Di[bis(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)].[1a] An Infrared Study

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Abstract: An evaluation of the solid-state infrared spectrum of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ indicates that the ligand $[(CH_3)_2N]_2BCl$ utilizes both nitrogens in coordinate-covalent bridging between two tetrachlorotitanium(IV) moieties. Assignments for the fundamental vibrational modes of the complex are presented along with reassignments for several group vibraions previously reported for several aminoborane derivatives. Conclusions based on additional infrared studies indicate that the complex $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ is partly dissociated in CH_2Cl_2 to $TiCl_4$, $[(CH_3)_2N]_2BCl$, and unidentified intermediate complexes. Complete dissociation to $TiCl_4$ and $[(CH_3)_2N]_2BCl$ takes place in the gas phase at temperatures >23° at a total pressure <9 torr.

The synthesis of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ from $TiCl_4$ and tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, or bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, is described in a previous paper.[1a] The ligand $[(CH_3)_2N]_2BCl$ was suggested to function as a bidentate chelate utilizing both nitrogens in coordination. An evaluation of the solid-state infrared spectrum of the complex is discussed in detail and is in accord with this mode of bonding.

Results and Discussion

Infrared Spectroscopic Study. General Background and Some Reassignments of Vibrational Absorption Modes. Because the infrared assignments for the spectrum of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, hereafter referred to as I (see Table I), are based on correlations with spectral data for $[(CH_3)_2N]_2BCl$, general assignments for aminoboranes are necessarily reviewed.

Assignments in the literature were found to vary for several vibrational modes, *i.e.*, $\nu_{as}(NC_2)$, $\nu_s(NC_2)$, $\nu_s(BN_2)$, and $\rho(CH_3)_2$.[2-5] Therefore, a systematic correlation of frequencies observed in the spectra of aminoboranes was carried out utilizing $\nu_s(NC_2)$ and $\rho(CH_3)$ infrared assignments for dimethylamine.[6,7] Dimethylamine may be classed in the point group C_s, but the $-N(CH_3)_2$ moiety possesses C_{2v} symmetry. Because aminoboranes of the general type X_2BY (X and Y representing permutations of $-N(CH_3)_2$, $-CH_3$, halogen, or $-H$) generally are of C_{2v} symmetry, *e.g.*, $Cl_2BN(CH_3)_2$, a correlation between absorptions arising from vibrational modes of the dimethylamino portion of these compounds and those of dimethylamine would be expected.

For bis(dimethylamino)boranes, several reassignments between 1376 and 1415 cm^{-1} have been made involving $\nu(BN_2)$ and $\delta(CH_3)$ based on comparison with the infrared spectrum of $HN(CH_3)_2$. Dimethylamine exhibits an infrared absorption at 1412 (m) cm^{-1}, assigned to $\delta_s(CH_3)$.[6,7] Absorptions of similar intensity in the spectra of mono(dimethylamino)borane derivatives, 1409–1415 cm^{-1}, have also been assigned to $\delta_s(CH_3)$.[8] However, bis(dimethylamino)borane derivatives exhibit infrared absorptions in the range 1376–1408 cm^{-1} (m) which have been previously assigned to the $\nu_s(BN_2)$.[3] The frequency range of these absorptions strongly suggests that they arise from methyl deformations and therefore they are reassigned to $\delta_s(CH_3)$. The medium intensity absorptions of bis(dimethylamino)boranes, 1349–1364 cm^{-1}, previously assigned to $\delta_s(CH_3)$, are accordingly reassigned to $\nu_s(BN_2)$.[3] The consistency of all assignments may be most readily determined by comparison of the appropriate data in Table I.[3-10]

The spectra of aminoboranes generally contain absorptions of strong to medium intensity, 1027–1077 and 1100–1194 cm^{-1}, which have previously been assigned to $\nu_s(NC_2)$ or $\nu_{as}(NC_2)$ and $\rho(CH_3)$, respectively.[2-5] However, absorptions occurring in the intervals 1022 and 1145–1079 cm^{-1} in the spectrum of $HN(CH_3)_2$ have been assigned to $\nu_{as}(NC_2)$ and $\rho(CH_3)$, respectively.[6,7] Some ambiguity in these latter assignments was implied, but in support of these assignments are the following facts. Upon complexation of $N(CH_3)_3$ with a Lewis acid, the absorption at 1104 cm^{-1}, assigned to $\rho(CH_3)$ in the noncomplexing base,[6,7] shifts 6–14 cm^{-1} to higher energy.[11] The absorption at 1043 cm^{-1}, assigned to $\nu_{as}(NC_2)$,[6,7] shifts 42–79 cm^{-1} to lower energy. A significant shift of $\nu_{as}(NC_2)$ to lower energy is expected upon complexation of $N(CH_3)_3$ with a Lewis acid; therefore, the 1043-cm^{-1} absorption is in accordance with the $\nu_{as}(NC_2)$ assignment. The absorption at 1104 cm^{-1}, in $N(CH_3)_3$, by process of elimination is assigned to $\rho(CH_3)$. Absorptions centered in the vicinity of 1100 and 1050 cm^{-1} in the spectra of aminoboranes are therefore reassigned to $\rho(CH_3)$ and $\nu_{as}(NC_2)$, respectively. The absorptions of medium intensity, 862–990 cm^{-1}, in the spectra of aminoboranes have been previously assigned to $\nu_s(NC_2)$ and are consistent with the fact that $HN(CH_3)_2$ exhibits absorptions of medium intensity at 928 cm^{-1} previously assigned to

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Table I. Infrared Correlations for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, $TiCl_4$, and Aminoboranes

