

Hydrodefluorination of non-activated C–F bonds by diisobutyl-aluminiumhydride via the aluminium cation [*i*-Bu₂Al]⁺

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Abstract—A novel system for the hydrodefluorination (HDF) of non-activated C–F bonds at room-temperature is described. The reaction of *i*-Bu₂AlH with [Ph₃C][B(C₆F₅)₄] (**1**), [Ph₃C][Al(C₆F₅)₄] (**2**) and [Ph₃C][Al{OC(CF₃)₃}₄] (**3**) as precatalysts leads under formation of triphenylmethane to the aluminium cation [*i*-Bu₂Al]⁺ and the non-coordinating anions [M(C₆F₅)₄][−] (M = B, Al) and [Al{OC(CF₃)₃}₄][−]. The formed aluminium cation is very reactive towards C–F bonds and easily forms *i*-Bu₂AlF releasing a carbocation that abstracts the hydride of excess *i*-Bu₂AlH and yields the corresponding hydrocarbon. Thereby, the active species [*i*-Bu₂Al]⁺ is regenerated and can realize a catalytic cycle. For 1-fluorohexane as an example including non-activated C–F bonds different activities were found (TON: **1**: 20; **2**: 12; **3**: 30) in cyclohexane as solvent.
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The activation of C–F bonds is one of the great challenges of modern organometallic chemistry and catalysis. This is due to the fact that the C–F bond is the strongest single bond which carbon can form.¹ The special strength results from the high bond energy that arises from the small size and the high electronegativity of the fluorine atom. Several reviews and papers described the C–F bond activation by transition metal complexes.^{2–8} Both, stoichiometric and catalytic C–F bond activations for aromatization reactions of cyclic perfluorocarbons were achieved by using titanocene and zirconocene fragments. These are formed from Cp₂MCl₂ (M = Ti, Zr) with Mg/HgCl₂ or Cp₂ZrCl₂ with Al/HgCl₂.⁹ Zirconocene generating systems, such as Cp₂ZrPh₂ or Cp₂ZrCl₂/2 *n*-BuLi, are able to effectively defluorinate perfluorodecaline to perfluoronaphthalene.¹⁰

2-Fluoropyridine and 3-fluoropyridine as compounds with activated C–F bond were catalytically defluorinated

by various complexes Cp'₂MCl₂ (M = Ti, Zr, Hf; Cp' = Cp, Cp*) in combination with reducing agents.¹¹ Jones and co-workers described in a series of papers the activation of several types of C–F bonds in alkanes, arenes and olefins by using the zirconocene hydride complex Cp₂^{*}ZrH₂.^{12–17}

We studied the C–F bond activation firstly by stoichiometric reactions and found consequences for the olefin polymerisation and hydrodefluorination (HDF) reactions.^{18–22}

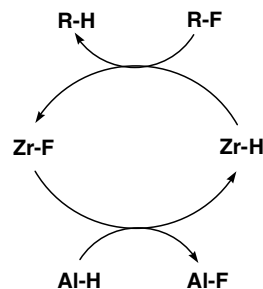


Figure 1.

Keywords: Bond activation; Hydrodefluorination; Organoaluminium compounds; Homogeneous catalysis; Boranates; Aluminates.

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The $\text{Cp}'_2\text{ZrH}_2$ catalysts ($\text{Cp}' = \text{Cp}_2, \text{rac}(\text{ebthi})$) were used for the catalytic HDF of activated C–F bonds. Mixtures of zirconocene difluorides $\text{Cp}'_2\text{ZrF}_2$ as pre-catalyst and diisobutyl-aluminiumhydride $i\text{-Bu}_2\text{AlH}$ as an activator were found to be active catalysts in the HDF of activated C–F bonds (Fig. 1). Complexes such as $\text{rac}(\text{ebthi})\text{ZrF}_2$ and $\text{Cp}'_2\text{ZrF}_2$ together with $i\text{-Bu}_2\text{AlH}$ were established as systems for the room-temperature HDF of pentafluoropyridine (TON = 67; 24 h). The turnover number (TON) is defined as mol product formed per mol catalyst. The in situ formed hydrides $[\text{rac}(\text{ebthi})\text{ZrH}(\mu\text{-H})_2]$ and $[\text{Cp}'_2\text{ZrH}(\mu\text{-H})_2]$ are assumed as the active species for this conversion and one can speculate about ate complexes such $[i\text{-Bu}_2\text{Al}][\text{Cp}'_2\text{ZrH}_3]$ as intermediates.²² Similar reactions with dichlorides gave no results because the chloride ligands are not replaced by the hydrides of $i\text{-Bu}_2\text{AlH}$.²³ An analogous system, that consists of LFeF and Et_3SiH , was introduced by Holland and co-workers (TON = 3.5; 12 h; 45 °C).²⁴

