Synthesis and Characterization of Borane Adducts of Some Diazines

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Received July 23, 1984

Abstract

Borane adducts of pyridazine, pyrimidine and pyrazine and some of its methyl derivatives have been synthesized and characterized by elemental analyses, infrared spectral data, and ^{1}H and ^{11}B nuclear magnetic resonance spectral data. The adducts of the pyrazines and pyrimidine were found to contain two mol of BH_3 whereas only one mol of BH_3 was found with pyridazine. The ^{11}B NMR chemical shift of the pyrazine adducts was found to contain two mol of BH_3 whereas only one mol with δ_{11B} (ppm) = $-29.6 + a(-1.8) + b(-0.4) + c + d$, in which a represents the number of methyl groups ortho to the nitrogen donor atom and b represents the number of methyl groups meta to the nitrogen donor atom. Terms c and d have values only when two or more methyl groups are present. Term c represents the effect of two methyl groups ortho to the nitrogen donor atom and d represents two *cis*-methyl groups which are ortho and meta to the nitrogen donor (*e.g.*, 2,3-dimethylpyrazine). To our knowledge, this is the first correlation of ^{11}B chemical shift data for the effect of substituents on a boron–nitrogen bond.

Introduction

Recently the research in this laboratory has continued to be concerned with the preparation and characterization of molecular adducts of boranes with nitrogen-containing Lewis bases. Specifically, studies have been completed in which the reactions of trifluoroborane, tribromoborane [1] and borane [2] have been allowed to react with 3- and 4-substituted pyridines in which the substituents were fluorine, chlorine, bromine and/or cyanide entities. Earlier the adducts of analogous 2-substituted pyridines with borane and tribromoborane were studied [3]. Borane adducts with the alkyl groups in the 2-, 3- and 4-positions of pyridine have been reported [4]. The above studies provided information on molecular adducts of boranes in which the environment of the nitrogen atom in the pyridine ring was changed systematically by placing substituents having different electronegativities in the 2-, 3- and 4-positions of the ring. As a consequence of these studies, it became of interest to see if any detectable changes could be observed in the properties of adducts comprised of diazines and substituted diazines with boranes. Accordingly, a study was made of trifluoro- and tribromoborane adducts of methyl-substituted pyrazines [5] and a study of borane adducts of methyl-substituted pyrazines is herein reported.

Experimental

All reactions and transfers were conducted in an atmosphere of dry nitrogen. Infrared spectra were recorded in a nujol mull between cesium iodide plates on a Perkin-Elmer model 599 spectrometer. Due to the sensitivity of the adducts towards moisture, the infrared samples were prepared in a glove box and immediately transferred to the spectrometer. Proton nuclear magnetic resonance spectra were obtained on a Varian T-60 spectrometer using tetramethylsilane (TMS) as an internal reference in a $CDCl_3$ solution. Boron-11 NMR spectra were measured at 64.2 MHz on a Nicolet NT-200 wide bore spectrometer. Trimethoxyborane was used as an external standard with a solvent comprised of 30% C_6D_6 and 70% C_6H_6.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., the Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York, and/or in this laboratory using an F&M model 185 CHN Analyzer.

Diethyl ether, which was used as the solvent, was deoxygenated by bubbling dry nitrogen gas through it for 30 min, after which it was dried, purified by refluxing over sodium and benzophenone, and distilled under a nitrogen atmosphere. It was used immediately. Benzene was refluxed over sodium and benzophenone and distilled under N_2.

All of the reactants were supplied by Aldrich Chemical Company, Milwaukee, Wisconsin. Pyrazine (99+%) was used without further purification.

0020-1693/85/$3.30

2,6-Dimethylpyrazine (98%) was sublimed before use. The other reactants 2-methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,3,5-trimethylpyrazine, pyrimidine and pyridazine were distilled prior to use. Dimethylsulfideborane was kept refrigerated and used without further purification.

Pyrazinebis(borane)

A solution of 1.20 g (15 mmol) of pyrazine in 20 mL of dry ether was added, with stirring, over a period of 5 minutes to a solution of 2.40 g (30 mmol) of dimethylsulfideborane [$(CH_3)_2SBH_3$] in 20 mL of dry ether under an atmosphere of dry nitrogen. The resulting white precipitate was collected quickly by suction filtration and washed three times with dry ether, then dried in a vacuum. A yield (1.32 g, 12.2 mmol, 81%) of $C_4H_4N_2 \cdot 2BH_3$ was isolated and characterized.

