Lewis Basicity of 2-Dimethylaminoborazine[1]

O. T. BEACHLEY, Jr.,* and T. R. DURKIN

The basicity of the dimethylamino group in $H_2[(CH_3)_2N]B_3N_3H_3$ has been investigated. The simple adduct $H_2[(CH_3)_2N\cdot BH_3]B_3N_3H_3$, prepared by the reaction of $H_2[(CH_3)_2N]B_3N_3H_3$ with B_2H_6, has been characterized according to its infrared and ^1H and ^{11}B nmr spectra. The compound is stable at room temperature in the presence of excess B_2H_6 but reacts with B_2H_6 if diethyl ether is present. The products of this reaction are $H_3B_3N_3H_3$ and $\mu\text{-}(CH_3)_2NB_2H_5$. The relative basicity of $H_2[(CH_3)_2N]B_3N_3H_3$ has been determined by studying a series of competition reactions with other bases using B_2H_6 as the reference acid. The observed order of base strength is $C_6H_5N(CH_3)_2 > H_2[(CH_3)_2N]B_3N_3H_3 > B[N(CH_3)_2]_3 \sim \overline{CH_3NC_2H_4N(CH_3)}BN(CH_3)_2$. These results indicate that the π electrons of borazine are partially delocalized and have a significant influence on the chemical properties of a ring substituent.

Introduction

Our understanding of the bonding in the borazine ring requires the elucidation of the nature of the π electrons. The hypothesis that the π electrons are delocalized, at least partially, is consistent with the nmr data observed for B-monosubstituted borazines.[2] Substituents apparently interact with the π system by means of a resonance effect to alter the π-electron density at the ortho and para positions. Additional experimental data are necessary to support the hypothesis of π-electron delocalization. Therefore, we have investigated the effects of the borazine ring on the chemical properties of a substituent. If the π electrons are delocalized, a substituent bound to a boron atom in the borazine ring should have significantly different properties than if it were bound to a boron atom in a simple molecule. For comparison, aromatic amines are less basic than amines with aliphatic substituents. In this paper we report the results of our study of the basicity of the dimethylamino group in 2-dimethylaminoborazine. Its basicity has been compared to the dimethylamino group in *N,N*-dimethylaniline, tris(dimethylamino)borane, and 1,3-dimethyl-2-dimethylaminodiazaboracyclopentane.[3] In all basicity studies, diborane was used as the reference acid.

Experimental Section

Manipulations involving air-sensitive materials were performed in a conventional vacuum line. Nonvolatile air-sensitive compounds were handled in a drybox with a purified nitrogen atmosphere.

Materials. Diborane[4] was prepared from $NaBH_4$ and H_3PO_4. Diborane-d_6 was prepared in a similar manner using $NaBD_4$. The compound 2-dimethylaminoborazine,[5] $H_2[(CH_3)_2N]B_3N_3H_3$, was prepared from $H_2ClB_3N_3H_3$ and $HN(CH_3)_2$. Tris(dimethylamino)-borane,[6] $B[N(CH_3)_2]_3$, was prepared from BCl_3 and $HN(CH_3)_2$. The heterocyclic ring compound[3] 1,3-dimethyl-2-dimethylaminodiaza-

boracyclopentane[7] was prepared from $B[N(CH_3)_2]_3$ and $CH_3HNCH_2\text{-}CH_2NHCH_3$. Commercial *N,N*-dimethylaniline, $C_6H_5N(CH_3)_2$, was dried over KOH pellets and distilled. All solvents were dried by conventional means.

Reaction of 2-Dimethylaminoborazine with Diborane. The basicity of the dimethylamino group in $H_2[(CH_3)_2N]B_3N_3H_3$ was investigated by studying its reaction with B_2H_6 under neat and solution conditions. In a typical experiment using only the neat reagents, 0.640 mmol of B_2H_6 was condensed onto 0.1399 g (1.126 mmol) of $H_2[(CH_3)_2N]B_3N_3H_3$ in a flask connected to the vacuum line. Upon warming the mixture to room temperature a white crystalline solid rapidly formed. After stirring for 1 hr at room temperature, 0.084 mmol of excess B_2H_6 was recovered. Thus, 1 mol of diborane reacted with 2 mol of $H_2[(CH_3)_2N]B_3N_3H_3$. This stoichiometry was further verified by tensimetric titrations between $H_2[(CH_3)_2N]\text{-}B_3N_3H_3$ and B_2H_6 in *n*-heptane at room temperature and $-78°$. In all cases the adduct $H_2[(CH_3)_2N\cdot BH_3]B_3N_3H_3$ precipitated as a colorless crystalline solid. Further observations for 18 hr indicated that there was no reaction between the adduct and B_2H_6 using neat conditions or in *n*-heptane at room temperature.

