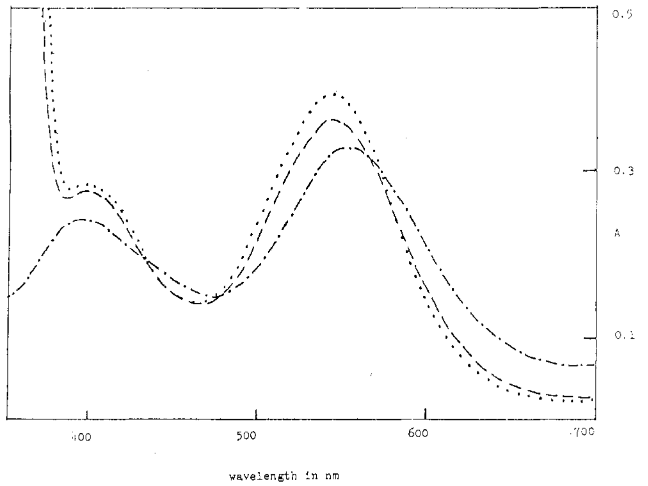

Figure 2. Spectra in acetone solution (0.003 M): -·-, [Cr(py)$_3$(NCO)$_3$]; ---, *mer*-[Cr(py)$_3$(NCS)$_3$]; ···, *fac*-[Cr(py)$_3$(NCS)$_3$].

Table II. Spectra in Acetone Solution[a]

mer-[Cr(py)$_3$(NCS)$_3$]: λ_{max} 546 nm, ϵ 121; λ_{max} 399 nm, ϵ 93
fac-[Cr(py)$_3$(NCS)$_3$]: λ_{max} 545 nm, ϵ 133; λ_{max} 398 nm, ϵ 97
[Cr(py)$_3$(NCO)$_3$]: λ_{max} 556 nm, ϵ 110; λ_{max} 393 nm, ϵ 83

[a] ϵ is the molar absorptivity in L mol^{-1} cm^{-1}.

200–300 cm^{-1} region was not well-defined to assign characteristic Cr–py vibrations.

Visible spectra in acetone solutions recorded on a 118 Cary spectrophotometer are given in Figure 2. The results are summarized in Table II. While the spectra are practically identical, higher molar absorptivitiy of the facial isomer is in keeping with the higher dipole moment of the isomer. N-Bonded cyanates have been found to produce a weaker crystal field in complexes[17] compared to the corresponding *N*CS compounds.

The lowest energy d–d transition band in the *N*CS compounds has shifted by 10 nm in the *N*CO compound. This red shift is of a magnitude expected for a transition from *N*CS to *N*CO.

The polar cis octahedral compounds of the type MA_4B_2 are found to have a lower R_f value in thin-layer chromatograms compared to the corresponding trans compounds. The same effect was reported for *fac* isomers.[13] The three Cr(III) complexes are soluble in acetone, *fac*-[Cr(py)$_3$(NCS)$_3$] being the most and [Cr(py)$_3$(NCO)$_3$] the least of the three. On silica gel all the three compounds ran with the solvent front in acetone. Ethanol effected a separation, but nitromethane was found to be the most suitable solvent. Sample sizes of 2–5 μL in acetone solutions of the compounds were applied, and chromatograms developed in nitromethane. The compounds are highly colored and can be spotted directly on the chromatograms. The R_f values were fairly reproducible. Table III summarizes the results.

On the basis of infrared and visible spectra we have designated the ethanol-soluble [Cr(py)$_3$(NCS)$_3$] prepared by Patel as the facial isomer. The ethanol-insoluble [Cr(py)$_3$(NCS)$_3$] was prepared from *trans*-[Cr(NCS)$_4$(NH$_3$)$_2$]$^-$ and pyridine. It is reasonable to assume that the two trans NH$_3$ groups were first displaced by pyridine, forming the *mer* isomer. This is supported by infrared and visible spectra, as well as its higher R_f value in TLC. Very high R_f for the [Cr(py)$_3$(NCO)$_3$] may indicate its *mer* or low-polarity character.

