Donor-Acceptor Strengths in Substituted Pyridine Complexes of Trifluoroborane and Tribromoborane

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Molecular complexes of some 3- and 4-substituted pyridines with trifluoro- and tribromoborane have been synthesized and characterized. Infrared and proton magnetic resonance spectra are reported. The ^{11}B NMR chemical shifts were measured. With an individual haloborane, there is little change in the value of the chemical shift among the substituted pyridine bases indicating little difference in the stability of the complexes. The 3- and 4-cyanopyridine adducts were found to be slightly less stable than the 3-halopyridine adducts. The change in the electron density within the pyridine ring as a result of adduct formation is discussed.

Introduction

Trihaloboranes, being coordinatively unsaturated, form adducts with a wide variety of donor molecules. Adducts of borane and trihaloboranes with pyridine and substituted pyridines have been the subject of many studies to ascertain the relative donor–acceptor strengths [1–3]. ^{11}B chemical shifts have been used as a criterion to determine the strength of the dative bond [4–7]. The ^{11}B chemical shifts may not be used unambiguously for the quantitative evaluation of the coordinate bond in borane complexes because of the variation in the rehybridization energy in the transition from sp^2 to sp^3 states [8] or because the interpretation of the spectra may be complicated due to the existence of intermolecular hydrogen bonding [9]. However, ^{11}B chemical shifts have been used successfully with the adducts of trihaloboranes [4–6]. It has been observed that the chemical shifts serve as a measure of the donor–acceptor strengths and reveal that the donor strengths of the substituted pyridines follow the series 2-alkyl- > 4-alkyl- > 3-alkylpyridines while the Lewis acid order of boron trihalides is $BF_3 < BCl_3 < BBr_3$. In an earlier paper [7], we have reported that the stability of the 2-halopyridine complexes of BBr_3, as observed from the ^{11}B chemical shifts, decreases as the size of the halogen substituent increases, clearly showing the steric effect of the substitutent at the 2-positions. The donor strength of the halopyridines generally increases as the halogen atom is moved away from the donor atom [10].

In the present study we report the synthesis and characterization of adducts of BF_3 and BBr_3 with 3-fluoro-, 3-chloro-, 3-bromo-, 3-cyano- and 4-cyanopyridine. An attempt has been made to correlate the inductive effect of the electronegative substituent on the pyridine ring to the ^{11}B chemical shifts. Also included are ^1H NMR and IR spectral studies.

Experimental

All reactions and transfers were conducted either in a glass high vacuum system or in an atmosphere of dry nitrogen. Infrared spectra were recorded in a nujol mull between cesium iodide plates on a Perkin-Elmer 257 spectrometer. Due to the sensitivity of the complexes towards moisture, IR samples were prepared in a dry nitrogen atmosphere in a glove box and the spectra taken immediately. ^{11}B chemical shifts were measured on a Nicolet 200 spectrometer at 200 MHz. Proton NMR spectra were recorded either on a Varian T-60 or on a Nicolet 200 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York.

All the substituted pyridines (Aldrich) were used without further purification except for 3-fluoropyridine (Pfaltz & Bauer) which was dried over calcium hydride before use. Trifluoroborane etherate was purified by distillation under reduced pressure and tribromoborane was distilled under vacuum

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and stored over mercury. The solvent, dichloromethane, was distilled from P_4O_{10} before use.

3-Fluoropyridinetrifluoroborane

In a typical preparation, a solution of 2.1 g (21.6 mmol) of 3-fluoropyridine in 50 ml of dichloromethane was immersed in a stream of dry nitrogen. The solution was frozen in liquid nitrogen. To this, 2.7 ml (21.6 mmol) of $BF_3 \cdot Et_2O$ was injected by a syringe. The top layer of the etherate was then frozen. The contents of the reactor were allowed to warm slowly to room temperature with stirring.

