Inorganica Chimica Acta, 58 (1981) 131–134
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Preparation and Characterization of Borane Adducts of 3- and 4-Substituted Pyridines

STEVEN FERRENCE, JAMES IWAMOTO, SARITA LEVY, NANCY MASSEY, ROBERT WILLIAMS and DONALD R. MARTIN

Department of Chemistry, The University of Texas at Arlington, Arlington, Tex. 76019, U.S.A.

Received June 29, 1981

The borane adducts of 3-fluoro-, 3- and 4-chloro-, 3- and 4-bromo-, and 3- and 4-cyanopyridine were prepared and characterized by chemical analyses, ^1H and ^{11}B NMR spectroscopy, IR, and differential scanning calorimetry. The 4-halopyridines as well as the two cyanopyridine derivatives were found upon heating to exhibit exothermic transtions, in contrast to the endothermic transitions of the 3-substituted pyridineboranes.

Introduction

In 1937 one of the authors [1] became interested in the behavior of trifluoroborane as a Lewis acid and its relative strength compared with the other trihaloboranes. In the interim there have been hundreds of papers published on molecular adducts of borane and substituted boranes. More recently, there have been reported [2–8] studies which have been concerned with the relative acid-base bond strengths of the components of adducts comprised of borane and trihaloboranes as acids and pyridine and substituted pyridines as bases.

Included in these studies was an investigation of the borane and tribromoborane adducts of the 2-halopyridines [8]. As an extention of these studies, the borane adducts of 3- and 4-chloropyridine, 3- and 4-bromopyridine, 3- and 4-cyanopyridine, and 3-fluoropyridine were prepared and characterized by elemental analyses, IR, ^1H and ^{11}B NMR, and differential scanning calorimetry.

Experimental

All of the preparations were performed under an atmosphere of dry nitrogen. IR spectra were recorded on a 621 Perkin-Elmer spectrophotometer using CH_2Cl_2 solutions except for the 3-fluoropyridineborane which was recorded as a thin film between NaCl plates. The ^1H NMR spectra were recorded on a Varian T-60 spectrophotometer using TMS (tetramethylsilane) as an internal standard. The ^{11}B NMR spectra were recorded on a JEOL JNM-FX200 spectrophotometer at an observation frequency of 63.98 MHz. The chemical shifts are reported relative to TMB (trimethylborate) as an external reference. Melting or decomposition temperatures were determined on a Perkin-Elmer Differential Scanning Calorimeter Model DSC-1B. Decomposition enthalpies were determined using the heat of fusion of tin as a standard. Elemental analyses were determined by Schwarzkopf Microanalytical Laboratory, Ind., Woodside, New York.

3-Fluoropyridineborane

To a solution of 2.43 g (25 mmol) of 3-fluoropyridine in 25 ml of CH_2Cl_2 was added 2.5 ml (25 mmol) of dimethylsulfideborane (BMS). The mixture was allowed to stir at room temperature for 30–45 minutes. The solvent was removed under vacuum to yield 2.56 g (92.4%) of clear liquid 3-fluoropyridineborane. *Anal.* Calc.: C = 54.14; H = 6.36; N = 12.63%. Found: C = 54.15; H = 6.59; N = 12.72%. IR Spectra: 2475(s), 1630(m), 1585(s), 1485(s), 1445(s), 1310(m), 1165(s), 885(s) (s = strong, m = medium).

3-Chloropyridineborane

A procedure similar to that described for 3-fluoropyridineborane was used. This yielded 2.84 g (89.1%) of white 3-chloropyridineborane crystals. *Anal.* Calc.: C = 47.15; H = 5.54; N = 11.00%. Found: C = 46.81; H = 5.54; N = 11.08%. Melting point 33–34 °C. IR Spectra: 2390(s), 1580(m), 1480(s), 1435(s), 1140(s), 920(m), 810(s).

3-Bromopyridineborane

A procedure similar to that used to prepare 3-fluoropyridineborane was followed. The yield was 4.06 g (94.%%) of white crystals of 3-bromopyridineborane. *Anal.* Calc.: C = 34.95; H = 4.11; N = 8.15%. Found: C = 34.76; H = 4.36; N = 8.06%. Melting point 48–50 °C. IR Spectra: 2405(s), 1475(m), 1185(s), 1095(m).