Reaction of the Borane Adduct of 2-Dimethylaminoborazine with Diborane in Diethyl Ether. In a typical experiment 0.652 mmol of B_2H_6 was condensed onto 0.0803 g (0.646 mmol) of $H_2[(CH_3)_2N]\text{-}B_3N_3H_3$ in a flask connected to the vacuum line. Upon warming to room temperature the solid adduct formed. The mixture was then cooled to $-196°$ and 0.642 mmol of diethyl ether was added. The mixture was warmed to room temperature at which point a reaction ensued as evidenced by vigorous bubbling. After stirring for 12 hr the volatile components (1.910 mmol *via* PVT data) were removed by condensation into a cold trap at $-196°$. There was no nonvolatile residue remaining in the original reaction flask. The volatile material was identified as a mixture of $H_3B_3N_3H_3$, $\mu\text{-}(CH_3)_2\text{-}NB_2H_5$, and diethyl ether by comparison of its infrared spectrum to that of authentic samples. Repeated attempts to separate the compounds in the mixture on a vacuum line were unsuccessful due to the similar volatilities of the components. However, gas chromatography confirmed the presence of three components.

The reaction between $H_2[(CH_3)_2N]B_3N_3H_3$ and B_2H_6 in the presence of ether was repeated using B_2D_6. This reaction was significantly slower than that observed for the undeuterated system.

Competition Reaction between 2-Dimethylaminoborazine and *N,N*-Dimethylaniline with Diborane. The relative basicity of $H_2[(CH_3)_2N]B_3N_3H_3$ was compared to that of $C_6H_5N(CH_3)_2$ by a competition reaction using B_2H_6 as the reference acid. Nmr was used to monitor the reaction. The components, 0.0685 g (0.575 mmol) of $C_6H_5N(CH_3)_2$, 0.0555 g (0.447 mmol) of $H_2[(CH_3)_2N]B_3N_3H_3$, and 0.321 mmol of B_2H_6, were condensed in an nmr tube at $-196°$. The mixture was dissolved in *ca.* 0.5 ml of diethyl ether and the tube sealed *in vacuo*. After allowing the mixture to warm to room temperature, the ^1H nmr spectrum was recorded. It consisted of sharp singlets at -2.99 and -2.57 ppm (relative to TMS) which may be assigned to $C_6H_5N(CH_3)_2\cdot BH_3$ and $H_2[(CH_3)_2N]B_3N_3H_3$, respectively, by comparison to spectra of authentic samples. There were no lines in the spectrum which could be assigned to $C_6H_5N(CH_3)_2$ or $H_2\text{-}[(CH_3)_2N\cdot BH_3]B_3N_3H_3$. The compound $C_6H_5N(CH_3)_2$ has a sharp singlet at -2.86 ppm due to the $N(CH_3)_2$ group. A spectrum of
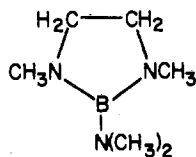
(1) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

(2) O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, 92, 5372 (1970).

(3) The compound 1,3-dimethyl-2-dimethylaminodiazaboracyclopentane has the following structure. This compound will be referred to as the "heterocyclic ring compound."

(4) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1970, pp 492–496.

(5) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, 6, 575 (1967).

(6) J. Goubeau, M. Rahtz, and H. J. Bechen, *Z. Anorg. Allg. Chem.*, 275, 161 (1954).

(7) K. Niedenzu, P. Busse, and C. Miller, *Inorg. Chem.*, 9, 977 (1970).

