Supporting Online Material for

Hydrodefluorination of Perfluoroalkyl Groups Using Silylium-Carborane Catalysts

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Supporting Online Material

Hydrodefluorination Of Perfluoroalkyl Groups

Using Silylium-Carborane Catalysts

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Materials and Methods

All manipulations were performed either in an argon-filled glovebox or using Schlenk line techniques. The atmosphere of the box was strictly kept free of donor solvents. All glassware was dried at 140°C for 8 hours before use. α-Dichlorobenzene, benzene, triethylsilane, trihexylsilane, hexafluorobenzene, bromopentafluorobenzene, dichloromethane and all the substrates used (Table 1), were dried with CaH₂, distilled under argon atmosphere, and stored in a glovebox. Ph₃CB(C₆F₅)₄ was donated by Albemarle Corp. It was recrystallized and dried under high vacuum before use. Cs[HCB₁₁H₁₁] was purchased from Katchem (Czech Republic) and the trityl salts of the carborane anions ([HCB₁₁H₅Cl₆], [HCB₁₁H₅Br₆], [HCB₁₁Cl₁₁]), were synthesized from it following methods reported in the literature (S1-S4). These salts then were recrystallized from toluene, washed with hexanes and dried under high vacuum for 24-48 h before use. NMR spectra were recorded either on a Varian Inova 400 spectrometer or a Varian Inova 500 (¹H NMR, 399.755 MHz, ¹⁹F NMR, 376.104 MHz, ¹¹B NMR, 160.323 MHz). Et₃SiF (-178.1 ppm) and Et₂SiF₂ (-146.2 ppm) were identified by ¹⁹F NMR (in o-dichlorobenzene, δ –178.1 and –146.2, respectively. GC/MS spectra were recorded on a Hewlett Packard GCD System (EI mode) employing HP-5MS from Agilent Technologies (30m×0.25mm) and 1227032 from J&W Scientific (30m×0.25mm). Helium was used as a carrier gas. The following were typical temperature programs for analyzing the products using the HP-5MS column: A. Initial temperature: 40°C, increase at a rate: 40°C until final temperature: 260°C, hold temperature for 10 minutes at 260°C. Solvent delay:
1.6 minutes. B. Initial temperature 40°C, increase at a rate: 40°C until final temperature: 260°C, hold temperature for 10 minutes at 260°C. Solvent delay: 0.1 minutes.

**CAUTION:** In certain cases, C-F activation reactions may proceed very rapidly, self-accelerating and releasing dangerous amounts of heat. In addition, these reactions may generate hydrogen and possibly even other gases. Great care and preliminary testing of safe conditions are necessary for performing reactions in closed vessels.

**Comparison of activity of carborane-based catalysts with that based on** \([\text{B(C}_6\text{F}_5)_4]^\text{-}\** in the HDF reaction with \text{C}_6\text{F}_5\text{CF}_3**. Four J. Young tubes were loaded with \(\text{Ph}_3\text{C[HCB}_{11}\text{H}_5\text{Cl}_6}\), \(\text{Ph}_3\text{C[HCB}_{11}\text{Cl}_{11}\), Ph\text{3C[HCB}_{11}\text{H}_5\text{Br}_6}\) or \(\text{Ph}_3\text{C[B(C}_6\text{F}_5)_4]}\) (10 µmol), respectively. To each was added \(\text{C}_6\text{F}_6\) (10 µL, 0.08 mmol), \(\alpha\)-dichlorobenzene (0.30 mL), \(\text{C}_6\text{F}_5\text{CF}_3\) (0.80 mmol), and \(\text{Et}_3\text{SiH}\) (0.80 mL, 7.5 mmol). The tubes were closed and were immediately shaken well. Then they were opened and allowed to stand open in the glovebox for 1 h. The reactions were analyzed by \(^1\text{H}^\text{F}\) NMR spectroscopy after 1, 10 and 24 h. The results are summarized in Table S1 in terms of observed turnover numbers.

