Contribution from the Evans Chemical Laboratories,
The Ohio State University, Columbus, Ohio 43210

# Preparation and Characterization of (1,2-Dibromo)[1,2-bis(dimethylamino)]diborane(4)-Titanium(III) Bromide

MONIM R. SULIMAN[1] and E. P. SCHRAM*

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Treatment of $TiBr_4$ with $B_2[N(CH_3)_2]_4$ affords $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$ which is characterized as a binuclear species based on magnetic data and infrared and electronic spectroscopy. Pyrolysis of $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$ affords $B_2Br_2[N(CH_3)_2]_2$ and subsequent treatment of the pyrolysis residue with $N(CH_3)_3$ yields $TiBr_3 \cdot 2N(CH_3)_3$. In a similar fashion, treatment of $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$ with $N[(CH_3)_2]_3$ quantatively yields $TiBr_3 \cdot 2N(CH_3)_3$ while reaction with HBr produces $B_2Br_4$-$[N(CH_3)_2H]_2 \cdot TiBr_3$.

## Introduction

Treatment of $TiCl_4$ with $B_2[N(CH_3)_2]_4$ affords the binuclear species, $Ti_2Cl_6 \cdot B[N(CH_3)_2]_2Cl$, which exhibits antiferromagnetic behavior.[2] A structure was suggested for this latter species which incorporated Cl bridges and coordinated $N(CH_3)_2$ moieties.[3] As a logical extension to the synthesis of other binuclear Ti derivatives, $TiBr_4$ was treated with $B_2[N(CH_3)_2]_4$. Rather than production of the analogous Ti bromide species, formation of $B_2Br_2$-$[N(CH_3)_2]_2 \cdot TiBr_3$ resulted. The characterization and chemistry of this species are presented and discussed.

## Experimental Section

**Apparatus and Procedures.** All reactions were carried out in a vacuum line equipped with Kontes greaseless Teflon stopcocks and operated at $10^{-5}$ Torr. Equipment was attached to the vacuum line with Viton A O-ring closure assemblies while nonvolatile samples were handled in a drybox containing stirred Na-K alloy. **Infrared spectra** of solid samples were recorded with a Perkin-Elmer 457 spectrometer employing combination Nujol-Fluorolube mulls and KBr or CsBr windows. Nonvolatile liquid samples were run neat while volatile materials were contained in a 10-cm gas cell. Spectra were calibrated with reference to the 1601.4-$cm^{-1}$ band of polystyrene. **Nmr spectra** were obtained on solutions sealed in 5-mm Pyrex tubes employing a Varian A-60A spectrometer. **Electronic spectra** were recorded with a Cary 14 spectrophotometer equipped with a reflectance attachment. **Magnetic measurements** were carried out with a Gouy balance at room temperature and at four different currents using $Hg[Co(NCS)_4]$ as a calibrant.[4] **Analyses** for boron, nitrogen, titanium, and $H_2$ were carried out as previously described while bromide titrations were performed potentiometrically (Ag-AgBr couple).[2]

**Reagents. 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.[5] 185 Torr.

**Titanium tetrabromide, $TiBr_4$,** obtained from Ventron Corp., Beverly, Mass., was sublimed at 30–31° under vacuum prior to use. Titanium tetrabromide was collected as a yellow-orange crystalline solid on the cold tip of the sublimator. This material had ir absorptions in agreement with the literature[6] at 796 (m), 781 (m, sh), 629 (w, sh), 612 (w), 472 (m, sh), 455 (m), 402 (w, sh), 392 (s, sh), 338 (vs), 374 (w), and 321 (w) $cm^{-1}$.

**Trimethylamine, $N(CH_3)_3$,** obtained from the Matheson Co., 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.[5] 6.6 Torr at −78°. Treatment of a sample of this material with bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, still affords some tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, and $(CH_3)_3NHCl$.

**HBr** was obtained from Air Products and Chemicals, Inc., Allentown, Pa., and purified by fractional condensation through a −126° to a −196° trap. The vapor tension of the purified HBr, at −126°, 5.3 Torr, agreed with the literature value.[7]

**$(CH_3)_3NHBr$** was prepared in the gas phase with equimolar portions of $(CH_3)_3N$ and HBr. Infrared data: 3050 (w), 3005 (w, sh), 2900 (vs), 2680 (vs, b), 2510 (m), 2460 (s), 1460 (vs), 1420 (m), 1395 (m), 1255 (vs), 1240 (w, sh), 1198 (w), 1055 (s), 980 (vs), 890 (w), 815 (s), 810 (m, sh), 630 (w), and 460 (m) $cm^{-1}$.

