BORON

ANNUAL SURVEY COVERING THE YEAR 1974

PART II

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CONTENTS

Boron. Part II; Annual Survey covering the year 1973 see J. Organometal. Chem., 75(1974)193-261.

As in the past several years, this survey reports on organoboron and related species containing only isolated boron atoms. The only exceptions involve diborane(4) derivatives, which exhibit a similar chemistry. Carborane and typical organoboron hydride chemistry (hydroboration) are reviewed in Part I of this survey. Although the present material is divided into 14 major sections strict adherence to this classification has not been attempted.

1 REVIEWS AND SUMMARIES

A supplementary volume of the GMELIN HANDBUCH DER ANORGANISCHEN CHEMIE entitled "Borverbindungen 1" has been published (11 Its contents comprise three major areas: (a) binary boron-nitroge compounds, particularly boron nitride; (b) polymeric derivatives containing a boron-nitrogen backbone; and (c) boron-nitrogen-carbo heterocyclic systems. This latter part (155 pages) which is of special interest to the organoboron chemist contains an exhaustiv survey of the area up to 1972 and a brief but interesting proposal for the naming of organoboron heterocycles. Despite its high cost, this book is a most certainly worthwhile addition to the library. Another supplement, "Borverbindungen 2", includes an initial description of carborane chemistry (275); a second volume treating large carboranes, heterocarboranes, metallo carboranes, and polyme species will be published later. The descriptive part of this supplement is a comprehensive documentation of small carborane chemistry; however, the 138 pages devoted to "nomenclature and compound types" seem overly lengthy and - at least to the casual reader - confusing and (sometimes) irritating. It should be noted that both cited supplementary volumes deviate (to a degree) from the "normal" GMELIN tradition in their presentation of material which, however, does not diminish the value.

Structural data on various organoboron species studied during the period 1960-1965 are compiled elsewhere (103) and detailed procedures for the analysis of organoboron species have been summarized (104). An article on the reaction chemistry of diborane(6) lists 683 references, many of which deal with organometallic species (144). Mass spectral data on inorganic and organic boron derivatives have been assembled (73) and the abstracts of the papers presented at the Second International Meeting on Boron Chemistry are available (154).

Comprehensive reviews describe structural and bonding aspects of elemental boron and metal borides (251), metalloboranes and metal-boron bonding (260), and the technology of boron derivatives, particularly binary compounds such as boron carbide, metal borides, boron nitride, and also boron whiskers (255). Recent results in boron-sulfur, -selenium, and -tellurium chemistry (252) as well as boron-nitrogen chemistry (253) have been summarized. VOELTER (254) reports on the structures, determination, separation, and applications of carbohydrate-boric acid complexes.

In a review of "organometallic compounds and living organisms" the role of boron derivatives in this area is discussed by citing some 22 references (237). Additional summaries treat metalloboroxanes and related compounds (147) and the chemistry of sugars in boric acid solution (134). The reactions of isonitriles, cyanides, carbon mo oxide and other LEWIS bases with organylboranes have been reviewe in an article listing 71 references (217) and the uses of thexylborane (= 2,3-dimethyl-2-butylborane) as hydroboration agent in organic syntheses have been summarized (324).

2 GENERAL ORGANOBORON-HYDRIDE CHEMISTRY

Methyl sulfide-borane has been suggested as a hydroboration agent since it is a liquid and stable source of BH_3 (136). As an example, the hydroboration/oxidation of alkenes has been describe and was found to be a facile regioselective and stereoselective method for the preparation of the corresponding alcohols. Reducti of aromatic carboxylic acids with methyl sulfide-borane was effect particularly well in the presence of tris(methoxy)borane (314).

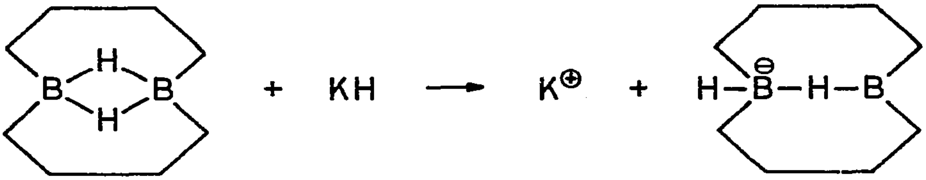
Hydroboration of alkenes with sodium tetrahydroborate and acetic acid in tetrahydrofuran is another new method using the *in situ* formation of BH_3 as hydroboration agent (143); also, poly(4-vinylpyridine-borane) has been suggested as a polymeric reducing agent (202) and chloroborane, dichloroborane, and catechol-borane have been advocated as new hydroborating agents (326).

Of particular interest to the spectroscopist may be the observation that, in the presence of catalytic amounts of $[(C_6H_5)_3P]_3RuHCl$, hydrogen atoms can be exchanged by deuterium at boron atoms but not at carbon atoms (114). The reaction proceeds smoothly at temperatures from 65-100°C with deuterium gas; triphen phosphine-Rh-carborane derivatives can also function as catalysts for this exchange.

The symmetric (C_{2h}) approach of two BH_3 molecules to form B_2H was compared with the unsymmetric (C_s) approach *via* extensive self-consistent field calculations (50); the data indicate a strong preference for the C_{2h} transition state. Simple harmonic force fields of the tetrahydroborate ion, methane, and the ammonium ion have been computed by the FSGO method (227); the calculated main force constants are larger than the values that were determined experimentally.

An improved method for the determination of boron in organoboron species has been described (233) and boron nitride, boron phosphide, and boron oxide have been used for the detection of thermal neutrons (173).

A facile laboratory procedure for the preparation of tetraalkyldiboranes and dimeric 9-borabicyclo(3.3.1)nonane has been described in detail (269). Also, the preparation of a singly hydrogen bridged organoboron anion, $(C_4H_8)_2B_2H_3^{\ominus}$, containing a single transannular hydrogen bridge, has been reported (61); its formation is illustrated by the following equation:



The hydrogen bridge of the ion is resistent to nucleophilic displacement and the structure of the species was confirmed by X-ray diffraction data. The heterocyclic hydridic species $HB(O\text{-}CHCH_3)_2CH_2$ has been obtained by the reaction of diborane(6) with pentane-2,4-diol (187). The same compound is also found along with other products on reaction of acetylacetone with $\left[(\underline{t}\text{-}C_4H_9O)_3Be\right]BH_4$.

The reaction of lithium hydride with (fluoro)dimesitylborane yields, depending on the conditions employed, dimesitylborane or lithium dihydrodimesitylborate (56). The latter salt was initial isolated as its complex with two molecules of solvent, e.g., 1,2-dimethoxyethane. All three of the cited species are crystall materials; the last one shows exceptional stereoselectivity for reduction of ketones. Disiamylborane has been used to hydroborat acetylenic acetals and the reaction was developed to provide a novel synthesis of α-keto ethers and cis-allylic ethers (12). Hydrogen peroxide oxidation of the (not isolated) products formed from aryl halides and diborane(6) in the presence of metallic lithium, potassium, or calcium in tetrahydrofuran yields phenols (236). Presumably, the process occurs via an arylboron intermedia

Vinylborane, $CH_2=CH-BH_2$, has been studied by ab initio calculations (15). The barrier to rotation about the B-C bond was found to be 7.6 kcal/mol and optimized values for the C-C and B-C bond distances were calculated as 1.32 Å and 1.57 Å for the planar molecular form and 1.32 Å and 1.57 Å for the orthogonal species. The latter value is in virtual agreement with the experimentally determined B-C distance of trimethylborane (18).

Decomposition of carbon monoxide-triborane(7) leads to bis(carbon monoxide)-diborane(4), $B_2H_4(CO)_2$ (40). As shown by a X-ray crystal structure study, the latter has a 1,2-disubstituted ethane-like structure in which bond distances and angles appear to be "normal" (distances: B-C, 1.52 Å; B-B, 1.78 Å; C-O, 1.125 Å; B-H, 1.14 Å; $B-H_2$, 1.11 Å). An ab initio molecular orbital calcula on carbon monoxide-borane has shown that among the various electronic configurations of the complex a charge-transfer species plays an essential role (76); the influence of hyperconjugation on the properties of carbon monoxide-borane has been studied by CN/INDO calculations (322).

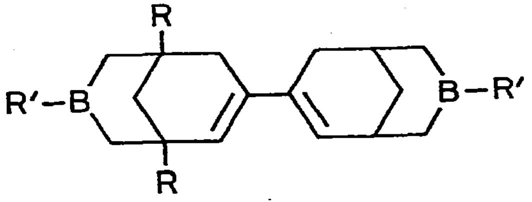
Carbon monoxide-borane reacts with NO at temperatures below -130°C in a redox reaction to yield N_2O, N_2, CO, and boric acid (130); the adduct $H_3B{\cdot}NO$ is formed as an intermediate. Carbon monoxide-borane forms a 1:1 adduct with trimethylamine wherein the nitrogen is bonded to the carbon atom of the CO moiety (329). The adduct is stable at low temperatures but it thermally dissociates into the initial reactants. At still higher temperatures base displacement occurs and trimethylamine-borane is formed. Triethylamine and triphenylphosphine also react with carbon monoxide-borane but pyridine does not. Infrared spectral evidence (288) supports the proposed structure of $H_3B{\cdot}CO{\cdot}N(C_2H_5)_3$. High resolution infrared spectra have also been recorded on $^{11}BD_3{\cdot}CO$ and $^{10}BD_3{\cdot}CO$ but no definite conclusion with respect to the structure of carbon monoxide-borane could be reached on that basis (310).

3 TRIORGANYLBORANES

3.1 Syntheses and Reactions

A facile laboratory procedure for the preparation of triphenylborane has been described in detail (267). (Dialkyl)allylboranes have been prepared via hydroboration reactions using 9-bora-bicyclo(3.3.1)nonane (282) and the reaction of triorganylboranes such as tri-n-propylborane or triallylborane with bicyclo(1.1.0)butane affords butenylboranes, $CH_2{=}CH{-}CHR{-}BR_2$ (42). The latter reaction is highly exothermic and the formation of the unsymmetrical triorganylboranes was confirmed by spectroscopic data although the materials were not actually isolated. Lithium chloropropargylide, $Li{-}C{\equiv}C{-}CH_2Cl$, reacts with trialkylboranes to yield allenic boranes of the type $CH_2{=}C{=}CR{-}BR_2$ (350) and (dialkyl)-allylboranes have been obtained by the reaction of trialkylboranes with allylmagnesium bromide; the resultant materials were identi by elemental analysis and infrared data (142).

Biacetylene reacts with triallylborane or tris(2-methylally borane according to the "usual" allylboron-acetylenic condensati (153); at 120-150°C compounds of type 1 (R = H, R' = CH_2-CH=CH_2; R = CH_3, R' = CH_2-CCH_3=CH_2) are obtained.



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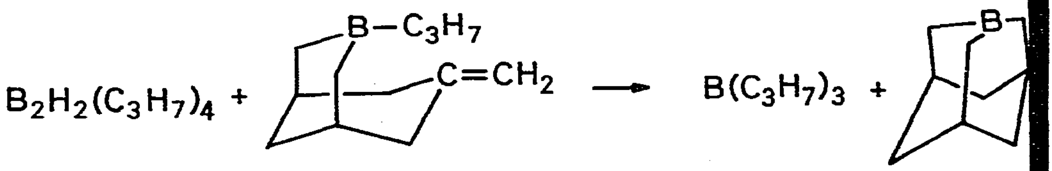
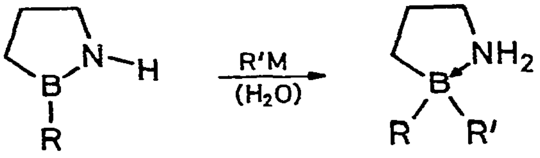
A new procedure for the preparation of 1-boraadamantane involves the reaction of tetra-*n*-propyldiborane(6) with 3-*n*-propyl-7-methylene-3-boracyclo(3.3.1)nonane (151); tri-*n*-propylborane is formed as a byproduct:



The reaction of $(C_2H_5)_2O \cdot BF_3$ with indenyllithium leads to the formation of tris(inden-1-yl)borane (44). The compound exists in the allyl form which, as evidenced by magnetic resonance studies, undergoes a permanent allyl rearrangement at high temperatures. Complex formation of tris(inden-1-yl)borane was observed on treatment of the compound with nitrogen bases such as trimethy amine, diethylamine, or pyridine.

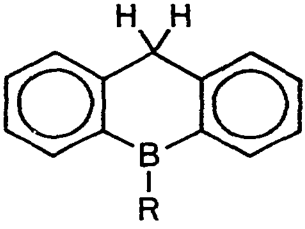
(Dialkyl)methoxyboranes react with organolithium reagents to provide mixed triorganylboranes according to the reaction $R_2BOCH_3 + R'Li \longrightarrow R_2BR' + LiOCH_3$ (148). The desired unsymmetri triorganylborane is formed in high yield and purity in hydrocarbon solvents; the alkali metal alkoxide precipitates.

Treatment of 1,2-azaborolidines with metal alkyls leads to the formation of γ-functional trialkylboranes with an internal coordinate B-N bond (45):



M = MgBr, Li

The preparation of 9-mesityl-9,10-dihydro-9-boraanthracene, 2, has been described in detail. Proton abstraction with organolithium reagents gives the corresponding anion, which was converted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R = mesityl

by reaction with various electrophiles such as D_2O, CO_2, or CH_3I into 10-substituted derivatives of 2. Proton nuclear magnetic resonance and ultraviolet spectra of the various species have been discussed (241). Equilibrium acidities of 9-mesityl-9,10-dihydro-9-boraanthracene and of its 10-phenyl derivative have been determined toward lithium cyclohexylamide in cyclohexylamine. From these data, along with ultraviolet spectroscopic studies, it was concluded that the 9-boraanthracene anion shows aromatic stabilization (216).

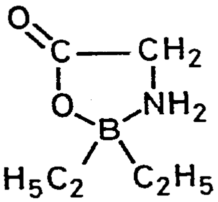
The hydrolysis of linear and cyclic trialkylboranes at room temperature is catalyzed by diethylborylpivalate, $(CH_3)_3C-CO_2-B(C_2H_5)_2$

(256). Cleavage of one boron-carbon bond of the trialkylborane occurs quite readily and bis(dialkylboryl) oxides, $(R_2B)_2O$, can isolated in good yield. Other proton-active materials such as alcohols or amines react with triethylborane in the presence of diethylborylpivalate to provide for O- or N-diethylboronation. The catalytic effect of the diethylborylpivalate has been studie by the reaction of triethylborane with primary alkylamines and a two-step catalytic cycle was formulated (250). The suggested mechanism is supported by the isolation of reaction intermediates in a preparative scale.

Amino acids react with triethylborane to yield O-diethylboryl derivatives (27):

$$HRN-(CH_2)_n-COOH + B(C_2H_5)_3 \longrightarrow C_2H_6 + HRN-(CH_2)_n-CO-O-B(C_2H_5)_2.$$

The speed of this reaction is also catalyzed by diethylborylpivalate. If n = 3 or 5, simultaneous diethylboronation of the amin group can be effected. The lack of N-boronation in the case of n = 1 or 2 may be interpreted as being due to the formation of coordinated cyclic structures such as 3, which may render the nit inactive. The existence of such species is supported by nuclear magnetic resonance data. On the other hand, diethylborylpivalate may deactivate intramolecular coordination to provide for a boronation reaction according to:



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$$(CH_3)_3C-CO-O-B(C_2H_5)_2 + HRN-(CH_2)_n-CO-O-B(C_2H_5)_2 \longrightarrow$$
$$C_2H_6 + (CH_3)_3C-CO-O-BC_2H_5-NR-(CH_2)_n-CO-O-B(C_2H_5)_2.$$

Amino acid esters such as glycine methyl ester react with triethylborane even in the presence of the cited catalyst to form only simple 1:1 adducts.

In the presence of sufficient quantities of diethylborylpivalate, triethylborane may react with amino acids to yield, for example, $(CH_3)_3C\text{-}CO\text{-}O\text{-}BC_2H_5\text{-}NH\text{-}(CH_2)_2\text{-}CO\text{-}O\text{-}BC_2H_5\text{-}O\text{-}CO\text{-}C(CH_3)_3$. Such doubly boronated amino acids are colorless solid materials which probably do not have any intramolecular B-N coordination (27).

Triorganylboranes add across the multiple bond of unsaturated species such as N-benzylidenemtheylamine, N-diethylaminopropyne, or methacrylonitrile (185). Addition of the dialkylboron moiety occurs at the most electron-rich site, e.g.:

$$CH_2{=}CCH_3\text{-}CN + BR_3 \longrightarrow CH_2{=}CCH_3\text{-}CR{=}N\text{-}BR_2.$$

However, reaction of these same organic molecules with boron trichloride leads mostly to simple adducts:

$$CH_2{=}CCH_3\text{-}CN + BCl_3 \longrightarrow CH_2{=}CCH_3\text{-}CN\cdot BCl_3.$$

Trialkylboranes react with carbon monoxide in the presence of excess ethylene glycol to yield cyclic glycol esters of trialkylcarbonylboric acids (152). Addition of small amounts of metallic sodium to the reaction mixture appears to change the direction of the reaction (mechanism?) affording secondary alcohols by decomposition of the carbonylation product.

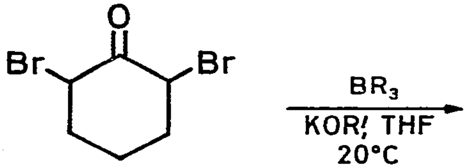
Additional work on the free radical reaction of organylboranes with α,β-unsaturated ketones leading to (vinyloxy)boranes has now been shown to provide a ready means of preparing α-bromoketones (58). In this procedure, the (vinyloxy)borane is brominated and subsequently is treated with methanol. The overall reaction can be summarized as follows:

$$BR_3 + CH_2{=}CH{-}CO{-}CH_3 \xrightarrow{O_2} RCH_2{-}CH{=}CCH_3{-}O{-}BR_2 \xrightarrow{Br_2}$$

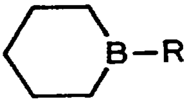
$$RCH_2{-}CHBr{-}CBrCH_3{-}O{-}BR_2 \xrightarrow[(H_2O)]{CH_3OH} RCH_2{-}CHBr{-}CO{-}CH_3.$$

The intermediate products need not to be isolated. In the presenc of base triorganylboranes react with α,β-dibromoketones by attack of bromine on the initial ketone-borane adduct (228). This step is followed by the rate-determining transfer of an organyl group from boron to carbon.