COMPOUND	$\nu(CH_3)$	$_{^{10}B}\nu(BN)_{^{11}B}$	$_{^{10}B}\nu_{as}(BN_2)_{^{11}B}$	$\delta_{as}(CH_3)$	$_{^{10}B}\nu_s(BN_2)_{^{11}B}$	$\delta_s(CH_3)$	$\rho(CH_3)$	$\rho(CH_3)$	$\nu_{as}(NC_2)$	$\nu_s(NC_2)$	$_{^{10}B}\nu(BCl)_{^{11}B}$	$_{^{10}B}\nu_{as}(BCl_2)_{^{11}B}$	$_{^{10}B}\nu_s(BCl_2)_{^{11}B}$	$_{^{10}B}\delta(BN_2)_{^{11}B}$	$_{^{10}B}\delta(BCl_2)_{^{11}B}$	$\nu(TiCl_4)$
$\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ (s)	3171 w† 3036 w 3017 w 2938 w		1644 s 1609 vvs	1465 vs 1452 vs	1441 m (sh)	1413 m	1250 vs 1201 s(sh) 1190 s(sh) 1185 vs 1160 m (sh) 1144 vs	1096 w 1072 vw 1054 s	1036 w 1017 vvs 974 m	888 m 857 vvs (b) 829 vvs (b) 828 vs (sh)	922 w 914 m			680 w 658 m		598 vw 528 vw 425 vvs (b) 405 vvs (sh)
$TiCl_4$ 9ǂ (g)																610 w, 518 s(sh) 498 vvs
$TiCl_4$ (ℓ)																598 w(b), 481 vvs
$(CH_3)_2NH$ 7 (g)				1441 vvs		1412 m	1240 vw	1145 vs 1137 vs 1079 m	1022 m	928 m						
$(CH_3)_3N$ 6 (g)				1466 vvs		1402 m	1272 s	1183 s 1104 s	1043 m	826 s						
$[(CH_3)_2N]_2BCl$ 3ǂ (g)	3014 w, 2942 s(sh) 2908 vs, 2883 w(sh) 2825 m		1560 m (sh) 1528 vvs	1460 s	1355 m	1409 vvs 1407 vvs	1218 s 1201 s (sh)	1144 s 1136 s(sh) 1123 m(sh)	1077 s	966 w 912 s				598 w‡ 581 w‡		
$[(CH_3)_2N]_2BCl$ (ℓ)	3017 m, 2933 s(sh) 2895 vs, 2845 m(sh) 3805 s(sh)		1544 vs (sh) 1530 vvs	1482 w 1452 s	1349 s*	1408 vs (sh)* 1400 vvs*	1215 vvs 1191 vs	1152 vs*, 1143 vvs* 1107 vw*	1074 vvs* 1022 vw*	922 m 907 vs				600 w‡ 579 vs‡		
$[(CH_3)_2N]_2BCH_3$ 3 (ℓ)	2796 s 2840 vs 2972 s		1521 s(sh) 1502 vvs	1469 vs (sh) 1452 vs(sh) 1409 vs	1364 vs (sh)*	1392 vs (sh)* 1376 vvs*	1219 vs	1194 vs 1151 s (sh) 1143 vs(b) * 1130 vs(b) 1111 w	1063 vs*	949						
$[(CH_3)_2N]_2BH$ 3 (ℓ)			1548 vs (sh) 1530 vvs	1485 s (sh) 1462 vs 1455 vs	1354 s*	1398 vvs* 1409 s (sh)	1237 vs 1225 vs	1189 m 1163 vs * 1142 s 1080 vs	1058 vs*	962 m 878 s 862 s						
$[(CH_3)_2N]_3B$ 5ǂ (g)	3008 s 3862 vvs 2805 s		1525 w(sh) 1507 vvs	1448 s	1383 vvs (overlap ?)		1222 vs 1202 m(sh)	1119 vvs*	1065 m*	959 vw 909 m				689 m 665 m		
$[(CH_3)HN]_3B$ 10 (ℓ)	2911 2865 2770		1499	1435	1386 ?		1277 1189	1139*	1027*							
$[(CH_3)_2N]B(CH_3)_2$ 4 (g)	3015 m 2953 vvs 2905 vvs 2812 m	1527 vvs 1518 vvs		1463 s		1415 vvs	1219 s	1111 s * 1101 m *	1066 m* 1056 m*	990 m 947 (sh) 935 m						
$[(CH_3)HN]B(CH_3)_2$ 4 (g)	3005 (sh) 2945 vvs 2830 m	1515 vvs 1504 vvs		1444 m 1434 m			1285 (sh)	1176*	1060*	949 (sh) 936 m 968 m						
$[(CH_3)_2N]BCl_2$ 3ǂ (g)	3034 w, 2954 vs 2902 m (sh) 2828 w, 2780 w	1538 vs(sh) 1522 vvs		1461 m		1409 vs	1202 s	1142 vs*	1068 vw*	overlap with $\nu(BCl_2)$?		974 m 944 vs	932 s		533 m 524 m 515 m 503 m	

† s = strong; v = very; m = medium; w = weak; (b) = broad; (sh) = shoulder; (g) = gas; (ℓ) = liquid; (s) = solid; ‡ Absorption previously unassigned;

ǂ Data from our work and partial assignments of bands obtained from references cited; * Assignment in reference changed, justification in text.

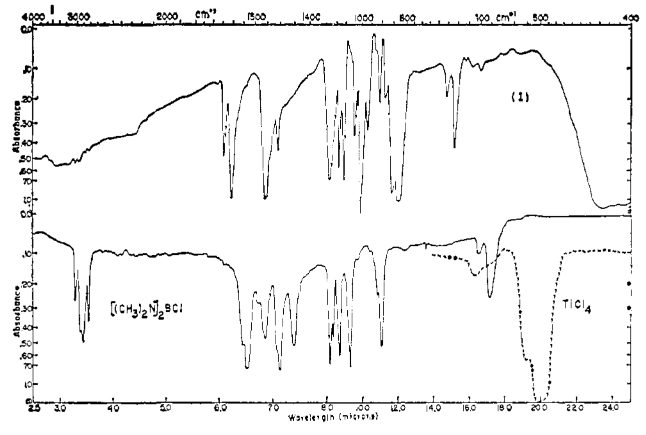

Figure 1. Infrared spectra of I, $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}$, and $\mathrm{TiCl_4}$.