$H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$ in ether solution exhibits a sharp singlet at -2.64 ppm due to the $N(CH_3)_2$ group and a broad triplet at -5.55 ppm for the NH protons. Therefore, the B_2H_6 reacted exclusively with $C_6H_5N(CH_3)_2$. Thus, *N,N*-dimethylaniline is a stronger base than 2-dimethylaminoborazine.

Competition Reaction between Tris(dimethylamino)borane and 2-Dimethylaminoborazine with Diborane. A mixture of 0.0224 g (0.180 mmol) of $H_2[(CH_3)_2N]B_3N_3H_3$ and 0.0403 g (0.281 mmol) of $B[N(CH_3)_2]_3$ was condensed at $-196°$ into a flask connected to the vacuum line. To this mixture 0.103 mmol of B_2H_6 was added. The reaction mixture was warmed to room temperature and a white crystalline solid formed. The volatile component was then removed after 10 min of reaction time and identified as pure $B[N(CH_3)_2]_3$ by its infrared spectrum. The mass of the nonvolatile residue was 0.0250 g compared to a calculated value of 0.0249 g for $H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$. Thus, $H_2[(CH_3)_2N]B_3N_3H_3$ is a stronger base than $B[N(CH_3)_2]_3$. In order to determine if $B[N(CH_3)_2]_3$ reacts with $H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$, the $B[N(CH_3)_2]_3$ from the competition experiment was recondensed onto the adduct and allowed to stand for an additional 18 hr at room temperature. The volatile components were removed again and identified as a mixture of $H_3B_3N_3H_3$, $H_2BN(CH_3)_2$, and $HB[N(CH_3)_2]_2$ by their infrared spectra. The compounds $H_2BN(CH_3)_2$ and $HB[N(CH_3)_2]_2$ have characteristic bands[8] at 960 and 880 cm^{-1}. Bands at 3480 and 720 cm^{-1} were used to identify $H_3B_3N_3H_3$ in the mixture. The mass of the nonvolatile residue was 0.0034 g.

Competition Reaction between 1,3-Dimethyl-2-dimethyl-aminodiazaboracyclopentane and 2-Dimethylaminoborazine with Diborane. A mixture of 0.0658 g (0.466 mmol) of the heterocyclic ring compound[3] and 0.0688 g (0.554 mmol) of $H_2[(CH_3)_2N]B_3N_3H_3$ was condensed into an nmr tube and dissolved in $CHCl_3$. To this mixture 0.233 mmol of B_2H_6 was added by condensation at $-196°$. After the tube was hermetically sealed, the mixture was warmed to room temperature and the spectrum was immediately recorded. The spectrum consisted of a complex set of peaks at $-2.44, -2.48, -2.52, -2.59, -2.62, -2.69, -2.94,$ and -3.05 ppm (relative to TMS) with relative intensities of *ca.* 2, 5, 20, 3, 6, 12, 2, and 1, respectively. The relative intensities of these peaks varied with time. These nmr data indicate that a simple competition reaction with one product did not occur.

In order to determine the nature of the reaction in the previously described competition experiment, 0.0162 g (0.115 mmol) of the heterocyclic ring compound[3] and 0.074 mmol of B_2H_6 were allowed to react in $CHCl_3$ in an nmr tube. The mixture was warmed to room temperature and the ^1H nmr spectrum was immediately recorded. The spectrum consisted of peaks at $-2.51, -2.57, -2.62, -2.68, -2.72, -2.78, -3.04,$ and -3.17 ppm (relative to TMS) with relative intensities of *ca.* 1, 4, 6, 6, 3, 5, 5, and 2, respectively. This spectrum was also time dependent. Thus, the data suggest that the products from the competition reaction with B_2H_6 are quite different from the products from the reaction of only the heterocyclic ring compound[3] and B_2H_6. Attempts to observe the borane adducts, before further reactions occurred, using low temperatures for reaction and observations proved futile. The use of solvents selectively to precipitate the adducts and B_2D_6 to inhibit hydride-transfer reactions were also unsuccessful.

