Ammonia-Borane and Related N-B-H Compounds and Materials: Safety Aspects, Properties and Applications

(A survey completed as part of a project for the DOE Chemical Hydrogen Storage Center of Excellence, Contract # DE-FC36-05GO15060)

Clinton F. Lane
Department of Chemistry and Biochemistry
Northern Arizona University
PO Box 5698
Flagstaff, AZ 86011-5698
Phone: 928-523-6296
e-mail: clint.lane@nau.edu

Outline

1. Introduction
2. Safety Aspects
3. Synthesis
4. Physical Properties
5. Theoretical Studies
6. Chemical Properties
7. Synthetic Applications
8. Industrial Applications
9. Conclusions
10. References

1. Introduction

Amine-borane complexes have great potential for use as a key component in hydrogen storage fuels due to their stability and the high gravimetric content of hydrogen in these compounds. For example, the simplest complex, ammonia-borane (H_3NBH_3), contains 19.5 wt% H, which is higher than the wt% H in $LiBH_4$. The 2015 DOE goal is to develop and achieve an on-board hydrogen storage system with at least 9 wt% H. Thus, it appears that an amine-borane-based system has reasonable potential to meet this goal. However, many issues need to be addressed.

Technical and economic issues related to the possible use of ammonia-borane (AB) for the generation of hydrogen for fuel cell applications were evaluated in prior DOE funded reports.[1, 2] Regardless of the issues, the potential use of AB for hydrogen storage in automobiles has even reached the popular scientific press.[3, 4] Also, AB is being investigated as a hydrogen storage material for portable fuel cell powered devices.[5, 6]

Safety may also be an issue. Diborane is an obvious precursor for AB, but B_2H_6 is pyrophoric and toxic.[7] The amine adducts of borane have increased stability and reduced reactivity in comparison to B_2H_6, which means the safety concerns may be less than those for B_2H_6. However, the safety of amine-borane complexes must be examined and will be addressed in this survey.

A number of reviews have appeared covering the chemistry of amine-borane adducts.[8-10] Also, an older survey of synthetic procedures for almost all known boron-nitrogen compounds (except for boron nitrides) is available.[11] The present survey will overlap the earlier reviews as necessary to give a complete picture of the chemistry of AB and related N-B-H containing materials. If a B-N compound does not contain B-H, then it is omitted from this survey. A few references to the synthesis of boron nitride from AB are included, but full coverage of the various routes to BN can be found elsewhere.[12] Iminoboranes of the type R-B≡N-R' can be converted to N-B-H compounds, but this chemistry is not included since a survey of these R-BN-R' compounds is available.[13]

The amine-cyanoboranes and amine-carboxyboranes are not covered in this survey since the main interest in these compounds appears to be related to the physiological activity of various derived boronated biomolecules. A recent theoretical study of the role of a B-N dative bond in the biochemical activity of these boronated biomolecules provides a listing of these B-N compounds and their physiological activity.[14]

Finally, it is interesting to note that the reviews of boron and its commercial uses by the US Geological Survey seldom mention any B-N or B-H compounds.[15-17] B-O compounds completely dominate the current commercial uses and applications of boron chemistry.

2. Safety Aspects

Before discussing the stability and reactivity (safety aspects) of amine-borane adducts, it is important to consider how the compounds are prepared. The direct reaction of ammonia with diborane does not give a Lewis acid-base complex. Instead an unsymmetrical cleavage occurs. This is in contrast to the direct reaction of trimethylamine with diborane, which gives the expected Lewis acid-base complex. When ammonia is added to a tetrahydrofuran (THF) solution of borane-THF, the result is a 50/50 mixture of the products from symmetrical and unsymmetrical cleavage. These reactions are illustrated in equations 1-3.

$$2NH_3 \; + \; B_2H_6 \; \longrightarrow \; [(NH_3)_2BH_2]^{+} \, [BH_4]^{-} \qquad\qquad (1)$$
$$\text{the diammoniate of diborane}$$

$$2(CH_3)_3N \; + \; B_2H_6 \; \longrightarrow \; 2(CH_3)_3N{-}BH_3 \qquad\qquad\qquad (2)$$
$$\text{trimethylamine-borane}$$

$$3THF{-}BH_3 \; + \; 3NH_3 \; \longrightarrow \; [(NH_3)_2BH_2]^{+} \, [BH_4]^{-} \; + \; NH_3{-}BH_3 \; + \; 3THF \;\; (3)$$
$$\text{ammonia-borane}$$
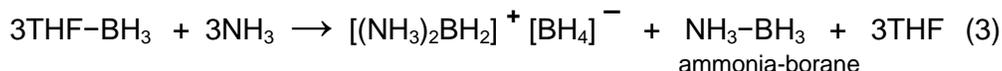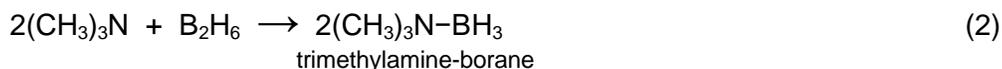
Sheldon Shore extensively studied the above chemistry of diborane and ammonia and a scientific biography of this work covers all the details with references to the original literature.[18]

As can be expected, the properties and stability of AB and the diammoniate of diborane are quite different. At ambient temperatures the diammoniate slowly undergoes decomposition with evolution of hydrogen resulting in pressure build-up in storage vessels.[19] The recommendation is to store the compound at -78 ^{o}C.[19] It is possible to prepare AB from the diammoniate and this is reported to give a material that is somewhat unstable at room temperature.[20] However, when AB is prepared from $(CH_3)_2S-BH_3$ and ammonia and is recrystallized from diethyl ether to remove the diammoniate by-product, then the produced high-purity crystalline AB is found to be stable for 5 days at 70 ^{o}C.[21] Another investigator also found that high purity AB with a sharp melting point did not show any sign of decomposition (no pressure build-up) over a 2 month period at room temperature and could be sublimed at temperatures up to almost 100 ^{o}C under high vacuum with no decomposition.[22] This same high purity AB did not undergo any detectable conversion to $[(NH_3)_2BH_2]$ $[BH_4]$ when held at 50 ^{o}C for 13 days.[23] Finally, when AB of good apparent purity was prepared by the reaction between NaBH4 and an ammonium salt, the solid AB appeared to be stable indefinitely at room temperature.[24] A THF solution of this AB slowly decomposed upon standing with precipitation of an unidentified white solid.[24]

It appears that high purity AB can be safely stored in a closed vessel at room temperature, but mixtures or solutions need to be vented until the absence of pressure build-up is assured.

The decomposition of AB at high temperatures with hydrogen evolution is well documented and is reported to become vigorous at near 120 ^{o}C.[25] If this thermal decomposition is run in air with oxygen present, then an interesting light emission is observed at 180-190 ^{o}C, which is thought to be the result of an oxidation reaction of a decomposition product.[26] Obviously, it seems prudent to use inert atmosphere techniques when doing any work that involves hydrogen generation or active boron hydride formation. It is a good idea to always store AB under an inert atmosphere since a mass spec study of the vapor above solid AB showed the presence of diborane.[27]

Two fires recently occurred during the handling of AB.[28, 29] In January 2005 a sample of AB on mesoporous carbon was observed to inflame in air when contacted with a stainless steel spatula.[28] The best explanation is that this incident may have been caused by a static discharge.[28] Interestingly, a Material Safety Data Sheet (MSDS) for pyridine-borane warns that if charcoal is used to decolorize a solution of this amine-borane, then special care must be taken during filtration because the carbon on the filter paper can burst into flames upon drying in air.[30] However, this might be a result of the known instability of pyridine-borane, which will be discussed later in this section. In April 2005 a fire occurred in a vendor's packaging department during clean-up of equipment following packaging of AB.[29] An investigation into the cause of this fire showed that when acetone is added to residues of AB in the open air, then a reaction occurs in a few seconds with gas evolution and the generation of heat.[29] If water or methanol is used in place of acetone, then AB simply dissolves with no observed reaction.[29] A sample of the AB involved in the fire was tested to see if the material was pyrophoric using the Filter Paper Char Test[31, 32] and the results were negative.[29] A stock check (reassay following a standard QC method[33]) of AB product in packaged units for 10 months showed a slight improvement in % purity.[34]

The recommendations here are to avoid initial use of acetone in the open air for clean up of lab equipment that contains residues of AB and to not allow mixtures of finely divided carbon and amine-boranes to dry in the open air. The direct use of water for clean up in the absence of flammable liquids is the best method to follow to avoid these fire hazards.

Ammonium borohydride is closely related to AB, but this salt can only be prepared at low temperatures and decomposes at temperatures above -20 ^{o}C with evolution of hydrogen.[35] This may be more than a simple thermal decomposition because when ultra-dry solvents are used a mixture of $(BH_4)^-$ and $(NH_4)^+$ does not react to give hydrogen.[36] Regardless, even though ammonium borohydride appears attractive based on wt% H, it must be treated with caution since it is usually an unstable material.

Another material to treat with caution is hydrazine-bisborane ($H_3B-NH_2NH_2-BH_3$).[37, 38] It can be prepared from diborane and anhydrous hydrazine at low temperatures, but the white solid product explodes when heated in air.[37] It is also reported to be shock sensitive and will detonate upon impact.[38] Solid pellets of hydrazine-bisborane can be ignited to provide hydrogen gas via a self-sustaining thermal decomposition.[39]

It is now generally accepted that amine-boranes prepared from primary and secondary amines are stable and do not evolve hydrogen under normal conditions. However, early workers reported that $(CH_3)NH_2-BH_3$ and $(CH_3)_2NH-BH_3$ decompose slowly even at 0 ^{o}C with evolution of hydrogen.[40] A later report states that both of these adducts are stable white solids with no tendency to evolve hydrogen at room temperature.[41a] This apparent discrepancy is now understood as being due to unsymmetrical cleavage of diborane.[41b] Interestingly, a patent claims the manufacture of "stable" $(CH_3)_2NH-BH_3$ which shows no decomposition when heated up to 110 ^{o}C.[42] More recently, a melt of neat $(CH_3)_2NH-BH_3$ was kept at 45 ^{o}C for 7 days with no observed decomposition.[43]

It is recommended that all new amine-borane adducts prepared from 1° or 2° amines need to be treated as potentially unstable until tested for the absence of pressure build-up upon storage.

As mentioned earlier, pyridine-borane is known to be thermally unstable. Early workers observed the adduct decomposing during an attempted vapor pressure measurement.[44] Also, a violent decomposition occurred during an attempted distillation of pyridine-borane.[45] These reports are in contrast to a comment in a patent that pyridine-borane can be heated up to 100 ^{o}C without any disadvantage.[46] Neat pyridine-borane is a clear yellow liquid at room temperature, but it can often slowly become a clear gummy to wax-like solid upon long-term storage. This result lead to a serious industrial accident where a 55-gal drum of pyridine-borane was moved to a hot room and later ruptured and started a fire.[47] This company also learned about other incidents and fires involving pyridine-borane when it was stored or shipped at higher than ambient temperatures. It is recommended that bulk containers must only be stored or transported at 30 ^{o}C or less.[47]

Although it is not an amine-borane, a discussion of the instability of the related Lewis acid-base adduct, borane-THF, is needed since it does reveal a problem when a system contains an internal route from a reactive B-H to a thermodynamically more stable B-O. Borane-THF, as a 1M solution in THF, is available commercially, but was initially only offered as a $NaBH_4$ stabilized solution. Borane-THF undergoes a slow internal reductive ring opening to give butoxy-B compounds,[48] and this reaction can be retarded if a small amount of $NaBH_4$ (0.005M) is present.[49] Later it was claimed in a patent that borane-THF can be stored "unstabilized" if never allowed above 20 ^{o}C.[50] Unfortunately, whether stabilized with $NaBH_4$ or not, this reagent can decompose violently when stored in bulk at ambient temperatures as witnessed by a very serious industrial accident.[51-53] This explosion resulted in a safety alert[54] from the manufacturer of the material involved in the incident, and a revision of the MSDS by both commercial manufacturers.[55, 56] A recent investigation into means to improve the stability of the commercial borane-THF reagent lead to the development of an amine-stabilized product.[57-59]

The lesson to be learned from the problems with borane-THF is that a mixture of any boron hydride plus an oxygen containing organic needs to be evaluated carefully to see if there is a temperature at which a self-accelerating decomposition can occur. This is especially critical if the mixture is ever produced and shipped in large quantities.

The generation of hydrogen from AB or other amine-borane adducts may involve the formation of borazine, $(HNBH)_3$. Thus, a short discussion of the stability/safety of borazine is needed. Early work on the synthesis of borazine showed that liquid borazine slowly decomposes to give hydrogen and a non-volatile white solid with small amounts of diborane in the volatiles.[60] Later the decomposition of liquid borazine was studied at 50 ^{o}C and 100 ^{o}C with only about 50% of the borazine being recovered after 160 hours.[61] The recommendation is to store borazine at or below 4 ^{o}C.[62]

Finally, a report of the synthesis of $(CH_3)_3N-BH_2N_3$ warns that this compound will detonate upon rapid heating.[63]

The stability, reactivity and utility of amine-borane complexes have lead to the commercial availability of many of these compounds. The following table lists the products where an MSDS can be obtained from a supplier.

Table 1. Commercial amine-borane products with MSDS and technical data sheet.

Amine	MSDS reference	Data sheet reference
Ammonia	64	
Dimethylamine	65	
Trimethylamine	66, 67	
Triethylamine	68, 69	
tert-Butylamine	70, 71	72
Pyridine	30, 73	74
Pyridine (as a 50 wt% solution in pyridine)	75	74
Morpholine	76, 77	
N-Methylmorpholine	78	
N-Ethylmorpholine	79	
N,N-Diisopropylethylamine	80	
N,N-Diethylaniline	81, 82	83

In addition to the two suppliers that offer the amine-borane products listed above, a few of these products are available from non-USA sources. Aviabor[84] lists a number of boron products including AB.[85] Boroscience Canada[86] recently announced the availability of AB and borazine.[87] Finally, Katchem[88] has posted spec sheets for dimethylamine-borane[89] and borazine[90] on the Internet and Gelest[91] is a new supplier for borazine.[92]

The toxicity of diborane is well known and well documented[7] and is listed in detail in the MSDS for diborane supplied by Airgas.[93] Even when supplied as a 10% solution in hydrogen, the MSDS clearly lists the mixture as highly toxic.[94] Much less is known about the toxicity of the amine-borane adducts. A review of the MSDS's supplied by the manufacturers seems to indicate that the amine-borane product is only listed as toxic if the free amine is classified as toxic. This probably means that the authors of the MSDS's could not find any reported toxicological studies in the open literature. A search of the government report archives at US Borax uncovered one study from Project ZIP.[95] The acute toxicity of dimethylamine-borane, pyridine-borane and trimethylamine-borane was

measured by injection in rats.[96] The LD_{50} when expressed as mg B/kg showed that the toxicity of dimethylamine-borane and pyridine-borane is approximately equal to the toxicity of pentaborane, while trimethylamine is much less toxic. Pentaborane is known to be highly toxic.[7c-d, 97]

The safety aspects of amine-borane compounds will not be complete without a discussion of handling procedures and techniques. Gases that are reactive to the atmosphere are best handled using vacuum line techniques. Solids that are reactive to the atmosphere are best manipulated in a glove box. Air-sensitive liquids and solutions can be easily handled using syringe and double-ended needle techniques along with appropriate glassware equipped with sleeve stoppers.[98] Obviously, many of the amine-borane adducts are unreactive to water and oxygen, but it is still a good idea to run all reactions and to handle and store these materials under inert atmospheres.

