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Synthesis and Structure of Triphenylmethylphosphonium Tetrakis(tetrahydroborato)aluminate, $[Ph_3MeP][Al(BH_4)_4]$, an Example of Eight-Coordinate Aluminum(III)

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Complex cation, $[(Ph_3P)_2N]^+$ and $[Ph_3MeP]^+$, salts of the tetrakis(tetrahydroborato)aluminate anion $[Al(BH_4)_4]^-$ were prepared as white crystalline solids in good yield from the reactions of $[Ph_3MeP][BH_4]$ and $[(Ph_3P)_2N][BH_4]$ with $Al(BH_4)_3$ in CH_2Cl_2 solutions. These salts are thermally stable above 100 °C. They have been characterized by ^1H, ^{11}B, and ^{27}Al NMR spectroscopy, and the structure of $[Ph_3MeP][Al(BH_4)_4]$ has been determined by single crystal X-ray analysis. Crystal data for $[Ph_3MeP][Al(BH_4)_4]$ (−60 °C): space group $Pca2_1$, $a = 17.701(3)$ Å, $b = 9.030(2)$ Å, $c = 14.993(3)$ Å, $V = 2396.4$ Å^3, ϱ(calcd) = 1.008 g cm^{-3}, MW = 363.67, $Z = 4$. Four BH_4^- units form eight apparent 3c−2e Al−H−B bonds with the Al^{3+} center. This is the first molecular structure of an aluminum compound which contains an eight-coordinate aluminum atom. The four BH_4 units are arranged in a distorted tetrahedral fashion around the aluminum atom. Each BH_4 unit contributes two hydrogen bridges to the aluminum. The eight bridging hydrogens form a slightly distorted dodecahedral coordination geometry around the aluminum center. Other previously reported salts $M[AlH(BH_4)_3]$, $M[AlH_2(BH_4)_2]$, and $M[AlH_3(BH_4)]$ (M^+ = Li^+, Bu_4N^+) were studied further in solution by NMR spectroscopy.

Introduction

Aluminum borohydride anions $[AlH_3(BH_4)]^-$, $[AlH_2(BH_4)_2]^-$, $[AlH(BH_4)_3]^-$, and $[Al(BH_4)_4]^-$ have attracted attention because they are likely to contain 3-center−2-electron Al−H−B bonds.[1−5] Questions of interest are whether they contain single Al−H−B bridge bonds, double Al−H−B bridge bonds, or triple Al−H−B bridge bonds. But the syntheses and structure determinations of such anions present significant challenges because of their limited stabilities. Formation of $Li[AlH_3(BH_4)]$, $Li[AlH_2(BH_4)_2]$, $Li[AlH(BH_4)_3]$, and $Li[Al(BH_4)_4]$ from the reaction of $LiAlH_4$ with diborane was first reported in 1960 by Wiberg and co-workers[1] and was later studied in several laboratories.[2,3] A comprehensive NMR study reported by Nöth and co-workers[4] described the complex chemistry of these "triple hydrides" in THF solutions. Later, in an effort to isolate stable aluminum borohydride anions, the preparation of similar compounds with large complex cations—$[(C_8H_{17})_3NC_3H_7][Al(BH_4)_4]$, $[Bu_4N][AlH_3(BH_4)]$, $[Bu_4N][AlH_2(BH_4)_2]$, $[Bu_4N][AlH(BH_4)_3]$, and $[Bu_4N][Al(BH_4)_4]$—was reported by Nöth[6] and by Titov.[7−9] However, these compounds were only partially characterized. Thus far, no structural determinations of these aluminum borohydride anions appear in the literature. Herein we report further characterizations of the $[AlH_3(BH_4)]^-$, $[AlH_2(BH_4)_2]^-$, $[AlH(BH_4)_3]^-$, and $[Al(BH_4)_4]^-$ anions and the single-crystal X-ray structure of $[Ph_3MeP][Al(BH_4)_4]$. This is the first structure determination for an aluminum borohydride anion and the first example of an aluminum compound which contains an eight-coordinate aluminum atom.

Experimental Section

General Comments. All manipulations were performed using standard high vacuum line techniques or in a drybox under N_2. Benzene, toluene, Et_2O, and hexane were dried over sodium metal, while CH_2Cl_2 was dried over P_2O_5. Previously dried solvents were freshly distilled into reaction flasks prior to use. $Li[BH_4]$ and $[Bu_4N][BH_4]$ were purchased from Aldrich Chemical Co. and used as received. $Li[AlH_4]$ (Aldrich) was purified by a standard method.[10] B_2H_6,[11] $[Bu_4N][AlH_4]$,[12] $Al(BH_4)_3$,[13] $[Ph_3PMe][BH_4]$,[14] and $[(Ph_3P)_2N][BH_4]$[15] were prepared by literature procedures. Extreme caution needs be to exercised in handling of B_2H_6 and $Al(BH_4)_3$. Both are volatile, highly flammable, and potentially explosive upon exposure to air. All IR spectra were recorded with 2-cm^{-1} resolution using a Mattson-Polaris FT-IR spectrometer. Boron-11 NMR {$\delta(Et_2OBF_3) = 0.00$ ppm}, ^{27}Al NMR {$\delta[Al(NO_3)_3] = 0.00$ ppm}, and proton NMR spectra {$\delta[Si(CH_4)_4] = 0.00$ ppm} were obtained on either a Bruker MSL-300 NMR spectrometer operating at 96.3, 78.2, and 300 MHz or a Bruker AM-250 NMR spectrometer operating at 80.2, 65.2, and 250 MHz respectively.

