STABILITY RELATIONSHIPS AMONG ANALOGOUS MOLECULAR ADDITION COMPOUNDS OF GROUP III ELEMENTS

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I. INTRODUCTION

A very great number of molecular addition compounds of the Group III elements of the periodic table have been described. This is not surprising, since the tendency of boron and its congeners to form this type of compound has been recognized for nearly one hundred and fifty years. Thus monoammonia-boron trifluoride, $H_3N \cdot BF_3$, was prepared by Gay-Lussac (56) and studied by Davy (54).

The long existence of this well-defined field of chemistry has prompted the periodic appearance of review articles. These reviews have been concerned largely with complex compounds formed by one specific acceptor molecule, or by one class of acceptor molecule, usually boron-containing, e.g., boron tribromide (74), boron trichloride (73), boron trifluoride (6, 61), borane (BH_3) (37, 98), and the trialkylboranes (65).

In spite of the large number of coördination compounds of Group III elements mentioned in the chemical literature, few properties of many of them have been recorded. In several instances, it is known only that the compound exists. Because of this a survey of all known addition compounds of Group III elements would be of little value. However, knowledge in this field has now developed sufficiently to support a broad discussion of principles. This has come about through many systematic investigations, often of a physicochemical nature, in which only one factor has been changed in passing from one complex to the next. This review will be limited, therefore, to comparing the stability of complexes of the Group III elements where there is enough information available to make comparisons among related compounds worthwhile.

Treatment of a Group III acceptor molecule with an electron donor does not always yield as the final product a true molecular addition compound. Formation of an addition compound gives rise to a donor–acceptor bond with considerable polarity, and this situation favors ionization of the molecule, or the elimination of small molecules, like hydrogen or methane, from the complex. The tendency of addition compounds of the Group III atoms to decompose via intramolecular elimination reactions has been known for a long time, and in recent years this type of reaction has been exploited extensively for the synthesis of new compounds. Section V of this article will survey this topic.

Aromatic electron donors form weak adducts even with the strongest of Group III acceptors. Indeed, these molecular complexes dissociate so readily into their components that they are often not regarded as real *compounds.* They will be omitted from this article, especially since they have been reviewed (1) recently.

Before surveying addition compounds of Group III elements it is necessary to consider briefly the energetics of the formation of complex compounds and the methods used to evaluate relative stabilities.

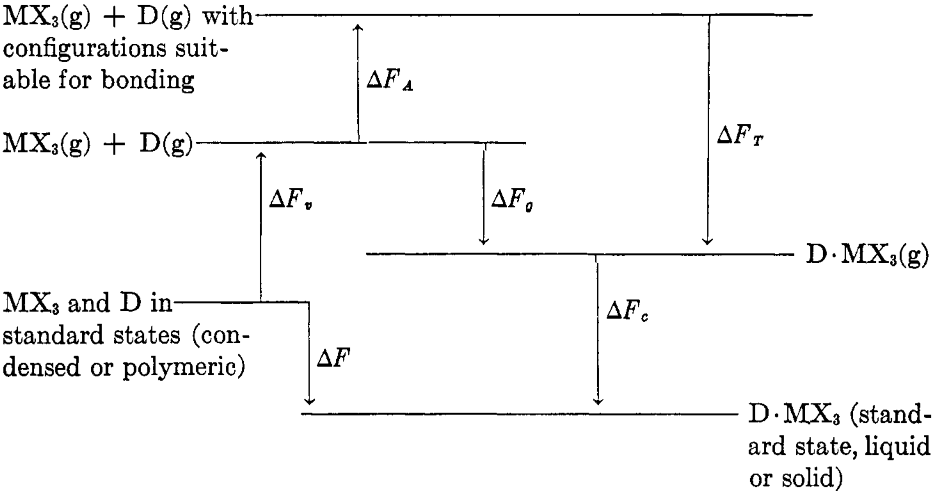
II. Formation of Molecular Addition Compounds

A. ENERGETICS OF ADDITION-COMPOUND FORMATION

According to the concepts of modern valence theory the bonding electrons of a Group III atom M in a molecular compound MX_3 occupy three nsp^2 hybrid orbitals at angles of 120°, leaving a vacant or perhaps partially vacant np_π orbital perpendicular to the plane containing the three σ bonds. Thus in terms of the octet rule the electronic environment of the Group III atom is incomplete. The atom is thus predisposed to act as an electron-pair acceptor in the presence of suitable donor molecules. Formation of addition compounds in this manner enables the atom M to use in full all energetically suitable bonding orbitals. This donor–acceptor principle of bonding was used by Lewis (69) to define the terms acid and base. Classification of MX_3-type acceptor molecules as acids has permitted the correlation of much information which otherwise would have appeared unrelated, but Lewis' generalized acid-base theory has many limitations, the chief of which is that it supplies no information concerning the energetics of complex-compound formation, or the stability of dative bonds once they are produced. Thermochemical studies of Skinner and Smith (94) have shown that a coördinate link in a molecular addition compound is much less strong than the analogous covalent link. This is not unexpected, however, because of differences in hybridization, and due allowance must often be made for strengthening of the covalent link by multiple bonding.

The existence of a coördination compound should be considered in terms of an energy cycle of formation (38). Although complete data for the component parts of such a cycle are lacking, the cycle can be used qualitatively for discussion of real or possible compounds. For an adduct $D \cdot MX_3$, formed from a donor D and a vacant orbital acceptor MX_3, the various energy steps shown in the figure below must be considered. It should be understood that every donor–acceptor reaction requires adjustment of the energy levels in relation to each other to accord with the actual properties of the system.

Energy steps in the formation of addition compounds



ΔF_v = vaporization energy required to convert donor and acceptor to the gas phase from their standard states
ΔF_A = adjustment energy required to convert gaseous donor and acceptor to moieties having configurations present in the final product
ΔF_T = total energy released in dative-bond formation, giving the adduct in the gas phase
ΔF_g = gas-phase energy of formation
ΔF_c = energy released when addition compound condenses to standard state
ΔF = free-energy change accompanying the reaction $MX_3 + D \rightarrow D \cdot MX_3$, reactants and products being in their standard states

In some instances the adjustment energy may be greater than the energy released by dative-bond formation so that there is no combination, the gas-phase free energy of formation being positive instead of negative. This may well be true for some of those extreme cases where no reaction takes place between acceptors and donors having large alkyl groups attached to them. On the other hand, from recent work (55, 64) on the kinetics of coördinate-bond formation in the vapor phase, the energy of readjustment for reactions between some classes of donor and acceptor can be quite small. This is true for complex compound formation between certain amines and boron halides. Alternatively, the $D \cdot MX_3$ standard state may lie above the ($MX_3 + D$) standard states so that the adduct would not form. All these energy steps are complex. Thus, with respect to the acid, adjustment for bonding involves energy of rehybridization, with a drawing of M out of the MX_3 plane to form a vacant sp^3 orbital. Sometimes the existence of π bonding between M and X in MX_3 makes this step energetically more costly than in other situations where such π bonding is less, or absent. Rehybridization considerations also apply to the basic molecules, although usually the changes are not as drastic as in the case of acceptors. A further complication occurs if the acceptor molecule exists as a polymer. Then conversion of MX_3 (standard state) to $MX_3(g)$ requires energy for depolymerization. This happens during complex formation by the dimeric aluminum halides or by electron-deficient molecules like trimethylaluminum and diborane. Of all these factors the most complex relation is between the adjustment energy and the hypothetical total energy released in dative-bond formation, both being affected by steric and electronic influences of the groups on donor and acceptor. Various electronic and steric factors will be discussed later in more appropriate parts of this review.

Even from this brief consideration of the energy steps in complex-compound formation, it is readily seen, and moreover was recognized by Lewis (69, 80), that it is impossible to assign definite strengths to electron-pair donors and acceptors valid for every acid-base reaction.

B. METHODS OF STUDYING STABILITIES OF ADDITION COMPOUNDS

Because of its pertinence to the question of the nature of dative bonds, the most important relationship existing between Group III addition compounds is the variation in *strength* of the coördinate bond in passing from compound to compound. Strength of a metal–ligand bond is most satisfactorily defined as the enthalpy change, ΔH, accompanying the gas-phase dissociation of the complex. Sometimes, however, the strength of the donor–acceptor bond is interpreted in terms of the magnitude of the equilibrium constant, K_p, for the reaction:

$$D \cdot MX_3(g) \rightleftharpoons D(g) + MX_3(g)$$

When equilibrium constants are used as a criterion of stability, and they often are, care has to be taken in interpreting the results. This is because equilibrium constants are a measure of a free-energy change. Therefore, if K_p for one addition compound is greater than for a second at a given temperature, it does not necessarily follow that the dissociation of the former is accompanied by the smaller enthalpy change. This is only true if the entropy of dissociation in both reactions is very similar. Fortunately, from those studies in the gas phase made so far, it is evident that for many closely related addition compounds of Group III elements the entropy changes accompanying dissociation are rather similar. This is in contrast to equilibria involving transition metal complexes where entropy changes are sometimes quite different even with compounds of very similar type. Studies on the subgroup elements, however, are carried out in solution, where entropy changes are probably affected by difference in solvation.

1. Thermal dissociation of the complex in the gas phase

As indicated above, the most satisfactory method of investigating the stability of an adduct $D \cdot MX_3$ is by studying, in the gas phase, dissociation of the compound into its component parts. A knowledge of how the degree of dissociation varies with temperature permits the thermodynamic functions, ΔH, ΔF°, and ΔS to be calculated, and this enables a *quantitative* measure of the strength of the metal–ligand bond to be obtained. The experimental techniques for studying gas-phase dissociation of molecular addition compounds have been developed by Brown, Taylor, and Gerstein (17, 34) to give precise results.

Molecular addition compounds of the Group III elements which have been studied in the gas phase are listed in table 1.

2. Calorimetric studies

The gas-phase dissociation technique for the study of addition compounds has certain limitations. Thus, it is difficult to study in the gas phase adducts which have already attained a high (ca. 90 per cent) degree of dissociation a few degrees above saturation point. The dissociation method is also unsuitable for the study of complex compounds which do not give a measurable dissociation at a convenient temperature (below ca. 170°C.). For these two classes of complexes representing compounds at either ends of the stability range, it is possible to determine the stability by calorimetry. Calorimetric studies have been applied so far chiefly, but not exclusively, to addition compounds of boron. The types of reaction investigated fall into a number of different categories:

$$D(g) \text{ or } (l) + MX_3(g) \text{ or } (l) = D \cdot MX_3(l) \text{ or } (s)$$

$$D(\text{solution}) + MX_3(\text{solution}) = D \cdot MX_3(\text{solution})$$

$$D'(\text{solution}) + D \cdot MX_3(\text{solution}) = D' \cdot MX_3(\text{solution}) + D(\text{solution})$$

$$D(\text{solution}) + MX_3(g) = D \cdot MX_3(\text{solution})$$

None of these reactions gives the dative-bond strength (ΔH(g)) in an adduct $D \cdot MX_3$ directly, but the results in some instances can be converted to the gas phase when other data are available, e.g., heats of sublimation, vaporization, or solution. In a few cases where results are available from both gas-phase and calorimetric studies, it has been found (25) that the heat of formation of the

TABLE 1

Gas-phase dissociation data for molecular addition compounds of Group III elements

