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BCN-SEQUENCED, VALENCE SATURATED COMPOUNDS. SYNTHESIS AND STRUCTURE *

NORMAN E. MILLER

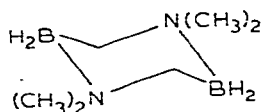
Chemistry Department, University of South Dakota, Vermillion, South Dakota, 57069 (U.S.A.)

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Summary

The synthesis and characterization are presented of a series of compounds having the common structural features of four-coordinate BCN sequences. The discovery of a novel difunctionally substituted borohydride ion, $(\text{CH}_3)_2\text{NCH}_2\text{-BH}_2\text{CH}_2\text{N}(\text{CH}_2)_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2^-$, provides for a more complete understanding of the general synthesis mechanism.

The development of a series of stable compounds with the common structural feature of a saturated BCN sequence began with the first report [2] of the heterocycle I, 2,2,5,5-tetramethyl-1,2,4,5-bis(borazonia)cyclohexane, by the low yield reaction of sodium hydride on the borane cation $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{Cl}^-$.



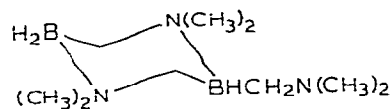
(I)

The structure as originally proposed [2] has been corroborated by other chemical [3,4] and physical studies, including the X-ray structure determination by Hseu and Larsen [5]. A white solid with a camphor-like odor, this compound, hereafter to be designated heterocycle I for simplicity, proved to be exceptionally stable, thermally, up to temperatures near 170°C , and in neutral and aqueous basic solution. Substitution at the boron site leads to stable halogen derivatives [2], so a skeletal sequence has been established which has sufficient ambient integrity to warrant further chemical elaboration.

Further study indeed has led to the synthesis of other members of the series:

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a novel strong base, $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (II) * [6] herein called linear free base; a coordinated lithium derivative $(\text{CH}_3)_2\text{NCH}_2\text{BH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{Li}$ (III) [6], herein called lithium chelate **; and more recently a dimethylaminomethyl derivative of heterocycle I namely, compound IV, hereafter identified as heterocyclic base *** [7].



(IV)

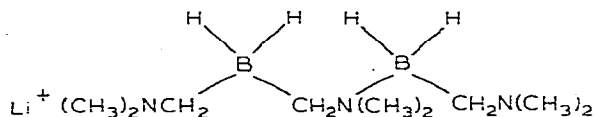
Several other new members have been synthesized, and their isolation and characterization are reported along with new perspectives on the mechanism of synthesis.

Results and discussion

Replacement of sodium hydride by butyllithium in the synthesis of I according to reaction 1 not only improved the yield but also led to several new species



However, the yields are not very high and considerable difficulty is experienced in achieving reproducibility. When the counter anion was changed from chloride to iodide or hexafluorophosphate, no product was isolated. Change to the different alkyl lithium, *t*-butyllithium, however, made a remarkable difference in the results and permitted reproducible, good yields of I, II, or III depending on conditions. From the non-volatile solid pot residue, previously known with butyllithium as an uncharacterizable viscous oil, a new reactive member of the BCN-sequenced series was isolated by solvent extraction. It is identified chemically and physically as a disubstituted lithium borohydride salt soluble in hexane, benzene, ether, and water (V). This salt, called herein lithium amino-



(V)

borohydride †, is a fusible, air-sensitive white solid with an odor characteristic of unstable borohydrides.

Reaction of the borane salt $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{Cl}^-$ with a molar equivalent of *t*-butyllithium occurs in a heterogeneous mixture in hexane with stirring at room temperature for 12 h. Product isolation by fractional condensation and

* A systemic name for this compound which does not obscure the amine functionality is (trimethylamineborylmethyl)dimethylamine.

** (Lithiomethyl dimethylamineborylmethyl) dimethylamine.

*** 1-Dimethylaminomethyl-2,2,5,5-tetramethyl-1,2,4,5-bis(boratazonia)cyclohexane.

† μ -C,N-Dimethylaminomethylbis(dimethylaminomethyldihydroborate)(1-).