Stirring was continued for about 10 hours. The solvent was removed under vacuum to yield 3.04 g (85.4%) of white 3-fluoropyridinetrifluoroborane crystals (m.p. 32–36 °C). *Anal.* Calc.: C, 36.41; H, 2.45; N, 8.50%. Found: C, 35.37; H, 2.49; N, 7.41%. IR spectra: 3125(w), 3087(m), 1637(s), 1595(s), 1564(sh), 1551(s), 1492(sh), 1265(m), 920(sh), 872(s), 825(s), 810(sh), 770(sh), 708(sh), 698(s), 673(s), 627(s), 542(s), 522(s), 482(m), 426(m), 407(s), 322(s) cm^{-1} (s-strong, m-medium, w-weak, sh-shoulder).

3-Chloropyridinetrifluoroborane

A procedure similar to that described for 3-fluoropyridinetrifluoroborane was used to yield 97.0% of white crystalline 3-chloropyridinetrifluoroborane (m.p. 44–45 °C). *Anal.* Calc.: C, 33.11; H, 2.23; N, 7.73%. Found: C, 32.83; H, 2.40; N, 7.98%. IR spectra: 3115(m), 3082(m), 1623(s), 1568(s), 1533(s), 1485(sh), 1435(sh), 1252(w), 903(sh), 811(s), 782(s), 729(s), 688(s), 670(s), 620(s), 541(m), 518(m), 455(s), 430(s), 355(m), 310(s) cm^{-1}.

3-Bromopyridinetrifluoroborane

Following the procedure described for the preparation of the 3-fluoropyridine analogue, an 86.6% yield of white crystals of 3-bromopyridinetrifluoroborane (m.p. 74–78 °C) was obtained. *Anal.* Calc.: C, 26.60; H, 1.78; N, 6.20%. Found: C, 25.97; H, 2.05; N, 5.67%. IR spectra: 3130(m), 3088(w), 1622(s), 1600(w), 1563(m), 1530(s), 1484(s), 1436(s), 1252(w), 907(s), 814(s), 802(s), 762(s), 708(m), 698(s), 680(s), 627(s), 537(sh), 515(m), 462(m), 457(sh), 374(m), 324(m) cm^{-1}.

3-Cyanopyridinetrifluoroborane

A similar procedure to that described for 3-fluoropyridinetrifluoroborane was followed. When the solution was allowed to warm to room temperature, a crystalline white insoluble product was formed. The solid was filtered and washed with a little (~5 ml) 1,2-dichloromethane to yield 58.7% 3-cyanopyridinetrifluoroborane (m.p. 123–125 °C). *Anal.* Calc.: C, 41.92; H, 2.35; N, 16.30%. Found: C, 40.07; H, 2.74, N, 15.67%. IR spectra: 3118(w), 3072(m), 2245(s), 1637(s), 1600(s), 1544(s), 1482(s), 1437(sh), 917(sh), 829(s), 802(s), 775(m), 705(s), 690(s), 668(s), 550(s), 522(m), 473(m) cm^{-1}.

4-Cyanopyridinetrifluoroborane

A procedure similar to that used for the 3-cyanopyridine analogue was used. This yielded 38.1% of white crystalline 4-cyanopyridinetrifluoroborane (m.p. 105 °C dec.). *Anal.* Calc.: C, 41.92; H, 2.35; N, 16.30%. Found: C, 41.36; H, 2.38; N, 15.78%. IR spectra: 3120(m), 3073(m), 2243(m), 1635(s), 1552(s), 1505(s), 1433(s), 1210(s), 1200(s), 1060(s), 895(sh), 858(s), 661(s), 577(s), 550(m), 507(m), 311(m) cm^{-1}.

