Inorg. Chem. **2006**, *45*, 6549–6554

Inorganic Chemistry
Article

Cesium Hydridotris(trifluoromethyl)borate, $Cs[(CF_3)_3BH]$[†]

Jens Geier,* Gottfried Pawelke, and Helge Willner*

Bergische Universität Wuppertal, FB C - Anorganische Chemie, Gaussstrasse 20,
D-42097 Wuppertal, Germany

Received March 14, 2006

Treatment of $Cs[(CF_3)_3BNH_2]$ with the aminating agent H_2NOSO_3H in aqueous solution allowed the isolation of pure $Cs[(CF_3)_3BH]$, which is stable up to 300 °C. Due to the strong electron-withdrawing effect of the CF_3 substituents, the $[(CF_3)_3BH]^-$ anion behaves as a very unreactive hydride. It is stable in concentrated hydrochloric acid for many days but reacts cleanly with F_2, Cl_2, and Br_2 to the corresponding haloborates. The molecular structure was determined by single-crystal X-ray diffraction. Crystal data: orthorhombic, space group *Pnma*; $a = 11.4296(5)$ Å, $b = 7.9510(4)$ Å, $c = 9.7268(5)$ Å; $V = 883.94(7)$ Å^3, $Z = 4$; R1 = 0.0294, wR2 = 0.0818. The anions exhibit only C_s symmetry in the lattice. The natural and deuterated anions were characterized by IR, Raman, and multinuclear NMR spectroscopy; vibrational assignments were supported by DFT calculations. QTAIM charges derived from the B3LYP electron density are given for $[(CF_3)_3BH]^-$ and several related anions.

Introduction

Although the Lewis superacid $(CF_3)_3B$[1] is a very short-lived molecule, the corresponding Lewis acid−base adducts such as $(CF_3)_3BNH_3$[2] and the borates $[(CF_3)_3BX]^-$, X = F, Cl, Br,[3] CN, NC,[4] are stable species. All perfluoroalkylborates are promising weak coordinating anions with interesting applications. One example of the long-sought hydridotris(perfluoroalkyl)borate anions $[(R_f)_3BH]^-$, the hydridotris(perfluoroethyl)borate $[(C_2F_5)_3BH]^-$, was recently detected as an impurity that was not isolable during the synthesis of $[(C_2F_5)_3BF]^-$.[5] The isolation of such a hydridotris(perfluoroalkyl)borate is of interest because it constitutes the parent member in the series of the $[(R_f)_3BX]^-$ species. Moreover, it may exhibit unusual spectroscopic properties and, due to the very strong electron-withdrawing effect of the perfluoroalkyl substituents, one may speculate about the possibility of generating a dianion $[(R_f)_3B]^{2-}$ by deprotonation with strong bases. In recent years, we attempted several syntheses of the $[(CF_3)_3BH]^-$ anion by reacting $(CF_3)_3BCO$[6] with different hydride sources, but all failed. In some instances, (i) ArF laser photolysis of $[(CF_3)_3BCO_2]^{2-}$ in H_2O,[7] (ii) reduction or UV irradiation of dissolved $Cs[(CF_3)_3BN{=}NCF_3]$,[8] and (iii) treatment of $Cs[(CF_3)_3BNCl_2]$[3] with Ph_3P in MeO^{t}Bu, traces of $[(CF_3)_3BH]^-$ were indicated by NMR spectroscopy, but its isolation proved to be impossible. In this article, we report an unusual reaction of the ammine complex $(CF_3)_3BNH_3$,[2] which allows, for the first time, the isolation of small quantities of pure $Cs[(CF_3)_3BH]$.

Experimental Section

$(CF_3)_3BNH_3$ was prepared according to the published procedure.[2] All other chemicals were commercial products (Fluka/Honeywell) of ≥95% ($CsOH{\cdot}H_2O$ and H_2NOSO_3H) or >99% (solvents) purity and were used as received.

Cesium Hydridotris(trifluoromethyl)borate. $(CF_3)_3BNH_3$ (1.17 g, 5.0 mmol) and $CsOH{\cdot}H_2O$ (1.68 g, 10.0 mmol) were dissolved in 15 mL of water. Solid H_2NOSO_3H (1.13 g, 10.0 mmol) was added as a powder at room temperature within 15 min in 8−10 portions. After a few portions had been added, an exothermic reaction with evolution of gas was noted. The solution was stirred for 0.5 h and, upon addition of $CsOH{\cdot}H_2O$ (3.36 g, 20.0 mmol),

---

[†] Dedicated to Professor Karl Otto Christe on the occasion of his 70th birthday.

* To whom correspondence should be addressed. Phone: +49(0)202-439-2517. Fax: +49(0)202-439-3053. E-mail: geier@uni-wuppertal.de (J.G.); willner@uni-wuppertal.de (H.W.).