An area of special safety concern is the use of liquid nitrogen in the cold traps on vacuum distillation apparatus. If a B-H compound is distilled and there is any possibility for disproportionation to give diborane, then these cold traps can collect diborane. If the system is opened to the air following the distillation, then **these traps will explode**. It is always a good idea to use high purity nitrogen to relieve the vacuum in any system using cold traps, but an extra measure of safety can be obtained by first putting a small amount of methanol in the cold traps before distilling the B-H compound.

Care must be taken to properly vent all reaction set-ups and to make sure any generated hydrogen is diluted with nitrogen and vented to an efficient hood. By using aqueous mineral acids, it is possible to completely destroy any B-H bonds in amine-borane adducts with evolution of hydrogen. This can be used to make sure any by-products are safe for proper disposal.

This generation of hydrogen upon hydrolysis can be quantitatively measured and used to determine the concentration of B-H containing solutions and the purity of B-H containing compounds.[99]

3. Synthesis

This section will highlight the reactions that can be used to prepare AB, various 1°, 2° and 3° amine-borane adducts, aminoboranes (mainly R_2N-BH_2 dimers and trimers) and borazines [$(HNBH)_3$ or $(RNBH)_3$]. The use of these compounds to prepare other N-B-H will be included in the section on chemical properties. The use of these compounds as reagents for synthetic chemistry will be included in the section on synthetic applications.

Before discussing the synthetic routes to AB, it is important to remember that the symmetrical cleavage product (AB) is not formed by direct reaction of NH_3 with B_2H_6. Ammonia reacts with diborane via an asymmetrical cleavage to give an ionic solid,[100] which is called the diammoniate of diborane (eq 1). Detailed procedures are available for the preparation of the diammoniate of diborane and all involve passing diborane into liquid ammonia at low temperatures.[19, 101, 102] The dimethylammoniate of diborane can be prepared from methylamine by an analogous reaction (eq 4).[103]

$$2MeNH_2 \; + \; B_2H_6 \; \longrightarrow \; [(MeNH_2)_2BH_2]^+ \, [BH_4]^- \qquad\qquad (4)$$
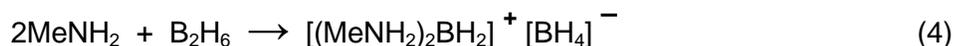
If diborane is first symmetrically cleaved to give a reactive borane-base adduct, then the direct reaction with ammonia is reported to give a mixture of AB plus the diammoniate of diborane (eq 3).[102] Interestingly, borane-THF gives a 50:50 mixture,[102] borane-OMe$_2$ gives almost entirely the diammoniate[104] and borane-SMe$_2$ gives mainly AB.[21]

Ammonia-Borane (AB)

When AB is prepared from borane-THF[102] or borane-SMe$_2$[21], pure AB can be obtained by recrystallization from Et$_2$O due to the insolubility of the ionic diammoniate of diborane.[105] Early workers claimed that AB slowly rearranges at room temperature to give the thermally more stable diammoniate.[103] However, as stated before, a later worker found that AB of high purity does not undergo conversion to the diammoniate even when heated at 50 ^{o}C for 13 days.[23] In the presence of trace amounts of diborane, the diammoniate can be converted cleanly to AB without hydrogen evolution (eq 5).[23]

$$[(NH_3)_2BH_2]^+ [BH_4]^- \xrightarrow[\text{Diglyme, 25 }^o\text{C/40 hrs}]{\text{trace of B}_2\text{H}_6} 2NH_3BH_3 \qquad (5)$$
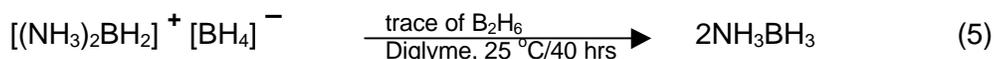
The reaction of lithium borohydride with ammonium salts gives AB without the need to work with diborane or a borane complex (eq 6 and 7).[106]

$$LiBH_4 + NH_4Cl \longrightarrow NH_3BH_3 + LiCl + H_2 \qquad (6)$$

$$2LiBH_4 + (NH_4)_2SO_4 \longrightarrow 2NH_3BH_3 + Li_2SO_4 + 2H_2 \qquad (7)$$

The above reactions are run in diethyl ether and give isolated yields of AB of around 45%. Any by-product diammoniate is removed during the filtration to remove the insoluble lithium salts. Later workers developed a more convenient and improved procedure using the reaction shown in equation 8.[24]

$$NaBH_4 + (NH_4)_2CO_3 \xrightarrow[\text{40-45 }^o\text{C}]{\text{THF}} NH_3BH_3 + NaCO_3(NH_4) + H_2 \qquad (8)$$

Sodium borohydride is less expensive than lithium borohydride and is much easier to handle. Also, the yield of pure AB is greatly improved (80% isolated).[24]

Organoamine-Borane Complexes

Mono-, di- and trialkylamine-borane adducts can be prepared directly from diborane (see equation 2)[107] or from an active borane-base complex. A few specific examples are given in Table 2 for various alkylamines.

Table 2. Synthesis of alkylamine-borane complexes from "borane" precursors.

Amine	Borane	Yield	Reference
Methylamine	THF-BH$_3$	98%	108
Dimethylamine	B$_2$H$_6$[a]	90%	42
Dimethylethylamine	B$_2$H$_6$[b]	84%	109
Diethylmethylamine	B$_2$H$_6$[b]	86%	109
Ethylenediamine	THF-BH$_3$	66%[c]	110
Ethylenediamine	THF-BH$_3$[d]	72%[c]	111
Trialkylamines[e]	THF-BH$_3$	NR[f]	112

Table 2. (continued)

Triethylenediamine	$Me_2S\text{-}BH_3$	96%[c]	113
Dimethyl(2-methoxyethyl)amine	$Me_2S\text{-}BH_3$	NR[f]	114
Trialkylamines[g]	$B_2H_6{}^a$	NR[f]	115

[a] No solvent. [b] Diethyl ether as solvent. [c] Product is the bisborane adduct. [d] Using preformed in situ borane-THF. [e] Wide variety. [f] Not reported but assumed to be quantitative. [g] Variety with bulky groups.

The second major route to alkylamine-borane adducts is the reaction of an amine hydrochloride salt with a borohydride. The original investigators used lithium borohydride in diethyl ether and obtained an 86% isolated yield of amine-borane based on equation 9.[116] Sodium borohydride in THF is now the reagent of choice for the synthesis of amine-boranes from amine-HCl and a few specific examples are given in Table 3.

$$LiBH_4 + (CH_3)_3N \cdot HCl \longrightarrow (CH_3)_3NBH_3 + LiCl + H_2 \qquad (9)$$
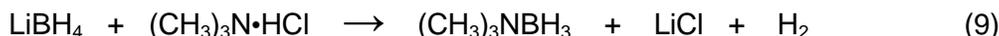
Table 3. Synthesis of amine-boranes from amine-HCl by reaction with $NaBH_4$.

Amine (as HCl salt)	Solvent	Yield	Reference
Trimethylamine	THF	67%	117
Methylamine	Monoglyme	NR[a]	118
Methylamine	THF	83%	119
Ethylenediamine	THF	55%[b]	120
Pyridine	Pyridine	93%	121

[a] Not reported. [b] Product is the bisborane adduct.

Two patents claim an improvement is obtained when the amine and $NaBH_4$ are treated with carbon dioxide in an inert solvent in the presence of water.[122, 123] The reaction for this process is shown in equation 10, which gives an 80% isolated yield of amine-borane.

$$NaBH_4 + (CH_3)_3N + CO_2 + H_2O \longrightarrow (CH_3)_3NBH_3 + NaHCO_3 + H_2 \qquad (10)$$
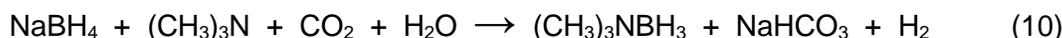
A major disadvantage of the above $NaBH_4$ processes is the generation of hydrogen as a by-product with a loss of ¼ of the valuable B-H. This is somewhat improved (no evolution of hydrogen) by reacting an amine with $NaBH_4$ in liquid SO_2[124] or under anhydrous conditions with CO_2.[125] The by-product for the CO_2 process is believed to be sodium formate (eq 11).[126] Thus, one of the hydrides in $NaBH_4$ is still lost.

$$NaBH_4 + R_3N + CO_2 \longrightarrow R_3NBH_3 + NaOCHO \qquad (11)$$

A major improvement in B-H utilization is possible if borane-THF is generated in the presence of an amine as illustrated in equation 12.[46, 127] The isolated yields are excellent. The only disadvantage of this process is the loss of boron in the fluoroborate by-product.

$$3NaBH_4 + 4BF_3\text{-}OEt_2 + R_3N \longrightarrow 4R_3NBH_3 + 3NaBF_4 + 4Et_2O \qquad (12)$$

It is possible to generate "borane" in situ by reacting $NaBH_4$ with iodine, and this reaction can be run in the presence of an amine to produce 62-97% isolated yields of a wide variety of amine-borane complexes (eq 13).[128] However, this process is inefficient in utilization of B-H.

$$2NaBH_4 + 2R_3N + I_2 \longrightarrow 2R_3NBH_3 + 2NaI + H_2 \qquad (13)$$

Finally, lithium aluminum hydride can be used to reduce dialkyl arylboronates[129] or trialkylboroximes[130] in diethyl ether in the presence of a trialkylamine to give trialkylamine-RBH2 adducts. The required aluminum hydride can even be prepared in situ to give an interesting process for the synthesis of amine-borane complexes (eq 14).[131]

$$2(PhO)_3B + 2Et_3N + 2Al + 3H_2 \longrightarrow 2Et_3NBH_3 + 2Al(OPh)_3 \qquad (14)$$

Aminoboranes

The simplest aminoborane, $H_2N\text{-}BH_2$, can only be isolated at very low temperatures. The vapor phase pyrolysis of AB produces the monomer $H_2N\text{-}BH_2$, which can be trapped, but it is only stable at very low temperatures.[132] When the solid monomer is allowed to warm, it coverts to a polymer $(H_2N\text{-}BH_2)_n$. Alternatively, poly(aminoborane) can be prepared by simple thermal decomposition of AB[133] or by the reaction of lithium amide with diborane (eq 15).[134, 135]

$$nLiNH_2 + nB_2H_6 \longrightarrow nLiBH_4 + (H_2N\text{-}BH_2)_n \qquad (15)$$
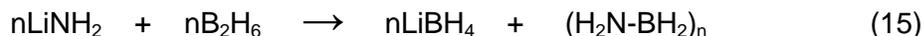
Cyclotriborazane, $(H_2N\text{-}BH_2)_3$, can be prepared using a two step process starting with borazine as shown in equations 16 and 17.[136] The trimer is a solid that decomposes at 150 ^{o}C with hydrogen evolution.

$$(HNBH)_3 + 3HCl \longrightarrow (HNBH)_3\bullet 3HCl \qquad (16)$$

$$2(HNBH)_3\bullet 3HCl + 6NaBH_4 \longrightarrow 2(H_2N\text{-}BH_2)_3 + 6NaCl + 3B_2H_6 \qquad (17)$$
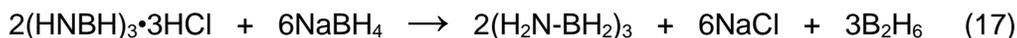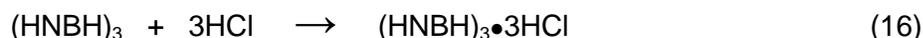
The reaction of sodamide with the diammoniate of diborane in liquid ammonia gives mainly the product where n=5 (50% yield) along with very small amounts of the products with n=2 and n=3 (eq 18).[137] Cyclopentaborazane can also be synthesized via a thermal decomposition of the diammoniate in monoglyme in the presence of ammonia (eq 19).[138]

$$5NaNH_2 + 5[(NH_3)_2BH_2][BH_4] \longrightarrow 5NaBH_4 + (H_2N\text{-}BH_2)_5 + 10NH_3 \quad (18)$$

$$5[(NH_3)_2BH_2][BH_4] \xrightarrow[NH_3]{Monoglyme} (H_2N\text{-}BH_2)_5 + 5H_3NBH_3 + 5H_2 \quad (19)$$
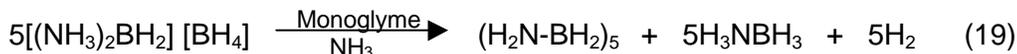
Heating methylamine-borane at 100 ^{o}C gives N,N,N-trimethylcyclotriborazane.[119, 139-141] This aminoborane trimer can also be prepared by the reaction of the amine hydrochloride with sodium borohydride (eq 20), which gives the product as two isomers both in a chair conformation.[118] Similar results are obtained when methylamine-borane is heated at reflux in diglyme.[108] The two isomers were separated and identified with the major isomer having all three methyl groups equatorial and the other isomer having two equatorial and one axial.[118]

$$3MeNH_2\bullet HCl + 3NaBH_4 \longrightarrow (MeNHBH_2)_3 + 3NaCl + 6H_2 \qquad (20)$$

Early studies of the reaction of diborane with 2° amines showed that the initially formed material can be converted to dialkylaminoborane by heating to above 100 ^{o}C.[142, 143] Also,

an early report of the reaction of dimethylamine hydrochloride with lithium borohydride followed by heating, is reported to give dimethylaminoborane.[116] A detailed preparative procedure is available based on the reaction given in equation 21.[117]

$$Me_2NH \bullet HCl \ + \ NaBH_4 \ \longrightarrow \ Me_2NBH_2 \ + \ NaCl \ + \ 2H_2 \qquad (21)$$