TABLE 1
PRODUCT AND YIELD DEPENDENCE ON STOICHIOMETRY

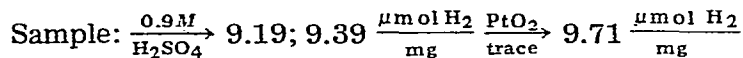
t-BuLi/B	Product	Yield (%)
1	linear free base	35
	aminoborohydride	54
2	lithium chelate	60

solvent extraction typically gives yields of 43% lithium aminoborohydride (V) and 28% linear free base II, with recovery of 20% unreacted borane cation, and a trace of heterocyclic I. Based on consumed boron reagent, the yields were 54, and 35%, respectively. If a twice molar equivalent of t-butyllithium is used, a 60% yield of lithium chelate III is isolated (Table 1).

Characterization of lithium aminoborohydride (V)

Structural assignment for V is based upon analyses, neutralization equivalent, spectra, and chemical conversions. Dissolution of V in water gives a basic solution sufficiently stable to titrate under a blanket of nitrogen. A measured equivalent weight of 108 is in modest agreement with 103.5 theory, and about as good as might be expected considering the decomposition evidenced by onset of bubbling at pH 7, see Fig. 1.

A more definitive analysis is that for hydrolytic hydrogen which proceeds in two steps. One-half of the hydrolytic hydrogen is liberated by contact with acid, and the second half is released on addition of platinum black:



Theory: $9.67 \frac{\mu\text{mol } H_2}{\text{mg}}$ for each step

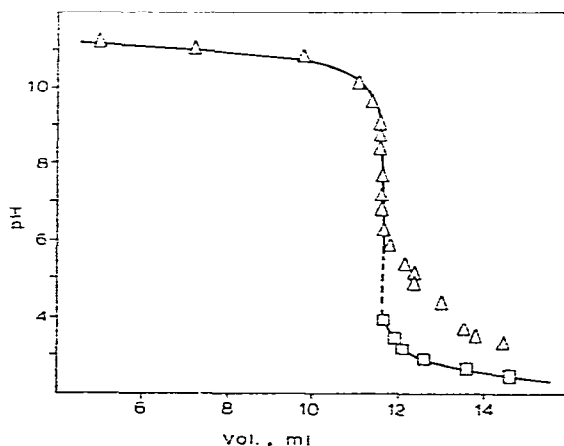
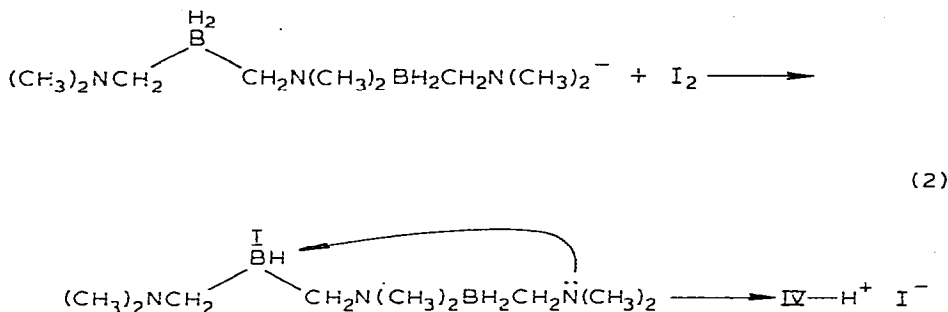


Fig. 1. Titration of aminoborohydride V with 0.1012 M HCl. Δ observed, \square calculated for strong acid—strong base titration.

The structure proposed for V has the requisite chemically different BH environments: one ($\text{NCH}_2\text{BH}_2\text{CH}_2\sim$) relatively unhindered and chemically much like borohydride, an ion known to hydrolyze in acid [8], and one ($\sim\text{N}(\text{CH}_3)_2\text{BH}_2\text{CH}_2-$) like that in I and II which are known to require platinum catalysis [6].

Elemental analyses are concordant with the empirical structure, and the infrared spectrum shows the absorption at 2800 cm^{-1} characteristic of $-\text{N}(\text{CH}_3)_2$ groups [9]. ^1H NMR data are not helpful in establishing structures because of peak overlapping.

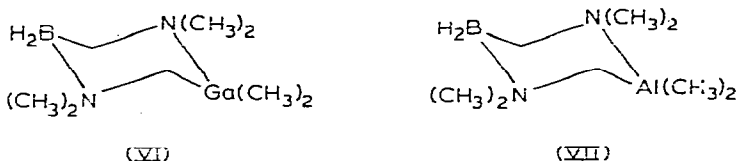
Key evidence for structure V is the chemical conversion of V into the proton salt of heterocyclic base IV. About one molar equivalent of iodine (I_2) reacts with V to produce a high yield >80% of the salt of IV (eq. 2).



