Dodecaborates

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Synthesis, Crystal Structure, and Reactivity of the Strong Methylating Agent $Me_2B_{12}Cl_{12}$**

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The efficiency of methylating reagents strongly depends on the weakly coordinating properties of the anion. The introduction of carborane anions $[CHB_{11}R_5X_6]^-$ (R = Me, Cl; X = Cl, Br) and the synthesis of the methylating agents $Me(CHB_{11}Me_5X_6)$ (X = Cl, Br) by Reed was a recent breakthrough.[1] The replacement of triflate anions by the more weakly coordinating carborane anions $[CHB_{11}R_5X_6]^-$ (R = Me, Cl; X = Cl, Br) significantly increased the methylating power.[2] $Me(CHB_{11}Me_5X_6)$ (X = Cl, Br) methylates benzene and converts alkanes into the corresponding alkyl cations with concomitant formation of methane.[1] Very recently, perhalogenated dodecaborate cluster anions $[B_{12}X_{12}]^{2-}$ (X = F,[3] Cl[4]) came to attention as weakly coordinating dianions. Improved syntheses for $[B_{12}F_{12}]^{2-}$ [3b] and $[B_{12}Cl_{12}]^{2-}$ [4a] have been developed and make these dianions available on a large scale. They have been applied to stabilize unusual dications[4b] and the first diprotic superacid $H_2B_{12}Cl_{12}$.[4c] These anions are thus of great interest as weakly coordinating dianions for methylating agents and stabilization of the resulting cations.

We therefore attempted to methylate the perchlorinated dodecaborate cluster $[B_{12}Cl_{12}]^{2-}$ and explore its properties. In a well-known reaction, methyl fluoride was treated with the Lewis acid AsF_5 in liquid sulfur dioxide at temperatures below −30 °C to give $[MeOSO][AsF_6]$ [Eq. (1)], which can be subsequently used to methylate very weak donor molecules.[5] Treatment of $[MeOSO][AsF_6]$, prepared in situ, with $M_2[B_{12}Cl_{12}]$ (M = Li, Na, K) in liquid sulfur dioxide at −70 °C yielded methylated $[B_{12}Cl_{12}]^{2-}$ [Eq. (2)].

$$MeF + AsF_5 \xrightarrow{SO_2} [MeOSO][AsF_6] \quad (1)$$

$$2\,[MeOSO][AsF_6] + M_2[B_{12}Cl_{12}] \xrightarrow{SO_2} [MeOSO][MeB_{12}Cl_{12}] + 2\,M[AsF_6]\downarrow \quad (2)$$

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$M[AsF_6]$ is only sparingly soluble in liquid SO_2 and was partly removed by filtration. Subsequent removal of all volatiles results in a bulk material with the composition $M[MeB_{12}Cl_{12}]$, which corresponds to a mixture of the two very soluble compounds $M_2[B_{12}Cl_{12}]$ and $Me_2B_{12}Cl_{12}$. Colorless crystals of $Me_2B_{12}Cl_{12}$ were obtained by slow evaporation of the solvent and fractional crystallization. The structure of neutral $Me_2B_{12}Cl_{12}$ could be determined by single-crystal X-ray diffraction (Figure 1) and is the first structurally characterized example of a carborane or dodecaborate anion bound to a methyl cation.[6] Neutral dodecaborate clusters are rare; other examples are 1,12-$B_{12}H_{10}(CO)_2$ and 1,12-$B_{12}H_{10}(CO_2H_2)_2$.[7]

