JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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$HCB_{11}(CF_3)_nF_{11\text{-}n}{}^{-}$: Inert Anions with High Anodic Oxidation Potentials

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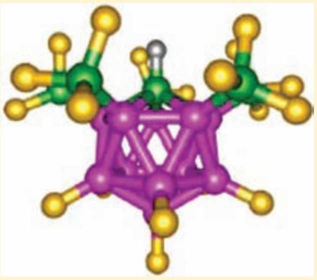
S *Supporting Information*

ABSTRACT: Cs salts of four of the title anions were prepared by fluorination of salts of partly methylated (n = 11, 10) or partly methylated and partly iodinated (n = 6, 5) $CB_{11}H_{12}{}^{-}$ anions. The CH vertex is acidic, and in the unhindered anion with n = 6 it has been alkylated. Neat $Cs^+[1\text{-}H{-}CB_{11}(CF_3)_{11}]^-$ is as treacherously explosive as $Cs^+[CB_{11}(CF_3)_{12}]^-$, but no explosions occurred with the salts of the other three anions. BL3YP/6-31G* gas-phase electron detachment energies of the title anions are remarkably high, 5-8 eV. Treated with $NiF_3{}^+$ in anhydrous liquid HF at −60 °C, anions with n = 11 or 10 resist oxidation, whereas anions with n = 6 or 5 are converted to colored EPR-active species, presumably the neutral radicals $[HCB_{11}(CF_3)_nF_{11\text{-}n}]^{\bullet}$. These are stable for hours at −60 °C after extraction into cold perfluorohexane or perfluorotri-*n*-butylamine solutions. On warming to −20 °C in a Teflon or quartz tube, the color and EPR activity disappear, and the original anions are recovered nearly quantitatively, suggesting that the radicals oxidize the solvent.



INTRODUCTION

Anions with very high anodic oxidation potentials are of interest in many contexts, e.g., as counterions for strongly oxidizing cations and as battery electrolytes. Salts of several such anions, such as $BF_4{}^-$ and $PF_6{}^-$, are in common use in electrochemistry. Anions that have a strongly positive redox potential and can be oxidized reversibly to strong electroneutral oxidants would be particularly useful but are rare. Perhaps the best known examples are transition metal fluorides, especially the $PtF_6{}^-/PtF_6$ pair, with a gas-phase electron detachment energy of the anion most recently calculated as 7.09 eV[1] and previously reported as 7.0 ± 0.35[2−4] and ~8[5] eV.

Parent carborate anions, especially the icosahedral $[CB_{11}H_{12}]^-$ (Figure 1),[6] have attracted attention in this context as well. They are not oxidized reversibly themselves, but some of their sterically hindered derivatives are. The anodic oxidation potentials of the parents are not nearly as high as that of $PtF_6{}^-$,[7] but they are much less reactive than metal fluorides and easier to prepare and handle. Among the reversibly oxidizable derivatives, the dodecamethylated anion[8] and radical[9] redox pair as well as other methylated anions[10,11] have been electrochemically characterized the best but are even more easily oxidized than the parent. Halogenated derivatives of $[CB_{11}H_{12}]^-$ appear to be a superior choice in that their anodic oxidation potentials are likely to be higher than that of the parent. However, to our knowledge their oxidation has not been studied, and it is not known whether it is reversible and the radicals isolable. Some of the halogenated anions have seen considerable use as weakly coordinating anions and their proton salts are among the strongest known Brønsted acids.[12−14] Among such halogenated species, the fluorinated derivatives can be expected to have the highest oxidation potentials, and we have turned our attention to the anions **1**-**24** (Table 1).

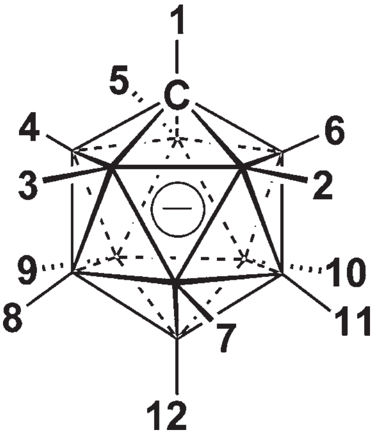


Figure 1. Vertex numbering in CB_{11}.

There are several early reports of partially fluorinated $[CB_{11}H_{12}]^-$ anions[15−19] and a trifluoromethylated derivative.[20] The first example of a symmetric and very highly fluorinated carborate anion potentially useful for our purposes was $[1\text{-}H\text{-}(2{-}12)\text{-}F_{11}{-}CB_{11}]^-$ (**1**).[21] Since the F substituent is a σ acceptor but a π donor, whereas the CF_3 substituent is a σ and π acceptor, it seemed to us that the latter would be preferable to the former if the highest anodic oxidation potential was desired. The synthesis of dodecakis(trifluoromethyl)carba-*closo*-dodecaborate, $[CB_{11}(CF_3)_{12}]^-$ (**3**), was then published along with density functional theory (DFT) results.[22] The calculations predicted an impressive gas-phase electron detachment energy of 8.8 eV, rivaling that of PtF_6,[2−5] and also an amazingly low gas-phase proton affinity, in

Received: December 8, 2010
Published: February 22, 2011

Table 1. Vertical Electron Detachment Energies of the Anions $[CB_{11}(CF_3)_nF_{12-n}]^-$ and $[1\text{-}HCB_{11}(CF_3)_nF_{11}]^-$

	subst.					
compd	1	2−6	7−11	12	$-E_{HOMO}$/eV	ΔE/eV
1	H	F	F	F	3.6	5.2
2	F	F	F	F	3.8	5.4
3	CF_3	CF_3	CF_3	CF_3	6.8	7.9
4	F	F	F	CF_3	4.0	5.5
5	F	CF_3	F	F	5.2	6.5
6	F	F	CF_3	F	5.5	6.8
7	F	F	CF_3	CF_3	5.6	7.0
8	F	CF_3	F	CF_3	5.5	6.8
9	F	CF_3	CF_3	F	6.4	7.6
10	F	CF_3	CF_3	CF_3	6.9	8.0
11	H	F	F	CF_3	3.8	5.3
12	H	CF_3	F	F	5.2	6.5
13	H	F	CF_3	F	5.4	6.7
14	H	F	CF_3	CF_3	5.5	6.8
15	H	CF_3	F	CF_3	5.3	6.7
16	H	CF_3	CF_3	F	6.4	7.5
17	H	CF_3	CF_3	CF_3	6.8	8.0
18	CF_3	F	F	F	3.9	5.4
19	CF_3	F	F	CF_3	4.1	5.5
20	CF_3	CF_3	F	F	5.3	6.6
21	CF_3	F	CF_3	F	5.6	6.9
22	CF_3	F	CF_3	CF_3	5.7	7.0
23	CF_3	CF_3	F	CF_3	5.4	6.8
24	CF_3	CF_3	CF_3	F	6.4	7.5

the vicinity of 200-250 kcal/mol.[22] The exact value of proton affinity could not be calculated because in the computer the isolated protonated form fell apart into HF and the ylide, $^-CB_{11}(CF_3)_{11}CF_2^+$, but it is possible that this would not occur in solution. The record-breaking gas-phase acidity of $H^+[CB_{11}(CF_3)_{12}]^-$ (H^+ **3**) and similar Brønsted acids was confirmed by subsequent more extensive calculations.[23,24]

The perfluorination of the much cheaper $[B_{12}H_{12}]^{2-}$ dianion to $[B_{12}F_{12}]^{2-}$ has been reported[25] and improved[26−28] repeatedly, but the presently unknown anodic oxidation potential of the latter is most likely less positive than that of $[1\text{-}H{-}CB_{11}F_{11}]^-$ (**1**).[29] Trifluoromethylated uncharged carboranes are also known.

