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Synthesis and Characterization of Ammonioundecafluoro-*closo*-dodecaborates(1–). New Superweak Anions

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The ammonioborane monoanion $H_3NB_{12}H_{11}^-$ was per-B-fluorinated with elemental fluorine in liquid hydrogen fluoride to yield the first member of a new class of weakly coordinating anions, $H_3NB_{12}F_{11}^-$ (isolated as $[N(n\text{-}Bu)_4]_2[H_2NB_{12}F_{11}]$ in 41% yield). The pK_a of the $H_3NB_{12}F_{11}^-$ anion is 9.6. Several salts of the tri-N-alkylated anions $Me_3NB_{12}F_{11}^-$ and $Dd_3NB_{12}F_{11}^-$ (Dd = n-$C_{12}H_{25}$) were also prepared. The structure of $[CPh_3][Me_3NB_{12}F_{11}]$ was determined by single-crystal X-ray diffraction: monoclinic, space group $P2_1/c$, $a = 18.053(3)$ Å, $b = 33.139(5)$ Å, $c = 9.600(2)$ Å, $\beta = 91.459(4)°$, $V = 5742(2)$ Å^3, $Z = 8$, $T = 173(2)$ K, $R_1 = 0.045$. It revealed that the only direct interactions between the undecafluoroammonioborate monoanions and the trityl cations in the two independent ion pairs were long and weak $BF\cdots CPh_3$ interactions of 2.992(6) and 2.942(6) Å. Salts of the new anions were chemically, electrochemically, and thermally stable. The conductivity of $Li(Me_3NB_{12}F_{11})$ in dimethoxyethane was comparable to that of $LiPF_6$ but less than half the value of $Li(1\text{-}Me\text{-}CB_{11}F_{11})$.

Ever since the seminal reports by Reed and co-workers that $CB_{11}H_{12}^-$ is a robust weakly coordinating anion,[1] several groups have prepared more weakly coordinating derivatives (i.e., superweak anions[2]) by substituting some or all of the hydrogen atoms with halogen atoms and/or hydrocarbyl or haloalkyl groups.[3−7] Many of these derivatives are even more robust than $CB_{11}H_{12}^-$ with respect to thermal or electrochemical degradation, to strong acids, bases, electrophiles, or nucleophiles, or to strong oxidizing or reducing agents.

We recently reported that $B_{12}F_{12}^{2-}$, in spite of its 2− charge, is more weakly ion paired with the CPh_3^+ cation in the solid state than is the BF_4^- anion with related triarylcarbenium ions.[8] We proposed that if a 1− derivative of $B_{12}H_{12}^{2-}$ could be highly fluorinated, the resulting anion might be a useful (and potentially less expensive) alternative to the 1-R-$CB_{11}F_{11}^-$ class of superweak anions.[9] We now report that the ammonioborane monoanion $H_3NB_{12}H_{11}^-$, first prepared in 1964,[10] can be per-B-fluorinated and then trialkylated to yield the first two members of a new class of weakly coordinating anions, $Me_3NB_{12}F_{11}^-$ and $Dd_3NB_{12}F_{11}^-$ (Dd = n-$C_{12}H_{25}$).

In contrast to the monofluorination of $CB_{11}H_{12}^-$ in liquid anhydrous HF (LAHF) in 4 h at 25 °C,[11] $Cs(H_3NB_{12}H_{11})$ was recovered unchanged after treatment with LAHF for 2 days at 25 °C. However, $Cs(H_3NB_{12}H_{11})$ was converted to $Cs(H_3NB_{12}F_{11})$ with elemental fluorine in LAHF, as shown below:

$$H_3NB_{12}H_{11}^- + \text{excess } F_2 \xrightarrow{\text{LAHF}} xH_3NB_{12}F_{11}^- + 11xHF + yBF_4^- + zNH_4^+$$

[**CAUTION:** Both HF and F_2 are extremely hazardous materials and should be handled only by trained personnel].[12]

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(12) Details of the synthesis of new compounds and the determination of the pK_a of the $H_3NB_{12}F_{11}^-$ anion are given in the Supporting Information.