$\nu_s(\mathrm{NC_2})$.[6,7] However, for aminoboranes containing B–$\mathrm{CH_3}$ or B–Cl bonds, overlap of $\nu(\mathrm{BCl})$ and $\rho(\mathrm{CH_3})$ with $\nu_s(\mathrm{NC_2})$ may occur and assignments in this region become very difficult.[3,4,8] Assignments for $\delta(\mathrm{BN_2})$ in the spectrum of $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}$ are based on previously reported data for $[(\mathrm{CH_3})_2\mathrm{N}]_3\mathrm{B}$.[5] In summary, concerning aminoboranes, some assignments for $\nu_s(\mathrm{BN_2})$, $\delta(\mathrm{CH_3})$, $\nu_{as}(\mathrm{NC_2})$, and $\rho(\mathrm{CH_3})$ have been revised.

Infrared Frequency Shifts Associated with the Coordinated Dimethylamino Moiety. By comparison of the infrared spectra obtained for free and complexed $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}$ with similar data pertaining to other methylamine bases, the mode of bonding in I may be determined with some degree of certainty. Unfortunately, $\mathrm{HN(CH_3)_2}$ adducts with titanium and boron halides tend to eliminate HCl with formation of Ti–N or B–N bonds. However, infrared spectral data for $\mathrm{N(CH_3)_3}$ adducts with $\mathrm{BX_3}$ (X = H, F, Cl, Br, and I) have been evaluated and assignments made to the various vibrational modes.[11-15]

Adducts of type $(\mathrm{CH_3})_3\mathrm{N}\rightarrow\mathrm{BX_3}$ exhibit absorptions at 1485 (s), 1460 (s), 1452 (m), and 1408 (m) $\mathrm{cm^{-1}}$, while the corresponding absorptions in the spectrum of $\mathrm{N(CH_3)_3}$, occurring at 1466 (s) and 1402 (m) $\mathrm{cm^{-1}}$, have been assigned to $\delta(\mathrm{CH_3})$.[6,7,15] Similarly, absorptions at 1265 (w), 1230 (m), and 1110 (s) $\mathrm{cm^{-1}}$ in the adduct spectrum, assigned to $\rho(\mathrm{CH_3})$,[11-15] are found at 1272 (m), 1183 (s), and 1104 (s) $\mathrm{cm^{-1}}$ in the spectrum of $\mathrm{N(CH_3)_3}$.[6,7] Absorptions at 970 (vvs) and 833 (vvs) $\mathrm{cm^{-1}}$ in the spectra of $(\mathrm{CH_3})_3\mathrm{N}\rightarrow\mathrm{BX_3}$ were assigned to $\nu_{as}(\mathrm{NC_2})$ and $\nu_s(\mathrm{NC_2})$ found at 1043 (m) and 826 (s) $\mathrm{cm^{-1}}$ in the spectrum of of $\mathrm{N(CH_3)_3}$. The lack of apparent shift exhibited by $\nu_s(\mathrm{NC_2})$ is surprising and may result from strong coupling of $\nu_s(\mathrm{NC_2})$ with vibrational modes of the same symmetry in that region of the spectrum, or else the assignment for this absorption is incorrect because complex bands of similar intensity present at lower energies could just as well be attributed to $\nu_s(\mathrm{NC_2})$. In the spectrum of the adduct $(\mathrm{CH_3})_3\mathrm{N}\rightarrow\mathrm{TiCl_3}$, $\nu_{as}(\mathrm{NC_2})$ and $\nu_s(\mathrm{NC_2})$ occur as intense absorptions at 988 and 813 $\mathrm{cm^{-1}}$, respectively,[16] −55 and −13 $\mathrm{cm^{-1}}$ from the corresponding values in the spectrum of $\mathrm{N(CH_3)_3}$.

In summary, the following characteristics may be expected for the absorptions arising from vibrational modes of the complexed dimethylamino moieties in I: (1) small shifts in absorptions assigned to $\delta(\mathrm{CH_3})$ and $\rho(\mathrm{CH_3})$ with slight change in relative intensities; (2) a large negative shift in $\nu_{as}(\mathrm{NC_2})$, *ca.* −60 $\mathrm{cm^{-1}}$, while $\nu_s(\mathrm{NC_2})$ should exhibit a small shift to lower energy. Both absorptions should exhibit an increase in intensity with respect to those for other vibrational modes.

Interpretation of the Solid-State Infrared Spectrum of $\{[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}\}_2\{\mathrm{TiCl_4}\}_3$. The solid-state vibrational spectrum of I, $\mathrm{TiCl_4}$(g), and $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}$(l) are shown in Figure 1; the spectral data are summarized in Table I. The absorptions located at 425 and 405 $\mathrm{cm^{-1}}$ in the spectrum of I are assigned to TiCl bond stretching which occurs at 610, 518, and 498 $\mathrm{cm^{-1}}$ in the spectrum of $\mathrm{TiCl_4}$(g). Similarly, infrared absorptions of nitrile–titanium tetrachloride complexes, in the 400–436-$\mathrm{cm^{-1}}$ region, have been attributed to TiCl bond stretching, *e.g.*, in $\mathrm{TiCl_4\cdot 2L}$ at 400, 410, and 425 $\mathrm{cm^{-1}}$ where L = $\mathrm{C_6H_5CN}$, $\mathrm{CH_3CN}$, and $\mathrm{C_2H_5CN}$, respectively.[17] The absorptions above 600 $\mathrm{cm^{-1}}$, in the spectrum of I, are attributed to vibrations of the complexed ligand, $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}$.

