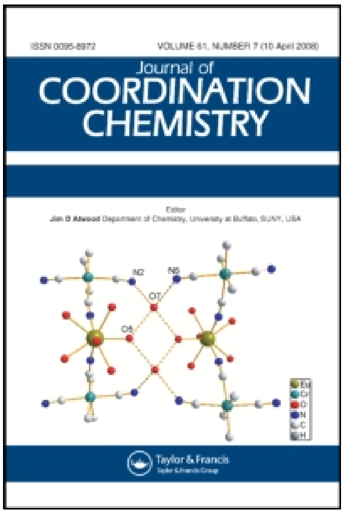

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THE BEHAVIOR OF RIGID AND SEMI-RIGID BIDENTATE DONOR MOLECULES TOWARD SOME SIMPLE BORON ACCEPTORS

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Synthesis of a series of complexes of the type $LLBX_2{}^+BX_4{}^-$ where $X = F^-$ and Cl^- and LL = 1,10-phenanthroline, 2,2′-bipyridine and 1,8-bis(dimethylamino)naphthalene was achieved by the direct interaction of the ligand and BX_3. No reaction was observed for $X = CH_3$. The reactions provide a direct route for the preparation of tetra-coordinate boronium cations. The boron-11 nmr and infrared spectra of these complexes confirm the ionic nature of the compounds. 2,2′-Bipyridine functions as a chelating agent rather than as a bis-monodentate donor. 1,8-Bis(dimethylamino)naphthalene is found to be able to chelate cations much larger than protons. The steric implications of donor-acceptor interactions of boron with rigid and semi-rigid chelating donor molecules are discussed.

INTRODUCTION

There is a general absence of knowledge concerning the reactions of boron Lewis acids with rigid or semi-rigid polydentate chelating donors. While the literature dealing with boron donor-acceptor complexes is indeed vast, most of the work has dealt with monodentate ligands. The use of chelating donors provides an opportunity to study acid-base interactions under conditions that require formation of unsymmetric products, *i.e.* ionic compounds. This work is an effort to investigate the possible formation of such species and to examine their steric properties.

Review of the chemistry of the boron halides[1] (the simplest boron compounds) reveals that most of the complexes observed are tetracoordinate neutral boron species of the general form base · BX_3. If the donor is bidentate, the boron can remain tetracoordinate only if an X^- group is displaced, producing a boronium cation, as in Eq. 1.

$$BX_3 + LL \rightarrow LLBX_2{}^+ + X^- \qquad (1)$$

Boronium cations have been obtained with various nitrogen donors,[2–6] including some bidentate tertiary amines.[7–13] The latter form cations containing one or two sterically favored five-membered chelate rings. They are generally stable toward hydrolysis and will undergo various metathetical reactions.[10,12] The X^- group which is displaced in equation (1) may retain its identity, as in the case of I^-,[6] or it may react with an additional molecule of BX_3 to produce a $BX_4{}^-$ anionic species as described in Eq. 2.

$$LL + 2BX_3 \rightarrow LLBX_2{}^+ + BX_4{}^- \qquad (2)$$

The present investigation describes in detail the reactions between some bidentate nitrogen donors and some simple Lewis acid acceptors, BX_3, which may be described by Eq. 2, where LL denotes a bidentate nitrogen donor molecule.

EXPERIMENTAL SECTION

Instrumentation and Analyses.

Standard high-vacuum, inert-atmosphere and Schlenk techniques[14] were employed for all manipulations. Infrared spectra were determined as Nujol mulls or as KBr or KCl pellets with Beckman IR-12 and Perkin-Elmer 337 spectrophotometers. Proton nmr spectra were measured on a Varian T-60 spectrometer and are reported in ppm downfield from TMS (external). ^{11}B spectra were measured at ambient temperature with a Varian HA-100 instrument at 32.1 MHz; ^{11}B chemical shifts, reported in ppm relative to $BF_3 \cdot OEt_2$, were determined by tube-interchange. Melting points were determined in sealed capillaries using a Uni-Melt apparatus and are uncorrected. C, H, F, and Cl microanalyses were done by Huffman Laboratories, Wheatridge, Colorado.

Boron was determined by flame emission spectroscopy or by volumetric titration of the *D*-Mannitol complex of boric acid with standard sodium hydroxide solution.

Solvents.

