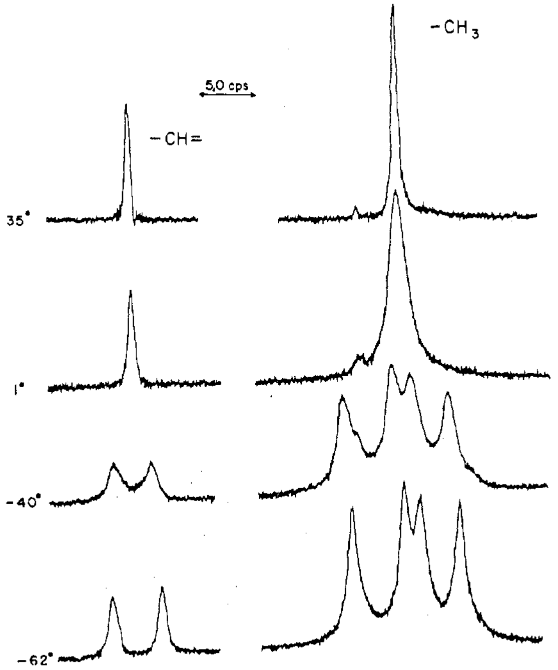

Figure 3. Variable-temperature pmr spectra of an equimolar mixture of Ti(acac)$_2$F$_2$ and Ti(acac)$_2$(OEt)$_2$ in dichloromethane solution; total solute molarity is 0.32 *M*. The weak peak on the low-field side of the methyl resonance in the 35° spectrum and the very weak, broad shoulder on the high-field side of this resonance are due to Ti(acac)$_2$F$_2$ and Ti(acac)$_2$(OEt)$_2$, respectively. The intense lines are all due to the mixed complex Ti(acac)$_2$F(OEt).

the same configuration. This was checked for Ti(acac)$_2$F(OEt) by low-temperature nmr. Pmr spectra of an equimolar mixture of Ti(acac)$_2$F$_2$ and Ti(acac)$_2$(OEt)$_2$ (Figure 3) are dominated by the resonance lines of Ti(acac)$_2$F(OEt) because of the large value of *K* (Table III) for F-OEt exchange; resonances of the parent complexes are weak and do not complicate interpretation of the spectra. The low-temperature spectra exhibit four equally intense methyl resonances and two equally intense -CH= resonances, as expected for the cis isomer (point group C_1). There is no evidence for any appreciable concentration of the trans isomer. Above −40°, rapid intramolecular rearrangement collapses the spectrum to a single, time-averaged methyl resonance and a single, time-averaged -CH= line.

Thompson, *et al.*,[32] have recently reported the preparation and isolation of the mixed chloroalkoxy complexes, Ti(acac)$_2$Cl(OR). These compounds also exist in solution as stereochemically nonrigid cis isomers.

Acknowledgments. The support of this research by the National Science Foundation is gratefully acknowledged. We also thank Mr. J. K. Howie for recording variable-temperature pmr spectra of the Ti(bztf)$_2$F$_2$–Ti(dpm)$_2$F$_2$ mixture.

Registry No. Ti(acac)$_2$F$_2$, 16986-93-9; Ti(bzac)$_2$F$_2$, 51064-85-8; Ti(bzbz)$_2$F$_2$, 17967-65-6; Ti(dpm)$_2$F$_2$, 51022-45-8; Ti(tfac)$_2$F$_2$, 51022-46-9; Ti(bztf)$_2$F$_2$, 51022-47-0; Ti(thtf)$_2$F$_2$, 51022-48-1; Ti(hfac)$_2$F$_2$, 51025-52-6; Ti(acac)$_2$(OEt)$_2$, 23072-30-2; Ti(tfac)$_2$(OEt)$_2$, 51022-49-2; Ti(hfac)$_2$(OEt)$_2$, 51022-50-5; Ti(acac)$_2$Cl$_2$, 16986-94-0; Ti(acac)$_2$FCl, 51025-53-7; Ti(acac)$_2$FBr, 51022-51-6; Ti(acac)$_2$ClBr, 51025-54-8; Ti(acac)$_2$F(OEt), 51022-52-7; Ti(acac)$_2$Br$_2$, 16986-95-1; Ti(acac)(bzac)F$_2$, 51022-53-8; Ti(acac)(bzbz)F$_2$, 51022-54-9; Ti(acac)(dpm)F$_2$, 51022-55-0; Ti(bzac)(bzbz)F$_2$, 51022-26-5; Ti(bzbz)(dpm)F$_2$, 51022-27-6; Ti(tfac)(acac)F$_2$, 51022-28-7; Ti(tfac)(bzac)F$_2$, 51022-29-8; Ti(tfac)(bzbz)F$_2$, 51022-30-1; Ti(bztf)(acac)F$_2$, 51022-31-2; Ti(bztf)(bzac)F$_2$, 51022-32-3; Ti(bztf)(dpm)F$_2$, 51022-33-4; Ti(thtf)(acac)F$_2$, 51022-34-5; Ti(thtf)(bzac)F$_2$, 51022-35-6; Ti(thtf)(dpm)F$_2$, 51022-36-7; Ti(tfac)(thtf)F$_2$, 51022-37-8; Ti(tfac)(bztf)F$_2$, 51022-38-9; Ti(bztf)(thtf)F$_2$, 51022-39-0; Ti(tfac)(hfac)F$_2$, 51022-40-3; Ti(acac)(hfac)F$_2$, 51022-41-4; Ti(acac)(tfac)(OEt)$_2$, 51022-42-5; Ti(tfac)(hfac)(OEt)$_2$, 51022-43-6; Ti(acac)(hfac)(OEt)$_2$, 51022-44-7.