However, it is now known that dimethylaminoborane actually exists as a dimer[140] and it was isolated and identified as 1,1,3,3-tetramethyldiborazane as a low yield by-product when the starting materials in equation 21 were used to prepare dimethylamine-borane complex.[144] Recently, an efficient catalytic dehydrocoupling of Me_2NHBH_3 was discovered which results in the quantitative formation of the cyclic dimethylaminoborane dimer under very mild conditions (eq 22).[43]

$$2Me_2NHBH_3 \ \xrightarrow[25-45\ ^oC]{Rh(I)\ or\ Rh(II)\ catalyst} \ (Me_2NBH_2)_2 \ + \ H_2 \qquad (22)$$

This exciting new development is under continuing investigation.[145-148]

Borazines

One of the earliest synthetic routes to borazine (30-35% yield) involved the reaction of lithium borohydride with ammonium chloride in the absence of a solvent at a temperature around 300 ^oC (eq 23).[149]

$$3LiBH_4 \ + \ 3NH_4Cl \ \longrightarrow \ (HNBH)_3 \ + \ 3LiCl \ + \ 9H_2 \qquad (23)$$

Later the reduction of B-trichloroborazine with $LiBH_4$ in Et_2O is claimed to be an improved process, but results in the generation of diborane as a major by-product.[60] The use of $NaBH_4$ provides a less expensive source of B-H and, by running the reaction in the presence of a trialkylamine, the diborane is trapped to provide a significantly safer process.[150] A detailed preparative procedure is available for this reaction (eq 24).[151]

$$(ClBNH)_3 \ + \ 3NaBH_4 \ + \ 3(n\text{-}Bu)_3N \ \longrightarrow \ (HBNH)_3 \ + \ 3NaCl \ + \ 3(n\text{-}Bu)_3NBH_3 \quad (24)$$
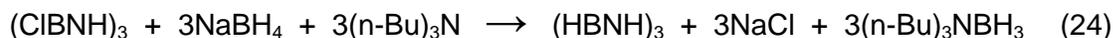
When the above procedure was published, B-trichloroborazine was commercially available. Unfortunately, this chemical is currently only available in small research quantities,[152] and the literature preparation from boron trichloride and ammonium chloride is rather inconvenient.[153]

The direct thermal conversion of AB to borazine is claimed in a patent (69-73% yield), but the process requires specialized equipment.[154] This process can be run in laboratory glassware using tetraglyme as the solvent giving a 67% isolated yield of borazine.[155, 156]

A greatly improved laboratory-scale synthetic procedure (50-60% yield) is now available based on the reaction in equation 25.[62, 155-158]

$$3(NH_4)_2SO_4 \ + \ 6NaBH_4 \ \longrightarrow \ 2(HBNH)_3 \ + \ 3Na_2SO_4 \ + \ 18H_2 \qquad (25)$$

When methylamine-borane is heated to 200 ^oC, the main product is N-trimethylborazine.[119, 139, 159] In general, heating monoalkylamine-boranes to 200° C or higher gives N-trialkylborazines.[156, 160] These products can also be prepared by reacting

an alkylamine hydrochloride with lithium borohydride[116] or sodium borohydride[117] followed by heating and by reducing B-trichloro-N-trialkylborazines with sodium borohydride.[161]

Mixtures of mono-, di-, and tri-N-methylborazines can be prepared by heating mixtures of ammonia and methylamine with diborane[162] or pentaborane.[163]

When the rhodium-catalyzed dehydrocoupling reaction was extended to methylamine-borane, a 40% yield of N-trimethylborazine was obtained (eq 26).[43, 148]

$$3MeNH_2BH_3 \quad \xrightarrow[\text{25-45 }^{o}\text{C, monoglyme}]{\text{Rh(I) or Rh(II) catalyst}} \quad (MeNBH)_3 \;+\; 6H_2 \qquad (26)$$
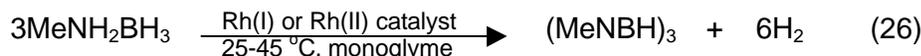
Finally, the reduction of acetonitrile with diborane in THF at reflux gives N-triethylborazine, which can be isolated in 50% yield (eq 27).[164]

$$6MeCN \;+\; 3B_2H_6 \quad \longrightarrow \quad 2(CH_3CH_2NBH)_3 \qquad\qquad (27)$$
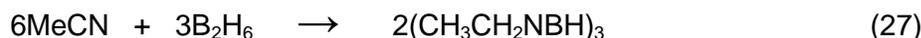
N-Trialkylborazines are assumed to be the intermediate (not isolated) in the borane-methyl sulfide reduction of organonitriles, which gives primary amines upon hydrolysis with methanolic HCl.[165]

4. Physical Properties

The review by Geanangel and Shore provides a listing of the physical properties for a large number of boron-nitrogen compounds.[11] Also, the MSDS's can be consulted to obtain the physical properties for the commercially available compounds. This section will mainly provide a listing of where to find the experimental results for various physical measurements. The N-B-H chemicals and materials covered will only be those previously discussed.

Even though the previous review[11] lists the melting point and boiling point for the early N-B-H compounds, the listing in Table 4 is provided to give the values for the simple compounds plus a few more recent measurements.

Table 4. Physical constants for a few simple B-N-H chemicals.

Compound	mp, ^{o}C	bp, ^{o}C (mm)	Ref.
Ammonia-borane	112-114		22
	110-112		23
	125		105
Methylamine-borane	58		156
Dimethylamine-borane	36	49 (0.01)	11
Trimethylamine-borane	94-94.5	172	11
Dimethylaminoborane dimer	74-76		145
Methylaminoborane trimer	>250		156
Borazine	-58	55	11
N-Trimethylborazine		134	156

AB is a quite simple yet very interesting molecule and many workers have investigated the physical properties of this Lewis acid-base complex. Likewise, the three methylamine-

borane adducts, the aminoboranes and borazine have also been studied experimentally. Tables 5-8 provide lists for most of the major studies.

Table 5. Experimental studies on ammonia-borane.

Method	Property studied/determined	Ref.
X-ray diffraction	Crystal structure	166, 167
Heterodyne beat	Dipole moment	168, 169
Microwave spectrum	B-N bond distance & dipole moment	170
IR spectra (matrix isolated)	Force constants	171
^1H & ^{11}B NMR	Correlation of chemical shifts with enthalpies of formation	172
^{11}B, ^{10}B & ^{14}N NQR	Nitrogen nuclear quadrupole moment	173
^{11}B, ^{10}B & ^{14}N NMR	Activation energy for B-N bond rotation	174
Microwave spectrum	Rotational constants, dipole moment, torsional barrier, etc.	175
Deuterium NMR	B-N bond rotation & dihydrogen bonding[a]	176
Neutron diffraction	Dihydrogen bonding	178
Raman spectroscopic	Dihydrogen bonding	179
IR spectra (matrix isolated)	Structure of pyrolysis products	180-182
^{11}B NMR	Products from thermal decomposition	183
X-ray crystallography	Structure of AB complex with crown ether	184, 185
Water calorimeter	Heat of combustion	186
Adiabatic calorimeter	Thermochemical properties	187
DSC, TG, TG-FTIR & TG-MS	Study of thermal decomposition	188, 189

[a] For a review of dihydrogen bonding where AB is a prime example, see reference 177.

Table 6. Experimental studies on $(H_2NBH_2)_n$

n=	Method	Property studied/determined	Ref.
1	Microwave spectrum	Rotational constants & dipole moment	190
3	Effusion technique	Heat of sublimation	191
3	Dielectric cell	Dipole moment	191
3	X-ray diffraction	Crystal structure	192
2-5	IR & x-ray diffraction	Structural study	133
2-5	MS & x-ray photoelectron Spectra	Structural study	193

Table 7. Experimental studies on amine-borane adducts.

cmpd[a]	Method	Property studied/determined	Ref.
A	X-ray diffraction	B-N bond length	194
A	Raman & IR spectra	Electronic charge distribution	195
A-C	Vapor-pressure depression	MW (showed all are monomeric)	196
A-C	Heterodyne beat	Dipole moment	169
A	Microwave spectra	B-N bond length & dipole moment	197
D	X-ray diffraction	Molecular & crystal structure	198
A	IR	Hydrogen bonding in methanol	199
E	IR (various special)	Dihydrogen bonding in gas phase	200-203
F	^{11}B NMR	B-N bond strength	204

Table 7. (continued)

G	^{1}H, ^{11}B & ^{13}C NMR	Configurational stability	205, 206
H	Calorimetric	Enthalpies of formation	207

[a] A is trimethylamine-borane, B is dimethylamine-borane, C is methylamine-borane, D is ethylenediamine-bisborane, E is a phenol-dimethylamine-borane complex, F is a series of substituted pyridine-borane adducts, G is a series of amine-borane adducts that are configurationally complex, H is a series of primary and secondary and tertiary alkylamine-borane adducts.

Table 8. Experimental studies on borazine.

Method	Property studied/determined	Ref.
Electron diffraction	Structure & B-N bond length	208
UV absorption	Comparison with benzene	209
Classical	Density, viscosity, surface tension & refractive index	210
^{1}H & ^{11}B NMR	Chemical shifts & spin coupling constants	211
Heterodyne beat	Dipole moment	212
Gouy magnetic balance	Diamagnetic susceptibility	213
Vibrational spectrum	Assignment of frequencies	214
Electron diffraction	Molecular structure	215
IR & Raman spectra	Vibrational analysis	216
IR spectra & ^{1}H NMR	Absence of hydrogen bonding	217
X-ray crystallography	Molecular & solid state structure	218

Two additional experimental studies of note that do not fit cleanly in the above tables are as follows:
   a. an x-ray diffraction study of the cyclic trimer of Me_2NBH_2 shows the molecule to be a 6-member ring with repeating B-N atoms in a chair configuration.[219]
   b. an x-ray absorption fine structure spectroscopy and ^{11}B NMR study of the rhodium-catalyzed dehydrogenation of dimethylamine-borane.[220]

A number of lists of NMR chemical shifts and coupling constants for various B-N-H compounds are available. Table 9 provides a chronological summary.

Table 9. Lists of NMR data for B-N-H compounds.

NMR	Types of compounds included in list	Ref.
^{11}B	Mainly inorganic plus a few amine-boranes	221
^{11}B	Good list with additional amine-boranes and aminoboranes	222
^{1}H	Borazine plus various substituted borazines	223
^{11}B	AB plus the three methylamine-boranes	224
^{1}H	Substituted borazines	225
^{11}B	Various amine-boranes plus a comparison with ^{13}C values for the analogous alkanes	226, 227
^{1}H	B-substituted amine-boranes	228
^{15}N	AB and trimethylamine-borane	229
^{11}B	A few amine-boranes and aminoboranes along with an extensive listing of organoboron compounds	230
^{11}B	Primary and secondary alkylamine-boranes	231

Finally, this survey of physical properties can not be complete without at least a mention that a number of excellent experimental studies clearly established the structure of the diammoniate of diborane.[20, 196, 232-238]

5. Theoretical Studies

For the past 50+ years, chemists and theoreticians have found N-B-H compounds to be particularly interesting. Efforts continue to date at exploring the many unusual structures using high level *ab initio* quantum computations. The various N-B-H compounds present challenging aspects that test the reliability of current *ab initio* programs to account for experimental data. No attempt will be made in this section to cover any of this work in detail. Table 10 simply provides a list of many of these studies in chronological order.

Table 10. Theoretical studies on B-N-H compounds.

Compound(s)[a]	Focus of study	Ref.
Borazine	UV spectra	239
Borazine	Diamagnetic anisotropy	213
AB, borazine, etc.	B-N compounds compared to C analogs	240
Borazine	π-electron system	241
AB	Electronic structure	242
Borazine	π-electron density compared to ^{11}B ^{14}N NMR	243
Me-borazines	Electronic spectra & ionization potentials	244
AB	Potential surfaces & molecular properties	245
AB	Internal rotation barrier	246, 247
AB	Electronic structure & heat of formation	248
H_2NBH_2	Electronic structure	249
AB	Internal rotation barrier	250, 251
AB	Rotational barrier & structure	252, 253
AB	Electronic structure	254
AB	Electronic fields, diamagnetic shielding, dipole moment & diamagnetic susceptibility	255
H_2NBH_2 & AB	Geometry, stability & charge distribution	256
AB, MAB & TMAB	Electron donor-acceptor interaction energies	257
AB	Complexation energy	258-260
$(B-N)_x$ various	π-electron conjugation	261
AB	Various physical properties	262
Borazine, etc.	Bond order approach to aromaticity[b]	263
Borazine	Electronic & structural properties	266
Borazine	Electronic excitation & π-electron interaction	267
AB & DD	Symmetric & asymmetric cleavage of diborane	268
H_2NBH_2	Potential energy surfaces	269
AB	Geometry & energy	270
H_nNBH_n (n=1,2,3)	Equilibrium geometrics & vibrational frequencies	271
AB & TMAB	B-N bond length & formation energy	272
Borazine	Electronic structure	273
AB, etc.	Covalent vs. dative bonds, a discussion	274
AB	B-N bond length	275
Borazine	Aromaticity relative to benzene	276

Table 10. (continued)

AB, MAB, DMAB & TMAB	Enthalpies of formation	277
AB	Rotational barrier & electric field gradients	174
H_2NBH_2	Formation from ammonia and diborane	278
AB	Bond energies, dipole moment, vibrational frequencies & rotational barrier	279
Borazine & TMB	Magnetic anisotropies & charge distributions	280
H_2NBH_2	Formation from ammonia and diborane	281
AB	Binding energy	282
AB & TMAB	Geometries & bonding energies	283
Borazine	Energetics of prismane analog	284
AB	Geometry & binding energy	285
AB	Dihydrogen bonding	286
AB	Geometry & binding energy	287
$B_2H_6 + NH_3$	Reaction mechanism	288
AB	Donor-acceptor interactions	289
AB & F-AB	Substitution effects on binding energy, etc.	290
Borazine	Magnetic properties & ring current	291
AB & various NBH	Thermochemical values	292
AB, etc.	Stability of borane-adduct complexes	293
AB	Dihydrogen bonding	294
Borazine	Aromaticity	295
AB, MAB, DMAB & TMAB	Geometrics & complexation energies	296
AB	Dihydrogen bonding	297
AB, F-AB & Cl-AB	Structure, bonding & stability	298
AB	Dihydrogen bonding	299
AB & M-AB	Substitution effects on binding energy, etc.	300
Borazine, etc.	Structural aspects of aromaticity	301
AB	Dipole-bound anion in a charge-transfer adduct	302
Borazine	Protonation & methylation of aromatic?	303
AB, TMAB, etc.	Polarization & charge-transfer effects	304
AB	Dihydrogen bonding	305
AB	Gas/solid phase structural differences	306
Borazine	Structure & stability	307
AB, etc.	Structural aspects of donor-acceptor interactions	308
AB	B-N stretching frequency in solid state	309
AB	dihydrogen bonding in solid state	310
AB	Charge transfer in donor-acceptor adduct	311
AB	Proton affinity & structure of cation	312
AB	Dihydrogen bonding	313

[a] AB is ammonia-borane, MAB is methylamine-borane, TMAB is trimethylamine-borane, DD is the diammoniate of diborane, DMAB is dimethylamine-borane, TMB is N-trimethylborazine, F-AB is various fluoro-substituted ammonia-borane complexes, Cl-AB is various chloro-substituted ammonia-borane complexes, M-AB is all possible methyl-substituted ammonia-borane complexes. [b] For a more recent discussion and calculations of what defines aromaticity, see references 264 and 265.