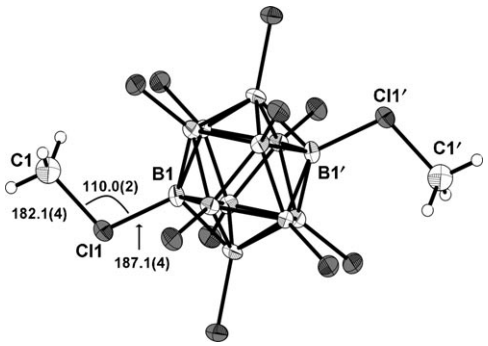
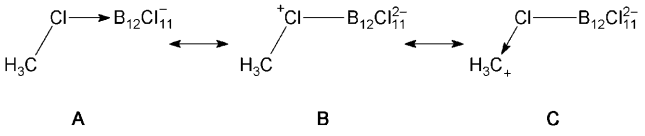


Figure 1. Part of the X-ray crystal structure of $Me_2B_{12}Cl_{12}$ including selected bond lengths [pm] and angles [°]. Thermal ellipsoids are set at 50% probability.

In solid $Me_2B_{12}Cl_{12}$ two methyl groups are connected to the anion in the 1- and 12-positions similar to the coordination of two $[Et_3Si]^+$ cations in $(Et_3Si)_2B_{12}Cl_{12}$.[4c,8] In contrast to the rather long silicon–chlorine bond in solid $(Et_3Si)_2B_{12}Cl_{12}$ (231.75(8) pm versus 208.63(9) pm in Me_3SiCl),[9] the carbon–chlorine bond in $Me_2B_{12}Cl_{12}$ (C1−Cl1 182.1(4) pm, 180.6 pm calculated at the PBE0/def2-TZVPP level for comparison) is only slightly longer than the carbon–chlorine single bond in methyl chloride (180.5 pm (solid state),[10a] 178.2 pm (gas phase)[10b]). Dimethylchloronium [Me-Cl-Me]$^+$ has been reported,[11] and very recently experimental structural data was obtained.[12] The C−Cl bond length in [Me-Cl-Me]$^+$ (calcd (PBE0/def2-TZVPP) 180.5 pm; exp. 181.0(2) pm[12]) is in good agreement with the experimentally observed bond length in $Me_2B_{12}Cl_{12}$. Only very recently, the crystal structure of the disilylated chloronium cation $[Me_3Si\text{-}Cl\text{-}SiMe_3]^+$ was determined;[13] the silicon–chlorine bond (223.8(5) pm)[13] is significantly longer than the silicon–chlorine bond in the corresponding neutral Me_3SiCl

(208.63(9) pm).[9] The carbon–chlorine distances in $Me_2B_{12}Cl_{12}$ and $[Me\text{-}Cl\text{-}Me]^+$ are thus extremely short and should be best described as covalent carbon–chlorine single bonds. The differences between the compounds having $[H_3C]^+$ and $[Me_3Si]^+$ groups can be attributed to the intrinsically better stabilization of $[Me_3Si]^+$ compared to $[H_3C]^+$. Correspondingly, the chlorine–bond Cl1–B1 (187.1(4) pm) is almost 10 pm longer than the typical boron–chlorine bond (178.9 pm) in free $[B_{12}Cl_{12}]^{2-}$ [4a] and is also longer than in the silylium compounds $(R_3Si)_2B_{12}Cl_{12}$ (R = Et, *i*Pr; av. 184.1 pm),[4c,8] thus indicating a very strong carbon–chlorine and a weak chlorine–boron bond in $Me_2B_{12}Cl_{12}$.

The bonding situation should thus be described by equal contributions of mesomeric structures **A** and **B** (Scheme 1). This view is supported by calculated NPA charges (H_3C +0.18, Cl1 +0.46, av. Cl −0.08, B1 −0.09, av. B −0.07) for



Scheme 1. Mesomeric structures for $[MeB_{12}Cl_{12}]^-$.

$[MeB_{12}Cl_{12}]^-$ at the PBE0/def2-TZVPP level, which show only a very small positive charge on the methyl group but a significant positive charge on the bridging chlorine atom and the remaining negative charge of about −1.5 total on the anion. Thus, significant positive charge transfer from the methyl cation to the anion and mainly the bridging chlorine atom occurs.

