C-F Activation

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Formation of Zirconocene Fluoro Complexes: No Deactivation in the Polymerization of Olefins by the Contact-Ion-Pair Catalysts $[Cp'_2ZrR]^+[RB(C_6F_5)_3]^{-**}$

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In memory of Erhard Kurras

Certain ion pairs $[Cp'_2MMe]^+[MeB(C_6F_5)_3]^-$ (M = Ti, Zr; Cp' = substituted or unsubstituted η^5 -cyclopentadienyl), formed by the formal abstraction of methyl anions from dimethyl complexes $[Cp'_2MMe_2]$ of the Group 14 transition metals by the strong Lewis acid $B(C_6F_5)_3$, are highly active catalysts for the polymerization of α -olefins.^[1] Zirconocene complexes of olefins, alkynes, and butadiene were also later activated for catalytic olefin polymerization in a similar way.^[2]

Recently, we described the reactions of complexes containing two M–C σ bonds, including the zirconacyclopropenes $[Cp'_2Zr(\eta^2-RC_2R)]$ (R = SiMe₃)^[3a] and several five-membered zirconacycles,^[3b,c] with B(C₆F₅)₃. A typical example is [*rac*-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃)] (A; ebthi = 1,2-ethylene-1,1'bis(η^5 -tetrahydroindenyl)),^[4a] which undergoes electrophilic substitution at the five-membered ring of the ebthi ligand upon reaction with B(C₆F₅)₃, forming the alkenyl complex **B** [Eq. (1)].^[4b] In this complex, the boranate group is substituted at the 3-position of the five-membered ring, and one of its *ortho* fluorine atoms is coordinated to the zirconium center. The σ -bound alkenyl group at the zirconium center participates in an additional agostic interaction.^[4b]

Upon thermolysis of **B** [Eq. (1)], bis(trimethylsilyl)acetylene is eliminated, and with the cleavage of one B–C bond,

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one C_6F_5 group is transferred from boron to zirconium. The resulting complex **C** contains one bridging μ -hydrogen atom between the boron and zirconium centers.^[4b]

Complexes **B** and **C** can serve as model compounds for the two most frequently reported side reactions leading to catalyst poisoning and decreased productivity.^[5a] The first deactivation pathway is the transfer of a C_6F_5 group to the cationic metal centre (**C**).^[4b,5] The second consists of the transfer of a fluoride anion to the metal center (via intermediates such as **B**). It has been proposed that the formation of catalytically inactive zirconocene fluorides is an important deactivation process.^[5a]

Nevertheless, we recently found that the difluoride [rac-(ebthi) ZrF_2] (1),^[6b,c] in contrast to the analogous dichloride,^[6a] is an efficient catalyst for ethylene polymerization after activation with *i*Bu₃Al (or *i*Bu₂AlH).^[7a-c] In the literature, there are several empirical reports of Ti-F and Zr-F olefinpolymerization catalysts.^[7d-f] To understand these results, we studied the reaction of 1 with two equivalents of iBu₂AlH and found that hydride anions replace the fluoride ligands of 1 to give the complex $[{rac-(ebthi)ZrH(\mu-H)}_2]$ (2) (Scheme 1).^[8a,b] Interestingly, the reaction of the dichloride [rac-(ebthi)ZrCl₂] with iBu2AlH under analogous conditions does not lead to a hydride; rather, only the starting material is isolated.^[8a] The fluoride anion is apparently a more labile ligand than the chloride anion in this system, which explains the easier abstraction of a fluoride ligand to give an active catalyst system. The cleavage of the Zr-F bonds by Al-H groups with the formation of Zr-H and Al-F bonds is accepted as the reason for this "fluoride effect".^[7,8]

Zirconocene hydrides have frequently been used for the activation of C–F bonds. In a series of outstanding papers, Jones and co-workers have described the cleavage of C–F bonds in alkanes, arenes, and olefins using $[Cp*_2ZrH_2]$ ($Cp* = \eta^5$ -pentamethylcyclopentadienyl).^[9]

In light of the surprising results mentioned above for zirconocene difluorides in the catalytic polymerization of olefins, we describe herein the effective cleavage of C–F bonds in $B(C_6F_5)_3$ by complex **2**, which is formed by the reaction of Zr–F and Al–H species.