Molecular weight measurement by cryoscopy in benzene supports association, possibly to a dimer form. The solution structure in poorly polar solvents for an ionic species like V would understandably be complicated by association.

Heteroatom replacement in I

Two new heterocyclic compounds with BCN sequences and structures like heterocycle I were made by simple reaction of lithium chelate III with dimethylaluminum iodide and dimethylgallium chloride (VI and VII). Hydrolytic



stability of the gallium compound permitted handling in the open atmosphere; the aluminum analogue was reactive toward water, however, a typical difference for gallium and aluminum alkyls [10].

Characterization of lithium chelate III

Further characterization of III not presented in the early report [6] include, elemental analyses (Table 2), solution molecular weight, and ^1H NMR spectrum (Table 3).

Molecular weight measurements of 288 and 285 were obtained, respectively,

TABLE 2
CHARACTERIZATION AND ANALYSES OF BCN SEQUENCED COMPOUNDS

Species	Physical properties	Analyses (Found (calcd.)) (%)			
		C	H	N	
I	$[\text{H}_2\text{BCH}_2\text{N}(\text{CH}_3)_2]_2$	a	a	a	a
II	$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	b	b	b	b
III	$\text{LiCH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	52.3 (53.0)	13.7 (13.3)	20.0 (20.6)	
IV	$(\text{CH}_3)_2\text{NCH}_2\text{BHCH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	c	c	c	c
V	$\text{Li}^+(\text{CH}_3)_2\text{NCH}_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2^-$	52.7 (52.2)	13.8 (13.6)	19.3 (20.3)	
VI	$\text{H}_2\text{BCH}_2\text{N}(\text{CH}_3)_2\text{Ga}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2$	42.6 (42.0)	11.6 (10.6)	12.8 (12.2)	
VII	$\text{H}_2\text{BCH}_2\text{N}(\text{CH}_3)_2\text{Al}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2$	49.4 (51.6)	12.8 (13.0)	8.0 (15.0)	

^a Analyses previously reported, ref. 1. ^b Analyses previously reported, ref. 3. ^c Analyses previously reported, ref. 6. ^d Reactive compound not obtained in purified state.

by cryoscopy and vapor pressure depression in benzene. As the theoretical molecular weight of structure III is 136.0, association to a dimer is documented. No proposal is forwarded about the mode of dimerization though several explanations are plausible.

Proton NMR

Resonances for compounds I–VI, collected in Table 3, are for the most part reasonably accounted by the structures proposed. The broad, low intensity BCH_2 proton peaks make it difficult to do more than assign the major structural features. It is of interest to note that the high field, sharp peak in VI at 0.628 above TMS is typical of gallium methyl resonances; it compares well with the 0.27 upfield shift of cyclic dimethylgallium complex of hydroxamide, $(\text{CH}_3)_2\text{-GaON}(\text{CH}_3)\text{CCH}_3\text{O}$ [11].

