BORON

ANNUAL SURVEY COVERING THE YEAR 1975

PART II

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Boron, Part II; Annual Survey covering the year 1974 see J. Organometal. Chem., 98 (1975) 369-443.

1 REVIEWS AND SUMMARY ACCOUNTS

About two years ago the GMELIN Institute began to issue new supplements to update the coverage of the element boron within the GMELIN HANDBUCH DER ANORGANISCHEN CHEMIE. All of these new volumes fall within the framework of the "Ergänzungswerk" (New Supplement Series) and the material is arranged by topics rather than by a completely systematic approach to the presentation. Individual volumes may be obtained separately and it is noteworthy that the coverage by topics extends beyond the traditional GMELIN system whereby only compounds of elements with a lower "system number" than the one under consideration are discussed. On the other hand, the extended coverage is somewhat less detailed than to what one is accustomed to and one has to consult the system numbers (given inside the back-cover of each volume) in order to establish whether or not complete discusssion of a given compound or type of compound is called for. However, the referencing of the literature does not seem to have suffered by this new approach. – During the past year a total of five such supplement volumes have been published and others are to follow in rapid order of succession. The first of these volumes (10) contains comprehensive chapters on sigma-bonded boron-sulfur species as well as B-S donor acceptor complexes, boron-selenium and boron-tellurium compounds. A chapter on boron-phosphorus derivatives covers the literature from 1960 through 1973; it is not as detailed as those chapters mentioned first though it seems exhaustive in the literature survey. The lack of detail is readily explained by the fact that phosphorus comes after boron in the GMELIN system and, hence, the data up to 1960 are found in the phosphorus volumes. Further accounting is dedicated to boron-arsenic, boron-antimony and boron-silicon compounds and the two concluding chapters of the volume describe those species containing a boron-to-metal bond. – The second volume (11) presents a detailed accounting of such boron-nitrogen compounds that contain trigonal isolated boron atoms with at least one sigma bond to nitrogen; included are linear as well as cyclic species and the literature is stated to be covered from 1950 through 1973 though many later dated references (including several from 1975) are given. – Vibrational, mass, photoelectron and nuclear magnetic resonance spectroscopic data on these compounds are summarized in a third new supplement volume (12), that also contains a comprehensive chapter on boron-pyrazole derivatives including a section devoted to the coordination chemistry of poly(1-pyrazolyl)borates. - The fourth volume (229) is the second one describing carborane chemistry (the first one dealing with this subject was published in 1974) and deals with the electronic nature of closo-carboranes, the chemistry of metallo-carboranes (including extensive tables summarizing nuclear magnetic resonance data) and with polymeric carboranes. The fifth volume (230) is of no direct interest to the organometallic chemist since it deals with boron oxides, boric acids, borates and peroxoborates only.

The year 1975 also brought about the publication of a number of new books dealing with various aspects of boron chemistry. A broad survey of this area is given by N. N. GREENWOOD (221) and a critical perspective of boron hydride chemistry including carboranes is presented elsewhere (220). A comprehensive and impressive collection of physical and chemical properties of compounds containing boron-carbon bonds has been compiled by T. ONAK (140); the presentation includes three- and four-coordinate species as well as polyborane derivatives.

Organic syntheses via boranes have been summarized by the pioneer in this field, H. C. BROWN (231), who also traces the development of this area in a review article (331). The topics of other reviews range from polymers derived from boranes and carboranes (297) and those containing B-N and B-P units (37) to the industrial applications of boron compounds (116).

Surveys on the preparation of organoboranes for use in organic syntheses have been compiled (9, 31), another summary of this area includes organoborate anions (75), while still another one centers on homolytic reactions of organoboranes (118). Syntheses employing triallylboranes (6, 117), trialkylhydroborates (39), sodium cyanotrihydroborate (40), methane tetraboronic esters of the type $C[B(OR)_2]_4$ and triboronic esters of the type $R'C[B(OR)_2]_3$ (41) have also been reviewed.

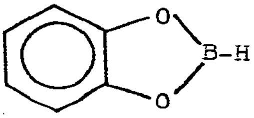
A brief survey on the reduction of organic functional groups with methylsulfide-borane lists 10 references (30), recent advances in the chemistry of boron hydrides have been summarized (119) and gas-phase electron diffraction data of organoboron species have been compiled (122). A review on oxime and hydroxylamine derivatives of metals and metalloids includes various boron compounds (13) and an accounting of condensed-phase isotope effects for $B(OR)_3$ species ($R = CH_3$, C_2H_5, C_4H_9) and BX_3 ($X = F$, Cl) is given elsewhere (8). Finally, boron-containing polymers have been surveyed briefly (199).

2 SOME DATA OF GENERAL INTEREST

Part I of this review deals in detail with the aspects of hydroboration; hence, only a few species containing boron-hydrogen bonds and that are of general interest are mentioned here.

The BH and the BH_3 species have been treated by PNO-CI (pair natural orbital configuration interaction) and CEPA-PNO (complete electron pair approximation with pair natural orbitals) calculations (190) and a theoretical study of the ionization potential and electron affinity of BH has been reported (191).

H. NÖTH (113) has discussed the nature of one of the original hydroboration agents, i.e., a 3:1 molar mixture of $NaBH_4$ with $AlCl_3$ in diglyme; it is suggested that $B_2H_7^-$ is the active agent in that mixture. The reduction of carboxylate esters with $NaBH_4$ was found to be activated by thiols (348) and the hydroboration of 1,5-cyclooctadiene offers a direct synthesis of 9-borabicyclo(3.3.1)nonane (74, 171). The utilization of benzodioxaborole



as hydroboration agent has been elaborated upon (252). Ab initio calculations on hydroxyborane, H_2BOH, show that a partial π-bond is superimposed on the B-O sigma bond in the most stable planar form of this molecule (97); the barrier to rotation about the B-O bond of H_2BOH is 16.4 kcal/mol if partial geometry optimization is carried out in both the planar and orthogonal forms. Remarkably, the B-O bond of the molecule exhibits less multiple bond character than the B-S bond in H_2BSH. The geometry of the linear molecule HBO has been investigated within restricted HARTREE-FOCK LCAO-MO-SCF approximation (121).

The reaction of B_2H_6 with arylthallium derivatives seems to proceed <u>via</u> an arylborane species, $ArBH_2$ (80). A LEWIS orbital model for CH_3BH_2 has been presented (338) and electronic spectra and rotational barriers of the vinylboranes RBH_2, R_2BH and BR_3 have been studied by the INDO method and RBH_2 was also probed by <u>ab initio</u> calculations (70); the calculated spectra show large systematic errors due mainly to the neglect of hyperconjugation.

Tetraalkyldiboranes(6) interact with (1-alkinyl)dialkylboranes to yield 1,1-bis(dialkylboryl)-1-alkenes (240):

$$2\ R_2B\text{-}C{\equiv}C\text{-}R' + (HBR_2)_2 \longrightarrow 2\ (R_2B)_2C{=}CH\text{-}R'$$

The latter species can be converted to yield pentaalkyl-1,5-dicarba-<u>closo</u>-pentaboranes(5). Byproducts of the reactions are polymeric organylboranes which are formed <u>via</u> 1,2-bis(dialkylboryl)alkenes, 1,1,2-tris(dialkylboryl)alkenes or 1,2,2-tris(dialkylboryl)alkenes.

Tris(diethylboryl)methane is obtained from tris(dimethoxyboryl)methane and triethylborane in the presence of ethyldiborane(6) (240); thermal rearrangement of tris(diethylboryl)methane at 150°C in the presence of $Al(C_2H_5)_3$ gives a boraadamantane derivative.

Experimentally determined ^{11}B-^{13}C coupling constants of a variety of organoboron species such as $1\text{-}CH_3B_5H_8$, $B(CH_3)_3$, $OCBH_3$ and $[H_3BCN]^-$ agree well with the calculated data (59); it appears that the finite perturbation theory of spin couplings can account for the major patterns of substituent effects on boron-carbon coupling constants. Multifrequency resonance methods have been used for the indirect measurement of coupling constants in various organylboranes, e.g., trimethylamine-borane, trimethylborane and (oxy)diorganylboranes (15). Similarly, double and triple resonance techniques were used to determine ^{11}B and ^{13}C chemical shift data as well as coupling constants for a series of simple organylboranes of the type $R_{3-n}BX_n$ ($R = CH_3$; $X = N(CH_3)_2$, OCH_3, SCH_3; $n = 0$ to 3) (263); there is no ready explanation yet for the observed linear correlation between $\delta^{13}C$ and $\delta^{11}B$. A correlation coefficient of 0.987 has been suggested for the ^{13}C chemical shifts of carbenium ions with $\delta^{11}B$ of isoelectronic trigonal borane analogs (177).

Finally, some calculations on the energy of formation of B_2H_6 from BH_3 have been performed (139).

3 TRIORGANYLBORANES AND RELATED SPECIES

3.1 PREPARATIVE CHEMISTRY

(Dialkyl)bromoboranes may be converted into unsymmetrical trialkylboranes via sodium hydride reduction in the presence of an alkene (314); the yields of the process, which can be formulated:

$$R_2BBr + NaH \longrightarrow Na[HBrBR_2] \longrightarrow NaBr + HBR_2$$

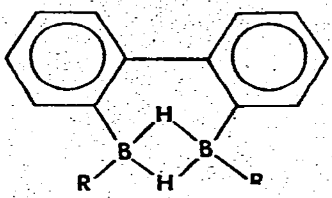
$$HBR_2 + {>}C{=}C{<} \longrightarrow R_2B{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H$$

range from 81 to 99%. (Thexyl)monoalkylboranes are readily converted to monoalkylboranes(175). The hydroboration of olefins with (thexyl)monoalkylboranes provides a convenient route to (thexyl)dialkylboranes, mixed dialkylboranes and mixed trialkylboranes (174). Cis-alkenylboranes are formed in a highly stereoselective manner by the reaction of dialkylboranes with 1-halo-1-alkynes followed by treatment with either $Li[HB(C_2H_5)_3]$ or $K[HB(s\text{-}C_4H_9)_3]$ (152) as is illustrated in the following sequence:

$$RC{\equiv}CX + HBR'_2 \longrightarrow RHC{=}CX{-}BR'_2 \longrightarrow RHC{=}CH{-}BR'_2$$

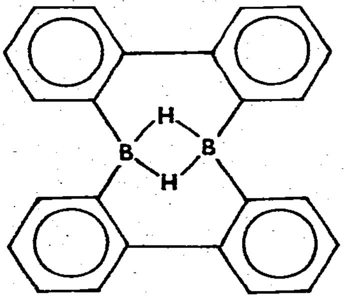
Protonation of lithium (trialkyl)ethynylborates with concentrated hydrochloric acid at low temperatures provides the borane with the opposite stereochemistry from that realized in the hydroboration of the corresponding acetylene (309); lithium (trialkyl)-alkenylborates react in a similar manner.

