SUPPORTING INFORMATION

# Substitution of H atoms in unsaturated (vinyl-type) carbocations by Cl or O atoms

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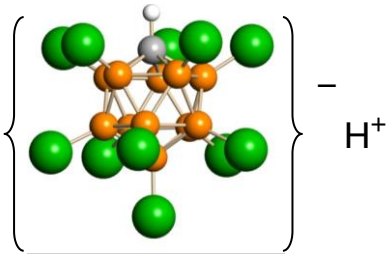


Figure S1. The super acid with icosahedral carborane anion $CHB_{11}Cl_{11}^-$, which was used for obtaining the carbocation salts

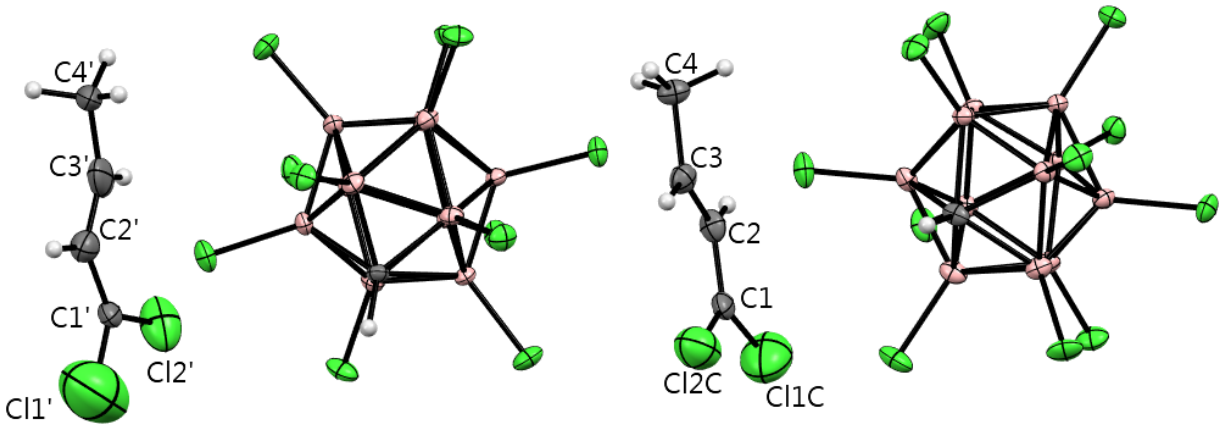


Figure S2. Crystallographically independent 1,1-dichlorobutylene cations and $\{Cl_{11}^-\}$ anions in the crystal lattice of their salt.