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Reduction of Vanadium Tetrachloride by Tetrakis(dimethylamino)diborane(4). Preparation of Bis(dimethylaminomethane)vanadium(III) Chloride

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Treatment of vanadium tetrachloride, VCl$_4$, with excess tetrakis(dimethylamino)diborane(4), B$_2$[N(CH$_3$)$_2$]$_4$, affords bis(dimethylaminomethane)trichlorovanadium(III), VCl$_3$·[N(CH$_3$)$_2$]$_2$CH$_2$ (I). Reaction of I with pyridine, py, quantitatively displaces CH$_2$[N(CH$_3$)$_2$]$_2$ and affords VCl$_3$·3py. Treatment of I with gaseous HCl results in the formation of the cationic species (CH$_3$)$_2$N=CH$_2^+$ and (CH$_3$)$_2$NH$^+$ and liberation of VCl$_3$. For comparison, the reaction of HCl with CH$_2$[N(CH$_3$)$_2$]$_2$ is also described. Electronic and infrared spectral data for I are consistent with vanadium in the five-coordinate state, and the magnetic moment is normal for a V(III) d^2 system.

Introduction

The reduction of anhydrous metal halides (periodic groups IVb, Vb) by tetrakis(dimethylamino)diborane(4), B$_2$[N(CH$_3$)$_2$]$_4$, has led to the formation of metal halide complexes involving bridging and chelate groups derived from oxidation of B$_2$[N(CH$_3$)$_2$]$_4$, *i.e.*, B[N(CH$_3$)$_2$]$_2$X, X = Cl and Br. Reduction of TiCl$_4$ affords the ligand-bridged species (TiCl$_4$)$_3$$\{$[N(CH$_3$)$_2$]$_2BCl\}_2$ and the binuclear antiferromagnetic complex (TiCl$_3$)$_2$[N(CH$_3$)$_2$]$_2$BCl.[2] A similar reaction with TiBr$_4$ results in the formation of (TiBr$_4$)$_3$$\{$[N(CH$_3$)$_2$]$_2Br\}_2$ and (TiBr$_3$)$_2$$\{B_2Br_2$[N(CH$_3$)$_2$]$_2$$\}_2$.[3] In an effort to prepare binuclear V(III) complexes the reduction of VCl$_4$ with B$_2$[N(CH$_3$)$_2$]$_4$ was investigated.

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[1] Work completed in partial fulfillment of the Ph.D. degree, 1971.