Unfortunately, the cesium salt of the most promising anion **3** is treacherously explosive,[22] and work with it was discontinued. The main products of the explosion are BF_3 and graphite. The calculated detonation energy density (heat of explosion) is ~1.3 kcal/g,[22] higher than that of trinitrotoluene (1.05 kcal/g[30]). The large value is attributed to the relative weakness of the C−F bond energy (110-130 kcal/mol[31]) compared with the B−F bond energy (154 kcal/mol in BF_3[32]). It thus appeared desirable to replace a sufficient number of the CF_3 substituents with F substituents in an attempt to provide nonexplosive anions that would be safe to work with but would still have oxidation potentials higher than **1**. The present report describes the results of this endeavor.

■ RESULTS

Calculations. The electron detachment energies of the fluorinated and trifluoromethylated derivatives of $CB_{11}H_{12}^-$ are of primary interest, and we have used the BL3YP/6-31G* method to calculate the energy difference between the gas phase anion and radical at their respective optimized geometries for anions **1**-**24**. Vibrational frequencies were computed at all optimized geometries to verify that they correspond to true potential energy minima. Table 1 lists the adiabatic electron detachment energies along with the vertical energies at the geometries of the anions, estimated by using Koopmans' theorem. The adiabatic electron detachment energy of **3** was originally reported as 8.8 eV using the same method of calculation,[22] whereas the present more reliable result is 7.9 eV. We suspect that the old value was obtained at an incompletely optimized radical geometry, since at the time computer resources for a calculation of vibrational frequencies were not available.

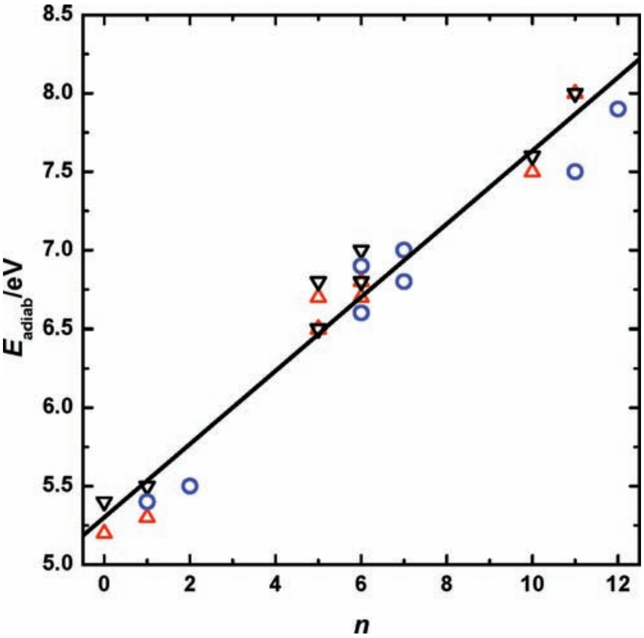


Figure 2. Plot of B3LYP/6-31G* adiabatic electron detachment energy E_{adiab} against the number n of trifluoromethyl substituents present. ○ (blue) $1\text{-}CF_3{-}CB_{11}(CF_3)_{n-1}F_{11-n}$, ▽ $1\text{-}FCB_{11}(CF_3)_nF_{11-n}$, △ (red) $1\text{-}H{-}CB_{11}(CF_3)_nF_{11-n}$, $E_{adiab} = 0.23n + 5.30$ ($r = 0.98$).

The calculated electron detachment energies correlate with the number of CF_3 groups in the anion (Figure 2), and as expected, these groups are clearly much more effective in making the anion hard to oxidize than the fluorine substituents. The location of the CF_3 substituent on the cage plays a secondary role.

Although the neutral radical is Jahn−Teller distorted, the adiabatic and vertical electron detachment energies in Table 1 are strongly correlated (Figure 3). For future estimates of electron detachment energies for anions of this type, it should be sufficient to calculate the orbital energy at the geometry of the anion.

The Jahn−Teller distortion of the geometries of the radicals is expected to reduce their symmetry, and it is useful to recall the more accurate CASSCF(13,12)/6-31+G* results for the parent $CB_{11}H_{12}^\bullet$ radical (Figure 4).[10] The distortion of its C_{5v} icosahedral cage can be performed in two ways, one producing an optimized geometry with a ground state wave function of A′ symmetry and the other, an optimized geometry with a ground state wave function of A″ symmetry. At the CASSCF(13,12)/6-31+G* level of calculation, the energy of the A′ state is about 4 kcal/mol higher. In Figure 4, the best C_s A′ and A″ structures of the distorted $CB_{11}H_{12}^\bullet$ radical are compared with the C_{5v} symmetric structure of the parent anion $CB_{11}H_{12}^-$. The distortions are slight, and the most obvious among them is the strong off-axis bend of the C−H bond in position 12 in the A′ state.

In the substituted anions the situation is somewhat more complicated, since the CF_3 substituents do not have cylindrical symmetry. If they did, the $[CB_{11}(CF_3)_nF_{12\text{-}n}]^-$ and $[1\text{-H}{-}CB_{11}(CF_3)_nF_{11\text{-}n}]^-$ anions would have C_{5v} symmetry. Although this is not exactly true, it is nearly true, and typical differences in the energies of the members of the HOMO and HOMO-1 orbital pairs at the optimized anion geometries are only ~0.03 eV. Geometry optimizations of all of the fluorinated radicals derived from the anions **1**-**24** led to C_s symmetry and an A″ ground state, independent of the starting cage symmetry, A′ or A″. When these optimizations were started from the equilibrium geometries of the anions, the structure oscillated between A′ and A″ symmetry as the calculation approached completion and convergence to the final C_s A″ state was difficult. The optimizations were much faster when started from an initial carborane cage geometry that was already A″ Jahn−Teller distorted.

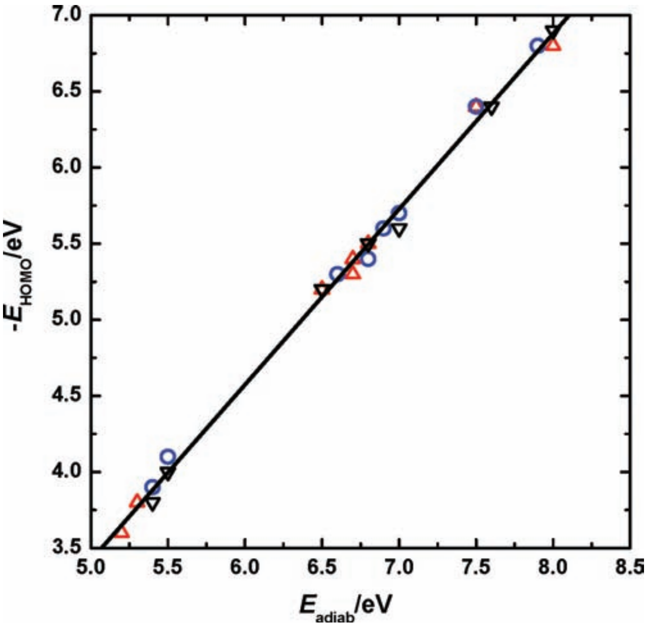


Figure 3. B3LYP/6-31G* vertical electron detachment energies at optimized anion geometries obtained from Koopmans' theorem ($-E_{HOMO}$) plotted against adiabatic electron detachment energies. ○ (blue) $1\text{-}CF_3{-}CB_{11}(CF_3)_{n-1}F_{11-n}$, ▽ $1\text{-F-}CB_{11}(CF_3)_nF_{11-n}$, △ (red) $1\text{-H}{-}CB_{11}(CF_3)_nF_{11-n}$, $-E_{HOMO} = 1.15\ E_{adiab} - 2.35$ ($r = 0.998$).

