# BORON

## ANNUAL SURVEY COVERING THE YEAR 1976

## PART II

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CONTENTS

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Boron, part II, Annual Survey covering the year 1975 see J. Organometal Chem., 119(1976)57-130.

## 1 REVIEWS AND SUMMARY ACCOUNTS

Reviews dealing with organylboranes include one article on the preparation and properties of allylboranes (100), the versatility of organylboranes with respect to their chemical behavior (328), a brief summary on the use of organylboranes as alkylating agents (107), recent work on aromatic boron-containing heterocycles (274), and the formation of organoboron heterocycles <u>via</u> cyclic hydroboration of dienes (315), a compilation of data on various (perfluoroorganyl)borane species (5), and a survey of the chemistry of organylborates (48). Applications of organoboron compounds as nucleophiles in organic syntheses have also been compiled (197) and the use of catecholborane as hydroboration agent (286) is surveyed elsewhere. An article on structural and bonding patterns in cluster chemistry centers about borane and carborane species (304) and the influence of these patterns as affected by coordination number preferences is discussed in another accounting (305).

Various topics are discussed in a new book on boron hydride chemistry, reviewing theoretical and experimental data on boron hydrides and carboranes and derivatives thereof (43). A compilation of recent advances in poly(1-pyrazolyl)borate chemistry centers on the use of the species as coordinating ligands (185) and further short reviews deal with metalloboranes containing ligand-to-metal single bonds (186), reductions involving diborane(6) and its derivatives (302), and borane anions (187). A general guide to the literature on the organometallic chemistry of the main group elements (16) may be of interest to some readers.

Three additional volumes of the New Supplement Series of the GMELIN HANDBUCH DER ANORGANISCHEN CHEMIE dealing with boron compounds have been published during this past year; see some relevant remarks in J. Organometal. Chem., 119 (1975) 58. The first one of these new additions to the boron literature (194) describes the tetrahydroborate ion and a variety of derivatives thereof in which the hydrogen is partially or completely replaced by ligands such as halogen, hydroxy, organyloxy, hydrothio, organylthio, amino, or organic groups. Another volume (195) deals with boron-halogen derivatives and contains chapters on (halo)hydroboranes and ether adducts thereof as well as on (organyl)haloboranes containing trigonal boron. The third volume (196) presents various compounds containing tetra-coordinate boron. Specifically, μ-derivatives of diborane(6) and some related species, boronium salts, and tetrahaloborate ions are discussed. In addition, carbon monoxide-boranes and some boron derivatives with noble gases are presented.

## 2 SOME DATA OF GENERAL INTEREST

Localized molecular orbitals of diborane(6) have been calculated by the ab initio method (217), and another molecular orbital study (75) elaborates on the role of $BH_5$ in the hydrolysis of the tetrahydroborate ion; for some computations of energy differences for motions in $B_2H_6$ and $CH_3BH_2$, see (190).

The catalytic hydroboration of ethylene in the gas phase and employing diborane(6) has been described (69) and the photochemically-catalyzed reduction of ketones with sodium tetrahydroborate has been studied (180). Elsewhere (179), evidence is presented disputing a four-center transition state in the borohydride reduction of ketones. Asymmetric induction in the hydroborative reduction of carbonyl compounds by means of a chiral phase-transfer catalyst has been described (192) and the hydroboration of poly(alkadienes) and their models by bis(boracyclanes) has been studied (239).

The mercury-sensitized photochemical reaction of boranes and carboranes at 2537 Å seems to be a convenient method for the synthesis of the corresponding B-B coupled species (158). High-resolution nuclear magnetic resonance measurements on small boron hydrides illustrate that the magnitude of the coupling constant J(BB) is related to the bonding between the coupled nuclei (171). For some $^{11}B$ nuclear magnetic resonance shift data and coupling constants of diboranes, polyboranes, and carboranes, see (313).

Trimethylborane reacts with closo-1,5-$C_2B_3H_5$ to provide a monomethylation according to the equation

$C_2B_3H_5 + B(CH_3)_3 \longrightarrow 2\text{-}CH_3\text{-}C_2B_3H_4 + \frac{1}{2}(CH_3)_4B_2H_2$ (76).

Reaction of trialkylboranes $BR_3$ (R = $C_2H_5$, i-$C_3H_7$) with $BH_3$ in tetrahydrofuran has been studied by $^{11}B$ nuclear magnetic resonance spectroscopy at various temperatures. The first step in a ligand exchange reaction was found to be the formation of the unsymmetrical dialkyldiborane(6); consecutive steps depend on the molar ratio of the two initial reactants. Steric effects are considered to interpret the equilibrium compositions and the significance of a base-catalyzed exchange of terminal and bridging hydrogen is discussed (199). For the gas-phase reaction of deuterium atoms with triethylborane, see (218).

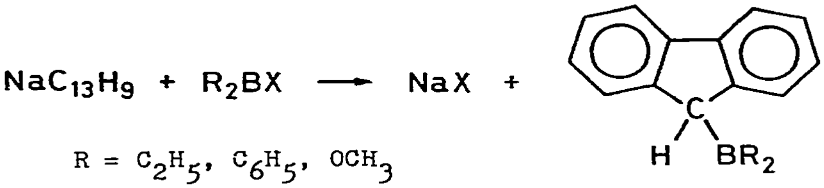
Ab initio calculations on $H_2B\text{-}O\text{-}O\text{-}BH_2$ predict a simple minimum for the barrier to internal rotation in the trans position (89). Non-empirical LCAO-MO-SCF calculations on μ-aminodiborane indicate electron donation to the amino group from the diborane moiety; π-bonding within the BHBN ring of the species is negligible (140). Bonding and properties of carbon monoxide-borane, $(OC)BH_3$, have been examined by a single-determinant approximation (72) and a new ab initio calculation on the electronic structure of the molecule has also been reported (60); for additional molecular orbital studies on the compound, see (292). The electronic structures of $(OC)_2B_2H_4$, $(OC)B_3H_7$, and their parent boranes have also been examined by non-empirical molecular orbital techniques (139). The $\nu_7$ perpendicular band of $(OC)BH_3$ has been studied by high-resolution infrared spectroscopy (62).

Boron-11 chemical shift data on two series of boranes, i.e., $R_{3-n}BX_n$ (R = alkyl; X = $N(CH_3)_2$, Cl, Br; n = 0, 1, 2) and $R'_{3-n}BX_n$ (R' = phenyl, thienyl, furyl, vinyl, etc.; X = alkyl, Cl, Br, $N(CH_3)_2$; n = 0, 1, 2), respectively, indicate an increase of dative π-backbonding from cyclic systems to boron that is correlated to a decrease of the aromaticity of the rings (26); the conjugated system of cyclopentadienylboranes results in a high-field shift of $\delta^{11}B$ as compared to vinylboranes.

## 3 TRIORGANYLBORANES AND RELATED SPECIES

### 3.1 PREPARATIVE CHEMISTRY

(Dimethyl)phenylborane, $(CH_3)_2BC_6H_5$, has been prepared from $(CH_3)_2BCl$ and $Hg(C_6H_5)_2$ and the $^1H$ NMR band-shape method has been used to determine exchange parameters of this compound (and of trimethylborane) with methylphosphines (260). 9-Borylfluorenes have been prepared from the corresponding haloboranes and sodium fluorenide as depicted in the following equation (24):



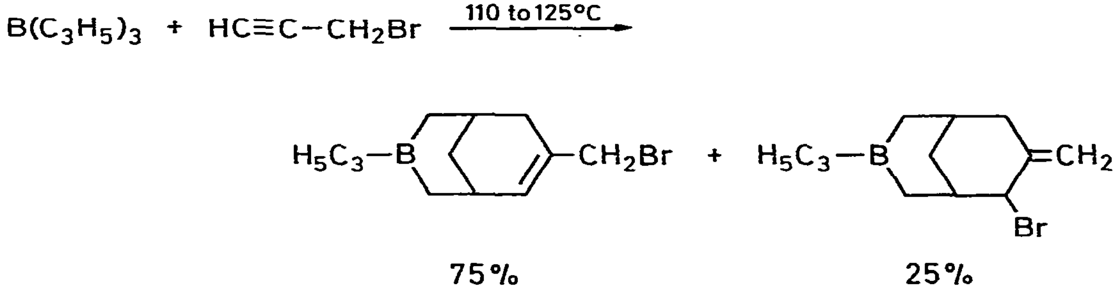
R = $C_2H_5$, $C_6H_5$, $OCH_3$

The 9-borylfluorene with R = $C_2H_5$ can be deprotonated with the use of $Na[HB(C_2H_5)_3]$ to yield $Na[(C_2H_5)_2BC_{13}H_8]$ as a diglyme adduct. Reaction according to

$$2\ Sn(C_5H_5)_2 + BI_3 \longrightarrow (C_5H_5)SnI \cdot SnI_2 + B(C_5H_5)_3$$

supposedly occurs in quantitative fashion (77). Tris(organylsilyl)-boranes of the type $B(CH_2\text{-}Si(CH_3)_2\text{-}X)_3$ with X = $Si(CH_3)_3$, $OSi(CH_3)_3$, or halogen have been obtained, in principle, via a Grignard procedure. The compounds are distillable liquids that oxidize in air (319).

Triallylborane reacts with 3-bromopropyne to yield a mixture of compounds as illustrated by the equation:



Various organic reactions at the Br sites of the two species are possible with retention of the original skeletal arrangement (37). In a series of chemical transformations 3,6-dibutyloxy-7-methylene-3-borabicyclo[3.3.1]nonane was also obtained (37). (Allyl)dialkylboranes are prepared by the reaction of allylboranes with $R_2BSR'$ (R and R' = alkyl groups) according to (73):

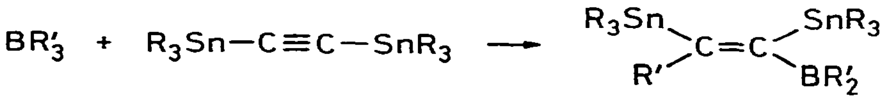
$$(C_2H_5)_2BSC_6H_5 + B(C_3H_5)_3 \longrightarrow (C_2H_5)_2B\text{-}CH_2\text{-}CH{=}CH_2$$

The products are obtained in 95 % yield and are stable towards symmetrization to 115°C; however, intramolecular allylic rearrangement does occur. (Allyl)dialkylboranes as well as (diallyl)alkylboranes can be obtained according to the following schemes (68):

$$R_2BOR' + BrCH_2\text{-}CH{=}CH_2 + Al \longrightarrow R_2B\text{-}CH_2\text{-}CH{=}CH_2$$

$$RB(OR')_2 + BrCH_2\text{-}CH{=}CH_2 + Al \longrightarrow RB(CH_2\text{-}CH{=}CH_2)_2.$$

The compounds $(CH_3)_2B\text{-}CF{=}CF_2$ and $CH_3B(CF{=}CF_2)_2$ were prepared by transfer of $C_2F_3$ groups from tin to boron (49). The two cited species are thermally stable at 100°C but decompose rapidly at 200°C. Spectral data show that B-C π-bonding may be more significant in these two compounds than in analogous vinylboranes. The compound $(CH_3)_2B\text{-}C{\equiv}CC_6H_5$ has been prepared by the reaction of $(CH_3)_2BI$ with $IC{\equiv}CC_6H_5$ (94). At room temperature trialkylboranes react with bis(trimethylstannyl)acetylene in a cis-addition (46) according to the equation:



R = $CH_3$; R' = $CH_3$, $C_2H_5$, i-$C_3H_7$, n-$C_4H_9$

Reactivity differences in the R' groups were briefly evaluated and products were identified by $^1H$ and $^{11}B$ NMR data. Various (vinyl)-diethylboranes have been prepared by the interaction of the salt $Na[(C_2H_5)_3B\text{-}C{\equiv}C\text{-}Si(CH_3)_3]$ with nucleophiles (82). The reaction proceeds primarily with the formation of the (E)-isomers, thus illustrating a pronounced effect of the silicon on the stereochemistry of the final product.

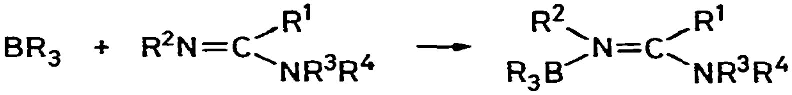
In a brief note the hydroboration of bicyclo[3.3.1]-2,6-nonadiene is described (67). Thermal treatment of the resultant polymer at 200 to 250°C yields 2-ethyl-2-boraadamantane, whereas on refluxing with $B(OCH_3)_3$ the corresponding 2-ethoxy derivative is obtained.

## 3.2 PHYSICOCHEMICAL STUDIES

The vibrational spectra of triallylborane, tricrotylborane, and tris(methylallyl)borane and their complexes with pyridine have been recorded and assignments of the fundamentals are suggested (19); the data are interpreted with a localized double bond in the allyl moiety and pure sigma bonding between boron and carbon. On the other hand, various spectroscopic data on alkenylboranes seem to indicate an appreciable conjugation of the carbon-carbon π-systems with boron (198). An ab initio study on 1-aza-4-boratricyclo[2.2.2.0]octane and 1-aza-4-borabicyclo[2.2.2]octane demonstrates a bond-stretch isomerism as depicted below:

## 3.3 CHEMICAL BEHAVIOR

Trialkylboranes, $BR_3$ (R = n-$C_3H_7$, i-$C_3H_7$), react with amidines (295) to form 1:1 molar complexes via nitrogen-to-boron coordination:



Infrared and NMR spectroscopic data support the suggested structures. However, if $R^3$ and/or $R^4$ is hydrogen, heating of the complexes results in the formation of N-dialkylboryl-amidines with the elimination of RH, probably via an intermediate cyclic state. The reactions of tri-n-butylborane and tetra-n-butyldiborane(6) with alkylbutyn-2-yl ethers (129), methylenediamines (128), isovaleraldehyde diethyl acetal (127), and alkyl-3-chloro-buten-2-yl ethers have been studied.

Oxygen-induced 1,4-addition reactions of trialkylboranes with α,β-unsaturated carbonyl compounds give evidence for the hypothesis that coordination of the boron of trialkylboranes to the carbonyl oxygen plays an important role in the process (223). Alkylative cleavage of the pyridine ring by trialkylboranes appears to be a stereospecific process (287). The reaction of trialkylboranes with iron(III) azide in the presence of $H_2O_2$ presents a new synthesis of azidoalkanes (178); for reactions of amide compounds in the presence of trialkylboranes, see (207). Utilizing sodium methoxide as base presents a substantial improvement of yields in the conversion of trialkylboranes to the corresponding alkyl iodides (193). Trialkylboranes react with α-methoxyvinyllithium to yield dialkylmethylcarbinols (95) and the reaction of organylboranes with lithium aldimines presents a new approach for the synthesis of partially mixed trialkylcarbinols (56). The reaction of trialkylboranes with ferric selenocyanates has been used as a new procedure for the preparation of alkyl selenocyanates (99), see also (232), and electrolysis of trialkylboranes and nitromethane is a new route to nitroalkanes (176). For the reaction of trialkylboranes with carbonyl compounds, see (52), and with aromatic sulfonyl chlorides, see (53).

Electrophilic substitution of a primary alkylborane can proceed with inversion of configuration at carbon, provided the electrophile can coordinate to the boron (201). Consistent inversion has been observed in the base-induced reaction of elemental iodine with diisocamphenyl-2-butylborane, tri-exonorbornylborane, and B-methoxy 9-borabicyclo[3.3.1]nonane (151).

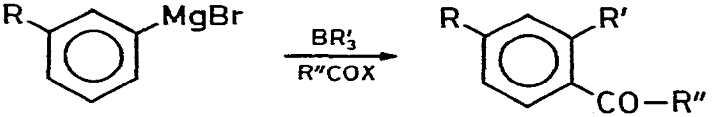
The utility of 9-borabicyclo[3.3.1]nonane as selective reducing agent has been studied in detail (202). Also, the reaction of the reagent with olefins provides for the synthesis of various 9-alkyl derivatives of the species (202), and conjugate addition of B-alkenyl-9-borabicyclo[3.3.1]nonanes to methyl vinyl ketones provides a convenient synthesis of γ,δ-unsaturated ketones (303). Methoxide ion promotes the protonolysis of orgnosilylboranes which are obtained from the interaction of 9-borabicyclo[3.3.1]nonane (or dicyclohexylborane) and vinylsilanes (326). Alkaline peroxide decomposition of the products obtained from the interaction of B-n-hexyl-9-borabicyclo[3.3.1]nonane with the lithium aldimine derived from n-butyllithium gives the unsymmetrical ketones 5-undecanone (227).

