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, $(CH_3)_2\ddot{N}CH_2BH_2CH_2N(CH_3)_2BH_2CH_2\ddot{N}(CH_3)_2^-$. 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 $(CH_3)_3N\cdot BH_2CH_2\ddot{N}(CH_3)_2$ 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.

$(CH_3)_2\overline{NCH_2BH_2C}H_2$ (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.

References and Notes

(1) N. E. Miller and D. L. Reznicek, *Inorg. Chem.*, **8**, 275 (1969).
(2) N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964); N. E. Miller, M. D. Murphy, and D. L. Reznicek, *ibid.*, **5**, 1832 (1966).
(3) B. R. Gragg and G. E. Ryskewitsch, *J. Am. Chem. Soc.*, **96**, 4717 (1974).
(4) N. E. Miller, *J. Am. Chem. Soc.*, **92**, 4564 (1970).
(5) N. E. Miller, *J. Organomet. Chem.*, **137**, 131 (1977).
(6) (a) N. E. Miller, *Inorg. Chem.*, **16**, 2664 (1977). (b) T. H. Hseu and L. A. Larsen, *ibid.*, **14**, 330 (1975).
(7) B. R. Gragg and G. E. Ryskewitsch, *Inorg. Chem.*, **15**, 1201 (1976).
(8) O. E. Edwards, G. Fodor, and L. Marion, *Can. J. Chem.*, **44**, 13 (1966).
(9) E. J. Goethals and E. H. Schacht, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 497 (1973).

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

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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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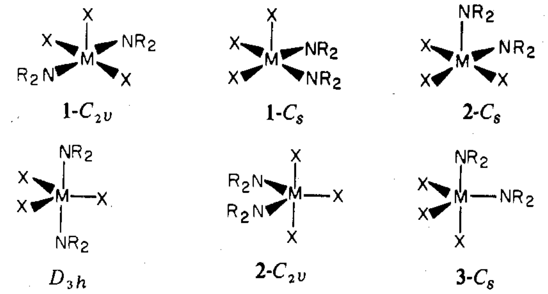
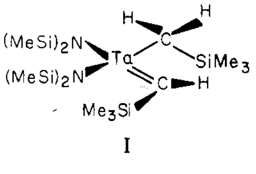
Chart I



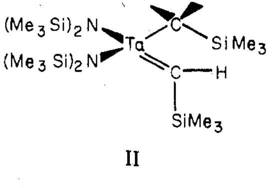
among the other possible isomers. The $^{13}C\{^1H\}$ spectrum confirms the proton NMR result in that two different methyl–tantalum envionments are observed whose chemical shifts are δ 65.0 and 56.5. The carbon spectrum of the trimethylsilyl groups is more informative since it shows two equal-area resonances at δ 3.57 and 3.34. This latter datum shows that isomer **2**-C_{2v} cannot exist in solution if it is assumed that the Me_3Si groups are orientated orthogonal to the equatorial (N_2TaX) plane. Thus, we can reduce the isomer count to 4 and we can go no further. Of the four remaining idealized geometric isomers we favor the C_{2v} one since the sterically voluminous silylamide groups will doubtless prefer to be as far away from each other as possible. This is only possible in the C_{2v} isomer as the C_s isomers all have idealized N–M–N bond angles of 90°.

It should be possible to provide a further stereochemical distinction between the solution isomers by using an alkyl group bonded to tantalum that has potentially nonequivalent methylene groups; the β-elimination-stabilized Me_3SiCH_2 group is an ideal one. Reaction of the chloro amide with $LiCH_2SiMe_3$ does not afford the trialkyl but instead yields the alkyl–alkylidene complex $(Me_3SiCH_2)(Me_3SiCH)Ta[N(SiMe_3)_2]_2$. The yellow, pentane-soluble, monomeric (by mass spectroscopy) complex is essentially air stable. The carbene formulation is assigned with certainty by the ^{13}C NMR spectrum which shows the $(Me_3Si)_2N$ groups at δ 5.80 and the Me_3Si groups bonded to the methylene and methine carbon atoms at δ 3.53 and 2.45. A definitive assignment of these latter two equal-area resonances cannot be made though this is not germane to the arguments presented here. The methylene carbon atom resonates at δ 62.8 which yields a triplet in the ^1H-coupled spectrum, J_{CH} being 104 Hz. The proton-coupled spectrum shows the methine carbon atom as a doublet (J_{CH} = 95 Hz) at δ 231, in the region for carbene–metal resonances.

The formulation of this complex as an alkyl–alkylidene complex is thus substantiated. However, two rotational isomers (I or II) are possible depending upon whether the carbene ligand is orientated perpendicular (I) or parallel (II) to a plane which bisects the N_2Ta unit. In I the methylene protons are nonequivalent and will yield an AB pattern, whereas in II the hydrogen atoms are equivalent and will yield a single resonance in the ^1H NMR spectrum. The observed spectrum at +35 and −85 °C shows a single resonance at δ 0.57. Unfortunately, the observation of a single methylene resonance is not sufficient to prove which conformation is present in solution since the Ta═C rotation barrier could be small or the methylene protons could be degenerate. The methylene protons in $Cp_2Ta(CH_2Ph)(CHPh)$[8] and $Cp_2Ta(CH_2SiMe_3)(CHSiMe_3)$[9] are nonequivalent, but those in $(Me_3CCH_2)_3Ta(CHCMe_3)$[10] are equivalent. Thus, no definitive conclusion can be reached on the basis of the ^1H NMR spectrum. However, conformation II, with equivalent methylene protons, is sterically the most favorable one.