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Tetrabutylammonium Tetrakis(tetrahydroborato)aluminates. $[Bu_4N][Al(BH_4)_4]$ **(1a)** was prepared by the literature procedure[8] and by the following alternative method. $Al(BH_4)_3$ (0.020 g, 0.28 mmol) was measured in a closed vessel by weight and then dissolved in 5 mL of toluene. This solution was then combined with $[Bu_4N][BH_4]$ (0.072 g, 0.28 mmol) at room temperature. After brief stirring, a clear solution was obtained. NMR samples were obtained directly using this solution. A white solid was obtained in 97.8% yield (0.090 g, 0.27 mmol) when the solvent was pumped away. No further purification was required. Its IR spectrum given below is in accord with the reported spectrum recorded in benzene.[8] IR (CH_2Cl_2): 2472 (m), 2411 (m), 2240(w), 2150 (w), 2127 (sh), 1481 (w), 1470 (w), 1461 (w), 1421 (w), 1265 (m), 1118 (w), 1034 (w), 742 (s), 735 (s), 729 (m), 717 (m), 710 (m), 704 (m) cm^{-1}. NMR(CD_2Cl_2): ^{11}B, −34.0 (q) ppm, $^1J_{B-H}$ = 85.0 Hz; ^{27}Al, 49.5 (s) ppm; ^1H, 3.1 (Bu_4N), 1.6 (Bu_4N), 1.4 (Bu_4N), 1.0 (Bu_4N), 0.5 (BH_4^-) ppm.

Tetrabutylammonium (Tetrahydroborato)aluminates. $[Bu_4N][AlH(BH_4)_3]$ **(2a)**, $[Bu_4N][AlH_2(BH_4)_2]$ **(3a)**, and $[Bu_4N][AlH_3(BH_4)]$ **(4a)** were prepared by redistribution reactions between **1a** and $[Bu_4N][AlH_4]$ in procedures like those reported earlier.[9] All solid samples were stored at −35 °C. NMR (toluene-d_8) for **2a**: ^{11}B, −33.8 (q) ppm, $^1J_{B-H}$ = 83.9 Hz. NMR for **3a**: ^{11}B, −36.7 (q) ppm, $^1J_{B-H}$ = 83.1 Hz. NMR for **4a**: ^{11}B, −39.2 (q) ppm, $^1J_{B-H}$ = 83.3 Hz, ^{27}Al, 106 (br, s) ppm.

$Li[Al(BH_4)_4]$ **(1b)** was prepared by either a reaction of $LiAlH_4$ with B_2H_6 or the reaction of $Al(BH_4)_3$ with $LiBH_4$ similar to the synthesis of **1a**. $Li[AlH(BH_4)_3]$ **(2b)**, $Li[AlH_2(BH_4)_2]$ **(3b)**, and $Li[AlH_3(BH_4)]$ **(4b)** were prepared by reaction of **1b** with $LiAlH_4$ analogous to syntheses of $[Bu_4N][Al(BH_4)_4]$ and $[Bu_4N][AlH_4]$. All reactions were carried out in Et_2O solutions. Isolation of pure solid samples by recrystallization failed. No other purification efforts were made. Fresh reaction solutions containing these compounds were analyzed by NMR spectroscopy. NMR (Et_2O-d_{10}, 23 °C) for **1b**: ^{11}B, −33.9 (q) ppm, $^1J_{B-H}$ = 79.4 Hz; ^{27}Al, 49.2 (s) ppm; ^1H, 0.5 ppm (br); NMR for **2b**: ^{11}B, −37.1 (q) ppm, $^1J_{B-H}$ = 83.8 Hz; ^{27}Al, 80.5 (br, s) ppm; ^1H, 0.1 (q) ppm. NMR for **3b**: ^{11}B, −38.1 (q) ppm, $^1J_{B-H}$ = 82.9 Hz; ^{27}Al, 104.6 (br, s) ppm, ^1H, −0.1 (q) ppm. NMR for **4b**: −39.6 (q) ppm, $^1J_{B-H}$ = 81.3 Hz; ^{27}Al, 111.7 (br, s) ppm; ^1H, −0.4 (q) ppm.