In contrast, in sulfur dioxide solution, only one methyl group is bound to the $[B_{12}Cl_{12}]^{2-}$ anion regardless of the temperature, and a strongly bound $[MeB_{12}Cl_{12}]^-$ anion is formed. The ^{11}B NMR spectrum has three signals in a 1:5:6 pattern (Figure 2). The cross-peaks in the ^{11}B COSY NMR spectrum show that these signals arise from the same cluster. The chemical shift for the boron atom connected to the $(Me\cdots Cl)^+$ unit is shifted downfield by about 3.0 ppm compared to free $[B_{12}Cl_{12}]^{2-}$.

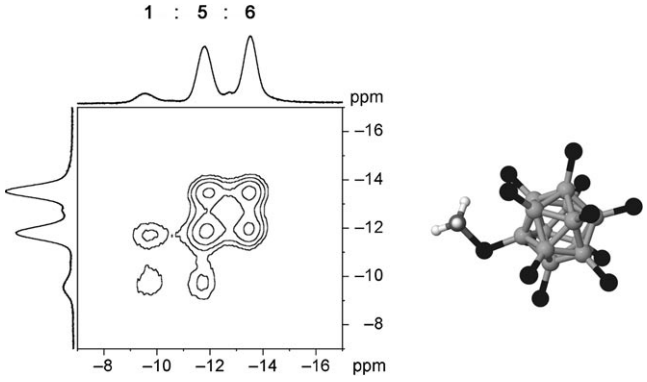


Figure 2. $^{11}B,^{11}B$ COSY spectrum (double quantum-filtered) of $[MeB_{12}Cl_{12}]^-$ in $Na[MeB_{12}Cl_{12}]$ in SO_2 solution at RT (calibrated on $[B_{12}Cl_{12}]^{2-}$) and the calculated structure of $[MeB_{12}Cl_{12}]^-$.

The second methyl cation is solvated by sulfur dioxide. Computed energetics for the binding of one and two methyl cations to $[B_{12}Cl_{12}]^{2-}$ in SO_2 solution confirm these experimental findings (see the Supporting Information). Binding of one methyl cation to the anion in solution is feasible, whilst the second methyl cation remains solvated, and is thus much more reactive. For comparison, the single methyl cation in $Me(CHB_{11}Me_5Br_6)$ is bound to the $[CHB_{11}Me_5Br_6]^-$ anion in SO_2 solution, as shown by NMR spectroscopy.[1b] Therefore, it can be concluded that $[MeB_{12}Cl_{12}]^-$ is a more weakly coordinating anion than the carborane $[CHB_{11}Me_5Br_6]^-$ with the same total charge of −1.

Despite the strong coordination of one methyl cation to the $[B_{12}Cl_{12}]^{2-}$ anion in solution, and a structure that is similar to covalent MeCl bound to $[B_{12}Cl_{11}]^-$ in the solid state, methyl chloride elimination has not been observed under normal laboratory conditions. However, in the gas phase, the situation is different, as shown by mass spectrometric analysis. Isolation and fragmentation (Figure 3) of ions with *m*/*z* 629 from the isotopic distribution of the anionic ion pair $[(NMe_4)\text{-}(B_{12}Cl_{12})]^-$ showed the loss of NMe_3 and formation of the methylated anion $[MeB_{12}Cl_{12}]^-$ (*m*/*z* 570), which subsequently eliminated methyl chloride. However, the expected remnant,

