

BORON-NITROGEN COMPOUNDS

BY

K. NIEDENZU J. W. DAWSON



**ANORGANISCHE UND ALLGEMEINE CHEMIE
IN EINZELDARSTELLUNGEN
BAND VI**

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HERAUSGEGEBEN VON
MARGOT BECKE-GOEHRING

BAND VI

BORON-NITROGEN COMPOUNDS

BY

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Titel No. 4273

Vorbemerkung des Herausgebers

Die Chemie der Bor-Stickstoff-Verbindungen geht in ihren präparativen Anfängen auf ALFRED STOCK zurück und ihre Sonderstellung im Rahmen der anorganischen Chemie wurde zuerst von EGON WIBERG erkannt. Die Bor-Stickstoff-Verbindungen sind in der Folgezeit von einer ganzen Anzahl hervorragender Chemiker bearbeitet worden und seit etwa acht Jahren kann man von einer fast stürmischen Entwicklung auf diesem Gebiet sprechen. Obgleich heute die präparativen Möglichkeiten noch lange nicht erschöpft sind und obgleich man immer noch recht wenig über die Bindungsverhältnisse, die die Besonderheiten der Bor-Stickstoff-Bindung bestimmen, weiß, erschien es doch zweckmäßig, eine zusammenfassende Übersicht über dieses Gebiet der anorganischen Chemie zu geben. Es ist zu hoffen, daß das vorliegende Bändchen alle diejenigen, die sich für das weite Feld der Chemie der nichtmetallischen Elemente interessieren, über den Stand unserer Kenntnis auf dem Gebiet der Bor-Stickstoff-Verbindungen informieren und sie zu neuen Versuchen und Überlegungen anregen möge.

November 1964

M. BECKE-GOEHRING

Preface

Although the chemistry of boron is still relatively young, it is developing at a pace where even specific areas of research are difficult to compile into a monograph. Besides the boron hydrides, boron-nitrogen compounds are among the most fascinating derivatives of boron. Nitrogen compounds exist in a wide variety of molecular structures and display many interesting properties. The combination of nitrogen and boron, however, has some unusual features that are hard to match in any other combination of elements. This situation was first recognized by ALFRED STOCK and it seems proper to pay tribute to his outstanding work in the area of boron chemistry. One should realize that about forty years ago, STOCK and his coworkers had to develop completely new experimental techniques and that no guidance for the interpretation of their rather unusual data had been advanced by theoretical chemists.

In this monograph an attempt has been made to explore the general characteristics of structure and the principles involved in the preparation and reactions of boron-nitrogen compounds. It was a somewhat difficult task to select that information which appears to be of the most interest to "inorganic and general chemistry" since the electronic relationship between a boron-nitrogen and a carbon-carbon grouping is reflected in the "organic" character of many of the reactions and compounds. Due to this fascinating interplay and the limited scope of a monograph, the description of some areas of boron-nitrogen chemistry has been restricted to a very brief resume. Also, the chemistry of the nitrogen derivatives of the higher boron hydrides has been deliberately curtailed in the present description; it is felt that this area should more properly be considered as boron hydride chemistry rather than that of boron-nitrogen compounds.

This monograph is being offered as an example of what can evolve from a close integration of several areas of chemistry. In boron-nitrogen chemistry rarely are there examples that are strictly inorganic, organic or physical in nature. Rather, this area of chemistry exemplifies what can be accomplished through healthy cross-fertilization. The influences of the various subdisciplines have contributed much toward promoting a lively interest in the chemistry of boron-nitrogen compounds.

The authors gratefully acknowledge the invitation by Prof. M. BECKE-GOEHRING for us to write this monograph and particularly for her meticulous and careful review of the manuscript and her helpful and constructive suggestions leading to its improvement.

August 1964

JOHN W. DAWSON
KURT NIEDENZU

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Introduction

Boron, a black metallic appearing element, was prepared by GAY-LUSSAC and THENARD as far back as 1808¹. However, its best known derivative, borax, was known to the Arabs as TINKAL and was used in melting processes in the sixteenth century. Boric acid was prepared by HOMBERG² in 1702 and found wide application as "sal sedativum". Also in 1808, DAVY³ obtained amorphous boron by the electrolysis of boric acid and a crystalline modification was described by WÖHLER and SAINTE-CLAIRE DEVILLE in 1856⁴. Large deposits of boron minerals are found in various parts of the world. The most important stocks are located in Tuscany (Italy), in the southwestern part of the United States, and in Northern Chile and neighboring parts of Argentina, Peru and Bolivia. Smaller deposits of commercial interest are found in Turkey, Central Asia (Tibet) and near Stassfurt, Germany. The percentage of boron in the earth's crust is estimated at about 0.001%.

