

## SUPPORTING INFORMATION

**Spontaneous transition of alkyl carbocations to unsaturated vinyl-type carbocations  
in organic solutions**

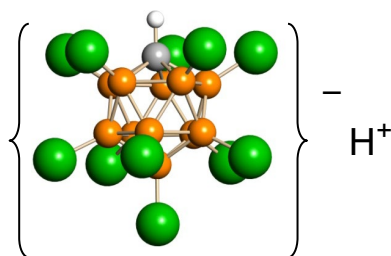
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## Experimental details

The carborane acid,  $\text{H}(\text{CHB}_{10}\text{Cl}_{11})$  (Figure S1), used for obtaining carbocation salts was prepared as described previously.<sup>1</sup> Methods for obtaining salts of cations  $t\text{-Bu}^+$  and methylcyclopentyl<sup>+</sup> are given in refs. 2 and 3, respectively. Nonetheless, we found easier ways to prepare them. The  $t\text{-Bu}^+(\text{CHB}_{10}\text{Cl}_{11})^-$  salt is easily obtained by wetting the acid powder with drops of liquid 1-chlorobutane followed by rinsing with a small volume of dichloromethane (DCM) and drying in a glove box with a water vapor content of <0.5 ppm. Salt methylcyclopentyl<sup>+</sup> $(\text{CHB}_{10}\text{Cl}_{11})^-$  can be prepared as follows: the solid acid is dissolved in DCM to form a solution of  $\text{CH}_3\text{-CHB}_{10}\text{Cl}_{11}$  and  $(\text{CH}_2\text{Cl})_2\text{Cl}^+(\text{CHB}_{10}\text{Cl}_{11})^-$  salts<sup>4</sup> followed by the addition of hexane. Hexane is protonated and converted into the methylcyclopentyl<sup>+</sup> cation, the salt of which precipitates as a white solid. It is separated, washed with DCM, and dried in a glove box. All the procedures were performed in a Vacuum Atmospheres Corp. glove box in an atmosphere of  $\text{N}_2$  ( $\text{O}_2$  and  $\text{H}_2\text{O}$  concentrations <0.5 ppm).



