

Chiral Poly(pyrazolyl)borate Ligands and Complexes. 1

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Reaction of 3,5-dimethylpyrazole hydrochloride with lithium borohydride gives 3,5-dimethylpyrazole-borane. This compound loses hydrogen at 114 °C to give the 1,3,5,7-tetramethylpyrazabole. Treatment of 3,5-dimethylpyrazole-borane with sodium hydride gives trihydrido(3,5-dimethylpyrazolyl)borate $[(H_3B(3,5-Me_2Pz))]^-$, whose reaction with pyrazole in dimethylacetamide gives the unsymmetric (pyrazolyl)borate $[H_2B(Pz)(3,5-Me_2Pz)]^-$. The dichelate complexes of this ligand with Ni^{2+} , Zn^{2+} and Co^{2+} were prepared and studied. These complexes fall into two categories corresponding to the square-planar (Ni) and tetrahedral (Zn, Co) chelates. The 1H NMR spectra of the diamagnetic Ni and Zn complexes show in each case the presence of several distinct isomers. In contrast to the case of the symmetric bis(pyrazolyl)borates the puckered metallacycle $M(Pz)(3,5-Me_2Pz)B$ presents no plane of symmetry. In the temperature range 0–110 °C no interconversion of the isomers could be observed.

Introduction

One of the challenging objectives in organometallic stereochemistry¹ and asymmetric catalysis² is to develop suitable optically active ligands. A great number of chiral monodentate, bidentate, and also tridentate ligands have been studied. A family of compounds that can act as bidentate as well as tridentate ligands are the poly(pyrazolyl)borates. They are of general structure $[R_nB(Pz)_{4-n}]^-$, where R is a noncoordinating substituent, Pz is a 1-pyrazolyl group, and n may be 0, 1, or 2.³ One of the outstanding characteristics of the poly(pyrazolyl)borate complexes is their high stability.³ We reported recently the first optically active (pyrazolyl)borate complexes in which the central metal is a chiral center,⁴ but we had to use optically active aminophosphines as ligands in order to obtain separable diastereoisomers, although it should be possible to prepare these complexes directly from optically active poly(pyrazolyl)borates. Optically active poly(pyrazolyl)borates are possible in principle because, with three different pyrazoles, the tris(pyrazolyl)borate $[RB(Pz')(Pz'')(Pz''')]^-$ would be chiral with an asymmetric boron atom. Although the bis(pyrazolyl)borate $[R_2B(Pz')(Pz'')]^-$ would still be achiral, it could form chelates containing the puckered $R_2B(Pz')(Pz'')M$ ring (Figure 1), and this puckered metallacyclic ring in the boat form³ presents no plane of symmetry having a local symmetry of C_1 , in contrast to the symmetrical poly(pyrazolyl)borate chelates with local C_s symmetry.

The great number of existing pyrazoles with a wide range of electronic and steric properties permits the construction of many unsymmetrical bis(pyrazolyl)borates, chiral tripod bis(pyrazolyl)borates,⁵ and chiral tris(pyrazolyl)borates with different electronic and steric properties. This possibility of tailoring the poly(pyrazolyl)borates, in addition to the great stability of their complexes, led us to attempt the synthesis of unsymmetric poly(pyrazolyl)borates. In this paper we describe the synthesis and properties of the first unsymmetric dihydridobis(pyrazolyl)borate and the properties of some of its complexes.

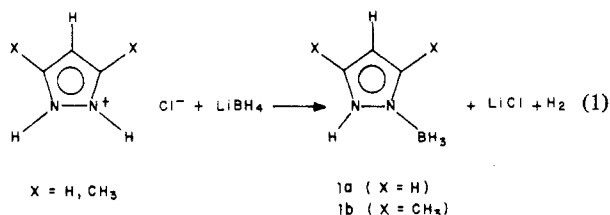
Results and Discussion

In Trofimenko's⁶ synthesis of poly(1-pyrazolyl)borates by reaction of potassium borohydride with pyrazoles in a melt, the first isolable product that is obtained is the dihydridobis(1-pyrazolyl)borate. For the synthesis of chiral (pyrazolyl)borates it is necessary to introduce the different pyrazoles into the borohydride consecutively and to avoid scrambling.