Unfortunately, when equimolar mixtures of $H_2[(CH_3)_2N]B_3N_3H_3$ and the heterocyclic ring compound[3] are exposed to B_2H_6, a complex mixture of products instead of a simple borane adduct was observed. These results indicate that a borane adduct is formed but decomposes or further reacts rapidly. Furthermore, in a separate experiment under identical conditions it was observed that the heterocyclic ring compound[3] reacts with B_2H_6 to form products which are different from those of the competition reaction. Our interpretation of these data is that $H_2[(CH_3)_2N]B_3N_3H_3$ is probably the stronger Lewis base but undergoes further reaction before the products can be observed. Thus, the aminoborazine forms an initial borane adduct which in turn acts as a hydride source to react with the heterocyclic ring compound[3] and yield the products. This type of reaction would be similar to that observed between $H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$ and $B[N(CH_3)_2]_3$. The other possibility is that the heterocyclic ring compound[3] is the stronger base. It could form a borane complex which then rapidly decomposes or further reacts with the aminoborazine. The facts that such different products are formed in the competition reaction than in the reaction of only the heterocyclic ring compound[3] with B_2H_6, the resistance of $H_2[(CH_3)_2N]B_3N_3H_3$ toward reaction with other amine-boranes, plus the similarities between $B[N(CH_3)_2]_3$ and the

heterocyclic ring compound,[3] lead us to believe that $H_2[(CH_3)_2N]$-$B_3N_3H_3$ is the stronger base.

Infrared Spectra. Infrared spectra were recorded by means of a Perkin-Elmer 457 grating spectrometer. Gas-phase spectra were observed using a 10-cm gas cell equipped with KBr optics. Solid samples were prepared as a combination of Kel-F (4000–1350 cm^{-1}) and Nujol (1350–400 cm^{-1}) mulls between KBr plates. Absorption intensities were measured using the method of Durkin, DeHayes, and Glore.[9] The infrared frequencies (cm^{-1}) of pertinent compounds follow.
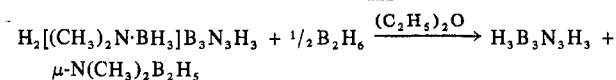
$H[(CH_3)_2N \cdot BH_3]B_3N_3H_3$: 3410 (vs), 3020 (m), 2995 (m), 2640 (w, sh), 2618 (m), 2520 (s), 2390 (s), 2300 (s), 1460 (vs, br), 1294 (vw), 1267 (w), 1200 (w), 1160 (m), 1121 (w, sh), 1102 (m), 1059 (m), 1028 (m), 963 (m), 920 (s, sh), 908 (s), 894 (s, sh), 853 (w), 757 (s), 730 (s), 721 (s, sh), 661 (w), 620 (vw). $H_2[(CH_3)_2N \cdot BD_3]B_3N_3H_3$: 3460 (m), 3410 (vs), 3020 (m), 2995 (m), 2615 (m), 2525 (vs), 2440 (w), 2325 (m), 1891 (vs), 1770 (vs), 1720 (w), 1655 (m), 1460 (vs, br), 1345 (m, sh), 1320 (w, sh), 1260 (w), 1190 (vw), 1149 (w), 1105 (m), 1055 (m), 1021 (w), 960 (w), 920 (s, sh), 910 (s), 895 (m, sh), 881 (m), 800 (s, sh), 791 (s), 780 (s), 733 (m), 701 (m). C_6H_5N-$(CH_3)_2 \cdot BH_3$: 3115 (m), 3080 (m), 3040 (s), 2400 (vs), 2322 (s), 2280 (s), 1955 (w), 1875 (w), 1800 (vw), 1597 (m), 1495 (s), 1404 (m), 1390 (w), 1260 (m), 1210 (m, sh), 1165 (s), 1129 (m), 1080 (m), 1033 (m), 1015 (m), 976 (m), 911 (m), 878 (s), 779 (s), 752 (m), 696 (s), 672 (m, sh), 619 (vw), 545 (s), 462 (w).

$CH_3\overline{NCH_2CH_2N(CH_3)}BN(CH_3)_2$: 2980 (m), 2870 (vs), 2785 (s), 1543 (m, sh), 1522 (vs), 1490 (m), 1450 (m, sh), 1435 (s), 1402 (vs), 1390 (vs), 1367 (s), 1290 (vs), 1226 (s), 1182 (w), 1128 (m), 1070 (w), 1041 (vw), 921 (s), 667 (w, sh), 643 (m), 623 (w, sh).

