$[CpRu(\eta^4\text{-arene})S]^+$ and $[CpRuS_3]^+$ intermediates that are generated as the reaction coordinate in Figure 7 is crossed will be much larger in dichloromethane than in acetonitrile, giving rise to the energy gap between these solvated intermediates in the two solvents. The dichloromethane-solvated $[CpRuS_3]^+$ product is a high-energy species that either rapidly complexes the dye arene ring to form the η^4-slipped-ring intermediate, complexes the dye carbonyl groups to form the emissive intermediate (designated "I" in Figure 7), or simply decomposes to an unknown, unreactive ruthenium species with the irreversible liberation of free dye in solution.

This scheme is consistent with the observed generation of a metastable, carbonyl-complexed intermediate during complexation of the dye in dichloromethane solution even though the source of $CpRu^+$ in our experiments was the tris(acetonitrile) adduct. Recent kinetic studies in our laboratory of the complexation of arenes by $[CpRu(CH_3CN)_3]^+$ indicate that the tris(acetonitrile) adduct is quite inert and that the reactive species in these reactions is the "unsaturated" $[CpRu(CH_3CN)_2(S)]^+$ solvate in which an acetonitrile ligand has been replaced by a solvent molecule.[3]

Traversing the excited-state reaction coordinate involves the initial population of the lowest singlet state, S_1, of the η^6-complex and subsequent rapid intersystem crossing to the distorted a^3E_1 state. Distortion of the triplet state to form the slipped-ring, η^4-arene complex channels the molecule into an excited-state funnel from which it readily back-intersystem crosses and relaxes to the ground-state potential surfaces that lead to the characteristic reactions previously discussed.

Conclusions

An emissive intermediate is observed in the photolysis of the η^6-$CpRu^+$ complexes of 3-acyl-7-aminocoumarin laser dyes in noncoordinating media. The perturbed, dye-centered emission observed from the intermediate indicates that the $CpRu^+$ moiety is bound to the dye in the intermediate but is not bound to the dye arene ring as this complexation mode would be expected to completely quench the dye emission. The observation that the intermediate is only observed from 3-substituted coumarin laser dyes and consideration of the IR spectra of the intermediates suggests that they consist of the laser dye coordinating the $CpRu^+$ group through its two carbonyl groups. The ability to observe the intermediate in both the thermal complexation and photochemical decomplexation of laser dye suggests that these two processes occur through a common transition state that may be a "slipped-ring" complex of reduced arene hapticity. In the future we intend to pursue the synthesis and isolation of other transition-metal-laser dye complexes that retain the emissivity of the free laser dye.

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Notes

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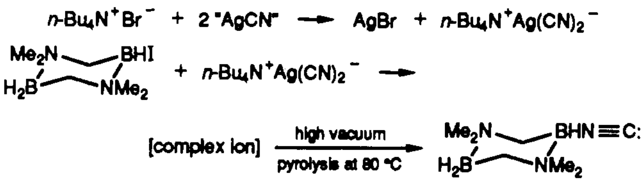
Borane Isonitriles and Carboxylates. Synthesis and Characterization of the 2-Carboxylic Acid Derivative of 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane

Norman E. Miller

Received October 16, 1990

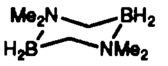
Carboxylic acid substitution onto boranes is a desirable transformation because it provides a means of conjugating borane moieties to organic structures or vice versa. Bringing about such substitution has been difficult, and a general route for substituting intact nonpolyhedral boranes has not existed. The first carboxylate derivative of a borane is the carbonyl adduct of borane $BH_3{\cdot}C{\equiv}O$,[1] which can be considered the anhydride of the acid $H_3O^+BH_3CO_2H^-$, known only as the divalent salt ion $BH_3CO_2^{2-}$, and derivatives.[2] Carboxylate substitutions onto $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ ions proceed via hydration of the anhydride carbonyl derivatives. The B_{10}-bis(carbonyl) is obtained by displacement of the nitrogen in $B_{10}H_8(N_2)_2$ inner salt, and the B_{12}-bis(carboxylic acid), by carbonylation of the crystalline, hydrated acid of $B_{12}H_{12}^{2-}$ under pressure at elevated temperature.[3] More recently, carboxylic acid derivatives of nominally BH_3 adducts were made by the two-stage hydrolysis of nitrilium salts of preformed cyanoboranes.[4]

Scheme I



2

Bringing about carboxylate substitution on 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**) is an objective



1

of long standing. This ring system has been shown[5] to be robust enough to withstand reasonable chemical processing. Once obtained, the carboxylate and other functions to which it could be converted would be capable of being conjugated to organic structures of interest.