Series	Compound	ΔH	ΔS	$\Delta F°$ *	K_p *	References
Ligand atom from Group V						
		kcal. mole^{-1}	*cal. deg.$^{-1}$ mole^{-1}*	*kcal. mole^{-1}*		
1...	$H_3N \cdot B(CH_3)_3$	13.75	39.9	−1.13	4.62	(9,13)
	$CH_3NH_2 \cdot B(CH_3)_3$	17.64	40.6	2.46	0.0360	(9, 13)
	$(CH_3)_2NH \cdot B(CH_3)_3$	19.26	43.6	2.89	0.0214	(9, 13)
	$(CH_3)_3N \cdot B(CH_3)_3$	17.62	45.7	0.56	0.472	(9, 13, 34)
2...	$(CH_3)_3N \cdot BF_3$	Too stable to permit study in the gas phase				(40, 42)
	$(CH_3)_3N \cdot BF_2CH_3$	23.1	—	—	0.01275 (at 140°C.)	(40)
	$(CH_3)_3N \cdot BF(CH_3)_2$	18.3	—	—	0.152 (at 86°C.)	(40)
	$(CH_3)_3N \cdot B(CH_3)_3$	17.62	45.7	0.56	0.472	(9, 13, 34)
3...	$H_3P \cdot B(CH_3)_3$	Not formed even at −78°C.				(22)
	$CH_3PH_2 \cdot B(CH_3)_3$	—	—	—	∞ (at 20°C.)	(9, 32)
	$(CH_3)_2PH \cdot B(CH_3)_3$	11.41	35.1	−1.69	9.8	(9, 32)
	$(CH_3)_3P \cdot B(CH_3)_3$	16.47	40.0	1.52	0.128	(9, 32)
4...	$H_3P \cdot BF_3$	Formed only at low temperatures				(16, 107)
	$CH_3PH_2 \cdot BF_3$	Too highly dissociated to be measured				(9, 16)
	$(CH_3)_2PH \cdot BF_3$	14.7	44.1	−1.74	10.5	(9, 16)
	$(CH_3)_3P \cdot BF_3$	18.9	45.3	1.99	0.0669	(9, 16)
5...	$(CH_3)_3N \cdot B(CH_3)_3$	17.62	45.7	0.56	0.472	(9, 13, 34)
	$(CH_3)_3P \cdot B(CH_3)_3$	16.47	40.0	1.52	0.128	(9, 32)
	$(CH_3)_3As \cdot B(CH_3)_3$	—	—	—	1.6 (at 0°C.)	(22)
	$(CH_3)_3Sb \cdot B(CH_3)_3$	Not formed even at −78°C.				(22)
6...	$H_3N \cdot B(CH_3)_3$	13.75	39.9	−1.13	4.6	(9, 13)
	$C_2H_5NH_2 \cdot B(CH_3)_3$	18.00	43.0	1.96	0.705	(9, 33)
	$(C_2H_5)_2NH \cdot B(CH_3)_3$	16.31	44.1	−0.15	1.22	(9, 33)
	$(C_2H_5)_3N \cdot B(CH_3)_3$	~10	—	—	∞	(9, 33)
7...	$CH_3NH_2 \cdot B(CH_3)_3$	17.64	40.6	2.47	0.0350	(9, 13)
	$C_2H_5NH_2 \cdot B(CH_3)_3$	18.00	43.0	1.96	0.0705	(9, 33)
	$C_3H_7NH_2 \cdot B(CH_3)_3$	18.14	43.0	2.09	0.0598	(9, 35)
	$C_4H_9NH_2 \cdot B(CH_3)_3$	18.41	43.2	2.27	0.0470	(9, 35)
	$C_5H_{11}NH_2 \cdot B(CH_3)_3$	18.71	43.9	2.36	0.0415	(9, 35)
	$C_6H_{13}NH_2 \cdot B(CH_3)_3$	18.53	43.2	2.40	0.0390	(9, 35)
8...	$CH_3NH_2 \cdot B(CH_3)_3$	17.64	40.6	2.47	0.0350	(9, 13)
	$C_2H_5NH_2 \cdot B(CH_3)_3$	18.00	43.0	1.96	0.0705	(9, 33)
	$i\text{-}C_3H_7NH_2 \cdot B(CH_3)_3$	17.42	44.7	0.74	0 368	(9, 12)
	$s\text{-}C_4H_9NH_2 \cdot B(CH_3)_3$	17.26	44.3	0.73	0.373	(9, 12)
	$t\text{-}C_4H_9NH_2 \cdot B(CH_3)_3$	12.99	39.3	−1.66	9.46	(9, 12)
9...	$C_4H_9(CH_3)_2N \cdot B(CH_3)_3$	15.3	45.6	−1.72	10.2	(27)
	neo-$C_5H_{11}(CH_3)_2N \cdot B(CH_3)_3$	Too highly dissociated to be measured				(27)
10...	$(CH_3)_3N \cdot BF_3$	Too stable to permit study in the gas phase				(40, 42)
	$(CH_3)_3P \cdot BF_3$	18.9	45.3	1.99	0.0669	(9, 16)
	$(CH_3)_3As \cdot BF_3$	—	—	—	0.4 (at 5°C.)	(22)
	$(CH_3)_3Sb \cdot BF_3$	Not formed even at −78°C.				(22)
11...	$(CH_3)_2NH \cdot B(CH_3)_3$	19.26	43.6	2.88	0.0214	(9, 13)
	$(CH_2)_2NH \cdot B(CH_3)_3$	17.59	40.1	2.64	0.0284	(9, 18)
	$(CH_2)_3NH \cdot B(CH_3)_3$	22.48	44.3	5.96	0.000332	(9, 18)
	$(CH_2)_4NH \cdot B(CH_3)_3$	20.43	43.5	4.19	0.00350	(9, 18)
	$(CH_2)_5NH \cdot B(CH_3)_3$	19.65	45.0	2.86	0.0210	(9, 18)
12...	$(C_2H_5)_3N \cdot B(CH_3)_3$	~10	—	—	∞	(9, 33)
	cyclo-$C_7H_{13}N \cdot B(CH_3)_3$†	19.94	45.6	2.92	0.0196	(9, 31)

TABLE 1—*Concluded*

Series	Compound	ΔH	ΔS	$\Delta F°$ *	K_p *	References
		kcal. mole^{-1}	*cal. deg.*$^{-1}$ *mole*$^{-1}$	*kcal. mole*$^{-1}$		
13....	$C_5H_5N \cdot B(CH_3)_3$	17.00	43.2	0.89	0.301	(9, 11)
	$2\text{-}CH_3C_5H_4N \cdot B(CH_3)_3$	~10	—	—	∞ (at 55°C.)	(9, 11)
	$3\text{-}CH_3C_5H_4N \cdot B(CH_3)_3$	17.81	43.9	1.47	0.138	(9, 11)
	$4\text{-}CH_3C_5H_4N \cdot B(CH_3)_3$	19.40	47.5	1.67	0.105	(9, 11)
14....	$(CH_3)_3N \cdot Ga(CH_3)_3$	21	—	—	—	(46, 48)
	$(CH_3)_3P \cdot Ga(CH_3)_3$	18	—	—	0.03 (at 130°C.)	(46)
	$(CH_3)_3As \cdot Ga(CH_3)_3$	10	—	—	1.34	(46)
	$(CH_3)_3Sb.Ga(CH_3)_3$	—	—	—	∞	(46)
15....	$(CH_3)_3N \cdot In(CH_3)_3$	19.9	—	—	—	(49)
	$(CH_3)_3P \cdot In(CH_3)_3$	17.1	—	—	—	(49)
	$(CH_3)_3As \cdot In(CH_3)_3$	Too highly dissociated to be measured				(49)
16....	$(CH_3)_3N \cdot B(CH_3)_3$	17.62	45.7	0.56	0.472	(9, 34)
	$(CH_3)_3N \cdot Al(CH_3)_3$	Too stable to permit study in the gas phase				(53)
	$(CH_3)_3N \cdot Ga(CH_3)_3$	21.0	—	—	—	(46, 48)
	$(CH_3)_3N \cdot In(CH_3)_3$	19.9	—	—	—	(49)
	$(CH_3)_3N \cdot Tl(CH_3)_3$	—	—	—	Appreciably dissociated at 0°C.	(49)
	Ligand atom from Group VI					
17....	$(CH_3)_2O \cdot BF_3$	13.3	32.3	1.25	0.184	(10, 66)
	$(CH_3)_2S \cdot BF_3$	Too highly dissociated to be measured				(59, 60)
	$(CH_3)_2Se \cdot BF_3$	—	—	—	∞ (at 20°C.)	(59, 60)
18....	$(CH_3)_2O \cdot BH_3$	—	—	—	∞ (at 20°C.)	(37, 89)
	$(CH_3)_2S \cdot BH_3$	5.2‡	14.6‡	0.44 (at 50° C.)‡	0.505 (at 50°C.)‡	(59, 60)
	$(CH_3)_2Se \cdot BH_3$	—	—	—	∞ (at 20°C.)	(59, 60)
19....	$(CH_3)_2O \cdot Al(CH_3)_3$	Too stable to permit study				(53)
	$(CH_3)_2S \cdot Al(CH_3)_3$	8.5§	—	—	27% dissociated at 100°C.§	(53)
	$(CH_3)_2Se \cdot Al(CH_3)_3$	6¶	—	—	40% dissociated at 100°C.¶	(46)
	$(CH_3)_2Te \cdot Al(CH_3)_3$	Too highly dissociated to be measured				(46)
20....	$(CH_3)_2O \cdot Ga(CH_3)_3$	9.5	—	—	1.07	(46)
	$(CH_3)_2S \cdot Ga(CH_3)_3$	~8	—	—	~2.5	(46)
	$(CH_3)_2Se \cdot Ga(CH_3)_3$	10	—	—	1.5	(46)
	$(CH_3)_2Te \cdot Ga(CH_3)_3$	~8	—	—	~2.5	(46)
21....	$(CH_3)_2O \cdot BF_3$	13.3	32.3	1.25	0.184	(10, 66)
	$(C_2H_5)_2O \cdot BF_3$	10.9	27.5	0.64	0.420	(10)
	$(i\text{-}C_3H_7)_2O \cdot BF_3$	—	—	1.34 (at 50°C.)	0.0445 (at 50°C.)	(10)
	$(CH_2)_4O \cdot BF_3$	13.4	27.1	3.31	0.0011	(10)

* $\Delta F°$ and $K_{p(\text{atm.})}$ are referred to a temperature of 100°C. unless otherwise stated.

† Quinuclidine-trimethylborane.

‡ The results quoted refer to the dissociation:

$$(CH_3)_2S \cdot BH_3(g) = (CH_3)_2S(g) + \tfrac{1}{2}B_2H_6(g) \qquad K_{p(\text{atm.}^{1/2})}$$

§ The results quoted refer to the dissociation:

$$(CH_3)_2S \cdot Al(CH_3)_3(g) = (CH_3)_2S(g) + \tfrac{1}{2}Al_2(CH_3)_6(g) \qquad K_{p(\text{atm.}^{1/2})}$$

¶ The results quoted refer to the dissociation:

$$(CH_3)_2Se \cdot Al(CH_3)_3(g) = (CH_3)_2Se(g) + \tfrac{1}{2}Al_2(CH_3)_6(g) \qquad K_{p(\text{atm.}^{1/2})}$$

addition compound in solution is nearly the same as the heat of dissociation in the vapor phase. However, in other instances where data have been obtained under the two different experimental conditions, the heats of reaction have been found to differ by a somewhat larger amount (19). Fortunately, however, these differences are unlikely to be large enough to make orders of stability for a series of closely related addition compounds dependent on whether the results are obtained in solution or in the gas phase.

Heats of reaction between boron trifluoride, trimethylborane, or diborane and pyridine or its alkyl derivatives have been measured (14, 19, 20, 21, 25, 26) in order to determine the chemical effects of steric strains in displacement reactions. These studies have been important to organic chemistry, but since this work has recently been reviewed (9, 29) it will not be discussed in this article. However, the heats of reaction of some boron acceptor molecules with certain donors acting as *reference* bases are sometimes important to an understanding of coördination chemistry. Such heats of reaction will be discussed in later sections of this review.

3. Displacement reactions

In many instances the relative stabilities of molecular addition compounds have been established by displacement reactions. Although the method gives only a qualitative indication of the magnitude of the equilibrium constant for displacement from an addition compound of one donor (or acceptor) molecule by another donor (or acceptor) molecule, it has proved useful for the more stable complexes.

Since a displacement reaction depends on differences in free energy between products and reactants, entropy effects can conceivably determine the results. Furthermore, complications could be introduced by lattice energy and volatility effects. However, in all cases where displacement reactions have been used to establish an order of stability for a group of addition compounds, the order has not had to be changed when quantitative data on the same compounds have subsequently been reported from gas-phase dissociation studies. This fortunate situation is probably due both to the similarities often found in the entropies of closely related complex compounds (table 1) and to lattice energies of comparable magnitude arising through similarities in structure. Series 7 in table 1 provides one example where an entropy effect makes the order of variation in K_p different from the order of variation of ΔH (29, 35).

4. Relative volatilities

It has long been customary to infer orders of relative stability from measurements of saturation pressure. Again, only a qualitative indication of dative-bond strength can be obtained in this manner. As a general rule (30), for two addition compounds of closely similar type and molecular weight, the less stable exhibits the higher saturation pressure. For addition compounds differing in molecular weight it is to be expected that the lighter would be the more volatile.