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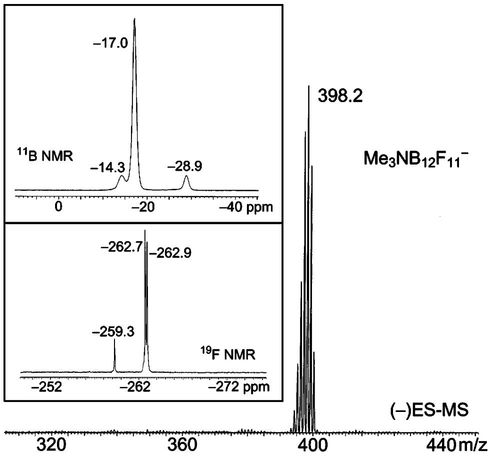

Figure 1. Negative-ion electrospray-ionization mass spectrum (H_2O solution), ^{11}B NMR spectrum (96.3 MHz, CD_3CN, $\delta(BF_3{\cdot}OEt_2) = 0$), and $^{19}F\{^{11}B\}$ NMR spectrum (282.4 MHz, anhydrous CD_3CN, $\delta(CFCl_3) = 0$) of anhydrous $Li(Me_3NB_{12}F_{11})$.

The BF_4^- anion and the NH_4^+ cation, which are attributed to the degradation of some of the $H_3NB_{12}H_{11}^-$ anions under the reaction conditions, were observed in NMR spectra of the crude product. No other boron-containing products were observed by ^{11}B NMR spectroscopy.

Neither the Cs^+ nor the $N(n\text{-}Bu)_4^+$ salts of $H_3NB_{12}F_{11}^-$ and BF_4^- could be efficiently separated from one another because their solubilities in water are too similar. However, when the mixture of $(Cs/NH_4)(H_3NB_{12}F_{11})$ and $(Cs/NH_4)BF_4$ was dissolved in a large volume of 0.5 M aqueous KOH and treated with $N(n\text{-}Bu)_4Cl$, the compound $[N(n\text{-}Bu)_4]_2[H_2NB_{12}F_{11}]$, containing the aminoborate dianion $H_2NB_{12}F_{11}^{2-}$, precipitated with virtually no $N(n\text{-}Bu)_4BF_4$ contamination.[12] After drying, the yield of $[N(n\text{-}Bu)_4]_2[H_2NB_{12}F_{11}]$ was 41% based on $Cs(H_3NB_{12}H_{11})$.

The ammonioborate monoanion $H_3NB_{12}F_{11}^-$ is a weak Brønsted acid in water. Its pK_a value, 9.6, was determined by monitoring ^{19}F NMR peaks at various pH values:[12] only $H_3NB_{12}F_{11}^-$ was observed at pH 1 and below; only $H_2NB_{12}F_{11}^{2-}$ was observed at pH 12.6 and above; an average set of resonances for rapidly exchanging $H_3NB_{12}F_{11}^-$ and $H_2NB_{12}F_{11}^{2-}$ were observed at intermediate pH values.

The ammonio group can be mono-, di-, or trialkylated. Details about mono- and dialkylation will be reported in the full paper. Here we report the trimethyl and tridodecyl derivatives. When the fluorination product mixture containing $H_3NB_{12}F_{11}^-$, BF_4^-, and NH_4^+ was dissolved in 0.5 M aqueous KOH and treated with excess $(MeO)_2SO_2$, the compound $[NMe_4][Me_3NB_{12}F_{11}]$ was isolated in 27% yield based on $Cs(H_3NB_{12}H_{11})$.[12] The salts $Li(Me_3NB_{12}F_{11})$ and $[CPh_3][Me_3NB_{12}F_{11}]$ were prepared by metathesis reactions.[12] Similarly, the compound $Li(Dd_3NB_{12}F_{11})$ was prepared in 42% yield by treatment of $[N(n\text{-}Bu)_4]_2[H_2NB_{12}F_{11}]$ in 0.5 M aqueous KOH with excess DdBr followed by $Li^+/N(n\text{-}Bu)_4^+$ metathesis.[12] The ^{11}B and $^{19}F\{^{11}B\}$ NMR spectra and a negative-ion electrospray ionization mass spectrum of $Li(Me_3NB_{12}F_{11})$ are shown in Figure 1. Other spectroscopic data are given in the Supporting Information.

