Table IV. Comparison of Relative Rates of Ozonation of Olefins

Olefin	Vrbaski and Cvetanović[a]	Wei and Cvetanović[b]		Bufalini and Altshuller[c]	This work
		O_2	N_2		
1-Hexene	1.0	1.0	1.0	1.0	1.0
1-Pentene	0.8	0.9	0.8	...	1.1
Isobutylene	0.8	0.8	1.0	2.0	1.3
cis-2-Butene	2.9	2.7	1.4	29	2.1
2-Hexene	2.7	2.9	2.5	...	1.9
Trimethylethylene	2.5	2.8	3.0	65	2.2
Tetramethylethylene	3.0	3.8	5.2	...	2.6
Cyclopentene	...	...	...	...	2.6

[a] Reference 5. [b] Reference 6. The two columns refer, respectively, to values obtained with O_2 and N_2 as the diluent gas. [c] Reference 7.

of the corresponding rates in the gas phase. This can be seen, for example, by comparing the rates of ozonation of hexene-1 in the two media. For this reaction the gas-phase values of k_1 obtained by different workers agree quite well.[7] The present value of k_1 for hexene-1 in CCl_4 solution is 13 ± 4 times greater than the gas-phase values for the same reaction. Such a large ratio ($R_{s/g}$) of the rate constants k(solution)/k(gas) need not be regarded as unexpected since order-of-magnitude calculations[9,10] predict for second-order reactions $R_{s/g}$ values as large as one to two powers of ten. However, it would seem at the moment that few experimental data can be quoted in support of these predictions and, in some cases, there is little or no difference between the rates in the gas phase and in solution. Relative rates of a series of reactions of the same type should be affected little on going from the gas phase to solution. This seems to be borne out by the present results and the gas-phase results obtained previously in this laboratory.

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(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

(10) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 504–510.

Reactions of Titanium Tetrachloride with BCl_3, $(CH_3)_2NBCl_2$, $[(CH_3)_2N]_2BCl$, $[(CH_3)_2N]_3B$, $[(CH_3)_2N]_2BCH_3$, and $B_2[N(CH_3)_2]_4$[1a]

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Abstract: Treatment of titanium tetrachloride with bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, or tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, results in the formation of di[bis(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)], $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. Reaction with bis(dimethylamino)methylborane, $[(CH_3)_2N]_2BCH_3$, affords dimethylaminochloromethylborane, $(CH_3)_2NBClCH_3$, and dimethylaminotrichlorotitanium(IV), $(CH_3)_2NTiCl_3$; with tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, the products of reaction are $[(CH_3)_2N]_2BCl$, dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, bis(dimethylamino)dichlorotitanium(IV), $[(CH_3)_2N]_2TiCl_2$, and $(CH_3)_2NTiCl_3$. Boron trichloride was found to be unreactive as would be expected, while dimerization of $(CH_3)_2NBCl_2$ took place in the presence of excess $TiCl_4$.

The reaction of titanium tetrachloride with tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, was investigated as a possible route to the synthesis of compounds containing Ti–Ti covalent bonds. Rather than formation of species containing metal–metal bonds, bis(dimethylamino)chloroborane was produced and subsequently complexes with $TiCl_4$ to afford $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. In order to elucidate the factors associated with this stoichiometry, reactions of $TiCl_4$ with $[(CH_3)_2N]_2BCl$, $[(CH_3)_2N]_2BCH_3$, $[(CH_3)_2N]_3B$, $(CH_3)_2NBCl_2$, and BCl_3 were investigated.

Experimental Section

Apparatus. All reactions were carried out in a section of a standard vacuum line isolated from mercury and equipped with stopcocks lubricated with a Kel-F 200 wax–Fluorolube blend which was found to be inert to gaseous and liquid titanium tetrachloride. Manipulations of nonvolatile materials were effected in a dry nitrogen atmosphere inside a glove box. General Dynamics "Hi-Pure" nitrogen was dried by passage through a tube containing Linde Molecular Sieve 4A, and the absence of residual moisture was assured by employing a P_2O_5 dessicant. Vapor-tension measurements were performed with a triple Pyrex spoon gauge (P_{obsd} ±0.2 torr in the range 1.0–80.0 torr). Melting points of volatile materials were determined, *in vacuo*, using the falling rod method.[2] Analyses for titanium, boron, chlorine, and nitrogen were by ignition to TiO_2

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(1) (a) G. S. Kyker and E. P. Schram, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O-063; (b) work carried out in partial fulfillment of the M.S. degree; (c) to whom correspondence should be addressed.

(2) A. Stock, *Ber.*, 50, 156 (1917).