3-Cyanopyridineborane

A procedure similar to that used for 3-fluoropyridineborane was used to prepare this compound. The yield was 2.77 g (94.1%) of white crystals of 3-cyanopyridineborane. *Anal.* Calc.: C = 61.10; H = 5.98; N = 23.75%. Found: C = 58.36; H = 6.05; N = 22.45%. This compound decomposes at 93–95 °C. IR Spectra: 2380(s), 2315(m), 1605(m), 1465(s), 1420(m), 1150(s), 905(m), 800(s).

4-Cyanopyridineborane

A procedure similar to that used to prepare 3-fluoropyridineborane yielded 1.74 g (59.0%) of white 4-cyanopyridineborane crystals. *Anal.* Calc.: C = 61.10; H = 5.98; N = 23.75%. Found: C = 60.91; H = 6.05; N = 23.53%. This compound decomposed at 148–150 °C. IR Spectra: 2390(s), 2285(s), 1630(m), 1500(m), 1435(m), 1175(s), 1080(s), 835(s).

4-Chloropyridineborane

A different procedure was used to prepare this borane adduct. A solid mixture of 3.75 g (25 mmol) of 4-chloropyridine hydrochloride and 0.95 g (25 mmol) sodium borohydride were placed in a round-bottom flask fitted with a constant pressure addition funnel. After flushing the system with dry nitrogen, 50 ml of dimethoxyethane (glyme) was added to the addition funnel and allowed to drip slowly into the reaction flask. The mixture bubbled vigorously during the addition. After all of the glyme had been added, the mixture was stirred at room temperature for 1.5 hours. The solvent was removed under vacuum and the solid residue was extracted with dry CH_2Cl_2. The solution was filtered and solvent removed under vacuum. This procedure yielded 2.38 g (74.8%) of yellow crystals of 4-chloropyridineborane. *Anal.* Calc.: C = 47.15; H = 5.54; N = 11.00%. Found: C = 46.94; H = 5.80; N = 10.72%. This compound decomposed at 133–135 °C (Lit. 140–2° [13]). IR Spectra: 2340(s), 1580(s), 1460(m), 1150(s), 805(m).

4-Bromopyridineborane

A procedure similar to that used to synthesize 4-chloropyridineborane was used and yielded 2.47 g (57.6%) of yellow crystals. *Anal.* Calc.: C = 34.95; H = 4.11; N = 8.15%. Found: C = 34.85; H = 4.43; N = 8.25%. The compound decomposed at 130–132 °C (Lit. 151–2° [13]). IR Spectra: 2390(s), 1610(s), 1485(s), 1432(m), 1175(s), 1065(m), 830(m).

Discussion

The chemical shifts in ^{11}B NMR spectra of boron adducts have been used as a measure of the dative bond strength [5, 6, 8, 9] however, there is a question as to whether the absolute bond strength can be measured in this way [10]. For a similar series of adducts, however, the chemical shfits do serve as a guide to the relative strengths of the donor-acceptor bonds.

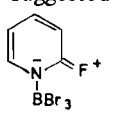
TABLE I. ^{11}B NMR Data for Substituted pyridineborane Compounds.

Boranes	δ ^{11}B[a]	$^1J^{11}B-^1H$ (Hz)	Solvent	Ref.
pyridine	30.1[b]	104	–	[6]
2-bromopyridine	27.9	95	$CHCl_3$	[8]
3-bromopyridine	30.2	98	$CHCl_3$	[e]
4-bromopyridine	30.5	98	$CDCl_3$	[e]
2-chloropyridine	29.6	98	$CHCl_3$	[8]
3-chloropyridine	30.1	98	$CDCl_3$	[e]
4-chloropyridine	30.5	98	$CDCl_3$	[e]
2-cyanopyridine	29.9	98	CH_3CN	[8]
3-cyanopyridine	29.5	95	$CDCl_3$	[e]
4-cyanopyridine	29.6	98	$CDCl_3$	[e]
2-fluoropyridine	32.9	96	$CHCl_3$	[8]
3-fluoropyridine	29.9	98	$CDCl_3$	[e]
2-methylpyridine	32.7[b]	104		[6]
3-methylpyridine	30.6[b]	104		[6]
4-methylpyridine	31.5[b]	103		[6]
2-ethylpyridine	33.1[b]	104		[6]
3-ethylpyridine	30.8[b]	103		[6]
4-ethylpyridine	31.6[b]	103		[6]

[a]Shifts with respect to $(CH_3O)_3B$ as an external standard. [b]Originally reported with respect to $(CH_3)_2O{\cdot}BF_3$ as an external standard. These values were calculated by adding 18.3 ppm to the reported value. [e]This work.