Ozerov and co-workers established an approach for the HDF without transition metals.²⁵ In a recent paper, they described a system for the HDF of non-activated C–F bonds consisting of Et_3SiH and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, in which the Et_3Si^+ acts as the catalytically active species. Müller and co-workers took a similar way to hydrodefluorinate non-activated C–F bonds but with a different silicon-based compound.²⁶ They applied a hydrogen-bridged disilyl cation with a 1,8-naphthalenediyl backbone (Fig. 2).

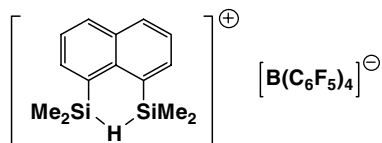
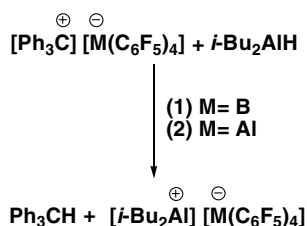


Figure 2.

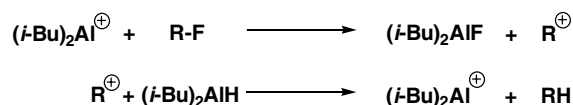
On the basis of our recently published results²² with $i\text{-Bu}_2\text{AlH}$ this knowledge was extended to new systems without zirconium for hydrodefluorination reactions. These results are reported in this Letter.

The reaction of $i\text{-Bu}_2\text{AlH}$ with the precatalysts $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**), $[\text{Ph}_3\text{C}][\text{Al}(\text{C}_6\text{F}_5)_4]$ (**2**) and $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**3**) leads under formation of triphenylmethane Ph_3CH to the aluminium cation $[i\text{-Bu}_2\text{Al}]^+$ and the weakly coordinating anions $[\text{M}(\text{C}_6\text{F}_5)_4]^-$ (M = B, Al) and $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ which remain as counterparts (Scheme 1).



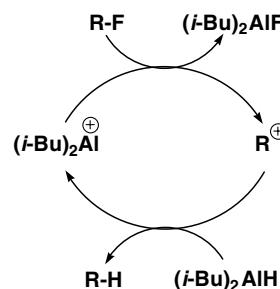
Scheme 1.

This reaction proceeds in a similar way compared to R_3SiH and $[\text{Ph}_3\text{C}][\text{M}(\text{C}_6\text{F}_5)_4]$, in which the silylium cation is formed. The initially formed aluminium cation is very reactive towards C–F bonds and easily forms $i\text{-Bu}_2\text{AlF}$ releasing a carbocation. This carbocation reacts with additional $i\text{-Bu}_2\text{AlH}$, which is used in excess, to the corresponding hydrocarbon (Scheme 2).



Scheme 2.

The active species $[i\text{-Bu}_2\text{Al}]^+$ is regenerated and the cycle is closed which leads to the catalytic cycle shown in Scheme 3.



Scheme 3.

The driving force for this reaction is the higher bond energy of the Al–F bond (665 kJ/mol) compared to the C–F bond (485 kJ/mol).^{27,28} The existence of the catalytically active species was proven by single crystals which were obtained by the reaction of $i\text{-Bu}_2\text{AlH}$ with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) in THF. However, the crystal quality of the complex $[i\text{-Bu}_2\text{Al}(\text{THF})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**4**) was insufficient to discuss the structural data in detail. Nevertheless the structural principle could be verified. The X-ray structure of **4** is shown in Figure 3. The aluminium cation is stabilised by two molecules of THF, acting as donor ligands.