A method is reported here to convert a B-I substituent to a $B{-}CO_2H$ function on extant borane derivatives. It began with the development of a new cyaniding reagent to make isonitrilo-substituted boranes.

Exchange of isonitrile for iodide in Me_3NBH_2I is reported by Vidal and Ryschkewitsch[6] using silver cyanide to form a complex

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[1] Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1937**, *59*, 780.

[2] (a) Malone, L. J.; Parry, R. W. *Inorg. Chem.* **1967**, *6*, 817. (b) Parry, R. W.; Nordman, C. E.; Carter, J. C.; Terharr, G. *Adv. Chem. Ser.* **1964**, *42*, 302. (c) Carter, J. C.; Parry, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 2354.

[3] (a) Knoth, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 935. (b) Knoth, W. H.; Sauer, J. C.; Balthis, J. H.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 115; **1967**, *89*, 4842.

[4] (a) Spielvogel, B. F.; Wojnowich, L.; Das, M. K.; McPhail, A. T.; Hargrave, K. D. *J. Am. Chem. Soc.* **1976**, *98*, 5703. (b) Spielvogel, B. F.; Das, M. K.; McPhail, A. T.; Onan, K. D.; Hall, I. H. *Inorg. Chem.* **1980**, *102*, 6343. (c) Spielvogel, B. F.; Ahmed, F. U.; Morse, K. W.; McPhail, A. T. *Inorg. Chem.* **1984**, *23*, 1776. (d) Spielvogel, B. F.; Ahmed, F. U.; Silvey, G. L.; Wisian-Nielson, P.; McPhail, A. T. *Inorg. Chem.* **1984**, *23*, 4322. (e) Kemp, B.; Kalbag, S.; Geanangel, R. A. *Inorg. Chem.* **1984**, *23*, 3063. (f) Gyori, B.; Lazar, I.; Emri, J. *J. Organomet. Chem.* **1988**, *344*, 29.

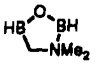
[5] Miller, N. E.; Reznicek, D. L. *J. Organomet. Chem.* **1988**, *349*, 11.

[6] Vidal, J. L.; Ryschkewitsch, G. E. *Inorg. Chem.* **1977**, *16*, 1898.

0020-1669/91/1330-2228$02.50/0

Table I. High-Resolution Mass Data[a]

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HO_2CH$[b]					$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCO_2H$ (3)			
m/e	%	calcd[c]	dev mass		*m/e*	%	calcd[c]	dev mass
186.1683	7.7	3.4		$^{13}CC_6H_{19}N_2O_2{}^{11}B_2$	186.1665			
185.1633	43.8	*	0	$C_7H_{19}N_2O_2{}^{11}B_2$	185.1630	3.3	*	−0.2
184.1662	20.9	21.6	−0.7	$C_7H_{19}N_2O_2{}^{11}B^{10}B$	184.1670	1.5	1.6	0
141.1732	7.1	*	−0.2	$C_6H_{19}N_2{}^{11}B_2$	141.1731	26.7	*	−0.9
140.1771	3.9	3.5	0	$C_6H_{19}N_2{}^{11}B^{10}B$	140.1765	15.2	13.2	−0.6
98.0945	100	*	−0.3	$C_3H_{10}NO^{11}B_2$	98.0948	7.8	*	0
97.0982	48.6	49.3	−0.2	$C_3H_{10}NO^{11}B^{10}B$	97.1001	7.7	3.8	1.7



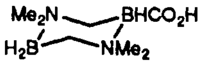
[a] Data from MCMS, University of Nebraska/Lincoln. [b] Formate isomer data from ref 9. [c] Based upon abundancies and normalized to most intense peak of pair.

salt from which the isonitrile derivative is isolated by treatment with hydrogen sulfide in a tandem three-vessel Schlenk apparatus. Need of a less heroic method was apparent, and a one-pot method was found that used a cyaniding solution of n-$Bu_4N^+Ag(CN)_2^-$ in methylene chloride, according to Scheme I.

