J. Am. Chem. Soc. **2000,** *122,* 10255−10256 10255

# The Explosive “Inert” Anion $CB_{11}(CF_3)_{12}^-$

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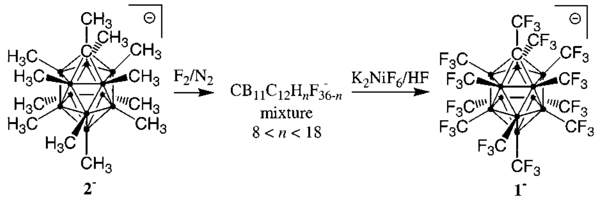
*Received May 8, 2000*
*Revised Manuscript Received August 16, 2000*

We have prepared the icosahedral anion $CB_{11}(CF_3)_{12}^-$ ($\mathbf{1}^-$), dodecakistrifluoromethylcarba-*closo*-dodecaborate, whose large size, absence of strongly basic sites, sterically protected delocalized charge, oxidation resistance, and chemical stability promise to make it a superior weakly coordinating[1] counterion for extremely acidic, electrophilic, and/or oxidizing cations. However, $Cs^+\mathbf{1}^-$ is explosive[2] and the nearly spherical symmetry of $\mathbf{1}^-$ hinders crystallographic characterization of its salts.

In previous attempts to decrease their coordinating ability, icosahedral carborate anions were partially[3] or fully[4] halogenated or fully methylated.[5] We expected that perfluorination would suppress the sensitivity[6,7] of the $CB_{11}(CH_3)_{12}^-$ anion ($\mathbf{2}^-$)[5] to strong acids and oxidants. Halomethyl persubstituted carborate anions were not previously reported, but the neutral 1,12-$C_2B_{10}(CHCl_2)_{12}$ has been described,[8] fluorination of 1,12-$C_2B_{10}(CH_3)_{12}$ and 1,12-$(H)_2$-1,12-$C_2B_{10}(CH_3)_{10}$ has been investigated,[9] and simple trifluoromethylborates are known.[10]

Fluorination[11] of $Cs^+\mathbf{2}^-$ in $CFCl_3$ with excess 10% $F_2/N_2$ gave a mixture of partially fluorinated anions $CB_{11}C_{12}H_nF_{36-n}^-$, $\sim 8 < n < \sim 18$.[12] Repeated attempts at perfluorination using $F_2$ with and without irradiation at various pressures, temperatures, and stirring rates were unsuccessful. Unlike $\mathbf{2}^-$,[6] the partially fluorinated mixture is unaffected by anhydrous HF and hence the Simmons electrochemical fluorination[13] procedure was feasible. It provided the first samples of $\mathbf{1}^-$ in ~1% yield after HPLC separation.[12,14] Perfluorination of the partially fluorinated mixture with Bartlett’s reagent[15] ($K_2NiF_6$) is superior and provides $Cs^+\mathbf{1}^-$ in 25% overall isolated yield (96% for each of 36 successive substitutions).[12] Structure (effective $C_{5v}$ symmetry) and purity were established by spectroscopy.[16] Attempted combustion analyses resulted in detonation. The cesium salt has been converted to others by ion exchange in methanol[5] or repeated partitioning (3×) of an ethereal solution against a concentrated (~20%) aqueous solution of a salt of another cation.



Numerous attempts at single-crystal X-ray diffraction analysis of $Cs^+$, $Rb^+$, $PPN^+$, and $Ph_2EtMeP^+$ salts failed because the essentially spherical anion was disordered (many such structures of salts of $\mathbf{2}^-$ have been solved successfully[5,17] and the difficulty appears to be specific to the Teflon-like surface of $\mathbf{1}^-$). The low-symmetry ($P\bar{1}$ or $P1$) $Ph_2EtMeP^+\mathbf{1}^-$ crystal yielded a well-defined cation structure with reasonable thermal parameters, but no suitable model for the anion was found (R1 > 40%).[18] Electron density maps showed $\mathbf{1}^-$ to be essentially spherical, with a ~8.0 Å outer F sphere diameter and 3.38 Å inner $CB_{11}$ sphere diameter, in agreement with the 8.12 and 3.42 Å respective average diameters in a B3LYP/6-31G*[12] optimized structure (Figure 1).

