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An Intramolecularly Stabilized Arylboron Dibromide

David S. Brown, Claire J. Carmalt, Alan H. Cowley,*
Andreas Decken,† and Harold S. Isom

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712

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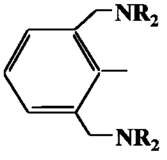
ABSTRACT

*A new boron dibromide featuring intramolecular Lewis base coordination, $ArBBr_2$ (***4***; Ar = 2-[(dimethylamino)methyl]phenyl) has been prepared via the salt-elimination reaction of [2-(Me_2NCH_2)C_6H_4]Li with BBr_3. Single-crystal X-ray diffraction experiments reveal that* **4** *rystallizes in two polymorphs, both of which are orthorhombic. The principal difference between the two polymorphs is the presence or absence of weak Br. . .Br intermolecular contacts. The metrical parameters for the individual molecules of* **4** *are very similar for both polymorphs; the amine "arm" is coordinated strongly, and the boron atom adopts a somewhat distorted tetrahedral geometry. Compound* **4** *is surprisingly unreactive toward a variety of hydride transfer reagents.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9:**79–83, 1998

INTRODUCTION

Supplemental Lewis base interaction represents a viable approach to the stabilization of a number of unusual main group compounds [1]. For example, use of the "two-arm" ligand **1** [2] has permitted the isolation of, e.g., monomeric aluminum and gallium dihydrides [3] and remarkably stable group 13 bis(azides) [4]. The "one-arm" ligand **2** [5] has proved useful for, e.g., the preparation of several intermetallic derivatives [6] and indium iodides with diverse solid-state structures [7]. Curiously, ligands **1** and **2** have been employed very little in the context of boron chemistry [8,9]. It is the recently reported reaction of [2,6-(Et_2NCH_2)$_2C_6H_3$]Li with BCl_3 [9] that is of particular relevance to the present work [10]. As shown in Scheme 1, the product of this reaction involves both intra- and intermolecular coordination of the amine "arms." Given the unusual nature of this product, we were prompted to explore the consequences of employing the one-arm ligand **2** to support boron halide moieties.



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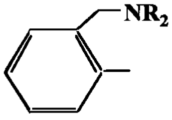

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RESULTS AND DISCUSSION

Colorless, crystalline **4** was prepared by treatment of [2-(Me_2NCH_2)C_6H_4]Li with one equivalent of BBr_3 in toluene solution at −78°C (Scheme 2). Following workup, the yield of **4** was 39%. A satisfactory elemental analysis was obtained for **4** and the CI mass

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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday and in recognition of his exceptional scholarly work and leadership in main group chemistry.

*To whom correspondence should be addressed.

†Current address: Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5AB.

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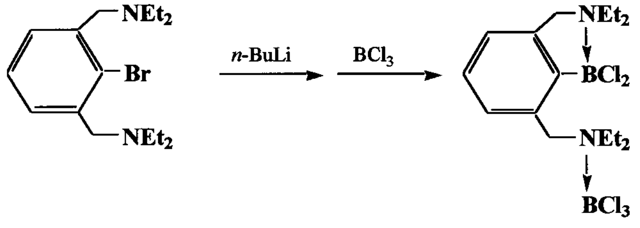

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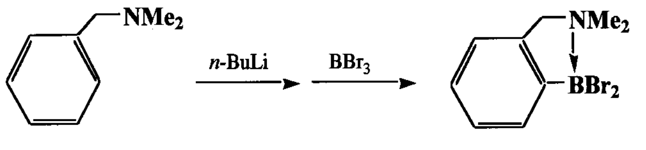
SCHEME 1