Two examples of converged geometries are shown in Figure 5, which displays the structures of $1\text{-H-}(7{-}12)\text{-}F_6\text{-}(2{-}6)\text{-}(CF_3)_5\text{-}CB_{11}^{\bullet}$ and $1\text{-H-}(2{-}6,12)\text{-}F_6\text{-}(7{-}11)\text{-}(CF_3)_5\text{-}CB_{11}^{\bullet}$, the radicals derived from the anions **12** and **13**, respectively. Similarly as in the optimized geometry of the A″ state of the parent radical $CB_{11}H_{12}^{\bullet}$, in these structures the fluorine in position 12 is not bent off-axis. In the F and/or CF_3 substituted radicals the C_s A′ state appears to be more strongly destabilized with respect to the C_s A″ state than is the case in the parent $CB_{11}H_{12}^{\bullet}$ radical. This could be an electronic effect, but it could also be a simple result of steric hindrance provided by the substituents in positions 7−11.

Synthesis. The preparation of **3** by fluorination of $[CB_{11}(CH_3)_{12}]^-$ in two steps[22] provided the initial protocol for the preparation of the desired $[1\text{-H}{-}CB_{11}(CF_3)_nF_{11\text{-}n}]^-$ anions, starting with partially methylated or partially methylated and partially iodinated anions $[CB_{11}(CH_3)_nH_{12\text{-}n}]^-$ or $[CB_{11}(CH_3)_nI_{12\text{-}n}]^-$, prepared according to reported procedures.[10] We have worked with cesium salts throughout. As described below, a considerable departure from the initial protocol was found to be beneficial in the end.

The reported exhaustive fluorination of $[CB_{11}(CH_3)_{12}]^-$ was only successful in anhydrous liquid HF.[22] Since this medium

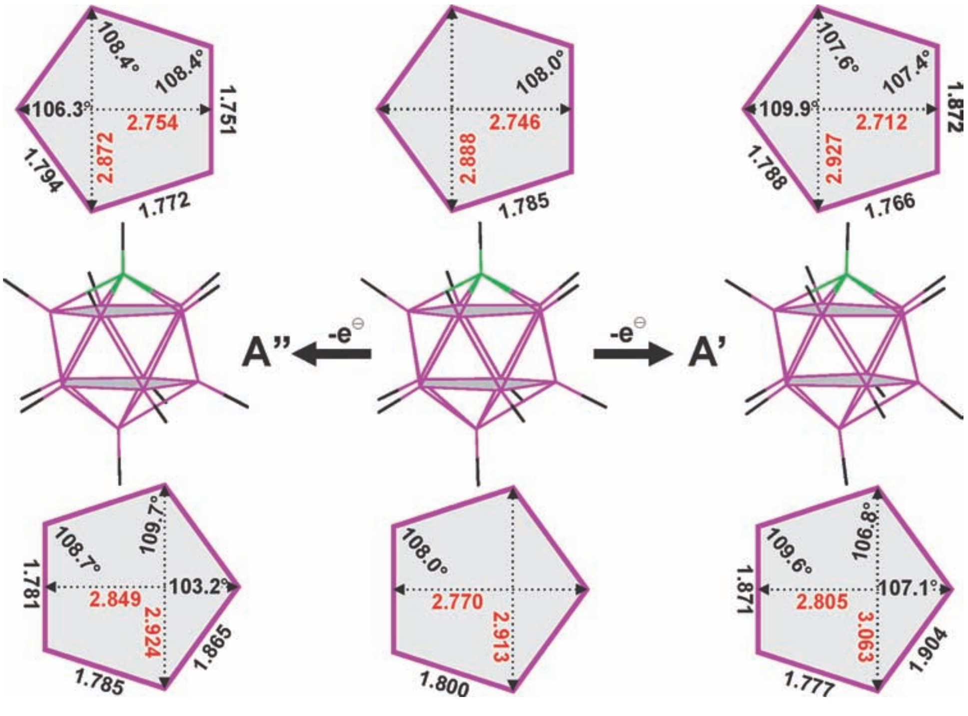


Figure 4. B3LYP/6-31G* optimized structures of the C_s A′ (right) and A″ (left) states of the radical $CB_{11}H_{12}^{\bullet}$ and the C_{5v} anion $CB_{11}H_{12}^-$ (center). The carbon vertex is on top, the geometry of the proximate pentagon is above, and that of the distal pentagon is below.

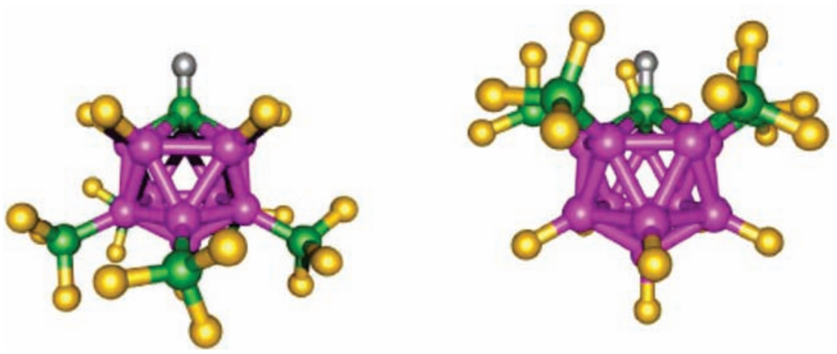


Figure 5. B3LYP/6-31G* structures of radicals 1-H-(7−12)-F_6-(2−6)-$(CF_3)_5$-$CB_{11}^{\bullet}$ C (right, derived from anion **12**) and 1-H-(2−6,12)-F_6-$(CF_3)_5$-$CB_{11}^{\bullet}$ (left, derived from anion **13**).

attacks the starting anion $[CB_{11}(CH_3)_{12}]^-$, replacing one of the methyl substituents with a fluorine atom,[9] the fluorination had to be performed in two steps. About half of the fluorine atoms were introduced at first by direct fluorination with 10% F_2 in N_2 in a CF_3Cl solvent containing the methylated anion adsorbed on silica, which effectively removes the HF byproduct. The resulting mixture of the isolated partially fluorinated anions was then stable to anhydrous liquid HF, and the fluorination was completed in this solvent with Bartlett's reagent, K_2NiF_6.[33]

[1-H−$CB_{11}(CF_3)_{11}$]$^-$ (17). This was the first new anion whose preparation was tried, starting with 1-H−$CB_{11}Me_{11}^-$. Attempted fluorinations using K_2NiF_6 without the initial partial fluorination gave a product mixture whose mass spectra suggested the presence of anions in which one or two of the methyl groups were replaced by a fluorine atom. The two-step fluorination using elemental fluorine initially and K_2NiF_6/HF subsequently avoided this problem. However, the desired product **17** and the undesired 1-F-$CB_{11}(CF_3)_{11}$ (**10**) were produced in nearly equal amounts. The formation of **10** was avoided by quenching the HF/K_2NiF_6 mixture resulting from the second step at low temperature, instead of warming it up and distilling the HF back into a reservoir in an attempt to recycle and reuse it, as was done previously in the preparation of **3**.[22] The quenching involves pouring the product mixture containing K_2NiF_6 dissolved in HF over an ice bath contained in a Teflon vessel and requires great care. The yield of **17** was often only 10% and at best 15%. Attempts to increase the yield and to make the preparation safer by avoiding the use of the HF/K_2NiF_6 mixture altogether, using only elemental fluorine and CF_3Cl as a solvent, resulted in incomplete fluorination. The anion **17** was found to be stable to strong acids (BF_3/HF, GeF_4/HF, AsF_5/HF, and CF_3SO_3H).

