Room-temperature catalytic hydrodefluorination of pentafluoro-pyridine by zirconocene fluoro complexes and diisobutylaluminumhydride

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Dedicated to Professor Bernhard Lücke on the occasion of his 70th birthday

Abstract

Mixtures consisting of zirconocene difluorides Cp'_2ZrF_2 (Cp' = substituted or nonsubstituted η^5-cyclopentadienyl) as pre-catalysts and diisobutylaluminumhydride i-Bu$_2$AlH as activator were found to be active catalysts in the room-temperature hydrodefluorination (HDF) of fluorinated pyridines. Evaluation of these systems established rac-(ebthi)ZrF$_2$ (**1**) and Cp$_2$ZrF$_2$ (**3**) together with i-Bu$_2$AlH as active catalysts in the room-temperature hydrodefluorination (HDF) of pentafluoro-pyridine. The active species for the conversion were the actually formed hydrides [rac-(ebthi)ZrH(μ-H)]$_2$ (**2**) and [Cp$_2$ZrH(μ-H)]$_2$ (**4**). The results we obtained (rt, 24 h, turn over number 67) showed a significantly better performance compared to other investigations published before for this HDF reaction.
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1. Introduction

Fluorocarbons are chemically inert as a consequence of the great strength of the C—F bond which arises from the small size and the high electronegativity of the fluorine atom. Nevertheless, the activation of several carbon–fluorine bonds by transition-metal complexes was summarized in many reviews [1–6]. There are examples for the activation of C—F bonds by group four electron-deficient transition-metal reagents from zirconium and titanium with C—F bond cleavage, too. One of the first examples for titanium was reported from Stone and co-workers [7], who pyrolysed Cp$_2$Ti(C$_6$F$_5$)$_2$ to obtain Cp$_2$Ti(C$_6$F$_5$)F. Later Burk and co-workers described the elimination of a cyclopropane (CH$_2$)$_2$CR$_2$ in the reaction of a tetrakis(trifluoromethyl)cyclopentadienone-titanacyclobutane [Cp$_2$Ti(CH$_2$)$_2$CR$_2$][O=C(CCF$_3$)$_4$] and the subsequent F-abstraction to a titanocene-fluoro-dienone

complex Cp$_2$Ti(F)[(O–C(CCF$_3$)$_3$C=CF$_2$)] [8]. Beckhaus and co-workers [9] published the complete defluorination of trifluoromethyl-substituted Cp-ligands by titanium amide complexes. Similar reactions were reported by Deck et al. [10] for corresponding pentafluorophenyl-substituents of cyclopentadienyl and indenyl ligands. Hessen and co-workers published that the complex [Cp$_2^*$Ti(η^1-FC$_6$H$_5$)][BPh$_4$] yields with trifluorotoluene 1,2-diphenyl-1,1,2,2-tetrafluoroethane and Cp$_2^*$TiF$_2$ [11]. Stoichiometric and certain catalytic C–F bond activations for the aromatization of cyclic perfluoro-carbons were achieved by using titanocene and zirconocene, generated by Cp$_2$MCl$_2$ (M = Ti, Zr) and Mg/HgCl$_2$ or Cp$_2$ZrCl$_2$ and Al/HgCl$_2$ [12]. Zirconocene forming systems, such as Cp$_2$ZrPh$_2$ or Cp$_2$ZrCl$_2$/2 n-BuLi can defluorinate effectively perfluorodecaline to perfluoronaphthalene [13].

2-Fluoro- and 3-fluoropyridine were defluorinated by various complexes Cp$'_2$MCl$_2$ (M = Ti, Zr, Hf; Cp$'$ = Cp, Cp*) in combination with different aluminum compounds as reduction agents [14]. 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 Cp$_2^*$ZrH$_2$. The mechanistic investigations had shown different pathways depending on
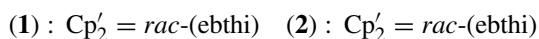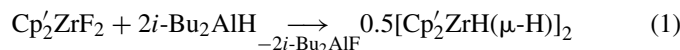
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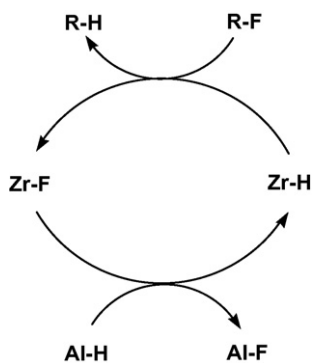
Scheme 1. Catalytic cycle.