So far our attempts to isolate any cyanato-*O* isomer in the pure state have been unsuccessful. It was, however, found that a cold acetone solution of *mer*-[Cr(py)$_3$Cl$_3$] reacts with solid silver cyanate, AgNCO, which is known to be N bridged[18] to yield a blue-violet solution with absorption bands at 572 and 447 nm, with a shoulder at 430 nm. The shift of d–d band from 556–572 nm may indicate formation of cyanato-*O* coordination. Even though the infrared spectra of solids isolated from such reaction products indicated a possible Cr–OCN coordination, the purity was unsatisfactory and indicated that cyanato-*O* initially formed led to OCN bridging by eliminating pyridine and resulting in polymeric forms.

Table III[a]

	R_f	R_f/R_f(*fac*-[Cr(py)$_3$(NCS)$_3$])
fac-[Cr(py)$_3$(NCS)$_3$]	0.41	1.00
mer-[Cr(py)$_3$(NCS)$_3$]	0.49	1.20 ± 0.02
mer(?)-[Cr(py)$_3$(NCO)$_3$]	0.86	2.10 ± 0.03

[a] Solvent nitromethane; TLC Eastman Chromagram Sheet 6061; silica gel without fluorescent indicator; room temperature 24 °C.

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Registry No. *mer*-[Cr(py)$_3$(NCS)$_3$], 71629-72-6; *mer*-[Cr(py)$_3$(NCO)$_3$], 71606-77-4; *fac*-[Cr(py)$_3$(NCS)$_3$], 71629-73-7; NH$_4$[Cr(NH$_3$)$_2$(NCS)$_4$], 13573-16-5.

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Contribution from the Chemistry Department,
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1,1-Dimethyl-1,3-azoniaboratacyclobutane

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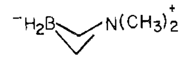
The title four-membered heterocycle, **1**, with two coterminus



1

BCN sequences, has been isolated and characterized among the products from the reaction of *tert*-butyllithium and the BCN-sequenced salt[1] (CH$_3$)$_3$NBH$_2$CH$_2$N(CH$_3$)$_3$$^+Cl^-$. The heterocycle is named as a cyclobutane replacement derivative

Table I. Characterization Data

	analyses, %						hydrolytic H, μmol/mg	
	C		H		N			
compd	calcd	found	calcd	found	calcd	found	calcd	found
I	56.5	57.0	14.2	14.2	16.5	16.0	22.8	23.5
4	29.2	29.0	7.0	6.8	9.7	9.5		

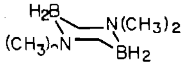
Table II. Low-Resolution Mass Spectral Data of **1**[a]

m/e	intens	*m/e*	intens
84	15.4	59	32
83	3.8	58 $(CH_3)_2NCH_2^+$	100
70	3.7	57	3.7
68	1.7	56	9.0
66	1.5	42	40.2
60	1.0	41	15.4

[a] Finnigan 3200 quadrupole; direct inlet; Battelle Memorial Institute.

and is shown in one of the rapidly inverting "butterfly" conformations which accord with the observed ^1H NMR. It is a white crystalline solid, melting at 88–89 °C, which sublimes under high vacuum at 40 °C. It is stable and soluble in water with barely noticeable hydrolysis, but it hydrolyzes rapidly in dilute acid. It is soluble in polar organic solvents but not in hexane.

Structurally, **1** is closely related to two other known valence-saturated, BCN-sequenced heterocycles, **2**[2] and **3**,[3] yet



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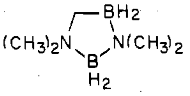

3

it differs from these in two important ways: there are no B–N bonds in **1**, and the B atom in **1** is sterically less shielded. Both features strongly influence the chemical and physical properties.

The fixed, separated formal charges on the $-BH_2-$ and $-N(CH_3)_2-$ moieties of **1** are much like those on $-CO_2$ and $-N(CH_3)_3$ moieties of betaines, and a polar structure—more pronounced than that of **2** or **3**—results, with concomitant lower solubility in nonpolar solvents. The formal charges from dative bonds in **2** and **3** do not lead to as much polarity because the charges are not separated and are offset by electron drift via the σ bond.