Crystals of $[CPh_3][Me_3NB_{12}F_{11}]$ suitable for X-ray diffraction were grown from a saturated dichloromethane solution.[13] The structure of one of the two independent ion pairs is shown in Figure 2. The B−B and B−F distances are similar to those observed in $[CPh_3]_2[B_{12}F_{12}]$ and in compounds containing various $1\text{-R-CB}_{11}F_{11}^-$ ions.[7b,c,8,14] The two B−N distances, 1.576(5) and 1.568(6) Å, can be compared with the B−N distance in $Cs(H_3NB_{12}H_{11}){\cdot}2MeOH$, 1.54(1) Å.[15] The most significant feature of the structure is the long, weak C1···F5 distance of 2.992(6) Å, which is only 0.18 Å shorter than the 3.17 Å sum of van der Waals radii for carbon and fluorine.[16] The next longest C1···F contact is greater than 3.6 Å. Furthermore, the sum of the three C−C1−C angles is 359.9(3)°, indicating no significant distortion of the carbenium carbon atom geometry from planarity. The shortest and next shortest C···F distances for the second ion pair are 2.942(6) and >3.5 Å, respectively. Note that the shortest C···F distance in each of the two $[CPh_3][Me_3NB_{12}F_{11}]$ ion pairs is far longer than the related $BF{\cdots}CAr_3$ distances in $[CPh_2(p\text{-OMe-}C_6H_4)][BF_4]$ and $[CPh(p\text{-OMe-}C_6H_4)_2][BF_4]$, 2.68 and 2.58 Å, respectively.[17] This indicates that $Me_3NB_{12}F_{11}^-$ is a more weakly basic anion than BF_4^-.

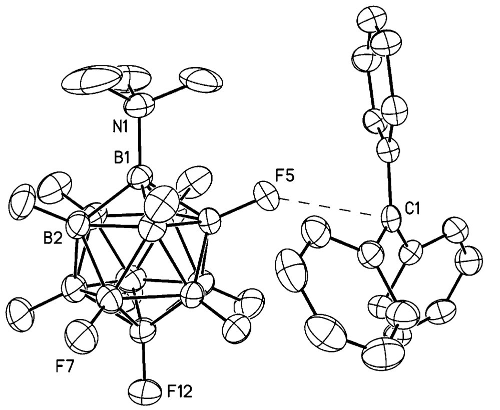

Figure 2. Thermal ellipsoid plot of one of the two nearly identical ion pairs in $[CPh_3][Me_3NB_{12}F_{11}]$ (50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (deg): C1···F5, 2.992(6); C1−C, 1.437(5)−1.454(5); C−C1−C, 119.4(3)−120.7(4); N1−C, 1.475(5)−1.493(5); C−N1−C, 105.1(4)−108.3(4); B1−N1, 1.576(5); B−F, 1.378(4)−1.394(5). The C···F distance in the other ion pair is 2.942(6) Å.

To further probe the weakly basic nature of $Me_3NB_{12}F_{11}^-$, we measured the conductivity of $Li(Me_3NB_{12}F_{11})$ and several related salts as 0.01 M solutions in dimethoxyethane.[18] The conductivity (σ) of $Li(Me_3NB_{12}F_{11})$, 68 μS cm^{-1}, is considerably higher than that of $LiCF_3SO_3$ (4 μS cm^{-1}), somewhat

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(13) Crystal data for $[CPh_3][Me_3NB_{12}F_{11}]$: red-orange; monoclinic; $P2_1/c$, $a = 18.053(3)$ Å, $b = 33.139(5)$ Å, $c = 9.600(2)$ Å; $\beta = 91.459(4)$°; $Z = 8$; $T = 173(2)$ K; $R = 0.045$, $R_w = 0.110$; GOF = 0.686.

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(18) Solution conductances were measured in a helium-filled glovebox at 24 ± 1 °C using a YSI model 3403 conductivity cell calibrated for inverted use ($k = 0.9988$ cm^{-1}) and a YSI model 32 conductivity bridge operated at 1 kHz. All of the lithium salts were anhydrous as determined by ^{1}H NMR spectroscopy.