6. Chemical Properties

AB and most amine-borane complexes that are prepared from 1°, 2° and 3° alkylamines are inert to oxygen and moisture in the air. These materials can generally be stored indefinitely at room temperature. As discussed previously, AB and the amine-borane

complexes prepared from 1° and 2° alkylamines liberate hydrogen upon heating and all amine-boranes can be forced to react with active hydrogen-containing chemicals under the right conditions with generation of hydrogen. Finally, any B-H containing compound can be expected to act as a reducing agent when allowed to react under certain conditions.

All of these chemical reactions will now be discussed in more detail with an emphasis in this section on processes that result in new B-N containing products. If a chemical property of a B-N-H compound is used to prepare a new organic, then the reaction will be included in the section on synthetic applications.

<u>Hydrolysis plus Related Reactions</u>

Only amine-borane complexes with N-arylamines[112, 314] and N-(bulky)alkylamines[315-317] are hydrolyzed by water and alcohols. Most other amine-borane adducts are unaffected by hydrolytic solvents at neutral pH after many hours at room temperature.[112] Hydrolysis does occur in a strong acid medium and rapidly goes to completion at ambient temperature if the amine-borane adduct is water soluble (eq 28).[112]

$$R_3NBH_3 + HCl + 3H_2O \xrightarrow[25\,°C]{ethylene\ glycol} B(OH)_3 + R_3NHCl + 3H_2 \quad (28)$$
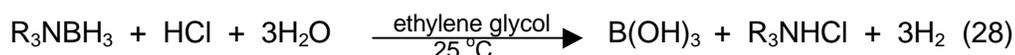
The above reaction is not as simple as depicted. Both the acid catalyzed and uncatalyzed hydrolysis of a number of amine-borane adducts was studied kinetically by a few investigators to better understand the mechanism.[318-323] The reaction is proposed to involve the formation of an activated complex as the rate-determining step where nitrogen has some degree of bonding to both the entering H^+ and leaving BH_3.[323] The BH_3 is believed to exist as a solvated and highly reactive intermediate.[323]

Tertiary amine-borane complexes are formed when tertiary amides are reduced with Me_2SBH_3 and aqueous HCl at 100 °C is used to achieve complete hydrolysis in a short time period.[165]

During a study of the slow acidic hydrolysis of trimethylamine-borane, it was discovered that the hydrogens in B-H exchange with the protons in the solvent faster than they hydrolyze to give hydrogen gas.[324] If excess D_2O is used in the presence of DCl, then this process can be used to give good yields of the BD_3 adduct (eq 29).[324]

$$Me_3NBH_3 + 3D_2O \xrightarrow[excess\ D_2O,\ 25\,°C]{DCl} Me_3NBD_3 + 3DOH \quad (29)$$
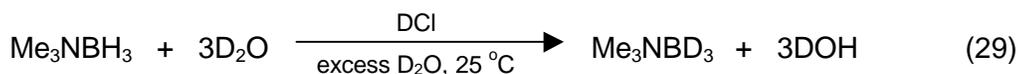
Subsequently, this exchange reaction was used as the first step in a procedure to prepare sodium borodeuteride (eq 30).[325]

$$4Me_3NBD_3 + 3NaOMe \xrightarrow[120-150\,°C]{Diglyme} 3NaBD_4 + 4Me_3N + B(OMe)_3 \quad (30)$$
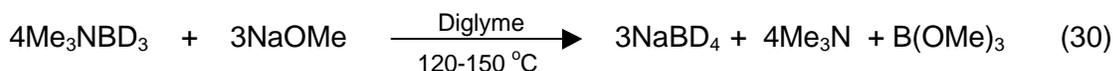
A study of the exchange of hydrogen in borazine with various deuterium-containing compounds showed that D_2 and B_2D_6 only exchange with B-H and ND_3 only exchanges with N-H.[326] Similarly, the reaction of B_2H_6 with excess ND_3 does not result in the contamination of the excess ND_3 with protons.[327]

A reaction related to hydrolysis is the conversion of trimethylamine-borane into trialkylthioborates at 100 °C in 65-70% yield(eq 31).[328]

$$Me_3NBH_3 \ + \ 3RSH \ \longrightarrow \ (RS)_3B \ + \ Me_3N \ + \ 3H_2 \qquad (31)$$
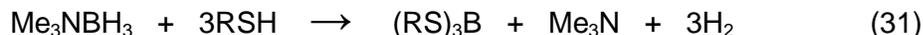
The relatively harsh conditions required for the complete hydrolysis of stable 3° amine-boranes provided an incentive to develop a mild procedure to free the amine from the amine-borane intermediate that results from borane reduction of amides.[329] The process involves simply treating the complex with a catalyst in methanol (eq 32).

$$R_3NBH_3 \ + \ 3MeOH \ \xrightarrow[\text{room temp}]{\text{Pd or Ni/Al}} \ R_3N \ + \ B(OMe)_3 \ + \ 3H_2 \qquad (32)$$
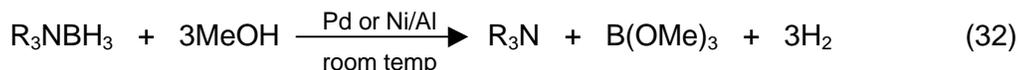
When applied to AB, complete methanolysis occurred in 0.2hr in the presence of 10% Pd/C but was only 24% complete after 60 days in MeOH alone.[329] A recent article described a similar metal-catalyzed hydrolysis of AB at room temperature (eq 33).[5] Also, the use of ion exchange resins in the acid form or even simply CO_2 result in the complete hydrolysis of AB at room temperature.[6]

$$H_3NBH_3 \ + \ 2H_2O \ \xrightarrow[\text{room temp}]{\text{Pt or Pd}} \ NH_4BO_2 \ + \ 3H_2 \qquad (33)$$

Aminoboranes and borazines are sensitive to atmospheric moisture and any source of hydrolytic hydrogen. Only a limited amount of work is reported on these systems as summarized below:
   a. Borazine reacts with excess MeOH at room temperature to give a 1:3 adduct, $B_3N_3H_3$-3MeOH, that probably contains the fragment H-N-B-OMe which loses hydrogen upon heating to give ammonia plus $B(OMe)_3$.[330]
   b. Acid-catalyzed methanolysis of N-trimethylcyclotriborazane produces a B-OMe product at 0° C.[331]
   c. Cyclotriborazane is unaffected by ice-cold water if diethyl ether is absent.[332]

Finally, N-trialkylborazines are assumed to be the intermediate in the borane reduction of organonitriles, and the amine-HCl is obtained in high yield upon hydrolysis with methanolic HCl (eq 34).[165]

$$[(RCH_2)NBH]_3 \ + \ 3HCl \ + \ 3MeOH \ \longrightarrow \ 3RCH_2NH_3Cl \ + \ B(OMe)_3 \ + \ 3H_2 \qquad (34)$$

Thermolysis

Various thermolysis processes were previously mentioned in the synthesis section. A few additional studies will now be covered. The thermal decomposition of AB and polymeric H_2NBH_2 was studied by thermogravimetry, differential thermal analysis and decomposition product measurements to better define the chemical steps in the decomposition reaction.[25, 333, 334] An old patent reports that the pyrolysis of monoisopropylaminoborane at 250-350 ^oC gives a polymer along with loss of one equivalent of hydrogen.[335] A recent study reports that hydrogen is released from AB at a relatively low temperature when the AB is infused in nanoporous silica.[336] Also, the purity of the generated hydrogen is greatly improved. Both the lower temperature and the hydrogen purity are promising developments for the potential use of AB as a chemical hydrogen storage material for fuel cell applications.[336]

An investigation of the elimination of H_2 from Me_2NHBH_3 at 100 ^oC gave results that rule out a unimolecular process and favor a bimolecular reaction.[337]

The decomposition of borazine and borazine derivatives has been studied for many years. As noted previously, borazine is thermally unstable and must be stored at or below 4 ^{o}C. The pyrolysis of gaseous borazine at 340-440 ^{o}C in an all-glass cell gives hydrogen plus nonvolatile polycyclic B-N solids.[338] Similar B-N ring compounds were found in the products formed during the room temperature decomposition of liquid borazine.[339] Interestingly, both N-trimethylborazine and B-trimethylborazine appear to be completely stable in the gas phase at 450 ^{o}C.[340]

Simply heating liquid borazine at moderate temperatures under vacuum results in a dehydrocoupling reaction to produce polyborazylene as a soluble polymer in excellent yields.[62, 341] This polymer provides a useful precursor to boron nitride.[342]

<u>Halogenation Reactions</u>

The reaction of various halogenation reagents with N-B-H compounds provides routes to the corresponding N-B-X compounds where X = F, Cl, Br or I. Specific examples are given in equations 35-43.

$$Me_3NBH_3 + (CH_2CO)_2N\text{-}Cl \xrightarrow[\text{reflux}]{\text{Benzene}} Me_3NBH_2Cl + (CH_2CO)_2NH \qquad (35)^{[343]}$$
$$\text{65-70\%}$$

$$Me_3NBH_3 + (CH_2CO)_2N\text{-}Br \xrightarrow[\text{reflux}]{\text{Benzene}} Me_3NBH_2Br + (CH_2CO)_2NH \qquad (36)^{[343]}$$
$$\text{65-70\%}$$

$$2Me_3NBH_3 + I_2 \longrightarrow 2Me_3NBH_2I \qquad (37)^{[344]}$$

$$Me_3NBH_3 + 2SOCl_2 \longrightarrow Me_3NBHCl_2 + S + SO_2 + 2HCl \qquad (38)^{[345]}$$
$$\text{73\%}$$

$$Me_3NBH_3 + HCl \longrightarrow Me_3NBH_2Cl + H_2 \qquad (39)^{[346]}$$
$$\text{94\%}$$

$$Me_3NBH_3 + HBr \longrightarrow Me_3NBH_2Br + H_2 \qquad (40)^{[346]}$$
$$\text{94\%}$$

$$Me_3NBH_3 + Br_2 \longrightarrow Me_3NBHBr_2 + HBr \qquad (41)^{[347]}$$
$$\text{95\%}$$

$$Me_3NBH_3 + HF \longrightarrow Me_3NBH_2F + H_2 \qquad (42)^{[348]}$$

$$Me_3NBH_3 + (C_6H_5)_3C\text{-}Cl \longrightarrow Me_3NBH_2Cl + (C_6H_5)_3C\text{-}H \qquad (43)^{[349]}$$
$$\text{72\%}$$

In addition to the above examples, the reaction of tert-butylamine-borane with HF and HCl to give the corresponding amine-monohaloborane has been reported,[350] and detailed procedures for B-halogenation of TMED-2BH$_3$ using HCl, HBr and Br2 are available.[351] When the reaction with a chloramine is extended to a 2° amine-borane, the initially formed products continue to react to give a boron cation type of final product (eq 44).[352]

$$Me_2NHBH_3 + Me_2N\text{-}Cl \longrightarrow Me_2NHBH_2Cl + Me_2NH \longrightarrow [(Me_2NH2)BH_2]^+ \ Cl^- \qquad (43)^{[349]}$$
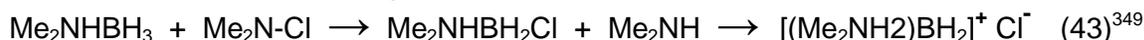
The reaction of borazine with HCl gives a 1:3 adduct which is reported to be B-trichlorocyclotriborazane.[353] Extension of this reaction to N-trimethylborazine gives an analogous B-trichloro compound, which is converted to B-trichloro-N-trimethylborazine plus hydrogen upon heating at 165 ^{o}C.[354] The direct reaction of HCl with N-trimethylcyclotriborazane can be controlled to give either the B-monochloro or B-dichloro products.[331]

Finally, B-halogenation of AB has been studied by NMR.[355] The ammonia-haloborane products were prepared by the reaction of AB with BF_3, BCl_3 and BBr_3.