The α-position of B-isopropyl-9-borabicyclo(3.3.1)nonane is activated by the boron moiety to an even greater extent than by a phenyl group as is evidenced by competitive bromination (57). Thi feature makes it possible to synthesize and isolate α-bromoalkyl derivatives and to employ them in syntheses. The reaction of α,α'-dibromoketones with triorganylboranes can be used to prepare monoalkylated ketones (8); this is illustrated in the following scheme:



Six-membered boracyclanes of type 4 when treated with bromin in the presence of water undergo a ring contraction to produce the corresponding five-membered carbocyclic compound (191). Trialkylboranes react with α-bromosulfenyl compounds in the presence



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of potassium t-butoxide to yield the corresponding α-alkylated sulfenyl derivatives (135):

$$BR_3 + BrCH_2SO_2Y \xrightarrow{KOC_4H_9} RCH_2SO_2Y.$$

γ,γ-Dimethylallylamines isomerize under the influence of tributylborane (96); also, the reaction of tributylborane with ethers containing a γ,γ-dimethylallyl group has been studied (212). Triallylboranes react with ethyldiazoacetate in tetrahydrofuran at low temperatures to produce, after hydrolysis of the reaction mixture, the esters of γ,δ-unsaturated acids (180); this reaction is similar to that of trialkylboranes (182). The oxygen induced 1,4-addition reaction of organylboranes to croton aldimine has been described (208). The reaction of styryl sulfoxides or sulfanes with trialkylboranes provides for ready access to β-alkylated styrene (291). Trialkylboranes have been used to prepare tertiary alcohols (341) and the anodic oxidation of trialkylboranes using graphite as the anode seems to proceed through a carbonium ion mechanism (302). The copolymerization of vinylhydroquinone and acrylonitrile by tributylborane has been described (206).

The trialkylboranes $B[CH_2-Si(CH_3)_2-O-Si(CH_3)_3]_3$ and $B[CH_2-Si(CH_3)_2-O-Si(CH_3)_2-C_6H_5]_3$ undergo a base-catalyzed β-elimination which appears to generate 1-silaethylene species (273).

3.2 Physicochemical Studies

The vibrational spectrum of trivinylborane has been recorded (1,64). The spectrum was assigned on the basis of a planar (C_{3h}) symmetry and the data were interpreted as evidence for the presence of B-C π-bonding (64). Two conformers seem to exist in the liquid state (1) but only one planar species is observed in the solid material. A complete vibrational assignment has been given for the molecule in the solid state (1). Also, the photoelectron and ultraviolet spectra of trimethylborane, (fluoro)dimethylborane, and (dimethylamino)dimethylborane have been recorded and were assigne (335).

The structure of triphenylborane has been determined by X-ra diffraction studies (150). No intermolecular interaction was observed and the phenyl groups were found to be tilted about 30^{o} with respect to the BC_3 valence plane. A two-ring flip mechanism is supposedly the threshold mechanism for the stereoisomerizatio of triarylboranes (331).

The trimethylborane exchange with trimethylphosphine-trimeth borane is first order in complex concentration (188); this observ ation is consistent with a dissociative mechanism.

Chemical shifts in carbon-13 nuclear magnetic resonance spectra of tetraalkylammonium ions, tetraalkylborate ions, and trialkylboranes correlate linearly with the shifts calculated fo the corresponding isoelectronic hydrocarbons (34). Also, additiv substituent effects on chemical shifts for charged and neutral boron were clarified and it was found that aromatic solvent induc shifts of tetraalkylammonium tetraalkylborates are smaller (in pp in carbon-13 spectra than in proton nuclear magnetic resonance spectra.

4 HALOBORANES

Detailed procedures have been described for the facile laboratory preparation of (chloro)diethylborane and (chloro)diphenylborane (270). (Alkenyl)dichloroboranes may be prepared by t hydroboration of alkynes with dichloroborane-etherate; the reaction is initiated by boron trichloride and proceeds cleanly with virtually no formation of byproducts (15).

Ferrocene reacts with boron triiodide at 10°C in benzene to form a precipitate of (ferrocenyl)diiodoborane (17). Additional interaction of the latter with boron triiodide provides for the boronation of the second cyclopentadienyl ring. Both of the boronated compounds are susceptible to halogen exchange and the corresponding chlorine and bromine derivatives have been prepared using this latter procedure.

Thermal degradation of 1,2-bis(dichloroboryl)ethane gives a white solid of the composition $(BCl)_6(CH)_4$ in low yield (243). On the basis of mass, proton magnetic resonance, and Raman spectroscopic data an adamantane-like structure was assigned to the material. Methylation of the compound with tetramethyltin gives the B-methyl derivative, which is identical with the species obtained by the pyrolysis of trimethylborane (244). Also, the exchange of boron bonded chlorine by bromine via treatment of $(BCl)_6(CH)_4$ with boron tribromide has been described (243). The reaction of (dialkyl)chloroboranes with lithium aldimines can be used for the synthesis of unsymmetrical ketones (54).

The vibrational spectrum of (ethynyl)difluoroborane and that of (ethynyl)dichloroborane have been studied (174); B-F valence absorptions were assigned at 1292 and 1390 cm^{-1}, B-Cl stretching modes at 960 and 1076 cm^{-1}, and $\nu(BC)$ was found near 740 (fluorine derivative) and 498 cm^{-1} (chlorine derivative), respectively.

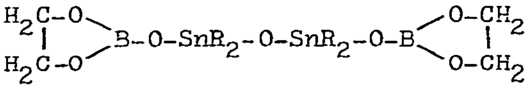
Chemical shift data have been used to establish the relative acidities of a series of haloboranes which were found to decrease in the order $BCl_3 > (C_2F_3)BCl_2 > (C_2F_3)_2BCl > B(C_2F_3)_3 > BF_3$ (5). A study of the microwave, Raman, and infrared spectrum of (vinyl)difluoroborane indicates that the molecule is planar (41) it has an experimentally determined total dipole moment of 1.74 Assignment of the fundamental vibrations suggests B-C stretching to occur at 766 cm^{-1} and ν(C=C) at 1624 cm^{-1}; B-F stretching mod were assigned at 1373 and 1316 cm^{-1}, respectively. The Raman, infrared, and proton magnetic resonance spectra of (X = F, Cl) $X_2B\text{-}CH_2\text{-}CH_2\text{-}BX_2$ and $X_2B\text{-}CH{=}CH\text{-}BX_2$ have been recorded. The proton magnetic resonance spectrum suggest the existence of a dipolar species $Cl_2B\text{-}\overset{\ominus}{C}H\text{-}CH{=}\overset{\ominus}{B}Cl_2$, and the vibrational data indicate a cis modification for the molecule which converts to a trans species prolonged standing.

The microwave spectrum of $F_2B\text{-}SiF_3$ indicates a B-Si bond length that is larger than that expected for a single bond (168); this observation is consistent with the extremely low value for the barrier to internal rotation about this bond.

5 ORGANOBORON-OXYGEN SYSTEMS

5.1 Compounds Containing a BO_3 Moiety and Related Systems

Boric acid reacts with trialkyltin hydroxides or bis(trialkyltin) oxides to yield tris(trialkylstannyloxy)boranes, $B(OSnR_3)$ (35). The latter interact with boric anhydride to form the corresponding boroxines, $(\text{-}BOSnR_3\text{-}O\text{-})_3$. Dialkyltin oxides and pyr borate (or boric acid) react with glycol to yield 1,3-bis(boryloxy)tetraalkyldistannoxanes, 5 (36). All stannyloxyboranes are



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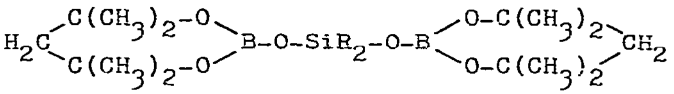
quite sensitive to moisture. 2-(Trimethylsilyloxy)-1,3,2-dioxaborolanes and -dioxaborinanes have been prepared by the reaction of the corresponding trialkyltin or trialkylgermanium derivatives with (trimethyl)chlorosilane (22). Using (dimethyl)dichlorosilane, borosiloxanes such as 6 are obtained by an analogous procedure.



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The silyloxyboranes are colorless but moisture sensitive materials; the proton magnetic resonance spectra of the liquids are consistent with the suggested structures.

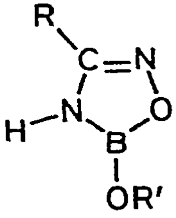
Various 2-substituted 1,3,5,2-oxadiazaborols, 7, have been prepared by

(a) the reaction of the appropriate bis(triorganyltin) oxide with boric aicd and an amidoxime,

(b) by the reaction of 7 (R' = H) with R_3SnCl in the presence of a tertiary amine, or

(c) by a similar procedure based on the reaction of 2,2'-oxybis(1,3,5,2-oxadiazaboroles and R_3SiCl or $(R_3Sn)_2O$.

All compounds of type 7 are monomeric in benzene and are moisture sensitive; selected infrared data have been presented (242).



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R = CH_3, C_2H_5, C_3H_7, C_6H_5

R' = $Sn(C_4H_9)_3$, $Sn(C_6H_5)_3$, $Si(CH_3)_3$

Tris(pentafluorotelluryloxy)borane, $B(OTeF_5)_3$, is readily obtained by the reaction of boron trichloride with pentafluoroorthotelluric acid (60). The compound is thermally stable up to 140°C and forms 1:1 adducts with donor molecules such as pyridine or acetonitrile. A modified procedure has been described for the preparation of triacetylborate, $B(O\text{-}CO\text{-}CH_3)_3$ (351) and tris(alkoxy)boranes were found to react with N,N-diethylhydroxylamine to give *O*-diethylamino derivatives of the type $B(OR)_n[ON(C_2H_5)_2]_{3-n}$ ($n = 2,3$) (230).

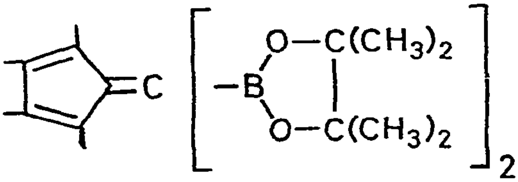
The CO bonds in straight chain tris(organyloxy)boranes cleav when subjected to electron bombardment, whereas tris(sec. alkyloxy)boranes undergo α-cleavage reactions under the same condition (231). Both types of fragmentation are observed for cyclic specie and the B-O bond was found to be remarkably stable to electron impact. 2-Phenyl-1,3,2-dioxaborolanes undergo rearrangements indu by electron impact to form hydrocarbon ions (234).

5.2 (Organyl)oxyboranes

Arylmercury halides react with BH_3 in tetrahydrofuran soluti to yield a material which, on hydrolysis, affords (aryl)dihydroxyboranes (284). Linear and cyclic 2-unsaturated (organyl)oxyborane of the backbone $C{=}C\text{-}C\text{-}B(OR)_2$ or $C{\equiv}C\text{-}C\text{-}B(OR)_2$ have been prepared by conventional organometallic syntheses (272). The final structu of the boron-bonded carbon framework is related to a tetracoordina metal borate intermediate; various intermolecular rearrangement and ligand exchange reactions as well as reactions with carbonyl compounds of the cited species were studied. (But-1-en-3-yl)(dimethylamino)methoxyborane and (but-1-en-3-yl)bis(dimethylamino)borane have been prepared by conventional organometallic syntheses

(16). Both species, which are examples of α-methylallylboranes, were found to be inert to allylic rearrangement at ambient temperatures.

Continuing their studies with tetrakis(dimethoxyboryl)methane MATTESON and coworkers reacted $C[B(OCH_3)_2]_4$· with pinacol to produce the corresponding pinacol ester (79). This ester reacts with alkyllithium to form the corresponding triboryl methide anion, which can be converted by treatment with bromine to give the bromomethanetriboronic ester. Further abstraction of a oxyboryl group and subsequent bromination leads to the dibromodiboronic ester, whereas reaction with triphenyltin chloride gives $(C_6H_5)_3Sn\text{-}CBr\text{-}[B(O\text{-}CR_2\text{-})_2]$. Similarly, the reaction of the triboryl methide ion with (trimethyl)-chlorosilane produces the corresponding $Si(CH_3)_3$ derivative and the reaction with tetraphenylcyclopentadienone gives the expected fulvene <u>8</u> <u>via</u> β-elimination (81).



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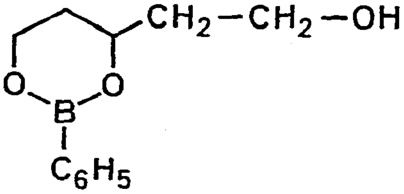
The triboryl methide ions condense readily with ketones, acetaldehyde or benzaldehyde in a general reaction (80); with ketones, R'_2CO, derivatives of the type $R'_2C{=}C[B(O\text{-}R)_2]_2$ are formed. These alkene-1,1-diboronic esters appear to be quite versatile synthetic intermediates (80).

Esters of glycerol and other triols with the $C_6H_5BO_2$ moiety usually form mixtures of isomers, the individual abundance of which is related to conformational effects (298). Pentane-1,3,5-triol, however, reacts with (dihydroxy)phenylborane with the exclusive formation of 9 (301). Derivatives of sugars such as D-glucose or D-fructose containing the RBO_2 moiety (R = n-C_4H_9, C_6H_5) have been prepared by a condensation reaction (343); ν(BO) of these species was assigned in the 1310-1360 cm^{-1} region and the diester show a strong resistance to fragmentation under electron impact. Phenyl(or butyl)oxyboron-oxygen derivatives obtained by the interaction of arabinose or xylose with (dihydroxy)organylboranes are 1,2:3,4 and 1,2:3,5 diboronic esters, respectively (300).

Syntheses and properties of 2-substituted 4H-1,3,2-benzodioxaborinanes, 10, have been described (70). Mass spectral data indicate the facile loss of one hydrogen at the 4-position of the species and the resultant ions may have substantial heteroaromati character. Assignments of ν(BO) and ν(BN) near 1235-1325 cm^{-1} and 1500-1525 cm^{-1}, respectively, have been suggested.



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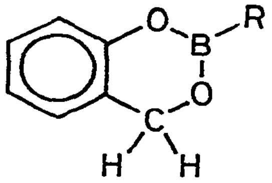

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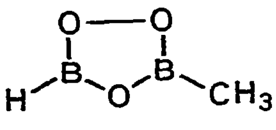
Methyldiborane(6) and oxygen react at temperatures above 150°C to yield the unsymmetrically substituted 2-methyl-1,3,4-trioxadiborolane 11 as one of the major products. The compound was



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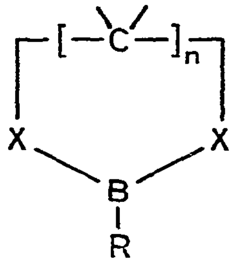
identified by mass spectroscopic data and by the observation of two infrared absorptions at 2628 and 883 cm^{-1}, respectively, which were assigned to ν(BH) and the B-H out-of-plane deformation (138).

The bromine in (α-bromo-*p*-tolyl)boroxine is highly reactive towards triethylamine or hexamethylenetetramine (139). This feature has been utilized for the preparation of derivatives of (dihydroxy)-*p*-tolylborane containing a primary amino group or a trialkylammonium function in the aliphatic moiety. The interaction of triphenylboroxine, $(-BC_6H_5-O-)_3$, with vicinal aminoalcohols leads to cyclic N-B-O-C species (299). In the case of a *cis* aminoalcohol grouping, the 2-phenyl-1,3,2-oxazaborolidine ring is formed, whereas a *trans* grouping leads to 2,4-diphenyl-1,3,5-dioxaza-2,4-diborepine systems. Also, a number of heterocyclic species of types 12 and 13 have been prepared. These compounds will form LEWIS acid-base type adducts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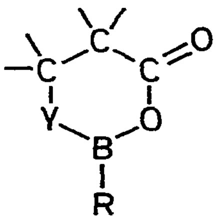
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R = Br, CH_3, C_6H_5
n = 2, 3
X = O, S
Y = C, NH

with cyclic nitrogen bases such as pyridine, picoline, or collidine if the annular carbon atoms are simultaneously part of an aromatic system or if a carbonyl group is incorporated into the heterocycle. Enthalpies of the acid-base interactions have been measured and an attempt has been made to correlate such enthalpies with the LEWIS acidity of the boron atom in the various compounds. Mass spectral data on heterocycles of type <u>12</u> with either amino or alkylthio gr as exocyclic boron substituents indicate that the cyclic boronium ions resulting from electron impact can exhibit considerable stability (62). Boron substituted 1,3,2-oxathiaborinanes are ther stable liquids which are, however, sensitive to hydrolysis (186). The B-S stretching frequency in these compounds was tentatively assigned in the 940-1000 cm^{-1} region.

The photoelectron spectra of (methoxy)boranes and (methylthi boranes of the type $(CH_3X)_nB(CH_3)_{3-n}$ with X = O or S have been compared (133); in conjunction with the boron-11 nuclear magnetic resonance spectra of the compounds, the data have been interprete to indicate a noticeable π-contribution in the B-S bond. ZAHRUDNIK and MATOUSEK (97) have reported on the electronic structure of 1,3,2-trioxadiborolane and the corresponding 1,3,4-trithiadiborola

Treatment of (diorganyl)organyloxyboranes, R_2BOR', with α,α-dichloromethyl methyl ether yields (β-chloroorganyl)organylmethoxyboranes in a base induced reaction (74):

$$R_2BOR' + Cl_2CH\text{-}O\text{-}CH_3 \longrightarrow R_2ClC\text{-}BOCH_3\text{-}OR'.$$

Mild thermal treatment of (α-chloroorganyl)dimethoxyboranes result in a novel α-elimination (313) and may be used as a novel synthesi for olefins according to:

$$R_2ClC\text{-}B(OCH_3)_2 \longrightarrow ClB(OCH_3)_2 + R\text{-}CH{=}CH\text{-}R.$$

The reaction of 2-chloro-1,3,2-dioxaborolane or -dioxaborinanes with bis(trimethylsilyl)amine or tris(trimethylsilyl)ami proceeds <u>via</u> the expected cleavage of the boron-halogen bond and formation of a B-aminosilylated species (94). It is of interest to note that the 2-bis(trimethylsilyl)amino derivatives can underg a second silazane cleavage reaction with the formation of (diboryl)-(trimethylsilyl)amines, though considerable quantities of polymeric byproducts are also formed in this instance.