**Tris(dimethylamino)bromodiborane(4), $B_2Br[N(CH_3)_2]_3$,** was prepared according to the literature method.[8] Tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$ (21.6 mmol), in *ca.* 20 ml of ether, was treated with $BBr_3$ (10.8 mmol) in *ca.* 10 ml of benzene at −22°. After stirring the reaction mixture for 2 hr at room temperature the solution was slightly brown. Removal of ether and benzene at room temperature, *in vacuo*, followed by distillation of all materials volatile at 40° afforded a low volatile liquid which was subsequently distilled in the range 50–55° (0.6 Torr), lit.[8] 51° (0.5 Torr). A neat sample had ir bands at 3005 (s, sh), 2940 (vs), 2900 (s), 2810 (vs), 1550 (w, sh), 1535 (m, sh), 1510 (s), 1468 (s), 1415 (vw, sh), 1410 (vs), 1355 (w), 1192 (vs), 1170 (s), 1123 (vs), 1060 (vs), 980 (vvs), 890 (vw, sh), 875 (vw, sh), 863 (vvs), 820 (vw), 790 (w), 710 (vvs), 525 (w, br), and 460 (m) $cm^{-1}$.

**(1, 2-Dibromo)[1,2-bis(dimethylamino)]diborane(4), $B_2Br_2$-$[N(CH_3)_2]_2$,** was prepared by the literature method and observed to have two $^1H$ nmr signals of equal intensity as reported, −2.98 and −2.89 ppm from TMS.[8] Infrared data: 2990 (w), 2900 (m), 2890 (m), 2800 (s), 2830 (vs), 1502 (s), 1453 (s), 1410 (m), 1375 (vs), 1339 (m, sh), 1220 (s), 1190 (m), 1145 (m, sh), 1120 (vs), 1080 (m), 1065 (s), 1050 (w), 970 (s), 890 (m), 870 (w), 860 (w), 830 (w), 760 (s), 680 (w), and 610 (w) $cm^{-1}$.

**Tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$,** obtained from U. S. Borax Research Corp., Anaheim, Calif., was distilled in the range 69–71° (3.6 Torr), lit.[9] 69° (3.5 Torr). Infrared data: 3010 (m, sh), 2900 (m), 2865 (vs), 2800 (s), 1515 (w, sh), 1503 (vs), 1465 (w, sh), 1455 (s), 1410 (s), 1380 (vs), 1342 (s), 1225 (vs), 1192 (s), 1150 (m, sh), 1135 (vs, sh), 1125 (vs), 1108 (w, sh), 1070 (s), 1055 (m), 905 (w, sh), 892 (vs), 845 (w, sh), 835 (m), 800 (w), and 618 (w) $cm^{-1}$.

**Titanium tetrabromide-trimethylamine, $TiBr_4 \cdot N(CH_3)_3$,** was prepared by the literature method[10] and has infrared bands at 3120 (m), 3020 (w), 2970 (w), 2710 (w), 1465 (s), 1415 (w), 1315 (w), 1250 (m), 1215 (w), 1155 (m), 1075 (w, b), 1020 (w), 985 (s), 940 (w, sh), 820 (m), and 725 $cm^{-1}$.

**Titanium tribromide-bis(trimethylamine), $TiBr_3 \cdot 2N(CH_3)_3$,** prepared by the literature method,[10] has infrared bands at 3080 (m), 3010 (m), 2980 (m), 2900 (s), 2860 (m, sh), 2800 (m, sh),

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2460 (w), 1480 (vs), 1460 (vs), 1445 (s, sh), 1408 (s), 1240 (m), 1230 (w, sh), 1105 (vs), 985 (vs), 890 (w), 812 (vs), 725 (m), 510 (vs), 435 (s), and 320 (s) cm$^{-1}$.