The isonitrile **2** is a new derivative of the parent ring system and is a borane structure in the class termed multipolar framework compounds in this laboratory because of the repeating formal charges of datively bonded atoms with tetrahedral valency. Characterization of the product as the isonitrile rather than the cyanide comes from the ^{13}C NMR signal at δ 169 ppm and the intense "cyanide" stretch at 2127 cm^{-1}. (The isonitrile stretch in $Me_3N{\cdot}BH_2N{\equiv}C{:}$ is much stronger than the stretch in the cyano derivative.[6])

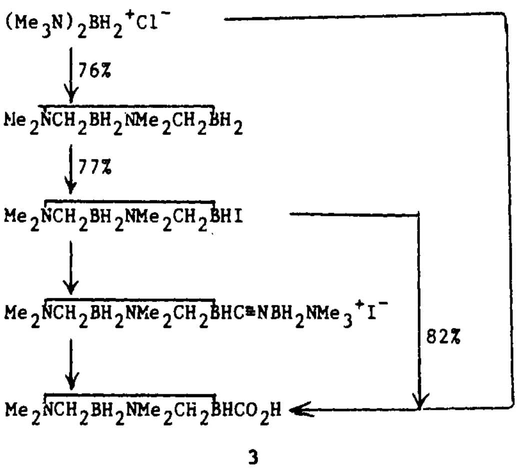
Application of Scheme I to the synthesis of known $Me_3N{\cdot}BH_2N{\equiv}C{:}$ gave better than 60% yields, allowing rather large quantities of this isonitrile to be made.

Previous experience with cyanide-bridged borane cations[7] and the hydrolytic instability of amide-bonded borane cations in basic solution,[8] taken together, suggested a route to the carboxylate of **1**. The iodo derivative of **1** may be able to undergo iodide displacement by $Me_3N{\cdot}BH_2N{\equiv}C{:}$ to produce a cyanide-bridged cation. The analogous reaction with methyl isocyanide, however, failed under a number of conditions including forcing conditions. The $Me_3N{\cdot}BH_2$-substituted isonitrile, on the other hand, would be expected to be a better base and nucleophile from the evidence of base enhancement of $Me_3N{\cdot}BH_2$-substitution.[9] No reaction was observed in either chloroform or toluene solution. A slow reaction goes if but a trace of chloroform is used to "melt" the $Me_3N{\cdot}BH_2N{\equiv}C{:}$ into a liquid phase. The bridged salt product was obtained as a syrup that could be induced to crystallize in the presence of trace amounts of toluene. Because of the crystallization difficulty and an aqueous lability, characterization as $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HC{\equiv}NBH_2NMe_3{}^+I^-$ has depended primarily on spectral data. It proved to be the right intermediate for the synthesis of the long-desired carboxylate derivative **3**. It slowly hydrolyzed in 0.5 M OH^- solution to give a clear solution and nearly quantitatively twice the molar amount of hydrogen.



3

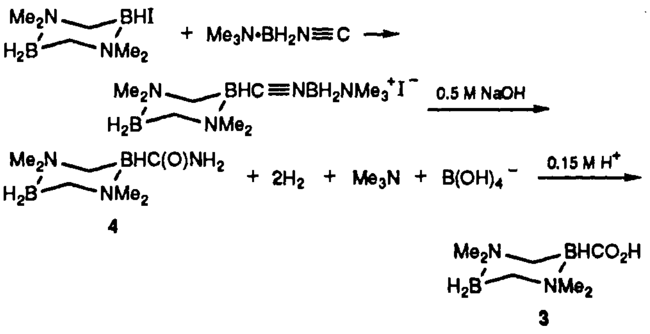
Acidification of the solution to about 0.15 M in H^+ leads to slow precipitation of **3** after a short induction of a minute or two. Since acidification of the salt form of **3** leads to immediate and rapid precipitation, an amide intermediate is implicated. Indeed, when the base hydrolyzate is neutralized and evaporated, a water-soluble amide, **4**, is obtained. This amide exhibited unusual solvation tendencies which made isolation and purification difficult. Chloroform was retained so tenaciously that a solid could not be obtained on vacuum pumping, but trituration with a few drops of water rapidly converted the translucent semisolid into a white crystalline solid.



3

Figure 1. Yield charting for synthesis of **3**.