Triphenylmethylphosphonium Tetrakis(tetrahydroborato)aluminate $[Ph_3MeP][Al(BH_4)_4]$ (1c). $Al(BH_4)_3$ (0.076 g, 1.07 mmol) dissolved in 10 mL of CH_2Cl_2 was combined with $[Ph_3MeP][BH_4]$ (0.31 g, 1.06 mmol). The reaction mixture was stirred at 23 °C for 10 min. Solvent was then slowly removed until the majority of the product precipitated. A white solid was obtained after filtration and drying of the filtrate *in vacuo*; yield 75.5% (0.29 g, 0.80 mmol). Hydridic hydrogen was determined by hydrolysis of the sample with excess aqueous HCl solution (96.2% yield). IR spectrum (CH_2Cl_2): 2474 (m), 2411 (m), 2241 (w), 2150 (m), 2124 (m, sh), 1440 (s), 1421 (m), 1117 (s) 998 (w), 897 (m) cm^{-1}. NMR spectra (CD_2Cl_2): ^{11}B, −34.2 (q) ppm, $^1J_{B-H}$ = 85.0 Hz; ^{27}Al, 49.5 (s) ppm; ^1H, 7.5−8.0 ppm (Ph), 2.8 (d, CH_3), $^2J_{P-H}$ = 13.2 Hz; 0.5 (br, BH_4) ppm.

Bis(triphenylphosphoranylidene)ammonium Tetrakis(tetrahydroborato)aluminate $[(Ph_3P)_2N][Al(BH_4)_4]$ (1d). $Al(BH_3)_3$ (0.27 g, 3.8 mmol) was diluted in 20 mL of CH_2Cl_2 solution and then mixed with $[(Ph_3P)_2N][BH_4]$ (2.06 g, 3.7 mmol) at room temperature. After brief stirring, the solvent was removed. A colorless crystalline solid was isolated in 60.2% yield (1.4 g, 2.2 mmol). Hydrogen analysis revealed that 93.0% of the expected hydridic hydrogen was released upon hydrolysis with excess aqueous HCl solution. IR spectrum (CH_2Cl_2): 2472 (s), 2412 (s), 2235 (m), 2150 (s), 2124 (sh), 1260 (m), 1250 (m), 1186 (m), 1117 (vs), 999 (m), 690 (s), 547 (vs) cm^{-1}. NMR spectra (CD_2Cl_2): ^{11}B, −34.0 (q) ppm, $^1J_{B-H}$ = 85.2 Hz; ^{27}Al, 49.5 (s) ppm; ^1H, 7.4−7.8 (Ph), 0.5 (br, BH_4) ppm.

X-ray Crystal Structure Determination. A crystal of suitable size (0.3 × 0.4 × 0.4 mm) was mounted in a glass capillary under N_2. Crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well-distributed in reciprocal space and lying in a 2θ range of 24−30°. Crystallographic data are given in Table 1. All reflection data were corrected for Lorentz and polarization effects.

Table 1. Crystallographic Data for $[Ph_3MeP][Al(BH_4)_4]$

formula	$C_{19}H_{34}AlB_4P$	T, °C	−60
fw	363.67	scan mode	$\omega-2\theta$
space group	$Pca2_1$	2θ limits, deg	4−50
a, Å	17.701(3)	no. of reflcns collcd	4687
b, Å	9.030(2)	no. of unique reflcns $[I \geq 3.0\sigma(I)]$	1406
c, Å	14.993(3)	no. of variables	302
vol, $Å^{-3}$	2396.4	R_F[a]	0.028
Z	4	R_{wF}[b]	0.033
ϱ(calcd), g cm^{-3}	1.008	κ[c]	0.02
μ(Mo Kα), cm^{-1}	1.5		

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. [c] $w = [\sigma(I)^2 + (\kappa I)^2)]^{-1/2}$.

Table 2. Positional Parameters of Atoms and Their Esd's for $[Al(BH_4)_4]^-$

atom	x	y	z	B,[a] $Å^2$
Al	0.16897(5)	0.8189(1)	0.03936(9)	3.54(2)
B1	0.1131(2)	0.7709(4)	0.1719(3)	4.02(9)
B2	0.2479(3)	1.0026(5)	0.0803(4)	5.5(1)
B3	0.0657(3)	0.8088(6)	−0.0455(4)	5.5(1)
B4	0.2502(3)	0.6933(5)	−0.0460(3)	5.5(1)
H1b1	0.111(2)	0.883(4)	0.127(2)	3.3(9)
H1b2	0.146(2)	0.710(3)	0.138(2)	2.7(8)
H1t1	0.058(2)	0.724(4)	0.180(3)	5(1)
H1t2	0.135(2)	0.785(3)	0.218(2)	2.2(8)
H2b1	0.248(2)	0.890(3)	0.103(2)	2.1(7)
H2b2	0.197(2)	1.014(4)	0.038(3)	3.2(8)
H2t1	0.292(2)	1.023(4)	0.039(3)	5(1)
H2t2	0.242(2)	1.050(4)	0.132(2)	4(1)
H3b1	0.099(2)	0.907(4)	−0.029(3)	3.3(9)
H3b2	0.096(2)	0.710(3)	−0.013(2)	2.2(8)
H3t1	0.073(2)	0.804(5)	−0.107(3)	6(1)
H3t2	0.016(2)	0.820(4)	−0.015(2)	2.5(8)
H4b1	0.228(2)	0.666(3)	0.017(2)	2.0(8)
H4b2	0.226(2)	0.804(4)	−0.062(3)	3.5(9)
H4t1	0.303(2)	0.716(4)	−0.041(3)	6(1)
H4t2	0.232(2)	0.625(4)	−0.092(2)	3.1(9)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The structure was solved by the direct-method MULTAN 11/82 and difference Fourier syntheses with analytical atomic scattering factors used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. All the crystallographic computations were carried out on a DEC VAX Station 3100 computer using the SDP (Structure Determination Package).[16] Full-matrix least-squares refinements were employed. After all non-hydrogen atoms were located and refined, all hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the anion $[Al(BH_4)_4]^-$ and hydrogen atoms of the methyl group on the cation $[Ph_3MeP]^+$ were refined isotropically. The terminal B−H hydrogen H1t2 refined to an unusually short B−H distance 0.80(5) Å. It might be an artifact. Calculated H atom positions of the phenyl rings on the cation were used. The positional and thermal parameters of hydrogen atoms on the phenyl rings were fixed during the final refinement. Atomic coordinates for $[Al(BH_4)_4]^-$ are given in Table 2.

