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Chlorination of Icosahedral Carborane Anions. X-ray Crystal Structure of $[Me_3NH][CH_3\text{-}1\text{-}CB_{11}Cl_{11}]$

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Icosahedral carboranes constitute a new class of very weakly coordinating anions.[1,2] They are finding many applications in metathesis, catalysis, and oxidation chemistry.[3−11] The 7−12-hexahalogenated derivatives, $CB_{11}H_6X_6^-$ (X = Cl, Br, I), are larger, more thermodynamically stable, more chemically inert, less coordinating, and less nucleophilic than the parent $CB_{11}H_{12}^-$ ion.[3] These anions are playing a very important role in stabilizing coordinatively unsaturated cations such as the silylium ion (R_3Si^+),[4−7] the four-coordinate (tetraphenylporphyrinato)iron(III) ion ($Fe(tpp)^+$),[8] and hydronium ion ($H_9O_4^+$).[12] The partially fluorinated[13] and permethylated[14] derivatives have just been reported very recently, which are, however, either similar in coordinating ability to $CB_{11}H_{12}^-$ [13] or less stable toward oxidant and concentrated acids than the parent ion.[14] The search for the most stable, the least coordinating, and the most soluble anion is still of great interest and a challenging synthetic problem. It has been known that the halogenation of $CB_{11}H_{12}^-$ leads to not only increased stability but also decreased nucleophilicity.[3] The origin of this decreased coordinating ability may lie in a steric effect, that is, the five halogen atoms in the pentagonal belt (7−11 positions) can prevent the coordination of the most basic one (the 12-halo substituent) to the cation.[3−7] The hexachlorocarborane is the least coordinating anion in this series at least with respect to R_3Si^+.[7] With this in mind, it seemed logical that the perchlorinated carborane should be the more stable and even less coordinating anion than the other derivatives. A summary of our initial efforts is presented herein.

Perchlorinated or perbrominated polyhedral boranes are known and were readily prepared from the reaction of the polyhedral analogues with excess of *N*-chlorosuccinimide or *N*-bromosuccinimide, respectively.[15] Under similar conditions, however, only partially halogenated products of the 12-vertex carborane anion were obtained. A stronger chlorination reagent must be employed in order to make the perhalogenated carborane anions. Direct chlorination of $Cs[CH_3\text{-}1\text{-}CB_{11}H_{11}]$[14] in glacial acetic acid at 85−90 °C for 1 week led to the isolation of the single product $Cs[CH_3\text{-}1\text{-}CB_{11}Cl_{11}]$ (Cs[**1**]) in 85% yield, which can then be converted into the Me_3NH^+ and Ag^+ salts by cation exchange reactions.[16] Addition of the Lewis acid catalyst such as $AlCl_3$ into the reaction system can slightly shorten the reaction time but on the other hand causes much difficulties in the workup process, resulting in the low isolation yield. Under similar or more vigorous reaction conditions, the chlorination of $Cs[CB_{11}H_{12}]$ did not proceed to completion, giving a mixture of hepta-, octa-, nona-, deca- and undecachlorocarborane anions, $CB_{11}Cl_xH_{12-x}^-$ ($x = 7-11$), based on analyses of the LSIMS mass spectra. This mixture can be methylated on carbon in 90% yield using the general procedure for *C*-alkylation,[17] followed by the method mentioned above to generate the single product Cs[**1**]. The presence of the methyl group on the carborane cage is essential for converting all *BH* to *BCl* vertices, probably due to its electron donating ability that can increase the overall electron density of the cage and activate the *BH* vertices closer to the *CH* vertex.

The structure of **1** in $[NMe_3H]$[**1**] is shown in Figure 1.[18] This anion has crystallographically imposed C_3 symmetry which prohibited differentiation of the carbon atom from the boron atoms within the cage. The exohedral CH_3 group is thus completely mixed up with the eleven chlorine atoms of the cage anion. The average B−Cl bond distance of 1.767(10) Å is shorter than the 1.803(9) Å average in $Pr^i_3Si(CB_{11}H_6Cl_6)$.[7] The distances between the centers of pairs of the antipodal chlorine