2-Methylpyrazinebis(borane)

In a typical synthesis, the procedure described above was employed with 1.41 g (15 mmol) of 2-methylpyrazine being added to 2.40 g (30 mmol) of dimethylsulfideborane. An off-white colored solid, $2\text{-}(CH_3)C_4H_3N_2 \cdot 2BH_3$ (0.84 g, 6.85 mmol, 46% yield), was obtained and characterized.

2,3-Dimethylpyrazinebis(borane)

Following the procedure described to prepare pyrazinebis(borane), 1.62 g (15 mmol) of 2,3-dimethylpyrazine was added to 2.40 g (30 mmol) of dimethylsulfideborane. A white solid, $2,3\text{-}(CH_3)_2\text{-}C_4H_2N_2 \cdot 2BH_3$ (0.69 g, 5.08 mmol, 34% yield), was obtained and characterized.

2,5-Dimethylpyrazinebis(borane)

The procedure described above for the preparation of pyrazinebis(borane) was modified to use 10 mL of dry ether to dissolve each of the reactants. Accordingly, 1.62 g (15 mmol) of 2,5-dimethylpyrazine was added to 2.40 g (30 mmol) of $(CH_3)_2S \cdot BH_3$. The solid white adduct, 2,5-dimethylpyrazinebis(borane) (1.44 g, 10.6 mmol, 71% yield) was characterized.

2,6-Dimethylpyrazinebis(borane)

The procedure used to synthesize pyrazinebis(borane) was applied to the preparation of 2,6-dimethylpyrazinebis(borane). Thus, 1.62 g (15 mmol) of 2,6-dimethylpyrazine was allowed to react with 2.40 g (30 mmol) of dimethylsulfideborane. White, plate-like crystals of 2,6-dimethylpyrazinebis(borane) were characterized (0.99 g, 7.29 mmol, 49% yield).

To better understand the reaction of 2,6-dimethylpyrazine with dimethylsulfideborane, a solution of 0.19 g (2.0 mmol) of 2,6-dimethylpyrazine in 12 mL of 70% C_6H_6/30% C_6D_6 was placed in an NMR tube and titrated with 1.0 mmol aliquots of dimethylsulfideborane (10 M BH_3 in dimethylsulfide). ^{11}B NMR spectra were recorded about 15 min after each addition. The results displayed in Fig. 1 clearly indicate that BH_3 adds first to the nitrogen atom in the 4-position and then to the nitrogen atom in the 1-position.

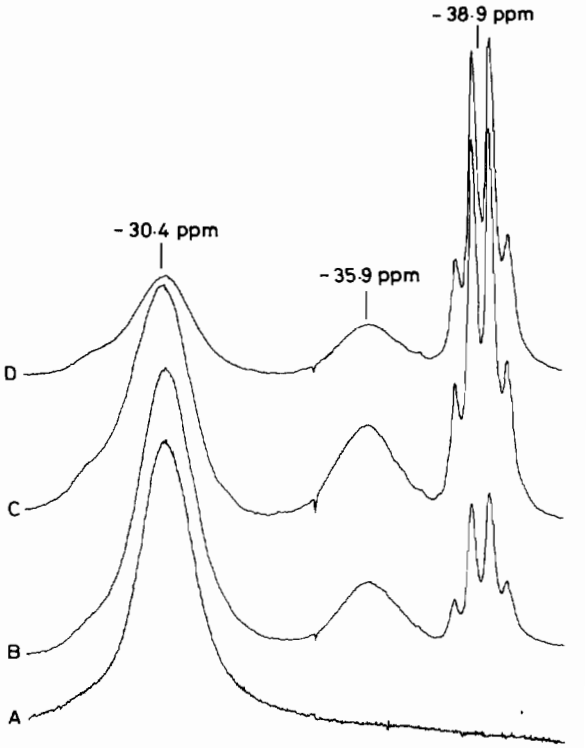


Fig. 1. ^{11}B NMR spectra of the titration of 2,6-dimethylpyrazine with dimethylsufideborane. A – 1 mol borane: mol pyrazine. B – 1 1/2 mol borane: mol pyrazine. C – 2 mol borane: mol pyrazine. D – 2 1/2 mol borane: mol pyrazine. The quartet at –38.9 ppm is unreacted dimethylsulfideborane. The peak at –35.9 ppm is B–N(1), and at 30.4 ppm is B–N(4).