The reaction of pyrazole with an excess of KBH_4 in toluene or monoglyme at low temperatures always gave products of disubstitution instead of the monosubstituted compound required. Recent studies of hydrolysis of BH_4^- in MeOH/ H_2O mixtures at -78 °C⁷ have permitted the identification of the following intermediates after the initial hydrolysis step: H_2OBH_3 and $(H_2O)BH_2OH$. These intermediates hydrolyze at rates slower than BH_4^- , presumably due to solvent conditions and the less hydridic nature of the B-H hydrogens.

These findings led us to suppose that a pyrazole with strong electron-withdrawing groups would reduce the hydridic nature of the B-H hydrogens in $[BH_3(1-Pz)]^-$ sufficiently in order to allow the isolation of the product of monosubstitution. In order to do this, we selected 3,5-bis(trifluoromethyl)pyrazole, that is, a compound already so acidic that it forms salts with aqueous sodium hydroxide solutions. The reaction of KBH_4 with 3,5-bis(trifluoromethyl)pyrazole proceeded faster than with pyrazole in a melt as well as in the solvents toluene and monoglyme. In all these cases we recovered unreacted KBH_4 and disubstituted product. Owing to the failure of the supposedly direct method of obtaining the monosubstituted (pyrazolyl)borate we attempted a two-step synthesis of the required monosubstituted compound.

Synthesis of Polypyrazole-Boranes. Schaeffer⁸ and Nöth⁹ reported a method for the synthesis of alkylamine-boranes by reacting the amine hydrochloride with lithium borohydride. In analogy we reacted pyrazole hydrochlorides with lithium borohydride (eq 1).



From the reaction of pyrazole hydrochloride ($X = H$) with KBH_4 a product was obtained whose IR spectra showed no NH-stretch band and the same BH-stretch pattern as pyrazabole,¹⁰ synthesized by Trofimenko. Pyrazabole is the dimer of (1-pyrazolyl)dihydroborane $((PzBH_2)_2)$, and its formation requires hydrogen elimination from **1a** to give $PzBH_2$ prior to dimerization. The combination in **1a** of the hydridic borane hydrogen with the relatively acidic pyrazole hydrogen (pK_a of pyrazole 2.52)¹¹ makes this elimination feasible. $PzBH_2$

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Table I. Analytical Data

compd	formula (mol wt)	Anal. found (calcd)				mp, °C
		% C	% H	% B	% N	
3,5-dimethyl-4-pyrazole-borane	C ₅ H ₁₁ BN ₂ (109.98)	54.64 (54.61)	9.99 (10.08)	9.65 (9.84)	25.26 (25.47)	114 dec
sodium trihydrido(3,5-dimethyl-1-pyrazolyl)borate	C ₅ H ₁₀ BN ₂ Na (131.97)	45.48 (45.51)	7.70 (7.64)	8.00 (8.20)	21.20 (21.23)	295 dec
hydrogen dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate	C ₈ H ₁₃ BN ₄ (171.03)	54.30 (54.58)	7.30 (7.44)	6.41 (6.24)	31.76 (31.83)	122 dec
cobalt bis(dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl))borate	C ₁₆ H ₂₄ B ₂ CoN ₈ (408.97)	47.71 (46.99)	5.79 (5.92)		26.99 (27.40)	159
zinc bis(dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl))borate	C ₁₆ H ₂₄ B ₂ N ₈ Zn (415.47)	46.26 (46.26)	5.99 (5.82)		26.73 (26.97)	169
nickel bis(dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl))borate	C ₁₆ H ₂₄ B ₂ N ₈ Ni (408.74)	47.37 (47.02)	5.90 (5.92)		26.94 (27.41)	213 dec

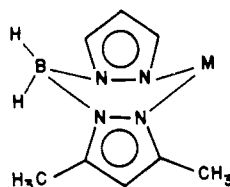
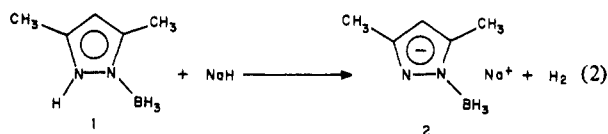


Figure 1.

once formed can dimerize to give pyrazabole. To reduce the possibility of hydrogen elimination, we reacted LiBH₄ with the hydrochloride of the less acidic 3,5-dimethylpyrazole (pK_a 4.12).¹¹ In this case there was obtained in a yield of 38% the 3,5-dimethylpyrazole-borane adduct **1b**, the properties and spectra of which are given in Tables I and II.