the used substrate [15–21]. Caulton and co-workers reported that Cp_2ZrHCl reacts with fluoroethylene to give Cp_2ZrFCl, $Cp_2Zr(CH_2CH_3)Cl$ and Cp_2ZrF_2 (3) [22]. In the reaction of *rac*-(ebthi)Zr(Me)(NHtBu) with pentafluoro-pyridine Bergman and co-workers obtained via the monomeric imidozirconocene complex [*rac*-(ebthi)Zr=NtBu] an activation of the *ortho* C–F bond and the formation of an amininopyridinato complex *rac*-(ebthi)ZrF(-NtBu-2-C_5NF_4) [23]. Mostly zirconocene hydride complexes were used in C–F bond activation reactions.

$$Cp_2'ZrF_2 + 2i\text{-}Bu_2AlH \xrightarrow[-2i\text{-}Bu_2AlF]{} 0.5[Cp_2'ZrH(\mu\text{-}H)]_2 \qquad (1)$$

(1) : Cp_2' = *rac*-(ebthi)   (2) : Cp_2' = *rac*-(ebthi)

(3) : Cp_2' = Cp_2 (4) : Cp_2' = Cp_2

Recently, we published that, in contrast to the dichloride *rac*-(ebthi)$ZrCl_2$ [24], the difluoride *rac*-(ebthi)ZrF_2 (1) [25,26] reacted with two equivalents of *i*-Bu$_2$AlH to form the complex [*rac*-(ebthi)ZrH(μ-H)]$_2$ (2) (Eq. (1)) [27,28]. Interestingly, under analogous conditions the Cl-ligands of *rac*-(ebthi)$ZrCl_2$ were not replaced by H upon treatment with *i*-Bu$_2$AlH and only unchanged starting material was isolated [27]. Fluoride, obvi-

ously, is the more labile ligand compared with chloride. In the light of these results of zirconocene difluorides, we tried to realize a catalytic cycle (Scheme 1) in which cleavage of the Zr–F bond by interaction with Al–H yields Al–F and Zr–H from which the latter reacts with C–F to form C–H and again starting Zr–F bonds. Driving force for this cycle is the formation of strong Al–F bonds.

2. Results and discussion

2.1. Basic stoichiometric reactions

To evaluate the best pre-catalysts, experiments were conducted to find out if the exchange of fluoride by hydrogen proceeds for other zirconocene complexes, too. In NMR experiments of the reaction of Cp_2ZrF_2 (3) with two equivalents of *i*-Bu$_2$AlH, the formation of [$Cp_2ZrH(\mu$-H)]$_2$ (4) was observed (Eq. (1)). At room-temperature, nearly quantitatively clean complex 4 was formed, whereas at 70 °C, the spectra indicated several byproducts. In contrast to these results, the difluoride $Cp_2^*ZrF_2$ and *i*-Bu$_2$AlH did not form dihydride $Cp_2^*ZrH_2$. At higher temperature, decomposition reactions occured. It was published, that $Cp_2^*ZrH_2$ and $Cp_2^*ZrF_2$ under hydrogen conproportionate at 150 °C to $Cp_2^*Zr(H)F$ [29]. In contrast to this result, a mixture of *rac*-(ebthi)ZrF_2 (1) and [*rac*-(ebthi)ZrH(μ-H)]$_2$ (2) did not change its NMR spectra after several weeks at 100 °C.

The complexes $Cp_2'ZrCl_2$ (Cp_2' = *rac*-(ebthi), Cp_2, Cp_2^*) upon treatment with *i*-Bu$_2$AlH gave no appreciable exchange reactions of Cl by H. This was the reason why for further experiments *rac*-(ebthi)ZrF_2 (1), [*rac*-(ebthi)ZrH(μ-H)]$_2$ (2), Cp_2ZrF_2 (3) and [$Cp_2ZrH(\mu$-H)]$_2$ (4) were used.