2,3,5-Trimethylpyrazinebis(borane)

Following the modified procedure used to prepare 2,5-dimethylpyrazinebis(borane), 1.83 g (15 mmol) of 2,3,5-trimethylpyrazine was added to 2.40 g (30 mmol) of dimethylsulfideborane. The desired product, 2,3,5-trimethylpyrazinebis(borane), was obtained as a white powder (1.11 g, 7.41 mmol, 49% yield).

Pyrimidinebis(borane)

Under an atmosphere of dry nitrogen, 2.40 g (30 mmol) of dimethylsulfideborane in 25 mL of dry ether was frozen in liquid nitrogen. Pyrimidine (1.20 g, 15 mmol) in 25 mL of dry ether was added. The reaction mixture was allowed to warm

to the temperature of an acetone-dry ice bath and then stirred for one hour. A white precipitate formed which turned yellow upon attaining room temperature. The yellow precipitate, pyrimidinebis-(borane), was collected on a suction filter and dried in a vacuum (1.44 g, 13.4 mmol, 89 % yield.

Pyridazineborane

Under an atmosphere of dry nitrogen, 1.20 g (15 mmol) of dimethylsulfideborane in 30 mL of dry ether was frozen in liquid nitrogen. To this was added 0.60 g (7.5 mmol) of pyridazine in 30 mL of dry ether. The reaction mixture was allowed to warm to ice temperature. A white precipitate, pyridazineborane (0.35 g, 3.25 mmol, 47% yield), was collected on a suction filter and dried in a vacuum.

Results and Discussion

The elemental analyses and the physicial properties of the adducts are given in Tables I and II. Some of the analyses are not as good as desired due to the instability of these compounds. A solution of 2,3,5-trimethylpyrazinebis(borane) in benzene in a sealed tube is very unstable. In addition, the rate of adduct formation at each nitrogen site is not necessarily equal, leading to the possible synthesis of mixtures (see Discussion below and Fig. 1). Spectral analyses support the elemental analyses of the bis(borane) adducts of the pyrazines. No suitable solvent was found for the product of the reaction of pyrimidine and borane consequently no nuclear magnetic resonance spectra could be obtained. The elemental analyses indicate the formation of pyrimdinebis(borane).

The yields of some of the adducts are low due to their solubility in diethyl ether. The solid product obtained upon evaporating the solvent from the filtrate was found, using ^1H NMR data, to be a mixture of the adduct and the pyrazine base.

The infrared spectral data for the borane frequencies of the adducts are given in Table III. Generally, the frequencies of the diazines changed little upon adduct formation. Among the characteristic vibrations which are also observed are the BH_3 stretching vibrations in the 2445 to 2240 cm^{-1} region.

TABLE I. Elemental Analysis of Borane Adducts.

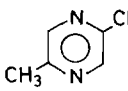
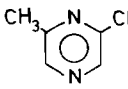
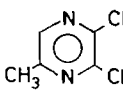
		%C	%H	%N
	Calc.	44.59	9.35	26.00
	Found	44.41	9.24	25.89
	Calc.	48.99	10.53	22.85
	Found	50.96	10.36	20.80
	Calc.	53.06	10.39	20.63
	Found	52.86	10.50	20.64
	Calc.	53.06	10.39	20.63
	Found	53.50	10.49	19.05
	Calc.	53.06	10.39	20.63
	Found	53.79	11.31	22.12
	Calc.	56.11	10.76	18.70
	Found	56.58	11.26	19.81
	Calc.	51.16	7.52	29.82
	Found	51.25	7.18	29.73
	Calc.	44.59	9.35	26.00
	Found	43.76	7.49	24.36

TABLE II. Physical Properties of Borane Adducts.