Table I. Physical Properties of Aminoboranes

Aminoborane	Mp, °C		Vapor tension (±0.5 torr)		δ (ppm) B^{11} nmr[a]		δ (ppm) H^1 nmr		d (±0.05 g/ml)[b]	
	Found	Lit.	Found	Lit.	Found	Lit.	Found	Lit.	Found	Lit.
$[(CH_3)_2N]_2BCl$	−37.5	−54[g]	5.0 (25)[c]	6.42 (25)[g]	−27.8	−27.9[h]	+4.58[d]	...	1.02 (0°)	...
$[(CH_3)_2N]_2BCH_3$	...	...	14.0 (26)	13.0 (26–28)[i]	...	−33.5[h]	...	...	...	0.799 (20)[i]
$[(CH_3)_2N]_3B$	−16.0	−16.1 to −16.5[j]	5.0 (25)	5.2 (25)[g] 4.6 (25)[j]	−27.2	−27.3[h]	+4.59[d]	...	0.88 (0°)	...
$[(CH_3)_2N]BCl_2$	−42.5	−43[k]	26.0 (25)	27.5 (25)[g]	−30.2	−30.2[h]	+4.69[d]	...	...	1.1634 (0°)[k]
$\{[(CH_3)_2N]BCl_2\}_2$	135.5[e]	142.5[k]	...	...	−10.4	−10.4[h]	+2.56[f] (Septet J_{B-H} = 3.19 cps)	+2.60[l] (Septet J_{B-H} = 3.10 cps)	...	...

[a] From $BF_3{\cdot}O(C_2H_5)_2$. [b] Obtained by weighing a known volume of liquid. [c] Temperature, °C, in parentheses. [d] From C_6H_6. [e] Sealed capillary under dry nitrogen. [f] From CH_2Cl_2. [g] E. Wiberg and K. Schuster, *Z. Anorg. Allgem. Chem.*, **213**, 77 (1933). [h] H. Nöth and H. Vahrenkamp, *Ber.*, **99**, 1049 (1966). [i] Reference 6. [j] A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **73**, 953 (1951). [k] C. A. Brown and R. C. Osthoff, *ibid.*, **74**, 2340 (1952). [l] A. J. Banister and N. N. Greenwood, *J. Chem. Soc.*, 1534 (1965).

(1000–1200°), standard manitol titration, potentiometric titration employing $AgNO_3$, and the Kjeldahl method, respectively. Infrared spectra were recorded with a Perkin-Elmer Model 337 grating spectrophotometer. Spectra of volatile materials were obtained on samples contained in a 10-cm gas cell equipped with potassium bromide optics. Spectra of nonvolatile solids were obtained as Nujol or Fluorolube mulls between potassium bromide plates or as solutions contained in 0.10-mm matched liquid cells equipped with potassium bromide optics.

Reagents. **Boron trichloride**, obtained from the Matheson Co., Inc., Joliet, Ill., was distilled through a trap maintained at −63.5° into one maintained at −126° until its 0° vapor tension was 476 torr and its −78° vapor tension was 4.5 torr; lit.[3] 477 and 4.5 torr, respectively. **Tetrakis(dimethylamino)diborane(4)**, obtained from the U. S. Borax Research Corp., Anaheim, Calif., was distilled *in vacuo* utilizing a Nester-Faust spinning-band column. The boiling point of the colorless liquid was found to be 69° (3.5 torr); lit.[4] 69° (3.6 torr).

Dimethylamine, obtained from the Matheson Co., was dried over calcium hydride and distilled through a trap maintained at −63.5° into one maintained at −126° until its 0° vapor tension was 565 torr and its −78° vapor tension was 2.8 torr; lit.[3] 565 and 2.8 torr, respectively. **Hydrogen chloride**, obtained from the Matheson Co., was purified by distillation through a trap maintained at −126° into one maintained at −196°. The colorless liquid in the −196° trap exhibited a vapor tension of 121 torr at −111.6; lit.[3] 120 torr. **Methylene chloride**, obtained from Matheson Coleman and Bell, East Rutherford, N. J., was dried over calcium hydride and distilled through a −63.5° trap into one maintained at −126°. The vapor tension of the colorless liquid, collected in the −126° trap, was 145 torr at 0° and did not change with successive expansions. ***n*-Pentane**, obtained from Matheson Coleman and Bell, was dried over calcium hydride and distilled through a trap maintained at −63.5° into one maintained at −126°. The fraction collected in the trap maintained at −126° had a vapor tension of 187 torr at 0°; lit.[3] 185 torr. **Titanium tetrachloride** (CP grade), obtained from Stauffer Chemical Co., was distilled *in vacuo* utilizing a Nester-Faust spinning-band column. The colorless distillate had a constant boiling point of 48° (31 torr); lit.[5] 48° (26 torr). **Aminoboranes** were prepared by standard procedures described in the literature: $[(CH_3)_2N]_2BCl$,[4] $[(CH_3)_2N]_2B(CH_3)$,[6] $B[N(CH_3)_2]_3$,[7] and $(CH_3)_2NBCl_2$;[7] their physical properties are compared to literature values in Table I.