**Preparation and Characterization of (1, 2-Dibromo)[1,2-bis(dimethylamino)diborane(4)]-Titanium(III) Bromide, $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$.** Titanium tetrabromide, $TiBr_4$ (10.5 mmol), 3.864 g, in benzene (15 ml), was treated with $B_2[N(CH_3)_2]_4$ (5 mmol) in benzene (15 ml) at 25° affording an initial deep red solution and subsequently a brown precipitate. This reaction mixture was stirred vigorously for 5 hr at room temperature. The volatile materials were removed under vacuum and fractionated through a −22° trap into one at −196°. Benzene, identified by vapor-phase ir and by its 0° vapor tension of 25 Torr, lit.[7] 25.0 Torr, was recovered from the −196° trap. The −22° condensate was identified as tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, by vapor-phase ir.[11] Distillation of all materials volatile at 28° afforded (1,2-dibromo)[1,2-bis(dimethylamino)]diborane(4), $B_2Br_2[N(CH_3)_2]_2$, identified by $^1H$ nmr and ir.[8] The liquid-state infrared spectrum of this material was identical, as expected, with that of a pure sample of (1,2-dichloro)[1,2-bis(dimethylamino)]diborane(4), $B_2Cl_2[N(CH_3)_2]_2$, except for the boron–halide stretching frequencies.

The insoluble nonvolatile brown residue was washed with $CH_2Cl_2$ leaving a nonvolatile brown solid on the surface of the frit and a deep black-red filtrate. The insoluble brown solid, ground into a fine powder, was washed again with $CH_2Cl_2$ and subsequently desolvated at 28° for 10 hr, *in vacuo*. When a sample of this material (219.7 mg) was treated with 25% $H_2SO_4$, a deep violet solution immediately developed from which no $H_2$ was evolved within 10 hr at 25°. Treatment of this acidic solution with previously degassed 25% aqueous NaOH resulted in the formation of a blue-black precipitate and evolution of $H_2$. The blue-black precipitate, characteristic of Ti(III), slowly transformed into a white solid over a period of 7 days with slow evolution of additional $H_2$. The contents of the hydrolysis flask were dissolved in aqueous $H_2SO_4$. Samples of this hydrolysis solution were analyzed for B, N, and Br. *Anal.* Calcd: B, 3.9; Br, 71.6; N, 4.78; Ti, 8.6. Found (for a 319.7-g sample): B, 3.8; Br, 71.6; N, 4.90; Ti, 9.09, 8.93. Ti analyses were obtained by quantitative conversion of $TiBr_3$, associated with I, to $TiBr_3 \cdot 2N(CH_3)_3$—see $N(CH_3)_3$ reaction section. A molecular weight determination was not carried out because of lack of a suitable solvent. Compound I was found to be insoluble in methylene chloride, benzene, *n*-pentane, and carbon tetrachloride and to react with acetonitrile and trimethylamine.

**Thermal Decomposition of $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$.** A 150-mg (0.27 mmol) sample (hereafter referred to as I was heated, *in vacuo*, with decomposition initiated at 110° as evidenced by evolution of $B_2Br_2[N(CH_3)_2]_2$. Characterization of this latter species was by ir. Treatment of the red-black residue with $N(CH_3)_3$ afforded green $TiBr_3 \cdot 2N(CH_3)_3$ which was characterized by comparison of ir data with that of an authentic sample.

**Reaction of $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$ with $N(CH_3)_3$.** Treatment of I with a 50 molar excess of $N(CH_3)_3$ at −78°, followed by slow warming of the reaction mixture to *ca.* −5°, resulted in the formation of a green solution as well as a mixture of amine-insoluble yellow and white solids. Filtration of the green solution, followed by removal of excess $N(CH_3)_3$ and volatile materials, afforded a green crystalline solid and a mixture of insoluble yellow and white solids. The green solid was identified as $TiBr_3 \cdot 2N(CH_3)_3$ by ir. Compound I, 551.1 and 363.3 mg, afforded 50.08 and 31.00 mg of $TiBr_3 \cdot 2N(CH_3)_3$, respectively (duplicate runs). The mixture of the amine-insoluble yellow and white solids contained on the surface of the frit was subjected to a second filtration employing $CH_2Cl_2$. The yellow solid partially dissolved affording a light yellow solid which was shown to contain halide ions, boron, volatile amines, and no titanium based on qualitative tests. Examination of the white solid, insoluble in $CH_2Cl_2$, by ir indicated the presence of $(CH_3)_3NHBr$.