(2-Biphenylyl)diethylborane reacts with ethyldiborane(6) to give an approximately 80% yield of 1,2-diethyl-1,2-(2,2'-biphenylene)diborane(6):

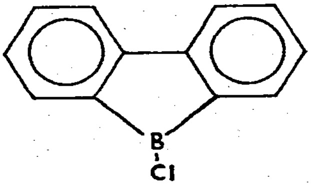


$R = C_2H_5$

The ethyl groups can be replaced by H via reaction with additional B_2H_6 whereas the reaction with $(C_2H_5)_2O \cdot BF_3$ yields



and with BCl_3 the species



is obtained (110). All of the proposed structures were verified by nuclear magnetic resonance data and the chemical behavior of the various compounds.

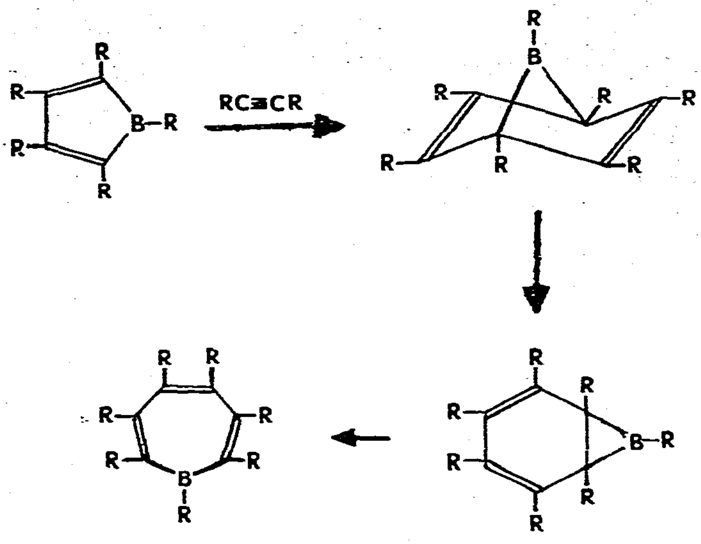
Triorganylboranes react with N,N-diethylaminopropyne according to the following sequence (112):

$$(C_2H_5)_2N\text{-}C{\equiv}C\text{-}CH_3 + BR_3 \longrightarrow (C_2H_5)_2N\text{-}C(BR_2){=}CR\text{-}CH_3$$

Methacrylonitrile interacts with triallylborane to yield species of the type $CH_2=CCH_3-CR=N-BR_2$ whereas with BCl_3 and adduct, $CH_2=CCH_3-C\equiv N\cdot BCl_3$ is formed (112). Similarly, benzylidenemethylamine and triallylborane form the compound $C_6H_5-CHR-N(BR_2)-CH_3$ whereas with BCl_3 an adduct is obtained. These data illustrate the greater reactivity of the B-C bond as compared to the B-Cl linkage toward C-C multiple bonds. The allylboronation of alkoxyacetylenes with (2-methylallyl)boranes proceeds <u>via</u> <u>cis</u>-addition of the 2-methylallyl and borane fragments to the triple bond to yield vinylboranes (210). On the basis of proton magnetic resonance data, tris(2-methylallyl)borane reacts with alkoxyacetylenes in three successive stages (212).

On the basis of proton magnetic resonance data a permanent allyl rearrangement occurs on heating of tris(3-methyl-2-butenenyl)borane or of 1-allyl-5-(3-butenyl)-2-(chloromethylene)-3,3-dimethylborolane (213). The influence of permanent allyl rearrangement on the NMR parameters of allylborane derivatives has been studied by double heteronuclear magnetic resonance spectroscopy (16). The data indicate the preservation of the allyl-boron and the (2-methylallyl)-boron sigma bond under the conditions of rapid permanent allyl rearrangement. The B-C bond of (2-methylallyl)boranes undergoes protolytic cleavage with considerably greater ease than in unsubstituted allylboranes (210).

The first non-condensed borepin has been prepared by a sigmatropic rearrangement and subsequent ring opening as is depicted below (369):



R = C_6H_5

The pyrolysis of trimethylborane to yield the adamantane-type species $(CH_3B)_6(CH)_4$ has now been described in detail (84). The boron-carbon cage is formed in approximately 25% yield. Though the compound is stable toward water, degradation occurs with various reagents such as oxygen, propanoic acid or ammonia; the species is only a weak acceptor toward the donors trimethylamine or trimethylphosphine and, at room temperature, no stable complex can be isolated.

3.2 PHYSICOCHEMICAL STUDIES

Some geometry-optimized _ab initio_ calculations have been reported for trimethylborane and trivinylborane (206) and the latter molecule was also the object of a gas-phase electron diffraction study (146).

The carbon-13 nuclear magnetic resonance shifts of the terminal vinyl carbons in trivinylborane, various (vinyl)haloboranes and several LEWIS acid-base adducts of the vinylboranes have been determined (329). The boron-11 chemical shifts of these species are discussed in the same paper (329) and a boron-11 nuclear magnetic resonance study of the scrambling between tri-_n_-propylborane and its oxidation products is described elsewhere (339). For a detailed nuclear magnetic resonance study of the nature of the B-C bond in vinylboranes see also (310), for carbon-13 nuclear magnetic resonance studies of alkenyl- and alkynylboranes see (160, 325).

The He(I) photoelectron spectra of trimethylborane and (methyl)haloboranes have been analyzed in (318) and a detailed analysis of the mass spectrum of tri-_n_-butylborane has been reported elsewhere (157). The ion cyclotron resonance spectrum of the compound shows the formation of only low molecular weight ions with m/e values smaller than 59 (71). This observation is interpreted in terms of a lesser stability of boron-containing cations relative to pure hydrocarbon species.

Some speculations on the electrophilic decomposition of organometallic species include comments on tribenzylborane (251). The stereoisomerization of trimesitylborane has been examined by empurical force field calculations (68). The calculated energies for the idealized transition state point to a two-ring flip mechanism as the pathway of lowest energy.

For some comments on the structure of diborane(6) see (154).

3.3 REACTIONS

The utilization of organylboranes in organic syntheses is now such a common occurrence that only a brief mentioning of such reactions can be made here. For example, the reaction of alkyl or aryl crotyl ethers with tetrabutyldiborane(6) (287) and tributylborane (286) has been studied and reactions of trialkylboranes with aromatic amine N-oxides (352), aromatic nitro compounds (353) and α-bromoketones have been investigated (288).

Trialkylboranes are readily oxidized in acetonitrile solution containing tetraalkylammonium halides as supporting electrolyte by transfer of an alkyl group from boron to the acetonitrile (295). The nature of the electrochemical reduction of triarylboranes is largely in accord with chemical reduction studies (305).

Trialkylboranes react with $FeCl_2$ and thiocyanate in aqueous THF to yield alkyl chlorides and cyanates in good yield (32). The vic. diorganylborane obtained by hydroboration of diphenylacetylene reacts with CrO_3 to form trans-stilbene via a seven-membered transition state (203). The reaction of organylboranes and lithium diallyl cuprates with 1-acyl-2-vinyl cyclopropanes is a convenient new route to γ,δ-unsaturated ketones (342) and bicyclic organylboranes react with $AgNO_3$ in alkaline solution to give a mixture of a monocyclic ketone and a cis-monoolefinic ketone (105), and with an excess of chromic acid only monocyclic ketones are obtained (370). For the reaction of organylboranes with lithium aldimines see (327), with lithium chloroacetylide see (345), and for the action of triorganylboranes and acyl halides on phenylmagnesium bromide see (350). The oxidation of organylboranes with trimethylamine N-oxide dihydrate is a mild and convenient route to the corresponding alcohols (193).

The displacement of alkyl groups of mixed trialkylboranes by butylthiyl radicals (derived from butanethiol) follows the sequence primary $<$ secondary $<$ tertiary alkyl substituent (104). Ligand exchange reactions of triallylboranes with (organylthio)boranes, (organyloxy)boranes and haloboranes have been studied by nuclear magnetic resonance spectroscopy and the resultant data substantiate the formation of a six-center transition state and the occurrence of an intermolecular permanent allyl rearrangement (233, 234). The major pathway for the β-elimination of a (silyloxy)organylborane moiety from a β-silyloxylated organylborane is a <u>cis</u> elimination that occurs even in the presence of $(C_2H_5)_2O \cdot BF_3$ (333).

Cyclic and acyclic ketones react with triethylborane in the presence of diethylboryl pivalate to form (vinyloxy)diethylboranes by elimination of ethane (241):

$$B(C_2H_5)_3 + R\text{-}CO\text{-}CHR'R'' \longrightarrow R\text{-}C\left[OB(C_2H_5)_2\right]{=}CR'R''$$

The reaction may be viewed as enolysis of triethylborane and the action of the diethylboryl pivalate is strictly catalytic in nature. On the absence of the catalyst higher reaction temperatures are required and provide for various side reactions.

A reinvestigation of the previously reported preparation of (acyl)dialkylboranes (= borylketones) has shown the earlier data to be erroneous (313).

The diethylboronation of alcohols, phenols or dihydroxy derivatives with triethylborane proceeds readily in the presence of diethylboryl pivalate (109). Trialkylboranes interact with $LiBH_4$ in ethereal solvents in a 1:1 molar ratio (214). Based on boron-11 nuclear magnetic resonance data, lithium trialkyltetrahydrodiborates are formed which are in equilibrium with the original reactants.