Reactions of Titanium Tetrachloride with Tetrakis(dimethylamino)diborane(4). Tetrakis(dimethylamino)diborane(4), 12.9 mmoles dissolved in 20 ml of CH_2Cl_2, was added dropwise with stirring at −78° to $TiCl_4$, 77.6 mmoles, dissolved in 40 ml of CH_2Cl_2. The following color changes were observed: black, −78 to −30°; green, −30 to 0°; and brown after *ca.* 2 hr at 0°. All materials volatile at 0° were distilled from the reaction vessel through a −45° trap into one maintained at −196°. A small amount of red liquid was retained in the −45° trap; CH_2Cl_2, collected from the −196° trap, was identified by its 0° vapor tension, 145 torr, and its vapor-phase infrared spectrum. A nonvolatile brown solid remained in the reaction vessel. Heating this brown solid in the temperature interval 35–60° resulted in large quantities of red liquid distilling into a trap maintained at −78°. This red liquid was observed to convert to a yellow crystalline solid between 0 and 25°. After continuous heating of the brown solid at 60° for 72 hr, the evolution of red liquid ceased and a tan homogeneous-appearing solid remained in the bottom of the reaction vessel. During the heating period a small quantity of green crystals sublimed away from the brown solid; $(CH_3)_2NTiCl_3$ is a green solid which sublimes at *ca.* 70°.[8] The remaining tan solid was slightly soluble in benzene, producing a red-tan solution. A sample of this brown solid, *ca.* 800 mg, was washed three times with benzene and dried *in vacuo* for 12 hr. A sample of the purified tan solid, *ca.* 50 mg, was hydrolyzed with 25% sulfuric acid. The solution bubbled vigorously and a violet color, indicative of $Ti(H_2O)_6{}^{3+}$, developed in the aqueous phase. Qualitative testing of this solution indicated the presence of B, N, Cl, and Ti.

Reactions of Titanium Tetrachloride with Bis(dimethylamino)chloroborane. Treatment of $TiCl_4$, 34.2 mmoles, dissolved in 60 ml of CH_2Cl_2 with $[(CH_3)_2N]_2BCl$, 11.4 mmoles, resulted in the formation of a red solution at −78°. All materials volatile at 0° were distilled from the reaction vessel and fractionally condensed through a −63.5° trap into one maintained at −196°. CH_2Cl_2 was recovered from the −196° trap and a red liquid recovered from the −63° trap. This red liquid converted to a yellow solid. After this conversion took place, $TiCl_4$ was recovered and characterized by its vapor-phase infrared spectrum.

Purification and Analytical Characterization of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. Procedure A. Conversion of Red Liquid to Yellow Solid in the Temperature Interval 0–20°. A sample of the yellow crystalline solid, *ca.* 200 mg, was obtained by the red liquid-phase change in the temperature interval 0–20°. This sample was freed from small amounts of green solid, $(CH_3)_2NTiCl_3$, by heating at 45° and distilling the resultant volatile materials into a trap maintained at −196°. The initial yellow solid was transformed almost quantatively into a red liquid which collected in the −196° trap over a period of 7 hr. A trace of white residue remained in the bottom of the vessel originally containing the yellow solid. The contaminant, $(CH_3)_2NTiCl_3$, sublimed from the hot zone, *ca.* 45°, but not into the −196° trap. The red liquid, *ca.* 0.3 ml, converted to a nonvolatile, yellow, crystalline solid over a span of 2 min when maintained in the temperature interval 0–20°. A trace of colorless volatile liquid which formed during the conversion was identified by vapor-phase infrared spectroscopy as $(CH_3)_2NBCl_2$ and could be separated from the yellow solid at 20° by condensation into an adjacent trap maintained at −196°. A homogeneous-appearing yellow crystalline solid, *ca.* 150 mg, remained in the trap maintained at 20°. This yellow solid melts at 109–112°, sealed capillary, with decomposition to a red-brown liquid.

Procedure B. Recrystallization of the Yellow Solid from a 50% by Volume Solution of Titanium Tetrachloride and Methylene Chloride. A sample of the red liquid, *ca.* 5 ml, was distilled into a $TiCl_4$-CH_2Cl_2 mixed solvent contained in a 50-ml vessel cooled to −78°. The color of the resultant solution was red in the temperature interval −78–0°. When the solution was maintained at 25°, the red color of the solution slowly decreased in intensity and yellow needle-like crystals precipitated. After 72 hr the intensity of the red

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(3) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(4) R. J. Brotherton, A. L. McCloskey, L. Petterson, and H. Steinbreg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).

(5) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(6) H. Nöth and P. Fritz, *Z. Anorg. Allgem. Chem.*, **322**, 297 (1963).

(7) J. Goubeau, M. Rahtz, and H. J. Becher, *ibid.*, **275**, 161 (1954).

(8) E. Benzing and W. Kornicker, *Ber.*, **94**, 2263 (1961).

color and the amount of yellow crystalline precipitate appeared to remain constant. At 100° the yellow crystals redissolved to produce a red solution. Cooling of the red solution to 25° again resulted in precipitation of needle-like yellow crystals. These crystals were filtered, *in vacuo*, employing the $TiCl_4$–CH_2Cl_2 mixed solvent. Yellow needle-like crystals collected on the frit and the filtrate was red-brown. These crystals were washed with CH_2Cl_2 and dried *in vacuo* for 6 hr at 25°. The yield of crystals was very small, *ca.* 100 mg. Heating of the crystals *in vacuo* at 45° and quenching of the resultant vapors at −196° produced a red liquid. Hydrolysis of a sample of the crystals, *ca.* 10 mg, with 25% sulfuric acid and subsequent qualitative tests indicated the presence of B, N, Cl, and Ti(IV). An infrared spectrum (mull) of this yellow crystalline solid was identical with that of the yellow solid obtained by procedure A and is summarized in Table II. The decomposition point of this material also occurred at 109–112°.