**Table S1.** Comparison of activity of carborane-based catalysts with that based on \([\text{B(C}_6\text{F}_5)_4]^\text{-}\** in the HDF reaction with \text{C}_6\text{F}_5\text{CF}_3**.

<table>
<thead>
<tr>
<th>Anion</th>
<th>TON in 1 h</th>
<th>TON in 10 h</th>
<th>TON in 24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{HCB}_{11}\text{H}_5\text{Cl}_6)</td>
<td>180</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>(\text{HCB}<em>{11}\text{Cl}</em>{11})</td>
<td>180</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>(\text{HCB}_{11}\text{H}_5\text{Br}_6)</td>
<td>140</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>(\text{B(C}_6\text{F}_5)_4])</td>
<td>4</td>
<td>11</td>
<td>14</td>
</tr>
</tbody>
</table>

**Observation of the absence of decomposition of the** \([\text{HCB}_{11}\text{H}_5\text{Cl}_6]^\text{-}\** anion. **A J. Young tube was loaded with catalyst \(\text{Ph}_3\text{C[HCB}_{11}\text{H}_5\text{Cl}_6}\) (15 mg, 25 µmol), \(\alpha\)-
dichlorobenzene (0.20 mL), substrate C₆F₅CF₃ (0.10 mL, 0.70 mmol), and Et₃SiH (0.37 mL, 2.3 mmol) and the tube was closed and was taken out of the glovebox. ¹⁹F NMR spectroscopy was recorded after an hour and showed that the HDF reaction had run to completion (no CF₃ group resonance). At this point, a ¹¹B{¹H} NMR spectrum was recorded and showed that the resonances corresponding to the carborane anion CB₁₁H₆Cl₆⁻ had remained unchanged (Figure S1).

![Figure S1. ¹¹B{¹H} NMR spectra of before and after the HDF reaction of C₆F₅CF₃ with a [HCB₁₁H₆Cl₆]-based catalyst](image)

**Observation of the decomposition of the [B(C₆F₅)₄]⁻ anion.** A J. Young tube was loaded with Ph₃C[B(C₆F₅)₄]⁻ (30 mg, 33 µmol), o-dichlorobenzene (0.20 mL), substrate C₆F₅CF₃ (0.10 mL, 0.70 mmol), and Et₃SiH (0.37 mL, 2.3 mmol) and the tube was closed and was taken out of the glovebox. An ¹⁹F NMR spectrum was recorded after 1 hour and
showed that the HDF reaction had proceeded with generation of Et$_3$SiF (19 turnovers), but the B(C$_6$F$_5$)$_4^-$ anion peaks had disappeared (Figure S2).

**Figure S2.** $^{19}$F NMR spectra before and after the HDF reaction of C$_6$F$_5$CF$_3$ with a [B(C$_6$F$_5$)$_4$]-based catalyst. Degradation of [B(C$_6$F$_5$)$_4$]$^-$ is evident from the disappearance of the corresponding resonances.