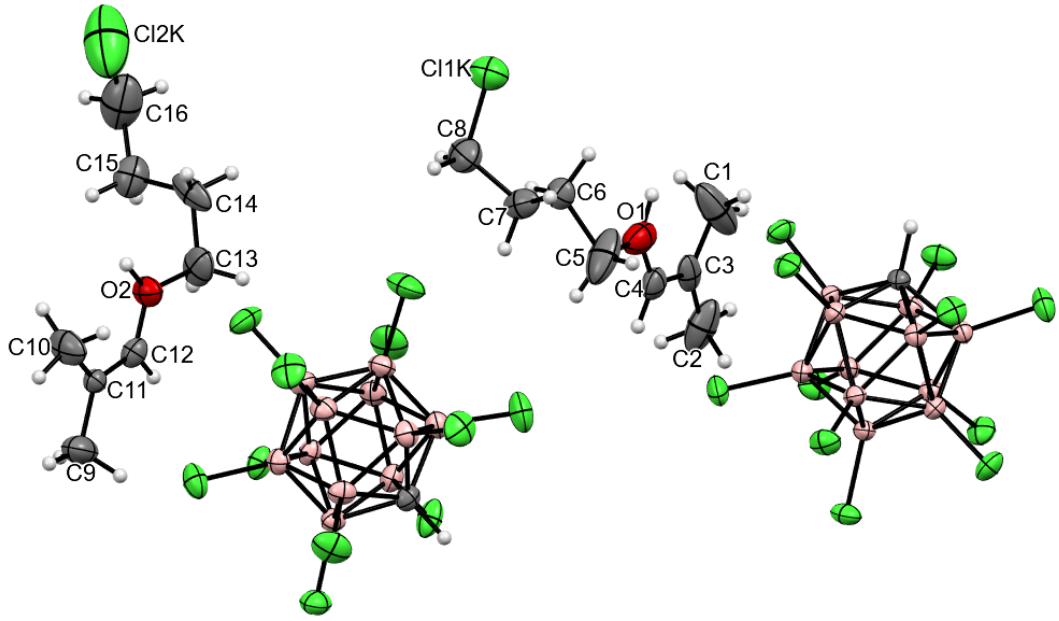


Figure S3. Crystallographically independent cations **I** and $\{Cl_{11}^-\}$ anions in the crystal lattice of their salt.

# Crystal phase data

## Table S1

X-ray data for compounds 1,1-dichloro-1-butylene carbocation and cations **I** and **II**

| Compound | 1,1-dichloro-1-butylene$^+$ | **I** | **II** |
|---|---|---|---|
| Empirical formula | $C_4H_5Cl_2$+$CHB_{11}Cl_{11}$ | $C_8H_{16}OCl$ + $CHB_{11}Cl_{11}$ | $C_8H_{13}OCl_2$ + $CHB_{11}Cl_{11}$ |
| Formula weight | 645,86 | 685.54 | 717.96 |
| Temperature K | 200(2) | 200(2) | 200(2) |
| Wavelength Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | P-1 | $P2_1/c$ | $P2_1/c$ |
| Unit cell dimensions *a* Å | 12.5834(5) | 16.258(4) | 16.355(5) |
| *b* Å | 14.4684(8) | 23.118(5) | 9.979(3) |
| *c* Å | 15.0626(8) | 15.126(3) | 17.462(5) |
| $\alpha$ ° | 104.414(2) | 90 | 90 |
| $\beta$ ° | 110.117(2) | 103.689(9) | 96.166(11) |
| $\gamma$ ° | 100.501(2) | 90 | 90 |
| Volume Å$^3$ | 2383.3(2) | 5524(2) | 2833.3(14) |
| Z | 4 | 8 | 4 |
| Density (calcd.) Mg.m$^{-3}$ | 1.760 | 1.649 | 1.683 |
| Abs. coefficient mm$^{-1}$ | 1.391 | 1.210 | 1.275 |
| F(000) | 1240 | 2704 | 1408 |
| Crystal size mm$^3$ | 0.04 x 0.15 x 0.30 | 0.20 x 0.30 x 0.30 | 0.005 x 0.01 x 0.30 |
| Θ range for data collection ° | 1.52 – 26.09 | 1.29 - 30.26 | 2.35 – 25.03 |
| Index ranges | $-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$ | $-23 \leq h \leq 23$, $-32 \leq k \leq 32$, $-19 \leq l \leq 21$ | $-19 \leq h \leq 19$, $-11 \leq k \leq 11$, $-20 \leq l \leq 20$ |
| Reflections collected | 25683 | 93831 | 24561 |
| Independent reflections | 9386 R(int) = 0.071 | 16365 R(int )= 0.056 | 4986 R(int )= 0.155 |
| Completeness to θ % | 99.7 | 99.7 | 99.6 |
| Data / restraints / parameters | 9386 / 0 / 531 | 16365 / 16 / 633 | 4986/42 / 308 |
| Goodness-of-fit on $F^2$ | 1.03 | 1.05 | 1.12 |
| Final R indices $I > 2\sigma(I)$ | $R_1 = 0.0627$, $wR_2 = 0.1659$ | $R_1 = 0.0573$, $wR_2 = 0.1613$ | $R_1 = 0.1180$, $wR_2 = 0.2667$ |
| Final R indices (all data) | $R_1 = 0.1028$, $wR_2 = 0.1938$ | $R_1 = 0.0722$, $wR_2 = 0.1733$ | $R_1 = 0.2138$, $wR_2 = 0.2893$ |
| Largest diff. peak / hole e.Å$^{-3}$ | 1.28 / -1.25 | 1.57 / -1.30 | 0.96/ -0.78 |
| CCDC | | | |

