

Zirconocene Dichloride Catalyzed Hydrodefluorination of C_{sp²}-F bonds**

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In recent years synthetic methods for the activation and functionalization of inert C–F σ bonds with organometallic complexes have attracted increased attention.^[1,2] In the presence of a reductant such as H₂ or a silane, a number of late-transition-metal and main-group catalysts are known to effect the hydrodefluorination of C_{sp²}-F and C_{sp³}-F bonds.^[3,4] While the use of early-transition-metal catalysts for this transformation is rare,^[2] in a series of seminal papers, Jones and co-workers have documented stoichiometric C–F bond cleavage with group 4 metallocenes.^[5–7] The related cerium complex $[\{\eta^5\text{-}1,2,4\text{-}(t\text{Bu})_3\text{C}_5\text{H}_2\}_2\text{CeH}]$ is known to effect C–F bond activation of hydrofluorocarbons.^[8] During these studies it has often been postulated that the strength of the newly formed M–F bond provides not only a thermodynamic driving force for C–F bond cleavage but also a barrier to catalytic turnover.

Comparison of the gas-phase bond dissociation energies for Zr–F + Al–H and Al–F + Zr–H combinations suggests that aluminum hydrides should act as reagents for catalytic turnover in zirconium-mediated hydrodefluorination.^[9,10a] Successful studies in this area, however, are limited to two heteroaromatic substrates. Hence, pentafluoropyridine may be selectively hydrodefluorinated to yield 2,3,5,6-tetrafluoropyridine by employing 0.5–10 mol % $[\text{Cp}_2\text{ZrF}_2]$ (Cp = cyclopentadienyl) or $[\{\text{Cp}_2\text{ZrH}(\mu\text{-H})_2\}]$ as a pre-catalyst and DIBAL-H as a terminal reductant.^[10a] Similarly, Red-Al has been reported as a hydride source for the conversion of 2-fluoropyridine into pyridine albeit with 10 mol % $[\text{Cp}_2\text{MCl}_2]$ (M = Ti, Zr) as a catalyst.^[10b] In related studies, Kiplinger and co-workers have shown that toxic M/HgCl₂ (M = Mg, Al) mixtures act as reductants for the defluorination and aromatization of a handful of cyclic perfluorinated hydrocarbons with catalytic $[\text{Cp}_2\text{ZrCl}_2]$,^[11] while Lentz and co-workers reported the use of primary and secondary silanes as reductants for the hydrodefluorination of fluoropropenes using $[\text{Cp}_2\text{TiF}_2]$ as a catalyst.^[12] We now report four-coordinate aluminum dihydrides as reductants for the hydrodefluorination of fluoroarenes catalyzed by $[\text{Cp}_2\text{ZrCl}_2]$.

As evidenced by ¹⁹F NMR spectroscopy, the reaction of **1a** (for structure see Table 1) with C₆F₆ in the presence of 5 mol % $[\text{Cp}_2\text{ZrCl}_2]$ in C₆D₆ at 80 °C led to the slow production of C₆F₅H and *p*-C₆F₄H₂. Under the same conditions, a reaction with **1b** appeared, qualitatively, to proceed more rapidly, whereas **1c** did not display any advantages over **1b**.^[13]

Control reactions conducted without $[\text{Cp}_2\text{ZrCl}_2]$ or with PhSiH₃, or DIBAL-H in place of **1a–c** did not lead to significant consumption of C₆F₆. The complexes **1a–c** were synthesized from LiAlH₄ and the pro-ligand may potentially be recovered following the hydrodefluorination reaction.

Based upon these observations, we investigated the hydrodefluorination of a series of fluoroarenes using 5 mol % of $[\text{Cp}_2\text{ZrCl}_2]$ and 0.6–1.05 equivalents of **1b** (Table 1). The catalytic reactions were followed by a methanol work up at 80 °C for 14 hours. As a result of substrate bias, reactions were conducted at a series of temperatures [25 °C (C₆D₆), 80 °C (C₆D₆), and 110 °C ([D₈]toluene)] and for each substrate a control reaction was conducted without the catalyst present. Data from catalyzed experiments are included in Table 1, while full details of the control reactions are presented in Table S1 in the Supporting Information.