Compounds	Color	M.P.* °C	Yield %
Pyrazine•$2BH_3$	White	128	81
2-Methylpyrazine•$2BH_3$	Off-white	94	46
2,3-Dimethylpyrazine•$2BH_3$	White	105	34
2,5-Dimethylpyrazine•$2BH_3$	White	106	71
2,6-Dimethylpyrazine•$2BH_3$	White	90	49
2,3,5-Trimethylpyrazine•$2BH_3$	White	108	49
Pyrimidine•$2BH_3$	Yellow	222	89
Pyradazine•BH_3	White	90	47

*Melted with decomposition.

TABLE III. Infrared Spectra of Borane Adducts.

Compound	ν_{BH_3} (cm^{-1})
Pyrazine•$2BH_3$	2410(s)[a],2370(s),2302(sh), 2283(sh)
2-Methylpyrazine•$2BH_3$	2380(s),2337(s),2298(s), 2260(m)
2,3-Dimethylpyrazine•$2BH_3$	2400(sh),2373(s),2338(s), 2304(s),2277(s),2240(m)
2,5-Dimethylpyrazine•$2BH_3$	2405(s),2360(s),2330(s), 2300(s),2280(m),2260(s)
2,6-Dimethylpyrazine•$2BH_3$	2445(m),2382(s),2343(s), 2296(sh),2256(m)
2,3,5-Trimethylpyrazine•$2BH_3$	2410(s),2370(s),2340(s), 2308(m),2262(m)
Pyrimidine•$2BH_3$	2380(s),2270(s)
Pyridazine•BH_3	2360(s),2300(m),2260(m)

[a]s = strong, m = medium, sh = shoulder.

The ^1H NMR spectral data are listed in Table IV. All aromatic and aliphatic proton resonances for the pyrazine adducts shift downfield upon adduct formation as a consequence of a decrease in electron density around the nitrogen atom. The aliphatic resonances shift from 0.30 to 0.46 ppm downfield. The aromatic protons, which are more strongly affected by the reduction of electron density in the ring, have resonances which show a greater variation in shift upon adduct formation. Pyrazine protons, already relatively deshielded upon adduct formation, shift downfield only 0.24 ppm, whereas, 2,3,5-trimethylpyrazine protons shift 0.63 ppm downfield. The chemical shifts of all aromatic protons in the adducts are more alike than those in the free ligands, implying that the electrons donated by the methyl groups are now in the nitrogen–boron bond rather than in the ring. This conclusion is supported by the ^{11}B NMR spectral data (see below). These results are in contrast to those reported for borane and phenylborane adducts of alkyl-substituted pyridines [4]. In the alkylpyridines systems, shifts in the resonances of the aromatic protons upon reaction with borane were generally upfield and followed no discernible pattern.

The resonance of the *beta* protons in pyridazine is also shifted downfield upon formation of the adduct; however, the *alpha* proton resonance is unaffected. It is reasonable to assume that these protons, which resonate at 9.28 ppm in both the free ligand and the borane adduct, are already very deshielded and further reduction of electron density about the proton as a result of complexation with borane does not occur.

Table V lists the ^{11}B NMR chemical shift data for the borane adducts. Boron-proton coupling constants, J_{B-H} (not shown), are in the range of 95–105 Hz [4, 6]. Pyridazine, unlike the pyrazines, is able to add only one molecule of borane to form pyridazineborane which has a ^{11}B resonance 0.3 ppm downfield from pyrazinebis(borane). Assignment of the ^{11}B NMR chemical shifts to borane

TABLE V. ^{11}B-NMR Data of Borane Adducts.

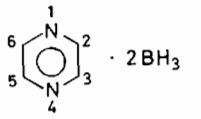
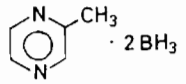
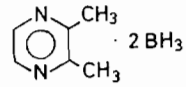
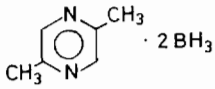
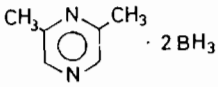
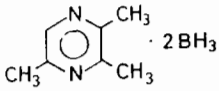
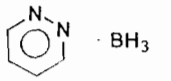
Compound	$\delta_{B-N(1)}$	$\delta_{B-N(4)}$
	−29.59	
	−31.45	−30.00
	−30.64	
	−31.80	
	−35.88	−30.37
	−31.04	−35.21
	−29.37	

TABLE IV. ^1H-NMR Data of the Borane Adducts.