(1) Sheldrick, G. M. *SHELX-97*, University of Göttingen: Göttingen, Germany, 1997.
(2) Ansorge, A.; Brauer, D. J.; Bürger, H.; Krumm, B.; Pawelke, G. *J. Organomet. Chem.* **1993**, *446*, 25.
(3) Brauer, D. J.; Bürger, H.; Chebude, Y.; Pawelke, G. *Inorg. Chem.* **1999**, *38*, 3972.
(4) Finze, M.; Bernhardt, E.; Lehmann, C. W.; Willner, H. *J. Am. Chem. Soc.* **2005**, *127*, 10712.
(5) Pawelke, G.; Willner, H. *Z. Anorg. Allg. Chem.* **2005**, *631*, 759.
(6) Finze, M.; Bernhardt, E.; Terheiden, A.; Berkei, M.; Willner, H.; Christen, D.; Oberhammer, H.; Aubke, F. *J. Am. Chem. Soc.* **2002**, *124*, 15385.
(7) Bernhardt, E.; Willner, H. unpublished results.
(8) Brauer, D. J.; Bürger, H.; Chebude, Y.; Pawelke, G. *Z. Naturforsch., B: Chem. Sci.* **2000**, *55b*, 269.

10.1021/ic0604361 CCC: $33.50

solid H_2NOSO_3H (1.13 g, 10.0 mmol) was slowly added again. After stirring for 1 h, the sequence of adding at first $CsOH{\cdot}H_2O$ (3.36 g, 20.0 mmol) and then H_2NOSO_3H (1.13 g, 10.0 mmol) was repeated 3−4 times more until the ^{19}F NMR spectrum indicated more than 80% conversion of $[(CF_3)_3BNH_2]^-$ (the solution was occasionally diluted with a small amount of water). After 12 h, the solution was made strongly alkaline with CsOH, the solvent was evaporated, the solid residue kept under dynamic vacuum for 12 h (to remove also the H_2NNH_2 formed in the synthesis) and then extracted with ten 30 mL portions of hot tetrahydrofurane. The solvent was removed, and the residue (mainly $Cs[(CF_3)_3BOH]$ with a smaller amount of the less soluble $Cs[(CF_3)_3BH]$) was crystallized four to five times from a boiling mixture of 1,4-dioxane (30−40 mL) and 1,2-dimethoxyethane (2−5 mL). The obtained colorless crystals lost solvent completely upon drying in a vacuum ($\approx 10^{-3}$ mbar) for 24 h. $Cs[(CF_3)_3BH]$ remained as a colorless powder (92 mg, 0.26 mmol, 5% with respect to $(CF_3)_3BNH_3$) which was pure according to its NMR (^{19}F, ^{1}H, ^{11}B, ^{13}C) spectra. Single crystals suitable for X-ray diffractometry were grown by slow evaporation of a solution in diethyl ether/*n*-hexane.

The deuterated compound was prepared analogously in D_2O instead of H_2O solution. The starting materials $[(CF_3)_3BNH_3$, $CsOH{\cdot}H_2O$, and $H_2NOSO_3H]$ were dissolved in D_2O and evaporated to dryness several times before use. The degree of deuteration of $Cs[(CF_3)_3BD]$, estimated by vibrational spectroscopy, was >95 mol%.

Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on an FTIR spectrometer IFS 66v (Bruker, Karlsruhe, Germany) equipped with a DTGS detector and a KBr/Ge or Mylar/Ge beam splitter operating in the region 4000−400 or 700−100 cm^{-1}, respectively. For each spectrum, 64 scans were added with an apodized resolution of 2 cm^{-1}. The solid samples were measured as KBr pellets or Nujol mulls between polyethylene disks. Raman spectra were recorded at room temperature on a Bruker EQUINOX 55 FT Raman spectrometer (Bruker, Karlsruhe, Germany) using the 9394.8 cm^{-1} exciting line (500 mW) of a Nd:YAG laser. Solid samples were used for recording spectra in the region 3000−50 cm^{-1} with a resolution of 2 cm^{-1}. For each spectrum, 2000 scans were added.

NMR Spectroscopy. NMR spectra of $Cs[(CF_3)_3B(H/D)]$ were measured in D_2O at room temperature on Bruker Avance DRX-250 (^{1}H, 250.13 MHz; ^{19}F, 235.34 MHz; ^{11}B, 80.25 MHz) and DRX-400 (^{13}C, 100.6 MHz) spectrometers. The chemical shifts are relative to external TMS (^{1}H and ^{13}C), $CFCl_3$ (^{19}F), and $BF_3{\cdot}OEt_2$ (^{11}B).

Differential Scanning Calorimetry. Thermo-analytical measurements were performed with a Netzsch DSC 204 (Netzsch GmbH, Selb, Germany) instrument. Temperature and sensitivity calibrations in the temperature range of 20−600 °C were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 3 mg of solid $Cs[(CF_3)_3BH]$, contained in a sealed aluminum crucible, were heated from 20 to 600 °C at a rate of 10 °C min^{-1} under an atmosphere of dry nitrogen. The data were processed with the Netzsch Protens 4.0 software.

Single-Crystal X-ray Diffraction. Diffraction data were collected at room temperature on a P4 Smart 1000 diffractometer (Bruker AXS, Karlsruhe, Germany) using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. They were corrected with SADABS, version 2.10.[9] The crystal structure was solved by direct methods using SHELXS-97,[10] and full-matrix least-squares refinement based on F^2 was performed using SHELXL-97.[10] Molecular structure diagrams were generated with the program XP.[11] A summary of crystal data is contained in Table 1. CCDC reference number: 299071. Crystallographic data in cif format can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Data of $Cs[(CF_3)_3BH]$ at Room Temperature

formula	C_3CsBF_9H
molecular weight [g mol^{-1}]	351.76
color	colorless
cryst syst, space group	orthorhombic, *Pnma*
a [Å]	11.4296(5)
b [Å]	7.9510(4)
c [Å]	9.7268(5)
V [Å^3]	883.94(7)
Z	4
ρ_{calcd} [g·cm^{-3}]	2.643
θ range [°]	2.75−28.19
R1 ($I > 2\sigma$)[a]	0.0294
wR2 (all data)[b]	0.0818
GOF on F^2	1.107

