pathology of localized bonding in $B_4H_4$ is related to its nondiscovery. Studies of localized orbitals in reactions, intermediates, and transition states may be useful, especially in reactions in which pairing schemes are conserved. Perhaps the only clear experimental fact is that $B_4Cl_4$ does exist, and we suggest that a study, which may soon be possible, of localized orbitals in this molecule may be of interest. There is a set of vacant E orbitals in $B_4H_4$ at an eigenvalue of only 0.055 au, perhaps placing this molecule in the vacant-orbital class, like $BH_3$. Back-$\pi$-bonding is possible in $BCl_3$, but not in $BH_3$, which dimerizes to $B_2H_6$. Longuet-Higgins[25] has shown that the E pair is of the appropriate symmetry to accept localized back-$\pi$-donation from Cl in $B_4Cl_4$, and he suggested that $B_4Cl_4$ might be stabilized in a way that $B_4H_4$ cannot. This is a more detailed and informative statement than the topological theory of King,[26] who proposed that vertices of order 3 (boron bound to three other borons) should result in molecular instability. The existence of $B_4Cl_4$ is inconsistent with this proposal of King and is also not compatible with his contention that stable, closed neutral borane frameworks must have either $BH_2$ groups or bridge hydrogens. Thus, purely topological arguments shed little light on the $B_4H_4$ problem.

In conclusion, $B_4H_4$ should be one of a reasonable set of molecules to serve as a prototype for future SCF calculations on polyhedral boranes and carboranes. Analysis of the $B_4H_4$ localization indicates that the LMO's are, in some cases, very dependent on symmetry and other constraints placed upon LMO's. Thus one should be extremely careful with regard to similarity of local chemical environment and molecular symmetry when constructing approximate molecular wave functions from the localized bond components.[27]

**Registry No.** $B_4H_4$, 27174-99-8.

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(27) Note Added in Proof. *Ab initio* SCF calculations have been completed on the molecules $B_4F_4$ and $B_4Cl_4$. We will publish the results shortly.

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# Preparation and Proposed Structure for Bis[bis(dimethylamino)bromoborane]-Tris(titanium tetrabromide)

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Treatment of $[(CH_3)_2N]_2BBr$ with $TiBr_4$ affords $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$. The stoichiometry of the latter was established by determination of the reactant ratio and by nucleophilic degradation affording $TiBr_4 \cdot N(CH_3)_3$ and $[(CH_3)_2N]_2BBr$. A structure is proposed for $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$ based on infrared assignments and the unusual stoichiometry of this compound.

## Introduction

Treatment of $TiCl_4$ with $[(CH_3)_2N]_2BCl$ has been reported to afford the labile species $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ (I).[2] Several possible structures were suggested including an ionic formulation involving hexachlorotitanate, $TiCl_6^{2-}$, as well as two different molecular formulations with $[(CH_3)_2N]_2BCl$ moieties bridging between three $TiCl_4$ species. One example of the latter consisted of all three Ti being six-coordinate with single Cl bridges, whereas the other involved mixed five- and six-coordinate Ti with no Cl bridges. Based on the ease of dissociation of I, a molecular formulation was favored rather than one involving ionic species. The reaction of $TiBr_4$ with $[(CH_3)_2N]_2BBr$ was investigated in order to prepare a compound stoichiometrically analogous to I but with the larger Br moieties more sterically limiting compared to those of Cl, thus allowing a distinction between molecular structures.

## Experimental Section

**Equipment.** Chemical reactions and procedures were followed as previously described while infrared spectra were recorded with a Perkin-Elmer 457 spectrometer employing KBr and CsBr cell windows.[2]

**Reagents. Bis(dimethylamino)bromoborane,** $[(CH_3)_2N]_2BBr$, was prepared by treatment of $BBr_3$ with a twofold molar excess of tris(dimethylamino)borane, $[(CH_3)_2N]_3B$, in *n*-pentane.[3] The reaction mixture was stirred for 3 hr followed by removal of solvent under vacuum, affording a colorless liquid which was distilled in the range 35-37° (2 Torr), lit.[3] 25-28° (0.5 Torr). Infrared data: 3015 (ms), 2940 (s, sh), 2900 (vs), 2820 (ms), 1555 (s, sh), 1535 (vvs), 1482 (w, sh), 1465 (vs), 1412 (vvs), 1408 (vs, sh), 1358 (vs), 1212 (vvs), 1195 (s, sh), 1185 (w, sh), 1145 (vvs), 1118 (w, sh), 1070 (vvs), 900 (s, sh), 880 (ms), 838 (s), 582 (w, sh), and 565 (ms) cm$^{-1}$.