Results and Discussion

Although the synthesis of aluminum borohydride anions has been studied earlier,[1−9] the structures of these anions were unknown. Questions of interest are the coordination geometries of hydrogen atoms around the aluminum center, whether they contain single 3-center−2-electron Al−H−B bridge bonds, double Al−H−B bridge bonds, or triple Al−H−B bridge bonds.

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(16) SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, to apply corrections, and to solve and refine the structures.

In the present study, these anions were prepared with different cations with emphasis on obtaining the suitable cyrstals for structure determinations. In one case, we were successful in elucidating the molecular structure of $[Ph_3MeP][Al(BH_4)_4]$ by X-ray crystallography. Aluminum borohydride salts **1**−**4** were prepared by the following synthetic reactions (eqs 1−5). The

$$AlH_4^- + 2B_2H_6 \rightarrow [Al(BH_4)_4]^- \qquad (1)$$

1a, $[Bu_4N]^+$; **1b**, Li^+

$$[BH_4]^- + Al(BH_4)_3 \rightarrow [Al(BH_4)_4]^- \qquad (2)$$

1a, $[Bu_4N]^+$; **1b**, Li^+; **1c**, $[Ph_3MeP]^+$; **1d**, PPN^+

$$3[Al(BH_4)_4]^- + AlH_4^- \rightarrow 4[AlH(BH_4)_3]^- \qquad (3)$$

2a, $[Bu_4N]^+$; **2b**, Li^+

$$[Al(BH_4)_4]^- + AlH_4^- \rightarrow 2[AlH_2(BH_4)_2]^- \qquad (4)$$

3a, $[Bu_4N]^+$; **3b**, Li^+

$$[Al(BH_4)_4]^- + 3AlH_4^- \rightarrow 4[AlH_3(BH_4)]^- \qquad (5)$$

4a, $[Bu_4N]^+$; **4b**, Li^+

$[Bu_4N]^+$ salts were obtained from the procedures developed by Titov and co-workers.[7−9] However, we found that by adjustment the ratios of reactants in the reactions of $[Bu_4N][Al(BH_4)_4]$ with $[Bu_4N][AlH_4]$, cleaner products were obtained than from the reactions of $[Bu_4N][AlH_4]$ with B_2H_6. $Li[AlH(BH_4)_3]$ (**2b**), $Li[AlH_2(BH_4)_2]$ (**3b**), and $Li[AlH_3(BH_4)]$ (**4b**) were prepared by the reactions of $Li[Al(BH_4)_4]$ (**1b**) with $LiAlH_4$ in Et_2O solutions.

Large alkyl ammonium cations were shown to enhance the stabilities of the salts and increase their solubilities in hydrocarbon solvents. Indeed, **1a**, **2a**, and **3a** are stable white solids under inert atmosphere at room temperature. However, **4a** slowly decomposes into a dark gray solid within a day at room temperature. **1a**, **2a**, **3a**, and **4a** are soluble in benzene and toluene. Unfortunately, no single crystals for X-ray analysis could be obtained despite many attempts at crystallization from toluene, benzene or toluene-benzene with ether or hexane. **1a** and **2a** are soluble in CH_2Cl_2 solution, while **3a**, and **4a** decompose in CH_2Cl_2.

Ether solutions of **4b** are unstable at room temperature or at temperatures near −10 °C. Precipitation of $AlH_3(Et_2O)_x$ was observed within 30 min. Similar observations for **4b** in THF solution were reported by Nöth and co-workers.[4] Subsequently, freshly prepared samples were analyzed by ^{11}B, ^{27}Al, and ^1H NMR spectroscopy. Several attempts were made to isolate crystalline samples of the lithium salts. However, crystals of the desired products were not obtained. Instead, $LiBH_4$ was isolated from the cold concentrated ether solutions containing **2b**, **3b**, and **4b**. Isolation of $LiBH_4$ suggests that **2b**, **3b**, and **4b** are unstable in solution and may partially dissociate into $LiBH_4$ and other related aluminum boron hydride compounds. An extraction experiment was performed in an effort to separate any neutral aluminum borohydrides from **2b** and **3b**. Solvent was removed *in vacuo* and the solid was extracted with benzene. The benzene insoluble fraction was redissolved in Et_2O and identified as $LiBH_4$ by ^{11}B NMR (−39.6 ppm). The benzene-soluble fraction was analyzed by NMR spectroscopy, and the results are discussed in the NMR studies below.