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$; $a = 0.0443$, $b = 0.90$, $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Theoretical Calculations. The molecular structures were optimized with the Gaussian program package[12] at the B3LYP/6-311++G(2d,2p) level,[13−16] starting with RHF/6-311++G(2d,-2p) orbitals as initial guess (SCF convergence criteria for density matrix [rms] and energy: 10^{-8} and 10^{-6}; optimization convergence criteria for maximum force and maximum displacement: 4.5×10^{-4} and 1.8×10^{-3}). Cartesian d functions were used throughout. All structures are minima according to their Hessian eigenvalues. Frequencies are unscaled. All occupied B3LYP orbitals had negative energies, and the validity of the single reference calculations was checked in all cases by a stability analysis.[17] The B3LYP orbitals were saved in wfn output files by means of the Keywords: 6d, DENSITY = CURRENT, OUTPUT = WFN. The topological analysis of the electron density was performed with the program AIM2000 ver. 2.0,[18] which uses the wfn files as input. The integrations over atomic basins were done in natural coordinates with relative and absolute accuracies of 10^{-5}. The magnitudes of the integrated values of $L(\mathbf{r}) = -1/4\nabla^2\rho(\mathbf{r})$ were smaller than 10^{-3} au in all cases.

---

(9) *SADABS Bruker Nonius area detector scaling and absorption correction − V2.10*; Bruker-Nonius: Madison, WI, 2003.

(10) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Univerisity of Göttingen: Göttingen, Germany, 1997.

(11) *SHELXTL program package V. 6.10*; Bruker AXS: Karlsruhe, Germany, 2000.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

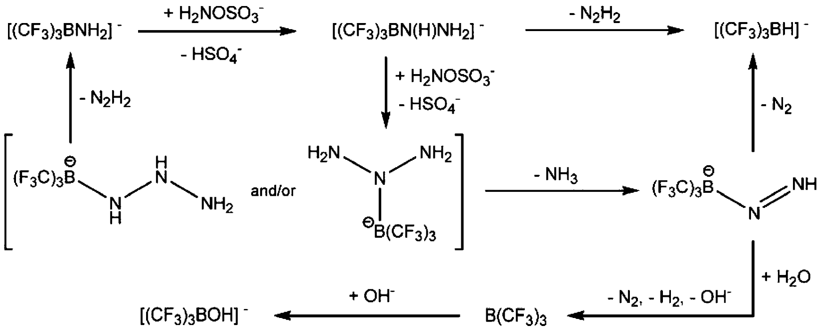
(15) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8558.

(16) Becke, A. D. *J. Chem. Phys* **1996**, *104*, 1040.

(17) Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047.

(18) Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 545.

Scheme 1. Proposed Mechanism for the Reaction of $[B(CF_3)_3NH_2]^-$ with $H_2NOSO_3^-$



Results and Discussion

Synthesis. The amidoborate, $[(CF_3)_3BNH_2]^-$,[2] reacts in aqueous alkali metal hydroxide solution exothermically under gas evolution with the electrophilic aminating agent hydroxylamine-*O*-sulfonic acid. The latter must be employed in a large excess (10−15 times) in order to achieve more than 80% conversion. The main product is, instead of the expected hydrazidoborate, $[(CF_3)_3BN(H)NH_2]^-$, the hydroxoborate, $[(CF_3)_3BOH]^-$,[19] together with 5−10 mol% of the desired hydridoborate $[(CF_3)_3BH]^-$. Fortunately, the latter can be isolated from the reaction mixture in the form of its cesium salt, $Cs[(CF_3)_3BH]$, by repeated crystallization from a mixture of 1,2-dimethoxyethane and 1,4-dioxane as a colorless, nonhygroscopic and air-stable solid in about 5% yield. It is reasonable to assume, that the first step of this obviously complicated reaction consists of an electrophilic amination of the amidoborate, $[(CF_3)_3BNH_2]^-$, to give the hydrazidoborate, $[(CF_3)_3BN(H)NH_2]^-$, (Scheme 1), which then either undergoes β-elimination, leading to the desired product and diazene, N_2H_2, or is attacked again by the aminating agent.

In the latter case, two isomeric triazanidoborates, $[(CF_3)_3BN_3H_4]^-$, may arise, which are expected to eliminate either NH_3 with formation of the diazenidoborate, $[(CF_3)_3BN_2H]^-$, or N_2H_2 with formation of the starting material. This regeneration of $[(CF_3)_3BNH_2]^-$ is consistent with the low conversion of the reaction. The intermediate diazenidoborate may then decompose under β-elimination, forming N_2 and $[(CF_3)_3BH]^-$, or it may fragment heterolytically to the neutral borane $B(CF_3)_3$. The latter reaction resembles the decomposition of N_2H_2 in strongly basic solution: $H{-}N{=}N^- + H_2O \rightarrow N_2 + H_2 + OH^-$. The unstable Lewis acid $B(CF_3)_3$ is expected to react immediately to the main product $[(CF_3)_3BOH]^-$. This reaction sequence was, however, not proved. It was not possible to identify any intermediates, and the reaction becomes even more complicated through the fast decomposition of H_2NOSO_3H in basic solution, which generates NH_3, N_2H_4, N_2, and H_2.