Scheme II



The carboxylic acid **3**, purified by recrystallization from aqueous methanol, is a crystalline solid melting at 194 °C, is stable in air, and is practically insoluble in water. A charting of yields of the preparation, beginning with the starting material $(Me_3N)_2BH_2{}^+Cl^-$ is summarized in Figure 1, and the reaction sequence beginning with iodo derivative of **1** is shown in Scheme II. **3** is a linkage isomer with the known formate ester[5] of **1**, so a comparison of high-resolution mass data of the two, Table I, is instructive in the characterization of **3** and the understanding of fragmentation.

The carboxylic acid **3** is soluble in strong ammonia or alkali solution from which it can be recovered unchanged by evaporation and neutralization, respectively. Since the multipolar borane ring moiety in **3** is electron releasing, a pK_a higher (by 2 or 3 units) than that of acetic acid might be expected. A similar inductive effect of the multipolar ring increasing the basicity of the (dimethylamino)methyl derivative of **1** in comparison to trimethylamine has been observed.[9] It was of interest then to see if a stable salt of the latter base and **3** could be obtained. These

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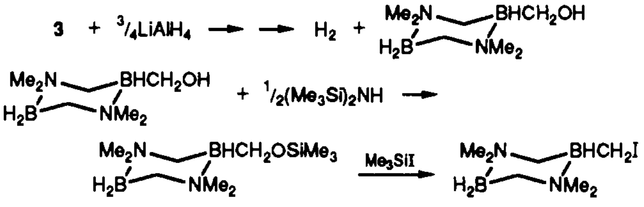
(7) Reznicek, D. L.; Miller, N. E. *Inorg. Chem.* **1972**, *11*, 858.
(8) Miller, N. E. Unpublished work.
(9) Miller, N. E.; Reznicek, D. L. *Inorg. Chem.* **1969**, *8*, 275.

Scheme III



components were found to be separable by distillation under vacuum at room temperature. Like most derivatives of **1**, **3** is sensitive to strong aqueous acid and nonaqueous hydrogen halides, a factor that is a consideration in the interconversions of functionality on **1**.

The synthesis method was applied to the preparation of the known borane carboxylate $Me_3N{\cdot}BH_2CO_2H$. A yield in excess of 50% based on $Me_3N{\cdot}BH_2I$ was achieved. The workup was modified to accommodate its greater water solubility than **3**.

A beginning has been made on converting **3** into other functionalities that should be useful in conjugation of the multipolar framework ring to organic structures. Reduction of the carboxylate function to the hydroxylmethyl and then conversion to the iodomethyl go according to Scheme III. The carboxylate and other monosubstituted derivatives of **1** generally show four nonequivalent *N*-methyl environments in proton and carbon-13 NMR data. This is common to other reported[5] monosubstituted derivatives, and is as expected for the chair conformation of the ring, either dynamic or static. Ring methylene or other boron-bonded methylene in these compounds have broadened multiplet NMR resonances. The two boron environments are nonequivalent but are not enough different to give differentiated triplet and doublet boron resonances of BH_2 and BH sites for **2–4**, the precursor salt, and the iodomethyl derivative. The Hydroxymethyl compound and its trimethylsilyl ether derivatives have well-separated boron environments of the expected multiplicities.

The isolation of **3** and derivatives opens new avenues of research to examine the relationships of structure and function of multipolar framework compounds, with an eye toward practical utility. Additionally, the synthetic work suggests that, for the first time, a general route is available to carboxylate boranes provided there is replaceable halogen and that the borane has no alkali-labile functionality. This is a finding with important implications because of the biological effects of borane amides and carboxylates being documented.[10]

Experimental Section

Where required, standard high-vacuum-line procedures were employed. A line equipped with Delmar-Urry O-ring joints and PTFE needle stopcocks, with pumping capability to 10^{-5} Torr of noncondensible gas, provided for reactions, transfer, and sublimations. Melting points were measured in a Thomas-Hoover capillary melting point apparatus and are uncorrected for emergent stem. Analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. NMR, IR, and GC/MS data were obtained on Bruker AC300, Biorad Digilab FTS-40, and Hewlett-Packard 5988A instrumentation, respectively. High-resolution mass spectral data were obtained from the Midwest Center for Mass Spectrometry, University of Nebraska/Lincoln, NE. Chloroform was freed of ethanol by repeated extraction with water, followed by drying over sodium sulfate and distillation from phosphoric anhydride. Hexane was freed of olefin traces by repeated extraction with concentrated sulfuric acid, followed by water washing, drying, and distillation from calcium hydride. Other solvents and reagents were reagent grade and used as received. Trimethylamine–iodoborane and iodo-**1** were made by iodination of trimethylamine-borane and 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane,[5] followed by sublimation. NMR data of deuteriochloroform solutions are reported as chemical shifts, δ, ppm referenced to $CDCl_3$, TMSi, and external boron trifluoride etherate for C, H, and B, respectively.