Tris(o-alkoxyphenyl)boranes form 1:1 molar complexes with 4-aminopyridine (90). The resultant compounds exhibit two strong infrared absorptions in the 3300 to 3500 cm^{-1} frequency region corresponding to N-H stretching modes of a free amino group. Hence, the annular nitrogen of the pyridine ring appears to coordinate to the boron atom.

Ate complexes of 9-borabicyclo(3.3.1)nonane are a new type of reducing agents for the selective reduction of tertiary alkyl, benzyl and allyl halides to hydrocarbons (176) but an anomalous course for the hydrogen peroxide oxidation has been observed for ate complexes of the cited organylborane (328). The latter species is a highly selective reducing agent for the conversion of α,β-unsatutated aldehydes or ketones to the corresponding alcohols in the presence of other functional groups (148).

Interaction of trimethylborane with adiponitrile causes polymerization of the latter (351). The copolymerization of 4-propenyl pyrocatechol derivatives with vinyl monomers is readily effected by tributylborane (111). Other applications in the polymer field include the polymerization of methyl methacrylate by tri-n-butylborane in the presence of amino acid esters (227), the grafting of vinyl polymers onto chlorophyll and related compounds with the aid of tributylborane (356) and the copolymerization of vinylhydroquinone and vinyl polymers by tri-*n*-butylborane (107).

4 HALOBORANES

Fluorination of $C_2B_5H_7$ with elemental fluorine yields $H_2C(BF_2)_2$ among other products (216). The compound is a volatile and explosive liquid that decomposes at room temperature.

The reaction of (methylthio)dialkylboranes, CH_3SBR_2, with elmental bromine has been advocated as a new method for the preparation of (dialkyl)bromoboranes (180) and redistribution reactions in (phenyl)dihaloborane/trihaloborane systems have been studied.

Geometry-optimized *ab initio* molecular orbital studies have been reported for the series R_nBF_{3-n} ($R = CH_3$, C_2H_3) (206) and the microwave spectrum of (phenyl)difluoroborane, $C_6H_5BF_2$, has been recorded; the resultant data were used to calculate a barrier to internal rotation about the B-C bond of the molecule of 13.3 kJ/mole (86). A value of 1.551 Å was calculated for the B-C distance of (phenyl)difluoroborane and the B-F distance was calculated to be 1.330 Å; the bond angle F-B-F was found to be 116.0°.

A laser-specific product formation has been observed in the exchange reaction of HBr with $B(CH_3)_3$, $(CH_3)_2BBr$ and CH_3BBr_2 whereby CH_3 is displaced by Br (259).

Single-crystal X-ray diffraction studies in $(H_2BCN)_6$ substantiate a cyclic structure for the species (319); the eighteen-membered ring formed of B-C-N-B-C-N moieties exists in chair conformation with average bond lengths of B-C and N-B = 1.56 Å, C-N = 1.14 Å and B-H = 1.14 Å. The C and N atoms could not be differentiated.

Some work in simple haloboranes includes the preparation of dichloro- and dibromoisocyanatoborane (165) and a report that the yield in the preparation of tetrachlorodiborane(4), B_2Cl_4, by passing BCl_3 through an electrical discharge between two mercury pools can be increased by increasing the BCl_3 pressure (20). Pentachloroborosilane, $Cl_3Si\text{-}BCl_2$, is synthesized by passing a mixture of BCl_3 and $SiCl_4$ through a d.c. pulse discharge (19); the colorless liquid is stable at room temperature but decomposes above 70°C. Cyclopropane reacts with $Cl_3Si\text{-}BCl_2$ according to the equation

$$Cl_3Si\text{-}BCl_2 + C_3H_6 \longrightarrow Cl_3Si\text{-}(CH_2)_3\text{-}BCl_2.$$

An interesting laser-induced enrichment of boron isotopes has been observed on irradiation of BCl_3/H_2S mixtures (125). The experiments were performed in a small static system and chemical procedures for recovering selectively enriched BCl_3 are described.

The electronic structure of B_2F_4 has been calculated by <u>ab initio</u> computations. The rotational barrier about the boron-boron bond of the molecule slightly favors the D_{2d} conformer with a B-B force constant of 3.0 mdyn/Å (24); for some vibrational spectroscopic studies on the solid molecule see (106).

The RAMAN and infrared spectra of solid $B_2Cl_4 \cdot 2PH_3$ and $B_2Cl_4 \cdot 2PD_3$ have been interpreted on the basis of a <u>trans</u> molecular conformation (C_{2h} symmetry) (62). On the basis of the suggested assignments of torsional modes the barrier of rotation about the B-P bond was calculated to be 2.92 kcal/mol ; the B-P valence stretching mode was assigned at 651/713 cm^{-1} (IR, RAMAN) for $B_2Cl_4 \cdot 2PH_3$ and at 620/658 cm^{-1} for $B_2Cl_4 \cdot 2PD_3$.

The reaction

$$3\ PF_5 + BCl_3 \longrightarrow 3\ PF_4Cl + BF_3$$

proceeds slowly in the gas phase at ambient temperatures (219) and comparative proton affinity studies indicate that HBF_2 and BF_3 are protonated by H_3^+ but not by CH_5^+ (57). The reaction of N_2O_5 with BF_3 yields nitryl hexafluoro-μ-oxodiborate(2-) (166).

Halogen redistribution reactions of trihaloborane adducts of $P(CH_3)_3$, $OP(CH_3)_3$ and $SP(CH_3)_3$ have been studied by nuclear magnetic resonance techniques (159) and the enthalpies of complexation of BF_3 with various ketones have been measured (167). The valence force field for the acetone adduct of BF_3 has been calculated based on experimental data that include those obtained on six different isotopically labelled species (95). Also, a direct carbon-13 nuclear magnetic resonance study of BF_3 and BCl_4 complexes with ethers has been reported (322), and BCl_3 was found to catalyze the isomerization of cyclopropane to yield propene at 360 to 470°C (289). Methylcopper induces rapid coupling of (dialkenyl)chloroboranes at 0°C to yield 1,3-dienes (308).

Fluorine-19 nuclear magnetic resonance data recorded at -155°C confirm the existence of $B_2F_7^-$ as a fluorine-bridged species (126). A nuclear magnetic resonance study on $B(BF_2)_3$ in the $N(CH_3)_3/F_3P{\cdot}B(BF_2)_3$ system indicates adduct formation of the BF_2 moieties with trimethylamine (316). B_8F_{12} is very reactive towards $N(CH_3)_3$ in dichloromethane and, at -90°C, $(CH_3)_3N{\cdot}B(BF_2)_3$ was tentatively identified (316).

Mixtures of BCl_3 and H_2 have been irradiated by a pulsed CO_2 laserto yield $HBCl_2$ and HCl as the only products; approximately 50% conversion of the reagents was observed (296).

5 BORON-OXYGEN COMPOUNDS

Several (aryl)hydroxyboranes have been prepared by conventional syntheses involving the interaction of organolithium species with tris(organyloxy)boranes (236). Ionization constants of these acids have been measured and the data suggest an increase in the degree of dissociation of the acid with the presence of a dipolar structure. The effect of the pH on the stability of (phenyl)dihydroxyborane in aqueous solution has been studied (292). Also, (2-furanyl)dihydroxyborane and (3-furanyl)dihydroxyborane were found to resemble in their chemical behavior the corresponding carboxylic acids (17); the acidity of the $B(OH)_2$ group is affected by essentially the same factor as that of a furan-bonded COOH group. For the synthesis of (μ-aminophenyl)hydroxyborane see (135), for a study of complex formation of (phenyl)dihydroxyborane with oxalic acid see (306).

A ready method for the preparation of (organyloxy)diethylboranes, $ROB(C_2H_5)_2$, is provided by the reaction of triethylborane with alcohols or phenols in the presence of (diethylboryl)pivalate as a catalyst (109). Similarly, 2-ethyl-1,3,2-dioxaboracycloalkanes have been prepared from alkane diols and activated triethylborane (242) and various carbohydrate derivatives containing 2-phenyl-1,3,2-dioxaboracycloalkane moieties have also been described (143).

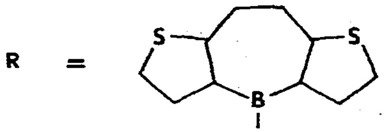
2-Phenyl-1,3,2-dioxaboracycloalkanes undergo rearrangements under electron impact whereby hydrocarbon ions are formed, specifically the tropylium and the methyltropylium ion (330). For complete mass spectra of various 1,3,2-dioxaboracycloalkanes and a detailed discussion of the fragmentation patterns see (88), for a nuclear magnetic resonance study on conformational isomers of 1,3,2-dioxaboracyclohexanes see (202).

Various 1,3,2-benzoxathiaboroles have been prepared by the reaction of 2-hydroxythiophenol with diborane(6), trichloroborane or (phenyl)dichloroborane, respectively (18). The B-H species reacts with cyclohexene to yield the B-C_6H_{11} derivative (18) and reaction of the B-H compound or similar cyclic species with $(C_6H_5)_3$PRhX (X = Cl, Br) gives a species with a sigma metal-to-boron bond that is, however, readily cleaved by reaction with triethylsilane (294).

(Diorganyloxy)organylboranes react readily with dichloromethyl methyl ether to give tertiary α-chloro derivatives; the latter undergo a remarkable rearrangement with hydride or methide shift and elimination during solvolysis in aqueous solvents to produce the corresponding olefins in high yield (100). The reaction of (alkenyl)hydroxyboranes with bromine in the presence of sodium methoxide and methanol provides a simple one-stage synthesis of α-bromoacetals (196). For the stereochemistry of the reaction of (organyloxy)propargyl- and allenylboranes with aldehydes see (153).

The eight-membered heterocycles obtained by condensation of (phenyl)dihydroxyborane with HO-$(CH_2)_2$-X-$(CH_2)_2$-OH (X = O, S) shows no transannular coordination of the X atom to boron; this conclusion is based on the chemical behavior of the compounds and the observation of a boron-11 chemical shift near -30 ppm (226). The crystal structure of the corresponding species with X = NH has been studied by X-ray diffraction (134) and a B-N bond distance of 1.666 Å was found. The crystal structure of the compound consists of discrete molecules with a O-N distance of 2.914 Å to form continuous spirals along the b axis.