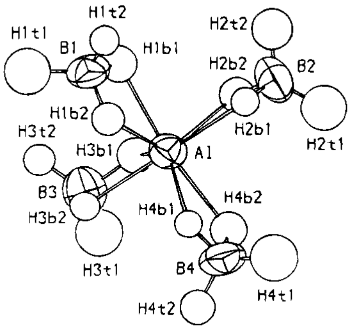

Figure 1. ORTEP Plot for $[Al(BH_4)_4]^-$ anion with 50% probability thermal ellipsoids.

Up to now, all efforts to isolate stable and crystalline samples of $[Al(BH_4)_4]^-$ (**1**), $[AlH(BH_4)_3]^-$ (**2**), $[AlH_2(BH_4)_2]^-$ (**3**), and $[AlH_3(BH_4)]^-$ (**4**) with Bu_4N^+ or Li^+ as counterions have been unsuccessful. However, crystalline samples of $[Ph_3MeP][Al(BH_4)_4]$ (**1c**) were obtained from the reaction of $[Ph_3MeP][BH_4]$ and $Al(BH_4)_3$ in CH_2Cl_2 solution. $[(Ph_3P)_2N][Al(BH_4)_4]$ (**1d**) and the previously known $[Bu_4N][Al(BH_4)_4]$ (**1a**) were prepared in the same fashion. Use of CH_2Cl_2 is important since both starting materials and products are soluble in CH_2Cl_2, and crystals of the products were readily obtained from CH_2Cl_2 solutions. However, we were unable to prepare $[Ph_3MeP][AlH_4]$ and $[(Ph_3P)_2N][AlH_4]$ due to reactions of the anion with the cations. Therefore this synthetic procedure is limited to the preparation of $[Al(BH_4)_4]^-$. Compounds of $[AlH(BH_4)_3]^-$, $[AlH_2(BH_4)_2]^-$, and $[AlH_3(BH_4)]^-$ with $[Ph_3MeP]^+$ and $[(Ph_3P)_2N]^+$ could not be synthesized. Solid samples of $[Ph_3MeP][Al(BH_4)_4]$ (**1c**) and $[(Ph_3P)_2N][Al(BH_4)_4]$ (**1d**) are stable above 100 °C under vacuum.

Structure of $[Ph_3MeP][Al(BH_4)_4]$. Colorless crystals of $[Ph_3MeP][Al(BH_4)_4]$ (**1c**) were grown by slowly cooling a concentrated CH_2Cl_2 solution to −10 °C. The molecular structure of **1c** was determined by a single-crystal X-ray diffraction analysis. An ORTEP plot of the $[Al(BH_4)_4]^-$ anion is shown in Figure 1. Selected bond distances and bond angles are given in Table 3.

The molecular structure of $[Al(BH_4)_4]^-$ consists of a central aluminum atom surrounded by four BH_4 groups arranged as a distorted tetrahedron. Four of the B-Al−B angles are within the range 97−101° while the remaining angles B1−Al−B4 and B2−Al−B3 are 133.4(2) and 134.0(3)°, respectively. Two of the four hydrogen atoms around each boron form apparent hydrogen bridges with the aluminum atom. These eight bridging hydrogens that surround the aluminum center establish a slightly distorted dodecahedral coordination geometry (Figure 2). Consistent with dodecahedral coordination,[24] the trapezoidal least squares planes (within 0.05(4) Å) defined by H1b1, H1b2, H4b1, H4b2, Al and H2b1, H2b2, H3b1, H3b2, Al have a dihedral angle of 91(1)° vs 90° for the idealized dodecahedron.

The aluminum−boron distances (2.229(6)−2.261(5) Å), aluminum−hydrogen distances (1.77(4)−1.83(4) Å), bridging hydrogen B−H distances (0.95(5)−1.22(5) Å), and terminal hydrogen B−H distances (0.80(5)−1.07(5) Å) are generally consistent with those structural parameters observed in $Al(BH_4)_3$-NMe_3 from a single-crystal X-ray structure determination based upon photographic data.[17] Although $[Al(BH_4)_4]^-$ possesses apparent 2-electron, 3-center hydrogen bridges, there is probably

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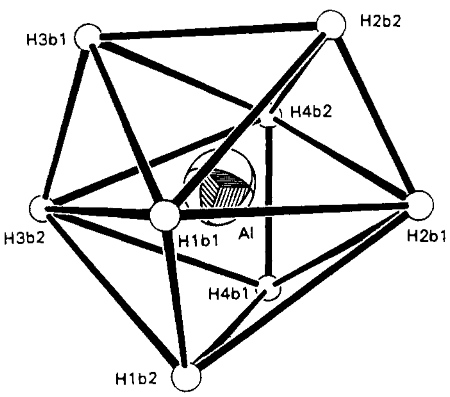

Figure 2. Dodecahedral coordination geometry of bridging hydrogens around aluminum.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[Al(BH_4)_4]^-$