Reagent grade chloroform, benzene and toluene were purified by standard methods, distilled under nitrogen, and stored over P_4O_{10} in evacuated vessels. n-Heptane was distilled under nitrogen and stored over $LiAlH_4$ in an evacuated bulb. When needed, solvents were condensed directly into the reaction vessel.

Donors.

1,10-Phenanthroline, $C_{12}H_8N_2$, was prepared by the method of Madeja[15] and was dehydrated by heating *in vacuo* at 80°. Melting point of the white needles was 117-118.5°, lit.[16] 117-118°.

2,2'-Bipyridine, $C_{10}H_8N_2$, (Eastman Chemical Company) was sublimed *in vacuo* at 65°. Melting point of the white needles was 71.0-71.5°, lit.[16] 71-73°.

1,8-Bis(dimethylamino)naphthalene, [1,8-BDN], $C_{14}H_{18}N_2$, (Aldrich Chemical Company), was sublimed *in vacuo.* Melting point of the solid was 49.5-50.0°, lit.[17], 47-48°.

Acceptors

Boron Trifluoride, BCl_3, obtained from the Matheson Company, Inc., was fractionated prior to use through −126° into −196°.

Boron Trichloride, BCl_3, obtained from the Matheson Company, Inc., was fractionated prior to use through −45° into −196°.

Trimethyl Boron, $B(CH_3)_3$, was prepared by the treatment of diborane with a 3.5 molar excess of trimethylaluminum in a sealed, evacuated bulb. The reaction mixture was allowed to stand at 25° for 68 hours, then fractionated on the vacuum line to remove any unreacted diborane. The product was passed through −126° into −196°. The $B(CH_3)_3$ recovered from the −196° trap was identified by its vapor-phase infrared spectrum[18] and by its −83.6° vapor pressure of 20 Torr, lit.[14], 20 Torr.

1,10-Phenanthroline–Boron Trifluoride System. A 4.27 mmol sample of BF_3 was condensed onto 0.1833 g (1.02 mmol) of phenanthroline in 15 ml of benzene at −196°. As the mixture was warmed to 25°, an insoluble white solid rapidly formed, m.p. 317-318° (dec.). Separation of volatile materials resulted in the recovery of 2.21 mmol BF_3, implying 2.06 mmol consumption and a mole ratio BF_3: phenanthroline of 2.02. *Anal.* Calcd for $C_{12}H_8N_2B_2F_6$: C, 45.7; H, 2.6; F, 36.1. Found: C, 45.5; H, 2.7; F, 35.9.

2,2'-Bipyridine–Boron Trifluoride System. A 2.96 mmol sample of BF_3 was condensed onto 0.1014 g (0.65 mmol) of 2,2'-bipyridine in 10 ml of toluene. As the mixture was warmed to 25°, an insoluble white solid rapidly formed, m. p. 260°+ (dec.). Separation of volatile materials resulted in the recovery of 1.64 mmol BF_3, implying 1.32 mmol consumption and a mole ratio BF_3: 2,2'-bipyridine of 2.03. *Anal.* Calcd for $C_{10}H_8N_2B_2F_6$: C, 41.2; H, 2.8; F, 39.1. Found: C, 41.3; H, 2.7; F, 39.4.

1,8-Bis(dimethylamino)naphthalene–Boron Trifluoride System. A 2.83 mmol sample of BF_3 was condensed onto 0.0917 g (0.43 mmol) of 1,8-bis(dimethylamino)naphthalene in 5 ml of toluene. Upon warming to −23°, an insoluble white solid appeared, m. p. 150–175° (dec). Separation of volatile materials resulted in the recovery of 1.94 mmol of BF_3, implying 0.89 mmol consumption and a mole ratio BF_3: 1,8-BDN of 2.07.

1,10-Phenanthroline–Boron Trichloride System. A 5.05 mmol sample of BCl_3 was condensed onto 0.2236 g (1.24 mmol) of phenanthroline in 10 ml of toluene. As the mixture was warmed to 25°, a hygroscopic white solid formed rapidly, m. p. 200° (dec.). Separation of the volatile materials resulted in the recovery of 2.52 mmol of BCl_3, implying 2.53 mmol consumption and a mole ratio BCl_3: phenanthroline of 2.04. *Anal.* Calcd for $C_{12}H_8N_2B_2Cl_6$: B, 5.22; Cl, 51.4. Found: B, 5.22; Cl, 51.0.