Reduction

The use of amine-boranes as reducing agents for organic functional groups will be covered in the section on synthetic applications. N-B-H compounds can also be used to reduce metal salts. An early report on the properties of pyridine-borane states that this complex reduces silver nitrate to Ag(0) and Fe(III) to Fe(II).[121] The reaction of borazine with a variety of silver(I) salts gives the corresponding B-monosubstituted borazine (see equation 44, where X = -CN, -OCN, -SCN, CH_3CO_2- or CH_3SO_3-).[356]

$$H_3N_3B_3H_3 \ + \ AgX \ \longrightarrow \ H_3N_3B_3H_2X \ + \ Ag \ + \ \tfrac{1}{2}H_2 \qquad (44)$$
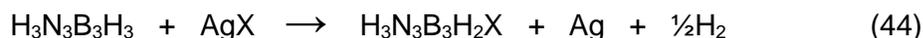
Aminoborohydride Reagents

Hutchins prepared sodium dimethylaminoborohydride (eq 45) and studied the reducing properties of this reagent.[357]

$$Me_2NHBH_3 \ + \ NaH \ \longrightarrow \ Na(Me_2NBH_3) \ + \ \tfrac{1}{2}H_2 \qquad (45)$$

Singaram reasoned that the corresponding lithium salt would be a more powerful reducing agent and prepared a number of reagents from 2° amine-boranes (eq 46).[358-361] A recent review covers the chemistry of these lithium aminoborohydride reagents.[362]

$$R_2NHBH_3 \ + \ n\text{-BuLi} \ \longrightarrow \ Li(R_2NBH_3) \ + \ n\text{-Butane} \qquad (46)$$
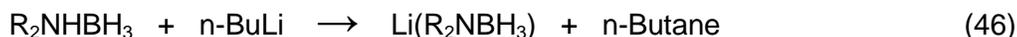
Myers extended equation 46 to AB and reported that $Li(H_2NBH_3)$ is a superior reagent for the reduction of 3° amides to 1° alcohols.[363] Later he reported that this reagent can be prepared by reacting AB with lithium diisopropylamide (eq 47).[364]

$$H_3NBH_3 \ + \ LiN(CHMe_2)_2 \ \longrightarrow \ Li(H_2NBH_3) \ + \ (Me_2CH)_2NH \qquad (46)$$
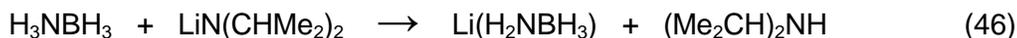
Lewis Base Exchange

Both electronic and steric effects can influence the stability of a Lewis base-borane complex. For example, trimethylamine forms a more stable adduct with BH_3 than does pyridine.[365] Also, this chemical property can be used to convert the more reactive borane-THF and borane-SMe_2 complexes to amine-borane adducts, see section on synthesis. When BH_3 is the reference acid, the base strength of Me_3P is greater than that of Me_3N,[366] which provides a synthetic route to a variety of organophosphine-borane complexes (eq 47).[45]

$$Et_3NBH_3 \ + \ R_3P \ \longrightarrow \ R_3PBH_3 \ + \ Et_3N \qquad (47)$$
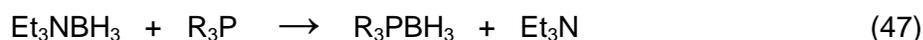
The direct reaction of diamines with borane-THF or borane-SMe$_2$ gives only the bisborane adduct.[110,111,113] However, it is possible to prepare the monoborane adduct by dissolving the bisborane complex in excess diamine.[367, 368] In the case of TMED, the monoborane adduct is unstable above its mp of -3 $^{\circ}$C and disproportionates back to the bisborane adduct (eq 48)[367] while the monoborane adduct of triethylenediamine is stable at temperatures up to 100 $^{\circ}$C.[368]

$$2(Me_2NC_2H_4NMe_2)BH_3 \quad \longrightarrow \quad Me_2NC_2H_4NMe_2 \; + \; H_3B(Me_2NC_2H_4NMe_2)BH_3 \qquad (48)$$

Miscellaneous

The following table provides a summary of a number of additional reactions and studies.

Table 11. Miscellaneous reactions and studies of N-B-H compounds

Compound(s)[a]	Reaction and/or Study	Ref.
Me$_2$NBH$_2$	Disproportionation	369
Pyridine-borane	Single-bridged compound with additional BH$_3$	370
Me$_3$NBH$_2$R	Rx with NH$_3$ to give B-trialkylborazine	371
TRB	Rx with Grignard reagents to give B-substitution	372
Me$_2$NBH$_2$	Vapor phase polymerization with MeNH$_2$	373
Borazine	Photochemical Rx with O$_2$, H$_2$O and NH$_3$	374
Borazine	Photochemical Rx with MeOH	375
Borazine	Photochemical exchange with deuterium	376
Borazine	Photolysis with HCl, CH$_3$Cl, CHCl$_3$, etc. to give B-Cl	377
Borazine	H$_2$NBH$_2$ monomer via radiofrequency discharge in vapor phase	378
Borazine	Photolysis in gas phase	379
TMB	Photochemical Rx with H$_2$	380
AB	Rx with NH$_3$ to give (H$_2$N)$_2$BH in low yield	381
Borazine	Electrophilic substitution in gas phase	382, 383

[a] TRB is N-trialkylborazine, TMB is N-trimethylborazine, AB is ammonia-borane.

7. Synthetic Applications

The use of amine-borane complexes for selective reductions and as hydroboration reagents was last reviewed in 1999.[10] This section will only cover the more recent reports plus a few reports of the synthetic applications for N-B-H compounds other than amine-borane adducts.

Preceramic precursors containing Al-N-B linkages can be produced from the reaction of AB with Me$_3$NAlH$_3$ followed by treatment with NH$_3$.[384] Another application of amine-borane adducts that does not fit in the following subsections is the regioselective metallation of benzylamine-borane complexes.[385] This reaction was studied in detail and the intermediate benzylic anion was reacted with a wide range of electrophiles to give good yields of the substitution product.[385]

Selective Reductions

N-Ethyl-N-isopropylaniline-borane is reported to be a superior reagent for selective reductions in THF at room temperature.[314] Simple aldehydes, ketones, carboxylic acids

and aliphatic esters are cleanly reduced to alcohols. Under similar conditions, acid chlorides, anhydrides and aromatic carboxylic esters are unreactive. Imines, tertiary amides and nitriles are reduced to the corresponding amines, but primary and secondary amides and nitro groups are not reduced. The reduction of esters, amides and nitriles is often slow at room temperature, but becomes reasonably fast when the reaction mixture is heated to reflux.[314] tert-Butyldialkylamine-borane adducts show similar reactivity for selective reductions.[315]

Recently, a number of investigators reported selective reductions using an amine-borane complex in the presence of an active metal catalyst as summarized in table 12.

Table 12. Selective reductions using amine-borane plus metal catalyst.

Amine-borane	Catalyst	Group reduced	Product	Ref.
Me_2NHBH_3	Pd	Allyl carbamates	Amines[a]	386
Me_2NHBH_3	Pd	Monoepoxides of diene-esters	Homoallylic alcohols	387
Me_3NBH_3	Pd	Nitrobenzenes	Anilines	388
$t-BuNH_2BH_3$	Pd	Arylalkene/alkyne	Arylalkane	389
Me_2NHBH_3	Ni	Aryl chloride	Aryl-H	390
Me_2NHBH_3	Rh	Alkene	Alkane	391

[a] Useful method for removal of an amine protecting group in solid-phase peptide synthesis.

Hydroborations

The use of various amine-borane adducts as hydroboration reagents is well documented and the older literature is covered in the most recent review.[10] Borazine can also be used as a hydroboration reagent when catalyzed by rhodium.[62, 392-395] Hydroboration (HB) of acetylene with borazine gives B-vinylborazine,[62, 392] HB of alkynes gives trans-B-alkenylborazines[393] and HB of alkenes gives B-alkylborazines.[394, 395]

Recently, a large number of aryl- and "bulky" alkylamine-borane adducts were investigated as convenient and mild HB reagents. Table 13 provides a listing of the studies.

Table 13. Amine-borane hydroboration reagents.

Amine-borane adduct	Reference
N, N-Dialkylaniline-borane	396, 397
N-Ethyl-N-isopropylaniline-borane	314, 398
N,N-Diisopropylalkylamine-borane	115, 316, 399
N,N-Dialkyl-tert-butylamine-borane	315, 400
N,N-Dialkyl-tert-alkylamine-borane	317
Trialkylsilylamine-borane	401, 402

Finally, Vedejs reports that pyridine-monoiodoborane is a convenient reagent for room temperature HB of alkenes and alkynes.[403]

8. Industrial Applications

The use of amine-borane complexes for various industrial applications was last reviewed in 1973.[8] This section will only cover the subsequent reports and patents, which are summarized in table 14.

Table 14. Industrial applications of N-B-H and related materials.

Material/mixture	Application	Ref.
$NaBH_4$ & hydrazine sulfate	Combustible composition for H_2 generation	404
$LiBH_4$ & hydrazine-2HCl	Combustible composition for H_2 generation	405
$NaBH_4$ & hydrazine-2HCl	Combustible composition for H_2 generation	406
B_2H_6, NH_3 & H_2	Chemical vapor deposition (CVD) BN film	407
B_2H_6 & NH_3	Reactive plasma deposition of BN film	408
$NaBH_4$ & ammonium salts	Solid propellant for H_2 generation	409
Water soluble amine-borane	Plating of gold	114
AB, Fe2O3 & $NaBH_4$	Solid propellant for H_2 generation	410
$MeNH_3B_3H_8$, Si & Al	Solid propellant for H_2 generation	411
B_2H_6 & NH_3	Chemical vapor deposition of BN film	412
AB, Al & Ni	Solid propellant for H_2 generation	413
Hydrazine-bisborane	Solid propellant for H_2 generation	39
AB, etc.	Solid propellant for H_2 generation	414
Polyborazines	Ceramic precursors	341, 415
Tertiary amine-borane adducts	Epoxy curing agents	125
Poly(B-alkenylborazine)	Ceramic precursors	416
Borazine oligomer	Carbon fiber/BN composite	417
Borazine	CVD of BN nanotubes	418

9. Conclusions

The possible use of boron hydrides for chemical hydrogen storage is just the most current in a long line of government funded projects involving B-H compounds. During World War II a National Defense Research Committee contract was initiated at the University of Chicago under the direction of Schlesinger and Brown with the initial goal to prepare volatile compounds of uranium.[419] Since aluminum and beryllium borohydride were already known to be the most volatile compounds of these metals, the proposal was to prepare uranium borohydride. The goal was never accomplished, but the research did lead to the development of improved processes for the preparation of $NaBH_4$ and B_2H_6, which are used today (with only minor modifications) as the basis for the commercial manufacture of both of these chemicals in the USA. Unfortunately, the full results of these projects carried out at the University of Chicago during the war were not made public until a series of eleven articles appeared in 1953.[419, 420] This work lead to the next major government funded project which occurred during the Cold War.

In the mid to late 1950's a concerted effort was made to develop a boron-hydride-based high-energy fuel for jets and rockets.[421] This was code-named Project Hermes by the US Army and Project Zip by the US Navy. Both projects funded many academic investigations and the industrial partners even built pilot-scale production plants.[421] The goal of a boron-based high-energy fuel for jets was never accomplished, but the research

did result in a wealth of technical information about the chemistry of boron hydrides, which was ultimately made public in the 1960's.[422]

Again we are faced with a project where boron hydrides could hold the key to success. However, we must learn from our past mistakes. One of the most serious mistakes during the high-energy fuels projects was the rush to achieve results at the expense of safety. This resulted in a total of five major accidents with eight people being killed.[421] All of these accidents could have been prevented. We must not allow safety to be compromised during our work on Chemical Hydrogen Storage.

10. References

(1)   http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/32405b15.pdf
(2)   Section V.A.1 in
        http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/33098_sec5.pdf
(3)   Jacoby, M. *Chem. Eng. News* **2004**, *82*(January 5), 22-25.
(4)   Schneider, D. *Am. Scient.* **2005**, *93*, 410-411.
(5)   Chandra, M.; Xu, Q. *J. Power Sources* **2006**, in press1.
(6)   Chandra, M.; Xu, Q. *J. Power Sources* **2006**, in press2.
(7)   (a) http://www.osha.gov/SLTC/healthguidelines/diborane/recognition.html (b)
        Rozendaal, H. M. *Indust. Hyg. Occup. Med.* **1951**, *4*, 257-260. (c) *Boron Hydrides*;
        Data Sheet 508, National Safety Council: Chicago, 1961. (d) *Properties and
        Essential Information for Safe Handling and Use of Boron Hydrides*; Chemical
        Safety Data Sheet SD-84, Manufacturing Chemists Association: Washington, DC,
        1961.
(8)   Lane, C. F. *Aldrichimica Acta* **1973**, *6*, 51-58.
(9)   Hutchins, R. O.; Learn, K.; Nazer, B.; Pytlewski, D.; Pelter, A. *Org. Prep. Proc. Int.*
        1984, *16*, 335-372.
(10)   Carboni, B.; Monnier, L. *Tetrahedron* **1999**, *55*, 1197-1248.
(11)   Geanangel, R. A.; Shore, S. G. *Prep. Inorg. React.* **1966**, *3*, 123-238.
(12)   Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73-91.
(13)   Paetzold, P. *Pure & Appl. Chem.* **1991**, *63*, 345-350.
(14)   Fisher, L. S.; McNeil, K.; Butzen, J.; Holme, T. A. *J. Phys. Chem. B* **2000**, *104*,
        3744-3751.
(15)   http://minerals.usgs.gov/minerals/pubs/commodity/boron/120495.pdf
(16)   http://minerals.usgs.gov/minerals/pubs/commodity/boron/boronmyb03.pdf
(17)   http://minerals.usgs.gov/minerals/pubs/commodity/boron/boronmyb04.pdf
(18)   Parry, R. W. *J. Chem. Ed.* **1997**, *74*, 512-518.
(19)   Shore, S. G.; Boddeker, K. W.; Patton, J. A. *Inorg. Syn.* **1967**, *9*, 4-9.
(20)   Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8-12.
(21)   Beres, J.; Dodds, A.; Morabito, A. J.; Adams, R. M. *Inorg. Chem.* **1971**, *10*, 2072-
        2074.
(22)   Mayer, E. *Inorg. Chem.* **1972**, *11*, 866-869.
(23)   Mayer, E. *Inorg. Chem.* **1973**, *12*, 1954-1955.
(24)   Hu, M. G.; Van Paasschen, J. M.; Geanangel R. A. *J. Inorg. Nucl. Chem.* **1977**, *39*,
        2147-2150.
(25)   Hu, M. G.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta.* **1978**, *23*, 249-
        255.
(26)   Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta.* **1987**, *113*, 383-385.
(27)   Kuznesof, P. M.; Shriver, D. F.; Stafford, F. E. *J. Am. Chem. Soc.* **1968**, *90*, 2557-
        2560.
(28)   Aardahl, C. L. Pacific Northwest National Laboratory, personal communication.