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SCHEME 2

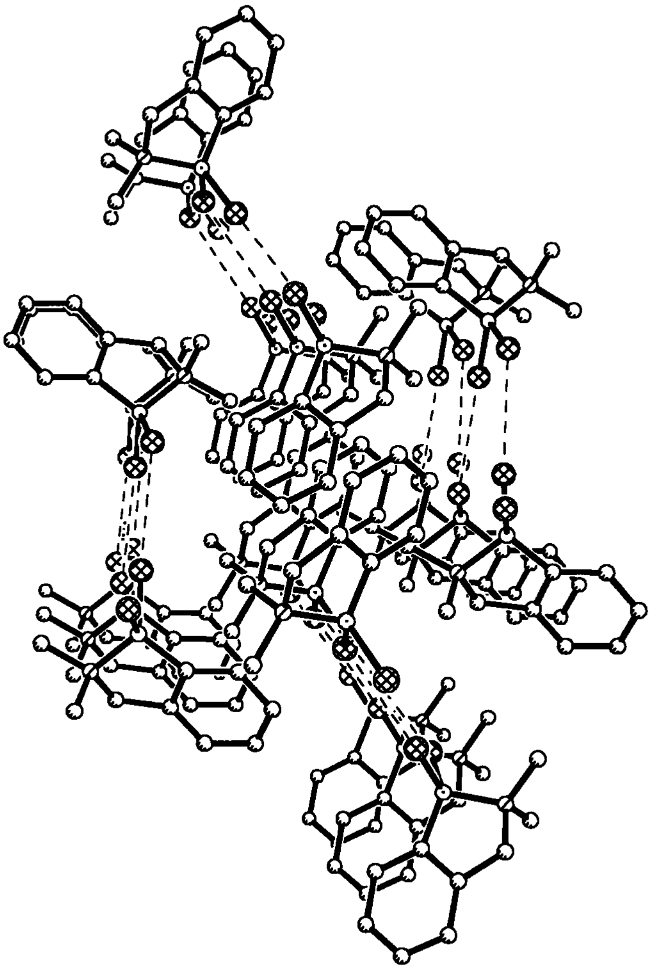

FIGURE 1 Packing diagram for the $P2_12_12_1$ polymorph of **4** showing the stacking along the C axis.

spectrum exhibited a molecular ion at m/z 306 ($M^+ + H$) and fragmentation peaks at m/z 224 and 136, which correspond to the loss of bromine and (ligand + H), respectively. The ^1H and ^{13}C {^1H} NMR data (Experimental) were also consistent with the formula proposed in Scheme 2. The ^{11}B chemical shift of 4 (δ 20.46) is suggestive of the formation of intramolecular coordination in solution due to the upfield shift from dibromophenylborane (δ 57.7 [11]. However, it was not clear whether the amine arm is coordinated, hence, it was necessary to appeal to X-ray crystallography. X-ray quality crystals were grown from either toluene or diethyl ether solution at −20°C. Interestingly, two different polymorphs were obtained: the crystals grown from toluene solution belong to the orthorhombic space group $P2_12_12_1$, while those grown from diethyl ether solution are also orthorhombic but belong to the space group $Pna2_1$. Examination of the packing diagrams revealed the presence of weak Br. . .Br intermolecular contacts in the $P2_12_12_1$ polymorph that results in an interesting stacking of individual molecules of **4** along the C axis (Figure 1). The intermolecular Br. . .Br distance is 3.760 Å (c.f., the van der Waals radius for Br is 1.85 Å). There are no unusual intermolecular contacts in the case of the $Pna2_1$ polymorph. Despite the foregoing differences in crystal packing, the metrical parameters for **4** are identical in the two polymorphs within experimental error; hence, only those for the $P2_12_12_1$ polymorph are reported here (Table 1). The X-ray analysis revealed that the amine arm of **4** is coordinated and, as a consequence, the boron center assumes a tetrahedral geometry (Figure 2). However, the bond angles at boron vary over a range of ~11°. This distortion is due to the constraints of the five-membered NBC(1)C(2)C(7) ring that enforces a C(1)-B-N angle of less than the ideal tetrahedral value [100.2(8)°]. The NBC(1)C(2)C(7) ring is nonplanar on account of the protrusion of the nitrogen atom from the BC_3 least-squares plane of 0.231°. A similar nonplanarity is evident in the NBC_3 five-membered rings of **3** [9] and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]B(OCH_2CPh_2O)$ [8] and the NMC_3 rings of the heavier congeners of **4**, $[2\text{-}(Me_2NCH_2)C_6H_4]MX_2$ (M = Al, Ga, In; X = Cl, Br, I) [12]. The N → B donor–acceptor bond length of 1.625(1) Å is very similar to that reported for **3** [9] [1.649(5) Å].