	Bond Distances		
Al−H1b1	1.77(4)	B2−H2b1	1.07(4)
Al−H1b2	1.82(4)	B2−H2b2	1.11(5)
Al−H2b1	1.81(5)	B2−H2t1	1.01(6)
Al−H2b2	1.83(4)	B2−H2t2	0.90(5)
Al−H3b1	1.79(5)	B3−H3b1	1.09(5)
Al−H3b2	1.80(4)	B3−H3b2	1.15(4)
Al−H4b1	1.77(4)	B3−H3t1	0.94(6)
Al−H4b2	1.83(5)	B3−H3t2	0.99(4)
B1−H1b1	1.22(5)	B4−H4b1	1.04(4)
B1−H1b2	0.95(5)	B4−H4b2	1.11(5)
B1−H1t1	1.07(5)	B4−H4t1	0.96(6)
B1−H1t2	0.80(5)	B4−H4t2	0.98(5)
	Selected Nonbonding Distances		
B1⋯Al	2.261(5)	B2⋯Al	2.254(7)
B3⋯Al	2.229(6)	B4⋯Al	2.234(6)
	Selected Bond Angles		
H1b1−Al−H2b1	87(2)	H1b1−Al−H1b2	56(2)
H1b1−Al−H2b2	81(2)	H1b2−B1−H1t1	113(4)
H1b1−Al−H3b1	83(2)	H1b2−B1−H1t2	105(4)
H1b1−Al−H3b2	95(2)	H1t1−B1−H1t2	114(5)
H1b1−Al−H4b1	138(2)	Al−H1b1−B1	97(3)
H1b1−Al−H4b2	165(2)	Al−H1b2−B1	105(3)
H1b2−Al−H2b1	87(2)	H2b1−B2−H2b2	106(3)
H1b2−Al−H2b2	126(2)	H2b1−B2−H2t1	111(4)
H1b2−Al−H3b1	123(2)	H2b1−B2−H2t2	101(4)
H1b2−Al−H3b2	84(2)	H2b2−B2−H2t1	105(4)
H1b2−Al−H4b1	82(2)	H2b2−B2−H2t2	111(4)
H1b2−Al−H4b2	139(2)	H2t1−B2−H2t2	123(5)
H2b1−Al−H2b2	57(2)	Al−H2b1−B2	100(3)
H2b1−Al−H3b1	133(2)	Al−H2b2−B2	97(3)
H2b1−Al−H3b2	167(2)	H3b1−B3−H3b2	106(3)
H2b1−Al−H4b1	85(2)	H3b1−B3−H3t1	101(5)
H2b1−Al−H4b2	92(2)	H3b1−B3−H3t2	107(4)
H2b2−Al−H3b1	76(2)	H3b2−B3−H3t1	109(4)
H2b2−Al−H3b2	136(2)	H3b2−B3−H3t2	107(3)
H2b2−Al−H4b1	126(2)	H3t1−B3−H3t2	126(4)
H2b2−Al−H4b2	85(2)	Al−H3b1−B3	98(3)
H3b1−Al−H3b2	60(2)	Al−H3b2−B3	96(2)
H3b1−Al−H4b1	130(2)	H4b1−B4−H4b2	105(3)
H3b1−Al−H4b2	87(2)	H4b1−B4−H4t1	110(4)
H3b2−Al−H4b1	85(2)	H4b1−B4−H4t2	111(3)
H3b2−Al−H4b2	90(2)	H4b2−B4−H4t1	102(4)
H4b1−Al−H4b2	57(2)	H4b2−B4−H4t2	106(4)
H1b1−B1−H1b2	102(3)	H4t1−B4−H4t2	121(5)
H1b1−B1−H1t1	112(4)	Al−H4b1−B4	102(3)
H1b1−B1−H1t2	111(4)	Al−H4b2−B4	96(3)
	Selected Nonbonding Angles		
B1−Al−B2	100.0(2)	B1−Al−B3	97.7(3)
B1−Al−B4	133.4(2)	B2−Al−B3	134.0(3)
B2−Al−B4	97.5(3)	B3−Al−B4	100.4(2)

significant ionic interaction between the aluminum center and borohydride groups.

The distorted tetrahedral arrangement of BH_4 groups around the aluminum, as indicated by the B−Al−B angles, reflects the dominance of the dodecahedral arrangement of the bridging hydrogens. An alternative explanation for the distortion may be the interaction between the cation and the anion. However, this is unlikely since the closest contact between the $[Ph_3MeP]^+$ cation and the $[Al(BH_4)_4]^-$ anion in the unit cell is a P⋯Al nonbonding distance of 5.419(2) Å. To explore this point further, a second single-crystal structure using $[(Ph_3P)_2N]^+$ as the cation was undertaken.[18] In this case, the same type of distortion involving the boron atoms was observed. Unfortunately this structure could not be refined in as much detail as the $[Ph_3MeP]^+$ salt. Not all of the hydrogen atoms could be located.

Gas-phase electron diffraction studies on $Al(BH_4)_3$[19] showed that the aluminum atom is coordinated by six bridging hydrogens in three double bridges. Each boron atom forms an unsymmetrical rhombus with the central Al atom and the two bridging hydrogen atoms. One bridging hydrogen atom lies closer to the Al atom while the other hydrogen atom lies closer to the B atom, as also indicated by the B−H distances in $[Al(BH_4)_4]^-$ in the present study (Table 3).

