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Derivatives of the Dimethylbis(2-pyridyl)borate(1−) Ion: Synthesis and Structure

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The syntheses and structures of derivatives of a novel uninegative bidentate ligand, the dimethylbis(2-pyridyl)borate anion, $(py)_2BMe_2^-$, are reported. Lithium dimethylbis(2-pyridyl)borate, $Li(py)_2BMe_2$, was prepared by adding a solution of bromodimethylborane to a solution of 2-lithiopyridine in a 1:2 molar ratio, respectively; subsequent hydrolysis afforded hydrogen dimethylbis(2-pyridyl)borate, $H(py)_2BMe_2$, in 44% yield. Reaction of $Li(py)_2BMe_2$ with either bromodimethylborane or bromodiphenylborane afforded the corresponding tricyclic bis(organo)boronium dimethylbis(2-pyridyl)borate species $R_2B(\mu\text{-py})_2BMe_2$ ($R = CH_3$, C_6H_5) in approximately 90% yields. Reaction of $H(py)_2BMe_2$ with anhydrous zinc(II) chloride or nickel(II) chloride hexahydrate in a 4:1 molar ratio gave the tetrahedral complex bis[dimethylbis(2-pyridyl)borato-*N*,*N′*]zinc(II), $Zn\{(\mu\text{-py})_2BMe_2\}_2$, or the square planar complex bis[dimethylbis(2-pyridyl)borato-*N*,*N′*]nickel(II), $Ni\{(\mu\text{-py})_2BMe_2\}_2$, respectively. $H(py)_2BMe_2$ is monoclinic, $P2_1/m$, with $a = 8.836(2)$ Å, $b = 7.1825(5)$ Å, $c = 9.2789(11)$ Å, $\beta = 99.81(2)°$, $V = 580.29(13)$ Å^3, and $Z = 2$. $Ph_2B(\mu\text{-py})_2BMe_2$ is monoclinic, $P2_1/n$, $a = 8.0334(12)$ Å, $b = 10.9169(9)$ Å, $c = 22.981(2)$ Å, $\beta = 94.653(9)°$, $V = 2008.8(4)$ Å^3, and $Z = 4$. $Zn\{(\mu\text{-py})_2BMe_2\}_2$ is monoclinic, *Cc*, with $a = 8.010(2)$ Å, $b = 31.256(3)$ Å, $c = 18.753(3)$ Å, $\beta = 90.83(2)°$, $V = 4694.8(13)$ Å^3, and $Z = 8$. $Ni\{(\mu\text{-py})_2BMe_2\}_2$ is triclinic, $P\bar{1}$, with $a = 7.675(2)$ Å, $b = 8.819(2)$ Å, $c = 9.459(2)$ Å, $\alpha = 115.72(3)°$, $\beta = 96.89(3)°$, $\gamma = 94.02(3)°$, and $Z = 1$.

Introduction

The first examples of the pyrazaboles, which possess the ring system shown in Figure 1a, were reported in 1966.[1] Subsequent research involving this class of compounds is now quite substantial.[2] Pyrazaboles can be viewed as two BR_2 moieties bridged by two pyrazolyl groups. Since the pyrazolyl groups are bonded to each of the boron atoms through the nitrogen atoms, these groups may be referred to as "N^1:N^2-pyrazolyl" groups, where "N^1:N^2" represents the two pyrazolyl atoms that are directly bonded to boron. Recently, pyrazabole analogs containing the bridging groups 1-methyl-C^2:N^3-imidazolyl,[3] 1-methyl-N^4:C^5-triazolyl,[3] C^2:N^3-thiazolyl,[3] and N^1:C^2-pyridyl[4] were prepared.

Unlike symmetrically substituted pyrazolyl groups in a pyrazabole, each of the latter bridging groups can, in theory, give rise to an isomeric pair of ring systems, depending on their orientation with respect to each other. In fact, the first preparation and isolation of each member of a pair of this type have only recently been reported[4] (Figure 1b). As noted in this report, the major product of the slow addition of bromodimethylborane, $BrBMe_2$, to an equimolar quantity of 2-lithiopyridine, 2-Li(py), is not dimeric dimethyl(2-pyridyl)borane,[5] **I**, but dimethylboronium dimethylbis(2-pyridyl)borate,[6] **II**.

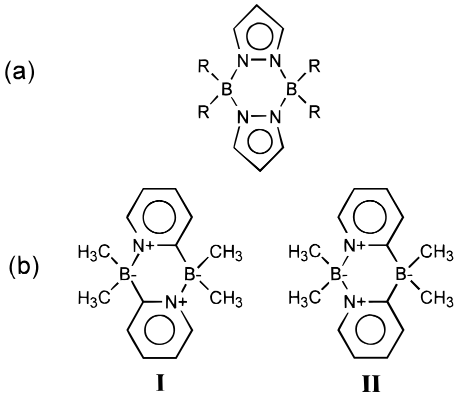

Figure 1. (a) Structure of a pyrazabole. (b) Structure of **I**, dimeric dimethyl(2-pyridyl)borane, and **II**, dimethylboronium bis(2-pyridyl)-dimethylborate.

In order to explain why **II** is the major product, the formation of the dimethylbis(2-pyridyl)borate ion, **III**, was proposed.[4] Herein we report the isolation and structure of a versatile derivative of this ion, hydrogen dimethylbis(2-pyridyl)borate, **IV**, and examples of the application of **III** as a new uninegative bidentate ligand in coordination chemistry. The synthesis of poly(2-pyridyl)borate ions such as **III** may be of interest to coordination chemists. The electronic and steric properties of these ligands may be similar to, but significantly different from, those of their well-known poly(1-pyrazolyl)borate analogs.[7] An example may be the use of metal complexes of these ligands in catalysis.

There is increasing interest in metal complexes containing bulky nitrogen ligands in catalysis, such as in polymerization reactions.[8,9] Poly(1-pyrazolyl)borato ligands in which the

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(5) Alternative name: 9,9,10,10-tetramethyl-4a,8a-diaza-9,10-dibora-9,-10-dihydroanthracene.

(6) Alternative name: 9,9,10,10-tetramethyl-4a,10a-diaza-9,10-dibora-9,-10-dihydroanthracene.

(7) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115−209. (c) Niedenzu, K.; Trofimenko, S. *Top. Curr. Chem.* **1986**, *131*, 1−37.

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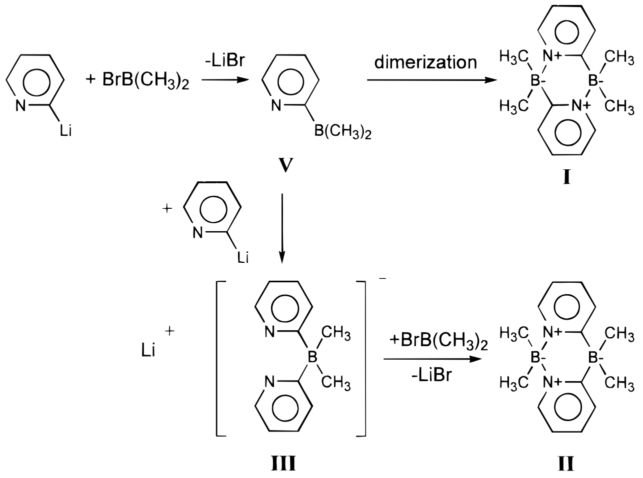
Scheme 1



3-positions of the pyrazolyl rings are occupied by such groups as isopropyl,[10] *tert*-butyl,[11,12] or neopentyl[13] sometimes undergo 1,2-borotropic rearrangements at temperatures ranging from 25[11] to 240 °C.[13] The bulky substituent is thus effectively moved from the 3- to the 5-position on some of the pyrazolyl rings in these complexes, limiting their use as catalysts. However, this type of rearrangement may not occur with the poly(2-pyridyl)borato ligands. Research on the synthesis and chemistry of poly(2-pyridyl)borate ions, eventually leading to the preparation of metal complexes of these ions that contain bulky groups in the 6-positions of the pyridyl rings, may thus be quite fruitful. The first results of research in this area are reported here.

Results and Discussion

General Remarks on the Addition of Solutions of Bromodimethylborane to Solutions of 2-Lithiopyridine. The addition of bromodimethylborane, $BrBMe_2$, to an equimolar quantity of 2-lithiopyridine, 2-Li(py), results in the formation of the isomeric analogs of a pyrazabole, dimeric dimethyl(2-pyridyl)borane, **I**, and dimethylboronium dimethylbis(2-pyridyl)borate, **II**, in a ratio of ca. 15:85, respectively.[4] A hypothetical mechanism which may explain the observed ratio of these isomers is shown in Scheme 1.

