BORON

ANNUAL SURVEY COVERING THE YEAR 1981*
Part II

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CONTENTS

The present discussion is primarily concerned with the chemistry of organoboron derivatives containing isolated boron atoms, thus excluding the polyboron hydrides as well as carboranes. In addition, hydroboration reactions are generally not considered. Although the material is grouped into major sections, this classification is not always strictly adhered to. Furthermore, some data are included that are not directly organometallic but should be of interest within the framework of this treatise.

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* Boron, Annual Survey covering the year 1980 see J. Organometal. Chem., 227 (1982) 199 - 240.

1 REVIEWS AND SUMMARY ACCOUNTS

The application of organylboranes in organometallic syntheses (30) and of dimethylsulfide-borane in organic synthesis (42) have been reviewed. Also, the synthesis and application of vinylic organylboranes (8), the chemistry of 1,3,2-diazaboracycloalkanes (14), and the photochemistry of boron compounds (205) have been summarized. A recent issue of the GMELIN handbook (89) treats elemental boron and boron carbides.

2 SELECTED DATA OF GENERAL INTEREST

Some general experiments have been described concerning the use of $(CH_3)_3N\text{-}BH_3$, $C_5H_5N\text{-}BH_3$, $H_3P\text{-}BH_3$, $(C_6H_5)_3P\text{-}BH_3$, and $(C_6H_5O)_3P\text{-}BH_3$ in hydroboration reactions (121). Also, aluminoborane analogs of the lower boron hydrides have been reported (201).

The first sign determination for a $^{11}B\text{-}^{11}B$ spin coupling constant (in methylpentaborane) and signs and magnitude of other coupling constants of selected organylboranes (as determined by double- and triple-resonance techniques) have been reported (87).

3 TRIORGANYLBORANES AND SOME RELATED SPECIES

Reaction of dialkylboranes with alkali metal hydrides in the presence of alkenes provides for a synthesis of mixed trialkylboranes in solution (41). Similarly, the reaction of dialkylboranes with lithium diorganylcuprates has been developed as a new synthesis of organylboranes (116). The hydroboration of 3-methyl-1,3-butadiene with 1,2:1,2-bis(tetramethylene)diborane(6) (3) proceeds by retention of the cyclic structure in the first step, followed by exchange of B-H and B-C bonds, and final cyclic hydroboration to yield

Triethylborane reacts with alkynylstannes to yield 1-stannyl-2-boryl-alkenes (2); the latter interact with additional alkynylstanne to yield metallated allenes of the type $R_3Sn\text{-}CR^2{=}C{=}CR^1\text{-}CR^3(BR'_2)(SnR_3)$ ($R = CH_3$, $R' = C_2H_5$). Various mesitylboranes $(mes)_2BR$ (R = aryl, ethenyl, allenyl, allyl) have been synthesized (6). On the basis of ^{11}B and ^{13}C chemical shift data it is concluded that the unsaturated ligands stabilize these systems by pi back-donation in the order aryl $\ll$ allenyl $<$ alkenyl $<$ alkynyl. Dynamic ^{13}C NMR data have been reported for a series of dimesitylboranes $(mes)_2BX$ where X = SR, OR, NHR (79). The data are interpreted in terms of a low temperature perpendicular structure in which one of mesityl rings is assumed to be perpendicular to the X-B-mes plane involving the second mesityl ring. The barrier to internal rotation is attributed to steric interactions. Elsewhere, the dimesitylboryl group has been established as a new auxochrome (148) and the **HAMMETT** substituent constant for the p-dimesitylboryl group was determined (151).

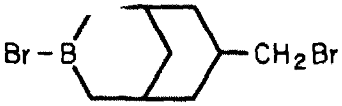
The thermal isomerization of 3-hexyl-bis(2,5-dimethylcyclohexyl)borane is exceptionally fast (175). The degenerate 1,3-shift rearrangement of allylboranes was found to conform to the pseudopericyclic concept (172).

A new preparation of 9-borabicyclo(3.3.1)nonane involves the hydroboration of 1,5-cyclooctadiene with $(CH_3)_2S\text{-}BH_3$ in monoglyme (212). Various new hydroboration reactions employing 9-borabicyclo(3.3.1)nonane have been reported (24, 44, 173) and new derivatives of the cited borane have been described elsewhere (204); see also (36). The reaction of GRIGNARD reagents with 7-substituted 3-methoxy-3-borabicyclo-(3.3.1)nonanes gave the corresponding B-alkylated species; also, some beta-diketonate derivatives have been described (95). Based on NMR studies, derivatives of 3-borabicyclo(3.3.1)nonane containing three-coordinate boron have a flattened double-chair conformation (93). However, species containing four-coordinate boron usually prefer the chair-boat conformation although exceptions are known.

Reaction of 9-borabicyclo(3.3.1)nonane with alkynylstannanes is not consistent with a hydroboration process (214); rather, it involves exchange reactions, alkynylborate intermediates, and organoboration. Reaction of the borane with the heterocycle $(R_2NB)_2S_3$ ($R = CH_3$) gives access to $(HB)_2S_3$ (255), although the latter polymerizes readily (but could be obtained as a trimethylamine adduct). Interaction of 9-ethyl-9-borabicyclo(3.3.1)nonane and alkynylstannes appears to yield borate type intermediates which undergo a temperature-dependent rearrangement and ultimately provide access to organoboron alkene derivatives (105).

The reaction of 3-allyl-7-methoxymethyl-3-borabicyclo-(3.3.1)non-6-ene and the corresponding 3-methoxy derivative with acetylacetone, ethanolamine or other bidentate ligands occurs by displacement of the boron substituent and subsequent formation of an inner complex (35). A new synthesis of 1-boraadamantane has been described which originates from propargyl esters and proceeds via the 3-borabicyclo(3.3.1)-non-6-ene system (136).

