

Supplementary Information

Hydrodehalogenation of organohalides by Et₃SiH catalysed by group 4 metal complexes and B(C₆F₅)₃

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Contents:

1. Experimental section	S2
1.1 General experimental details	S2
1.2 Catalytic HDF reaction – typical procedure	S2
1.3 NMR observation of the reaction kinetics	S4
1.4 Solvent dehalogenation – identification of products	S4
1.5 Determination of Friedel-Crafts side-products of HDF reaction	S4
1.6 HDF of PhCF ₃ catalysed by TiCl ₄ without borane	S5
1.7 Attempted HDF reaction catalysed by Cp ₂ TiMe ₂ /Ph ₃ C ⁺ [B(C ₆ F ₅) ₄] ⁻	S5
2. References	S6

1. Experimental section

1.1 General experimental details

All reactions and manipulations with air- and moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox Labmaster 130 (mBraun) under purified nitrogen. All solvents (typically HPLC grade HiPerSolv Chromanorm, VWR Prolabo Chemicals) were appropriately dried: THF, toluene, *n*-hexane, dichloromethane, and chloroform were purified by a solvent purification system (PureSolv MD 7; Innovative Technology, Inc.). Water content was periodically monitored by Karl–Fisher titration to be within the range 1–3 ppm. 1,2-Dichloroethane, chlorobenzene, fluorobenzene, trifluorotoluene, and triethylsilane were refluxed with CaH₂, then distilled under argon and stored over 4Å molecular sieves. 4-(trifluoromethyl)anisole, 1-fluoro-4-(trifluoromethyl)benzene, and perfluorotoluene were degassed and stored over 4Å molecular sieves. Deuterated solvents were dried as follows: benzene-*d*₆, toluene-*d*₈ were refluxed with Na/benzophenone ketyl, distilled under argon, and stored over 4Å molecular sieves; chloroform-*d*, bromobenzene-*d*₅ were refluxed with CaH₂, then distilled under argon and stored over 4Å molecular sieves. The precatalysts Cp₂MCl₂ (M = Ti, Zr, Hf), CpTiCl₃, TiCl₄, Cp*₂TiCl₂, Cp₂TiMe₂ (as a 5 wt. % solution in toluene), and B(C₆F₅)₃ were purchased from Strem Chemicals, M-Cat, or Sigma Aldrich and were used as received. Cp₂TiF₂ [1] and Cp*₂TiF₂ [2] were prepared by literature methods and were purified by recrystallization or sublimation.

¹H (300.0 MHz) and ¹⁹F (282.2 MHz) NMR spectra were recorded on a Varian Unity 300 spectrometer at 293 K. Chemical shifts (δ/ ppm) are given relative to solvent signals (benzene-*d*₆: δ_H 7.16; C₆D₅Br: δ_H 7.30, CDCl₃: δ_H 7.26), ¹⁹F NMR spectra were referenced to the PhCF₃ signal at –63.72 ppm (external reference was alternatively used).

GC-MS analyses were performed with a Thermo Focus DSQ instrument using a capillary column Thermo TR-5MS (15 m, ID 0.25 mm). GC-FID measurements were performed on an Agilent 6890 with a DB-5 column (length: 50 m, ID 0.32 mm, stationary phase thickness: 1 μm) with *n*-decane as an internal standard.

1.2 Catalytic HDF reaction – typical procedure

The solid metal pre-catalyst (5 mol%) and B(C₆F₅)₃ (5 mol%) were placed in a Schlenk tube under argon atmosphere and dissolved in the selected solvent. PhCF₃ (100 μL, 0.81 mmol) and then Et₃SiH (0.52 mL, 4.0 equiv) were added to the solution (addition of the silane typically induced a colour change to deep green-brown and sometimes led to a slight heat evolution). The total volume of the reaction mixture was set to 3 mL. The reaction was stirred for 20 h at room temperature (22 °C), then exposed to air and after the addition of appropriate internal standard (*n*-decane, mesitylene, or hexafluorobenzene) aliquots were immediately analysed by ¹H, ¹⁹F NMR (see representative figures S1-S3) after dilution with an appropriate deuterated solvent (typically CDCl₃), and other portions were filtered through a short pad of silicagel and analysed by GC, and/or GC-MS.