NOZAKURA and KIDA (323) report the synthesis and polymerization of (phenyl)vinyloxyboranes; the GLC assay of sorbitol in the form of cyclic (n-butyl)oxyboranes has been described (315). Tris(i-propyl)boroxine, $(-BC_3H_7-O-)_3$, can be used as a reducing agent for substituted benzaldehydes (284). (Dialkoxy)allylboranes react with aldehydes or ketones to give unsymmetrical tri(organyloxy)boranes (238,239):

$$R'B(OR)_2 + OC= \longrightarrow =CR'-O-B(OR)_2.$$

With sterically unhindered carbonyl compounds, the reaction proceeds with propargyl-allenyl rearrangement (238). In the case of ketones, however, acetone, acetophenone, or cyclohexanone give only acetylenic derivatives; all other ketones studied give mixtures of acetylenic and allenic derivatives (239).

(Alkoxy)difluoroboranes form 1:1 addition compounds with amines (L) at low temperature. At temperatures above -30°C ligand exchange occurs with the formation of $L \cdot BF_3$ and tris(alkoxy)boranes (118).

5.3 Peroxyboranes

The oxidation of tri-n-propylborane with hydroperoxides results in the formation of a complex mixture of products (141). The nature of these products suggests a free radical mechanism for the process which may be initiated by the formation of an unstable donor-acceptor complex. Evidence for a free radical mechanism in the reaction of triorganylboranes with $(RO)_2B-O-OR'$ or $(RO)_2B-O-O-B(OR)_2$ has also been presented (356). Bis(alkoxy)chloroboranes, $ClB(OR)_2$, with R =

C_3H_7 or C_4H_9, react with hydrogen peroxide in ether to give the corresponding organoboron peroxides (49):

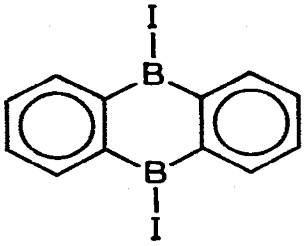
$$2\ ClB(OR)_2 + H_2O_2 \longrightarrow (RO)_2B-O-O-B(OR)_2 + 2\ HCl.$$

Thermal decomposition of these peroxides seems to occur *via* a free radical mechanism in which the initial stage is the homolytic cleavage of the oxygen-oxygen bond.

Several new peroxyboron derivatives, *i.e.*, (alkoxy)alkyl-(α,α-dimethylbenzyldioxy)boranes, have been prepared by the reacti of (alkoxy)alkylchloroboranes with sodium α,α-dimethylbenzyl peroxide (140). Thermal decomposition of these organoboron peroxides follows first order kinetics and the temperature dependence of the rate constant K conforms to the ARRHENIUS equation. The main cours of the decomposition seems to include an intramolecular rearrangem wherein an alkyl group migrates from a boron to an oxygen atom; subsequently, homolytic cleavage of the oxygen-oxygen bond occurs.

6 BORON-SULFUR AND BORON-SELENIUM COMPOUNDS

Boron triiodide reacts with 1,3- or 1,4-diiodobenzene to yiel the corresponding bis(diiodoboryl)benzene but the reaction of 1,2-diiodobenzene or 3,4-diiodothiophene with BI_3 leads to the polycyclic systems 14 and 15, respectively (31,360). Either of the two latter compounds can then be reacted with $(-BI-S-)_3$ under mild conditions to yield 16 or 17, respectively; 16 has also been been obtained from the reaction of 1,2-diiodobenzene with BI_3 and elemental sulfur. When 15 is reacted with $CH_3-S-S-CH_3$, 18 is obtained in a clean reaction. The B-S-B bridge in 16 to 18 and other boron-substituted derivatives thereof is readily cleaved, *e.g.*, with secondary amines to give 19, with primary amines to yield 20, and with hydrazines to yield 21 (31). 1-Diiodoborylnaph-



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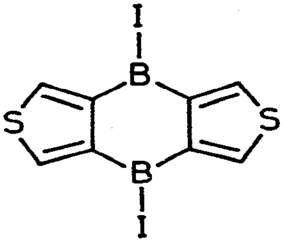

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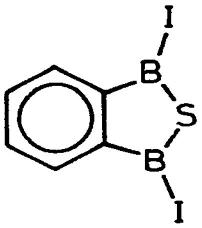

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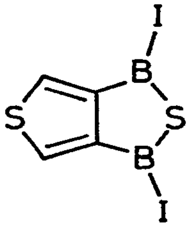

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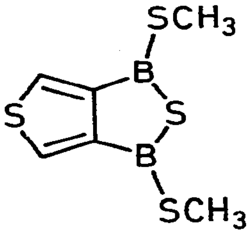

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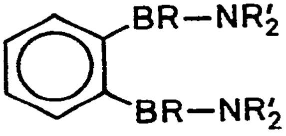

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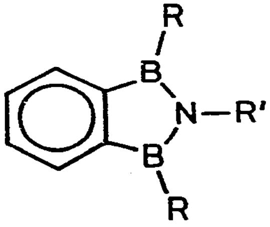

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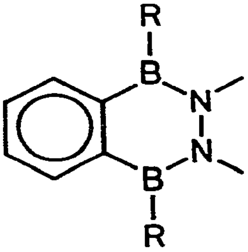

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thalene was found to react with (-BI-S-)$_3$ to yield a naphthathiodiborole derivative analogous to *16* (360).

(Dihalo)organylboranes react with di-*t*-butylsulfane to yield the *t*-butyl halide and the corresponding borthiine (126):

$$3\ RBX_2 + 3\ R'_2S \longrightarrow (-BR-S-)_3 + 6\ R'X.$$

Mass spectral data seem to indicate a considerable stability (?) for triphenylborthiine, (-BC$_6$H$_5$-S-)$_3$, which could be due to charg delocalization within the boron-sulfur ring (190). The thermodyna stability of trihaloborthiines, (-BX-S-)$_3$ with X = Cl, Br, or I, greater than is normally assumed and the compounds can be purifie by sublimation without decomposition (219). They crystallize in t monoclinic system and their vibrational spectra were compared wit those of (-BSH-S-)$_3$ and (-BSD-S-)$_3$; B-S ring stretching vibration were assigned in the 850-1000 cm^{-1} region. A redetermination of t crystal structure of tribromoborthiine, (-BBr-S-)$_3$, gave the foll mean values for bond distances and annular angles: B-S = 1.807 Å, B-Br = 1.895 Å, angle B-S-B = 109.2°, angle S-B-S = 130.7° (359).

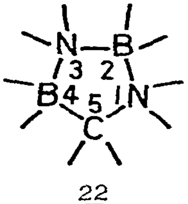
Vibrational spectroscopic data on B(SH)$_3$ and XB(SH)$_2$ (X = Br and their deuterated analogs have been collected (307). The speci have an essentially planar skeleton and ν(BS) is assigned in the 880-990 cm^{-1} region. Extended HÜCKEL calculations on (hydrothio)di boranes, HSBX$_2$ with X = Cl, Br, I, have given values in the order of 28 kcal/mol for the barrier to internal rotation about the B-S bond in these species (131). Calculations on these same molecules by the CNDO/2 method yield much lower values (by a facto of about ten); they are, however, in better agreement with the experimental data. *Ab initio* calculations of the barrier to interna rotation for HSBH$_2$ have shown (312) that the B-S distance calculat for a planar model agrees with that which was experimentally determined for the corresponding methylated derivative. The calculated rotational barrier of about 20 kcal/mol suggests a fairly strong B-S π-bonding; calculations on the basis of an orthogonal molecule disclose a weakening of the B-S bond strength and a decrease of the rotational barrier to about 10 kcal/mol.

The ZEEMAN microwave spectrum of HBS has been recorded on a flow system comprising H_2S gas passed over boron at ca. 1100°C; molecular magnetic data were also reported (218). Computed molecular properties of the ground state of HBS (303) were found to be in reasonable agreement with the experimental data and the photoelectron spectrum of the species (304) indicates that the highest occupied molecular orbital is essentially non bonding and is localized at the sulfur atom.

Adducts of pyridine with (methyl)methylthioboranes $R_nB(SR)_{3-n}$ ($R = CH_3$) are more stable than the corresponding adducts of trimethylamine (279). The pyridine adducts react with CH_2Cl_2 to form boronium salts such as $[R_2B(C_5H_5N)_2]Cl$; their formation depends on the dissociation of the amine-boranes and the nucleophilic displacement of CH_3S groups followed by S_N2 substitution at the carbon atom of the dichloromethane.

Dimethyltin selenide reacts with (iodo)diorganylboranes to yield compounds of the type R_2B-Se-BR_2 (361). If $R = C_6H_{11}$ or C_6H_5, the diborylselenanes are thermally stable and can be isolated; however, if $R = CH_3$ or C_4H_9, the products readily decompose to polymeric $(RBSe)_n$ species. Routes to the diboryldiselenanes, R_2B-Se-Se-BR_2, involve the reaction of $(C_5H_5)_2TiSe_5$ with R_2BI or the interaction of a cyclic borolane with elemental selenium. At elevated temperatures the diboryldiselenanes decompose to yield triorganylboranes and triselenadiborolanes (361).

As representative of a novel type of B-N-C heterocycle, the 1,1,3,3-tetramethyl derivative of the 1,3-diazonia-2,4-diborato-cyclopentane system 22 has been prepared (334). The compound is isomeric with the cyclic adduct formed from (dimethylamino)dimethylborane and (dimethylamino)methylborane (338) and



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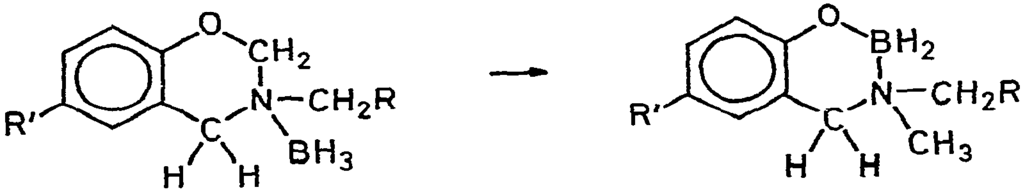
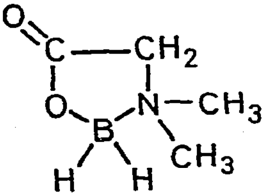
structurally links the cyclic dimeric aminoboranes with the six-membered 1,4-diazonia-2,5-diboratocyclohexane species (339).

Thermal treatment of amine-borane type adducts of 3,4-dihydro-2H-1,3-benzoxazines provides (4H)-1-oxa-3-azonia-2-boranaphthalenes as shown in the following scheme (69):



The structure of the reaction products was confirmed by nuclear magnetic resonance and infrared data.

The cyclic borane 23 is an intermediate in the hydrolysis of the (ethyl dimethylglycine)trimethylamine-boron(1+) cation (340). It can be methylated at the annular methylene carbon atom. Cyclization displacements in borane cations (boronium ions) with iodine and/or trimethylamine leaving groups as well as borane cleavage of amino acid esters lead to various similar five- or six-membered heterocycles (111). These can formally be considered as cyclized amino acid-boranes, which have now been studied in detail (111); 24 was found to be a novel strong base. Also, O-diethylborylated amino acids exists in analogous coordinated cyclic structures (27).



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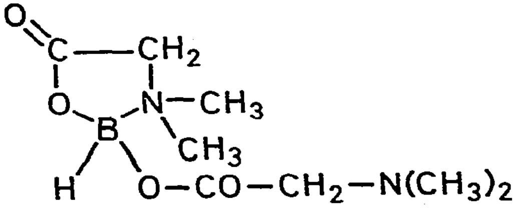

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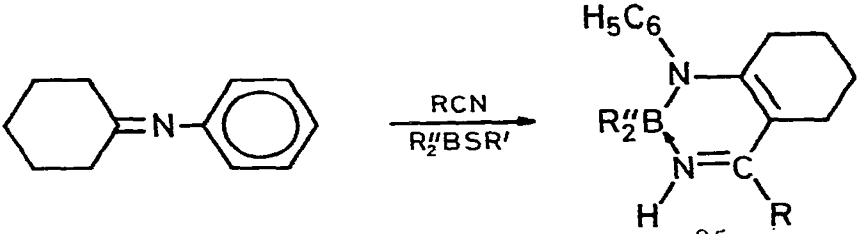
(Dialkyl)alkylthioboranes react with cyclohexanone anil and aliphatic nitriles to form aminoborane chelates of type 25 (179):



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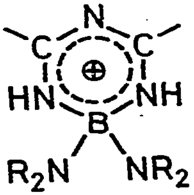
Species of type 25 can undergo hydrolytic cleavage and condensation to yield acridine derivatives. Biguanidides react with tris(diethylamino)borane to form chelates of type 26 (229) and lactic acid gives a 1:1 complex with (dihydroxy)phenylborane (349) which was formulated as 27.



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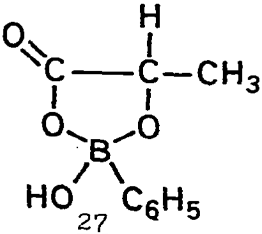

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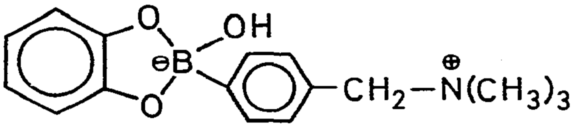
The cyclic dipolar complex 28, derived from *o*-phenylene-α-amino-*p*-toluene borate, is stable in aqueous solution (159).



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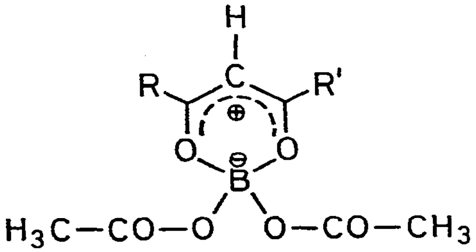
Boroacetate complexes of various β-diketones, 29, and β-keto esters have been prepared (224). The infrared spectra of these materials show good agreement with previous assignments for simil complexes. Ultraviolet absorption maxima and chemical shift data of 2-H can be correlated, in most cases, with the electronic natu of the substituents R and R'.



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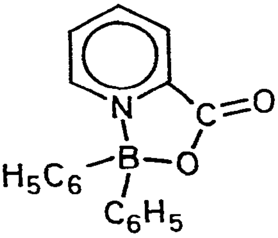
Anionic dinuclear complexes containing two tetracoordinate boron atoms with two xylitol molecules are obtained from the reaction of boric acid with xylitol in water/alcohol. The structure of the species and several salts thereof was determined by infrared spectroscopy, thermogravimetric analysis, and cryoscopic measurements (184).

Complexes of boric acid with 2,2-bis(hydroxymethyl)-3-methyl-1-butanol (trimethylisobutane borates) have been described (195) and the thermal decomposition of pentaerythrol borates has been studied (162). The extraction of boric acid with 1,3-nonanediol occurs *via* borate formation (161).

The nuclear magnetic resonance spectra of some methriol and ethriol borates have been recorded (160) and the electrolytic conductivity of methanol solutions of boric acid complexes with methriol and trimethylisobutane have been investigated (316). The double tridentate complex of triquinoyl with boric acid is strongly acidic and the dipotassium salt thereof is almost water insoluble (290).

The formation of borate and diphenylborate complexes of polyhydroxy compounds has been studied by carbon-13 nuclear magnetic resonance spectroscopy (286). Carbon-13/boron-11 coupling does not seem to occur and the spectra of complexes of sugars containing the $BO_4^\ominus$ moiety are broadened due to the presence of multiple species.

The mass spectra of boron chelates with pyridine and quinoline derivatives of the types 30 and 31 have been discussed (132). In aqueous solution (3-pyridyl)dihydroxyborane and (4-pyridyl)dihydroxyborane exist predominantly in the pyridiniumborate form (233). These acids are thermally stable but decompose on treatment with methyl iodide; a photo induced deboronation to give pyridine and borate occurs in neutral or slightly basic solution (233).



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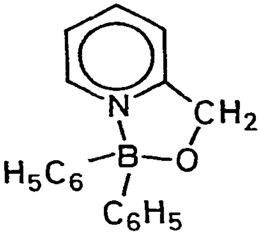

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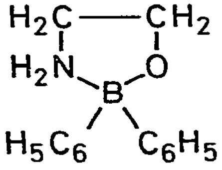
B,*B*-Diphenylboroxazolidine, 32, exists in a half-chair conformation (248). The X-ray study of the molecule provided the following distances: B-C = 1.611 Å, B-N = 1.653 Å, B-O = 1.484 Å. Annular angles range from 99.7 to 110.1°. The crystal and molecular structure of the corresponding *B*,*B*-bis(*p*-fluorophenyl) derivativ has also been determined by X-ray diffraction (247). The B-N bon (1.652 Å) is somewhat longer than the B-C bond (1.618 Å) and the B-O distance was found to be 1.471 Å; the O-B-N angle is 99.9° and the angle B-O-C is 108°. The five-membered ring of 33 was fo



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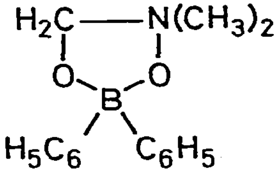
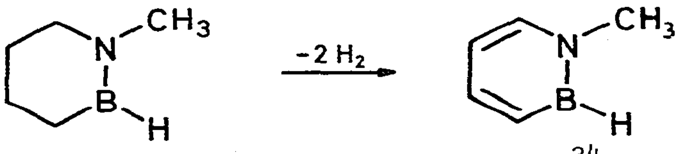


33

to be distorted to a half-chair configuration with the distances B-O = 1.506 Å and B-C = 1.632 Å (294). The angle O-B-O is 107°. In the triethanolamine complex $B(OCH_2CH_2)_3N$ the boron is tetrahedrally surrounded by the three oxygen and the one nitrogen atom the B-O bond distances are 1.431, 1.432, and 1.475 Å, respectivel and the B-N distance is 1.693 Å (129); there exists no hydrogen bonding between individual complexes.