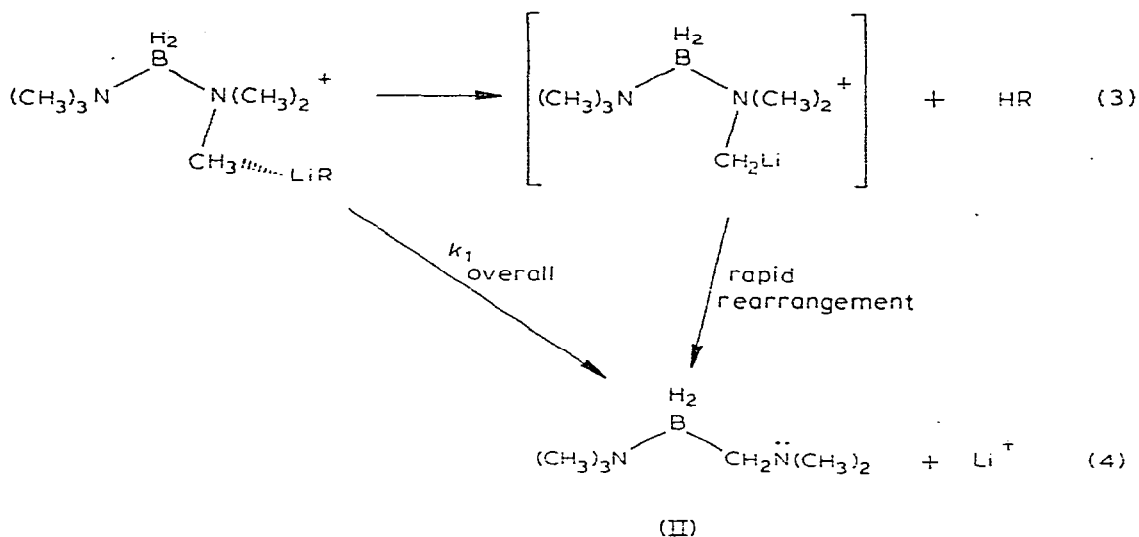
Mechanism for synthesis

The discovery of the aminoborohydride salt V provides for material balances near 90% and suggests a likely mechanism for the synthesis reaction (eq. 3). Original reaction of the borane cation with butyllithium is heterogeneous and observably slow. Products of this reaction are suggested to be lithiomethyl derivatives produced by lithium–hydrogen exchange, and these products are soluble in the hydrocarbon solvent, a notable product being the linear free base II (eq. 4).

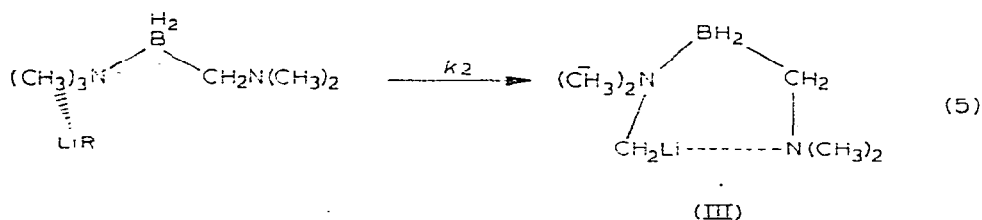
TABLE 3
 ^1H NMR RESONANCES

Compound	Chemical shift ^b	Area ratio
I	in CH_2Cl_2	$\text{N}(\text{CH}_3)_2$
		CH_2
II	as H^+PF_6^- salt, in D_2O	$\text{N}(\text{CH}_3)_2$
		$\text{N}(\text{CH}_3)_3$
III	in C_6D_{12}	$\text{BN}(\text{CH}_3)_2$ 5.4
		$\text{LiN}(\text{CH}_3)_2$ 6.3
		BCH_2 2.2
		LiCH_2 1.6
		ring $\text{N}(\text{CH}_3)_2$ 4.9
IV	in C_6D_{12}	ring $\text{N}(\text{CH}_3)_2$ 5.4
		ring $\text{N}(\text{CH}_3)_2$ 9
		$(\text{CH}_3)_2\text{N}$ substituent 9.3
		CH_2 9.8
		approximately equal
V ^c	in C_6D_{12}	$\text{N}(\text{CH}_3)_2$
VI	in CH_2Cl_2	$-\text{CH}_2-$ broad
		$\text{BN}(\text{CH}_3)_2$ 3
		$\text{GaN}(\text{CH}_3)_2$ 3
		BCH_2 2
		$\text{Ga}(\text{CH}_3)_2$ 3

^a Obtained on Varian A60A and Perkin–Elmer Hitachi R24A Spectrometers. ^b Chemical shifts in ppm downfield from internal tetramethylsilane unless noted otherwise. ^c External reference. ^d Shift upfield from tetramethylsilane.



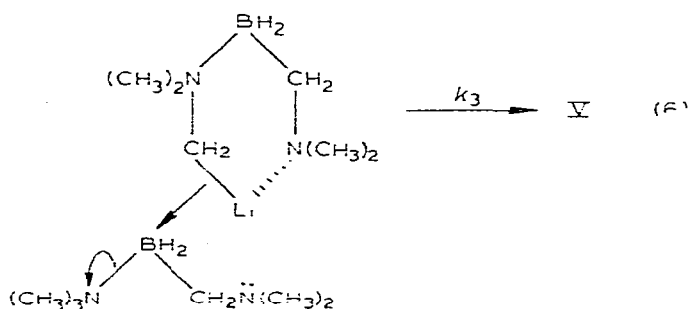
A lithium-hydrogen exchange reaction of II with RLi would be favored by a homogenous reaction but hindered by a lesser positive charge on protons of II relative to borane salt, but it might be expected to proceed to give lithium chelate III (eq. 5).