Table II. Solid-State Infrared Data for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$[a]

Frequency ± 5 cm^{-1}	
3171 w	1072 w
3036 w	1054 s
3017 w	1036 w
2938 w	1017 vvs
1644 s	974 m
1609 vvs	922 w
1465 vs	914 m
1452 vs	888 m
1441 m (sh)	857 vvs (b)
1413 m	829 vvs (b)
1250 vs	828 vs (sh)
1201 s (sh)	680 w
1190 s (sh)	658 m
1185 vs	598 vw
1160 m (sh)	528 vw
1144 vs	425 vvs (b)
1096 w	405 vvs (sh)

[a] v = very; s = strong; m = medium; w = weak; b = broad; and sh = shoulder.

The analytical data pertaining to the yellow crystalline solid obtained from both the diborane(4) synthesis and the monoboron synthesis are as follows.

	% Ti	% Cl	% B	% N
Diboron synthesis	16.50	60.30	2.70	6.43
Monoboron synthesis	16.97	59.50	2.61	6.83
Calcd for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$	17.15	59.30	2.59	6.70

Reaction of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ with Hydrogen Chloride. A 251.2-mg sample of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ (hereafter referred to as I) was contained in a 100-ml reaction vessel equipped with a magnetic stirrer and treated with 8.55 mmoles of HCl (571 torr) at 29° for 30 hr. Hydrogen chloride, 8.54 mmoles, was recovered. Subsequent repeated treatment with liquid HCl also resulted in no loss of this reagent. The infrared spectrum (mull) of I after treatment with HCl was identical with that of the starting material.

Reactions of Borane Derivatives with Titanium Tetrachloride. With Bis(dimethylamino)methylborane. 1. Mole Ratio of $TiCl_4$/$[(CH_3)_2N]_2BCH_3$ *ca.* 3.0/1.0. $[(CH_3)_2N]_2BCH_3$, 1.3 ml (9.09 mmoles), was dissolved in 30 ml of CH_2Cl_2 contained in a 100-ml reaction vessel equipped with a magnetic stirrer. $TiCl_4$, 3.0 ml (27.3 mmoles), was slowly distilled into the CH_2Cl_2–borane solution with vigorous stirring at −95°; a green solution immediately developed with subsequent precipitation of a green solid. Attempts to isolate this green solid by filtration at temperatures above 20° resulted in the formation of an unidentified brown solid with an observed decrease in the amount of green solid collecting on the filtration frit. However, recrystallization of the green solid from CH_2Cl_2 and filtration at *ca.* −5° *in vacuo* resulted in retention of a homogeneous-appearing green solid on the frit. This green solid was identified as $(CH_3)_2NTiCl_3$ from elemental analyses. *Anal.* Calcd: Ti, 24.16; N, 7.06; Cl, 53.64. Found: Ti, 25.66; N, 6.65; Cl, 53.40. Infrared data for $(CH_3)_2NTiCl_3$ are presented in Table III. Assignments for absorptions in the spectrum of $(CH_3)_2NTiCl_3$ were made by correlations to those assignments appearing in the literature for $Ti[N(CH_3)_2]_4$.[9]

Table III. Infrared Data and Assignments for $(CH_3)_2NTiCl_3(s)$

Assignments	Frequency ± 5 cm^{-1}
$\nu(CH_3)$	3181 s
	3017 w
	2946 w
	2920 w
	2853 vw
	2805 vw
	2766 vw
?	1561
	1464 m (sh)
	1460 s (sh)
$\delta_{as}(CH_3)$	1445 s (sh)
	1433 vs
	1404 vw
$\delta_s(CH_3)$	1383 m
$\rho(CH_3)$	1155 w
$\rho(CH_3)$	1118 vs
	1036 vvs
$\nu_{as}(NC_2)$	1016 s (sh)
$\nu_s(NC_2)$	972 w
	923 vvs
?	809 m
ν(Ti–N)	579 vvs
$\nu_{as}(Ti\text{–}Cl_3)$	420 vvs

2. Mole Ratio of $TiCl_4$/$[(CH_3)_2N]_2BCH_3$ *ca.* 1.0/1.0. $[(CH_3)_2N]_2BCH_3$, 0.82 ml (5.72 mmoles), was treated with $TiCl_4$, 0.57 ml (5.14 mmoles), at −196° in a reaction vessel equipped with a magnetic stirrer. As the reaction mixture warmed from −196 to 0°, with stirring, a green solid formed. Removal of all materials volatile at 0° from the reaction mixture resulted in isolation of a nonvolatile green solid characterized as $(CH_3)_2NTiCl_3$ by comparison of the infrared spectrum of this material with that of an authentic sample of $(CH_3)_2NTiCl_3$. The volatile colorless liquid which collected in a −196° trap was purified by fractionation through a trap maintained at −22.9° into one maintained at −196°. A small amount of low-volatile colorless liquid, retained in the −22.9° trap, was identified as $[(CH_3)_2N]_2BCH_3$ by its vapor-phase infrared spectrum. The colorless liquid in the −196° trap was identified as $(CH_3)_2NBClCH_3$, 0.55 ml (4.98 mmoles), by its 0° vapor tension of 11.8 torr (lit.[10] 11.8 torr), B^{11} nmr absorption of −38.3 ppm from $BF_3 \cdot O(C_2H_5)_2$ (lit.[11] −38.5 ppm), and conversion to a white crystalline dimer, mp 99–102° (lit.[10] 100–102°). No $TiCl_4$ was present in the volatile section of the reaction mixture as proven by vapor-phase infrared spectroscopy.

