Crystal data for **1a**: $[(C_{48}H_{48}N_{32}O_{16})(C_8H_{20}N_4)]\cdot 4\,HCl\cdot 19.67\,H_2O$, $M_r = 2001.50$, rhombohedral, space group $R\bar{3}$ (No. 148), $a = b = 29.1533(10)$, $c = 26.7471(13)$ Å, $V = 19687.1(14)$ Å^3, $Z = 9$, $\rho_{calcd} = 1.519\,g\,cm^{-3}$, $T = 188$ K, Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$), $\mu = 2.42\,cm^{-1}$. The structure was solved by the Patterson method (SHELXS-86). All non-hydrogen atoms were refined anisotropically (SHELXL-93). Final block-diagonal matrix least-squares refinement on F^2 with all 6967 reflections and 628 variables converged to $R1$ ($I > 2\sigma(I)$) $= 0.0923$, $wR2$ (all data) $= 0.2737$, and GOF $= 1.068$. Crystal data for **1b**: $[(C_{48}H_{48}N_{32}O_{16})(C_{10}H_{24}N_4)]\cdot 4\,HCl\cdot 18\,H_2O$, $M_r = 1999.64$, rhombohedral, space group $R\bar{3}$ (No. 148), $a = b = 29.3372(7)$, $c = 26.6945(10)$ Å, $V = 19897.1(10)$ Å^3, $Z = 9$, $\rho_{calcd} = 1.502\,g\,cm^{-3}$, $T = 213$ K, $\mu = 2.38\,cm^{-1}$. $R1$ ($I > 2\sigma(I)$) $= 0.1005$, $wR2$ (all data) $= 0.2957$, and GOF $= 1.088$. Crystal data of **2a**: $[(C_{48}H_{48}N_{32}O_{16})(CuC_8H_{20}N_4)(H_2O)]\cdot 2\,NO_3\cdot 16\,H_2O$, $M_r = 1995.30$, rhombohedral, space group $R\bar{3}$ (No. 148), $a = b = 29.8575(3)$, $c = 24.8758(4)$ Å, $V = 19205.0(4)$ Å^3, $Z = 9$, $\rho_{calcd} = 1.553\,g\,cm^{-3}$, $T = 188$ K, $\mu = 3.70\,cm^{-1}$. $R1$ ($I > 2\sigma(I)$) $= 0.1015$, $wR2$ (all data) $= 0.3134$, and GOF $= 1.063$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156566 (**1a**), -156567 (**1b**), and -156568 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Perfluorinated Nanosphere: Synthesis and Structure of Perfluoro-deca-*B*-methyl-*para*-carborane**

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In the early stages of the chemistry of polyhedral boranes the direct, exhaustive halogenation of *closo*-boranes and carboranes was one of the first reactions studied in detail.[1] The most challenging endeavor in this context, their perfluorination, led to the synthesis of $B_{12}F_{12}^{2-}$,[2] 1,2-$(H)_2$-1,2-$C_2B_{10}F_{10}$,[3] 1,7-$C_2B_{10}F_{12}$,[3, 4] and 1,12-$(H)_2$-1,12-$C_2B_{10}F_{10}$.[3] While the existence of $B_{12}F_{12}^{2-}$ was never confirmed,[5] all three carborane fluorides can be isolated and 1,12-$(H)_2$-1,12-$C_2B_{10}F_{10}$ can even be handled in the presence of moist air. In aqueous media however, they hydrolyze to form boric acid as the final product.[3] The recently reported anion 1-$HCB_{11}F_{11}^-$ has been shown to undergo the nucleophilic substitution at the B–F moieties by OH^- as well, but under basic aqueous conditions.[6]

