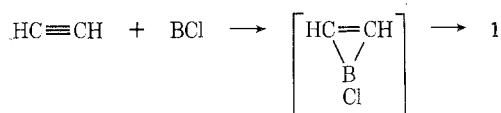
Three-membered rings have not been isolated in reactions of these carbenoids, although the boracyclopropenes are isoelectronic with "aromatic" cyclopropenium ions. In the reaction of SiCl₂ with propene, it is difficult to avoid the formation of the catenated compound 12 in addition to 11, as SiCl₂ inserts easily into Si–Cl bonds.

It is probable that the reactions of BF with acetylene and propene also involve the initial formation of three-membered rings but that these are sensitive to fluorine transfer reactions and ring opening. Strong B—F⋯B interactions are known to occur in boron fluorides at low temperatures, and some BF₃ is always present with BF condensed on a cold surface.

Thus, there is the possibility of a reaction

(structure showing F-B-C-C ring → bis(difluoroboryl) product)
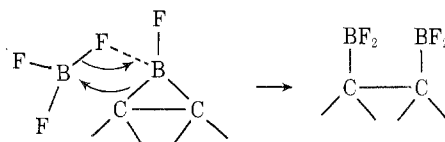
This process can account for the good yields of 1,2-bis(difluoroboryl)propane (18) formed from BF and propene. This compound is certainly not formed on the cold surface by addition of B₂F₄ to propene, as this reaction is known to be slow below 0°.

In the acetylene–BF reaction, fluorine transfer and ring opening may go one stage further. Addition of BF₃ to the boracyclopropene could give 1,2-bis(difluoroboryl)ethylene, which then interacts with a second molecule of the boracyclopropene as shown.

(structure with BF₂, C=C, B, F → 8)

→ 8
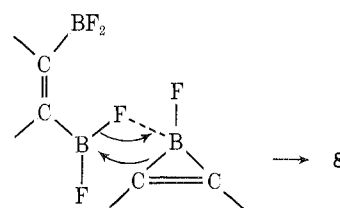
Cyclization of 8 occurs in the gas phase with elimination of BF₃ to give the boracyclohexadiene 9, a compound which is quite stable as a vapor but which decomposes rapidly in the condensed phase above 0°. This instability is also observed with the other cyclohexadiene derivatives, 1 and 2, but analogs of these compounds formed from dimethylacetylene are more stable.

From infrared and nmr spectroscopic data, it seems certain that the 1,4-diboracyclohexadienes 1 and 9 are planar.[9] Other compounds containing the C₄B₂ ring system, notably C₄B₂H₆,[10] adopt a *nido*-carborane structure, a pentagonal pyramid with an apical boron atom. It is thought that p-pπ bonding from the halogen atoms to the boron p_z orbitals and the interaction of these orbitals with the carbon–carbon π orbitals stabilizes the planar structures.

Silicon difluoride is believed to react with alkenes and alkynes by a free-radical mechanism.[5] Monomeric SiF₂ does not attack carbon–carbon multiple bonds, but at −196° polymerization of SiF₂ yields diradicals ·SiF₂SiF₂·, ... ·(SiF₂)ₙ·, which are very reactive. Thus, in the reaction of SiF₂ with acetylene and propene, the diradicals ·SiF₂SiF₂CH=CH· and ·SiF₂SiF₂CH₂ĊHCH₃, will be among the initial products. These can either cyclize to 3 or 13, respectively, or add a further molecule of acetylene or propene to give ·HC=CHSiF₂SiF₂CH=CH· or CH₃ĊHCH₂SiF₂CH₂ĊHCH₃. These diradicals can stabilize in two ways, either by cyclization or by proton shifts. Acetylene gives only the product 4 by a 2,5-proton shift,[11] but substituted acetylenes also

(9) P. L. Timms, *J. Amer. Chem. Soc.*, **90**, 4585 (1968).

