water may be detected by this method since hydrolysis produces a characteristic brown precipitate.

Analysis. Gallium was determined gravimetrically as the 8-hydroxyquinolate. Halogen was determined by argentometric titration. Raman spectra were recorded on a Cary 81L spectrometer and compared with previously recorded spectra.[2,3]

Discussion

The methods describe the preparation of pure Ga_2X_4 (X = Cl, Br, I) and Ga_4I_6 and are clearly superior to the normal high-temperature methods. Purity is assessed by chemical analysis, melting points for Ga_2Cl_4 and Ga_2Br_4 (Ga_2I_4 and Ga_4I_6 decompose when heated), and Raman spectra which compare very favorably with those obtained from samples prepared by other methods.

The subhalides Ga_4X_6 (X = Br, I) are of interest since they are believed to contain metal–metal bonds and may thus be formulated $(Ga^+)_2Ga_2X_6^{2-}$. Evidence for this formulation rather than one based upon a gallium cluster[6] comes from their Raman spectra which compare very favorably with those of the salts $(R_4N^+)_2Ga_2X_6^{2-}$. A crystal structure determination has unequivocally shown that the metal–metal bonded ions are present in the chloride salts.[7] Ga_4Br_6[5] cannot be prepared by the reduction of gallium(III) bromide with excess gallium metal in benzene solution. A separate experiment has shown that the following decomposition occurs in benzene: $2Ga_4Br_6 \rightarrow 3Ga_2Br_4 + 2Ga$.

Registry No. Ga_2I_4, 17845-89-5; Ga_4I_6, 33088-29-8; Ga_2Cl_4, 24597-12-4; Ga_2Br_4, 18897-61-5; GaI_3, 13450-91-4; $GaCl_3$, 13450-90-3; $GaBr_3$, 13450-88-9.

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A Convenient Synthesis of $N(CH_2CH_2CH_2NH_2)_3 \cdot 4HCl \cdot 0.5H_2O$

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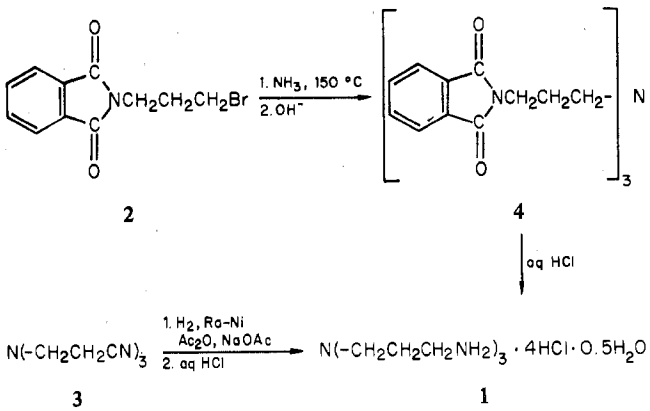
In order to synthesize certain polyamine chelating agents, we required as an intermediate 3,3′,3″-triaminotripropylamine tetrahydrochloride (**1**). This ligand may be prepared from 1-bromo-3-phthalimidopropane (**2**, Scheme I) in extremely low[1] yield by the procedure of Mann and Pope.[2] Workers who recently have studied metal complexes of the free base derived from **1** were unable to obtain the ligand by other methods, including the catalytic reduction of tris(β-cyanoethylamine) (**3**). However, others have succeeded in preparing **1** in 44% yield by reducing **3** with Raney nickel (Ra-Ni) and hydrogen (3200 psi) at 120 °C.[3] Conducting the reduction in the presence of ammonia presumably suppressed polymerization and/or cyclization products expected from the inter- and intramolecular addition of $CH_2CH_2CH_2NH_2$ fragments with $CH_2CH_2CH{=}NH$ fragments.[4] These side reactions also may be blocked by performing nitrile reductions in acetic anhydride solvent using Ra-Ni and sodium acetate.[4] The resulting amine functions are trapped as the *N*-acetyl derivatives; hydrolysis of the reduction products under either basic or acidic conditions may be used to obtain the amines as free bases or salts, respectively. We report here the application of this procedure to the hydrogenation of **3** at low pressure (50 psig). Subsequent acid hydrolysis of the reduction product has afforded **1** in 86% overall yield.

Scheme I



Experimental Section

1. Reduction of 3. The trinitrile (**3**) was prepared in 90% yield from the reaction of acrylonitrile with aqueous ammonia following a published procedure.[3] Excess acrylonitrile and water were removed by rotary evaporation (aspirator pressure, ~95 °C). The resulting brown syrup was dried by the addition of 50 mL of absolute ethanol and further rotary evaporation. Instead of purifying **3** by distillation,[3] we obtained this crystalline product by stirring a mixture of the brown syrup and absolute alcohol at room temperature. The crude product was collected by filtration. After a single recrystallization from warm ethanol, the product melted at 56–58 °C (lit.[3] mp 58–59 °C).