The crystal structure of the diboryl oxide R_2O with



has also been studied by X-ray diffraction (25). Each half of the molecule is approximately planar, the molecule is propeller-shaped and the B-C distances are 1.533 Å.

The syntheses of several 2-phenyl-1,3,2-oxazaborolans have been described (185) and some properties of these compounds including the infrared spectra and some mass spectral features are discussed.

(Dimethyl)bromoborane reacts with organic oximes to yield (alkylideniminoxy)dimethylboranes, $(CH_3)_2B\text{-}O\text{-}N{=}CRR'$ (283). At room temperature only the species with $R = R' = C_6H_5$ is monomeric whereas the others form cyclic dimers _via_ coordination of boron to nitrogen of a second molecule.

(Diethyl)chloroborane interacts with sodium or potassium salts of primary nitroalkanes, α-phenylnitroethane and nitroparaffins that contain ester or amide functions α to the nitro group to yield esters of the corresponding nitronic acid (239). Primary nitroalkanes react as follows:

$$2\ \mathrm{Na\ CRR'(NO_2)} + 2\ \mathrm{(C_2H_5)_2BCl} \longrightarrow \mathrm{[RR'C{=}N(O){-}O{-}B(C_2H_5)_2]_2} + 2\ \mathrm{NaCl}$$

$R = CH_3$, *n*-C_3H_7 $\quad$ $R = C_6H_5$

$R' = H$ $\quad$ $R' = CH_3$

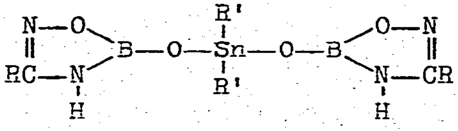
Boron-11 chemical shift values of -12 to -13 ppm suggest the presence of tetracoordinated boron in these species and the dimeric structure is further supported by the proton nuclear magnetic resonance data. - The esters decompose rapidly at *ca.* 20°C to yield a species of the composition $(C_2H_5)_2B{-}O{-}B(C_2H_5){-}O{-}N{=}CRR'$ in which the terminal boron is coordinated to the nitrogen to form a cyclic species. Identical products can be obtained from the reaction of bis(diethylboryl) oxide with $(C_2H_5)_2B{-}O{-}N{=}CHR$. The O-diethylboryl esters of the corresponding nitronic acids are formed in simlar fashion from the sodium salts of amides of α-nitro acids.

(Acyloxy)(3-aminopropyl)butylboranes form internal complexes of the amine-borane type (235); in addition, intermolecular hydrogen bonding as well as intramolecular hydrogen bonding seems to occur in these species as is indicated by infrared and nuclear magnetic resonance data

Butyllithium reacts with $HC[B(-OCH_2CH_2CH_2)-)]_2$ in tetrahydrofuran with precipitation of the corresponding lithium methide (151). The anion is sufficiently basic in order to abstract a proton from dimethyl sulfoxide and triphenyltin and bromo derivatives were obtained from the lithium salt. For the reaction with carbonyl compounds see (307).

The synthesis and polymerization of (vinyloxy)phenylboranes has been described (115). Polystyrene beads can be coated with poly(p-vinylphenyl-dihydroxyborane) and the resulting material reversibly sorbs vicinal diols in a highly pH dependent process (87). This feature can be used for the column chromatographic separation of diol mixtures. For the use of (organyloxy)butylboranes in the gas-liquid chromatography of some carbohydrates see (228), and for the O-dialkylborylation of polyols and saccharides see (243).

Condensation of dibutyltin oxide with boric acid and amidoximes (290) leads to species of the type ($R' = C_4H_9$)



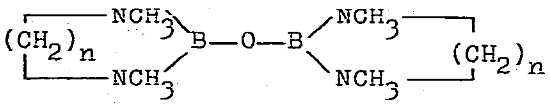
and bis(boryloxy)dibutylgermanes and related compounds have been described elsewhere (169).

Semi-empirical molecular orbital calculations on boroxines, $(-BR-O-)_3$ (R = H, OH, F, Cl), indicate a sigma electron drift within the boroxine ring towards oxygen ; the π-electron drift is directed towards boron (149).

The LEWIS acidity of boron in tris(aryloxy)boranes, $B(OC_6H_4X)_3$, varies with the electronic nature of X (54); thermochemical measurements show a maximum variation of about 60 kJ/mol between the 4-CN and the 4-OCH_3 derivatives. For the kinetics of the hydrolysis of tris(alkoxy)boranes see (355).

The photoelectron spectrum of $B(O-CH_2-CH_2)_3N$ is interpreted in terms of a close approachment of nitrogen and boron resulting in intramolecular bonding interaction (85).

Trioxazaboratricycloalkanes (362) and related species (363) have been prepared. The infrared spectra of 2-iminoxy-1,3,2-dioxaborinane exhibit a weak C=N stretching mode in the 1630 to ≈ 1660 cm^{-1} frequency region (35); the N-O valence vibration of the compounds is observed near 900 to 940 cm^{-1} and B-O ring modes are assigned near 1414 and 1110 cm^{-1}, respectively. The B-O stretch of diboryl oxides of the type



with n = 2 or 3 is observed near 1350 cm^{-1} (33).

The interaction of boric acid with ethriol systems has been studied (360) and infrared spectra of borate species and their thermal dehydration products have been recorded (361). Various metriolborates have been synthesized by the reaction of metriol with boric acid and alkali or alkaline earth metal hydroxides (209); the data indicate the exclusive formation of the anion $[CH_3C(CH_2O)_3BOH]^-$. For the formation of ethylene glycol-borates in aqueous medium see (127) and for the preparation and anodic peak potentials of salts of coordination compounds derived from boric acids and polyhydridic phenols see (192). Fourier transform nuclear magnetic resonance studies have been described for the $[B(OH)_4]^-$ ion (264), and polarimetric data indicate that D-glucose interacts with $B_4O_7^{2-}$ in a 1:1 molar ratio only (48).

6 COMPOUNDS CONTAINING B-S AND B-Se BONDS

Tris(methylthio)borane, $B(SCH_3)_3$, is readily obtained from $Li[Al(SCH_3)_4]$ (prepared <u>in situ</u> by the reaction of $LiAlH_4$ with $(CH_3)_2S$) and $(C_2H_5)_2O \cdot BF_3$ (266), whereas $B(SCF_3)_3$ is prepared by the reaction of $Hg(SCF_3)_2$ with BBr_3 (22). However, $B(SCF_3)_3$ is unstable at room temperature and decomposes with the formation of BF_3 and SCF_2. $B(SCF_3)_3$ is a stronger LEWIS acid than $B(SCH_3)_3$

as is evidenced by the ready formation of $(CH_3)_3N{\cdot}B(SCF_3)_3$. This latter adduct decomposes slowly to yield $(CH_3)_3N{\cdot}BF_3$ and an unidentified solid byproduct (22).

(Hydrothio)diorganylboranes, $HSBR_2$, have been prepared from the corresponding haloboranes and H_2S (198). At elevated temperatures the reaction

$$3\ HSBR_2 \longrightarrow (\text{-BR-S-})_3 + 3\ RH$$

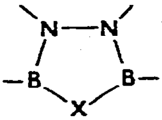
occurs; in addition, H_2S is eliminated to yield diborylsulfanes, $(R_2B)_2S$. The latter species rearrange with the formation of BR_3 and $(\text{-BR-S-})_3$.

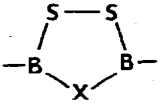
(Organylthio)boranes of the type $R'SBR_2$ react with ethoxyacetylene <u>via</u> thioboronation of the carbon-carbon triple bond (208):

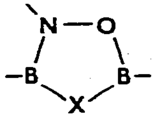
$$R_2BSR' + HC{\equiv}C\text{-}OC_2H_5 \longrightarrow R_2B\text{-}CH{=}C(SR')\text{-}OC_2H_5$$

Tris(organylthio)boranes, $B(SR)_3$, react in analogous fashion and, in the presence of excess ethoxyacetylene, $B(CH{=}C(SR')\text{-}OC_2H_5)_3$ is obtained (208). However, this reaction may be stopped at the intermediate stage of $(RS)_2B\text{-}CH{=}C(SR)\text{-}OC_2H_5$ and the boron-bonded SR groups can be replaced by OR' on treatment with alcohols and by NR'_2 on treatment with amines (144). For the redistribution of methilthio and dimethylamino ligands at trigonal boron see (164).

The fundamental ν_1 of linear H-B=S is observed near 2750 cm^{-1} (96) and in the spectrum of μ-HS-B_2H_5 the ring puckering mode is assigned at 306.5 cm^{-1} (94). *Ab initio* calculations have shown that the B-S bond of H_2BSH exhibits more multiple bond character than the B-O bond in H_2BOH (97). In this conjunction it is of interest to note that the He(I) photoelectron spectra of 30 derivatives of five-membered isoelectronic heterocycles of the following skeletal arrangements (all of which contain six π-electrons)

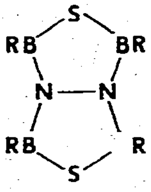

X = S, NR


X = O, S, NR


X = S, NR

suggest cyclic π-conjugation within all of these ring systems (262); however, that π-conjugation decreases with successive replacement of NR groups by S.

The ring system

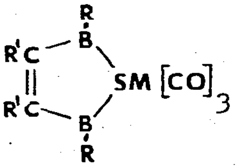


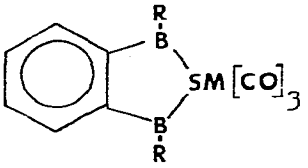
with R = CH_3 contains two CBNBC plains that are tilted by 18° (260). The average B-N distance in the molecule is 1.42 Å and the B-C distance is abnormally short with only 1.445 to1.455 Å.

The N-N distance of 1.45 Å is analogous to that of hydrazine and the B-S distance is about 1.80 Å. A B-S distance of 1.805 Å was found in gaseous bis(dimethylboryl)disulfane, $(CH_3)_2B{-}S{-}S{-}B(CH_3)_2$, by electron diffraction (237). The molecular arrangement about the B-S bonds of the molecule were found to be planar; the S-S distance is rather long with 2.078 Å and the torsional angle about the S-S bond is about 120°.