3-Fluoropyridinetribromoborane

In a typical preparation, 1.65 ml (25.0 mmol) of 3-fluoropyridine in ~200 ml of dichloromethane was frozen and evacuated in a vacuum line. To this solution was transferred 2.4 ml (25.0 mmol) of BBr_3. The contents of this flask were frozen and allowed to warm slowly to room temperature with stirring. The solvent was removed leaving a yellowish white product. The solid was recrystallized from dichloromethane to give 5.88 g (67.6% yield) of 3-fluoropyridinetribromoborane (m.p. 121 °C). *Anal.* Calc.: C, 17.28; H, 1.16; N. 4.03; B, 3.11; Br, 68.96; F, 5.47%. Found: C, 17.50; H, 1.44, N, 4.04; B, 3.45; Br, 69.40; F, 5.78%. IR spectra: 3114(w), 3072(m), 1635(s), 1585(s), 1551(m), 1481(s), 1442(sh), 1311(s), 1280(s), 1251(s), 1192(s), 1102(s) 1080(s), 1035(m), 940(m), 909(s), 893(s), 805(s), 745(s), 635(s), 592(m), 581(s), 528(s), 433(m), 306(s) cm^{-1}.

3-Chloropyridinetribromoborane

A procedure similar to that described for 3-fluoropyridinetribromoborane was followed resulting in a 57.8% yield of recrystallized 3-chloropyridinetribromoborane (m.p. 153 °C). *Anal.* Calc.: C, 16.49; H, 1.11; N, 3.85; B, 2.97; Br, 65.84, Cl, 9.74%. Found: C, 16.63; H, 1.16; N, 3.73; B, 2.90; Br, 65.13; Cl, 9.39%. IR spectra: 3100(w), 3053(w), 1610(sh), 1557(m), 1424(s), 1400(w), 1249(w) 1198(m), 1132(s), 1115(s), 1097(s), 1031(sh), 819(s), 807(s), 740(s), 640(s), 590(m), 579(s), 450(s), 435(m) cm^{-1}.

3-Bromopyridine tribromoborane

3-Bromopyridinetribromoborane was prepared following the procedure used for the 3-fluoropyridine analogue. A yield of 86.2% of 3-bromopyridinetribromoborane (m.p. 137 °C) was obtained. *Anal.* Calc.: C, 14.70; H, 0.99; N, 3.43; B, 2.65; Br, 78.24%. Found: C, 14.97; H, 1.12, N, 3.51; B, 2.40; Br, 78.73%. IR spectra: 3098(m), 3045(w), 1617(m), 1607(m), 1591(m), 1552(w), 1517(s), 1467(s), 1420(s), 1240(m), 1196(s), 1120(s), 1095(s),

1030(w), 901(m), 802(s), 790(s), 633(s), 590(w), 578(s), 440(m), 349(m) cm^{-1}.

3-Cyanopyridinetribromoborane

Following a procedure similar to that described for 3-fluoropyridinetribromoborane, a yield of 55.5% of 3-cyanopyridinetribromoborane (m.p. 192 °C; a decomposition temperature of 150–155 °C reported [7] earlier is believed to be in error) was obtained. *Anal.* Calc.: C, 20.32; H, 1.14; N, 7.90; B, 3.05; Br, 67.60%. Found: C, 20.49; H, 1.45; N, 7.91; B, 2.94; Br, 67.29%. IR spectra: 3060(w), 2241(w), 1665(sh), 1630(s), 1599(s), 1550(sh), 1495(sh), 1344(s), 1251(w), 1195(sh) 1115(m), 1091(s), 1028(w), 862(m), 815(sh), 630(w), 572(w), 560(m) cm^{-1}.

4-Cyanopyridinetribromoborane

A method similar to that described for the synthesis of 3-fluoropyridinetribromoborane was used to obtain a yield of 55.7% of 4-cyanopyridinetribromoborane (m.p. 141 °C). *Anal.* Calc.: C, 20.32; H, 1.14; N, 7.90; B, 3.05; Br, 67.60%. Found: C, 19.88; H, 1.22; N, 7.97; B, 3.07; Br, 67.16%. IR spectra: 3057(w), 1684(sh), 1662(sh), 1630(s), 1590(s), 1543(sh), 1515(sh), 1232(w), 1192(sh), 1071(m), 1000(m), 822(s), 752(sh), 650(m), 637(m) cm^{-1}.