If, however, the heavier complex is found to be more volatile, this is taken to indicate that it is also more highly dissociated.

III. Compounds Formed by Group III Acceptor Molecules and Ligands of Group V Atoms

In this field there has been a tendency to follow the difficult but more satisfactory procedure of attempting to establish underlying principles by studying selected systems. This has been done mostly with compounds formed by acceptor molecules of Group III atoms and donor molecules of the elements of Groups V and VI. Such complexes have proved to be very useful for comparative work, often showing a definite gradation in properties, varying from very stable or fairly stable adducts to unstable compounds, or situations in which no interaction is detectable between donor and acceptor even at low temperatures (table 1). Consequently, nowhere else in this field are the factors determining dative-bond strength in complex compounds better understood.

Some of the addition compounds mentioned in this section and in the following section of this review decompose irreversibly under certain conditions of temperature and pressure. These decomposition reactions are discussed in Section V of this survey.

A. COMPOUNDS OF BORON

The classic work of Burg and Green (40) by which the order of stability

$$(CH_3)_3N \cdot BF_3 > (CH_3)_3N \cdot BF_2CH_3 > (CH_3)_3N \cdot BF(CH_3)_2 > (CH_3)_3N \cdot B(CH_3)_3$$

was established (table 1, series 2) has been referred to several times in the chemical literature (47, 82, 92, 93). Reference to this order is made because of a frequent desire to provide an example of supposedly well understood polar effects. Trimethylamine-boron trifluoride is the most stable member of the series because attachment of three highly electronegative fluorine atoms to an acceptor atom increases its Lewis acidity over a situation in which it is bonded to electron-releasing alkyl groups. The nitrogen–boron dative bond in $(CH_3)_3N \cdot BF_3$ is highly polar. It was suggested by Sidgwick (91) that this type of bond should be represented by an arrow ($N \rightarrow B$), but the use of positive and negative signs ($\overset{+}{N}—\overset{-}{B}$), due to Lowry (70), is more precise since it implies an electron-transfer process. The donor–acceptor principle of bonding has recently been expressed by Mulliken (79, 80) in quantum-mechanical terms. Thus for the compound $(CH_3)_3N \cdot BF_3$, b^2 is much greater than a^2 in the wave function, ψ_N, of the ground state:

$$\psi_N \approx a\psi_0((CH_3)_3N \cdot BF_3) + b\psi_1((CH_3)_3\overset{+}{N}\ \overset{-}{B}F_3)$$

In this equation ψ_0 is the no-bond wave function, and ψ_1 is the donor wave function corresponding to complete transfer of an electron from $(CH_3)_3N$ to BF_3 in forming a bond by the odd electrons in $(CH_3)_3N\cdot^+$ and $\cdot BF_3^-$. In the more stable addition compounds the second term, which involves ψ_1, predominates.

In theory, the classical coördinate link may vary between complete sharing of the lone pair, with transfer of one electronic charge to the acceptor atom, giving a strong bond, and incomplete sharing, with little charge transfer, giving a weak bond. In actual practice, the range of electrical asymmetries of dative σ bonds is less than theoretically attainable.

Dative-bond strength is affected by the nature of the groups on the donor atom, just as it is by the nature of the groups on the acceptor atom. Again the effect is usually in the direction expected from considerations of electronegativity. Hence the ability of a ligand atom to donate a lone pair is often reduced by the attachment of electron-attracting groups. Thus the compound $H_3P \cdot BF_3$ (16, 107) is known, whereas the adducts $F_3P \cdot BF_3$ and $Cl_3P \cdot BF_3$ are not known (24). However, the stability of an addition compound is not always that to be expected from predictions based on Pauling's (84) electronegativity values even when donor and acceptor atoms are from the first row of the periodic system where complications arising through bonding above the $2sp^3$ octet are impossible. This is illustrated by the relative acceptor powers of the boron halides, long thought to be in the order $BF_3 > BCl_3 > BBr_3$ (74). It has even been stated that boron trifluoride is the strongest acceptor molecule known (7). This idea has no doubt arisen through the characterization of far more adducts of boron trifluoride than complex compounds of other boron halides. Using pyridine and nitrobenzene as reference bases, it has been shown (23) that the acceptor power of the boron halides is in the sequence $BF_3 < BCl_3 < BBr_3$ (table 2). Pyridine-boron trifluoride has been studied in the gas phase by van der Meulen and Heller (76). The results of these workers led to a value of 50.6 kcal. mole^{-1} for the heat of dissociation of $C_5H_5N \cdot BF_3$ in the gas phase. As pointed out by Brown and Horowitz (25), this value is seriously in error. The true enthalpy change, with a small correction to obtain the gas-phase value, must be near 25.0 kcal. mole^{-1}, the value obtained for formation of the adduct with all components in nitrobenzene.

TABLE 2

Heats of reaction of boron halides with pyridine and nitrobenzene

Chemical Reaction	Heat of Reaction $-\Delta H$
	kcal. mole^{-1}
C_5H_5N(solution) + BF_3(solution) = $C_5H_5N \cdot BF_3$(solution)	25.0*
C_5H_5N(solution) + BCl_3(solution) = $C_5H_5N \cdot BCl_3$(solution)	30.8*
C_5H_5N(solution) + BBr_3(solution) = $C_5H_5N \cdot BBr_3$(solution)	32.0*
$C_6H_5NO_2$(l) + BF_3(g) = $C_6H_5NO_2 \cdot BF_3$(solution)	9.2
$C_6H_5NO_2$(l) + BF_3(l) = $C_6H_5NO_2 \cdot BF_3$(solution)	6.7†
$C_6H_5NO_2$(l) + BCl_3(l) = $C_6H_5NO_2 \cdot BCl_3$(solution)	8.7
$C_6H_5NO_2$(l) + BBr_3(l) = $C_6H_5NO_2 \cdot BBr_3$(solution)	12.5
C_5H_5N(solution) + BF_3(l) = $C_5H_5N \cdot BF_3$(solution)	31.7
C_5H_5N(solution) + BCl_3(l) = $C_5H_5N \cdot BCl_3$(solution)	39.5
C_5H_5N(solution) + BBr_3(l) = $C_5H_5N \cdot BBr_3$(solution)	44.5

* The high heats of solution of BX_3 in nitrobenzene show that the heat evolved in the reaction of pyridine with BX_3, with both donor and acceptor in nitrobenzene, represents the heat of the displacement reaction:

$$C_5H_5N + C_6H_5NO_2 \cdot BX_3 = C_5H_5N \cdot BX_3 + C_6H_5NO_2$$

† Calculated using a value of 2.5 kcal. mole^{-1} for the heat of vaporization of BF_3; see reference 23.

An order of Lewis acidity in the boron halides contrary to electronegativity predictions is also probably true when arsine is the donor. Thus $H_3As\cdot BCl_3$ (96) and $H_3As\cdot BBr_3$ (97) are known, whereas $H_3As\cdot BF_3$ does not form even below −100°C. (75). Similarly, the adduct $Cl_3P\cdot BBr_3$ exists, but $Cl_3P\cdot BCl_3$ and $Cl_3P\cdot BF_3$ do not (24), contrary to a previous report (4). Furthermore, although $CH_3CN\cdot BF_3$ and $CH_3CN\cdot BCl_3$ are completely dissociated in the gas phase, their relative heats of sublimation suggest that $CH_3CN\cdot BCl_3$ is the more stable adduct (68).

An explanation for the relative acidity of the boron halides can be found in terms of π bonding between X and B in BX_3 molecules. This would increase along the series BBr_3, BCl_3, BF_3, thereby reducing the acceptor power of boron by successive but not necessarily equal amounts (23). Reduction of acid strength through resonance between lone-pair electrons on fluorine and the boron $2p_\pi$ orbital may be responsible for the irregularities observed in the enthalpy increments in series 2 of table 1.

A mesomeric effect also probably accounts for the weak Lewis acidity of alkyl borates like $(CH_3O)_3B$ (15, 95). Although alkoxy groups are electronegative, and because of this should enhance the acceptor power of boron, there is the possibility of π bonding between the oxygen lone-pair electrons and the boron p_π orbital, so that readjustment energy to free this orbital for chemical bonding to a base is high. Unlike the alkyl compounds, aryl borates form adducts with ammonia and amines (50, 51). In the aryl compounds boron–oxygen p_π–p_π bonding would be less because of the electronegativity of the phenyl groups (65), and so a stronger Lewis acidity should be observed.

The boron–nitrogen bond strength in the compound $(CH_3)_3N\cdot BF_3$ is not known with certainty. The adduct is not dissociated to a sufficient extent in a convenient temperature range to permit study in the gas phase. Indeed it was reported to be undissociated at a temperature as high as 230°C. Moreover, the results suggested that the complex was actually associated to some extent (40). These observations were later shown to be incorrect when it was found that $(CH_3)_3N\cdot BF_3$ was monomeric and undissociated at 177°C. (42). The original results arose through uncertainties in the corrections to be applied for the vapor pressure of mercury. It has been calculated that the dissociation of $(CH_3)_3N\cdot BF_3$ in the gas phase should be readily observed below 200°C. but difficult to detect below 175°C. (3). Several estimates of the dative-bond strength in the compound $(CH_3)_3N\cdot BF_3$ have been made, since a value was required for comparison with the dative-bond strength in other adducts. Thus, from calorimetric studies of Brown and Lawton (28) and of Brown and Horowitz (25), made using nitrobenzene as solvent, it is possible to calculate (60) the enthalpy change in the dissociation

$$(CH_3)_3N\cdot BF_3(\text{solution}) = (CH_3)_3N(\text{solution}) + BF_3(\text{solution})$$

as 30.9 kcal. mole^{-1}. Since heats of formation of molecular addition compounds apparently do not differ very greatly in nitrobenzene solution and in the gas phase, it may be presumed that ΔH for the gas-phase dissociation is also close to 30.9 kcal. mole^{-1}. Another estimate (ΔH = 26.6 kcal. mole^{-1}) has been made by Bauer and McCoy (3), using heat capacity data for solid $(CH_3)_3N \cdot BF_3$.

Studies in the gas phase (22) (table 1, series 10) show that the boron trifluoride adducts of trimethyl derivatives of Group V elements decrease in stability in the order $N > P > As > Sb$. As will be discussed in Section IV, in Group VI the order of coördination towards boron trifluoride is $O > S > Se$. The same sequences of coördination are observed towards the majority of Group III acceptor molecules, and this demonstrates that the ability to form classical dative bonds decreases down Groups V and VI with increasing atomic size. The prevalence of these orders of coördination has led to the incorrect conclusion that when alkyl derivatives of elements from both Groups V and VI act as ligands to the Group III atoms, the molecular addition compounds formed *always* decrease in stability with increasing size of the donor atom (52). This generalization came about through a desire to contrast the coördination chemistry of Group III elements, where metal–ligand bonds were regarded as always being adequately described in terms of classical coördinate links, with recent important advances in the chemistry of transition metal complexes, where multiple bonding is now fairly well recognized (52, 82).

