more labile cobalt system. Unfortunately, the kinetic behavior differences reported, although outside of experimental error, are quite small and therefore the reactivity variations are difficult to interpret quantitatively.

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Boron–Nitrogen Compounds. XXXVII.[1a] Synthesis and Characterization of 2-Hydrido-1,3,2-diazaboracycloalkanes

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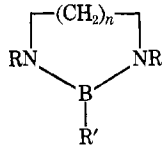
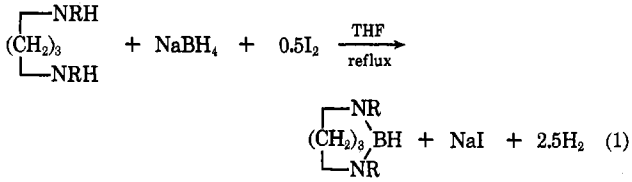
Although 1,3,2-diazaboracycloalkanes, I, have been known for some time, most of these heterocycles which have been prepared have been the *B*-alkyl and -aryl derivatives.[2] A few *B*-chloro compounds have also



I

been synthesized,[3,4] and recently the remaining *B*-halo derivatives have been described.[5] However, only one of the parent compounds with R′ = H has been reported.[6] This latter compound was obtained from a transamination reaction of bis(dimethylamino)borane, $HB[N(CH_3)_2]_2$, with 1,3-diaminopropane. Some similar *B*-hydrido heterocycles have been prepared from the interaction of aromatic diamine monohydrochlorides with sodium tetrahydroborate,[7] but this method failed to give the desired products when aliphatic diamines were treated with $NaBH_4$.

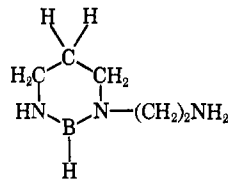
The present work reports on the synthesis of several 2-hydrido-1,3,2-diazaboracyclohexanes by the method illustrated in eq 1 which represents an extension of the procedure of Nainan and Ryschkewitsch[8] for the preparation of borane adducts.



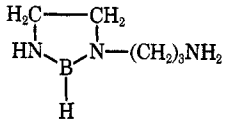
(1)

In an alternate procedure trimethylamine–borane was utilized as source of the borane and was found to serve equally well as sodium tetrahydroborate in the synthesis of 2-hydrido-1,3,2-diazaboracycloalkanes. This latter method yields trimethylamine as a by-product and thus facilitates the purification of the desired heterocycles.

Furthermore, *N*-(ω-aminoethyl)-1,3-diaminopropane, $H_2N(CH_2)_2NH(CH_2)_3NH_2$, was treated with sodium tetrahydroborate. Previously,[9] this same amine had been treated with tris(dimethylamino)borane to yield 1,7,9,8-triazaborahydrindane, IV. In the present work it was possible to isolate a monocyclic intermediate. Two structures, II and III, can be suggested for the intermediate product. However, spectroscopic data clearly substantiate structure II. On heating II to 160° hydrogen is split off and IV is obtained in virtually quantitative yield.



II



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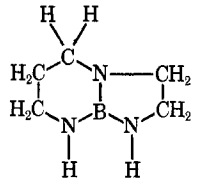

IV

Experimental Section

All diamines used in the present work were obtained from the Ames Laboratories, Milford, Conn.; they were dried over potassium hydroxide and were vacuum distilled before use. Elemental analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra of the materials were recorded on the neat liquids and/or vapor phases on a Perkin-Elmer Model 621 spectrophotometer. Raman spectra of the neat liquids were obtained with a Jarrell-Ash Raman spectrometer equipped with a He–Ne laser as exciting device through the courtesy of Dr. E. B. Bradley, Department of Electrical Engineering, University of Kentucky. Nuclear magnetic resonance spectra were recorded with a Varian HA60-IL and/or Model T-60 spectrometer; mass spectra were provided by the University of Kentucky Mass Spectroscopy Center and were obtained with a Hitachi Perkin-Elmer double-focusing spectrometer, Model RMU-6E.