In Table I are shown the ^{11}B chemical shifts for the halo-substituted pyridineboranes as well as those for the methyl and ethyl analogs. It can be seen by the magnitude of the shifts for the 3- and 4-chloro- and bromopyridineboranes that moving the halogen from the 2 position causes the chemical shift to increase, indicating a stronger B–N bond. The smaller shift for the 2-halopyridineborane compounds was attributed primarily to a steric interaction [8]. Inductive effects would be expected to decrease the bond strength and may account for the slightly lower shift of the 3-fluoropyridineborane as compared to pyridineborane.

Resonance stabilization of the 4-chloro- and 4-bromopyridineboranes similar to that suggested for 2-fluoropyridinetribromoborane,



could account for the slightly larger shifts of the 4-halopyridine adducts.

TABLE II. ^{1}H NMR Chemical Shifts[a] for 3- and 4-Halopyridineboranes.

Pyridine base	H_2	H_3	H_4	H_5	H_6	solvent
3-fluoropyridine	8.25	–	7.20	7.10	8.13	C_6D_6
3-chloropyridine	8.62	–	7.98	7.53	8.52	$CDCl_3$
3-bromopyridine	8.72	–	8.15	7.45	8.57	$CDCl_3$
3-cyanopyridine	8.92	–	8.19	7.67	8.85	$CDCl_3$
4-chloropyridine	8.43	7.52	–	7.52	8.43	$CDCl_3$
4-bromopyridine	8.44	7.68	–	7.68	8.44	$CDCl_3$
4-cyanopyridine	8.85	7.80	–	7.80	8.85	$CDCl_3$

[a]Relative to TMS as an internal standard.

TABLE III. Changes in Chemical Shift for Pyridine Ring Protons upon Borane Adduct Formation.[a]

pyridine base	H_2	H_3	H_4	H_5	H_6
3-fluoropyridine	+3.0	–	–4.8	–31.2	–3.0
3-chloropyridine	–4.8	–	–22.2	–25.2	–6.0
3-bromopyridine	–4.2	–	–27.0	–21.0	–6.0
3-cyanopyridine	0.0	–	–8.4	–10.2	–3.0
3-methylpyridine[b]	+4.0	–	–19.4	–18.2	+2.4
3-ethylpyridine[b]	+1.3	–	–24.5	–22.7	–1.0
4-chloropyridine	–5.4	–14.4	–	–14.4	–5.4
4-bromopyridine	–4.8	–18.6	–	–18.6	–4.8
4-cyanopyridine	–6.0	–19.8	–	–19.8	–6.0
4-methylpyridine[b]	+2.8	–20.2	–	–20.2	+2.8
4-ethylpyridine[b]	+7.7	–12.4	–	–12.4	+7.7

[a]Shifts are in Hertz upfield (+) or downfield (–) from the free pyridine signals. [b][6].

The chemical shifts observed for the ring protons in the borane adducts are listed in Table II. In Table III are the changes in the chemical shifts for the protons upon adduct formation. The shifts reported for 3- and 4-methyl- and ethylpyridines have been included for comparison. It can be seen that the magnitudes of the proton shifts do not correlate with the ^{11}B NMR shifts nor with the B–N bond strength if the ^{11}B chemical shifts truly reflect this parameter.

There are three different factors which influence the changes in the chemical shift of the pyridine protons upon adduct formation [4, 11]. The first is the inductive effect of placing a formal positive charge on the nitrogen atom. This inductive influence results in a decrease in the diamagnetic shielding which will cause a downfield shift of the proton resonances, especially at the 2 and 6 positions.

The second effect is a decrease in the π electron density of the pyridine ring upon adduct formation. This decrease causes a reduction of the paramagnetic anisotropic effect. This will result in an almost uniform upfield shift for all of the ring protons.

In pyridine, the lone pair of electrons on the nitrogen causes a paramagnetic shielding of the 2 and 6 protons [4, 12]. Formation of the dative bond using this electron pair greatly reduces this paramagnetic shielding to produce a significant upfield shift for the adjacent protons. The 3-, 4-, and 5-hydrogens are farther removed from the lone pair and so are not influenced much by this effect. The shifts actually observed represent the sum of all of these effects.

Differential Scanning Calorimetry

All of the borane adducts except the 3-fluoropyridineborane were examined by differential scanning calorimetry. The 3-chloropyridineborane and the 3-bromopyridineborane were found to give small endotherms which are attributed to the melting of the compounds.