Comparison of activity of different carboranes in the HDF reaction with C$_6$F$_5$CF$_3$. Stock solutions of the catalysts Et$_3$Si[HCB$_{11}$H$_5$Cl$_6$], Et$_3$Si[HCB$_{11}$Cl$_{11}$], and Et$_3$Si[HCB$_{11}$H$_5$Br$_6$] were made as follows. In a glass vial equipped with a stir bar, 0.050
mmol of the corresponding trityl carborane salt was dissolved in 3.0 mL of o-dichlorobenzene and the solution was stirred for 5 min. Then, 0.080 mL (0.50 mmol) of Et₃SiH was added and the solution stirred for 2 h upon which time the solution turned clear. A stock solution of C₆F₅CF₃ was made by combining 1.0 mL (7.1 mmol) of C₆F₅CF₃, 0.10 mL (0.79 mmol) of C₆F₅Br (internal standard) and 3.6 mL (22.6 mmol) of Et₃SiH in a glass vial equipped with a stir bar and stirring for 10 min. For the experiments, 0.50 mL of the substrate solution (760 µmol of C₆F₅CF₃) was added to a glass vial equipped with a stir bar and 50 µL of the catalyst solution (0.83 µmol) was added to it. The vial was closed and the mixture was stirred for 1 h. After 1 h, Bu₄N[BH₄] was added in order to stop the reaction. All contents were transferred to a J. Young tube and analyzed by ¹⁹F NMR (Table 4). Each catalyst was tested in duplicate and the results are summarized in Table S2 in terms of observed turnover numbers (TON).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Carborane anion</th>
<th>TON</th>
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<tbody>
<tr>
<td>1a</td>
<td>[HCB₁₁H₅Cl₆]</td>
<td>880</td>
</tr>
<tr>
<td>1b</td>
<td>[HCB₁₁H₅Cl₆]</td>
<td>870</td>
</tr>
<tr>
<td>2a</td>
<td>[HCB₁₁Cl₁₁]</td>
<td>370</td>
</tr>
<tr>
<td>2b</td>
<td>[HCB₁₁Cl₁₁]</td>
<td>370</td>
</tr>
<tr>
<td>3a</td>
<td>[HCB₁₁H₅Br₆]</td>
<td>220</td>
</tr>
<tr>
<td>3b</td>
<td>[HCB₁₁H₅Br₆]</td>
<td>210</td>
</tr>
</tbody>
</table>

**Table S2.** Activity of catalyst supported by different carboranes in the HDF reaction with C₆F₅CF₃.

**Observation of H₂ in and HDF reaction of C₆F₅CF₃ in o-dichlorobenzene.** A J-Young tube was loaded with Ph₃C[HCB₁₁H₅Cl₆] (5.0 µmol), C₆F₆ (5.0 µL, 43 µmol), o-
dichlorobenzene (0.20 mL), C₆F₅CF₃ (0.10 mL, 0.70 mmol), and Et₃SiH (0.36 mL, 2.3 mmol) and the tube was quickly closed and was taken carefully out of the glovebox. (CAUTION: When the tube was opened at the end, it was found to be under pressure). After 1h, the reaction mixture was analyzed by ¹H NMR and the presence of H₂ (δ 4.42 ppm) was detected. The H₂ resonance was confirmed by comparison with the ¹H NMR resonance of an authentic sample of H₂ in o-dichlorobenzene. The TON was calculated to be 380 based on the Et₃SiF resonance in the ¹⁹F NMR spectrum of the reaction.

Table S3 (same as Table 1 from the main text). HDF reactions with Ph₃C[HCB₁₁H₅Cl₆] as catalyst; catalyst loading is given per number of C(sp³)-F bonds. Si-F conversion is calculated as fraction of F from the original aliphatic C-F bonds, found in the Si-F bonds of R₃SiF and R₂SiF₂ (by ¹⁹F NMR). Turnover numbers (TON) are calculated based on the C-F conversion (by ¹⁹F NMR).

<table>
<thead>
<tr>
<th>#</th>
<th>Substrate</th>
<th>Silane</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Cat. mol %</th>
<th>Solvent</th>
<th>Si-F Conv. %</th>
<th>C-F Conv. %</th>
<th>TON</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆F₅CF₃</td>
<td>Et₃SiH</td>
<td>25</td>
<td>24</td>
<td>0.080</td>
<td>o-C₆H₄Cl₂</td>
<td>84</td>
<td>&gt;97</td>
<td>1250</td>
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<tr>
<td>2</td>
<td>C₆F₅CF₃</td>
<td>Et₃SiH</td>
<td>25</td>
<td>6</td>
<td>0.080</td>
<td>neat</td>
<td>82</td>
<td>&gt;97</td>
<td>1250</td>
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<tr>
<td>3</td>
<td>C₆F₅CF₃</td>
<td>Et₃SiH</td>
<td>25</td>
<td>72</td>
<td>0.036</td>
<td>o-C₆H₄Cl₂</td>
<td>76</td>
<td>&gt;97</td>
<td>2700</td>
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<tr>
<td>4</td>
<td>Ph(CH₂)₂CF₃</td>
<td>Et₃SiH</td>
<td>25</td>
<td>24</td>
<td>0.13</td>
<td>neat</td>
<td>79</td>
<td>&gt;97</td>
<td>780</td>
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<tr>
<td>5</td>
<td>Ph(CH₂)₂CF₃</td>
<td>Et₃SiH</td>
<td>25</td>
<td>48</td>
<td>0.13</td>
<td>C₆H₆</td>
<td>75</td>
<td>&gt;97</td>
<td>780</td>
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<tr>
<td>6</td>
<td>C₄F₇C₂H₅</td>
<td>Hex₃SiH</td>
<td>50</td>
<td>120</td>
<td>0.50</td>
<td>neat</td>
<td>92</td>
<td>&gt;97</td>
<td>200</td>
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**Descriptions of experiments in Table S3/Table 1 of the main text, by entry.**