The anion $\mathbf{1}^-$ is destroyed by heating to 250 °C and by $Na^0$ in anhydrous $NH_3$, but is not affected by 20% KOH/EtOH. It is

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(1) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133. Lupinetti, A. J.; Strauss, S. H. *Chemtracts* **1998**, *11*, 565.

(2) Scratching $Cs^+\mathbf{1}^-$ (300 mg) contained in a Pyrex flask with a metal spatula caused an explosion that broke glassware 2 m distant. It is likely that other salts of $\mathbf{1}^-$ will also be explosive and *should be treated with extreme care.*

(3) Ivanov, S. V.; Ivanova, S. M.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chim. Acta* **1999**, *289*, 76. Ivanov, S. V.; Lupinetti, A. J.; Solntsev, K. A.; Strauss, S. H. *J. Fluorine Chem.* **1998**, *89*, 1. Ivanov, S. V.; Ivanova S. M.; Miller, S. M.; Anderson, O. P.; Kuznetsov, N. T.; Solntsev, K. A.; Strauss S. H. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1310. Ivanov, S. V.; Rockwell, J. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 7882. Ivanov, S. V.; Ivanova, S. M.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 6914. Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922. Jelínek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982. Jelínek, T.; Plešek, J.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.

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(5) King, B. T.; Janoušek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313.

(6) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10902.

(7) Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10253−10254.

(8) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2536.

(9) Callahan, R. P.; Lagow, R. J.; Herzog, A.; Hawthorne, M. F. (private communication) found that at all reaction temperatures and times tried, only product mixtures inseparable by column chromatography, crystallization, or sublimation resulted from the fluorination [$F_2$/He, ratios from 1:4 to 3:1, in Freon 113 or perfluoro(isopropyldecalin); a detonation occurred once] of 1,12-$C_2B_{10}(CH_3)_{12}$ and 1,12-$H_2$-1,12-$C_2B_{10}(CH_3)_{10}$ on a 300-fold excess of NaF. The major products were 1-F-1,12-$C_2B_{10}(CF_3)_{11}$ and 1,12-$C_2B_{10}(CF_3)_{12}$ from the former and 1,12-$H_2$-1,12-$C_2B_{10}(CF_3)_{10}$, 1-F-12-H-1,12-$C_2B_{10}(CF_3)_{10}$, and 1,12-$F_2$-1,12-$C_2B_{10}(CF_3)_{10}$ from the latter (this sublimed mixture exploded upon contact with a Teflon-coated spatula). The work was discontinued as too dangerous.

(10) Brauer, D. J.; Bürger, H.; Chebude, Y.; Pawelke, G. *Inorg. Chem.* **1999**, *38*, 3972 and references therein.

(11) ***Caution:*** *Fluorine and hydrogen fluoride are extremely reactive, corrosive, and poisonous and must be handled with the utmost care. The experimentalist must become familiar with their safe handling before their use.* See, e.g.: Hudlicky, M. *Chemistry of Organic Fluorine Compounds: a Laboratory Manual with Comprehensive Literature Coverage*; Chichester: Ellis Horwood: New York, 1992. $K_2NiF_6$ can explode when treated with oxidizable substrates, *including water*. Plans for $F_2$ and anhydrous HF manifolds and reactors used are included in the Supporting Information.

(12) See Supporting Information for experimental and computational details.

(13) Simons, J. H. *J. Electrochem. Soc.* **1949**, *95*, 47. Burden, J.; Tatlow, J. C. *Adv. Fluorine Chem.* **1969**, *1*, 129.

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(15) Whalen, J. M.; Chacón, L. C.; Bartlett, N. *Proc. Electrochem. Soc.* **1997**, *97*, 1. Bartlett, N.; Chambers, A. J.; Roche, A. J.; Spink, R. C. H.; Chacón, L.; Whalen, J. M. *Chem. Commun.* **1996**, 1049.