Despite the widespread occurrence of boron compounds and the early recognition of boron as an element, studies of boron chemistry have long been confined to a relatively small area. This was due mainly to the instability of many boron compounds towards hydrolysis or oxidation and the inherent difficulties in handling many of the materials. However, when STOCK developed his now famous experimental vacuum techniques, a door was opened for the investigation of a completely new field of boron chemistry. The boron hydrides were exhaustively studied and, it is indicative of STOCK's outstanding work that, until a few years ago, no new boron hydride had been discovered for about thirty years.

Reports on boron-nitrogen compounds date back about 150 years. However, it was the inspired work of ALFRED STOCK and his coworkers⁵ and the experimental techniques developed in their basic investigation of boron hydrides some forty years ago which provided the necessary impetus for a detailed study of boron-nitrogen derivatives. In 1926 STOCK and POHLAND⁶ studied the reaction of diborane with ammonia which resulted in the discovery of borazine, $(-\text{BH}-\text{NH}-)_3$, the "inorganic

¹ GAY-LUSSAC, J. L., and L. J. THENARD: *Ann. Chim. Phys.* [1] **68**, 169 (1808).

² HOMBERG, G.: *Mem. Acad. polon Sci Letters. Cl. Sci. math. natur., Ser. A.* **33**, 50 (1702).

³ DAVY, H.: *Philos. Trans. Roy. Soc. London Ser. A.* **98**, 333 (1808).

⁴ WÖHLER, F., and H. SAINTE-CLAIRE DEVILLE: *C. R. hebdom. Seances Acad. Sci.* **43**, 1088 (1856).

⁵ STOCK, A.: *Hydrides of Boron and Silicon*, Ithaca, N.Y.: Cornell University Press 1933.

⁶ STOCK, A., and E. POHLAND: *Ber. deutsch. chem. Ges.* **59**, 2215 (1926).

benzene". This event might be considered as the birth of modern boron-nitrogen chemistry. Nevertheless, until about 1950, few research groups devoted any real effort to the exploration of this area. Since that time, however, an increasing number of scientists have become interested in boron-nitrogen compounds and recent methods have been developed which provide for at least partial replacement of the high vacuum techniques previously used in STOCK's classic work, by more conventional methods.

Historical Dates of Boron-Nitrogen Chemistry

1809	GAY-LUSSAC	adduct of ammonia and trifluoroborane
1842	BALMAIN	first reports on boron nitride
1850	WÖHLER, ROSE	characterisation of boron nitride
about 1905	STOCK, JOANNIS	studies on the interaction of ammonia with trihalogenoboranes
1926	STOCK and POHLAND	synthesis of borazine
since 1935	WIBERG, SCHLESINGER	basic studies of boron-nitrogen compounds
1955	BROWN and LAUBENGAYER	preparation of B-trichloroborazine with standard laboratory equipment
since 1956	DEWAR and coworkers	heteroaromatic boron-nitrogen compounds
1958	PARRY and coworkers	structure of the diammoniate of diborane

It is of interest to note that the more recent efforts are independent of any commercial interest in boron-nitrogen compounds and are based primarily on the pursuit of basic research.

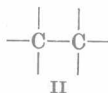
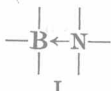
As direct neighbors of carbon in the Periodic Table of Elements, the combination of boron and nitrogen has the same number of electrons as the carbon-carbon entity. Moreover, the sum of the atomic radii of boron and nitrogen is of the same order of magnitude as that of two carbon atoms.

Elemental Characteristics of Boron, Carbon and Nitrogen

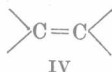
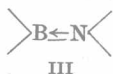
	number of outer electrons	covalent single- bond radii, Å	electronegativity
boron . . .	3	0.88	2.0
carbon . . .	4	0.771	2.5
nitrogen . .	5	0.70	3.0

The tervalent nitrogen has a pair of unshared electrons which are available to complete the octet of a tervalent, electron-deficient, boron atom. Thus a close relationship in behavior and characteristics between some substances having boron-nitrogen bonds and others with similar carbon-carbon linkages is to be expected since the two bonds are of similar size. Indeed, considerable attention has been drawn to the existence of a number of boron-nitrogen compounds similar in many respects to their analogous organic counterparts.