Table S2. Selected bond lengths (Å) and bond angles (°) for the 1,1-dichloro-1-butylene cation (two independent molecules):

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| Bond | Length (Å) | Bond | Length (Å) |
| C1–Cl1c | 1.629(9) | C1'–Cl1c' | 1.601(9) |
| C1–Cl2c | 1.671(8) | C1'–Cl2c' | 1.621(8) |
| C1–C2 | 1.395(10) | C1'–C2' | 1.359(11) |
| C2–C3 | 1.325(11) | C2'–C3' | 1.299(13) |
| C3–C4 | 1.497(10) | C3'–C4' | |
| Bond angles | (°) | Bond angles | (°) |
| Cl1c–C1–Cl2c | 119.6(5) | Cl1c'–C1'–Cl2c' | 117.5(6) |
| Cl1c–C1–C2 | 118.0(6) | Cl1c'–C1'–C2' | 115.3(7) |
| Cl2c–C1–C2 | 122.2(6) | Cl2c'–C1'–C2' | 126.9(6) |
| C1–C2–C3 | 121.8(7) | C1'–C2'–C3' | 124.0(9) |
| C2–C3–C4 | 125.0(6) | C2'–C3'–C4' | 129.7(10) |

Table S3. Selected bond lengths (Å) and bond angles (°) for cation **I** (two independent molecules):

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| Bond | Length (Å) | Bond | Length (Å) |
| Cl1K–C8 | 1.775(5) | Cl2K–C16 | 1.738(9) |
| O1–C4 | 1.269(5) | O2–C12 | 1.287(4) |
| O1–C5 | 1.435(9) | O2–C13 | 1.475(6) |
| O1–C5' | 1.435(9) | O2–C13' | 1.475(6) |
| C1–C3 | 1.451(9) | C9–C11 | 1.456(5) |
| C2–C3 | 1.455(8) | C10–C11 | 1.456(7) |
| C3–C4 | 1.274(6) | C11–C12 | 1.278(5) |
| C5–C6 | 1.565(9) | C13–C14 | 1.524(10) |
| C5'–C6' | 1.50(2) | C13'–C14' | 1.40(2) |
| C6–C7 | 1.518(9) | C14–C15 | 1.547(13) |
| C6'–C7' | 1.52(3) | C14'–C15' | 1.50(2) |
| C7–C8 | 1.528(8) | C15–C16 | 1.563(12) |
| C7'–C8' | 1.50(2) | C15'–C16' | 1.55(1) |
| Bond angles | (°) | Bond angles | (°) |
| C4–O1–C5 | 117.1(4) | C12–O2–C13 | 115.8(3) |
| C1–C3–C2 | 119.6(5) | C9–C11–C10 | 117.5(4) |
| C1–C3–C4 | 120.4(5) | C9–C11–C12 | 120.4(3) |
| C2–C3–C4 | 120.1(4) | C10–C11–C12 | 121.9(3) |
| O1–C4–C3 | 121.8(4) | O2–C12–C11 | 121.5(3) |
| O1–C5–C6 | 98.8(5) | O2–C13–C14 | 108.0(4) |
| O1–C5'–C6' | 132(1) | O2–C13'–C14' | 109.5(8) |
| C5–C6–C7 | 105.1(5) | C13–C14–C15 | 107.5(7) |
| C5'–C6'–C7' | 109(2) | C13'–C14'–C15' | 128(2) |
| C6–C7–C8 | 109.0(5) | C14–C15–C16 | 112.1(7) |
| C6'–C7'–C8' | 111(2) | C14'–C15'–C16' | 112(1) |
| Cl1K–C8–C7 | 114.2(4) | Cl2K–C16–C15 | 129.6(7) |
| Cl1K–C8'–C7' | 113.2(9) | Cl2K–C16'–C15' | 92.6(6) |