For sulfatoboric acids and anhydrides see (163). Proton nuclear magnetic resonance studies on the adducts $R_2S{\cdot}BX_3$, $R_2S{\cdot}BRX_2$, $R_2S{\cdot}BR_2X$ and the corresponding R_2Se derivatives ($R = CH_3$; $X = Br, I$) demonstrate a displacement of the resonance signals to higher field with increasing methylation of the boron (49). This observation is interpreted to indicate an accompanying decrease in the B-S and B-Se bond order, respectively.

Infrared, proton magnetic resonance and X-ray data on the two complexes

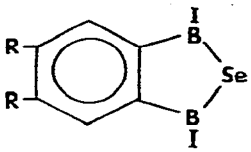




($R = CH_3$; $R' = C_2H_5$; $M = Fe$) indicate that both of the boron ligands act as 2-electron donors (132).

Tris(methylseleno)borane, $B(SeCH_3)_3$, is readily obtained on reaction of Li $[Al(SeCH_3)_4]$ with $(C_2H_5)_2O \cdot BF_3$ (266) and the formation of (hydroseleno)diorganylboranes, $HSeBR_2$, by interaction of the corresponding (halo)diorganylboranes with H_2Se has been described (198). The molecular structure of gaseous $B(SeCH_3)_3$ has been studied by electron diffraction techniques (130); the B-Se bond length of 1.936 Å appears to dispute a double bond character for the B-Se bond. For the vibrational spectra of (hydroseleno)haloboranes, $(HSe)_nBX_{3-n}$, see (43).

The reaction of (3,4-xylenyl)diiodoborane with polymeric $(-BI-Se-)_n$ at 180°C (267) gives a good yield of a yellow solid, melting from 138 to 140°C, to which the following structure has been assigned (R = CH_3):



Reaction of X_2, HX or BX_3 (X = Br, I) with dimethylsulfane-borane, $(CH_3)_2S \cdot BH_3$, leads to boron halogenation and $(CH_3)_2S \cdot BH_2X$ or $(CH_3)_2S \cdot BHX_2$ are formed (123). No acid exchange was observed and proton magnetic resonance data on the series $(CH_3)_2S \cdot BH_nX_{3-n}$ suggest an increase in the donor-acceptor bond strength with decreasing n.

7 BORON-NITROGEN CHEMISTRY

7.1 AMINOBORANES

Pyrolysis of $H_3N{\cdot}BF_3$ at 185°C yields $H_2N{-}BF_2$ as the primary volatile product (270); the appearance potential of the species is 12.4 eV. (Dialkylamino)hydrophenoxyboranes, $R_2N{-}BH{-}OC_6H_5$, are readily prepared by the following reaction sequence (271):

$$4\ BF_3 + 3\ NaBH_4 \longrightarrow 3\ NaBF_4 + 2\ B_2H_6$$

$$B_2H_6 + 2\ HNR_2 \longrightarrow 2\ R_2HN{\cdot}BH_3$$

$$R_2HN{\cdot}BH_3 + C_6H_5OH \longrightarrow R_2N{-}BH{-}OC_6H_5.$$

Molecular association and proton magnetic resonance studies in benzene solution are consistent with a planar, monomeric configuration of these species with considerable π-interaction between boron and nitrogen. A novel synthesis of $B[N(CH_3)_2]_3$ involves the reaction of $LiAlH_4$ with dimethylamine to generate $LiAlR_4$ ($R = (CH_3)_2N$) in situ which is subsequently reacted with $(C_2H_5)_2O{\cdot}BF_3$ (266). Also, the reaction of $LiN(CH_3)_2$ with $HB[N(CH_3)_2]_2$, $[(CH_3)_2N{-}BH_2]_2$, $LiNR_2{\cdot}BH_3$ and similar species leads, in general, to the ready formation of tris(dimethylamino)-borane (61).

(Dialkylamino)dibromoboranes, $R_2N{-}BBr_2$ ($R = C_2H_5$, n-C_3H_7, n-C_4H_9, C_5H_{11}), have been prepared by conventional syntheses, i.e., dehydrohalogenation of the corresponding dialkylamine-tribromoborane with the aid of a tertiary amine. (1-Imidazolyl)-

boranes have been prepared via a silazane cleavage reaction (34) und dimeric bis(3,5-dimethyl-1-pyrazolyl)dihydroborane is readily obtained by the reaction of triethylamine-borane with 3,5-dimethylpyrazole (28). X-Ray diffraction data on bis(3,5-dimethyl-1-pyrazolyl)dihydroborane indicate that each molecule of the dimer lies in a center of of symmetry and is slightly chair-shaped with a dihedral andle of 12.7° between the N-B-N plane and the central plane. The Cl_2BNC_2 skeleton of (diphenylamino)dichloroborane is virtually planar and the B-N distance is short with 1.380 Å (223); however, the two phenyl rings of the molecule are considerably distorted out of the cited plane.

The fluorescence spectra of aminoborane analogs of stilbenes and styrenes are generally structureless, are significantly red-shifted in polar solvents and are in-plane polarized (197), and a LCAO-MO-CNDO/2 analysis of tris(dimethylamino)borane (278) presents no particular surprises.

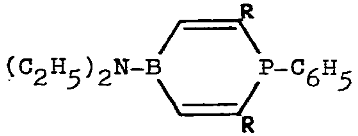
Lithium amide and diborane(6) interact in ether according to the equation (92):

$$LiNH_2 + B_2H_6 \longrightarrow 1/n\ (H_2N\text{-}BH_2)_n + LiBH_4.$$

The resultant amorphous species has a degree of association, n, averaging from 3 to 4.5. Protolysis with water or methanol indicates the presence of two types of boron-bonded hydrogen, one of which is readily attacked; this observation is interpreted to indicate the existence of chain-like rather than cyclic species although the given infrared data are inconclusive in this respect. Non-empirical LCGO-MO-SCF calculation of the boat and chair conformers of cyclic $(H_2N\text{-}BH_2)_3$ indicate that, in the gas phase, the molecule can indeed exist in the boat form with electrostatic attraction being a contributing factor (78).

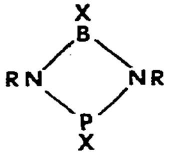
Radical-initiated hydrophosphination of (diethylamino)-dipropynylborane with phenylphosphine leads to a novel heterocyclic system as is shown in the following equation (256):

$$(C_2H_5)_2N\text{-}B(C{\equiv}C\text{-}CH_3)_2 + H_2PC_6H_5 \longrightarrow$$



$(R = CH_3)$

Another new heterocyclic system, the 1,3,2,4-diazaphosphaboretidine ring $(R = Si(CH_3)_3;\ X = Cl,\ Br)$



has been obtained from the reaction of RNH-P=NR with BX_3 (4).

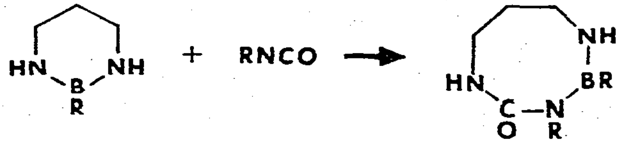
A new and general method for the preparation of iminoboranes containing the skeletal unit C=N-B involves the interaction of imines with (alkylthio)dialkylboranes according to the equation (170):

$$C_6H_5\text{-}CR{=}NH + R'SBR''_2 \longrightarrow R'SH + C_6H_5\text{-}CR{=}N\text{-}BR''_2.$$

Though no experimental details are given, physical data on several compounds obtained by this procedure are presented.

7.2 BORON-NITROGEN-CARBON HETEROCYCLES

Addition of the B-N bonds of $C_6H_5B(\text{-}NCH_3\text{-}CH_2\text{-})_2$ across the multiple bond of small unsaturated molecules such as CO_2 and SO_2 has been reported but no defined products were isolated (52). However, the reaction of the corresponding 2-phenyl-1,3,2-diazaboracyclohexane with phenyl isocyanate was found to proceed according to the equation (371):



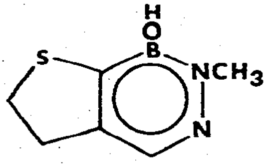
$R = C_6H_5$

Controlled hydrolysis of 2-methylthio-1,3,2-diazaboracycloalkanes yields the corresponding diboryl oxides (33); the B-O stretching mode in such species is observed near 1350 cm^{-1}. The structure of $Cl\text{-}B(\text{-}NCH_3\text{-}CH_2\text{-})_2CH_2$ has been studied by electron diffraction (228). The data illustrate planar environment about boron and nitrogen and the short B-N bond distance of 1.415 Å indicates considerable -bond character in the B-N bonds.

Benzoyl chloride cleaves the hetero ring of 2-phenyl-benzodiazaborolidine with the formation of N,N'-dibenzyl-o-phenylene diamine (38); in the presence of pyridine, however, small amounts of boronium salts are also formed.

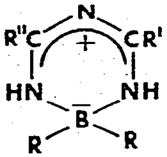
New borazaromatic species include boroaromatic sulfamides (46) and various nitro compounds such as the one obtained by nitration of 3,4-dimethyl-4,3-borazaroisoquinoline with N-nitropicolinium tetrafluoroborate (129); these nitro derivatives can be reduced to the corresponding amino compounds, which appear to have substantial utility for further reactions. Derivatives of 3,2-borazaropyridines are also readily brominated with elemental bromine in pyridine/CCl_4 or iodinated with iodine in pyridine/CH_3CN (128). Benzo- and thieno-fused ring systems react at the remaining CH group of the B-N-C heterocycle. In some cases dihalogenation was observed with excess of the reagents; some mechanistic speculations for the halogenation procedure are based on the observeation that the corresponding isoelectronic pyridines are not halogenated with the cited reagents under similar conditions.

The electron spectra of some 3,2-borazaropyridines have been studied (51) and all of the annular atoms of the following pyridine analog

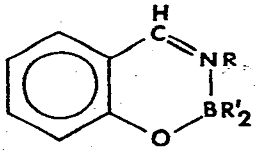


are approximately coplanar (26); bond distances of the species as found by X-ray diffraction are B-N = 1.435 Å and B-C = 1.528 Å.