With Tris(dimethylamino)borane. $[(CH_3)_2N]_3B$, 1.63 g (11.47 mmoles), dissolved in 25 ml of *n*-pentane was cooled at −78° and treated with $TiCl_4$, 1.25 ml (11.47 mmoles). A brown solution developed at −78° and, as the solution warmed to *ca.* −30°, a yellow solid precipitated. At temperatures above −30°, the yellow solid converted to a mixture of yellow, green, and brown solids; the color of the solution changed to orange-red. Removal of all materials volatile at 30° resulted in the isolation of a mixture of nonvolatile yellow, green, and red-brown solids in the reaction vessel. Distillation of the volatile materials through traps maintained at 0, −63.5, and −196° resulted in the following separations: 0°, yellow solid and red-brown solids; −63.5°, pale red liquid; and −196°, *n*-pentane identified by its 0° vapor tension. A vapor-phase infrared spectrum of the red liquid, retained in the −63.5° trap, contained absorptions characteristic of $[(CH_3)_2N]_2BCl$ and $(CH_3)_2NBCl_2$ but no absorptions characteristic of $TiCl_4$. Vacuum sublimation, 46–62°, of the mixture of solids resulted in the vaporization of a red-brown amorphous material. $[(CH_3)_2N]_2TiCl_2$ is a brown solid which sublimes at 60° (0.001 torr).[8] A green, needle-like crystalline material which remained in the bottom of the sub-

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(9) H. Buerger, H. Stammreich, and T. H. Teixirasans, *Monatsh. Chem.*, 97, 1276 (1966).

(10) F. C. Gunderloy and C. E. Erickson, *Inorg. Chem.*, 1, 349 (1962).

(11) See footnote *h*, Table I.

limator was identified as $(CH_3)_2NTiCl_3$ by its sublimation point of 70°[8] and comparison of its infrared spectrum with that of an authentic sample of $(CH_3)_2NTiCl_3$.

With Monomeric and Dimeric Dimethylaminodichloroborane. $(CH_3)_2NBCl_2$ monomer, 1.4 ml (12.96 mmoles), dissolved in 30 ml of CH_2Cl_2 was cooled to −78° and treated with $TiCl_4$, 4 ml (35.8 mmoles). The color of the solution at −78°, light yellow, slowly changed to light green as the solution warmed to 25°. Removal of all materials volatile at 25° resulted in the retention of a small quantity of nonvolatile blue-green crystals in the reaction vessel; a light yellow solution collected in a trap maintained at −196°. All materials were recombined in the reaction vessel and stirred for 2 hr at 30°. The blue-green crystals disappeared and white crystals slowly precipitated from a light yellow solution. All materials volatile at 25° were distilled from the reaction vessel and fractionally condensed through traps maintained at −63.5 and −196°. CH_2Cl_2, recovered from the −196° trap, was identified by its vapor-phase infrared spectrum and 0° vapor tension of 145 torr. A light yellow liquid, retained in the −63.5° trap, was repeatedly distilled through traps maintained at −30.6, −63.5, and −196°. The liquid distilled through the −30.6° trap and was retained in the −63.5° trap. A vapor-phase infrared spectrum of this yellow material was identical with a composite spectrum of $(CH_3)_2NBCl_2$ and $TiCl_4$. Separation of the yellow solution on a vacuum fractionation column yielded $(CH_3)_2NBCl_2$ (identified by its vapor-phase infrared spectrum, mp −42.4° (lit.[12a] −43.0°), and 25° vapor tension of 25.8 torr (lit. 26 torr)) and $TiCl_4$ (identified by its vapor-phase infrared spectrum). $TiCl_4$ and $(CH_3)_2NBCl_2$ were again distilled into the reaction vessel maintained at −78°. While the mixture was being stirred for 54 hr at 60°, under 745 torr of dry nitrogen, a white crystalline material precipitated from the light yellow solution. After removal of all materials volatile at 25°, there remained a nonvolatile white crystalline solid. This white crystalline solid was washed with dry benzene and dried for 24 hr *in vacuo*, and subsequently identified as dimeric $(CH_3)_2NBCl_2$ by its melting point of 135.4° (found 135.4° for pure dimeric $(CH_3)_2NBCl_2$) and its H^1 nmr signal (septet) centered at +2.56 ppm from CH_2Cl_2 ($J_{B-H} = 3.19$ cps); lit.[12b] +2.6 ppm from CH_2Cl_2 ($J_{B-H} = 3.10$ cps).

With Boron Trichloride. Treatment of BCl_3 (8.86 mmoles), cooled to −196°, with $TiCl_4$, 1.0 ml (9.1 mmoles), resulted in no apparent reaction. The solution was colorless after stirring at 0° for 1 hr. Distillation of the volatile materials through traps maintained at −78, −126, and −196° resulted in the retention of $TiCl_4$, 1.0 ml (9.1 mmoles), in the −78° trap, identified by its vapor-phase infrared spectrum. BCl_3, 8.84 mmoles, recovered from the −126° trap had a 0° vapor tension of 477 torr (lit.[3] 477 torr).