higher than that of Li($Dd_3NB_{12}F_{11}$) (54 μS cm^{-1}), comparable to that of $LiPF_6$ (73 μS cm^{-1}), and less than half that of Li(1-Me-$CB_{11}F_{11}$) (190 μS cm^{-1}). The difference in σ values for Li($Me_3NB_{12}F_{11}$) and Li($Dd_3NB_{12}F_{11}$) is probably due to the lower anion mobility of the larger $Dd_3NB_{12}F_{11}^-$ anion. The difference in σ values for Li($Me_3NB_{12}F_{11}$) and Li(1-Me-$CB_{11}F_{11}$) is more significant. Although the $Me_3NB_{12}F_{11}^-$ anion has the same icosahedral shape, the same number of B−F bonds, and the same overall 1− charge as the 1-Me-$CB_{11}F_{11}^-$ anion, it is a zwitterion with a 1+ ammonium moiety connected to a $B_{12}F_{11}^{2-}$ moiety. The individual fluorine atoms in $Me_3NB_{12}F_{11}^-$ may accumulate more negative charge density than the fluorine atoms in 1-Me-$CB_{11}F_{11}^-$, and therefore $Me_3NB_{12}F_{11}^-$ is more strongly ion pairing, and is probably more strongly coordinating, than 1-Me-$CB_{11}F_{11}^-$. An alternative explanation is that the zwitterionic nature of $Me_3NB_{12}F_{11}^-$ results in a much greater charge asymmetry along the pseudo-5-fold symmetry axis in $Me_3NB_{12}F_{11}^-$ than along the corresponding axis in 1-Me-$CB_{11}F_{11}^-$. The greater charge asymmetry renders $Me_3NB_{12}F_{11}^-$ a more "polar" anion than 1-Me-$CB_{11}F_{11}^-$.

The $H_3NB_{12}F_{11}^-$ anion did not react with 20% aqueous DCl or, except for deprotonation to $H_2NB_{12}F_{11}^{2-}$, with 0.5 M aqueous NaOH during 18 days. As far as electrochemical stability is concerned, a cyclic voltammogram of Cs($Dd_3NB_{12}F_{11}$) showed no oxidation wave up to 2.0 V vs Ag/AgCl (0.001 M acetonitrile solution containing 0.1 M N(*n*-Bu)$_4$PF$_6$). The compounds Li($Dd_3NB_{12}F_{11}$) and Cs($Dd_3NB_{12}F_{11}$) were recovered unchanged after heating (in a purified dinitrogen atmosphere) at 185 °C for 18 h and 200 °C for 0.5 h, respectively. When Cs($Dd_3NB_{12}F_{11}$) was heated at 300 °C for 0.5 h, the Hofmann-degradation products $Dd_2HNB_{12}F_{11}^-$ and $DdH_2NB_{12}F_{11}^-$ were observed in ^{1}H NMR and mass spectra along with intact $Dd_3NB_{12}F_{11}^-$, but no degradation of the B_{12} cage and no cleavage of B−N bonds were observed. Finally, the ^{1}H and ^{19}F NMR spectra of Cs($Dd_3NB_{12}F_{11}$) in toluene-d_8 were unchanged after the addition of 3 or 100 equiv of $AlEt_3$ except for the resonances due to $AlEt_3$ in the ^{1}H NMR spectrum.

As far as other halogen derivatives of $H_3NB_{12}H_{11}^-$ are concerned, Miller and co-workers reported the synthesis of a series of $R_3NB_{12}H_{11-n}X_n^-$ salts in 1965 (R = Me, X = Br, n = 1, 8; R = Et, X = Br, n = 6; R = Et, X = Cl, n = 7).[19] Surprisingly, the only evidence reported at that time was elemental analysis, and no followup reports have appeared since then. Accordingly, we have started to re-explore the chlorination and bromination of the $H_3NB_{12}H_{11}^-$ anion. When Cs($H_3NB_{12}H_{11}$) was heated with *N*-chlorosuccinimide or bromine in refluxing acetic acid, mixtures of $H_3NB_{12}Cl_{11}^-$/$H_3NB_{12}HCl_{10}^-$ or $H_3NB_{12}Br_{11}^-$/$H_3NB_{12}HBr_{10}^-$, respectively, were observed by negative-ion electrospray-ionization mass spectrometry. Compositionally pure salts of the $H_3NB_{12}Cl_{11}^-$ and $H_3NB_{12}Br_{11}^-$ anions, free from $H_3NB_{12}HX_{10}^-$ contamination, have not yet been isolated. We are continuing to investigate the N-alkylated and per-B-halogenated derivatives of $H_3NB_{12}H_{11}^-$.

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Supporting Information Available: Synthetic details and selected NMR spectral data for new compounds and crystallographic data in CIF format for [CPh_3][$Me_3NB_{12}F_{11}$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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