The molecular structures of the 1:1 molar complexes of 1-boraadamantane with pyridine and quinoline have been examined by X-ray diffraction (220). 1-Boraadamantane interacts with aldehydes or ketones by initial formation of a 1:1 molar complex (137); thermal treatment of the latter leads to various new heterocyclic cage compounds. The amination of 1-boraadamantane has also been investigated (109). The reaction of bromine with 1-boraadamantane gives 3-bromo-7-bromomethyl-3-borabicyclo(3.3.1)nonane (31):

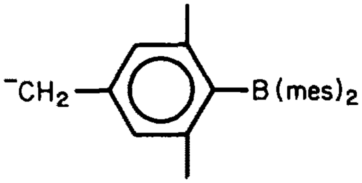


The boron-bonded bromine of the latter is readily displaced by OH or OR. The compound was also utilized for the preparation of the 4-oxa-3-borahomoadamantane dimer and of 7-alkoxy-7-butylaminomethyl-3-borabicyclo(3.3.1)nonanes (31). Complexed (with tetrahydrofuran, trimethylamine or pyridine) 3-borahomoadamantane was obtained from the THF-complex of 1-boraadamantane and trimethylammonium methide (33). The molecular structure of the 4-oxa-3-borahomoadamantane dimer was determined by X-ray diffraction (94).

Vibrational and NMR spectra of $CH_3B(CH=CH_2)_2$ have been studied (50) and various spectroscopic data of 1-phenyl-1-boracyclohexane have been reported (125). Radical organoboron anions which are isoelectronic with tertiary alkyl, allyl and benzyl radicals have been obtained by reduction of the appropriate triorganylboranes with Na/K alloy and were characterized by ESR spectroscopy (229).

Trialkylboranes react with chloramine-T or N,N-dichlorourethane to yield alkyl chlorides (223), and triorganylboranes react with NH_4OH in the presence of NaOCl at 0^oC to yield alkylamines (174). The intermolecular redox reaction of trialkylboranes and $(CH_3)_2BOOCH_3$ in solution has been studied by ^1H NMR spectroscopy and a general mechanism for such processes was proposed (111). The complexation of organylboranes with peroxides has been studied by infrared spectroscopy (143). For the reaction of organylboranes with alkyl(alkoxymethyl) formals, see (184); and for the reaction of B-(1-alkenyl)dialkylboranes with isocyanates, see (192).

The Pd-catalyzed carbonylation of 1-alkenylboranes leads to carboxylic esters (114); for the Pd-catalyzed reaction of 1-alkenylboranes with 1-alkenyl bromides, see (132); and for the reaction of (alkenyl)dialkylboranes to yield conjugated enynes via alkenylcopper intermediates, see (23). The Pd-catalyzed reaction ofphenyl or 1-alkenyl iodides with 1-alkenyl-1,3,2-bezodioxaboroles gives the corresponding cross-coupled products (145). For the synthesis of organic iodides via trialkylboranes, see (82, 134); see also (120). Trimesitylborane reacts with strong bases (43) to form the boron-stabilized carbanion

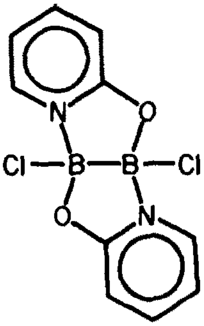


Details for the synthesis of tetraorganyldiboranes(4), R_2B-BR_2, have now been reported (62). The thermal stability of the species is discussed in terms of steric effects exerted by the organi moieties. The radical anion $R_2B-BR_2{}^{\cdot -}$ (R = $CH_2C(CH_3)_3$) has been obtained by reduction of the corresponding tetraalkyldiborane(4), and the ESR spectrum of the species has been described (92). The compound $(B\text{-}t\text{-}C_4H_9)_4$ has been prepared by reaction of B_4Cl_4 with $Li\text{-}t\text{-}C_4H_9$ (118).

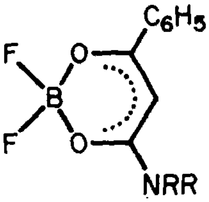
The THF complex of 1-pyrrolylborane has been advocated as a new bifunctional hydroborating agent (75). For the hydroboration of silylacetylenes, see (76).

Dissolving $(CH_3)_nSnX_{4-n}$ (n = 1 to 4, X = halogen) in liquid BY_3 (Y = Cl, Br) either halogen exchange alone or halogen exchange accompanied by cleavage of the CH_3 moiety from the tin may occur (197); the specific processes depend on the halogen involved.

2-(Trimethylsilylamino)pyridine or 2-(trimethylsilyloxy)-pyridine react with BCl_3 under displacement of $Si(CH_3)_3$ by BCl_2 (51). 2-(Trimethylsilyloxy)pyridine reacts with B_2Cl_4 in 2:1 molar ratio to yield the cyclic species



2,4-Pentanedione (Hacac) reacts with BCl_3 ti yield $(B(acac)_2)HCl_2$, whereas reaction of $(acac)B(C_3H_7)_2$ with BCl_3 yields $(acac)BCl_2$ (73). For a ^1H NMR study on the related species



see (81).

The conversion $R_2BX \longrightarrow R_2BH$ (X = Cl, Br) utilizing various hydriding agents has been developed as a general procedure (152). (Dialkyl)haloboranes react with silyl enol ethers to give the corresponding boron enolates (163).

The isotopically selective infrared photodissociation of (trans-2-chloroethenyl)dichloroborane has been described (78) and the vibrational spectrum of (cyclopropyl)dichloroborane has been investigated (85).