As indicated, the reaction of one $BrBMe_2$ molecule with one 2-Li(py) molecule should give one molecule of monomeric dimethyl(2-pyridyl)borane, **V**. This intermediate may either dimerize to form **I** or react with a second molecule of 2-Li(py) to form **III**. Once **III** appears, it can react with $BrBMe_2$ to form **II**, but not **I**. Therefore, the formation of **I** must occur only in the early stages of the addition of solutions of $BrBMe_2$ to solutions of 2-Li(py).

When $BrBMe_2$ is added dropwise to 2-Li(py) in 1:2 molar ratio, respectively, the major product should be **III**. Smaller yields of **I** and **II** should also be expected. Furthermore, a much higher ratio of **I** to **II** than that reported in the earlier work (15:85) should be observed. This last prediction is justified on the grounds that $BrBMe_2$ should preferentially react with 2-Li(py), which is a stronger Lewis base than is **III**, and that, according to this mechanism, only **II** can be formed from the reaction of $BrBMe_2$ with **III**.

The above predictions have been confirmed in the present work. Of the $BrBMe_2$ used, ca. 45% was converted to **III** (which was isolated as hydrogen dimethylbis(2-pyridyl)borate, **IV**) while ca. 34% was converted to a mixture of **I** and **II** consisting of 57% **I**, as compared to the 15% **I** that was formed when the ratio of $BrBMe_2$ to 2-Li(py) was 1:1.[4]

Synthesis of III and Its Hydrolysis To Form IV. The reaction conditions used in the synthesis of **III** were similar to those used in the earlier work[4] for the synthesis of mixtures of **I** and **II**, including the temperatures employed, the nature of the solvents, and the concentrations of the reactants. As before, the method of Gilman and Spatz was used for the generation of solutions of 2-lithiopyridine.[14] The chief difference between the work described here and the earlier work[4] was in the mole ratio of $BrBMe_2$ to 2-Li(py) employed (1:2, respectively, in the present work but 1:1 in the earlier work). Copious tarry byproducts are typically formed in reactions involving 2-Li(py), significantly lowering the yields of the desired products.

Extraction of the reaction mixture with water hydrolyzes **III** to **IV** and also removes LiBr, LiOH, and some colored byproducts. Subsequent extraction of the organic layer with aqueous 1.00 M acetic acid produces protonated **IV**; a mixture of **I**, **II**, and unidentified colored materials remains in the organic layer. The product, **IV**, is precipitated as a yellowish solid when the acetic acid solution is made strongly alkaline with aqueous 6 M NaOH solution. Final purification of **IV** was achieved by repetition of the above, followed by recrystallization from hexane. The reactions used to generate **IV** are illustrated in eq 1.

$$2\{2\text{-Li(py)}\} + BrB(CH_3)_2 \xrightarrow{-LiBr} \text{Li salt of } \mathbf{III} \xrightarrow{+H_2O} \mathbf{IV} + LiOH \quad (1)$$

The ^{1}H NMR spectra of **II**[4] and **IV** in $CDCl_3$ feature the expected 2-pyridyl ring pattern as well as a partially resolved quartet in the high-field region (0.06 ppm for **II** and 0.07 ppm for **IV**) that is attributable to the dimethylborate protons. The spectrum of **IV** contains a signal at 18.70 ppm that is dependent on both the nature of the solvent and the presence of moisture. In fact, upfield shifts for this peak of as much as 8−9 ppm can be ascribed to the presence of moisture in the sample. When the solvent is $CDCl_3$, the intensity of this peak decreases over a period of hours as exchange with the deuterium atom in the solvent occurs. These properties are consistent with the assignment of this singlet with the nitrogen-bonded proton in **IV**.

The ^{11}B and ^{13}C NMR spectra of **II** and **IV** also have much in common. The ^{11}B NMR spectra of these compounds both show a sharp singlet near −18 ppm; this signal in the spectrum of **II** has previously been assigned to the dimethylborate boron atom.[4] The ^{13}C NMR spectra of these two compounds each exhibit quartets near 14 ppm ($J = 41.0$ Hz) and near 190 ppm ($J = 48.5$ Hz), which are assigned to the dimethylborate carbon atoms and the boron-bonded pyridyl carbon atoms, respectively. The number and positions of the remaining peaks in the ^{13}C NMR spectrum of **IV** are consistent with their assignment to the pyridyl ring carbon atoms.

Hydrogen dimethylbis(2-pyridyl)borate, **IV**, is a colorless crystalline air-stable compound. It consists of long needles, rods, or long, narrow platelets that melt at 80−81 °C. It is not hygroscopic and is nearly odorless.

The molecular structure of **IV** is illustrated in Figure 2. An X-ray crystal study of **IV** established that it is planar, with the exception of the methyl groups. The boron atom lies in an approximately tetrahedral environment, as expected.

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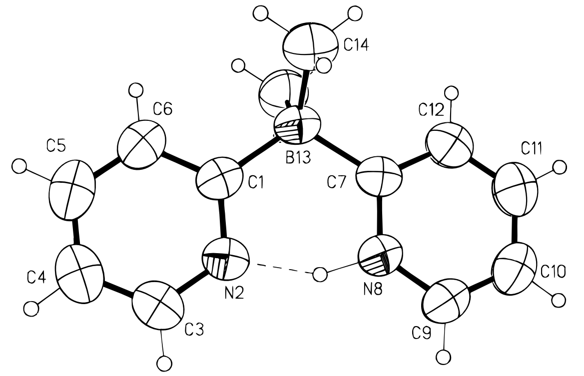

Figure 2. Displacement ellipsoid diagram (50% thermal ellipsoids) of **IV**, hydrogen dimethylbis(2-pyridyl)borate.

Table 1. Selected Crystallographic Data

	IV	VI	VII	VIII
formula	$C_{12}H_{15}BN_2$	$C_{24}H_{24}B_2N_2$	$(C_{12}H_{14}BN_2)_2Zn$	$(C_{12}H_{14}BN_2)_2Ni$
fw	198.07	362.07	459.49	452.83
space group	$P2_1/m$ (No. 11)	$P2_1/n$ (No. 14)	Cc (No. 9)	$P\bar{1}$ (No. 2)
a, Å	8.836(2)	8.0334(12)	8.010(2)	7.675(2)
b, Å	7.1825(5)	10.9169(9)	31.256(3)	8.819(2)
c, Å	9.2789(11)	22.981(2)	18.753(3)	9.459(2)
α, deg				115.72(3)
β, deg	99.81(2)	94.653(9)	90.83(2)	96.89(3)
γ, deg				94.02(3)
V, Å^3	580.29(11)	2008.8(4)	4694.8(13)	567.3(2)
Z	2	4	8	1
ρ_{calcd}, g cm^{-3}	1.134	1.197	1.300	1.326
T, °C	22	−160	−125	22
λ, Å	0.710 73	1.541 78	0.710 73	0.710 73
μ, mm^{-1}	0.067	0.518	1.064	0.873
$R(F_o)$	0.0380	0.0460	0.0667	0.0308
$R_w(F_o{}^2)$	0.1126	0.1302	0.1958	0.0767

A comparison of the structure of **IV** with that of the related compound hydrogen dihydrobis(1-pyrazolyl)borate, $H[(pz)_2BH_2]$,[15] shows some differences. The most obvious difference is that the hydrogen bonding in **IV** is intramolecular, while that in $H[(pz)_2BH_2]$ is intermolecular. Therefore, at least in the solid state, molecules of $H[(pz)_2BH_2]$ exist as hydrogen-bonded dimers, unlike **IV**, which is monomeric. The annular bond lengths in these two compounds are typical of those within the corresponding heteroaromatic ring systems. The NBN bond angle in $H[(pz)_2BH_2]$ (109.7(3)°) is very close to the tetrahedral bond angle, while the C(pyridyl)BC(pyridyl) bond angle in **IV** is slightly larger (112.8(2)°). The pyridyl rings in **IV** may be forced apart by intramolecular hydrogen bonding, which appears to explain both the coplanarity of the pyridyl rings and the fact that this compound has few acidic properties.

Synthesis of II from IV. A suspension of the lithium salt of **III** was generated by adding a solution of *n*-butyllithium to a solution of **IV** at −78 °C. A solution of $BrBMe_2$ was then added to this slurry, according to eq 2. The reaction conditions

$$\mathbf{IV} + n\text{-BuLi} \xrightarrow{-C_4H_{10}} \text{Li salt of } \mathbf{III} \xrightarrow{+BrBR_2} R_2B(\mu\text{-py})_2BMe_2 + LiBr \quad (2)$$

$$\mathbf{II}\ (R = Me)$$

$$\mathbf{VI}\ (R = Ph)$$

employed were very similar to those used earlier for the synthesis of **II** in terms of reaction temperature, solvent composition, and concentration of the reactants.[4] However, yields of **II** in the present work were 89%, in contrast to the low yields of **II** reported previously.[4]

A ^1H NMR spectrum of the crude reaction product of the lithium salt of **III** with $BrBMe_2$ showed no evidence for the formation of **I** in this reaction. Therefore, the formation of **I** upon the addition of $BrBMe_2$ to an *equimolar* quantity of 2-Li-(py) must occur only during the early stages of this addition.