Triarylboranes form 1:1 molar complexes with hydrazine or semicarbazide (8). Irradiation of tribenzylborane produces toluene as the major product (235); similarly, irradiation of ammine-tribenzylborane in protic solvents gives a 26 % yield of toluene, but the process is solvent-dependent. The reaction of trimesitylborane with metallic Li, Na, or K in diethyl ether gives a blue paramagnetic solution which, on standing, turns red and diamagnetic (3). This color change is interpeted with a formation of a trimesityl borane di-anion by reacting the species with an electron acceptor, i.e., trimesitylborane or naphthalene.

The ion-molecule reaction of trimethylborane (alone and in mixture with other species) has been studied by ion cyclotron spectroscopy (150). No protonated trimethylborane species could be observed but proton transfer reactions lead exclusively to the formation of $(CH_3)_2B^+$ and $CH_4$.

Several studies report on the use of trialkylboranes as polymerization agents (109, 213, 214).

Various alicyclic products have been obtained by annelation of organoboranes derived from geraniol (220) and perhydroboraphenalen is readily converted to 13-azabicyclo[7.3.1]tridecan-5-ol and perhydroazaphenalene (210). The reaction of an aryl-Grignard with trialkylborane and acyl halides yields o-alkylacylphenones (284)



Secondary alcohols have been obtained from the interaction of trialkylboranes with bis(phenylthio)methyllithium; the process amounts to a transfer of two alkyl groups from boron to the methyl carbon of the lithium derivative under displacement of the two phenylthio groups via a saltlike intermediate (285).

## 4 HALOBORANES

The reaction of trihaloboranes with tetraalkyllead has been advocated as a new method for the prepration of organylhaloboranes of the type $R_nBX_{3-n}$ ($R = CH_3, C_2H_5$; $X = Cl, Br$; $n = 1, 2$) (112). Reaction of stannocene, $Sn(C_5H_5)_2$, with trihaloboranes, $BX_3$ ($X = Cl, Br, I$), in a 1:1 molar ratio results in ligand exchange and formation of dicyclopentadienylhaloboranes (77). Various cyclopentadienyldihaloboranes are readily obtained by the reaction of trimethylsilylated cyclopentadienes with trihaloboranes (124); even the diborylated species

X = Cl, Br, I

were obtained by this procedure.

In a detailed report on the hydroboration of α,ω-dienes with $(C_2H_5)_2O \cdot BH_2Cl$ the syntheses of various cyclic 1-chloroboraalkanes such as $ClB(-CH_2-)_5$ as well as their methanolysis products and some intermediates have been described (81). Also, details for the hydroboration of alkenes and alkynes with etherates of $BH_2Cl$ have been described to present a convenient procedure for the preparation of dialkyl-, monoalkyl-, and dialkenylchloroboranes (90). Similarly, hydroboration of alkenes and alkynes with $BHCl_2$-etherates provides for the convenient preparation of alkyl- and alkenyldichloroboranes, respectively (91). $BI_3$ interacts with ICN to yield $I_2BCN$ and reaction of $(CH_3)_2BI$ with $IC{\equiv}CC_6H_5$ yields $(CH_3)_2B\text{-}C{\equiv}C\text{-}C_6H_5$ (94). $(CH_3)_2BCN$ is obtained from the reaction of $(CH_3)_2BF$ with ICN (94).

The kinetics of atomic hydrogen/deuterium exchange in the reaction of $BHF_2$ with molecular deuterium has been studied (237).

Boron-11 and $^1H$ nuclear magnetic resonance studies of the reaction between $BX_3$ (X = F, Cl, Br, I) and $BR_3$ (R = $C_3H_7$, $C_4H_9$) show that the mixed (organyl)haloborane species are not uniformly favored in ligand exchange reactions (311); the effects of Lewis acidity and steric hindrance are discussed in this connection.

Higher trialkylboranes react with $CH_3SH$ to yield dialkylmethylthioboranes that, without isolation, are readily converted to the corresponding (dialkyl)bromoboranes by reaction with elemental bromine at low temperatures (259). Reaction of $BCl_3$ with $CF_3SNH_2$ results in the formation of $Cl_nB(NHSCF_3)_{3-n}$ (n = 0, 1, 2) (268). $Cl_2B\text{-}N(SCF_3)_2$ reacts with $CF_3SNH_2$ to yield unsymmetrical aminoboranes and $Cl_2B\text{-}NHSCF_3$ reacts with chlprine to yield a sublimable material, supposedly dimeric $Cl_2B\text{-}NCl\text{-}SCF_3$.

Several 2-chloro-1,3-butadienylboranes have been prepared by the following sequence (71):

$$CH_2{=}CH\text{-}C{=}CH \longrightarrow CH_2{=}CH\text{-}CCl\text{-}CH\text{-}HgCl \longrightarrow CH_2{=}CH\text{-}CCl{=}CH\text{-}BCl_2$$

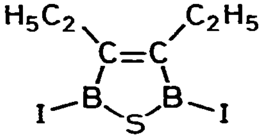
$$\longrightarrow CH_2{=}CH\text{-}CCl{=}CH\text{-}B(OCH_3)_2.$$

Similarly, the addition of $BCl_3$ to vinylacetylene and subsequent methanolysis was found to give a mixture of <u>cis</u> and <u>trans</u> products (71).

The electronic nature of R in nitroso compounds of the type R-N=O governs their reactivity with haloboranes (1). For example, N-nitrosoamines form 1:1 molar adducts with $BCl_3$ or organylboranes whereas 1,1-dichloronitrosoethane interacts with $BCl_3$ or $BBr_3$ <u>via</u> haloboronation of the N=O bond and subsequent dehalogenation to yield iminoxyborane dimers; individual structures were determined by spectroscopic and elemental analysis data. (Dialkenyl)chloroboranes undergo cross-coupling with organic halides under the influence of methylcopper to yield monoolefins and 1,4-dienes (254). Diiodoborane was found to be a regioselective reagent for the conjugate reduction of enones (209). Unsymmetrical ketones are obtained in good yield via the reaction of (dialkyl)chloroboranes with lithium aldimines followed by treatment with thioglycolic and alkaline hydrogen peroxide (227).

The mixed halide-pseudohalides $BX_n(NCS)_{3-n}$ (n = 1, 2) have been obtained for X = F (136). Vibrational spectroscopic data show that the boron is bonded to the nitrogen of the NCS group of the species.

As determined by X-ray diffraction data (121), the crystal structures of $Cl_2BSCH_3$ and $Br_2BSCH_3$ are isostructural. Both compounds exist as trimers in the form of a six-membered ring system of alternating boron and sulfur atoms in chair conformation. The compound



is obtained from the reaction of $(C_2H_5)CI{=}CC_2H_5{-}BI_2$ with $(-BI-S-)_3$ (94). It crystallizes in a triclinic system and contains two molecules in the unit cell (113). The two moieties are associated by a center of symmetry forming a four-membered $B_2S_2$ ring. This leads to the presence of two differently coordinated boron atoms in each thiadiborolene ring (each of the latter is nearly coplanar).

The photoelectron spectra of (methyl)haloboranes of the composition $(CH_3)_{3-n}BX_n$ (X = F, Cl, Br; n = 1, 2) have been compared with those of the corresponding trihaloboranes and that of trimethylborane utilizing ab initio calculations (98). The resultant data are compared with those on various additional trigonal methylborane derivatives in terms of π-bonding activities.

Mössbauer spectra of (ferrocenyl)dihaloboranes,

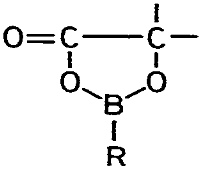
$Fe(\pi-C_5H_4BX_2)_2$ (X = F, Cl, Br, I) show a decrease in the quadrupole splitting with increasing Lewis acidity of the $BX_2$ group whereas the isomer shift remains constant (111). The vibrational spectra of (organyl)haloboranes $R_nBX_{3-n}$ (R = $CH_3$, $C_2H_5$, $C_6H_5$; X = Cl, Br; n = 1, 2) have been recorded and several new assignments of fundamentals are suggested (112). For an analysis of the vibrational spectrum of $B_4Cl_4$ see (188). The microwave spectra of $CH_2$=CH-$BF_2$ and isotopically labelled derivatives thereof have been recorded (165); on that basis structural parameters of the molecule were elucidated.

Carbon-13 nuclear magnetic resonance data of complexes of $BF_3$ with various alkyl and cyclic ketones indicate that at temperatures from -85 to -125°C exchange is slow enough (on the NMR time scale) to permit the observation of separate $^{13}C$ resonance signals for bound and free ligands (264).

## 5 BORON-OXYGEN COMPOUNDS

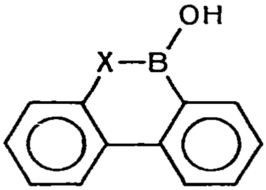
The carborane 1,5-$C_2B_3H_5$ reacts rapidly with methanol or water to form initially $ROB[CH_2B(OR)_2]_2$ (R = H, $CH_3$) (160); other small closo-carboranes, however, give smaller cleavage products such as $B(OR)_3$, $CH_3B(OR)_2$, and $CH_2[B(OR)_2]_2$. Tris(dimethoxyboryl)-methane, $HC[B(OCH_3)_2]_3$, can be reacted with ethylene glycol to yield $HC[B(-O-CH_2-)_2]_3$ (45). The latter compound can be converted to $Li^+[HC[B(-O-CH_2-)_2]_2]^-$ via reaction with $LiCH_3$ (50). The lithium salt reacts with aldehydes to give trans-RHC=CH-$B(-O-CH_2-)_2$ in exceedingly high stereoselectivity, a reaction which is also possible with ketones. Reaction of the lithium salt with $(C_6H_5)_3MCl$ (M = Ge, Sn, Pb) yields species of the type $(C_6H_5)_3M-CH[B(-O-CH_2-)_2]_2$; treatment of this tin compound with $LiCH_3$ followed by addition of $(C_6H_5)_3SnCl$ will produce the compound $[(C_6H_5)_3Sn]_2CH-B(-O-CH_2-)_2$ (45). The cited lithium salt can also be alkylated with benzyl bromide to give 1,1-bis(ethylenedioxyboryl)-2-phenylethane, $C_6H_5CH_2\text{-}CH[B(\text{-}O\text{-}CH_2\text{-})_2]_2$ (50). Treatment of this latter species with $HgCl_2$ and $NaOCH_3$ gives the compound $C_6H_5CH_2\text{-}CH(HgCl)\text{-}B(\text{-}O\text{-}CH_2\text{-})_2$, which reacts with bromine to produce $C_6H_5CH_2\text{-}CHBr\text{-}B(\text{-}O\text{-}CH_2\text{-})_2$.

1-Methoxy-cycloboraalkanes are readily obtained by the hydroboration of α,ω-dienes with $(C_2H_5)_2O\cdot BH_2Cl$ and subsequent methanolysis (81). Reaction of $LiCHCl_2$ with $B(OCH_3)_3$ and subsequent hydrolysis yields $CHCl_2\text{-}B(OH)_2$ in impure form (330). The hydroxyborane was converted, however, to several well-characterized organyloxy derivatives. Reaction of (diethyl)chloroborane with the corresponding silver salt has been used to prepare the O-diethylboron derivative of p-toluene-N-nitrosulfonamide, $CH_3\text{-}C_6H_4\text{-}SO_2\text{-}N{=}N(O)\text{-}O\text{-}B(C_2H_5)_2$ (32) and reaction of (dibutyl)chloroborane with Na/K alloy followed by treatment with benzoyl chloride yields (benzyloxy)dibutylborane (308). (Organyl)dihaloboranes and α-hydroxy carboxylic acids interact to yield cyclic species of the type

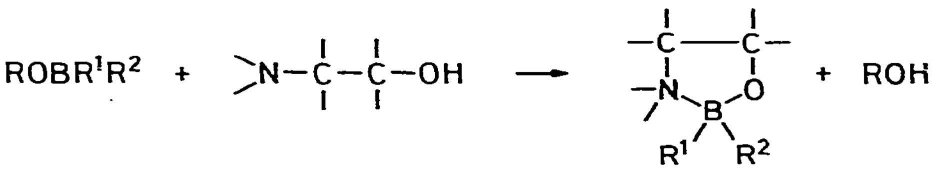


These compounds are closely related to the condensation products derived from $RBX_2$ and oxalic acid but are considerably weaker Lewis acids than the latter (114). Thermal and mass spectral fragmentation of the species are discussed.

10-Hydroxy-10,9-boroxaro( and azaro)phenanthrene



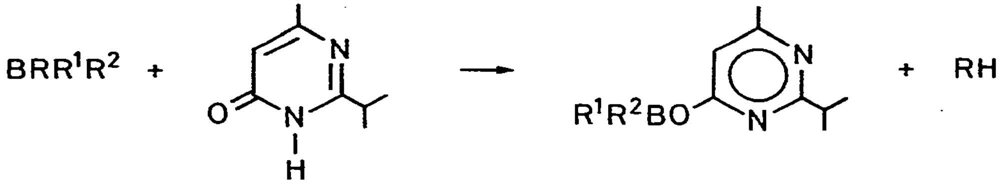
can behave as protonic as well as Lewis acid and $^{11}B$ nuclear magnetic resonance data on the species are interpreted to demonstrate a lack of aromatic character in the heterocycle (78). The relative hydrolytic stability of the species is assumed to be due to the B-X bond strengthening via rehybridization of the heteroatom orbitals. Unsymmetrical (organyloxy)diarylboranes have been reacted with amino-hydroxy compounds to yield boroxazolidines containing an asymmetric boron atom (103):



The structures of the resultant products were confirmed by infrared data.

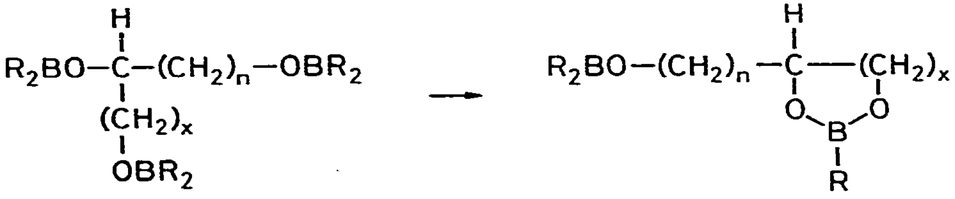
(Vinyloxy)diethylboranes are obtained by the 1,4-addition of triethylborane to methacrolein, methyl vinyl ketone, isopropenyl methyl ketone, phenyl vinyl ketone, or phenyl isopropenyl ketone at temperatures between -78 to 100°C (85). The stereoselectivity of the reaction varies widely but structures were unequivocally assigned with the aid of nuclear magnetic resonance data. Similarly, various trialkylboranes add in 1,4-fashion to 2-methylacrolein to yield (alkenyloxy)dialkylboranes at various rates (84); however, (E)-vinyloxydialkylboranes are formed predominantly. Analogous reactions of 2-methylacrolein with (diethyl)organylboranes, triallylboranes, triphenylborane, and ethyldiborane(6) have been described (84). A new cross-aldol reaction via vinyloxyboranes has also been reported (234).

Trialkylboranes, $BR_3$ (R = $C_2H_5$, i-$C_3H_7$), and the dimeric 9-borabicyclo[3.3.1]nonane react with 2-isopropyl-6-methyl-4-pyrimidine according to (276):

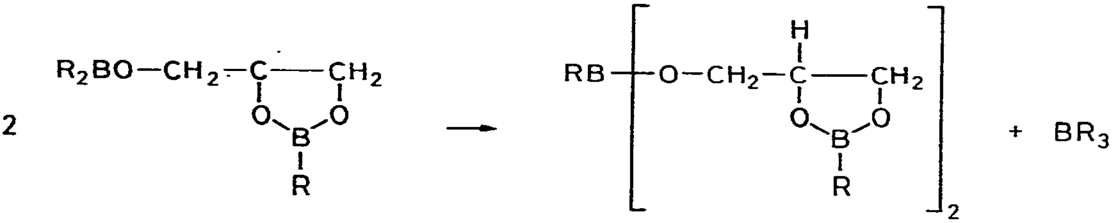


Subsequent reaction of the boron-containing species with aldehydes yields (2,2-dialkylvinyloxy)dialkylboranes in virtually quantitative yield.