(10) T. P. Onak and G. T. F. Wong, *J. Amer. Chem. Soc.*, **92**, 5226 (1970).

(11) C. S. Liu, J. L. Margrave, J. C. Thompson, and P. L. Timms, *Can. J. Chem.*, **50**, 459 (1972).

give 1,2-disilacyclohexadienes.[12] The diradical from propene appears to undergo both cyclization and a 1,7-proton shift to give 14 and 15, respectively. The bicyclic compound 5 from the acetylene–SiF_2 reaction could result from rearrangement of a seven-membered ring formed by cyclizing the diradical $\cdot HC{=}CHSiF_2SiF_2SiF_2CH{=}CH\cdot$.

In these, as in many other reactions of SiF_2, it is only the compounds containing two or three silicon atoms which have been characterized, more complex compounds derived from higher diradicals being less easily purified and handled. Thus, in general, the yields of products which are isolated are lower than in corresponding reactions of the other silicon and boron subhalides which react as monomers and give a smaller range of products.

The reactions of silicon monoxide with unsaturated organic compounds at $-196°$ provide a unique direct route to silicone polymers.[6] There is chemical and spectroscopic evidence that the reaction products from alkenes and alkynes contain Si–O–Si linked 1,4-disilacyclohexane and 1,4-disilacyclohexadiene rings, respectively, as shown in structures 16 and 6.

However, the reactions with silicon monoxide are complicated in two ways. First, it seems that oxygen-bridged polymers of SiO may be at least as reactive as monomeric SiO, as it has not proved possible to make products which contain a 1:1 mole ratio of an organic molecule to SiO. For example, the average composition with propene is $C_3H_6(SiO)_3$. This is consistent with matrix isolation studies on SiO[13] which show that a cyclic dimer, a cyclic trimer, and higher polymers are formed very easily.

Second, the products contain Si–H bonds, showing that there is some insertion of SiO or its polymers into C–H bonds. This is a reaction with no parallel in reactions of the silicon and boron subhalides. Both these complicating factors adversely affect the properties of the silicone products, the first causing strong cross-linking, and the second causing some oxidation sensitivity. Nevertheless, the reactions products from SiO and some organic compounds, e.g., propene and benzene, are very thermally stable materials.

This discussion has been restricted to reactions of the high-temperature species with acetylene and propene so that a complete set of results could be presented. It is clear that SiF_2, $SiCl_2$, and SiO react with almost every unsaturated organic compound, including aromatic hydrocarbons. However, the boron monohalides are more sensitive to acceptor–donor interactions and it is possible, for example, that the failure of BF to react with benzene can be attributed to this cause. No addition of B_2O_2 to alkenes or alkynes has been observed.

The Silicon–Boron Halides

Relatively few compounds are known which contain silicon–boron bonds, but reactions of the high-temperature species now provide good ways of forming these bonds.

The first perfluorinated silicon–boron compounds were made by condensing SiF_2 with BF_3 at $-196°$, and this reaction was studied in some detail chemically and spectroscopically.[14] The products of the reaction were $SiF_3SiF_2BF_2$, $SiF_3(SiF_2)_2BF_2$, and traces of higher homologs. No SiF_3BF_2 was formed. These observations gave good support for the theory that the reactions of silicon difluoride are dependent on polymerization to reactive diradicals[5] and that monomeric SiF_2 often appears unreactive. At the time of this study, silicon difluoride was being made from silicon and SiF_4 at $1200°$ and was pumped at 0.2 Torr pressure along a glass tube before it was condensed with BF_3 at $-196°$.