Further attempts to improve the synthesis were abandoned when it was discovered that the neat cesium salt is similarly explosive as that of **3**. When a minute amount on the tip of a spatula is brought close to an open flame, it detonates violently. Several times very small samples detonated when touched with a Teflon-coated spatula, and once even an only incompletely fluorinated mixture exploded.

1-H-(2−6)-F_5-(7−12)-$(CF_3)_6$-CB_{11}^- (14) represented our second choice. It was first prepared from (7−12)-Me_6-$CB_{11}H_6^-$ in two steps using the procedure described for **17**, as a mixture with other products that were difficult to separate. As was the case with **17**, one of these impurities was the 1-fluoro derivative **7**. This impurity can be once again minimized by very cautiously quenching the reaction mixture by pouring it over ice while it is still at −78 °C, but it was very difficult to eliminate completely. The other impurities identified by ES/MS contained oxygen and were present in amounts that varied from one reaction to the next, from as little as 10% to as much as 50% of the crude product. These byproducts were also difficult to separate. Once again, attempts to avoid the use of the HF/K_2NiF_6 mixture and to use only elemental fluorine in CF_3Cl solvent resulted in incomplete fluorination.

Finally, a safer and higher yielding procedure was discovered when the use of K_2NiF_6 in the second step was replaced with fluorination in a Monel reactor charged with anhydrous HF and 200 psi of 20% F_2/80% N_2. After two days, the yield based on (7−12)-Me_6-$CB_{11}H_6^-$ was 48%, and the crude product was more than 93% pure. Neither **7** nor any oxygen insertion products were formed. The same sequence of reactions also provided **17** in good yield, but due to its explosive nature, we have not pursued its synthesis further. In contrast, all attempts to make the cesium salt of **14** explode, using a hammer, scraping, and an open flame, failed. However, this does not necessarily mean that other salts of **14** or the free radical resulting from its oxidation could not be explosive, and each should be handled in small quantities and with extreme care until proven safe.

[1-H-12-F-(2−11)-$(CF_3)_{10}$-CB_{11}]$^-$ (16). The first step in the preparation is the synthesis of 12-X-$CB_{11}H_{11}^-$ (X = F or I). Both fluorination[16] with HF and iodination[34] with I_2 are successful, but iodination proceeds much faster and is more convenient. The next step is the methylation of positions 2−11 using methyl triflate in the presence of calcium hydride to give 1-H-12-I-(2−11)-Me_{10}-CB_{11}^- [10]or 1-H-12-F-(2−11)-Me_{10}-CB_{11}^-.[35] Fluorination of either 12-halogenated anion in the optimized two-step procedure that avoids the use of K_2NiF_6 gave the desired anion **16**. It is stable to BF_3/HF, GeF_4/HF, AsF_5/HF, and CF_3SO_3H. We have not experienced any explosions of its neat salts but have not examined the limits of stability extensively and recommend that they be viewed as potentially explosive.

1-H-(7−12)-F_6-(2−6)-$(CF_3)_5$-CB_{11}^- (12) was prepared by a one-step fluorination of 1-H-(7−12)-I_6-(2−6)-Me_5-CB_{11}^- [10] in a Monel reactor charged with anhydrous HF and 200 psi 20% F_2/80% N_2. It is not necessary to partially fluorinate the material before using the high pressure fluorination procedure, because iodines in positions 7−12 render the anion stable to HF. We have experienced no explosions with its neat cesium salt but have not made extensive attempts to induce them.

Alkylation. Attempts to alkylate **17** after deprotonation of the carbon vertex ran into difficulties. While spectral evidence indicated that methylation was possible, attempts to introduce longer akyl groups clearly failed, and these efforts were abandoned. We suspect that the steric hindrance by the trifluoromethyl groups

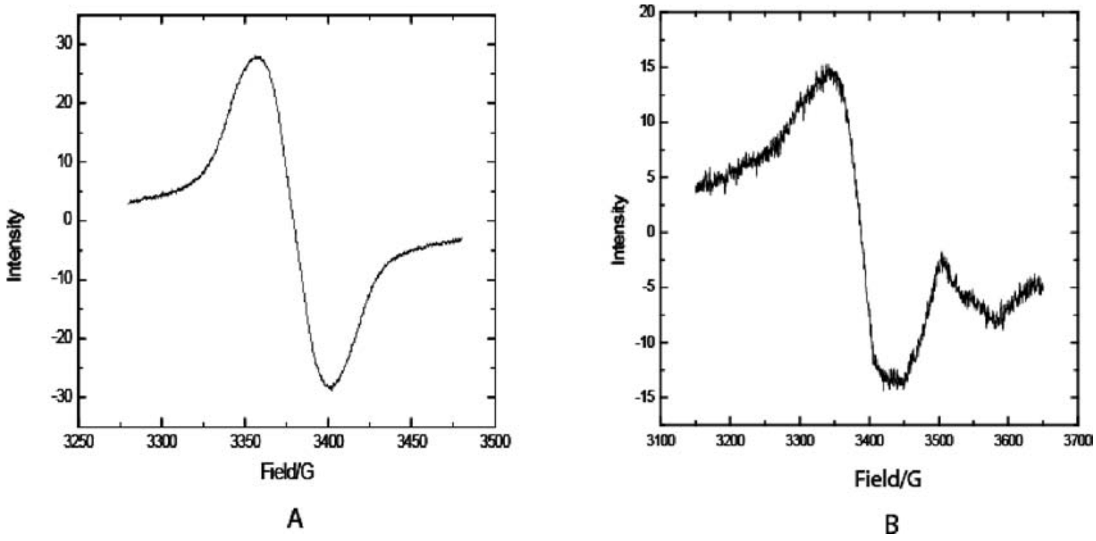


Figure 6. EPR spectra of **27** (A, derived from anion **14**) and **28** (B, derived from anion **12**).

in positions 2−6 is excessive, in line with recent observations of severe steric hindrance at the carbon vertex by five methyl groups in the same positions.[35] In contrast, the alkylation of the much less hindered anion **14** is facile, and 1-allyl (**25**) and 1-pentenyl (**26**) derivatives were prepared in good yield.

Anion Oxidation Tests. The stability of several of the anions to the strong oxidant, "NiF_3^+", was examined. This reagent needs to be prepared[36] and used in anhydrous liquid HF. The addition of more than a 3-fold molar excess of BF_3 to a solution of K_2NiF_6 in anhydrous HF below −60 °C gives yellowish brown solutions of an ill-characterized $Ni^{IV}_{(solv)}$ cation, presumably NiF_3^+. This species, and the analogous $Ag^{III}_{(solv)}$ cation, are believed to be the strongest chemical oxidants known in the bulk to date.[36] Both fail to oxidize the cesium salts of **3**, **16**, and **17** to the respective neutral radicals.

In contrast, the cesium salt of anion **14** appears to be oxidized with the $Ni^{IV}_{(solv)}$ reagent to produce the neutral radical 1-H-(2−6)-F_5-(7−12)-$(CF_3)_6$-$CB_{11}^{\bullet}$ (**27**). The reaction was run using a two-layer system containing anhydrous HF and either perfluorohexane or perfluorotri-*n*-butylamine. The densities of the solvents are such that the HF layer is always on the top. K_2NiF_6 and **14** dissolve in the HF layer at −78 °C. Upon addition of a large excess of BF_3 the HF layer turns deep brown. This color is characteristic of the $Ni^{IV}_{(solv)}$ cation. Upon warming the reaction mixture to −60 °C the perfluorohexane or perfluorotri-*n*-butylamine layer develops a deep blue color, similar to that of the well characterized $CB_{11}Me_{12}^{\bullet}$ radical.[9]

The blue solution gives no NMR signals at −60 °C but yields a strong broad EPR signal (Figure 6A). The blue color disappears upon warming above −20 °C in either a Teflon vessel or a quartz tube, and the only boron containing product isolated is **14**. Perfluorohexane can be cannulated into another flask at −60 °C and washed with HF and again removed by cannulation. Allowing the washed, isolated material to warm above −20 °C again leads to a loss of the blue color and **14** is isolated. Alternatively, perfluorotri-*n*-butylamine can be used instead of perfluorohexane. Its freezing point is 26 °C above that of HF (−78 °C), and it can be frozen while the liquid HF layer is decanted into a separate arm of a Teflon T-reactor for safe disposal. However, it turned out to be fairly difficult to keep the reactor at low enough temperature, and we consider this procedure inferior.