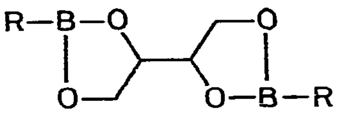
Alkane triols react with trialkylborane in the presence of diethylboryl pivalate as a catalyst to yield the corresponding O-diethylborylated species (87). Pyrolysis of the products at temperatures above 150°C or interaction with ethyldiborane(6) at room temperature have been employed to prepare 2-ethyl-1,3,2-dioxaboracycloalkanes, <u>e.g.</u>:



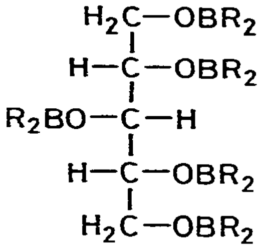
At temperatures above 220°C (or below 50°C in the presence of B-H groups) the resultant species condense in an intermolecular reaction

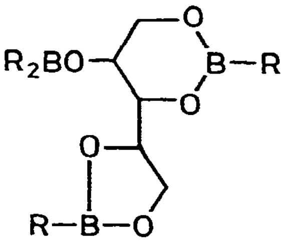


with the elimination of $BR_3$. Alternatively, the exocyclic $BR_2$ moiety can be displaced by H <u>via</u> interaction with $CH_3OH$; ring opening occurs simultaneously but to a minor degree. Subsequent substitution reactions at the OH site of the molecules are feasible. Tetraols react in similar fashion as outlined above and species of the type

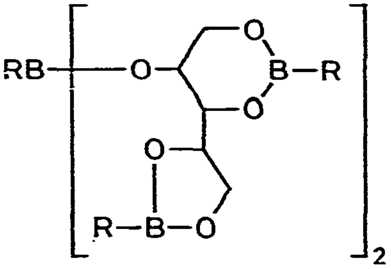


can be obtained (87). The structures of all products were ascertained by infrared, mass, and nuclear magnetic resonance spectroscopic data. The pentaol xylitol reacts in similar fashion (86) to yield the following two species:

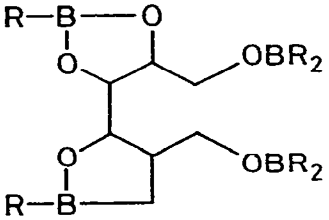




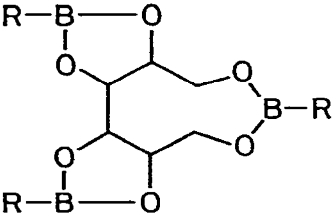
The exocyclic $R_2B$ group of the latter compound is readily displaced by H via reaction with acetylacetone whereas treatment with $CH_3OH$ results in partial ring opening; subsequently, the hydrogen has been replaced by $C_6H_5CO$ through treatment with benzoyl chloride/ pyridine. Also, the bicyclic species depicted above undergoes an intermolecular condensation (86) to form the following compound:



This latter reaction is reversible by treating the product with a large excess of triethylborane. It is worth noting that in the bicyclic species the six-membered heterocycle undergoes a ring opening more readily than the five-membered ring system. The reaction of the hexol dulcitol with triethylborane proceeds in quite similar fashion as outlined above (88). The polydiethylboryloxy derivative can be isolated but undergoes an intramolecular condensation to yield



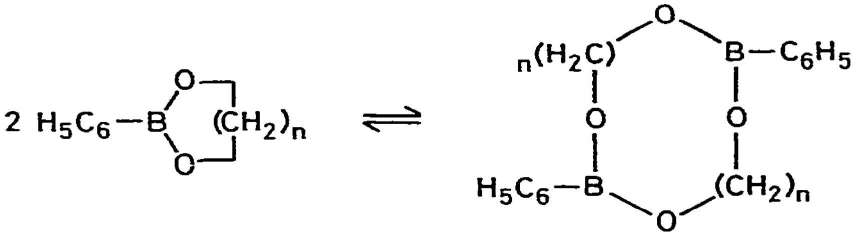
The two exocyclic $BR_2$ groups of this latter species can again be displaced by H which, in turn, can be replaced by various organic groups such as $CH_3CO$. Also, the molecule undergoes an additional intramolecular condensation to form the following compound:



However, the structural information on the latter two species illustrated above is not completely conclusive and alternate structures involving 1,3,2-dioxaboracyclohexane moieties rather than the depicted five-membered ring system are possible. For similar reactions of D-mannitol with triethylborane, see (83). Two routes are described for the preparation of ethylboronated

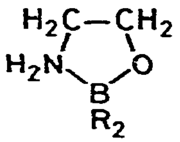
O-derivatives of some methyl glycosides in a regioselective synthesis (294).

Condensation of (phenyl)dihydroxyborane with $HO(CH_2)_nOH$ (n = 5, 6) yields heterocyclic species which equilibrate as illustrated by the following scheme (316):

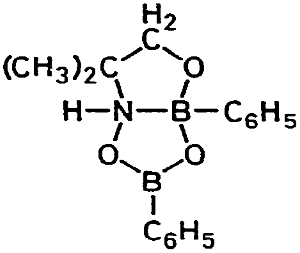


The N-oxides of 1-alkyl-3,5-piperidindiol interact with (aryl)-hydroxyboranes to yield betaines with an adamantanoid or a bicyclic ring system (306):

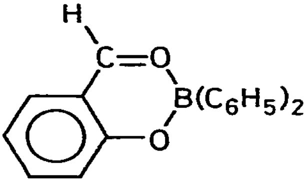
The crystal and molecular structure of the following compound with R = $C_6H_5$ or $C_6H_4$-4-$CH_3$ , respectively, has been studied by X-ray diffraction (317) and features intermolecular NH...O bonding.



The structure of

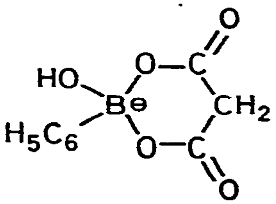


features one nearly planar BOBON ring in which the two boron atoms are in different coordination (318); intermolecular NH...O bonding is also observed. X-ray data on (salicylaldehydato)-diphenylborane



show that the heterocycle is almost planar, the boron atom being 0.33 Å from the mean plane of the other five atoms (135).

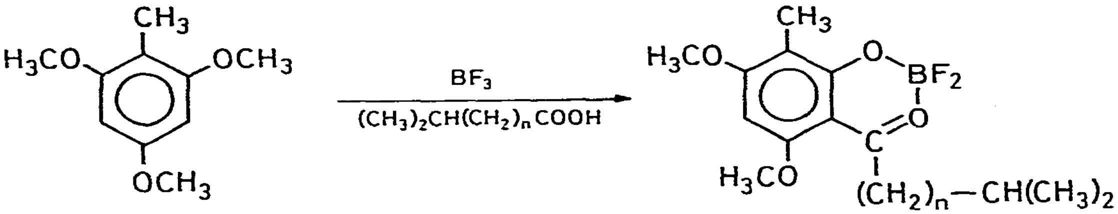
The stability constant for the reaction $C_6H_5B(OH)_2$ + 2 $H_2$mal $\rightleftharpoons$ $C_6H_5B(OH)(mal^-)$ + $H_3O^+$ ($H_2$mal = malonic acid) is 0.026 suggesting the formation of a tetrahedral anionic complex as illustrated below (14):



For a study of the $pk_a$ and the protodeboronation of (2-furyl)-dihydroxyborane, see (332).

Cyclic derivatives of several sugar phosphates containing $CH_3BO_2$ and $C_4H_9BO_2$ groupings as structural unit have been examined by mass spectrometry (169); the data seem to substantiate the formation of rearrangement ions containing a B-O-P linkage. For mass spectral data on cyclic bis(alkaneboronates) of various monoacetylated carbohydrates see (293). The mass spectral fragmentation patterns of various chelates containing the $BF_2$ or $B(C_6H_5)_2$ moiety are substituent dependent (117); boron-bonded fluorine-containing species form trigonal boron moieties by chelate ring opening whereas the boron-phenyl species lose a phenyl group.

2,4,6-Trimethoxytoluene reacts with $(CH_3)_2CH-(CH_2)_n-COOH$ (n = 0, 1) and $BF_3$ to form boron-containing heterocycles in a selective demethylation process as is illustrated by the following equation (275):



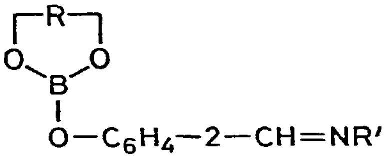
The resultant species can be hydrolyzed and the process may be of potential use in natural product chemistry, particularly since a similar reaction, i.e., formation of boron-containing heterocycles, is also observed with 1,3,5-trimethoxybenzene.

The pulse radiolysis of aqueous solutions of (phenyl)dihydroxyborane and its m-nitro and m-amino derivatives have been studied (219); a band observed at 297 nm is assigned to the $[C_6H_5B(OH)_2]^-$ anion which is formed in an electron-capture reaction; electron inductive effects are discussed.

Poly(styryldihydroxyborane) resin has been used successfully in the selective functionalization at glycosides (278) and cyclic boronate species have been utilized in gas chromatographic analysis (215) and in gas-liquid chromatography-mass spectrometry studies (216, 267). The deboronation of (p-vinylphenyl)dihydroxyborane polymers has been utilized for the synthesis of p-deuterated polystyrenes (54). For copolymers of (p-vinylphenyl)dihydroxyborane with styrene see (277).

*Ab initio* molecular orbital calculations on $H_3BOH_2$, $(H_2BOH)_2$, and some related compounds have been made (47). Based on these data it is concluded that the bonding in the cited species is very similar to that of related aluminum compounds and that the reorganization energy due to conjugation in $H_2BOH$ is responsible for a very low dissociation energy for the $(H_2BOH)_2$ molecule. Electron diffraction data on gaseous $[(CH_3)_2B]_2O$ indicate the existence of coplanar $C_2BO$ units in the molecule with a B-O distance of 1.359 Å and a B-C bond length of 1.573 Å (41). The structure of $B(OCH_3)_3$ as determined by electron diffraction involves a planar $B(OC)_3$ skeleton of $C_{3h}$ symmetry with a B-O distance of 1.367 Å (40). Tris(organyloxy)boranes, $B(OR)_3$, hydrolize in organic solvents in the presence of KOH to yield anhydrous potassium polyborates (115); the rate of hydrolysis is dependent upon the size of the organic moiety, the reaction temperature, and the polarity of the solvent. Several polyborate and fluoropolyborate ions have been identified in solution by Raman spectroscopic measurements (247).

Four routes involving condensation reactions have been developed for the synthesis of 2-(N-alkylsalicylaldimino)borinanes, -borolanes, and -boroles (101):



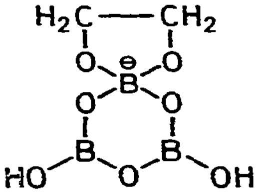
These compounds are reasonably stable toward moisture indicating back-coordination of the azomethine-nitrogen to boron.

Tetrachlorosilane, metallic lithium, and $ClB(OCH_3)$ interact to form solid $Si[B(OCH_3)_2]_4$ (155); the B-Si bond is sufficiently stable to survive transesterification. Tris(trimethylstannyloxy)-borane and the corresponding Ge and Sn compounds have been prepared by condensation reactions and were characterized by infrared and proton magnetic resonance data (241).

The vibrational spectrum of $B(OCH_3)_3$ has been studied in detail (337) and the data were interpreted in terms of a $C_{3h}$ model; the calculated forceconstant f(BO) is 4.75 mdyn/Å. The cell parameters of $B(-O-CH_2-CH_2-)_3N$ have been re-determined (168) and the $^{14}N$ nuclear magnetic resonance spectrum of the compound has been recorded (222). The synthesis of $B(O-CH_2-CH_2NHC_6H_5)_3$ has been described and thermal cracking of the compound was found to lead to indole (224).

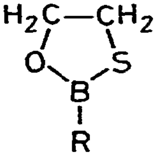
Complex formation equilibria in the system $MF/B(OCH_3)_3$ (M = alkali metal) were determined by the solubility of MF in the reaction medium (2). The resulting salts of the type $M[FB(OCH_3)_3]$ are readily soluble in $CH_3OH$ in which solvent, however, decomposition occurs. For vapor-liquid equilibria of the trimethoxyborane/carbon tetrachloride and trimethoxyborane/benzene systems, see (253).

Boric acid and ethylene glycol form equilibria in aqueous medium in the presence of $NaClO_4$ that contain polyborate ions as well as glycol complexes such as the following species (17):



For the thermal condensation of boric acid with pentitols and hexitols (166) as well as with pentaerythriols and analogous compounds (167), see the cited references. Also, complexes of sodium tartrate with boric acid have been studied (273) and several borate-polyol complexes have been investigated by Raman spectroscopy (231). For anion-exchange chromatography of alditols in borate medium see (175). The reaction of boric acid with various monobasic bidentate ligands in refluxing acetic anhydride gives chelates of boroacetate of the type $(L\text{-}L)B(O\text{-}CO\text{-}CH_3)_2$ (271). In the 1:1 molar interaction of boric acid and benzoyl acetone a chelate is formed that has an intramolecular charge-transfer band at 310 nm; photo-excited species of the ligand are discussed (248). For a benzylamine-borotartrate complex, see (298), and for solid solutions in the Mn, Co, and CU pentaerythritolborate series, see (297).

Heterocylces of the structure



with R = $C_6H_5$, $N(C_2H_5)_2$, $NHC_4H_9$, and $SC_2H_5$ have been prepared by condensation of 2-mercaptoethanol and an appropriate borane such as $C_6H_5B(SC_2H_5)_2$ (164).

Boric acid and (phenyl)dihydroxyborane have been used in the partial acetonation of monosaccharides (230).

## 6 BORON-SULFUR COMPOUNDS

Various 2-substituted 1,3,2-dithiaboracyclohexanes, $CH_2(\text{-}CH_2\text{-}S\text{-})_2BX$ with X = $C_6H_5$, $N(C_2H_5)_2$, $NHC_3H_7$, $NHC_4H_9$, $NHC_6H_5$, and $SC_2H_5$ have been prepared and mass spectral data on the species were recorded (327). For the preparation of some arylthiopolyboranes, see (242); the preparation and structure of a thiadiborolene derivative (113,121) has been discussed above.

Ab initio calculations on HBS (63) and $H_2B$-S-S-$BH_2$ (29) have been reported; the results on the latter compound indicate a substantially higher barrier to internal rotation for the syn as compared to the anti form of the molecule. On $CO_2$-laser irradiation of a mixture of $B_2H_6$ and $H_2S$ ($D_2S$) the species $HB(SH)_2$ and $HB(SD)_2$, respectively, are formed (as unstable materials) besides μ-HS-$B_2H_5$; the compounds are not produced in an analogous thermal reaction (183).

Bis(methylthio)methylborane, $(CH_3S)_2BCH_3$, has a molecular skeleton which is nearly coplanar but with non-equivalent $SCH_3$ groups (18); the electron diffraction data on the gaseous species give values of 1.796 Å for the B-S bond distance and 1.818 Å for the C-S bond. Bis(trifluoromethylthio)methylborane has been obtained from the reaction of (methyl)dihaloborane with $Hg(SCF_3)_2$ (110); various other haloboranes react in analogous fashion and $Cl_2BSCF_3$, $ClB(SCF_3)_2$, $B(SCF_3)_3$, and others have also been prepared by this procedure. The compounds are chemically unstable and decompose readily with the formation of fluoroboranes.

For kinetics and mechanism of the reduction of ketones employing $Na[H_2BS_3]$ as agent, see (342).

## 7 BORON-NITROGEN COMPOUNDS

### 7.1 AMINOBORANES

(Dimethylamino)haloboranes of the type $(CH_3)_2N$-BHX with X = Cl, Br have been obtained by the reaction of dimeric (dimethylamino)dihydroborane with $HgX_2$ at 110°C (13); monomer-dimer equilibria persist in the gas phase, the dimer involving a $B_2N_2$

ring system. Diphenylamine and $BBr_3$ interact in refluxing benzene to form $(C_6H_5)_2N-BBr_2$; the colorless solid interacts with pyridine to yield a boronium salt (181). Pyrrole reacts with $THF{\cdot}BH_3$ at 0°C to yield (1-pyrrolyl)dihydroborane as a 1:1 molar adduct with THF (6). Further reaction with pyrrole yields Tris(1-pyrrolylborane) besides a polymeric species, most likely resulting from a hydroboration of the pyrrolyl moiety with (1-pyrrolyl)dihydroborane. This polymer is the exclusive product in the reaction of $B_2H_6$ with pyrrole in the absence of solvent. (1-Pyrrolyl)dihydroborane is also obtained when $THF{\cdot}BH_3$ is reacted with tris(1-pyrrolyl)borane and pyridine-trichloroborane was found to react with (1-pyrrolyl)potassium to yield pyridine-(1-pyrrolyl)dihydroborane (6). Trihaloboranes, $BX_3$ (X = F, Cl, Br) react with tris(-trimethylsilyl)amine N-silylated (amino)haloboranes (20), and $(CF_3S)_2NH$ reacts in similar fashion (95). Reaction of $X_2B-N(SCF_3)_2$ with $Hg(SCF_3)_2$ gives $(F_3CS)_2N-B(SCF_3)_2$ and with $LiBH_4$ the corresponding dihydroborane is obtained. All of these species appear to contain an extremely electron-poor boron-nitrogen bond.