Alternatively, the catalyst solution (such as TiCl₄ in CHCl₃) was added as the last component to the mixture of the substrate PhCF₃, Et₃SiH, and B(C₆F₅)₃ in the same solvent to initiate the reaction. This procedure was tested also for the Cp₂TiCl₂-catalysed reaction and gave the same results as the above described procedure.

¹H NMR revealed the conversion of Et₃SiH to Et₃SiF (and/or Et₃SiCl in the presence of aliphatic chlorinated solvents such as CHCl₃) – see Fig. S1. In case of a successful HDF reaction, ¹⁹F NMR signal for Et₃SiF (δ_F –176.7 ppm) [3] appeared as the only fluorine-containing product (see Fig. S2) and its amount corresponded to the converted C-F bonds, i.e. the sum of the C-F bonds in PhCF₃ and Si-F bonds in Et₃SiF corresponded to the starting amount of the substrate as evaluated by comparison with an internal standard hexafluorobenzene.

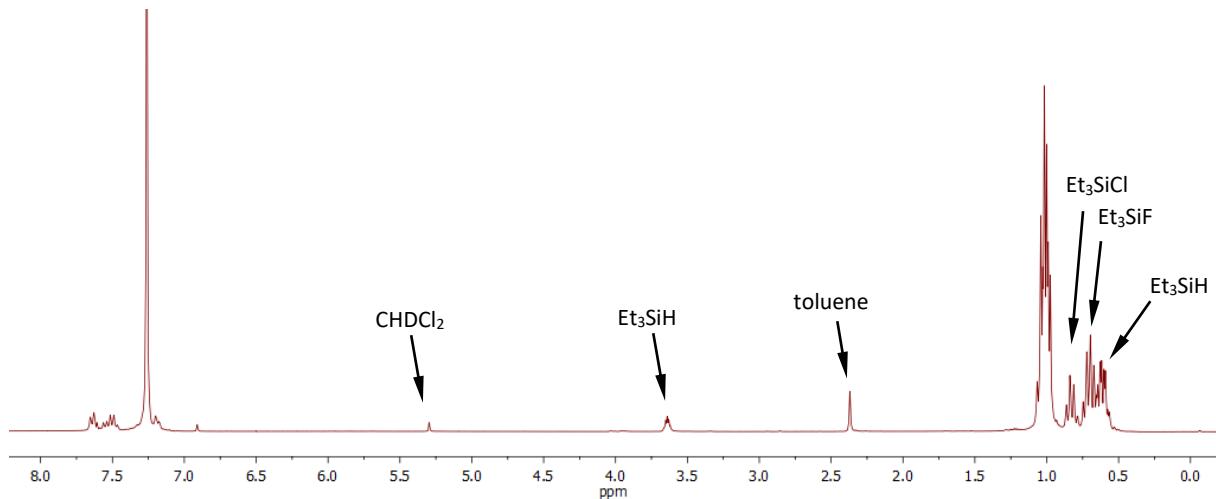


Fig. S1 ^1H NMR spectrum of the HDF reaction of PhCF_3 with 4 equiv Et_3SiH catalysed by Cp_2TiCl_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ performed in CHCl_3 20 h at room temperature.