Results and Discussion

Titanium tetrachloride was found to react with both tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, and bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, to afford di[bis(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)], $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. The reaction with $[(CH_3)_2N]_2BCl$ is described by eq 1.

$$2[(CH_3)_2N]_2BCl + 3TiCl_4 \longrightarrow \{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3 \quad (1)$$

When an excess of either reactant was employed over that of the indicated stoichiometry, that species was always recovered during purification of the reaction product I. The 2:3 stoichiometry observed for I would most likely not be predicted, *a priori*, but is not unique because $TiCl_4$ has been observed to afford compounds of similar stoichiometry with 1,3-triphenyltriazene[13] and ethylenebis(diphenylphosphine).[14] In these cases[13,14] characterization consisted of elemental analyses and a far-infrared study,[14] but no structures or bonding schemes were suggested.

Dissociation of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. The labile nature of I is quite interesting. The 2:3 complex is a yellow crystalline solid which has a dissociation pressure of *ca.* 0.1 torr at 25°. Heating I at 25°, *in vacuo*, results in dissociation to gaseous $TiCl_4$ and $[(CH_3)_2N]_2BCl$ as described by eq 2. Condensation of the vapor mixture at −196° *in vacuo* and subsequent warming to −78° results in a blood-red liquid. Further warming to *ca.* 10° results in the formation of I. This process is reversible with only *ca.* 1–3% of a side reaction taking place, affording the exchange products $(CH_3)_2NTiCl_3$ and $(CH_3)_2NBCl_2$. This facile dissociation of I has also been observed in solution; *e.g.*, when I is dissolved in benzene or methylene chloride, red solutions result. Investigation of such solutions has been *via* infrared, ultraviolet, and H^1 nmr spectroscopic methods and has lead to the conclusion that I is not present in solution but rather that intermediate complexes are formed as well as $[(CH_3)_2N]_2BCl$ and $TiCl_4$.[15] Because of these results, it has not been possible to obtain a solution molecular weight for I.

$$\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3 \rightleftharpoons 2[(CH_3)_2N]_2BCl + 3TiCl_4 \quad (2)$$

Reaction of $TiCl_4$ with $[(CH_3)_2N]_3B$, $(CH_3)_2NBCl_2$, $[(CH_3)_2N]_2BCH_3$, and BCl_3. In an effort to elucidate the factors involved with both the 2:3 stoichiometry of I and its labile nature, $TiCl_4$ was treated with several related borane derivatives. Treatment with $[(CH_3)_2N]_3B$ resulted in exchange of Cl and $(CH_3)_2N$ moieties between Ti and B (eq 3); the products formed are dependent on the initial reaction stoichiometry.

$$[(CH_3)_2N]_3B + TiCl_4 \xrightarrow{CH_2Cl_2} [(CH_3)_2N]_{3-x}BCl_x + TiCl_{4-x}[N(CH_3)_2]_x \quad (3)$$

$$x = 1 \text{ or } 2$$

Reaction of $TiCl_4$ with $[(CH_3)_2N]_2BCH_3$ even at −78° resulted in Cl–$N(CH_3)_2$ moiety exchange according to eq 4. This reaction affords an excellent method for preparing dimethylaminochloromethylborane. Titanium tetrachloride was found not to afford stable products with either BCl_3 or $(CH_3)_2NBCl_2$ at 25° *in vacuo*. In fact, $(CH_3)_2NBCl_2$ was observed to dimerize at 25° even in the presence of the strong Lewis acid, $TiCl_4$.

$$TiCl_4 + [(CH_3)_2N]_2BCH_3 \xrightarrow{-78°} (CH_3)_2NTiCl_3 + (CH_3)_2NBCl(CH_3) \quad (4)$$

The 2:3 stoichiometry observed for I and its labile dissociation appears to be unique for $[(CH_3)_2N]_2BCl$ and may be associated with the attainment of a balance between Lewis basicity of the dimethylamino moieties and the strength of the B–N bond. Nitrogen must be a strong enough base to coordinate with the Lewis acid $TiCl_4$, but the BN bond strength must be great enough to resist exchange such as that which takes place in the case of $[(CH_3)_2N]_2BCH_3$ affording $(CH_3)_2NBClCH_3$. The electron-withdrawing effect of Cl is thought to increase the BN bond order relative to that in $[(CH_3)_2N]_2BCH_3$, thus inhibiting exchange. If exchange took place the bidentate would be destroyed.

Nature of the Bidentate Ligand, $[(CH_3)_2N]_2BCl$. The 2:3 stoichiometry of I, coupled with the various mole ratios of reactants employed in its synthesis, suggests the ligand to be functioning as a bidentate with no free

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(12) (a) See footnote *k*, Table I. (b) See footnote *l*, Table I.

(13) O. C. Dermer and W. C. Fernelius, *Z. Anorg. Allgem. Chem.*, **221**, 83 (1934).

(14) A. D. Westland and L. Westland, *Can. J. Chem.*, **43**, 426 (1965).

(15) G. S. Kyker and E. P. Schram, *J. Am. Chem. Soc.*, **90**, 3678 (1968).