(Dimethylthiophosphorylamino)boranes of the type $B[NR-PS(CH_3)_2]_3$ and $XB[NR-PS(CH_3)_2]_2$ are monomeric whereas $X_2B-NR-PS(CH_3)_2$ species (X = Br, $CH_3$) form monomer-dimer equilibria in which B-S coordination seems to prevail (80).

Molecular orbital calculations suggest an eclipsed boat conformation for $(H_2B-NH_2)_3$ and indicate that the molecule is thermodynamically unstable with respect to disproportionation (261). The electronic influence of the substitutents on the free enthalpy of rotation about the B-N bond of aminoboranes of the type $(CH_3)_2N-BClR$ and $RCH_3N-B(CH_3)_2$ where R is a <u>para</u>-substituted phenyl group has been studied by nuclear magnetic resonance spectroscopy (212), and the stereochemical rigidity and enantiomerization of bis(diisopropylamino)dialkylaminoboranes has been studied by $^1H$ and $^{13}C$ NMR spectroscopy and was established for $R = C_2H_5$ (334).

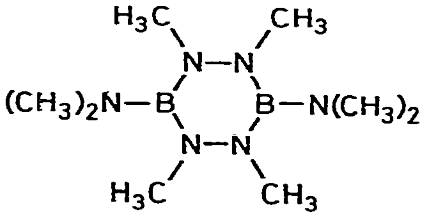
For electroless plating baths containing (dimethylamino)borane as the reducing agent and the properties of the deposits, see (299).

## 7.2 BORON-NITROGEN RING SYSTEMS

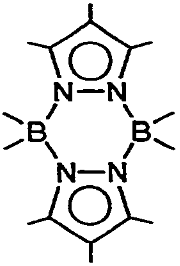
Excess $BBr_3$ reacts with $Cl_3VNCl$ to yield the novel borazine $[-BBr-N(BBr_2)-]_3$ (21); the compound was characterized by its vibrational spectrum exhibiting the B-N ring frequency at 1450 $cm^{-1}$ and by nuclear magnetic resonance and mass spectroscopic data. Boron-deuterated borazines can readily be prepared in a gas phase reaction with a $D_2/HBF_2$ mixture, in which the $HBF_2$ acts as an H/D exchange catalyst (148). Borazine cations are formed by 10.2 eV photon impact on borazine, B-trimethylborazine, or N-trimethylborazine; the ions react with their precursors by proton transfer. In the methylated cations the odd electron seems to be located at a carbon atom (338).

Boron-11 and $^{14}N$ chemical shift values of borazines can be interpreted in terms of delocalized $p_z$ electron pairs of the nitrogen atoms in the ring system (182); $\delta^{14}N$ correlates linearly with the calculated $\pi$-charge densities at the nitrogen atoms. Coriolis constants of the E" species of borazine have been determined by a study of the vapor phase Raman spectrum of the compound (61). For force constant calculations on the borazine ring by the Coulsen and Longuet-Higgins method, see (96), and for the pure rotational spectrum of borazine, see (270).

The molecular structure of the compound



was investigated by X-ray diffraction techniques (118). The $B_2N_4$ ring is non-planar with a B-N distance of 1.43 Å and a N-N distance of 1.43 Å. The mass spectra of dimeric (1-pyrazolyl)-boranes (= pyrazaboles) of the structure



give evidence for three major fragmentation processes (341). Common to all spectra is the symmetrical cleavage of the molecule under electron impact whereas the occurrence of rearrangement processes <u>via</u> $B_2N_3$ and $B_2N_2$ ring systems is depending on the nature of the carbon substituents.

## 7.3 IMINOBORANES

Bisiminoboranes and trisiminoboranes have been prepared via thioboranes (74):

$$RB(SR')_2 + 2\ C_6H_5R''C{=}NH \longrightarrow RB(N{=}CR''C_6H_5)_2$$

$$B(SR')_3 + 3\ C_6H_5R''C{=}NH \longrightarrow B(N{=}CR''C_6H_5)_3$$

Diarylketimine hydrochlorides react with aminoboranes to yield (diarylketimino)boranes (307):

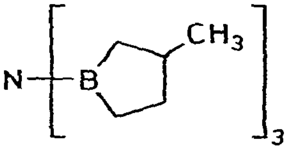
$$Ar_2C{=}NH\cdot HCl + R_2B{-}N(C_2H_5)_2 \longrightarrow Ar_2C{=}N{-}BR_2 + (C_2H_5)_2NH\cdot HCl$$

Dipole measurements on the resultant species give relatively low values in the order of approximately 1.5 to 2.5 D; this observation seems to dispute allene-like structures for the compounds. On the other hand, $^{13}C$ nuclear magnetic resonance data on $(CF_3)_2C{=}N{-}B(CH_3)_2$

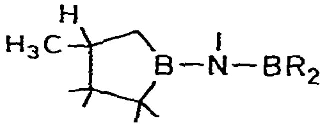
suggest that the CNB ckeleton is linear with an allene-like structure (12). The cited compound exhibits a vapor pressure of 488 Torr at 19°C and is readily obtained by a dehydrohalogenation reaction between $(CF_3)_2CNH$ and $(CH_3)_2BBr$.

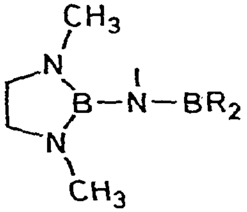
## 7.4 COMPOUNDS CONTAINING ANNULAR BORON

The reaction of tris(trimethylstannyl)amine with the corresponding 1-bromoborolane yields the compound



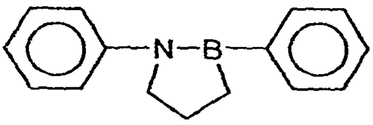
Nuclear magnetic resonance data on this tris(boryl)amine demonstrate that the borolanyl group withdraws electron density from the nitrogen via B-N interactions (39). A number of novel diborylamines have been described in which the boron is incorporated into an annular system (23). The species of the types



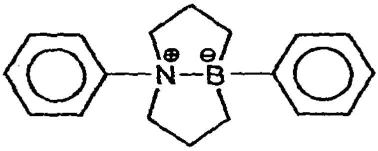


are relatively stable toward hydrolysis and can be distilled without noticeable decomposition.

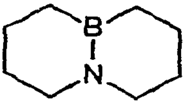
The reaction of triethylamine-phenylborane with N,N-diallylaniline yields 1,2-diphenyl-1,2-azaborolidine



and 1,5-diphenyl-1-aza-5-borabicyclo [3.3.0] octane

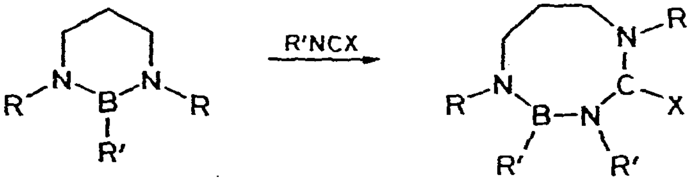


as the major boron-containing products (163). The species

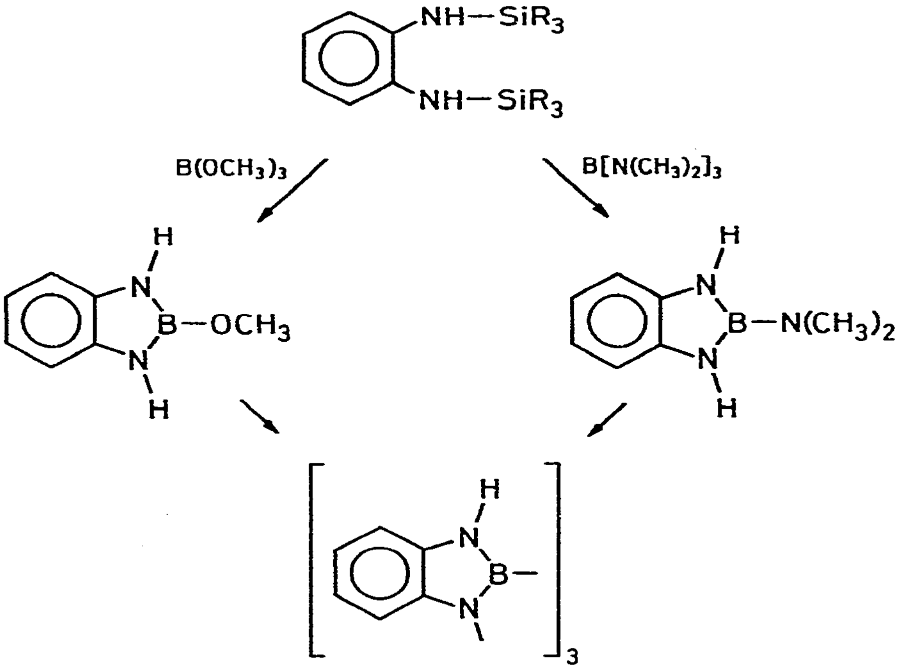


normally exists as a dimer; however, at temperatures near 180°C monomer formation occurs and the He(I) photoelectron spectrum of the monomer has been recorded (22).

2-Phenyl-1,3,2-diazaboracyclohexane reacts with phenyl isocyanate or isothiocyanate in a 1:1 molar ratio according to (7):

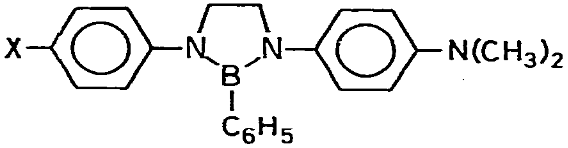


The structures of the products were confirmed by infrared and nuclear magnetic resonance data that clearly dispute the presence of alternate species. Additional derivatives of this triazaboracyclooctane heterocyclus have been obtained by such an aminoboronation procedure (329). The following reaction series has been briefly described (184):



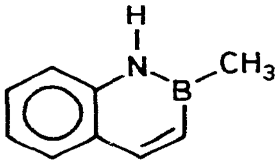
and X-ray data on B,B'-bis(1,3-dimethyl-1,3,2-diazaborolidin-2-yl, $(-CH_2-NCH_3-)_2B-B(-NCH_3-CH_2-)_2$, have been gathered (312). These data clearly support the suggested structure and dispute the interpretation of earlier mass spectroscopic results.

The transmission of substituent effects in the system

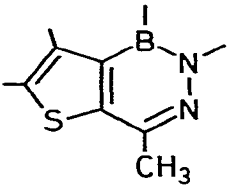


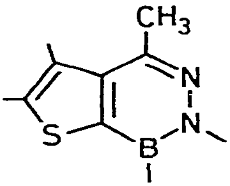
with X = Cl, $OCH_3$, $NO_2$ and similar heteroimidazolidine systems has been studied by $^1H$ nuclear magnetic resonance investigations (154). The transmission does not seem to be affected by the hetero atom.

Some electronic properties of 2-methyl-2,1-borazaronaphthalene



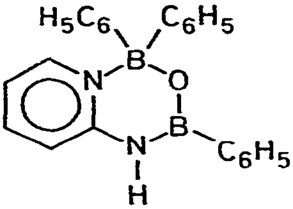
have been studied by CNDO/2 approximation (333). The rotational barrier of the methyl group was found to be approximately 1 kcal/mol and there exists a net charge transfer from the heterocycle to the methyl group along the B-$CH_3$ bond. The preparation, bromination and nitration of some thieno-fused 3,2-borazaropyridines



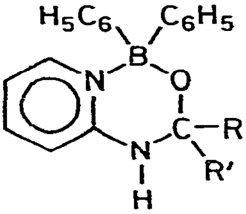


have been described (31) and halogen-metal exchange has been found possible by reacting iodo- or bromo-substituted 3,2-borazaropyridines with butyllithium (30).

2-Aminopyridine and triphenylborane form a 1:1 molar adduct in which the pyridyl nitrogen is coordinated to the boron (11); pyrolysis of the compound yields B-triphenyl-N-2-pyridylborazine. Similarly, 2-aminopyridine coordinates with the boron atom of (2-pyridylamino)diphenylborane and the latter reagent was also found to form a 1:1:1 molar adduct with (diphenyl)hydroxyborane and 2-aminopyridine. Pyrolysis of this latter adduct yields (diphenylboryl)(2pyridylaminophenylboryl) oxide, which has a coordinated bicyclic structure:

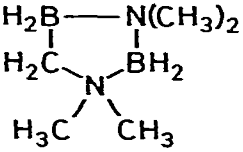


(2-Pyridylamino)diphenylborane reacts cleanly with aldehydes or ketones in a 1,2-addition of the pyridylamino and diphenylboryl fragments of the aminoborane across a carbonyl group (10). The resultant products, however, have again a bicyclic coordinated structure

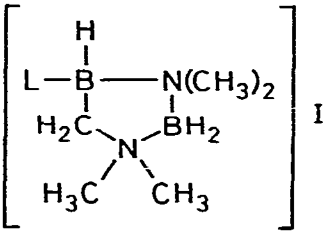


as is evidenced by their $^{11}B$ nuclear magnetic resonance spectra and their high hydrolytic stability. A similar species is obtained on reaction of (2-pyridylamino)diphenylborane with carbon dioxide, whereas with molecular oxygen or water the diboryl oxide cited above is obtained (11).

The reaction of bis(trimethylamine)-dihydroboronium iodide with potassium metal yields the following heterocyclic species (33):

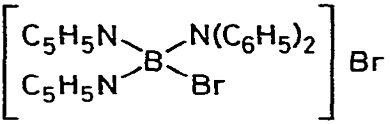


This same compound is also obtained via the reduction of $(CH_3)_3N\cdot BH_2X$ (X = Br, I) with sodium-potassium alloy (35). For this latter process, a reactive intermediate $[(CH_3)_3NBH_2:]^-$ was formulated. Monohalogenation of the heterocycle with HX (X = Cl, Br, I) under mild conditions occurs at the C-B-N boron atom. A second halogen can be attached to the other boron atom, a third halogen again bonds to the C-B-N boron and displacement of all four boron-bonded hydrogens has also been accomplished (33). The monoiodinated product reacts with Lewis bases L such as pyridine or trimethylamine by iodide ion displacement to yield a novel type of boronium salt (34):



## 7.5 AMINE-BORONIUM IONS

(Diphenylamino)dibromoborane interacts with pyridine to form the following boronium salt (181):



Several boronium salts of the type $[LL'BH_2]I$ were obtained in a two-step process (27). Initially, adducts of iodoborane, $L\cdot BH_2I$ with L = trimethylamine, pyridine, triphenylphosphine, are obtained by combination of the reactants; addition of a second donor molecule L' = trimethylamine, trimethylphosphine or triphenylphosphine yields the cited salts. The various species were characterized by elemental analysis as well as $^1H$ and $^{11}B$ nuclear magnetic resonance data.

A newly defined class of O and N bonded boron cations derived of betaines and amino acid esters, e.g., $[(CH_3)_3N\text{-}BH_2\text{-}O\text{-}CO\text{-}(CH_2)_nN(CH_3)_3]^+$, has also been described (145).

## 7.6 AMINE-BORANES

Simmons-Smith reagent, an organometallic complex formed between Zn and $CH_2I_2$, interacts with $(CH_3)_3N\cdot BH_3$ by transferring methylene groups to a B-H bond (44). It appears that the B-N bond is destroyed in the initial stage of the reaction; if the reagent is prepared in the presence of trimethylamine-borane on a 3:1 molar ratio, a yield of trimethylborane is obtained that is close to the theoretical value. However, interaction of the two species in a 1:1 molar ratio does not yield any trimethylborane.