Synthesis and Structure of Diphenylboronium Dimethylbis(2-pyridyl)borate,[16] VI. This compound was formed by addition of bromodiphenylborane, $BrBPh_2$, to a slurry of the lithium salt of **III**, according to eq 2. The conditions were very similar to those used in the synthesis of **II** from **IV**. However, the product, **VI**, was much less soluble in the reaction mixture at ambient temperature than was **II**, although the solvent composition and the molar concentration of the reactants were the same. The yield of crude **VI** was 94%.

The ^1H NMR spectrum of **VI** shows the expected 2-pyridyl ring pattern (doublets at 8.08 and 7.98 ppm, triplets at 7.74 and 7.08 ppm). The unresolved multiplets at ca. 7.25 and 7.02 ppm are assigned to the phenyl group protons. The position of the broad singlet at −0.01 ppm is that expected for the methyl groups. The appearance of this signal is similar to that reported in the ^1H NMR spectrum of $Li(CH_3)_4$ at −51 °C.[17]

The sharp singlet at −17.6 ppm in the ^{11}B NMR spectrum of **VI** is assigned to the dimethylborate moiety on the basis of its position and width. The much broader singlet at +4.0 ppm is assigned to the diphenylboronium moiety. The ^{11}B NMR spectrum of **VI** is thus similar to that of **II** reported earlier.[4]

The ^{13}C NMR spectrum of **VI** bears some resemblance to that of **II**. The quartet at 13.4 ppm (J = 41.5 Hz) in the spectrum of **VI** is assigned to the dimethylborate carbon atoms on the basis of its position, multiplicity, and coupling constant; these values are similar to those reported for the dimethylborate carbon atoms in the spectrum of **II** (δ = 14.7 ppm, q, J = 41.0 Hz).[4] The boron-bonded annular carbon atoms most likely give rise to the quartets at 187.0 ppm (J = 48.5 Hz)[4] and 189.5 ppm (J = 47.5 Hz) in the spectra of **II** and **VI**, respectively. The broad signal at 150.0 ppm in the spectrum of **VI** is assigned to the boron-bonded phenyl carbon atoms. A comparison of the spectrum of **VI** with that of **II** suggests that the peaks at 119.2, 130.3, 136.9, and 143.9 ppm in the spectrum of **VI** arise from the pyridyl carbon atoms.

The mass spectrum of **VI**, like that of **II**, does not exhibit a parent ion cluster but does exhibit an intense cluster due to the loss of CH_3. It also shows clusters of peaks corresponding to the loss from the parent ion of two methyl groups and the loss of one methyl group and one phenyl group. However, no ion clusters of significant intensity were observed corresponding to the loss of phenyl groups without the simultaneous loss of a methyl group. This observation implies that the boron−carbon bonds involving phenyl groups are stronger than those involving methyl groups.

Although a crystal structure of **II** was attempted, the central $B_2C_2N_2$ ring in this compound was found to be disordered. To obtain some information on this ring system, a crystal study of **VI** was performed; the molecular structure of **VI** is illustrated in Figure 3. The central ring of **VI** has a shallow boat conformation. The annular boron−carbon bonds in **VI** (1.615(3) and 1.617(3) Å) are shorter than those in **IV** (1.631(3) and 1.632(3) Å). The B−N bonds (both 1.598(3) Å) in **VI** are

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(16) Alternative name: 9,9-dimethyl-10,10-diphenyl-4a,10a-diaza-9,10-dibora-9,10-dihydroanthracene.

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **IV**

	x	*y*	*z*	*U*(eq)[a]
C(1)	10030(2)	2500	2182(2)	56(1)
N(2)	11089(2)	2500	1297(2)	62(1)
C(3)	12592(3)	2500	1853(3)	78(1)
C(4)	13147(3)	2500	3302(3)	85(1)
C(5)	12109(3)	2500	4240(3)	86(1)
C(6)	10578(3)	2500	3690(2)	77(1)
C(7)	7836(2)	2500	−256(2)	55(1)
N(8)	8983(2)	2500	−1040(2)	59(1)
C(9)	8758(3)	2500	−2505(2)	72(1)
C(10)	7338(3)	2500	−3297(3)	81(1)
C(11)	6112(3)	2500	−2564(3)	86(1)
C(12)	6363(3)	2500	−1075(3)	76(1)
B(13)	8196(3)	2500	1529(3)	57(1)
C(14)	7410(2)	4372(3)	2086(2)	79(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **VI**

	x	*y*	*z*	*U*(eq)[a]
C(1)	2089(2)	5801(2)	4333(1)	19(1)
N(2)	1371(2)	5995(1)	3781(1)	18(1)
C(3)	1558(3)	5172(2)	3349(1)	24(1)
C(4)	2468(3)	4126(2)	3434(1)	27(1)
C(5)	3241(3)	3901(2)	3985(1)	28(1)
C(6)	3024(3)	4729(2)	4421(1)	26(1)
C(7)	188(3)	7559(2)	4712(1)	20(1)
N(8)	−474(2)	7725(1)	4150(1)	18(1)
C(9)	−1853(2)	8429(2)	4031(1)	23(1)
C(10)	−2651(3)	9007(2)	4455(1)	27(1)
C(11)	−2021(3)	8868(2)	5029(1)	30(1)
C(12)	−640(3)	8145(2)	5149(1)	28(1)
B(13)	1869(3)	6767(2)	4855(1)	22(1)
C(14)	1799(3)	6017(2)	5470(1)	28(1)
C(15)	3478(3)	7708(2)	4910(1)	26(1)
B(16)	471(3)	7262(2)	3605(1)	18(1)
C(17)	1883(2)	8256(2)	3472(1)	18(1)
C(18)	1663(3)	9510(2)	3567(1)	23(1)
C(19)	2829(3)	10373(2)	3429(1)	29(1)
C(20)	4277(3)	10015(2)	3184(1)	28(1)
C(21)	4515(3)	8784(2)	3076(1)	27(1)
C(22)	3338(3)	7926(2)	3219(1)	23(1)
C(23)	−891(2)	7060(2)	3050(1)	19(1)
C(24)	−856(3)	7766(2)	2544(1)	22(1)
C(25)	−2037(3)	7637(2)	2073(1)	27(1)
C(26)	−3299(3)	6785(2)	2093(1)	31(1)
C(27)	−3368(3)	6064(2)	2588(1)	31(1)
C(28)	−2186(3)	6203(2)	3058(1)	25(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **VII**