To find out well-suited substrates, we checked the reactions of different organofluorides with [*rac*-(ebthi)ZrH(μ-H)]$_2$ (2) (Scheme 2) or [$Cp_2ZrH(\mu$-H)]$_2$ (4) (Scheme 3). With complex 2 no reactions were noticed with fluorobenzene, hexafluorobenzene and with 1-fluoro-hexane at 80 °C, 24 h in toluene solu-
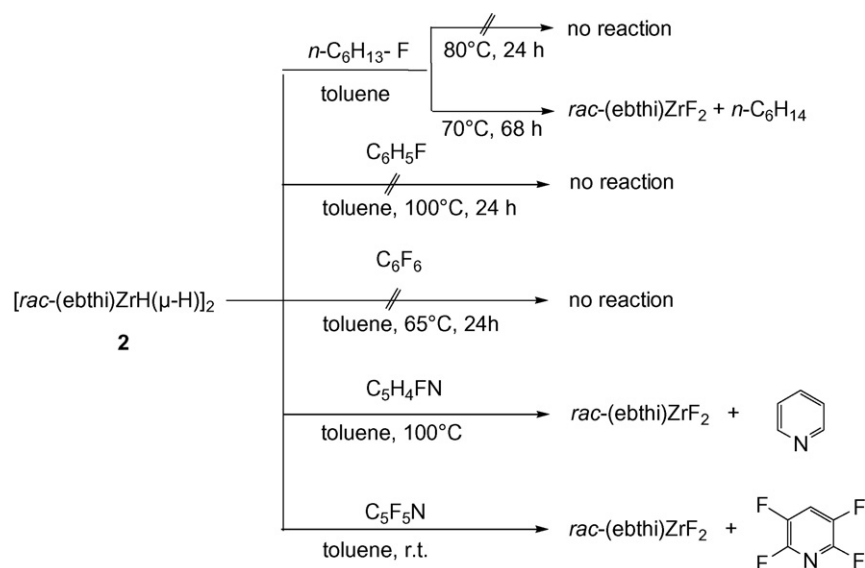
Scheme 2. Stoichiometric reactions of [*rac*-(ebthi)ZrH(μ-H)]$_2$ (2) with different fluorinated substrates.
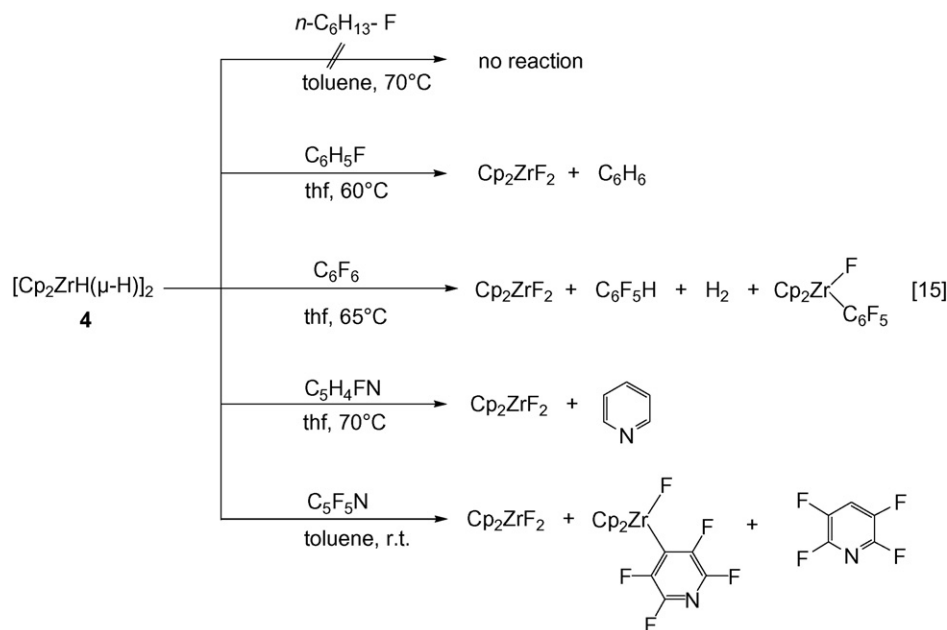
Scheme 3. Stoichiometric reactions of [Cp₂ZrH(μ-H)]₂ (**4**) with different fluorinated substrates.