Exchange at the quaternary nitrogen of II would take place because of larger positive charge of protons as compared to those on the $-\text{CH}_2\text{N}(\text{CH}_3)_2$ moiety, a consequence of the inductive effect of the $(\text{CH}_3)_3\text{NBH}_2-$ group.

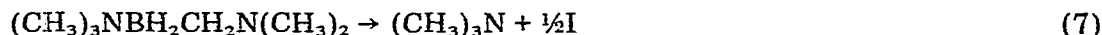
Since some (20%) of starting borane salt is recovered, it is possible to conclude that the lithium-hydrogen interchange between III and the borane cation is not important; rather a concerted attack on II occurs to produce the amino-borohydride V (eq. 6).

That large amounts of linear free base and amino-borohydride V and no chelate



III result from a 1/1 ratio of reactants, whereas good yields of chelate III result from a 2/1 ratio requires comment. If $k_1/k_2 > 1$ is such that all RLi is consumed to produce 0.23 mole equivalent III and 0.54 mole equivalent II, there will be 0.23 mole equivalent unreacted borane cation. The chelate III reacts with II much slower than k_1 , k_2 ($k_3 \ll k_2$) or III would not be produced at the expense of V with larger amounts of RLi in the 2/1 runs. Eventually, in the 1/1 runs, k_3 would produce 0.23 mole V and leave 0.31 mole of II. This result would correspond to 59% yield of V and 40% yield of II based on consumed boron, in concordance with experimental values of 54 and 35%, respectively. When a 2/1 portion of RLi is employed, a nearly quantitative yield of III would be expected apart from a small amount of V. The isolated yield of better than 60% III is in agreement with this suggestion.

The observed increase of yield of II and V and concomitant decrease of I in the presence of trimethylamine appears to be a kinetic inhibition of the decomposition of II noted earlier [4] (eq. 7). This decomposition proceeds to



completion in a closed vessel for neat II; all attempts to reverse it have been negative.

Experimental details

Where required, standard vacuum line procedures were employed [12]. A line equipped with Delmar-Urry O-ring joints and needle stopcocks, with pumping capable of 10^{-5} mmHg noncondensable gas provided for reactions, transfers, and sublimations.

Solvents were reagent grade quality, certain of which were rendered anhydrous by common procedures and kept under vacuum or pure nitrogen in stainless or mild steel containers. Chloroform was purified by distillation from excess phosphorus pentoxide, ether from LiAlH_4 , and hexane from CaH_2 after prolonged shaking with sulfuric acid.

Melting points, uncorrected, were measured on a Thomas-Hoover capillary apparatus. Analyses were commercially obtained from PCR, Gainesville, Florida, and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

t-Butyllithium was used as received in pentane from Foote Mineral Co., Route 100, Exxon, Penn. Concentration was estimated by hydrolysis and titration with standard hydrochloric acid to phenolphthalein end point.

Gallium trichloride was prepared from gallium (Alcoa, 99.99%) and anhydrous hydrogen chloride (prepared from sulfuric acid and sodium chloride) at 200–210°C [13]. Product was sublimed from the hot zone onto a cold surface. Yield was 96% or better.

Trimethylgallium etherate was prepared using a reported procedure from gallium chloride, 7.07 g (20.1 mmol dimer) in 25 ml dry ether, and 60 ml of 3.0 *M* methylmagnesium bromide in ether [14]. Volatiles were removed after reaction and were fractionated in a short path still. The material boiling at 95–98°C and ambient pressure amounted to 6.5 g, 75% yield, of product etherate.