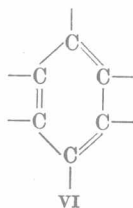
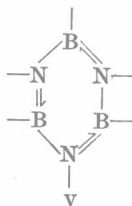
WIBERG¹ classified boron-nitrogen derivatives into the three major groups of amine-boranes (Borazane), aminoboranes (Borazene) and borazines (Borazole) according to the nature of the B—N bond in the molecules. *Amine-Boranes* are characterized by having a tervalent boron bonded to a tervalent nitrogen by the two unshared electrons of the nitrogen (I). This structure is roughly comparable to that of alkanes, in the sense that in alkanes two carbon atoms are linked by a single two-electron bond (II).



In the *Aminoborane* system, boron and nitrogen are linked together by one normal covalent bond; but the unshared electron pair of the nitrogen can participate in this linkage² thereby introducing a degree of double bond character (III). Aminoboranes, therefore, often exhibit physical characteristics analogous to those of alkenes (IV).



The third major group of boron-nitrogen compounds comprises the cyclic *Borazines* (V), whose formal analogy to aromatic carbon compounds (VI) is illustrated by the structures.



However, any such comparison between boron-nitrogen compounds and organic materials should not be pursued excessively. Although B—N and C—C linkages are isoelectronic and very similar, they are not identical. The C—C bond involves atoms of the same element, while that of B—N resides between atoms of differing electronegativity and, therefore, the electron cloud representing the B—N bond is not symmetrical. Differences between the two systems might very well outweigh the similarities. Nevertheless, the concept of isosterism of B—N and C—C compounds serves well to effect a general classification of boron-nitrogen derivatives and has been adopted as a model for the following chapters. It seems proper to mention in this introduction, two reactions which have been found to be of major importance in this area of chemistry.

¹ WIBERG, E.: *Naturwissenschaften* 35, 182, 212 (1948).

² In the following, arrows (→) will be used to emphasize lone-pair electron bonding and to distinguish from the normal covalent bond illustrated by a straight line (—).

Boron compounds have a distinct tendency to disproportionate, apparently more so than those of any other nonmetallic element. This tendency is readily explained in terms of the electron deficiency of trivalent boron, which provides a center for nucleophilic attack. Although often annoying in preparative work, disproportionation reactions of boron compounds have nevertheless been put to good use. This is illustrated by the interaction of triorganoboranes with trihalogenoboranes to yield various organohalogenoboranes, which are not readily available by other synthetic methods. Of equal importance in boron-nitrogen chemistry is the transamination reaction. The potentialities of this reaction are only now beginning to be exploited. During the past three or four years, transamination has already provided for a remarkably simple access to several major classes of boron-nitrogen compounds.

Interest is also quickening in the extent to which certain boron-nitrogen compounds may be applied for technical purposes. This upsurge resulted mainly from the proposed military uses of boron compounds as high energy fuels. Although this application has not realized its full potential, diborane for example has now become commercially available. B-Trichloro-borazine is offered in developmental quantities and a variety of other boron-nitrogen compounds have appeared on the market. The use of boron nitride as a possible semiconductor is being explored and, in the search for inorganic and semi-inorganic polymers applicable for high temperature uses, various boron-nitrogen derivatives demonstrate interesting possibilities.

The reader interested in a more detailed study of the progress and aspects of boron chemistry is referred to some recent articles and books listed below.

Books:

GMELIN's Handbuch der anorganischen Chemie, "Bor", System Nummer 13, Ergänzungsband. Verlag Chemie: Weinheim 1954.

LIPSCOMB, W. N.: Boron Hydrides. New York/Amsterdam: W.A. Benjamin Inc. 1963.

BROWN, H. C.: Hydroboration. New York: W. A. Benjamin Inc. 1962.

GERRARD, W.: The Organic Chemistry of Boron. New York/London: Academic Press 1961.

Advances in Chemistry Series, Vol. 42, Boron-Nitrogen Chemistry. Washington, D.C.: American Chemical Society.

Advances in Chemistry Series, Vol. 32, Borax to Boranes. Washington, D.C.: American Chemical Society.