A new type of heterocyclic inner complex



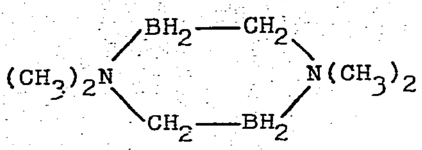
is obtained when equimolar mixtures of trialkylboranes, BR_3, and a primary amide, "RCONH$_2$, are heated in a large excess of a nitrile, R'CN, at 80 to 100°C andthe resultant cyclic product is subsequently treated with ammonia or propylamine (14). The fragmentation of the inner complex



R' = C_6H_5

under electron impact is characteristically influenced by the nature of the substituent R though the ion P minus C_6H_5 is always the most abundant one (205).

Trimethylamine-bromoborane, $(CH_3)_3N\cdot BH_2Br$, reacts with sodium/potassium alloy in trimethylamine to give the cyclic species of the following structure (63):

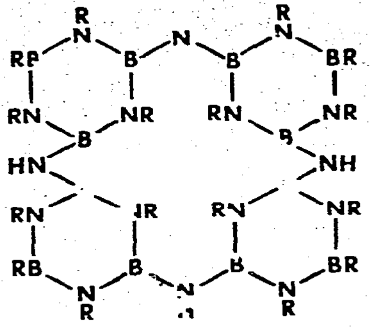


As shown by X-ray diffraction, the ring has chair conformation and the following annular bond distances were found: C-B = 1.609 Å, B-N = 1.615 Å, N-C = 1.511 Å; the N-C bond distances to the equatorial and axial CH_3 groups are 1.482 Å.

7.3 BORAZINE CHEMISTRY

Borazines of the type $(-BX-NR-)_3$ with X = F, Cl and R = H, CH_3, C_6H_5 react with bis(trimethylsilyl)acetamide to yield the corresponding borazines with X = $OSi(CH_3)_3$ (284). However, $(-BCl-NCH_3-)_3$ reacts with the same reagent to yield products containing both $OSiR_3$ and $OCR(SiR_3)$ (R = CH_3) bonded to boron. N-Trimethylborazine undergoes a reversible addition reaction with HX (X = Cl, Br, I) in a 1:3 molar ratio (215). At elevated temperatures hydrogen-halogen exchange occurs to yield B-halogenated species. Elemental bromine interacts with N-trimethylborazine under equivalent conditions to yield B-dibromo-N-trimethylborazine. B-Trichloroborazine reacts with HBr to yield a 1:3 molar adduct but an analogous reaction between B-tribromoborazine and HCl could not be effected (215).

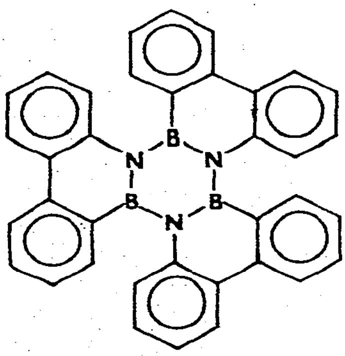
Photolysis of a mixture of borazine with hexafluoroacetone yields a mixture of B-monosubstituted borazine with either $OC(CF_3)_3$ or $OCH(CF_3)_2$ bonded to one of the annular boron atoms (1); both compounds were identified by spectroscopic data. Photolysis of pure N-methylborazine yields hydrogen, methane, borazanaphthalene, N-methylborazanaphthalene and N-dimethylborazanaphthalene (56); photolysis in the presence of ammonia, methanol or dimethylamine yields predominantly a B-monosubstituted borazine derivative. Ion-molecule reactions have been observed for borazines underphoton impact with 10.2 eV radiation (276). Protonation occurs and the resultant borazine cation $B_3N_3H_7^+$ can further react to yield the species $B_6N_6H_{11}^+$. CNDO Calculations support mass spectroscopic evidence that the ptrotonation occurs at a nitrogen site and dissociative proton transfer at a boron site. The mercury sensitized photolysis of hydrogen with N-trimethylborazine produces a new borazine derivative, 1,2-di(3',5'-dimethylborazinyl)ethane (91). A novel pentacyclic borazine species containing a $(BN)_{12}$ ring is obtained in about 60% yield when 1,2,3,5-tetramethylborazine is reacted with hexamethyldisilazane (3). Minor byproducts of the reaction are a B,B'-trimethylsilylaminated species and the corresponding diborazinylamine. For other polycyclic borazine derivatives see (317).



R = CH_3

The borazine $[-B(C_6H_4-2-CH_3)-NC_2H_5-]_3$ is the first example of an arylsubstituted borazine where the absence of coplanarity of the aromatic and borazine rings is clearly demonstrated (55). The compound exists as a pair of diastereomers due to steric hindrance of rotation about the B-C bonds; partial separation of the isomers was accomplished but they are thermally interconvertable.

Borazines and B-monosubstituted amine-boranes have been



compared on the basis of their chemical reactivity and proton magnetic resonance spectral properties (2). The structure of was solved by weighted multi-solution tangent formula place refinement from X-ray diffraction data (29). The central borazine ring suffers severe distortion from planarity to a shallow chair conformation as a result of the crowding of the biphenyl groups. The B-N distances of the molecule are not equal; they are shorter (with a mean of 1.430 Å) when bridged by a biphenyl than when not (mean = 1.488 Å), the latter B-N distance representing the longest one known for any borazine.

The vibrational spectra of N-trimethylborazine and some isotopically labelled derivatives thereof have been recorded (224). The N-methylation does not seem to cause fundamental changes in the electronic structure of the borazine heterocycle. The ion kinetic energy spectra of a series of N-trimethylborazines suggest the possible formation of a cyclopentadienyl-like ion by metastable decomposition in the first field-free region of a mass spectrometer (359). For an *ab initio* study of the electronic structure of borazine as compared to that of boroxine see (147), and for some theoretical investigations of symmetrically trisubstituted borazines see (343).

Various silaborazines containing B_2SiN_3 and BSi_2N_3 heterocycles have been described (261); nuclear magnetic resonance data seem to indicate that these ring systems are not planar.

Hexamethylborazinechromium tricarbonyl reacts with tetraphenylarsonium trichlorostannate or trichlorogermanate in THF _via_ displacement of the borazine ring from the chromium (302).

7.4 AMINE-BORANES AND SOME RELATED SPECIES

Dialkylamine-trihaloboranes are obtained in good yield and purity by halogenation of the corresponding dialkylamine-boranes, $R_2HN{\cdot}BH_3$ with elemental halogen. Partial chlorination is also feasible and the resulting $R_2HN{\cdot}BH_2Cl$ may be utilized for the subsequent synthesis of bisamine-boronium salts via interaction with additional amine (225). Triallylboranes such as tris(2-methylallyl)borane complex readily with nitrogen bases such as trimethylamine, pyridine or picolines to form amine-borane species (16) and 1:1 molar adducts of piperazine and triethylene diamine with $BH_{3-n}F_n$ (n = 0 to 3) have been obtained _via_ base displacement reactions from the corresponding trimethylamine-boranes (47). Also, the preparation of poly(4-vinylpyridine-borane) and its action as polymeric reducing agent have been described (108).

Trimethylamine-haloboranes exhibit a shift to lower field in the proton magnetic resonance spectrum with increasing size of the halogen as well as with an increase in the number of halogen atoms bonded to the boron atom (275). For additional nuclear magnetic resonance studies and boron quadrupole-induced relaxation of tertiary amine adducts of trihaloboranes see (93), for carbon-13 nuclear magnetic resonance studies in $(CH_3)_3N \cdot BX_3$ with X = F, Cl, Br, H (including some mixed species) see (138). Nuclear magnetic resonance studies on hydrazine-borane (in hydrazine) have been reported elsewhere (244, 245), for the kinetics and mechanism of the thermal decomposition of methylhydrazine-borane see (124).

Electron spin resonance data and theoretical studies of radicals formed from trimethylamine-borane have been presented (155) and molecular orbital studies of the dipole moments of methylamine-boranes have been reported (280).

The UV photoelectron spectrum of pyridine-borane exhibits three assignable peaks below 12 eV and this basic pattern persists in the spectra of the 4-substituted pyridine-boranes (281).

Microwave spectroscopic studies gave a value of 1.638 Å for the B-N distance of trimethylamine-borane (64); the C-N distance is 1.483 Å and the dipole moment of the molecule is 4.84 D.

Infrared spectroscopic data indicate that the adducts of $Cl_3C\text{-}CO\text{-}NH_2$ and $(CH_3)_2N\text{-}CO\text{-}Cl$, respectively, with boron trichloride contain a B-O bond (265); the chlorine-35 NQR spectrum exhibits an extraordinary high shift of the C-Cl resonance signal as compared to the free donor molecule. Supposedly this effect can be interpreted by a substantial C-Cl double bond character.

Triethylamine-trifluoroborane is an effective agent for the dehydrofluorination of monohydrofluoroalkanes to yield perfluoroolefins (282). Mixing $(C_2H_5)_2O{\cdot}BF_3$ with an alcohol provides BF_3-etherate-alcohol, which is a mild and effective esterification agent. For some complexes of BCl_3 with dicarboxylic esters see (168)

8 PHOSPHORUS, ARSENIC AND ANTIMONY DERIVATIVES

Lithium diethylphosphide, $LiP(C_2H_5)_2$, reacts with the diethyl ether adduct of BCl_3 to yield a wide variety of compounds containing B-P bonds, the nature of which depends on the ratio of the reactants and the temperature conditions (204). Among the species identified as products from this reaction are ($R = C_2H_5$) $Li[B(PR_2)_4]$, $[B(PR_2)_3]_2$, $[ClB(PR_2)_2]_2$, $[Cl_2B\text{-}PR_2]_2$, $R_3P{\cdot}BCl_2(OR)$ and $B(OR)_3$. Also described are preparative routes to give $[HB(PR_2)_2]_3$, $[Cl_2B\text{-}PR_2]_3$, $R_3P{\cdot}BH_3$ and $R_3P{\cdot}BCl_3$ (204).