**Tris(dimethylamino)borane,** $[(CH_3)_2N]_3B$, was prepared by the treatment of $BCl_3$ with more than a sixfold molar excess of $HN(CH_3)_2$.[4] The resulting liquid was freed of any traces of bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, by further treatment with $HN(CH_3)_2$ followed by fractional distillation through a −22° trap into one at −196°. Tris(dimethylamino)borane recovered from the −22° trap was identified by its vapor-phase infrared spectrum[5] and by its 25° vapor tension of 5.2 Torr, lit.[6] 5.2 Torr.

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**$BCl_3$** was obtained from the Matheson Co., Inc., Joliet, Ill., and fractionated prior to use through a −63° trap into one at −196°. The $BCl_3$ recovered from the −196° trap had a vapor tension of 4.2 Torr at −78°, lit.[7] 3.9 Torr.

**$BBr_3$** was obtained from the Ventron Corp., Beverly, Mass., and used without further treatment.

**Dichloromethane,** $CH_2Cl_2$, spectral grade, obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J., was stirred over $CaH_2$ for 48 hr and fractionated through a −63° trap into one at −196° prior to use.

***n*-Pentane** obtained from Mallinkrodt Chemical Works, St. Louis, Mo., was dried over $CaH_2$ and fractionated through a −63° trap into one at −196°, prior to use. The −196° condensate had a vapor tension of 186 Torr at 0°, lit.[7] 185 Torr.[7]

**Trimethylamine,** $N(CH_3)_3$, obtained from the Matheson Co., Inc., Joliet, Ill., was dried over $LiAlH_4$ for 7 days at room temperature to remove water and species containing labile hydrogen, followed by fractionation through a −78° trap into one at −196°. The trimethylamine recovered from the −196° trap had a vapor tension of 7.2 Torr at −78°, lit.[7] 6.6 Torr at −78°. Treatment of a sample of this material with bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, afforded more than trace amounts of tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, and $NH(CH_3)_3Cl$ both of which arise from residual $HN(CH_3)_2$ in the $N(CH_3)_3$.

**Titanium tetrabromide,** $TiBr_4$, obtained from the Ventron Corp., Beverly, Mass., was sublimed at 30–31° under vacuum and consisted of yellow-orange crystals. Infrared data: 796 (m), 781 (m, sh), 629 (vw), 612 (w), 472 (m, sh), 455 (m), 402 (vw, sh), 392 (s, sh), 338 (vvs), 374 (w), 321 (m) $cm^{-1}$.[8]

**Titanium Tetrabromide–Trimethylamine Adduct, $TiBr_4 \cdot N(CH_3)_3$.** Treatment of equimolar amounts of $TiBr_4$ and $N(CH_3)_3$ in pentane affords the red solid, $TiBr_4 \cdot N(CH_3)_3$, which was washed and desolvated *in vacuo* at 30°. Infrared data: 3120 (m), 3020 (w), 2970 (w), 2710 (w), 1465 (s), 1415 (w), 1315 (w), 1250 (m), 1215 (w), 1155 (m), 1075 (w, br), 1020 (w), 985 (s), 940 (w, sh), 820 (m), and 725 (m) $cm^{-1}$.