Results and Discussion

Adducts of trihaloboranes in solution may undergo ionization giving $BX_2(py)_2^+BX_4^-$ or $BX_2py^+X^-$ (X = F, Cl or Br). The ionization is usually prevented when the fourth coordination site of boron is occupied by strong basic molecules such as pyridine. Adducts of pyridine with BCl_3 are molecular in benzene solution [11]. In a strong basic solvent like acetonitrile, the pyridine adducts of BCl_3 and BBr_3 apparently behave as nonconductors [12]. In the present study all of the BBr_3 adducts were synthesized twice: with excess of BBr_3 and with an excess of the substituted pyridine. Elemental analyses in both samples are consistent with the formation of the same molecular adducts. The existence of molecular adducts as the only product was confirmed also by spectral analyses. The infrared spectra of the materials in nujol mull and in dichloromethane solution are essentially identical. Adducts of BBr_3 show a broad absorption in the region 731–650 cm^{-1}, characteristic of BBr_3 vibrations in its molecular adducts [13, 14]. No absorption was observed for BBr_4^- vibrations at ~605 cm^{-1} [15]. Adducts of BF_3 gave a combination of bands with shoulders in the region 1170–1050 cm^{-1}, as observed [16] for the acetonitrile adduct of BF_3. The C≡N stretch in adducts of BF_3 and BBr_3 with 3-cyanopyridine appears ~20 cm^{-1} higher while that for 4-cyanopyridine-BF_3 shifts only slightly to higher wavelengths when compared to the corresponding cyanopyridine spectra. $\nu_{(C\equiv N)}$ for 4-cyanopyridine-BBr_3 could not be identified due to decomposition of the complex on the cesium iodide plate, as indicated by the white mull turning into a yellow product. While there may be a difference in the details in the IR spectra of all of the adducts, the $\nu_{(C-C)}$ and $\nu_{(C-N)}$ modes generally fell to lower wavelengths on complex formation. The B–N stretch could not be identified due to the complicated nature of the spectra.

TABLE I. ^{11}B Chemical Shifts[a] for Substituted Pyridine Complexes of BF_3 and BBr_3.

Pyridine	BF_3	BBr_3
3-fluoropyridine	17.91	25.99
3-chloropyridine	17.90	25.99
3-bromopyridine	17.90	26.04
3-cyanopyridine	17.77	25.87
4-cyanopyridine	17.75	25.83

[a]Shifts (ppm) were measured in $CDCl_3$ and are upfield with respect to $(CH_3O)_3B$ as an external standard.

The ^{11}B NMR data are listed in Table I. All signals are on the high field side of the standard which indicates that the coordination number of boron increases from three to four. The appearance of a single resonance band at ~17.9 ppm for BF_3 adducts and at ~26.0 ppm for BBr_3 adducts is consistent with the existence of 1:1 molecular species in dichloromethane. Although no peak has been observed for the presence of BF_4^- in the solid state (IR), ^{11}B spectra of some BF_3 adducts show weak bands (*ca.* <5%) at 19.6 ppm. This band may indicate the presence of BF_4^- (19.9 ppm in CH_2Cl_2 [22]) which might result from a slight ionization of the compound:

$$[3\text{-Xpy}\cdot BF_3]_2 \rightleftarrows [(3\text{-Xpy})_2BF_2]^+BF_4^-$$

A comparison of the chemical shifts shows that the acceptor strength of BBr_3 is greater than that of BF_3 as observed in earlier studies [1(b), 4]. The extent of chemical shifts for BBr_3 and BF_3 adducts implies that the transfer of charge from nitrogen to boron is greater with the formation of BBr_3 adducts than with the BF_3 adducts. This has been rationalized from the study of molecular complexes of boranes and trihaloboranes with a variety of donor molecules [17].