**Reaction of $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$ with HBr.** A sample of $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$, 190.9 mg (0.34 mmol), was treated with HBr (65 Torr), 2.75 mmol, in the presence of *ca.* 20 ml of $CH_2Cl_2$ at room temperature. The reaction was allowed to proceed for 1 hr with vigorous stirring. All materials volatile at 27° were then removed, *in vacuo*, affording a light brown solid. Fractionation of the volatile material through a series of traps maintained at −78, −126, and −196°, afforded $CH_2Cl_2$ in the −78 and −126° traps, identified by vapor-phase infrared spectroscopy. The material isolated from the −196° trap was identified as HBr (2.03 mmol) by its −126° vapor tension of 5.3 Torr, lit.[7] 5.3 Torr. The light brown solid was washed twice with $CH_2Cl_2$ and subsequently desolvated, *in vacuo*, at 27° for 2 hr. Infrared data: 3120 (vs, b), 2950 (m), 2760 (w), 1690 (w), 1570 (m), 1450 (s), 1400 (w), 1380 (w), 1010 (s), 970 (w), 900 (w), 873 (w), 809 (m), 715 (m), 595 (w), and 420 (w) cm$^{-1}$.

## Results and Discussion

**Preparation and Analytical Characterization of 1,2-Dibromo)[1,2-bis(dimethylamino)]diborane(4)-Titanium(III) Bromide, $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$.** Titanium tetrabromide, $TiBr_4$, reacts with tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, over a wide range of mole ratios to afford $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$. Maximum product yield is obtained for a 2:1 $TiBr_4$:$B_2[N(CH_3)_2]_4$ mole ratio. Purification of insoluble I was effected by repeated washings, *in vacuo*, with $CH_2Cl_2$. Removal of unreacted $TiBr_4$ or $B_2[N(CH_3)_2]_4$ is ensured by the absence of ir bands in I at 455 (ms), 392 (s, sh), and 338 (vs) cm$^{-1}$ ($TiBr_4$)[6] and bands at 1503 (vvs), 1342 (s), and 892 (s) cm$^{-1}$ associated with $B_2[N(CH_3)_2]_4$.[12] Also, $B_2Br[(CH_3)_2]_3$ is proven absent by the absence of the absorption at 980 (vvs) cm$^{-1}$. Investigation of the by-products associated with formation of I indicate no oxidation of the B–B bond takes place in contrast to the corresponding reduction of $TiCl_4$.[2] In the present case the reduction of Ti(IV) to Ti(III) involves oxidation of a $N(CH_3)_2$ moiety to a methylenimine derivative. This type of redox reaction will be discussed in detail shortly.[13]

Quantative transformation of $TiBr_3$, associated with I, to green $TiBr_3 \cdot 2N(CH_3)_3$ (characterized by comparison ir spectroscopy) was effected with liquid $N(CH_3)_3$

$$B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3 + 2N(CH_3)_3 \rightarrow B_2Br_2[N(CH_3)_2]_2 + TiBr_3 \cdot 2N(CH_3)_3 \qquad (1)$$

Because amines are known to function as reducing agents toward early transition metal(IV) halides, it was necessary to show a similar reaction had not occurred with I.[10] Under reaction conditions, similar to those associated with eq 1, treatment of $TiBr_4$ with $N(CH_3)_3$ afforded red $TiBr_4 \cdot N(CH_3)_3$ with less than 5% reduction to green $TiBr_3 \cdot 2N(CH_3)_3$. Concerning eq 1, a high yield of $B_2Br_2[N(CH_3)_2]_2$ was not realized; a rather substantial quantity of $B_2[N(CH_3)_2]_4$ was isolated. This is explained by the fact that $N(CH_3)_3$ contains trace quantities of $HN(CH_3)_2$ even after treatment with $LiAlH_4$. Further evidence for the presence of the diborane(4) ligand, eq 1, is the fact that heating I at 110°, *in vacuo*, affords $B_2Br_2[N(CH_3)_2]_2$ which was characterized by comparitive ir and $^1H$ nmr spectroscopy.

Degradation of I in aqueous base is summarized by

$$B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3 + 7OH^- \rightarrow 2BO_2^- + TiO_2 + H_2O + 5Br^- + 2HN(CH_3)_2 + 1.5H_2 \qquad (2)$$

The $H_2$ produced was 78% of the theoretical amount after 5 days at 25°. Incomplete B–B bond oxidation is indicated by the fact that fresh hydrolysis solutions, with pH adjusted to <7, affords $Ag^0$ when treated with $AgNO_3$. Similar results are found when treating aqueous solutions of B–B bonded species (pH <7) with $AgNO_3$.[14] Successful $Br^-$ analyses were effected only after $H_2O_2$ treatment of the basic hydrolysis solution.