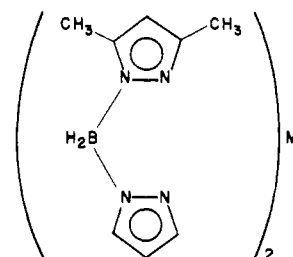
The ¹H NMR spectrum shows only one methyl signal contrary to that expected, although other N-substituted 3,5-dimethylpyrazoles, for example, *N*-methyl- and *N*-benzyl-3,5-dimethylpyrazoles, also show only one methyl signal.¹² The compound **1b** melts at 114 °C with gas evolution; after gas evolution ceases, the melt solidifies and melts again at 175 °C. The spectra of this solid and its comparison with authentic material show it to be 1,3,5,7-tetramethylpyrazabole. Also the pyrazole-borane adduct **1b** eliminates hydrogen easily to give the pyrazolylborane 3,5-Me₂PzBH₂ that dimerizes to the pyrazabole.

Synthesis of Trihydridomono(pyrazolyl)borates. The second step in the formation of the trihydridomono(pyrazolyl)borate is the abstraction of the N-2 hydrogen. Muettetries¹³ describes a simple route to substituted borohydrides by protolysis of sodium hydride and amine-borane complexes. The desired compound trihydrido(3,5-dimethyl-1-pyrazolyl)borate (**2**) was obtained by similar reaction of **1b** with NaH (eq 2).



The compound **2** is very hygroscopic, and its ¹H NMR spectrum shows the expected two methyl signals. After exposure to water the two signals collapse to give one signal.

Sodium Dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate. While the reaction of **2** with pyrazole in the melt



M = Ni(4), Zn(5), Co(6)

Figure 2.

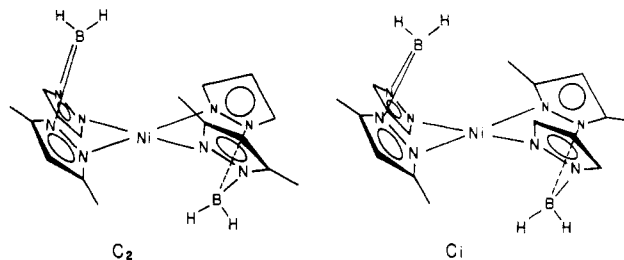
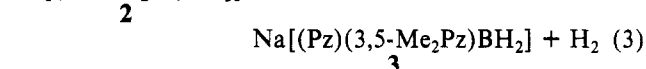


Figure 3.

produces a mixture of several products, in dimethylacetamide (DMAA) the reaction proceeds smoothly, liberating the calculated amount of hydrogen to form the desired compound **3** (eq 3). In this reaction care must be taken to control the



temperature, which must not exceed 140 °C; otherwise scrambling results to give the symmetric compounds. The compound **3** is obtained associated with DMAA that cannot be eliminated by repeated recrystallization from toluene or anisole. For its analytical characterization the free acid H[(Pz)(3,5-Me₂Pz)BH₂] was precipitated from the aqueous solution of **3** by treatment with acetic acid.

Metal Chelates. The aqueous solution of **3** was also used to prepare the chelates **4**, **5**, and **6** by reacting it with the corresponding metal salts (Figure 2). The colors of the complexes **4**, **5**, and **6**, orange, white, and violet, respectively, are similar to those of their symmetric analogues [H₂B(Pz)₂]₂M and [H₂B(3,5-Me₂Pz)₂]₂M. The electronic configuration and the structures of **4**, **5**, and **6** should therefore be analogous to their corresponding symmetric counterparts.

The nickel bis(1-pyrazolyl)borate complexes studied by Trofimenko¹⁷ are square planar; this was indicated by their

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Table II. NMR^a and Infrared^b Data