	x	*y*	*z*	*U*(eq)[a]
Zn(1A)	1476(1)	4377(1)	7177(1)	23(1)
N(1A)	1224(10)	3744(2)	7163(4)	19(2)
C(2A)	725(15)	3548(3)	6549(5)	30(3)
C(3A)	742(16)	3120(4)	6462(6)	35(3)
C(4A)	1236(16)	2868(3)	7027(6)	32(2)
C(5A)	1703(14)	3066(4)	7656(6)	32(3)
C(6A)	1642(13)	3517(3)	7746(5)	25(2)
B(7A)	2099(18)	3753(4)	8501(6)	30(3)
C(8A)	3626(13)	4112(3)	8383(5)	24(2)
C(9A)	4995(14)	4155(4)	8854(5)	30(2)
C(10A)	6181(15)	4467(4)	8762(6)	34(3)
C(11A)	6008(14)	4748(4)	8190(6)	35(3)
C(12A)	4652(14)	4701(4)	7748(6)	33(3)
N(13A)	3528(12)	4398(2)	7836(5)	24(2)
N(14A)	213(10)	4914(3)	7435(4)	21(2)
C(15A)	473(13)	5089(3)	8089(5)	27(2)
C(16A)	−107(14)	5483(3)	8264(6)	30(2)
C(17A)	−956(15)	5727(3)	7758(6)	34(3)
C(18A)	−1165(14)	5558(4)	7074(6)	34(3)
C(19A)	−549(13)	5141(3)	6900(5)	25(2)
B(20A)	−856(15)	4920(4)	6133(6)	24(3)
C(21A)	928(14)	4794(3)	5781(5)	23(2)
C(22A)	1467(13)	4924(3)	5100(5)	27(2)
C(23A)	2970(14)	4805(3)	4823(5)	30(2)
C(24A)	4037(14)	4535(4)	5220(5)	33(2)
C(25A)	3494(15)	4422(3)	5892(6)	30(3)
N(26A)	2012(10)	4543(2)	6162(4)	18(2)
C(27A)	448(13)	4003(3)	8762(5)	25(2)
C(28A)	2711(18)	3404(4)	9104(6)	48(3)
C(29A)	−1928(15)	4471(4)	6230(6)	31(3)
C(30A)	−1867(15)	5234(4)	5584(6)	41(3)
Zn(1B)	6082(1)	2022(1)	7048(1)	20(1)
N(1B)	7281(10)	1484(2)	6748(4)	22(2)
C(2B)	7031(13)	1328(3)	6078(5)	26(2)
C(3B)	7560(13)	936(3)	5866(5)	27(2)
C(4B)	8462(14)	687(3)	6367(6)	28(3)
C(5B)	8695(13)	849(3)	7045(5)	27(2)
C(6B)	8098(12)	1247(3)	7251(5)	23(2)
B(7B)	8411(15)	1449(4)	8043(6)	26(3)
C(8B)	6613(12)	1577(3)	8419(5)	21(2)
C(9B)	6233(13)	1450(3)	9101(6)	27(2)
C(10B)	4716(14)	1571(4)	9395(5)	34(3)
C(11B)	3655(13)	1826(4)	9014(6)	33(2)
C(12B)	4078(15)	1951(3)	8345(6)	31(3)
N(13B)	5593(10)	1831(3)	8055(4)	17(2)
N(14B)	6336(11)	2655(2)	7155(5)	21(2)
C(15B)	6836(15)	2822(3)	7796(6)	33(3)
C(16B)	6920(15)	3254(4)	7919(6)	37(3)
C(17B)	6446(15)	3525(4)	7379(6)	35(3)
C(18B)	5984(15)	3359(3)	6740(6)	35(3)
C(19B)	5935(13)	2912(3)	6609(5)	24(2)
B(20B)	5479(15)	2711(4)	5821(6)	25(3)
C(21B)	3997(12)	2352(3)	5873(5)	24(2)
C(22B)	2614(12)	2330(4)	5395(5)	28(2)
C(23B)	1428(15)	2019(4)	5434(7)	36(3)
C(24B)	1538(14)	1700(4)	5968(6)	32(3)
C(25B)	2858(13)	1733(3)	6420(5)	21(2)
N(26B)	4075(10)	2032(2)	6384(4)	20(2)
C(27B)	9564(13)	1882(4)	7934(5)	27(3)
C(28B)	9521(15)	1124(4)	8553(5)	33(3)
C(29B)	7139(14)	2470(3)	5555(6)	27(2)
C(30B)	4944(15)	3084(3)	5261(6)	35(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

longer than the 1.55 Å average found in many pyrazaboles.[18] However, B−N bond lengths associated with the Ph_2B moiety in the pyrazabole $Ph_2B(\mu\text{-pz})_2BCl_2$ are only slightly shorter (1.575(5) and 1.586(5) Å)[19] than those found in **VI**.

The methyl carbon−boron bond lengths in **VI** are comparable to those in **IV**. However, the phenyl carbon−boron bonds in **VI** (1.622 Å average) are slightly longer than the phenyl carbon−boron bonds in the pyrazabole $Ph_2B(\mu\text{-pz})_2BCl_2$ (1.608(5) and 1.609(5) Å).[19] Steric effects are probably responsible for the fact that the PhBPh bond angle is wider than the MeBMe bond angle in **VI**. In **VI**, the NBN bond angle (108.0(2)°) is slightly narrower than the annular CBC bond angle; a “scissoring” effect caused by the bulky phenyl substituents may be responsible for this difference.

Synthesis of the Divalent Metal Complexes of III. The nickel(II) and zinc(II) complexes were synthesized by treating a solution of the metal(II) chloride in 95% ethanol with an ethanolic solution of **IV** at ambient temperature, according to

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(18) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(19) Clarke, C. M.; Das, M. K.; Hanecker, E.; Mariategui, J. F.; Niedenzu, K.; Niedenzu, P. M.; Nöth, H.; Warner, K. R. *Inorg. Chem.* **1987**, *26*, 2310−2317.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **VIII**

	x	*y*	*z*	*U*(eq)[a]
Ni(1)	0	0	0	28(1)
C(1)	2538(3)	−1941(3)	540(3)	33(1)
N(2)	2015(3)	−1176(3)	−385(2)	30(1)
C(3)	2877(4)	−1268(3)	−1577(3)	37(1)
C(4)	4297(4)	−2147(4)	−1935(4)	45(1)
C(5)	4835(4)	−2972(4)	−1053(4)	50(1)
C(6)	3965(4)	−2861(4)	171(4)	46(1)
C(7)	1642(3)	399(3)	2993(3)	33(1)
N(8)	1058(3)	1267(3)	2175(2)	29(1)
C(9)	1222(4)	2973(3)	2892(3)	35(1)
C(10)	1971(4)	3931(4)	4449(3)	45(1)
C(11)	2549(5)	3106(4)	5319(4)	52(1)
C(12)	2372(4)	1358(4)	4598(3)	47(1)
B(13)	1497(4)	−1672(4)	2028(4)	37(1)
C(14)	−582(4)	−2527(4)	1374(4)	44(1)
C(15)	2424(5)	−2469(4)	3138(4)	57(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

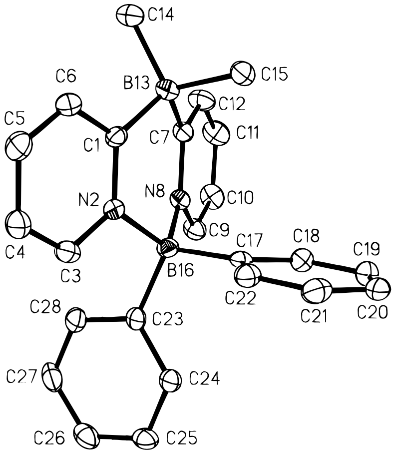

Figure 3. Displacement ellipsoid diagram (50% thermal ellipsoids) of **VI**, diphenylboronium dimethylbis(2-pyridyl)borate. The hydrogen atoms have been omitted for clarity.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for **IV**, Hydrogen Dimethylbis(2-pyridyl)borate

	Bond Lengths		
B(13)−C(1)	1.631(3)	N(8)−H(1a)	1.08(2)
B(13)−C(7)	1.632(3)	N(2)−H(1a)	1.59(2)
B(13)−C(14)	1.637(2)	N(2)···N(8)	2.60(2)
	Bond Angles		
C(1)−B(13)−C(7)	112.8(2)	C(7)−N(8)−H(1a)	108.5(6)
C(14)−B(13)−C(14)[a]	110.4(2)	C(9)−N(8)−H(1a)	127.9(6)
C(1)−B(13)−C(14)	109.3(2)	N(8)−H(1a)···N(2)	153.5(6)
C(7)−B(13)−C(14)	107.5(2)		

[a] Coordinates transformed by (*x*, 0.5 − *y*, *z*).

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **VI**, Diphenylboronium Dimethylbis(2-pyridyl)borate

	Bond Lengths		
B(13)−C(1)	1.617(3)	B(16)−N(2)	1.598(3)
B(13)−C(7)	1.615(3)	B(16)−N(8)	1.598(3)
B(13)−C(14)	1.639(3)	B(16)−C(17)	1.616(3)
B(13)−C(15)	1.649(3)	B(16)−C(23)	1.627(3)
	Bond Angles		
C(1)−B(13)−C(7)	109.8(2)	N(2)−B(16)−N(8)	108.0(2)
C(14)−B(13)−C(15)	109.1(2)	C(17)−B(16)−C(23)	112.4(2)
C(1)−B(13)−C(14)	109.2(2)	N(2)−B(16)−C(17)	108.6(2)
C(1)−B(13)−C(15)	109.3(2)	N(2)−B(16)−C(23)	110.1(2)
C(7)−B(13)−C(14)	110.9(2)	N(8)−B(16)−C(17)	108.7(2)
C(7)−B(13)−C(15)	108.6(2)	N(8)−B(16)−C(23)	109.0(2)