The cesium salt of the anion **12** is also oxidized with $NiF_3^+{}_{(solv)}$, presumably to yield the neutral radical 1-H-(2−6)-$(CF_3)_5$-(7−12)-F_6−$CB_{11}^{\bullet}$ (**28**). This reaction was also carried out at −60 °C using a two-layer system with anhydrous HF and perfluorohexane. Upon the addition of a large excess of BF_3 to the reaction mixture, the purple color characteristic of K_2NiF_6 dissolved in HF turned to the deep brown color of $Ni^{IV}_{(solv)}$ and the perfluorohexane layer turned bright pink. Isolation of the colored perfluoroalkane layer and warming above −20 °C caused a loss of color, and the starting anion **12** was isolated as the only boron containing product. At −60 °C, the pink solutions gave no NMR signals and yielded an EPR spectrum exhibiting a very broad signal (Figure 6B). The spectrum contains an additional weaker broad feature that could be due to the presence of a smaller amount of a second radical but could also be an artifact. It was not investigated further at this time. Using perfluorotri-*n*-butylamine instead of perfluorohexane worked but provided no advantage.

It is unclear what is being oxidized by the colored radicals upon warming to temperatures above −20 °C. The EPR spectra of the solutions were taken in sealed NMR tubes in perfluorohexane. The perfluorohexane was purchased from Aldrich, dried, degassed, and distilled before use. No EPR signals were observed after the color of the solutions faded. The faded solutions displayed ^{11}B spectra identical to the spectra measured for the anions **12** and **14**. The reactions were worked up, and the cesium salts of the anions were isolated. Over 85% of the starting carborane salt was recovered.

Most likely, the radicals oxidize the perfluorohexane or perfluorotri-*n*-butylamine solvent. Although the ionization potential of perfluorohexane is over 11 eV,[2] and although perfluoroalkanes and perfluoroalkylamines are generally viewed as inert, in Material Safety Data Sheets all are listed as incompatible with strong oxidants. It remains to be seen what the oxidation products are and whether an inert solvent can be found for the radicals **27** and **28** at room temperature. We anticipate that the neat solid radicals may well be explosive even if the neat cesium salts of the parent anions are not.

■ DISCUSSION

The discussion of the results will be facilitated by summarizing the results of calculations first. The method for calculating electron detachment energy has been claimed[37] to be accurate to within ±0.2 eV. Even if this claim is correct, in our case the accuracy may be lower, since a single-reference method of calculation is questionable for radicals that have a nondegenerate ground state, but whose geometries differ only by a small Jahn–Teller distortion from the high-symmetry equilibrium geometry of the anion, where the radical ground state is degenerate or very nearly degenerate. Unfortunately, at present a two-reference level of calculation is not accessible to us for molecules of this size. We therefore view the results listed in Table 1 as a rapid initial survey rather than a definitive quantitative prediction. The calculated values of electron detachment energies are so extreme that even approximate values represent a sufficient encouragement for synthetic work.

It is noteworthy that the calculated electron detachment energy depends approximately linearly on the total number of CF_3 groups (Figure 2) but is nearly independent of their positions and of the choice of the H, F, or CF_3 group located on the carbon vertex. The largest difference noted when comparing anions with the same number of trifluoromethyl groups is between **10**, 1-F-$CB_{11}(CF_3)_{11}^-$ (8.0 eV), and **24**, 12-F-$CB_{11}(CF_3)_{11}^-$ (7.5 eV). The vertical (Koopmans) and adiabatic (state energy difference) values are correlated with each other (Figure 3).

Our first target, the per(trifluoromethyl) anion **3**, initially appeared to be an ideal choice for a non-nucleophilic, nonbasic, and nonoxidizable anion. Its large size, considerably exceeding that of C_{60}, reduces the electric field strength at its surface, the only nucleophilic and basic sites are the very inert fluorine lone pairs, and a calculated electron detachment energy of ~8 eV is competitive with the current champions such as PtF_6^-.[1−5] The discovery of its treacherously explosive nature[22] dampened our enthusiasm for this choice.

The two factors responsible for the high heat of detonation,[22] the weakness of the C−F bond relative to the B−F bond, and the steric crowding of the CF_3 substituents, can be alleviated by replacement of a suitable number of CF_3 groups with F substituents. Only the minimum number of such replacements should be made, since the fluorines of BF bonds carry considerable negative charge and are likely nucleophilic and basic sites, and since the replacement makes the anion easier to oxidize (Table 1, Figure 2). Since the removal of a CF_3 group from the carbon vertex and its replacement with F or even H is calculated to carry essentially no penalty with respect to the ease of oxidation, the undeca(trifluoromethyl) anion **17** was the next logical choice. It offered the additional advantage of providing opportunities for substitution at the carbon vertex and thus for attachment to other molecular structures.

We prepared **17** and found that it resembles the previously known[22] **3** in that it also resists even the strongest known bulk oxidant, NiF_3^+.[36] Unfortunately, the resemblance is too perfect and extends to explosive behavior. Moreover, although **17** can be easily deprotonated at the carbon vertex, the introduction of substituents larger than methyl onto the highly hindered carbon atom is very hard.

The desire to prepare an anion that would be safe and if possible easy to substitute, yet would still provide acceptably weak nucleophilicity and resistance to oxidation, led us to choose **14**. Here, we unfortunately must expect to lose ~1.5 V in resistance to oxidation (Table 1), and indeed we find that unlike the anions **3** and **17**, the anion **14** is oxidized with NiF_3^+. The EPR spectrum of the resulting radical **27** is very broad as expected, given the 3 spin of the ^{10}B nuclei and the 3/2 spin of the ^{11}B nuclei (in 20% and 80% abundance, respectively), the presence of 23 fluorine atoms (spin 1/2) in 3 nonequivalent groups, and a proton. The low-temperature stability of the radical appears to be limited by reaction with the perfluorohexane or perfluorotri-*n*-butylamine solvents but suggests that in a more resistant solvent it might be useful as a potent one-electron oxidant soluble in nonpolar and aprotic media. This could make it represent a valuable alternative to NiF_3^+, which is currently available only as a solution in anhydrous liquid HF.

In spite of having given up ~1.5 V in resistance to oxidation, we believe that the anion **14** will be useful. Even an electron detachment energy of 6.8 eV is still ~1.5 V higher than those of the known[21] anion **1**, and nucleophilicity as well as basicity are undoubtedly lower. The steric hindrance at the carbon vertex of **14** should be greatly reduced relative to **17**, and substitution of the carbon atom is indeed facile.

In order to test the generality of our synthetic approach to this class of anions, we have prepared also the anions **12** and **16**, whose behavior still remains to be investigated in greater detail. The former seems to behave similarly to **14**, but the latter should be only 0.5 V easier to oxidize than **3** and **17**. If it is nonexplosive, it may end up being the "inert" carborane anion of choice.

Finally, we note that the conversion of the anions to radicals with NiF_3^+/HF will apparently only be possible for anions whose electron detachment energy is lower than about 7-7.5 eV. The preparation of neutral radicals from anions that are harder to oxidize, such as **16**, will require either the development of new oxidizing agents or an electrochemical approach.