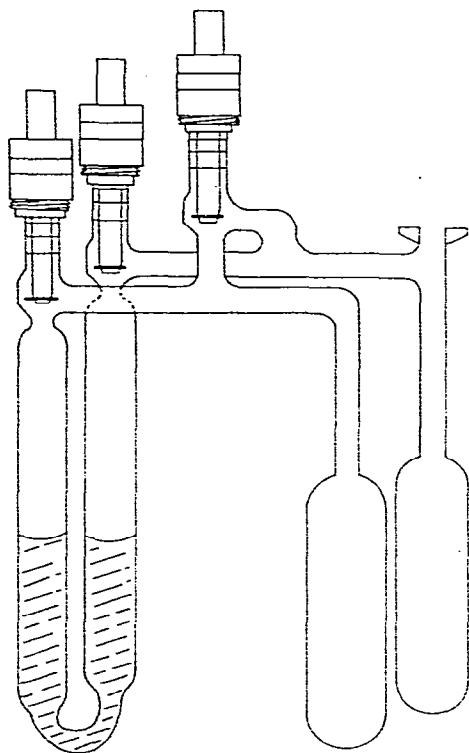
Dimethylaluminum iodide was prepared from 18 g (0.67 mol) of iodine activated aluminum turnings and 140 g (0.99 mol) methyl iodide [15]. After about one-third of the methyl iodide had been introduced, the vigorous reaction was

moderated by cooling with ice. After addition, reflux for 2 h, and filtration, the product was distilled in a short path still. The fraction boiling 171–180°C/100 mmHg was redistilled and the distillate (b.p. 110–113°C/50 mmHg) was collected.

Dimethylgallium chloride was prepared by combining 3.3 g of trimethylgallium etherate and 3.1 g reagent grade aluminum chloride under vacuum. The mixture went to a clear melt with gas evolution. Fractionation through a –30°C U trap gave 1.78 g dimethylgallium chloride (74%, m.p. 45–46°C; lit. [16] (45.3–45.6°C)).

Molecular weights by cryoscopy were obtained in a magnetically stirred solution under rigorous exclusion of moisture. Freezing point depression was measured with a mercury thermometer graduated in 0.10° intervals; temperatures were estimated to nearest 0.01°.

Molecular weights by vapor pressure depression were obtained using a special apparatus incorporating a 15 mm OD, 100 mm high glycerine manometer, see Fig. 2. Both solution and pure solvent reservoirs were magnetically stirred with the same driver and immersed in a dewar of water. Pressures were read with a cathetometer to the nearest 0.1 mm. Mole fraction solute was calculated using Raoult's law, $N_2 = \Delta P/P_0$ where ΔP , P_0 are respectively vapor pressure depression



VAPOR PRESSURE DEPRESSION APPARATUS

Fig. 2. Vapor pressure depression apparatus. Glycerine manometer is 16 mm O.D. Solvent and sample vessels are left and right, respectively.

and vapor pressure of benzene at temperatures of measurement *; $\Delta P = P_g \times 1.26/13.6$, where P_g is the height of glycerine column and 1.26/13.6 is the ratio of glycerine and mercury densities. Trial runs with standards gave reasonable measurements; naphthalene, 133, 132, 133, 138 found, 128.2 calcd.; diphenyl, 151, 156, 159 found, 154.2 calcd. Using hexane as a solvent and a measured 17.2°C vapor pressure of 108.0 mmHg, observed molecular weight for diphenyl was 144, 137 compared to 128.2 theory. This method appears to have some promise in that it avoids thermometers, but in our hands the expected precision and utility are yet to be realized.

Synthesis of gallium and aluminum heterocycles VI, VII

A mixture of 127 mg (0.93 mmol) lithium chelate and 125 mg (0.46 mmol dimer) dimethylgallium chloride was stirred under vacuum for 2 days. Solvent was evacuated via a U-trap cooled to -15°C. Trap contents were dissolved in pentane, and the resulting solution was washed with water, dried over sodium sulfate, and fractionated through a -60°C trap. The white solid (at -60°C) melted to a clear liquid at room temperature; it was identified by NMR and chemical analyses to be VI; yield 48 mg, 23%.

Similarly, the combining of 190 mg (1.40 mmol) lithium chelate III with 260 ± 20 mg (0.71 mmol dimer) dimethylaluminum iodide in 6 ml total pentane led to immediate precipitation. (Accurate matching of reagents required use of 1.7 ml of a solution of 431 mg of aluminum compound contained in 2.8 ml pentane.) After several hours stirring at room temperature, volatile products were fractionated through a -25°C U-trap. The product was a clear liquid at room temperature; it reacted readily with water in contrast to the gallium analogue. Identification as the aluminum heterocycle was made based on elemental analyses and an infrared spectrum which was strikingly similar to that of VI.