Table 8. Selected Bond Lengths (Å) and Angles (deg) for **VII**, Bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]zinc(II)

	a	b
	Bond Lengths	
Zn−N(1)	1.988(7)	2.018(8)
Zn−N(13)	2.044(9)	2.024(8)
Zn−N(14)	2.024(8)	2.019(7)
Zn−N(26)	2.024(8)	2.019(8)
B(7)−C(6)	1.63(2)	1.63(2)
B(7)−C(8)	1.68(2)	1.66(2)
B(7)−C(27)	1.62(2)	1.65(2)
B(7)−C(28)	1.64(2)	1.65(2)
B(20)−C(19)	1.61(2)	1.64(2)
B(20)−C(21)	1.63(2)	1.64(2)
B(20)−C(29)	1.65(2)	1.61(2)
B(20)−C(30)	1.63(2)	1.62(2)
	Bond Angles	
N(1)−Zn−N(13)	97.0(3)	96.5(3)
N(14)−Zn−N(26)	97.2(3)	97.2(3)
N(1)−Zn−N(26)	105.5(3)	102.7(3)
N(1)−Zn−N(14)	141.1(3)	143.5(4)
N(13)−Zn−N(14)	103.2(3)	102.6(3)
N(13)−Zn−N(26)	112.3(3)	114.6(3)
C(6)−B(7)−C(8)	110.0(8)	110.9(8)
C(27)−B(7)−C(28)	110.5(9)	106.2(9)
C(6)−B(7)−C(27)	107.9(9)	106.4(8)
C(6)−B(7)−C(28)	111.1(9)	111.3(9)
C(8)−B(7)−C(27)	108.4(9)	110.2(8)
C(8)−B(7)−C(28)	108.9(10)	111.5(9)
C(19)−B(20)−C(21)	110.0(8)	111.2(8)
C(29)−B(20)−C(30)	109.0(9)	110.2(9)
C(19)−B(20)−C(29)	109.8(8)	106.5(8)
C(19)−B(20)−C(30)	111.9(9)	111.0(9)
C(21)−B(20)−C(29)	107.4(9)	107.6(8)
C(21)−B(20)−C(30)	108.6(8)	110.2(9)

eq 3. It should be noted that **IV** is both the ligand source and the proton acceptor in reactions of this type.

$$4\mathbf{IV} + \mathrm{MCl_2} \rightarrow 2\mathbf{IV}\cdot\mathrm{HCl} + \mathrm{M}\{(\mu\text{-py})_2\mathrm{BMe_2}\}_2 \qquad (3)$$

$$\mathrm{M} = \mathrm{Zn, Ni}$$

The metal complexes precipitate from the reaction mixtures over the course of several minutes; the reaction mixtures were stirred for several hours to ensure maximum yields in each case (>90%). Although the zinc complex was somewhat soluble in the reaction medium, the nickel complex was not.

Both metal complexes of **III** are air-stable, high-melting solids that are insoluble in both water and hexane. Bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]zinc(II), **VII**, is soluble in such solvents as tetrahydrofuran, methylene chloride, chloroform, carbon tetrachloride, acetone, ethyl acetate, and toluene at ambient temperature. Bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]nickel(II), **VIII**, is moderately soluble only in tetrahydrofuran at room temperature and in benzene, dimethyl sulfoxide, and *o*-xylene at higher temperatures.

Characterization of the Metal Complexes of III. NMR spectra of the nickel complex could not be obtained due to its insolubility in the available deuterated solvents. The ^{1}H NMR spectrum of the zinc complex in $CDCl_3$ showed the expected 2-pyridyl ring pattern of two doublets and two triplets. The methyl signal consisted of a broadened singlet at 0.34 ppm, somewhat farther downfield than those corresponding to the boron-bonded methyl protons in other compounds described in this work but not as far downfield as those in bis[dimethylbis(1-pyrazolyl)borato-*N*,*N*′]zinc(II), $\mathrm{Zn}[(\mu\text{-pz})_2\mathrm{BMe_2}]_2$, which are located at 0.51 ppm.[20]

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(20) Breakell, K. R.; Patmore, D. J.; Storr, A. *J. Chem. Soc., Dalton Trans.* **1975**, 749−754.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **VIII**, Bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]nickel(II)

Bond Lengths			
Ni−N(2)	1.906(2)	Ni−N(8)	1.902(2)
B(13)−C(1)	1.638(4)	B(13)−C(7)	1.637(4)
B(13)−C(14)	1.639(4)	B(13)−C(15)	1.623(4)
Bond Angles			
N(2)−Ni−N(8)	89.34(9)	N(2)−Ni−N(8)[a]	90.66(9)
C(1)−B(13)−C(7)	102.7(2)	C(14)−B(13)−C(15)	109.5(3)
C(1)−B(13)−C(14)	110.6(2)	C(1)−B(13)−C(15)	111.9(3)
C(7)−B(13)−C(14)	110.4(2)	C(7)−B(13)−C(15)	111.6(2)

[a] Coordinates transformed by (−*x*, −*y*, −*z*).

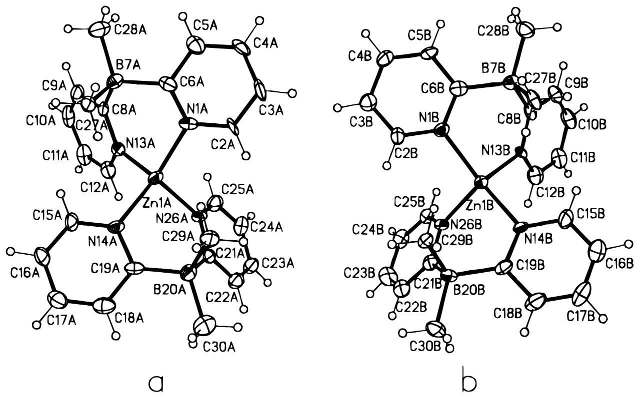

Figure 4. Displacement ellipsoid diagram (50% thermal ellipsoids) of the two molecules of **VII**, bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]-zinc(II).

The shape of the methyl signal in **VII** may be due to a boat-to-boat interconversion of the Zn(NC)$_2$B rings that is fairly rapid on the NMR time scale. Such a boat-to-boat interconversion has been observed in complexes such as Ni[(μ-pz)$_2$GaMe$_2$]$_2$.[21] However, the line shape of this signal is similar to that reported for LiB(CH$_3$)$_4$ at −51 °C,[17] and differences in transverse relaxation times, T_2, between the methyl protons in **VII** and the methyl protons in other compounds described in this work cannot be ruled out.

As expected, the ^{11}B NMR spectrum of the zinc complex displays one singlet at −16.6 ppm ($h_{1/2} = 15.0$ Hz); its position and line width are similar to those found for the borate boron atoms in **II**,[4] **IV**, and **VI**.

The mass spectra of these two complexes have much in common. Neither exhibits parent ion clusters, but ion clusters were observed that correspond to the loss of one methyl group in each case. An ion cluster corresponding to the species M(py)$_3$BMe$^+$ was also observed in each complex. The mass spectra of both complexes also contain ion clusters corresponding to the ions (py)$_2$BMe$_2$$^+$, (py)$_2BMe^+$, and (py)BMe$^+$; these arise from ligand fragmentation. An ion cluster was also observed in the spectra of both complexes that may arise from an ion with the structure MeB(μ-py)$_3$BMe$^+$. If this structure is correct, a significant rearrangement of the parent ion is implicated.

An ion cluster corresponding to the species M(py)$_2$BMe$_2$$^+$ (loss of one ligand per molecule) was observed only for the zinc complex. On the other hand, a significant ion cluster corresponding to the loss of two methyl groups from the parent ion as well as an ion cluster corresponding to the species M(py)BCH$_2$$^+$ was observed only for the nickel complex.

The molecular structure of **VII** is shown in Figure 4. An X-ray crystal study of this compound showed that the zinc atom occupies a pseudotetrahedral environment. As previously noted, the ^{1}H NMR spectrum of this complex in CDCl$_3$ exhibited only one signal due to the methyl protons, implying that in solution the Zn(NC)$_2$B rings either are planar or undergo rapid boat-to-boat interconversions. In the solid state, however, the Zn(NC)$_2$B rings in this complex exist in pronounced boat-shaped conformations. As a result, this complex is chiral in the solid state; the two enantiomers are present in equimolar amounts.

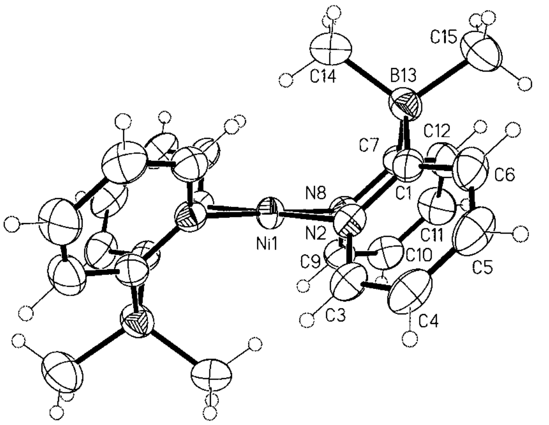

Figure 5. Displacement ellipsoid diagram (50% thermal ellipsoids) of **VIII**, bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]nickel(II).