8 BORON-NITROGEN-CARBON HETEROCYCLES

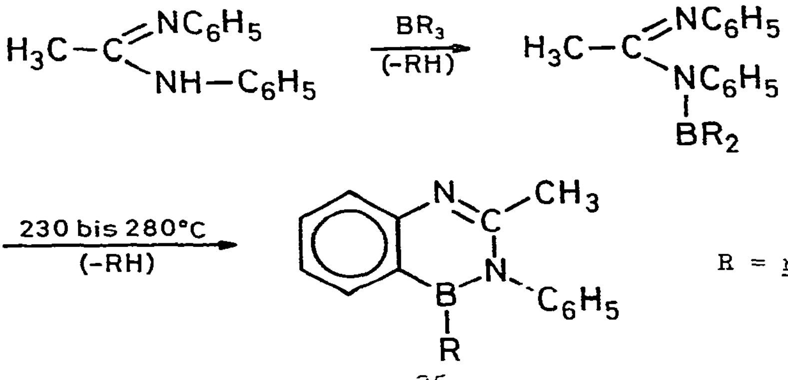
The B-N bond of 1,2-azaborolidines is readily cleaved by treatment with metal alkyls (45); advantage can be taken of this characteristic in preparing γ-functional triorganylboranes. Dehyd



34

genation of N-methyl-tetrahydro-2,1-borazarene gives N-methyl-2,1-borazarene, 34, as an unstable intermediate, which could not be isolated but was identified by mass spectroscopic data and the observation of a B-N stretching frequency at 1620 cm^{-1} (32).

Refluxing a mixture of N,N-diphenylacetamidine and tri-n-propyl borane in tetrahydrofuran yields N-di-n-propylboryl-N,N'-diphenylacetamidine (181). Pyrolysis of the associated (probably dimeric) compound gives a boron-containing analog of 3,4-dihydroquinazoline, 35, as illustrated in the following sequence:



R = n-C_3H_7

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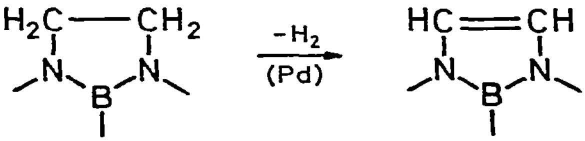
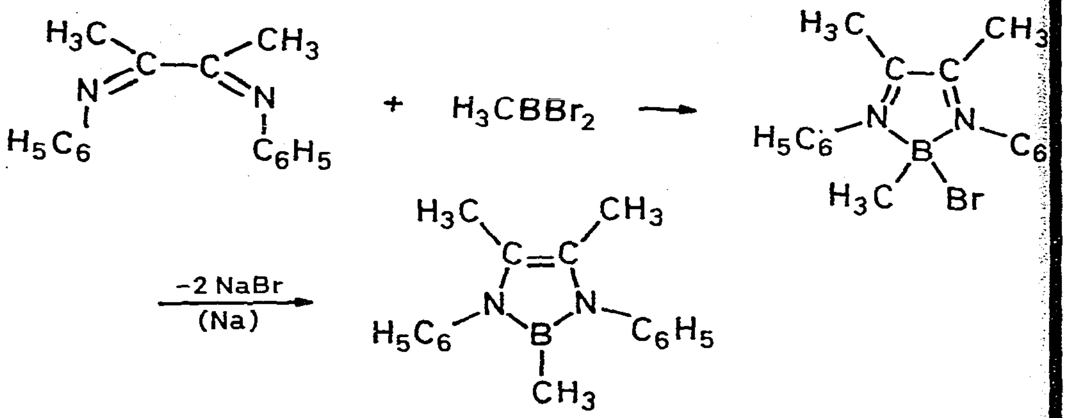
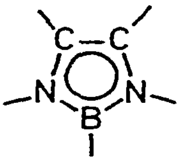
The structure of the final product was established by elemental analysis and infrared, nuclear magnetic resonance, and mass spectral data.The synthesis of 1,3,2-diazaborolines by the catalytic dehydrogenation of 1,3,2-diazaborolidines according to:



has now been described in detail (25). As an alternate route to the unsaturated five-membered heterocycle it was found that the reaction of diacetyldianil with (dibromo)methylborane gives a boronium salt (198), which is readily reduced with sodium amalgam as illustrated in the following reaction sequence:



Boron-11 and nitrogen-14 nuclear magnetic resonance data indicate a decrease in the electron density about nitrogen and an increase about boron for the 1,3,2-diazaboroline system (25). Ultraviolet spectroscopic studies in conjunction with molecular orbital calculations support the concept of extensive electron delocalizati within this ring, which is isoelectronic with the cyclopentadieni anion. On this basis, the heterocycle can be considered as a pseud aromatic system, 36 (25). This assumption is further substantiated by a comparison the the He(I) photoelectron spectra of 1,3,2-diazaborolidines with those of 1,3,2-diazaborolines (121). The considerable π-delocalization within the ring is supported by CNDO/S calculations.



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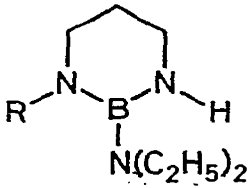

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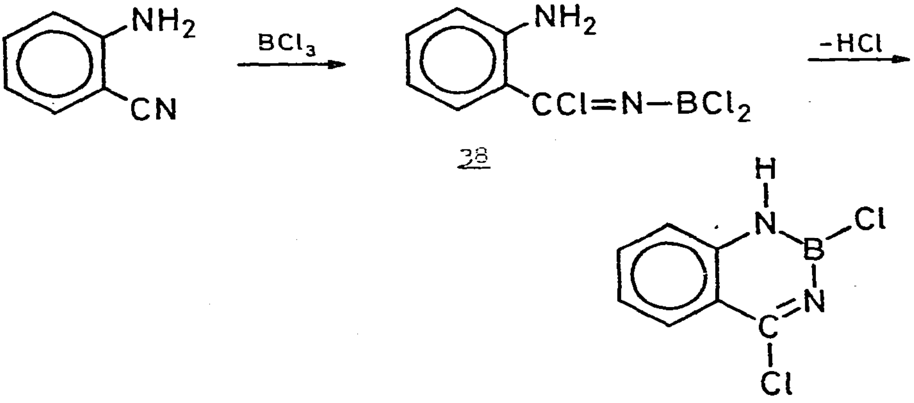
Tris(diethylamino)borane and N-alkyl propylenediamines can interact to give a 2-diethylamino-1,3,2-diazaboracyclohexane (= 1,3,2-diazaborolane) in which only one of the annular nitrogen atoms is not vulnerable to polymerization, 37 (129). Although yields of up to 53% were obtained, polycyclic borazine derivatives are also formed in substantial quantities by loss of diethylamine and simultaneous trimerization.

Haloboranes undergo a 1,2-addition across the nitrile group of 2-aminobenzonitrile (128). Using BCl_3 in this reaction, the resultant product 38 can cyclicize with the amino group to form the 1,3,2-diazaboranaphthalene derivative 39. Both 38 and 39 are representatives of ketiminoboranes. The cyclization reaction does not occur when (dihalo)organylboranes are used in the cited reaction.



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39

Recently (146), colored compounds which were obtained by 1,2-addition of haloboranes to phthalodinitrile have been described. The proposed structure of a phthalocyanine like ring system (see structure 53, p. 379 of the review covering the year 1972) has now been confirmed by an X-ray diffraction study (145). The relatively short B-N distances of 1.467 Å are quite remarkable and probably reflect steric hindrance; in principle, the polycyclic system can also be considered as a ketiminobornae.

A general method has been described (117) for the preparati of tris(organylamino)boranes by the interaction of boron triflu etherate with N-lithio dialkyl-, diaryl- or alkylarylamines in tetrahydrofuran. (But-1-en-3-yl)bisdimethylaminoborane has been prepared by conventional organometallic synthesis (16). This rep sentative of α-methylallylboranes was found to be stable up to 200°C; some isomarization could be detected near 225°C.

Trimeric (azido)dihaloboranes, $(N_3\text{-}BX_2)_3$ (X = F, Cl, Br), ha been prepared by the reaction of the corresponding boron trihali with (azido)trimethylsilane (125). The reaction of (dialkylamino diborane(6) with amines or hydrazines provides a mixture of amin boranes and amine-boranes as the final product (46). Formaldehyd dimethylhydrazone reacts with BH_3, amine-boranes or hydrazine-boranes in a simple hydroboration process (47):

$$CH_2\text{=N-N}(CH_3)_2 + BH_3 \longrightarrow H_2B\text{-N}CH_3\text{-N}(CH_3)_2.$$

Ketiminoboranes in which the ketimino group C=N-B is conjugated with a carbon-carbon double bond have been obtained by the follo ing reaction (185):

$$CH_2\text{=C}CH_3\text{-CN} + BR_3 \longrightarrow CH_2\text{=C}CH_3\text{-CR=N-B}R_2.$$

Both 3- and 4-aminobenzonitrile react with haloboranes to yield primarily the corresponding amine-haloboranes along with some de halogenation products (128). (Diphenylketiminc)diethylborane, $(C_6H_5)_2C\text{=N-B}(C_2H_5)_2$, reacts with bis(benzonitrile)palladium dich to yield the complex $[(C_2H_5)_2B\text{-N=C}(C_6H_5)_2]_2PdCl_2$ (67). Based on boron-11 nuclear magnetic resonance and infrared spectroscopic studies the ketiminoborane is coordinated to the palladium via th C=N group.

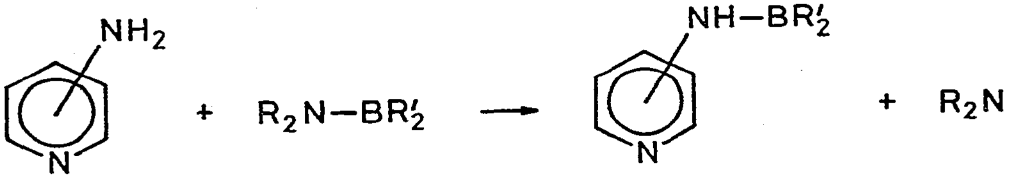
Reactions of alkali metal derivatives of (trimethylsilyl)-alkylamines with haloboranes have been used for the preparation of silylaminoboranes of the type $(CH_3)_3Si-NR-BC_6H_5-X$ with R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, and X = Cl, $N(CH_3)_2$ (4). If R = CH_3 or C_2H_5 and X = Cl, the resultant aminoboranes are thermally unstable and only their condensation products, $(-BC_6H_5-NR-)_3$, could be isolated. The reaction of (bromo)dimethylborane with $B\left[NCH_3-Si(CH_3)_3\right]_3$ can be manipulated to give, via successive cleavage of Si-N bonds, all possible members of the series $\left[(CH_3)_2B-NCH_3\right]_nB\left[NCH_3-Si(CH_3)_3\right]_{3-n}$ (122); the reactions are strongly temperature dependent. On the basis of proton and boron-11 nuclear magnetic resonance data, the final member of the cited series (n = 3) is a particularly electron poor trisaminoborane. This latter characteristic accounts for the great thermal instability of the compound which can lose trimethylborane at temperatures as low as 50°C.

(Dichloroamino)dichloroborane, Cl_2N-BCl_2, has been prepared from NCl_3 and an excess of boron trichloride (165). The vibrational spectrum of the compound shows an unusual low B-N valence frequency at 1312 cm^{-1}; B-Cl stretching modes were assigned at 986 and 446 cm^{-2}, N-Cl stretching at 735 and 541 cm^{-1}. The boron-11 chemical shift of the compound with $\delta = -34.7$ ppm is very close to that of (chloroethylamino)dichloroborane, $C_2H_5-NCl-BCl_2$, $\delta(^{11}B) = -32.4$ ppm.

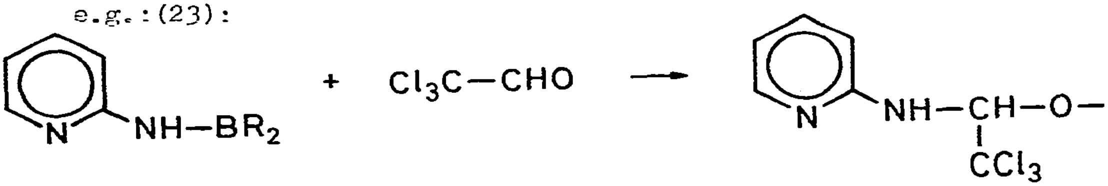
Chloroborane adducts (ethers, amines) react with disilazanes to cleave the Si-N bond in facile manner (48). However, the reaction cannot be utilized for the preparation of diborylamines of the type $(H_2B)_2NR$ which apparently seem to rearrange to yield $(-BH-NR-)_3$ and BH_3. However, simple (silylamino)boranes of the type $H_2B-NR-SiR'_3$ could be isolated as reaction intermediates. The preparation of some new diborylamines of the type $(R_2B)_2NR'$ (94)

has already been described above (see section 5).

(Pyridylamino)boranes have been obtained by a transamination reaction as is shown in the following equation (23):

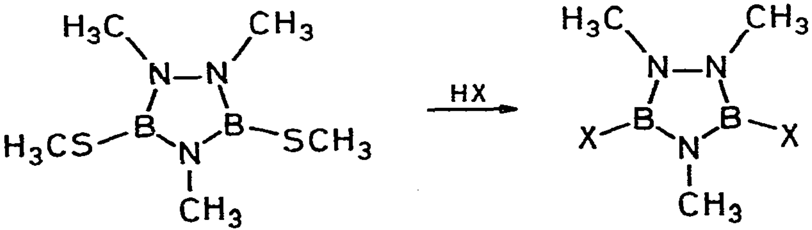


As was noted last year (24), the (pyridylamino)boranes react with multiple bonds via 1,2-addition of the boron-nitrogen link, e.g.: (23):



Preparative details have now also been presented for the synthesis of (2-pyridylamino)boranes by thermal condensation of 2-aminopyridine with trialkylboranes (357). It is of interest to note that steric overcrowding at the nitrogen site of aminoborane is apparently relieved by molecular distortions other than those involving significant B-N bond rotation (358).

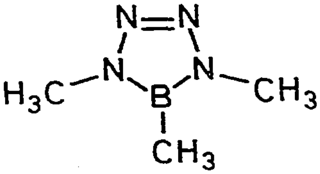
Several 1,2,4-triaza-3,5-diborolidines have been prepared by displacement of boron bonded methylthio groups (26):



40 41

Since <u>40</u> is readily accessible from the interaction of tris(methylthio)borane, <u>N</u>,<u>N</u>'-dimethylhydrazine, and methylamine (28), this heterocyclic system can now be studied in detail. For example, if methylamine is replaced by ammonia in the latter reaction, the 4-hydro derivative is obtained. Subsequently, the 4-nitrogen may be metallated by reaction with lithium alkyl; the resultant <u>N</u>-lithio compound is very reactive and various groups such as $B(NR_2)_2$, $P(NR_2)_2$, $Si(CH_3)_3$, or $Sn(CH_3)_3$ have been attached to the 4-position of the heterocycle. Magnetic resonance studies indicate that the six π-electron system of the 1,2,4-triaza-3,5-diborolidine ring has considerable aromatic character which may explain the rather unusual chemical stability of this system.

In complexes of <u>42</u> with $TiCl_4$ and aromatic hydrocarbons the latter are only loosely held in the crystal lattice (345); infrared and Raman data on 1:1 complexes of <u>42</u> with $SnCl_4$ or $SbCl_5$ have been recorded on the solid materials.



<u>42</u>

Details for the synthesis of a heterocycle comprised of four silicon (exocyclic substituents: phenyl groups) and one boron (exocyclic dimethylamino group) as annular atoms have now become available (55). Vibrational, ultraviolet, and proton magnetic resonance data suggest the complete absence of delocalized electrons within the ring.

Cleavage of the boron-boron bond is characteristic for the electron impact induced fragmentation of bis(amino)diborane(4) derivatives, $R_2N{-}BR'{-}BR'{-}NR_2$ (163). The ions with $m/2$ frequently are base peaks but are not observed in the mass spectra of specie in which boron and nitrogen are annular members of the same heter cyclic system.

The nitrogen-14 and boron-11 nuclear magnetic resonance spec of some 19 (silylamino)boranes have been recorded in conjunction with the nitrogen-14 spectra of 39 silylamines (123). The resultant data are readily interpreted in terms of sp^2 hybridization of the nitrogen together with a B-N double bond character but they also reflect geometric factors. Bonding boron to the nitrogen of silylamines leads to a decrease in the shielding about the nitrogen atom and illustrates the greater strength of (pp)π-bonding for the B-N bond as compared to the (pd)π-bonding of the Si-N linkage. Nitrogen-14 chemical shift values of organic amido derivatives (N-methylated urea, acetamide, etc.) and their isoster aminoboranes correlate linearly as do the $\delta(^{14}N)$ values of carbonium ions and their isoelectronic aminoborane analogs (278).

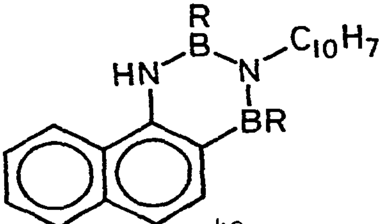
The B-N bond length of aminoborane, $H_2N{-}BH_2$, has been determined by ab initio calculations to be 1.38 Å for a planar model and 1.47 Å for the orthogonal form (14). The barrier to internal rotation was estimated to be 33.3 kcal/mol. The electronic structu of (amino)difluoroborane, $H_2N{-}BF_2$, has been calculated by the CNDO and INDO methods (89); the calculated dipole moment of about 3.0 D for the molecule is in satisfactory agreement with the exper mental data.

(Anilino)dimesitylboranes fluoresce showing the largest Stokes shifts as yet reported, corresponding to energy losses of 35.3 to 61.8 kcal/mol (102).

10 BORAZINES

B-Tris(alkylamino)-N-trialkylborazines and B-tris(arylamino)-N-triarylborazines have been prepared almost quantitatively by employing the appropriate stoichiometry in the reaction of boron trichloride and an alkyl- or arylamine (124). The borazines so formed react with boron trifluoride or boron trifluoride-etherate to give good yields of B-trifluoro-N-triorganylborazines. It has also been found that, in the presence of aluminum dust, primary alkylamine-trifluoroboranes readily dehydrogenate to give B-trifluoro-N-trialkylborazines (10). However, in the case of the alkyl group being methyl a liquid byproduct, m.p. 20-24°C, is obtained which was shown to be the tetrameric species $(-BF-NCH_3-)_4$. This latter compound represents the first example of the eight-membered borazocine ring in which the N-substituent is not a bulky group.