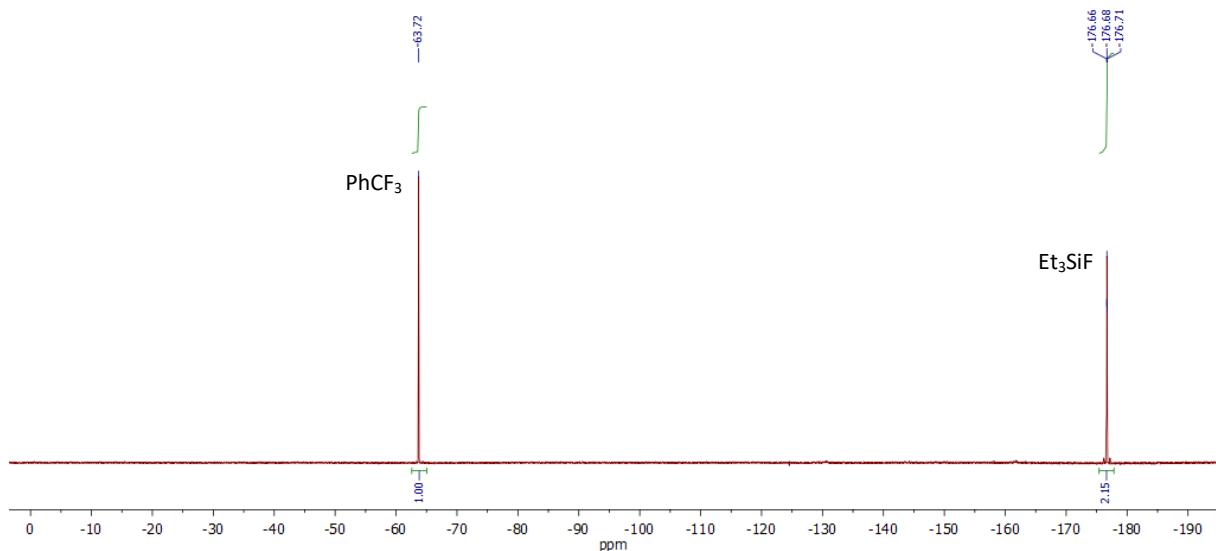


Fig. S2 ^{19}F NMR spectrum of the HDF reaction of PhCF_3 with 4 equiv Et_3SiH catalysed by Cp_2TiCl_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ performed in CHCl_3 20 h at room temperature. C-F conversion determined: 68%.

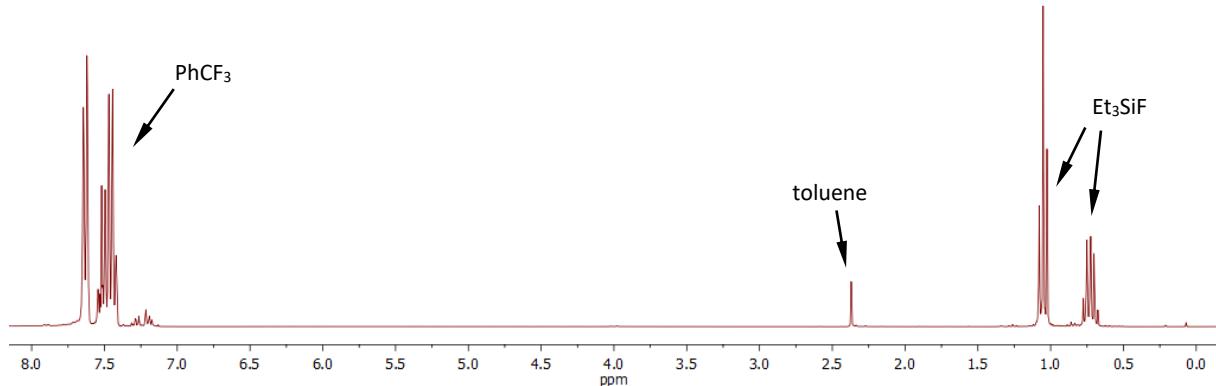


Fig. S3 ^1H NMR spectrum of the HDF reaction of neat PhCF_3 with Et_3SiH catalysed by Cp_2TiCl_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ after 20 h at room temperature. Only Et_3SiF , toluene, and excess PhCF_3 can be observed.