One of the objectives of preparing **4** had been to effect its conversion into the corresponding boron hydride, $[2\text{-}(Me_2NCH_2)C_6H_4]\ BH_2$ (**5**). Interestingly, however, **4** is a remarkably robust compound and

TABLE 1 Important Bond Lengths (Å) and Angles (°) for **4.**

B–C(1)	1.56(2)
B–N	1.62(1)
B–Br(1)	2.01(1)
B–Br(2)	2.02(1)
N–C(7)	1.50(1)
N–C(8)	1.50(1)
N–C(9)	1.51(1)
C(1)–C(6)	1.39(2)
C(1)–C(2)	1.40(1)
C(2)–C(3)	1.38(1)
C(2)–C(7)	1.47(1)
C(3)–C(4)	1.37(2)
C(4)–C(5)	1.37(2)
C(5)–C(6)	1.38(2)
C(1)–B–N	100.2(8)
C(1)–B–Br(1)	111.4(7)
N–B–Br(1)	109.0(7)
C(1)–B–Br(2)	116.2(7)
N–B–Br(2)	111.5(7)
Br(1)–B–Br(2)	108.2(5)
C(7)–N–C(9)	113.7(9)
C(7)–N–C(8)	107.6(8)
C(9)–N–C(8)	106.5(9)
C(7)–N–B	101.8(7)
C(9)–N–B	115.3(8)
C(8)–N–B	111.8(8)
C(6)–C(1)–C(2)	117.7(1)
C(6)–C(1)–B	134.2(1)
C(2)–C(1)–B	108.1(9)
C(3)–C(2)–C(1)	120.3(1)
C(3)–C(2)–C(7)	128.1(1)
C(1)–C(2)–C(7)	111.6(9)
C(4)–C(3)–C(2)	120.7(1)
C(3)–C(4)–C(5)	120.2(1)
C(4)–C(5)–C(6)	119.7(1)
C(5)–C(6)–C(1)	121.4(1)
C(2)–C(7)–N	105.0(9)

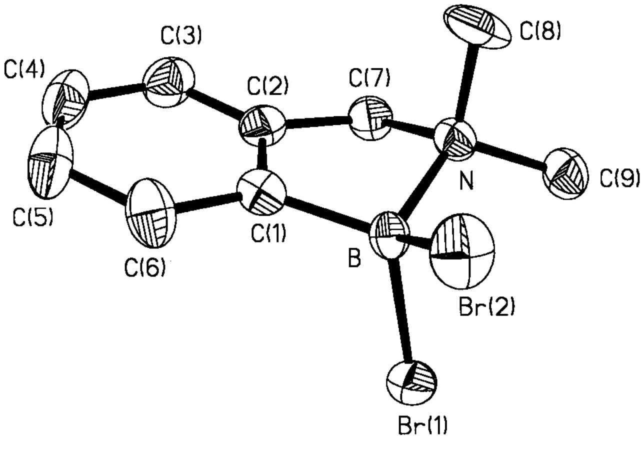

FIGURE 2 Molecular structure of **4** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% probability level.

failed to react with a wide variety of hydride transfer reagents. Since [2-(Me_2NCH_2)C_6H_4]$GaCl_2$ has been found [13] to undergo facile transmetallation to afford the corresponding (dimeric) aluminum hydride, the analogous reaction of [2-(Me_2NCH_2)C_6H_4]$GaCl_2$ and [2-(Me_2NCH_2)C_6H_4]$AlBr_2$ with $LiBH_4$ were attempted. However, conversion to **5** did not occur in either case.

EXPERIMENTAL

General Procedures

All manipulations were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or a HE-493 Vacuum Atmosphere dry box. Unless otherwise stated, all solvents were dried over sodium and distilled from sodium benzophenone ketyl under argon prior to use. The reagent [2-(Me_2NCH_2)C_6H_4]Li [12] was prepared according to the literature method. All other reagents were purchased from commercial sources and used without further purification. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

TABLE 2 Crystal Data and Structure Refinement for **4**

Empirical formula	$C_9H_{12}BBr_2N$
Formula weight	304.83
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 9.759(2)$ Å $b = 9.761(2)$ Å $c = 11.919(2)$ Å $\alpha = \beta = \gamma = 90°$
Volume	1135.4(4) Å^3
Z	4
Density (calculated)	1.783 g/cm^3
Absorption coefficient	70.94 cm^{-1}
F(000)	592
Theta range for data collection	2.70 to 24.96°
Index ranges	$-11 \langle h \rangle 1$, $-11 \langle k \rangle 11$, $-14 \langle l \rangle 1$
Reflections collected	1674
Independent reflections	1470 [R(int) = 0.0599]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$])	$R1 = 0.0518$, $wR2 = 0.1118$
R indices (all data)	$R1 = 0.0801$, $wR2 = 0.1296$

$wR2 = (\Sigma[w(F_0^2 - F_c^2)^2/\Sigma[wF_0^4])^{1/2}$, $R1 = \Sigma\|F_0| - |F_c\|/\Sigma|F_0|$.
Weight $= 1/[\sigma^2 (F_0^2) + (0.0733 * P)^2 + (0.000 * P)]$ where $P = [\max (F_0^2, 0) + 2 * F_c^2]/3$.