The reaction of α-naphthylamine with triethylamine-borane or boron trichloride gives the expected borazines, $(-BX-NR-)_3$ with $X = H, Cl$, and $R = \alpha-C_{10}H_7$ (240). Reaction of either species with CH_3MgI results in B-methylation. Mass, proton magnetic resonance, and ultraviolet spectra of the three borazines cited have been recorded and were compared with data obtained on α-naphth-3-yl-2,4-dibora-1,3-diazarophenanthrenes, 43. The reaction of tri(organyloxy)boranes with o-phenylenediamine apparently does not afford a polycyclic borazine derivative (308) but rather a polymeric species



43

which is reasonably stable towards hydrolytic attack is obtained.

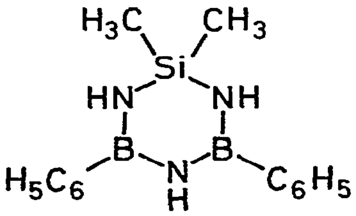
A two-step synthesis has been developed for the specific preparation of 2,4-dichloroborazine (109). The procedure involves the initial preparation of 2-dimethylamino-4,6-dichloroborazine in essentially quantitative yield and subsequent reaction of this product with diborane(6) in ether.

A reinterpretation of the earlier (221) X-ray diffraction data on hexachloroborazine on the basis of CNDO/BW semi-empirical molecular orbital calculations is consistent with a regular hexagonal ring structure for the compound (120). No meaningful potent curves can be obtained for π-π type molecular interactions by standard CNDO/2 methods (352). A modification in which pairs of atoms are associated with the same molecule and with different molecules leads to reduced intermolecular bonding and provides reasonable stabilization energies. Calculations based on this var tion suggest that borazine/benzene and borazine/borazine complexe in which the molecules are symmetrically disposed in parallel pla can exist in the ground state.

The proton magnetic resonance spectra of several borazines have been studied in an attempt to elucidate the electronic effec in the borazine ring system (235). The results were interpreted to indicate that the anisotropy of the borazine ring might not be caused by a ring current. On the other hand, the proton magnetic resonance spectra and magnetic susceptibilities of *N*-trialkyl-*B*-t fluoro, -tribromo, and-tri(organyloxy)borazines seem to suggest t these species may be considered as aromatic moieties (173). Methyl methyl proton spin-spin coupling constants, however, indicate onl a relatively weak transmission of spin density information *via* the presumed π-electron system of the borazine ring (292). Other authors (85) report that the chemical shift values of *N*-bonded methyl groups of borazines are virtually unaffected by increasing the number of *N*-methyl groups whereas a systematic change to higher field is observed with increasing *B*-methylation. No final conclusion can yet be reached from the first analysis of fine splitting in the FOURIER transfer proton magnetic resonance spectra of nitrogen-15 labeled borazines (319).

The acetonitrile groups of *fac*-$Cr(CO)_3(CH_3CN)_3$ have been displaced by borazines to yield $(CO)_3Cr(\text{-}BR\text{-}NR'\text{-})_3$ complexes with $R = CH_3$, *n*-C_3H_7, *i*-C_3H_7 and $R' = CH_3$, *n*-C_3H_7, *i*-C_3H_7 (287); infrared, mass, and proton magnetic resonance spectroscopic data of these borazine complexes are also presented. A ligand exchange reaction was also observed on reacting *B*-trimethylborazine with the complex $(CO)_3Cr(\text{-}BC_2H_5\text{-}NH\text{-})_3$ (342). In the presence of an excess of the free ligand the equilibrium of the interaction is readily shifted to permit the isolation of $(CO)_3Cr(\text{-}BCH_3\text{-}NH\text{-})_3$.

(Dichloro)phenylborane and $[\text{-}Si(CH_3)_2\text{-}NH\text{-}]_3$ interact to yield B-triphenylborazine, $(\text{-}BC_6H_5\text{-}NH\text{-})_3$, or either of the two silaborazines 44 and 45, respectively, depending on the molar ratio of the reactants (289). The silaborazines are hydrolytically relatively stable materials but the B-N bond strength seems to increase with decreasing number of annular silicon atoms.



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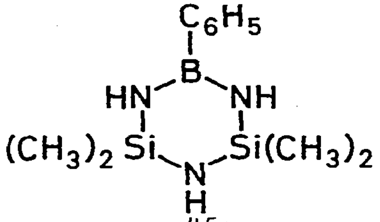

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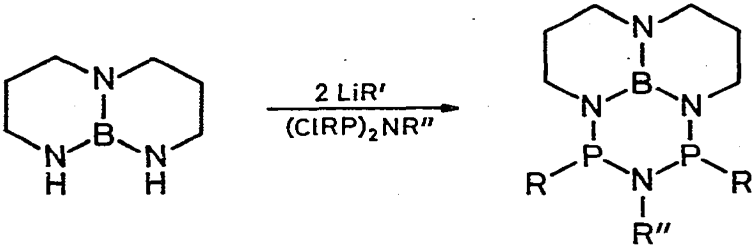
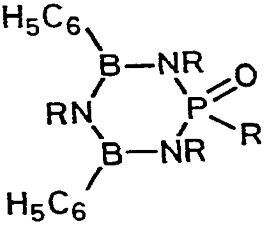
The cyclic trisaminoborane 46 reacts with lithium alkyl to give the N-dilithio derivative which, in turn, can be reacted with $R''N(PRCl)_2$ or $R''N[P(O)RCl]_2$ to yield phosphaborazines such as



46 47

47 (368). The monophosphaborazine 48 was obtained by silazane cleavage of $(CH_3)_3Si-NCH_3-BC_6H_5-NCH_3-BC_6H_5-NCH_3-Si(CH_3)_3$ and subsequent condensation. The cyclic structures of the cited phosphaborazines were confirmed by elemental and spectroscopic analysis. The ^1H and ^{31}P nuclear magnetic resonance data suggest the existe of some stereoisomers which might be caused, e.g., in the case of 48, by non-planarity of the ring system.



48

11 AMINE-BORANES

11.1 Hydridic Adducts

A detailed procedure has been described for the facile labor tory preparation of dimethylamine-borane (265) and the four possi adducts of BH_3 with hexamethylenetetramine have been described (3 They were found to be antagonistic to boronium cation formation and pyrolysis of the tetra adduct proceeded with rearrangement by hydride migration to form (dimethylamino)borane derivatives such as bis(dimethylamino)borane and dimeric (dimethylamino)borane.

The heats of formation have been determined for hydrazine-borane (92) and hydrazine-bis(borane) (91) and the vibrational spectrum of the latter has been studied (90). The thermal decomposition of hydrazine-borane is a multistage process, the first of which involves the loss of hydrogen from the amine-borane type grouping. In addition to standard manometric methods, infrared and mass spectroscopy were used to investigate the kinetics of the process and a free radical mechanism has definitely been ruled out (93, 183). The kinetics and the mechanism of the thermal decomposition of 1,1-dimethylhydrazine-borane have also been studied (327).

The infrared and RAMAN spectra of trimethylamine-borane and deuterated derivatives thereof have been recorded from solid state samples and the spectra were assigned on the basis of a C_{3v} molecular symmetry. The B-N stretch was observed in the 610-680 cm^{-1} region but it is extensively mixed with the symmetric N-C stretch. The calculated B-N force constant of 2.58 mdyn/Å seems to be consistent with the adduct stability (337). A conformational study has been performed on trimethylamine-borane <u>via</u> CNDO/2 calculations (88) and the structural effects of an amine-borane on the latter's activity in electroless plating have been investigated (306).

The basicity of a series of phosphites has been correlated with ν(BH) and the relative stability of their BH_3 adducts (352). A slow tertiary butyl rotation has been observed in tris(<u>t</u>-butyl)-phosphine-borane and di(<u>t</u>-butyl)chlorophosphine-borane using proton magnetic resonance spectroscopy (72). The coordinated BH_3 was found to be significantly more hindering to the <u>t</u>-butyl rotation than the free electron pair in the free bases.

A convenient preparation for amine-haloboranes involves the halogenation of amine-boranes of the type $R_3N{\cdot}BH_3$ with elemental halogen or hydrogen halides (21). The halogenation process can be monitored by boron-11 nuclear magnetic resonance spectroscopy , thus permitting the isolation of partially halogenated species. The bis(borane) adduct of N,N,N',N'-tetramethyl ethylenediamine was similarly halogenated at the boron sites by treatment with hydrogen halide (F, Cl, Br) or elemental bromine (158). Reaction monitoring was accomplished by proton magnetic resonance spectros and the new compounds TMED·$2BH_2X$ (X = F, Cl, Br; TMED = tetrameth ethylenediamine) and TMED·$2BHX_2$ (X = Br) were isolated. Exchange reactions of the type

$$(CH_3)_3N{\cdot}BH_2I = MX \longrightarrow (CH_3)_3N{\cdot}BH_2X + MI$$

where X = NCS, NCO, CN, F, Cl, or Br proceed exceedingly well in tetrahydrofuran as solvent (363).

The infrared spectra of $(CH_3)_3N{\cdot}BH_2X$ and $(CH_3)_3N{\cdot}BHX_2$ (X = C Br, I) have been recorded (245); using the group vibration assignment the following fundamentals could be identified:

$(CH_3)_3N{\cdot}BH_2X$: $\nu(BH) = 2328\text{-}2480\ cm^{-1}$
$\nu(BN) = 693\text{-}703\ cm^{-1}$
$(CH_3)_3N{\cdot}BHX_2$: $\nu(BH) = 2471\text{-}2514\ cm^{-1}$
$\nu(BN) = 712\text{-}716\ cm^{-1}$.

Most of the other important fundamentals were also assigned. The rotational barriers about the B-N bond for $H_3N{\cdot}BF_3$, $H_3N{\cdot}BHF_2$, $H_3N{\cdot}BH_2F$, and $H_3N{\cdot}BH_3$ have been calculated by *ab initio* molecula orbital methods (157); fluorine substitution causes the rotational energies to decrease.

Adducts of cyanoborane of the type $L{\cdot}BH_2CN$ with L = dimeth amine, trimethylamine, morpholine, N-methylmorpholine, 4-picolin, or tetramethyl ethylenediamine have been prepared and their mechanism of hydrolysis has been studied (108). In alkaline solution the hydrolysis can be described by the equation:

$$L\cdot BH_2CN + 2\ H_2O + 2\ OH^{\ominus} \longrightarrow L + B(OH)_4^{\ominus} + 2\ H_2 + CN^{\ominus}.$$

Boron-11 and nitrogen-14 chemical shifts of a large number of B-N derivatives containing tetracoordinate boron have been recorded (277). A nearly linear correlation between the chemical shift values of amine-boranes $L\cdot BR_3$ (L = aliphatic amine, R = H, CH_3) and the carbon-13 chemical shift values of the corresponding isoelectronic alkanes was noted. Furthermore, stability and structural information of the $L\cdot BR_3$ adducts (L = heteroaromatic nitrogen base, R = H, CH_3, C_2H_5) can be deduced from the nuclear magnetic resonance data.

Both nitrogen atoms of the LEWIS base 1,4-diazabicyclo(2.2.2)-octane coordinate with BX_3 (X = hydrogen or halogen) (175); the in-phase B-N mode of the BH_3 complex was observed near 720 cm^{-1}.

11.2 Boron Halide Complexes

A detailed procedure has been described for a simple laboratory preparation of dimethylamine-tribromoborane (266). Halogen exchange of trimethylamine-BX_3 species in solution with BY_3 yields the mixed adducts $(CH_3)_3N\cdot BX_2Y$ (293). Apparently, the B-N bond remains intact during the reaction which proceeds in either direction and probably occurs via a bridged transition state involving five-coördinate boron. However, in the gas phase halogen exchange occurs even in the absence of excess acid and probably involves a B-N bond cleavage.

The 1:1 adduct of tetramethyl urea with boron trifluoride can rearrange to give the ionic species $(OC[N(CH_3)_2]_2BF_2)^+(BF_4)^-$ (78).

A more convenient source of the cited cation is the 1:1 adduct of tetramethyl urea with (chloro)difluoroborane which is obtained from the reaction of the BF_3 adduct with that of BCl_3 in solution subsequent displacement of chlorine via nucleophilic attack of tetramethyl urea provides the desired cation.

Complexes of boron trifluoride with methyl, ethyl, and n-butyl ethers of α-naphthol have been described (209) and exchange react of aromatic amine adducts with boron trichloride and (dichloro)-phenylborane have been examined by nuclear magnetic resonance techniques (71). In the presence of an excess of free base the ra determining step of the ligand exchange is normally a unimolecula ionization of the initial adduct according to:

$$L\cdot BRX_2 \rightleftharpoons L\cdot BRX^{\oplus} + X^{\ominus}.$$

The electronic structures and heats of formation of some adducts of boron trifluoride have been calculated by the ab initi method (100). An experimental carbon-13 nuclear magnetic resonanc study of boron trihalide adducts with several ethers has shown tha the C-13 chemical shifts of the α-carbon atom in the complexes are to lower field than in the free ethers (7); a variation in the ord tetrahydrofuran $> (C_2H_5)_2O > (C_3H_7)_2O \simeq (C_4H_9)_2O$ was observed. The carbon-13 signals of all other carbon atoms are displaced to a hig field.

The infrared spectra of boron trifluoride adducts with aromatic ethers and carboxylic esters have been recorded (204) and it has been shown by a nuclear magnetic resonance study (189) that in the boron trihalide adducts of methyl acetate and its sulfur analogs, the coordinating site is always the multiple bonded chalocgen, eve in the case of CH_3-CS-OCH_3. The ν(CO) frequency of ethyl acetate and benzophenone changes when the latter form a complex with boron trihalides (296). Mixed halide adducts can be formed by simple ligand exchange; they are less stable than the unmixed species. A brief theoretical evaluation of the proton, boron-11, fluorine-19, and phosphorus-31 nuclear magnetic resonance data on complexes of boron trifluoride with amine oxides, phosphine oxides, and arsine oxides has been reported (305); the base strengths decrease in the order $R_3NO \gtrsim R_3AsO > R_3PO$. Boron-11 and fluorine-19 chemical shift data on boron trifluoride adducts of a variety of donors such as nitrogen bases, ethers, and other oxygen donors have been studied (112). Donor-halogen interaction parameters appear to permit the determination of the donor atom within a multidonor site molecule. Nuclear magnetic resonance studies also indicate a close relationship between the complexing ability of various cyclohexanones with boron trifluoride and the π-electron density of the carbonyl group (328).

Ground state properties of BF_3 complexes with aromatic aldehydes have been investigated by nuclear magnetic resonance and infrared spectroscopic studies (200). Very good correlations were observed between ν(CO) and the proton chemical shifts of the formyl proton with the respective BROWN σ^+ substituent constants; this observation emphasizes the dependence of these quantities on the charge density on the carbonyl carbon atom of the complexes. An infrared analysis of the acetone-BF_3 complex has also been reported (309) and acrylate estersadducts with BF_3 have been used for the polymerization of α-olefins (207).

The basicity of various aromatic carbonyl compounds (cyclic ketones, benzaldehyde, acetophenone, <u>etc.</u>) as inferred from the enthalpy of complex formation with boron trifluoride appears to be a function of inductive effects, steric factors, and possible conjugation (167). Phosphine and methylphosphine form 1:1 adducts with mixed boron trihalides (346). Boron trichloride, tribromide, and triiodide also form 1:1 adducts with (methyl)dichlorophosphin (2) but boron trifluoride does not interact with the same LEWIS base. Infrared data on $H_3P{\cdot}BX_3$ and $D_3P{\cdot}BX_3$ (X = F, Br, I) produce a force constant of the B-P bond of about 2.0 mdyn/Å (344). Tertiary phosphines and their chalcogenide derivatives form 1:1 complexes with boron tribromide and boron triiodide (116), the proton and boron-11 nuclear magnetic resonance spectra of which h been studied. Also, complexes of the type $X_3B{\cdot}PR_3Y$ with X = Cl, B I; R = CH_3, C_6H_5, C_6H_{11}; Y = S, Se, have been prepared (170) and was noted that ν(PY) shifts drastically upon coordination by abou 40 cm^{-1} to indicate B-Y interaction. Phosphine oxides react with diborane(6) *via* symmetrical cleavage of the latter to give 1:1 BH adducts whereas amine oxides promote unsymmetrical cleavage of th diborane(6) molecule (336). In contrast, trimethylamine(*N*)oxide hydrochloride reacts with sodium tetrahydroborate to yield the trimethylamine(*N*)oxide-borane. The 1:1 adduct of $As(CH_3)_3$ with BX_3 (X = Br, I) is stable at room temperature whereas the analogou adduct with $Sb(CH_3)_3$ slowly rearranges under the same conditions to form $(CH_3)_3SbX_2$ (347).

12 IONIC COMPOUNDS

The electronic structures of borane and the tetrahydroborate ion have been examined by *ab initio* calculations (176). The vibrational frequencies calculated from the data are in good agreement with the experimental values and the heat of formation of the gas phase reaction

$BH_3 + H^{\ominus} \longrightarrow BH_4^{\ominus}$

was calculated to be -278.6 kJ/mol.

The compound $[H_2B(N(CH_3)_2)_2][Al(BH_4)_2]$ and similar species have been prepared by the reaction of diborane(6) with various alanes in ether solvents (330). Also, the reactions of sodium tetrahydroborate and sodium cyanotrihydroborate with divalent chlorides of Co, Ni, Cu, Pd, and Pt in the presence of tertiary phosphines (285) and a facile laboratory preparation of trans-carbonyl(cyanotrihydroborato)bis(triphenylphosphine)rhodium(I) (271) have been described.

The reaction of sodium tetrahydroborate with open-chain conjugated nitrones results in deoxygenation of the nitrone function only (231). Reductive alkylation of proteins is readily accomplished using aromatic aldehydes and sodium cyanotrihydroborate (353) and the same reagent can be used in the preparation of biologically active nitroxides (311).