NMR Study. NMR spectra for, $M[Al(BH_4)_4]$ (**1**), $M[AlH(BH_4)_3]$ (**2**), $M[AlH_2(BH_4)_2]$ (**3**), and $M[AlH_3(BH_4)]$ (**4**) ($M^+ = [Bu_4N]^+$ or Li^+) were recorded in toluene or Et_2O solutions respectively. Room temperature NMR data are summarized in Table 4.

The tetrabutylammonium salts **1a**, **2a**, **3a**, and **4a** each show a single ^{11}B resonance in the chemical shift range δ −33 to −40 ppm that is a quintet due to proton coupling. Boron-11 chemical shifts move upfield in the series $[AlH_x(BH_3)_{4-x}]^-$ as x goes from 0 to 3. (Table 4). The resonance at δ −33.0 ppm for **1a** is downfield with respect to $Al(BH_4)_3$ (δ −36.9 ppm).[20] Similar downfield shifts are also observed for **1c** and **1d** (δ −34.1 ppm in CD_2Cl_2). Both boron-11 resonances are sharp ($W_{1/2h}$ = 35 Hz) and there is no indication of dissociation in solution.

The sharp ^{27}Al resonance at δ 49.5 ppm ($W_{1/2h}$ = 257 Hz), for **1a** is upfield with respect to $Al(BH_4)_3$ (δ 98.4 ppm, CD_2Cl_2) and is consistent with the formation of the $[Al(BH_4)_4]^-$ monoanion with symmetrical Al chemical environment. The ^{27}Al NMR spectra of **1c** and **1d** show an equally sharp singlet with chemical shifts identical to that of **1a**. A very broad singlet is observed for **4a** at δ 106.2 ppm. ^{27}Al resonances for **2a** and **3a** are too broad to be detected. Also, in all cases, there is no apparent ^{27}Al-^1H coupling.

The proton spectra of **1a**, **2a**, **3a**, and **4a** recorded in toluene-d_8 show broad resonances for the $[Bu_4N]^+$ cation, thereby obscuring the Al−H and $[BH_4]^-$ signals. The ^1H NMR spectra of **1c** and **1d** show resonances consistent with $[Ph_3PMe]^+$ and $[(Ph_3P)_2N]^+$ cations and a very broad resonance centered at 0.55

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(18) Single-crystal structure of $[(Ph_3P)_2N][Al(BH_4)_4]$ (**1d**): space group $P2_12_12_1$, a = 10.836(7) Å, b = 15.932(4) Å, c = 21.727(5) Å; V = 3751(1) Å^3, Z = 4, ϱ(calcd) = 1.107 g cm^{-3}, μ(Mo Kα) = 1.6 cm^{-1}; T = −60 °C; R_F = 0.045; R_{wF} = 0.055; $I \geq 3.0\sigma(I)$. B1−Al−B2 = 99.4(3)°, B1−Al−B3 = 97.7(4)°, B1−Al−B4 = 130.0(3)°, B2−Al−B3 = 125.5(4)°, B2−Al−B4 = 100.5(4)°, and B3−Al−B4 = 106.9(5)°. B1⋯Al = 2.25(1) Å, B2⋯Al = 2.27(1) Å, B3⋯Al = 2.24(1) Å, and B4⋯Al = 2.28(1) Å.

(19) Almenningen, A.; Gundersen, G.; Haaland, A. *Acta Chem. Scand.* **1968**, 22, 328. With only minor uncertainty, the electron diffraction experiment revealed that the molecular structure of $Al(BH_4)_3$ has a D_{3h} symmetry and each BH_4 unit forms two bridging hydrogen bonds with the Al atom. Six bridging hydrogen atoms occupy the vertexes of a trigonal prism.

(20) (a) Phillips, W. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 4496. (b) Bird, P. H.; Wallbridge, M. G. H. *J. Chem. Soc.* **1965**, 3923.

Table 4. Summary of NMR Data for $[AlH_{4-x}(BH_4)_x]^-$ ($x = 1-4$)[a]

	$[Al(BH_4)_4]^-$	$[AlH(BH_4)_3]^-$	$[AlH_2(BH_4)_2]^-$	$[AlH_3(BH_4)_3]^-$
^{11}B NMR ppm	−33.0 (Bu_4N^+)	−33.8 (Bu_4N^+)	−36.7 (Bu_4N^+)	−39.2 (Bu_4N^+)
	−33.9 (Li^+)	−37.1 (Li^+)	−38.1 (Li^+)	−39.6 (Li^+)
J_{B-H}, Hz	84.8 (Bu_4N^+)	83.9 (Bu_4N^+)	83.1 (Bu_4N^+)	83.3 (Bu_4N^+)
	79.4 (Li^+)	83.8 (Li^+)	82.9 (Li^+)	81.3 (Li^+)
^{27}Al NMR, ppm	49.5 (Bu_4N^+)			106 (Bu_4N^+)
	49.2 (Li^+)	80.5 (Li^+)	104.6 (Li^+)	111.7 (Li^+)
^{1}H NMR, ppm	0.5 (Li^+)	0.1 (Li^+)	−0.1 (Li^+)	−0.4 (Li^+)