**Reactions of Titanium Tetrabromide with Bis(dimethylamino)-bromoborane. Preparation and Purification.** Titanium tetrabromide (1.1172 g, 3.04 mmol), dissolved in 15 ml of *n*-pentane, was contained in a 100-ml flask fitted with a 50-ml tip flask joined *via* a standard O-ring joint. Bis(dimethylamino)bromoborane (0.589 g, 3.30 mmol) dissolved in *n*-pentane and contained in the tip flask was added dropwise to the stirred solution of $TiBr_4$ over a period of 30 min at room temperature. The resulting clear red solution was then stirred vigorously for 3 hr, during which no further color change or precipitation was observed. Addition of $CH_2Cl_2$ resulted in the immediate precipitation of a homogeneous orange solid. All material volatile at room temperature was removed, *in vacuo*, and subsequently fractionated through a series of traps maintained at −22, −45, and −196°. Methylene chloride, $CH_2Cl_2$, recovered from the −196° trap was identified by vapor-phase ir spectroscopy and vapor tension, 145 Torr at 0°.[7] The material collected from the −45° trap was identified as $[(CH_3)_2N]_2BBr$ (0.2377 g, 1.33 mmol) by vapor-phase ir. The orange solid was washed repeatedly with $CH_2Cl_2$ and *n*-pentane and subsequently desolvated, *in vacuo*, at room temperature for 2 hr. Investigation of this material by ir indicated the absence of absorptions at 338 (vvs) and 392 (s, sh) $cm^{-1}$, characteristic of $TiBr_4$. The absence of strong absorption bands at 2900 $cm^{-1}$ ($\nu(CH_3)$), 1535 $cm^{-1}$ ($\nu_{as}(BN_2)$), 1212 $cm^{-1}$ ($\rho(CH_3)$), and 1070 $cm^{-1}$ ($\nu_{as}(NC_2)$), characteristic of $[(CH_3)_2N]_2BBr$, indicated that the orange solid was free of unreacted $[(CH_3)_2N]_2BBr$. *Anal.* Calcd for the orange solid: N, 3.83; B, 1.48; Ti, 9.84; Br, 76.62. Found: N, 3.75; B, 1.45; Ti, 9.91; Br, 76.84.

A molecular weight determination was not possible because a suitable solvent has not been found. Insolubility was noted with dichloromethane, *n*-pentane, carbon tetrachloride, and benzene while solution with reaction was observed with tetrahydrofuran, pyridine, 1,2-dibromoethane, and nitromethane.

**Thermal Degradation of $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$.** A sample of $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$ (150 mg, 0.10 mmol) was placed in a vacuum sublimator equipped with a side tube maintained at −196°. The sample reservoir of the sublimator was gradually heated by means of a small resistance furance; decomposition began at 61° as evidenced by the condensation of a volatile liquid and a red smear-like substance in the −196° trap. The sample, maintained in the interval 61-95°, decomposed without melting to afford a mixture of red and black materials which spread above the hot zone. The volatile material, collected from the −196° trap, was freed of small amounts of an orange solid and subsequently identified as $[(CH_3)_2N]_2BBr$ (32 mg, 0.18 mmol) by vapor-phase ir. When the mixture of solids collecting on the sides of the sublimator was gently warmed in the interval 35–39°, an orange-yellow crystalline solid sublimed in the side tube maintained at 0°. This solid was identified as $TiBr_4$ by ir spectroscopy; however, it was not possible to obtain a quantitative measurement of $TiBr_4$ because of the difficulties encountered in separation.

**Reactions of $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$ with Trimethylamine.** A sample of $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$ (197 mg, 0.13 mmol) maintained in a 50-ml reaction flask, fitted with a stopcock and a Teflon-covered magnet, was treated with excess $N(CH_3)_3$ at −196°. The reaction mixture was then allowed to warm gradually and reaction occurred in the interval −5 to 0° to afford a deep red solid and red solution. The flask was finally maintained at room temperature with vigorous stirring for 2 hr. A small amount of a green solid together with traces of a white solid slowly formed on the sides of the reaction flask. Removal of unreacted $N(CH_3)_3$ and all material volatile at 28° afforded a deep red solid and traces of a mixture of green and white solids. Fractionation of the volatile materials through a −78° trap into one at −196° afforded $N(CH_3)_3$ identified by ir spectroscopy and by its −78° vapor tension of 7.2 Torr, lit.[7] 6.6 Torr. The material isolated from the −78° trap, identified as $[(CH_3)_2N]_2BBr$ (37.5 mg), contained appreciable amounts of $[(CH_3)_2N]_3B$ as evidenced by ir.