For the HDF experiments different types of C–F bonds were tested. One can assume that C–F bonds with a sp^2 -hybridised carbon atom are hardly accessible for HDF reactions (Table 1, entries 1–5). In contrast to this observation the C–F bond of a sp^3 -hybridised carbon atom is cleaved more easily (entries 6–17). A possible explanation can be found in the different stability of the formed carbocation, and therefore the different reactivity. In a sp^2 -system the positive charge can be better delocalised and, therefore, the carbocation is less reactive. Moreover, the first C–F bond in C_6F_6 is very strong ($D_0 = 650 \text{ kJ mol}^{-1}$), further reducing the likelihood of the desired transformation. These could be reasons for the lower TONs of the HDF of sp^2 -C–F bonds, for example, in the case of hexafluorobenzene and fluorobenzene. The HDF of 1,1,1-trifluorotoluene did not yield toluene as the desired product. The reaction stopped with mono- and dihydrodefluorinated products, even though sufficient equivalents of $i\text{-Bu}_2\text{AlH}$ were

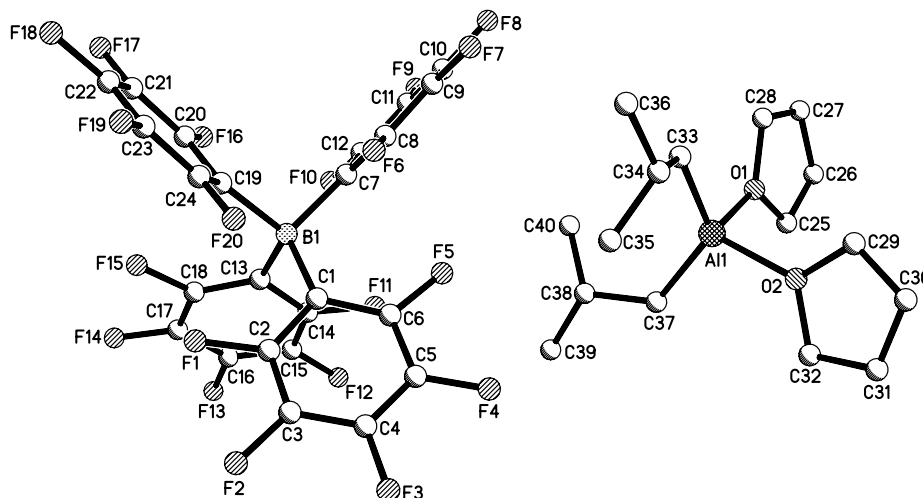


Figure 3.

Table 1. Hydrodefluorination of substrates with non-activated C–F bonds^a

Entry	RF	RH	Pre-cat.	Solvent	TON	Conversion (%)
1 ^b	C ₆ F ₆	C ₆ F ₅ H	A 1	Toluene	0	4
2 ^c	C ₆ F ₆	C ₆ F ₅ H	A 1	Toluene	2	8
3	C ₆ F ₆	C ₆ F ₅ H	A 1	Toluene	3	9
4 ^d	C ₆ F ₆	C ₆ F ₅ H	A 1	Toluene	3	9
5	C ₆ H ₅ F	C ₆ H ₆	A 1	Toluene	5	12
6	C ₆ H ₅ CF ₃	C ₆ H ₅ CH ₃	A 1	<i>n</i> -Heptane	Does not react to desired product toluene	5
7 ^e	C ₆ H ₅ CF ₃	C ₆ H ₅ CH ₃	B 1	<i>o</i> -Dichlorobenzene	60	100
8 ^f	C ₆ H ₅ CF ₃	C ₆ H ₅ CH ₃	C Disilylation	Benzene	19	
9 ^e	<i>n</i> -C ₅ H ₁₁ F	<i>n</i> -C ₅ H ₁₂	B 1	<i>o</i> -Dichlorobenzene	28	100
10 ^f	<i>n</i> -C ₁₀ H ₂₁ F	<i>n</i> -C ₁₀ H ₂₂	C Disilylation	Toluene	45	
11	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 1	Toluene	Alkylation products of toluene	
12	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 1	<i>o</i> -Dichlorobenzene	3	95
13	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 1	<i>o</i> -Difluorobenzene	9	95
14	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 1	Diethyl ether	14	99
15	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 1	Cyclohexane	20	100
16	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 2	Cyclohexane	12	100
17	<i>n</i> -C ₆ H ₁₃ F	<i>n</i> -C ₆ H ₁₄	A 3	Cyclohexane	30	99

A: Pre-catalyst: [Ph₃C][B(C₆F₅)₄] (1), [Ph₃C][Al(C₆F₅)₄] (2), [Ph₃C][Al{OC(CF₃)₃}₄] (3).