Based on its reactivity with deuterium gas difluoroborane, HBF_2, has been found to be an effective hydrogen-deuterium exchange catalyst (28). cis-1,2-Dichloroethylene reacts with BH_3 in THF at 20°C to convert approximately 95% of the BH_3 to H_2BCl via beta-elimination of the initial hydroboration product (158). Both $HBCl_2$ and $HBBr_2$ have been generated in the gas phase from the reaction of gaseuous BX_3 with solid $NaBH_4$ at temperatures near 250°C (64). The He(I) photoelectron spectra of the two species were recorded and interpreted by ab initio calculations. For a theoretical study on $BF_n(OH)_{3-n}$, see (140).

Tetrabromodiborane(4), B_2Br_4, is readily accessible by reaction of BBr_3 with $B_2(OCH_3)_4$; since the latter is conveniently prepared bia the reaction sequence $ClB(NR_2)_2 \longrightarrow B_2(NR_2)_4 \longrightarrow B_2(OR)_4$ ($R = CH_3$), the procedure provides for simple access to B_2Br_4 (13).

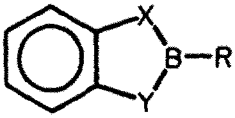
5 OXYGEN DERIVATIVES

Acylation of boron-stabilized carbanions with methyl benzoate yields phenyl-substituted vinyloxyboranes according to the following pathway: $Li(CH(BR'_2)(CH_2R)) + C_6H_5C(O)OCH_3 \longrightarrow LiOCH_3 + C_6H_5C(O)\text{-}CH(BR'_2)(CH_2R)$ (83). Organoboron siloxanes have been prepared by the reaction: $R_3SiH + R'_2BH \longrightarrow R_3Si\text{-}O\text{-}BR'_2 + H_2$ (234); alkyl peroxides cleave the B-C linkage via an intermediate where R_3SiO has exchanged with $R''O_2$ species.

The molecular structures of $(CH_3)_2BOCH_3$ and $CH_3B(OCH_3)_2$

have been studied by electron diffraction (96) and minimum energy geometries, rotational barriers and charge distributions have been calculated for H_2BOH, $HB(OH)_2$ and $(H_2B)_2O$ by ab initio studies (7).

Boron-11 and carbon-13 chemical shifts of benzannellated heteroborolanes of the type



with X = O, S, NH, NCH_3, NC_6H_5 or $NSi(CH_3)_3$ and R = H, Cl, $N(CH_3)_2$, CH_3 or C_6H_5 have been determined (58). Based on the ^{13}C data it is concluded that the BX(Y) interaction weakens the mesomeric donor effect on the aromatic ring.

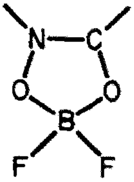
The Pd-catalyzed cross-coupling of (dihydroxy)phenylborane with haloarenes in the presence of bases has been described (129). (Hydroxy)vinylboranes can be reacted with ICl to give vinyl iodides (74). For the reaction of (vinyloxy)boranes with SCHIFF bases to yield beta-amino acid derivatives, see (181).

Laser or microwave discharge promoted reduction of $B(OCH_3)_3$ by hydrogen occurs only partially but smooth reaction is observed using SiH_4 and laser (67). For reactions of $B(OC_2H_5)_3$ with alkanolamines, see (139); for alkanolamine ligand exchange reactions with cyclic bis(oxy)boranes, see (72).

$B(OCH_3)_3$ interacts with organic peroxides to yield 1:1 molar complexes but exchange of alkoxy and alkyldioxy groups may also occur (141). $(C_4H_9O)_2B$-O-O-t-C_4H_9 interacts with ether solvent in a bimolecular reaction but homolytic cleavage of the peroxide link does also occur (142).

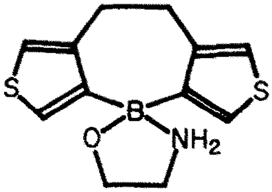
For studies on the reduction of organic compounds with bis(trifluoroacetoxy)borane, see (45). Bis(dialkylamino)-bromoboranes interact with salts of carboxylic acids to yield the corresponding acyloxyboranes, $(R_2N)_2B\text{-}O\text{-}C(O)R'$ (104). Various applications of oxyboranes in chromatography (99, 100, 122, 123) and analysis (185) have been described. For some applications of oxyboranes in organic syntheses, see (11, 12, 47, 130, 131, 183, 203).

Boron heterocycles of the general type

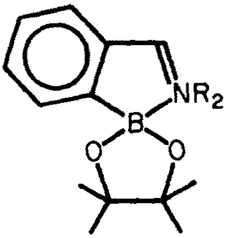


have been described (196) and fluoro- and acetoxyboron complexes of semicarbazones and thiosemicarbazones have been prepared (198). Also, boron complexes of monofunctional bidentate and difunctional tridentate SCHIFF bases (193), and 2-isopropoxyborolane, -borinane and -borole complexes of N,N'-ethylene bis(salicylaldimine) (195) have been reported. For some boron derivatives of azines, see (194).

The crystal structure of



has been determined by X-ray diffraction (170). The B-N bond of 2-(aminomethyl)phenyl derivatives of the type



is labile and opens and closes rapidly (110).

Boric acid interacts with ethylenediamine in aqueous medium to form a 3:1 molar complex of salt-like nature involving a B-O heterocycle as anion (207). A substituted ammonium salt of similar structure is obtained by reaction of boric acid with aqueous 2-aminoethanol (208). For reactions of boric acid with acetals, see (233).

6 SULFUR, SELENIUM AND TELLURIUM DERIVATIVES

(Organylthio)dimesitylboranes, $RSB(mes)_2$ (mes = mesityl), have been prepared by reacting RSMgBr with $FB(mes)_2$. The steric hindrance of the four ortho-methyl groups is insufficient to prevent hydrolysis of the B-S bond when R = alkyl, but the species with R = aryl were found to be hydrolytically stable (1).