**Entry 1.** A J. Young tube was loaded with Ph$_3$C[HCB$_{11}$H$_5$Cl$_6$] (3.0 mg, 5.0 µmol), C$_6$F$_6$ (20 µL, 0.17 mmol), o-dichlorobenzene (0.3 mL), C$_6$F$_5$CF$_3$ (0.30 mL, 2.1 mmol). Et$_3$SiH (1.1 mL, 6.9 mmol) was added slowly and the mixture was allowed to stand for 1 h. After this time, the tube was closed and taken out of the glovebox. $^{19}$F NMR analysis revealed that all C$_6$F$_5$CF$_3$ (δ -58.5 ppm for the CF$_3$ group) had reacted after 24 h. Products that were detected included: C$_6$F$_5$CH$_3$ (-146.7, -162.1, -165.6 ppm), Et$_3$SiF and Et$_2$SiF$_2$ (84% Si-F yield). Other unidentified peaks appeared at -145.2 ppm, -160.1 ppm, and -167.5 ppm (presumably Friedel-Crafts products). GC/MS showed formation of C$_6$F$_5$CH$_3$ (M/$Z^+$ 182) (53% yield) and also the Friedel-Crafts products C$_6$F$_5$CH$_2$C$_6$H$_3$Cl$_2$, two isomers with M/$Z^+$ 326 (M$^+$) (32% yield).

Determination of the yield of C$_6$F$_5$CH$_3$ by GC/MS was as follows. A solution containing a 1.00:1.00 molar ratio of C$_6$F$_5$CH$_3$ and C$_6$F$_5$H was prepared by mixing the corresponding volumes (57 µL and 50 µL respectively). GC-MS analysis was carried out and integration of the chromatogram gave a 0.91 ratio. For analysis of the reaction in entry 1 C$_6$F$_5$H (50 µL) was added to the mixture upon the completion of the reaction and prior to the GC-MS analysis. The mixture was filtered, diluted in diethyl ether and analyzed by GC/MS. The yield of C$_6$F$_5$CH$_3$ was calculated using the integral of C$_6$F$_5$H as reference and taking into account the coefficient of 0.91.

**Entry 2.** A J. Young tube was loaded with Ph$_3$C[HCB$_{11}$H$_5$Cl$_6$] (3.0 mg, 5.0 µmol), C$_6$F$_6$ (15 µL, 0.13 mmol) and C$_6$F$_5$CF$_3$ (0.30 mL, 2.1 mmol), and cooled down using a
pre-cooled (glovebox refrigerator set at -35ºC) copper shot bath. Then, Et₃SiH (1.1 mL, 6.9 mmol) was added and the mixture was allowed to reach room temperature. The reaction proceeded quickly, developing an exotherm, and then cooled to room temperature. The tube was closed and taken out of the glovebox. After 24 h (¹⁹F NMR evidence), Et₃SiF and Et₂SiF₂ had been formed (82% Si-F conversion), and all substrate had been consumed. The ¹⁹F NMR measured yield for C₆F₅CH₃ was 86%. GC/MS analysis showed formation of Et₃SiF (M/Z⁺ 134) Et₂SiF₂ (M/Z⁺ 124), Et₄Si (M/Z⁺ 144), C₆F₅CH₃ (M/Z⁺ 182), and no Friedel-Crafts products.