There is little variation in either the Zn−N bond lengths (1.988(7)−2.044(9) Å, 2.018 Å average of eight) or the intraannular NZnN bond angles (those in which the nitrogen atoms belong to the same Zn(NC)$_2$B ring) (96.5(3)−97.2(3)°, 97.0° average of four) in **VII**. The Zn−N bond lengths in this complex are thus comparable to those in the only bis[bis(1-pyrazolyl)borato]zinc(II) complex whose structure has been determined, Zn((pz*)(pz**)BH$_2$)$_2$, where Hpz* = 3,5-dimethylpyrazole and Hpz** = 3,5-diphenylpyrazole (1.982(2)−2.019(2) Å, 1.998 average of four).[22] However, the intraannular NZnN bond angles in Zn((pz*)(pz**)BH$_2$)$_2$ (100.3(1), 100.9(1)°) are slightly wider than those in **VII**. Furthermore, one of the interannular NZnN bond angles in each enantiomer of **VII** is much wider than the others (141.1(3)° vs 103.2(3), 105.5(3), 112.3(3)°; 143.5(4)° vs 102.6(3), 102.7(3), 114.6(3)°). By contrast, there is much less variation in the interannular NZnN bond angles in Zn((pz*)(pz**)BH$_2$)$_2$ (106.4(1)−119.5(1)°, 113.9° average of four). Crystal packing forces, coupled with the inherent polarizability of the zinc atoms, may be responsible for these variations.

The molecular structure of the nickel complex, **VIII**, is shown in Figure 5. An X-ray crystal study of this compound showed that the nickel atom is surrounded by the ligand nitrogen atoms in a square planar arrangement. As in the case of the zinc complex, the Ni(NC)$_2$B rings exist in a pronounced boat-shaped conformation. This conformation places one of the methyl group hydrogen atoms almost directly over the nickel atom. The complexes Ni[(μ-pz)$_2$BGaMe$_2$]$_2$[21] and Ni[(μ-pz)$_2$BR$_2$]$_2$ (R = C$_2$H$_5$,[23,24] C$_4$H$_9$[24]) have a similar shape. The Ni−N bond lengths in **VIII** are 0.116 Å shorter than the Zn−N bond lengths in **VII**. This difference may be ascribed to a limited degree of overlap of the empty ligand π^* orbitals with filled d$_{xz}$ and d$_{yz}$ orbitals on the metal atom in the nickel complex.

Some interesting comparisons can be made between the dimethylbis(2-pyridyl)borato ligand and bis(1-pyrazolyl)borato

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(21) Herring, F. G.; Patmore, D. J.; Storr, A. *J. Chem. Soc., Dalton Trans.* **1975**, 711−717.

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(23) Echols, H. M.; Dennis, D. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2173−2176.

(24) Trofimenko, S. *J Am. Chem. Soc.* **1967**, *89*, 6288−6294.

Table 10. Shape of the Ligands in $Ni((py)_2BMe_2)_2$, **VIII**, and [Bis(pyrazolyl)borato]nickel(II) Complexes

	dihedral angle between heteroaromatic rings in ligand, deg	dist from boron to N_2E_2 plane,[a] Å	dist from nickel to N_2E_2 plane,[a] Å	dihedral angle between MN_2 plane and heteroaromatic ring, deg	calcd from data given in ref
$Ni((py)_2BMe_2)_2$	66.3(1)	0.728(5)	0.946(1)	52.9(1), 52.3(1)	this work
$Ni((pz)_2BH_2)_2$	68.3	0.707	0.700	47.8, 28.9	25a
$Ni((pz)_2BEt_2)_2$	66.6	0.711	0.714	44.7, 42.0	23
$Ni((pz)_2BPh_2)_2$	63.0	0.695	0.788	44.9	26

[a] See Figure 6.

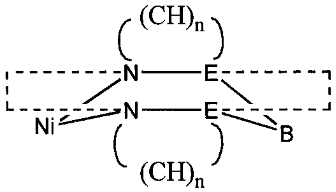

Figure 6. The N_2E_2 plane in bis(2-pyridyl)borato complexes (E = C, $n = 4$) and bis(1-pyrazolyl)borato complexes (E = N, $n = 3$).

ligands. Data regarding the general shape and orientation of the ligands in the square planar complexes **VIII** and $Ni((pz)_2BR_2)_2$ (pz = pyrazolyl, R = H,[25] C_2H_5,[23] and C_6H_5[26]) are given in Table 10. A comparison of the data in the first two columns of this table reveals that the two types of ligands have similar shapes. However, the data in the third column indicate that the ligands in **VIII** are "tilted" to a greater extent, relative to the NiN_4 plane, than are the ligands in the bis(1-pyrazolyl)borato complexes. Therefore, the acute dihedral angles between the NiN_4 plane and the planes defined by each of the heteroaromatic rings are significantly wider in **VIII** than in the bis(1-pyrazolyl)borato complexes. This implies that the degree of overlap between the filled nickel d_{xz} and d_{yz} orbitals and empty π^* orbitals in the heteroaromatic rings should be somewhat less in **VIII** than in the bis(1-pyrazolyl)borato complexes. This may explain the slightly longer Ni−N bond lengths in **VIII** (1.902(2), 1.906(2) Å) as compared to those in $Ni((pz)_2BH_2)_2$ (1.889(2), 1.895(2) Å),[25b] $Ni((pz)_2BEt_2)_2$ (1.875(8), 1.880(4) Å),[23,25b] or $Ni((pz)_2BPh_2)_2$ (1.891(3) Å).[26]

Summary

The reaction of 2-lithiopyridine with bromodimethylborane, $BrBMe_2$, in a 2:1 mole ratio, respectively, and the subsequent hydrolysis of the crude reaction product lead to the formation of hydrogen dimethylbis(2-pyridyl)borate, **IV**, which was isolated in 44% yield. Strong intramolecular hydrogen bonding makes molecules of this compound planar (except for the methyl group atoms) and appears to account for the lack of acidic properties of this compound in most of its reactions. Derivatives of the dimethylbis(2-pyridyl)borate anion can be synthesized by two general methods:

(1) The lithium salt of this anion can be regenerated by allowing **IV** to react with an equimolar quantity of *n*-butyllithium; subsequent reaction of this salt with equimolar quantities of either bromodimethylborane or bromodiphenylborane yields dimethylboronium dimethylbis(2-pyridyl)borate, **II**, or diphenylboronium dimethylbis(2-pyridyl)borate, **VI**, respectively, in ca. 90% yield. An X-ray crystal study of **VI** showed that the central $B(NC)_2B$ ring is boat-shaped.

(2) Reaction of **IV** with either anhydrous $ZnCl_2$ or $NiCl_2{\cdot}6H_2O$ in a 4:1 molar ratio, respectively, gives 1 mole of the corresponding bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]metal(II) complex. X-ray crystal studies of these complexes showed that the environment around the metal atom is pseudotetrahedral for the zinc complex and square planar for the nickel complex. The $M(NC)_2B$ ring adopts a boat-shaped conformation in each complex. This conformation leads to the zinc complex existing as an enantiomeric pair in the solid state.

Experimental Section

General Considerations. Bromodimethylborane, 2-bromopyridine, and hexane were purchased from Aldrich and used as received. Diethyl ether (Mallinckrodt) was stirred over sodium metal and then filtered before use. A solution of *n*-butyllithium in hexane, ca. 1.6 M, was purchased from Aldrich; its precise concentration was determined by titration.[27] A sample of bromodiphenylborane was kindly donated by Professor Emeritus Dr. Kurt Niedenzu of the University of Kentucky. Reagent grade anhydrous zinc(II) chloride (J. T. Baker, Inc.) was dried for 30 min at 110 °C immediately before use. Temperatures of −78 °C were attained using a dry ice−acetone bath. Transfer of air-sensitive solutions was performed using needle and cannula techniques under a nitrogen cover.[28]

NMR spectra were recorded on a Bruker 500-MHz NMR spectrometer. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference (external $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR); $h_{1/2}$ = peak width at half-height. Mass spectral data were obtained on a Kratos MS-80 spectrometer operating in the electron impact mode and are listed to *m/z* 100 (referenced to the species with ^{11}B, ^{58}Ni, and ^{64}Zn) with relative abundances in parentheses (abbreviations: M = parent ion, Me = CH_3, Ph = C_6H_5, py = C_5H_4N); the observed isotope pattern matches the calculated isotope pattern for $M - CH_3$. Infrared spectra were obtained using a BOMEM Michelson MB-100 FTIR spectrometer having 4 cm^{-1} resolution; samples were prepared as KBr pellets. Melting points (uncorrected) were determined on a Mel Temp block. Elemental analyses for **IV** and **VI** were performed by Galbraith Laboratories, Knoxville, TN; elemental analyses for **VII** and **VIII** were performed by Desert Analytics Laboratory, Tucson, AZ.