Isonitrile Synthesis. A solution of 41.0 g (0.127 mol) of $n\text{-}Bu_4N^+Br^-$ in 80 mL of methylene chloride was added in four batches to a suspension of 34.4 g (0.257 mol) of silver cyanide in 250 mL methylene chloride under stirring to give a yellow precipitate, 22.3 g (0.119 mol), judged to be silver bromide from color and absence of cyanide infrared absorption; 94% yield. After filtration, the nearly colorless solution appears to be stable indefinitely in brown bottles away from light.

$Me_3N{\cdot}BH_2N{\equiv}C$. A solution of 25.8 g (0.130 mol) of trimethylamine–iodoborane in 30 mL of methylene chloride was added slowly over 4 h to the $n\text{-}Bu_4N^+Br^-$ solution with protection from light. The resulting slightly yellowish solution with traces of black insolubles was evaporated slowly under vacuum, finally leaving a viscous oil that was pyrolyzed by bringing the temperature slowly to 80 °C with continued heating and stirring for 8 h and then for an additional 12 h at 85 °C. The white sublimate was resublimed twice under high vacuum at 50 °C; yield 8.4 g, 68%, white crystals of $Me_3NBH_2N{\equiv}C$. Infrared absorptions agreed with the literature, and the melting point of another sample prepared similarly was 46–48 °C (45–46 °C, reported[6]).

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HN{\equiv}C$ (**2**) was prepared in a similar manner from 207 mg (1.17 mmol) of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HI$ and 11 mL of 0.16 M cyaniding solution. After two sublimations, 112 mg of white crystals of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HN{\equiv}C$ were obtained. Another sample prepared in like manner melted at 80–82 °C. A purified 6-mg sample for NMR use was obtained by multiple injections on a C18 analytical HPLC column using acetonitrile eluent. High-resolution mass spectral data (composition, *m/e* observed, deviation in mass, intensity) confirm the composition by presence of $C_7H_{18}N_3B_2$ parent − 1 and rational framentation peaks: $C^{13}C_6H_{18}N_3{}^{11}B_2$, 167.1715, −0.5, 0.9; $C_7H_{18}N_3{}^{11}B_2$, 166.1690, 0.3, 9.1; $C_7H_{18}N_3{}^{11}B^{10}B$, 165.1722, −1.2, 4.8; $C_5H_{17}N_2{}^{11}B_2$, 127.1576, −0.1, 11.5; $C_5H_{17}N_2{}^{11}B^{10}B$, 126.1609, 2.9, 5.3; $C_5H_{14}N_2{}^{11}B$, 113.1238, 1.0, 41.8; $C_5H_{14}N_2{}^{10}B$, 112.1265, −2.1, 10.4; C_3H_8N 58.0678, 2.2, 100. Typically for the multipolar framework compounds the highest mass is the parent less one (P − 1). The $C_5H_{17}N_2B_2$ fragment is the P − 1 peak expected for the five-membered ring $Me_2\overline{NCH_2BH_2NMe_2B}H_2$,[12] from which the $C_5H_{14}N_2B$ fragment could be explicable by loss of BH_3 to form $Me_2NCH_2B{=}NMe_2{}^+$. IR data (frequency in cm^{-1}, intensity): BH 2331 m (2461, 2356, 2301 w shoulders), N≡C 2127 s, 1300 w, 1181 s, 1140 w, 1106m, 1092 m, 1027 w, 1007 w, 998 w, 968 m, 932 w, 894 w, 849 m, 819 w, 736 w. NMR data: ^{13}C N≡C 169.44, NMe 57.10, 54.72, 49.40, 43.74; ^1H NMe 2.68, 2.62, CH_2 2.38 (br), 2.09–2.02 (br); ^{11}B overlapping peaks interpretable as doublet and triplet −9.0, −10.3, −11.3, decouples to broad signal −10.7.