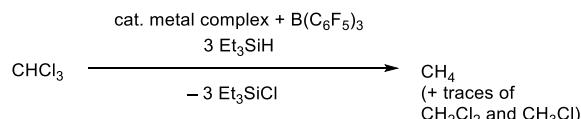
1.3 NMR observation of the reaction kinetics

The reaction mixtures were prepared in a Schlenk vessel as described above using half amount of the reagents and CDCl_3 as the solvent. The mixtures were immediately transferred to a NMR tube cooled in liquid nitrogen. The mixture was briefly degassed and the tube flame-sealed under vacuum. NMR spectra were then taken in regular time intervals to determine the conversion of PhCF_3 (see Fig. 2 in the main article).

In the case of $\text{Cp}^*_2\text{TiF}_2$ catalyst, Et_3SiH (4 equiv.) was consumed after ca 5 h by a concurrent reaction with CDCl_3 and the conversion of PhCF_3 stopped. After opening the tube, additional Et_3SiH (4 equiv.) was added and the reaction was further monitored by NMR. The reaction proceeded at a slightly lower rate (possibly due to some catalyst decomposition), but reached 60% PhCF_3 conversion after 20 h, showing that the catalyst was still active.

1.4 Solvent dehalogenation – identification of products

Notably, a product of hydrodechlorination of CDCl_3 , CH_3D (1:1:1 triplet at δ 0.22 ppm, see Fig. S4), was observed in a sealed NMR tube containing a CDCl_3 solution of catalytic HDF reaction as described above. The reaction scheme for HDF of chloroform is depicted below (Scheme S1). The reactivity of dichloromethane or 1,2-dichloroethane is analogous.



Scheme S1 Hydrodechlorination (HDF) of chloroform by Et_3SiH catalysed by group 4 metal complex and $\text{B}(\text{C}_6\text{F}_5)_3$.

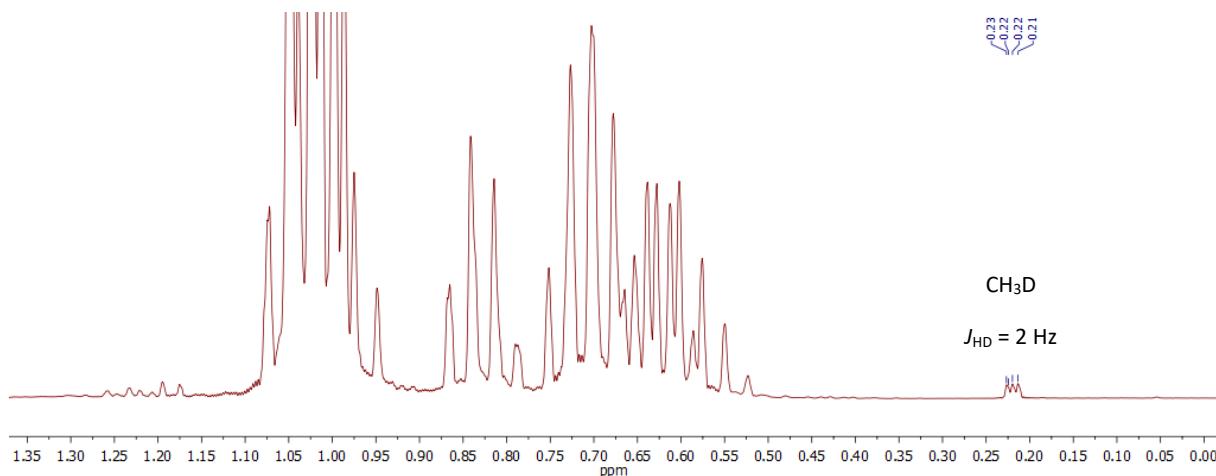
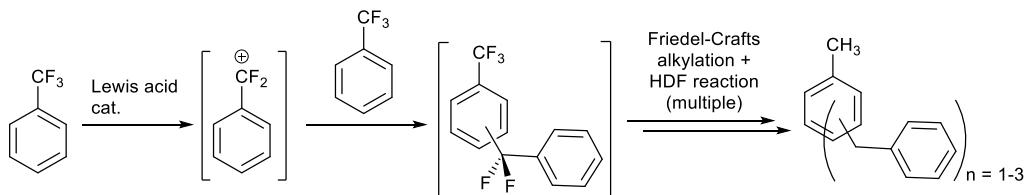