A repetition of the reported rapid and quantitative reduction of adiponitrile to *N*,*N*′-diacetyl-1,6-hexanediamine[4] was used to calibrate the Parr hydrogenation apparatus and to demonstrate the activity of the Ra-Ni catalyst.[5a] A water suspension of the catalyst was dried immediately before using by repeated washing (decantation) with absolute ethanol and, finally, with acetic anhydride. About 3 mL of the catalyst (wet with acetic anhydride) was added to a 500-mL Parr bottle along with 26.4 g (0.15 mol) of **3**, 12.0 g (0.15 mol) of sodium acetate, and 200 mL of acetic anhydride. The quantitative amount of hydrogen was absorbed after 6 h when the reaction was performed at 65–75 °C and 50 psig hydrogen pressure. The sodium acetate was removed by filtration, and the filtrate was concentrated to a thick yellow syrup by rotary evaporation (aspirator pressure, 95 °C). We did not attempt to obtain the *N*-acetyl derivative in crystalline form. The ^1H NMR spectrum of the yellow syrup in deuteriochloroform solution was consistent with the reduction product being the monoacetate salt of tris(3-acetamidopropyl)amine. The nitrile infrared absorption at ~2250 cm^{-1} of the starting material could not be detected in the reduction product.

2. Acid Hydrolysis of the Reduction Product. A solution of the yellow syrup in 100 mL of 37% aqueous hydrochloric acid was refluxed for 12 h. During this time the color of the mixture turned dark brown. Rotary evaporation (aspirator pressure, 95 °C) of the reaction mixture yielded a dark brown solid residue. The residue was dried further by the azeotropic rotary evaporation of remaining water with two 50-mL portions of absolute ethanol. The addition of 200 mL of absolute ethanol to the residue followed by extensive stirring and shaking yielded a tan solid and a brown supernatant liquid which was decanted and discarded. The tan solid was triturated again with 100 mL of absolute ethanol, collected by filtration, and dried in a vacuum oven (aspirator pressure, 90 °C). Forty-four grams (86%) of tan solid was obtained which melted with foaming at 220–222 °C (lit.[2] mp 227–229 °C). Anal. Calcd for $C_9H_{29}N_4Cl_4O_{0.5}$ (**1**): C, 31.49; H, 8.45; N, 16.33; Cl, 41.34. Found: C, 31.61; H, 8.66; N, 16.07; Cl, 40.74.

The product was adequately pure for our needs, and further purification was not attempted. The chemical identity of the product was established further by the high-yield preparation of two known derivatives.

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3. Preparation of Tris(3-phthalimidopropyl)amine (4) and 1-Tetrapicrate (5). Treatment of **1** with a mixture of sodium acetate, acetic acid, and phthalic anhydride[5b] afforded the tris(phthalimido) derivative (**4**) only in poor yield. However, an adaptation of a more forcing procedure used to prepare *N*-alkylphthalimido derivatives for peptide syntheses[6] allowed **4** to be obtained in good yield. A melt of 8.0 g (0.054 mol) of phthalic anhydride, 1.2 g (0.0146 mol) of sodium acetate, and 1.0 g (0.0029 mol) of **1** was maintained at ~200 °C for 15 min, cooled, and then transferred to a beaker containing 400 mL of water. The resulting suspension was heated to boiling and neutralized to pH ~8 by the addition of 10 g of sodium bicarbonate. A tan solid was separated from the aqueous phase by filtration, washed with water, and dried in air. This crude tris(phthalimido) derivative was obtained in 71% yield (1.2 g) and melted at 140–145 °C (lit.[2] mp 150–151 °C). Two recrystallizations from a mixture of 20 mL of dimethylformamide, 8 mL of water, and ~2 g of activated charcoal afforded colorless needles which melted at 150–152 °C. Anal. Calcd for $C_{33}H_{30}N_4O_6$ (**4**): C, 68.51; H, 5.19; N, 9.69. Found: C, 68.28; H, 5.15; N, 9.82.

Addition of a solution of 0.34 g (0.001 mol) of **1** in 100 mL of water to a warm solution of 1.6 g (0.007 mol) of picric acid in 225 mL of water resulted in the immediate precipitation of a yellow solid. A nearly saturated solution of this yellow material was obtained by adding an additional 300 mL of water and heating the mixture to boiling. The hot solution was filtered and stored overnight at 5 °C. The filtrate deposited yellow needles (0.88 g, 79%) which were collected by filtration and dried in a vacuum oven (aspirator pressure, 85 °C). The product melted (with decomposition to a red liquid) in a sealed capillary at 223–224 °C (lit.[2] mp 222 °C). Anal. Calcd for $C_{33}H_{38}N_{16}O_{29}$ (**5**): C, 35.29; H, 3.39; N, 19.96. Found: C, 34.88; H, 3.35; N, 19.95.

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Registry No. **1**, 66322-79-0; **3**, 7528-78-1; **4**, 66322-78-9; **5**, 66322-77-8; phthalic anhydride, 85-44-9; picric acid, 88-89-1.