The reaction of **2** with $B(C_6F_5)_3$ in toluene at 90 °C for 14 days leads to a nearly quantitative formation of **1** (Scheme 1). A small amount of complex **5** is formed as a byproduct. To elucidate the reaction pathway, not only was the intermediate **3** isolated, but NMR spectroscopic experiments were also carried out. In these experiments, compounds such as **4** and **5**, which are difficult to characterize or isolate because of their instability, were detected. Note that the system is extremely sensitive with respect to slight changes in reaction conditions. Variations in the conditions can change



Scheme 1. Elementary steps of C–F bond activation in the reaction of ${\bf 2}$ with $B(C_6F_5)_3.$

the product composition or lead to inseparable mixtures of other complexes, which could not yet be characterized.

Orange crystals of complex **3** form very quickly at 20 °C in toluene, *n*-hexane, or benzene. The insolubility and instability of this complex prevents a detailed NMR spectroscopic investigation or recrystallization. Therefore, only low-quality crystals could be obtained for X-ray crystal-structure analysis. Nevertheless, it was possible to confirm that **3** consists of an ion pair of the type [{*rac*-(ebthi)Zr(μ -H)}₂]⁺[HB(C₆F₅)₃]⁻;^[14] in analogy to the ion pair [Cp*₂ZrH]⁺[HB(C₆F₅)₃]⁻;^[10] the presence of one terminal hydrogen atom in the cation is postulated (Scheme 1), but could not be located.

Complex **3** reacts slowly (60 °C, 5–7 h) with additional $B(C_6F_5)_3$ to give the yellow mononuclear complex [*rac*-(ebthi)Zr(μ -H){o-C₆F₄B(C₆F₅)₂]] (**4**) and varying amounts of complex **5**. The molecular structure of **4** contains the typical {*rac*-(ebthi)Zr} unit; the zirconium center is bonded to an *ortho*-metalated phenyl ring of the boranate anion, as well as a hydride ligand (H1; Figure 1).^[15] The positional and thermal parameters of H1 could not be refined. However, in the ¹H{¹¹B} NMR spectrum of **4** a signal (δ = 1.27 ppm) assigned to the hydride ligand is detected in the region of the *rac*-(ebthi)-ligand signals. Further NMR spectroscopic investigations were hampered by the instability of **4** in solution. Nevertheless, high yields of **1** can be obtained by the reaction of **2** with B(C₆F₅)₃ or by the thermolysis of complex **3**.

Only one other example of a similar fluoride transfer from $B(C_6F_5)_3$ to zirconium has been described: starting from



Figure 1. ORTEP representation of **4**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms (with the exception of H1) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1–C1 2.222(4), C1–C2 1.414(6), B1–C2 1.647(7); Zr1-C1-C2 103.4(3), C1-C2-B1 121.9(4).

 $[Cp*_2ZrMe]^+[MeB(C_6F_5)_3]^-$, Marks and co-workers obtained $[Cp*_2(Me)Zr(\mu-F)Zr(Me)Cp*_2]^+[MeB(C_6F_5)_3]^-$,^[5c] which can be viewed as an adduct of $[Cp*_2ZrMe]^+[MeB(C_6F_5)_3]^-$ and $[Cp*_2Zr(Me)F]$. This product is probably formed through either a transfer of one C_6F_5 group to the metal center, with the formation of $[Cp*_2Zr(Me)C_6F_5]$ and $MeB(C_6F_5)_2$, followed by an *ortho*-fluoride abstraction to give $[Cp*_2Zr(Me)F]$ and organoboron species, or through a direct fluoride transfer to the zirconium centre.

Complex 5, which is formed in 10 to 30 % yield depending on the reaction temperature and time, was shown by X-ray crystallography to be an isomer of complex $C^{[4b,16]}$ In 5, the *rac*-(ebthi) ligand is substituted by the boranate group at the 2-position of the cyclopentadienyl ring, whereas in **C**, the ring is substituted at the 3-position. Additionally, one *ortho* fluorine atom of the zirconium-bound C₆F₅ group weakly coordinates the zirconium center in 5 (Figure 2).^[4b]



Figure 2. ORTEP representation of **5**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms (with the exception of H1) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1-C13 2.319(8), Zr1...F1 2.604(5), F1-C14 1.389(8), B1-C4 1.593(10); C13-C14-F1 114.0(7).

The formation of the difluoride **1** (by nucleophilic aromatic substitution on $B(C_6F_5)_3$), as well as complexes **5** and **C** (by C_6F_5 -group migration) is relevant for the catalytic polymerization of olefins. Complexes such as **5** and **C** are completely inactive, and their formation clearly represents a deactivation process. The formation of **1** from **2** and $B(C_6F_5)_3$ by C–F bond cleavage, often described as a deactivation process, is not in fact a deactivation, because **1** can be reconverted into **2** through treatment with *i*Bu₂AlH (Scheme 1).