Tris(organylthio)boranes, $B(SR)_3$, react with pyrazole to yield pyrazaboles = dimeric pyrazolylboranes of the type $((RS)_2B\text{-}N_2C_3H_3)_2$ and the compound $((C_2H_5S)(C_6H_5)B\text{-}N_2C_3H_3)_2$ has been obtained similarly (68). Corresponding species have been obtained by condensation of pyrazabole, $(H_2B\text{-}N_2C_3H_3)_2$, with α,ω-dithiols. The boron-bonded RS groups are stable towards nucleophilic attack by such reagents as pyrazole or alcohols.

Substituent exchange between 1,2,4,3,5-trithiadiborolanes of the types $(XB)_2S_3$ and $(YB)_2S_3$ occurs via two processes. An exo exchange provides for mixed species $(XYB_2)S_3$ without site exchange of boron atoms and an endo process occurs via BX or BY exchange, respectively. In general, the exo process is the faster one but in the case of $(CH_3B)_2S_3$ as one of the reactants, only the endo process is observed (56). Analogous processes occur between $(YB)_2S_3$ and BX_3. In this latter case, the exo reaction predominates if Y is more basic than the annular S atoms, and the endo reaction predominates if Y does not contain free electron pairs. In addition, steric factors can influence the ratio of endo to exo process. These studies were based on isotopic labelling of the boron (57). The first examples of the 1,2,4-trithia-3,5-diborolane heterocycle containing exocyclic (B)-O-C bonds have also been reported (107). The thermal stability of these compounds increases with increasing size of the organyl group and from aliphatic to aromatic substituents.

Nuclear magnetic resonance data on tris(bis(organylthio)-boryl)amines, $N(B(SR)_2)_3$, indicate the existence of chemically equivalent SR groups. However, in the solid state one of the three $B(SR)_2$ groups is different as is evidenced by a longer B-N distance as compared to the two other B-N bonds (61). The vibrational spectra of 1,3-dithia-2-boracyclopentanes (with boron-bonded Cl, Br, $N(CH_3)_2$, C_6H_5) have been examined (86).

Selenoboranes of the type $B(SeR)_3$ have been converted to beta-hydroxyselenides by reaction with epoxides (182). The preparation of $B(OTeF_5)_3$ and its 1:1 molar acetonitrile adduct as well as that of $Cs(B(OTeF_5)_4)$ have been described.

7 BORON-NITROGEN COMPOUNDS

The reaction of propargylamines with haloboranes or methylthioboranes usually yields the corresponding (propargylamino)boranes but haloboration of the triple bond presents an alternate reaction pathway (159). (Vinylamino)-diethylboranes of the type $(C_2H_5)_2B\text{-}NR(C(CH_2R')\text{=}CHR'')$ have been obtained by the reaction of triethylborane with N-alkyl ketimines, $RN\text{=}C(CH_2R')(CH_2R'')$ (88).

2-Aminomethypyridine and 2-aminoethylpyridine, when reacted in a 1:2 molar ratio with trialkylboranes, form intermediates which on pyrolysis yield (2-pyridylalkylamino)dialkylboranes, $C_5H_4N\text{-}2\text{-}(CH_2)_n\text{-}NH\text{-}BR_2$ (n = 1 or 2; R = C_2H_5, n-C_3H_7) (16). Nuclear magnetic resonance data show that if R = C_2H_5 the compound exists in an intramolecular coordinated bicyclic structure containing four-coordinate boron which is bonded to the pyridyl nitrogen. If R = C_3H_7, the species with n = 1 exists in both the non-coordinated (with trigonal boron) as well as the bicyclic coordinated form, but with n = 2 the compound exists exclusively in the open form with trigonal boron.

N-Lithiated (amino)fluorosilanes, $LiR'N\text{-}SiR_3$, react with BF_3 to yield $FB(NR'\text{-}SiR_3)_2$ and with $F_2B\text{-}N(SiR_3)_2$ to yield $R_3Si\text{-}NR'\text{-}BF\text{-}N(SiR_3)_2$ (164). Various N-silylated aminoboranes have been reported elsewhere (226) and the barriers to rotation about the B-N bond of the species were determined. Reaction of $(R_3Si)_2N\text{-}P\text{=}NSiR_3$ with BR_3 (R = CH_3) proceeds to yield $(R_3Si)_2N\text{-}PR\text{-}N(SiR_3)(BR_2)$ (37).

Species of the type $(t\text{-}C_4H_9P)_2B\text{-}NRR'$ have been prepared by the interaction of $K(t\text{-}C_4H_9)P\text{-}P(t\text{-}C_4H_9)K$ with (organylamino)dichloroboranes (69); the resultant products contain a P_2B ring system and the structure of $(t\text{-}C_4H_9P)_2B\text{-}N(C_2H_5)_2$ has been determined by X-ray diffraction (70).

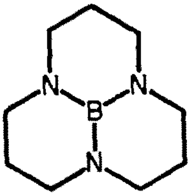
The heterocycle $ClB(\text{-}NCH_3\text{-}CH_2\text{-})_2$ (= Cl-L) reacts with N-silylated sulfur-nitrogen compounds to yield thermally stable materials such as $(CH_3)_2S(O)\text{=}N\text{-}L$, O=S=N-L or L-N=S=N-L (26);

if L = $B(C_6H_5)_2$, $B(C_6H_5)Cl$ or $B(-O-CH_2-CHCH_3-O-)$, the resultant products are considerably less stable. Cleavage of the Si-N bond in N-methyl-N-trimethylsilyl-methylsulfinamide with haloboranes or of N,N-organyl-trimethylsilylaminoboranes with methylsulfinyl chloride yields sulfinamidoboranes of the type $R-S(O)-N(CH_3)(BRR')$ (106). In other work (63), stannylboranes of the types $R_3SnB(NR'_2)_2$, $R_3SnB(NR'_2)R''$ and $(R_3Sn)_2B-NR'_2$ ($R = CH_3$; $R' = CH_3$, C_2H_5) and some of their properties have been described.