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Results and Discussion

Preparation and Characterization of $VCl_3 \cdot [N(CH_3)_2]_2CH_2$. Treatment of $B_2[N(CH_3)_2]_4$ with VCl_4 affords $VCl_3 \cdot [N(CH_3)_2]_2CH_2$, I, in *ca.* 30% yield based on VCl_4 consumed. Analytical data associated with I (presented in the Experimental Section) are in agreement with the indicated stoichiometry; however, the presence of a methylene group as well as ligand distribution must be established. In an effort to resolve these questions, nucleophilic displacement was effected with pyridine (py) by eq 1. Quantitative evolution of $CH_2[N(CH_3)_2]_2$ resulted and was subsequently characterized by comparison of ir and vapor tension data with those of an authentic sample and with literature values.[4] Vanadium(III) chloride-tris(pyridine), $VCl_3 \cdot 3py$, was identified by elemental analyses, and comparison of ir data with an authentic sample. The isolation of $CH_2[N(CH_3)_2]_2$, *via* nucleophilic displacement, provides evidence that I is a complex of VCl_3 rather than a complex of an aminochlorovanadium(III) species with dimethylmethyleneimmonium chloride, $(CH_3)N{=}CH_2^+Cl^-$. The latter cation has been shown to react with nucleophiles by complex formation as well as deprotonation.[5] In order to determine whether both nitrogens, associated with I, were coordinated to V, treatment with HCl was carried out. Noncomplexed nitrogen would be expected to be rapidly protonated by HCl. In order to understand this reaction it proved necessary also to investigate the interaction of $CH_2[N(CH_3)_2]_2$ with HCl.

$$VCl_3 \cdot [N(CH_3)_2]_2CH_2 + 3py \rightarrow VCl_3 \cdot 3py + CH_2[N(CH_3)_2]_2 \tag{1}$$

Reaction of $CH_2[N(CH_3)_2]_2$ with HCl. Treatment of $CH_2[N(CH_3)_2]_2$ with HCl is described by eq 2. The ir spectrum of the products consists of a composite of that of $(CH_3)_2N{=}CH_2^+Cl^-$ and $(CH_3)_2NH_2^+Cl^-$. For example, $(CH_3)_2N{=}CH_2^+Cl^-$ has distinct strong absorptions at 1678, 1172, 992, 500, and 430 cm^{-1} while $(CH_3)_2NH_2^+Cl^-$ is identified by strong absorptions at 2438, 1599, 1258, 1029, and 890 cm^{-1}.[6] Furthermore, the band shapes for the cited coincidental absorptions are identical. Finally, the other ir absorptions for the product species, eq 2, may be simulated by overlap of the ir spectra of the component species.

$$CH_2[N(CH_3)_2]_2 + 2HCl \rightarrow (CH_3)_2N{=}CH_2^+ + (CH_3)_2NH_2^+ + 2Cl^- \tag{2}$$

Reactions of $VCl_3 \cdot [N(CH_3)_2]_2CH_2$ with HCl. Treatment of I with HCl (*ca.* 1 atm) affords matter of overall composition I·0.6HCl. This material contains unreacted I based on ir data. Figure 1, B and C, reproduces the ir spectra of I and I·0.6HCl, respectively, and contains major coincident bands at 1470, 1246, 1046, 1007, 966, 865, 478, 393, and 359 cm^{-1}. A comparison of the ir spectrum of I·2HCl, Figure 1D, to that of I·0.6HCl indicates that I·0.6HCl contains I·2HCl based on the coincident bands at 3118, 3020, 1695, 1573, 1403, 839, 820, and 423 cm^{-1}. The intermediate material I·0.6HCl is a mixture of I and I·2.0HCl. The lack of rapid reaction of I with HCl, at 1 atm, to afford I·1.0HCl, is interpreted to indicate the absence of noncoordinated amino moieties.

Treatment of I with HCl at 5 atm is summarized by eq 3.

$$VCl_3 \cdot [N(CH_3)_2]_2CH_2 + 2HCl \rightarrow (CH_3)_2NH_2^+ + (CH_3)_2NCH_2^+ + VCl_3 + 2Cl^- \tag{3}$$