Properties. $Cs[(CF_3)_3BH]$ is stable up to 300 °C (DSC) and then decomposes exothermically. It is easily soluble in water, tetrahydrofuran, 1,2-dimethoxyethane, diethyl ether, and acetonitrile, hardly soluble in 1,4-dioxane, and insoluble in methylene chloride and aromatic or aliphatic hydrocarbons. Remarkably, it is stable in concentrated hydrochloric acid solution at room temperature for many days. On the other hand, it is destroyed readily by aqua regia or anhydrous hydrogen fluoride. In the latter case, its decomposition products indicate the intermediate formation of unstable $B(CF_3)_3$.[1] $Cs[(CF_3)_3BH]$ shows no reaction with H_2NOSO_3H under the conditions employed for its synthesis. It is not affected by heating in D_2O solution with catalytic amounts of CsOH in a sealed glass tube to 120 °C for 1 week, in particular there is no H−D exchange observed. $Cs[(CF_3)_3BH]$ cannot be deprotonated to the hypothetical dianion $[(CF_3)_3B]^{2-}$ by $CsNH_2$ in liquid ammonia at −40 °C or by $^nBuLi/KO^tBu$ in tetrahydrofuran at −78 °C: upon addition of D_2O to such reaction mixtures, only unchanged $[(CF_3)_3BH]^-$ is detected by NMR spectroscopy. Iodine shows no reaction in aqueous solution at room temperature, but heating $Cs[(CF_3)_3BH]$ with excess iodine in a sealed tube to 160 °C for several hours gives an unidentified mixture of compounds. In contrast, bromine or chlorine react cleanly in aqueous solution at room temperature to give the known haloborates $[(CF_3)_3BBr]^-$ and $[(CF_3)_3BCl]^-$.[3] Even the reaction of a solid film of $Cs[(CF_3)_3BH]$ on the wall of a PFA flask with fluorine (20 mbar for 1 day at room temperature, then 200 mbar for an additional day) gives almost clean $Cs[(CF_3)_3BF]$. Obviously the hydrogen atom in $Cs[(CF_3)_3BH]$ behaves as a very unreactive hydride due to the strong electron-withdrawing CF_3 substituents.

Molecular Structure and Charge Distribution. Crystallization of $Cs[(CF_3)_3BH]$ from a dme/dioxane mixture is a convenient method for its purification (cf. the Experimental Section), but it affords strongly disordered crystals, which contain solvent-coordinated cesium cations. Solvent-free crystals of good quality can, however, be obtained by slow evaporation of a solution in diethyl ether/*n*-hexane as colorless cuboids. Their structure was determined by single-crystal X-ray diffractometry and belongs to space group *Pnma* (cf. Table 1). The $[B(CF_3)_3H]^-$ anions have crystallographic C_s symmetry, with H1, B1, C2, and F5 being located on the mirror plane (see Figure 1).

The bond lengths and angles within the $(CF_3)_3B$ fragment (cf. Table 2) are essentially identical with those found in the analogous haloborates $[(CF_3)_3BX]^-$, X = F,[20] Cl, Br.[3]

---

[19] Brauer, D. J.; Bürger, H.; Chebude, Y.; Pawelke, G. *Eur. J. Inorg. Chem.* **1999**, 247.

[20] Bernhardt, E.; Finze, M.; Willner, H.; Lehmann, C. W.; Aubke, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 2077.

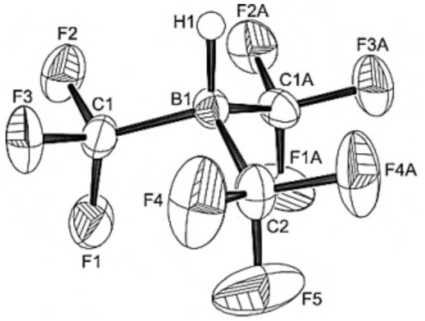


Figure 1. Structure of $[(CF_3)_3BH]^-$ in $Cs[(CF_3)_3BH]$ (thermal ellipsoids for 30% probability).

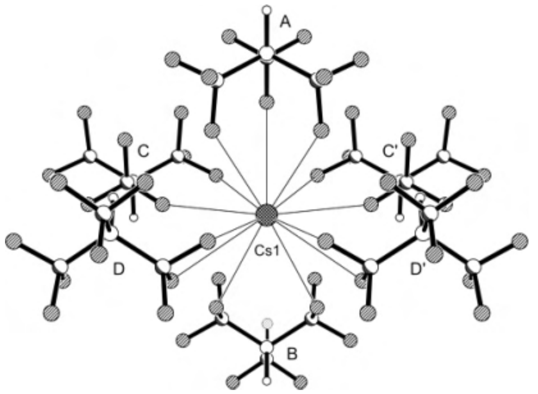


Figure 2. Coordination sphere of a cesium cation in $Cs[(CF_3)_3BH]$.