Fig. S4 ^1H NMR spectrum of the HDF reaction of PhCF_3 with Et_3SiH catalysed by $\text{Cp}^*_2\text{TiF}_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$ after 2 h at room temperature.

1.5 Determination of Friedel-Crafts side-products of HDF reaction

The selectivity of catalytic HDF reactions was analysed by the determination of toluene yield in the product mixture by GC (or NMR – integration of the toluene signal against mesitylene internal standard gave results comparable to GC analysis). Friedel-Crafts products were identified in the reaction mixtures, especially in the presence of stronger Lewis acids such as TiCl_4 . Suggested mechanism of formation is depicted in Scheme S2.



Scheme S2 Suggested mechanism of formation of Friedel-Crafts by-products during HDF of PhCF₃.

Identity of selected Friedel-Crafts by-products was elucidated from GC-MS (Fig. S5).

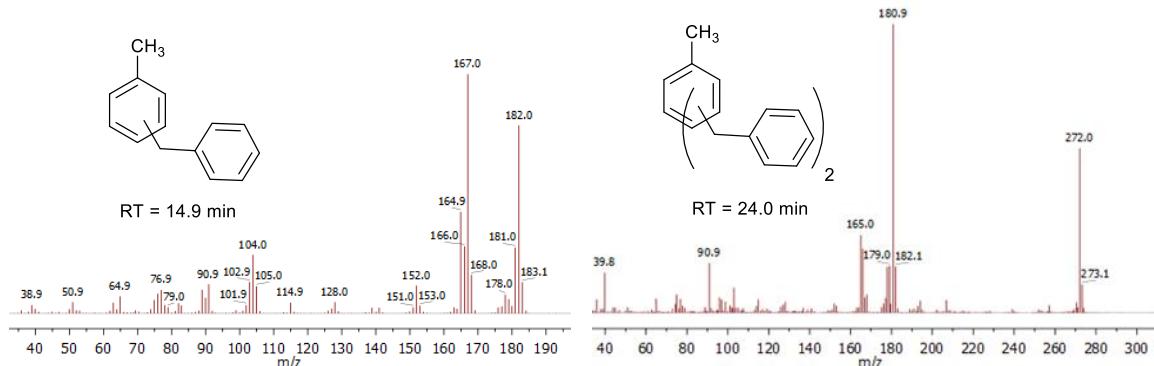


Fig. S5 Mass spectra of benzylated toluenes obtained from the HDF reaction of PhCF₃ with Et₃SiH catalysed by TiCl₄ and B(C₆F₅)₃ in CHCl₃.

1.6 HDF of PhCF₃ catalysed by TiCl₄ without borane

We attempted to reproduce the reaction conditions reported for HDF by Yamada et al.,[4] who used only TiCl₄ as the catalyst. In our hands, however, reactions in the presence of up to 30 mol% of TiCl₄ did not proceed at all, unlike those, where B(C₆F₅)₃ was employed (see Table 1, entry 6 in the main article). It is important to note, that the reactions were performed under strictly anaerobic and moisture-free conditions. As soon as such a reaction mixture was exposed to air, the catalytic process was initiated and complete conversion of PhCF₃ was observed typically in the course of several hours. Notably, however, only traces of toluene were present in the final mixture, whereas the Friedel-Crafts products dominated (see Fig. S6).