Nuclear Magnetic Resonance Spectra. The ^1H nmr spectra were recorded at 100 MHz by means of a Jeolco HM 100 spectrometer. The ^{11}B nmr spectra were recorded at 15.871 and 32.1 MHz by means of a Varian Associates HR-60 and HA-100 spectrometers, respectively. The reference compounds were tetramethylsilane and boron trifluoride etherate. The chemical shifts of the ^{11}B spectra were determined using the side-band technique.

Results and Discussion

Diborane reacts rapidly and quantitatively with 2-dimethyl-aminoborazine in a heptane solution or neat to form a simple adduct I, $H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$, which is a white crystalline solid. The solid adduct decomposes slowly at room temperature. The rate of decomposition, however, is retarded by the presence of excess B_2H_6. For example, the adduct has been kept in the solid state for 18 hr at room temperature in the presence of excess B_2H_6 without any evidence of decomposition. In contrast to our observations that the adduct is stable in the presence of excess B_2H_6, diethyl ether accelerates the rate of decomposition. The pure adduct I in ether decomposes at room temperature in several hours to form $H_3B_3N_3H_3$, μ-$(CH_3)_2NB_2H_5$, $HB[N(CH_3)_2]_2$, H_2BN-$(CH_3)_2$, and a nonvolatile residue. If excess diborane is present in addition to the diethyl ether, the adduct consumes the diborane to form $H_3B_3N_3H_3$ and μ-$(CH_3)_2NB_2H_5$ quantitatively according to the equation

$$H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3 + {}^1/_2B_2H_6 \xrightarrow{(C_2H_5)_2O} H_3B_3N_3H_3 + \mu\text{-}N(CH_3)_2B_2H_5$$

The formation of μ-$(CH_3)_2NB_2H_5$ probably results from *in situ* generation of monomeric $H_2BN(CH_3)_2$ which in turn reacts with diborane. When B_2D_6 was used in this reaction, a large isotope effect was qualitatively observed. Although the reaction is complicated by hydride exchange[10] between the H(B) on the borazine ring and B_2H_6, a large isotope effect suggests that the rate-determining step in this reaction is the breaking of a boron–hydrogen bond.

The proposed structure of $H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$, a simple Lewis adduct with the exocyclic nitrogen electron

(8) A. B. Burg and J. S. Sandhu, *Inorg. Chem.*, **4**, 1467 (1965).

(9) T. Durkin, J. Glore, and L. DeHayes, *J. Chem. Educ.*, **48**, 452 (1971).
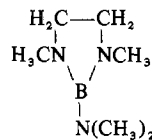
(10) G. H. Dahl and R. Schaeffer, *J. Amer. Chem. Soc.*, **83**, 3034 (1961).

pair as the base site, is consistent with all of our chemical and spectral data. The infrared spectrum of adduct I has absorptions at 3410 and 2520 cm^{-1} which are assigned to the stretching modes of the N-H and B-H bonds of the borazine moiety, respectively. The peaks at 2390 and 2300 cm^{-1} are due to the asymmetric and symmetric stretching modes of the BH_3 group. It should also be noted that there is a very broad peak centered at 1460 cm^{-1} which is in the proper region[11] for a B-H-B stretching mode. Therefore, a structure in which there is a hydride bridge between the exocyclic boron and the boron of the ring might be theoretically possible but is eliminated when one considers the spectrum of the BD_3 adduct. The compound $H_2[(CH_3)_2N \cdot BD_3] \cdot B_3N_3H_3$ also has the same broad absorption at 1460 cm^{-1}. This peak might be due to a combination of borazine ring and exocyclic B-N vibrations instead of a B-H-B stretching mode. The ^{11}B nmr spectrum further confirms the simple adduct structure. The spectrum of a diethyl ether solution of the adduct at -25° consists of a broad line at -30.0 ppm and a quartet at +9.0 ppm ($J = 100$ Hz). The broad low-field line is assigned to the overlap of the B-H doublet with the B-X singlet of the borazine ring boron atoms. The quartet is assigned to the BH_3 group indicating a simple borane adduct. It should also be noted that in the presence of excess B_2H_6 the position of the quartet is not shifted. Thus, there is no BH_3 exchange in adduct I on the nmr time scale.