[a] Spectra for Bu_4N^+ salts were recorded in toluene-d_8 and spectra for Li^+ salts were recorded in Et_2O-d_{10}.

ppm ($W_{1/2h}$ = 262 Hz) for BH_4 units. Upon ^{11}B decoupling, the broad BH_4 resonance slightly narrows ($W_{1/2h}$ = 240 Hz). When the temperature is lowered this resonance narrows further, but even at −70 °C, a broad singlet was observed ($W_{1/2h}$ = 210 Hz). The resonances for bridging and terminal hydrogens are not resolved. This is an indication that Al−H−B bridging bonds are not strong and hydrogen atoms of each BH_4 unit are exchanging positions at a rate faster than the NMR time scale. A similar dynamic proton NMR spectrum was previously reported for $Al(BH_4)_3$ by Ogg.[21] In the IR spectrum bridging and terminal hydrogen absorptions are observed. Two absorption bands at 2474 and 2411 cm^{-1} are assigned to unsymmetrical and symmetrical stretching modes of terminal B−H bonds, and three bands at lower frequencies—2241, 2150 and 2124 cm^{-1}—belong to absorptions of bridging Al−H−B bonds. A similar IR spectrum was reported for $Al(BH_4)_3$.[22]

The NMR spectrum of **1b** in Et_2O was originally reported by Nöth,[3] and NMR spectra of **2b**, **3b**, and **4b** were also studied by Nöth in THF solution.[4] In the present study, **2b**, **3b**, and **4b** were prepared in less basic Et_2O solutions, and in this solvent the spectra are less complex than in THF. ^{11}B, ^{27}Al, and ^{1}H NMR data are summarized in Table 4. **4b** might be fully dissociated in solution, since the ^{11}B resonance observed is identical to the chemical shift for $LiBH_4$, δ −39.6 ppm, in the same solvent. The ^{27}Al NMR spectrum of **4b** at δ 111.7 ppm is also indicative of the dissociation product $AlH_3(Et_2O)_x$ (δ 105 ppm, THF).[4] **2b** may partially dissociate into $HAl(BH_4)_2(Et_2O)_x$ and $LiBH_4$. The benzene soluble fraction of **2b** contains a single ^{11}B resonance at δ −35.1 ppm (q, J_{B-H} = 85.7 Hz), an ^{27}Al signal (δ 89.0 ppm), and a ^{1}H signal (δ 0.94 (q), J_{B-H} = 85 Hz) which correspond to $HAl(BH_4)_2(Et_2O)_x$.[23] The benzene-insoluble fraction contains $LiBH_4$. Similarly **3b** may partially dissociate into $HAl(BH_4)_2(Et_2O)_x$ and $AlH_3(Et_2O)_x$. The benzene extract shows a ^{11}B signal at δ −35.1 ppm (q, J_{B-H} = 85.7 Hz) and two equally intense ^{27}Al NMR signals at δ 89.0 and 117 ppm which are consistent with $HAl(BH_4)_2(Et_2O)_x$[23] and $AlH_3(Et_2O)_x$.[4] In Et_2O solutions these species coexist in equilibria. Low temperature ^{11}B NMR of **2b** and **3b** in Et_2O solutions confirm the partial dissociation and in general are in agreement with an earlier study performed in THF solutions.[4] Complex **1b** was also demonstrated to be in equilibrium with $Al(BH_4)_3$ and $LiBH_4$ by Nöth and co-workers[3] using low temperature NMR spectroscopy.

Overall, the Li^+ salts of the $[Al(BH_4)_4]^-$, $[AlH(BH_4)_3]^-$, $[AlH_2(BH_4)_2]^-$, and $[AlH_3(BH_4)]^-$ anions are much less stable than those with large complex cations. Complexes **1c** and **1d** show unusual stability and they are fully characterized. The structures for the remaining aluminum boron hydride anions $[AlH(BH_4)_3]^-$, $[AlH_2(BH_4)_2]^-$, and $[AlH_3(BH_4)]^-$ were not accessible because of the limited stabilities of the salts containing these anions.

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Supplementary Material Available: Full listings of crystal data, positional parameters of nonhydrogen atoms, positional parameters of hydrogen atoms, complete bond distances and bond angles, and anisotropic thermal parameters and a labeled ORTEP diagram showing the cation (8 pages). Ordering information is given on any current masthead page.

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(21) Ogg, R. A.; Ray, K. D. *Discuss. Faraday Soc.* **1955**, *19*, 239.

(22) Price, W. C. *J. Chem. Phys.* **1949**, *7* (11), 1044.

(23) NMR data for $HAl(BH_4)_2(Et_2O)_x$ containing some $Al(BH_4)_2Et(Et_2O)$ impurity were reported previously, Oddy P. R.; Wallbridge M. G. H. *J. Chem. Soc., Dalton Trans.* **1978**, 572. (^{11}B: −34.8 (q) ppm, J_{B-H} = 86.1 Hz. ^{27}Al: 84 ppm.)

(24) (a) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235. (b) Lippard, S. J.; Russ, B. J. *Ibid.* **1968**, *7*, 1686.