History repeated itself with the discovery of C_{60}.[7] Shortly thereafter its exhaustive fluorination was intensively investigated[8] and it is now widely accepted that $C_{60}F_{48}$ is the most fluorine-rich fullerene which can be isolated.[9] However, $C_{60}F_{48}$ is metastable in solution, decomposing according to the reaction $C_{60}F_{48} \rightarrow C_{60}F_{36} + 6\,F_2$,[10] and hydrolyzing rapidly in aqueous media.[11] The idea of a chemically resistant "fluorinated ball" based on C_{60} was further pursued through its perfluoroalkylation.[12] Up to 14 perfluoroalkyl addends (R_f) ($R_f = CF_3$, C_2F_5, C_3F_7, C_6F_{15}) can be added to C_{60}, about half the number needed to achieve a perfluorinated surface. Solutions of the mixtures of $C_{60}(R_f)_nH_m$ have been shown to be resistant to acids and bases.[12]

The generation of a neutral perfluorinated nanosphere by replacement of all H atoms of per-*B*-methylated carboranes by fluorine appeared to us to be a feasible goal. Previously, the radical chlorination of 1,12-$(H)_2$-1,12-$C_2B_{10}Me_{10}$ (**1**), yielding 1,12-$(H)_2$-1,12-$C_2B_{10}(CHCl_2)_{10}$,[13] as well as the synthesis of the 1-hydroxymethyl-2-hydroxyimino derivative of **1**[14] demonstrated the viability of radical reactions to transform the methyl substituents of camouflaged species such as **1**, leaving

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the underlying B–B framework intact. In fact, the explosive "inert" anion 1-$CB_{11}(CF_3)_{12}^-$ was synthesized starting from the permethylated anion 1-$CB_{11}(CH_3)_{12}^-$ by using F_2 and K_2NiF_6 as fluorination reagents.[15] This report cited our preliminary results on the fluorination of **1**[16] and its 1,12-dimethyl derivative 1,12-$C_2B_{10}Me_{12}$ (**2**).[16a]

Initially, the fluorination of **2** was studied, and it was found that at 25 °C using various F_2/N_2 (10–100% F_2) concentrations only partial fluorination occurred to yield 1,12-$C_2B_{10}C_{12}H_nF_{36-n}$ ($n = 3$–6). At a reaction temperature of 60 °C the formation of the desired 1,12-$C_2B_{10}(CF_3)_{12}$ (**3**) was observed. However, under these conditions partial disruption of the C–C bonds of **2** also led to the formation of 1-CF_3-12-F-1,12-$C_2B_{10}(CF_3)_{10}$ (**4**) and 1,12-$(F)_2$-1,12-$C_2B_{10}(CF_3)_{10}$ (**5**). Under no conditions examined did compound **3** form without the concomitant formation of **4** and **5**. All attempts to separate compounds **3**–**5** were unsuccessful.

Fluorination of **1** was initially conducted at low temperature (< 35 °C) using various F_2/N_2 concentrations with the goal of 1,12 C–H retention. However, under the varied reaction conditions employed only mixtures of **5**, 1,12-$(H)_2$-1,12-$C_2B_{10}(CF_3)_{10}$ (**6**), and 1-H-12-F-1,12-$C_2B_{10}(CF_3)_{10}$ (**7**) were obtained in ratios which depended on the reaction temperature and time. Attempts to separate compounds **5**–**7** from each other by gradient sublimation[17] or column chromatography were unsuccessful. Single crystals of 1-H-12-X-1,12-$C_2B_{10}(CF_3)_{10}$ (X = 92% H, 8% F) (**8**), obtained from sublimation, were suitable for an X-ray diffraction study.[18] The refined structure revealed that all methyl groups were converted into CF_3 groups.