(16) $ESI^-$ MS (mass: calcd, obsd): 955: 3.0, 5.5; 956: 12.0, 13.11; 957: 35.1, 34.35; 958: 72.0, 77.80; 959: 100, 100; 960: 86, 80.91; 961: 37.6, 32.32; 962: 4.4, 7.5. FT-ICR exact mass for $^{12}C_{13}{}^{11}B_{11}{}^{19}F_{36}$: calcd 961.04541, found 961.0443. $\{^{11}B\}^{19}F$ NMR (acetone-$d_6$, reference $CFCl_3$ at $\delta$ 0.0) $\delta$ −42.72 (3F, $CF_3$(1)), −45.58 (15F, $CF_3$(7−11), −45.70 (15F, $CF_3$(2−6), −46.60 (3F, $CF_3$(12)). $^{11}B$ NMR (reference $B(OMe)_3$ at $\delta$ 18.1) $\delta$ −0.130 (1B, B(12)), −8.997 (5B, B7−11), −12.257 (5B, B2−6). Assignments are based on $^{11}B$ COSY and CW $\{^{11}B\}^{19}F$ spectra. IR ($Cs^+$ salt, KBr) 1631, 1251, 1120, 1143, 748, 582, 481 $cm^{-1}$. Raman ($Rb^+$ salt) 737, 237 $cm^{-1}$. A single peak by HPLC (Econosil ODS 250 × 4.6 mm, 85:15 $MeOH/H_2O$ with 1% $Et_3N$, 0.7% AcOH, ELS detection).

(17) King, B. T.; Noll, B. C.; Michl, J. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1001.

(18) Crystal data for $Ph_2EtMeP^+\mathbf{1}^-$: triclinic, $a = 9.9173(2)$ Å, $b = 14.3937(2)$ Å, $c = 15.0998$ Å, $\alpha = 74.6100(10)°$, $\beta = 84.9900(10)°$ $\gamma = 79.8110(10)°$. Intensity data were collected at −180 °C on a Siemens SMART CCD diffractometer, with graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å).

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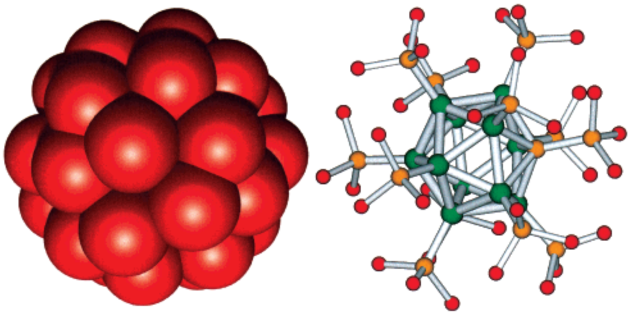

**Figure 1.** Space filling and stick representations of the calculated (B3LYP/6-31G*) structure of $CB_{11}(CF_3)_{12}^-$. F atoms are red, C atoms are yellow, and B atoms are green. The calculated structure of $\mathbf{1}^{\bullet}$ is visually indistinguishable from that of $\mathbf{1}^-$.

stable in concentrated $H_2SO_4$, anhydrous $CF_3SO_3H$, and $BF_3$/anhydrous HF mixtures, and may remain unprotonated in these acids.[19] It is electrochemically inert within the entire electrochemical window of $MeCN/Bu_4N^+PF_6^-$ and is not oxidized by $O_2^+AsF_6^-$ in anhydrous HF.

The perfluorinated analogue $\mathbf{1}^{\bullet}$ of the stable[6] neutral radical $\mathbf{2}^{\bullet}$ is calculated[12] (B3LYP/6-31+G*//B3LYP/6-31G*) to be stable, with a structure (Figure 1) very similar to that of $\mathbf{1}^-$, and is expected to be an extremely potent oxidant. The calculated[12] (B3LYP/6-31+G*//B3LYP/6-31G*) adiabatic electron detachment energy (in eV)[20] of $\mathbf{1}^-$ is 8.80; the value calculated for $\mathbf{2}^-$ is 4.57 (4.32[21]); cf. $F^-$ 3.40;[22,23] $PtF_6^-$ 7.00 ± 0.35,[23] ~8;[24] $IrF_6^-$ 6.50 ± 0.38;[23] $SbF_6^-$ >6.00;[23,25] $AuF_6^-$ 9.56,[26] >10.0.[23] Since the reversible $E_{1/2}$ of $\mathbf{2}^-$ in MeCN is 1.6 V vs NHE, this formally places the $E_{1/2}$ of $\mathbf{1}^-$ at ~5.8 V, or ~2.9 V above the $2\ F^- \rightarrow F_2$ couple[27] and ~2.1 V above the $F^- \rightarrow F^{\bullet}$ couple.[28]