Using boron compounds with small steric requirements as reference acids, it has been shown (13) that trimethylamine is a better base than ammonia and that trimethylphosphine is a better base than phosphine (32). The difference in donor power between ammonia and trimethylamine is much less than that between phosphine and trimethylphosphine (table 1). Indeed, whereas the well-established compounds $(CH_3)_3P \cdot B(CH_3)_3$ and $(CH_3)_3N \cdot B(CH_3)_3$ are of comparable stability, the adduct $H_3P \cdot B(CH_3)_3$ does not exist, in contrast to $H_3N \cdot B(CH_3)_3$. It is doubtful if any single suggestion can be used to explain these results satisfactorily. Inductive, steric, and hybridization effects are some of the factors involved. Substitution of hydrogen on a ligand atom by methyl causes a change in hybridization, probably because of the electron-releasing properties of the methyl group. This change in hybridization is greater for second row elements than for first (57). Thus the readjustment energies required for ammonia and trimethylamine to acquire tetrahedral configurations are not only small but similar. The appropriate bond angles are 107° and 108°, respectively. On the other hand, in phosphine the bond angle is 93°, while in trimethylphosphine the relevant bond angle is 100°. Phosphine, therefore, should be a much weaker base than trimethylphosphine. Moreover, both these phosphorus compounds would be expected to be weaker bases than their nitrogen analogs. In most instances this is true, but in a few cases trimethylphosphine appears to form more stable adducts than trimethylamine with Group III acceptors even when steric factors are not important. Moreover, if stabilities of addition compounds were determined only by the effect of bond angles on the rehybridization energies of ligands, ammonia should always be a better donor than trimethylphosphine towards a common acceptor molecule. With trimethylborane as the acid this is not so. The slight decrease in stability in passing from $(CH_3)_3N \cdot B(CH_3)_3$ to $(CH_3)_3P \cdot B(CH_3)_3$, and the large stability difference between $H_3N \cdot B(CH_3)_3$ and $H_3P \cdot B(CH_3)_3$, can also be interpreted in terms of steric effects (22). The nitrogen–boron bond is shorter than the phosphorus–boron bond, so there would be greater interference between groups on donor and acceptor atoms in $(CH_3)_3N \cdot B(CH_3)_3$ than in $(CH_3)_3P \cdot B(CH_3)_3$. In $H_3N \cdot B(CH_3)_3$ and $H_3P \cdot B(CH_3)_3$ steric factors would be negligible and, as would be expected from this, nitrogen then becomes a much better donor relative to phosphorus. Indeed, in the absence of steric effects the heat of dissociation of the adduct $(CH_3)_3N \cdot B(CH_3)_3$ has been estimated (27) as 25.4 kcal. mole^{-1}, 8 kcal. mole^{-1} above the observed value (13). Moreover, when boron trifluoride, with lower steric requirements than trimethylborane, is the reference acid, trimethylamine functions as a much better base than trimethylphosphine. Nevertheless, it is just possible that boron trifluoride would have a different effect on the orbitals used by phosphorus in bonding than would trimethylborane. Hence it may not be entirely correct to interpret the similar stabilities of $(CH_3)_3P \cdot B(CH_3)_3$ and $(CH_3)_3N \cdot B(CH_3)_3$ solely on the basis of a steric effect.

The compound $(CH_3)_3P \cdot BF_3$ is not one of the more stable addition compounds containing boron. The displacement reaction

$$(CH_3)_3P \cdot BF_3 + \tfrac{1}{2}B_2H_6 = (CH_3)_3P \cdot BH_3 + BF_3$$

proceeds quantitatively (59), whereas the analogous displacement reaction involving trimethylamine does not occur (60). The discovery that borane forms a more stable adduct with trimethylphosphine than does boron trifluoride is another illustration of the dangers of making predictions based entirely on steric and electronegativity concepts. A similar order of stability is shown by borane and boron trifluoride when phosphorus trifluoride is the ligand. Although the adduct $F_3P \cdot BF_3$ does not form (8), the compound $F_3P \cdot BH_3$ is known (83). Furthermore, on the basis of a displacement reaction the order of stability $(CH_3)_3P \cdot BH_3 > (CH_3)_3N \cdot BH_3$ has been established (60).

Two important facts arise from these observations: borane appears to show an order of coördination $(CH_3)_3P > (CH_3)_3N \gg (CH_3)_3As > (CH_3)_3Sb$, since $(CH_3)_3As \cdot BH_3$ is much less stable than $(CH_3)_3N \cdot BH_3$ or $(CH_3)_3P \cdot BH_3$ (37, 98), and $(CH_3)_3Sb \cdot BH_3$ forms only at low temperatures (39). It is to be noted, however, that the order $P > N$ is based on a displacement reaction, and not on exact knowledge of enthalpy of dissociation. The order $P > N$ is not shown by any other Group III acceptor, except perhaps trimethylthallium (discussed below). Furthermore, borane is the only Group III acceptor so far reported to be able to bond phosphorus trifluoride, although attempts have been made to make phosphorus trifluoride adducts of a few other Group III acceptors. Diborane does not form the adduct $F_3N \cdot BH_3$. In these respects borane coördination chemistry resembles somewhat the chemistry of certain transition metals (82). It is also interesting that the only known carbonyl of the Group III elements is $OC \cdot BH_3$, and that attempts to make others, notably $OC \cdot BF_3$, have been unsuccessful. Possible reasons for these observations will be discussed in Section IV.

The physical properties of borane addition compounds are summarized in table 3. Attempts have been made to evaluate quantitatively the dative-bond strength in several borane adducts. Since borane exists in its standard state as

TABLE 3

*Addition compounds of the borane group**

Compound	Melting Point	Boiling Point†	$\log_{10} p$ (mm.) $= -\frac{A}{T} + B$		ΔH (vapor)	Trouton Constant†	References
			A	*B*			
	°C.	°C.			kcal. mole^{-1}	e.u.	
$CH_3H_2N\cdot BH_3$‡	5-10	Unstable	—	—	—	—	(105, 106)
$CH_3H_2P\cdot BH_3$	−49.3	150	2329	8.400	10.7	25.3	(44)
$CH_3H_2As\cdot BH_3$	Solid at −78.5 ($p_{\text{diss.}}$ = 10.5 mm.)	Unstable	—	—	—	—	(99)
$(CH_3)_2HN\cdot BH_3$‡	11	Unstable	—	—	—	—	(105, 106)
$(CH_3)_2HP\cdot BH_3$	−22.6	174	2337	8.100	10.7	23.9	(44)
$(CH_3)_2HAs\cdot BH_3$	−22.4 to −21.5	85.5	2263	9.191	10.3	28.9	(99)
$(CH_3)_3N\cdot BH_3$	94	171	2202	7.846	10.1	22.7	(43)
$(CH_3)_3P\cdot BH_3$ (solid)	103	—	2933	9.531	—	—	(44)
$(CH_3)_3As\cdot BH_3$	73.5-74.5	154	2420	8.553	11.1	26.0	(99)
$(CH_3)_3Sb\cdot BH_3$	−33	Unstable	—	—	—	—	(39)
$F_3P\cdot BH_3$	−116.1	−61.8	1038.9	7.8061	4.760	22.5	(83)
$OC\cdot BH_3$	−137	−64	1040	7.850	4.750	23	(43)
$(CH_3)_2O\cdot BH_3$	Solid at −78.5 ($p_{\text{diss.}}$ = 18 mm.)	Unstable	—	—	—	—	(89)
$(CH_2)_4O\cdot BH_3$	−34	Unstable	—	—	—	—	(87)
$(CH_3)_2S\cdot BH_3$	−40 to −38	97	2346	9.220	10.7	29.0	(37, 60)
$(CH_2)_4S\cdot BH_3$	—	132.5	2321	8.602	10.6	26.2	(63)
$(CH_3)_2Se\cdot BH_3$	−34 to −32	63.2	1732	8.030	7.9	23.5	(60)

* Physical properties of a series of adducts formed between borane and various substituted pyridines have been tabulated by Brown and Domash (14).

† In order to calculate the boiling point, a large extrapolation of the vapor pressure equation is often involved, so these values must be considered as approximate. Furthermore, whenever vaporization of an addition compound is accompanied by an increase in dissociation, extrapolation of the vapor pressure equation cannot give the true boiling point. The large entropies of vaporization of molecular addition compounds are a consequence of further dissociation on vaporization, although dipole association in the condensed phase probably enhances the effect to some extent. A few addition compounds do not have high Trouton constants even though they are known to be highly dissociated in the gas phase. Such adducts are no doubt partially dissociated even as liquids.

‡ This compound may not be a true molecular addition compound of the BH_3 group, since the molecular weight is unknown.

a dimer, an exact knowledge of the enthalpy change in the reaction $B_2H_6(g) = 2BH_3(g)$ is needed to permit calculation of the stability of borane compounds. Estimates of this enthalpy change have varied from 13.6 (5) to 50 kcal. mole^{-1} (45), but recently a much more reasonable value, 28.4 kcal. mole^{-1}, has been obtained by thermochemical extrapolation (71). This value is supported by an analysis of kinetic data (2). McCoy and Bauer (71) have studied calorimetrically the reactions:

$$(CH_3)_3N(g) + \tfrac{1}{2}B_2H_6(g) = (CH_3)_3N\cdot BH_3(s) \quad -\Delta H = 31.3 \text{ kcal. mole}^{-1}$$

$$(CH_3)_2NH(g) + \tfrac{1}{2}B_2H_6(g) = (CH_3)_2NH\cdot BH_3(s) \quad -\Delta H = 32.5 \text{ kcal. mole}^{-1}$$

$$(CH_3)NH_2(g) + \tfrac{1}{2}B_2H_6(g) = (CH_3)NH_2\cdot BH_3(s) \quad -\Delta H = 31.1 \text{ kcal. mole}^{-1}$$

$$(CH_3)_3N(g) + \tfrac{1}{2}(CH_3)_4B_2H_2(g) = (CH_3)_3N\cdot BH(CH_3)_2(l) \quad -\Delta H = 20.6 \text{ kcal. mole}^{-1}$$

Knowing the heat of sublimation of $(CH_3)_3N \cdot BH_3$ and the calculated enthalpy change for dissociation of diborane into borane groups, the stability of $(CH_3)_3N \cdot BH_3$, in terms of gas-phase dissociation into $(CH_3)_3N$ and BH_3, was calculated as 31.5 kcal. mole^{-1}. The stabilities of $(CH_3)_3N \cdot BF_3$ (ΔH estimated as 30.9 to 26.6 kcal. mole^{-1}) and $(CH_3)_3N \cdot BH_3$ (ΔH = 31.5 kcal. mole^{-1}) thus appear to be quite close, with perhaps a slightly stronger dative bond in $(CH_3)_3N \cdot BH_3$ than in $(CH_3)_3N \cdot BF_3$ (71), although some reservations have been expressed on this (60).

The heat of the reaction

$$\tfrac{1}{2}B_2H_6(g) + C_5H_5N \text{ (in nitrobenzene)} = C_5H_5N \cdot BH_3 \text{ (in nitrobenzene)}$$

has been measured calorimetrically and found to be 17.91 kcal. (14). Using McCoy and Bauer's (71) estimate for the diborane–borane equilibrium, the enthalpy change accompanying the reaction

$$BH_3(g) + C_5H_5N \text{ (in nitrobenzene)} = C_5H_5N \cdot BH_3 \text{ (in nitrobenzene)}$$

is calculated as 32.15 kcal. The heat of reaction of born trifluoride gas with pyridine in nitrobenzene is 32.9 kcal. (19). Thus the heats of formation in nitrobenzene of the addition compounds $C_5H_5N \cdot BH_3$ and $C_5H_5N \cdot BF_3$ are very similar, assuming that the estimate of the heat of dissociation of diborane is correct.

Reduction in the acceptor power of a Group III atom by substituting electron-releasing methyl groups for hydrogen atoms is illustrated by the following order of stability:

$$(CH_3)_3N \cdot BH_3 \ (\Delta H = 31.5 \text{ kcal. mole}^{-1}) > (CH_3)_3N \cdot BH_2CH_3 \ (\Delta H, ?)$$
$$> (CH_3)_3N \cdot BH(CH_3) \ (\Delta H = 23.4 \text{ kcal. mole}^{-1})$$
$$> (CH_3)_3N \cdot B(CH_3)_3 \ (\Delta H = 17.6 \text{ kcal. mole}^{-1})$$

first established by displacement reactions (90) before quantitative data were available. A steric effect alone is insufficient to account for the observed order. The steric requirements of $BH(CH_3)_2$ are not much less than those of $B(CH_3)_3$, yet the difference in the stability of their trimethylamine adducts, 6 kcal., is large. The electron-releasing effect of methyl groups on boron may be responsible for the monomeric character of trimethylborane, a molecule which Mulliken (77) considers to be highly stabilized by hyperconjugation. However, it has also been suggested that the monomeric character of trimethylborane is due to steric factors (88).

Although silicon is more electropositive than carbon on any atomic scale of electronegativity, and on this basis should be more electron-releasing, the compound $(SiH_3)_3N$ is a much weaker base than $(CH_3)_3N$. It does not bond diborane or trimethylborane, but with boron trifluoride at low temperatures it does form a weak adduct (41). The inability of trisilylamine to form an adduct with borane is due to the base being incapable of supplying sufficient energy to break the B—H—B bridge bonds in the hydride. A similar situation exists with diethyl ether. The compound $(C_2H_5)_2O \cdot BF_3$ is well known (table 1, series 21), but diethyl ether-borane does not exist. However, it is interesting that although boron trifluoride does not form an adduct even at −80°C. with the very weak donor trimethylstibine (22), the compound $(CH_3)_3Sb \cdot BH_3$ (m.p. −33°C.) is formed at low temperatures (39). It is doubtful if differences in lattice energy are sufficient to account for this result, and it is more probable that the antimony–boron bond in $(CH_3)_3Sb \cdot BH_3$ is not a classical dative bond (see Section IV).