Recently, silicon difluoride has been made in the apparatus of Figure 1. When this is condensed with BF_3, difluoro(trifluorosilyl)borane, SiF_3BF_2, is among the products in addition to the silicon–boron compounds described above.[15] The simplest interpretation of this result is that the reaction of SiF_4 with silicon forms SiF_2 in both its singlet ground electronic state and an excited state. The singlet, which is known to be long-lived, gives $SiF_3SiF_2BF_2$ and $SiF_3(SiF_2)_2BF_2$ as before. However, the excited state is expected to be short-lived and decays unless passed by a collision-free path from the furnace to the cold surface, but on the surface it can insert directly into a B–F bond in BF_3 to give SiF_3BF_2. The yield of SiF_3BF_2 relative to $SiF_3SiF_2BF_2$ increases from a mole ratio of 1:3 when the silicon difluoride is formed at $1200°$ to a mole ratio of 2:1 when the difluoride is formed at $1850°$. From these figures a crude calculation suggests an energy difference between the two forms of SiF_2 of about 70 kJ/mol.

In the absence of a detailed spectroscopic study of the system, there remains a possibility that other short-lived species such as SiF or SiF_3 are present in the furnace off-gases and are responsible for the formation of SiF_3BF_2 by complex reactions on the cold surface. So far, the SiF_2–BF_3 reaction is the only case in which there is a major difference in the chemistry of silicon difluoride prepared in the two types of apparatus.

Other silicon–boron halides are also made from reactions of the high temperature species. When SiF_4 is passed over boron at $1800°$ in the apparatus of Figure 1, the off-gases are thought to contain mainly BF, SiF_2, and BF_3.[16] On condensation at $-196°$, these yield $SiF_2(BF_2)_2$ which may be formed by the reaction sequence

$$SiF_2 + BF \longrightarrow \cdot SiF_2BF\cdot \xrightarrow{BF_3} SiF_2(BF_2)_2$$
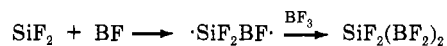
Silicon atoms, made by vaporizing silicon, have some the properties of a molecular carbenoid; their reaction with B_2F_4 at $-196°$ is complex, but $SiF(BF_2)_3$ is formed in small yield.

When $SiCl_2$ is condensed with BCl_3, $SiCl_3BCl_2$[17] is the main product, but further insertion of $SiCl_2$

(12) C. S. Liu, J. L. Margrave, and J. C. Thompson, *Can. J. Chem.*, **50**, 465 (1972).

(13) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *Inorg. Chim. Acta*, 3, 601 (1969).

(14) J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, 5, 729 (1966).

(15) D. L. Smith, R. Kirk, and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 295 (1972).

(16) R. W. Kirk and P. L. Timms, *J. Amer. Chem. Soc.*, 91, 6315 (1969).

(17) P. L. Timms, *Inorg. Chem.*, 7, 387 (1968).

into the Si–Cl bonds to give SiCl₃SiCl₂BCl₂ also occurs unless a huge excess of BCl₃ is present. The reaction certainly does not involve the diradical intermediates postulated for the SiF₂–BF₃ reaction.

The physical properties of the silicon–boron fluorides are strikingly similar to the properties of catenated silicon analogs. This can be seen from the boiling points of the compounds containing two and three skeletal atoms: SiF_3BF_2, bp $-19°$; SiF_3SiF_3, bp $-19°$; $BF_2SiF_2BF_2$, bp $39°$; $SiF_3SiF_2BF_2$, bp $42°$; $SiF_3SiF_2SiF_3$, bp $42°$. The slight change in boiling point when BF_2 is replaced by SiF_3 suggests that there is almost no polarity in the Si–B bond. A chemical application of this "electronic equivalence" of BX_2 and SiX_3 groups is discussed below. The melting points of the silicon–boron fluorides and the perfluorosilanes are less similar because of the different symmetries of the molecules.