2,2'-Bipyridine–Boron Trichloride System. A 2.87 mmol sample of BCl_3 was condensed onto 0.1574 g (1.01 mmol) of 2,2'-bipyridine in 10 ml of toluene. Upon warming to 25°, a hygroscopic white solid formed, m. p. 212–215° (dec.). Sparation of the volatile materials yielded 0.79 mmol of BCl_3, implying 2.08 mmol consumption and a mole ratio

BCl_3 : 2,2′-bipyridine of 2.06. *Anal.* Calcd for $C_{10}H_9H_8N_2B_2Cl_6$: C, 30.8; H, 2.01; B, 5.5 Found: C, 30.7; H, 2.3; B, 5.4.

1,8-Bis(dimethylamino)naphthalene–Boron Trichloride System A 2.99 mmol sample of BCl_3 was condensed onto 0.1096 g (0.51 mmol) of 1,8-BDN in 10 ml of n-heptane at −196°. When the BCl_3 came into contact with the surface of the frozen sample, the colorless mixture immediatly turned yellow-orange. As the reaction mixture was warmed to 25°, an orange solid separated from the pale yellow liquid. No further changes were noted after three days at 25°. Removal of volatile materials resulted in the isolation of a hygroscopic yellow-gold powder, m. p. 155–165° (dec). Separation of the volatile materials resulted in the recovery of 1.97 mmol of BCl_3, identified by its vapor-phase infrared spectrum, implying 1.02 mmol consumption and a mole ratio BCl_3 : 1,8-BDN of 2.00.

1,10-Phenanthroline-Trimethylboron System. Treatment of phenanthroline in toluene solution with $B(CH_3)_3$ resulted only in the recovery of unchanged starting materials.

2,2′-Bipyridine-Trimethylboron System, Condensation of $B(CH_3)_3$ onto an n-heptane solution of 2,2′-bipyridine and subsequent warming to 25° resulted only in the recovery of unchanged starting materials.

1,8-Bis(dimethylamino)naphthalene-Trimethylboron System. Treatment of an n-heptane solution of 1,8-BDN with $B(CH_3)_3$ resulted only in the recovery of unchanged starting materials.

RESULTS AND DISCUSSION

NMR Spectra.

Boron-11 nmr chemical shifts are presented in Table 1. The presence of two boron species in the reaction products is clearly indicated by the observation of two boron-11 resonances. The resonances are generally of equal size and shape. The higher field signal of each of the complexes closely corresponds to that of known BX_4^- species and is thus taken as arising from BX_4^-. The lower chemical shifts must, therefore, arise from the cation and are so assign

The fluoride complexes are very stable, and their spectra do not change upon standing for 24 hours. Solutions of the chloro complexes, however, are unstable and the two resonances observed in a fresh solution are converted into several peaks within a few hours. Similar behavior has been observed for DMSO solutions of tetramethylammonium tetrachloroborate,[20] probably owing to the reaction of BCl_4^- with DMSO itself.[21]

Proton spectra of the complexes soluble in $CDCl_3$ showed the distinctive patterns of the ligands shifted to lower field strengths upon coordination. Proton spectra in DMSO also showed the expected down-

TABLE I
Boron-11 NMR chemical shifts

Compound	Solvent	BX_3 ppm	$(LLBX_2^+)$ ppm	BX_4^- ppm
BF_3 [a]	Methylcyclohexane	−10.0		
KBF_4 [b]	HF(−5°)			+1.81
NH_4BF_4 [c]	DMSO			+1.5
Phen/BF_3 [c]	DMSO		+0.6	+1.2
Bipy/BF_3 [c]	DMSO		+0.6	+1.2
1,8-BDN/BF_3 [c]	DMSO		−1.9	+1.2
BCl_3 [b]	Methylcyclohexane	−46.5		
$N(CH_3)_4BCl_4$ [b]	DMSO			−6.84
Phen/BCl_3 [c]	DMSO		−9.0	−6.8
Bipy/BCl_3 [c]	DMSO[d]		[d]	[d]
1,8-BDN/BCl_3 [c]	DMSO[e]		[e]	[e]

[a] M. F. Lappert, M. R. Litzow, J. B. Pedley and A. Tweedale, *J. Chem. Soc.* (A), 2426 (1971).

[b] Reference 19.

[c] This Work.

[d] Resonance was not observed because of very limited solubility.