All experiments were performed under rigorous exclusion of moisture in a prepurified nitrogen atmosphere. The cited yields represent only one or two experiments in most cases and no attempt has been made to improve the yields. Analytical data and physical constants of the products are summarized in Table I.

1,3-Dimethyl-2-hydridodiazaboracyclohexane (Typical Experiment).—*N*,*N*′-Dimethyl-1,3-diaminopropane (10.2 g, 0.10 mol) and sodium borohydride (4.2 g, 0.11 mol) were mixed with 75 ml of dry tetrahydrofuran in a dry, nitrogen-filled flask with a magnetic stirring bar. A solution of iodine (12.7 g, 0.10

(1) (a) Part XXXV: K. Niedenzu, C. D. Miller, and F. C. Nahm, *Tetrahedron Lett.*, **28**, 2441 (1970). Part XXXVI: K. E. Blick, I. A. Boenig, and K. Niedenzu, *Inorg. Chem.*, in press. (b) Postdoctoral Fellow, 1970–1971.

(2) K. Niedenzu and C. D. Miller, *Fortschr. Chem. Forsch.*, **15**, 191 (1970).

(3) M. P. Brown, A. E. Dann, D. W. Hunt, and H. B. Silver, *J. Chem. Soc.*, 4648 (1962).

(4) A. Meller and H. Maracek, *Monatsh. Chem.*, **98**, 2336 (1967).

(5) T. Wang, P. J. Busse, and K. Niedenzu, *Inorg. Chem.*, **9**, 2150 (1970).

(6) K. Niedenzu, P. Fritz, and J. W. Dawson, *ibid.*, **3**, 1077 (1964).

(7) J. Goubeau and H. Schneider, *Justus Liebigs Ann. Chem.*, **675**, 1 (1964).

(8) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **8**, 2671 (1969).

(9) K. Niedenzu and W. Weber, *Z. Naturforsch. B*, **21**, 811 (1966).

TABLE I
2-HYDRIDO-1,3,2-DIAZABORACYCLOHEXANES

No.	Compd	Bp, °C (mm)[a]	% yield	Mol wt Calcd	Mol wt Found[b]	Boron analysis, % Calcd	Boron analysis, % Found	^{1}H nmr data,[c] δ, ppm
1	$H_2C(CH_2NCH_3)_2BH$	116–118 (758)	51	111.98	111	9.73	9.7	1.88 (q, 2H), 2.67 (s, 6H), 2.76 (t, 4H)
2	$H_2C(CH_2NC_2H_5)_2BH$	105 (155)	72	140.04	140	7.75	7.9	1.15 (t, 6H), 1.94 (q, 2H), 2.89 (t, 4H), 3.09 (f, 4H)
3	$CH_3CH(CH_2NCH_3)_2BH$	85 (128)	54	126.01	126	8.60	8.6	1.10 (d, 3H), 2.1 (m, 1H), 2.57 (d, 4H), 2.69 (s, 6H)
4	$H_2C(CH_2NH)_2BH$	102–104 (764)[d]	61	83.93	84	12.93	...	2.00 (q, 2H), 3.27 (x, 4H), 3.6 (s, b, 2H)

[a] Uncorrected. [b] By mass spectroscopy. [c] Neat liquids, external TMS standard. Abbreviations: s, singlet; d, doublet; t, triplet; f, quartet; q, quintuplet; x, sextet; m, multiplet; b, broad. [d] Lit.[5] bp 97–99°.

mol) in 75 ml of dry tetrahydrofuran was slowly added while stirring the mixture. When the addition was completed, the reaction mixture was refluxed for 4 hr. The solution was filtered, removing most of the slightly soluble sodium iodide, and the solvent was distilled off. The remaining product was distilled through a 15-cm Vigreaux column yielding 5.8 g (51%) of product, bp 116–118°.

In a similar manner and by using various α,ω-diamines, the compounds listed in Table I were prepared. The sodium iodide produced was frequently extremely fine and passed the filter. On subsequent distillation some of the desired product remained on the solid. In two cases, no. 2 and 4, the solutions were decanted, leaving behind most of the solid and higher yields of product resulted.