Fluorination of **1** at elevated temperatures (> 35 °C) using a high F_2 to N_2 ratio (1:3) for 14 days provided **5** in quantitative yield. Product formation was monitored by both mass spectrometry and ^{11}B NMR analysis. Compound **5** is a colorless solid that sublimes at 65 °C/0.01 mmHg to give colorless crystals. It has a melting point of 186 °C (sealed tube) and the molten compound remains colorless and inert up to 300 °C. In contrast to 1-$CB_{11}(CF_3)_{12}^-$, **5** does not detonate on percussion.[17] It is sparingly soluble in all common organic solvents, does neither hydrolyze in the presence of H_2O and nor oxidize on air. In acidic medium (CH_2Cl_2/CF_3COOH) **5** remains unchanged, whereas under basic conditions (CH_2Cl_2/NEt_3) it slowly decomposes. The ^{11}B NMR spectrum reveals that deboronation occurs initially to produce *nido* species which finally decompose to borates. The nature of the decomposition products has not yet been determined. The ^{19}F NMR spectrum of **5** shows a signal for the F atoms of its C–F vertices at $\delta = -157.5$ comparable with the shifts of the ^{19}F NMR resonance signals observed for $BF_3 \cdot THF$[19] ($\delta = -155.7$) or the *para*-F atom in *trans*-$C_6F_5CH{=}CHCl$ ($\delta = -155.3$).[20] Single crystals of **5** were obtained by the slow evaporation of a solution of **5** in toluene and Freon 113. The structure of **5** determined by X-ray analysis[21] is shown in Figure 1. It represents the first structurally characterized perfluorinated icosahedral borane derivative.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with one carborane per unit cell. Each molecule of **5** occupies a crystallographic inversion center. There are no unusually short intermolecular contacts. The C_2B_{10} core is indistinguishable from those reported for analogous carboranes such as **1**[16a] and 1,12-$(H)_2$-1,12-$C_2B_{10}(CHCl_2)_{10}$.[13] As predicted by Michl and King for the anion 1-$CB_{11}(CF_3)_{12}^-$,[15] the average diameter (as calculated by F ⋯ F distances) of the fluorinated sphere is approximately 8.04 Å. All other metrical parameters are typical and do not warrant further comment. Aside from the difference in the crystal packing, these findings account as well for **8**.[18]

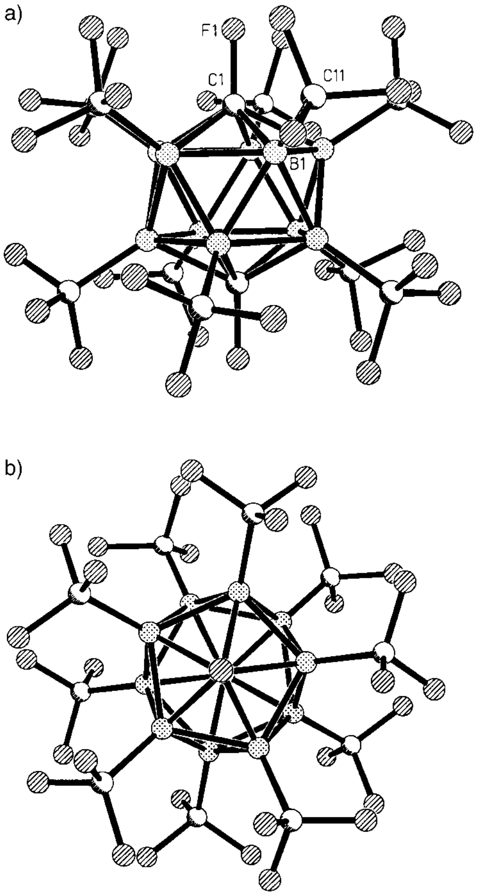

Figure 1. Molecular structure of **5**. a) View roughly perpendicular to the apical axis, showing the C–F bonds, b) view approximately along the apical axis. Selected bond lengths [Å]: C1-F1 1.326(11), B-C_{apical}(av) 1.741(15), B-CF_3(av) 1.627(15), C-F(av) 1.337(13).

We are currently exploring the feasibility of performing reactions at the C–H vertices of mixtures such as **8**.[22] Their 1- and 1,12-functionalization would allow their separation by column chromatography and open an avenue for further chemistry. At the same time we are probing the fluorination of other camouflaged carborane compounds[16b] including the possibility of generating fluorinated sticks and ropes from rigid rods consisting of tethered species derived from **1**.[23]

Experimental Section[24]

Caution!: Fluorine is a powerful oxidizer and should not be handled except in carefully controlled environments.[25, 26]

Caution!: Compounds such as **5** are potentially explosive.[15] In spite of having not experienced explosions when preparing or handling **5**, we advise extreme caution in doing so.