Synthesis conditions

A typical preparation using a 1/1 ratio of borane cation and t-butyllithium is described. The reaction vessel is a 50 ml vessel with a side arm that can be fitted with a serum adapter or an O-ring cap, connected to a vacuum line via another O-ring joint **.

A portion of $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{Cl}^-$ *** is placed in the tared reactor containing a magnetic stirring bar. After high vacuum pumping of 4 h at room temperature the mass of anhydrous borane salt is determined by weighing; 3.4706 g (20.82 mmol). About 8 ml of purified hexane are condensed in under vacuum, followed by about 8 mmol trimethylamine. Nitrogen is introduced, and a serum cap adapter is fitted to side-arm. With stirring at room temperature, 16.8 ml (20.8 mmol) of 1.24 M t-butyllithium in pentane is added with a syringe in 15 min. The resulting faintly yellow mixture is allowed to stir overnight, whereupon volatile material is pumped off via a -35°C U-trap. Pumping was continued at room

* Calculated from $\log P$ (mmHg) = $-1784.8/T + 7.9622$ [17].

** See apparatus described in ref. 18.

*** Synthesized by the iodide displacement method; purified via recrystallization as hexafluorophosphate salt; converted to chloride by ion exchange methods. See procedures in ref. 19.

temperature for an hour and then an additional hour at 50°C. Material stopping in the U-trap amounted to 764 mg (5.88 mmol), linear strong base II with a trace of I, as judged by physical properties. The solid residue was treated with about 15 ml dry ether introduced by condensation. Filtration under nitrogen, using an airless O-ring apparatus containing a fritted glass filter, separated 1.381 g of a mixture of unreacted cation (judged from infrared spectrum) and lithium salt (infrared transparent) as insoluble precipitate, and a clear filtrate. Evaporation and subsequent extraction of the crystalline residue with about 15 ml hexane in an airless O-ring filtration apparatus gave 928 mg (4.49 mmol) of crystalline, hexane-soluble, white salt characterized as V, lithium aminoborohydride, m.p. 118–120°C. If the insoluble reaction residue is assumed to be 691 mg lithium chloride (20.8–4.5 mmol) and the remainder cation, namely 690 mg (4.16 mmol), a material balance can be made. Thus 14.9 mmol of boron is incorporated in II and V and another 4.2 mmol remains unreacted, amounting to 19.1 mmol boron accounted, or 92% of original. Yields of 35% II and 54% V are calculated on 16.6 mmol boron consumed. Based on originally charged boron, the yield was 28% and 43% V, with 20% unreacted borane salt recovered.

If the synthesis reaction is carried out without addition of trimethylamine, yields of III and V are reduced to 12 and 18%, respectively, and there is produced about 50% yield of I.

Structure proof of V, reaction with iodine

Iodine in chloroform solution was added dropwise with stirring to V dissolved in chloroform and contained in the synthesis reaction apparatus. The chloroform solution of V, 738 mg in 8 ml, rapidly became opalescent on standing, suggestive of reaction with solvent. Addition of iodine solution, 897 mg in 23 ml chloroform, was stopped when the solution no longer rapidly decolorized. At this stage, 81% of iodine had been added. The mixture contained considerable solid that was removed by filtration; it was hygroscopic and flame tested for lithium and assumed to be LiI. The filtrate left an oil on evaporation under vacuum; on treatment with a small amount of water, 239 mg of the hydrogen iodide salt of IV was separated by filtration. The filtrate on treatment with ammonium hexafluorophosphate gave 536 mg white solid identified as the H^+PF_6^- salt of IV by infrared analysis. In all, 2.28 mmol of protonated IV was obtained, or 79% yield based on iodine consumed (see reaction 2).

Synthesis of lithium chelate III

In a similar manner as the synthesis of V, 1.5228 g (9.21 mmol) of $[(\text{CH}_3)_3\text{N}]_2\text{-BH}_2^+\text{Cl}^-$ was slurried with 4 ml hexane containing about 5 mmol of trimethylamine. Addition of 14.8 ml 1.24 M *t*-butyllithium (9.21 mmol) was made via syringe and the mixture was allowed to stir overnight. Solvent was removed via a -35°C trap; nothing stopped in trap. The reactive residue was transferred to a sublimator and sublimed under high vacuum at 90–110°C to give white, crystalline III, 740 mg (5.48 mmol), or 60% based on boron charged. Infrared analysis was used for identification (Table 4).