1-(ω-Aminoethyl)-3,2-diazaboracyclohexane (II).—*N*-(ω-Aminoethyl)-1,3-diaminopropane (11.8 g, 0.10 mol) and sodium tetrahydroborate (4.1 g, 0.11 mol) were mixed in 100 ml of dry tetrahydrofuran. A solution of 12.7 g (0.10 mol) of iodine in tetrahydrofuran was added dropwise with stirring. The mixture was refluxed for 3 hr and was allowed to stand for several hr. The clear solution was decanted from the solids, solvent was removed, and the remaining product was distilled under reduced pressure to yield 10.4 g (82%) of material, bp 74° (2 mm). *Anal.* Calcd for $C_5H_{14}N_2B$: B, 8.5; mol wt 127.128. Found: B, 8.5; mol wt (by mass spectroscopy) 127.129.

1,7,9,8-Triazaborahydrindane (IV).—Eight grams of II was heated for 4 hr at 160° in an oil bath. Hydrogen was evolved and the material turned slightly yellow and attained a syrupy consistency. Distillation *in vacuo* gave a nearly quantitative yield of IV, bp 69–71° (2 mm), lit.[9] bp 70° (2 mm).

1,3-Dimethyl-2-hydridodiazaboracyclopentane.—A quantity, 7.3 g (0.10 mol), of trimethylamine–borane was dissolved in 150 ml of chlorobenzene and a solution of 8.8 g (0.10 mol) of *N,N'*-dimethylethylenediamine in 100 ml of chlorobenzene was added. The mixture was refluxed for 4 hr and trimethylamine and hydrogen evolved from the system. A crude distillation of the mixture gave 7 g of product collected over the range 60–75°. The crude material was rectified by distillation through a 15-cm silver mantle column filled with stainless steel helices to provide for pure product, bp 67–68°. *Anal.* Calcd for $C_4H_{11}N_2B$: B, 12.9. Found: B, 12.8.

In a second experiment 9 g of crude product, bp 60–95°, was collected and was rectified to give 4 g of pure material.

Discussion

The 2-hydrido-1,3,2-diazaboracyclohexanes listed in Table I are all mobile liquids which are moisture sensitive although much less so than the corresponding 2-halo derivatives.[5] They have a heavy musky odor which causes severe headaches.

The proton magnetic resonance spectra of the compounds (see Table I) conform closely with those reported for similar compounds[5,10] and they confirm the structure of the heterocycles. The spectra consist of a triplet (two equivalent annular methylene groups), a quintet (the central annular methylene group), and the various peaks due to the exocyclic substituents at the nitrogen atoms. Compound 3 (Table I) is somewhat different due to the methyl group bonded to the center annular carbon atom. However, all of the observed peaks are readily assigned. While the general appearance of these spectra is analogous to that of the corresponding 2-halo derivatives,[5] the chemical shifts are at higher field for the 2-hydrido compounds thereby indicating that a BH group in 1,3,2-diazaboracycloalkanes has less Lewis acidity than a corresponding *B*-halogen grouping.

The mass spectra of the 2-hydrido-1,3,2-diazaboracyclohexanes would seem to indicate that the ring system is quite stable since the peaks due to species containing the ring are of much higher intensity than those of lower masses. The base peak was $(P - 1)^+$ in each case except for the 1,3-diethyl-2-hydridodiazaboracycloalkane where the base peak was $(P - 15)^+$. This observation might indicate that it is not the boron-bonded hydrogen which is primarily lost on electron impact. The parent peaks, P^+, occur in about 50–60% relative abundance.

The infrared spectra of the 2-hydrido-1,3,2-diazaboracyclohexanes all exhibit strong ν(BH) absorptions near 2500 cm^{-1} (*i.e.*, in the 2480–2490-cm^{-1} range for the *N,N'*-dialkylated rings and at 2515 cm^{-1} for compound 4, Table I). A BN stretching mode is also readily recognized in the 1510–1530-cm^{-1} region in close analogy to the same vibration in the corresponding *B*-halo compounds.