The ligand associated infrared assignments for I are based on correlations of the frequencies, intensities, shapes, and isotope shifts ($\mathrm{B^{10}}$ and $\mathrm{B^{11}}$) with those of the previously discussed aminoborane derivatives. With regard to the spectrum of I, the low-intensity absorptions in the interval 2938–3171 $\mathrm{cm^{-1}}$ are assigned to $\mathrm{CH_3}$ stretching modes. The low intensity of these absorptions is a result of diffraction of relatively high-energy radiation by the large particle size of I in the mull. The absorptions centered at 1644 (s) and 1609 (vvs) $\mathrm{cm^{-1}}$ are assigned to $\nu_{as}(\mathrm{B^{10}N_2})$ and $\nu_{as}(\mathrm{B^{11}N_2})$, respectively, which exhibit shifts of 100 and 79 $\mathrm{cm^{-1}}$ to higher energy compared with corresponding absorptions in the spectrum of $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}$(l). The shift of $\nu_{as}(\mathrm{BN_2})$ to high energy might arise from the presence of noncomplexed dimethylamino moieties in the solid-state complex which would exhibit appreciable BN double-bond character; likewise, coupling of the $\nu_{as}(\mathrm{BN_2})$ with other vibrations of the same symmetry, *i.e.*, $\nu_{as}(\mathrm{NC_2})$, would account for this relatively high energy absorption. The high-energy $\nu_{as}(\mathrm{BN_2})$, 1583 $\mathrm{cm^{-1}}$, found in diazoborocyclopentane is considered to arise from coupled vibrations.[18] Also, it is known that treatment of $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCH_3}$ with excess HI affords $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCH_3\cdot HI}$,[19] and this salt exhibits an infrared absorption at 1576 $\mathrm{cm^{-1}}$, assigned to $\nu_{as}(\mathrm{BN_2})$, which is indicative of a fairly high BN bond order; $\nu_{as}(\mathrm{BN_2})$ is found at 1502 $\mathrm{cm^{-1}}$ in the spectrum of $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCH_3}$(l). This salt further reacts with 1 equiv of HCl to afford $[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCH_3\cdot HI\cdot HCl}$; the absorption at 1576 $\mathrm{cm^{-1}}$ then disappears since the double-bond character of the noncoordinated $>\mathrm{B}\underset{--}{\leftarrow}\mathrm{N(CH_3)_2}$ is destroyed. In a similar manner, if free $-\ddot{\mathrm{N}}(\mathrm{CH_3})_2$ moieties were present in $\{[(\mathrm{CH_3})_2\mathrm{N}]_2\mathrm{BCl}\}_2\{\mathrm{TiCl_4}\}_3$, salt formation should occur upon treatment with HCl and the high-energy $\nu_{as}(\mathrm{BN_2})$ bond should

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disappear. The fact that this does not occur indicates the absence of noncoordinated nitrogen moieties in the solid-state complex.[19]

The intense absorptions in the spectrum of I at 1465 and 1452 cm^{-1} are attributed to $\delta_{as}(CH_3)$ which occur at 1482 and 1452 cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCl(l)$. The overlapping absorptions at 1441 (m) cm^{-1} are assigned to $\nu_s(B^{10}N_2, B^{11}N_2)$ which are at 1349 (s) cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCl(l)$, a shift of +92 cm^{-1}. This result is attributed to strong coupling between $\nu_s(BN_2)$ and other vibrational modes. The absorption centered at 1413 (m) cm^{-1} is assigned to $\delta_s(CH_3)$ found at 1408 cm^{-1} in the spectrum of the noncoordinated ligand. Absorptions occuring at 1250 (vs), 1201 (s), 1190 (s), and 1185 (vs) cm^{-1} are assigned to $\rho(CH_3)$ found at 1215 (vvs) and 1191 (vs) cm^{-1} in the spectrum of the ligand. Those at 1160 (m), 1144 (vs), 1096 (w), 1072 (w), and 1054 (s) cm^{-1} are also assigned to $\rho(CH_3)$ found at 1152 (vs), 1143 (vs), and 1107 (vs) cm^{-1} in the ligand spectrum.

Absorptions, in the spectrum of I, at 1036 (w), 1017 (vvs), and 974 (m) are assigned to $\nu_{as}(NC_2)$ found at 1074 (vvs) and 1022 (vw) cm^{-1} in the ligand spectrum. The absorption at 1017 cm^{-1} is very intense and is shifted −57 cm^{-1} as is expected for the complexed dimethylamino moiety. The bands at 922 (w) and 914 (m) cm^{-1} are assigned to $\nu(B^{10}Cl)$ and $\nu(B^{11}Cl)$, respectively, and exhibit small shifts from the corresponding absorptions in the spectrum of $[(CH_3)_2N]_2BCl$, 922 (m) and 907 (vs) cm^{-1}. Thus, the involvement of the chlorine atom in coordination appears unlikely since a substantial shift to lower energy would be expected. Compound I has infrared absorption at 888 (m), 857 (vvs), 829 (vvs), and 828 (vs) cm^{-1} which are assigned to $\nu_s(NC_2)$ and are shifted −78 cm^{-1} from the corresponding ligand absorptions. The 680 (w) and 658 (m) cm^{-1} bands are assigned to $\delta(B^{10}N_2)$ and $\delta(B^{11}N_2)$, respectively, which are shifted +80 and +79 cm^{-1} from the free ligand absorptions, 600 (w) and 579 (vs) cm^{-1}. The spectrum of I contains no intense absorptions in the region of 580 cm^{-1} thus indicating the absence of the $TiN(CH_3)_2$ moiety because the $\nu(TiN)$ occurs at 580 (s) cm^{-1} in $Cl_3TiN(CH_3)_2$.[1a]

From the infrared spectrum of I the following conclusions may be drawn: (1) the lowering of $\nu_{as}(NC_2)$ and $\nu_s(NC_2)$ of −57 and −78 cm^{-1}, respectively, suggests coordination through the nitrogen moieties; (2) the consistency of the $\nu(BCl)$ frequency indicates the noncoordinating status of this type of Cl, thus eliminating the possibility of mixed Cl and N bridging (associated with B) in I; (3) the absence of an intense band at 1074 cm^{-1}, $\nu_{as}(NC_2)$, indicates the absence of noncomplexed nitrogen moieties because such groups should exhibit an absorption close to that frequency assignment found in $[(CH_3)_2N]_2BCl$.