**Entry 3.** A stock solution of Ph₃C[HB₁₁H₅Cl₆] was made as follows. In a glass vial equipped with a stir bar, 50 μmol of the corresponding Ph₃CCB₁₁H₆Cl₆ was dissolved in 3.0 mL of o-dichlorobenzene and the solution was stirred for 5 min. Then, 0.080 mL (0.50 mmol) of Et₃SiH was added and the solution stirred for 2 h upon which time the solution turned clear (presumed formation of Et₃Si[HB₁₁H₅Cl₆]). A stock solution of C₆F₅CF₃ was made by combining 1.0 mL (7.1 mmol) of C₆F₅CF₃, 0.10 mL (0.79 mmol) of C₆F₅Br (¹⁹F NMR internal standard) and 3.6 mL (22.6 mmol) of Et₃SiH in a glass vial equipped with a stir bar and stirring for 10 min. Then, 0.50 mL of the substrate solution (760 μmol of C₆F₅CF₃) was added to a glass vial equipped with a stir bar and 50 μL of the catalyst solution (0.83 μmol) was added to it. The vial was closed and the mixture was stirred for 1 h. After this time, all contents were transferred in a J. Young tube and it was monitored by ¹⁹F NMR until all C₆F₅CF₃ was consumed after 72 h.