■ COMPUTATIONAL AND EXPERIMENTAL METHODS

Calculations. The structures of the anions and neutral radicals were optimized at the DFT level using the B3LYP functional and the 6-31G* basis set. The calculations were performed with the Gaussian 03 program suite (Supporting Information).[38,39]

General Experimental Methods. Standard Schlenk and inert-atmosphere techniques were used for handling air-sensitive reagents. THF and Et_2O were distilled from Na^0/benzophenone. Pentane was boiled in $KMnO_4/H_2SO_4$, distilled, and stored over K^0. MeOTf was prepared using the procedure of Stang et al.[40] Other reagents were reagent grade and were used as purchased. $Me_3NH^+ CB_{11}H_{12}^-$ was either purchased from Katchem Ltd. (E. Krásnohorské 6, 11000 Prague 1, Czech Republic) or prepared from $Me_3NH^+B_{11}H_{14}^-$.[41] Solution ^1H, ^{11}B, ^{19}F, and ^{13}C NMR spectra were measured with Varian XRS-300, Varian 400-Unity, and Varian Unity-500 spectrometers. ^1H and ^{13}C chemical shifts were measured relative to the lock solvent. ^{11}B chemical shifts were measured using a $B(OCH_3)_3$ external standard (18.1 ppm relative to $BF_3.Et_2O$ at 0 ppm). ^{19}F chemical shifts were measured relative to CF_3COOH (−76.55 ppm relative to CCl_3F at 0 ppm). Peak assignments are based on ^{11}B COSY, $^1H-^{11}B$ HETCOR, $^{13}C-^1H$ and $^{13}C-^{19}F$ HMQC, and $^{13}C-^1H$ HMBC experiments. Mass spectra were recorded with a Hewlett-Packard 5989 ESI. EPR spectra were measured with a Bruker ESP-300 spectrometer. UV spectra were measured with a Hewlett-Packard 8452A diode array spectrometer in spectral grade quality solvents.

All work with anhydrous hydrogen fluoride and elemental fluorine was done in an efficient fume hood. A face shield, rubber apron, and leather or neoprene gloves were worn. *These reagents are very dangerous and extreme care is required when handling them.*

Cs^+[1-H-(7−12)-F_6-(2−6)-$(CF_3)_5$-CB_{11}]$^-$ (12). Cs^+[(7−12)-I_6-(2−6)-Me_5-HCB_{11}]$^-$ [10] (0.2 g, 0.28 mmol) was added to a 45 mL Monel reactor (Parr Instruments). The material was dried at 100 °C and 0.05 Torr for 1 h. Anhydrous HF (5−10 mL) was distilled into the reactor at −78 °C, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was again cooled to −78 °C, and fluorine, 20% in nitrogen, was added to a pressure of 200 psi. The reaction mixture was allowed to warm to room temperature and stirred for 48 h. The HF was removed under reduced pressure and the reactor was opened. (*Caution: since anhydrous HF can still be present in the reactor, it should be handled with proper protective gear and in a hood*). The remaining solids were triturated with 80/20 Et_2O/THF (3 × 50 mL), and the combined ethereal solution was then washed with aqueous 20% CsCl (3 × 50 mL). The aqueous CsCl solution was washed with Et_2O (3 × 50 mL), and the combined organic solutions were evaporated to dryness using a rotary evaporator. The solid was washed with Et_2O (3 × 50 mL), and the solution was filtered to remove any remaining CsCl. The solution was evaporated to dryness using a rotary evaporator. The remaining solid was dissolved in boiling water (3 × 10 mL) and filtered through a glass wool plug. Water was removed providing 100 mg of pure Cs salt of **12**. Yield: 76%. ^{11}B NMR (ref $B(OMe)_3$ at δ 18.1, acetone-d_6): δ −32.50 [s, 5B, B(2−6)], −4.46 [(s, 5B, B(7−11)], 0.98 [s, 1B, B(12)]. ^{1}H NMR δ 4.70 (s, 1H, C−H). ^{19}F NMR (ref CF_3COOH, acetone-d_6) −223.7 [(m, 5F, B−F(7−11)], −205.0 [q, 1F, B−F(12)], −50.1 (m, 15F, C−F). ^{13}C NMR (ref CF_3COOH, C−F HMQC, acetone-d_6): δ 126.8 (s, B-CF_3). IR (NaCl) cm^{-1}: 1290, 1201, 1120, 1100, 1050, 500 . ESI MS(-) *m*/*z* 591, expected isotopic distribution. HRMS: calcd. for monoisotope: 593.0772 Found: 593.0792 (ppm error =3.4).

Partial Fluorination of $Cs^+[(7{-}12)\text{-}Me_6\text{-}CB_{11}H_5]^-$. To a solution of $Cs^+[(7{-}12)\text{-}Me_6\text{-}CB_{11}H_5]^{-}$[10] (0.4 g, 1.11 mmol) in methanol (150 mL) was added silica gel (10 g). Toluene (100 mL) was added, and the solvents were removed using a rotary evaporator. The silica gel with the adsorbed material was dried for 1 h at 100 °C and 0.05 Torr. The material was then placed with $CFCl_3$ (50 mL) into a PTFE reaction vessel equipped with a mechanical stirrer, and the solution was deoxygenated for 0.5 h with nitrogen. Fluorine, 10% in N_2, was added at 75 mL/min for 8 h, and the mixture was stirred at 25 s^{-1} at −78 °C. After sparging with N_2 for 1 h the silica was washed 6 times with methanol (100 mL portions). The wash was made basic with NH_4OH (100 mL) and evaporated to dryness. The solids were triturated with 80/20 Et_2O/THF (3 × 50 mL), and this organic solution was then extracted with aqueous 20% CsCl (3 × 50 mL). The aqueous CsCl solution was washed with 80/20 Et_2O/THF (3 × 50 mL). The organic solutions were combined and evaporated to dryness. The solids were triturated with Et_2O/THF, and the solution was filtered to remove any remaining CsCl. The organic solution was evaporated to dryness on a rotary evaporator. The material was dissolved in boiling water (3 × 10 mL) and filtered through a glass wool plug. Water was removed providing 500 mg of a colorless mixture $Cs^+[1\text{-}H{-}CB_{11}C_6H_nF_{23\text{-}n}]^-$, ∼10 < *n* < ∼18.

$Cs^+[1\text{-}H\text{-}(2{-}6)\text{-}F_5\text{-}(7{-}12)\text{-}(CF_3)_6\text{-}CB_{11}]^-$ (14) by Fluorination with K_2NiF_6. The $Cs^+[HCB_{11}C_6H_nF_{23\text{-}n}]^-$ mixture (250 mg), dry KF (0.5 g), and K_2NiF_6 (1 g) were added to a PTFE reaction vessel equipped with a PTFE-clad magnetic stir bar. Anhydrous HF (15 mL) was distilled into the reaction vessel at −78 °C. The reaction mixture was stirred for 1 h at −78 °C. The reactor was opened without warming (*Caution: the reaction mixture contains HF and K_2NiF_6*) and poured carefully onto ice (*exothermic!*). The solution was made basic with NH_4OH (*exothermic!*) and extracted with 80/20 Et_2O/THF (3 × 100 mL). The organic solution was then washed with aqueous 20% CsCl (3 × 50 mL). The aqueous CsCl solution was extracted with 80/20 Et_2O/THF (3 × 50 mL). The organic solutions were combined and evaporated to dryness. The remaining solid was dissolved in boiling water (3 × 50 mL) and filtered through a plug of glass wool. Water was removed providing 48 mg of Cs salt of **14** (95% pure). Yield: 10% overall from $Cs^+[(7{-}12)\text{-}Me_6\text{-}CB_{11}H_5]^-$.