Carboxylate Synthesis. $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCO_2H$ (3). A mixture of 2.363 g (8.824 mmol) of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HI$ and 8.615 g (8.794 mmol) of $Me_3NBH_2N{\equiv}C$ in 2.6 mL of anhydrous chloroform was allowed to stir protected from light for 2 days at which time a yellow viscous solution with a vapor tension of less than 100 mmHg was present. To this was added 6 mL of dry toluene and the resulting mixture allowed to stir 2 h before solvent was removed slowly at 30 mmHg and then at 10 mmHg backing pressure, to give a thick syrup. When this syrup was allowed to stand for 2 days, a light yellow-tinged crystalline solid, $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H\text{-}C{\equiv}NBH_2NMe_3{}^+I^-$, was formed. High-vacuum pumping for several hours removed residual solvent, but the crystals still contained solvent in some fashion, since a similarly prepared sample analyzed as $C_{10}H_{30}N_4B_3I(CHCl_3)_{0.73}(C_7H_8)_{0.106}$. Anal. Calcd: C, 29.76; H, 6.86; N, 12.15. Found: C, 29.76; H, 6.85; N, 12.10. NMR data: ^{13}C NMe_3 51.47; NMe_2 56.78, 56.31, 48.53, 47.45; ^1H NMe_3 2.91; NMe_2 2.75, 2.70 and peak(s) under NMe_3 resonance; CH_2 (broad) 2.62, 2.57, 2.54, 2.39, 2.36, 2.24, 2.19; ^{11}B −12.6 and multi-shouldered peak at −9.3, decoupled to resonances at −6.8, −9.4 and −13.0.

Hydrolysis of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HC{\equiv}NBH_2NMe_3{}^+I^-$ was conducted in two stages. The product from the 8.8-mmol run described above was dissolved in 44 mL of deoxygenated water and filtered. To this solution was added 50 mL of deoxygenated 1.0 M sodium hydroxide under nitrogen. Measurable gas evolution began in 10 min and continued for 2 days to give about 85% of the expected 17.6 mmol of gas. When the salt solution is not filtered before base hydrolysis, a much faster rate of gas evolution is measured, with about the same yield. If the salt is not obtained in the crystalline state, only slightly over 1 mol of gas/mol of salt is observed, yet the yield of **3** ultimately obtained is undiminished. The hydrolyzate is pumped under high vacuum pumping for about an hour to remove as much trimethylamine as possible along with some water. The solution remaining has some insolubles present, which dis-

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(10) Work of B. F. Spielvogel and co-workers, beginning with ref 4. See also reference summary cited by: Mittakanti, M.; Morse, K. W. *Inorg. Chem.* **1990**, *29*, 554.

(11) Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 3145.

(12) Gragg, B. R.; Ryschkewitsch, G. E. *Inorg. Chem.* **1976**, *15*, 1201.

solve as the solution is neutralized carefully to pH = 7.0. Evaporation in a rotary evaporator at aspirator vacuum and temperature less than 30 °C left a solid that was then pumped under high vacuum for several hours to remove traces of water. The solid was extracted with chloroform and the solvent removed under high-vacuum pumping to leave a semisolid. Stirring with a few drops of water caused crystallization to white crystals that were then dried under high vacuum, giving 1.20 g (80%) of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCONH_2$ (**4**). A sublimed sample (65–70 °C/high vacuum) melted sharply at 158–159 °C as opposed to a melting range beginning at 127 °C for the product as obtained, even though the infrared spectra were identical. NMR data: ^1H NMe_2 2.85, 2.69, 2.65, 2.61; NH_2 broad doublet 5.5 and 5.4; CH_2 broad ca. 1:3:3:1 quartet 2.42, broad ca. 1:2:1 triplet 1.90; ^{11}B unsymmetrical and shouldered triplet −8.4, −9.4, −10.0 decouples to a singlet −8.9. GC/MS data: one major GC peak and one minor one; *m/e* 184 (21%) and 183 (11%) parent − 1 with $^{11}B_2$ and $^{10}B^{11}B$ isotopic composition; 141 (100%) and 140 (52%) parent − 1 for **1**. Infrared data (cm^{-1}): NH 3435, 3282, 3166 s; BH 2343/2313 s with multiple shoulders; amide carbonyl 1621, 1575 s; 1306 w with shoulders, 1235 w, 1175 w, 1330–1320 m doublet, 1070 m multiplet, 1030–1010 m doublet, 966 m, 930 m, 889 w, 852 m, 830 w, 734 m.