The solid mixture remaining in the reaction flask was transferred to a filtration apparatus and treated with excess $N(CH_3)_3$. A red solution formed and was subsequently filtered at −78° leaving a red solid and a trace amount of white solid on the surface of the frit. The ir spectrum of the red solid contained bands at 3080 (s), 3020 (w, sh), 2940 (s, br), 2700 (vs), 2520 (w), 2480 (m), 1520 (w, sh), 1460 (vs), 1400 (m), 1380 (m), 1310 (w), 1265 (m), 1220 (vw), 1130 (vw), 985 (s), 820 (m), and 725 (m) $cm^{-1}$.

## Results and Discussion

Treatment of titanium tetrabromide, $TiBr_4$, with excess bis(dimethylamino)bromoborane, $[(CH_3)_2N]_2BBr$, is described by

$$3TiBr_4 + 2(CH_3)_2NBBr \rightarrow \underset{\text{II}}{\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3} \qquad (1)$$

The product, II, dissociates to its molecular components with partial decomposition at 61° *in vacuo*. In an effort to displace $[(CH_3)_2N]_2BBr$ from II, treatment of the latter with $N(CH_3)_3$ was carried out and is summarized by

$$\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3 + 3N(CH_3)_3 \rightarrow \underset{\text{III}}{3TiBr_4 \cdot N(CH_3)_3} + 2[(CH_3)_2N]_2BBr \qquad (2)$$

An 80% yield of the bromoborane was realized with the remaining material being converted to tris(dimethylamino)-borane, $[(CH_3)_3N]_3B$. Formation of the latter is accompanied by production of $HN(CH_3)_3Br$, both species being positively characterized by ir spectroscopy.[5,9] Formation of these two materials results from trace quantities of $HN(CH_3)_3$ present in the utilized $N(CH_3)_3$. The titanium derivative, III (eq 2), was characterized by comparison of its ir spectrum with that of an authentic sample: principally the band shapes and frequencies at 985 (s), 820 (m), and 725 $cm^{-1}$. Because I and II have the same unusual stoichiometry and behave similarly when treated with $N(CH_3)_3$[10] the structures associated with I and II are most likely quite similar.

**Nature of Bonding of II by Infrared Spectroscopy.** The infrared spectrum of II is shown in Figure 1 and summarized in Table I. The absorptions of primary interest, concerning the bonding associated with II, are $\nu$(B-Br), $\nu(B\text{-}N_2)$, and $\nu(NC_2)$. A decrease in $\nu(NC_2)$, in I, has been discussed in detail with regard to coordinated *vs.* noncoordinated $N(CH_3)_2$ moieties.[5]

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**Table I.** Infrared Data and Assignments for $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$

| Assignment | Freq, $cm^{-1}$ | Assignment | Freq, $cm^{-1}$ |
|---|---|---|---|
| $\nu(CH_3)$ | 3115 w | $\nu_{as}(NC_2)$ | 1052 |
| | 3040 w | | 1032 s, sh |
| | 2950 vw | | 1022 vs |
| | | | 993 vs |
| $\nu_{as}(B^{10,11}N_2)$ | 1675 m, sh | | |
| | 1647 w, sh | $\nu(BBr) + \nu_s(NC_2)$ | 897 w |
| | 1617 vvs | | |
| | | $\nu(BBr)$ | 800 s |
| $\delta_{as}(CH_3)$ | 1470 ms | | |
| | | $\delta(BN_2)$ | 683 w |
| $\delta_s(CH_3)$ | 1419 vs | | 660 s |
| | 1422 vs, sh | | |
| | | $\nu(TiBr)$ | 338 m |
| $\nu_s(BN_2)$ | 1450 s | | 310 s |
| | | | 270 m |
| $\rho(CH_3)$ | 1283 w | | |
| | 1250 vs | $\nu(TiN)$ | 280 m |
| | 1219 m | | |
| | 1183 vs | | |
| | 1145 vs | | |
| | 1130 s, sh | | |