tion. Nevertheless, after a longer reaction time of 68 h at 70 °C in a NMR tube, a mixture of [*rac*-(ebthi)ZrH(μ-H)]₂ (**2**) and 1-fluoro-hexane in toluene gave the complex *rac*-(ebthi)ZrF₂ (**1**) together with *n*-hexane and, the ^{19}F resonance of 1-fluoro-hexane disappeared, but these reaction conditions were unuseful for catalytic experiments.

Fluorbenzene reacted with [Cp₂ZrH(μ-H)]₂ (**4**) to benzene and the difluoride **3**, and hexafluorobenzene gave a mixture of pentafluorobenzene, hydrogen and the complexes Cp₂ZrF₂ (**3**) and Cp₂Zr(C₆F₅)F [38] according to results by Jones and co-workers [15].

Best stoichiometric results were obtained with 2-fluoro-pyridine, giving pyridine and pentafluoro-pyridine which reacted at rt to 2,3,5,6-tetrafluoro-pyridine and Cp₂Zr(4-C₅F₄N)F.

An additional point was to check the reactivity of the substrates towards *i*-Bu₂AlH as the activator (Scheme 4). As shown in Schemes 2 and 3, only fluorobenzene and the fluorosubstituted pyridines reacted with the zirconocene hydrides (**2** and **4**).

Fluorobenzene and pentafluoro-pyridine gave no reaction with *i*-Bu₂AlH. With 2-fluoro-pyridine the formation of an adduct with *i*-Bu₂AlH or with the formed *i*-Bu₂AlF is assumed.

According to these results, we considered only fluorobenzene and pentafluoro-pyridine to be suitable as substrates for a clean investigation of the catalytic HDF reaction.

2.2. Catalytic reaction

For fluorobenzene, the catalytic reaction was complicated by an unexpected problem. The difluoride Cp₂ZrF₂ (**3**) reacted as expected with *i*-Bu₂AlH to the zirconocene hydride [Cp₂ZrH(μ-H)]₂ (**2**) and *i*-Bu₂AlF. But before reacting productively with the fluorobenzene, the zirconocene hydride formed with *i*-Bu₂AlF a stable complex. In this case, the hydride reacts very slowly with the substrate and is desactivated by the formed diisobutylaluminumfluoride *i*-Bu₂AlF. In the case of the pentafluoro-pyridine, its activated C–F bond reacts faster with [Cp₂ZrH(μ-H)]₂ (**4**) to form regioselectively the 2,3,5,6-tetrafluoro-pyridine. This was
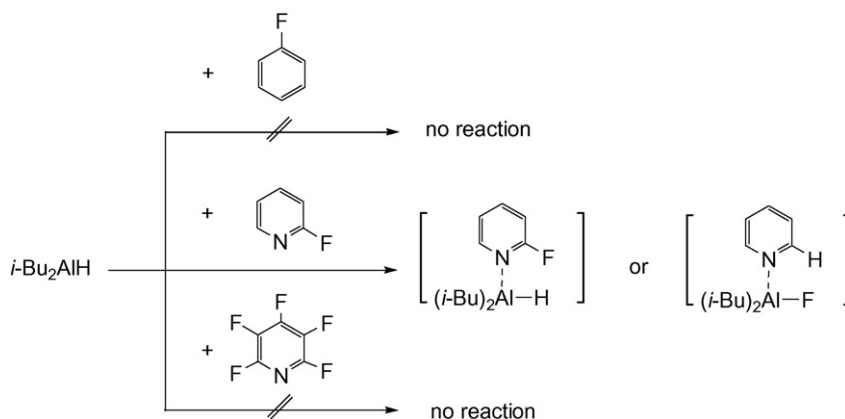
Scheme 4. Stoichiometric reactions of *i*-Bu₂AlH with different fluorinated substrates.
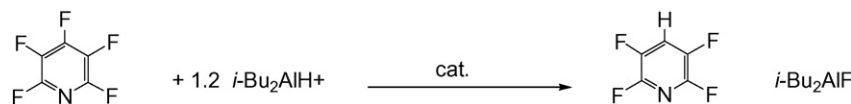
Scheme 5. Catalytic hydrodefluorination (HDF) of pentafluoro-pyridine.

the reason why pentafluoro-pyridine was used as a model for the HDF (Scheme 5).