If the basic hydrolysis solution is treated with 1 M HCl to approximately 0.15 M H^+, the carboxylate derivative $Me_2\overline{NCH_2BH_2CH_2NMe_2B}HCO_2H$ (**3**) settles slowly from the solution after a few minutes induction. Yields were better than 80%; for example, from 25.9 mmol of $Me_2\overline{NCH_2BH_2CH_2NMe_2B}HI$ and 25.8 mmol of $Me_3N{\cdot}BH_2N{\equiv}C$ precursors was obtained 3.96 g of **3**, 82%. Recrystallization from 30% methanol in water gives recovery of better than 70% as white needles, mp 196 °C/sealed capillary. Anal. Calcd for $C_7H_{20}B_2N_2O_2$: C, 45.23; H, 10.84; N, 15.07. Found: C, 45.52; H, 10.89; N, 14.93. **3** can be sublimed at 80 °C/high vacuum. Infrared data (cm^{-1}): OH under mineral oil CH stretch; BH 2373, 2353, 2328 s (shouldered); CO 1651 s; 1301 w, 1244 s, 1175 s (1195 m shoulder), 1128/1118 w doublet, 1074 s, 1025 w, 1004 m, 966 m, 928 m, 887 w, 855 w, 746 m. NMR data: ^{13}C NMe_2 57.56, 56.02, 48.08, 43.54; ^1H NMe_2 2.81, 2.77, 2.66, 2.61; CH_2 (broad multiplets) 2.47, 2.28, 2.20, 1.87; ^{11}B unsymmetrical triplet −8.1, −9.4, −10.4 decoupled to unsymmetrical doublet −9.1, −9.9.

$Me_3N{\cdot}BH_2CO_2H$. A solution of 297 mg (0.94 mmol) of $(Me_3NBH_2)_2C{\equiv}N^+PF_6^-$[7] in 8 mL of degassed 1 M NaOH was heated to 40 °C to initiate hydrolysis and then allowed to stir overnight. Noncondensible gas at −196 °C amounted to 1.8 mmol (100% of theory). The solution was filtered and adjusted to pH 4 and evaporated and the solid extracted with chloroform. Removal of solvent left a solid with amide infrared bands present, so it was dissolved in 5 mL of 0.3 M HCl and evaporated under high vacuum. Extraction with chloroform, followed by evaporation and sublimation, gave 58 mg (53%) of $Me_3N{\cdot}BH_2CO_2H$ identified by its infrared spectrum.[4a]

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OH$. A solution of 53 mg (0.285 mmol) of **3** in about 3 mL of dry glyme was added to 0.57 mL of 0.5 M $LiAlH_4$ in glyme under nitrogen. Brisk gas evolution occurred, resulting in a clear solution. After the solution was stirred overnight, 1 mL of 2-propanol and 1 mL of saturated aqueous NaF were added sequentially with stirring. The solid was removed by filtration and the filtrate evaporated to dryness under vacuum. Extraction with methylene chloride followed by solvent removal and sublimation at 55 °C/high vacuum, gave 73 mg, 62%, of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OH$, mp 85–86 °C sealed cap under nitrogen. Anal. Calcd for $C_7H_{22}N_2OB_2$: C, 48.91; H, 12.90; N, 16.29. Found: C, 49.21; H, 12.35; N, 16.38. Infrared data (cm^{-1}): OH 3470 m, BH 2391 m shoulder, 2347 s, 2300 s, 2260 m shoulder; 1308 w, 1293 m, 1237, 1179, 1135/1125 m doublet, 1095 s (1085 shoulder), 1026 m, 1001 s, 975 s, 956 w, 926 m, 877 m, 857 m, 816 m, 774 m, 734. Mass spectral data: 172, P + 1; 171, P; 169, P − 2. NMR data: ^1H NMe_2 2.68, 2.65, 2.58, 2.56; CH_2OH broad ab-type quartet, 3.18, 3.15, 3.08, 3.04; CH_2 broad triplet 2.18, broad doublet 1.89, 1.85; ^{11}BH 1:1 doublet −5.6 and −6.6 (J_{BH} = 96 Hz); BH_2 1:2:1 triplet −9.0, −10.1, −11.0 (J_{BH} = 96 Hz).