Adducts of iodoborane of the type $L\cdot BH_2I$ where L is a nitrogen donor molecule (or a phosphine) are readily obtained by direct combination of the two reactants (27). Trimethylamine-iodoborane reacts with AgCN to form $(CH_3)_3N\cdot BH_2NC\cdot AgCN$ whereas interaction of the cited amine-borane with $K[Ag(CN)_2]$ in $CH_2Cl_2$ yields a precipitate of $[(CH_3)_3NBH_2]_2CNAg_2I_3$; evaporation of the solution yields $(CH_3)_3N\cdot BH_2CN$ (157).

For species of the type $L\cdot BH_2X$ (L = trimethylamine, pyridine, trimethylphosphine; X = F, Cl, Br, I, NCS, NCSe) there seems to exist a correlation between the B-H coupling constant , the electronegativity of X and the (estimated) B-X distance (28). This observation appears to be useful for the prediction of coupling constants of yet unknown compounds of this type. The $^{13}C$ nuclear magnetic resonance spectra of trimethylamine-trihaloboranes exhibit trends of the chemical shift values that reflect the order of Lewis acidity of the trihaloboranes (143). Elsewhere (64), the preparation and some physical data of amine-haloboranes of the type $R_3N\cdot BX_nY_{3-n}$ (R = organic substitutent, X = halogen, Y = cyanate or thiocyanate group) are reported.

Trimethylamine-iodoborane reacts slowly in liquid ammonia to transform into bisamminedihydroboronium iodide (263); the reaction rate is greatly increased in the presence of halide salts. Reaction of $(CH_3)_3N \cdot BH_2I$ with NaCN gives mainly $H_3N \cdot BH_2CN$ (in liquid ammonia), and with $NaNH_2$ polymeric $(H_2B\text{-}NH_2)_n$ is obtained.

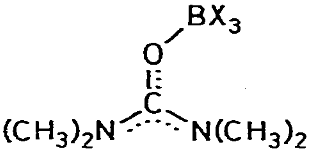
The annular atom of 2-aminopyridine serves as donor site in the complex with triphenylborane (11) and, based on molecular orbital calculations, the principle contribution to the stabilization of $H_3N \cdot BH_3$ and the corresponding N-methylated species is the electrostatic interaction (292). For molecular motion studies on solid trimethylamine-borane by nuclear magnetic resonance techniques, see (132).

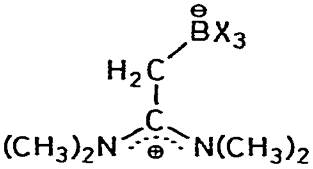
The hydrolysis of $(CH_3)_3N \cdot BH_2F$ occurs <u>via</u> acid-independent and acid-catalyzed pathways, each of which is first order in substrate (93). The mechanism of the thermal decomposition of solutions of hydrazine-borane in hydrazine has also been studied (55).

$(CH_3)_3N \cdot BBr_2CN$ has been obtained by direct bromination of $(CH_3)_3N \cdot BH_2CN$ in aqueous solution (170). $(CH_3)_3N \cdot BH_2(COOH)$ has been obtained by the reaction sequence (149) $R_3N \cdot BH_2CN \longrightarrow R_3N\text{-}BH_2\text{-}CNC_2H_5{}^+BF_4{}^- \longrightarrow R_3N \cdot BH_2(CONHC_2H_5) \longrightarrow R_3N \cdot BH_2(COOH)$ (where $R = CH_3$). The molecular structure of the product was determined by single crystal X-ray analysis and dimensions were found to be similar to those of other carboxylic acids. The compound, which may be viewed as the boron analog of an amino acid, exhibits significant antitumor activity. Various amine-boranes derived from amino acid esters have been prepared in another study (282); the amino groups serve as donor sites to the boron.

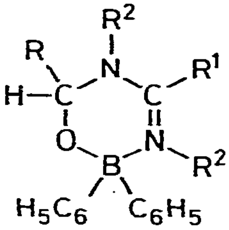
Tetramethylthiourea and tetramethylselenourea form 1:1 molar adducts with $BF_3$ which are partially converted into ionic species

(133), and the adducts of tetramethylurea and 1,1-bis(dimethylamino)ethylene with trihaloboranes were found to show similar complexation shifts and restricted rotation about the central C-N bonds (134).

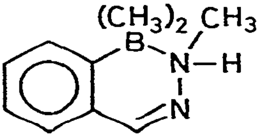




Consecutive addition of aqueous alkali, an aldehyde and acetamidine hydrochloride to (butyloxy)diphenylborane yields chelates of the following type (4):



The intramolecular adduct 3,4-dihydro-3,4,4-trimethyl-4,3-borazaroisoquinoline



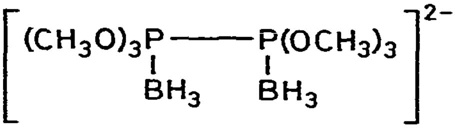
contains an asymmetric nitrogen atom. One of the two possible isomers has been studied by X-ray diffraction techniques (336) and was found to contain a B-N bond distance of 1.645 Å and a N-N distance of 1.463 Å.

## 8 PHOSPHORUS-CONTAINING SPECIES

When $H_3P\text{-}BH_3$ is dissolved in liquid ammonia at -45°C, the salt $NH_4\left[H_2P(BH_3)_2\right]$ is the final product of the reaction (141). At higher temperatures, increasing amounts of $H_3N\text{-}BH_3$ are formed besides the cited species. In contrast, methylamine and dimethylamine from the corresponding amine-boranes at -45°C whereas at higher temperatures salts corresponding to the one cited above are obtained. Trimethylamine forms the amine-borane under all conditions that were studied.

The compound $F_2B\text{-}NH\text{-}PF_2$ has been obtained by the interaction of $BF_3$ with $F_2P\text{-}NH_2$ (262). Controlled halogenation of the species $\left[(CH_3)_2P\text{-}BH_2\right]_3$ to yield partially halogenated species is possible with several reagents of which N-halosuccinimides are the most selective (244); B-monohalo derivatives are nucleophilic attacked by amides to yield the corresponding organyloxy derivatives besides ammonium halides (243). Detailed multinuclear magnetic resonance studies of various derivatives of the cited six-membered heterocyclic system have been utilized for structural assignments (245). Detailed nuclear magnetic resonance studies on aryldifluorophosphine-boranes, $RF_2P\text{-}BH_3$, have been recorded and chemical shift data are presented elsewhere (161). Based on $^{11}B$ nuclear magnetic resonance data on haloborane adducts with various phosphines (as well as arsines) both the $^{11}B$ chemical shift increment as well as the P-B coupling constant are sensitivie to the donor-acceptor bond strength (189).

Single-crystal electron spin resonance studies on triphenylphosphine-trichloroborane indicate the formation of the triphenylchlorophosphine radical during X-irradiation (238). $OP\left[N(CH_3)_2\right]_3$ forms adducts with $BF_3$ and $BCl_3$ that have been characterized (205); however, interaction of the phosphor amide with $BBr_3$ and $BI_3$ is more complex and results in the cleavage of a P-N bond as implicated by the isolation of the iodide of the cation $[(CH_3)_2N]_3PO\text{-}BH_2\text{-}[(CH_3)_2N]_2PIO^+$. These studies led to the discovery of a new type of boronium cations in which the boron is bonded to one nitrogen and two oxygen bases, e.g., the cation $|L\cdot BH[[(CH_3)_2N]PO]_2|^{2+}$. Reduction of trimethylphosphite-borane with sodium naphthalide seems to yield the dianion depicted below (142).



$$\left[(CH_3O)_3\underset{BH_3}{\underset{|}{P}}-\!\!-\!\!-\underset{BH_3}{\underset{|}{P}}(OCH_3)_3\right]^{2-}$$

## 9 BORATES

Various tetraalkylammonium tetrahydroborates have been prepared from the corresponding ammonium iodides by an exchange reaction with $BH_4^-$-loaded exchange resin in aqueous alcoholic media at 0°C (9) and on a cationic exchange resin (225) according to the equation:

$$(R_4N)X + MBH_4 \longrightarrow (R_4N)BH_4 + MX.$$

Quaternary ammonium hydroxides undergo a metathesis reaction with $Na(H_3BCN)$ (170) and the latter salt has been utilized as a selective reducing agent in acidic ethanol at ambient temperatures (203). For the mechanism of the reduction of α,β-unsaturated tosylhydrazones with the cited salt, see (289).

(1-Pyrrolyl)borane reacts with metal hydrides to yield alkali metal trihydro(1-pyrrolyl)borates (6). The lithium salt is also obtained as the sole product on interaction of $LiBH_4$ with pyrrole at temperatures below 160°C; however, on prolonged reflux the lithium tetrakis(1-pyrrolyl)borate can be obtained whereas an analogous reaction involving $NaBH_4$ proceeds at much slower pace.

Dihydrobis(1-pyrrolyl)borates are also described (6). Sodium trifluoroacetoxytrihydroborate is a convenient reagent for the reduction of nitriles to the corresponding amines under mild conditions (211). Fluorine-19 nuclear magnetic resonance data suggest that in the presence of alkali the first step in the hydrolysis of methoxytrifluoroborate ion is the displacement of $F^-$ via a dissociative mechanism (339); acid hydrolysis, however, proceeds via the hydroxytrifluoroborate ion as the initial product.

Thermogravimetric analysis of tetraalkylammonium tetrahaloborates shows the products of the thermal decomposition to be trialkylamine-trihaloboranes and (dialkylamino)dihaloboranes (226). The reaction of $BCl_3$ with various alkali metal and ammonium nitrates proceeds slowly at 20°C and leads ultimately to the decomposition of the nitrate ion and formation of tetrachloroborates (36); the species $M(Cl_3BONO_2)$ is an intermediate in the process but the salt $[(C_2H_5)_4N][B(ONO_2)_4]$ could be isolated and identified. Tetraalkylammonium perchlorates react with $BF_3$ to give 1:1 molar adducts in which the boron is coordinated to an oxygen atom of the $ClO_4$ group (102). The $^{11}B$ chemical shift values of tetrabutylammonium trihaloperchloratoborates are very close to that of $(C_2H_5)_2O \cdot BF_3$ (70); at room temperature a rapid chemical exchange of free and complexed trihaloborane is observed. Boron trichloride and boron tribromide as well as boric acid and oxide interact with disulfuric acid to form condensed structures with bridging $SO_4$ groups (240).

The reaction of lithium lithioethynyltrialkylborates with alkyl halides provides a facile route for the preparation of lithium trialkyl-1-alkynylborates (309). Sodium triethyl(trimethylsilylethynyl)borate is readily obtained by the interaction of sodium triethylhydroborate with trimethylsilylacetylene (82). Various reactions of the new reagent with electrophiles to yield vinylborane derivatives have been studied. The coupling reaction of copper(I) methyltrialkylborate with benzyl bromides has provided a convenient synthesis of alkylbenzenes (177). Lithium "ate" complexes derived from the addition of alkyllithium to B-alkyl-9-borabicyclo[3.3.1]nonane react with a variety of reducible organic compounds to form cis-bicyclo[3.3.1]oct-1-yldialkylboranes (92). The high stereo-, chemo- and regioselectivities of lithium di-n-butyl "ate" complexes of 9-borabicyclo[3.3.1]nonane in the reduction of carbonyl groups are elaborated upon elsewhere (288). Trialkylboranes derived from hydroboration of olefins with 9-borabicyclo[3.3.1]nonane are remarkably resistent to thermal isomerization (172).

Alkynyltrialkylborates undergo β-alkylation with alkyl migration from boron to the α-carbon atom under mild conditions to give (dialkyl)vinylboranes (320, 321) and protonation of trialkylalkynylborates followed by oxidation provides a very general route for the synthesis of ketones (322). Alkenyltrialkylborates react with aqueous NaOH in a selective protonolysis to give excellent yields of the corresponding alkenes (173). Treatment of alkenyltrialkylborates with hydrochloric acid produces primarily an olefin (105). The latter is formed via migration of an alkyl group from boron to the alkenyl α-carbon atom followed by extremely facile dehydroboronation of the triorganylborane intermediate. The reaction of lithium dialkynyldialkylborates with iodine has been used for the preparation of unsymmetrical conjugated dienes (58).

The reaction of lithium triethylhydroborate with alkyl tosylates is an advantageous procedure for the deoxygenation of alcohols (162) and lithium as well as potassium trialkylhydroborates are reagents for the direct reduction of α,β-unsaturated carbonyl compounds to yield synthetically useful enolate anions

(59). Alkali metal triethylhydroborates react with nitriles to form the corresponding triethyliminoborates (200) and lithium trisiamylhydroborate has been prepared and was found to be an exceptionally stereoselective agent for the reduction of cyclic ketones (291).

For new uses of copper(I) methyltrialkylborates in organic syntheses, see (283), and for reactions of lithium trialkylalkynylborates with several group III to V electrophiles, see (279).

The crystal structure of the anion $[B(C{=}CH)_4]^-$ has been studied by X-ray diffraction tecniques (120). For solubilities of potassium, cesium, and ammonium tetraphenylborate, see (108), for a study of the interaction of the anion with pinacyanole in solvent extraction, see (228), and for a kinetics study on the thermal decomposition of sodium tetraphenylborate, see (191).

The salt triethyl-n-hexylammonium triethyl-n-hexylborate is a liquid at room temperature; the viscosity of the species decreases non-exponentially with 1/T by a factor of 15 in the range of 20 to 80°C while its equivalent conductance increases similarly by a factor of 13 (42). Dilution of the salt with an equal volume of benzene increases the specific conductance at 25°C by a factor of 10.5 (42). Carbon-13 spin-lattice relaxation times of the cited salt have been measured (290).

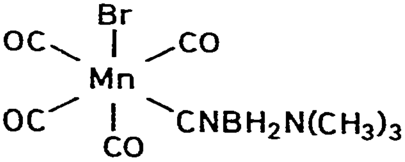
## 10 BORON-METAL COMPOUNDS

Metallic potassium reacts with $Al(BH_4)_3$ to give $KBH_4$ or $K[Al(BH_4)_4]$ though the latter complex is obtained only from non-solvated starting materials (340). $TiCl_4$ reacts with $LiBH_4$ in ether to yield $Ti(BH_4)_3{\cdot}O(C_2H_5)_2$ (335); the ether is readily displaced by stronger bases such as tetrahydrofuran. Pyridine, however, yields a 1:2 molar adduct and displaces $BH_3$ from the salt.

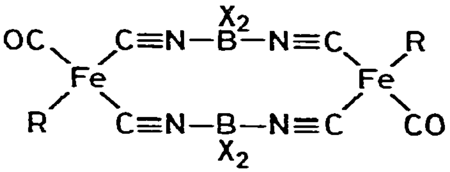
The vibrational spectrum of $(C_5H_5)_2Zr(BH_4)_2$ can be interpreted in terms of pentahapto cyclopentadienyl ligands and doubly-bridged $BH_4$ groups(206); the compound loses hydridic hydrogen near 200°C as the initial thermal event in TG-DTA analysis.

Metal tetrahydroborates are readily carbonylated to yield metal carbonyls (156). The reaction of Ti(salen)$Cl_2$ with $LiBH_4$ gives a dimeric complex containing seven-coordinate Ti(IV) and an amine-borane donor group (258). The latter is formed by addition of $BH_4^-$ to the imino function of the ligand. Several addition complexes of ammonium and sodium tetraphenylborate with [N,N'-ethylenebis(salicylidene iminato)]Ni(II) have been described and X-ray data on $[[Ni(salen)]_2Na(NCCH_3)_2[B(C_6H_5)_4]]\cdot 2CH_3CN$ have been obtained (314).

Trimethylamine-cyanoborane reacts with $[Mn(CO)_5]Br$ to give the following complex (157):



The reaction of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ with boranes ($BX_3$, X = F, Cl, Br, H, $C_6H_5$) yields iron(II) complexes containing $[CNBX_3]^-$ or $[CNBX_2NC]^-$ ligands (106). Infrared data and molecular weight determinations suggest structures such as



for the lattter species (in which R = $C_5H_5$). Triamminechromium tricarbonyl reacts with (phenyl)dihydroxyborane in boiling dioxane according to the equation (104):

$$C_6H_5B(OH)_2 + (H_3N)_3Cr(CO)_3 \longrightarrow [C_6H_5B(OH)_2]Cr(CO)_3 + 3\ NH_3$$

The yellow crystalline complex is relatively stable in air but is readily oxidized in solution. On heating in vacuum, water is lost with the formation of $(C_6H_5BO)Cr(CO)_3$, whereas reaction with n-$C_3H_7OH$ yields the extremely moisture-sensitive species $[C_6H_5B(OC_3H_7)_2]Cr(CO)_3$.