Three structure possibilities for I, which are consistent with these three conclusions, have been suggested in a previous paper.[1a] The ionic form consists of the hexachlorotitanate anion, $TiCl_6^{2-}$, and the cation comprises two six-coordinate $TiCl_3^+$ species bridged by Cl (originating from Ti) and two ligand species. Alternate molecular structure possibilities include mixed five- and six-coordinate Ti(IV) moieties with two bridging ligands and a model involving Cl bridging. The infrared data obtained to date do not aid in distinguishing between these suggested models.

Vapor-Phase Infrared Studies. The infrared spectrum of the vapor above I, maintained in several temperature ranges, is shown in Figure 2, and the corresponding spectral data are summarized in Table II. Spectra a, b, and c in Figure 2 were obtained when I was maintained at 27, 36–64, and 40–100, respectively. Spectrum d was obtained after all materials, volatile at 25°, were distilled from the gas cell and represents absorptions arising from yellow and brown solids which had sublimed to the cell windows during the experiments. Volatile species which gave rise to the absorptions in spectra a–c were identified as $[(CH_3)_2N]_2BCl$, $TiCl_4$, and $(CH_3)_2NBCl_2$ by reference to the spectral data for the pure compounds, taking into consideration intensities and band shapes. The absorptions above 600 cm^{-1} arise from the species $[(CH_3)_2N]_2BCl(g)$ and $(CH_3)_2NBCl_2(g)$ because $TiCl_4(g)$ exhibits no absorptions above that frequency. Some absorptions in the 3200–600-cm^{-1} range appear to undergo frequency shifts in proceeding from spectrum a to c. The origin of these apparent shifts is attributed to difficulties in locating band maxima since the solids which sublimed to the cell windows exhibit absorptions in the same frequency ranges as the volatile species. It should be noted that the amount of solids on the windows increased as the temperature was raised, hence the increase in intensity of their characteristic absorptions.

Table II. Infrared Frequencies and Assignments for Vapor above $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$[a]

	Frequency ±5 cm^{-1}			
	27°	36–64°	40–100°	27°
Assignment	a	b	c	d
$\nu(CH_3)$	3168 vw (b)	3119 vs (b)	3199 w	3172 w
	3006 vw	2988 vw	3015 w	2930 w
	2926 m (sh)	2926 m (sh)	2952 s	2888 w
	2901 s	2876 s	2909 s	2799 w
	2803 m	2787 m	2827 m	
	1578 w	1584 w	1604 w	1608 m
$\nu(BN)$	1554 m (sh)	1566 m (sh)	1556 m (sh)	1558 s
	1542 s (sh)	1544 m (sh)	1546 s (sh)	1534 w
	1525 vvs	1530 vvs	1527 vvs	5527 w
$\delta_{as}(CH_3)$	1460 s	1462 s	1460 s	1464 vs
$\delta_{as}(CH_3)$	1418 vs (sh)	1412 vs	1410 vvs	1410 vs
	1404 s			
$\nu_s(BN)$	1350 m	1360 m	1356 m	1353 vw
$\rho(CH_3)$	1195 vs	1199 vs	1197 vs	1192 vs
				1179 s (sh)
$\rho(CH_3)$	1149 s	1148 s	1145 vs	1141 vs
				1120 s (sh)
$\nu_{as}(NC_2)$	1071 m	1072 m	1068 m	1056 vm
			1015 s	1016 s
	974 s	975 s	977 s	973 s
	948 s	945 m (sh)	941 s	929 w
	905 m	913 m (sh)	916 m (sh)	895 m
$\nu(BCl)$	858 vw	858 vw	855 m	856 s
$\nu_s(NC_2)$	840 w	839 vw	826 m	828 vs
	829 w	777 w	728 s	775 m
	779 w	718 vs	650 w	731 vs
	732 vs			653 w
	498 vs	498 vs	516 w	
$\nu(TiCl)$	477 s	477 s	495 vvs	473 m
	404 vvs	404 vvs	474 vw	402 vvs
			401 vvs	

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

The bands in the region of $\nu(CH_3)$ centered at 3015 (w), 2909 (s), and 2825 (m) cm^{-1} in spectrum c, Table