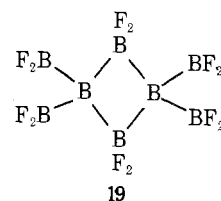## Borane Carbonyl Analogs: the Formation of "Superacids"

When boron monofluoride was first made in an apparatus similar to that of Figure 1 and condensed at $-196°$, a minor product isolated on warmup was found to be $(BF_2)_3BCO$.[18] Traces of oxygen in the boron are thought to have reacted with carbon at high temperatures to form carbon monoxide which was then trapped by reactions on the cold surface. This carbonyl is an analog of borane carbonyl, H_3BCO, with BF_2 groups replacing hydrogen. Subsequently it was found that condensation of BF at $-196°$ with other electron-pair donors of the type classified as soft bases is a general way of making complexes of formula $(BF_2)_3BL$, where L is a molecule of base. The compounds with CO, PF_3, PCl_3, PH_3, AsH_3, and SMe_2 are very stable at room temperature in the absence of air or water.[19] An X-ray structure determination on $(BF_2)_3BPF_3$ shows that there is a tetrahedral arrangement of three BF_2 groups and a PF_3 molecule about the central boron atom.[20]

The way in which complexes of $(BF_2)_3B$ could be formed from a reaction of BF became clearer as the chemistry of the system was studied. Reaction of BF with BF_3 yields B_2F_4, then $(BF_2)_2BF$. The last compound is very unstable and it disproportionates above $-50°$ according to

$$4(BF_2)_2BF \longrightarrow 2B_2F_4 + B_8F_{12}$$

The volatile, unstable compound B_8F_{12} behaves chemically like the dimer of $(BF_2)_3B$. Thus, it reacts quantitatively with CO at $-70°$ to give $(BF_2)_3BCO$.

The spectroscopic and chemical properties of B_8F_{12} can be mostly understood in terms of a diborane-like structure, **19**. The facile reaction with CO or with other soft bases is then seen as a simple cleavage of $B_2(BF_2)_6$. There is no evidence that $B_2(BF_2)_6$ is dissociated to $(BF_2)_3B$ in the gas phase at room temperature, and it is quite likely that the

(18) P. L. Timms, *J. Amer. Chem. Soc.*, **89**, 1629 (1967).

(19) R. W. Kirk, D. L. Smith, W. Airey, and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1392 (1972).

(20) B. G. De Boer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 836 (1969).

19

dimerization energy of $(BF_2)_3B$ is of similar magnitude to the dimerization energy of BH_3.

No displacement of one base by another has yet been observed with the complexes $(BF_2)_3BL$. This is in contrast to the BH_3 complexes which undergo rapid base exchange under suitable conditions. It also seems that $(BF_2)_3B$ will form stable complexes with very weak bases, *e.g.*, arsine, with which BH_3 does not complex. Thus, $(BF_2)_3B$ appears to be a stronger acid than BH_3, and $B_2(BF_2)_6$ must be among the strongest Lewis acids which have been isolated. The usefulness of $B_2(BF_2)_6$ as a superacid is somewhat restricted by its properties. It is a pyrophoric liquid which is unstable above $-10°$ in an inert atmosphere. It is also destroyed by hard bases such as ethers or amines giving boron-rich polymers and the BF_3 adduct of the base.

The driving force for the disproportionation of $(BF_2)_2BF$ to B_2F_4 and $B_2(BF_2)_6$, seems to be the electron deficiency of the central boron atom in $(BF_2)_2BF$. The p_z orbital of this three-coordinate boron atom can interact with the filled p orbitals of only one fluorine atom. However, in B_2F_2 each boron atom is joined to two fluorine atoms and in $B_2(BF_2)_6$ multicenter bonding improves the electron distribution around the two skeletal boron atoms. A similar disproportionation may occur with H_2BF. Attempts to make this molecule yield only HBF_2 and B_2H_6.