Compound	Chemical shift (ppm)			
	Aliphatic protons		Aromatic protons	
	δ	$\Delta\delta$	δ	$\Delta\delta$
Pyrazine·2BH_3	–	–	8.86	0.24
2-Methylpyrazine·2BH_3	2.83	0.35	8.93 8.73	0.46 0.35
2,3-Dimethylpyrazine·2BH_3	2.93	0.40	8.73	0.51
2,5-Dimethylpyrazine·2BH_3	2.77	0.30	8.80	0.53
2,6-Dimethylpyrazine·2BH_3	2.88	0.35	8.53	0.30
2,3,5-Trimethylpyrazine·2BH_3	2.93 2.84	0.46 0.37	8.70	0.63
Pyridazine·BH_3	–	–	9.28 7.90	0.00 0.27

bound to either N(1) or N(4) for each methyl-substituted pyrazine was determined by assuming that the upfield resonance resulted from borane molecule being bonded to the nitrogen atom having the most adjacent methyl groups. Alkyl-substitutions in the 2- and 6-positions of pyridine result in an upfield shift of the ^{11}B NMR resonance in pyridine-(borane) adducts [4]. Previous attempts in this laboratory to correlate the ^{11}B NMR chemical shift data for adducts of methyl-substituted pyrazines with trifluoro- or tribromoborane were unsuccessful [5].

The change in ^{11}B chemical shift from the pyrazinebis(borane) adduct upon methyl-substitution in the pyrazine ring can be expressed as the sum of four parameters:

$$\Delta\delta(\text{ppm}) = a(-1.8) + b(-0.4) + c + d \quad (1)$$

In the first two terms, a equals the number of methyl groups ortho to the nitrogen atom and b equals the number of methyl groups meta to the nitrogen donor atom. Methyl groups in the ortho position are better able to furnish electrons to the boron–nitrogen bond than those in the meta position. This results in the upfield shift of 1.8 ppm for each ortho methyl group and only 0.4 ppm for each meta methyl goup.

The third term, c, has a value of −2.6 ppm and contributes to the equation only when there are two methyl groups in the ortho position [*e.g.*, 2,6-dimethylpyrazinebis(borane)]. This term may be the result of an increased accumulation of electron charge in the boron–nitrogen bond due to an inductive effect of the two ortho electron-releasing groups, or as a result of a steric effect.

Figure 1 shows the titration of 2,6-dimethylpyrazine with dimethylsulfideborane. Addition of up to one mol of borane per mol of pyrazine results in the appearance of only one ^{11}B resonance at −30.4 ppm, assigned to borane complexed at N(4). Further addition of borane results in the appearance of a resonance at −35.9 ppm. The area of the signal at this resonance increases compared to that at −30.4 ppm as more borane is added. However, the signal areas never become equal, even in the presence of large amounts of unreacted dimethylsulfideborane.

This result demonstrates that the less shielded nitrogen reacts with borane first and becomes saturated before the more shielded nitrogen reacts. The upfield resonance is clearly due to borane addition at the nitrogen site with a higher electron density. Since borane reacts completely with the weaker Lewis base site first, factors other than Lewis base strength must determine the order of reactivity. While steric effects are probably important, it is beyond the scope of this study to determine the relative importance of the various factors.

The presence of two methyl groups in a *cis* position, as in 2,3-dimethylpyrazine, results in the need for the fourth parameter in the equation, d, which equals +1.15 ppm. The observation that two methyl groups in a *cis* position (but not in a *trans* position, as in 2,5-dimethylpyrazine) lead to a downfield shift in the ^{11}B resonance implies that a methyl group is less able to increase the electron density at the boron–nitrogen bond when there is an adjacent methyl group. This result may be due to inductive and/or steric effects. It is beyond the scope of this study to determine the nature of each effect.

In summary, borane adducts of methyl-substituted pyrazines have changes in ^{11}B NMR chemical shifts that can be related to the number and position of the methyl groups in a systematic manner. The result of methyl-substitution is to increase the electron density in the boron-nitrogen bond, leading to an upfield shift of the ^{11}B resonance.

Acknowledgement

The support of the Robert A. Welch Foundation is gratefully acknowledged.

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