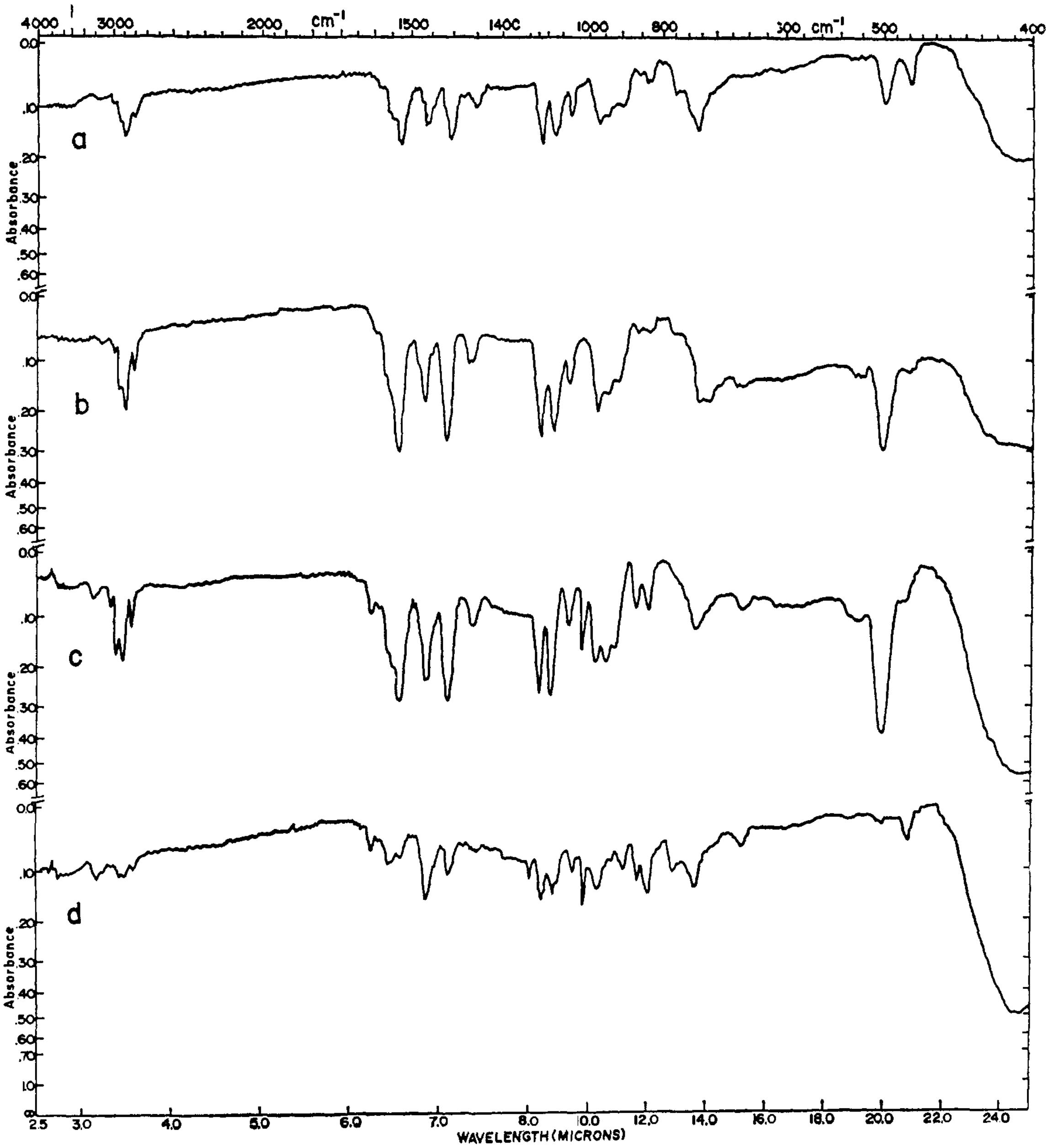

Figure 2. Infrared spectra of vapor above I at several temperature intervals.

II, appear at 3014 (w), 2908 (vs), and 2825 (m) cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCl(g)$, while the 2952 (s) cm^{-1} absorption in spectrum c occurs as an intense band at 2954 cm^{-1} in the spectrum of $(CH_3)_2NBCl_2$. Furthermore, the intense band centered at 1527 cm^{-1} is attributed to overlapping absorptions found at 1528 (vvs) and 1522 (vvs) cm^{-1} in the spectra of $[(CH_3)_2N_2]$-$BCl(g)$ and $(CH_3)_2NBCl_2(g)$, respectively. The 1460 (s) cm^{-1} absorption in spectrum c is considered to arise from overlapping absorptions occurring at 1460 (s) and 1461 (m) cm^{-1} [$\delta_{as}(CH_3)$] in the spectra of $[(CH_3)_2N]_2BCl(g)$ and $(CH_3)_2NBCl_2(g)$, respectively. The band at 1410 (vvs) cm^{-1} is assigned to overlapping bands found at 1409 (vvs) cm^{-1} [$\delta_s(CH_3)$] in both $[(CH_3)_2N]_2BCl(g)$ and $(CH_3)_2NBCl_2(g)$.

The 1356 (m) cm^{-1} absorption in spectrum c (see Table II) serves to establish the presence of $[(CH_3)_2N]_2BCl$ because a band of similar intensity is found at 1355 (m) cm^{-1} [$\nu_s(BN_2)$] in the spectrum of $[(CH_3)_2N]_2BCl(g)$, while the spectrum of $(CH_3)_2NBCl_2(g)$ contains no similar absorption. *The presence of this 1356-cm^{-1} absorption establishes the presence of* $[(CH_3)_2N]_2BCl$ *in the vapor above I and substantiates the correlations made in the* $\nu(CH_3)$ *region.* The band centered at 1197 (vs) cm^{-1} in spectrum c arises from overlapping frequencies attributed to $\rho(CH_3)$ found at 1218 (s) and 1202 (s) cm^{-1} in $[(CH_3)_2N]_2BCl(g)$ and $(CH_3)_2NBCl_2(g)$, respectively. The absorption centered at 1145 (vs) cm^{-1} results from overlapping frequencies attributed to $\rho(CH_3)$ found at 1144 (s) and 1142 (vs) cm^{-1}, respectively, in both aminoboranes.