^aReaction conditions: 5 mol % pre-catalyst, C–F bond to *i*-Bu₂AlH ratio at 1:1.1, *T* = 25 °C, *t* = 24 h; analysis via GC.

^b0.5 mol % pre-cat.

^c1 mol % pre-cat.

^d10 mol % pre-cat.

B: ^eResults from Ozerov and co-workers²⁵: 3.35 mol %, 8 equiv Et₃SiH.

C: ^fResults from Müller and co-workers²⁶: entry 8: 2.9 mol % pre-cat.; entry 10: 2.2 mol % pre-cat.; 1 equiv Et₃SiH.

TON: turnover number.

Conversion of substrate in %.

used. The reason for the incomplete conversion is unknown.

The most convincing results were achieved with 1-fluorohexane. Therefore, several investigations were done with this substrate. At first we tested precursors **1** and **2**, this showed that **1** (TON = 20; entry 15 in Table 1) is more reactive than **2** (TON = 12; entry 16 in Table 1). Based on this information further investigations were performed with **1** as the precursor. The main aspect was to change the solvent: on the one hand to achieve a higher solubility and on the other hand to control the reactivity of the intermediate by interaction with the solvent. According to the Ozerov system *o*-dichlorobenzene was

used as the solvent, but only an extremely low TON was achieved. Neither ¹⁹F NMR, showing signals which could not be assigned to a certain species, nor the GC–MS gave any hints. The occurrence of the side reactions of 1-fluorohexane can also be seen from the consumption of 1-fluorohexane but it gives only a low yield of *n*-hexane. This is a great disadvantage of *o*-dichlorobenzene and leads to the consideration that it is an inappropriate solvent for our investigations. The *o*-difluorobenzene was tested because it provides a relatively high polarity. So it is possible to dissolve the precursor completely. The results were slightly better but not outstanding. Toluene, the most common aromatic solvent, was used in the HDF investigations too.

But here a side reaction became prevailing. The carbocation reacted with toluene to give only alkylated products of toluene and no formation of *n*-hexane was observed. The different behaviour of the reagents and the thereby limited application is demonstrated by comparison of the systems (see entries 10 with 11 and entries 9 with 12 in Table 1).

We also tested some aliphatic solvents though these provide a lower solubility, but they should be more inert in our reactions. *n*-Heptane could not be used because the reactions are analysed via gas chromatography and the difference in the retention time of *n*-heptane and 1-fluorohexane is too small for a proper signal integration to make an accurate quantitative conclusion.

The use of ethers combines a higher polarity with a good inertness. The simplest example for this solvent class is diethyl ether. The results with it were slightly worse than with cyclohexane. This maybe due to the strong coordinating properties of the ether (cf. Fig. 3).

By using $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**3**) instead of $[\text{Ph}_3\text{C}][\text{M}(\text{C}_6\text{F}_5)_4]$ ($\text{M} = \text{B}, \text{Al}$) the highest turnover numbers were achieved in our investigations (TON = 30; entry 17 in Table 1).²⁹ Comparing the counteranions seems to reveal a trend in which the decreasing coordinating power is responsible for the different results of the used precursors.

In conclusion, we have shown that a system consisting of *i*-Bu₂AlH and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**), $[\text{Ph}_3\text{C}][\text{Al}(\text{C}_6\text{F}_5)_4]$ (**2**) or $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (**3**) is potentially useful for the room-temperature hydrodefluorination of non-activated C–F bonds. Nevertheless, the formed aluminium cation $[i\text{-Bu}_2\text{Al}]^+$ as the active species does not have the required properties like triethylsilane for the HDF. Possibly, the reactivity of the aluminium cation as an intermediate is too unselective and not only C–F bonds are activated, this is shown in the experiments by entries 11 and 12 in toluene and *o*-dichlorobenzene.

A deeper discussion and comparison of the three systems: Et₃SiH/[Et₃Si]⁺,²⁵ the disilyl cation²⁶ and the *i*-Bu₂AlH/[*i*-Bu₂Al]⁺ (this work) is not justified by the partly different reaction conditions and the limited data.

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