The catalytic system consists of i-Bu$_2$AlH to which in the ratio of 1:1.2 the complexes **1–4** were added in toluene in a concentration of 0.5–10 mol% together with pentafluoro-pyridine as the substrate. After a reaction time of 24 h at rt, the products were analyzed by gaschromatography. The results are summarized in Table 1.

Generally, the "turn over number" (T.O.N.) of the here investigated systems depends on the ligands used. Higher yields were obtained with the ebthi-ligand compared to the Cp-ligands (Table 1 entries 1–4 versus 9–12 and entries 5–8 versus 13–15). On one side this result is explained by the sterical hindrance of the ebthi-ligand. On the other, starting from [Cp$_2$ZrH(μ-H)]$_2$ (**4**), used as a pure complex or formed from Cp$_2$ZrF$_2$ (**3**) and pentafluoro-pyridine, the formation of complex Cp$_2$Zr(4-C$_5$F$_4$N)F as an inactive by-product, could explain lower activity of complexes with Cp-ligands.

There is no big difference, if the systems are started with the difluorides (**1**, **3**) as pre-catalysts or directly with the hydrides (**2**, **4**) as the real catalysts (Table 1 entries 9–12 versus 13–15 and entries 1–4 versus 5–8). One can assume that there is a nearly quantitative conversion of the difluorides to the hydrides. This is supported by the NMR investigation of the stoichiometric reactions which came to the same result.

To compare our result to a similar reaction, one can consider a very recently published investigation in which low-coordinate iron(II) fluorides were converted by Et$_3$SiH to the corresponding hydrides [30]. Compared to our systems, these catalysts were found to hydrodefluorinate pentafluoro-pyridine at higher tem-

Table 1
HDF of pentafluoro-pyridine with i-Bu$_2$AlH and catalysts **1–4**

Number	Catalyst	Catalyst (%)	Yield (%)	Conversion (%)	T.O.N.
1	**1**	0.5	26	53	**57**
2	**1**	1.0	40	57	40
3	**1**	5.0	67	83	15
4	**1**	10.0	80	82	8
5	**2**	0.5	33	44	**67**
6	**2**	1.0	42	60	41
7	**2**	5.0	48	79	10
8	**2**	10.0	67	90	7
9	**3**	0.5	8	37	**18**
10	**3**	1.0	8	37	9
11	**3**	5.0	40	56	8
12	**3**	10.0	60	75	6
13	**4**	1.0	17	70	**18**
14	**4**	5.0	64	86	11
15	**4**	10.0	67	86	6

Pre-catalyst: rac-(ebthi)ZrF$_2$ (**1**), Cp$_2$ZrF$_2$ (**3**). Catalyst: [rac-(ebthi)ZrH(μ-H)]$_2$ (**2**), [Cp$_2$ZrH(μ-H)]$_2$ (**4**).

Table 2
Comparison of relevant bond enthalpies

Bond	Bond enthalpy (kJ/mol)
Al−F	663.6 ± 6.3
Al−H	284.9 ± 6.3
Zr−F	616 ± 15
C−F	552
C−H	338.4 ± 1.2
Si−F	552.7 ± 21

perature of 45 °C with longer reaction time of 4 days and a small turn over number of only 3.5.

In principle, one could think to use Si−H instead of Al−H to activate Zr−F bonds. Comparison showed a bigger bond enthalpy of Zr−F (616 kJ/mol) compared to Si−F (552 kJ/mol). That is the reason why we preferred Al−H bonds as activators. Driving force for our catalytic system is the high stability of the Al−F bond [31] (Table 2).