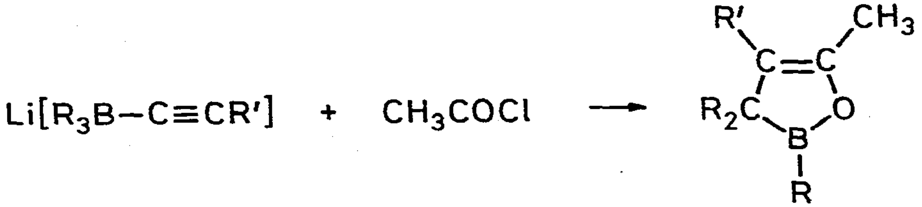
Bis(cyanotrihydroborato)-1,1,4,7,7-pentamethyldiethylenetriaminecopper(II) crystallizes in the orthorhombic system with eight monomeric molecules in the unit cell (77). The compound is a pentacoordinate complex of copper(II) and, on the basis of single-crystal X-ray diffraction data, the coordination polyhedron is a distorted square-based pyramid with one of the $NCBH_3$ ligands occupying the apical position. The structure of μ-bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I) has also been determined by single-crystal X-ray analysis (11). The H_3BCN ligands bridge the two copper atoms forming a ten-membered nonplanar ring.

Sodium cyanotrihydroborate reacts with metal hexacarbonyls $M(CO)_6$ with M = Cr, Mo, W, to give the anions $[H_3BCNM(CO)_5]^{\ominus}$ in which the cyano group acts as an electron donor (33). On the other hand, sodium tetraphenylborate reacts with such metal carbonyls form $[(C_6H_5)_2B\langle C_6H_5M(CO)_3\rangle_2]^{\ominus}$, in which two of the four phenyl groups are π-complexed to the metal tricarbonyl moieties. Sodium cyanotriphenylborate in the same reaction affords a complex of th cyano group to give the anions $[(C_6H_5)_3BCNM(CO)_5]^{\ominus}$.

The direct fluorination of alkali metal tetrahydroborates yields the corresponding tetrafluoroborates (156). Nitrosyl tetrafluoroborate, $(NO)(BF_4)$, has been prepared by the reaction of sol boron nitride in a quartz reactor with a 4:1 mixture of fluorine and oxygen (205), and a detailed procedure for the preparation of $(NF_4)(BF_4)$ via the interaction of BF_3, NF_3, and fluorine has been described (43).

Triethyloxonium tetrafluoroborate has been used as agent for the cyclization of δ- and γ-alkenenitriles (137) and for the polymeri ation of propylene sulfide (232). Stable carbonium ion salts are exceedingly rare and, in general, exist only in solution. However one of the best examples of such a stable species is (ferrocenyl) diphenylcyclopropenium tetrafluoroborate, the structure of which has been studied by X-ray diffraction (38). Silver tetrafluorobor complexes of organic species such as oxaziridine (105) or ketones (106) have recently been studied. Also, an example has been prese of a copper complex containing a weakly coordinate tetrafluorobor anion (107). Copper(I) and silver(I) complexes of O-ethylboranocarbonate are the first reported metal derivatives of the cited anion (332).

The reaction chemistry of alkali metal trialkylalkynylborates seems to be expanding rapidly. For example, the reaction of lithiu trialkylalkynylborates with propionic acid can be used for the syntheses of terminal and internal olefins, in which the acid acts as a protonylizing agent (197). Also, the reaction of the same reagent with acetyl chloride leads to 2-oxa-3-borolenes (164):

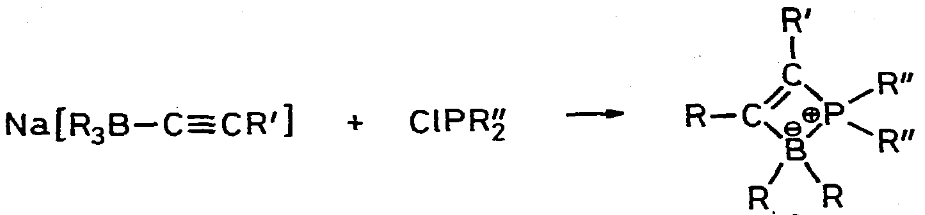


Since the latter are readily oxidized, the overall reactions represents a novel synthesis of highly substituted α,β-unsaturated ketones. Cationic metal complexes such as $[\mathrm{C_6H_5OCH_3Fe(CO)_3}][\mathrm{BF_4}]$ react with trialkylalkynylborates in stereo- and regioselective manner (365) and the reaction of lithium trialkylalkynylborates with methanesulfenyl chloride leads to (β-methanesulfinylvinyl)-boranes,

$$\mathrm{Li}[\mathrm{R_3B\text{-}C{=}CR'}] + \mathrm{CH_3SOCl} \longrightarrow \mathrm{R_2B\text{-}CR{=}CR'\text{-}SO\text{-}CH_3},$$

which lose the methanesulfinyl and dialkylboryl groups in a cis elimination to yield acetylenes (115). The reaction of lithium trialkylalkynylborates with oxiranes gives nonisolable intermediates which lose lithium alkyl to form oxaborinenes (281). This reaction has been used for the preparation of γ-hydroxyketones and the stereoselective preparation of trisubstituted ethylenes.

Efficient laboratory procedures for the syntheses of sodium triethylhydroborate, sodium tetraethylborate, and sodium triethyl-1-propynylborate have been described in detail (269). Sodium trialkylalkynylborates react with (chloro)diorganylphosphines to give organosubstituted 1,2-phosphaboret-3-enes, 49, in high yield (178). The structure of this novel type of compounds was ascertained by nuclear magnetic resonance data. In general, the materials react fairly rapidly with nucleophiles such as trimethylamine(N)oxide



49

but are stable in boiling methanol.

A novel double migration was observed in the reaction of trialkyl alkynylborates with dihalomethanes (261). Hydrolysis of the reaction products gives good yields of terminal olefins.

The nucleophilic reactivities of halide ions in liquid triethyl-n-hexylammonium triethyl-n-hexylborate have been studied (3 The halide ions follow the same order of reactivity as dissociate halide ions in normal polar aprotic solvents though the range of relative rate constants is much narrower.

The crystal structures of potassium tetraphenylborate and tha of tetramethylammonium tetraphenylborate have been determined by single-crystal X-ray diffraction (75); the B-C bond distance was found to be 1.64 Å. Bis(trimethylphosphite)tetraphenylboron rhodium(I), $[(CH_3O)_3P]_2Rh[B(C_6H_5)_4]$, is monoclinic and one aromati ring of the tetraphenylboron moiety is π-bonded to the rhodium atom which is situated symmetrically with respect to the ring (22

The B-C coupling constants for the tetraphenylborate ion hav been redetermined (320) and thallium(I) tetraphenylborate has bee used as a stationary phase for the gas chromatographic separation of some unsaturated hydrocarbons (66). The tetraphenylborate ion is an effective shift reagent for aminosulfonium ions and as such can be used for the solution of diastereotropic problems (318).

The hydrolysis of phenyl-1-pyrrolylborates, $[B(C_6H_5)_n(C_4H_4N)_{4-}$

..s second order and is catalyzed by hydrogen ion (274). The thermal decomposition of salts of the type $M[RB(OH)_3]$ with M = Li, Na, K, and R = C_6H_5 or C_6H_{11}, and $M[C_6H_5B(OH)_3]_2$ with M = Ca, Sr, Ba, leads to the anhydrous metaborate salts (84). Thermogravimetric data suggest that the initial process is a condensation in which two molecules lose one hydrocarbon molecule.

13 BORON-METAL DERIVATIVES

Perfluoroalkylmetal carbonyl halides of iron and cobalt have been reacted with potassium poly(1-pyrazolyl)borates (51); the 1-pyrazolylborate ligands of the resultant complexes are bidentate. Similar reactions have been described for trimethylplatinum derivatives (52); however, in this latter case, the 1-pyrazolylborate moiety serves as a tridentate ligand. It is intersting to note that through-space hydrogen-fluorine couplings between the axial methyl hydrogens or the axial 3-H pyrazole ring hydrogen and the the fluorine of $[HB(pz)_3]PtCH_3(R_f)$ complexes (pz = 1-pyrazolyl, R_f = fluoroolefin) have been observed (194).Bis hydrotris(1-pyrazolyl)borato copper(I) is the first example of a compound where the 1-pyrazolylborate ligand bridges two metal atoms (355). X-Ray diffraction studies indicate a centrosymmetric structure for the dimeric molecule with each $HB(pz)_3$ unit contributing two terminal 1-pyrazolyl ligands (one to each copper atom) and one 1-pyrazolyl group bridging crosswise. The major feature of the structure is the result that each copper atom is in a highly distorted tetrahedral environment and that the Cu-Cu distance is longer than in the bridged Cu(I) acetate structure. In solution, however, all 1-pyrazolyl rings appear to be magnetically equivalent.

A variety of 1-pyrazolylborate species derived from allyliron tricarbonyl iodide have been described (53) and several (1-pyrazc ylborato)carbonyl derivatives of manganese(I) have been studied b infrared and nuclear magnetic resonance spectroscopy (3). Data or these compounds of the type $[\mathrm{pzB(pz)_3}]\mathrm{Mn(CO)_2L}$ with L being vario phosphines indicate that the steric properties of the ligands influence the intercarbonyl angles.

[Diethylbis(1-pyrazolyl)borato]pyrazolato-trihaptoallyl-dicarbonylmolybdenum contains both a unidentate pyrazole ligand and a bidentate (1-pyrazolyl)borate ligand (9). The structure of [diethylbis(1-pyrazolyl)borato](trihapto-2-phenylallyl)(dicarbony molybdenum as determined by X-ray diffraction (37) reveals an ext ly strong interaction between an aliphatic CH bond and a metal. T α-carbon atom of one ethyl group of the cited compound is directe toward the molybdenum atom with a C-Mo distance of 3.06 Å; the rotational barrier about the B-C bond is such as to direct one of the α-hydrogen atoms toward the molybdenum resulting in an appare H-Mo distance of 2.15-2.27 Å. On that basis, a three-center C-H-M two-electron bond is postulated in order to account for this stro interaction and to provide molybdenum with an effective closed sh configuration. Proton magnetic resonance studies have revealed th a dissymmetric structure for $[(\mathrm{C_2H_5})_2\mathrm{B(pz)_2}]\mathrm{Mo(CO)L}$ with L = $\mathrm{CH_2{=}CC_6H_5{-}CH_2}$ or $\mathrm{CH_2{=}CH{-}CH_2}$; the fluxional molecules also contain a three-center C-H-Mo two-electron bond (348).

On the basis of a crystal structure analysis, the $\mathrm{B(pz)_4}$ ligand of $[(\mathrm{C_6H_5})\mathrm{Ru}[\mathrm{B(pz)_4}]]\,[\mathrm{PF_6}]$ is tridentate and the benzene ri is hexahapto (193). The crystal structure of bis[diethylbis(1-pyrazolyl)borato]nickel(II) has been determined by X-ray diffraction (249). It is noteworthy that two of the ethyl groups, one from eac boron ligand, are either above or below the Ni-N plane and one hydrogen from each of the methylene groups is directed toward nickel. These data dispute the results of a previous nuclear magnetic resonance study whereby it was concluded that methylene hydrogens occupy equivalent environments.

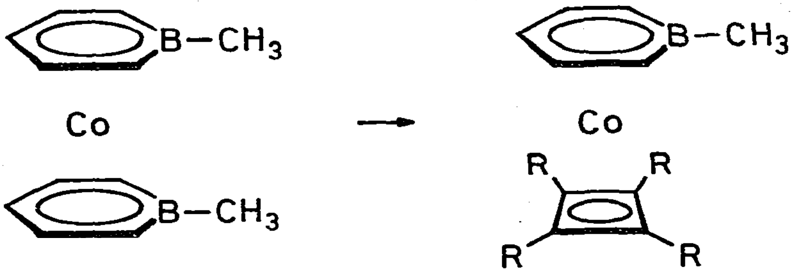
Reaction of the 1,5-cyclooctadiene complex $(C_8H_{12}RhCl)_2$ with potassium poly(1-pyrazolyl)borates of the type $K[H_{4-n}B(pz)_n]$ gives compounds of the type $(C_8H_{12})Rh[(pz)_nBH_{4-n}]$ as stable materials (149). Reaction of $[Rh(CO)_2Cl]_2$ with potassium bis(1-pyrazolyl)-borate gives $[H_2B(pz)_2]Rh(CO)_2$. Complexes of the general type $[RB(pz)_3]Rh(alkene)_2$ have been shown to involve a fluxional h_2-poly(1-pyrazolyl)borate ligand (29). The alkene groups are readily displaced by phosphines, nitrogen, or carbon monoxide, but only the latter yields a stable product. Similar observations have been reported for some other poly(1-pyrazolyl)borate complexes of rhodium (30). However, in this latter study, the formation of rhodium-dimethylpyrazolyl complexes is also described; their formation must occur via boron-carbon bond cleavage of a 1-pyrazolylborate species.

Five-coordinate methylplatinum(II)-acetylene complexes can be stabilized by tridentate poly(1-pyrazolyl)borate ligands (110) and the mixed sandwich compound $(C_5H_5)UCl_2[HB(pz)_3]$ has been prepared by the reaction of $(C_5H_5)UCl_3 \cdot 2THF$ with $K[HB(pz)_3]$ (246). The B-H stretching frequency of the complex is observed near 2500 cm^{-1}. The crystal structure of $[HB(pz)_3]PtCH_3(CO)$ has been determined by X-ray diffraction; the coordination about platinum is a slightly distorted square-planar arrangement and the six-membered PtN_4B ring is in the boat conformation.

The N=N stretching frequency of some poly(1-pyrazolyl)borates of the type $[RB(pz)_3]M(CO)_2(N_2Ar)$ (R = H, pz; M = Mo, W; Ar = C_6H_5, C_6D_5,

p-C_6H_4F) was assigned to the 1530-1580 cm^{-1} region (295).

1-Methylborinato(tetraphenylcyclobutadiene)cobalt has been prepared by ligand displacement as depicted below (203):



Dicarbonyl(1-phenylborinato)cobalt was also obtained by a ligand displacement when $Ni(CO)_4$ was reacted with bis(1-phenylborinato)-cobalt: One of the organylboron groups is displaced with the formation of the desired compound, m.p. 80°C (276). Nickel tetracarbonyl reacts with $(C_6H_5-BC_5H_5)_2Co$ to displace one of the two 1-phenylborinato groups to yield $(C_6H_5-BC_5H_5)Co(CO)_2$ (362) and the reaction of $(R-BC_5H_5)_2Co$ ($R = CH_3$, C_6H_5) with iron carbon can be directed to yield $(R-BC_5H_5)Fe(CO)_2{}_2$; these species proba contain a doubly CO-cis-bridged structure (366). Pyrolysis of the compounds at 230°C yields $(R-C_5H_5)_2Fe$.

The structures of $(CH_3-BC_5H_5)_2Fe(CO)_4$ and $(C_6H_5-BC_5H_5)Mn(CO)$ have been determined by X-ray diffraction (367). Both molecules contain virtually planar π-bonded "borabenzene" groups.

14 PHYSIOLOGICAL ASPECTS

Complexing of nucleosides and nucleotides with a boryl-group modified sephadex (95) and the binding of (organyloxy)boranes to chymotysin has been studied (263). Also, the comparative action of (dihydroxy)phenylborane and (dihydroxy)-4-methylphenylborane o the central nervous system has been investigated (264) and (hydro organylboranes have been found to inhibit subtilism (20). Several reports are concerned with the thermal isomerization of steroidal boranes (82, 159, 192) and the hydroboration of steroids (354).

The tetraphenylborate ion exhibits a detergent like action on phospholipid labeling in guinea pig cortex subfractions (213) and was found to effect the spontaneous transmitter release at frog neuromuscular junctions (225). The effects of tetraphenylborate ion on the automatic nervous system have also been studied (169).

Boric acid affects the catalytic activity of streptomyces griceus protease 3 (262). In this connection it seems of interest to note that the boron-free hydrolysis product of boromycin is remarkably similar in constitution, configuration, and even conformation to the antibioticum showing that its overall molecular shape is retained on removal of the spiro boron atom (220).

A general concept of the physiological role of boron in plants has been suggested (214) and the factors affecting the boron uptake by grasses have been studied (210). CHAPMAN and JACKSON (226) have reported an increased RNA labeling in boron deficient root tip segments and the effects of a boron deficiency on the activity of B-glucosidase in sunflowers have been studied (111). Also, the effect of boron on alfalfa weevil opposition (99) and on the anti-caries action of fluorine in drinking water (19) have been investigated.

Boron derivatives of sulfadizine have been studied as potential carriers for polymers into cancer tissue (261) and the syntheses of potential protein-modifying reagents containing borane cages for use in boron-10 neutron capture therapy have been described (257). The agents, which were obtained from orthocarborane and from decahydrodecaborate(2-), contain either amine, imido ester, or aldehyde functions besides ionic centers and were bound to human γ-globuline and bovine serum albumin (258). Similar work centers on the incorporation of sulfur-containing polyhedral boranes into antibodies (259) but the need for water-solubilizing groups in order to increase the number of boron atoms which may be attached to an antibody carrier is still apparent.