Identification of cationic species, eq 3, was achieved by correlation of ir absorptions to those of $(CH_3)_2NH_2^+Cl^-$ and $(CH_3)_2NCH_2^+Cl^-$. Small shifts in band frequency occur when comparing these ir spectra. These shifts are probably caused by the presence of anions other than Cl^-, perhaps VCl_5^{2-}; such anion effects have been previously observed.[6,7] The ion $(CH_3)_2NH_2^+$ has characteristic ir bands at 2770 and 2430 cm^{-1} (ν(N-H- - -Cl)), 1609 cm^{-1} ($\delta(NH_2)$), 1010 or 998 cm^{-1} ($\nu_{as}(NC_2)$), and 883 cm^{-1} ($\nu_s(NC_2)$).[8] Characterization of $(CH_3)_2N{=}CH_2^+$ is based on coincident frequencies and band shapes at 3118 and 3020 cm^{-1} (ν_{as} and $\nu_s(CH_2)$), 1695 cm^{-1} ($\nu(C{=}N)$), 1051 and 1010 or 998 cm^{-1} (ν_{as} and $\nu_s(NC_2)$), and 820 cm^{-1} ($\rho_w(CH_2)$).[9] The very strong broad absorption centered at 315 cm^{-1} is assigned to ν(V-Cl). The stretching frequency for bridging V-Cl-V in VCl_3 occurs at 295 cm^{-1}.[10] Terminal ν(V-Cl) stretching frequencies in four-coordinate V species are found at 485 cm^{-1} in VCl_4 and 406 cm^{-1} in VCl_4^-.[11] As the coordination number increases, the frequency of absorption decreases; thus VCl_5^- absorbs at 420 and 320 cm^{-1} while VCl_6^{2-} is expected to absorb *ca.* 320 and 312 cm^{-1} ($TiCl_6^{2-}$ absorbs at these frequencies and the vanadium species should be similar).[11,12] The anion present in the reaction product, eq 3, is either a bridged V(III) species or an anion of V(III) with a higher coordination number. The higher energy $\nu(C{=}N)$ frequency 1695 cm^{-1}, as compared to 1678 cm^{-1} for $(CH_3)_2N{=}CH_2^+Cl$, as well as other band shifts, is also consistent with a large anion.[6]

Concerning the reaction of I with HCl, based on ir data for I·0.6HCl, the initial relatively slow protonation of a dimethylamino moiety affording $VCl_3 \cdot N(CH_3)_2CH_2N(CH_3)_2H^+Cl^-$ is followed by the rapid second protonation and heterolytic bond cleavage to yield the cations $(CH_3)_2NCH_2^+$ and $(CH_3)_2NH_2^+$. This cleavage is expected to be assisted by the electronic withdrawing effect of coordinated VCl_3. The lack of a rapid initial protonation of I by HCl to afford I·HCl is interpreted to indicate both nitrogens, associated with I, are coordinated to vanadium. In order to gain insight concerning the coordination number of V, associated with I, the electronic and ir spectra were recorded.

Electronic Spectrum of I. The coordination number of 5 is assigned to V, associated with I, based on the four observed absorptions. Solutions of I in CH_2Cl_2 exhibit absorption maxima at 20.8 (vs), 14.1 (m), 6.9 (w), and 4.5 (mw) kK in the indicated approximate relative intensity ratios. Recent calculations have predicted four electronic absorptions for five-coordinated d^2 systems.[13] Analogous systems of the type $VCl_3 \cdot 2L$, where L is a monodentate ligand, have been shown to be five-coordinate when dissolved in an inert solvent based on the appearance of absorption bands in the near-infrared spectral region. Other species of the same type are five-coordinate in the solid state (four absorptions) and are six-coordinate when dissolved in excess ligands (two absorptions).[14]

Infrared Study. The ir spectrum of I is duplicated in Figure 1B and that of the free ligand, $CH_2[N(CH_3)_2]_2$, is