(29)   Gorr, K. Aldrich Chemical Company, personal communication.
(30)   BASF, MSDS for PYB.
(31)   Test N.3 in sub-section 33.3 of Division 4.2 of the UN Regulations gives the test method for classification of a liquid as pyrophoric for shipping.
(32)   Test Method B in EPA Method 1050 for classification of hazardous waste gives a procedure for determining if a liquid is pyrophoric, see http://www.epa.gov/epaoswer/hazwaste/test/pdfs/1050.pdf
(33)   Standard Operating Procedure for Analysis of Borane Ammonia Complex, Aldrich Chemical Company, 1994.
(34)   Sarafin, J. R. Aldrich Chemical Company, personal communication.
(35)   Parry, R. W.; Schultz, D. R.; Girardot, P. R. *J. Am. Chem. Soc.* **1958**, *80*, 1-3.
(36)   Parry, R. W.; Shore, S. G. Book of Abstracts, 210th ACS National Meeting, Chicago, IL, August 1995, Abstract INOR-642.
(37)   Emeleus, H. J.; Stone, F. G. A. *J. Chem. Soc.* **1951**, 840-841.
(38)   Gunderloy, Jr., F. C. *Inorg. Syn.* **1967**, *9*, 13-16.
(39)   Grant, L. R.; Flanagan, J. E. US Patent 4381206, April 26, 1983.
(40)   McCoy, R. E.; Bauer, S. H. *J. Am. Chem. Soc.* **1956**, 7*8*, 2061-2065.
(41)   (a) Alton, E. R.; Brown, R. D.; Carter, J. C.; Taylor, R. C. *J. Am. Chem. Soc.* **1959**, *81*, 3550-3551. (b) Shore, S. G.; Hickam, Jr., C. W.; Cowles, D. *J. Am. Chem. Soc.* **1965**, *87*, 2755-2756.
(42)   Schechter, W. H.; Adams, R. M.; Huff, G. F. US Patent 3122585, February 25, 1964.
(43)   Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun.* **2001**, 962-963.
(44)   Brown, H. C.; Domash, L. *J. Am. Chem. Soc.* **1956**, 7*8*, 5384-5386.
(45)   Baldwin, R. A.; Washburn, R. M. *J. Org. Chem.* **1961**, *26*, 3549-3550.
(46)   Lang, K.; Schubert, F. US Patent 3037985, June 5, 1962.
(47)   Smrz, D. C. Abbott Laboratories, personal communication.
(48)   Kollonitsch, J. *J. Am. Chem. Soc.* **1961**, *83*, 1515.
(49)   Brown, H. C. US Patent 3634277, January 11, 1972.
(50)   Burkhardt, E. R.; Corella, II, J. A. US Patent 6048985, April 11, 2000.
(51)   Reisch, M. *Chem. Eng. News* **2002**, *80*(July 1), 7.
(52)   Dzhelali, A. The Day Newspaper in Groton, CT, personal communication1.
(53)   Dzhelali, A. The Day Newspaper in Groton, CT, personal communication2.
(54)   Callery Chemical Company, Safety Reminder Memo, December 5, 2002.
(55)   BASF, MSDS for BTHF-1M.
(56)   Sigma-Aldrich, MSDS for product 176192.
(57)   Aldrich Chemical Company, Technical Bulletin AL218.
(58)   Sigma-Aldrich, MSDS for product 650390.
(59)   Sigma-Aldrich, MSDS for product 650412.
(60)   Schaeffer, R.; Steindler, M.; Hohnstedt, L.; Smith, Jr., H. S.; Eddy, L. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1954**, *76*, 3303-3306.
(61)   Haworth, D. T.; Hohnstedt, L. F. *J. Am. Chem. Soc.* **1960**, *82*, 3860-3862.
(62)   Wideman, T.; Fazen, P. J.; Lynch, A. T.; Su, K.; Remsen, E. E.; Sneddon, L. G. *Inorg. Syn.* **1998**, *32*, 232-242.
(63)   Miller, N. E.; Chamberland, B. L.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1064-1065.
(64)   Sigma-Aldrich, MSDS for product 287717.
(65)   Sigma-Aldrich, MSDS for product 180238.
(66)   Sigma-Aldrich, MSDS for product 178985.
(67)   BASF, MSDS for TMAB.
(68)   Sigma-Aldrich, MSDS for product 178977.
(69)   BASF, MSDS for TEAB.

(70)   Sigma-Aldrich, MSDS for product 180211.
(71)   BASF, MSDS for TBAB.
(72)   BASF, Technical Data Sheet for TBAB.
(73)   Sigma-Aldrich, MSDS for product 179752.
(74)   BASF, Technical Data Sheet for PYB.
(75)   BASF, MSDS for PYM50wt%.
(76)   Sigma-Aldrich, MSDS for product 180203.
(77)   BASF, MSDS for MPB.
(78)   Sigma-Aldrich, MSDS for product 262323.
(79)   Sigma-Aldrich, MSDS for product 235644.
(80)   Sigma-Aldrich, MSDS for product 253111.
(81)   Sigma-Aldrich, MSDS for product 179043.
(82)   BASF, MSDS for DEANB.
(83)   BASF, Technical Data Sheet for DEANB.
(84)   http://www.aviabor.com
(85)   http://www.aviabor.ru/eng-products.php?id=001-spec
(86)   http://www.boroscience.com
(87)   http://www.boroscience.com/product.htm
(88)   http://www.katchem.cz/about.htm
(89)   http://www.katchem.cz/hydrides.htm#dmab
(90)   http://www.katchem.cz/boranes.htm#borazine
(91)   http://www.gelest.com/company/aboutGelest.asp
(92)   Gelest, MSDS for Borazine.
(93)   Airgas, MSDS for Diborane.
(94)   Sigma-Aldrich, MSDS for product 463051.
(95)   Owen, J. US Borax, personal communication.
(96)   (a) US Borax Library Document 89392. (b) See also, Levinskas, G. J. "Toxicology
        of Boron Compounds." In *Boron, Metallo-Boron Compounds and Boranes*;
        Adams, R. M., Ed.; Interscience: New York, 1964; pp 693-737.
(97)   Callery Chemical Company, Safety Bulletin for Pentaborane.
(98)   Aldrich Chemical Company, Technical Bulletin AL134.
(99)   Aldrich Chemical Company, Technical Bulletin AL123.
(100)   Parry, R. W.; Edwards, L. J. *J. Am. Chem. Soc.* **1959**, *81*, 3554-3560.
(101)   Schaeffer, G. W.; Adams, M. D.; Koenig, F. J. *J. Am. Chem. Soc.* **1956**, *78*, 725-
        728.
(102)   Shore, S. G.; Boddeker, K. W. *Inorg. Chem.* **1964**, *3*, 914-915.
(103)   Beachley, O. T. *Inorg. Chem.* **1965**, *4*, 1823-1825.
(104)   Schlesinger, H. I.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 290-299.
(105)   Storozhenko, P. A.; Svitsyn, R. A.; Ketsko, V. A.; Buryak, A. K.; Ul'yanov, A. V.
        Russ. J. Inorg. Chem. **2005**, *50*, 980-985.
(106)   Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084-6085.
(107)   Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1937**, *59*, 780-787.
(108)   Narula, C. K.; Janik, J. F.; Duesler, E. N.; Paine, R. T.; Schaeffer, R. *Inorg. Chem.*
        1986, *25*, 3346-3349.
(109)   Brown, H. C. US Patent 2860127, November 11, 1958.
(110)   Kelly, H. C.; Edwards, J. O. *J. Am. Chem. Soc.* **1960**, *82*, 4842-4846.
(111)   Moore, R. C.; White, Jr., S. S.; Kelly, H. C. *Inorg. Syn.* **1970**, *12*, 109-115.
(112)   Brown, H. C.; Murray, L. T. *Inorg. Chem.* **1984**, *23*, 2746-2753.
(113)   Brown, H. C.; Singaram, B. *Inorg. Chem.* **1980**, *19*, 455-457.
(114)   Burke, A. R.; Hough, W. V. US Patent 4080381, March 21, 1978.
(115)   Brown, H. C.; Zaidlewicz, M.; Dalvi, P. V.; Narasimhan, S.; Mukhopadhyay, A.
        Organometallics **1999**, *18*, 1305-1309.
(116)   Schaeffer, G. W.; Anderson, E. R. *J. Am. Chem. Soc.* **1949**, *71*, 2143-2145.

(117) Bonham, J.; Drago, R. S. *Inorg. Syn.* **1967**, *9*, 8-12.
(118) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1963**, *85*, 395-397.
(119) Volkov, V. V.; Myakishev, K. G. *Izvest. Sibirsk. Otdel. Akadem. Nauk SSSR, Ser. Khim. Nauk* **1988**, *5*, 140-145 (*Chem. Abst.* **1989**, *110*, 192209).
(120) Kelly, H. C.; Edwards, J. O. *Inorg. Chem.* **1963**, *2*, 226-227.
(121) Taylor, M. D.; Grant, L. R.; Sands, C. A. *J. Am. Chem. Soc.* **1955**, *77*, 1506-1507.
(122) Farbenfabriken Bayer Akt.-Ges. British Patent 822229, October 21, 1959 (*Chem. Abst.* **1960**, *54*, 8634d).
(123) Hinckley, A. A. US Patent 3127448, March 31, 1964.
(124) Matsumura, S.; Tokura, N. *Tetrahedron Lett.* **1968**, *9*, 4703-4705.
(125) Arduengo, A. J. US Patent 5144032, September 1, 1992.
(126) Thorn, D. L. Los Alamos National Laboratory, personal communication.
(127) Camacho, C.; Uribe, G.; Contreras, R. *Synthesis* **1982**, 1027-1030.
(128) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1969**, *8*, 2671-2674.
(129) Hawthorne, M. F. *J. Am. Chem. Soc.* **1958**, *80*, 4291-4293.
(130) Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 831-833.
(131) (a) Ashby, E. C.; Foster, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3407-3408. (b) When this process is applied to dialkylamines under conditions that could lead to dialkylaminoboranes, the actual product is the bis(dialkylamino)borane which can be isolated in high yield, see Kovar, R. A.; Culbertson, R.; Ashby, E. C. *Inorg. Chem.* **1971**, *10*, 900-905.
(132) Pusatcioglu, S. Y.; McGee, Jr., H. A.; Fricke, A. L.; Hassler, J. C. *J. Appl. Polym. Sci.* **1977**, *21*, 1561-1567.
(133) Komm, R.; Geanangel, R. A.; Liepins, R. *Inorg. Chem.* **1983**, *22*, 1684-1686.
(134) Schaeffer, G. W.; Basile, L. J. *J. Am. Chem. Soc.* **1955**, *77*, 331-332.
(135) Denton, D. L.; Johnson, II, A. D.; Hickam, Jr., C. W.; Bunting, R. K.; Shore, S. G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1037-1038.
(136) Dahl, G. H.; Schaeffer, R. *J. Am. Chem. Soc.* **1961**, *83*, 3032-3034.
(137) Boddeker, K. W.; Shore, S. G.; Bunting, R. K. *J. Am. Chem. Soc.* **1966**, *88*, 4396-4401.
(138) Mayer, E. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 343-346.
(139) Bissot, T. C.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 3481-3482.
(140) Beachley, Jr., O. T. *Inorg. Chem.* **1967**, *8*, 870-874.
(141) Brown, M. P.; Heseltine, R. W.; Sutcliffe, L. H. *J. Chem. Soc. (A)* **1968**, 612-616.
(142) Burg, A. B.; Randolph, Jr., C. L. *J. Am. Chem. Soc.* **1949**, *71*, 3451-3455.
(143) Burg, A. B.; Good, C. D. *J. Inorg. Nucl. Chem.* **1956**, *2*, 237-245.
(144) Hahn, G. A.; Schaeffer, R. *J. Am. Chem. Soc.* **1964**, *86*, 1503-1504.
(145) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424-9434.
(146) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 1334-1335.
(147) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776-9785.
(148) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Phos. Sulf. Sil.* **2004**, *179*, 733-736.
(149) Schaeffer, G. W.; Schaeffer, R.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1951**, *73*, 1612-1614.
(150) Dahl, G. H.; Schaeffer, R. *J. Inorg. Nucl. Chem.* **1960**, *12*, 380-381.
(151) Niedenzu, K.; Dawson, J. W. *Inorg. Syn.* **1967**, *10*, 142-144.
(152) Strem Chemicals, Catalog Product # 93-0568.
(153) Brown, C. A.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 3699-3700.
(154) Hough, W. V.; Guibert, C. R.; Hefferan, G. T. US Patent 4150097, April 17, 1979.
(155) Wideman, T.; Sneddon, L. G. *Inorg. Chem.* **1995**, *34*, 1002-1003.
(156) Framery, E.; Vaultier, M. *Heteroatom Chem.* **2000**, *11*, 218-225.
(157) Sneddon, L. G.; Wideman, T. US Patent 5612013, March 18, 1997.

(158) Moon, K.-T.; Min, D.-S.; Kim, D.-P. *Bull. Korean Chem. Soc.* **1998**, *19*, 222-226.

(159) Hough, W. V.; Schaeffer, G. W.; Dzurus, M.; Stewart, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 864-865.

(160) Meller, A.; Schaschel, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 41-43.

(161) Hohnstedt, L. F.; Haworth, D. T. *J. Am. Chem. Soc.* **1960**, *82*, 89-92.

(162) (a) Schlesinger, H. I.; Ritter, D. M.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 1296-1300. (b) A mixture of methylborazines can also be prepared by reacting $NaBH_4$ with a mixture of NH_4Cl and $MeNH_3Cl$, see Beachley, Jr., O. T. *Inorg. Chem.* **1969**, *8*, 981-985.

(163) Bramlett, C. L.; Tabereaux, Jr., A. T. *Inorg. Chem.* **1970**, *9*, 978-979.

(164) Emeleus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614-2617.

(165) Brown, H. C.; Choi, Y. M.; Narasimhan, S. *J. Org. Chem.* **1982**, *47*, 3153-3163.

(166) Hughes, E. W. *J. Am. Chem. Soc.* **1956**, *78*, 502-503.

(167) Lippert, E. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1956**, *78*, 503-504.

(168) Weaver, J. R.; Shore, S. G.; Parry, R. W. *J. Chem. Phys.* **1958**, *29*, 1-2.

(169) Weaver, J. R.; Parry, R. W. *Inorg. Chem.* **1966**, *5*, 713-718.

(170) Suenram, R. D.; Thorne, L. R. *Chem. Phys. Lett.* **1981**, *78*, 157-160.

(171) Smith, J.; Seshadri, K. S.; White, D. *J. Mol. Spec.* **1973**, *45*, 327-337.

(172) Heitsch, C. W. *Inorg. Chem.* **1965**, *4*, 1019-1024.

(173) Lotz, A.; Voitlander, J. D. *J. Mag. Reson.* **1982**, *48*, 1-8.

(174) Penner, G. H.; Daleman, S. I.; Custodio, A. R. *Can. J. Chem.* **1992**, *70*, 2420-2423.

(175) Thorne, L. R.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1983**, *78*, 167-171.

(176) Penner, G. H.; Chang, Y. C. P.; Hutzal, J. *Inorg. Chem.* **1999**, *38*, 2868-2873.

(177) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348-354.

(178) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337-6343.

(179) Trudel, S.; Gilson, D. F. R. *Inorg. Chem.* **2003**, *42*, 2814-2816.

(180) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 3502-3506.

(181) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 3507-3511.

(182) Carpenter, J. D.; Ault, B. S. *Chem. Phys. Lett.* **1992**, *197*, 171-174.

(183) Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta* **1988**, *148*, 185-190.

(184) Colquhoun, H. M.; Jones, G.; Maud, J. M.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Dalton Trans.* **1984**, 63-66.

(185) Alston, D. R.; Stoddart, J. F.; Wolstenholme, J. B.; Allwood, B. L.; Williams, D. J. *Tetrahedron* **1985**, *41*, 2923-2926.

(186) Shaulov, Y. K.; Shmyreva, G. O.; Tubyanskaya, V. S. *Zh. Fiz. Khim.* **1966**, *40*, 122-124 (*Chem. Abst.* **1966**, *64*, 11950a).