[e] Complex reacts rapidly with DMSO and the desired resonance could not be observed.

field shift, but the spectra of the chloro species contained additional peaks which may have arisen from solvent-anion interactions (*vide supra*) or from hydrolytic reactions resulting from traces of moisture in the solvent or sample tube. The downfield shifts are more pronounced for BCl_3 than BF_3 complexes. The spectra of phenanthroline complexes are nearly unchanged except for the shifts resulting from coordination. In the case of 1,8-BDN, the singlet from the methyl protons and the ABX pattern from the ring protons are shifted downfield. The pattern also becomes more complex because of distortions in the molecule upon coordination. The 2,2′-bipyridine spectra are also shifted downfield, and in the BCl_3 complex, the symmetrical doublet of the protons adjacent to the atoms becomes extremely distorted. This distortion is not observed with the BF_3 complex and may reflect a steric interaction of the protons with the relatively bulky BCl_2^+ moiety. The proton spectra also demonstrate that the ligands have not undergone any reactions other than coordination. If there had been any attacks upon the ring systems of the ligands, the spectra would have shown alterations in the splitting patterns, which were not observed.

Infrared Spectra.

Infrared spectra of tetrahaloborate species have been reported by several workers. Waddington and Klanberg[22] examined the spectra of several BX_4^- salts and found that BCl_4^- species exhibit characteristic bands about 665(s), 690(s), 1275(w), 1380(w), and 1460(w) cm^{-1}. They also observed BF_4^- bands about 520(s), 535(s), 770(w), 1030(s) and 1060(s) cm^{-1}. Kynaston and co-workers[23] observed that BCl_4^- shows a strong band in the range 630-750 cm^{-1}, and that $KBCl_4$ also has weak bands at 1265, 1382, and 1449 cm^{-1}. For KBF_4, they observed 1032(s), 1054(s) and 1119(sh) cm^{-1}, and for $MeNH_3^+\ BF_4^-$, 1025(s) and 1063(s) cm^{-1}. A spectrum of KBF_4 run in our laboratory displayed two strong bands at 520 and 530 cm^{-1}, a medium intensity band at 770 cm^{-1}, and a very strong absorption envelope at 1000-1100 cm^{-1}.

The experimentally determined spectra of all complexes obtained in this work contain bands which may be attributed to the ligands, plus new bands which fall in the ranges reported for BX_4^- species. The spectrum of the phenanthroline/BF_3 complex is dominated by a massive band at 1000-1100 cm^{-1}. Other bands are observed at 350(w), 520(s), 550(s), 570(w), and 780 (m-s) cm^{-1}. The spectrum of the 2,2′-bypyridine/BF_3 complex contains a very intense absorption envelope at 1000-1250 cm^{-1}. 2,2′-Bipyridine itself has six absorptions in this range, but the shape and overwhelming intensity of the absorption indicates the presence of some absorbing species besides the ligand. Additional absorptions appear at 350(w), 520(s), 555(s), 890(s), and 925(s) cm^{-1}. The 780 cm^{-1} band of BF_4^- is obscured by a very strong ligand band, while the origin of the latter two bands is unclear at this time. As with the other two BF_3 complexes, the 1,8-BDN/BF_3 spectrum is characterized by a large envelope of bands at 1000-1150 cm^{-1} containing distinct bands at 1030(s), 1050(s), 1095(s),1110(m), and 1130(w) cm^{-1}. There are four ligand modes in this region, but the shape and intensity of the envelope clearly indicate the presence of BF_4^- in the complex. A weak band at 800 cm^{-1} and a medium intensity doublet at 900 cm^{-1} are also seen, but the origin of the latter is unknown.

The spectrum of the phenanthroline/BCl_3 complex reveals a strong absorption envelope at 625-750 cm^{-1} which contains distinct bands at 675, 695, 705, and 730 cm^{-1}, while 1,10-phenanthroline has only one band in this region at 740 cm^{-1}. The appearance of several bands within the envelope may be due to $^{10}BCl_4^-$ and $^{11}BCl_4^-$ species, but no isotopic studies have been conducted to examine this possibility. Medium intensity bands at 1370 and 1450 cm^{-1} are also observed Upon complete hydrolysis of the compound, all of these bands disappear and are replaced by absorptions attributable to boric acid. The 2,2′-bipyridine/BCl_3 product produces two strong bands at 710 and 675 cm^{-1} which are not present in 2,2′-bipyridine. Exposure of the product to water causes the disappearance of these bands. The spectrum of the hydrolyzed product is attributable to boric acid and free 2,2′-bipyridine. The spectrum of the 1,8-BDN/BCl_3 reaction product also reveals an absorption envelope at 630-730 cm^{-1} containing bands at 655, 670, 690, 705, and 715 cm^{-1}. The ligand shows only minor absorptions in this region. Two medium intensity bands are also found at 1250 and 1265 cm^{-1}. Upon exposure to the laboratory atmosphere for an hour, the yellow solid becomes white and the absorptions listed above disappear and are replaced by boric acid bands, plus bands which may be attributed to a protonated ligand species.