These results, obtained through the stepwise reactions of isolated complexes, have important consequences for catalytic olefin polymerization in general: mixtures of zirconocene halides such as $[Cp'_2ZrCl_2]$, methylalumoxane (MAO; as an activator and scavenger), and fluorosubstituted arylboranes such as $B(C_6F_5)_3$ are often used to produce catalytically active systems. Hydrogen gas is also added to the system to control the molecular weight of the polymer. Marks and coworkers have shown that the methyl complex $[Cp^*_2ZrMe_2]$ reacts with hydrogen to produce the hydride $[Cp^*_2ZrMe_2]$, with elimination of methane. The hydride subsequently reacts with $B(C_6F_5)_3$ to form the active ion pair $[Cp^*_2ZrH]^+[HB(C_6F_5)_3]^-$ (Scheme 2).^[10]



Scheme 2. Mechanisms of catalyst activation and deactivation. L-----L=Cp'_2.

In relation to these steps, the formation of fluoro complexes by C–F bond cleavage was only discussed as a deactivation process.^[5] Our results clearly show that Zr–F complexes can be reconverted into Zr–H complexes, which are very active catalysts, through interaction with Al–H groups (Scheme 2).

It has been noted that "In many instances organometallic fluorides have been the unexpected products of fluorine abstraction in the decomposition of complexes of fluorinated anions."^[11] This observation, in the case of reactions involving the fluorinated arylborane $B(C_6F_5)_3$ and the boranates [RB- $(C_6F_5)_3]^-$ (R = Me, H), was previously considered to be a marginal problem and interpreted exclusively as the result of a deactivation process.

There are, in fact, many examples of $B(C_6F_5)_3$ effecting electrophilic substitution at cyclopentadienyl ligands (leading to complexes such as **B**),^[3] but few examples of nucleophilic aromatic substitution involving $B(C_6F_5)_3$. Erker and co-workers,^[12a,b] and others^[12c] have described that the positive inductive effect of boron is sometimes overcompensated in $B(C_6F_5)_3$ by the fluoro substituents, making this special Lewis acid susceptible to nucleophilic attack at the electrondeficient arene rings.

The unexpected formation of **1** and its activity as a precatalyst in olefin polymerization, explained herein, con-

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firm the statement that "*early transition metal fluoride complexes do not preclude catalytic chemistry*."^[13] In this context, our results offer a new perspective on the deactivation of olefin-polymerization catalysts.

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- [14] Crystal-structure analysis of **3**: $C_{58}H_{51}BF_{15}Zr_2$, $M_r = 1226.24$, $0.2 \times 0.2 \times 0.1$ mm, orange prisms, space group $P2_1/n$, monoclinic, a = 10.946(2), b = 20.243(4), c = 22.602(5) Å, $\beta = 100.86(3)^\circ$, V = 4918.5(17) Å³, Z = 4, $\rho_{calcd} = 1.656$ g cm⁻³, 17564 reflections measured, 5159 independent, 3562 observed ($I > 2\sigma(I)$), R1 = 0.057, wR2(all data) = 0.141, 696 parameters. The terminal hydride ligand was not located.
- [15] Crystal-structure analysis of **4**: $C_{38}H_{25}BF_{14}Zr$, $M_r = 849.61$, $0.4 \times 0.3 \times 0.2$ mm, yellow prisms, space group $P2_12_12_1$, orthorhombic, a = 11.562(2), b = 12.493(2), c = 22.206(4) Å, V = 3207.5(10) Å³, Z = 4, $\rho_{calcd} = 1.759$ g cm⁻³, 17145 reflections measured, 5104 independent, 3749 observed $(I > 2\sigma(I))$, R1 = 0.034, wR2(all data) = 0.061, 487 parameters.
- [16] Crystal-structure analysis of **5**: $C_{39.67}H_{24}BF_{15}Zr$, $M_r = 887.62$, $0.3 \times 0.2 \times 0.1$ mm, colorless prisms, space group $P\bar{3}$, trigonal, a = 23.082(3), c = 12.474(3) Å, V = 5755.5(16) Å³, Z = 6, $\rho_{calcd} = 1.537$ g cm⁻³, 16976 reflections measured, 5992 independent, 2908 observed ($I > 2\sigma(I)$), R1 = 0.053, wR2(all data) = 0.153, 507 parameters. CCDC-295535 (**3**), CCDC-295534 (**4**), and CCDC- 295536 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

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