As other studies have supported,[4] steric hindrance of four-coordinate boron in simple borane structures is a prime factor affecting hydrolytic stability. The flanking of boron in **1** by the steric equivalent of two *sec*-butyl groups is not unlike that of the reactive borane in the aminoborohydride[5] $(CH_3)_2\ddot{N}CH_2BH_2CH_2N(CH_3)_2BH_2CH_2\ddot{N}(CH_3)_2^-$. The rather similar properties of moderate stability toward water, sensitivity toward acid hydrolysis, and facile iodination of **1** and the aminoborohydride can be attributed to the steric factor.

The composition and structure of **1** are supported by elemental analyses, hydrolytic hydrogen assay, and infrared and mass spectral data (Tables I–IV). The hydrolytic hydrogen assay clearly excludes $(CH_3)_3NCH_2BH_3$ as a structure possibility—if for no other reason. Mass spectral data at low resolution support the molecular weight and at higher resolution support the formulation. The high mass cluster is nicely explicable by a one-boron P – 1 fragment (Table III). Appropriately, there is little of the *m/e* 70 fragment characteristic of **2**,[6] **3**,[7] and other related derivatives,[6] since easy fragmentation via dative bonds is not possible for **1**.

^1H NMR of **1** shows two resonances (Figure 1), a multiplet at 3.25 ppm and a sharp singlet at 2.93 ppm of integrated intensity ratio 2:3. The sharpness of the upfield peak (3 Hz at half-height), assigned to *N*-methyl protons is comparable to that observed in the *N*-methyl peak of **2**. Broader *N*-methyl resonances in **3** (9 and 5 Hz) are attributed to quadrupole broadening from boron.[7] Multiplet features of the downfield methylene cluster are characteristic of methylene linked to boron and arise in part from ^{10}B and ^{11}B coupling. The chemical shift and position of the methylene downfield from

Table III. High-Resolution Mass Spectral Data[a]

	m/e		intens	
species	calcd	obsd	calcd[b]	obsd
$C_4H_{12}{}^{11}BN$	85.1063			
$C_4DH_{10}{}^{11}BN$	85.1047		0.14	
$^{13}CC_3H_{11}{}^{11}BN$	85.1018	85.1031	3.8	5.9
$C_4H_{11}{}^{11}B^{15}N$	85.0955		0.30	
$C_4H_{12}{}^{10}BN$	84.1099			
$C_4H_{11}{}^{11}BN$	84.0984	84.0978	84.6	84.6
$^{12}CC_3H_{10}{}^{11}BN$	83.1052			
$C_4H_{11}{}^{10}BN$	83.1021	83.1014	20.6	20.7
$^{13}CC_3H_{10}{}^{10}BN$	83.0976			
$C_4H_{10}{}^{11}BN$	83.0885	83.0895		2.4

[a] MS-9; Battelle Memorial Institute. [b] Based upon $C_4H_{11}{}^{11}BN$ normalized to 84.6%.

Table IV. Infrared Data[a]

compd	absn freq, cm^{-1}
1	2300 (s, br, d, sh), 2080 (w), 2050 (w), 2000 (w), 1420 (w), 1390 (w), 1310 (m), 1240 (w), 1220 (s), 1190 and 1180 (s, d), 1110 (w), 1050 (w), 1040 (s), 975 (s), 945 (s), 860 (s), 820 (w)
4	2425 and 2400 (m, d), 1420 (w), 1375 (m), 1320 (m), 1260 (s), 1240 (w), 1150 (s), 1120 (s), 1080 (w), 1060 (m), 980 (s), 850 (s, br, sh)

[a] As mineral oil mulls. Bands coincident with mineral oil excluded. Abbreviations: s = strong; m = moderate; w = weak; br = broad; d = doublet; sh = shoulders.