**Magnetic Susceptibility and Electronic Spectrum of I.** Compound I exhibits a field-independent magnetic moment

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of 1.45 BM at 25°. Antiferromagnetism is a common feature among titanium(III) halides and in most cases the moments are lower than spin-only values due to inter- or intramolecular antiferromagnetism. The unusually low magnetic moment of $\beta$-$TiCl_3$ (triple-Cl-bridged chain structure), 0.78 BM per titanium(III), is suggestive of a direct metal-metal bond while other titanium(III) halides (except $TiF_3$) are also antiferromagnetic with Curie points at 230 and >434° for $TiBr_3$ and $TiI_3$, respectively.[15] Recently the room-temperature magnetic moments of six-coordinate titanium complexes of the type $Br_3Ti \cdot 2L$ (where L = $S(CH_3)_2$ or tetrahydrothiophene) were measured, 1.61 and 1.64 BM, respectively, and interpreted in terms of weak antiferromagnetic interactions.[16] The room-temperature moment of 1.45 BM for I is consistent with an oxidation state of 3+ with weak magnetic interaction.

Crystal field theory has been useful for interpretation of the electronic spectra of transition metal complexes in terms of five- *vs.* six-coordinate central metal ions. However, this is only applicable to weak transitions between d-orbital levels and cannot account for the much stronger absorptions which invariably occur in the ultraviolet region and often extend into the visible region of the spectrum. The reflectance spectrum of I contains no d ← d transitions in the region expected for either five- or six-coordinate titanium(III) complexes. The absence of such transitions is interpreted in terms of weak magnetic interactions. This same reasoning has been suggested for the absence of d ← d transitions for $TiI_3 \cdot 2S(CH_3)_2$.[16] The two charge-transfer bands in the electronic spectrum of I have maxima at 27,700 and 23,300 $cm^{-1}$ and are tentatively assigned to Ti ← Br. It has been pointed out that an empirical correlation exists between the frequency of the first charge-transfer band and the coordination number of the central metal ion.[17] The ultraviolet spectra of titanium bromide complexes generally occur at lower energy (4000–6000 $cm^{-1}$) than the chloro complexes in agreement with the ease of Br oxidation compared with that of Cl. Although data on the bromo complexes are rather limited, the progressive shift to lower energy of the first charge-transfer band with increasing coordination numbers of titanium is apparent (Table I). For example, it has been suggested that complexes of the type $Br_3Ti \cdot 2S(CH_3)_2$ are six- rather than five-coordinate on the basis of their first charge-transfer bands in comparison with those of $Br_3Ti \cdot 2N(CH_3)_3$ ($D_{3h}$ by X-ray crystallography) and compounds known to be six-coordinate.[16]

Based on comparison of the energy of the first charge-transfer band (I) (23.3 kK) with data collected in Table I, Ti associated with I is considered six-coordinate. Furthermore, from the low magnetic moment for I, one may infer the presence of a binuclear Ti species undergoing spin exchange. Concerning possible modes of bonding for I, interpretation of the infrared data had been most informative.

**Table I.** Electronic Spectral Data for Titanium Bromide Complexes

| Species | Phase | Coord no. | Energy, kK |
|---|---|---|---|
| $TiBr_4$ | Gas | 4 | 27.75, 29.4, 35.9[a] |
| $TiBr_3 \cdot 2N(CH_3)_3$ | Solid | 5[b] | 27.7, 35.6, 44.8[c] |
| $TiBr_3 \cdot 2[C_4H_8O_2]$ | Soln | 6[c] | 20.8, 24.0, 29.4[c] |
| $TiBr_3 \cdot 2S(CH_3)_2$ | Soln | 6[c] | 17.5, 25.0[c] |
|  | Solid | 6[c] | 19.1, 26.6, 29.0, 45.3[c] |
| $TiBr_4 \cdot [(C_6H_5)_2AsCH_2]_2$ | Solid | 6[d] | 20.0[d] |
| $TiBr_6 \cdot [(C_2H_5)_2NH_2]_2$ | Soln | 6[e] | 22.0, 25.2, 27.0, 34.3[e] |
| $TiBr_4 \cdot 2CH_3CN$ | Solid | 6[f] | 21.8, 19.0, 27.6, 37.2, 45.6[e] |
| $TiBr_4 \cdot C_4H_8O_2$ | Solid | 6[f] | 22.2, 28.5, 36.6, 45.3[e] |
| $TiBr_4 \cdot 2[(C_6H_5)_2AsCH_2]_2$ | Solid | 8[d] | 17.9[d] |