compd	NMR	$\nu(\text{N-H})$	$\nu(\text{B-H})$
3,5-dimethylpyrazole-borane	2.26 (s, 6 H), ^c 5.93 (s, 1 H), 8.50 (s, ^d 1 H)	3280	2260-2400
sodium trihydrido(3,5-dimethyl-1-pyrazolyl)borate ^e	2.05 (d, $J = 0.5$, 3 H), 2.18 (d, $J = 0.5$, 3 H), 5.90 (s, 1 H)		2080, 2270, 2360
sodium dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate ^e	2.14 (s, 3 H), 2.23 (s, 3 H), 5.84 (s, 1 H), 6.24 (t, $J = 1.2$, 1 H), 7.53 (m, 2 H)		2260, 2360
dimethylacetamide	2.06 (s), 2.89 (s), 3.02 (s)		
nickel bis(dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate	1.68 (s, 34%), -1.81 (s, 66%, 3 H), 2.26 (s, 3 H), 5.51 (s, 1 H), 5.95 (t), 5.97 (t, 1 H), 6.69 (d, $J = 1.7$, 65%), -6.79 (d, $J = 1.7$, 35%, 1 H), 7.45 (d, $J = 2.3$, 34%), -7.50 (d, $J = 2.0$, 66%, 1 H)		2240-2455
zinc bis(dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate	1.84 (s), -1.87 (s), -1.97 (s, 3 H), 2.37 (s, 3 H), 5.81 (s, 1 H), 6.20 (t, $J = 2.2$, 1 H), 7.49 (dd, $J = 2.1$, 0.6, 1 H), 7.69 (dd, $J = 2.1$, 0.6, 1 H)		2245-2450
zinc bis(dihydridobis(3,5-dimethyl-1-pyrazolyl)borate	1.76 (s, 3 H), 2.38 (s, 3 H), 5.69 (s, 1 H)		
cobalt bis(dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate			2260-2440

^a NMR spectra were taken in CDCl₃ unless otherwise noted; chemical shifts (ppm) are relative to SiMe₄ as internal standard, with J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. ^b In KBr disk; all units of cm⁻¹. ^c Integral. ^d Broad, interchangeable with D₂O. ^e NMR spectra taken in D₂O with TSP as internal standard.

spectra and further proved by the X-ray structure of bis[dihydrido(1-pyrazolyl)borato]nickel(II).¹⁴ [H₂B(3,5-Me₂Pz)₂]₂Ni can only exist in the chair form and belongs to the C_{2h} point group; because of this symmetry all four 3-methyl and all four 5-methyl groups are equivalent, thus giving rise to only two NMR signals. However, it has not been possible to make an assignment of the 3- and 5-methyl groups.

Also, in the case of compound **4** only the chair form can be constructed from models, nonbonding interactions of the methyl groups precluding the construction of a boat form. This chair form allows two different geometric isomers with C₂ and C_i symmetry as shown in Figure 3. In each case the two 3-methyl groups are equivalent. The NMR spectrum of **4** at room temperature in CDCl₃ presents two methyl signals with a ratio 2:1 at high field and one methyl signal at low field. The sum of the integrals of the high-field signals is equal to the integral of the low-field signal. These data allow an assignment of the high-field signals to the resonances of the 3-methyl groups, because the environment of the 3-methyl groups close to the metal is quite different in the two isomers, while the environment of the 5-methyl groups pointing away from the metal is very similar. The ratio of 2:1 corresponds to the statistical weight of the different isomers of **4**, because the cis form C₂ allows for two enantiomers. In CDCl₃ up to 65 °C the NMR spectra show no variation, indicating that up to 65 °C there is no evidence of interconversion of the two isomers. At higher temperatures no variation could be detected because in higher boiling solvents such as C₆D₆ and toluene-*d*₈ the 3-methyl signals are not well separated, showing only one signal having a shoulder. All attempts to separate the isomers by column chromatography failed.

An X-ray study of unsubstituted bis[dihydridobis(1-pyrazolyl)borato]cobalt(II) by Guggenberger¹⁶ showed an essentially tetrahedral cobalt atom and a molecular symmetry of approximately C₂. Inversion of the Co(Pz)₂B rings would reproduce this geometry or its mirror image, so this symmetry makes the 3-pyrazolyl positions pairwise equivalent.

For the case of two bis(dihydridobis(1-pyrazolyl)borato)-zinc(II) analogues Trofimenko proposed and also confirmed the tetrahedral configuration of zinc. Again the C₂ symmetry makes the 3-pyrazole positions pairwise equivalent, and two NMR signals for the 3-pyrazolyl hydrogens would be expected. However, Trofimenko^{6,17} observed only one 3-pyrazolyl H signal. The NMR spectrum of [H₂B(3,5-Me₂Pz)₂]₂Zn in CCl₄ at room temperature shows also only one signal for the four

3-methyl groups. This fact can be due to an accidental equivalence of the signals of the two different 3-pyrazole positions or to a rapid interconversion of the B(Pz)₂Zn rings; both rigid¹⁵ and mobile¹⁹ B(Pz)₂M metallacycles are known. The zinc complex **5** allows one to distinguish between the two distinct possibilities, because ring interconversion would also interconvert the possible isomers. The compound **5** can present three different geometric isomers, two of C₂ and one of C_i symmetry. In each C₂ configuration the two 3-methyl groups are equivalent, while in the C_i configuration there are two different 3-methyl groups. In total one could expect a maximum of four signals for the 3-methyl groups.