As shown by X-ray diffraction data the compound 4-bromo-1,1-3,3,5,7,7,9,9-nonamethyl bicyclo[4.4.0]pentaborophane is an inorganic analog of decalin. The molecular framework consists of alternating B and P atoms arranged in two cis-fused cyclohexane rings; the CH_3 groups are bonded to phosphorus and Br is at B(1) (ring position 4) (133).

For the preparation of trimethylphosphine-boranes of the type $(CH_3)_3P{,}BX_3$ (X = H, F, Cl, Br, CH_3) and their order of adduct bond strength as determined by gas-phase calorimetry see (217). The B-P distance in $(CH_3)F_2P{\cdot}BH_3$ has been found to be 1.84 Å as determined by microwave spectral data on the compound as well as on those of isotopically labelled BH_3 derivatives (272). The vibrational spectrum of the solid compound has been assigned and a force constant of 2.44 mdyn/Å was calculated for the B-P stretching mode (366). A vibrational analysis has also been performed on solid phosphine-borane (145) and molecular orbital studies of the dipole moments of methylated phosphines and their borane adducts are reported elsewhere (280). The B-P bond distances in trimethylphosphine-trihaloboranes, $(CH_3)_3P{\cdot}BX_3$ (X = Cl, Br, I), range from 1.957 to 1.918 Å as based on X-ray diffraction data (27). Non-empirical calculations on $F_2HP{\cdot}BH_3$ give a value of 23.09 kJ/mol for the barrier to rotation about the B-P bond of the molecule (66). An X-ray crystal structure determination of $(CH_3)_3C(-CH_2-NCH_3-)_3P{\cdot}BH_3$ shows that there are two molecules in the unit cell and the B-P bond distance is 1.98 Å (114).

A variety of arsinoboranes has been obtained by three basic procedures (257):

a. Reaction of lithium diorganylarsenide with a haloborane,

b. reaction of silyl(or stannyl)organylarsanes with a haloborane, and

c. interaction of diborane(6) with tetramethyldiarsane.

The resultant arsino-bis(amino)boranes, $R_2As-B(NR'_2)_2$, are monomeric species, $(CH_3)_2As-B(CH_3)_2$ is trimeric, the corresponding B-diphenyl compound is unstable and partially associated, and $(CH_3)_2As-BH_2$ exists as trimer and tetramer.

The LEWIS acidity of simple boranes towards triphenylarsine and diphenylarsine decreases in the order $BBr_3 > BH_3 > CH_3BBr_2 > (CH_3)_2BBr > (CH_3)_2BSCH_3$ (258); triphenylarsine is the stronger of the two cited bases. Gas-phase calorimetric data on the interaction of $L(CH_3)_3$ (L = P, As, Sb) with BX_3 (X = H, F, Cl, Br, CH_3) give a relative base strength decrease in the order $P(CH_3)_3 > As(CH_3)_3 > Sb(CH_3)_3$ and an acid strength decrease in the order $BBr_3 > BCl_3 \approx BH_3 > BF_3 > B(CH_3)_3$ (65).

The reaction of $(CH_3)_2O \cdot B_3H_7$ or B_4H_{10} with PF_2X (X = F, Cl, Br) yields a mixture of $F_2XP \cdot BH_3$ and $(F_2XP)_2 \cdot B_2H_4$ (58); the latter species is prone to rearrange to yield $F_2XP \cdot BH_3$ and $(F_2XP \cdot BH)_n$.

9 BORONIUM SALTS AND BORATES

The salt $[(RH_2N)_2BF_2]BF_4$ ($R = \underline{n}\text{-}C_4H_9$) has been obtained from the reaction of n-butylamine with $(C_2H_5)_2O{\cdot}BF_3$ in $HCCl_3$ solution (249). - Vibrational assignments have been suggested for $[(H_3N)_2BH_2]I$ and the corresponding $N(CH_3)_3$ derivative on the basis of the group vibrational approximation; ν(BN) is assigned in the 690 to 775 cm^{-1} frequency region (23).

The rate law for the hydrolysis of the BH_4^- ion in dimethyl sulfoxide as solvent has the form of a general acid-catalyzed reaction (173). The kinetics of the reaction of NH_4^+ with BH_4^- in liquid ammonia have been studied (273). The reaction proceeds according to

$$(NH_4)_2SO_4 + 2\ NaBH_4 \longrightarrow Na_2SO_4 + 2\ H_2 + H_3N{\cdot}BH_3$$

and rate constants, a heat of activation and the effect of ionic strength have been determined.

$NaBH_4$/carboxylic acid systems have been studied as reagents for the alkylation of amines (326). In benzene sodium tetrahydroborate interacts with acetic acid to give $Na[HB(O\text{-}CO\text{-}CH_3)_3]$ (76). This latter salt may be viewed as a new and reasonably selective reducing agent; for example, although aldehydes are smoothly reduced by the salt, ketones apparently do not react. Sodium tris(2-methoxyethoxy)hydroborate has been prepared by the reaction of sodium hydride with tris(2-methoxyethoxy)borane (248). The crystal structure of $K[B(O-CO-CH_3]_4$ has been determined by X-ray diffraction techniques (141).

Dimeric (dimethylamino)borane reacts with lithium hydride in diethyl ether according to the equation (60):

$$[(CH_3)_2N-BH_2]_2 + 2\ LiH \longrightarrow 2\ Li\ [(CH_3)_2NBH_3].$$

However, this reaction is extremely slow with a 90% conversion completed at 25°C after two months.

$(C_5H_5)_3U(BH_4)$ reacts with triorganylboranes to form species of the type $(C_5H_5)_3U(H_3BR)$ (72). Vibrational spectrosoccpic data indicate that the BR moiety is connected to the U atom <u>via</u> a triple hydrogen bridge; for $(C_5H_5)_3U(NCBX_3)$ with X = H or C_6H_5 U-N≡C-B bonding was established.

Alkali metal salts of oxo acids reacts with BF_3 in carbon tetrachloride or pentane to form complexes such as $[CrO_4(BF_3)_2]^{2-}$, $[CrO_4(BF_3)_3]^{2-}$ or $[SO_4(BF_3)_3]^{2-}$ (222). Similar adducts are formed with NO_3^-, SO_3^{2-} and CO_3^{2-}; however, these latter species are unstable and readily decompose to yield BF_4^- and B_2O_3 as the only boron-containing species. Thermodynamic functions of $Rb(BCl_4)$ and $Cs(BCl_4)$ have been measured (83).

Using $HCCl_3$ or BCl_3 as solvent, tetraalkylammonium perchlorates interact with BCl_3 to form trichloroperchloratoborates, $[NR_4][Cl_3BClO_4]$ (207). The solid colorless products hydrolize readily though they are thermally reasonably stable. On heating to 170°C, the salt with R = CH_3 loses BCl_3. In the case of R = C_2H_5 or C_4H_9 decomposition occurs in the 205 to 230°C range without the loss of BCl_3 in an autoxidation-reduction process. Infrared data on the salts confirm the above structure rather than the formation of BCl_3-solvated cations. Standard heats of formation of $(PCl_4)BCl_4$ and $(PCl_4)BBr_4$ have been determined by a calorimetric method to be -223.9 and -135.5 kcal/mol, respectively (82).

Under mild conditions $[C(C_6H_5)_3]BF_4$ readily fluorinates Si-H bonds in dialkyl- or trialkylsilanes (103) and a mixture of $AgBF_4/CH_3I$ has been used a methylating agent in the preparation of 2-selenonaphthalene (73). Sodium cyanotrihydroborate has been used for the selective reduction of sugar iodides and p-toluene sulfonates (247)and reactions of conjugated carbonyl compounds with the cyanotrihydroborate ion in acidic media (323) as well as with α,β-unsaturated p-tosylhydrazones have been studied (98).

The synthetic utility of the reaction of trialkylcyanoborates with trifluoro acetic anhydride has been explored (188, 189) and new applications of such ions in organic syntheses have been described (186, 187).

Mixing of lithium aryls with trialkylboranes yields (trialkyl)arylborates (77); reactions of these salts with acyl halides have been utilized for a novel regiospecific aryl ketone synthesis.

The ^{7}Li chemical shift of $^7Li[B(CH_3)_4]$ is strongly solvent dependent due to the ready formation of ion pairs. The structure of this salt consists of planar sheets of Li atoms which are bridged by the tetramethylborate groups through linear B-CH_3-Li and multicenter fragments (304). For ^{1}H and ^{13}C nuclear magnetic resonance studies on tetraalkylborates see (293). The specific conductance of the liquid (at room temperature) salt $[N(C_2H_5)_3(\underline{n}\text{-}C_6H_{13})][B(C_2H_5)_3(\underline{n}\text{-}C_6H_{13})]$ increases by a factor of 7.8 when the salt is warmed from 25 to 75°C (42); the useful working range of the salt for recording cyclic voltammograms is about -0.5 to -2.5 V.

Various applications of organylborates in organic syntheses have been described. For example, the reduction of quaternary ammonium salts with $Li[HB(C_2H_5)_3]$ provides a convenient method for the demethylayion of substituted trimethylammonium salts (101). Alkali metal trialkyl(1-alkynyl)borates have been used for the preparation of Z/E substituted allyl methyl ethers (120). Similarly, addition of dimethylmethyleneammonium bromide to sodium trialkyl(1-propynyl)borates gives Z/E mixtures of N-(3-dialkylboryl-2-methyl-3-alkylallyl)dimethylamines (50). Additional studies describe the reaction of lithium tributyl-(1-propynyl)borate with oxiranes (161), protonation-iodination of lithium(trialkyl)alkynylborates to yield olefins (341), a facile double migration in the protonation of lithium trialkyl(alkynyl)borates with acid (324), and the reaction of lithium trialkyl(alkynyl)borates with propargyl bromide and iodoacetonitrile (349). The alkylation of thexyl(dialkyl)alkynylborates provides a new stereoselective synthesis of trisubstituted olefins (344), the reaction of BrCN with dilithium ethynyl-bis(trialkylborates) has been described (340), intermolecular alkyl transfer of tetraorganylborate ions with acyl halides is reported as a novel method for moderating carbanion reactivity (194), and the reaction of lithium (dialkyl)dialkynylborates with iodine in THF gives symmetrical conjugated dienes in excellent yields (311).