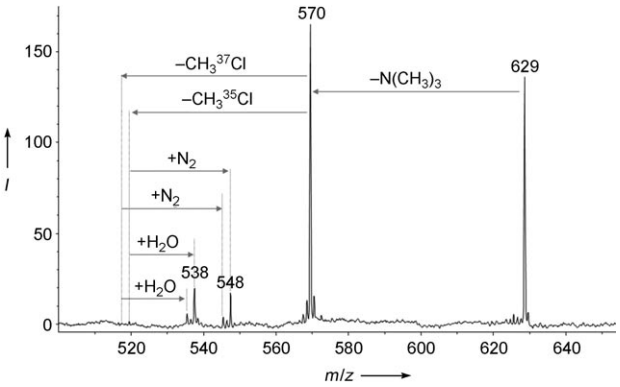
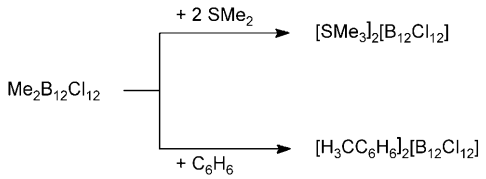


Figure 3. Fragmentation of ions with *m*/*z* 629 from the isotopic distribution of the anionic ion pair $[(NMe_4)(B_{12}Cl_{12})]^-$.

a $[B_{12}Cl_{11}]^-$ anion with a naked boron vertex, was not observed. Instead, the very reactive $[B_{12}Cl_{11}]^-$ anion immediately adsorbed H_2O and N_2 from the residual gases within the mass spectrometer, giving the experimentally observed $[B_{12}Cl_{11}(OH_2)]^-$ (*m*/*z* 538) and $[B_{12}Cl_{11}(N_2)]^-$ (*m*/*z* 548) anions. This situation is reminiscent of the reactivity of "$CB_{11}Me_{11}$" in solution, which instantaneously reacts with nucleophiles.[14] All the described gas-phase reactions in the mass spectrometer were verified by numerous experiments.[15]

$Me_2B_{12}Cl_{12}$ was applied in methylating reactions to investigate its reactivity (Scheme 2). The reaction with dimethyl sulfide gave $[SMe_3]_2[B_{12}Cl_{12}]$ as expected, which could be structurally characterized (see the Supporting Information). Both methyl cations in $Me_2B_{12}Cl_{12}$ react with benzene in a similar fashion to the carborane reagents $Me(CHB_{11}Me_5X_6)$ (X = Cl, Br) to give protonated toluene (shown by NMR spectroscopy; see the Supporting Information). These reac-



Scheme 2. Reactions of $Me_2B_{12}Cl_{12}$.

tions show the potential of $Me_2B_{12}Cl_{12}$ for methylating reactions. At the same time, the very weakly coordinating dianion $[B_{12}Cl_{12}]^{2-}$ is introduced to stabilize the cations formed.

Experimental Section

Air- and moisture-sensitive solid reagents were manipulated using vacuum and Schlenk techniques or in a glove box with an atmosphere of dry argon (H_2O and $O_2 < 1$ ppm). The reactions using liquid sulfur dioxide as solvent were carried out in H-shaped glass vessels with J. Young Teflon-in-glass valves and an incorporated G4 fine frit. The liquid sulfur dioxide solvent was dried over CaH_2 and distilled prior to use. $M_2[B_{12}Cl_{12}]$ was prepared by the reaction of $[NEt_3H]_2[B_{12}Cl_{12}]$ with two equivalents of MOH in aqueous solution.[4a] This product was thoroughly dried at 180 °C at 10^{-3} mbar for several days and subsequently treated with $SOCl_2$ in SO_2. Methyl fluoride[16] and arsenic pentafluoride[17] were prepared by published procedures. Full experimental details and spectra are given in the Supporting Information.