Evidence for restricted rotation about the B-N bond has been collected by ^{13}C NMR data on (amino)diphenylboranes (150), (dialkylamino)phenylfluoroboranes (149), (dialkylamino)phenylchloroboranes (108) and (alkylamino)(dialkylamino)phenylboranes (80). Minimum energy geometries, rotational berriers and charge distributions have been calculated for H_2B-NH_2, $HB(NH_2)_2$ and $(H_2B)_2NH$ by ab initio studies (7).

The formation of boron nitride films by pyrolysis of $(C_3H_7)_2N-BBr_2$ has been studied (209). Various NMR spectral data have been reported for a series of B- and N-trimethylstannylated aminoboranes (9). The chemical shifts $\delta^{13}C$ of monoaminoboranes of the type $R_2N-BR'_2$ with R' = halogen, organylamino, organyloxy, organylthio or organyl can be explained by the action of a gamma-effect exerted by R' on the shielding of $^{13}C(B)$ and $^{13}C(N)$ (55). The vibrational spectra of $((CH_3)_2N)_2BX$ species with X = H, D, CH_3 and CD_3 have been recorded and assignments to the fundamentals are supported by the results of a normal coordinate analysis (17). Similar studies have been reported for $B(NR_2)_3$, $(R_2N)_2B-B(NR_2)_2$ and $(R_2N)_2BBr$ (R = alkyl) (168).

The molecular structures of $(CH_3)_nB(NHCH_3)_{3-n}$ (n = 1 to 3) have been determined by electron diffraction (97). The observed changes in B-N bond distance confirm B-N pi-bonding. X-Ray diffraction data on



show that the BN_3 moiety is planar and the mean B-N bond distance is 1.4 Å (169). The structure of $(C_2H_5)_2N\text{-}B(t\text{-}C_4H_9)_2$ has been determined by X-ray diffraction (70). For MNDO studies on borazafulvenes, see (231).

The thermolysis of azidoboranes of the type $(R_2N)_2BN_3$ in the gas phase at 450 to 485°C yields various products which all can be considered to originate from iminoborane intermediates of the type $R_2N\text{-}B{\equiv}N\text{-}NR_2$; the latter are likely to be formed bia borylnitrenes, $(R_2N)_2BN$ (230). The thermal decomposition of liquid $R_2B\text{-}N(OSi(CH_3)_3)(Si(CH_3)_3)$ can be interpreted by assuming the formation of $RB{\equiv}NR$ as the key intermediate (10). In the presence of excess BR'_3, the diborylamine $RR'B\text{-}NR\text{-}BR'_2$ is formed; otherwise, the reaction proceeds with the elimination of hexamethyldisiloxane to yield a mixture of $R_2B\text{-}NR\text{-}N(OSi(CH_3)_3)(Si(CH_3)_3)$ and $(\text{-}BR\text{-}NR\text{-})_3$. Cyclotrisilazanes were found to react with $(C_2H_5)_2O\text{-}BF_3$ to yield, among other products, silaborazines (161).

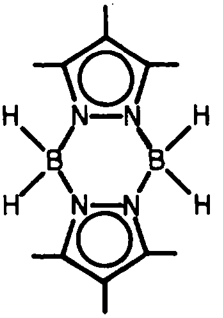
Hexamethylborazine, $(\text{-}BCH_3\text{-}NCH_3\text{-})_3$, forms a 1:1 molar adduct with $AlBr_3$ in which one annular nitrogen atom serves as donor site (60). X-Ray diffraction data on the species illustrate that this event results in a loss of planarity of the B-N heterocycle and provides for different B-N bond lengths. However, in solution and at temperatures above 276 K the adduct is fluxional.

The vibrational spectra of isotopically labelled B-trifluoroborazine and B-trichloroborazine have been reexamined (27). The chemical shift $\delta^{13}C$ of borazines of the type $(\text{-BR-NR'-})_3$ with R = halogen, organyloxy, organylthio, organylamino or organyl can be explained by the action of a gamma-effect exerted by R on the shielding of $^{13}C(B)$ and $^{13}C(N)$ (55).

The formation of boron nitride films by pyrolysis of $(\text{-BCl-NH-})_3$ has been studied (209). An airtight vibration-type apparatus for mechanico-chemical syntheses has been developed and its use for producing borazine has been described (217).

N,N-Diborylated hydrazines of the type $R_2N\text{-}N(BR_2)(BR'_2)$ have been obtained by the reaction of $R_2N\text{-}NLi(BR_2)$ ($R = CH_3$) with R'_2BX ($R' = CH_3$, C_6H_5; X = Cl, Br); similarly, the species $R_2N\text{-}N(BR_2)(SiR_3)$ was obtained by reaction of the N-lithio hydrazine with R_3SiCl (54). A polarographic study of 2,3-dihydro-4H-1,2,4,3-triazaboroles in dimethylformamide shows that the center of the electrolytic reduction is the C=N-N group (235).