Unfortunately, $\mathbf{1}^-$ and, presumably, $\mathbf{1}^{\bullet}$ are unsafe. The $Cs^+$ salt of $\mathbf{1}^-$ burns vigorously and has exploded with formation of soot upon scraping with a metal spatula,[2] providing the first example of an explosive compound based on the *closo*-$CB_{11}$ framework. Principal products of the explosive decomposition of $Cs^+\mathbf{1}^-$ in oxygen include $BF_3$, $BF_4^-$, and $CO_2$.[29] The calculated heat of combustion[30a] of $\mathbf{1}^-$ is 2358 kcal/mol, or 2.45 kcal/g (cf. TNT, 3.6 kcal/g), and the calculated heat of explosion[30b] of $\mathbf{1}^-$ is 1272 kcal/mol, or 1.32 kcal/g (cf. TNT, 1.05 kcal/g[31]), neglecting changes in Madelung energies (~100 kcal/mol) and differences in zero-point energies. For $\mathbf{1}^{\bullet}$, the calculated heat of combustion[30c] is 2450 kcal/mol, or 2.55 kcal/g, and the calculated heat of explosion[30d] is 1385 kcal/mol, or 1.45 kcal/g. The high-energy content of $\mathbf{1}^-$ is due to two chief factors. One is the higher strength of the B−F bond (154 kcal/mol in $BF_3$) relative to the C−F bond (116 kcal/mol). The other is the steric crowding of the $CF_3$ substituents.[32] In $\mathbf{1}^-$ the calculated[12,33] substituent crowding energy is 144 kcal/mol, comparable to the strain energy in cubane (157 kcal/mol).[34] The introduction of large substituent crowding by perfluorination has been noted before.[35]

The anion $\mathbf{1}^-$ approaches the ideal of inertness more closely than $\mathbf{2}^-$, but the disordered and explosive nature of crystals of its salts reduce its practicality.

**Acknowledgment.** This work is dedicated to Prof. R. Zahradník on the occasion of his 70th birthday and was supported by the National Science Foundation (CHE-9709195, CHE-9819179). B.T.K. is grateful to the American Chemical Society, Division of Organic Chemistry, and Organic Syntheses, Inc., for a graduate fellowship. CPU time on a NEC-SX4 computer (Grant No. LB98202, project INFRA2, Ministry of Education, Czech Republic) and a SUN Ultra-Enterprise (Institute of Physics, Academy of Sciences, Czech Republic) computer is gratefully acknowledged. We thank Dr. M. Olmstead for measuring a low-temperature X-ray diffraction data set and Dr. Z. Havlas for assistance with calculations. Measurement of exact mass by Dr. P. Jensen, Dr. L. Pasa-Tolic, and Dr. C. Masselon at Pacific Northwest National Laboratory (operated by Batelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830) is gratefully acknowledged. We are indebted to Prof. N. Bartlett for providing valuable advice.

**Supporting Information Available:** Details of the synthesis of $\mathbf{1}^-$, NMR spectra, a chromatogram, mass spectra, fluorine manifold description, X-ray electron density contour plots, and details of the crystallographic analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The protonated form appears to be unstable when isolated, with the adiabatic gas-phase proton affinity of $\mathbf{1}^-$ undefined. A B3LYP/6-31G* geometry optimization of $H^+\mathbf{1}^-$, starting with $H^+$ located above the center of the B(7)B(8)B(12) triangle, 2.5 Å from one of the F atoms in 12-$CF_3$, proceeded without a barrier to HF and the zwitterion, $CB_{11}(CF_3)_{11}CF_2$ (stabilization relative to $H^+$ at infinity, 252 kcal/mol); Havlas, Z.; King, B. T.; Michl, J. Unpublished results. This contrasts with the 197 kcal/mol value for the gas-phase proton affinity of $\mathbf{1}^-$ recently calculated with the PM3 method: Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. *J. Am Chem. Soc.* **2000**, *122*, 5114.