X-ray Crystal Data. The cell parameter and intensity data were collected on Siemens P4 diffractometers equipped with graphite monochromators. Selected crystallographic data are reported in Table 1. Atomic coordinates and thermal parameters for non-hydrogen atoms for **IV**, **VI**, **VII**, and **VIII** are listed in Tables 2−5, respectively. Selected bond lengths and bond angles for **IV**, **VI**, **VII**, and **VIII** are listed in Tables 6−9, respectively. Data for compounds **VI** and **VII** were collected at low temperatures using locally modified chilled N_2 gas devices. The space group for **VII** was assigned on the basis of systematic absences and the fact that the metals could not be related to one another by a center of symmetry because of the existing symmetry. All structures were solved by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were initially calculated and then refined using a riding model. The XSCANS program[29] was used to collect intensity data. The SHELXL-93 program[30] was used for atom parameter refinement. All other calculations were performed with the

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(25) (a) Clemente, D. A.; Cingi-Biagini, M. *Inorg. Chem.* **1987**, *26*, 2350−2359. (b) Echols, H. M.; Dennis, D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1627−1630.

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(28) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1969; pp 13−24.

(29) *XSCANS Software Users Guide*; Siemens Analytical X-ray Instruments: Madison, WI, 1993.

(30) Sheldrick, G. M. SHELXL 93: Program for the Refinement of Crystal Structures. University of Goettigen, Germany, 1993.

SHELXL+ package.[31] The complex, neutral-atom scattering factors were taken from ref 32.

Spectral Data for Dimeric Dimethyl(2-pyridyl)borane, I. IR (cm^{-1}): 2933 (vs), 2921 (vs), 1619 (s), 1485 (s), 1283 (s), 1191 (m), 1133 (m), 1095 (vs), 1007 (vs), 970 (vs), 758 (vs), 742 (vs).

Synthesis of Hydrogen Dimethylbis(2-pyridyl)borate, IV. A solution of 2-bromopyridine (10.516 g, 66.6 mmol) in 52 mL of anhydrous diethyl ether was chilled to −78 °C. It was then added over a 10 min period to a stirred solution of 1.60 M *n*-butyllithium in hexane (41.6 mL, 66.6 mmol) and 150 mL of diethyl ether at −78 °C under a nitrogen cover. The solution became red-brown to burgundy red. After 10 min, a solution of bromodimethylborane (4.018 g, 33.3 mmol) in 52 mL of hexane was added over a 20 min period. Stirring was continued while the reaction mixture warmed to room temperature over a 17 h period.

Subsequently, 0.81 g of a brownish solid was removed by filtration. The filtrate was stirred for 75 min with activated charcoal and was filtered again. The tea-colored filtrate was shaken with 100 mL of water, and the lower (aqueous) layer was discarded. The organic layer was shaken with three 75 mL portions of aqueous 1.00 M acetic acid solution.

The organic layer was subsequently evaporated to dryness; the residue, which consisted of a mixture of dark oily materials and crystalline solids, weighed 1.34 g. A ^{1}H NMR spectrum of this residue in $CDCl_3$ indicated that it was primarily a mixture of **I** and **II**.[4] Integration of this spectrum revealed that the area ratio of the 0.36 ppm peak to the 0.22 ppm peak was ca. 1:2.65, respectively.

The combined acetic acid layers were made alkaline with 75 mL of aqueous 6.0 M NaOH solution. A yellowish solid, mixed with a little darker oil, appeared. The oil was removed mechanically. After 30 min, the mixture was filtered, and the crude **IV** was washed thoroughly with water and air-dried for 30 min. The combined aqueous filtrate and washings also gave a little solid which, after being filtered off, washed, and dried, brought the total mass of crude **IV** to 3.061 g (46% yield).

The combined solids were stirred with 150 mL of hexane, and a small amount of tarry material was removed by decantation. An extraction and precipitation procedure similar to that used for the filtered reaction mixture was employed for the resulting yellowish solution in which two 40 mL portions of aqueous 1.00 M acetic acid and 40 mL of aqueous 6.0 M NaOH were used. The resulting cream-colored solid was washed with three 30 mL portions of water, and the solid was air-dried (mp 76−79 °C). The ^{1}H NMR spectrum of this solid in $CDCl_3$ solution was consistent with that expected for **IV**. Yield: 2.872 g, 44%. Repeated recrystallization from hexane gave colorless needles (mp 80−81 °C). Part of the latter sample (51 mg) was sublimed in an evacuated ampule at bath temperatures of 60−65 °C (the solid was deposited at a temperature of 30−35 °C) over a 3 month period to give an analytical sample (mp 80−81 °C).

This compound is very soluble in polar organic solvents such as acetone, chloroform, methylene chloride, 95% ethanol, diethyl ether, or tetrahydrofuran. It is less soluble in aliphatic hydrocarbons such as hexane. It is soluble in aqueous acidic solutions, only very sparingly soluble in water (ca. 4 mg/100 mL at 25 °C), and insoluble in aqueous alkaline solutions.

Anal. Calcd for $C_{12}H_{15}BN_2$ ($M_r = 198.08$): C, 72.77; H, 7.63; B, 5.46; N, 14.14. Found: C, 72.95; H, 7.78; B, 5.49; N, 14.11. ^{1}H NMR (δ, $CDCl_3$): 18.70 (1H, s), 8.34 (2H, d, $J = 5.4$ Hz), 7.81 (2H, d, $J = 8.0$ Hz), 7.68 (2H, td, $J = 7.7$, 1.3 Hz), 7.10 (2H, td, $J = 6.7$, 1.3 Hz), 0.07 (6H, partially resolved q, $J = 4.4$ Hz). ^{1}H NMR (δ, CD_2Cl_2): 17.92 (1H, s), 8.39 (2H, d, $J = 5.5$ Hz), 7.80 (2H, d, $J = 8.0$ Hz), 7.71 (2H, td, $J = 7.8$, 1.5 Hz), 7.14 (2H, td, $J = 6.4$, 1.5 Hz), 0.04 (6H, partially resolved q, $J = 4.5$ Hz). ^{11}B NMR (δ, $CDCl_3$): −18.4 (s, $h_{1/2} = 5.6$ Hz). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 191.8 (q, $J = 48.5$ Hz), 140.1, 136.7, 129.3, 118.8, 13.6 (q, $J = 41.0$ Hz). Mass spectrum, *m/z*(+) (relative intensity): 198.1343 (1.7) (M, calc 198.1328), 197 (2.2) (M − H), 183 (100) (M − Me), 120 (20) (M − (py)), 104 (99) ((py)BMe). IR (cm^{-1}): 2909 (vs), 2854 (s), 2508 (m, broad, $N-H\cdots N$), 2145 (m, broad, $N-H\cdots N$), 1626 (vs), 1584 (vs), 1509 (s), 975 (vs), 937 (s), 740 (vs), 606 (m, broad).

Synthesis of Dimethylboronium Dimethylbis(2-pyridyl)borate, II, from IV. A sample of 1.69 M *n*-butyllithium in hexane (1.9 mL, 3.2 mmol) was added to a stirred solution of 0.628 g (3.17 mmol) of **IV** in a mixture of 7.1 mL of hexane and 20.1 mL of anhydrous diethyl ether at −78 °C under a nitrogen cover. A large amount of white solid appeared. The resulting mixture was stirred for 10 min, and then a chilled (−78 °C) solution of 0.388 g (3.21 mmol) of bromodimethylborane in 5.2 mL of hexane was added over a 2 min period. Stirring was continued while the reaction mixture warmed to ambient temperature overnight; most of the solid dissolved during this time.

A colorless, gelatinous solid (0.084 g) was then removed by filtration, and the filtrate was evaporated to dryness under a nitrogen flow. The residue (1.042 g) was treated with three 10 mL portions of aqueous 1.00 M acetic acid solution. The undissolved solid was dried and identified as **II** by its melting point, 175−177 °C (lit.[4] 178−179 °C), and ^{1}H NMR spectrum in $CDCl_3$. The ^{1}H NMR spectrum of this solid showed no evidence that it contained either **I** (no signals near 0.22 ppm) or **IV** (no signals in the 8.4−18.8 ppm region). This solid weighed 0.678 g (89% yield). Neither the mass nor the melting point of this solid changed after it was treated with three additional 10 mL portions of aqueous 1.00 M acetic acid solution and recovered in the manner described above. IR (cm^{-1}): 2923 (vs), 1620 (vs), 1482 (vs), 1299 (s), 1108 (vs), 978 (s), 958 (s), 744 (vs).