The weakness of trisilylamine as a donor arises through the electron-attracting powers of the SiH_3 group when it is bonded to electronegative atoms (100). The Si_3N skeleton is coplanar (62), and it has been suggested (41) that this is due to π bonding in $(SiH_3)_3N$ between the nitrogen lone pair and the vacant silicon $3d$ orbitals. Trisilylamine is one of the few examples of a base where considerable rehybridization energy is required to assume an sp^3 configuration. The compound $(CH_3)_2(SiH_3)N \cdot B(CH_3)_3$ has been isolated, but no adduct is formed between $CH_3(SiH_3)_2N$ and trimethylborane (101). Thus the order of base strength $(CH_3)_3N > (SiH_3)(CH_3)_2N > (SiH_3)_2NCH_3$, $(SiH_3)_3N$ was established towards trimethylborane, but since no adducts were formed with $(SiH_3)_2NCH_3$ or $(SiH_3)_3N$ it was impossible to determine the relative donor power of these very weak bases. However, with boron trifluoride, a stronger reference acid than trimethylborane, the expected order of coördination $(SiH_3)_2NCH_3 > (SiH_3)_3N$ was demonstrated, despite secondary reactions leading to irreversible formation of silyl fluoride and aminoboron fluorides (102).

B. COMPOUNDS OF ALUMINUM

Comparative studies on the stabilities of addition compounds of aluminum have been mostly confined to complexes formed by the dimeric and therefore electron-deficient trimethylaluminum (table 4). In general the stability of addition compounds formed between ligands of Group V elements and aluminum acceptor molecules is so great that the complexes cannot be studied in the gas phase. Thus $(CH_3)_3N \cdot Al(CH_3)_3$ and $(CH_3)_3P \cdot Al(CH_3)_3$ are not measurably dissociated at 150°C. and 40 mm. pressure (53). An order of coördination $(CH_3)_3N > (CH_3)_3P$ was therefore established by the displacement reaction

$$(CH_3)_3P \cdot Al(CH_3)_3 + (CH_3)_3N = (CH_3)_3P + (CH_3)_3N \cdot Al(CH_3)_3$$

which proceeds quantitatively to the right.

Furthermore, as would be expected from polar effects, substitution of chlorine for methyl on aluminum results in an increase in the acceptor power of aluminum. Thus the reaction,

$$(CH_3)_3N \cdot Al(CH_3)_3 + \tfrac{1}{2}[(CH_3)_2AlCl]_2 = (CH_3)_3N \cdot Al(CH_3)_2Cl + \tfrac{1}{2}Al_2(CH_3)_6$$

proceeds largely to the right, even though $Al_2(CH_3)_6$ dissociates more readily than does $[(CH_3)_2AlCl]_2$.

Unlike $(CH_3)_3P \cdot Al(CH_3)_3$, the adduct $(CH_3)_2PH \cdot Al(CH_3)_3$ was found to be appreciably dissociated at 150°C. So towards trimethylaluminum, as a reference acid, trimethylphosphine is a better donor than dimethylphosphine, just as is the case when trimethylborane is the acid (table 1, series 3). This is a further

TABLE 4

Addition compounds formed between trimethylaluminum and alkyls of Group V and Group VI elements

Compound	Melting Point	Boiling Point*	$\log_{10} p$ (mm.) $= -\frac{A}{T} + B$		ΔH (vapor)	Trouton Constant*	References
			A	B			
	°C.	°C.			*kcal. mole⁻¹*	*e.u.*	
$(CH_3)_3N \cdot Al(CH_3)_3$	105	177	2380	8.19	10.9	24.4	(53)
$(CH_3)_3P \cdot Al(CH_3)_3$	62.5	189	2566	8.52	11.8	25.6	(53)
$(CH_3)_2NH \cdot Al(CH_3)_3$	51	186	2620	8.60	12.0	26.1	(53)
$(CH_3)_2PH \cdot Al(CH_3)_3$†	—	169	2429	8.388	11.1	25.2	(53)
$(CH_3)_2O \cdot Al(CH_3)_3$	−29.9	159	2148	7.832	9.85	22.9	(53)
$(CH_3)_2S \cdot Al(CH_3)_3$	−20	141	2462	8.740	11.3	27.2	(53)
$(CH_3)_2Se \cdot Al(CH_3)_3$†	—	146	2320	8.410	10.6	25.3	(46)
$(CH_3)_2Te \cdot Al(CH_3)_3$†	—	146	2022	7.708	9.3	22.1	(46)

* By extrapolation of the vapor pressure equation; see second footnote to table 3.

† Liquid at room temperature.

example of the rule that methyl groups increase the donor power of ligand atoms provided steric effects are not predominant.

C. COMPOUNDS OF GALLIUM, INDIUM, AND THALLIUM

Addition compounds formed between the trialkyls of gallium, indium, or thallium and alkyl derivatives of Group V elements have been studied by Coates (46) and by Coates and Whitcombe (49). With trimethylgallium or trimethylindium there is a decrease in the stability of the addition compounds with increasing size of the Group V ligand atom (table 1, series 14 and 15). Trimethylbismuth forms no compound with trimethylgallium even at low temperatures. The adducts $(CH_3)_3N \cdot Tl(CH_3)_3$, $(CH_3)_3P \cdot Tl(CH_3)_3$, and $(CH_3)_3As \cdot Tl(CH_3)_3$ are not amenable to study in the gas phase on account of their instability. Volatility considerations show clearly that $(CH_3)_3As \cdot Tl(CH_3)_3$ is the weakest adduct of this series, but that trimethylamine and trimethylphosphine are donors of comparable strength towards trimethylthallium. The adduct $(CH_3)_3P \cdot Tl(CH_3)_3$ has a higher melting point than $(CH_3)_3N \cdot Tl(CH_3)_3$, and it has been suggested (49) that this fact provides some evidence for the phosphorus compound being the more stable, since for all complexes formed by any given Group III trimethyl and the various Group V trimethyls the melting point of the complex increases with its enthalpy of dissociation. Unfortunately, lattice energies do not always permit a direct correlation between the melting point of an addition compound and its enthalpy of dissociation. This is especially true for adducts differing only in the acid moiety. Thus $(CH_3)_3N \cdot B(CH_3)_3$ ($\Delta H = 17.62$ kcal. mole^{-1}) has a melting point 62°C. higher than that reported for the more stable compound $(CH_3)_3N \cdot In(CH_3)_3$ ($\Delta H = 19.9$ kcal. mole^{-1}). The comparable stabilities of $(CH_3)_3N \cdot Tl(CH_3)_3$ and $(CH_3)_3P \cdot Tl(CH_3)_3$, however, suggest that it may not be correct to regard the phosphorus–thallium link in $(CH_3)_3P \cdot Tl(CH_3)_3$ as a classical dative σ bond (49).

The relative dative-bond strength in the trimethylamine addition compounds of Group III elements is in the order Al > Ga > In > B > Tl (table 1, series 16). This sequence, except for the position of boron, perhaps reflects to some degree a decreasing desire on the part of metals to accept partial negative charge with increasing electropositive character. Undoubtedly the position of boron in the order of acceptor power is at least partly due to steric factors. Steric interference between groups on the donor with those on the acceptor in adducts $(CH_3)_3N \cdot M^{III}(CH_3)_3$ would be at a maximum when M^{III} is the smallest element of the group, the N—M^{III} bond length then being at a minimum. Indeed, as mentioned earlier, the estimated enthalpy of dissociation for $(CH_3)_3N \cdot B(CH_3)_3$ is 25.4 kcal. mole^{-1} in the absence of steric effects (27). However, it cannot safely be argued from this that $(CH_3)_3N \cdot B(CH_3)_3$ is intrinsically more stable than $(CH_3)_3N \cdot Ga(CH_3)_3$ (ΔH = 21 kcal. mole^{-1}), since part of the strain in $(CH_3)_3N \cdot B(CH_3)_3$ may be due to interference of methyl groups on nitrogen with themselves. Since this B-strain (9) would be independent of the Group III atom, it would tend to weaken all $(CH_3)_3N \cdot M^{III}(CH_3)_3$ adducts to some extent. It is also necessary to consider the probability that the electron-releasing power of methyl groups depends on the Group III atom to which they are bonded. So if trimethylborane is more stabilized by hyperconjugation than is trimethylgallium, this would tend to weaken $(CH_3)_3N \cdot B(CH_3)_3$ relative to $(CH_3)_3N \cdot Ga(CH_3)_3$.

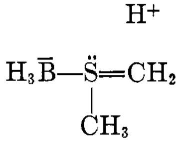
IV. Compounds Formed by Group III Acceptor Molecules and Ligands of Group VI Atoms

A. COMPOUNDS OF BORON

Ligands of Group VI atoms form less stable adducts than do analogous ligands of Group V atoms with Group III acceptor molecules. This apparently unbreakable rule was first observed by Davidson and Brown (53) in their studies on trimethylaluminum addition compounds, but there are many examples of the rule in boron chemistry. Thus orders of coördination $(CH_3)_3N > (CH_3)_2O > CH_3F$, and $(CH_3)_3P > (CH_3)_2S > CH_3Cl$, are observed towards borane, boron trifluoride, and trimethylborane. The increase in nuclear charge in passing across a row in the periodic classification may be responsible for the observed decrease in donor power.

The compound $(CH_3)_2O \cdot B(CH_3)_3$ does not exist even at −78.5°C., but the adduct $(CH_3)_2S \cdot B(CH_3)_3$ (m.p. −42°C.) is known, although it is completely dissociated in the gas phase and stable only at low temperatures (60). It is possible to account for the nonexistence of $(CH_3)_2O \cdot B(CH_3)_3$ and the existence of $(CH_3)_2S \cdot B(CH_3)_3$ in terms of a steric effect. The oxygen–boron bond is shorter than the sulfur–boron bond, so interference between methyl groups on donor and acceptor would be greater in $(CH_3)_2O \cdot B(CH_3)_3$ than in $(CH_3)_2S \cdot B(CH_3)_3$. Some support for this suggestion may be derived from the observation that with boron trifluoride, a Lewis acid stronger than trimethylborane but with lower steric requirements, the order of coördination is $(CH_3)_2O > (CH_3)_2S > (CH_3)_2Se$ (table 1, series 17). However, with borane, an acid with steric requirements even lower than those of boron trifluoride, the order of coördination in Group VI reverts to S > O (table 1, series 18). Thus towards borane the second row element, sulfur, is a better "donor" than the first row element, oxygen. Moreover, $(CH_3)_2S \cdot BH_3$ is much more stable than is $(CH_3)_2S \cdot BF_3$. As mentioned above, in Group V a similar situation between the first and second rows of the periodic classification also appears to occur when borane is the reference acid. To explain these unexpected orders of coördination, it has been suggested that borane adducts are stabilized to some extent by dative π bonds when the ligand atom is from the second or later rows of the periodic system. In the case of phosphorus or sulfur this could occur through overlap of the empty $3d$ orbitals with a filled pseudo p_π orbital provided by the three hydrogen atoms of the borane group (60). Indeed such supplementary π bonding, if it occurs, should be greater in Group VI than in Group V, since the sulfur $3d$ orbitals lie lower than those of phosphorus and are, therefore, even more energetically suitable for bonding. Similar π bonding in borane adducts of first row ligands is of course not possible, since they do not have d orbitals suitable for chemical bonding. This would qualitatively account for borane and boron trifluoride forming adducts of similar stability when nitrogen is the ligand atom, but forming compounds of widely different stability with ligands of second row atoms. It is true that $(CH_3)_2O \cdot BH_3$ is far more highly dissociated than is $(CH_3)_2O \cdot BF_3$, and at first sight this suggests that the strength of the dative bond in the boron trifluoride adduct must be very much greater than the strength of the dative bond in the borane adduct. However, this is not necessarily so, since dissociation of $(CH_3)_2O \cdot BH_3$ is promoted by the energy released in the dimerization of borane.