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**Table II.** Infrared Data and Assignment for $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$

| Freq, $cm^{-1}$ | Assignment | Freq, $cm^{-1}$ | Assignment |
|---|---|---|---|
| 3135 m | $\nu$(CH) | 1072 m | $\nu_{as}(NC_2)$ |
| 3000 w |  | 1063 m |  |
| 2920 s |  | 1050 m |  |
| 2880 s |  | 990 s | $\nu_s(NC_2)$ |
| 2800 w |  | 975 s |  |
| 1559 m, sh | $\nu$(B–N) | 925 s |  |
| 1540 s, sh |  | 890 m |  |
| 1521 s |  | 865 m |  |
| 1510 s |  | 835 m |  |
| 1496 s |  | 825 m |  |
| 1465 s | $\delta$(CH) | 725 s | $\nu$(BBr) |
| 1440 s |  |  |  |
| 1410 w |  | 682 m |  |
| 1390 s |  | 630 w |  |
| 1365 w |  | 610 w |  |
| 1320 s |  | 475 m |  |
|  |  | 425 w |  |
| 1245 s | $\rho$(CH) | 383 w, sh |  |
| 1220 s |  |  |  |
| 1200 m |  | 300 s, b | $\nu$(TiBr) |
| 1185 m |  |  |  |
| 1160 m |  |  |  |
| 1145 w |  |  |  |
| 1125 s |  |  |  |

**Inference of Molecular Geometry for $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$ by Infrared Spectroscopy and Chemical Reactivity.** One may infer from the treatment of I with $N(CH_3)_3$, as well as thermal dissociation, the presence of the ligand $B_2Br_2[N(CH_3)_3]_2$ in I. The questions to be answered involve the nature of coordination. Are the nitrogens or bromines, associated with boron, bridging to titanium? The infrared spectrum of I is shown in Figure 1 and summarized in Table II. A most important and surprising feature of this spectrum involves the conclusion that the $N(CH_3)_2$ moieties are noncoordinating. This conclusion is based on the assignment for $\nu_{as}(NC_2)$ associated with I, at 1072, 1063, and 1050 $cm^{-1}$ compared with the noncoordinated ligand bands at 1080, 1065, and 1050 $cm^{-1}$.[18] Similarly noncoordinated $\nu_s(NC_2)$ is found at 970 $cm^{-1}$ for the noncomplexed ligand and at 990 and 975 $cm^{-1}$ for I.[18] Also consistent with the noncoordinating nature of the $N(CH_3)_2$ moieties is the series of overlapping bands at 1559, 1540, 1531, 1520, and 1504 $cm^{-1}$ which are assigned to $\nu$(B=N).[18] In the noncomplexed ligand $\nu_{as}(BN_2)$ is found at 1502 $cm^{-1}$; hence the increased B–N bond order is a consequence of bromide bridging from boron to titanium increasing the effective electronegativity of B and as a consequence increasing $N_{p_\pi}$-$B_{p_\pi}$ interactions. It should be noted that the magnitude of increased $\nu$(B–N) is less than that observed for coupled B–N vibra-

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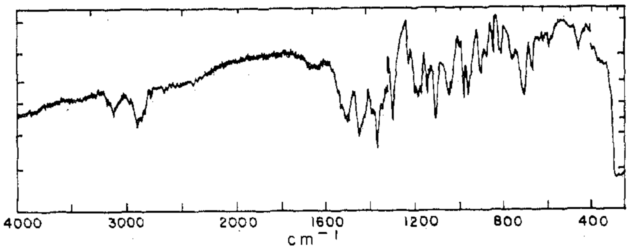

**Figure 1.** Infrared spectrum of $TiBr_3 \cdot B_2Br_2[N(CH_3)_2]_2$.

tions involving coordinated $N(CH_3)_2$ moieties, *i.e.*, to 1650 cm$^{-1}$.[3,11]

Further evidence for the noncomplexing $N(CH_3)_2$ moieties is the facile reactions with HBr

$$B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3 + 2HBr \rightarrow TiBr_3 \cdot B_2Br_4 \cdot 2NH(CH_3)_2 \quad (3)$$