Pentafluoropyridine and octafluorotoluene, known to contain activated C–F bonds, reacted readily within 1 hour at 25 °C in the presence of 1.05 equivalents of **1b** and 5 mol % of $[\text{Cp}_2\text{ZrCl}_2]$ (Table 1, entries 1 and 6), while more challenging substrates required elevated temperatures before hydrodefluorination was observed. Under the catalytic conditions C₆F₆ was completely consumed after 24 hours at 80 °C and both C₆F₅H and *p*-C₆F₄H₂ were observed after protic work up (Table 1, entry 10). Although the high C–F bond dissociation energy of hexafluorobenzene has meant that it is often employed as a substrate in hydrodefluorination catalysis,^[1–2] the stabilization of the $[\text{C}_6\text{F}_5\text{H}_2]$ anion may result in a relatively low activation energy for C–F bond cleavage by nucleophilic aromatic substitution. A similar argument could not be made for 1-fluoronaphthalene, which underwent hydrodefluorination albeit at a higher temperature of 110 °C and a longer reaction time of 4 days (Table 1, entry 13). An attempt to improve the efficiency of the latter reaction using $[\{\eta^5\text{-C}_5\text{Me}_4\text{H}\}_2\text{ZrCl}_2]$, a pre-catalyst with a more electron-rich cyclopentadienyl ligand,^[7] failed, yielding naphthalene in only 25 % conversion after 5.5 days at 110 °C.

Ozerov and co-workers have documented silylium and alumenium cations associated with noncoordinating carborane anions for the mild and selective hydrodefluorination of C_{sp³}-F bonds in the presence of C_{sp²}-F bonds.^[4a–d] In the current case, a selective hydrodefluorination of C_{sp²}-F bonds occurs and the data are reminiscent of those reported for the

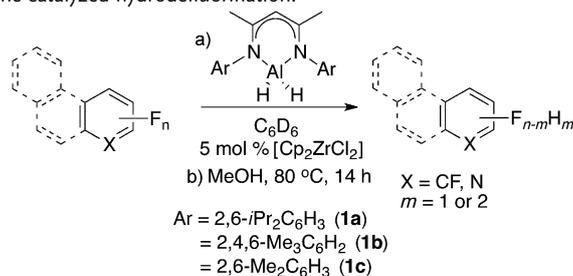
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Table 1: Zirconocene-catalyzed hydrodefluorination.



Entry	Substrate	Product(s)	Cat. (mol%)	Equiv. 1b	t	T [°C]	Yield [%] ^[a]
1 ^[b]			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.00	10 min	25	92
2 ^[b]			$[\text{Cp}^*_2\text{ZrCl}_2]$ (1)	1.05	24 h	25	64
3 ^[b]			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	0.6	1 h	80	83
4 ^[b]			$[\{\text{Cp}^*_2\text{ZrH}_2\}_2]$ (5)	1.05	24 h	25	93
5 ^[b]			$[\text{Cp}^*_2\text{ZrF}_2]$ (5)	1.05	30 min	25	77
6 ^[b]			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	10 min	25	79
7 ^[b]			4b (5)	1.05	1.5 h	25	81
8			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	3 h	80	82
		$\text{R}^1 = \text{H}; \text{R}^2 = \text{F}$ (25%) $\text{R}^1, \text{R}^2 = \text{H}$ (57%)					
9			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	1.5 h	80	82
		$\text{R}^1 = \text{H}; \text{R}^2, \text{R}^3 = \text{F}$ (50%) $\text{R}^1, \text{R}^3 = \text{H}; \text{R}^2 = \text{F}$ (26%) $\text{R}^1, \text{R}^2 = \text{H}; \text{R}^3 = \text{F}$ (6%)					
10		$\text{C}_6\text{F}_5\text{H}$ (49%) $p\text{-C}_6\text{F}_4\text{H}_2$ (41%)	$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	24 h	80	90
11		$\text{C}_6\text{F}_5\text{H}$ (40%) $p\text{-C}_6\text{F}_4\text{H}_2$ (37%)	$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	18 h	80	77
12			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	24 h	80	81
13 ^[b,c]			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	4 d	110	76
14 ^[b,c]			$[\text{Cp}^*_2\text{ZrCl}_2]$ (5)	1.05	4 d	110	18

[a] For 0.2 M of substrate, the yield was determined by NMR analysis of the reaction mixture relative to a capillary containing a 1.0 M solution of $\text{C}_6\text{H}_5\text{F}$ in $[\text{D}_6]$ benzene. Yields of the individual products are given with in the parentheses. [b] Yields recorded prior to (or without) MeOH work-up. [c] Reaction conducted in $[\text{D}_8]$ toluene.

stoichiometric reactions of $[\text{Cp}^*_2\text{ZrH}_2]$ and $[\{\text{Cp}^*_2\text{ZrH}(\mu\text{-H})\}_2]$ with hydrofluorocarbons.^[2,7]

During catalytic preparations, both $[\{(\text{MesNCMe})_2\text{CH}\}\text{AlF}_2]$ (**2b**) and $[\{(\text{MesNCMe})_2\text{CH}\}\text{AlHF}]$ (**3b**) were observed as reaction by-products by ^{19}F NMR spectroscopy.