From earlier experience of the similarity of compounds containing perhalosilyl and perhaloboryl groups, it seemed possible that silicon–boron analogs of $(BF_2)_2BF$ would also disproportionate and perhaps yield new superacids. Once again, the approach to making such compounds was through high-temperature species. Thus, by cocondensing $SiCl_2$ and B_2Cl_4 at $-196°$, it was hoped to make $SiCl_3BClBCl_2$ with an electron-deficient central boron atom. It has not yet proved possible to isolate $SiCl_3BClBCl_2$, but when the cocondensate of $SiCl_2$ and B_2Cl_4 is warmed to room temperature in the presence of carbon monoxide a good yield of a very stable complex, $(SiCl_3)_2(BCl_2)BCO$, is formed. This must be due to the disproportionation of $SiCl_3BClBCl_2$.

$$4SiCl_3BClBCl_2 \longrightarrow 2B_2Cl_4 + [(SiCl_3)_2(BCl_2)B]_2 ? \xrightarrow{CO} (SiCl_3)_2(BCl_2)BCO$$
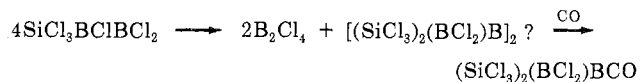
In the absence of CO, only $SiCl_4$, $SiCl_3BCl_2$, and boron-rich solids are formed on warming to room temperature. No equivalent of $B_2(BF_2)_6$ can be isolated. From the stability of its CO complex, it seems that $(SiCl_3)_2(BCl_2)B$ is an acid of strength comparable to $(BF_2)_3B$. Addition of PF_3 in place of CO in the above reaction gives $(SiCl_3)_2(BF_2)BPF_3$, the BF_2 group apparently being formed by halogen exchange between boron and phosphorus.

The condensation of SiF_2 with B_2F_4 at $-196°$ gives a very unstable, volatile compound which may be $SiF_3SiF_2BFBF_2$. In the presence of PF_3, $(Si_2F_5)_2(BF_2)BPF_3$ is formed. Characteristically, the overall yields of products isolated from the SiF_2-B_2F_4 reaction are much lower than from the $SiCl_2$-B_2Cl_4 reaction.

From the systems studied so far, it seems that compounds of type $RBXBX_2$ disproportionate according to

$$4RBXBX_2 \longrightarrow 2B_2X_4 + [R_2(BX_2)B]_2$$
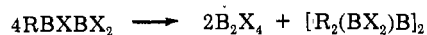
It is probable that compounds of type $RBXR'$ will also disproportionate to $R'BX_2$ and $(R_2R'B)_2$ provided that R and R' are both groups with no greater electron-donating power than a hydrogen atom or perhalosilyl or perhaloboryl groups. To test this idea, a synthesis of $(SiF_3)_2BF$ is being sought, a compound which should, according to theory, yield SiF_3BF_2 and either $B_2(SiF_3)_6$ or base-stabilized complexes of $(SiF_3)_3B$.

Poly(boron fluorides and chlorides)

As described above, condensation of BF in the presence of BF_3 at $-196°$ yields B_2F_4, $(BF_2)_2BF$, and, by disproportionation, $B_2(BF_2)_6$. In addition to these compounds, smaller amounts of more complex boron fluorides are formed which contain 10 to 16 boron atoms.[21] Slow decomposition of $B_2(BF_2)_6$ at $-20°$ also gives a higher fluoride, believed to be $B_{14}F_{18}$. Purification and characterization of these liquid and solid fluorides are difficult because they readily decompose to intractable polymers with liberation of BF_3. However, ^{19}F nmr studies on partly purified materials show resonances only in the region $+30$ to $+45$ ppm relative to CCl_3F, typical of fluorine in BF_2 groups. Resonances due to BF groups are expected at much lower field. It seems that the basic structural unit in these higher fluorides is a boron skeleton with terminal or bridging BF_2 groups as in $B_2(BF_2)_6$, and that $>B-BF-B<$ groups do not occur. The compound $B_{14}F_{18}$ may be $B_5(BF_2)_9$, a formal analog of B_5H_9, although an exact structural relationship between these two molecules is not firmly established.
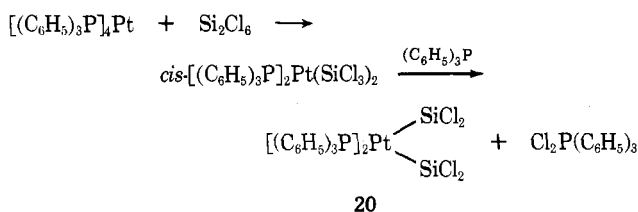
The situation in the polymerization of BCl is quite different. Condensation of BCl in the presence of BCl_3 at $-196°$ gives a good yield of B_4Cl_4, a well-known compound with a tetrahedral boron skeleton. On slow decomposition, B_2Cl_4 forms polyboron chlorides, B_nCl_n, of which B_8Cl_8 and B_9Cl_9 are particularly stable and well characterized.[22] These compounds contain boron cages with chlorine substituents.