As noted above, the first product of the reaction between BH_3 and *N*-(ω-aminoethyl)-1,2-diaminopropane can have either structure II or III, both of which, on heating, will lose hydrogen to yield IV. However, proton nmr data suggest structure II for this intermediate. The ^{1}H magnetic resonance spectrum consists of a broad line (3.92 ppm, 1H) assigned to the NH proton, an overlapping multiplet centered at 3.17 ppm (8H) due to the four nitrogen-bonded methylene groups, a quintuplet (2.15 ppm, 2H) for the center annular methylene groups, and a broad singlet (1.43 ppm, 2H) assigned to the protons of the NH_2 group. If the five-membered ring III had been formed, the annular methylene groups should give rise to a sharp and strong singlet, which was not observed. On the other hand, the spectrum of 1,3-dimethyl-2-hydridodiazaboracyclopentane exhibits only two sharp singlets (2.72 ppm, 6H; 3.2 ppm, 4H) in consonance with the expected structure. Moreover, the ring-breathing region of the infrared spectrum of II is much more similar to that of the 1,3,2-diazaboracyclohexanes than that of the five-membered heterocycles.

The successful isolation of II provides additional support for a previous suggestion[11] that the formation

(10) K. Niedenzu, C. D. Miller, and S. L. Smith, *Z. Anorg. Allg. Chem.*, **372**, 337 (1970).

(11) K. Niedenzu and P. Fritz, *ibid.*, **340**, 329 (1965).

of bicyclic tris(amino)boranes such as IV proceeds stepwise and involves a monocyclic intermediate.

The pmr spectrum of IV exhibits only three peaks. The overlapping multiplet centered at 3.4 ppm (8H) is due to the nitrogen-bonded methylene groups, a quintuplet (2.25 ppm, 2H) is observed for the CH_2–CH_2–CH_2 protons, and a broad singlet (1.34 ppm, 2H) can be assigned to the two NH protons.

In Table II the boron-11 nuclear magnetic resonance data for some boron-substituted 1,3-dimethyl-2-diazaboracycloalkanes are listed. It is noteworthy that the effect of the boron substituents on the deshielding of boron is analogous in order for the five-membered and the six-membered heterocycles independent of the ring size; however, the chemical shifts are slightly more negative for the smaller rings. On the other hand, the effect of nitrogen substituents on the boron-11 chemical shift appears to be much less pronounced. For example, in the series of 1,3,2-diazaboracyclohexanes, I, where $n = 3$, R′ = H, and R = H, CH_3, and C_2H_5, δ values of −25.1, −26.6, and −25.5 ppm, respectively, were observed with a coupling constant J_{BH} of 131, 132, and 128 Hz, respectively.

TABLE II
BORON-11 NMR DATA OF 1,3-DIMETHYL-2-DIAZABORACYCLOALKANES[a]

R′ of compd I	^{11}B nmr data, δ, ppm[b] $n = 2$	$n = 3$	R′ of compd I	^{11}B nmr data, δ, ppm[b] $n = 2$	$n = 3$
I	−21.3	−21.4	Cl	−27.0	−25.1
Br	−26.0	−24.8	H	−28.3	−26.0
$N(CH_3)_2$	−26.1	−25.2	CH_3	−31.6	−29.2

[a] Recorded at 19.3 MHz. [b] Neat liquids, external boron trifluoride etherate standard.

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Rates of Protonation of Some Amide and Peptide Nickel(II) Complexes

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A number of metal ions have the ability to promote proton ionization from a coordinated amide or peptide moiety. Nickel(II), for example, forms weak complexes with amino acid amides and glycine peptides in neutral solution but these lose protons from the ligand at about pH 9.[1] Judging from the structures of isolated solids,[2-4] as well as from indirect evidence, there is a Ni–O to Ni–N bond rearrangement at the amide or peptide site as a result of the proton ionization from the coordinated CONHR residue. This deprotonation is usually attended also by conformational change from an octahedral complex to a yellow or orange planar species.