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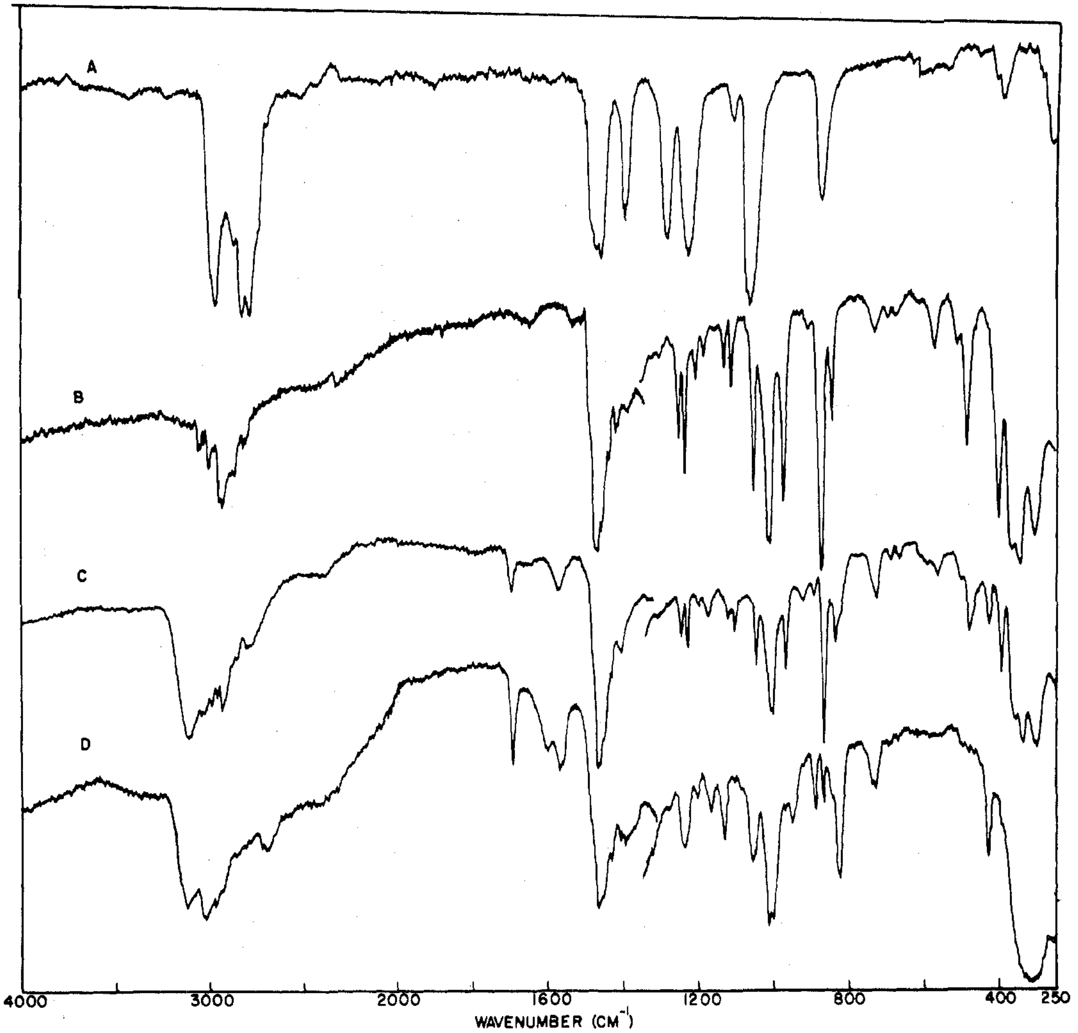

Figure 1. Infrared spectra of (A) $CH_2[N(CH_3)_2]_2$, (B) $VCl_3 \cdot [N(CH_3)_2]_2CH_2$, (C) $VCl_3 \cdot [N(CH_3)_2]_2CH_2 \cdot 0.6HCl$, and (D) $VCl_3 \cdot [N(CH_3)_2]_2CH_2 \cdot 2HCl$.

shown in Figure 1A. The ir assignments are based on considerations of assignments associated with $CH_2[N(CH_3)_2]_2$, $CD_2[N(CH_3)_2]_2$, and $N(CH_3)_3$.[9] Of particular importance are the low-energy shifts for $\nu(NC_2)$, both asymmetric and symmetric, from 1053 and 864 cm^{-1}, respectively, associated with the free ligand, to 1041, 1003, 963 (asymmetric) and 861, 831 (symmetric) cm^{-1} in I. These ir shifts are most consistent with both $N(CH_3)_2$ moieties coordinated. Also of importance are the $\nu(CH_2)$ at 2045, 3045, and 3017 cm^{-1}; these high-energy absorptions are similar to $\nu(CH_2)$ absorptions associated with aliphatic four-membered rings as is the apparent increase in $\delta(CH_2)$, from 1392 cm^{-1}, in the free complex, to under the $\delta(CH_3)$ band at 1460 cm^{-1} in I.[15]

Concerning the ir spectra of complexes of Ti(III) which we have prepared, we have noted very weak $\nu(CH_3)$ absorptions and previously attributed this phenomenon to insufficient fine mulling of the sample. These same samples, affording very weak $\nu(CH_3)$ bands, were suggested to involve five-coordinate Ti based on other data.[16,17] In this work we report an electronic absorption in the near-infrared spectrum and now suggest the absence of strong $\nu(CH_3)$ vibrations is due to the fact that these absorptions are masked by tailing of the low-energy electronic transition. Hence it appears that we have a simple tool to assign five-coordinate geometry, for these types of complexes, based on the absence of strong $\nu(CH_3)$ absorptions at *ca.* 2900 cm^{-1}.

Possible Structure of $VCl_3 \cdot [N(CH_3)_2]_2CH_2$. Because I is only slightly soluble in nonreacting solvent and decomposes prior to vaporization, a molecular weight determination could not be successfully carried out. The magnetic moment, 2.9 BM, precludes antiferromagnetic interaction; the electronic spectral data are consistent with five-coordinate V(III), while infrared data are interpreted to indicate chelated $CH_2[N(CH_3)_2]_2$. The structure most consistent with these conclusions is a distorted trigonal bipyramid with chelate ligands occupying an axial and equatorial position. This mode of chelation results in minimum internal strain.