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Stability and Stereochemistry of Some Amino(bis(trimethylsilyl)amino)boranes[1a]

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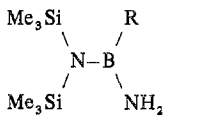
The thermal instability of most primary aminoboranes is illustrated by the results reported by Mikhailov[2] (eq 1) and Neilson[3] (eq 2).

$$PhBCl_2 \xrightarrow[-2NH_4Cl]{4NH_3} [PhB(NH_2)_2] \xrightarrow{-NH_3} {}^1/_3(PhBNH)_3 \quad (1)$$

$$PhB(Cl)NMe_2 \xrightarrow[-NH_4Cl]{2NH_3} [PhB(NH_2)NMe_2] \xrightarrow{-Me_2NH} {}^1/_3(PhBNH)_3 \quad (2)$$

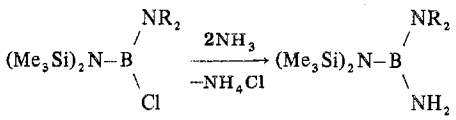
While reactions of this type are fairly well documented,[4] it has also been found that when large groups are attached to boron such condensation reactions are less likely to occur. In particular, we have observed that primary aminoboranes which contain the bis(trimethylsilyl)amino substituent,



R = Ph, $NHSiMe_3$, NMe_2

are indeed quite stable.[5–8]

This paper reports the preparation (eq 3) of three compounds (**4–6**) in this class and offers an explanation of their thermal stability which is consistent with the observation of high rotational barriers about the B–NR_2 bonds in all of the (bis(trimethylsilyl)amino)(dialkylamino)boranes (**1–6**).



(3)

1, R = Me
2, R = Et
3, R = *i*-Pr

4, R = Me
5, R = Et
6, R = *i*-Pr

Experimental Section

Materials. (Bis(trimethylsilyl)amino)chloro(dimethylamino)borane (**1**) was prepared according to the method reported by Paige and Wells.[9] Synthesis of the other *B*-chloro compounds (**2** and **3**) has been previously described by Geymayer and Rochow.[10] These compounds were converted to the corresponding B–NH_2 derivatives (**4–6**) by their reactions with an excess of ammonia according to the following procedures.

Amino(bis(trimethylsilyl)amino)(dimethylamino)borane (4).[5] Compound **1** (18.2 g, 0.073 mol) was dissolved in dry pentane (300 mL) in a flask equipped with a magnetic stirrer. The flask was attached to a vacuum system, cooled to −78 °C, and evacuated. Ammonia (2.5 g, 0.15 mol) was measured at −78 °C and allowed to condense into the reaction flask. The mixture was allowed to warm to room temperature and was stirred overnight. Ammonium chloride (3.9 g, 100% yield) was filtered from the mixture and identified by comparison of its infrared spectrum to that of an authentic sample. Solvent was removed from the filtrate and the liquid residue was distilled to yield compound **4** as a colorless liquid (16.4 g, 97% yield, bp 56–58 °C (2.0 Torr)). The infrared spectrum of the product had two bands between 3450 and 3550 cm^{-1} and a strong band at 1600 cm^{-1}, all indicative of a primary amino function. The proton NMR spectrum of a neat sample gave Me_3Si (δ −0.10):Me_2N (δ 2.38):NH_2 (δ 1.77) = 61:20:6 (calcd 18:6:2). Anal.[11] Calcd for $C_8H_{26}BN_3Si_2$: C, 41.54; H, 11.33; B, 4.67; N, 18.17; Si, 24.29; mol wt, 231. Found: C, 41.67; H, 11.32; B, 4.53; N, 18.05; Si, 24.55; mol wt, 231 (mass spectrum).

Amino(bis(trimethylsilyl)amino)(diethylamino)borane (5).[1b] The procedure used for the preparation of **4** was modified to allow the use of larger quantities of reactants. Thus, compound **2** (25.0 mL, 0.098 mol) and dry hexane (200 mL) were placed in a flask equipped with a cold finger condenser, a gas inlet tube and a magnetic stirrer. Both the condenser and the reaction vessel were cooled to −78 °C. Excess liquid ammonia (6.1 mL, 0.29 mol) was condensed into a graduated tube maintained at −78 °C. The ammonia container was attached to the gas inlet tube of the reaction flask and the ammonia was allowed to evaporate and condense into the cold reaction flask. The cold bath surrounding the flask was removed while maintaining the condenser at −78 °C. After 1 h the condenser was allowed to warm to room temperature and excess ammonia was allowed to escape. Workup of the reaction mixture proceeded as described in the preparation of **4**. Compound **5** was obtained as a colorless liquid (20.1 g, 79% yield, bp 86 °C (2.0 Torr)). The proton NMR spectrum of a neat sample gave Me_3Si (δ −0.03):CH_2 (δ 2.85):CH_3 (δ 0.90):NH_2 (δ 1.88) = 12.0:3.3:6.0:2.0 (calcd 18:4:6:2). The mass spectrum[12] contained a molecular ion at *m/e* 259.2078 (calcd for $^{12}C_{10}{}^1H_{30}{}^{11}B^{14}N_3{}^{28}Si_2$, 259.2071).

Amino(bis(trimethylsilyl)amino)(diisopropylamino)borane (6).[1b] Compound **6** was prepared by the same method described for **5**. In a typical preparation **3** (202 mL, 0.566 mol) was allowed to react