The absorption centered at 1068 cm^{-1} arises from $\nu_{as}(NC_2)$ found at 1077 (s) and 1068 (w) cm^{-1} in the bis- and mono(amino)chloroboranes, respectively. The 977 (s) and 941 (s) cm^{-1} bands arise from $\nu_{as}(B^{10}Cl_2)$ and $\nu_{as}(B^{11}Cl_2)$ found at 974 (m) and 944 (vs) cm^{-1} in the spectrum of $(CH_3)_2NBCl_2(g)$; the spectrum of $[(CH_3)_2N]_2BCl$ contains only one weak absorption at 966 cm^{-1}

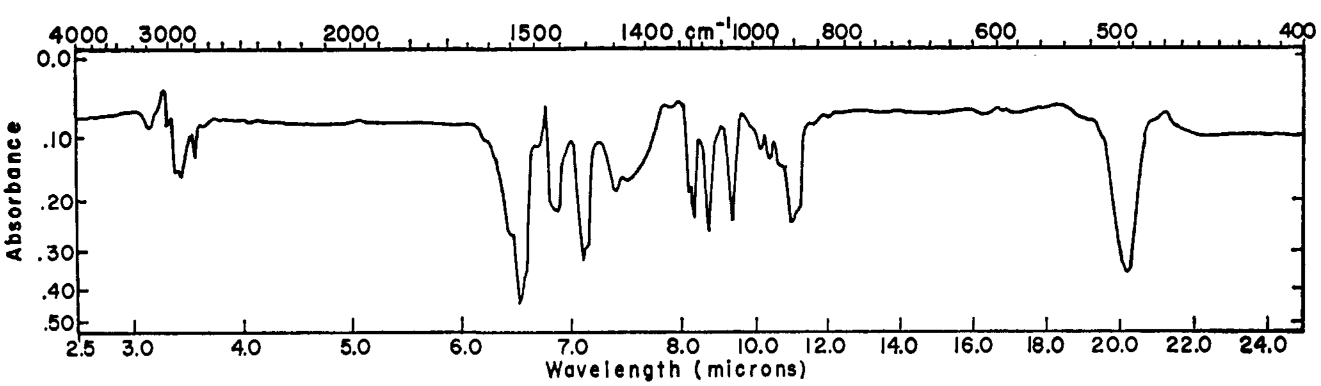

Figure 3. Infrared spectrum of I dissolved in methylene chloride.

(ν(BCl)). *The presence of the absorptions 944–974 cm^{-1} in spectrum c firmly establishes the existence of* $(CH_3)_2NBCl_2$ *in the vapor phase above I.* The absorption at 916 (m) cm^{-1} is considered to arise from $\nu_s(NC_2)$ + ν(BCl) found at 912 (s) and 932 (s) cm^{-1} in the spectra of $[(CH_3)_2N]_2BCl(g)$ and $(CH_3)_2NBCl_2(g)$, respectively. The intense absorption at 495 (vvs) cm^{-1} is attributed to ν_3(TiCl) found at 498 (vs) cm^{-1} in the spectrum of $TiCl_4(g)$. *This absorption establishes the existence of* $TiCl_4$ *in the vapor phase above I.* The bands at 474 and 401 cm^{-1}, spectrum c, Figure 2 (Table II), arise from the yellow and brown solids which sublimed to the windows of the gas cell. The yellow solid was identified as I by comparison of its infrared spectrum (d) with that of pure I (Figure 1).

Concerning the absorptions characteristic of $(CH_3)_2NBCl_2(g)$, the increase in intensity of the bands at 974 and 944 cm^{-1} in proceeding from spectrum a to c (Figure 2) indicates enhancement of the exchange reaction

$$TiCl_4(g) + [(CH_3)_2N]_2BCl(g) \longrightarrow Cl_3TiN(CH_3)_2(s) + (CH_3)_2NBCl_2(g)$$

with increasing temperature. Further evidence for this exchange process was obtained when I was warmed to 65°. The volatile materials were constantly removed under vacuum and identified as $(CH_3)_2NBCl_2(g)$ and $Cl_3TiN(CH_3)_2(s)$.[1a] Concerning the gas-phase spectra, if absorptions characteristic of associated $TiCl_4$–$[(CH_3)_2N]_2BCl$ species are present, they are masked by absorptions due to the dissociated species. An apparent molecular weight of 142.8 g/mole was obtained for the vapor above I at 23° (calculated: 167.6 g/mole for 100% dissociation of I). Because of experimental difficulties involved in the relatively low-pressure measurements of reactive species and condensation of $Cl_3TiN(CH_3)_2$, the calculated and observed apparent molecular weights are considered to be in satisfactory agreement for the complete dissociation of I in the gas phase at a total pressure <9 torr

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

The thermal instability of I with regard to dissociation to $TiCl_4(g)$ and $[(CH_3)_2N]_2BCl(g)$ suggests that the relative Lewis acidies of Ti in $TiCl_4$ and B in $[(CH_3)_2N]_2BCl$ must be comparable with $TiCl_4$ functioning as a slightly stronger acid in I.

Solution Infrared Studies. The infrared spectrum of I in CH_2Cl_2 (saturated solution) is shown in Figure 3, and the spectral data are summarized in Table III. A comparison of the solution spectrum of I with those obtained for the solid and vapor phases (see Tables I and II) is consistent with the presence of noncomplexed $[(CH_3)_2N]_2BCl$ and $TiCl_4$ in solution. The slight shifts in frequencies in the solution spectrum, with respect to the spectra of $[(CH_3)_2N]_2BCl(l)$ and $TiCl_4(g)$, most likely arise from solvent effects as well as phase change. The bands at 1214 (m) and 1198 (s) cm^{-1} appear to have undergone a reversal in relative intensity with respect to the corresponding absorptions at 1215 (vvs) and 1191 (vs) cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCl(l)$. Additional weak bands centered at 981 and 958 cm^{-1} in the solution spectrum are absent in $[(CH_3)_2N]_2BCl$; however, $(CH_3)_2NBCl_2$ exhibits intense absorptions at 974 and 944 cm^{-1}. Therefore, these bands may arise from a low concentration of $(CH_3)_2NBCl_2$ produced by Cl–N exchanges between B and Ti in solution. The ν_3(TiCl) centered at 498 (vs) cm^{-1} in the spectrum of $TiCl_4(g)$ is found at 492 (vs) cm^{-1} in the solution spectrum of I. This shift of −6 cm^{-1} may be attributed to solvent effects or association of $TiCl_4$ in the condensed phase. Indeed, the ν_3(TiCl) mode in $TiCl_4(g)$