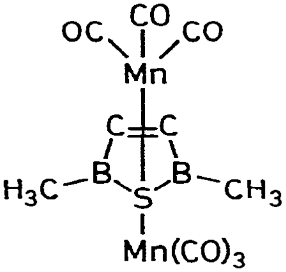
For the reaction of haloboranes with Pt(0) and Pt(II) species to yield complexes of the type $[(C_6H_5)_3P]_2Pt(BF_3)_2$, see (144). In the case of (diphenyl)haloboranes oxidative addition of the B-halogen bond has been observed to occur at the Pt(0) center to yield $[(C_6H_5)_3P]_2Pt[B(C_6H_5)_2]X$.

Various tetrahydroborate-, cyanotrihydroborate-, and hydridophosphine complexes of Ru(II) have been described (131) and similar Rh(I), Rh(II) and Rh(III) species have also been reported (130). The reaction of cis-$Cr(CO)_4[P(CH_3)_3][C(OCH_3)(CH_3)]$ with $BF_3$ proceeds via elimination of a $CH_3O$ group and substitution of a CO ligand to yield mer-$(BF_4)Cr(CO)_3[P(CH_3)_3](CCH_3)$, which contains a $BF_4$ group coordinated to the Cr atom (331); the species readily interacts with water to yield the compound $[\text{mer-}H_2OCr(CO)_3[P(CH_3)_3](CCH_3)]^+BF_4^-$. The structure of the cluster species $(OC)_9Co_3COBBr_2[N(C_2H_5)_3]$ has been determined by X-ray diffraction (116).

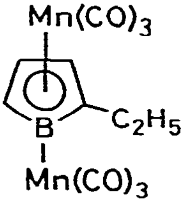
The crystal structure of $HB(pz)_3Mo(CO)_2(NO)$ (pz = 1-pyrazolyl) has been determined from single crystal X-ray data (38). Coordination about Mo is roughly octahedral and that of B is tetrahedral. A single crystal X-ray diffraction study on $[HB(pz)_3]Pt(CH_3)(CO)$ showed the compound to be square planar with only two of the three 1-pyrazolyl groups coordinated to the platinum (51). The metal is located slightly above the plane defined by the four donor atoms. X-Ray data on bis dihydro-bis(1-pyrazolyl)borato nickel(II) give no evidence for Ni-H interaction in the complex (65). The structures of $[HB(pz)_3Cu]_2$ and of the corresponding 3,5-dimethylpyrazolyl derivative have been studied in the solid state (X-ray diffraction) and in solution ($^1H$ NMR) (152); the methylated species is extensively dissociated in solution. X-Ray diffraction data show that in the complex $(CH_3)[HB(pz)_3]Pt[CNC(CH_3)_3]$ the Pt is in square planar environment with the hydrotris(1-pyrazolyl)borate anion functioning as a bidentate ligand (246). However, a significant difference in the Pt-N bond lengths is observed and is discussed in terms of a trans influence; the relation between the solution NMR spectral data and the solid state structure is also discussed.

$TiCl_4$ react with $K[HB(pz)_3]$ or the corresponding 3,5-dimethylpyrazolyl derivative to give $[HB(pz)_3]TiCl_3$ in a very clean reaction (147). New Mo complexes containing poly(1-pyrazolyl)-borate ligans include $[[(C_2H_5)_2B(pz)_2]_4]Mo_2$, the species $(CH_3CO_2)_2\ Mo_2[(pz)_2B(C_2H_5)_2]_2$ and $(CH_3CO_2)_2Mo_2[(pz)_3BH]_2$ (146); the structures of the latter two species were determined by X-ray diffraction techniques. Dihalonitrosyl(tris-1-pyrazolylborato)-molybdenum complexes have been described, their alcoholysis was studied, and $^1H$ and $^{13}C$ nuclear magnetic resonance spectra (159) were discussed. Also, the structure of $[(C_6H_5)_2B(pz)_2]_2Ni$ has been studied by X-ray spectroscopy (138). Several lanthanide poly-(1-pyrazolyl)borates of the type $L[HB(pz)_3]Cl_{3-n}$ (L = lanthanide element, n = 0, 1, 2) have been obtained by the interaction of the appropriate $LCl_3$ with $K[HB(pz)_3]$ in THF solution (137); infrared data suggest that the species contain coordinated THF. Stereochemically nonrigid five-coordinate methylplatinum(II) complexes containing the HB(pz)$_3$ ligand have been prepared and variable temperature nuclear magnetic resonance spectra were recorded (323); intramolecular exchange probably involves a rotation of the HB(pz)$_3$ ligand about the Pt-B axis. For some uranium(IV) pyrazolylborate complexes, see (204), and some palladium pyrazolylborate complexes containing Pd-C bonds, see (233).

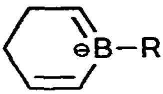
All acetonitrile moieties of $(CH_3CN)_3Cr(CO)_3$ are displaced on interaction of the compound with the cyclic ligand L = (-BR-NR-NR-BR-CR'=CR'-) (R = $CH_3$, R' = $C_2H_5$) to yield the complex $LCr(CO)_3$ (125). The diamagnetic complex



is obtained on interaction of $Mn_2(CO)_{10}$ with the thiadiborolene (122), whereas reaction of $Mn_2(CO)_{10}$ with $C_6H_5B$ $(-CH=CH-CH_2-)_2$ at 165°C (123) yields a novel type of triple-decker sandwich containing a borole as bridging ligand:

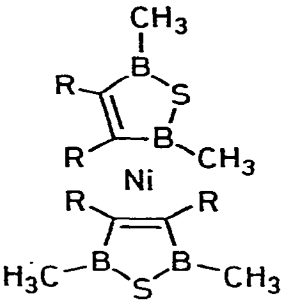


Bis(borabenzene)iron complexes are obtained by reacting $FeCl_3$ with the following anion (153):



$^{57}$Fe Mössbauer spectra and He(I) PE photoionization potentials suggest that the borabenzene ligands are more electron-demanding than the cyclopentadienyl ring of ferrocene. Fridel-Crafts acetylation and acid-catalyzed deuterium exchange occurs in the alpha position of the complexes.

The ligand $S(-BCH_3-CC_2H_5=)_2$ reacts with $Ni(CO)_4$ by displacement of two carbonyl groups from nickel (119); the resultant species reacts with additional ligand molecules to yield the corresponding bis(1,2,5-thiadiborolene)nickel(0) complex:



The suggested structure containing staggered ring moieties is supported by X-ray diffraction and nuclear magnetic resonance data on the sandwich complex.

Bis(borinato)cobalt complexes $Co(C_5H_5BR)_2$ (R = $CH_3$, $C_6H_5$) are degraded by interaction with alkali metal cyanides MCN to yield $M[C_5H_5BR]$. The latter compounds are versatile synthetic intermediates that can be used for the preparation of various transition metal borinato complexes (79).

Ferrocene and cymantrene as well as methylcymantrene react with $BBr_3$, $BI_3$, $C_6H_5BI_2$, or $CH_3BI_2$ to form the metallocenylhaloboranes (325); direct dichloroborylation is only possible with ferrocene. Ferrocene reacts with $BI_3$ or $BBr_3$ in $CS_2$ to give 1,1'-bis(dihaloboryl)ferrocenes (310); the cyclopentadienyl ring of cymantrene is doubly diiodoborylated on interaction with $BI_3$. Nuclear magnetic resonance data on these complexes are presented and various reactions at the $BX_2$ sites of the species are described.

## 11 PHYSIOLOGICAL ASPECTS

Organylhydroxyboranes have been used as reversible inhibitors in studies on the active center topography of pancreatic lipase (221) and the modulation of activity of glutaminase B in *Eschericia coli* by borate ions has been studied (251). Temperature jump (249) and potentiometric studies (250) on the interaction of (phenyl)dihydroxyborane with chymotrypsin have been described. Depletion of synaptic vesicles at the frog neuromuscular junctions by tetraphenylborate ion has been observed (301) and the effect of the tetraphenylborate ion on the uptake of the lipophile dibenzyldimethylammonium cation by yeast cells has been studied (66). For the use of spin labels as probes for the interaction of the tetraphenylborate ion with liposomes, see (229).

Toxicity, uptake and survey studies of boron in the marine environment have been reported (207) and acid extraction of plant boron has been studied (271). For some effects of boron on grain yield and boron concentration in barlay and wheat, see (296).

The dihydroxyboryl-benzyloxycarbonyl group, $(HO)_2B-C_6H_4-CH_2-O-CO-$, appears to permit the modification of solubility properties of peptides, thereby offering a great potential for facilitating manipulations of peptide chemistry (256).

Efforts continue for the preparation of organoboron derivatives for use in neutron capture therapy. For example, a series of polyhedral borane derivatives based on $B_{10}H_8$ moieties and containing protein-binding functional groups has been synthesized (174); gluconamide functions in the species provide for solubility of the materials in water. Also, L-*o*-carboranylalanine, a boron analog of phenylalanine, has been prepared (300) and the synthesis of borylated porphyrins has been described (272).

The attachment of the *p*-bromphenylboryl group to oxygen sites of complex physiologically active molecules aids in the structural elucidation of the latter. Utilizing this procedure, X-ray diffraction data have been obtained on the cyclic *p*-bromophenylboronate ester of the antibiotic streptovaricin C triacetate (324) and on the *p*-bromophenylboronate ester of a steroid (265).

## References:

1. A. Meller, W. Maringgele and H.-G. Köhn, Monatsh. Chem., **107** (1976) 89.
2. V. N. Plakhotnik, N. G. Parkhomenko and V. V. Ersikov, J. Gen. Chem. USSR (Engl. Transl.), **45** (1976) 1745.
3. V. I. Melnikova, E. S. Petrov, K. K. Pivnitskii and A. A. Shatenshtein, J. Gen. Chem. USSR (Engl. Transl.), **45** (1976) 1862.
4. V. A. Dorokhov, V. I. Seredenko and B. M. Mikhailov, J. Gen. Chem. USSR (Engl. Transl.), **45** (1976) 1737.
5. GMELIN Handbuch der Anorganischen Chemie, Erg.-Werk, Vol. **25** (1975) pp. 116-125.
6. B. Györi, J. Emri and P. Szarvas, Acta. Chim. (Budapest), **86** (1975) 235.
7. K.-D. Müller and U. Gerwarth, J. Organometal. Chem., **110** (1976) 15.
8. I. I. Lapkins, S. E. Ukhanov and G. A. Yuzhakova, J. Gen. Chem. USSR (Engl. Transl.), **45** (1975) 1479.
9. K. N. Semenenko, O. V. Kravchenko and S. P. Shilkin, Russ. J. Inorg. Chem. (Engl. Transl.), **20** (1975) 1293.
10. B. R. Gragg, R. E. Handshoe and K. Niedenzu, J. Organometal. Chem., **116** (1976) 135.
11. B. R. Gragg and K. Niedenzu, J. Organometal. Chem., **117** (1976) 1.
12. B. R. Gragg and K. Niedenzu, Syn. React. Inorg. Metal-org. Chem., **6** (1976) 275.
13. O. T. Beachley and B. Washburn, Inorg. Chem., **15** (1976) 725.
14. G. Lorber and R. Pizer, Inorg. Chem., **15** (1976) 978
15. K. P. Callahan and M. F. Hawthorne, Adv. Organometal. Chem., **14** (1976).

16. J. D. Smith and D. R. M. Walton, Adv. Organometal. Chem., 13 (1975) 454.

17. T. Paal and L. Barcza, Acta Chim. (Budapest), 87 (1975) 33.

18. S. Lindoey, H. M. Seip and R. Seip, Acta Chem. Scand., A30 (1976) 54.

19. W. Brüser, S. Schröder and H. Wittke, Z. Anorg. Allg. Chem., 421 (1976) 89.

20. W. Haubold and U. Kraatz, Z. Anorg. Allg. Chem., 421 (1976) 105.

21. K. Dehnicke and V. Fernandez, Chem. Ber., 109 (1976) 488.

22. H. Bock and W. Fuss, Chem. Ber., 109 (1976) 799.

23. H. Nöth and W. Storch, Chem. Ber., 109 (1976) 884.

24. P. Paetzold and B. Boeke, Chem. Ber., 109 (1976) 1011.

25. K. Seppelt, Chem. Ber., 109 (1976) 1046.

26. B. Wrackmeyer and H. Nöth, Chem. Ber., 109 (1976) 1075.

27. M. L. Denniston, M. Chiusano, J. Brown and D. R. Martin, J. Inorg. Nucl. Chem., 38 (1976) 379.

28. M. L. Denniston, M. A. Chiusano and D. R. Martin, J. Inorg. Nucl. Chem., 38 (1976) 979.

29. O. Gropen, Acta Chem. Scand., A29 (1975) 873.

30. S. Gronowitz and A. Maltessan, Acta Chem. Scand., B29 (1975) 1036.

31. S. Gronowitz and C. Roos, Acta Chem. Scand., B29 (1975) 990.

32. S. L. Ioffe, L. M. Leonteva, L. M. Makarenkova, A. L. Blyumenfeld, V. F. Pyaterikov and U. A. Tartakorskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1975) 1053.

33. B. R. Gragg and G. E. Ryschkewitsch, Inorg. Chem., 15 (1976) 1201.

34. B. R. Gragg and G. E. Ryschkewitsch, Inorg. Chem., 15 (1976) 1205.

35. B. R. Gragg and G. E. Ryschkewitsch, Inorg. Chem., 15 (1976) 1209.

36. K. V. Titova and V. Ya. Rosolovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1976) 2246.

37. B. M. Mikhailov, T. K. Kozminskaya and B. I. Bryantsev, J. Gen. Chem. USSR (Engl. Transl.), 46 (1976) 87.

38. E. M. Holt, S. L. Holt, F. Cavalito and K. J. Watson, Acta Chem. Scand., A30 (1976) 225.

39. W. Storch and H. Nöth, Angew. Chem. Int. Ed. (Engl.), 15 (1976) 235.

40. G. Gundersen, J. Mol. Structure, 33 (1976) 79.

41. G. Gundersen and H. Vahrenkamp. J. Mol. Structure, 33 (1976) 97.

42. W. T. Ford and D. J. Hart, J. Phys. Chem., 80 (1976) 1002.

43. E. L. Muetterties, ed., "Boron Hydride Chemistry," Academic Press (1975), 552 pages.

44. B. R. Gragg and G. E. Ryschkewitsch, Inorg. Chem., 15 (1976) 1988.

45. D. S. Matteson and P. K. Jesthi, J. Organometal. Chem., 110 (1976) 25.

46. B. Wrackmeyer and H. Nöth, J. Organometal. Chem., 108 (1976) 210.

47. E. Flood and O. Gropen, J. Organometal. Chem., 110 (1976) 7.

48. E. Negishi, J. Organometal. Chem., 108 (1976) 281.

49. E. J. Stampf and J. D. Odom, J. Organometal. Chem., 108 (1976) 1.

50. D. S. Matteson and P. K. Jesthi, J. Organometal. Chem., 114 (1976) 1.

51. J. D. Oliver and P. E. Rush, J. Organometal. Chem., 104 (1976) 117.

52. T. Kudo and A. Nose, Yakugaku Zasshi, 95 (1975) 1411.

53. A. Nose and T. Kudo, Yakugaku Zasshi, 96 (1976) 140.

54. M. Hartmann and H. Carlsohn, Z. Chem., 16 (1976) 53.

55. V. V. Zakharov, G. V. Lagodzinskaya, G. N. Nechiporenko and G. G. Manlis, Zh. Fiz. Khim., 49 (1975) 3087.

56. Y. Yamamoto, K. Kondo and I. Moritani, J. Org. Chem., 40 (1975) 3644.

57. D. J. Raber and W. C. Guida, J. Org. Chem., 41 (1976) 690.

58. J. A. Sinclair and H. C. Brown, J. Org. Chem., 41 (1976) 1078.

59. J. M. Fortunato and B. Ganem, J. Org. Chem., 41 (1976) 2194.

60. T. Ha, J. Mol. Structure, 30 (1976) 103.

61. B. Roussel, A. Chapput and G. Fluery, J. Mol. Structure, 31 (1976) 371.

62. C. Pepin, L. Lambert and A. Cabana, J. Mol. Spectroscopy, 59 (1976) 43.

63. O. Gropen and E. Wisloeffe-Nilssen, J. Mol. Structure, 32 (1976) 21.

64. J. Dazord, H. Mongeot, H. Atchekzai and J. P. Tuchagues, J. Less-Common Met., 47 (1976) 55.

65. H. M. Echols and D. Dennis, Acta Cryst., B32 (1976) 1627.

66. J. A. Hoeberichts and G. W. Borst-Panwels, Biochim. Biophys. Acta, 413 (1975) 248.

67. B. M. Mikhailov, T. A. Shchegoleva and E. M. Shashkova, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1975) 899.