The marked difference in structures of poly(boron fluorides and chlorides) must depend on the nature

of the B–F and B–Cl bonds. Both fluorine and chlorine donate electrons to the boron p_z orbital by p-pπ bonding, but as fluorine is more electronegative than chlorine, the electrons in the boron p_z orbital may be less able to delocalize over a boron cage from a B–F group than from a B–Cl group. Thus, boron fluorides adopt boranelike structures with $B-BF_2$ groups, but these do not achieve the high thermal stability of the polyhedral cages of BCl groups.

The Species as Ligands to Transition Metals

Like carbenes,[23] the carbenoid boron and silicon subhalides have some potential as ligands to transition metals. In 1970, Schmid[24] reported the synthesis of a bis(dichlorosilylene) complex of platinum, **20**, formed from tetrakis(triphenylphosphine)platinum(0) and hexachlorodisilane. However, other carbenoid complexes of comparable stability to **20** have not yet been found.

$$[(C_6H_5)_3P]_4Pt + Si_2Cl_6 \longrightarrow$$

$$cis\text{-}[(C_6H_5)_3P]_2Pt(SiCl_3)_2 \xrightarrow{(C_6H_5)_3P}$$

$$[(C_6H_5)_3P]_2Pt\begin{array}{c} \diagup SiCl_2 \\ \diagdown SiCl_2 \end{array} + Cl_2P(C_6H_5)_3$$

20

The approach to carbenoid complexes at Bristol has been *via* low-temperature reactions of metal atoms. It was hoped that cocondensation of a metal vapor, a strong ligand like a phosphine, and a carbenoid or a precursor of carbenoid would give the desired complex. Thus, condensation of iron vapor with a mixture of PF_3 and B_2F_4 gives two products of very similar volatility. One is $Fe(PF_3)_5$;[25] the other is very unstable but appears from its infrared, mass, and ^{19}F nmr spectra to be $Fe(PF_3)_4BF$. So far, the latter compound has not been obtained pure because of decomposition above $-50°$. Similarly unstable products have resulted from reactions of chromium, iron, nickel, or palladium vapors with a mixture of another ligand and B_2F_4, Si_2F_6, or SiF_2 as carbenoid sources. In each case, there is evidence for the formation of a carbenoid complex at low temperatures, but isolation of the pure compounds proves too difficult.

This failure brings out the important point that the synthetic method of low-temperature condensation of species is more powerful than present methods of purification and characterization. However, the quest for stable carbenoid complexes of transition metals seems worthwhile as they may provide useful sources of carbenoids in some reactions where the gaseous carbenoid species cannot be used successfully.

(21) R. W. Kirk, Ph.D. Thesis, University of California, Berkeley, 1969.
(22) G. F. Lanthier, J. Kane, and A. G. Massey, *J. Inorg. Nucl. Chem.*, 33, 1569 (1971).

(23) D. J. Cardin, B. Cetenkaya, and M. J. Lappert, *Chem. Rev.*, 72, 545 (1972).
(24) G. Schmid and H. J. Balk, *Chem. Ber.*, 103, 2240 (1970).
(25) P. L. Timms, *J. Chem. Soc. A*, 2526 (1970).