$Cs^+[1\text{-}H\text{-}(2{-}6)\text{-}F_5\text{-}(7{-}12)\text{-}(CF_3)_6\text{-}CB_{11}]^-$ (14) by High Pressure Fluorination. The $Cs^+[HCB_{11}C_6H_nF_{23\text{-}n}]^-$ mixture (200 mg) was added to a 45 mL Monel reactor (Parr Instruments) and converted to **14** using the procedure described above for **12**. Yield: 52% from $Cs^+[(7{-}12)\text{-}Me_6\text{-}CB_{11}H_5]^-$. ^{11}B NMR (ref $B(OMe)_3$ at δ 18.1, acetone-d_6): δ −26.63 [s, 5B, B(7−11)], −22.95 [(s, 1B, B(12)], −5.04 [s, 5B, B(2−6)]. ^{1}H NMR δ 5.76 (s, 1H, C−H). ^{19}F NMR (ref CF_3COOH, acetone-d_6) −212.4 (m, 5F, B−F), −46.3 [m, 15F, B-CF_3(7−11)], −44.3 [(m, 3F, B-CF_3(12)]. ^{13}C NMR (ref CF_3-COOH, C−F HSQC acetone-d_6): δ 128 [(s,6C, B-CF_3 (7−12)]. IR (NaCl) cm^{-1}: 1275, 1175, 1101, 1010, 500 . ESI MS(-) *m*/*z* 641, expected isotopic distribution. HRMS: calcd. for monoisotope: 643.0740. Found: 643.0732 (ppm error is 1.3).

Partial Fluorination of $Cs^+[1\text{-}H{-}CB_{11}Me_{11}]^-$. Cs^+ $[1\text{-}H{-}CB_{11}Me_{11}]^{-}$[10] (0.4 g, 0.93 mmol) was partially fluorinated using the procedure for partial fluorination of $Cs^+[(7{-}12)\text{-}Me_6\text{-}CB_{11}H_5]^-$ described above, affording 517 mg of colorless mixture $Cs^+[1\text{-}H{-}CB_{11}C_{11}H_nF_{33\text{-}n}]^-$, ∼15 < *n* < ∼25.

$Cs^+[1\text{-}H{-}CB_{11}(CF_3)_{11}]^-$ (17) by Fluorination with K_2NiF_6. The $Cs^+[1\text{-}H{-}CB_{11}C_{11}H_nF_{33\text{-}n}]^-$ mixture (250 mg) was completely fluorinated with K_2NiF_6 using the same conditions as in the preparation of **14**, providing 57 mg of the Cs salt of **17**. Yield: 7−10% (93% pure).

$Cs^+[1\text{-}H{-}CB_{11}(CF_3)_{11}]^-$ (17) by High-Pressure Fluorination. The Cs^+ $[1\text{-}H{-}CB_{11}C_{11}H_nF_{33\text{-}n}]^-$ mixture (200 mg) was added to a 45 mL Monel reactor (Parr Instruments) and converted to **17** by the procedure used to make **12**. Yield: 48% from $Cs^+[1\text{-}H{-}CB_{11}Me_{11}{}^-]$. ^{11}B NMR (ref $B(OMe)_3$ at δ 18.1, acetone-d_6): δ −14.26 [s, 5B, B(2−6)], −10.07 [(s, 5B, B(7−11)], −4.89 [s, 1B, B(12)]. ^{1}H NMR δ (s, 1H, C−H). ^{19}F NMR (ref CF_3COOH, acetone-d_6) −51.6 [(m, 15F, B-CF_3(2−6)], −48.5 [m, 15F, B-CF_3(7−11)], −47.5 [(m, 3F, B-CF_3(12)]. ^{13}C NMR (ref CF_3COOH, C−F HSQC acetone-d_6): δ 124 [(s, 5C, B-CF_3 (2−6)], 126 [s, 5C, B-CF_3(7−11)], 128 [s, 1C, CF_3(12)]. IR (NaCl) cm^{-1}: 3065, 1615, 1588, 1485, 1436, 1265, 1133, 1106, 998, 759, 722, 689. ESI MS(-) *m*/*z* 891, expected isotopic distribution. HRMS: calcd. for monoisotope: 893.0580. Found: 893.0611 (ppm error =3.4).

Partial Fluorination of $Cs^+[1\text{-}H\text{-}12\text{-}I\text{-}(2{-}11)\text{-}Me_{10}\text{-}CB_{11}]^-$. Partial fluorination of $Cs^+[1\text{-}H\text{-}12\text{-}I\text{-}(2{-}11)\text{-}Me_{10}\text{-}CB_{11}]^{-}$[10] (0.4 g, 0.74 mmol) using the above procedure for partial fluorination of $Cs^+[(7{-}12)\text{-}Me_6\text{-}CB_{11}H_5]^-$ provided 492 mg of colorless mixture $Cs^+[1\text{-}H{-}CB_{11}C_{10}H_nF_{31\text{-}n}]^-$, ∼13 < *n* < ∼24.

$Cs^+[1\text{-}H\text{-}12\text{-}F\text{-}(2{-}11)\text{-}(CF_3)_{10}\text{-}CB_{11}]^-$ (16) by High Pressure Fluorination. The $Cs^+[HCB_{11}C_{10}H_nF_{31\text{-}n}]^-$ mixture (200 mg) was added to a 45 mL Monel reactor (Parr Instruments) and converted to **16** using the procedure described above for the preparation of **12**. Yield: 39% from $Cs^+[1\text{-}H\text{-}12\text{-}I\text{-}(2{-}11)\text{-}Me_{10}\text{-}CB_{11}]^-$. ^{11}B NMR (ref $B(OMe)_3$ at δ 18.1, acetone-d_6): δ −17.29 [s, 5B, B(2−6)], −11.52 [(s, 5B, B(7−11)], 10.35 [s, 1B, B(12)]. ^{1}H NMR δ (s, 1H, C−H). ^{19}F NMR (ref CF_3COOH, acetone-d_6) −178.3 [(m, 1F, B−F(12)], −51.8 [m, 15F, B-CF_3(2−6)], −50.8 [(m, 15F, B-CF_3(7−11)]. ^{13}C NMR (ref CF_3COOH, C−F HSQC acetone-d_6): δ 125 [(s, 5C, B-CF_3 (7−11)], 127 [(s, 5C, B-CF_3 (2−6)] . IR (NaCl) cm^{-1}: 1397, 1275, 1147, 1111, 667, 500. ESI MS(-) *m*/*z* 841, expected isotopic distribution. HRMS: calcd. for monoisotope: 843.0612. Found: 843.0586 (ppm error =3.1).