68. B. M. Mikhailov, Y. N. Bubnov and A. V. Tsyban, Bull. Acad. Sci, USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1975) 897.

69. T. Matsuda, I. Seto and T. Tanaka, Bull. Chem. Soc. Japan, 49 (1976) 1713.

70. K. V. Titova, Y. I. Malov, E. I. Kolmakova and V. Y. Rosolovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl, Transl.), 24 (1975) 664.

71. B. M. Mikhailov, L. S. Vasilev, V. V. Veselovskii and V. G. Kiselev, Bull. Acad. Sci. USSR, Div. Chem. Sci., (Engl. Transl.), 24 (1975) 655.

72. W. C. Ermler, F. D. Glasser and C. W. Kern, J. Amer. Chem. Soc., 98 (1976) 3799.

73. B. M. Mikhailov, Y. N. Bubnov and A. V. Tsyban, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1975) 416.

74. B. M. Mikhailov, G. S. Ter-Sarkisyan, N. N. Govorov and Z. Yanoushek, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1975) 418.

75. I. M. Pepperberg, T. N. Halgren and W. N. Lipscomb, J. Amer. Chem. Soc., 98 (1976) 3442.

76. R. C. Dobbie, E. W. Distefano, M. Black, J. B. Leach and T. Onak, J. Organometal. Chem., 114 (1976) 233.

77. W. Siebert and K. Kinberger, J. Organometal. Chem., 116 (1976) C7.

78. B. M. Mikhailov and M. E. Kuimova, J. Organometal. Chem., 116 (1976) 123.

79. G. Herberich, H. J. Becker, K. Carsten, C. Engleke and W. Koch, Chem. Ber., 109 (1976) 2382.

80. G. Muckle, H. Nöth and W. Storch, Chem. Ber., 109 (1976) 2572.

81. H. C. Brown and M. Zaidlewicz, J. Amer. Chem. Soc., 98 (1976) 4917.

82. R. Köster and L. A. Hagele, Synthesis, (1976) 118.

83. W. V. Dahlhoff, W. Schuessler and R. Köster, Liebigs Ann. Chem., (1976) 387.

84. R. Köster, H.-J. Zimmermann and W. Fenzl, Liebigs Ann. Chem., (1976) 1116.

85. W. Fenzl, R. Köster and H.-J. Zimmermann, Liebigs Ann. Chem., (1975) 2201.

86. W. V. Dahlhoff and R. Köster, Liebigs Ann. Chem., (1975) 1926.

87. W. V. Dahlhoff and R. Köster, Liebigs Ann. Chem., (1975) 1914.

88. W. V. Dahlhoff and R. Köster, J. Org. Chem., 41 (1976) 2316.

89. O. Gropen, J. Mol. Structure, 32 (1976) 85.

90. H. C. Brown and N. Ravindran, J. Amer. Chem. Soc., 98 (1976) 1785.

91. H. C. Brown and N. Ravindran, J. Amer. Chem. Soc., 98 (1976) 1798.

92. G. W. Kramer and H. C. Brown, J. Amer. Chem. Soc., 98 (1976) 1964.

93. C. Weidig, J. M. Lakovits and H. C. Kelly, Inorg. Chem., 15 (1976) 1783.

94. W. Siebert, R. Full, T. Renk and A. Ospici, Z. Anorg. Allgem. Chem., 418 (1975) 273.

95. A. B. Levy and S. J. Schwartz, Tetrahedron Lett., (1976) 2201.

96. L. Y. Rikhter and L. M. Sverdlov, Teor. Eksp. Khim., 11 (1975) 672.

97. A. Haas, M. Haeberlein and C. Krüger, Chem. Ber., 109 (1976) 1769.

98. H.-O. Berger, J. Kroner and H. Nöth, Chem. Ber., 109 (1976) 2266.

99. A. Arase and Y. Masuda, Chem. Lett., (1976) 785.

100. B. M. Mikhailov, Usp. Khim., 45 (1976) 1102.

101. A. Singh and R. C. Mehrotra, Syn. React. Inorg. Metal-org. Chem., 6 (1976) 307.

102. K. V. Titova, E. I. Kolmakova and V. Ya. Rosolovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 24 (1976) 2711.

103. O. N. Shevtsova and A. M. Yurkevich, J. Gen. Chem. USSR (Engl. Transl.), 46 (1976) 345.

104. G. A. Razuvaev, A. N. Artemor, A. A. Aladjim and N. I. Sirotkin, J. Organometal. Chem., 111 (1976) 131.

105. K.-W. Chiu, E. I. Negishi, M. S. Plante and A. Silveira, J. Organometal. Chem. 112 (1976) C3.

106. J. Emri, B. Györi, A. Bakos and G. Czira, J. Organometal. Chem., 112 (1976) 325.

107. G. W. Kabalka, J. D. Baker and G. W. Neal, J. Chem. Education, 53 (1976) 549.

108. E. Siska, Magy. Kem. Foly., 82 (1976) 275.

109. E. Alouin, J. Cornejo and E. A. Lissi, Eur. Polym. J., 11 (1975) 779.

110. A. Haas and M. Haeberlein, Z. Anorg. Allgem. Chem., 424 (1976) 20.

111. J. Pebler, W. Ruf and W. Siebert, Z. Anorg. Allgem. Chem., 422 (1976) 39.

112. W. Haubold and J. Weidlein, Z. Anorg. Allgem. Chem., 420 (1976) 251.

113. F. Zettler, H. Hess, W. Siebert and R. Full, Z. Anorg. Allgem. Chem., 420 (1976) 285.

114. P. Paetzold, P. Böhm, A. Richter and E. Scholl, Z. Naturforsch., 31B (1976) 754.

115. G. Heller and H. Ross, Z. Naturforsch., 31B (1976) 714.

116. V. Baetzel, Z. Naturforsch., 31B (1976) 342.

117. E. Hohaus and W. Riepe, Z. Naturforsch., 31B (1976) 324.

118. J. C. Huffman, H. Fusstetter and H. Nöth, Z. Naturforsch., 31B (1976) 289.

119. W. Siebert, R. Full, C. Krueger and Y. Tsay, Z. Naturforsch., 31B (1976) 203.

120. A. I. Gusev, M. G. Los, A. F. Zhigach, R. A. Svitsin and E. S. Sobolev, Zh. Strukt. Khim., 17 (1976) 537.

121. S. Pollitz, F. Zettler, D. Forst and H. Hess, Z. Naturforsch., 31 B (1976) 897.

122. W. Siebert and K. Kinberger, Angew. Chem. Int. Ed. Engl., 15 (1976) 434.

123. G. E. Herberich, J. Hengesbach, U. Kölle, G. Huttner and A. Frank, Angew. Chem. Int. Ed. Engl., 15 (1976) 433.

124. P. Jutzi and A. Seufert, Angew. Chem. Int. Ed. Engl., 15 (1976) 295.

125. W. Siebert and R. Full, Angew. Chem. Int. Ed. Engl., 15 (1976) 45.

126. G. B. Bagdasaryan, S. M. Markaryan and M. G. Indzhickyan, Arm. Khim. Zh., 29 (1976) 48.

127. G. B. Bagdasaryan, L. S. Airiyan and M. G. Indzhikyan, Arm. Khim. Zh., 29 (1976) 88.

128. G. B. Bagdasaryan, K. S. Badalyan and M. G. Indzhikyan, Arm. Khim. Zh., 29 (1976) 179.

129. G. B. Bagdasaryan, S. M. Markaryan and M. G. Indzhikyan, Arm. Khim. Zh., 29 (1976) 186.

130. D. G. Holah, A. N. Hughes and B. Hui, Can. J. Chem., 53 (1975) 3669.

131. D. G. Holah, A. N. Hughes and B. C. Hui, Can. J. Chem., 54 (1976) 320.

132. T. T. Aug and B. A. Dunell, Can. J. Chem., 54 (1976) 1087.

133. J. S. Hartman, G. J. Schrobilgen and P. Stilbs, Can. J. Chem., 54 (1976) 1121.

134. J. S. Hartman and R. R. Yetman, Can. J. Chem., 54 (1976) 1130.

135. S. J. Rettig and J. Trotter, Can. J. Chem., 54 (1976) 1168.

136. J. Dazord, H. Monguet, H. Atchekzai and J. P. Tuchagues, Can. J. Chem., 54 (1976) 2135.

137. K. W. Bagnall, A. C. Tempest, J. Takats and A. P. Masino, Inorg. Nucl. Chem. Lett., (1976) 555.

138. F. A. Cotton and C. A. Murillo, Inorg. Chim. Acta, 17 (1976) 121.

139. D. R. Armstrong, Inorg. Chim. Acta, 18 (1976) 13.

140. D. R. Armstrong, Inorg. Chim. Acta, 18 (1976) 145.

141. E. A. Dietz, K. W. Morse and R. W. Parry, Inorg. Chem., 15 (1976) 1.

142. L. A. Peacock and R. A. Geanangel, Inorg. Chem., 15 (1976) 244.

143. J. M. Miller and T. R. B. Jones, Inorg. Chem., 15 (1976) 284.

144. M. Fishwick, H. Nöth, W. Petz and M. G. Wallbridge, Inorg. Chem., 15 (1976) 490.

145. N. E. Miller, Inorg. Chem., 15 (1976) 1735.

146. D. M. Collins, F. A. Cotton and C. A. Murillo, Inorg. Chem., 15 (1976) 1861.

147. J. K. Kouba and S. S. Wreford, Inorg. Chem., 15 (1976) 2313.

148. A. J. DeStefano and R. F. Porter, Inorg. Chem., 15 (1976) 2569.

149. B. F. Spielvogel, L. Wojnowich, M. K. Das, A. T. McPhail and K. D. Hargrave, J. Amer. Chem. Soc., 98 (1976) 5702.

150. M. K. Murphy and J. L. Beauchamp, J. Amer. Chem. Soc., 98 (1976) 1433.

151. H. C. Brown, N. R. De-Lue, G. W. Kabalka and H. C. Hedgecock, J. Amer. Chem. Soc., 98 (1976) 1290.

152. C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks and J. A. Ibers, J. Amer. Chem. Soc., 98 (1976) 711.

153. A. J. Ashe, P. Shu, T. von Lehmann and J. Bastide, J. Amer. Chem. Soc., 97 (1975) 6865.

154. M. K. Das and J. J. Zuckerman, J. Chem. Soc. Chem. Commun., (1976) 460.

155. R. J. Wilcsek, D. S. Matteson and J. G. Douglas, J. Chem. Soc. Chem. Commun., (1976) 401.

156. G. Fachinetti, G. Fochi and C. Floriani, J. Chem. Soc. Chem. Commun., (1976) 230.

157. J. L. Vidal and G. E. Ryschkewitsch, J. Chem. Soc. Chem. Commun., (1976) 192.

158. J. S. Plotkin and L. G. Sneddon, J. Chem. Soc. Chem. Commun., (1976) 95.

159. J. A. McCleverty, D. Seddon, N. A. Bailey and N. W. Walker, J. Chem. Soc. Dalton Trans., (1976) 898.

160. R. C. Dobbie, E. Wan and T. Onak, J. Chem. Soc. Dalton Trans., (1975) 2603.

161. C. Jonany, G. Jugie, G. V. Roschenthaler and O. Stelzer, J. Inorg. Nucl. Chem., 38 (1976) 1383.

162. S. Krishnamurthy and H. C. Brown, J. Org. Chem., 41 (1976) 3064.

163. C. L. McCormick and G. B. Butler, J. Org. Chem., 41 (1976) 2803.

164. R. H. Cragg, J. Dudman and J. P. N. Husband, J. Organometal. Chem., 116 (1976) 281.

165. J. R. Durig, L. W. Hall, R. O. Carter, C. J. Wurrey, V. F. Kalasinsky and J. D. Odom, J. Phys. Chem., 80 (1976) 1188.

166. E. M. Shvarts, V. Grundsteins and A. Ievins, J. Therm. Anal., 8 (1975) 461.

167. E. M. Shvarts, V. Grundsteins and A. Ievins, J. Therm. Anal., 8 (1975) 469.

168. M. Bonczek and H. Follner, Monatsh. Chem., 107 (1976) 283.

169. J. Wiecko and W. R. Sherman, Org. Mass Spectrom., 10 (1975) 1007.

170. J. E. Repashy, C. Weidig and H. C. Kelly, Syn. React. Inorg. Metalorg. Chem., 5 (1975) 337.

171. E. J. Stampf, A. R. Garber, J. D. Odom and P. D. Ellis, J. Amer. Chem. Soc., 98 (1976) 6550.

172. H. Taniguchi, L. Brener and H. C. Brown, J. Amer. Chem. Soc., 98 (1976) 7107.

173. E. Negishi and K. Chiu, J. Org. Chem., 41 (1976) 3484.

174. R. L. Sneath, J. E. Wright, A. H. Soloway, S. M. O'Keefe, A. S. Dey and W. D. Smolnycki, J. Med. Chem., 19 (1976) 1290.

175. K. Larsson and O. Samuelson, Carbohydr. Res., 50 (1976) 1.

176. Y. Takahashi, M. Tokuda, M. Itoh and A. Suzuki, Synthesis, (1976) 616.

177. N. Miyaura, M. Itoh and A. Suzuki, Synthesis, (1976) 618.

178. A. Suzuki, M. Ishidoya and M. Tabata, Synthesis, (1976) 687.

179. D. C. Wigfield and F. W. Gowland, Tetrahedron Lett., (1976) 3373.

180. D. C. Wigfield, S. Feiner and F. W. Gowland, Tetrahedron Lett., (1976) 3377.

181. E. A. Balabanova, T. G. Sevastyanova, I. D. Kolli and V. I. Spitsyn, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 25 (1976) 164.

182. B. Wrackmeyer and H. Nöth, Chem. Ber., 109 (1976) 3480.

183. H.-R. Bachmann, F. Bachmann, K. L. Kompa, H. Nöth and R. Rinck, Chem. Ber., 109 (1976) 3331.

184. R. Goetze and H. Nöth, Chem. Ber., 109 (1976) 3247.

185. S. Trofimenko, Adv. Chem. Ser., 150 (1976) 289.

186. L. J. Todd, Adv. Chem. Ser., 150 (1976) 302.

187. D. F. Gaines, M. B. Fischer, S. J. Hildebrandt, J. A. Ulman and J. W. Lott, Adv. Chem. Ser., 150 (1976) 311.

188. F. R. Brown, F. A. Miller and C. Sourisseau, Spectrochim. Acta, 32A (1976) 125.

189. E. Muylle, G. P. van der Kelen and E. G. Claeys, Spectrochim. Acta, 32A (1976) 1149.

190. C. Trindle and J. K. George, Theor. Chim. Acta, 40 (1975) 119.

191. K. N. Ninan and C. G. Nair, Thermochim. Acta, 15 (1976) 345.

192. J. Balcells, S. Colonna and R. Fornasier, Synthesis, (1976) 266.

193. N. R. De-Lue and H. C. Brown, Synthesis, (1976) 114.

194. Gmelin Handbuch der Anorganischen Chemie, Erg.-Werk Band 33, Borverbindungen Part 8 (1976).

195. Gmelin Handbuch der Anorganischen Chemie, Erg.-Werk Band 34, Borverbindungen Part 9 (1976).

196. Gmelin Handbuch der Anorganischen Chemie, Erg.-Werk Band 37, Borverbindungen Part 10 (1976).

197. E. I. Negishi in: New Applications of Organometallic Reagents in Organic Synthesis (D. Seyferth, editor), Elsevier, Amsterdam and New York (1976).