The structure of $K[B(C_6H_5)_4]$ has been determined by X-ray diffraction analysis (246) and previous experimental data on the conformation of the tetraphenylborate ion have been reconsidered (136).

4-Methylpyridinium hydrochloride reacts with $Na[B(C_6H_5)_4]$ in 4-methylpyridine to give the salt $[(4\text{-}CH_3\text{-}C_5H_4NH)(4\text{-}CH_3\text{-}C_5H_4N)]^+$ $[B(C_6H_5)_4]^-$ (21); the formulation of this rather unusual species is based on the elemental analysis data. The possible existence of a (pyridine-H-pyridine)$^+$ cation obtained as a tetraphenylborate is discussed elsewhere (365) and various complexes of alkali metals with macrocyclic polyethers have been prepared by using the tetraphenylborate as the counter ion (279). The tetraphenylborate anion has also been used for the determination of sparteine (53) and the anisotropic electrical conductivity of methoxybenzilidene butylaniline containing tetrabutylammonium tetraphenylborate has been studied (200). For rearrangement reactions of low-spin pentacoordinate Ni(II) complexes with sodium tetraphenylborate to produce polynuclear complex species see (89) and for the preparation and properties of sodium tetrakis(3-chlorophenyl)borate see (131).

The photolytic degradation of $Na[B(C_6H_5)_4]$ in aprotic media occurs _via_ two principal reactions (69):

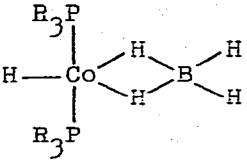
a. Direct formation of biphenyl and generation of a species (in solution) which has the properties of sodium diphenylborate; and

b. formation of a mixture of sodium triarylhydroborates, $Na[HBR_3]$, where R = phenyl, biphenyl, _m_-terphenyl or _p_-terphenyl.

10 BORON-METAL COMPOUNDS

Improved methods for the preparation of $(C_5H_5)_2Zr(BH_4)_2$ and $Zr(BH_4)_4$ have been described (36), for some proton nuclear magnetic resonance studies on $(C_5H_5)_2Zr(BH_4)_2$, $(C_5H_5)_2Hf(BH_4)_2$ and $(C_5H_5)_2ZrH(BH_4)$ see (172) and for some comments on the bonding of the BH_4^- ion to transition metals see (137). The species

$(C_5H_5)_2V(BH_4)$ can be viewed as covalent in nature with two V-H-B bridges (178); bridge-to-terminal hydrogen exchange has a relatively high free energy barrier of 7.6 kcal/mol. The Co-B distance in the paramagnetic complex

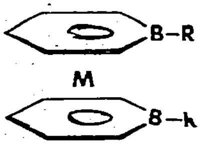


$R = C_6H_{11}$

is 2.13 Å; the complex shows distorted penta-coordination about the Co atom as shown by single crystal X-ray diffraction data (79).

$Al(BH_4)_3$, $ClAl(BH_4)_2$ and $Cl_2Al(BH_4)$ react with ammonia <u>via</u> unsymmetrical cleavage of the AlH_2B group resulting mainly in the formation of $[Al(NH_3)_6]^{3+}$, Cl^- and BH_4^- (7). Organylmercury chlorides interact with $NaBH_4$ to form a coordination species which transforms through a one-electron transfer leading to the generation of a radical pair (211).

Borinato (= borabenzene) complexes of the type



(M = Co; R = CH_3, C_6H_5) decompose on heating with alkali metal cyanides, M'CN (M' = Na, K), in acetonitrile to yield alkali metal borinates, $M'(C_5H_5BR)$ (5). The latter are excellent complexing agents as is illustrated by the following equation:

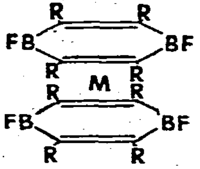
$$Rh(C_8H_{12})Cl_2 + 2\ K(C_5H_5BR \longrightarrow 2\ KCl + (C_8H_{12}Rh(C_5H_5BR)$$

Several (1-substituted borabenzene)iron complexes have been prepared by direct interaction of $FeCl_2$ with the ligand (303); the resultant species exhibit properties and show reactions that closely parallel the chemistry of ferrocene.

The C_5H_5 ring of $(C_5H_5)Co(C_2B_9H_{11})$ is expanded by insertion of B when the initial cobalt complex is treated with sodium and then $C_6H_5BCl_2$ is added (218). In a reverse of their synthesis, borinato complexes undergo a ring contraction (357). For electron spin resonance studies on bis(1-phenylborabenzene)cobalt(II) see (181).

$Fe_2(CO)_9$ reacts with $CH_3B(SCH_3)_2$ to yield among other products a boron-containing intermediate that decomposes with the formation of $[(CO)_3FeSCH_3]_2$ (354); however, reaction of $Fe_2(CO)_9$ with $[-BN(CH_3)_2-S-]_3$ yields $(CO)_6Fe_2(S_2B-N(CH_3)_2)$. Based on spectroscopic data on this latter compound there are two $Fe(CO)_3$ groups linked <u>via</u> two S-bridges, the two sulfur atoms being bonded to the boron atom. For the structure of $(CO)_9Co_3(CO)-[BCl_2\cdot N(C_2H_5)_3]$ see (322).

Single crystal X-ray data on



(M = Ni; R = CH_3) show that the two heterocycles are nearly planar and all six annular atoms are bonded to the central metal atom (315). For crystallographic data on the corresponding complex in which one of the rings is displaced by two CO groups see (321).

New transition metal complexes with (1-pyrazolyl)borate ligands include methylplatinum(II) derivatives of the type $[R_2B(pz)_2]PtCH_3L$ (pz = 1-pyrazolyl; L = tertiary phosphine, isocyanide, acetylene) (250) as well as rhodium(I) and iridium(I) species of the types $(CO)_2M(pz)_2BH_2$ and $(CO)(R_3P)M(pz)_2BH_2$ (R = C_6H_5) (102) and uranium(IV) tetrakis(1-pyrazolyl)borates (184). For some further complexes obtained from $K[HB(pz)_3]$ see (277, 312); see also (182).

Electron spin resonance and electronic spectra of complexes of the type $(C_5H_5)_2Ti[H_xB(pz)_{4-x}]$ indicate that the cyclopentadienyl groups are pentahapto and the (1-pyrazolyl)borate ligand is bidentate (334). High resolution nuclear magnetic resonance studies on $K[H_2B(pz\text{-}3\text{-}CH_3)_2]$ are consistent with a single isomeric structure (274).

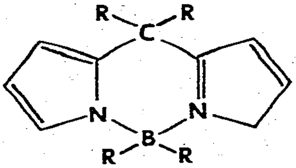
Single crystal X-ray diffraction data on the copper complex $[HB(pz)_3]Cu(CO)$ illustrate that there are two crystallographic distinct types of molecule within the unit sell (269). An X-ray diffraction study on $[(C_6H_5)_2B(pz)_2]Mo(CO)_2(CH_3-CCH_3=CH_2)$ shows the Mo atom to have a 16-electron configuration (67) and in $[(C_2H_5)_2B(pz)_2]Pt(CH_3)(C_6H_5C{=}CCH_3)$ the coordination about Pt is square planar (335); the conformation of the ring formed by the bidentate (1-pyrazolyl)borate ligand in the latter compound os that of a shallow boat. In $[HB(pz)_3]Pt(CH_3)(CO)$ the coordination about Pt is slightly distorted square planar (81); the PtN_4B ring of the molecule is in boat conformation with a (non-bonded) Pt-B distance of 3.36 Å; the N-B-N bond angle averages 109.7°.

The enthalpy of chelation of Co(II), Ni(II), Cu(II) and Zn(II) with four (1-pyrazolyl)borate ligands in water and acetonitrile has been determined (268) and some spectroscopic studies on (1-pyrazolyl)borate complexes of Cu(II) and Ni(II) are described elsewhere (183).

11 PHYSIOLOGICAL AND RELATED ASPECTS

The effects of the tetraphenylborate ion on frog skeletal and cardiac muscle (44) and neuromuscular transmission (253, 254) have been studied. - The stability of memerane acetylcholinesterase in human erythrocytes treated with tetraphenylborate has been investigated (298) and N,N-trimethylpropylammonium bromide methaneborinic acid was found to be a specific and reversible bifunctional inhibitor of acetylcholinesterase (158).

The acute ip toxicity of ($R = C_2H_5$)



was found to be LD_{50} = 69.5 mg/kg in mice (255). Initial toxic symptoms are noticed within 3 to 6 hours by an increase in the muscle tone followed by severe hyperreflexia and convulsive response; oral and sc LD_{50}'s appear to be in the order of 180 mg/kg and 420 mg/kg, respectively. The experimental data indicate a high propensity for the compound to concentrate in liver tissue and the most significant effect of the species appears to be the inducement of porphyria-like complications.

Monte Carlo calculations for determining boron dosis for neutron capture treatment of brain tumors have been described (156).

The boron tolerance and enhancement of boron toxicity by chloride ion in alkali solution during germination of _Sporabolus airoides torr_ has been studied (299). The amino acid composition and N-terminal groups of proteins in ribosomes of boron-deficient pea plants have been determined (301) and the effect of boron-deficiency on the level of the growth inhibitor flavanol-3-glycoside and other flavonoids has been investigated (300).

Chromatographic column materials such as Sephadex can be modified via reactions with (aryl)hydroxyboranes; such modified species interact with carbohydrates and the chemical stabilities of the resultant complexes are related to the conformation of the polyols which can thus be separated in a chromatographic procedure (368). Other (organyloxy)boranes have been used for the determination of sorbitol and mannitol by GLC in pharmaceuticals (336,337) and in conjunction with mass spectrometry for the identification of various carbohydrates (367). For the interaction of polyols with polymers (based on dextrose or cellulose) containing N-substituted [(4-boronophenyl)methyl]ammonio groups see (291). Arylboron polymers have been used for the isolation of nucleotides and amino acylated nucleotides (45).

Literature:

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