Neutralization equivalent of IV

This was determined by titration of 126.8 mg in 50 ml degassed water con-

TABLE 4
INFRARED SPECTRA^a

Species	Absorption ^d (cm ⁻¹)
$(\text{CH}_3)_2\text{NCH}_2\text{BH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{Li}$ chelate III	^b , 2780m, 2350m, 2300–2270w mt(sh), 1325w, 1255–1275m mt, 1180s, 1165s, 1145m, 1110m, 1055w(sh), 1040m, 1010w, 945w, 925vw(sh), 900w, 855s, 750w.
$\text{Li}^+(\text{CH}_3)_2\text{NCH}_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{CH}_2\text{N}(\text{CH}_3)_2^-$ aminoborohydride V	^b , 2120m, 2340(br), 2800s, 1400w, 1297m, 1305w d, 1270m, 1250vw(sh), 1245–1230m dd, 1210m, 1175m, 1165w(sh), 1155s, 1130m, 1110m, 1040m, 1010s, 980m, 935vw, 920vw, 905vw, 875s, 847m, 825w, 755w.
$(\text{CH}_3)_2\text{NCH}_2\text{BH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{Ga}(\text{CH}_3)_2$ gallium heterocycle VI	^c , 2480w, 2350s mt, 2260m d, 1315w, 1280m, 1255vw, 1225m; 1190, 1180s, mt; 1160s, 1140w, 1112m, 1095m, 1038w, 1020w, 1005m, 980m, 970w, 925w, 880m, 865w, 735s, 700m.
$(\text{CH}_3)_2\text{NCH}_2\text{BH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{Al}(\text{CH}_3)_2$ Aluminum heterocycle VII	^c , 2340s mt, 2260m, 1320w, 1285m, 1255w, 1230w, 1190–1180s mt, 1160s, 1140–1130 w d, 1115m, 1100m, 1075vw, 1035m, 1010s, 980m, 930w, 880m, 720m.

^a Recorded on Perkin–Elmer 237B Spectrometer. ^b Mineral oil mulls; absorption masked by mineral oil not listed. ^c Neat. ^d Abbreviations; s, strong; m, medium; w, weak; vw, very weak; (br), broad; (sh) shoulder; d, doublet; mt, multiplet.

tained in a beaker under a nitrogen purge. A combination glass electrode, microburet tip, and long hyperdermic needle nitrogen inlet were fitted to the beaker through a thin polyethylene film cover. Stirring was provided with a magnetic stirring bar. A neutralization equivalent to pH 7 was calculated: 11.612 ml of 0.1012 M HCl required; $NE = 107.9$, compared to 103.5 theory. Decomposition was noticeable near pH 7 as evidenced from bubble formation and deviation of pH versus volume plot (Fig. 1) from calculated values assuming strong base titration. The original pH of 11.6 would require K_1K_2 to be about 10^{-3} , and would mean 98% of base was in the salt form.

Hydrolytic hydrogen assay

A 38.3 mg-sample of V was contained in a small porcelain boat in a side-arm of a 50 ml reactor containing 6 ml of 1.8 M H_2SO_4 . Evacuation to high vacuum was accomplished by repeated cycles of freezing, pumping, thawing. The sample was introduced with a magnetic pusher, and the hydrogen evolved during room temperature stirring for 2 h, followed by mild warming, was Toppler-pumped through a -196°C trap to a calibrated volume. A second, 37.3 mg sample was then introduced and hydrolyzed in the same solution. Hydrolytic values of 9.19 and 9.39 $\mu\text{mol}/\text{mg}$ were determined. Then, a tiny (pinhead) quantity of PtO_2 was introduced via a platinum boat in a similar manner as were the original samples. Brisk hydrogen evolution set in and lasted 0.5 h. After a brief period of warming to 40°C , evolved hydrogen was Toppler-pumped into

measuring volume as before. A hydrolytic volume of 9.71 $\mu\text{mol}/\text{mg}$ was determined.

The observed values agree well with the 9.67 $\mu\text{mol}/\text{mg}$ per step calculated for release of half of the B-H hydrogen in acid and the other half with platinum catalysis. Overall total hydrolytic hydrogen observed was 19.00 $\mu\text{mol}/\text{mg}$ compared to 19.33 $\mu\text{mol}/\text{mg}$ theory.

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