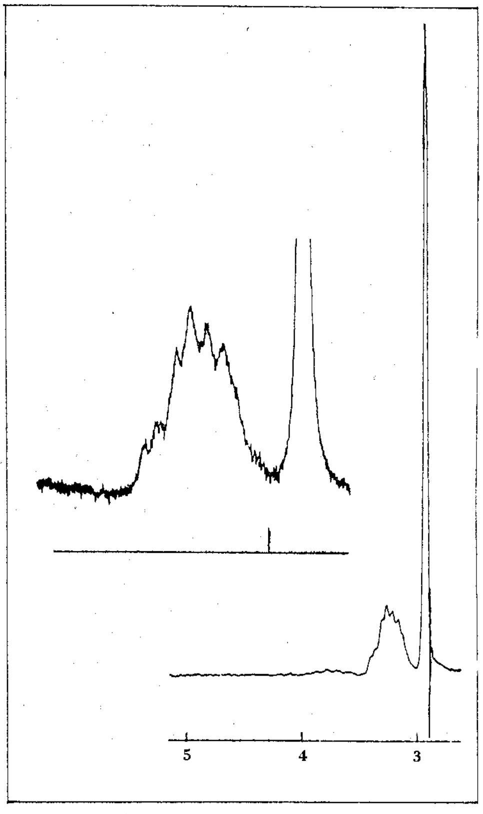

Figure 1. ^1H NMR spectrum of **1** in $CDCl_3$. Chemical shift is given in ppm. Inset shows the expanded field of methylene resonance.

N-methyl are upon first consideration surprising. Ordinarily the positions are inverted, and both are further upfield in other related BCN compounds such as **2** and **3**. However, four-membered rings and particularly nitrogen-containing heterocycles are known to display methylene protons "deshielded to an unusual extent".[8] In *N*-ethyl-*N*-methylazetidinium ion, for example, the α-methylene resonance is an AB quartet centered at 4.45 ppm and nearly 1 ppm downfield from *N*-methyl.[9] The absence of fine structure in the *N*-methyl resonances of **1** is explicable by planar or rapidly inverting "butterfly" conformations. It is more plausible to infer the butterfly conformation because of its decreased distance between charge centers and its similarity to *N*-dimethylazetidinium[8] ion which is nonplanar.

Exploration of the chemical properties of **1** reveals, beside the stated hydrolytic sensitivity, a facile iodination (and bromination). The qualitatively observed rate is more rapid than that of **2** or even that of trimethylamine–borane and in degree resembles that observed for the sterically similar borane in the aminoborohydride, $(CH_3)_2\dot{N}CH_2BH_2CH_2N(CH_3)_2BH_2CH_2\dot{N}(CH_3)_2^-$. Displacement of the iodine by trimethylamine led to a stable cation

Again, steric protection of borane is the key to aqueous stability. Further chemical characterization of this interesting and reactive heterocycle is a matter of continuing research.

Experimental Section

$(CH_3)_3NCH_2BH_2N(CH_3)_3^+Cl^-$. This compound was prepared by ion exchange of the corresponding iodide salt obtained from the reaction of methyl iodide and $(CH_3)_3N{\cdot}BH_2CH_2N(CH_3)_2$ (trimethylamine–[(dimethylamino)methyl]borane). Synthesis of the latter compound is reported elsewhere,[1] but the method has given erratic yields. Presently we are using 1 molar equiv of *n*-butyllithium in pentane, rapidly added to a stirred hexane suspension of $[(CH_3)_3N]_2BH_2^+Cl^-$ initially at −78 °C. After 2 h, fractional condensation of volatiles leads to 29% yield of $(CH_3)_3N{\cdot}BH_2CH_2\dot{N}(CH_3)_2$ in a −35 to −50 °C trap. A solution of the product in hexane when treated with excess methyl iodide precipitates the iodide salt mentioned earlier, as a finely divided white solid.

$(CH_3)_2\overline{NCH_2BH_2CH_2}$ (1). This compound is obtained from reaction of *t*-BuLi and $(CH_3)_3NCH_2BH_2N(CH_3)_3^+Cl^-$ in 1:1 molar ratio. A suspension of 524 mg (2.90 mmol) of chloride salt (rendered anhydrous by high-vacuum pumping at 50 °C) in about 5 mL of hexane is treated with 1.5 mL (2.90 mmol) of 2.0 M *tert*-butyllithium in pentane. In about 2 min a vigorous reaction ensues which causes solvent to reflux and imparts a temporary (0.5 h) yellow coloration to the mixture. After stirring of the mixture about 20 h, the volatiles are removed and the residue is sublimed under high vacuum at 40–80 °C: yield, 164 mg of crude product, 67%. Purification could not be effected by repeated sublimation. Trituration of 71 mg in 2 × 0.5 mL of deionized water and filtration yielded a solution from which 36 mg of pure **1** could be obtained by careful evaporation and sublimation; mp 88.5–89.5 °C. About 5 mg of a yet uncharacterized water-insoluble white solid remained from the first extraction. Its presence as an impurity in the crude product was verifiable by examination of infrared and ^1H NMR spectra of crude and purified products and isolated impurity.