Analytical instruments used: VG analytical ZAB2-E mass spectrometer (HR-MS); Varian Unity plus-300 (^{19}F NMR); Bruker ARX 400 (^{13}C NMR);

Bruker ARX 500 (^{11}B NMR); Nicolet Nexus 470 (FT-IR); Spex 1402 double monochromator, RCA C31034 photomultiplier tube, Stanford research systems SR400 photon counter (Raman).

5: The fluorination of **1** with the goal of 1,12 C–H conversion to 1,12 C–F was carried out in a solution-phase fluorination reactor which has been described in previous articles.[24, 25] The reactor was filled with perfluorononane (Exfluor Research Corp.) (300 mL, b.p. 125 °C) and NaF (25 g, 0.59 mol). The reactor was then purged with N_2 (100 cm^{3}min^{-1}, 1 h). Compound **1** (500 mg, 1.75 mmol), dissolved in perfluorononane (150 mL), was pumped into the reactor (25 mL h^{-1}). During the addition of **1** a mixture of F_2 and N_2 was bubbled through the reactor at a rate of 100 and 400 cm^{3}min^{-1}, respectively. After the addition of the solution containing **1** was completed, the F_2/N_2 flow rate was reduced to 25 and 25 cm^{3}min^{-1}, respectively, and the temperature was gradually raised to 110 °C (240 h). The reaction was held at 110 °C for an additional 4 days. The F_2 was turned off and the reactor was allowed to purge (4 h). The contents of the reactor were filtered and excess solvent was removed under reduced pressure. Sublimation of product (65 °C/0.01 mm, 181 °C/760 mm) furnished **5** as a colorless solid (1.39 g, 94 %). M.p. 186 °C (sealed tube); ^{11}B NMR (160.5 MHz, Freon 113, $BF_3 \cdot Et_2O$ external): $\delta = -15.8$ (s); ^{19}F NMR (376.5 MHz, Freon 113, 5 % $CDCl_3$): $\delta = -49.1$ (d, 30 F, ^2J(B,F) = 60 Hz; CF_3), -157.5 (s, 2 F; CF); ^{13}C NMR (100.6 MHz, Freon 113, 5 % $CDCl_3$): $\delta = 111$ (CF_3), 109 (d, ^2J(B,F) = 60 MHz; CF); IR (neat): $1/\lambda = 1258$, 1160, 1149, 1133, 1029, 980 cm^{-1}; Raman[27] (neat) $1/\lambda = 194$ (s), 219 (s), 266, 441, 539 (w), 641.5 (w), 715, 1166 (w), 1190 (w), 1258 (w) cm^{-1}; HR-MS (CI-): *m/z*: calcd 860.0496; found 860.0483.