REFERENCES

1. J. L. Odom, L. W. Hall, S. Riethmiller and J. R. Durig, Inorg. Chem., 13 (1974) 170
2. R. M. Kren, M. A. Mathur and H. H. Sisler, ibid., 13 (1974) 1
3. A. R. Schoenberg and W. P. Anderson, ibid., 13 (1974) 465
4. R. H. Neilson and R. L. Wells, ibid., 13 (1974) 480
5. N. Walker and A. J. Leffler, ibid., 13 (1974) 484
6. J. P. Brennan, ibid., 13 (1974) 490
7. A. Fratiello, G. A. Vidulich and R. E. Schuster, J. Inorg. Nucl. Chem., 36 (1974) 93
8. R. H. Prager and J. M. Tippett, Tetrahedron Lett., (1973) 519
9. F. A. Cotton, B. A. Frenz and A. G. Stanislowski, Inorg. Chim. Acta, 7 (1973) 503
10. V. I. Spitsyn, I. D. Kolli and T. G. Sevastyanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 22 (1974) 11
11. K. M. Melmed, T. Li, J. J. Mayerle and S. J. Lippard, J. Amer. Chem. Soc., 96 (1974) 69
12. G. Zweifel, A. Horng and J. E. Plamondon, ibid., 96 (1974) 31
13. H.M. Seip and H. H. Jensen, Chem. Phys. Letters, 25 (1974) 20
14. O. Gropen and H. M. Seip, ibid., 25 (1974) 206
15. H. C. Brown and N. Ravindran, J. Organometal. Chem. 61 (1973)
16. K. G. Hancock and J. D. Kramer, ibid. 64 (1974) C29
17. W. Ruf, M. Fueller and W. Sibert, ibid. 64 (1974) C45

18. L. S. Bartell and B. L. Carroll, J. Chem. Phys., 42 (1965) 3076

19. R. D. Gabovich and G. A. Stepanenko, Gig. Sanit., 73(12) (1973) 20

20. R. N. Lindquist and C. Terry, Arch. Biochem. Biophys., 160 (1974) 135

21. J. M. Van Paasschen, M. G. Hu, L. A. Peacock and R. A. Geanangel, Syn. React. Inorg. Metalorg. Chem., 4 (1974) 11

22. S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, ibid., 4 (1974) 27

23. W. L. Cook and K. Niedenzu, ibid., 4 (1974) 53

24. V. A. Dorokhov and B. M. Mikhailov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 21 (1973) 1847

25. K. Niedenzu and J. S. Merriam, Z. Anorg. Allg. Chem., 406 (1974) 251

26. D. Nolle, H. Nöth and W. Winterstein, ibid., 406 (1974) 235

27. R. Köster and E. Rothgery, Liebigs Ann. Chem., (1974) 112

28. D. Nolle and H. Nöth, Z. Naturforsch., 27b (1972) 1425

29. D. J. O'Sullivan and F. J. Lalor, J. Organometal. Chem., 65 (1974) C47

30. N. F. Borkett and M. I. Bruce, ibid., 65 (1974) C51

31. B. Asgarouladi, R. Full, K.-J. Schaper and W. Siebert, Chem. Ber., 107 (1974) 34

32. H. Wille and J. Goubeau, ibid., 107 (1974) 110

33. R. B. King and K. C. Nainan, J. Organometal.Chem., 65 (1974) 71

34. D. J. Hart and W. T. Ford, J. Org. Chem. 39 (1974) 363

35. S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, J. Organometal. Chem., 65 (1974) 361

36. S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, J. Organometal. Chem., 65 (1974) 367

37. F. A. Cotton, T. LaCour and A. G. Stanislowski, J. Amer. Chem. Soc., 96 (1974) 754

38. R. L. Sime and R. J. Sime, ibid., 96 (1974) 892

39. M. D. Riley and N. E. Miller, Inorg. Chem., 13 (1974) 707

40. J. Rathke and R. Schaeffer, ibid., 13 (1974) 760

41. J. R. Durig, R. O. Carter and J. D. Odom, ibid., 13 (1974) 701

42. B. A. Kazansky, Y. N. Bubnov, S. V. Zotova, N. M. Abramova, V. G. Kiselev and B. M. Mikhailov, Tetrahedron Lett., (1974)

43. V. Y. Rosolovskii, V. I. Nefedov and S. M. Sinelnikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 22 (1974) 1

44. B. M. Mikhailov, T. K. Baryshnikova and V. S. Bogdanov, J. Gen. Chem. USSR (Engl. Transl.), 43 (1974) 1932

45. V. A. Dorokhov, O. G. Boldyreva and B. M. Mikhailov, ibid., 43 (1974) 1938

46. A. F. Zhigach, R. A. Svitsyn and E. S. Sobolev, ibid., 43 (1974) 1941

47. A. F. Zhigach, R. A. Svitsyn and E. S. Sobolev, ibid., 43 (1974) 1946

48. A. F. Znigach, E. S. Sobolev, R. A. Svitsyn and V. S. Nikitin ibid., 43 (1974) 1949

49. V. F. Maslennikov, G. I. Makin, V. N. Alyasov and Y. A. Aleksandrov, ibid., 43 (1974) 1954

50. D. A. Dixon, I. M. Pepperberg and W. N. Lipscomb, J. Amer. Chem. Soc., 96 (1974) 1325

51. R. B. King and A. Bond, ibid., 96 (1974) 1334

52. R. B. King and A. Bond, ibid., 96 (1974) 1338

53. R. B. King and A. Bond, ibid., 96 (1974) 1343

54. Y. Yatamoto, K. Kondo and I. Moritani, Tetrahedron Lett., (1974) 793

55. E. Hengge and D. Wolfer, J. Organometal. Chem., 66 (1974) 413

56. J. Hooz, S. Akiyama, F. J. Cedar and M. J. Bennett, J. Amer. Chem. Soc., 96 (1974) 274

57. H. C. Brown and N. R. Delue, ibid., 96 (1974) 311

58. N. Miyaura, M. Harada, M. Itoh and A. Suzuki, Chem. Letters, (1973) 1145

59. G. G. Petukhov, L. I. Kachaeva, V. N. Kashaeva, L. F. Kudryav S. F. Zhiltsov and V. A. Sokolava, Tr. Khim. Khim. Tekhnol., (1973) 105

60. F. Sladky, H. Kropshofer and O. Leitzke, J. Chem. Soc. Chem. Commun., (1973) 134

61. W. R. Clayton, D. J. Saturnino, P. W. R. Corfield and S. G. Shore, ibid., (1973) 377

62. R. H. Cragg, M. Nazery, J. F. J. Todd and A. F. Weston, ibid., (1973) 386

63. R. H. Cragg and A. F. Weston, ibid., (1974) 22

64. A. K. Holliday, W. Reade, K. R. Seddon and I. A. Steer, J. Organometal. Chem., 67 (1974) 1

65. T. Yamamoto and L. J. Todd, ibid., 67 (1974) 75

66. G. E. Baiulesc and V. A. Ilie, Analyt. Chem. 46 (1974) 1847

67. G. Schmid and L. Weber, ibid., 107 (1974) 547

68. R. C. Larock, J. Organometal. Chem., 67 (1974) 353

69. R. E. Lyle and D. A. Walsh, ibid., 67 (1974) 363

70. R. H. Cragg and M. Nazery, J. Chem. Soc. Dalton Transact., (1974) 162

71. J. R. Blackborow, M. N. S. Hill and S. Kumar, ibid., (1974) 411

72. C. H. Bushweller and J. A. Brunelle, Tetrahedron Lett., (1974) 893

73. R. H. Cragg and A. F. Weston, J. Organometal. Chem., 67 (1974) 161

74. B. A. Carlson, J. J. Katz and H. C. Brown, ibid., 67 (1974) C39

75. K. Hoffmann und E. Weiss, ibid., 67 (1974) 221

76. S. Kato, H. Fujimoto, S. Yamabe and K. Fukui, J. Amer. Soc. 96 (1974) 2024

77. B. G. Segal and S. J. Lippard, Inorg. Chem. 13 (1974) 822

78. J. S. Hartman and G. J. Schrobilgen, ibid., 13 (1974) 874

79. D. S. Matteson, R. A. Davis and L. A. Hagelee, J. Organometal. Chem., 69 (1974) 45

80. D. S. Matteson and P. B. Tripathy, ibid. 69 (1974) 53

81. D. S. Matteson and M. Furue, ibid., 69 (1974) 63

82. E. Mincione, F. Feliciani and O. Rossi, Ann. Chim. 63 (1974) 297

83. M. Wieber and W. Kuenzel, Z. Anorg. Allg. Chem., 403 (1974) 107

84. C. L. Fields and J. R. Doyle, Thermochim. Acta, 8 (1974) 239

85. G. Beaumelon, M. Pasdeloup and J. P. Laurent, Org. Magn. Resonance, 5 (1973) 585

86. G. M. Rosen, J. Med. Chem., 17 (1974) 358

87. M. Lelental, J. Catal., 32 (1974) 429

88. F. Crasnier, J. Chim. Phys. Physicochim. Biol., 70 (1973) 17

89. C. Leibovici, J. F. Labarre and F. Gallais, C. R. Acad. Sci. Ser. C., 278 (1974) 327

90. F. Hanousek and T. Haruda, Collect. Czech. Chem. Commun., 38 (1973) 3692

91. G. L. Galchenko, E. P. Brykina, L. V. Kulakova, V. M. Eselso and A. F. Zhigach, Zh. Fiz. Khim., 48 (1974) 481 A

92. G. L. Galchenko, E. P. Brykina, B. M. Eselson and A. F. Zhig ibid., 48 (1974) 481 B

93. V. V. Zakharov, A. F. Zhigach and G. B. Manelis, ibid., 48 (1974) 492 B

94. G. Srivastava, J. Organometal. Chem., 69 (1974) 179

95. E. A. Ivanova, I. I. Koladkina and A. L. Yurkevitch, Zh. Obshch. Khim., 44 (1974) 430

96. G. B. Bag, V. S. Badalyan, S. M. Markaryan and M. G. Indzhik Arm. Khim. Zh., 26 (1973) 929

97. R. Zahradnik and I. Matousek, Coll. Czech. Chem. Commun., 39 (1974) 57

98. Y. A. Skkolnik, Fiziol. Rast., 21 (1974) 174

99. R. K. Smith, D. A. Miller and E. J. Armbrust, J. Econ. Entomo 67 (1974) 130 A

100. R. M. Archibald, D. R. Armstrong and P. G. Perkins, J. Chem. Soc. Faraday Trans., (1973) 1793

101. D. F. Gaines, S. Hildebrandt and J. Ulman, Inorg. Chem., 13 (1974) 1217

102. M. E. Glogowski, P. J. Grisdale, J. L. R. Williams and L. Co J. Organometal. Chem., 74 (1974) 175

103. "Molecular Structures and Dimensions" Vol. A 1 Crystallographic Data Centre Cambridge (1972) 397

104. T. R. Crompton, Chemical Analysis of Organometallic Compounds Vol. 1 (1974)

105. D. R. Crist, G. J. Jordan and J. A. Hashmall, J. Amer. Chem. 96 (1974) 4927

106. D. R. Crist, Z.-H. Hsieh, G. J. Jordan, F. P. Schinco and C. A. Maciorowski, ibid., 96 (1974) 4932

107. A. P. Gaughan Jr., Z. Dori and J. A. Ibers, Inorg. Chem., 13 (1974) 1657

108. C. Weidig, S. S. Uppal and H. C. Kelly, ibid., 13 (1974) 1763

109. O. T. Beachley and T. R. Durkin, ibid., 13 (1974) 1768

110. H. C. Clark and L. E. Manzer, ibid., 13 (1974) 1291

111. N. E. Miller, ibid., 13 (1974) 1459

112. J. S. Hartman and J. R. Miller, ibid., 13 (1974) 1467

113. K. M. Harmon, A. B. Harmon, B. C. Thompson, C. L. Spix, T. T. Coburn, D. P. Ryan and T. Y. Susskind, ibid., 13 (1974) 862

114. E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 96 (1974) 4676

115. M. Naruse, K. Utimoto and S. Yamada, Tetrahedron, 30 (1974) 2159

116. M. L. Denniston and D. R. Martin, J. Inorg. Nucl. Chem., 36 (1974) 1461

117. W. R. Purdum and E. M. Kaiser, ibid., 36 (1974) 1465

118. J. P. Tuchagues and J. P. Laurent, ibid., 36 (1974) 1469

119. Gmelin Handbuch der Anorganischen Chemie, Ergänzungswerk Vol. 13, Borverbindungen Teil 1

120. M. S. Gopinathans, M. A. Whitehead, C. A. Coulsen, J. R. Carruthers and J. S. Rollett, Acta Cryst. B, 30 (1974) 731

121. J. Kroner, H. Nöth and K. Niedenzu, J. Organometal. Chem., 71 (1974) 165

122. H. Nöth and W. Storch, Chem. Ber., 107 (1974) 1028

123. H. Nöth, W. Tinhof and B. Wrackmeyer, ibid., 107 (1974) 518

124. J. M. Miller and G. L. Wilson, J. Fluorine Chem., 4 (1974) 207

125. N. Wiberg, W. Ch. Joo and K. H. Schmid, Z. Anorg. Allgem. Chem., 394 (1974) 197

126. M. Schmidt and F. R. Rittig, ibid., 394 (1974) 152

127. M. Wieber and W. Künzel, ibid., 403 (1974) 107

128. A. Meller, W. Maringgele and G. Maresch, Monatsh. Chem., 105 (1974) 637

129. H. Follner, ibid., 104 (1973) 477

130. K. F. Hoffmann and U. Engelhardt, Z. Anorg. Allg. Chem., 389 (1972) 97

131. H. S. Randhawa, Z. Physik. Chem. (Frankfurt), 89(1974) 320

132. E. Hohaus and W. Riepe, Z. Naturforsch., 286 (1973) 440

133. J. Kroner, D. Nölle and H. Nöth, ibid., 286 (1973) 416

134. T. E. Acree, Adv. Chem. Ser., 117 (1973) 208

135. W. E. Truce, L. A. Mura, P. J. Smith and F. Young, J. org. Chem., 39 (1974) 1449

136. C. F. Lane, ibid., 39 (1974) 1437

137. F. Johnson, L. G. Duquette, W. L. Parker and W. A. Nasutaric ibid., 39 (1974) 1434

138. L. Barton, J. M. Crump and J. B. Wheatley, J. Organometal Ch 72 (1974) C1

139. E. I. Pichuzhkina, I.I. Kolodkina and A. M. Yurkevich, J. Gen. Chem. USSR (Engl. Transl.), 43 (1974) 2266

140. G. I. Makin, V. P. Maslennikov and Y. A. Aleksandrov, ibid., 43 (1974) 2260

141. V. P. Maslennikov, G. I. Makin and Y. A. Aleksandrov, ibid., 43 (1974) 2277

142. G. E. Kacheishvili, N. I. Pirtskhalava and B. D. Dzhioshvili ibid., 43 (1974) 2387

143. V. Hach, Synthesis, (1974) 340

144. L. H. Long, Adv. Inorg. Radiochem., 16 (1974) 201

145. H. Kietaibl, Monatsh. Chem., 105 (1974) 405

146. A. Meller and H. Ossko, ibid., 103 (1972) 150

147. S. K. Mehrotra, G. Srivastara and R. C. Mehrotra, J. Organometal. Chem., 73 (1974) 277

148. G. W. Kramer and H. C. Brown, ibid., 73 (1974) 1

149. R. B. King and A. Bond, ibid., 73 (1974) 115

150. F. Zettler, H. D. Hausen and H. Hess, ibid., 72 (1974) 157

151. B. M. Mikhailov and V. N. Smirnov, Bull. Acad. Sci. USSR. Div. Chem. Sci., (Engl. Transl.), 22 (1974) 2124

152. K. V. Puzitskii, S. D. Pirozhkov, K. G. Ryabora, I. V. Postuk and Y. T. Eidus, ibid., 22 (1973) 1760

153. B. M. Mikhailov, Y. N. Bubnov and M. S. Grigoryan, ibid., 22 (1974) 2351

154. IME BORON, University of Leeds, England (1974)

155. W. Haubold and J. Weidlein, Z. Anorg. Allg. Chem., 406 (1974) 171

156. R. J. Lagow and J. L. Margrave, Inorg. Chim. Acta, 10 (1974) 9

157. D. R. Armstrong and P. G. Perkins, ibid., 10 (1974) 77

158. M. G. Hu and R. A. Geanangel, ibid., 10 (1974) 83

159. E. Mincione, F. Feliziani and O. Rossi, Ann. Chim. (Rome), 63 (1973) 297

160. I. P. Biryukov, F. P. Smirnov, E. Svarcs, A. Ievins, A. Terauda and A. Vegnere, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1974) 142

161. E. Svarcs, R. Ignash, A. Putnins and A. Ievins, ibid., (1974) 145

162. E. Svarcs, R.G. Belousova and A. Ievins, ibid., (1974) 149

163. K. G. Hancock and A. K. Uriarte, Org. Mass Spectrom., 9 (1974) 289

164. M. Naruse, T. Tomita, K. Utimoto and H. Nozaki, Tetrahedron, 30 (1974) 835

165. J. G. Haasnoot and W. L. Groenveld, Z. Naturforsch., 29b (1974) 52

166. J. Kroner, D. Nölle and H. Nöth, ibid., 28b (1973) 416

167. J. F. Gal, L. Elegant and M. Azzaro, Bull. Soc. Chim. Fr., (1974) 411

168. T. Ogata, A. P. Cox, D. L. Smith and P. L. Timms, Chem. Phys. Letters, 26 (1974) 186

169. G. Guideri, E. Seifter and F. Seifter, Arch. Int. Pharmacodyn. Ther., 208 (1974) 224

170. P. M. Boorman and D. Potts, Canad. J. Chem., 52 (1974) 2016

171. A. N. Maevskaya, E. A. Troitskaya and G. Temp, Fisiol. Rast., 21 (1974) 619

172. G. Cros and J. P. Laurent, J. Chim. Phys. Physicochim. Biol., 71 (1974) 802

173. K. Ananthanarayanan, P. J. Gielesse and A. Choudry, Nucl. Instrum. Methods, 118 (1974) 45

174. J. M. Burke, J. J. Ritter and W. J. Lafferty, Spectrochim. Acta A, 30 (1974) 993

175. J. R. McDivitt and G. L. Humphrey, ibid., 30 (1974) 1021

176. D. R. Armstrong, P. G. Perkins and K. S. Sorbie, Rev. Roum. Chim., 19 (1974) 747

177. E. Hengge and D. Wolfer, J. Organometal. Chem., 66 (1974) 41

178. P. Binger and R. Köster, ibid., 73 (1973) 205

179. B. M. Mikhailov, V. A. Dorokhov and O. G. Boldyreva, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 22 (1974) 2587

180. B.M. Mikhailov and M. E. Gurskii, ibid., 22 (1974) 2588

181. B. M. Mikhailov and V. A. Dorokhov, ibid., 22 (1974) 2594

182. J. Hooz and S. Linke, J. Amer. Chem. Soc., 90 (1968) 6891

183. A. F. Zhigach, V. V. Zakharov, G. B. Manelis, G.N. Nechipore V. S. Nikitin and B. M. Eselson, Russ. J. Inorg. Chem. (Engl Transl.), (1973) 931