$\overline{CH_2(CH_3)_2NCH_2B}HN(CH_3)_3^+PF_6^-$ (4). A solution of an unpurified sample of **1** (150 mg, 1.76 mmol) in 10 mL of chloroform was treated with 10 mL of a solution containing 224 mg (0.88 mmol of I_2) iodine. About 80% of the iodine solution was added over a 2-min period when no further decoloration was observed, and addition was stopped. Solvent was removed under vacuum and the residue metathesized to the hexafluorophosphate salt; yield 77 mg, 15%.

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Registry No. **1**, 71371-27-2; **4**, 71370-66-6; $(CH_3)_3NCH_2BH_2N(CH_3)_3^+Cl^-$, 71370-68-8.

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Trimethylbis[bis(trimethylsilyl)amido]tantalum(V) and [(Trimethylsilyl)methyl][(trimethylsilyl)methylidene]bis[bis(trimethylsilyl)amido]tantalum(V)

Richard A. Andersen

Received April 3, 1979

Five-coordinate group 5B amides are limited to some binary ones of the type $(Me_2N)_5M$ where M is either niobium or tantalum.[1-3] The niobium complex has been examined crystallographically and shown to be square pyramidal.[4] Some dialkylamido derivatives, $(Et_2N)_2MF_3$ (M = Nb or Ta)[5] and $(Me_2N)_2TaMe_3$,[6] have also been described though their structures are not known. We now describe some bis(trimethylsilyl)amido derivatives of the type $[(Me_3Si)_2N]_2TaR_3$.

Tantalum pentachloride reacts with either 2 or 3 molar equiv of sodium bis(trimethylsilyl)amide in diethyl ether, yielding $[(Me_3Si)_2N]_2TaCl_3$ which crystallizes from pentane as yellow prisms. The monomeric (by mass spectroscopy), five-coordinate complex shows a single resonance in its ^1H and $^{13}C\{^1H\}$ NMR spectra at δ 0.57 and 4.69, respectively. The former is temperature independent to −80 °C, indicating that the compound is either fluxional or stereochemically rigid with equivalent $(Me_2Si)_2N$ groups.

The infrared spectrum of the chloro amide consists of five strong absorptions in the metal–nitrogen and metal–chloride regions at 415, 401, 374, 338, and 315 cm^{-1}. A group-theoretical analysis could offer a choice between the six possible idealized X_3Y_2M square-pyramidal or trigonal-bipyramidal geometric isomers (Chart I). The two C_{2v} and three C_s isomers will each have a maximum of six metal–chloride and three metal–nitrogen absorptions possible, whereas the D_{3h} isomer will only have one metal–chloride and one metal–nitrogen allowed absorption. The observed solid-state infrared spectrum definitely rules out the D_{3h} isomer but does not allow us to distinguish among the C_{2v} or C_s isomers.

The characterization of the idealized geometry of the five-coordinate complex would be facilitated by replacement of the chloride ligands with groups which would give nuclear magnetic resonance absorptions, e.g., a methyl group. Trimethylbis[bis(trimethylsilyl)amido]tantalum can be prepared from the chloro derivative and methyllithium. The yellow $Me_3Ta[N(SiMe_3)_2]_2$ is monomeric (by mass spectroscopy) and rather volatile (sublimation temperature 40–50 °C (10^{-2} torr)). The ^1H NMR spectrum at room temperature consists of three single resonances at δ 1.40, 1.27, and 0.52 in an area ratio of 6:3:36. The first two resonances are due to two different types of methyl–tantalum groups in a 2:1 area ratio and the latter is due to the trimethylsilyl resonance. This result eliminates the D_{3h} isomer (Chart I) but does not allow us to distinguish

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