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Journal of Molecular Catalysis A: Chemical 261 (2007) 184–189

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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

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Received 5 May 2006; received in revised form 9 June 2006; accepted 12 June 2006
Available online 11 September 2006

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 $i\text{-}Bu_2AlH$ 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_2ZrF_2 (**3**) together with $i\text{-}Bu_2AlH$ 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 $[Cp_2ZrH(\mu\text{-}H)]_2$ (**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.

Keywords: Zirconocene; C—F bond activation; C—H bond activation; Organometallics; Heterocycles

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 $Cp_2Ti(C_6F_5)_2$ to obtain $Cp_2Ti(C_6F_5)F$. Later Burk and co-workers described the elimination of a cyclopropane $(CH_2)_2CR_2$ in the reaction of a tetrakis(trifluoromethyl)cyclopentadienone-titanacyclobutane $[Cp_2Ti(CH_2)_2CR_2][O{=}C(CCF_3)_4]$ and the subsequent F-abstraction to a titanocene-fluoro-dienone complex $Cp_2Ti(F)[(O{-}C(CCF_3)_3C{=}CF_2)]$ [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 $[Cp^*_2Ti(\eta^1\text{-}FC_6H_5)][BPh_4]$ yields with trifluorotoluene 1,2-diphenyl-1,1,2,2-tetrafluoroethane and $Cp^*_2TiF_2$ [11]. Stoichiometric and certain catalytic C–F bond activations for the aromatization of cyclic perfluorocarbons were achieved by using titanocene and zirconocene, generated by Cp_2MCl_2 (M = Ti, Zr) and $Mg/HgCl_2$ or Cp_2ZrCl_2 and $Al/HgCl_2$ [12]. Zirconocene forming systems, such as Cp_2ZrPh_2 or Cp_2ZrCl_2/2 *n*-BuLi can defluorinate effectively perfluorodecaline to perfluoronaphthalene [13].

2-Fluoro- and 3-fluoropyridine were defluorinated by various complexes Cp'_2MCl_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 $Cp^*_2ZrH_2$. The mechanistic investigations had shown different pathways depending on

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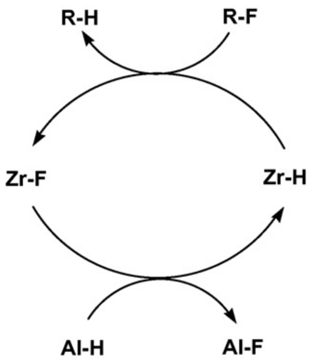
doi:10.1016/j.molcata.2006.06.027



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)(NH*t*Bu) with pentafluoro-pyridine Bergman and co-workers obtained via the monomeric imidozirconocene complex [*rac*-(ebthi)Zr=N*t*Bu] an activation of the *ortho* C–F bond and the formation of an amininopyridinato complex *rac*-(ebthi)ZrF(-N*t*Bu-2-C_5NF_4) [23]. Mostly zirconocene hydride complexes were used in C–F bond activation reactions.

$$Cp'_2ZrF_2 + 2i\text{-}Bu_2AlH \xrightarrow[-2i\text{-}Bu_2AlF]{} 0.5[Cp'_2ZrH(\mu\text{-}H)]_2 \qquad (1)$$

(**1**) : $Cp'_2 = rac\text{-}(ebthi)$ (**2**) : $Cp'_2 = rac\text{-}(ebthi)$
(**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_2AlH 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_2AlH and only unchanged starting material was isolated [27]. Fluoride, obviously, 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.

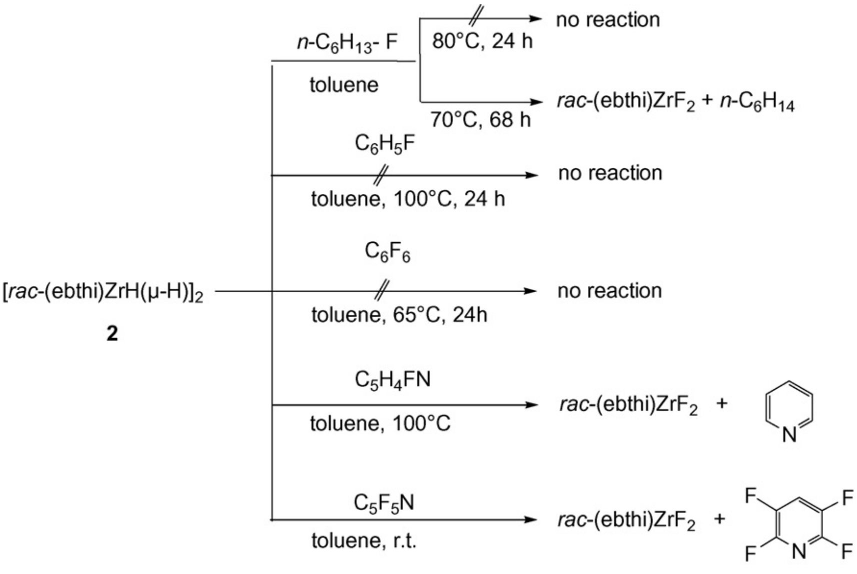
2. Results and discussion

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_2AlH, the formation of $[Cp_2ZrH(\mu\text{-}H)]_2$ (**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 $Cp^*_2ZrF_2$ and *i*-Bu_2AlH did not form dihydride $Cp^*_2ZrH_2$. At higher temperature, decomposition reactions occured. It was published, that $Cp^*_2ZrH_2$ and $Cp^*_2ZrF_2$ under hydrogen conproportionate at 150 °C to $Cp^*_2Zr(H)F$ [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'_2ZrCl_2 (Cp'_2 = *rac*-(ebthi), Cp_2, Cp^*_2) upon treatment with *i*-Bu_2AlH 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 $[Cp_2ZrH(\mu\text{-}H)]_2$ (**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 $[Cp_2ZrH(\mu\text{-}H)]_2$ (**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.