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$. A solution of 73 mg (0.42 mmol) of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OH$ in 1 mL of $CHCl_3$ was treated with 0.2 mL of hexamethyldisilazane under nitrogen and allowed to stir overnight. Evaporation of solvent left an oil characterized as $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OSiMe_3$. To this was added 1 mL of $CHCl_3$ containing 0.1 mL of Me_3SiI, and the mixture was allowed to stand overnight. Removal of solvent under vacuum followed by sublimation (80 °C/high vacuum) gave 64 mg, 54%, of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$ as a cream white solid. NMR data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OSiMe_3$: ^1H NMe_2 2.61, 2.59, 2.52, 2.50; ^{11}B BH doublet −5.8, −6.7 (J_{BH} = 87 Hz); BH_2 triplet −8.0, −9.0 −10.0 (J_{BH} = 96 Hz). NMR data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$: ^1H NMe_2 2.87, 2.74, 2.54, 2.43, NCH_2 broad 2.3, 1.65, BCH_2I broad −0.5; ^{11}B unsymmetrical triplet −4.6, −5.9, −6.9 decouples to unsymmetrical doublet −5.3, −6.4. Mass spectral data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OSiMe_3$: 1 Gc/Ms peak *m/e* 245 (1%), 244 (3%) parent, 243 (4%) parent − 1; 141 (100%) and 140 (54%), $^{11}B_2$, $^{10}B^{11}B$ $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H^+$. Mass spectral data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$: one GC peak *m/e* 281 (12.8%) and 280 (6.4%), parent − 1, $^{11}B_2$, $^{10}B^{11}B$ distribution, 155 (100%), 154 (52%) parent − iodine, $^{11}B_2$, $^{10}B^{11}B$. Infrared data (cm^{-1}) for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$: BH 2445 m, 2362 m doublet with multiplet shoulders, 1402 w, 1295 m, 1191 s, 1171 m, 1120 m, 1093 m, 1024 m, 1003 m, 988 s, 955 m, 878 m, 847 s, 820 w, 749 w, 684 m.

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Crystal and Molecular Structure of $(2,2,2\text{-crypt-}K^+)_2Pb_2Te_3^{2-}$

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Introduction

In a recent publication[3] we reported the preparation of a new family of dilead(II) chalcogenide anions $Pb_2Ch_3^{2-}$ (Ch = Se, Te) by extraction of the appropriate ternary or quaternary Zintl phases $KPb_{0.5}Se_{1-x}Te_x$ (where $x \approx 0.3$ or 0.71) with ethylenediamine (en) in the presence of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) and their characterization in solution by ^{207}Pb, ^{125}Te, and ^{77}Se NMR spectroscopy and by the X-ray analysis of a representative example, $(2,2,2\text{-crypt-}K^+)_2Pb_2Se_3^{2-}$. The NMR findings showed that the structures of the anions are all based upon a trigonal-bipyramidal structure[5] having axial Pb atoms bonded to three chalcogen atoms in the equatorial plane. Moreover, after the nuclear dependence had been removed and allowances for relativistic effects had been applied to the observed coupling constants $^1J(^{207}Pb{-}^{125}Te)$ and $^1J(^{207}Pb{-}^{77}Se)$ to give relativistically corrected reduced coupling constants $^1K_{RC}$, it was proposed that the effects of increasing Te substitution in the series $Pb_2Se_{3-n}Te_n^{2-}$ (n = 0–3) was additive and that the structure of the $Pb_2Te_3^{2-}$ anion would be "flatter" than that of the $Pb_2Se_3^{2-}$ anion with angles Se–Pb–Se < Te–Pb–Te and Pb–Se–Pb > Pb–Te–Pb.

In the present note, the structure of $(2,2,2\text{-crypt-}K^+)_2Pb_2Te_3^{2-}$ has been determined by X-ray crystallography at room temperature. The structures of the $Pb_2Te_3^{2-}$ and $Pb_2Se_3^{2-}$ anions are

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(3) Björgvinsson, M.; Sawyer, J. F.; Schrobilgen, G. J. *Inorg. Chem.* **1987**, *26*, 741.
(4) Enraf-Nonius Structure Determination Package, B. A. Frenz and Associates, College Station, TX, 1981.
(5) Jones, P. G. *Acta Crystallogr.* **1986**, *A42*, 57.

0020-1669/91/1330-2231\$02.50/0