I



II

Experimental Section

Analyses were by the microanalytical laboratory of this department. Proton nuclear magnetic resonance spectra were recorded on a modified Bruker 1180 machine operating at 180 MHz in benzene-d_6 or toluene-d_8. Carbon nuclear magnetic resonance spectra were recorded on the Bruker 1180 machine operating at 45.29 MHz in benzene-d_6 and referenced to Me_4Si (δ 0). All operations were performed under nitrogen.

Trichlorobis[bis(trimethylsilyl)amido]tantalum(V). Sodium bis(trimethylsilyl)amide (0.98 g, 0.0054 mol) in diethyl ether was added to tantalum pentachloride (0.96 g, 0.0027 mol) suspended in diethyl ether (30 mL) at 0 °C. The mixture was stirred at 0 °C for 24 h. The diethyl ether was evaporated under vacuum, and the residue was extracted with pentane (50 mL) and filtered. The filtrate was concentrated to ca. 10 mL under vacuum and cooled (−70 °C). The yellow needles were collected and dried under vacuum; mp 150–151 °C. The yield was 1.3 g (78%). Anal. Calcd for $C_{12}H_{36}Cl_3N_2Si_4Ta$: C, 23.7; H, 5.93; Cl, 17.5; N, 4.61. Found: C, 23.9; H, 5.96; Cl, 17.1; N, 4.52.

Trimethylbis[bis(trimethylsilyl)amido]tantalum(V). Methyllithium (9.5 mL of a 0.50 M diethyl ether solution, 0.0047 mol) was added to a solution of trichlorobis[bis(trimethylsilyl)amido]tantalum (0.96 g, 0.0016 mol) in pentane (40 mL) at 0 °C. The mixture was stirred at this temperature for 8 h. The suspension was allowed to settle, the supernatant was filtered, and the filtrate was evaporated under vacuum to dryness. The residue sublimed (40–50 °C (10^{-2} torr)) as light yellow plates, mp 65–67 °C. The yield was 0.44 g (50%). Anal. Calcd for $C_{15}H_{45}N_2Si_4Ta$: C, 33.0; H, 8.24; N, 5.13. Found: C, 32.6; H, 8.19; N, 5.03.

[(Trimethylsilyl)methyl][(trimethylsilyl)methylidene]bis[bis(trimethylsilyl)amido]tantalum(V). [(Trimethylsilyl)methyl]lithium (5.4 mL of a 0.80 M hexane solution, 0.0043 mol) was added to trichlorobis[bis(trimethylsilyl)amido]tantalum (0.87 g, 0.0014 mol) dissolved in diethyl ether (40 mL) at 0 °C. The mixture was stirred at this temperature for 12 h. The volatile material was removed under vacuum, and residue was extracted with pentane (40 mL). The extract was filtered, and the filtrate was concentrated to ca. 5 mL. Cooling (−70 °C) yielded yellow prisms in 77% (0.70 g) yield; mp 134–135 °C. Anal. Calcd for $C_{20}H_{57}N_2Si_6Ta$: C, 35.6; H, 8.46; N, 4.15. Found: C, 35.3; H, 8.53; N, 4.25. The proton nuclear magnetic resonance spectrum (180 MHz, benzene-d_6) consists of a singlet at δ 6.30 due to $Me_3SiC\mathit{H}Ta$, a singlet at δ 0.57 due to $Me_3SiC\mathit{H}_2Ta$, a singlet at δ 0.50 due to $[(\mathit{Me}_3Si)_2N]_2Ta$, and a slightly broadened singlet at δ 0.47 due to $(\mathit{Me}_3SiCH_2)(\mathit{Me}_3SiCH)Ta$ in an area ratio of 1:2:36:18.

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Registry No. $Cl_3Ta[N(SiMe_3)_2]_2$, 71616-54-1; $Me_3Ta[N(SiMe_3)_2]_2$, 71616-55-2; $(Me_3SiCH_2)(Me_3SiCH)Ta[N(SiMe_3)_2]_2$, 71616-56-3; tantalum pentachloride, 7721-01-9.

References and Notes

(1) Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 1335.
(2) Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 449.
(3) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. A* **1969**, 980.
(4) Heath, C.; Hursthouse, M. G. *Chem. Commun.* **1971**, 143.
(5) Fuggle, J. C.; Sharp, D. W. A.; Winfield, J. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1766.
(6) Santini-Scampucci, C.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 807.
(7) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.
(8) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. L. *J. Am. Chem. Soc.* **1978**, *100*, 3793.
(9) Lappert, M. F.; Milne, C. R. C. *J. Chem. Soc., Chem. Commun.* **1978**, 925.
(10) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.