$[Cs^+]$ $[1\text{-}C_3H_5\text{-}(2{-}6)\text{-}F_5\text{-}(7{-}12)\text{-}(CF_3)_6\text{-}CB_{11}]^-$ (25). The Cs salt of **14** (0.05 g, 0.06 mmol) was added to a 50 mL, three-neck round-bottom flask, and the material was dried for 1 h at 0.05 Torr. THF (distilled from Na^0) was added, and the reaction mixture was cooled to −78 °C. *n*-BuLi (0.24 mmol), 1.6 M in hexanes, was added over 0.5 h using a syringe pump. The reaction mixture was stirred for an additional 0.5 h, and allyl iodide (0.24 mmol) was added. Water (10 mL) was added, and the solvents were removed on a rotary evaporator. The remaining solid was triturated with 80/20 Et_2O/THF. The organic solution was washed with 20% aqueous CsCl (3 × 50 mL). The CsCl solution was extracted with 80/20 Et_2O/THF, and the combined organic solutions were evaporated to dryness. The remaining solid was again washed with 80/20 Et_2O/THF and filtered to remove any remaining CsCl. The organic solution was evaporated, and the remaining solid was recrystallized from boiling water to provide 48 mg of the Cs salt of **25**. ^{11}B NMR (ref $B(OMe)_3$ at δ 18.1, acetone-d_6): δ −4.93 [s, 5B, B(7−11)], −23.01 [(s, 1B, B(12)], −4.93 [s, 5B, B(2−6)]. ^{1}H NMR δ 5.22 (m, 2H, CH_2), 5.36 (m, 2H, CH_2), 5.93 (m, 1H, CH). ^{19}F NMR (ref CF_3COOH, acetone-d_6) −212.6 [(m, 5F, B−F(2−6)], −48.7 [m, 15F, B-CF_3(7−11)], −48.9 [(m, 3F, B-CF_3(12)]. IR (Cs^+ salt NaCl) cm^{-1}: 3115, 3088, 3060, 2973, 2936, 2923, 2883, 1700, 1276, 1112, 580. ESI MS(-) *m/z* 681, expected isotopic distribution. HRMS: calcd. for monoisotope: 683.1053. Found: 683.1061 (ppm error is 1.2).

Cs^+[1-C_5H_9-(2−6)-F_5-(7−12)-$(CF_3)_6$-CB_{11}]$^-$ (26). The preparation of the Cs salt of **26** from the Cs salt of **14** (0.06 g, 0.08 mmol) proceeded as described for the preparation of the Cs salt of **25** except that 1-bromo-4-pentene was used instead of allyl iodide. Yield: 91%. ^{11}B NMR (ref $B(OMe)_3$ at δ 18.1, acetone-d_6): δ −27.08 [s, 5B, B(2−6)], −23.20 [(s, 1B, B(12)], −4.69 [s, 5B, B(7−11)]. ^{1}H NMR δ: 1.84 (m, 2H, CH_2), 2.16 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 5.06 (m, 2H, CH_2), 5.82 (m, 1H, CH) . ^{19}F NMR (ref CF_3COOH, acetone-d_6) −212.5 [(m, 5F, B−F(2−6)], −48.7 [m, 15F, B-CF_3(7−11)], −46.9 [(m, 3F, B-CF_3(12)]. IR(NaCl) cm^{-1}: 3083, 2964, 2926, 1277, 1107, 650, 500. ESI MS(-) *m/z* 709, expected isotopic distribution. HRMS: calcd. for single isotope: 711.1366. Found: 711.1378 (ppm error is 1.2).

[1-H-(2−6)-F_5-(7−12)-$(CF_3)_6$-CB_{11}]$^•$ (27, in Perfluorotri-*n*-butylamine). One arm of a PTFE reactor was loaded with the Cs salt of **14** (0.025 g, 0.03 mmol), and material was dried for 1 h at 100 °C and 0.05 Torr. K_2NiF_6 (0.081 g, 0.30 mmol) and dry degassed perfluorotri-*n*-butylamine were added to the same arm of the T-reactor. Anhydrous HF (approximately 5 mL) was condensed onto the solids at −78 °C, and K_2NiF_6 was allowed to dissolve. The active $Ni^{IV}_{(solv)}$ species was prepared in situ, according to Bartlett's procedure,[33] by adding BF_3 to the solution. Upon addition of BF_3 to K_2NiF_6 a tan precipitate (NiF_4) appeared and the purple color of K_2NiF_6 disappeared. With addition of excess BF_3, a yellow solution appeared. Upon addition of a very large excess of BF_3 the solution turned from yellow to a very intense dark brown color. Upon formation of the dark brown solution the reaction mixture was allowed to warm to −60 °C. At this temperature the perfluorotri-*n*-butylamine layer turned deep blue. The reaction mixture was again cooled to −78 °C, and the perfluorotri-*n*-butylamine was frozen. The HF mixture was then poured into the other arm of the T-reactor. Anhydrous HF was again distilled onto the blue perfluorotri-*n*-butylamine layer at −78 °C, and the reaction mixture was warmed to −60 °C. The phases were shaken together, the mixture was cooled to −78 °C, and the perfluorotri-*n*-butylamine layer was again frozen and HF decanted to the other arm of the T-reactor. This process was performed three times, at which point the perfluorotri-*n*-butylamine was cannulated into a separate flask. The EPR spectrum of the solution gave a broad signal (peak to peak width 45 G) and no NMR signals. Warming the solution above −20 °C resulted in loss of color and regeneration of **14**. At −60 °C, the solutions lose their color completely after ~4 h. Above 0 °C, the solutions lose color and EPR signal simultaneously within a few min.

[1-H-(7−12)-F_6-(2−6)-$(CF_3)_5$-CB_{11}]$^•$ (28, in Perfluorotri-*n*-butylamine). The preparation of **28** from **12** (0.015 g, 0.02 mmol) was performed in the same way as the preparation of **27** from **14**. Solutions of **28** in perfluorotri-*n*-butylamine are pink. At −60 °C they give a broad EPR signal (peak to peak width over 80 G), and loss of color gives the anion **12**. Solutions of **28** at −60 °C exhibit complete loss of color after ~4 h. At room temperature the color disappears within a few min. No EPR signal is seen after color loss.

[1-H-(2−6)-F_5-(7−12)-$(CF_3)_6$-CB_{11}]$^•$ (27, in Perfluorohexane). One arm of a PTFE reactor was loaded with the Cs salt of **14** (0.025 g, 0.03 mmol), and the material was dried for 1 h at 100 °C and 0.05 Torr. K_2NiF_6 (0.081 g. 0.30 mmol) and dry degassed perfluorohexane were added to the same arm of the T-reactor. Liquid HF (~5 mL) was condensed onto the solids at −78 °C, and the K_2NiF_6 was allowed to dissolve. The active $Ni^{IV}_{(solv)}$ species was prepared in situ, according to Bartlett's procedure,[33] by adding BF_3 to the solution. Upon addition of BF_3 to K_2NiF_6 a tan precipitate (NiF_4) appeared and the purple color of K_2NiF_6 disappeared. With addition of excess BF_3, a yellow solution formed. Upon addition of a very large excess of BF_3 the solution turned from yellow to very intense dark brown, and the reaction mixture was then allowed to warm to −60 °C. At this temperature the perfluorohexane layer turned a deep blue color. The reaction mixture was again cooled to −78 °C, and the perfluorohexane was canulated into a separate Teflon vessel under positive nitrogen pressure. The colored solution yields a broad EPR signal (peak to peak width 45 G) and no NMR signals. Warming the solution above −20 °C results in loss of color, and these colorless solutions contain **14**. At −60 °C, the solutions become completely colorless after ~4 h. Above 0 °C the solutions lost color and EPR signal simultaneously within a few min.

[1-H-(7−12)-F_6-(2−6)-$(CF_3)_5$-CB_{11}]$^•$ (28, in Perfluorohexane). The procedure for the preparation of **28** from **12** (0.015 g, 0.02 mmol) is identical to that for the preparation of **27** from **14**. Solutions of **28** in perfluorohexane are pink. At −60 °C, they give a broad EPR signal (peak to peak width over 80 G) and after loss of color afford the anion **12**. Solutions of **28** at −60 °C exhibit complete loss of color after ~4 h. At room temperature the color and the EPR signal disappear within a few min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Computed optimized energies and geometries of the anions **1**-**24** and the corresponding neutral radicals, complete refs 37 and 38, and original spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

Work in Boulder was supported by the National Science Foundation (CHE-0848477) and the AFOSR (FA9550-10-1-0374). Work in Prague was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (IAA400550708) and by Research Project Z40550506 of the IOCB ASCR.

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