The NMR spectrum of **5** in CDCl₃ shows one low-field methyl resonance and three high-field methyl resonances in the ratio 9:2:1. For the same reasons as in the nickel complex we assign the high-field resonances to the 3-methyl groups. The spectrum in toluene-*d*₈ shows only two 3-methyl signals in a 3:1 ratio, possibly due to the coincidence of two signals. In the temperature range 0-110 °C the spectrum remains unchanged. In the case of CpCo[H₂B(Pz)₂]₂R_f King¹⁵ also found no interconversion of the B(Pz)₂Co metallacycle.

Experimental Section

Materials and Apparatus. All solvents were carefully dried and stored under an argon atmosphere. IR spectra were obtained with a Perkin-Elmer 283 infrared spectrophotometer. All melting points are uncorrected. The ¹H NMR spectra were obtained on a Varian XL-100 FT spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane or TSP as internal standard. Microanalyses were performed by the microanalytical laboratory Pascher, Bonn, Germany. Analytical and physical data are given in Table I. The ¹H NMR and IR data are given in Table II.

3,5-Dimethyl-4-pyrazole-Borane (1b). To 3,5-dimethylpyrazole hydrochloride (26.52 g, 200 mmol) suspended in 200 mL of ether cooled to 0 °C was added dropwise a filtered solution of lithium borohydride (4.14 g, 190 mmol) dissolved in 150 mL of ether. After the evolution of 4 L of hydrogen the temperature of the resulting heterogeneous reaction mixture was allowed to reach room temperature and stirred for a further 2 h. The solution was then filtered, and the solvent of the filtrate was evaporated to give a white residue. This residue was dissolved in benzene at 50 °C and filtered, and hexane was added. When the solution cooled, crystals of **1b** were deposited (yield 8.0 g, 38%).

Sodium Trihydrido(3,5-dimethyl-1-pyrazolyl)borate (2). To sodium hydride (0.48 g, 20 mmol) suspended in 5 mL of monoglyme was added 3,5-dimethyl-4-pyrazole-borane (1.1 g, 10 mmol) dissolved in 10 mL of monoglyme. After 1 h at a temperature of 40 °C, the mixture was

filtered and the solvent of the filtrate evaporated to give sodium trihydrido(3,5-dimethyl-1-pyrazolyl)borate in almost quantitative yield. The analytical sample was recrystallized from anisole.

Sodium Dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate (3). Sodium trihydrido(3,5-dimethyl-1-pyrazolyl)borate (2) (1.6 g, 12.1 mmol) and pyrazole (0.89 g, 13 mmol) were dissolved in dimethylacetamide, and the resulting solution was heated to 100–140 °C. After the evolution of 240 mL of hydrogen the solvent was evaporated under high vacuum. Although the resulting white residue was recrystallized several times from toluene, a white solid was obtained, which contained dimethylacetamide. This was used to prepare the metal chelates without further purification. For characterization, the free acid was prepared by dissolving a sample in water and adding several drops of acetic acid. The white precipitate that formed immediately was filtered, washed with cold water, and dried.

Transition-Metal Dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate Complexes. To a solution of sodium dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate in water was added, with stirring, a 50% excess of a 0.5 M solution of the appropriate metal

ion. The mixture was filtered, and the precipitate was dissolved in methylene chloride. The solution was washed several times with water, dried with MgSO_4 , and concentrated. After chromatography using a short column of silica gel (1-cm i.d., 10-cm length) and methylene chloride as the eluant, the solvent was evaporated and the residue recrystallized from toluene/hexane.

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Registry No. 1b, 82963-91-5; 2, 82963-92-6; 3, 82963-93-7; 4 (C_1 form), 83023-55-6; 4 (C_2 form), 82963-97-1; 5, 82963-96-0; 6, 82963-95-9; hydrogen dihydrido(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate, 82963-94-8; 3,5-dimethylpyrazole hydrochloride, 31705-88-1; lithium borohydride, 16949-15-8; sodium hydride, 7646-69-7; pyrazole, 288-13-1.