The observation[1,5-9] of slow rates associated with either the deprotonation or the reverse protonation reaction supports the idea of such an attendant bond rearrangement, since this might conceivably limit the rate of an otherwise expected rapid proton–base reaction. Recently Billo and Margerum[9] have carried out an extensive investigation of the kinetics of reaction of a number of acids HX, including H_3O^+ and H_2O, with the deprotonated species derived from the nickel–triglycine complex $Ni(Gly_3\text{-}2H^+)^-$. The rate of reprotonation was given by rate = $\{k_{HX}[HX]\}[Ni(Gly_3\text{-}2H^+)^-]$. Distinct mechanisms were suggested for the reaction with HX and with H_2O. We have measured the acid-independent values (corresponding to k_{H_2O}) for the reprotonation of deprotonated nickel complexes of a number of amides and peptides and reached some conclusions as to their structures and the mechanism of the protonation.

Experimental Section

Materials.—These were commercially available and used as supplied. Triglycine and tetraglycine from different sources gave identical results. Nickel perchlorate (G. Frederick Smith) was the source of nickel ions.

Kinetic and Other Experiments.—The concentration of nickel ions was estimated by EDTA titration, and that of the ligands by direct weighing. Freshly prepared solutions were used in all cases. The metal ion inhibited hydrolysis of glycinamide and peptides is slow at 25°.[10] It was observed that on standing for some days solutions of nickel–tetraglycine underwent marked spectral changes, specifically, enhancement of absorption at 275 nm and the appearance of a new intense band at 325 nm. These changes were particularly noticeable in concentrated solution.[6] The causes for these changes are not understood, but the problem was avoided by using solutions prepared within 1 hr or so. Reproducible kinetic results were then obtained.

In the measurement of the protonation rates, the complex solution was adjusted to a pH (usually 11–11.5) at which >95% deprotonation had occurred. This solution was then plunged into a buffer (final complex concentration $\sim 10^{-3}$ M) at a pH at which >95% reprotonation of the amide or peptide took place. To effect this, a borate buffer at pH ~9 was used for amide and dipeptide complexes and a lutidine buffer at pH ~7 for the higher peptides. The reactions were followed directly at the yellow peak, around 430 nm, and/or indirectly by incorporating indicators (phenolphthalein or bromothymol blue) to monitor the small pH increase (controlled by the buffer concentration) as a result of the removal of protons from solution. Usually the conditions were such that only a small amount of dissociation of the complex occurred. Since this occurred rapidly, it did not interfere with the indicator experiments and was unimportant in following the loss of yellow peak. The reactions were carried out in a stopped-flow apparatus of the Gibson design[11] or a Cary

(1) R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Amer. Chem. Soc.*, **82**, 495 (1960).

(2) A. Masuko, T. Nomura, and Y. Saito, *Bull. Chem. Soc. Jap.*, **40**, 511 (1967).

(3) Y. Nawata, H. Iwasaki, and Y. Saito, *ibid.*, **40**, 515 (1967).

(4) H. C. Freeman, J. M. Guss, and R. L. Sinclair, *Chem. Commun.*, 485 (1968).

(5) P. I. Chamberlain, J. Simplicio, and R. G. Wilkins, *Proc. Int. Conf. Coord. Chem., 1966*, **9**, 365 (1966).

(6) P. I. Chamberlain, Ph.D. Thesis, State University of New York at Buffalo, Buffalo, N. Y., 1968.

(7) T. Kaden, ref 5, p 196.

(8) K. S. Bai and A. E. Martell, *Inorg. Chem.*, **9**, 1126 (1970).

(9) E. J. Billo and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 6811 (1970).

(10) H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914 (1965); R. H. Andreatta, H. C. Freeman, A. V. Robertson, and R. L. Sinclair, *Chem. Commun.*, 203 (1967).

(11) Q. H. Gibson and L. Milnes, *Biochem. J.* **91**, 161 (1964).