The suggestion (72) that structures of the type,



$$H_3\bar{B}-\underset{CH_3}{\ddot{S}}=\overset{H^+}{CH_2}$$

make a significant contribution to the stability of dimethylsulfide-borane is interesting, but if such *methyl* hyperconjugation were the dominant factor, the groups on boron are not important and there is no reason why $(CH_3)_2S \cdot BF_3$ should not be more stable than $(CH_3)_2O \cdot BF_3$; however, it is not.

It has been suggested that it may not be correct to describe the bonding in $OC \cdot BH_3$ (37) or in $F_3P \cdot BH_3$ (60) entirely in terms of weak classical dative σ bonds. The physical properties of $OC \cdot BH_3$ and $F_3P \cdot BH_3$ are remarkably similar (83) (table 3). As has been pointed out earlier, the boron trifluoride analogs have not been prepared despite attempts to make them. This could be due to the inability of the deeply buried boron–fluorine bonding electrons to contribute to the empty $2p_\pi$ orbital in carbon monoxide, or to the $3d_\pi$ orbitals of phosphorus trifluoride, in a manner perhaps possible for boron–hydrogen electrons.

It should be noted that an alternative explanation for the failure to prepare boron trifluoride-carbonyl has been advanced. It has been suggested (2) that considerable activation energy is required before carbon monoxide can act as a base. The ionization potential of the lone-pair electrons in carbon monoxide is higher than that for the lone-pair electrons of trimethylamine or dimethyl ether. This, together with the energy required to overcome the resonance stabilization of boron trifluoride, might be sufficient to prevent the formation of $F_3B \cdot CO$. If this explanation is correct, it may be possible to prepare a carbonyl of the stronger Lewis acid boron trichloride.

The etherates of boron trifluoride (table 1, series 21) provide an interesting demonstration of the importance of steric effects (10). On the basis of inductive effects diethyl ether should be about as good a donor as tetrahydrofuran. The addition compound tetrahydrofuran-boron trifluoride is, however, considerably more stable than $(C_2H_5)_2O \cdot BF_3$. From data now available (87) it is possible to state that an order of coördination $(CH_2)_4O > (CH_3)_2O > (C_2H_5)_2O$ is also observed when borane is the acceptor. In the cyclic ether the base strength is much increased through reduction of the steric requirements. Similar behavior occurs with nitrogen, as was shown by Brown and Sujishi (31) in their demonstration of the much greater stability of quinuclidine-trimethylborane over triethylamine-trimethylborane (table 1, series 12).

Comparison of the strength of dative bonds in the etherates of boron trichloride with the strength of those in the etherates of boron trifluoride is difficult. Boron trichloride compounds often decompose irreversibly, so that gas-phase dissociation studies are meaningless in terms of evaluation of dative-bond strength. The higher melting points of the boron trichloride compounds (e.g., $(CH_3)_2O \cdot BCl_3$, m.p. 76°C.; $(CH_3)_2O \cdot BF_3$, m.p. -13°C.) merely show that the lattice energies are larger.

B. COMPOUNDS OF ALUMINUM

Etherates of aluminum trialkyls are so stable that it is not possible to prepare organoaluminum compounds by the Grignard method, in contrast to the alkyls of boron or thallium. The adduct $(CH_3)_2O \cdot Al(CH_3)_3$ (table 4) is undissociated in the gas phase at 150°C. (at 40 mm.) (53). The exchange reaction

$$[(CH_3)_2AlCl]_2 + 2(CH_3)_2O \cdot Al(CH_3)_3 = 2(CH_3)_2O \cdot Al(CH_3)_2Cl + Al_2(CH_3)_6$$

proceeds quantitatively to the right. The adducts $(CH_3)_2S \cdot Al(CH_3)_3$ (53), $(CH_3)_2Se \cdot Al(CH_3)_3$ (46), and $(CH_3)_2Te \cdot Al(CH_3)_3$ (46) are sufficiently dissociated in the gas phase to permit determination of relative stability (table 1, series 19). The observed order of coördination, $O > S > Se > Te$, is that expected for decreasing donor power with increasing size of the ligand atom.

Dissociation of the addition compounds of trimethylaluminum, like those of borane, is enhanced by the tendency of the acid moiety to polymerize. From studies in the gas phase it has been shown (67) that $\Delta H = 20.2$ kcal. mole^{-1} for the reaction $Al_2(CH_3)_6 = 2Al(CH_3)_3$. Thus it is possible to determine quantitatively the dative-bond strength in adducts of trimethylaluminum, if they dissociate at a low enough temperature, from a knowledge of the temperature variation of the equilibrium constant for dissociation of the complex into ligand and trimethylaluminum dimer (table 1, series 19).

C. COMPOUNDS OF GALLIUM, INDIUM, AND THALLIUM

For adducts formed by trimethylgallium and ligands of Group VI elements (table 5) the order of coördination is O > Se > S = Te (table 1, series 20) (46). The gallium–ligand atom bonds are relatively weak, and thus the ΔH values are only approximate. Therefore, the order of "stability" is best inferred from K_p values. The sequence of coördination is unusual, because dimethyl selenide forms a less dissociated adduct with trimethylgallium than does dimethyl sulfide. Coates (46) has suggested that this is due to the occurrence of d_π–d_π bonding in adducts of trimethylgallium when the ligand atom is from below the first row of the periodic system. Since gallium possesses a penultimate filled d-electron shell, these d electrons could be used in π bonding to ligands with empty low-energy d orbitals. Because aluminum has no d electrons, similar dative π bonding is not possible in any adduct formed by trimethylaluminum with a ligand with vacant orbitals. Thus, the sequence of coördination observed towards trimethylaluminum is O > S > Se > Te, since the ability to form classical dative bonds decreases down each group of the periodic table with increasing atomic weight. However, it is suggested (46) that the tendency of Group V or Group VI elements to form dative π bonds increases with atomic weight. Hence the stability of an

TABLE 5

Addition compounds formed between the trialkyls of gallium, indium, and thallium and alkyls of Group V and Group VI elements

Compound	Melting Point	Boiling Point*	$\log_{10} p$ (mm.) $= -\frac{A}{T} + B$		ΔH (vapor)	Trouton Constant*	References
			A	B			
	°C.	°C.			*kcal. mole*$^{-1}$	*e.u.*	
$(CH_3)_3N\cdot Ga(CH_3)_3$	96.2	164	2226	7.947	10.19	23.3	(46, 108)
$(CH_3)_2NH\cdot Ga(CH_3)_3$	33.3–33.6	170	2532	8.596	11.6	26.2	(46)
$CH_3NH_2\cdot Ga(CH_3)_3$	37–38	169	2760	9.119	12.6	28.6	(46)
$H_3N\cdot Ga(CH_3)_3$	31–32	179	1947	7.190	8.9	19.7	(46)
$(CH_3)_3P\cdot Ga(CH_3)_3$	56.4–56.7	173	2662	8.851	12.2	27.3	(46)
$(CH_3)_3As\cdot Ga(CH_3)_3$	23.4–23.7	121	2458	9.114	11.2	28.5	(46)
$(CH_3)_3Sb\cdot Ga(CH_3)_3$	0.3–2.2	95	2105	8.591	9.6	26.1	(46)
$(CH_3)_2O\cdot Ga(CH_3)_3$†	—	100	2078	8.453	9.5	25.5	(46)
$(CH_3)_2S\cdot Ga(CH_3)_3$†	—	116	2580	9.516	11.8	30.4	(46)
$(CH_3)_2Se\cdot Ga(CH_3)_3$	−43 to −42	111	2783	10.118	12.7	33.0	(46)
$(CH_3)_2Te\cdot Ga(CH_3)_3$	−32.5 to −32	122	2488	9.172	11.4	28.8	(46)
$(CH_3)_3N\cdot In(CH_3)_3$	66.2–66.4	171	2460	8.402	11.3	25.4‡	(49)
$(CH_3)_3P\cdot In(CH_3)_3$	46.5	189	2832	9.015	13.0	28.1‡	(49)
$(CH_3)_3As\cdot In(CH_3)_3$	28.2–28.8	155	2590	8.925	11.9	27.8‡	(49)
$(CH_3)_2O\cdot In(CH_3)_3$†	—	147	2175	8.066	10.0	23.8‡	(49)
$(CH_3)_2S\cdot In(CH_3)_3$	19.0–19.5	185	1808	6.825	8.3	18.1‡	(49)
$(CH_3)_3N\cdot Tl(CH_3)_3$§	—	—	—	—	—	—	(49)
$(CH_3)_3P\cdot Tl(CH_3)_3$	27–28	—	—	—	—	—	(49)
$(CH_3)_2O\cdot Tl(CH_3)_3$§	—	—	—	—	—	—	(49)
$(CH_3)_2S\cdot Tl(CH_3)_3$	−0.5	—	—	—	—	—	(49)
$(CH_3)_2Se\cdot Tl(CH_3)_3$§	—	—	—	—	—	—	(49)

* By extrapolation of vapor pressure equation; see second footnote to table 3.

† Liquid at room temperature.

‡ Calculated from results presented in reference 49.

§ Melts over a range, a little below 0°C.

adduct like $(CH_3)_2Se \cdot Ga(CH_3)_3$ depends on a balance between the two effects. The order of coördination O > Se > S = Te towards trimethylgallium is thus qualitatively accounted for. Multiple bonding should occur in trimethylgallium adducts of Group V ligands other than $(CH_3)_3N \cdot Ga(CH_3)_3$, but in Group V the classical dative bond is apparently sufficiently strong to mask π-bonding effects, since a "normal" order of coördination, N > P > As > Sb > Bi, is observed. However, the difference in degree of dissociation of $(CH_3)_2S \cdot Ga(CH_3)_3$ and $(CH_3)_2Se \cdot Ga(CH_3)_3$ could be due to an entropy effect, as was later pointed out (48), and this might be responsible for the sequence of coördination O > Se > S = Te.

The addition compounds formed between Group VI ligands and trimethylindium or trimethylthallium are much less stable than their gallium analogs (table 5). The compounds $(CH_3)_2O \cdot In(CH_3)_3$ and $(CH_3)_2S \cdot In(CH_3)_3$ are almost wholly dissociated in the vapor phase. Of the Group VI adducts of trimethylthallium only $(CH_3)_2S \cdot Tl(CH_3)_3$ has a sharp melting point. Trimethylthallium is an even weaker acceptor than trimethylindium.

It may be mentioned in passing that the orders of coördination $(CH_3)_3N > (CH_3)_3P > (CH_3)_3As > (CH_3)_3Sb$; $(CH_3)_2O > (CH_3)_2S > (CH_3)_2Se > (CH_3)_2Te$; and $(CH_3)_3N > (CH_3)_2O$ observed with the majority of Group III acceptor molecules are somewhat contradictory from one point of view. It has been suggested by several workers (2, 79, 93) that the electron-pair donor power of ligands should increase with decreasing ionization potential of the lone-pair electrons. The ionization potentials of trimethylamine [9.4 e.v. (86) or 7.82 e.v. (103)] and dimethyl ether [10.5 e.v. (86)] are such as to lead one to expect the order of coördination $(CH_3)_3N > (CH_3)_2O$. This order is found with all Group III acceptor molecules. Proton affinity also falls in the same sequence. Ionization potentials, however, should be at a maximum for first row ligands. This idea is supported by the fact that the ionization potential of dimethyl sulfide (9.4 e.v.) is lower than that for dimethyl ether (86). The order of donor power, therefore, should be $(CH_3)_3P > (CH_3)_3N$, and $(CH_3)_2S > (CH_3)_2O$. With most Group III acceptors the reverse order to this is found. Moreover, proton affinity is also in the order $(CH_3)_3N > (CH_3)_3P$ and $(CH_3)_2O > (CH_3)_2S$. Proton affinity, however, is a free-energy value, but if entropy changes are approximately equal, donor properties of various ligands can be compared by studying their proton affinities. The inability to correlate in the expected manner ionization potential with base strength, in Group V or Group VI, even when the proton with its negligible steric requirements is the reference acceptor, suggests that a determining factor in the formation of a classical dative σ bond is the size of the ligand atom and hence the length of the metal–ligand bond. Ionization potentials also fail to account for the variation in order of coördination sometimes shown by a given series of ligands when different Lewis acids are used as references. In attempting to correlate the base strength of a donor molecule with its first ionization potential further difficulties arise. As yet the ionization potentials of relatively few ligands are known; moreover, the value of the ionization potential depends on whether it was determined by the electron-impact (86) or the photoionization (103) method.