TABLE 3 Atomic Coordinates (x10^4) and Equivalent isotropic Displacement Parameters (Å × 10^3) for **4**

	x	*y*	*z*	*U*(*eq*)^a
B	2329(11)	8,311(12)	7,264(9)	42(3)
Br(1)	986(1)	7,817(1)	6,040(1)	68(1)
Br(2)	4221(1)	8,397(1)	6,582(1)	78(1)
N	1886(9)	9,772(8)	7,808(6)	50(2)
C(1)	2161(10)	7,361(12)	8,306(8)	52(3)
C(2)	1271(11)	8,006(11)	9,062(8)	56(3)
C(3)	930(13)	7,377(14)	10,065(8)	72(3)
C(4)	1413(13)	6,096(16)	10,314(11)	79(4)
C(5)	2297(14)	5,446(15)	9,593(12)	81(4)
C(6)	2648(13)	6,065(14)	8,588(11)	75(4)
C(7)	809(13)	9,345(10)	8,638(7)	54(3)
C(8)	3047(13)	10,417(13)	8,459(11)	81(4)
C(9)	1402(12)	10,836(11)	6,982(10)	65(3)

^{a}*U* (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Physical Measurements

Mass Spectra (CIMS) were run on a Finnagan MAT 4023 instrument, and NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.19 MHz; ^{13}C, 75.48 MHz, ^{11}B, 96.30 MHz). NMR spectra are referenced to C_6D_6, which was dried over sodium-potassium alloy and distilled prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $Si(CH_3)_4$ (0.00 ppm). ^{11}B chemical shifts are reported relative to BF_3 etherate (0.00 ppm). Melting points were obtained in sealed glass capillaries under argon (1 atm) and are uncorrected.

Synthesis of [2-(Me_2NCH_2)C_6H_4]BBr_2 (**4**). A slurry of 2-(Me_2NCH_2)C_6H_4Li (2.46 g, 17.4 mmol) in 100 mL of toluene was added via cannula to a stirred solution of BBr_3 (4.38 g, 17.4 mmol) in 30 mL of toluene at −78°C. The reaction temperature was maintained at −78°C for 1 hour, following which the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 hours, the reaction mixture was filtered and the volume of the filtrate was reduced until the solution became viscous. Cooling of this solution to −20°C overnight afforded a 39% yield (2.05 g) of colorless crystalline **4** (mp 150–152°C). Anal. calcd for $C_9H_{12}NBBr_2$: C, 35.46; H, 3.97; N, 4.60. Found: C, 35.53; H, 4.00; N, 4.70. CIMS (CH_4): *m/z* = 306 (M^+ +H), 224 (M-Br^-), 136 (ligand + H). ^{1}H NMR (C_6D_6): δ 2.11 (s, 6H, NMe_2), 3.25 (s, 2H, CH_2), 6.71 (d, 1H, C_6H_4), 7.04 (t, 1H, C_6H_4), 7.10 (t, 1H, C_6H_4), 7.81 (d, 1H, C_6H_4). ^{13}C{^{1}H} NMR (C_6D_6): δ 48.0 (s, CH_3), 67.1 (s, CH_2), 122.2 (s, CH, C_6H_4), 128.7 (s, CH, C_6H_4), 130.5 (s, CH, C_6H_4), 136.7 (s, CH, C_6H_4), 141.3 (s, C, C_6H_4); *ipso* carbon not detected. ^{11}B NMR (C_6D_6): δ 20.46.

X-ray Crystal Structure of [2-(Me_2NCH_2)C_6H_4]BBr_2 (**4**). Colorless crystals of **4** suitable for X-ray diffraction were grown from either a saturated toluene or diethyl ether solution at −20°C overnight. As pointed out earlier, different polymorphs crystallized from these solutions. The space groups of the polymorphs grown from toluene and diethyl ether solutions were $P2_12_12_1$ and $Pna2_1$, respectively. The crystals of the $P2_12_12_1$ polymorph were mounted in thin-walled glass capillaries and sealed under argon. The data for **4** were collected on an Enraf-Nonius CAD4 diffractometer at 25°C using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å). All calculations were performed using the Siemens SHELX programs [14]. The structure was refined to final *R* values of 0.0518 and 0.1296 for *R*1 and *wR*2, respectively. Details of the crystal data and a summary of intensity data collection parameters for **4** are given in Table 2. The atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of **4** are presented in Table 3.

ACKNOWLEDGMENTS

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