Articles:

MAITTLIS, P. M.: Heterocyclic Organic Boron Compounds. Chem. Review **62**, 223 (1962).

GERRARD, W., and M. F. LAPPERT: Reactions of Boron Trichloride with Organic Compounds, Chem. Review. **58**, 1081 (1958).

STONE, F. G. A.: Stability Relationships among Analogous Molecular Addition Compounds of Group III Elements, Chem. Review. **58**, 101 (1958).

WIBERG, E.: Neuere Entwicklungslinien der Borchemie. Experientia [Basel] Suppl. VII, 183 (1957).

Nomenclature of Boron-Nitrogen Compounds

In the following chapters, the nomenclature recommended by the Committee of the American Chemical Society on the Nomenclature of Organic Boron Compounds^{1,2} will be used. The principles of this nomenclature, insofar as they concern boron-nitrogen compounds, are outlined below.

I. Linear Systems

1. The combining form of boron is "bor-" and is used to designate the presence of boron in a compound.

2. For such compounds which can formally be considered as substituted BH_3 , the suffix "ane" is applied. Thus BCl_3 would be correctly named "trichloroborane", although in this case (and several others of common usage) the term "boron trichloride" is acceptable.



3. Whenever possible, substituents on the boron are named according to their accepted title as given in Chemical Abstracts. The order of the groups is governed by the practice used for substituted organic compounds.



4. In addition compounds (i.e. donor-acceptor complexes), both molecules are given their proper names and the title of the addition compound is formed by indicating the donor molecule first, and then joining this to the name of the acceptor by a hyphen.



¹ Chem. Engng. News **32**, 1441 (1954).

² *ibid.* **34**, 560 (1956).

5. If a need exists to indicate the addition linkage, the simple hyphen is replaced by the symbols of the two elements forming the donor-acceptor bond; the symbols are joined by a hyphen and enclosed in parentheses.

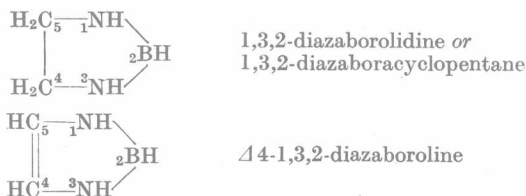


6. Hydrogen functioning as a ligand is named "hydro-" and the name is placed last in the order of ligands.

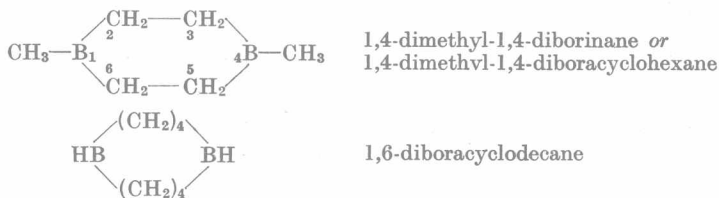


II. Ring Systems

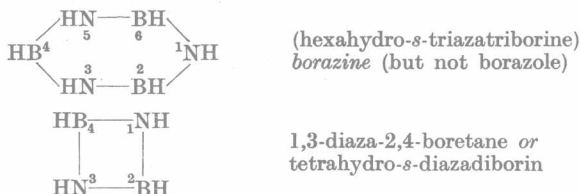
1. Names of small ring systems are most conveniently given by the practices established in the Ring Index.



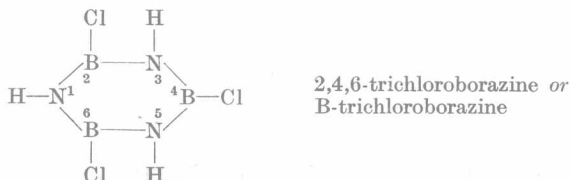
2. In larger rings, especially when these are in the highest stage of hydrogenation, names based on those of the corresponding hydrocarbons may be used.



3. Trivial names are to be used only if the ring possesses a particular feature (i.e. stability, great number of derivatives etc.).



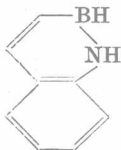
4. The numbering of the ring follows the usual practice for heterocyclic rings. In those cases where a high order of symmetry exists, a short form may be used.



5. When boron and nitrogen are incorporated in an aromatic six-membered ring system, nomenclature according to the Ring Index would not illustrate their essential features, i.e. that such compounds are isoelectronic with aromatic hydrocarbons. Consequently, the convention developed by DEWAR and DIETZ¹ is then adopted, wherein the compounds are named as derivatives of the isoelectronic hydrocarbon with the prefix "aro" to denote the existence of aromaticity in the system.