(187) Wolf, G.; van Miltenburg, J. C.; Wolf, U. *Thermochim. Acta* **1998**, *317*, 111-116.

(188) Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta* **2000**, *343*, 19-25.

(189) Baitalow, F.; Baumann, J.; Wolf, G.; Jaenicke-Robler, K.; Leitner, G. *Thermochim. Acta* **2002**, *391*, 159-168.

(190) Sugie, M.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* **1979**, *64*, 573-575.

(191) Leavers, D. R.; Long, J. R.; Shore, S. G.; Taylor, W. J. *J. Chem. Soc. A* **1969**, 1580-1581.

(192) Corfield, P. W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 1480-1487.

(193) Geanangel, R. A.; Rabalais, J. W. *Inorg. Chim. Acta* **1985**, *97*, 59-64.

(194) Bauer, S. H. *J. Am. Chem. Soc.* **1937**, *59*, 1804-1812.

(195) Rice, B.; Galiano, R. J.; Lehmann, W. *J. Phys. Chem.* **1957**, *61*, 1222-1226.

(196) Parry, R. W.; Kodama, G.; Schultz, D. R. *J. Am. Chem. Soc.* **1958**, *80*, 24-27.

(197) Cassoux, P.; Kuczkowski, R. L.; Bryan, P. S.; Taylor, R. C. *Inorg. Chem.* **1975**, *14*, 126-129.
(198) Ting, H.-Y.; Watson, W. H.; Kelly, H. C. *Inorg. Chem.* **1972**, *11*, 374-377.
(199) Brown, M. P.; Heseltine, R. W.; Smith, P. A.; Walker, P. J. *J. Chem. Soc. A* **1970**, 410-414.
(200) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2000**, *113*, 9885-9888.
(201) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2001**, *114*, 8877-8879.
(202) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2002**, *116*, 6056-6063.
(203) Patwari, G. N.; Ebata, T.; Mikami, N. *Chem. Phys.* **2002**, *283*, 193-207.
(204) Mooney, E. F.; Qaseem, M. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1439-1446.
(205) Tlahuext, H.; Santiesteban, F.; Garcia-Baez, E.; Contreras, R. *Tetrahedron Asym.* **1994**, *5*, 1579-1588.
(206) Martinez-Aguilera, L. M. R.; Cadenas-Pliego, G.; Contreras, R.; Flores-Parra, A. *Tetrahedron Asym.* **1995**, *6*, 1585-1592.
(207) Flores-Segura, H.; Torres, L. A. *Struct. Chem.* **1997**, *8*, 227-232.
(208) Bauer, S. H. *J. Am. Chem. Soc.* **1938**, *60*, 524-530.
(209) Jacobs, L. E.; Platt, J. R.; Schaeffer, G. W. *J. Chem. Phys.* **1948**, *16*, 116-117.
(210) Eddy, L. B.; Smith, Jr., S. H.; Miller, R. R. *J. Am. Chem. Soc.* **1955**, *77*, 2105-2106.
(211) Ito, K.; Watanabe, H.; Kubo, M. *J. Chem. Phys.* **1960**, *32*, 947-948.
(212) Watanabe, H.; Kubo, M. *J. Am. Chem. Soc.* **1960**, *82*, 2428-2430.
(213) Watanabe, H.; Ito, K.; Kubo, M. *J. Am. Chem. Soc.* **1960**, *82*, 3294-3297.
(214) Niedenzu, K.; Sawodny, W.; Watanabe, H.; Dawson, J. W.; Totani, T.; Weber, W. *Inorg. Chem.* **1967**, *6*, 1453-1461.
(215) Harshbarger, W.; Lee, G.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1969**, *8*, 1683-1689.
(216) Kaldor, A.; Porter, R. F. *Inorg. Chem.* **1971**, *10*, 775-785.
(217) Beachley, Jr., O. T.; Simmons, R. G. *Inorg. Chem.* **1977**, *16*, 2935-2938.
(218) Boese, R.; Maulitz, A. H.; Stellberg, P. *Chem. Ber.* **1994**, *127*, 1887-1889.
(219) Trefonas, L. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1959**, *81*, 4435.
(220) Chen, Y.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254-3255.
(221) Onak, T. P.; Landesman, H.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533-1535.
(222) Phillips, W. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 4496-4500.
(223) Ito, K.; Watanabe, H.; Kubo, M. *J. Chem. Phys.* **1961**, *34*, 1043-1049.
(224) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1964**, *86*, 1505-1507.
(225) Grace, A.; Powell, P. *J. Chem. Soc. A* **1966**, 1468-1471.
(226) Spielvogel, B. F.; Purser, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 5294-5295.
(227) Purser, J. M.; Spielvogel, B. F. *Inorg. Chem.* **1968**, *7*, 2156-2157.
(228) Beachley, Jr., O. T.; Washburn, B. *Inorg. Chem.* **1975**, *14*, 120-123.
(229) Wrackmeyer, B. *J. Mag. Reson.* **1986**, *66*, 172-175.
(230) (a) http://www.chemistry.sdsu.edu/research/BNMR/ (b) Ramachandran, P. V. "Boron NMR as a Tool for Organic Chemistry." In Brown, H. C.; Zaidlewicz, M. *Organic Syntheses via Boranes, Volume 2, Recent Developments*; Aldrich Chemical Company: Milwaukee, 2001; pp 325-358.
(231) Linehan, J. C. Pacific Northwest National Laboratory, personal communication.
(232) Schultz, D. R.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 4-8.
(233) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 12-15.
(234) Parry, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1958**, *80*, 15-20.
(235) Shore, S. G.; Girardot, P. R.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 20-24.
(236) Taylor, R. C.; Schultz, D. R.; Emery, A. R. *J. Am. Chem. Soc.* **1958**, *80*, 27-30.
(237) Nordman, C. E.; Peters, C. R. *J. Am. Chem. Soc.* **1959**, *81*, 3551-3554.

(238) Egan, B. Z.; Shore, S. G. *J. Am. Chem. Soc.* **1961**, *83*, 4717-4720.
(239) Roothaan, C. C. J.; Mulliken, R. S. *J. Chem. Phys.* **1948**, *16*, 118-122.
(240) Hoffmann, R. *J. Chem. Phys.* **1964**, *40*, 2474-2480.
(241) Chalvet, O.; Daudel, R.; Kaufman, J. J. *J. Am. Chem. Soc.* **1965**, *87*, 399-404.
(242) Veillard, A.; Levy, B.; Daudel, R.; Gallais, F. *Theoret. Chim. Acta* **1967**, *8*, 312-318.
(243) Hensen, K.; Messer, K. P. *Theoret. Chim. Acta* **1967**, *9*, 17-25.
(244) Kuznesof, P. M.; Shriver, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 1683-1688.
(245) Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1968**, *49*, 312-325.
(246) Moireau, M.-C.; Veillard, A. *Theoret. Chim. Acta* **1968**, *11*, 344-357.
(247) Veillard, A. *Chem. Phys. Lett.* **1969**, *3*, 128-130.
(248) Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1969**, 1044-1048.
(249) Armstrong, D. R.; Duke, B. J.; Perkins, P. G. *J. Chem. Soc. A* **1969**, 2566-2572.
(250) Gordon, M. S.; England, W. *Chem. Phys. Lett.* **1972**, *15*, 59-64.
(251) Palke, W. E. *J. Chem. Phys.* **1972**, *56*, 5308-5312.
(252) Gropen, O.; Seip, H. M. *Chem. Phys. Lett.* **1974**, *25*, 206-208.
(253) Armstrong, D. R.; Perkins, P. G. *Inorg. Chim. Acta* **1974**, *10*, 77-82.
(254) Fujimoto, H.; Kato, S.; Yamabe, S.; Fukui, K. *J. Chem. Phys.* **1974**, *60*, 572-578.
(255) Dixon, M.; Palke, W. E. *J. Chem. Phys.* **1974**, *61*, 2250-2254.
(256) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402-3409.
(257) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 7208-7220.
(258) Ahlrichs, R.; Koch, W. *Chem. Phys. Lett.* **1978**, *53*, 341-344.
(259) Redmon, L. T.; Purvis III, G. D. ; Bartlett, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 2856-2862.
(260) Zirz, C.; Ahlrichs, R. *J. Chem. Phys.* **1981**, *75*, 4980-4982.
(261) Haddon, R. C. *Pure & Appl. Chem.* **1982**, *54*, 1129-1142.
(262) Binkley, J. S.; Thorne, L. R. *J. Chem. Phys.* **1983**, *79*, 2932-2940.
(263) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344-1348.
(264) Schleyer, P. v. R.; Jiao, H. *Pure & Appl. Chem.* **1996**, *68*, 209-218.
(265) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669-12670.
(266) Boyd, R. J.; Choi, S. C.; Hale, C. C. *Chem. Phys. Lett.* **1984**, *112*, 136-141.
(267) Doering, J. P.; Gedanken, A.; Hitchcock, A. P.; Fischer, P.; Moore, J.; Olthoff, J. K.; Tossell, J.; Raghavachari, K.; Robin, M. B. *J. Am. Chem. Soc.* **1986**, *108*, 3602-3608.
(268) Purcell, K. F.; Devore. D. D. *Inorg. Chem.* **1987**, *26*, 43-48.
(269) Drewello, T.; Koch, W.; Lebrilla, C. B.; Stahl, D.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 2922-2924.
(270) McKee, M. L. *Inorg. Chem.* **1988**, *27*, 4241-4245.
(271) Brint, P.; Sangchakr, B.; Fowler, P. W. *J. Chem. Soc. Faraday Trans 2* **1989**, *85*, 29-37.
(272) Hirota, F.; Miyata, K.; Shibata, S. *J. Mol. Struct. (Theochem)* **1989**, *201*, 99-111.
(273) Cooper, D. L.; Wright, S. C.; Gerratt, J.; Hyams, P. A.; Raimondi, M. *J. Chem. Soc. Perkin Trans 2* **1989**, 719-724.
(274) Haaland, A. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992-1007.
(275) Buhl, M.; Steinke, T.; Schleyer, P. v. R.; Boese, R. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1160-1161.
(276) Fink, W. H.; Richards, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 3393-3398.
(277) Sana, M.; Leroy, G.; Wilante, C. *Organometallics* **1992**, *11*, 781-787.
(278) McKee, M. L. *J. Phys. Chem.* **1992**, *96*, 5380-5385.
(279) Holme, T. A.; Truong, T. N. *Chem. Phys. Lett.* **1993**, *215*, 53-57.
(280) Dennis, G. R.; Ritchie, G. L. D. *J. Phys. Chem.* **1993**, *97*, 8403-8409.
(281) Sakai, S. *Chem. Phys. Lett.* **1994**, *217*, 288-292.
(282) Glendening, E. D.; Streitwieser, A. *J. Chem. Phys.* **1994**, *100*, 2900-2909.

(283) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741-8753.
(284) Matsunaga, N.; Gordon, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 11407-11419.
(285) Bauschlicher, Jr., C. W.; Ricca, A. *Chem. Phys. Lett.* **1995**, *237*, 14-19.
(286) Richardson, T. B.; de Gala, S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 12875-12876.
(287) Branchadell, V.; Sbai, A.; Oliva, A. *J. Phys. Chem.* **1995**, *99*, 6472-6476.
(288) Sakai, S. *J. Phys. Chem.* **1995**, *99*, 9080-9086.
(289) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352-9362.
(290) Skancke, A.; Skancke, P. N. *J. Phys. Chem.* **1996**, *100*, 15079-15082.
(291) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997**, *101*, 1409-1413.
(292) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem. A* **1997**, *101*, 2670-2680.
(293) Anane, H.; Boutalib, A.; Tomas, F. *J. Phys. Chem. A* **1997**, *101*, 7879-7884.
(294) Cramer, C. J.; Gladfelter, W. L. *Inorg. Chem.* **1997**, *36*, 5358-5362.
(295) Jemmis, E. D.; Kiran, B. *Inorg. Chem.* **1998**, *37*, 2110-2116.
(296) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomas, F. *Chem. Phys. Lett.* **1998**, *287*, 575-578.
(297) Popelier, P. L. A. *J. Phys. Chem. A* **1998**, *102*, 1873-1878.
(298) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomas, F. *J. Phys. Chem. A* **1998**, *102*, 7070-7073.
(299) Kulkarni, S. A. *J. Phys. Chem. A* **1998**, *102*, 7704-7711.
(300) Anane, H.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomas, F. *J. Mol. Struct. (Theochem)* **1998**, *455*, 51-57.
(301) Madura, I. D.; Krygowski, T. M.; Cyranski, M. K. *Tetrahedron* **1998**, *54*, 14913-14918.
(302) Barrios, R.; Skurski, P.; Rak, J.; Gutowski, M. *J. Chem. Phys.* **2000**, *113*, 8961-8968.
(303) Kiran, B.; Phukan, A. K.; Jemmis, E. D. *Inorg. Chem.* **2001**, *40*, 3615-3618.
(304) Mo, Y.; Gao, J. *J. Phys. Chem. A* **2001**, *105*, 6530-6536.
(305) Li, J.; Zhao, F.; Jing, F. *J. Chem. Phys.* **2002**, *116*, 25-32.
(306) Merino, G.; Bakhmutov, V. I.; Vela, A. *J. Phys. Chem. A* **2002**, *106*, 8491-8494.
(307) Timoshkin, A. Y.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 60-69.
(308) Horvath, V.; Kovacs, A.; Hargittai, I. *J. Phys. Chem. A* **2003**, *107*, 1197-1202.
(309) Dillen, J.; Verhoeven, P. *J. Phys. Chem. A* **2003**, *107*, 2570-2577.
(310) Morrison, C. A.; Siddick, M. M. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 4780-4782.
(311) Mo, Y.; Song, L.; Wu, W.; Zhang, Q. *J. Am. Chem. Soc.* **2004**, *126*, 3974-3982.
(312) Patwari, G. N. *J. Phys. Chem. A* **2005**, *109*, 2035-2038.
(313) Meng, Y.; Zhou, Z.; Duan, C.; Wang, B.; Zhong, Q. *J. Mol. Struct. (Theochem)* **2005**, *713*, 135-144.
(314) Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M. *J. Org. Chem.* **1998**, *63*, 5154-5163.
(315) Brown, H. C.; Kanth, J. V. B.; Dalvi, P. V.; Zaidlewicz, M. *J. Org. Chem.* **1999**, *64*, 6263-6274.
(316) Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M. *Organometallics* **1999**, *18*, 1310-1317.
(317) Brown, H. C.; Kanth, J. V. B.; Dalvi, P. V.; Zaidlewicz, M. *J. Org. Chem.* **2000**, *65*, 4655-4661.
(318) Hawthorne, M. F.; Lewis, E. S. *J. Am. Chem. Soc.* **1958**, *80*, 4296-4299.
(319) Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 3290-3294.
(320) Kelly, H. C.; Marchelli, F. R.; Giusto, M. B. *Inorg. Chem.* **1964**, *3*, 431-437.
(321) Kelly, H. C. *Inorg. Chem.* **1966**, *5*, 2173-2176.
(322) Kelly, H. C.; Underwood, III, J. A. *Inorg. Chem.* **1969**, *8*, 1202-1204.
(323) Kelly, H. C.; Marriott, V. B. *Inorg. Chem.* **1979**, *18*, 2875-2878.
(324) Davis, R. E.; Brown, A. E.; Hopmann, R. ; Kibby, C. L. *J. Am. Chem. Soc.* **1963**, *85*, 487.