In an recent paper, Ozerov and co-workers described a very effective catalytic hydrodefluorination of aliphatic C(sp^3)−F bonds at room temperature by choosing a mixture of Et$_3$SiH and [Ph$_3$C][B(C$_6$F$_5$)$_4$] [32]. In these systems, [Et$_3$Si][B(C$_6$F$_5$)$_4$] as synthetic equivalent of R$_3$Si$^+$ was formed giving turn over numbers up to 126.

Our preliminary experiments with mixtures of i-Bu$_2$AlH and [Ph$_3$C][B(C$_6$F$_5$)$_4$] [33] or alternatively [Ph$_3$C][Al(C$_6$F$_5$)$_4$] [34] showed a similar reactivity in the catalytic HDF. In these systems, "[i-Bu$_2$Al][B(C$_6$F$_5$)$_4$]" or "[i-Bu$_2$Al][Al(C$_6$F$_5$)$_4$]" are assumed as synthetic equivalent of R$_2$Al$^+$. Similar complexes were described [35]. Such species are more active in the HDF with fluoroarene and aliphatic fluorides as substrates. As first examples for these non-activated fluorocarbons fluorobenzene, trifluorotoluene and 1-fluoro-hexane were investigated, reacting effectively at room temperature [36,37].

3. Experimental

3.1. Stoichimetric reactions

3.1.1. Cp$'_2$ZrF$_2$ with i-Bu$_2$AlH

In Schlenk tubes, the fluoro complexes **1** or **3** (0.2 mmol) were dissolved in benzene-d_6 (0.5 mL) and mixed with i-Bu$_2$AlH (0.4 mmol, 1 M in toluene) in benzene-d_6 (1.0 mL). The mixture was stirred under argon for 24 h at room-temperature and 70 °C and analyzed by NMR investigations. For Cp$'$ = Cp, the complex [Cp$_2$ZrH(μ-H)]$_2$ (**4**) was identified (^{1}H NMR (C$_6$D$_6$) δ [ppm]: −3.45 (t), 3.85, 5.75) [39]) and for Cp$'_2$ = ebthi, the complex [rac-(ebthi)ZrH(μ-H)]$_2$ (**2**) was found (same data as in ref. [27]). For Cp$'$ = Cp*, no Cp$^*_2$ZrH$_2$ [40] was detected.

3.1.2. Zirconocene hydrides with organofluoro compounds

In Schlenk tubes, the zirconocene hydrides **2** or **4** (0.5 mmol) were dissolved in solvent (0.5 mL). To this solution, the organofluoro compounds (0.5 mmol) in solvent (1.0 mL) were added. The products were analyzed by NMR investigations and/or GC–MS measurements.

Complex [rac-(ebthi)ZrH(μ-H)]$_2$ (**2**) gave in toluene solution after 24 h no reactions with 1-fluoro-hexane (at 80 °C), fluorobenzene (at 100 °C) and hexafluorobenzene (at 65 °C).

Complex **2** and 1-fluoro-hexane were solved in toluene-d_8 in a NMR-tube. After 68 h at 70 °C, the ^{19}F spectra show rac-(ebthi)ZrF$_2$ (**1**) [25] and the resonance of 1-fluoro-hexane disappeared. With 2-fluoro-pyridine (at 100 °C) as products pyridine and rac-(ebthi)ZrF$_2$ (same date as in refs. [25,26]) were indicated. With pentafluoro-pyridine as products 2,3,5,6-tetrafluoro-pyridine (^{1}H NMR (C$_6$D$_6$): δ = 6.37 (m, 1H, CH) [ppm], ^{19}F{^{1}H} NMR (C$_6$D$_6$): δ = −90.3 (o-C–F), −138.3 (m-C–F) [ppm]) and again rac-(ebthi)ZrF$_2$ (**1**) were identified (same data as described in refs. [25,26]).