The ^1H nmr spectral data of adduct I provide some interesting data on the question of π-electron interactions and delocalization. The spectrum in chloroform consisted of a sharp singlet at -2.67 ppm assigned to the $N(CH_3)_2$ group and a triplet at -5.55 ppm ($J = 54$ Hz) for the borazine NH protons. The BH protons were not observed. Therefore, upon complexation the field position of the line due to the $N(CH_3)_2$ group has been shifted downfield 0.15 ppm. The deshielding effect compares favorably in magnitude with the shifts exhibited in other amine–borane systems.[12] Furthermore, the borazine NH protons are also shifted downfield upon complexation. The electron pair of the exocyclic nitrogen is no longer available for a resonance interaction with the borazine ring. The field position of the NH resonance in $H_2[(CH_3)_2N \cdot BH_3]B_3N_3H_3$ is at slightly lower field than unsubstituted borazine (-5.45 ppm) and is probably related to the formal positive charge on the exocyclic nitrogen. It should also be noted that the ortho and para NH protons are magnetically equivalent in the borane adduct, whereas they are distinguished in $H_2[(CH_3)_2N]B_3N_3H_3$.

The basicity of the dimethylamino group in $H_2[(CH_3)_2N] \cdot$

(11) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. I, Methuen, London, 1967, p 293.

(12) H. Steinberg and A. L. McCloskey, "Progress in Boron Chemistry," Vol. 1, Macmillan, New York, N. Y., 1964, p 115.

$B_3N_3H_3$ has been compared with $C_6H_5N(CH_3)_2$, $B[N(CH_3)_2]_3$, and the heterocyclic ring compound.[3] Competition reactions using B_2H_6 as the reference acid suggest the following order of relative basicity

$$C_6H_5N(CH_3)_2 > H_2[(CH_3)_2N]B_3N_3H_3 > B[N(CH_3)_2]_3 \sim$$

$$\begin{array}{c} H_2C-\!\!-CH_2 \\ | \quad\quad | \\ H_3CN \quad NCH_3 \\ \backslash \quad / \\ B \\ | \\ N(CH_3)_2 \end{array}$$

The compound $C_6H_5N(CH_3)_2$ is the strongest base of the series. The relative base strength of the $N(CH_3)_2$ group can be related to the interactions of the electron pair on the nitrogen with appropriate π orbitals in the different molecules. Our results indicate that the electron pair of the $N(CH_3)_2$ group is more available as a base to B_2H_6 in $C_6H_5N(CH_3)_2$ than $H_2[(CH_3)_2N]B_3N_3H_3$ than $B[N(CH_3)_2]_3$. In other words, the basic electron pair on the $N(CH_3)_2$ group interacts less with the π orbital of the benzene ring than the borazine ring but more with the boron atom of $B[N(CH_3)_2]_3$. Thus, the borazine π-electron system is less resistant to electronic changes (the π electrons are less delocalized) than the benzene π system. The observation that $H_2[(CH_3)_2N]B_3N_3H_3$ is a stronger base than $B[N(CH_3)_2]_3$ indicates that the borazine ring has a significant effect on the extent of the interaction between the $N(CH_3)_2$ and the adjacent boron. Thus, the borazine ring should be considered to have significant π-electron delocalization. The borazine ring is probably not a series of isolated π systems. When one considers that $H_2[(CH_3)_2N]B_3N_3H_3$ is a stronger base than $B[N(CH_3)_2]_3$ and that $B[N(CH_3)_2]_3$ has three basic sites, one gets a qualitative feeling for the effect of the borazine ring. The $N(CH_3)_2$ group in $H_2[(CH_3)_2N]B_3N_3H_3$ is probably also more basic than the $N(CH_3)_2$ group in the heterocyclic ring compound.[3] However, it is unfortunate that our experimental results are not more definitive. This difference in basicity must also be related to the effects of π-electron delocalization in the borazine ring. Thus, our Lewis basicity studies clearly demonstrate that the borazine ring affects the chemical properties of a substituent and supports the hypothesis of π electron delocalization.