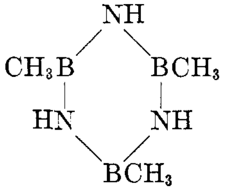
V. Irreversible Decomposition of Molecular Addition Compounds

As mentioned in the introduction, under appropriate conditions many addition compounds of the Group III elements decompose irreversibly, with loss of molecular hydrogen, methane, or other small molecules. The conditions required for elimination reactions depend markedly on the nature of the complex. Sometimes relatively high pressures and temperatures are necessary for irreversible decomposition of the addition compound, but in other instances donor and acceptor molecules react so rapidly, even at low temperatures, that the initially formed adduct can only be regarded as a reaction intermediate. Rapid decomposition of an adduct is only likely when the ligand atom is bonded to hydrogen. The ligand atom is electronegative relative to the hydrogen, but charge transfer from donor to acceptor increases the protonic character of the hydrogen still further, while at the same time groups on the acceptor atom acquire more electron density. These electrical strains are relieved when an elimination reaction occurs.

A. COMPOUNDS OF BORON

Addition compounds formed by the trialkyl- or triarylboranes with ammonia or with primary and secondary amines are relatively easily dissociated into their donor and acceptor parts. Because of this it is necessary to apply pressure to reduce the degree of dissociation, as well as to increase the temperature, in order to bring about loss of hydrocarbon and synthesis of an aminoboron type molecule, e.g.:

$$(CH_3)_3B\cdot NH_3 \xrightarrow[\text{20 atm.}]{\text{280°C.}} (CH_3)_2BNH_2 + CH_4 \xrightarrow[\text{20 atm.}]{\text{330°C.}}$$



$+ CH_4$

Reactions of this type have been used extensively, particularly by Wiberg and his coworkers (104), for the synthesis of compounds with boron–nitrogen bonds. However, these reactions have been mentioned in several reviews (58, 65, 98, 104), some of which are of recent date; hence they will not be discussed in this article.

Adducts formed by borane, monoalkylboranes, or dialkylboranes with ligands containing reactive hydrogen can decompose with loss of hydrogen, e.g.:

$$H_3N\cdot BH_3 \xrightarrow{-H_2} B_3N_3H_6$$

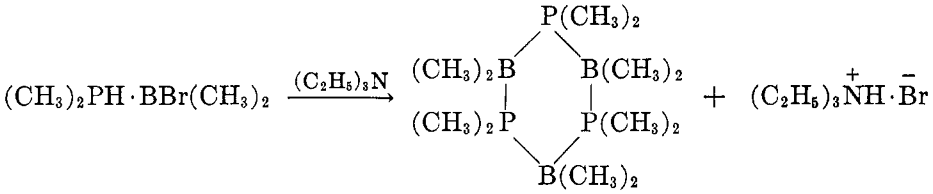
$$(CH_3)_2NH\cdot BH(CH_3)_2 \xrightarrow{-H_2} (CH_3)_2NB(CH_3)_2$$

$$(CH_3)_2PH\cdot BH_3 \xrightarrow{-H_2} ((CH_3)_2PBH_2)_n$$

$$CH_3SH\cdot BH(CH_3)_2 \xrightarrow{-H_2} CH_3SB(CH_3)_2$$

High pressures are not required for these reactions since, for reasons discussed in Sections III and IV above, these adducts possess boron–ligand bonds much more stable than those in the coördination compounds of the trialkylboranes. It is often necessary to heat the adduct, however, to obtain the theoretical amount of hydrogen. For reviews on the decomposition of borane addition compounds the reader is referred elsewhere (37, 98).

Addition compounds formed by boron halides, or their alkyl and aryl derivatives, with ligands containing active hydrogen tend to lose hydrogen halide. By treating the donor with the acceptor in the presence of a tertiary amine, or by treating the addition compound itself with tertiary amine, removal of hydrogen halide may be accomplished without secondary reactions, e.g. (44):



Removal of hydrogen halide with tertiary base in this manner was first used by Brown (36) in the synthesis of $(CH_3)_2NBCl_2$. Employment of this type of reaction to prepare organic compounds of boron has been reviewed by Lappert (65). Since this review, however, Musgrave (81) has prepared several new aminoboron dihalides by this method in a study of the factors controlling the dimerization of the halides.

B. COMPOUNDS OF ALUMINUM

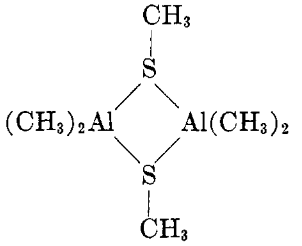
Comparative studies on the irreversible decomposition of molecular addition compounds of aluminum are chiefly confined to adducts of trimethylaluminum (53). The latter compound reacts with ligands containing active hydrogen according to the equation:

$$xAl_2(CH_3)_6 + 2xRH \rightarrow 2[(CH_3)_2AlR]_x + 2xCH_4$$

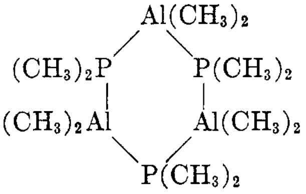
$x = 2$ or 3; $R = (CH_3)_2N$—, $(CH_3)_2P$—, CH_3O—, CH_3S—.

In the case of dimethylamine and dimethylphosphine, addition compounds may be isolated and then heated to give methane. With methanethiol and methanol, trimethylaluminum reacts spontaneously to give methane.

The derivatives $(CH_3)_2AlR$ are dimeric or trimeric in the gas phase and have been assigned ring structures like I or II. The ring bonding is strong, since only the sulfur compound can be depolymerized with trimethylamine, forming the adduct $(CH_3)_3N \cdot Al(CH_3)_2SCH_3$



I

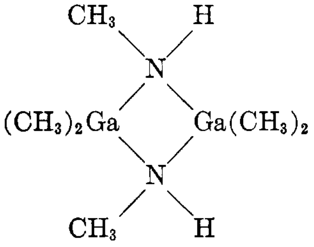


II

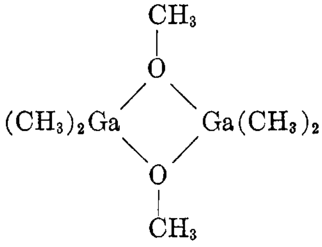
The compounds $(CH_3)_2AlNH_2$ and $(CH_3)_2AlNHCH_3$ have been obtained from the addition compounds $H_3N \cdot Al(CH_3)_3$ and $CH_3NH_2 \cdot Al(CH_3)_3$, respectively. So far relatively few organic derivatives of aluminum have been prepared via addition compounds as intermediates, but now that trialkyl- and dialkylaluminum compounds can be prepared more readily (109), this situation is likely to change.

C. COMPOUNDS OF GALLIUM, INDIUM, AND THALLIUM

Addition compounds of trimethylgallium with donor molecules like ammonia, methylamine, or dimethylamine decompose on heating in a manner similar to the analogous coördination compounds of trimethylaluminum. In this manner derivatives like III have been prepared (46). As long as reactive hydrogen remains on the ligand, further loss of methane can occur. Thus III, which is formed by the pyrolysis of $CH_3NH_2 \cdot Ga(CH_3)_3$ at 120–130°C., would eliminate methane if heated to a sufficiently high temperature,



III



IV

although it is stable to 180°C. Trimethylgallium undergoes an immediate reaction with methanol to give the dimeric methoxide (IV). The adduct $CH_3(H)O \cdot Ga(CH_3)_3$ apparently has only a transitory existence. Gallium derivatives similar to IV have been prepared from methanethiol, methaneselenol, phenols, thiophenols, and selenophenols. These dimeric derivatives are not detectably dissociated into the monomers in the gas phase. Some of the compounds, however, combine reversibly with the strong electron-pair donor trimethylamine (48). Loss of methane from complex compounds of boron, aluminum, and gallium is easiest in the order Ga > Al > B.

The adduct $H_3N \cdot In(CH_3)_3$ evolves methane slowly even at room temperature. At 70–80°C. the amide $[(CH_3)_2In \cdot NH_2]_n$ is rapidly formed (48). The compound

$[(CH_3)_2In \cdot N(CH_3)_2]_2$ is obtained when $(CH_3)_2NH \cdot In(CH_3)_3$ is heated at 140–160° C. With methanol, at its melting point (−98°C.), trimethylindium yields $[(CH_3)_2InOCH_3]_n$, a viscous liquid. The sulfur derivative $(CH_3)_2InSCH_3$, dimeric in benzene solution, has also been made.

A number of thallium compounds are known in which the dimethylthallium group is bonded to a donor group (49). However, many of these derivatives have not been obtained by the decomposition of a molecular addition compound. Dimethylthallium methoxide, like all other dimethylmetal methoxides of the Group III elements, does not form an adduct with trimethylamine (49).

In contrast to $[(CH_3)_2Al \cdot SCH_3]_2$, $[(CH_3)_2Ga \cdot SCH_3]_2$, and $[(CH_3)_2Ga \cdot SeCH_3]_2$, the compounds $[(CH_3)_2In \cdot SCH_3]_2$, $[(CH_3)_2Tl \cdot SCH_3]_2$, and $[(CH_3)_2Tl \cdot SeCH_3]_2$ do not absorb trimethylamine to form addition compounds.

From the work reviewed in this section it is seen that dimethylmetal derivatives of the type $(CH_3)_2M^{III}R$ (M^{III} = Al, Ga, In, Tl; R = H_2N—, $(CH_3)_2N$—, $(CH_3)_2P$—, CH_3O—, CH_3S—, CH_3Se—) are polymeric, with a degree of polymerization usually two or three. It is interesting to note that many of the boron analogs, $(CH_3)_2BR$, are monomeric: e.g., $(CH_3)_2BOCH_3$, $(CH_3)_2BN(CH_3)_2)$. Some of the boron compounds, however, can exist either as monomers or as dimers [e.g., $(CH_3)_2BNH_2$], while others are polymeric [e.g., $((CH_3)_2B \cdot P(CH_3)_2)_3$]. The existence of some of these boron compounds as monomers may be due to the boron–nitrogen and boron–oxygen bonds being of the σ,π type. This could occur through interaction of the lone-pair electrons on the donor atoms with the boron $2p_\pi$ orbital. The fact that Group III elements, other than boron, do not form monomeric derivatives may be understood in terms of the inability of these heavier atoms to form stable p_π–p_π bonds because of inner-shell repulsions (78, 85). By the same argument derivatives $(CH_3)_2BR$ in which the donor atom in R is from the second or later rows of the periodic system should also be polymeric. In agreement with this idea the compound $(CH_3)_2BP(CH_3)_2$ is trimeric, while $CH_3BH \cdot P(CH_3)_2$ and $(CH_3)_2B \cdot PH_2$ are even more polymerized. The derivatives $(CH_3)_2BSH$ and $(CH_3)_2BSCH_3$, however, are monomeric, but this is not necessarily due to the existence of sulfur–boron p_π–p_π internal dative bonds in these compounds. The classical dative-bonding power of sulfur is weaker than that of nitrogen, phosphorus, or oxygen, so that the inability of $(CH_3)_2BSCH_3$ or $(CH_3)_2BSH$ to polymerize could be due to insufficient $\overset{+}{S}$—$\overset{-}{B}$ external dative bonding to hold together a polymer. The boron–sulfur bond in $(CH_3)_2BSCH_3$ or $(CH_3)_2BSH$ might be a pure σ bond.

A similar explanation could account for the monomeric character of $(CH_3)_2SbBH_2$, since it is most unlikely that the large antimony atom could permit antimony–boron p_π–p_π bonding. However, in dimethylstibinoborane it has been suggested (39) that π bonding occurs through interaction of electrons in the antimony $5pd$ hybrid orbitals with the empty $2p_\pi$ orbital of boron. The compound $(CH_3)_2SbBH_2$, it should be noted, might be expected to dimerize via B—H—B bonds if it did not polymerize via external antimony–boron dative bonds.