(325) Atkinson, J. G.; MacDonald, D. W.; Struart, R. S.; Tremaine, P. H.; *Can. J. Chem.* **1967**, *45*, 2583-2588.

(326) Dahl, G. H.; Schaeffer, R. *J. Am. Chem. Soc.* **1961**, *83*, 3034-3037.

(327) Burg, A. B. *J. Am. Chem. Soc.* **1947**, *69*, 747-750.

(328) Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 1345-1347.

(329) Couturier, M.; Tucker, J. L.; Andresen, B. M.; Dube, P.; Negri, J. T. *Org. Lett.* **2001**, *3*, 465-467.

(330) Haworth, D. T.; Hahnstedt, L. F. *J. Am. Chem. Soc.* **1959**, *81*, 842-844.

(331) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1963**, *85*, 3592-3594.

(332) Shore, S. G.; Hickam, C. W. *Inorg. Chem.* **1963**, *2*, 638-640.

(333) Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta.* **1985**, *86*, 375-378.

(334) Sit, V.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta.* **1987**, *113*, 379-382.

(335) Hough, W. V.; Schaeffer, G. W. US Patent 2809171, October 8, 1957.

(336) Gutowska, A.; Li, L.; Shin, Y.; Wang, C. M.; Li, X. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 2-6.

(337) Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Chem.* **1970**, *9*, 314-317.

(338) Laubengayer, A. W.; Moews, Jr., P. C.; Porter, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 1337-1342.

(339) Mamantov, G.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1961**, *20*, 348-351.

(340) Newsom, H. C.; English, W. D.; McCloskey, A. L.; Woods, W. G. *J. Am. Chem. Soc.* **1961**, *83*, 4134-4138.

(341) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, *2*, 96-97.

(342) Fazen, P. J.; Remsen, E. E.; Beck, J. S.; Carroll, P. J.; McGhie, A. R.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 1942-1956.

(343) Douglass, J. E. *J. Org. Chem.* **1966**, *31*, 962-963.

(344) (a) Ryschkewitsch, G. E.; Garrett, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4240-4241. (b) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1968**, *7*, 1316-1319. (c) Ryschkewitsch, G. E.; Garrett, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 7234-7238.

(345) Wiggins, J. W.; Ryschkewitsch, G. E. *Inorg. Chim. Acta* **1970**, *4*, 33-39.

(346) Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Syn.* **1970**, *12*, 116-123.

(347) Mathur, M. A.; Ryschkewitsch, G. E. *Inorg. Syn.* **1970**, *12*, 123-127.

(348) VanPaasschen, J. M.; Geanangel, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 2680-2683.

(349) Ryschkewitsch, G. E.; Miller, V. R. *J. Am. Chem. Soc.* **1973**, *95*, 2836-2839.

(350) VanPaasschen, J. M.; Hu, M. G.; Peacock, L. A.; Geanangel, R. A. S*yn. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 11-24.

(351) Hu, M. G.; Geanangel, R. A. *Inorg. Chim. Acta* **1974**, *10*, 83-87.

(352) Miller, V. R.; Ryschkewitsch, G. E.; Chandra, S. *Inorg. Chem.* **1970**, *9*, 1427-1430.

(353) Laubengayer, A. W.; Beachley, Jr., O. T.; Porter, R. F. *Inorg. Chem.* **1965**, *4*, 578-582.

(354) Anderson, G. A.; Lagowski, J. J. *Inorg. Chem.* **1975**, *14*, 1845-1848.

(355) Hu, M. G.; Geanangel, R. A. *Inorg. Chem.* **1979**, *18*, 3297-3301.

(356) Beachley, Jr., O. T. *J. Am. Chem. Soc.* **1971**, *93*, 5066-5069.

(357) Hutchins, R. O.; Learn, K.; El-Telbany, F.; Stercho, Y. P. *J. Org. Chem.* **1984**, *49*, 2438-2443.

(358) Fisher, G. B.; Harrison, J.; Fuller, J. C.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1992**, *33*, 4533-4536.

(359) Fuller, J. C.; Strangeland, E. L.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 257-260.

(360) Fisher, G. B.; Fuller, J. C.; Harrison, J.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 1091-1094.

(361) Fisher, G. B.; Fuller, J. C.; Harrison, J.; Alvarez, S. G.; Burkhardt, E. R.; Goralski, C. T.; Singaram, B. *J. Org. Chem.* **1994**, *59*, 6378-6385.

(362) Pasumansky, L.; Singaram, B.; Goralski, C. T. *Aldrichimica Acta* **2005**, *38*, 61-65.

(363) Myers, A. G.; Yang, B. H.; Kopecky, D. J. *Tetrahedron Lett.* **1996**, *37*, 3623-3626.

(364) Myers. A. G.; Yang, B. H.; Chen, H.; McKinstry, L.; Kopecky, D. J.; Gleason, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6496-6511.

(365) Brown, H. C.; Schlesinger, H. I.; Cardon, S. Z. *J. Am. Chem. Soc.* **1942**, *64*, 325-329.

(366) Graham, W. A. G.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1956**, *3*, 164-177.

(367) Gatti, A. R.; Wartik, T. *Inorg. Chem.* **1966**, *5*, 329-330.

(368) Gatti, A. R.; Wartik, T. *Inorg. Chem.* **1966**, *5*, 2075-2076.

(369) Burg, A. B.; Randolph, Jr., C. L. *J. Am. Chem. Soc.* **1951**, *73*, 953-957.

(370) Brown, H. C.; Stehle, P. F.; Tierney, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 2020-2021.

(371) (a) Hawthorne, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 5836-5837. (b) Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 833-834.

(372) Grace, A.; Powell, P. *J. Chem. Soc. A* **1966**, 673-676.

(373) Brown, M. P.; Heseltine, R. W. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1197-1201.

(374) Lee, II, G. H.; Porter, R. F. *Inorg. Chem.* **1967**, *6*, 648-652.

(375) Nadler, M.; Porter, R. F. *Inorg. Chem.* **1967**, *6*, 1739-1741.

(376) Nadler, M. P.; Porter, R. F. *Inorg. Chem.* **1969**, *8*, 599-604.

(377) Oertel, M.; Porter, R. F. *Inorg. Chem.* **1970**, *9*, 904-907.

(378) Kwon, C. T.; McGee, Jr., H. A. *Inorg. Chem.* **1970**, *9*, 2458-2461.

(379) Neiss, M. A.; Porter, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 1438-1443.

(380) Turbini, L. J.; Mazanec, T. J.; Porter, R. F. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1129-1132.

(381) Briggs, T. S.; Gwinn, W. D.; Jolly, W. L.; Thorne, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 7762-7763.

(382) Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1999**, *121*, 2619-2620.

(383) Chiavarino, B.; Crestoni, M. E.; Marzio, A. D.; Fornarini, S.; Rosi, M. *J. Am. Chem. Soc.* **1999**, *121*, 11204-11210.

(384) Dou, D.; Ketchum, D. R.; Hamilton, E. J. M.; Florian, P. A.; Vermillion, K. E.; Grandinetti, P. J.; Shore, S. G. *Chem. Mater.* **1996**, *8*, 2839-2842.

(385) Ebden, M. R.; Simpkins, N. S.; Fox, D. N. A. *Tetrahedron* **1998**, *54*, 12923-12952.

(386) Gomez-Martinez, P.; Dessolin, M.; Guibe, F.; Albericio, F. *J. Chem. Soc. Perkin Trans 1* **1999**, 2871-2874.

(387) David, H.; Dupuis, L.; Guillerez, M.-G.; Guibe, F. *Tetrahedron Lett.* **2000**, *41*, 3335-3338.

(388) Couturier, M.; Tucker, J. L.; Andresen, B. M.; Dube, P.; Brenek, S. J.; Negri, J. T. *Tetrahedron Lett.* **2001**, *42*, 2285-2288.

(389) Couturier, M.; Andresen, B. M.; Tucker, J. L.; Dube, P.; Brenek, S. J.; Negri, J. T. S. *Tetrahedron Lett.* **2001**, *42*, 2763-2766.

(390) Lipshutz, B. H.; Tomioka, T.; Pfeiffer, S. S. *Tetrahedron Lett.* **2001**, *42*, 7737-7740.

(391) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2698-2699.

(392) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 5867-5868.

(393) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201-6209.

(394) Fazen, P. J.; Sneddon, L. G. *Organometallics* **1994**, *13*, 2867-2877.

(395) Wille, A. E.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1996**, *35*, 5101-5103.

(396) Brown, H. C. US Patent 5543569, August 6, 1996.

(397) Brown, H. C.; Zaidlewicz, M.; Dalvi, P. V. *Organometallics* **1998**, *17*, 4202-4205.

(398) Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M. *Tetrahedron* **1999**, *55*, 5991-6000.

(399) Brown, H. C. US Patent 5481038, January 2, 1996.

(400)   Brown, H. C. US Patent 6248885 B1, June 19, 2001.

(401)   Soderquist, J. A.; Medina, J. R.; Huertas, R. *Tetrahedron Lett.* **1998**, *39*, 6119-6122.

(402)   Soderquist, J. A.; Huertas, R.; Medina, J. R. *Tetrahedron Lett.* **1998**, *39*, 6123-6126.

(403)   Clay, J. M.; Vedejs, E. *J. Am. Chem. Soc.* **2005**, *127*, 5766-5767.

(404)   Hiltz, R. H. US Patent 3666672, May 30, 1972.

(405)   Beckert, W. F.; Dengel, O. H.; McKain, R. W. US Patent 3734863, May 22, 1973.

(406)   (a) Beckert, W. F.; Dengel, O. H.; McKain, R. W. US Patent 3862052, January 21, 1975. (b) Beckert, W. F.; Dengel, O. H.; McKain, R. W. US Patent 3931395, January 6, 1976.

(407)   Hirayama, M.; Shohno, K. *J. Electrochem. Soc.* **1975**, *122*, 1671-1676.

(408)   Hyder, S. B.; Yep, T. O. *J. Electrochem. Soc.* **1976**, *123*, 1721-1724.

(409)   (a) Chew, W. M.; Ayers, O. E.; Murfree, J. A.; Martignoni, P. US Patent 4061512, December 6, 1977. (b) Chew, W. M.; Ayers, O. E.; Murfree, J. A.; Martignoni, P. US Patent 4064225, December 20, 1977.

(410)   Chew, W. M.; Murfree, J. A.; Martignoni, P.; Nappier, H. A.; Ayers, O. E. US Patent 4157927, January 12, 1979.

(411)   Flanagan, J. E. US Patent 4166843, September 4, 1979.

(412)   Adams, A. C.; Capio, C. D. *J. Electrochem. Soc.* **1980**, *127*, 399-404.

(413)   English, W. D.; Chew, W. M. US Patent 4315786, February 16, 1982.

(414)   Artz, G. D.; Grant, L. R. US Patent 4468263, August 28, 1984.

(415)   Blum, Y. D.; Laine, R. M. US Patent 4801439, January 31, 1989.

(416)   (a) Sneddon, L. G.; Lynch, A. T. US Patent 5202399, April 13, 1993. (b) Sneddon, L. G.; Lynch, A. T. US Patent 5489707, February 6, 1996.

(417)   Kim, D.; Economy, J. *Chem. Mater.* **1993**, *5*, 1216-1220.

(418)   Lourie, O. R.; Jones, C. R.; Bartlett, B. M.; Gibbons, P. C.; Ruoff, R. S.; Buhro, W. E. *Chem. Mater.* **2000**, *12*, 1808-1810.

(419)   (a) Schlesinger, H. I.; Brown, H. C.; Abraham, B.; Bond, A. C.; Davidson, N.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H.; Horvitz, L.; Hyde, E. K.; Katz, J. J.; Knight, J.; Lad, R. A.; Mayfield, D. L.; Rapp, L.; Ritter, D. M.; Schwartz, A. M.; Sheft, I.; Tuck, L. D.; Walker, A. O. *J. Am. Chem. Soc.* **1953**, *75*, 186-190. (b) For a summary of this work, see pp 41-49 in Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.

(420)   (a) Schlesinger, H. I.; Brown, H. C.; Abraham, B.; Davidson, N.; Finholt, A. E.; Lad, R. A.; Knight, J.; Schwartz, A. M. *J. Am. Chem. Soc.* **1953**, *75*, 191. (b) Brown, H. C.; Schlesinger, H. I.; Sheft, I.; Ritter, D. M. *J. Am. Chem. Soc.* **1953**, *75*, 192-195. (c) Schlesinger, H. I.; Brown, H. C.; Gilbreath, J. R.; Katz, J. J. *J. Am. Chem. Soc.* **1953**, *75*, 195-199. (d) Schlesinger, H. I.; Brown, H. C.; Hoekstra, H. R.; Rapp, L R. *J. Am. Chem. Soc.* **1953**, *75*, 199-205. (e) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E. *J. Am. Chem. Soc.* **1953**, *75*, 205-209. (f) Schlesinger, H. I.; Brown, H. C.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 209-213. (g) Schlesinger, H. I.; Brown, H. C.; Mayfield, D. L.; Gilbreath, J. R. *J. Am. Chem. Soc.* **1953**, *75*, 213-215. (h) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H. R.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 215-219. (i) Schlesinger, H. I.; Brown, H. C. *J. Am. Chem. Soc.* **1953**, *75*, 219-222. (j) Schlesinger, H. I.; Brown, H. C.; Horvitz, L.; Bond, A. C.; Tuck, L. D.; Walker, A. O. *J. Am. Chem. Soc.* **1953**, *75*, 222-224.

(421)   Dequasie, A. *The Green Flame: Surviving Government Secrecy*; American Chemical Society: Washington, DC, 1991.

(422)   (a) *Borax to Boranes*; Advances in Chemistry Series 32; American Chemical Society: Washington, DC, 1961. (b) *Production of the Boranes and Related Research*; Academic Press: New York, 1967.