Table 2. Bond Lengths [Å] and Angles [deg] for $Cs[(CF_3)_3BH]$

B1−C1	1.602(4)	C1−F2	1.361(4)
B1−C2	1.603(7)	C1−F3	1.347(4)
B1−H1	1.15(6)	C2−F4	1.326(4)
C1−F1	1.339(5)	C2−F5	1.335(9)
C1−B1−C1A	110.4(4)	F1−C1−F3	104.8(3)
C1−B1−C2	109.6(3)	F2−C1−F3	102.7(3)
C1−B1−H1	109(2)	F4−C2−F4A	103.6(5)
C2−B1−H1	110(3)	F4−C2−F5	103.5(4)
F1−C1−F2	103.5(3)	F1−C1−B1−H1	−177(3)

Table 3. QTAIM Charges (q) of Hydrogen and Boron in Several Hydridoborates and the Delocalization Index δ(B,H) Determined at the B3LYP/6-311++G(2d,2p) Level

	q(H)	q(B)	δ(H, B)
$[BH_4]^-$	−0.662	+1.648	0.558
$[F_3BH]^-$	−0.663	+2.257	0.439
$[Cl_3BH]^-$	−0.628	+1.819	0.561
$[(CH_3)_3BH]^-$	−0.651	+1.797	0.493
$[(CF_3)_3BH]^-$	−0.556	+1.849	0.508
$[(NC)_3BH]^-$	−0.528	+1.902	0.506
$[(CN)_3BH]^-$	−0.580	+2.148	0.480
$[(HO)_3BH]^-$	−0.659	+2.189	0.442

The B−H bond distance was refined to 1.15(6) Å. There are no significant intermolecular contacts between hydrogen and fluorine; the shortest distance amounts to 3.14(3) Å. The cesium cation is irregularly surrounded by 13 fluorine atoms, with distances ranging from 3.040(3) to 3.552(3) Å. As shown in Figure 2, one anion (A) coordinates over three CF_3 groups (each with one fluorine atom), three anions (B, C, C′) coordinate over two CF_3 groups (again, each with one fluorine atom), and two anions (D, D′) coordinate over one CF_3 group (each with two fluorine atoms).

The structural parameters of $[(CF_3)_3BH]^-$ are reproduced by a B3LYP/6-311++G(2d,2p) calculation on the free, C_3-symmetric anion (B−H, 1.203 Å; B−C, 1.629 Å; F_{anti}−C−B−H, 172.56°; there is no stable structure with C_{3v} symmetry). The atomic charges, determined by the topological analysis of the electron density (QTAIM),[21] are contained in Table 3, together with the corresponding values for several other hydridoborates. In addition, the number of shared electrons between hydrogen and boron, the delocalization index[22] δ(H,B), is given. A hydrogen atom in the parent compound $[BH_4]^-$ carries a negative charge of −0.662. Substitution of three hydrogen atoms against fluorine leaves this value unchanged, but increases the positive charge of boron (by 37%) and the ionicity of the B−H bond (indicated by the lower δ value). By contrast, the CF_3 substituent in $[(CF_3)_3BH]^-$ decreases the negative charge of the hydrogen atom significantly, to −0.556, but has less effect on boron. These differences between fluorine and the CF_3 group are in line with the common view of fluorine as a π-donating substituent. Within the examples of Table 3, only the cyano group exhibits a slightly stronger electron-withdrawing effect than a CF_3 group; the negative charge of the hydrogen atom in the known $[(NC)_3BH]^-$ anion[23] amounts to −0.528.

NMR Spectra. The ^1H signal of $[(CF_3)_3BH]^-$ (Figure 3a) appears at 1.41 ppm (D_2O solution) as a quartet of decets due to coupling with one ^{11}B [$I = 3/2$; $^1J(^1H^{11}B) = 90.6$ Hz] and nine ^{19}F nuclei [$^3J(^1H^{19}F) = 12.2$ Hz].

The outermost lines and the ^{10}B satellites are not resolved. Although the symmetry of $[(CF_3)_3BH]^-$ enables the presence of an electric field gradient at boron, the ^{11}B signal (Figure 3b) is only marginally broadened. It appears as a doublet of decets at −22.2 ppm, due to coupling (cf. Table 4) with the ^1H and ^{19}F nuclei (again, the outermost lines are not observed).

Compared with the haloborates $[(CF_3)_3BX]^-$, X = F, Cl, and Br, it is significantly shifted to lower frequency (Table 4). Exhaustive NMR data for $[X_3BH]^-$, X = alkyl, perfluoroaryl, or (pseudo)halogen, are rare and often complicated by the presence of X_3B impurities, which lead to chemical exchange between anion, Lewis acid, and hydrogen-bridged structures. The ^1H chemical shift of $[(NC)_3BH]^-$ in CD_3CN is 1.77 ppm,[24] and $^1J(^1H^{11}B)$ amounts to 98.8 Hz.[24] For Li[$(CH_3)_3BH$] in hexane/thf, the latter is much smaller with 66.6 Hz[25] (cf. $[Et_4N][BH_4]$ in CD_3CN: $\delta(^1H) = -0.35$ ppm and $^1J(^1H^{11}B) = 80.9$ Hz[7]). In the tetrabutylammonium salt of hydridotris(pentafluorophenyl)borate[26] $[(C_6F_5)_3BH]^-$ (which

---

[21] Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

[22] Fradera, X.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem. A* **1999**, *103*, 304.

[23] Yao, H.; Kuhlman, M. L.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2005**, *44*, 6256.