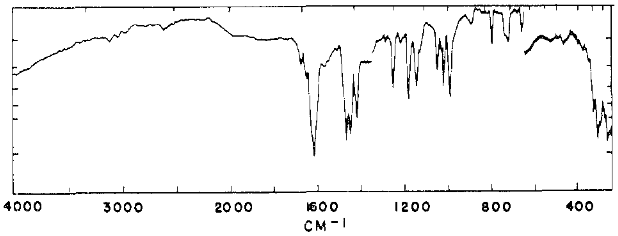

**Figure 1.** Infrared spectrum of $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$.

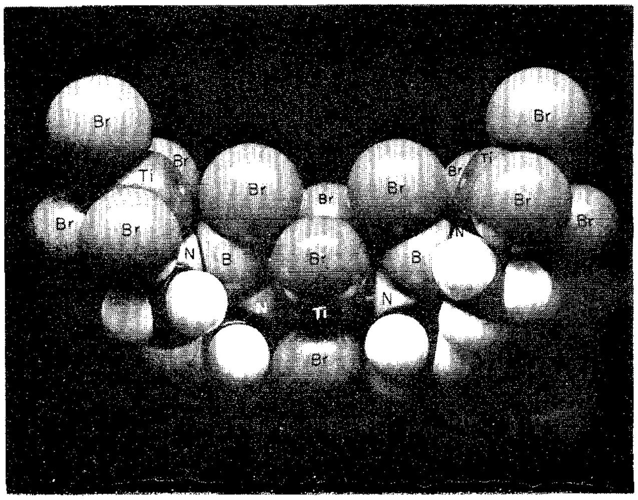

**Figure 2.** Proposed structure for $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$.

This absorption is at 1070 $cm^{-1}$ in the noncoordinated ligand, $[(CH_3)_2N]_2BBr$, but shifts to a series of bands at 1052, 1032, 1022, and 993 $cm^{-1}$ in II. Based on the lack of absorptions at 1070 $cm^{-1}$ in II, most assuredly there are no noncomplexed $N(CH_3)_2$ moieties associated with II. The $\nu_s(NC_2)$ in II is found at 897 $cm^{-1}$ while this absorption is located at 900 $cm^{-1}$ in the free ligand.

The Br bonded to B is considered noncomplexing based on the similar $\nu B^{10,11}Br$ frequency in II and $[(CH_3)_2N]_2BBr$, 897, 800 and 880, 838 $cm^{-1}$, respectively. The fact that $\nu(BBr)$ in II is at higher energy than in the free ligand is entirely consistent with noncomplexing BBr. The consistency of these ir assignments is most obvious by comparison of the ir spectra of $[(CH_3)_2N]_2BCl$,[2] $[(CH_3)_2N]_2BBr$ (see Experimental Section), and II, Table I. The $\nu_{as}(BN_2)$ vibrations are shifted from 1555 and 1535 $cm^{-1}$ in the noncomplexed ligand to 1675, 1647, and 1617 $cm^{-1}$ in II while $\nu_s(BN_2)$ shifts from 1358 to 1450 $cm^{-1}$. Similar $\nu(BN_2)$ shifts to higher energy were observed for I and attributed to $BN_2$ vibrations coupled with like-symmetry modes;[5] an identical explanation is suggested for II.

The most probable structure associated with II, and presumably I as well, is shown in Figure 2. The nature of coordination is as follows: $Br_4Ti \leftarrow N(CH_3)_2B(Br)(CH_3)_2N \rightarrow TiBr_4 \leftarrow N(CH_3)_2B(Br)(CH_3)_2N \rightarrow TiBr_4$. Concerning Figure 2, this structure involves five- and six-coordinate Ti and contains all Ti, B, and N, in the same plane; the N and B are $sp^3$ and $sp^2$ hybridized, respectively. Because the sixth coordination site of the terminal Ti atoms are blocked by Br (associated with B) the 2:3 stoichiometry is understandable as opposed to a 1:1 polymer. An equally probable structure would involve a 180° rotation of one N (and accompanying moieties, B and Ti). The suggested molecular structure, Figure 2, is completely consistent with the unusual stoichiometry for II and the infrared assignments.

**Registry No.** $[(CH_3)_2N]_2BBr$, 6990-27-8; $TiBr_4 \cdot N(CH_3)_3$, 38560-52-0; $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$, 38560-53-1.

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