Synthesis of Diphenylboronium Dimethylbis(2-pyridyl)borate, VI. A sample of 1.69 M *n*-butyllithium in hexane (2.21 mL, 3.73 mmol) was added to a stirred solution of 0.735 g (3.71 mmol) of **IV** in a mixture of 8.3 mL of hexane and 23.3 mL of diethyl ether at −78 °C under a nitrogen cover. The resulting slurry was stirred for ca. 15 min, and then a solution of 0.916 g (3.74 mmol) of bromodiphenylborane in 5.8 mL of hexane was added over a 1 min period. Stirring was continued while the reaction mixture warmed to room temperature over a 15 h period.

The reaction mixture was filtered, and the recovered solid was air-dried. It was treated with a total of 30 mL of aqueous 1.00 M acetic acid solution. The mixture was filtered, and the crude product was washed with a total of 20 mL of water and air-dried (0.959 g). It exhibited a ^{1}H NMR spectrum that was consistent with the desired product.

The solvent was removed from the filtrate from the original reaction mixture, and the residue was treated with a total of 20 mL of 1.00 M aqueous acetic acid solution. The resulting mixture was filtered, the insoluble portion was air-dried and then stirred with 80 mL of hot hexane, and 0.022 g of a brownish, tarry residue was removed by filtration. The resulting hexane solution was evaporated to dryness to give 0.303 g of a yellowish solid. A ^{1}H NMR spectrum of this solid in $CDCl_3$ indicated that it consisted mostly of the desired product (total yield of crude **VI**: 94%). When recrystallized from a hexane−THF mixture, **VI** melts at 213−215 °C; the melt was light yellow. When this sample was reheated, it melted at ca. 200−213.5 °C; this melt was orange.

Diphenylboronium dimethylbis(2-pyridyl)borate, **VI**, is air-stable. It is soluble in acetone, diethyl ether, benzene, tetrahydrofuran, chloroform, and methylene chloride at ambient temperature. It is also soluble in hot 1-propanol and hot hexane and sparingly soluble in hot ethanol. It is insoluble in aqueous solvents as well as hot methanol. Experiments involving heating evacuated ampules containing this compound indicate that the volatility of this compound is very low.

Anal. Calcd for $C_{24}H_{24}B_2N_2$ ($M_r = 362.09$): C, 79.61; H, 6.68; B, 5.97; N, 7.74. Found: C, 79.27; H, 6.50; B, 5.91; N, 7.93. ^{1}H NMR (δ, $CDCl_3$): 8.08 (1H, d, $J = 6.0$ Hz), 7.98 (1H, d, $J = 8.5$ Hz), 7.74 (1H, t, $J = 7.7$ Hz), 7.26−7.23 (3H, m), 7.08 (1H, t, $J = 7.2$ Hz), 7.03−7.01 (2H, m), −0.01 (3H, s, $h_{1/2} = 9$ Hz). ^{11}B NMR (δ, $CDCl_3$): 4.0 (s, $h_{1/2} = 174$ Hz), −17.6 (s, $h_{1/2} = 11.6$ Hz). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 189.5 (q, $J = 47.5$ Hz), 150.0 (broad, low intensity), 143.9, 136.9, 133.3, 130.3, 127.7, 126.6, 119.2, 13.4 (q, $J = 41.5$ Hz). Mass spectrum, *m/z*(+) (relative intensity): 347.1909 (100) (M − Me, calc 347.1891), 332 (6) (M − 2Me), 270 (11) (M − Me, Ph), 269 (10) (M − Me, (py)), 166 (15) ((py)BPh).

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(31) *SHELXTL+*, Version 4.0; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

(32) *International Tables for Crystallography*; Kluwer: Boston, 1993; Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2.

Synthesis of Bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]zinc(II). A solution of 68.1 mg of anhydrous $ZnCl_2$ was dissolved in 22 mL of 95% ethanol. The resulting solution was added to a stirred solution of 0.4221 g of **IV** in 28 mL of 95% ethanol, and a colorless precipitate formed slowly. The resulting mixture was stirred at room temperature overnight and then filtered. The colorless solid was washed with five 5 mL portions of 95% ethanol and then air-dried. It weighed 0.1977 g and began to melt at 237 °C (in vacuo) with extensive decomposition. A sample of this solid that was recrystallized from a hexane−THF mixture began to melt at 244 °C (in vacuo) with extensive decomposition.

The filtrate from the original reaction mixture was combined with the washings, and the solvent was removed under a nitrogen flow. The residue was treated with three 10 mL portions of aqueous 1.00 M acetic acid solution. The resulting mixture was filtered, and the insoluble material was dried (0.0250 g) and found to be identical to the original reaction precipitate by its melting point in vacuo (which began at 236 °C with decomposition) and its ^1H NMR spectrum. Total yield: ca. 97%.

Anal. Calcd for $C_{24}H_{28}B_2N_4Zn$ ($M_r = 459.51$): C, 62.73; H, 6.14; N, 12.19. Found: C, 62.67; H, 6.12; N, 12.00. ^1H NMR (δ, $CDCl_3$): 7.91 and 7.90 (2H, overlapping d, $J =$ ca. 7 and 4 Hz, respectively), 7.62 (1H, td, $J = 7.6$, ca. 1.5 Hz), 6.94 (1H, td, $J = 6.4$, ca. 1.5 Hz), 0.34 (3H, s, $h_{1/2} = 6.8$ Hz). ^{11}B NMR (δ, $CDCl_3$): −16.6 (s, $h_{1/2} =$ 15.0 Hz). Mass spectrum, *m/z*(+) (relative intensity): 443.1570 (100) (M − Me, calc 443.1557), 324 (22) ($Zn(py)_3BMe$), 286 (40) ($(py)_3B_2Me_2$), 261 (49) ($Zn(py)_2BMe_2$), 197 (8) ($(py)_2BMe_2$), 182 (42) ($(py)_2BMe$), 104 (33) ($(py)BMe$). IR (cm^{-1}): 2851 (m), 1598 (vs), 1463 (vs), 1422 (vs), 1212 (m), 983 (s), 952 (m), 749 (vs, doublet?), 657 (s), 416 (s).

Synthesis of Bis[dimethylbis(2-pyridyl)borato-*N*,*N*′]nickel(II). A solution of 50.1 mg of $NiCl_2{\cdot}6H_2O$ in 15 mL of 95% ethanol was added to a stirred solution of 0.253 g of **IV** in 25 mL of 95% ethanol at ambient temperature. A greenish, gelatinous precipitate formed almost immediately but was gradually replaced by a bright yellow solid over the next 30 min. The resulting mixture was stirred for another 4 h and was then filtered; the mother liquor did not produce a precipitate when treated with 6.0 M NH_3 and dimethylglyoxime solution. The yellow powder weighed 86.8 mg (91% yield) after it was washed with five 5 mL portions of 95% ethanol and air-dried. A sample of this solid that was recrystallized from *o*-xylene was obtained as small yellow-orange blocks. A sample of this solid slowly darkened at temperatures above 250 °C but did not melt below 400 °C; darkening was most rapid near 340 °C.

Anal. Calcd for $C_{24}H_{28}B_2N_4Ni$ ($M_r = 452.85$): C, 63.66; H, 6.23; N, 12.37. Found: C, 63.61; H, 6.24; N, 12.29. Mass spectrum, *m/z*(+) (relative intensity): 437.1608 (96) (M − Me, calc 437.1619), 422 (49) (M − 2Me), 318 (96) ($Ni(py)_3BMe$), 286 (34) ($(py)_3B_2Me_2$), 239 (35) ($Ni(py)_2BCH_2$), 197 (18) ($(py)_2BMe_2$), 182 (100) ($(py)_2BMe$), 161 (25) ($Ni(py)BCH_2$), 104 (23) ($(py)BMe$). IR (cm^{-1}): 1595 (s), 1460 (s), 1421 (vs), 1218 (s), 990 (s), 962 (m), 764 (vs), 755 (vs), 745 (s), 490 (m).

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Supporting Information Available: Tables of complete crystal and intensity collection data, hydrogen atomic coordinates and isotropic temperature factors, bond distances and angles, and anisotropic displacement parameters for **IV**, **VI**, **VII**, **VIII** and extensive infrared data for **I**, **II**, **IV**, **VII**, and **VIII** (33 pages). Ordering information is given on any current masthead page.

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