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Reduction of Potassium Ion in Liquid Ammonia by Hydrogen to Potassium Amalgam

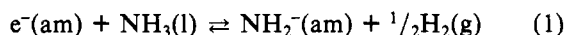
JAMES C. WARF

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The equilibrium constant at 25 °C of the reaction $\text{e}^-(\text{am}) + \text{NH}_3(\text{l}) \rightleftharpoons \text{NH}_2^-(\text{am}) + \frac{1}{2}\text{H}_2(\text{g})$ was recalculated on the basis of recently measured activity coefficients of potassium amide in liquid ammonia, with a result of $(5 \pm 2) \times 10^5$. The possibility of using mercury to extract potassium from H_2/KNH_2 in liquid ammonia was examined thermodynamically and found to be feasible ($\Delta G = -9.8$ kcal for the reaction $\text{K}^+(\text{am}) + \text{NH}_2^-(\text{am}) + \frac{1}{2}\text{H}_2(\text{g}) + \text{Hg}(\text{l}) \rightleftharpoons \text{K}/\text{Hg} + \text{NH}_3(\text{l})$, where the mole fraction of potassium in the amalgam is 0.05). This conclusion was confirmed experimentally, when amalgams of up to 0.044 mole fraction of potassium were prepared. Zinc also served as a successful reducing agent. Potassium bis(trimethylsilyl)amide in the solvent hexamethylphosphoramide was partially reduced by hydrogen to potassium amalgam. The densities of potassium amide solutions in liquid ammonia were determined.

Introduction

The formation of trace concentrations of the ammoniated electron, $\text{e}^-(\text{am})$, on reduction of potassium amide in liquid ammonia by hydrogen at high pressure, has been studied by Kirschke and Jolly.¹ They found for the reaction



an equilibrium constant of 5×10^4 at 25 °C. At a hydrogen pressure of 100 atm, concentrations of the ammoniated electron of approximately 10^{-5} M were noted. Since mercury readily extracts alkali metals (e.g., $\text{K}^+(\text{am}) + \text{e}^-(\text{am})$) from liquid ammonia,² there is the intriguing possibility of reducing appreciable quantities of potassium ion to potassium amalgam by hydrogen. The main purposes of this paper are to demonstrate both by calculation and by experiment that this proposition is valid. Use of zinc as a reducing agent instead of hydrogen and use of another potassium salt [$\text{KN}(\text{SiMe}_3)_2$] in a different solvent [$(\text{Me}_2\text{N})_3\text{PO}$] were also briefly investigated.

Equilibrium Constant of the NH_2^-/H_2 Reaction. Kirschke and Jolly measured the ammoniated electron concentration resulting from reaction 1, by both spectrophotometric and ESR techniques. Although measured activity coefficients of alkali metals in liquid ammonia were available, experimental data on potassium amide were not; consequently, activity coefficients of ammonium chloride were employed as an approxi-

mation. In the meantime, laboratory measurements of the activity coefficients of potassium amide in liquid ammonia have been made by Moreau and Lepoutre,³ who employed mole fraction rather than molarity (moles per liter of solution) as concentration units. So that the activity coefficients of Moreau and Lepoutre can be converted to the basis of molarity, by using the equations of Harned and Owen,⁴ the densities of KNH_2 solutions in liquid ammonia at 25 °C are needed. These densities were determined (see Experimental Section). These adjusted activity coefficients for KNH_2 in liquid ammonia at 25 °C proved to be much higher than the values for ammonium chloride used by Kirschke and Jolly. Similarly, Marshall's⁵ activity coefficients of potassium in liquid ammonia, with Johnson and Meyer's⁶ values of densities, were converted from values based on molality to those based on molarity (at -33 to -35 °C).

Equilibrium constants for reaction 1 were computed by using Kirschke and Jolly's data with the adjusted activity coefficients. The results ranged from 1×10^6 (0.067 M KNH_2) to 3×10^6 (1.0 M KNH_2). Plotting and extrapolating to zero concentration gave a constant of $(5 \pm 2) \times 10^5$, 10 times that of Kirschke and Jolly.

Standard free energies of formation at 25 °C of the species involved in reaction 1 are given by Lepoutre and Demortier,⁷

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