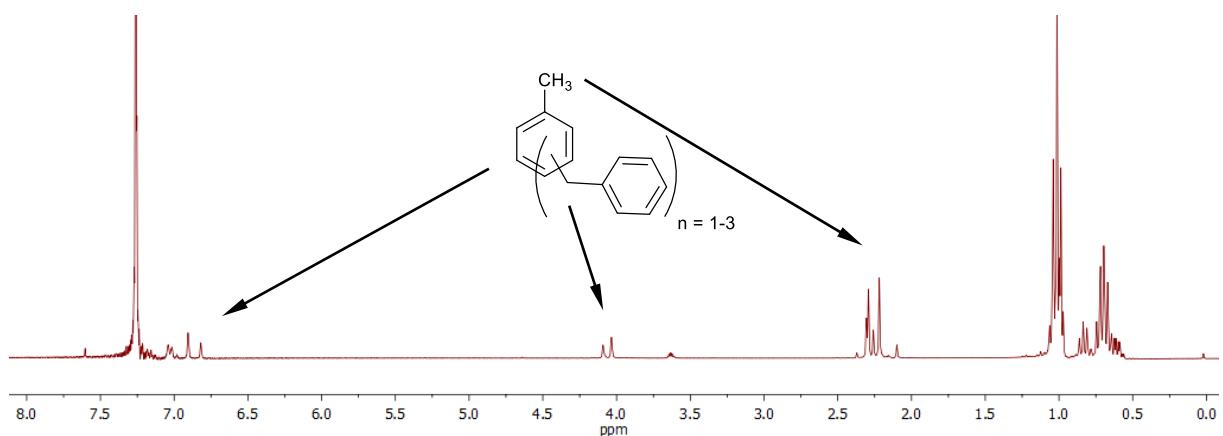


Fig. S6 ¹H NMR spectrum of the HDF reaction of PhCF₃ with Et₃SiH catalysed by 30 mol% TiCl₄ in CHCl₃ under air. Friedel-Crafts products of sequential self-alkylation/HDF of PhCF₃ are highlighted.

1.7 Attempted HDF reaction catalysed by Cp₂TiMe₂/Ph₃C⁺[B(C₆F₅)₄]⁻

This experiment should reveal the role of B(C₆F₅)₃ and the [HB(C₆F₅)₃]⁻ anion in the catalysis. A solution of Cp₂TiMe₂ (amount corresponding to 5 mol% vs. the substrate – i.e., 0.041 mmol Ti) in PhCl was

added to the solid $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (0.6 equiv vs Ti – substoichiometric amount to exclude formation of Et_3Si^+ cation by the reaction of Et_3SiH with Ph_3C^+), which dissolved to form a yellow-brown solution. Methyl abstraction from Cp_2TiMe_2 to form a cationic species by this method was studied by Baid et al. [5] After 5 min stirring at room temperature, PhCF_3 (100 μL , 0.81 mmol) and then Et_3SiH (0.52 mL, 4.0 equiv) were added. The colour of the mixture changed to amber-green, stirring at room temperature was continued for 20 h and the resulting mixture was analysed. Virtually no conversion of PhCF_3 was observed. When the experiment was repeated using stoichiometric amount of $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ vs Ti, complete conversion of PhCF_3 was achieved, the mixture contained predominantly Friedel-Crafts products and only traces of toluene. In a control experiment, Cp_2TiMe_2 was used in a catalytic amount without any additional activator (borane or borate), which exhibited no catalytic activity. In yet another control experiment, conditions reported by Ozerov et al. were applied [6], using only catalytic amount of $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, which gave complete PhCF_3 conversion forming predominantly Friedel-Crafts products. This suggested that the formation of Et_3Si^+ cation, even in small amounts, may have been responsible for the catalytic activity. When the silylum-catalysed route is excluded (with substoichiometric amount of Ph_3C^+), the role of $\text{B}(\text{C}_6\text{F}_5)_3$ as the hydride transfer agent in the metal-based catalysis is crucial and in its absence the system is inactive.

2. References

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