For example, the hydrodefluorination of $\text{C}_5\text{F}_5\text{N}$ using 1.05 equivalents of **1b** (Table 1, entries 1 and 3) proceeded with formation of **3b**, whereas use of 0.6 equivalents of **1b** produced **2b** as the major reaction by-product. The by-products have been assigned by the independent synthesis of each. Although reaction of **1b** with $\text{BF}_3\cdot\text{OEt}_2$ in Et_2O at -78°C gave **2b** in 86% yield upon isolation (^{19}F NMR $\delta = -174.5$ ppm, Figure 1),^[14] the synthesis of **3b** proved more complicated. As evidenced by NMR spectroscopy, a metathesis reaction of a 1:1 mixture of **1b** with **2b** in a C_6D_6 solution at 25°C resulted in incomplete consumption of the starting materials along with the formation of **3b** (^{19}F NMR $\delta = -157.4$ ppm). The equilibrium, represented in Scheme 1, suggested by these data could be shifted toward the product **3b** by using a 2:1 stoichiometry of **1b** to **2b**. Because of the propensity of **3b** to co-crystallize with the starting materials, attempts to isolate pure samples of this compound have, so far, failed.^[15]

In many instances, in addition to the fluoroarenes **2b** and **3b**, examination of reaction mixtures using ^1H and ^{19}F NMR spectroscopy prior to the methanol work-up revealed the presence of nonvolatile aluminum fluoroaryl complexes.^[16] Specifically, the reaction of 1.05 equivalent of **1b** with C_6F_6 and 5 mol % of $[\text{Cp}^*_2\text{ZrCl}_2]$ gave the fluoroarene-containing products $\text{C}_6\text{F}_5\text{H}$, $p\text{-C}_6\text{F}_4\text{H}_2$, $[\{(\text{MesNCMe})_2\text{CH}\}\text{Al}(\text{C}_6\text{F}_5)\text{F}]$, and $[\{(\text{MesNCMe})_2\text{CH}\}\text{Al}(p\text{-C}_6\text{F}_4\text{H})\text{F}]$ in 2, 23, 47, and 18% yield, respectively (Scheme 2). The latter complexes were characterized by peaks for m/z 398 and 546 in the EI mass spectrum. Upon treatment with excess methanol at 80°C , the aluminum complexes undergo protonolysis to yield the corresponding fluoroarenes (Scheme 2 and Table 1).

Facile transfer of not only fluoride but also fluoroaryl ligands from zirconium to aluminum explains the observed reaction intermediates, the aluminum fluoride by-products, and the ease of catalyst turnover. This hypothesis was probed by an NMR-scale reaction between a mixture of $[\text{Cp}^*_2\text{ZrF}_2]$

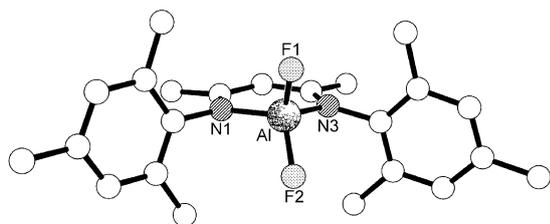
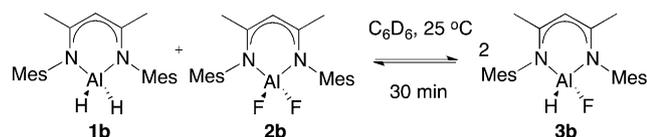
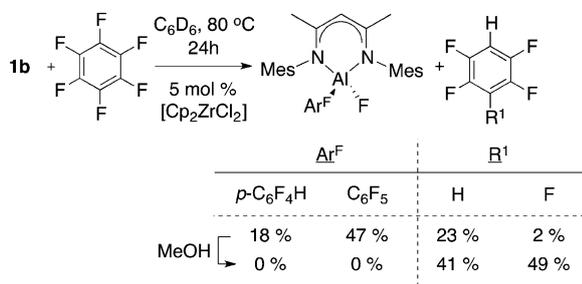


Figure 1. a) Crystal structure of **2b**. Selected bond angles [°] and bond lengths [Å]: Al–N1 1.8594(9), Al–N3 1.8594(9), Al–F1 1.6637(8), Al–F2 1.6647(8); N1–Al–N3 99.37(4), F1–Al–F2 107.91(5).^[21]



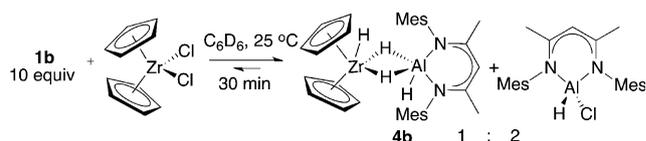
Scheme 1. Reaction of **1b** with **2b**.