[24] Bernhardt, E.; Hoppmann, S.; Willner, H., unpublished results for $K[(NC)_3BH]$ in CD_3CN. The ^1H chemical shift for $Na[(NC)_3BH]$ in D_2O was given as 1.94 ppm (a), while 1.76 ppm (b) was reported for the $[(Ph_3P)_2N]^+$ salt in CD_3CN: (a) Györi, B.; Emri, J.; Fehér, I. *J. Organomet. Chem.* **1983**, *255*, 17. (b) Yao, H.; Kuhlman, M. L.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2005**, *44*, 6256. The $^1J(^1H^{11}B)$ values for $[Cl_3BH]^-$ and $[Br_3BH]^-$ with $[Bu_4N]^+$ cations in CH_2Cl_2 were given as 158 and 176 Hz, respectively: Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1952.

[25] Biffar, W.; Nöth, H.; Sedlak, D. *Organometallics* **1983**, *2*, 579.

[26] Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.

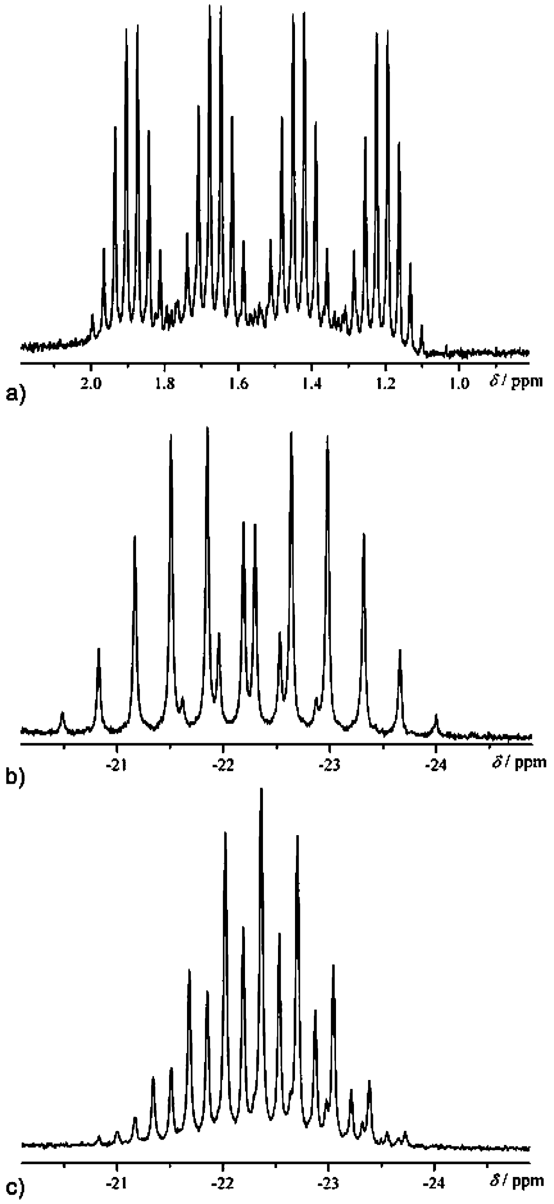


Figure 3. (a) ^{1}H NMR spectrum of $Cs[(CF_3)_3BH]$ in D_2O. (b) ^{11}B NMR spectrum of $Cs[(CF_3)_3BH]$ in D_2O. (c) ^{11}B NMR spectrum of $Cs[(CF_3)_3BD]$ in D_2O.

Table 4. NMR Data of $[(CF_3)_3BH]^-$ and Related $[(CF_3)_3BX]^-$ Anions

X	δ (^{11}B) [ppm]	δ (^{19}F) [ppm]	δ (^{13}C) [ppm]	$^{1}J(^{11}B^{13}C)$ [Hz]	$^{1}J(^{13}C^{19}F)$ [Hz]	$^{2}J(^{11}B^{19}F)$ [Hz]	ref
H[b]	−22.2	−58.7	136.0	71.8	∼310	27.3	[a]
D	−22.4	−58.8				27.0	[a]
F	−7.1	−68.8	132.6	80.0	309.4	28.3	3,28
Cl	−12.7	−65.8	134.2	77.9	308.0	27.4	3
Br	−14.9	−64.3	131.8	83.0	302.7	30.2	3
CN	−22.3	−62.1	132.4	76.2	303.2	29.0	4
C(O)F	−19.1	−61.2	132.8	74.6	303.9	27.1	29
CF_3	−18.9	−61.6	132.9	73.4	304.3	25.9	28
NC	−17.5	−67.0	131.7	78.4	304.8	29.0	4
OH	−10.6	−68.0	134.7	75.8	311.4	26.8	19

[a] This work [b] $^{2}J(^{1}H^{13}C) = 8.0$ Hz.

is directly accessible from the stable free Lewis acid $(C_6F_5)_3B$) the hydrogen atom is with $\delta(^{1}H) = 4.16$ ppm (in C_6D_6)[27] strongly deshielded relative to $[(CF_3)_3BH]^-$. In contrast, the boron signal appears at lower frequency [δ(^{11}B) $= -25.5$ ppm] and $^{1}J(^{1}H^{11}B)$ is 58 Hz smaller than in $[(CF_3)_3BH]^-$ (90.6 Hz). The ^{11}B signal of the deuterated anion $[(CF_3)_3BD]^-$ is shown in Figure 3c. The 30 lines of the expected decet of triplets ($I[^{2}H] = 1$) collapse into 15 lines because $^{1}J(^{2}H^{11}B)$ is, at 13.6 Hz, almost exactly half as large as $^{2}J(^{11}B^{19}F) = 27.0$ Hz.