Steric Considerations

The configuration and rigidity of 1,10-phenanthroline cause it to always act as a chelating ligand.[24]

2,2′-Bipyridine is not "locked into" a cis conformation and has been found to be trans-planar in the solid state.[25] In benzene solution the molecule assumes a transoid conformation with an interplanar angle about 20-30°.[26] While some trans-bridging 2,2′-bipyridine complexes have been suggested,[27] the complexed ligand is nearly always represented as a chelating ligand having a cis-planar conformation. However, one must consider the possibility of coordination in the transoid or trans-planar conformation. 1,8-Bis(dimethylamino)naphthalene is a rigid molecule, planar in nature, with the methyl groups arranged above and below the carbon-nitrogen skeleton. The presence of the methyl groups requires that the lone pair of electrons on each nitrogen point toward each other, making the molecule a chelating ligand similar to phenanthroline. X-ray determination of the structure[28] shows the free base to be distorted, with the lone pairs oriented toward each other, but skewed above and below the plane. The rings are distorted toward a chair-type configuration and the entire molecule possesses nearly exact two-fold symmetry. The conformation is rigid because of close interlocking of all hydrogen atoms in the staggered conformation. The compound is very basic (pk of 12.34 in aqueous solution)[17] and is sometimes called "proton sponge." X-ray studies[29] of salts of the protonated base reveal that upon coordination the system assumes a planar conformation having the nitrogens and the proton in the plane of the system with the methyl groups rotated to positions above and below the skeletal plane.

1,8-BDN is known to accommodate protons easily, but is often assumed to be unable to accept larger electrophiles. Space-filling molecular models suggest, however, that a BH_2 unit may be accommodated only with a great degree of distortion and steric interference; and a $B(CH_3)_2$ unit cannot be accommodated at all because of severe steric interferences.

No apparent steric interferences were detected in the phenanthroline complexes. The infrared and boron-11 nmr spectra clearly show the complexes are ionic and must, therefore, contain phenathroline as a chelating ligand of BX_2^+. The 2,2′-bipyridine complexes could be of the form $LL \cdot 2BX_3$ if the ligand were in the transoid form, or $LLBX_2^+\ BX_4^-$ if it were in the cisoid form. The spectral evidence clearly demonstrates the presence of the BX_4^- ion, and one must, therefore, conclude that 2,2′-bipyridine reacts in this case as a cis-planar chelating ligand. This may be contrasted to the reaction with diborane, in which B_2H_6 forms a non-ionic bisborane adduct with 2,2′-bipyridine.[30] 1,8-BDN complexes with BX_3 are ionic, as demonstrated by their spectral properties. There seems to be no steric interference in the fluoride system, but the chloride complex shows definite steric interactions. The complex is golden-yellow, the only colored complex obtained in this work. This color is possibly a result of ring distortion and subsequent modifications in the π energy levels of the system giving rise to transitions in the visible range and the observed color of the complex.

The failure of trimethylboron to react with the donors cannot be due to steric interferences only. While 1,8-BDN clearly cannot accommodate the $B(CH_3)_2$ group, there are no great steric hindrances with the other two ligands, so the failure to undergo reaction must be a result of other factors. The halide ions are good leaving groups and can form the BX_4^- species much more easily than a methyl group can be displaced to subsequently form $B(CH_3)_4^-$. While the boron-halogen bond strength is greater than that of the boron-carbon bond, the halides participate in bridge-bonds much more readily than carbon species. One might thus attribute the observed unreactivity of trimethylboron to the difficulty of forming an unfavorable methyl-bridged transition state as compared to the more favorable halogen-bridged transition state. The observed reaction of the boron halides may thus not be a simple displacement of X^- and subsequent reaction with a second BX_3 molecule, but a concerted reaction proceeding through a halogen-bridged transition state, forming both the cation and the anion simultaneously.

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