2,1-borazarobenzene *or*
2,1-borazarene (as trivial name for the parent
monocyclic system only)



2,1-borazonaphthalene

¹ DEWAR, M. J. S., and R. DIETZ: J. chem. Soc. (London) 1959, 2728.

Chapter I

Amine-Boranes and Related Structures

A. The Boron-Nitrogen Dative Bond

1. General Remarks

The ability of trivalent boron compounds of the type BR_3 to accept electron pairs from suitable electron donors has long been recognized. The driving force for such events is the tendency for boron to complete its outer shell of electrons in order to obtain the most favorable electronic configuration. Hence an extremely large number of molecular addition compounds of BR_3 molecules with a variety of nitrogen bases and, more general, nitrogen-containing compounds, have been described over the last 150 years. For instance, $H_3N \cdot BF_3$, the adduct of ammonia and trifluoroborane, was prepared by GAY-LUSSAC in 1809¹ and was studied in more detail by DAVY in 1812². In spite of the large number of such coordination compounds cited in the literature, it is amazing how few of their properties have been recorded and how little study of their behavior has been pursued.

Conventionally, coordination compounds of an amine with a borane, i. e. amine-boranes, are illustrated by the formula
$$\begin{array}{c} R \\ \diagdown \\ R \end{array} N \rightarrow B \begin{array}{c} R' \\ \diagup \\ R' \end{array}$$
. These compounds are obtained through direct combination of the components in equimolar amounts with or without the use of solvents at low temperatures.



However, treatment of an acceptor molecule BR_3 with an electron donor does not always yield a true molecular addition compound in which bonding is effected by the free electron pair of the donor nitrogen. Furthermore, a donor-acceptor linkage of this type possesses considerable polarity and this situation can favor ionization of the molecule or the intramolecular elimination of small molecules from the complex. Consequently, the intramolecular decomposition of amine-boranes leading to aminoboranes, $R_2N-BR'_2$, and borazines, $(-BR'-NR-)_3$ is one of the best known reactions of the amine-borane system. Reactions effected

¹ GAY-LUSSAC, J. L., and J. L. THENARD: *Mem. de phys. et de chim. de la soc. d'arcueil* **2**, 210 (1809).

² DAVY, J.: *Ann. Chimie* **86**, 178 (1813).

through cleavage of the boron-nitrogen linkage, e.g. reactions with suitable Lewis bases, are of equal importance. An example is illustrated in the following equation.



The following description of amine-boranes will not be confined to the addition products of simple nitrogen bases with a BR_3 acceptor. In view of the varying degree of stability residing in the basic amine-borane system, it seems reasonable to include those addition compounds which are, in general, derived by the coordination of a free electron pair of a nitrogen atom to a BR_3 molecule. Hence, borane complexes with nitriles, amides and related substances will also be considered if sufficient evidence suggests dative boron-nitrogen bonding in the resultant materials.

2. The Normal Coordination Structure (Donor-Acceptor Bonding)

The nature of the boron-nitrogen bond in an amine-borane, formed by donation of the free electron pair of a trivalent nitrogen to a boron component has not been established unequivocally and may vary between two extremes. Incomplete sharing of the electron pair results in a very weak bond whereas complete sharing involves a charge transfer to the acceptor atom resulting in a very strong bond. SIDGWICK¹ suggested that this type of bond should be represented by an arrow as illustrated in I, but the use of charges II, implying an electron-transfer process², has received more general acceptance.



The principle of such donor-acceptor bonding has been expressed by MULLIKEN^{3,4} in quantum-mechanical terms. Thus for the highly polar trimethylamine-trifluoroborane, $(\text{CH}_3)_3\text{N} \cdot \text{BF}_3$, b^2 is much greater than a^2 in the wave function, ψ_N , of the ground state.

$$\psi_N \approx a \psi_0[(\text{CH}_3)_3\text{N} \cdot \text{BF}_3] + b \psi_1[(\text{CH}_3)_3\text{N}^{\oplus} \cdot \text{BF}_3^{\ominus}] \quad (\text{I-3})$$

In this equation ψ_0 is the no-bond wave function, and ψ_1 is the donor wave function corresponding to a complete transfer of an electron from the nitrogen in trimethylamine to the boron in trifluoroborane in forming a bond by the odd electrons in $(\text{CH}_3)_3\text{N}^{\oplus} \cdot$ and $\cdot \text{BF}_3^{\ominus}$. In the more stable amine-boranes of similar type, the second term, which involves ψ_1 , predominates. In general, the nature of the donor-acceptor linkage

¹ SIDGWICK, N. V.: The Electronic Theory of Valence. Oxford: Clarendon Press 1927.