The mechanism of formation of I is under investigation and should prove very interesting because of the complicated nature of this reaction. That is, formation of $CH_2[N(CH_3)_2]_2$ from $B_2[N(CH_3)_2]_4$ must involve oxidation of a methyl group, dimethylamino group transfer, and methyl transfer to nitrogen.

Experimental Section

General procedures and techniques have been previously discussed as well as purification of solvents and some reactants.[18]

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Reagents. Tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, was obtained from Alfred Baker Chemicals, Milwaukee, Wis., or prepared by coupling $ClB[N(CH_3)_2]_2$ with NaK alloy, using pentane as the solvent. This reagent was distilled prior to use in a Bantam ware Vigreux column at 69° with 3.5 Torr He pressure; lit.[19] $P(69°) = 3.6$ Torr. Infrared data (neat, 0.1-mm path): 2990 (m, sh), 2979 (m), 2860 (vs), 2840 (vs), 2790 (s), 1498 (vs), 1450 (s), 1407 (ms), 1370 (vs), 1340 (s), 1220 (s), 1189 (ms), 1142 (ms), 1130 (ms), 1120 (vs), 1100 (ms), 1062 (s), 1050 (ms), 891 (ms), 830 (w), and 615 (w, br) cm^{-1}. **Bis(dimethylamino)methane, $H_2C[N(CH_3)_2]_2$,** was prepared from $LiN(CH_3)_2$, 274 mmol (14.00 g), in *ca.* 150 ml of $C_{10}H_{22}$ (slurry) by dropwise treatment with CH_2Cl_2, 140 mmol (8.5 ml); the resultant mixture was stirred for 2 days followed by reflux at 85° and 40 Torr He pressure. All products passing through a cold-water condenser were collected in a −196° trap and found to be a mixture of CH_2Cl_2, $NH(CH_3)_2$, and $CH_2[N(CH_3)_2]_2$ from which $CH_2[N(CH_3)_2]_2$ was separated by fractional condensation in a −45° trap. Vapor tension data agreed with the literature values.[4] Parent mass was *m/e* 104. Infrared data: 2958 (vs), 2860 (sh), 2820 (vs), 2780 (vs), 1465 (vs), 1454 (vs), 1392 (s), 1389 (s), 1276 (s), 1220 (s), 1101 (w), 1053 (s), 864 (m), 406 (w), and 384 (m) cm^{-1}. **Deuteriomethylene chloride, CD_2Cl_2,** obtained from Merck Sharp and Dohme, Montreal, Canada (99 atom % D), was dried over $LiAlH_4$ for 2 days at 25° followed by fractional condensation through a −63° trap to a −196° trap. Ir data: 2230 (m), 2211 (m), 1413 (w), 1010 (mw), 975 (vs), and 729 (vs) cm^{-1}. **Vanadium(III) chloride, VCl_3,** was prepared as previously reported.[6] **Vanadium(III) chloride–tris(pyridine), $VCl_3 \cdot 3py$,** was prepared by heating VCl_3, 0.422 mmol (66.5 mg), with py, 3.3 mmol, at 60° to afford a deep purple solution and precipitate. Pyridine was removed, *in vacuo*, over a 4-hr period to afford a purple solid, 0.1708 g. Infrared data: 3048 (w), 1675 (w), 1630 (w), 1601 (vs), 1580 (m), 1570 (m), 1559 (m), 1529 (m), 1480 (s), 1441 (vs), 1382 (w), 1239 (m), 1219 (s), 1157 (m), 1130 (w), 1070 (s), 1044 (s), 1013 (s), 958 (w), 880 (w), 780 (w), 760 (s), 740 (m), 698 (vs), 671 (m), 639 (m), 465 (mw), 440 (s), 392 (w), 380 (s), 350 (s), 333 (vs), 322 (vs), 290 (s), and 264 (w) cm^{-1}.