$Me_2B_{12}Cl_{12}$: $Li_2[B_{12}Cl_{12}]$ (0.41 g, 0.72 mmol) was charged into a H-shaped Schlenk vessel equipped with a G4 frit. SO_2 (10 mL) was condensed onto the solid at −196 °C and the solution was stirred at ambient temperature for 0.5 h. This side of the vessel was then closed and MeF (0.05 g, 1.55 mmol, 2.2 equiv), AsF_5 (0.32 g, 1.86 mmol, 2.6 equiv), and SO_2 (10 mL) were condensed at −196 °C into the other side of the vessel. This mixture was allowed to warm up to −70 °C and was then stirred at this temperature for 0.5 h. Thereafter the reaction mixture was poured to the solution of $Li_2[B_{12}Cl_{12}]$ in SO_2 at the same temperature. The reaction mixture was stirred for an additional 2.5 h at −70 °C. The solution turned orange in color and a white solid ($Li[AsF_6]$) precipitated. The solution was separated from the solid by filtration through the frit and all volatiles were subsequently removed, yielding a mixture of $Li_2[B_{12}Cl_{12}]$ and $Me_2B_{12}Cl_{12}$ (equivalent to a bulk composition of $Li[MeB_{12}Cl_{12}]$; 0.35 g, 0.60 mmol, 83 %) as a pale-brown solid. ^{1}H NMR (SO_2; calibrated on MeCl ($\delta =$ 3.01 ppm), 298 K): $\delta = 4.56$ ppm (s, $[MeB_{12}Cl_{12}]^-$). ^{7}Li NMR (SO_2; not referenced, 298 K): $\delta = -0.1$ ppm (Li^+). ^{11}B NMR (SO_2; calibrated on $[B_{12}Cl_{12}]^{2-}$ ($\delta = -12.7$ ppm), 298 K): $\delta = -13.5$ (br, 5 + 1 B), −11.8 (br, 5 B), −9.6 ppm (br, 1 B). ^{13}C NMR (SO_2; calibrated on MeCl ($\delta =$ 25.6 ppm), 298 K): $\delta = 45.8$ ppm ($[MeB_{12}Cl_{12}]^-$). IR: $\tilde{\nu} = 3067$ (vw), 1407 (w), 1332 (w), 1027 (vs), 709 (m), 594 (m), 532 cm^{-1} (vs). Raman: $\tilde{\nu} = 2961$ (10), 304 (100), 127 cm^{-1} (80). Fractional crystallization from liquid sulfur dioxide afforded colorless crystals of $Me_2B_{12}Cl_{12}$ suitable for X-ray diffraction.

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[6] Single-crystal X-ray structure determinations were carried out on a Rigaku R-AXIS Spider image-plate diffractometer using $Mo_{K\alpha}$ radiation (0.71073 Å). The crystals were selected at −30 °C and mounted onto a cryo loop using fluorinated oil and frozen in the cold nitrogen stream of the goniometer. The structures were solved by direct methods. Subsequent least-squares refinement on F^2 located the positions of the remaining atoms in the electron density maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model and were refined isotropically in blocks. (G. M. Sheldrick, SHELX-97 Programs for Crystal Structure Analysis, Universität Göttingen, **1997**). The data were corrected for absorption (semi-empirical from equivalents). $C_2H_6B_{12}Cl_{12}$: $M_r = 585.19$, orthorhombic, *Pbca*, $a =$ 1244.3(3), $b = 1193.0(2)$, $c = 1354.6(3)$ pm, $V = 2.0108(7)$ nm^3, $Z = 4$, $\mu = 1.640$ mm^{-1}, $T = 100(2)$ K, 29985 reflections measured, 1768 independent ($R_{int} = 0.1176$), $R1 = 0.0393$ ($I > 2\sigma(I)$), $wR2 = 0.0797$ (all data). $C_9H_{24}B_{12}Cl_{12}S_2$: $M_r = 751.54$, trigonal, $R\bar{3}m$, $a = b = 1082.9(3)$, $c = 2486.0(5)$ pm, $V = 2.5247(11)$ nm^3, $Z = 3$, $\mu = 1.117$ mm^{-1}, $T = 120(2)$ K, 16043 reflections measured, 754 independent ($R_{int} = 0.0460$), $R1 = 0.0299$ ($I > 2\sigma(I)$), $wR2 = 0.1073$ (all data). CCDC 755209 and CCDC 755210 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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