(20) It is ordinarily believed that this method predicts ionization potentials with an accuracy of ±0.2 eV: Brown, S. T.; Rienstra-Kiracofe, J. C.; Schaefer, H. F. *J. Phys. Chem. A* **1999**, *103*, 4065. Rienstra-Kiracofe, J. C.; Graham, D. E.; Schaefer, H. F. *Mol. Phys.* **1998**, *94*, 767. Tschumper, G. S.; Schaefer, H. F., *J. Chem. Phys.* **1997**, *107*, 2529. However, in radicals $\mathbf{1}^{\bullet}$ and $\mathbf{2}^{\bullet}$, whose ground state is nearly orbitally degenerate and the first excited state extremely low in energy,[6] the error could be larger.

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(23) Bartmess, J. E. Negative Ion Energetics Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, Feb. 2000 (http://webbook.-nist.gov). Korobov, M. V.; Kunznetsov, S. V.; Sidorov, L. N.; Shipachev, V. A.; Mit'kin, V. N. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *87*, 13. Compton, R. W.; Reinhardt, P. W. *J. Chem. Phys.* **1980**, *72*, 4655.

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(25) Compton, R. W.; Reinhardt, P. W. *J. Phys. Chem.* **1980**, *72*, 4655.

(26) Miyoshi, E.; Sakia, Y. *J. Chem. Phys.* **1988**, *98*, 7363.

(27) Kuhn, A. T. In *Encyclopedia of Electrochemistry of the Elements*, Bard, A. J., Ed.; Marcel Dekker: New York, 1975; Vol. 4, pp 44−45.

(28) Based on a $F_2$ BDE of 1.64 eV. Kerr, J. A. In *CRC Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1984; p F-173.

(29) The production of $CO_2$ is evident from the attempted combustion analyses. The production of $BF_3$ and $BF_4^-$ was established by igniting $Cs^+\mathbf{1}^-$ in a Pt boat in a PTFE bomb filled with 4 atm of $O_2$. Gaseous products were trapped in cold $d_6$-acetone and identified by $^{19}F$ NMR.

(30) Based on the assumed processes (reactants, B3LYP/6-31+G*//B3LYP/6-31G*, products B3LYP/6-31+G* and the heat of atomization of graphite): (a) $CB_{11}(CF_3)_{12}^- + {}^{25}/_2\ O_2 \rightarrow BF_4^- + 10\ BF_3 + {}^1/_2\ CF_4 + {}^{25}/_2\ CO_2$, (b) $CB_{11}(CF_3)_{12}^- \rightarrow BF_4^- + 10\ BF_3 + {}^1/_2\ CF_4 + {}^{25}/_2\ C_{graphite}$, (c) $CB_{11}(CF_3)_{12}^{\bullet} + {}^{49}/_4\ O_2 \rightarrow {}^3/_4\ CF_4 + 11\ BF_3 + {}^{49}/_4\ CO_2$, (d) $CB_{11}(CF_3)_{12}^{\bullet} \rightarrow {}^3/_4\ CF_4 + 11\ BF_3 + {}^{49}/_4\ C_{graphite}$.

(31) Köhler, J.; Rudolf, M. *Explosives*, 4th ed.; VCH: New York, 1993; p 371.

(32) The average calculated antipodal F−F distance in $\mathbf{1}^-$ is 8.12 Å; the surface area of a sphere with this diameter is 207 Å$^2$. Using a F van der Waals radius of 1.56 Å (Palmer, B. J.; Anchell, J. L. *J. Phys. Chem.* **1995**, *99*, 12239) and an average calculated CF bond length of 1.37 Å, a rotating tetrahedral $-CF_3$ group with the F atoms on this sphere defines a spherical segment of 25 Å$^2$; the twelve $CF_3$ groups require roughly 300 Å$^2$ for unhindered rotation.

(33) Based on the isodesmic reaction (B3LYP/6-31G*): $1\text{-}CF_3CB_{11}H_{11}^- + 5\ 2\text{-}CF_3CB_{11}H_{11}^- + 5\ 7\text{-}CF_3CB_{11}H_{11}^- + 12\text{-}CF_3CB_{11}H_{11}^- \rightarrow CB_{11}(CF_3)_{12}^- + 11\ CB_{11}H_{12}^-$.

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(35) The crowding energy in $HC(CF_2)_3CH$ is calculated to be 33 kcal/mol. Levin, M. D.; Hamrock, S. J.; Kaszynski, P.; Shtarev, A. B.; Levina, G. A.; Noll, B. C.; Ashley, M. E.; Newmark, R.; Moore, G. G. I.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 12750.