184. A. Y. Putnin, E. M. Shvarts and A. F. Ievenish, ibid., (1973

185. A. Meller and ". Gerger, Monatsh. Chem. 105 (1974) 684

186. R. H. Cragg and M. Nazery, J. Chem. Soc. Dalton Transact., (1974) 1438

187. R. A. Andersen and G. E. Coates, ibid., (1974) 1440

188. E. Alaluf, K. J. Alforo, E. O. Bishop and J. D. Smith, ibid.)1974) 669

189. M. J. Bula, J. S. Hartman and C. V. Raman, ibid., (1974) 725

190. R. H. Cragg and A. F. Weston, J. Chem. Soc. Chem. Communicat (1974) 22

191. Y. Yamamoto and H. C. Brown, ibid., (1973) 801

192. E. Mincione and F. Feliciani, ibid., (1973) 942

193. R. J. Restivo and G. Ferguson, ibid. (1973) 847

194. H. C. Clark and L. O. Manzer, ibid., (1973) 870

195. E. Vegnere, E. Svarcs and A. Ievins, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1973) 530

196. R. H. Prager and J. M. Tippett, Austr. J. Chem., 27 (1974) 1

197. N. Miyaura, T. Yoshinari, M. Itoh and A. Suzuki, Tetrahedron Lett., (1974) 2961

198. L. Weber and G. Schmid, Angew. Chem. 86 (1974) 519

199. R. H. Cragg and M. Nazery, Inorg. Nucl. Chem. Lett., 10 (1974) 481

200. A. Grinvald and M. Rabinowitz, J. Chem. Soc. Perkin Transact. II, (1974) 94

201. K. Erixon and G. Renger, Biochem. Biophys. Acta 333 (1974) 95

202. M. Hallensleben, ibid., 28b (1974) 540

203. G. E. Herberich and H. J. Becker, ibid., 28b (1974) 828

204. A. M. Volostchouk, S. G. Karetnikov, G. S. Katalnikov and T. A. Kozik, Kernenergie, 17 (1974) 150

205. J. L. Adcock and R. J. Lagow, J. Fluorine Chem., 2 (1973) 434

206. S. Iwabuchi, M. Ueda, M. Kobayashi and K. Kojima, Polym. J., 6 (1974) 185

207. A. L. Logothetis and J. M. McKenna, J. Polym. Sci. Polym. Lett. Ed., 12 (1974) 131

208. M. Miyaura, M. Kashiwagi, M. Itoh and A. Suzuki, Chem. Letters, (1974) 395

209. L. L. Drnitrerskii, T. U. Ivanova and S. G. Katalnikov, Zh. Fiz. Khim., 48 (1974) 1011

210. G. Tolgyesi and A. Kozma, Agrokem. Talajtan, 23 (1974) 83

211. K. Kitajima and N. Daimon, Nippon Kagaku Kaishi, (1974) 680

212. G. B. Bagdasaryan, S. M. Markaryan and K. S. Badalyan, Arm. Khim. Zh., 26 (1973) 855

213. J. Schacht and B. W. Agranoff, J. Neurochem., 22 (1974) 473

214. Y. A. Shkolnik, Fiziol. Rast., 21 (1974) 174

215. C. Stainier, Farmaco, Ed. Prat., 29 (1974) 3

216. R. Van Veen and F. Bickelhaupt, J. Organometal. Chem., 74 (1974) 393

217. J. Casanova Jr., "Isonitrile Chemistry", Academic Press, New York, (1971) 109

218. E. F. Pearson, C. L. Norris and W. H. Flygare, J. Chem. Phys., 60 (1974) 1761

219. R. Hillet, J. Bouix and H. T. Forel, Bull. Soc. Chim. Fr., (1974) 83

220. W. Marsh, J. D. Dunitz and D. N. J. White, Helv. Chim. Acta, 57 (1974) 10

221. J. G. Haasnot, G. C. Verschoer, C. Romers and W. L. Groeneve
Acta Cryst. B, 28 (1972) 2070

222. M. J. Nolte and G. Gafner, ibid., 30 (1974) 738

223. F. C. Fischer and E. Havinga, Recl. Trav. Chim. Pays-Bas, 93 (1974) 21

224. J. Simpson and G. B. Porter, J. Chem. Soc. Perkin Transact. (1973) 1796

225. I. G. Marshall and R. L. Parsons, Pharmacolog., 16 (1974) 23

226. K. S. R. Chapman and J. F. Jackson, Phytochem. 13 (1974) 131

227. J. R. Easterfield and J. W. Linett, J. Chem. Soc. Faraday Transact. II, (1974) 317

228. R. H. Prager and J. M. Tippett, Austr. J. Chem., 27 (1974) 1

229. A. Maitra and D. Den, Indian J. Chem., 12 (1974) 183

230. C. K. Sharma, V. D. Gupta and R. C. Mehrotra, ibid., 12 (1974) 218

231. K. Krishan and N. Singh, ibid., 12 (1974) 222

232. D. R. Van Doteghem and E. J. Goethals, Makromol. Chem., 175 (1974) 1513

233. N. A. Gradskova and E. A. Bondarevskaya, Zh. Anal. Khim., 29 (1974) 1237

234. R. H. Cragg, J. F. J. Todd and A. F. Weston, J. Organometal. Chem., 74 (1974) 385

235. J. L. Adcock and J. J. Lagowski, ibid., 72 (1974) 323

236. G. M. Pickles and F. G. Thorpe, ibid., 76 (1974) C 23

237. J. S. Thayer, ibid., 76 (1974) 265

238. E. Favre and M. Gaudemar, ibid., 76 (1974) 297

239. E. Favre and M. Gaudemar, ibid., 76 (1974) 305

240. A. Rizzo and B. Frange, ibid., 76 (1974) 1

241. R. Van Veen and F. Bickelhaupt, ibid., 77 (1974) 153

242. A. B. Goel and V. D. Gupta, ibid., 77 (1974) 183

243. M. S. Reason, A. G. Briggs, J. D. Lee and A. G. Massey, ibid. 77 (1974) C 9

244. M. P. Brown, A. K. Holliday and G. M. Way, J. Chem. Soc. Chem Communications, (1973) 532

245. P. J. Bratt, K. R. Seddon and I. A. Steer, Inorg. Chim. Acta, 10 (1974) 191

246. K. [illegible]. Bagnell and J. Edwards, J. Organometal. Chem., 80 (1974) C 14

247. S. J. Rettig and J. Trotter, Acta Cryst. B, 30 (1974) 2139

248. S. J. Rettig and J. Trotter, Canad. J. Chem., 51 (1974) 1288

249. H. M. Echols and D. Dennis, Acta Cryst. B, 30 (1974) 2173

250. E. Rothgery and R. Köster, Liebigs Ann. Chem., (1974) 101

251. G. Will, Chemiker-Ztg. 98 (1974) 471

252. W. Siebert, ibid. 98 (1974) 479

253. K. Niedenzu, ibid. 98 (1974) 487

254. W. Voelter, ibid. 98 (1974) 493

255. A. Graf von Matuschka, ibid. 98 (1974) 504

256. R. Köster, H. Bellut and W. Fenzl, Liebigs Ann. Chem. (1974) 54

257. H. S. Wong, E. I. Tolpin and W. N. Lipscomb, J. Medic. Chem. 17 (1974) 785

258. E. I. Tolpin, H. S. Wong and W. N. Lipscomb, ibid. 17 (1974) 792

259. R. L. Sneath, A. H. Soloway and A. S. Dey, ibid. 17 (1974) 796

260. N. N. Greenwood and I. M. Ward, Chem. Soc. Rev. 3 (1974) 231

261. A. Pelter and C. R. Harrison, Chem. Commun. (1974) 828

262. C. A. Bauer and G. Pettersson, Eur. J. Biochem. 45 (1974) 473

263. J. D. Rawn and G. E. Lienhard, Biochemistry 13 (1974) 3124

264. P. H. Chanh, I. Sokan and M. H. Quessada, Agressoldg. 15 (1974) 61

265. K. C. Nainan and G. E. Ryschkewitsch, Inorg. Syn. 15 (1974) 122

266. W. H. Myers and G. E. Ryschkewitsch, ibid. 15 (1974) 125

267. R. Köster, P. Binger and W. Fenzl, ibid. 15 (1974) 134

268. P. Binger and R. Köster, ibid. 15 (1974) 136

269. R. Köster and P. Binger, ibid. 15 (1974) 141

270. R. Köster and P. Binger, ibid. 15 (1974) 149

271. L. Vaska and M. V. Miller, ibid. 15 (1974) 72

272. J. Blais, A. L'Horne, J. Soulie and P. Cadiot, J. organometa
Chem. 78 (1974) 323

273. S. P. Hopper and J. S. Fine, ibid. 80 (1974) C 21

274. J. Emri, B. Györi and P. Szarras, Z. Anorg. Allg. Chem.
400 (1973) 321

275. Gmelin Handbuch der Anorganischen Chemie, Ergänzungswerk Vol.
Borverbindungen Teil 2

276. G. E. Herberich and H. J. Becker, Z. Naturforsch. 28b (1973)

277. H. Nöth and B. Wrackmeyer, Chem. Ber. 107 (1974) 3070

278. H. Nöth and B. Wrackmeyer, ibid. 107 (1974) 3089

279. H. Nöth and U. Schuchardt, ibid. 107 (1974) 3104

280. H. Nöth, W. Tinhof and T. Taeger, ibid. 107 (1974) 3113

281. M. Naruse, K. Utimoto and H. Nozaki, Tetrahedron 30 (1974) 3

282. L. Chevolot, J. Soulie and P. Cadiot, Tetrahedron Lett. (197

283. S. A. Breuer, F. G. Thorpe and J. C. Podesta, ibid. (1974) 37

284. H. Iida, H. Kitamura, K. Seita and K. Yamada, Bull. Chem. Soc
Japan 47 (1974) 1028

285. D. G. Holah, A. N. Hughes, B. C. Hui and K. Wright, Canad. J.
Chem. 52 (1974) 2990

286. P. A. Gorin and M. Mazurek, ibid. 51 (1973) 3277

287. M. Scotti and H. Werner, Helv. Chim. Acta 57 (1974) 1234

288. J. C. Carter, G. W. Luther and A. L. Moye, Appl. Spectrosc.
28 (1974) 427

289. R. N. Lindquist and C. Terry, Arch. Biochem. Biophys.
160 (1974) 135

290. T. Goto and M. Nagao, Bull. Chem. Soc. Japan 47 (1974) 246

291. N. Miyamoto, D. Fukuoka, K. Utimoto and H. Nozaki, ibid.
47 (1974) 503

292. J. B. Rowbotham and T. Schafer, Canad. J. Chem. 52 (1974) 489

293. B. W. Benton and J. M. Miller, ibid. 52 (1974) 2866

294. S. J. Rettig, J. Trotter and W. Kliegel, ibid. 52 (1974) 2531

295. D. Sutton, ibid. 52 (1974) 2634

296. J. S. Hartmann and R. R. Yetman, Canad. J. Spectrosc. 19 (1974) 1

297. K. X. To, E. J. Knystautas and R. Drouin, ibid. 19 (1974) 72

298. I. R. McKinley and H. Weigel, Carbohyd. Res. 31 (1973) 17

299. I. R. McKinley, H. Weigel, C. B. Barlow and R. D. Guthrie, ibid. 32 (1974) 187

300. P. J. Wood and I. R. Siddiqui, ibid. 33 (1974) 97

301. E. J. Bourne, I. R. McKinley and H. Weigel, ibid. 35 (1974) 141

302. T. Taguchi, Y. Takahashi, M. Itoh and A. Suzuki, Chem. Lett. (1974) 1021

303. C. Thomson, Chem. Phys. Lett. 25 (1974) 59

304. H. W. Kroto, R. J. Suffolk and N. P. C. Westwood, ibid. 22 (1973) 495

305. R. Bravo, M. Durano, J. P. Laurent and F. Galalais, C. R. Acad. Sci. C 278 (1974) 1489

306. M. Lelental, J. Catal. 32 (1974) 429

307. M. Fonassier, M. T. Forel, J. Bouix and R. Hiller, J. Chim. Phys. Physicochem. Biol. 70 (1973) 1518

308. S. H. Dandegaonker and A. S. Mane, J. Indian Chem. Soc. 50 (1974) 622

309. K. Sugiyama and S. Kono, J. Label. Compounds 9 (1973) 727

310. C. Pepin, L. Lambert and A. Cabana, J. Mol. Spectrosc. 53 (1974) 120

311. G. M. Rosen, J. Med. Chem. 17 (1974) 358

312. O. Gropen, E. W. Nilsson and H. M. Seip, J. Mol. Structure 23 (1974) 289

313. J. J. Katz, B. A. Carlson and H. C. Brown, J. org. Chem. 39 (1974) 2817

314. C. F. Lane, H. L. Myatt, J. Daniels and H. B. Hopps, ibid. 39 (1974) 3052

315. M. P. Rabinowitz, P. Reisberg and J. I. Bodin, J. Pharm. Sci. 63 (1974) 1601

316. A. Vegnere, E. Svarcs and A. Ievins, Latv. PSR Zinat. Akad. Vestis, Kim. Ser. (1974) 415

317. J. Bartulin, M. Przybylski, H. Ringsdorf and H. Ritter, Makromol. Chem. 175 (1974) 1007

318. G. P. Schiemenz and P. Klemm, Org. Magn. Reson. 6 (1974) 276
319. L. J. Turbini and R. F. Porter, ibid. 6 (1974) 456
320. J. D. Odom, L. W. Hall and P. D. Ellis, ibid. 6 (1974) 360
321. S. Hammerum and C. Djerassi, Org. Mass Spectrom. 8 (1974) 21
322. K. F. Purcell and R. L. Martin, Theor. Chim. Acta 35 (1974) 1
323. S. I. Nozakura and S. Kida, Org. Mass Spectrom. 6 (1974) 403
324. E. Negishi and H. C. Brown, Synthesis (1974) 77
325. F. Grein and K. Weiss, Theor. Chim. Acta 34 (1974) 315
326. Y. Yamamoto, Yuki Gosei Kagaku Kyokai Shi 32 (1974) 544
327. V. V. Zakharov, G. N. Nechiporenko, V. S. Nikitin and N. G. Yunda, Zh. Fiz. Khim. 48 (1974) 2150A
328. C. Paris, G. Torri, L. Elegant and M. Azzarro, Bull. Soc. Chi Fr. (1974) 1449
329. J. C. Carter, A. L. Moye and G. W. Luther, J. Amer. Chem. Soc 96 (1974) 3071
330. P. C. Keller, ibid. 96 (1974) 3073
331. J. P. Hummel, D. Gust and K. Mislow, ibid. 96 (1974) 3679
332. J. C. Bommer and K. W. Morse, ibid. 96 (1974) 6222
333. W. T. Ford, R. J. Hauri and S. G. Smith, ibid. 96 (1974) 4316
334. B. R. Cragg and G. E. Ryschkewitsch, ibid. 96 (1974) 4717
335. W. Fuss and H. Bock, J. Chem. Phys. 61 (1974) 1613
336. R. A. Geanangel, J. Inorg. Nucl. Chem. 36 (1974) 1397
337. J. D. Odom, J. A. Barnes, B. A. Hudgens and J. R. Durig, J. Phys. Chem. 78 (1974) 1503
338. W. Haubold and R. Schaeffer, Chem. Ber. 104 (1971) 513
339. N. E. Miller and E. L. Muetterties, Inorg. Chem. 3 (1964) 119
340. N. E. Miller, J. Amer. Chem. Soc. 92 (1970) 4564
341. R. J. Hughes, A. Pelter and K. Smith, Chem. Commun. (1974) 86
342. M. Scotti and H. Werner, J. Organometal. Chem. 81 (1974) C 17
343. P. J. Wood and I. R. Siddiqui, Carbohydrate Res. 36 (1974) 24

344. J. R. Durig, S. Riethmiller, V. F. Kalasinsky and J. D. Odom, Inorg. Chem. 13 (1974) 2729

345. J. H. Morris, J. Inorg. Nucl. Chem. 36 (1974) 2439

346. J. E. Drake and B. Rapp, ibid. 36 (1974) 2613

347. M. L. Denniston and D. R. Martin, ibid. 36 (1974) 2175

348. F. A. Cotton and J. M. Troup, J. Amer. Chem. Soc. 96 (1974) 5074

349. S. Friedman, B. Pace and R. Pizer, ibid. 96 (1974) 5381

350. T. Leung and J. Zweifel, ibid. 96 (1974) 5620

351. J. R. Ritscher, D. C. Kowalski and J. E. McKeon, J. Chem. Educ. 51 (1974) 688

352. D. W. White and J. G. Verkade, Phosphorus 3 (1974) 9

353. M. Friedman, L. D. Williams and M. S. Masri, Int. J. Rept. Protein Res. 6 (1974) 183

354. C. Kanako, A. Sugimoto, S. Yamada, M. Ishikawa, S. Sasaki and T. Suda, Chem. Pharm. Bull. 22 (1974) 2101

355. C. S. Arons, J. L. Wilkinson, C. Mealli, T. J. Marks and J. A. Ibers, J. Amer. Chem. Soc. 96 (1974) 7564

356. G. I. Makin, V. P. Maslennikov and Y. A. Aleksandrov, J. Gen. Chem. USSR (Engl. Transl.) 44 (1974) 1256

357. V. A. Dorokhov and B. M. Mikhailov, ibid. 44 (1974) 1259

358. J. Casanova and M. Geisel, Inorg. Chem. 13 (1974) 2783

359. W. Schwarz, H.-D. Hausen and H. Hess, Z. Naturforsch. 29b (1974) 596

360. W. Siebert, K.-J. Schaper and B. Asgarouladi, ibid. 29b (1974) 642

361. F. Riegel and W. Siebert, ibid. 29b (1974) 719

362. G. E. Herberich and H. J. Becker, ibid. 29b (1974) 439

363. P. J. Bratt, M. P. Brown and K. R. Seddon, J. Chem. Soc. Dalton Trans. (1974) 2161

364. P. E. Rush and J. D. Oliver, Chem. Commun. (1974) 996

365. A. Pelter, K. J. Gould and L. A. P. Kana-Maguire, ibid. (1974) 1029

366. G. E. Herberich, H. J. Becker and G. Greiss, Chem. Ber. 107 (1974) 3780

367. G. Huttner and W. Gartzke, ibid. 107 (1974) 3786

368. H. Nöth and W. Tinhof, ibid. 107 (1974) 3806