Preparation and Characterization of Bis(dimethylamino)methane Vanadium(III) Chloride, $VCl_3 \cdot [N(CH_3)_2]_2CH_2$. Treatment of VCl_4 with $B_2[N(CH_3)_2]_4$ was carried out 38 different times to determine the effect of reaction time, reaction temperature, concentration, solvent, order of reagent addition, phase of reagents combined, and final reagent stoichiometry on the yield of I. The highest yield was obtained from the following procedure. A solution of $B_2[N(CH_3)_2]_4$, 5.55 mmol (1.0983 g), in 5.8876 g of deuteriomethylene chloride, CD_2Cl_2, was prepared in a 20-ml tared bulb. Vanadium tetrachloride vapor, 2.23 mmol (0.429 g), was added to this solution at −78°. There was no immediate formation of insoluble material. The solution was maintained at 25° for 1 week during which red-orange and black material precipitated. The soluble red-orange product was isolated from the insoluble phases by washing with CD_2Cl_2. Maintaining the soluble product in CD_2Cl_2 for 4 days at 25° produced additional red-orange crystals. Volatile materials were removed, *in vacuo*, by maintaining the nonvolatile soluble phase at 10^{-4} Torr for 2 days. Fractionation of this volatile mixture through 0° and −45° traps into a trap maintained at −196° resulted in isolation of residual $B_2[N(CH_3)_2]_4$, 2.58 mmol (0.51 g), $B[N(CH_3)_2]_3$, 0.90 mmol (0.1288 g), and solvent. Characterization of these volatile materials was accomplished by vapor tension and ir data. Two solids were observed in the "insoluble phase," a red-orange crystalline material, I (which was found to be slightly soluble in CD_2Cl_2 and recrystallized therefrom), and a small amount of a gray-purple solid, completely insoluble in CD_2Cl_2. Separation of these two materials was effected by continuous extraction, *in vacuo*, employing a medium-porosity glass frit. *Anal.* Calcd for $VCl_3[N(CH_3)_3]_2CH_2$: V, 19.6; Cl, 41.0; N, 10.79. Found: V, 20.1; Cl, 40.4; N, 10.85. No H_2 is evolved during basic or acidic hydrolysis of I. The magnetic susceptibility of a 0.6038-g sample of I is $\chi_g = 14.23 \times 10^{-6}$ cgsu. Infrared data for I: 3045 (w), 3037 (w), 3017 (w), 2939 (s), 2920 (s), 2850 (w), 2809 (w), 2796 (w), 1459 (vs), 1450 (w, sh), 1429 (w, sh), 1411 (mw), 1403 (mw), 1376 (w, br), 1335 (w, sh), 1291 (w), 1241 (m), 1226 (ms), 1195 (w), 1173 (w), 1118 (mw), 1100 (mw), 1041 (s), 1003 (vs), 998 (vs), 963 (s), 895 (w), 861 (vs), 831 (m), 684 (w), 660 (w), 557 (m), 498 (m, sh), 474 (s), 391 (s), 357 (vs), 333 (vs), and 295 (s) cm^{-1}.

Reaction of I with Pyridine (py). Treatment of I, 1.53 mmol (0.3969 g), with *ca.* 10 ml of pyridine produces a purple solution. Volatile materials were removed, *in vacuo*, at 25° affording 1.59 mmol (0.6300 g) of $VCl_3 \cdot 3py$ which was characterized by comparison of its ir spectrum with one from an authentic sample. Volatile materials from this reaction were fractionated, from a trap warming from −196° through two −63° traps into a −196° trap. The contents of the −63° traps were characterized as pyridine by its ir spectrum and vapor tension, 4.5 Torr at 0°, (lit. 4.1 Torr). The −196° fraction was characterized as bis(dimethylamino)methane, $H_2C[N(CH_3)_2]_2$, by comparison of its ir spectrum with a spectrum of an authentic sample using the "Stadtler Index of Infrared Spectra" (No. 15389). A duplicate reaction, with 0.42 mmol (0.1090 g) of I, produced 0.401 mmol of $H_2C[N(CH_3)_2]_2$.