It might be expected that the adduct stability will decrease as the electronegativity of the substituent in the pyridine ring increases due to an inductive

TABLE II. ^{1}H NMR Chemical Shifts (ppm)[a] for Adducts of Substituted Pyridine Complexes in $CDCl_3$.

Compounds	H(2)	ΔH(2)	H(4)	ΔH(4)	H(5)	ΔH(5)	H(6)	ΔH(6)
3-Fluoropyridine–BF_3	8.66	0.14	8.04	0.66	7.88	0.62	8.63	0.17
3-Chloropyridine–BF_3	8.77	0.20	8.23	0.63	7.78	0.59	8.68	0.21
3-Bromopyridine-BF_3	8.87	0.22	8.38	0.63	7.71	0.56	8.72	0.24
3-Cyanopyridine–BF_3	9.07	0.12	8.51	0.45	7.99	0.46	8.99	0.16
4-Cyanopyridine–BF_3	8.97	0.17			8.05	0.52	8.97	0.17
3-Fluoropyridine–BBr_3	9.95	1.03	8.09	0.71	7.94	0.68	9.52	1.06
3-Chloropyridine–BBr_3	9.58	1.01	8.25	0.65	7.83	0.64	9.51	1.04
3-Bromopyridine–BBr_3	9.68	1.03	8.40	0.65	7.77	0.62	9.58	1.10
3-Cyanopyridine–BBr_3	9.97	1.02	8.55	0.49	8.06	0.53	9.89	1.06
4-Cyanopyridine–BBr_3	9.90	1.10			8.11	0.58	9.90	1.10

[a]Chemical shifts with respect to TMS as an internal standard.

effect. However, the data for adducts of BF_3 and BBr_3 with 3-halopyridines do not reflect such an effect. It may be best explained by the fact that the steric requirements for BF_3 and BBr_3 molecules are high enough to outweigh the inductive effect of the halogens attached to the pyridine ring. The data for the cyanopyridine adducts show an inductive effect of the cyanide substituent.

The proton chemical shifts resulting from adduct formation have been used to estimate the acceptor strengths of the trihaloboranes [18, 19]. The stronger acid produces a greater deshielding of the protons and results in a larger chemical shift. The ^{1}H NMR spectral data for the substituted pyridine adducts of BF_3 and BBr_3 are given in Table II.

Also shown are the changes in chemical shifts (ΔH) for the ring protons upon adduct formation. The interpretation of the complex spectra was in accordance with an earlier paper [2] which stated that the chemical shifts are influenced by three factors. These factors are: (1) a decrease in electron density around the ring hydrogens resulting from adduct formation (2) a decrease in the π electron density within the pyridine ring, and (3) a reduction in the paramagnetic shielding due to the absorption of the electron pair in the nitrogen atom into the N–B bond. The observed shift is the combination of all three factors, the effect due to the third factor being the greatest due to the local dipole moment of the B–N bond [20].

The ^{1}H chemical shifts for the BF_3 adducts of 3-chloro-, 3-bromo- and 4-cyanopyridine in $CDCl_3$ compare favorably with those obtained in ether [2]. The small differences may be a solvent effect [21]. Comparison of the data in Table II shows that the ΔH's are smaller in adducts of BF_3 than in adducts of BBr_3. The lone pair of electrons on the nitrogen donor is attracted by the formal charge on the boron atom and repelled by the negative charges on the halogen atoms of the trihaloboranes causing deshielding and shielding effects respectively, on the pyridine hydrogens. Since the repulsion varies inversely as the boron–halogen distance, the shielding effect is expected to be greater in the BF_3 adducts. This apparently results in comparatively smaller shifts for all the ring protons in the BF_3 adducts. The significant differences in ΔH(2)'s and ΔH(6)'s of BF_3 adducts with the corresponding ΔH's of BBr_3 adducts may be explained in terms of difference in the local dipole moments of the B–N bond in their adducts. It is reported that the dipole moment of the boron–nitrogen bond is less in BF_3-pyridine than in BBr_3-pyridine [11]. The same order would also be expected for the substituted pyridine adducts.

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