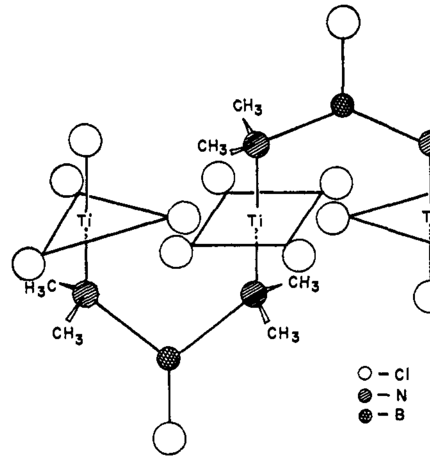
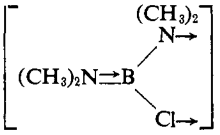
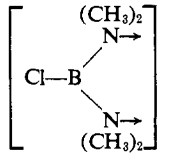


Figure 1. Possible molecular structure for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$.

chelate sites. Two possibilities exist; first, the ligand is bridging with a Cl and N (i)

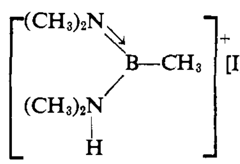


i

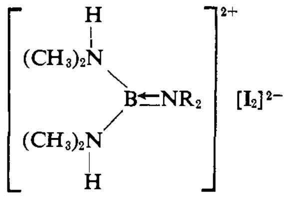


ii

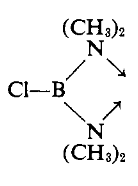
and second *via* both nitrogens (ii). The high-energy $\nu_{as}(BN_2)$ absorption frequency in the infrared suggests bonding of the first type, that is, assuming that $\nu_{as}(BN_2)$ is not a coupled vibration. Indeed, a relatively high energy absorption at 1576 cm^{-1} in the spectrum of $\{H[(CH_3)_2N]_2BCH_3\}^+I^-$ has been attributed to $\nu_{as}(BN_2)$ ($\nu_{as}(BN_2)$ is found at 1502 cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCH_3(g)$).[6] The relatively high value of 1576 cm^{-1} for $\nu_{as}(BN_2)$ was interpreted to indicate strong BN double-bond character, and the following valence-bond structure was proposed.



The infrared spectrum of $\{B[N(CH_3)_2N]_3H_2\}^{2+}\{I_2\}^{2-}$ also contains an absorption at 1558 cm^{-1} which was attributed to $\nu_{as}(BN_2)$ (found at 1507 cm^{-1} in $B[N(CH_3)_2]_3(g)$), and the complex was similarly formulated as[6]



The second mode of chelation



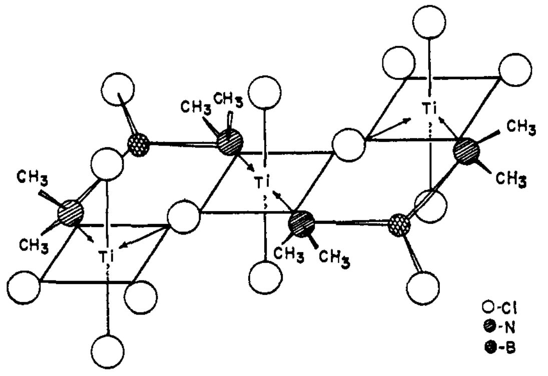


Figure 2. Possible molecular structure for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$.

would be that expected on the basis of stronger Lewis base strength of N compared with Cl. In order to determine if noncoordinated N was present, I was treated with gaseous HCl. No reaction took place, indicating $ClB[N(CH_3)_2]_2$ is acting as a bis (N) chelate because noncoordinated N would afford the amine hydrochloride salt.[16] Furthermore, in the infrared spectrum of I, the $\nu_{as}(NC_2)$ and $\nu_s(NC_2)$ exhibit shifts of −57 and −78 cm^{-1}, respectively, while $\nu(BCl)$ undergoes no significant change in frequency.[15] These data indicate both dimethylamino moieties of $[(CH_3)_2N]_2BCl$ are involved in coordination to $TiCl_4$ which is also in accord with the lack of reactivity of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ with HCl. The medium intensity infrared absorption at 1644 cm^{-1} and the very intense absorption at 1609 cm^{-1} must therefore be due to coupling of $\nu_{as}(B^{10}N)$ and $\nu_{as}(B^{11}N)$ with other vibrational modes of like symmetry, most likely $\nu_{as}(NC_2)$. A more complete infrared analysis and associated discussion of I, and aminoboranes in general, is the subject of a subsequent paper.[15]

Possible Molecular Formulations for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. The infrared spectrum of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ is consistent with both dimethylamino moieties being involved in coordinate covalent bridging between two molecules of $TiCl_4$; the formulation depicted in Figure 1, one possible isomer, is consistent with these facts and includes mixed five- and six-coordinate titanium. The isolation of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, as opposed to other stoichiometries such as $\{[(CH_3)_2N]_2BCl\}_3\{TiCl_4\}_2$, analogous to $\{C_2H_4P_2(C_6H_5)_4\}_3\{TiCl_4\}_2$,[14] is not a consequence of using excess $TiCl_4$. When equimolar quantities of reagents were mixed in CH_2Cl_2, I precipitated and $[(CH_3)_2N]_2BCl$ in excess of the required 2:3 stoichiometry was recovered. The lack of addition of $[(CH_3)_2N]_2BCl$ to the suggested terminal five-coordinate $TiCl_4$ moieties may result from steric effects or the insolubility of the yellow solid upon attaining the 2:3 stoichiometry. The addition of excess $TiCl_4$ to I is not considered likely since chlorine attached to boron is considered noncoordinating in nature as shown in the infrared study.[15]