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(16) Synthetic Procedure: Chlorine gas was continuously bubbled into a glacial acetic acid solution (30 mL) of $Cs[CH_3\text{-}1\text{-}CB_{11}H_{11}]$ (1.60 g, 5.52 mmol) at 85−90 °C under stirring for 1 week. The completion of this reaction can be monitored by ^{11}B NMR. After removal of most of the acetic acid, the viscous residue was dissolved in 5% sodium hydroxide (25 mL) and extracted with diethyl ether three times. The organic layer was concentrated and treated with aqueous solution of Me_3NHCl. The precipitate was filtered off, washed with water, and dried under vacuum to give $[Me_3NH]$**1** as white solid (2.80 g, 85%). Recrystallization from a mixture of CH_3CN and toluene yielded colorless prism X-ray-quality crystals. Anal. Calcd for $C_5H_{13}Cl_{11}B_{11}N$: C, 10.08; H, 2.20; N, 2.35. Found: C, 10.61; H, 2.30; N, 2.32. ^1H NMR (acetone-d_6, relative to external acetone): δ 1.55 (s, 3H), 3.18 (s, 9H). $^{11}B\{^1H\}$ NMR (160.5 MHz, acetone-d_6, relative to external $BF_3{\cdot}OEt_2$): δ −10.9 (s, 1B), −18.0 (s, 5B), −19.6 (s, 5B). $^{13}C\{^1H\}$ NMR (125.8 MHz, acetone-d_6, relative to external acetone): δ 49.67 (s, cage carbon), 44.98 [q, Me_3NH, $^1J(^{13}C-^1H) = 142.5$ Hz], 19.75 [q, CH_3, $^1J(^{13}C-^1H) = 128.6$ Hz]. IR (cm^{-1}, KBr): 3082 (m, br), 2803 (s), 1095 (s), 1035 (vs), 981 (s), 541(m). LSIMS for **1**: *m*/*e* 535.9. Found: *m*/*e* 535.8. The expected isotopic distribution of masses is also observed in LSIMS.
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(18) Crystal data for $[Me_3NH]$**1** ($C_5H_{13}Cl_{11}B_{11}N$; fw 596.02): Rhombohedral, space group $R\bar{3}c$, $a = 12.119(1)$ Å, $c = 29.726(2)$ Å, $V = 3783(2)$ Å^3, $d_{calcd} = 1.571$ g/cm^3, $Z = 6$, $R = 0.042$ ($F > 4.0\sigma(F)$), $R_w = 0.053$, data to parameter ratio 12.4. Data were collected at 294 K on a MSC/Rigaku RAXIS-IIC image plate using Mo Kα radiation ($\lambda = 0.710\,73$ Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. The structure was solved by direct methods and refined using the Siemens SHELXTL PLUS program package (PC version) (SHELXTL PLUS program set; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990). The icosahedral cage is defined by four independent B atoms and the four independent Cl atoms representing the exohedral groups which are each assigned the same occupancy factor of $(6 + 11 \times 7)/(12 \times 7) = 0.946$.

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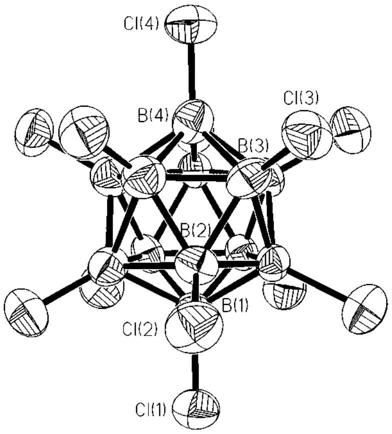

Figure 1. Perspective view of **1** in [Me_3NH]**1**. The thermal ellipsoids are drawn at the 50% probability level. Note that the C and B atoms of the icosahedral cage are indistinguishable, and the exohedral methyl group is completely scrambled with the eleven Cl atoms.

atoms (Cl···Cl diameters) fall in a narrow range from 6.937 to 6.947 Å with an average of 6.942 Å, indicating that **1** has an almost perfect spheroidal shape. With 1.75 Å for the van der Waals radius of Cl,[19] the average Cl···Cl diameter of **1** is 10.442 Å. This size is comparable to that of the C_{60} molecule which has an average C···C diameter of 7.074 or 10.474 Å after adding the van der Waals radii of its C atoms.[20] The molecular packing (illustrated in the synopsis) shows that the crystal structure consists of alternating layers of anions **1** and cations [NMe_3H]. The distance between two nitrogen atoms in neighboring layers, 8.57 Å, equals that between the centroids of two carborane cages in different layers. The closest Cl···N contact is 4.87 Å.

Compound [NMe_3H][**1**] has also been fully characterized by elemental analysis and IR, MS, and ^1H, ^{13}C, and ^{11}B spectroscopy.[16] The complete conversion of *BH* vertices into *BCl* vertices is indicated by the absence of B−H coupling in the ^{11}B NMR and of B−H absorption in the IR spectrum. The presence of the CH_3 substituent is clearly shown by the ^1H and ^{13}C NMR spectra as well as the MS spectrum. The Cs salt of **1** has high thermal stability, with no decomposition up to 260 °C. It is highly soluble in donor solvents such as acetone, acetonitrile, ether, and water and is also somewhat soluble in arenes. Like its parent CH_3-1-$CB_{11}H_{11}^-$ ion,[14] Cs[**1**] shows no oxidation wave up to 2.0 V in acetonitrile ([Bu_4N][PF_6]; Pt; ferrocene, 0.45 V) ($CB_{11}Me_{12}^-$: 1.6 V in acetonitrile[14]).

In summary, the first 12-vertex carborane anion containing eleven-*BCl* vertices has been prepared by direct chlorination in high yield. The presence of the electron-donating methyl substituent on the carbon position is essential for ensuring completely conversion of *BH* to *BCl* vertices. The application of **1** in the stabilization of coordinatively unsaturated cations is under investigation.

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Supporting Information Available: Tables of crystallographic data collection information, atom coordinates, bond distances and angles, and anisotropic thermal parameters and a figure showing the atom-numbering scheme for [Me_3NH]**1** (11 pages). Ordering information is given on any current masthead page.

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