**Entry 4.** A J. Young tube was loaded with Ph₃C[HB₁₁H₅Cl₆] (3.0 mg, 5.0 μmol), C₆F₆ (20 μL, 0.17 mmol), PhCH₂CH₂CF₃ (0.20 mL, 1.3 mmol) and Et₃SiH (0.60 mL, 4.0
mmol) and allowed to react for 1 h. After this time, the tube was closed, taken out of the glovebox and checked by $^{19}$F NMR spectroscopy. After 5 h, in addition to the resonance of PhCH$_2$CH$_2$CF$_3$ (-58.3 ppm), resonances corresponding to Et$_3$SiF and Et$_2$SiF$_2$ (60% Si-F conversion) had appeared. After 24 h, the peak corresponding to PhCH$_2$CH$_2$CF$_3$ had completely disappeared, signifying that all PhCH$_2$CH$_2$CF$_3$ had reacted while resonances for Et$_3$SiF and Et$_2$SiF$_2$ were present (79% Si-F conversion). A white solid had formed in the bottom of the tube. GC/MS indicated formation of indane (C$_9$H$_{10}$) (M/Z$^+$ 117) (5% yield calculated by GC/MS quantification versus a known amount of a C$_6$F$_5$H standard). Other products included: Et$_3$SiF (M/Z$^+$ 134), Et$_2$SiF$_2$ (M/Z$^+$ 124), Et$_4$Si (M/Z$^+$ 144). In the $^{13}$C NMR spectrum of the final reaction mixture, in addition to the resonances at 25.8, 35.5, 124.1, 125.9 and 142.1 ppm corresponding to indane (C$_9$H$_{10}$), the aromatic carbon resonances (o-dichlorobenzene etc.) and ethyl group (silanes) resonances, several resonances appeared were visible in the 32-36 ppm range (Figure S3), consistent with the presence of multiple ArCH$_2$CH$_2$CH$_2$Ar groups (PhCH$_2$CH$_2$CH$_2$Ph gives rise to resonances at 32.9, 35.4 ppm) (S5).
Entry 5. A J. Young tube was loaded with Ph3C[HCB11H5Cl6] (3.0 mg, 5.0 µmol), C6F6 (20 µL, 0.17 mmol), C6H6 (0.2 mL), PhCH2CH2CF3 (0.20 mL, 1.3 mmol) and Et3SiH (0.60 mL, 4.0 mmol), allowed to react for 1 h and then closed, taken out of the glovebox. The peak corresponding at -58.3 ppm had completely disappeared after 24 h, signifying that all PhCH2CH2CF3 had reacted, while Et3SiF and Et2SiF2 were present (75% Si-F conversion). GC/MS indicated formation of C8H5CH2CH2CH2C6H5; M/Z+ 196 (76% by GC/MS quantification versus a known amount of a C6F5H standard). Other products included: Et3SiF (M/Z+ 134) Et2SiF2 (M/Z+ 124), and Et4Si (M/Z+ 144).
Entry 6. A J. Young tube was loaded with Ph$_3$C[HCB$_{11}$H$_5$Cl$_6$] (12 mg, 20 µmol), $^{9}$C$_4$F$_9$C$_2$H$_5$ (0.080 mL, 450 µmol) and (hexyl)$_3$SiH (1.59 mL, 4.47 mmol). The tube was closed, taken out of the glovebox and placed in a heating bath at 50°C. After 5 h the color of the mixture had turned dark and $^{19}$F NMR analysis revealed formation of (hexyl)$_2$SiF$_2$ and (hexyl)$_3$SiF. The tube was returned to the bath and the $^{19}$F NMR spectrum was recorded after 10 h, 24 h, 36 h, 48 h, 72 h, 96 h and after 120 h upon which time the reaction had finished as all $^{9}$C$_4$F$_9$C$_2$H$_5$ had been consumed. Aliquots of the solution had been taken and analyzed by GC/MS after 10 h, 48 h, and at the end of the reaction (120 h) by first cooling down the tube at room temperature and the opening it inside the glovebox. After 10 h, in addition to the peak with (M/Z$^+$ 219 matching the CF$_3$CF$_2$CF$_2$CF$_2$ fragment) corresponding to $^{9}$C$_4$F$_9$C$_2$H$_5$ other products at this time included: (hexyl)$_3$SiF (M/Z$^+$ 302) (hexyl)$_2$SiF$_2$ (M/Z$^+$ 236), and (hexyl)$_3$Si (M/Z$^+$ 283) C$_6$H$_{12}$ (M/Z$^+$ 84), C$_6$H$_{11}$F (M/Z$^+$ 102), C$_6$H$_{10}$F$_2$ (M/Z$^+$ 120), and C$_6$H$_9$F$_3$ (M/Z$^+$ 138). After 48 h, in addition to the peaks corresponding to the CF$_3$CF$_2$CF$_2$CF$_2$ of $^{9}$C$_4$F$_9$C$_2$H$_5$, and (hexyl)$_3$SiF, (hexyl)$_2$SiF$_2$ (M/Z$^+$ 236), (hexyl)$_3$Si (M/Z$^+$ 283), other peaks at this time included: C$_6$H$_{12}$ (M/Z$^+$ 84), i. C$_6$H$_{14}$ (M/Z$^+$ 86), and ii. C$_6$H$_{14}$ (M/Z$^+$ 86). GC/MS analysis of the final mixture, in addition to (hexyl)$_3$SiF, (hexyl)$_2$SiF$_2$, (hexyl)$_3$Si, showed two peaks (M/Z$^+$ 86), corresponding to C$_6$H$_{14}$ which were the major peaks and were identified as 2,3-dimethylbutane and n-hexane by running authentic samples of different isomers of hexane. Methylcyclopentane, C$_6$H$_{12}$ (M/Z$^+$ 84) was also identified as a reaction product, while a very small peak of cyclohexane, C$_6$H$_{12}$ (M/Z$^+$ 84) was also present in the mixture. The molar amounts of these products were quantified by the
GC/MS using standardization of the authentic compounds vs. the C₆F₅H standard similarly to entry 1. The following amounts (yields) were thus calculated: \( n \)-hexane (28%), 2,3-dimethylbutane (13%), and methylcyclopentane (10%). The tube was found to be under pressure when opened inside the glovebox.
References and Notes for the Supporting Information