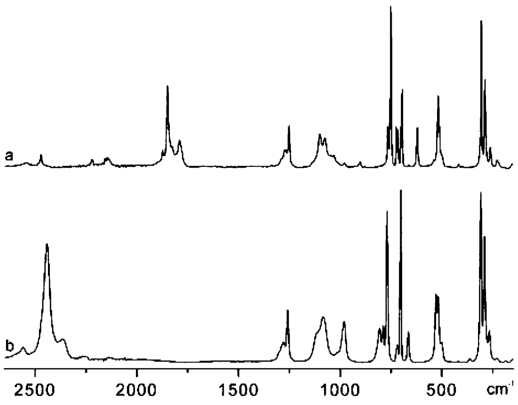


Figure 4. Raman spectra of (a) $Cs[(CF_3)_3BD]$ and (b) $Cs[(CF_3)_3BH]$.

Vibrational Spectra. The Raman spectra of both isotopomers, $Cs[(CF_3)_3BH]$ and $Cs[(CF_3)_3BD]$, are displayed in Figure 4.

They are surprisingly different due to strong vibrational coupling of the B(H/D) modes with the $(CF_3)_3B$ skeleton vibrations. The Raman and IR band positions of $[(CF_3)_3BH]^-$ and $[(CF_3)_3BD]^-$ are listed in Tables 5 and 6, together with the theoretical values obtained from DFT calculations. In C_3 symmetry, there are 24 IR- and Raman-active vibrational fundamentals:

$$\Gamma_{vib} = 12A\ (IR,\ Ra\ p) + 12E\ (IR,\ Ra\ dp)$$

From these, 19 were observed for $[(CF_3)_3BH]^-$ and 17 for $[(CF_3)_3BD]^-$. The missing modes (ν_{12}/ν_{24}) are outside the range of our spectrometers, overlap with each other (ν_7/ν_{20}) or are too weak for detection. As evident from Tables 5 and 6, the agreement between experimental and calculated band positions and band intensities is reasonable.

This allows the attribution of all observed fundamentals to the respective symmetry classes, but the description of modes, except ν(BH) and ν(BD), is arbitrary due to strong vibrational mixing. In general, all E mode bands are broader than the A mode bands, which indicates lifting of the E degeneracy. This is not unexpected due to the low rotation barrier of the CF_3 groups (cf. the C_s symmetry of the anion in the crystal structure). There is a large difference for the band positions of ν(BH) in the IR and Raman spectrum, possibly caused by exchange of Cs^+ with K^+ in the KBr pellet. Furthermore, the ν(BH) and ν(BD) bands are obviously disturbed by anharmonic resonances. They still behave like isolated B(H/D) oscillators, as indicated by the observed ν(BH)/ν(BD) ratio of 1.34, which is in agreement with the calculated value of 1.35. The six C−F stretching vibrations

---

(27) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247.

(28) Bernhardt, E.; Henkel, G.; Willner, H.; Pawelke, G.; Bürger, H. *Chem. Eur. J.* **2001**, *7*, 4696.

(29) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Chem. Eur. J.* **2005**, *11*, 6653.

Table 5. Vibrational Band Positions (cm^{-1}) and Band Intensities for Cs[(CF$_3$)$_3$BH]^d

Raman^a	IR^b	ν_{calcd}^{c}	I_{calcd}(Raman)^c	I_{calcd}(IR)^c	assignment (C_3)
2557, w	2484, m sh	2514			υ_1 A $\nu(^{10}BH)$
2442, vs br	2473, m	2504	124	121	υ_1 A $\nu(^{11}BH)$
2363, w	2366, vw				$\upsilon_{13} + \upsilon_3$
	2141, w				$2\upsilon_3$
	1385, m				$\upsilon_6 + \upsilon_{18}$
1300, vw sh	1297, s	1279			υ_{13} E $\nu_{as}(CF_3)$ ^{10}B
1279, w	1280, vs	1260	1.87	176	υ_{13} E $\nu_{as}(CF_3)$
1258, m	1257, s	1239	1.25	52.1	υ_2 A $\nu_s(CF_3)$
1118, m sh	1106, sh vs	1085	0.46	87.1	υ_{14} E $\nu_{as}(CF_3)$
1084, m br	1077, vs br	1069	6.75	631	υ_3 A $\nu_a(CF_3)$
1017, vw sh		1054	3.94	186	υ_{15} E $\nu_{as}(CF_3)$
		969	0.18	0.08	υ_4 A $\nu_s(CF_3)$
981, m br	977, vs br	965	2.49	206	υ_{16} E $\nu_{as}(BC_3)$
	904, w				$\upsilon_5 + \upsilon_{23}$
	881, w−m				
806, m	804, m	797	1.25	23.5	υ_{17} E $\delta(CBH)$
789, m	790, w−m	779			υ_5 A $\nu_s(^{10}BC_3)$
769, s	770, m	759	7.10	30.8	υ_5 A $\nu_s(BC_3)$
	705, m sh	696			υ_6 A $\delta_s(CF_3)$ ^{10}B
702, vs	701, m	693	5.88	11.5	υ_6 A $\delta_s(CF_3)$
664, m	663, s	655	0.42	30.4	υ_{18} E $\delta_{as}(CF_3)$
530, m	529, vw	518	0.49	0.00	υ_{19} E $\delta_{as}(CF_3)$
518, m	518, w	509	0.19	0.06	υ_7 A $\delta_s(CF_3)$
		508	1.28	1.42	υ_{20} E $\delta_{as}(CF_3)$
500, w	500, vw	489	0.89	1.16	υ_8 A $\delta_s(CF_3)$
309, s	308, vvw	299	1.32	0.03	υ_{21} E $\rho_{as}(CF_3)$
291, s	290, vvw	276	1.80	0.00	υ_9 A $\rho_s(CF_3)$
266, w	265, vvw	257	0.32	0.58	υ_{22} E $\rho_{as}(CF_3)$
		248	0.01	0.01	υ_{10} A $\rho_s(CF_3)$
	155, vvw	136	0.01	0.04	υ_{11} A $\delta_s(BC_3)$
	138, vvw	122	0.01	0.02	υ_{23} E $\delta_{as}(BC_3)$
		51	0.01	0.02	υ_{24} E $\tau_{as}(CF_3)$
		22	0.00	0.00	υ_{12} A $\tau_s(CF_3)$