The product, hereafter referred to as II, is considered a dimethylamine adduct of coordinated $B_2Br_4$, rather than a salt, based on analogous reactions with diborane(4) halides and on interpretation of the ir spectrum of II. Treatment of $B_2X_2[N(CH_3)_2]_2$ with HX (where X = Cl or Br) has been conclusively shown to afford the $NH(CH_3)_2$ adduct rather than a salt.[19] This referenced investigation which included an ir study indicates the presence of $\nu$(NH) at 3205 cm$^{-1}$ and the absence of hydrogen bonding, *i.e.*, no absorption at 2735 cm$^{-1}$, $\nu(N\cdot\cdot\cdot H\cdot\cdot\cdot Cl)$.[19] In a similar fashion the ir spectrum of II contains a strong broad absorption centered at 3135 cm$^{-1}$ but no bands at 2680 (vs, b), 2510 (m), and 2460 (s) cm$^{-1}$ found in $(CH_3)_3NHBr$ and assigned to $\nu(N\cdot\cdot\cdot H\cdot\cdot\cdot Br)$.[19]

With regard to $\nu$(BBr) assignments, associated with I, ir data collected on $B_2Br_2[N(CH_3)_3]_2$ and $B_2Cl_2[N(CH_3)_2]_2$ were compared and the $\nu$(BBr) assignment was concluded. $\nu$(BBr) is conclusively associated with the band at 760 cm$^{-1}$.[18] Because I is stable as an adduct and the bonding does not involve coordinated $N(CH_3)_2$ moieties, decreased $\nu$(BBr) (bridging bromine) from $B_2Br_2[N(CH_3)_2]_2$ to I is expected. With regard to the ir spectrum of I, no vibration occurs at 760 cm$^{-1}$ but a strong absorption occurs at 725 cm$^{-1}$ and is assigned to $\nu$(BBr) and associated with bromine bridging from boron to titanium. If follows that both bromines associated with the free ligand are coordinating.

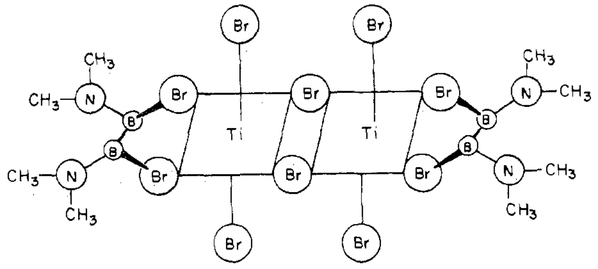

**Figure 2.** Proposed structure for $TiBr_3 \cdot B_2Br_2[N(CH_3)_2]_2$.

**Suggested Molecular Structures for $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$.** A mononuclear titanium formulation for I would be expected to exhibit a normal d$^1$ magnetic moment and a charge-transfer spectrum consistent with five-coordinate Ti. On the bases of the low magnetic moment and the energy of the first charge-transfer band being consistent with six-coordinate Ti, the binuclear species, Figure 2, is proposed. The low magnetic moment is suggested to result from a superexchange mechanism rather than direct metal-metal bonding because bromide-bridged titanium would result in very poor direct metal-metal orbital overlap.

The noncomplexed ligand (1,2-dibromo)[1,2-bis(dimethylamino)]diborane(4) exhibits two $^1H$ nmr signals in a 1:1 ratio. Based on molecular models, the sterric requirements of Br and $N(CH_3)_2$ do not allow cis-trans isomers with sp$^2$ hybridized boron. Furthermore, sp$^3$ hybridized boron would allow free rotation with the expected single $^1H$ nmr absorption. Concerning the structure of I, the high BN stretching frequency is most consistent with a B=N bond, and because of the sterric interactions between Br and $N(CH_3)_2$, bonded to adjacent B's, the N-B-B-N framework must be noncoplanar, Figure 2. Of course several isomeric forms of I are possible, these being the enantiomeric conformations $\delta\delta$ and $\lambda\lambda$ and the meso conformation $\delta\lambda$ due to the five-membered $B_2Br_2Ti$ ring.

**Registry No.** $TiBr_4$, 7789-68-6; $B_2[N(CH_3)_2]_4$, 1630-79-1; $B_2Br_2[N(CH_3)_2]_2 \cdot TiBr_3$, 37274-05-8; $N(CH_3)_3$, 75-50-3; HBr, 10035-10-6; $TiBr_3 \cdot B_2Br_4 \cdot 2NH(CH_3)_2$, 37274-02-8.

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