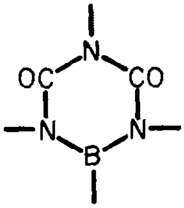
The pyrazabole skeleton



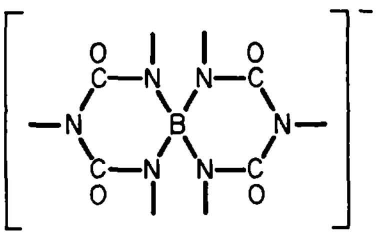
is symmetrically cleaved when pyrazaboles are treated with alpha-omega diamines ; monomeric 2-(pyrazol-1'-yl)-1,3,2-

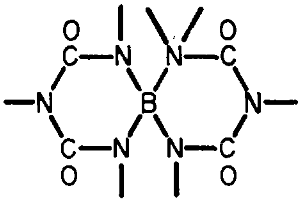
diazaboracycloalkanes result (68). Various N-borylated monomeric pyrazole (as well as imidazole) derivatives have also been obtained by condensation of 1,3-dimethyl-1,3,2-diazaboracycloalkanes with pyrazole or imidazole, respectively (4). The species are fluxional at room temperature and exhibit resilient coordination ability. 1,3-Dimethyl-2-(pyrrol-1'-yl)-1,3,2-diazaboracycloalkanes have been obtained in similar fashion as outlined above and the corresponding 1,3,2-diazaboracyclopent-4-ene was obtained by dehydrogenation of the saturated species (18). For transition metal complexes of the unsaturated boron-nitrogen ring system, see (165).

(Organyl)dihaloboranes, $R'BX_2$, react with $SC(NHR)_2$ ($R = t\text{-}C_4H_9$) to yield the four-membered heterocycle (-NR-BR'-NH-CS-) (221). Several heterocyclic species of the general structure of a 1,2-azaborauracil



have been obtained by condensation reactions of trigonal boranes with biurets (66) and also by reaction of N,N'-di-organylureas with (organyl)haloboranes (221). However, in this latter reaction, which also proceeds with thiourea derivatives, mixtures with heterocycles of the type $OC(\text{-}NR\text{-}BR'\text{-})_2NR$ are obtained. Various additional products which are formed may be explained by the complex pathway which proceeds via partial decomposition of the urea or thiourea to yield isocyanates (isothiocyanates) and primary amine. Bicyclic species of the types

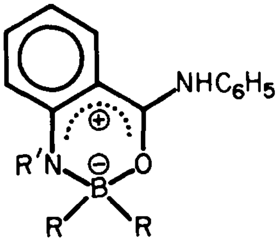




have been obtained on reaction of tris(dimethylamino)borane or trimethylamine-borane with biurets (66).

Mass spectral data on 1,2-azaboracyclopentanes have been evaluated and were compared with those of corresponding 1,2-oxaboracyclopentanes (32).

Reaction of (cyclohexenylamino)dialkylboranes with phenyl isocyanate under mild conditions results in aminoboronation of the C=N double bond according to (34): $R_2B\text{-}NR'R'' + C_6H_5NCO \longrightarrow R_2B\text{-}NC_6H_5\text{-}C(O)\text{-}NR'R''$. However, at elevated temperatures cyclic species containing tetracoordinated boron of the following type are obtained.



(Amino)dialkylboranes, $H_2N\text{-}BR_2$, react with nitriles, R'CN, under high pressure according to (213): $H_2N\text{-}BR_2 + R'CN \longrightarrow R_2B\text{-}N{=}CR'\text{-}NH_2$ (slow); $+ R'CN \longrightarrow N(\text{-}CR'\text{-}NH\text{-})_2BR_2$. The preparation of the final products is simplified by employing ammine-trialkylboranes as boron source. Similar species containing the same N_3C_2B ring system have been obtained from the reaction of 2-aminothiazole with either trialkylboranes and dicyclohexylcarbodiimide or with (amino)dialkylboranes and formamide (228).

8 LEWIS ACID-BASE TYPE ADDUCTS

Both 2-(aminomethyl)pyridine and 2-(aminoethyl)pyridine react with $(CH_3)_3N\text{-}BH_3$ by simultaneous base displacement and condensation to yield amine-aminoboranes, $2\text{-}(H_2B\text{-}NH\text{-}(CH_2)_n\text{-}C_5H_4N\text{-}BH_3$ (16). The incomplete oxidation of $(C_2H_5)_3N\text{-}BH_3$ in organic silvent has been studied (210). The process involves molecular oxygen dissolved in the solvent as well as in the amine-borane itself and yields a polymeric species likely to contain a cyclic tetrametaborate skeleton.

Molecular orbital calculations have been reported for the sigma-pi transmitted coupling over five or six bonds in pyridine-borane, $C_5H_5N\text{-}BH_3$ (215). The photoelectron spectrum of methylisocyanide-borane has been reported (77) and the microwave spectrum of ammine-borane, $H_3N\text{-}BH_3$ (124), as well as that of ethylphosphine-borane (126) have been examined.

The mode of action of monocarboxylates and thallous nitrate in the $(CH_3)_2HN\text{-}BH_3$ chemical nickel bath has been studied (219). For additional uses of amine-boranes as reducing agents, see (40, 138); and for a potentiometric study of the oxidation of dimethylamine-borane on a platinum electrode, see (240).

The compound $(CH_3)_3P\text{-}BH_2(CH_2N(CH_3)_2)$ has been prepared by a displacement reaction (206). Subsequent reaction of the species with B_2H_6 yields $(CH_3)_3P\text{-}BH_2(CH_2N(CH_3)_2\text{-}BH_3)$. Steric effects on the stability of amine-boranes have been studied amploying borinane, $(\text{-}CH_2\text{-})_5BH$, as LEWIS acid and a variety of amines as donor agents (176).

Dimethylsulfide-chloroborane, $(CH_3)_2S\text{-}BH_2Cl$, is formed in essentially quantitative yield by refluxing an equimolar mixture of $(CH_3)_2S\text{-}BH_3$ and CCl_4 (115). Triphenylphosphine-cyanoborane has been converted to $(C_6H_5)_3P\text{-}BH_2X$ species with X = COOH, $CONHC_2H_5$ or $COOC_2H_5$ (53).