198. G. Zweifel, G. M. Clark, T. Leung and C. C. Whitney, J. Organometal. Chem., 117 (1976) 303.

199. B. Wrackmeyer, J. Organometal. Chem., 117 (1976) 313.

200. H. Hoberg and V. Götz, J. Organometal. Chem., 118 (1976) C3.

201. D. E. Bergbreiter and D. P. Rainville, J. Organometal. Chem., 121 (1976) 19.

202. H. C. Brown, S. Krishnamurthy and N. M. Yoon, J. Org. Chem., 41 (1976) 1778.

203. R. O. Hutchins, D. Rotstein, N. Natale, J. Fanelli and D. Dimmel, J. Org. Chem., 41 (1976) 3328.

204. K. W. Bagnall and J. Edwards, J. Less-Common Met., 48 (1976) 159.

205. J. L. Vidal and G. E. Ryschkewitsch, J. Inorg. Nucl. Chem., 38 (1976) 1937.

206. B. E. Smith, B. D. James and J. A. Dilb, J. Inorg. Nucl. Chem., 38 (1976) 1973.

207. A. Nose and T. Kudo, Yakugaku Zaashi, 96 (1976) 988.

208. J. A. Thompson, J. C. Davis and R. E. Drew, Water Res., 10 (1976) 869.

209. E. C. Ashby and J. J. Lin, Tetrahedron Lett., (1976) 3865.

210. R. M. Mueller, Tetrahedron Lett., (1976) 2925.

211. N. Unino, T. Iwakuma and N. Itoh, Tetrahedron Lett., (1976) 2875.

212. H. Friebolin, R. Reusch and H. Wendel, Org. Magn. Reson., 8 (1976) 287.

213. K. Kojima, M. Yoshikuni, J. Ishizu and S. Umeda, Nippon Kagaku Kaishi, (1975) 2221.

214. S. Iwabuchi, K. Kojima, T. Nakahira and H. Hosoya, Makromol. Chem., 177 (1976) 1643.

215. M. Cagnasso and P. A. Biondi, Anal. Biochem., 71 (1976) 597.

216. S. J. Gaskell, C. G. Edmonds and C. J. Brooks, Anal. Lett., 9 (1976) 325.

217. J. Largo-Cabrerizo, An. Quim., 72 (1976) 315.

218. L. Larrondo and E. A. Lissi, An. Asoc. Quim. Argent., 63 (1975) 141.

219. B. J. Brown, P. G. Fitch and D. F. Sangster, Aust. J. Chem., 29 (1976) 941.

220. R. Murphy and R. H. Prager, Aust. J. Chem., 29 (1976) 617.

221. T. V. Rotanova, R. Claus, A. G. Ivanova, L. M. Ginodman and V. K. Antonov, Bioorg. Khim., 2 (1976) 837.

222. M. Witanowski, L. Stefaniak, H. Januszewski, M. G. Voronkov and S. N. Tandura, Bull. Acad. Pol. Sci., Ser. Chim., 24 (1976) 281.

223. A. Arase, Y. Masuda and A. Suzuki, Bull. Chem. Soc. Japan, 49 (1976) 2275.

224. J. Lieto, R. David, J. P. Aune, J. Villermaux and J. Metzger, Bull. Soc. Chim. Fr., (1976) 1246.

225. G. Guillevic, F. Maillot, H. Mongeot, J. Dazord and J. Cueilleron, Bull. Soc. Chim. Fr., (1976) 1099.

226. S. U. Sheikh, Bull. Chem. Soc. Japan, 49 (1976) 2879.

227. Y. Yamamoto, K. Kondo and I. Moritani, Bull. Chem. Soc. Japan, 48 (1975) 3682.

228. M. Tsubouchi and T. Sakai, Bunseki Kagaku, 24 (1975) 754.

229. N. G. Seidah, G. Roy, R. Laprade, T. Cyr and H. Dugas, Can. J. Biochem., 54 (1976) 327.

230. B. E. Stacey and B. Tierney, Carbohydr. Res., 49 (1976) 129.

231. J. B. Farmer, Chem. & Ind., (1976) 311.

232. A. Arase and Y. Masuda, Chem. Lett., (1976) 1115.

233. M. Onishi, Y. Ohama, K. Suzimura and K. Hiraki, Chem. Lett., (1976) 955.

234. T. Mukaiyama and T. Inone, Chem. Lett., (1976) 559.

235. Vo-Van-Chung, K. Inogaki, M. Tokuda and M. Itoh, Chem. Lett., (1976) 209.

236. Y. Kikogawa, Chem. Pharm. Bull., 24 (1976) 1059.

237. P. M. Curtis and R. F. Porter, Chem. Phys. Lett., 37 (1976) 153.

238. T. Berclaz, M. Geoffrey and E. A. Lucken, Chem. Phys. Lett., 36 (1976) 677.

239. C. P. Pinazzi, P. Guillaume and D. Reyx, Eur. Polym. J., 12 (1976) 9.

240. K. C. Malhotra and J. K. Puri, Indian J. Chem., 14A (1976) 384.

241. S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, Indian J. Chem., 14A (1976) 137.

242. D. A. Thompson, W. R. Pretzer and R. W. Rudolph, Inorg. Chem., 15 (1976) 2948.

243. M. H. Goodrow and R. I. Wagner, Inorg. Chem., 15 (1976) 2836.

244. M. H. Goodrow and R. I. Wagner, Inorg. Chem., 15 (1976) 2830.

245. M. A. Sens, J. D. Odom and M. H. Goodrow, Inorg. Chem., 15 (1976) 2825.

246. J. D. Oliver and N. C. Rice, Inorg. Chem., 15 (1976) 2741.

247. L. Maya, Inorg. Chem., 15 (1976) 2179.

248. M. Marcantonatos, Inorg. Chim. Acta, 16 (1976) 17.

249. K. Hanai, J. Biochem. (Tokyo), 80 (1976) 491.

250. K. Hanai, J. Biochem. (Tokyo), 79 (1976) 107.

251. S. Prusiner and E. R. Stadtman, J. Biol. Chem., 251 (1976) 3457.

252. G. K. Kabalke, J. D. Baker and G. W. Neal, J. Chem. Educ., 53 (1976) 549.

253. C. A. Plank and P. M. Christopher, J. Chem. Eng. Data, 21 (1976) 211.

254. Y. Yamamoto, H. Yatagai, A. Sonoda and S. Murahashi, J. Chem. Soc. Chem. Commun., (1976) 452.

255. M. N. Paddon-Row, L. Radom and A. R. Gregory, J. Chem. Soc. Chem. Commun., (1976) 427.

256. D. S. Kemp and D. C. Roberts, Tetrahedron Lett., (1976) 4629.

257. H. D. Empsall, E. Mentzer and B. L. Shaw, J. Chem. Soc. Chem. Commun., (1975) 861.

258. G. Fachinetti, C. Floriani, M. Mellini and G. Merlino, J. Chem. Soc. Chem. Commun., (1975) 300.

259. A. Pelter, K. Rowe, D. N. Sharrocks, K. Smith and C. Subrahmanyan, J. Chem. Soc. Dalton Trans., (1976) 2087.

260. K. J. Alford, E. O. Bishop and J. D. Smith, J. Chem. Soc. Dalton Trans., (1976) 920.

261. R. H. Findlay, J. Chem. Soc. Dalton Trans., (1976) 851.

262. D. E. J. Arnold, E. A. V. Ebsworth and D. W. H. Rankin, J. Chem. Soc. Dalton Trans., (1976) 823.

263. P. J. Bratt, M. P. Brown and K. R. Seddon, J. Chem. Soc. Dalton Trans., (1976) 353.

264. A. Fratiello, R. Kubo and S. Chow, J. Chem. Soc. Perkin Trans. 2, (1976) 1205.

265. P. J. Cox, P. O. Cradwick and G. A. Sim, J. Chem. Soc. Perkin Trans. 2, (1976) 110.

266. J. P. Costes, G. Cros and J. P. Laurent, J. Chim. Phys. Phys.-Chim. Biol., 73 (1976) 16.

267. S. J. Gaskell, C. W. Edmonds and C. J. Brooks, J. Chromatogr., 126 (1976) 591.

268. A. Haas and M. Haeberlein, J. Fluorine Chem., 7 (1976) 123.

269. K. Dey, J. K. Bhar, K. C. Ray and S. K. Sen, J. Indian Chem. Soc., 52 (1975) 999.

270. J. V. Kainnady and A. Weber, J. Raman Spectrosc., 5 (1976) 35.

271. M. K. John, J. Sci. Food Agric., 26 (1975) 1911.

272. G. V. Ponomarev, B. V. Rozynov, T. A. Babushkina and T. H. Ivanova, Khim. Geterotsikl. Soedin., (1975) 1518.

273. L. A. Slashcheva and E. Svarcs, Latv. PSR Zinat. Akad. Vestis, Khim. Ser., (1976) 256.

274. S. Gronowitz, Lect. Heterocycl. Chem., 3 (1976) 17.

275. G. P. Schiemenz and U. Schmidt, Liebigs Ann. Chem., (1976) 1514.

276. W. Fenzl, H. Kosfeld and R. Köster, Liebigs Ann. Chem., (1976) 1370.

277. M. Hartmann, H. Carlsohn and J. Pauls, Makromol. Chem., 177 (1976) 131.

278. E. Seymour and J. M. Frechet, Tetrahedron Lett., (1976) 1149.

279. J. Hooz and R. Mortimer, Tetrahedron Lett., (1976) 805.

280. G. M. Davies, P. S. Davies, W. E. Paget and J. M. Wardelworth, Tetrahedron Lett., (1976) 795.

281. N. Umino, T. Iwakuma and N. Itoh, Tetrahedron Lett., (1976) 763.

282. M. F. Grundon, D. G. McCleery and J. W. Wilson, Tetrahedron Lett., (1976) 295.

283. N. Miyaura, M. Hoh and A. Suzuki, Tetrahedron Lett., (1976) 255.

284. K. Utimoto, K. Okada and H. Nozaki, Tetrahedron Lett., (1975) 4239.

285. R. J. Hughes, A. Pelter, K. Smith, E. Negishi and T. Yoshida, Tetrahedron Lett., (1976) 87.

286. C. F. Lane and G. W. Kabalke, Tetrahedron, 32 (1976) 981.

287. K. Utimoto, N. Sakai, M. Obayashi and H. Nazaki, Tetrahedron, 32 (1976) 769.

288. Y. Yamamoto, H. Toi, A. Sonoda and S. Murahashi, J. Amer. Chem. Soc., 98 (1976) 1965.

289. E. J. Taylor and C. Djerassi, J. Amer. Chem. Soc., 98 (1976) 2275.

290. W. T. Ford, J. Amer. Chem. Soc., 98 (1976) 2727.

291. S. Krishnamurthy and H. C. Brown, J. Amer. Chem. Soc., 98 (1976) 3383.

292. H. Umeyama and K. Morokuma, J. Amer. Chem. Soc., 98 (1976) 7208.

293. J. Wiecko and W. R. Sherman, J. Amer. Chem. Soc., 98 (1976) 7631.

294. R. Köster and W. Dahlhoff, Liebigs Ann. Chem., (1976) 1925.

295. V. A. Dorokhov, V. I. Seredenko and B. M. Mikhailov, J. Gen. Chem. USSR (Engl. Transl.), 46 (1976) 1053.

296. U. C. Gupta, J. A. MacLeod and J. D. Sterling, Soil Sci. Soc. Am. J., 40 (1976) 723.

297. R. G. Belousova, E. Swarcs and A. Ievins, Latv. PSR Zinat. Akad. Vestis, Khim. Ser., (1976) 507.

298. A. Bernane and E. Svarcs, Latv. PSR Zinat. Akad. Vestis, Khim. Ser., (1976) 522.

299. K. Nishei, T. Ohsaka and H. Sawai, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 44 (1976) 656.

300. O. Luekart, M. Caviezil, E. Eberle, E. Escher, A. Tun-Kyi and R. Schwyzer, Helv. Chim. Acta, 59 (1976) 2184.

301. I. G. Marshall, R. L. Parsons and W. K. Paull, Experimentia, 32 (1976) 1423.

302. A. Pelter, Chem. & Ind., (1976) 888.

303. J. I. Jacob and H. C. Brown, J. Amer. Chem. Soc., 98 (1976) 7832.

304. K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 1.

305. R. E. Williams, Adv. Inorg. Chem. Radiochem., 18 (1976) 67.

306. W. Kliegel and E. Ahlensteil, Chem. Ber., 109 (1976) 3547.

307. B. M. Mikhailov, G. S. Ter-Sarkisyan, N. N. Govorov, N. A. Nikolaeva and V. G. Kiselev, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl,), 25 (1976) 348.

308. K. Smith and K. Swaminathan, J. Chem. Soc. Dalton Trans., (1976) 2297.

309. K. Utimoto, Y. Yabuki, K. Onada and H. Nozaki, Tetrahedron Lett., (1976) 3969.

310. W. Ruf, T. Renk and W. Siebert, Z. Naturforsch., 31B (1976) 1028.

311. J. P. Costes, G. Cros and J. P. Laurent, Can. J. Chem., 54 (1976) 2996.

312. H. Fusstetter, J. C. Huffmann, H. Nöth and R. Schaeffer, Z. Naturforsch., 31B (1976) 1441.

313. J. Kroner and B. Wrackmeyer, J. Chem. Soc. Faraday Trans. 2, 72 (1976) 2283.

314. N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Nardin, L. Randaccio, E. Zotti, G. Facchinetti and C. Floriani, J. Chem. Soc. Dalton Trans., (1976) 2310.

315. E. Negishi, S. U. Kulkarni and H. C. Brown, Heterocycles, 5 (1976) 883.

316. U. W. Gerwarth and W. Weber, Chem.-Ztg., 100 (1976) 498.

317. S. J. Rettig and J. Trotter, Can. J. Chem., 54 (1976) 3130.

318. S. J. Rettig, J. Trotter, W. Kliegel and H. Becker, Can. J. Chem., 54 (1976) 3142.

319. S. P. Hopper, M. J. Tremelling, J. S. Fine, D. S. Gilbert and R. J. Ginsberg, Syn. React. Inorg. Metal-org. Chem., 6 (1976) 373.

320. A. Pelter, T. W. Bentley, C. R. Harrison, C. Subramanyam and R. B. Laub, J. Chem. Soc. Perkin Trans. 1, (1976) 2149.

321. A. Pelter, K. J. Gould and C. R. Harrison, J. Chem. Soc. Perkin Trans. 1, (1976) 2428.

322. A. Pelter, C. R. Harrison, C. Subramanyam and D. Kirkpatrick, J. Chem. Soc. Perkin Trans. 1, (1976) 2435.

323. L. E. Manzer and P. Z. Meakin, Inorg. Chem., 15 (1976) 3117.

324. A. H. Wang and I. C. Paul, J. Amer. Chem. Soc., 98 (1976) 4612.

325. T. Renk, W. Ruf and W. Siebert, J. Organometal. Chem., 120 (1976) 1.

326. P. R. Jones and T. F. Oy Lim, J. Organometal. Chem., 120 (1976) 27.

327. R. H. Cragg adn M. Nazery, J. Organometal. Chem., 120 (1976) 35.

328. H. C. Brown, Pure Appl. Chem., 47 (1976) 49.

329. K.-D. Müller and U. W. Gerwarth, Chem.-Ztg., 100 (1976) 498.

330. M. W. Rathke, E. Chao and G. Wu, J. Organometal. Chem., 122 (1976) 145.

331. K. Richter, E. O. Fischer and C. G. Kreiter, J. Organometal. Chem., 122 (1976) 187.

332. D. Florentin, M. C. Fournie-Zaluski, M. Callaguin and B. P. Roches, J. Heterocycl. Chem., 13 (1976) 1265.

333. M. S. De-Giambiagi, M. Giambiagi and A. G. Schrott, J. Chim. Phys.-Chim. Biol., 73 (1976) 909.

334. K. K. Curry and J. W. Gilje, J. Amer. Chem. Soc., 98 (1976) 8262.

335. K. Franz, H. Fusstetter and H. Noth, Z. Anorg. Allgem. Chem., 427 (1976) 97.

336. C. Svensson, Acta Cryst., 32 B (1976) 3341.

337. A. Rogstad, B. N. Cyvin, S. J. Cyvin and J. Brunvoll, J. Mol. Struct., 35 (1976) 121.

338. A. J. DeStefano and R. F. Porter, J. Phys. Chem., 80 (1976) 2818.

339. V. N. Plakhotnik and V. V. Evsikov, Proc. Acad. Sci. USSR, Chem. Section (Engl. Transl.), 228 (1976) 417.

340. K. N. Semenko, S. E. Kravchenko and O. V. Kravchenko, Russ. J. Inorg. Chem. (Engl. Transl.), 20 (1975) 1872.

341. C. E. May, K. Niedenzu and S. Trofimenko, Z. Naturforsch., 31b (1976) 1662.

342. V. M. Ramanujam and N. M. Trieff, J. Chem. Soc. Perkin Trans. II, (1976) 1811.