Reaction of I with HCl. Treatment of finely ground I, 0.24 mmol (62.1 mg), contained in a 9.1-ml bulb, with HCl, 0.487 mmol, affords a homogeneous appearing purple solid over a 5-hr period at 25°. After 5 hr the rate of HCl uptake, as determined tensimetrically, was negligible; final HCl pressure was 715 Torr. HCl, 0.350 mmol, was recovered unreacted and a total of 67.1 mg of purple solid was obtained. Infrared data: 3120 (s, br), 3053 (sh), 3035 (sh), 2995 (sh), 2968 (sh), 2941 (s), 2860 (sh), 2800 (m, br), 1698 (m), 1573 (m, br), 1470 (vs), 1462 (vs), 1453 (s, sh), 1430 (m, sh), 1402 (m), 1247 (m), 1228 (m), 1199 (vs), 1173 (w), 1122 (w), 1107 (w), 1048 (m), 1008 (ms), 1000 (ms), 967 (m), 919 (vw), 890 (vs), 868 (s), 834 (m), 683 (vs), 663 (vw), 589 (vw, br), 560 (w), 400 (w, sh), 478 (m), 469 (m, sh), 425 (m), 392 (ms), 358 (s), 336 (s), 306 (s, sh), and 299 (s) cm^{-1}. Treatment of 58.0 mg of this material with 1.88 mmol of HCl produced vigorous bubbling. Residual HCl, 1.57 mmol, was recovered, and the residue mass was 70.6 mg. Infrared data: 3120 (s), 3045 (w), 3037 (w), 3017 (w), 2988 (m), 2939–2920 (s), 2840 (w), 2809 (w), 2796 (w), 2700 (ms), 2400–2500 (m), 1697 (m), 1604 (m), 1573 (m), 1561 (m, sh), 1459 (vs), 1450 (w, sh), 1429 (w, sh), 1411 (wm), 1403 (w), 1376 (w, br), 1335 (w, sh), 1291 (w, br), 1241 (m), 1226 (ms), 1195 (w), 1173 (w), 1118 (w), 1100 (s), 1041 (s), 1003 (vs), 998 (vs), 963 (s), 895 (w), 861 (vs), 831 (m), 684 (w), 660 (w), 557 (w), 498 (w, sh), 474 (s), 391 (s), 357 (vs, br), 333 (vs), and 295 (vs, sh) cm^{-1}.

Reaction of $CH_2[N(CH_3)_2]_2$ with HCl. A 5.00-mmol (0.5100-g) sample of $CH_2[N(CH_3)_2]_2$ was treated with excess HCl at −95° for 2 hr. Removal of volatile materials at 25° afforded 0.6881 g of nonvolatile white solid. This solid was heated at 100°, *in vacuo*, for 30 hr to a constant weight 0.8788 g (10.1 mmol of HCl absorbed). Infrared data: 3180 (w, sh), 3050 (m, sh), 3030 (m, sh), 2980 (s), 2940 (s), 2770 (s), 2510 (w), 2435 (m), 2350 (w), 2220 (m), 2110 (w), 1885 (w), 1770 (w), 1680 (m), 1598 (m), 1598 (m, sh), 1480 (s, sh), 1470 (s), 1465 (s), 1450 (m, sh), 1432 (w), 1410 (w), 1380 (w), 1330 (w), 1255 (w), 1168 (s), 1020 (m), 992 (m), 882 (m), 498 (m), and 428 (s) cm^{-1}.

Preparation of $(CH_3)_2NH_2^+Cl^-$. Equimolar quantities of $(CH_3)_2NH$ and HCl were combined in the gas phase. Ir data of the white solid residue: 3192 (w), 2972 (s, br), 2932 (s), 2822 (m), 2772 (s, br), 2435 (s), 1602 (w, sh), 1598 (w), 1467 (m), 1427 (w), 1410 (w), 1400 (w), 1252 (m), 1227 (sh), 1172 (w), 1152 (w, br), 110 (w), 1020 (s), and 882 (s) cm^{-1}.

Preparation of Dimethylmethyleneammonium Chloride, $(CH_3)_2NCH_2^+Cl^-$. According to the method of Bohme and Haake,[20] 9.11 mmol (0.9302 g) of $CH_2[N(CH_3)_2]_2$ was diluted with 1.81 g of CH_3CN in a 20-ml weighing vial. Acetyl chloride, 7.41 mmol (0.5815 g), was admitted slowly to this clear colorless solution with constant stirring. Volatile components were removed from the white nonvolatile solid *in vacuo*. The total amount of residual nonvolatile white solid was 0.6992 g. Ir data: 3080 (m), 3013 (sh), 2988 (m), 2910 (sh, br), 1893 (wm), 1678 (m), 1511 (sh), 1498 (m), 1481 (m), 1464 (m), 1450 (ms), 1381 (m), 1333 (m), 1172 (vs), 1078 (s), 992 (vs), 921 (w), 720 (w), 500 (s), 430 (s) 345 (w), and 280 (w, sh) cm^{-1}.

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Registry No. $VCl_3 \cdot [N(Me)_2]_2CH_2$, 51022-56-1; VCl_4, 7632-51-1; $B_2[N(Me)_2]_4$, 1630-79-1.

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