The borane adducts of 4-chloropyridine and 4-bromopyridine, which had been reported earlier [13], were found to give large exotherms in the region 130–135 °C. There was some indication of a very weak endotherm preceding the exotherm for 4-chloropyridineborane but none for the bromo analog.

The exothermic behavior of these two compounds could be a dissociation of the borane adduct followed by a dimerization (polymerization) of the free 4-halopyridines [14].

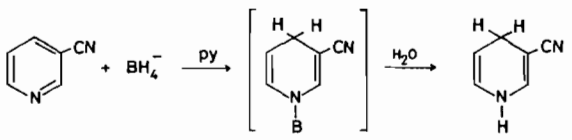
An alternative reaction is a reduction of the pyridine ring as suggested for the cyanopyridineboranes below. The enthalpy changes observed were –10.1 ± 1.8 Kcal/mol for 4-chloropyridineborane and –16.0 ± 1.6 Kcal/mol for 4-bromopyridineborane.

The two isomeric cyanopyridineboranes also were found to exhibit exothermic behavior upon heating. The 3-cyanopyridineborane, upon heating, gives some indication of a two step exothermic change, however the two exotherms were not well resolved. The total enthalpy change for this compound was found to be –20 ± 3.0 Kcal/mol. The 4-cyanopyridineborane gave only a single exothermic signal. The enthalpy was observed to be –20.7 ± 0.7 Kcal/mol.

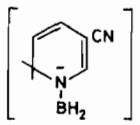
The products of these changes are not known. When a larger sample (<0.2 g) of 3-cyanopyridine was heated in a sealed, evacuated tube in an attempt to isolate the products, *the tube shattered violently*, destroying the oil bath in which it was being heated.

The products may be some reduced pyridine species. The reaction of 3-cyanopyridine and boro-

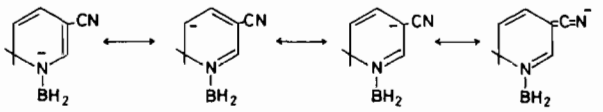
hydride ion in aprotic solvents was found to give the 1,4-dihydropyridine [15].



For the cyanopyridineboranes, the initial addition product might be expected to be a 1,2-addition,



since the hydrogens attached to the boron are quite close to these sites. Initial addition at either the 2 or 6 position might account for the lower initiation temperature and the resultant two step process because the cyano group in the 3 position could stabilize the negative charge generated. The possible resonance structures are:



With the cyanide in the 4 position, no stabilization of the intermediate by the –CN group is possible. The equivalent enthalpy changes suggest that the final products may be similar.

Acknowledgements

The assistance of Dr. A. Dean Sherry of the University of Texas at Dallas in obtaining the ^{11}B NMR spectra and the financial support of The Robert A. Welch Foundation, Houston, Texas, are gratefully acknowledged.

References

1 H. S. Booth and D. R. Martin, *J. Am. Chem. Soc., 64,* 2198 (1942).
2 H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc., 78,* 2173 (1956).
3 H. C. Brown, *J. Chem. Soc., (London),* 1248 (1956).
4 H. H. Perkampus and U. Krüger, *Ber. Bunsenges. Phys. Chem., 71,* 439 (1967).
5 E. J. McLauchlan and E. F. Mooney, *Spectrochim. Acta, 23A,* 1227 (1967).
6 E. F. Mooney and M. A. Qaseem, *J. Inorg. Nucl. Chem., 30,* 1439 (1968).
7 C. J. Foret, M. A. Chiusano, J. D. O'Brien and D. R. Martin, *J. Inorg. Nucl. Chem., 42,* 165 (1980).
8 C. J. Foret, K. R. Korzekwa and D. R. Martin, *J. Inorg. Nucl. Chem., 42,* 1223 (1980).
9 P. N. Gates, E. J. McLauchlan and E. F. Mooney, *Spectrochim. Acta, 21,* 1445 (1965).
10 H. Nöth and B. Wrackmeyer, NMR Basic Principles and Progress, Vol. 14, p. 84, Springer-Verlag, New York (1978).
11 V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc., 60,* 248 (1964).
12 J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.,* 304 (1961).
13 M. A. Weiner and M. Lattman, *Inorg. Nucl. Chem. Lett., 11,* 273 (1975).
14 J. P. Wibaut and F. W. Broekman, *Rec. Trav. Chim., 58,* 885 (1939).
15 S. Yamada, M. Kuramoto and Y. Kikugawa, *Tetra. Letters,* 3101 (1969).