² LOWRY, T. M.: Trans. Faraday Soc. 18, 285 (1923).

³ MULLIKEN, R. S.: J. physic. Chem. 56, 801 (1952).

⁴ MULLIKEN, R. S.: J. Amer. chem. Soc. 74, 811 (1952).

may vary between the two extremes cited above. The bond strength is affected by the nature of the groups attached to both the boron and the nitrogen atom and consequently, the stability of an amine-borane (which is directly dependent upon the nature of the bond) can vary tremendously. Some of these compounds may be stable only at low temperatures whereas others of comparable size can be distilled without decomposition even at atmospheric pressures.

The stability of selected systems of amine-boranes has been studied frequently in order to establish underlying principles. The classic work of BURG and GREEN¹ provides a relatively well understood example of polar effects. In the series $(\text{CH}_3)_3\text{N} \cdot \text{BF}_3$, $(\text{CH}_3)_3\text{N} \cdot \text{BF}_2\text{CH}_3$, $(\text{CH}_3)_3\text{N} \cdot \text{BF}(\text{CH}_3)_2$, $(\text{CH}_3)_3\text{N} \cdot \text{B}(\text{CH}_3)_3$, trimethylamine-trifluoroborane is the most stable member: The three highly electronegative fluorine atoms increase the LEWIS acidity of the boron acceptor atom compared to the situation where the boron is bonded to electron-releasing alkyl groups.

However, the stability of an addition compound is not always in agreement with expectations based on electronegativity data. For instance, trifluoroborane has long been considered as the strongest boron acceptor molecule known and the acceptor power of trihalogenoboranes was thought to be in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$. More recent work, using pyridine and nitrobenzene as reference bases, indicates a reversed sequence; an explanation for the relative acidity of halogenoboranes can be found in terms of π -bonding between the halogen and boron in BX_3 molecules².

It is not surprising that, under these circumstances, various types of bonding have been postulated for the amine-borane system. Besides the normal coordination structure, an ionic type and, in the case of aromatic organic amines, a π -complex model has been considered for those amine-boranes containing boron-halogen linkages. The classical formulation of a normal coordination structure is unquestionably the predominant situation in the amine-borane system. If there is no halogen substituent bonded to the boron, the formation of an ionic structure as discussed below seems to be excluded: The free electron pair of the nitrogen adds to the boron atom establishing a lone-pair electron bond and forming a normal molecular addition compound (I). This same concept of bonding holds true for amine-halogenoboranes. It was developed, in principle, by GOUBEAU and coworkers³ and was substantiated by GERRARD et al.⁴: As described below, there is some evidence that certain amine-boranes such as dimethylamine-trichloroborane, $(\text{CH}_3)_2\text{HN} \cdot \text{BCl}_3$, might have an ionic (i.e. salt-like) structure. However, a chloroform solution of such materials does not show a detectable conductivity³. This situation is in agreement with the behavior of other amine-boranes, such as trimethylamine-borane, $(\text{CH}_3)_3\text{N} \cdot \text{BH}_3$, trimethylamine-trimethylborane, $(\text{CH}_3)_3\text{N} \cdot \text{B}(\text{CH}_3)_3$, or trimethylamine-trichloroborane, $(\text{CH}_3)_3\text{N} \cdot \text{BCl}_3$. In contrast, trimethylammonium chloride, $[(\text{CH}_3)_3\text{NH}]\text{Cl}$, as a salt, is

¹ BURG, A. B., and A. A. GREEN: J. Amer. chem. Soc. **65**, 1838 (1943).

² BROWN, H. C., and R. R. HOLMES: *ibid.* **78**, 2173 (1956).

³ GOUBEAU, J., M. RAHTZ and H. J. BECHER: Z. anorg. allg. Chem. **275**, 161 (1954).

⁴ GERRARD, W., M. F. LAPPERT and C. A. PEARCE: J. chem. Soc. (London) **1957**, 381.