Table III. Infrared Frequencies and Assignments for $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ in Methylene Chloride

Assignment	Frequency ± 5 cm^{-1}
$\nu(CH_3)$	3173 w (b)
	3012 w
	2931 m
	2872 m
	2792 w
$\nu_{as}(BN_2)$	1604 w (sh)
	1556 s (sh)
	1535 vs
	1526 vs (sh)
	1487 w
$\delta_{as}(CH_3)$	1456 m
$\delta_s(CH_3)$	1409 s
	1403 s (sh)
$\nu_s(BN_2)$	1350 m
	1325 m
$\rho(CH_3)$	1214 m
	1198 s
$\rho(CH_3)$	1157 s
$\nu_{as}(NC_2)$	1070 s
ν(BCl)	981 w
	958 w
$\nu_s(NC_2)$	915 w
	905 s
ν(TiCl)	492 vs

at 498 (vvs) cm^{-1} is broadened and shifted to 481 (vvs) cm^{-1} in $TiCl_4$(l). *In conclusion, infrared data for I in CH_2Cl_2 are consistent with the presence of noncoordinated $[(CH_3)_2N]_2BCl$ and $TiCl_4$.* Low concentrations of I in CH_2Cl_2 afford yellow solutions while high concentrations yield red solutions. Also, cooling solutions containing low concentrations of I (yellow) from 25 to −78° results in the appearance of a red color. These color changes indicate the presence of low concentrations of intermediate complexes in solution as suggested by

$$\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3 \longrightarrow \{[(CH_3)_2N]_2BCl\}_{2-x}\{TiCl_4\}_{3-y} + x[(CH_3)_2N]_2BCl + yTiCl_4$$

The red coloration most likely is a result of these suggested intermediate complexes. Lack of observed infrared absorptions for such species is attributed to coincidence of frequencies arising from both associated and dissociated products.

Summary

The coordination complex $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ is formed by treatment of $TiCl_4$ with $[(CH_3)_2N]_2BCl$. Evaluation of infrared data for this complex in the solid state indicates the involvement of $[(CH_3)_2N]_2BCl$ as a nitrogen bidentate ligand bridging two molecules of $TiCl_4$. Dissociation of this complex *in vacuo* and in CH_2Cl_2 occurs to afford $TiCl_4$ and $[(CH_3)_2N]_2BCl$; these dissociations are accompanied by small amounts of intermolecular exchange affording $(CH_3)_2NBCl_2$ and $Cl_3TiN(CH_3)_2$.

Experimental Section

The preparation and purification of $[(CH_3)_2N]_2BCl$, $(CH_3)_2NBCl_2$, $TiCl_4$, and $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ have been described in a previous paper.[1a] Samples of the complex were ground in an agate mortar under a dry nitrogen atmosphere in a glove box, mixed with Nujol (previously dried over sodium) or Flurolube (previously dried over Linde Molecular Sieve Type 4A), and enclosed between KBr plates. Dichloromethane solutions of the complex were syringed into 0.1-mm matched liquid cells equipped with KBr optics. Dichloromethane was previously dried over CaH_2 and distilled in a vacuum line. Vapor-phase spectra of the volatile components in equilibrium with the solid complex were determined at various temperatures by immersing the condensation finger of the gas cell in heated dibutyl phthalate. The temperature of dibutyl phthalate was measured before and after the recording of each vapor-phase infrared spectrum to establish the temperature interval. All infrared measurements were carried out with a Perkin-Elmer Model 337 grating spectrophotometer.

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The Mass Spectra of Trifluorophosphinecarbonylcobalt Hydrides[1]

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Philadelphia, Pennsylvania 19104. Received November 20, 1967

Abstract: A mass spectral study has been carried out on the series of compounds: $HCo(CO)_x(PF_3)_{4-x}$, where $x = 0$ to 4. These studies, which included the measurement of the fragmentation patterns and appearance potentials of the five compounds, showed that the Co–CO and Co–PF_3 bond energies are essentially identical (56 ± 15 kcal/mole) and are much greater than the H–Co bond energy (4 ± 15 kcal/mole). The heats of formation of these compounds, calculated from the appearance potential data, become more negative by approximately 200 kcal/mole for each CO moiety that is replaced by PF_3. Since this variation is the difference between the heats of formation of PF_3 and CO, the nature of the Co–PF_3 and Co–CO bonds must be quite similar. The values for ΔH_f° ($HCo(CO)_x(PF_3)_{4-x}$) are (in kcal/mole): −173 ± 11, −381 ± 9, −579 ± 10, −783 ± 9, and −978 ± 14 for $x = 4$ to 0, respectively. Comparison of the relative intensity of the hydrogen-containing ions with ions that have lost a hydrogen atom in the mass spectra of these cobalt hydrides shows that ions containing H–Co bonds are more abundant until two or more of the covalently bonded ligands (CO or PF_3) are lost from the parent ion. This type of fragmentation can be explained by an interaction between the equatorial ligands around the Co atom and the axial hydrogen atom.

A number of mass spectral studies of metal carbonyl compounds have been reported in the literature recently.[2–9] While a few publications[6,10] have dealt with the mass spectra of substituted metal carbonyls, a mass spectral study, including both appearance potential and fragmentation data, of a complete series of substituted metal carbonyls has not been reported.

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