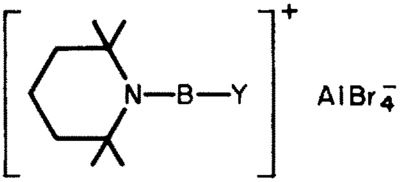
Ab initio calculations on the geometry of $(CH_3)_2O\text{-}BH_3$ have been reported (48) and the structure of $C_5H_5N\text{-}BCl_3$ has been determined by X-ray diffraction (154). Spectroscopic data have also been reported for the 1:1 molar adducts of boron trihalides, BX_3 (X = Cl, Br, I), with dimethylphosphine (103), trimethylarsine and triphenylarsine (102). The molecular structure of $(CH_3)_3P\text{-}BBr_3$ has been examined by electron diffraction (157). For the infrared multiphoton dissociation of $(CH_3)HS\text{-}BCl_3$, see (232).

In the formation of 1:1 molar complexes between triarylboranes and acetone phenylhydrazone the sp^2-hybridized nitrogen of the latter acts as the donor site (227).

The formation of boron nitride films by pyrolysis of $(CH_3)_3N\text{-}BF_3$ and $H_3N\text{-}BH_3$ has been described (209).

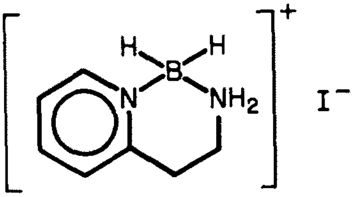
9 BORON CATIONS

The first boron cations involving a two-coordinate boron atom have been obtained by bromide ion abstraction from (2,2,6,6-tetramethylpiperidino)bromoboranes with $AlBr_3$ (91). The species



with Y = $N(CH_3)_2$, $N(C_2H_5)_2$, CH_3 or C_6H_5 were obtained in good yield and crystal structure data confirm a linear arrangement of the cation.

Reaction of either 2-(aminomethyl)pyridine or 2-(aminoethyl)pyridine with $(CH_3)_3N-BH_2I$ occurs by base displacement and concurrent iodide ion displacement to yield boronium(1+) salts containing a cyclic cation, e.g (16):



10 ANIONS OF THE BORATE(1-) TYPE

Dialkylboranes react rapidly with $LiAlH_4$ in diethyl ether in the presence of triethylenediamine (= L) according to: $R_2BH + LiAlH_4 \longrightarrow Li(R_2BH_2) + AlH_3$ (where the AlH_3 is complexed with L). Similarly, the reaction $L\text{-}BH_2R + LiAlH_4 \longrightarrow Li(RBH_3) + L\text{-}AlH_3$ proceeds quite readily (211).

The lithium tetramethylborate-dioxolane electrolyte has been evaluated for use in rechargeable cells (186). For reactions of alkyl fluorosulfonates with lithium (1,2-dimethoxyethenyl)trialkylborates to yield ketones, see (162); for reactions of lithium (alkenyl)trialkylborates with alkylidene derivatives, see (133); for that with benzo-1,3-dithiolium fluoroborate, see (117); and for reactions of lithium allylborates with allylis halides, see (52). Reductions employing lithium 9,9-dibutyl-9-borabicyclo(3.3.1)nonate have been described elsewhere (177).

The electronic structure of the $(HBpz_3)^-$ ligand (pz = pyrazol-1-yl) has been studied by photoelectron spectroscopy (187). The related ions $(H_2Bind_2)^-$, $(HBind_3)^-$ and $(Bind_4)^-$ (ind = indazolyl) have been synthesized and some 1:1 molar complexes of these new chelating ligands have been obtained by reaction with transition metal halides (19).

The ion $(H_3BSnR_3)^-$ ($R = CH_3$), $\delta^{11}B = -43.7$ ppm, has been obtained by reaction of THF-BH_3 with $LiSnR_3$ (9). A detailed study of the interaction of mono- and dialkylboranes with saline hydrides to yield the corresponding alkylhydroborates has now been published (84). For the reaction of trialkylboranes with $LiAlH_4$ in the presence of triethylenediamine to yield lithium trialkylhydroborates, see (178). Tris(aryloxy)hydroborates can be used for the reduction of aldehydes in the presence of ketones (112), and the anion $((R_3B)_2CN)^-$ ($R = C_6H_5$) has been found quite useful for the precipitation and crystallization of large cations (38).

The crystal structure of the oxonium tetrafluoroborates $(H_2O)BF_4$, $(H_5O_2)BF_4$ and $(H(CH_3OH)_2)BF_4$ have been determined (236).

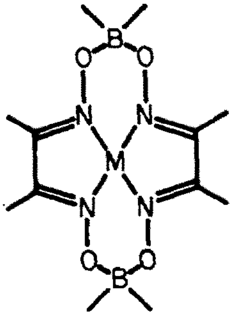
Sodium tetraphenylborate has been used for the determination of arenediazonium salts (155), and various tetraarylborates have been employed as NMR shift reagents (71). The ion $B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4^-$ has been described as the first efficient negatively charged phase-transfer catalyst (113). For reactions of Cs and Rb with $Na(B(C_6H_4\text{-}4\text{-}F)_4)$, see (224); and for activation parameters of the oxidation of the tetraphenylborate ion by hexahaloiridate(IV) complexes, see (222).

11 METAL DERIVATIVES AND COMPLEXES

There seems to exist a correlation between the metal ion radius, metal-boron distance, and the number of B-H-metal bridge bonds in metal tetrahydroborate complexes (29). However, the difference in energy between the various possible modes of bonding is small, and the coordination number of the metal ion and steric hindrance by other ligands are of significant impact.