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[18] a) X-ray crystal data for **8**: crystal dimensions: 0.2 × 0.2 × 0.16 mm, monoclinic, $a = 10.4450(5)$ Å, $b = 10.4002(5)$ Å, $c = 12.2536(6)$ Å, $\beta = 99.050(3)^\circ$, $V = 1314.54(11)$ Å^3, space group $P2_1/n$, $Z = 2$, formula: $C_{12}H_2B_{10}F_{30}$, $M_r = 824.21$, $\rho_{calcd} = 2.082$ g cm^{-3}, $\mu = 0.266$ mm^{-1}; 5745 reflections were measured in the range $6.18^\circ < 2\theta < 54.98^\circ$ on an Enraf Nonius KAPPA-CCD diffractometer ($Mo_{K\alpha}$, graphite monochromator, $T = -150$ °C), 3012 unique after merging ($R_{int} = 0.0368$). A correction was applied for Lorentzian polarization. The structure was solved by direct methods (SIR92) and refined by full-matrix least squares on F^2 using the Siemens SHELXL-97 (PC) software package. All non-hydrogen atoms were allowed anisotropic thermal motion. Number of parameters: 243. There appeared to be partial fluorine occupancy at the apical carbon atom of the molecule. Refinement with a hydrogen atom at the apical position resulted in a negative U_{iso} for the hydrogen atom. The C–H bond length was also longer than expected (1.15(3) Å). A possible explanation is the presence of a small percentage of fluorine which would increase the electron density at the apical position and have the effect of an elongated C–H bond. A model was generated where a partial occupancy fluorine atom and a partial occupancy hydrogen atom were refined. The sum of the site occupancy factors for the two atoms was fixed to be equal to 1. An isotropic displacement parameter was refined but constrained to be equal for the two atoms. The C–H and C–F bond lengths were constrained to be close to 0.96 Å and 1.30 Å, respectively. The B-C-H and B-C-F bond angles were kept nearly equal by constraining the five B-C-H contacts to be equivalent, at the same time the five B-C-F contacts were also constrained to be equal. In this way, the fluorine occupation was estimated to be 8(1) %. Final R factors: $R_1 = 0.1111$, $wR_2 = 0.1798$; max./min. residual electron density: 0.712/-0.284 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153963 (**8**) and CCDC-153964 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[21] X-ray crystal data for **5**: crystal dimensions: 0.3 × 0.3 × 0.2 mm, triclinic, $a = 8.571(5)$, $b = 9.771(5)$, $c = 9.981(5)$ Å, $\alpha = 117.601(5)^\circ$, $\beta = 113.317(5)^\circ$, $\gamma = 92.701(5)^\circ$, $V = 652.4(6)$ Å^3, space group $P\bar{1}$, $Z = 1$, formula: $C_{12}B_{10}F_{32}$, $M_r = 860.20$, $\rho_{calcd} = 2.190$ g cm^{-3}, $\mu = 0.284$ mm^{-1}; 4446 reflections were measured in the range $6.18^\circ < 2\theta < 58.81^\circ$ on an Enraf Nonius KAPPA-CCD diffractometer ($Mo_{K\alpha}$, graphite monochromator, $T = -20$ °C), 2987 unique after merging ($R_{int} = 0.0343$). A correction was applied for Lorentzian polarization. The structure was solved by direct methods (SIR92) and refined by full-matrix least squares on F^2 using SHELXL-93 in the WinGX software package. All non-hydrogen atoms were allowed anisotropic thermal motion. Number of parameters: 244. Final R factors: $R_1 = 0.1336$, $wR_2 = 0.4164$; max./min. residual electron density: 0.624/-0.682 e Å^{-3}.[18b)]

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[24] Preparation of **8**, spectroscopic data for 1,12-$(H)_2$-1,12-$C_2B_{10}(CF_3)_{10}$ (**6**) and 1-H-12-F-1,12-$C_2B_{10}(CF_3)_{10}$ (**7**). **Caution!**: Scraping the crystals that contained a mixture of compounds **5**, **6**, and **7** resulted in the detonation of those crystals[17] and extreme caution should be used in their handling. The reactor[25, 26] was filled with Freon 113 (300 mL) and NaF (16 g, 0.38 mol), cooled to -25 °C and purged with N_2 (100 cm^{3}min^{-1}) for 1 h. Compound **1** (250 mg, 0.88 mmol), dissolved in Freon 113 (150 mL), was pumped into the reactor (25 mL h^{-1}), while a mixture of F_2 and N_2 was bubbled through the reactor (100 and 400 cm^{3}min^{-1}, respectively). After the addition of the solution containing **1** was completed, the F_2/N_2 flow rate was reduced (25/25 cm^{3}min^{-1}) and the temperature was gradually raised to 35 °C (72 h). The reaction was held at 35° C for an additional 10 h. The F_2 was turned off and the reactor was allowed to purge (4 h). The contents of the reactor were filtered and all volatiles were removed under reduced pressure. Sublimation (110 °C/3 mmHg) furnished

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