A second possible molecular formulation for I is described in Figure 2.[17] This structure involves all three titaniums in the six-coordinate state. Greater stability would be associated with this structure as compared to the mixed five- and six-coordinate species with

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[16] H. Nöth and S. Lukas, *Ber.*, **95**, 1505 (1962).

[17] We are indebted to one of the referees for this suggestion.

regard to nucleophilic attack by nitrogen on titanium. Such attack would be expected to afford stoichiometries other than the observed 2:3 ratio.

Ionic Formulation of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. A third possible formulation consistent with the 2:3 stoichiometry is that of an ionic species. The existence of Ti(IV) and Ti(III) ionic complexes is well known. Compounds of type $(AH)_2TiCl_6$ (A = trimethylamine, dimethylamine, and pyridine) have been reported by Fowles and Nicholls to be yellow solids.[18] Goyal, *et al.*, have described the preparation of $[(CH_3)_3N(C_7H_7)]_2[TiCl_6]$ and $[(CH_3)_2NC_6H_5(C_7H_7)]_2[TiCl_6]$; both are yellow solids melting at 165–170° and 175–180°, respectively.[19] Complexes of type $[S{=}C(NR_2)_2][TiCl_4]_2$ (R = H, alkyl, or aryl), in which chlorine bridging was postulated, have been reported by Rivest to be low-melting brown or yellow solids.[20] Finally, the existence of chlorine bridging in the complex $(TiCl_4 \cdot POCl_3)_2$ has been proven by Bränden and Lindqvist in a crystal structure study.[21] In view of these facts, a complex of type $\{Ti_2Cl_6 \cdot 2[(CH_3)_2N]_2BCl\}^{2+}\{TiCl_6\}^{2-}$ involving Cl bridging is suggested (Figure 3). This structure incorporates all three titaniums in the six-coordinate state and implied stability with regards to nucleophilic attack. Although the yellow color and low solubility in organic solvents may suggest an ionic formulation, nonionic tertiary amine–$TiCl_4$ adducts are also yellow solids which have low solubility in organic solvents, *e.g.*, $(CH_3)_3N \cdot TiCl_4$.[22] Thus, the physical properties of I are not considered definitive insofar as ionic formulations are concerned. Although conductivity studies would distinguish between an ionic *vs.* covalent structure, measurements in solvent systems studied so far are impossible because dissociation of I takes place to afford $[(CH_3)_2N]_2BCl$, $TiCl_4$, and low concentrations of associated species; see infrared study.[15] Recent ultraviolet spectroscopy studies have shown that the diffuse reflectance spectra of $TiX_6{}^{2-}$ ($X = Cl^-$ and Br^-) and *cis*-$TiCl_4 \cdot 2L$ ($L = CH_3CN$ and bipy) exhibit identical absorptions in the region of $Cl(\pi) \rightarrow \gamma_5$, γ_5 representing a vacant metal d orbital.[23] Thus, the possibility of distinguishing between ionic and covalent formulations of I by this method is not likely. Far-infrared spectroscopy studies might prove to be rewarding since much data concerning ν(M-Cl bridge)[24] and $\nu(TiCl_6{}^{2-})$[25] are available; however, complications in the intrepretation of far-infrared data may arise since $\nu(N \rightarrow M)$ and ligand, *i.e.*, $\delta(NC_2)$, absorptions also occur in the 100–400-cm^{-1} region.[26,27]

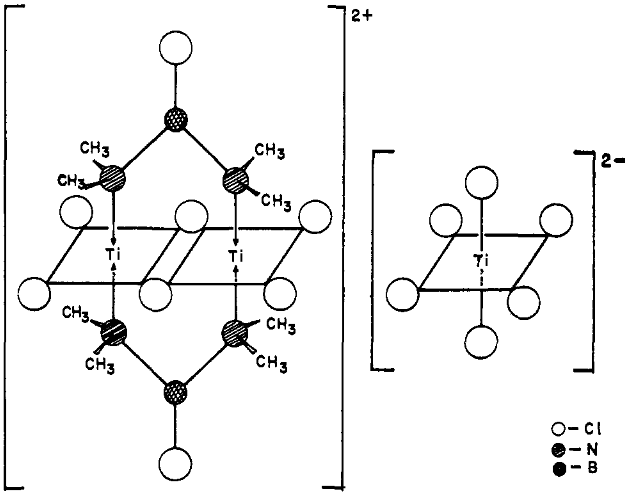

Figure 3. Possible ionic structure for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$.

We are continuing our investigation of I and related compounds in order to increase our understanding of the bonding and reactivity of these species.

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[27] H. J. Becher, *Z. Anorg. Allgem. Chem.*, **287**, 285 (1956).