The species $Li(CH_2P(CH_3)_2\text{-}BH_2\text{-}P(CH_3)_2CH_2)$ reacts with anhydrous metal halides (d^0 and d^{10} metals) to give spirocyclic complexes of the type $H_2B(P(CH_3)_2CH_2)_2M(CH_2P(CH_3)_2)_2BH_2$ (49). Employing organometallics rather than halides gives access to monocyclic derivatives of the type $H_2B(-P(CH_3)_2-CH_2-)_2MR_2$ (49, 166).

For macrocyclic transition metal complexes involving the species

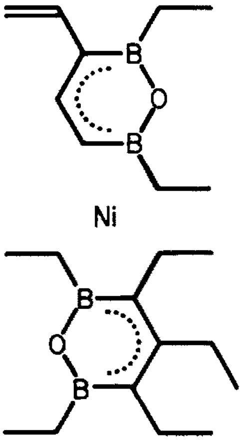


see (101, 189). For the reaction of nickel dioximates with $(-BOCH_3-O-)_3$ or dimethylammonium pentaborate hydrate to give similar species, see (15). The crystal structure of the 1:1 molar adduct of anthracene with bis(difluoroborondimethylglyoximato)nickel(II) has been studied by X-ray diffraction (188), as has the crystal structure of N,N-dimethylpiperidinium iodo bis(difluoroborondimethylglyoximato)nickel(II), the product of the reaction of bis(difluoroborondimethylglyoximato)-nickel(II) with piperidine and iodomethane (238).

New studies on metal complexes with (pyrazol-1-yl)borate ligands include derivatives of the following metals: Cu (20), Ag (21), Ti (22), Mo (119, 127, 190, 216), W (191), Tc (25) and Co (199).

Magnetic susceptibilities of Cu(II) complexes of (dihydroxy)phenylborane were found to obey the BLEANEY-BOWERS equation for dinuclear Cu(II) clusters (156). For skeletal electron counting in transition metal heteroboranes and related species, see (239).

INDO SCF MO claculations have been reported for some bis(borabenzene) complexes, $M(C_5H_5BH)_2$, M = Cr^-, Mn, Fe^+, and the findings are discussed in terms of the simple ligand field model (5). The sandwich complex



has been obtained as an unusual product of the interaction of a 1,3-diborolene with $Ni(CO)_4$ (147); X-ray diffraction data confirm the structure. When $(=CR\text{-}NR'\text{-})_2BR''$ (= L) is reacted with $(CH_3CN)_3Cr(CO)_3$, a sandwich of the type $LCr(CO)_3$ is obtained (165); however, in the case of R' = C_6H_5, this latter group serves as the coordinating site. The reaction of 2-methyl-1,2-azaboracyclopent-3-ene (= L) with $Fe(CO)_5$ yields $(L(Fe(CO)_2)_2$ (59).

The preparation of the solvated species $(OC)_5WC\text{-}(OB(n\text{-}C_4H_9)_2)CH_3\cdot L$ (L = diethyl ether, tetrahydrofuran, dioxane) has been briefly reported (153). $(OC)_5ReFBF_3$ is obtained from $(OC)_5ReH$ (or $(OC)_5ReCH_3$) by interaction with $(C_6H_5)_3CBF_4$ (146); it reacts with water vapor to yield $(OC)_5Re(OH)BF_3$, and with sigma or pi donors L to form the salts $((OC)_5ReL)BF_4$. Tetrafluoroborate complexes of the type $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PR_3)FBF_3$ have been prepared by hydride abstraction from the corresponding hydrido complex using $(C_6H_5)_3CBF_4$ (237).

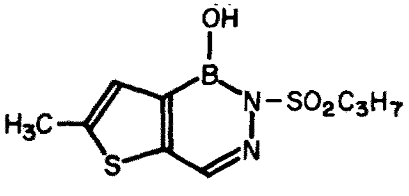
The carbamoyl complex $(C(N(CH_3)_2)_3)((OC)_4FeC(O)N(CH_3)_2)$ reacts with bromoboranes, $BrBR_2$ (R = CH_3, C_6H_5, $N(CH_3)_2$), at low temperatures to yield boroxy complexes of the type $(OC)_4Fe\text{-}C(OBR_2(N(CH_3)_2)$ (65). The latter decompose at ambient temperature with the formation of the aminoborane, $(CH_3)_2N\text{-}BR_2$ and $Fe(CO)_5$.

The NMR spectra of the paramagnetic triple-decker sandwich complex $(C_5H_5)Ni(C_2B_2(C_2H_5)_4CCH_3)Ni(C_5H_5)$ have been examined (144) and the first such species containing a bridging six-membered ligand, i.e., $(C_5R_5)Rh(CH_3B(CH{=}CH)_2\text{-}BCH_3)Rh(C_5R_5)^{2+}$, has been prepared from the corresponding mononuclear species by treatment with CF_3COOH (90).

12 BIOCHEMICAL AND MEDICINAL ASPECTS

A partial synthesis of boromycin (179) as well as the total synthesis and stereochemical identification of the $C_{18}H_{32}O_5$ degradation product thereof (200) have been reported. The biosynthetic pathway leading to boromycin seems to parellel that of aplasmomycin (180).

The antihyperlipidemic activity of amine-cyanoboranes, amine-carboxyboranes, and related compounds has been studied (39); and the inhibition of subtilism by substituted (aryl)-hydroxyboranes has been investigated (128). Gram-negative bacteria can be inhibited by



which blocks the biosynthesis of liposaccharide (171).

An improved monitoring system of neutron flux during boron-neutron capture therapy (135) and a design study of a relevant neutron irradiation facility (218) have been reported.

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