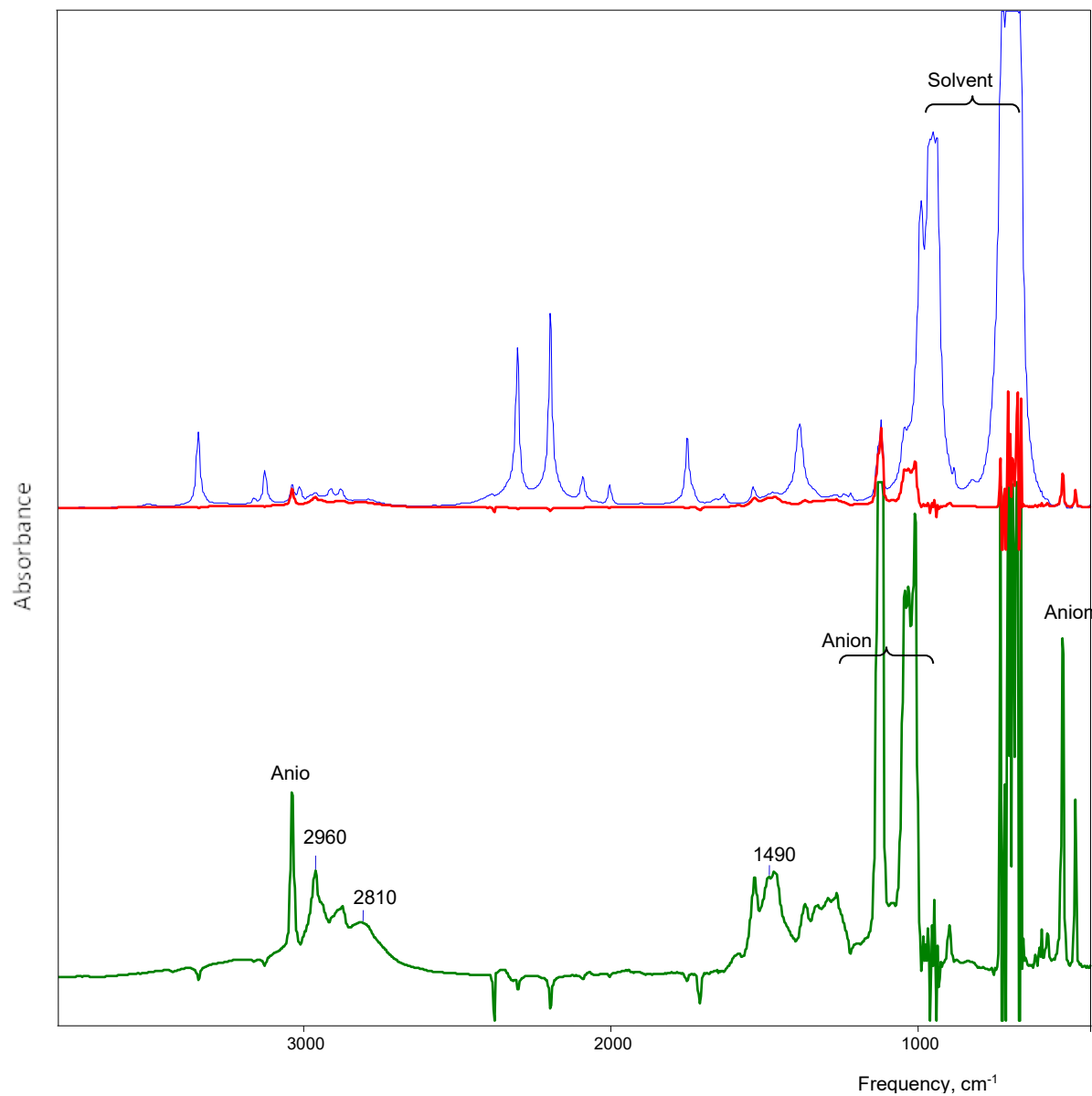
**Figure S1.** The superacid having icosahedral carborane anion  $\text{CHB}_{10}\text{Cl}_{11}^-$

Crystals of  $\text{C}_4$ -carbocation salts were grown from a solution via slow evaporation of the solvent in the glove box or by keeping the solutions over  $\text{CCl}_4$ . X-ray structural analysis of the crystals was carried out by us earlier.<sup>5-7</sup>

IR spectra were recorded on a Shimadzu IRAffinity-1S spectrometer housed inside a glove box in either transmission or attenuated total reflectance (ATR) mode ( $400\text{--}4000\text{ cm}^{-1}$ ). The IR data were processed in the GRAMMS/A1 (7.00) software from Thermo Fisher Scientific.

To record the IR spectra of the solutions, we used a cell with Si windows having 0.036 mm separation at the beam transmission point. To avoid interference effects, the cell configuration is wedge-shaped. The IR spectra of the solutions consist of overlapping spectra of the solute and solvent. To isolate a spectrum of a solute, the spectrum of the solvent was subtracted from the initial spectrum of the solution. Figure S2 shows a typical example of this procedure. Figures 1 and 2 in the main text present IR

spectra of the solutes in two frequency ranges: CH stretching vibrations and C=C stretching and CCH bending vibrations. The rest of the spectrum is not informative for our tasks.



**Figure S2.** The IR spectrum of the *t*-Bu{Cl<sub>11</sub>} solution in CD<sub>2</sub>Cl<sub>2</sub>, as recorded 2 min after preparation. Initial data are blue, and data with the subtracted spectrum of the solvent are red. The spectrum of the solute enhanced by a factor of 10 is green. In the main text, it is shown in Figure 1b, red.