[a] Powder. [b] KBr pellet, below 500 cm^{-1} Nujol mull. [c] B3LYP/6-311++G(2d,2p), Raman intensities in Å^4 amu^{-1}, IR intensities in km mol^{-1}. [d] Qualitative intensities: w = weak, m = medium, s = strong, v = very.

of symmetry types 3A + 3E are observed in the expected range of 1000−1280 cm^{-1}, although the A mode positions are disturbed by $\nu_s(BC_3)$ and $\delta_s(CF_3)$ and the E mode positions by $\delta(CBH)$ and $\nu_{as}(BC_3)$. Because of the considerably high mass change associated with the substitution of H against D, the spectral patterns of [(CF$_3$)$_3$BH]$^-$ and [(CF$_3$)$_3$BD]$^-$ differ quite strongly in the range 1000−500 cm^{-1}.

Table 6. Vibrational Band Positions (cm^{-1}) and Band Intensities for Cs[(CF$_3$)$_3$BD]^d

Raman^a	IR^b	ν_{calcd}^{c}	I_{calcd}(Raman)^c	I_{calcd}(IR)^c	assignment (C$_3$)
	2141, m				$\nu_3 + \nu_{15}$
1874, m	1873, w	1864			ν_1 A $\nu(^{10}BD)$
1850, s br	1851, w	1848	64.9	59.8	ν_1 A $\nu(^{11}BD)$
1791, m br	1790, w				$\nu_{14} + \nu_{17}$
	1670, w				$\nu_4 + \nu_6$
1290, w	1296, s sh	1267			ν_{13} E $\nu_{as}(CF_3)$ ^{10}B
1270, w	1280, vs	1251	1.56	120	ν_{13} E $\nu_{as}(CF_3)$
1252, m	1257, m	1237	0.91	53.1	ν_2 A $\nu_s(CF_3)$
1100, m br	1105, vs sh	1068	6.46	645	ν_3 A $\nu_s(CF_3)$
1076, m br	1080, vs	1055	3.46	212	ν_{14} E $\nu_{as}(CF_3)$
1044, w br					$\nu_5 + \nu_9$
1030, w br	1034, s sh	1016	1.57	16.7	ν_{15} E $\nu_{as}(CF_3)$
		969	0.18	0.09	ν_4 A $\nu_s(CF_3)$
929, vw	929, s	924			ν_{16} E $\nu_{as}(BC_3)$ ^{10}B
902, vw	903, vs	905	0.40	238	ν_{16} E $\nu_{as}(BC_3)$
767, m	767, w	758			ν_5 A $\nu_s(BC_3)$ ^{10}B
752, vs	753, m	743	9.70	18.6	ν_5 A $\nu_s(BC_3)$
724, m					
716, m	716, s	710	0.63	9.36	ν_{17} E $\delta_{as}(CF_3)$
695, s	695, s	688	3.95	14.7	ν_6 A $\delta_s(CF_3)$
621, m	621, s	615	1.05	13.1	ν_{18} E $\delta(CBD)$
519, s br	518, w	510	0.54	0.00	ν_{19} E $\delta_{as}(CF_3)$
		509	0.19	0.05	ν_7 A $\delta_s(CF_3)$
		507	1.51	1.51	ν_{20} E $\delta_{as}(CF_3)$
501, w sh	498, w	487	0.86	1.26	ν_8 A $\delta_s(CF_3)$
307, vs		298	1.30	0.04	ν_{21} E $\rho_{as}(CF_3)$
288, s		276	1.81	0.00	ν_9 A $\rho_s(CF_3)$
262, w		256	0.30	0.56	ν_{22} E $\rho_{as}(CF_3)$
230, vw		248	0.01	0.01	ν_{10} A $\rho_s(CF_3)$
		136	0.01	0.04	ν_{11} A $\delta_s(BC_3)$
		122	0.01	0.02	ν_{23} E $\delta_{as}(BC_3)$
		51	0.01	0.02	ν_{24} E $\tau_{as}(CF_3)$
		22	0.00	0.00	ν_{12} A $\tau_{as}(CF_3)$

[a] Powder. [b] KBr pellet. [c] B3LYP/6-311++G(2d,2p), Raman intensities in Å^4 amu^{-1}, IR intensities in km mol^{-1}. [d] Qualitative intensities: w = weak, m = medium, s = strong, v = very.

Acknowledgment. We thank Torsten Küppers for preparing the graphics from spectra and the DFG for financial support.

Supporting Information Available: Cartesian coordinates of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0604361