Complex [Cp$_2$ZrH(μ-H)]$_2$ (**4**) gave in analogous investigation at 70 °C in toluene solution no reaction with 1-fluoro-hexane. According to results obtained by Jones and co-workers, fluorobenzene reacted with [Cp$_2$ZrH(μ-H)]$_2$ (**4**) in THF at 60 °C to benzene and the difluoride **3** [15]. Hexafluorobenzene gave a mixture of pentafluorobenzene, hydrogen and the complexes Cp$_2$ZrF$_2$ (**3**) and Cp$_2$Zr(C$_6$F$_5$)F. [15] The 2-fluoro-pyridine formed in THF at 70 °C pyridine and difluoride **3**. Pentafluoro-pyridine reacted with [Cp$_2$ZrH(μ-H)]$_2$ (**4**) at rt to 2,3,5,6-tetrafluoro-pyridine, Cp$_2$ZrF$_2$ (**3**) and Cp$_2$Zr(4-C$_5$F$_4$N)F (same data as in ref. [38]).

3.1.3. i-Bu$_2$AlH with organofluoro compounds

In NMR tubes, the corresponding organofluoro compounds (0.9 mmol) were dissolved in benzene-d_6 (0.5 mL). To this solution i-Bu$_2$AlH (1.35 mmol) were added. The mixture was stirred under argon for 24 h at room-temperature and also at 70 °C. After reactions, the products were analyzed by NMR investigations and/or GC–MS measurements. Fluorobenzene and pentafluoropyridine gave only the starting materials.

3.2. Catalytic hydrodefluorination of pentafluoro-pyridine

3.2.1. i-Bu$_2$AlH and Cp$_2'$ZrF$_2$

In a Schlenk tube, Cp$_2'$ZrF$_2$ (0.4 mmol) (Cp$_2'$ = rac-(ebthi) (**1**) or Cp$_2$ (**3**)) as the pre-catalyst was dissolved in 20 mL of toluene and hexadecane (0.2 mL) was added as the internal standard. The solution was treated with i-Bu$_2$AlH (4.8 mmol) and pentafluoro-pyridine (0.44 mL, 4.0 mmol). The mixture was stirred at rt for 24 h. A sample was quenched in methanol and investigated by GC.

3.2.2. i-Bu$_2$AlH and [Cp$_2'$ZrH(μ-H)]$_2$

In a Schlenk tube, [Cp$_2'$ZrH(μ-H)]$_2$ (0.4 mmol) (Cp$_2'$ = rac-(ebthi) (**2**) or Cp$_2$ (**4**)) as the catalyst were dissolved in 20 mL of toluene and hexadecane (0.2 mL) was added as the internal standard. The solution was treated with pentafluoro-pyridine (0.44 mL, 4.0 mmol) and i-Bu$_2$AlH (4.8 mmol). The mixture was stirred at rt for 24 h. A sample was quenched in methanol and investigated by GC.

4. Conclusion

A new catalytic cycle was established in which cleavage of the Zr−F bond by interaction with Al−H yields Al−F and Zr−H from which the latter reacts with C−F to form C−H under recreation of Zr−F bonds. Driving force for this cycle is the formation of strong Al−F bonds. This cycle was realized in the room-temperature hydrodefluorination (HDF) of pentafluoro-pyridine. Evaluation of these systems established rac-(ebthi)ZrF$_2$ (**1**) and Cp$_2$ZrF$_2$ (**3**) as pre-catalysts which give together with i-Bu$_2$AlH as an activator active catalysts. The active species for the conversion were the formed hydrides [rac-(ebthi)ZrH(μ-H)]$_2$ (**2**) and [Cp$_2$ZrH(μ-H)]$_2$ (**4**). The results we obtained (rt, 24 h, turn over number 67) showed a significantly better performance compared to other investigations published before for this HDF reaction. Generally, the "turn over number" of the, here investigated, systems depends on the ligands used. Higher yields were obtained with the ebthi-ligand compared to the Cp-ligands. No big difference was found, if the systems are started with the difluorides as pre-catalysts or directly with the hydrides as the real catalysts. Bergman's monomeric imidozirconocene complex [rac-(ebthi)Zr=NtBu], gives an ortho C−F bond cleavage of pentafluoro-pyridine [23], and our alkyne complex Cp$_2$Zr(pyridine)(η^2-Me$_3$SiC$_2$SiMe$_3$), forms Cp$_2$ZrF(4-C$_5$NF$_4$) by para C−F bond cleavage of pentafluoro-pyridine [38]. These undesired side reactions are avoided if zirconium hydride complexes are used to catalyze HDF reactions.

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