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VI. References

(1) Andrews, L. J.: Chem. Revs. **54,** 713 (1954).
(2) Bauer, S. H.: J.Am. Chem. Soc. **78,** 5775 (1956).
(3) Bauer, S. H., and McCoy, R. E.: J. Phys. Chem. **60,** 1529 (1956).
(4) Baumgarten, P., and Bruns, W.: Ber. **80,** 517 (1947).
(5) Bell, R. P., and Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) **A183,** 357 (1945).
(6) Booth, H. S., and Martin, D. R.: *Boron Trifluoride and its Derivatives.* John Wiley and Sons, Inc., New York (1949).
(7) Booth, H. S., and Martin, D. R.: *Fluorine Chemistry* (edited by J. H. Simons), Vol. I, p. 208. Academic Press, Inc., New York (1950).
(8) Booth, H. S., and Walkup, J. H.: J. Am. Chem. Soc. **65,** 2334 (1943).
(9) Brown, H. C.: J. Chem. Soc. **1956,** 1248.
(10) Brown, H. C., and Adams, R. M.: J. Am. Chem. Soc. **65,** 2557 (1943).
(11) Brown, H. C., and Barbaras, G. K.: J. Am. Chem. Soc. **69,** 1137 (1947).
(12) Brown, H. C., and Barbaras, G. K.: J. Am. Chem. Soc. **75,** 6 (1953).
(13) Brown, H. C., Bartholomay, H., and Taylor, M. D.: J. Am. Chem. Soc. **66,** 435 (1944).
(14) Brown, H. C., and Domash, L.: J. Am. Chem. Soc. **78,** 5384 (1956).
(15) Brown, H. C., and Fletcher, E. A.: J. Am. Chem. Soc. **73,** 2808 (1951).
(16) Brown, H. C., and Fletcher, E. A.: Unpublished work; see E. A. Fletcher, Thesis, Purdue University, 1952.
(17) Brown, H. C., and Gerstein, M.: J. Am. Chem. Soc. **72,** 2923 (1950).
(18) Brown, H. C., and Gerstein, M.: J. Am. Chem. Soc. **72,** 2926 (1950).
(19) Brown, H. C., and Gintis, D.: J. Am. Chem. Soc. **78,** 5378 (1956).
(20) Brown, H. C., Gintis, D., and Domash, L.: J. Am. Chem. Soc. **78,** 5386 (1956).
(21) Brown, H. C., Gintis, D., and Podall, H.: J. Am. Chem. Soc. **78,** 5375 (1956).
(22) Brown, H. C., and Harris, R. H.: Unpublished work; see R. H. Harris, Thesis, Purdue University, 1952.
(23) Brown, H. C., and Holmes, R. R.: J. Am. Chem. Soc. **78,** 2173 (1956).
(24) Brown, H. C., and Holmes, R. R.: Abstracts of Papers presented at the 129th Meeting of the American Chemical Society, held in Cleveland, Ohio, May, 1956, p. 28q.
(25) Brown, H. C., and Horowitz, R. H.: J. Am. Chem. Soc. **77,** 1730 (1955).
(26) Brown, H. C., and Horowitz, R. H.: J. Am. Chem. Soc. **77,** 1733 (1955).
(27) Brown, H. C., and Johannesen, R. B.: J. Am. Chem. Soc. **75,** 16 (1953).
(28) Brown, H. C. and Lawton, E. A.: Unpublished work; see E. A. Lawton, Thesis, Purdue University, 1952.
(29) Brown, H. C., McDaniel, D. H., and Hafliger, O.: *Determination of Organic Structures by Physical Methods*, edited by E. A. Braude and F. C. Nachod, p. 567. Academic Press, Inc., New York (1956).
(30) Brown, H. C., and Pearsall, H.: J. Am. Chem. Soc. **67,** 1765 (1945).
(31) Brown, H. C., and Sujishi, S.: J. Am. Chem. Soc. **70,** 2878 (1948).
(32) Brown, H. C., and Sujishi, S.: Unpublished work; see S. Sujishi, Thesis, Purdue University, 1949.
(33) Brown, H. C., and Taylor, M. D.: J. Am. Chem. Soc. **69,** 1332 (1947).
(34) Brown, H. C., Taylor, M. D., and Gerstein, M.: J. Am. Chem. Soc. **66,** 431 (1944).
(35) Brown, H. C., Taylor, M. D., and Sujishi, S.: J. Am. Chem. Soc. **73,** 2464 (1951).
(36) Brown, J. F.: J. Am. Chem. Soc. **74,** 1219 (1952).
(37) Burg, A. B.: Record Chem. Progress (Kresge-Hooker Sci. Lib.) **15,** 159 (1954).

(38) Burg, A. B.: Abstracts of Papers Presented at the 127th Meeting of the American Chemical Society, held in Cincinnati, Ohio, April, 1955, p. 26q.

(39) Burg, A. B., and Grant, L. R.: Abstracts of Papers Presented at the 132nd Meeting of the American Chemical Society, held in New York City, September, 1957, p. 25s.

(40) Burg, A. B., and Green, A. A.: J. Am. Chem. Soc. **65,** 1838 (1943).

(41) Burg, A. B., and Kuljian, E. S.: J. Am. Chem. Soc. **72,** 3103 (1950).

(42) Burg, A. B., and Randolph, C. L.: 3rd Annual Technical Report to the Office of Naval Research, Project NR 052-050. Contract N6onr-238-TO-I.

(43) Burg, A. B., and Schlesinger, H. I.: J. Am. Chem. Soc. **59,** 780 (1937).

(44) Burg, A. B., and Wagner, R. I.: J. Am. Chem. Soc. **75,** 3872 (1953).

(45) Clarke, R. P., and Pease, R. N.: J. Am. Chem. Soc. **73,** 2132 (1951).

(46) Coates, G. E.: J. Chem. Soc. **1951,** 2003.

(47) Coates, G. E.: *Organo-Metallic Compounds*, p. 62. Methuen, London (1956).

(48) Coates, G. E., and Hayter, R. G.: J. Chem. Soc. **1953,** 2519.

(49) Coates, G. E., and Whitcombe, R. A.: J. Chem. Soc. **1956,** 3351.

(50) Colclough, T., Gerrard, W., and Lappert, M. F.: J. Chem. Soc. **1955,** 907.

(51) Colclough, T., Gerrard, W., and Lappert, M. F.: J. Chem. Soc. **1956,** 3006.

(52) Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. E., and Sutton, L. E.: J. Chem. Soc. **1954,** 332.

(53) Davidson, N., and Brown, H. C.: J. Am. Chem. Soc. **64,** 316 (1942).

(54) Davy, H.: Phil. Trans. **30,** 365 (1812).

(55) Garvin, D., and Kistiakowsky, G. B.: J. Chem. Phys. **20,** 105 (1952).

(56) Gay-Lussac, J.: Mémoires de la société d'Arcueil **2,** 211 (1809).

(57) Gibbs, J. H.: J. Chem. Phys. **22,** 1460 (1954).

(58) Goubeau. J.: *F.I.A.T. Reviews of German Science: Inorganic Chemistry*, Vol. I, p. 218.

(59) Graham, W. A. G., and Stone, F. G. A.: Chemistry & Industry **1956,** 319.

(60) Graham, W. A. G., and Stone, F. G. A.: J. Inorg. Nuclear Chem. **3,** 164 (1956).

(61) Greenwood, N. N., and Martin, R. L.: Quart. Revs. (London) **8,** 1 (1954).

(62) Hedberg, K.: J. Am. Chem. Soc. **77,** 6491 (1955).

(63) Kaesz, H. D., and Stone, F. G. A.: Unpublished work.

(64) Kistiakowsky, G. B., and Williams, R.: J. Chem. Phys. **23,** 334 (1955).

(65) Lappert, M. F.: Chem. Revs. **56,** 959 (1956).

(66) Laubengayer, A. W., and Finlay, G. R.: J. Am. Chem. Soc. **65,** 884 (1943).

(67) Laubengayer, A. W., and Gilliam, W. F.: J. Am. Chem. Soc. **63,** 477 (1941).

(68) Laubengayer, A. W., and Sears, D. S.: J. Am. Chem. Soc. **67,** 164 (1945).

(69) Lewis, G. N.: J. Franklin Inst. **226,** 293 (1938).

(70) Lowry, T. M.: Trans. Faraday Soc. **18,** 285 (1923).

(71) McCoy, R. E., and Bauer, S. H.: J. Am. Chem. Soc. **78,** 2061 (1956).

(72) McDaniel, D. H.: Science **125,** 545 (1954).

(73) Martin, D. R.: Chem. Revs. **34,** 461 (1944).

(74) Martin, D. R.: Chem. Revs. **42,** 581 (1948).

(75) Martin, D. R., and Dial, R.: J. Am. Chem. Soc. **72,** 852 (1950).

(76) Meulen, P. A. van der, and Heller, H. A.: J. Am. Chem. Soc. **54,** 4404 (1932).

(77) Mulliken, R. S.: Chem. Revs. **41,** 207 (1947).

(78) Mulliken, R. S.: J. Am. Chem. Soc. **72,** 4493 (1950).

(79) Mulliken, R. S.: J. Am. Chem. Soc. **74,** 811 (1952).

(80) Mulliken, R. S.: J. Phys. Chem. **56,** 801 (1952).

(81) Musgrave, O. C.: J. Chem. Soc. **1956,** 4305.

(82) Nyholm, R. S.: Revs. Pure Appl. Chem. **4,** 15 (1954).

(83) Parry, R. W., and Bissot, T. C.: J. Am. Chem. Soc. **78,** 1524 (1956).

(84) Pauling, L.: *The Nature of the Chemical Bond.* Cornell University Press, Ithaca, New York (1945).

(85) Pitzer, K. S.: J. Am. Chem. Soc. **70,** 2140 (1948).

(86) PRICE, W. C.: Chem. Revs. **41**, 257 (1947).
(87) RICE, B., LIVASY, J. A., AND SCHAEFFER, G. W.: J. Am. Chem. Soc. **77**, 2750 (1955).
(88) RUNDLE, R. E.: J. Am. Chem. Soc. **69**, 1327, 1719 (1947).
(89) SCHLESINGER, H. I., AND BURG, A. B.: J. Am. Chem. Soc. **60**, 290 (1938).
(90) SCHLESINGER, H. I., FLODIN, N. W., AND BURG, A. B.: J. Am. Chem. Soc. **61**, 1078 (1939).
(91) SIDGWICK, N. V.: *The Electronic Theory of Valency*, p. 60. Clarendon Press, Oxford (1927).
(92) SIDGWICK, N. V.: *The Chemical Elements and their Compounds*, p. 401. Clarendon Press, Oxford (1950).
(93) SKINNER, H. A.: *Cationic Polymerisation* (edited by P. H. Plesch), p. 35. Heffer, Cambridge (1953).
(94) SKINNER, H. A., AND SMITH, N. B.: J. Chem. Soc. **1953**, 4025.
(95) SKINNER, H. A., AND SMITH, N. B.: J. Chem. Soc. **1954**, 2324.
(96) STIEBER, A.: Compt. rend. **195**, 610 (1932).
(97) STOCK, A.: Ber. **34**, 949 (1901).
(98) STONE, F. G. A.: Quart. Revs. (London) **9**, 174 (1955).
(99) STONE, F. G. A., AND BURG, A. B.: J. Am. Chem. Soc. **76**, 386 (1954).
(100) STONE, F. G. A., AND SEYFERTH, D.: J. Inorg. Nuclear Chem. **1**, 112 (1955).
(101) SUJISHI, S., AND WITZ, S.: J. Am. Chem. Soc. **76**, 4631 (1954).
(102) SUJISHI, S., AND WITZ, S.: J. Am. Chem. Soc. **79**, 2447 (1957).
(103) WATANABE, K., AND MOTTLE, J. R.: J. Chem. Phys. **26**, 1773 (1957).
(104) WIBERG, E.: Naturwissenschaften **35**, 182, 212 (1948).
(105) WIBERG, E., BOLZ, A., AND BUCHHEIT, P.: Z. anorg. Chem. **256**, 285 (1948).
(106) WIBERG, E., HERTWIG, K., AND BOLZ, A.: Z. anorg. Chem. **256**, 177 (1948).
(107) WIBERG, E., AND HEUBAUM, U.: Z. anorg. Chem. **225**, 270 (1935).
(108) WIBERG, E., JOHANNSEN, T., AND STECHER, O.: Z. anorg. Chem. **251**, 114 (1943).
(109) ZIEGLER, K.: Angew. Chem. **68**, 721 (1956).