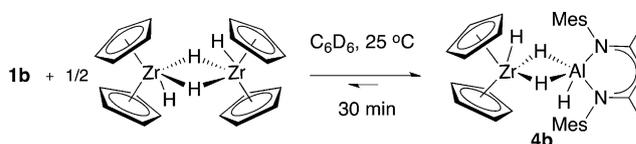
Scheme 2. Catalytic hydrodefluorination of C₆F₆ with **1b**.^[17]

(C₆F₅)/[Cp₂ZrF₂], formed from the reaction of [(Cp₂ZrH(μ-H))₂] with C₆F₆,^[7c] and excess **1b**. In a C₆D₆ solution after 30 minutes at 25 °C, the aforementioned reaction yielded a mixture of [(MesNCMe)₂CH]Al(C₆F₅)X (X = H or F) and **3b** as the major fluorine-containing products as evidenced by ¹⁹F NMR spectroscopy.^[18] An alternative explanation for the formation of aluminum fluoroaryl complexes under the catalytic conditions is C–H bond activation of the organic reaction products. Heating *p*-C₆F₄H₂ in the presence of **1b** and 5 mol% of [Cp₂ZrCl₂] in C₆D₆ for 24 hours at 80 °C, however, did not result in the formation of [(MesNCMe)₂CH]Al(*p*-C₆F₄H)H] by C–H activation of the fluoroarene.

The catalyst resting state at the early stages of the reaction was investigated by an additional series of experiments. Reaction of [Cp₂ZrCl₂] with **1b** in a 1:10 ratio resulted in formation of the heterobimetallic complex **4b** and [(MesNCMe)₂CH]AlHCl] (Scheme 3).^[19] The assignment of [(MesNCMe)₂CH]AlHCl] was confirmed by spiking reactions with authentic samples, while **4b** was synthesized on a preparative scale by reaction of **1b** with [(Cp₂ZrH(μ-H))₂] (Scheme 4). Although attempts to obtain single crystals of **4b** was unsuccessful, the analogue [(2,6-Me₂C₆H₃-NCMe)₂CH]Al(H)(μ-H)₂Zr(H)Cp₂] (**4c**) was the subject of an X-ray diffraction study. The results of this experiment are presented in Figure 2.



Scheme 3. Reaction of [Cp₂ZrCl₂] with 10 equiv **1b**.



Scheme 4. Reaction of [(Cp₂ZrH(μ-H))₂] with 1 equiv **1b**.

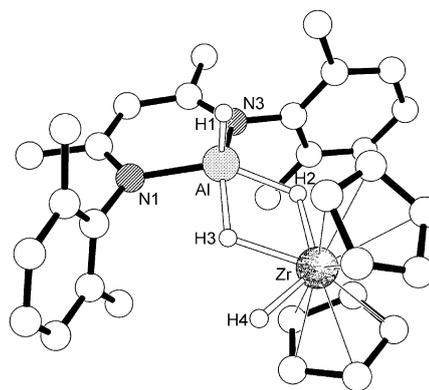


Figure 2. Crystal structure of **4c**. Selected bond angles [°] and bond lengths [Å]: Al–N3 1.9464(10), Al–N1 1.9493(10), Zr–C 2.4964(14)–2.5219(13); N1–Al–N3 93.14(4).^[21]

Upon dissolving crystalline samples of **4b** in C₆D₆ an equilibrium between **4b** and **1b**/[(Cp₂ZrH(μ-H))₂] was observed; [(Cp₂ZrH(μ-H))₂] was characterized by diagnostic ¹H NMR resonances at δ = –3.62 (t, *J* = 7.2 Hz) and +3.68 ppm (t, *J* = 7.2 Hz) for the bridging and terminal hydrides, respectively.^[20] The reversibility of alane binding to zirconocene dihydride was confirmed by a crossover experiment in which 1 equivalent of **4b** was reacted with 1 equivalent of **1c** and shown to form **4c**. Variable-temperature ¹H NMR data recorded across the –80 to +80 °C range in [D₈]toluene revealed a series of fluxional processes consistent with fast exchange between all possible hydride positions of **4b**. In the high temperature regime (> +20 °C) a single broad hydride resonance is observed for **1b** at δ = –0.71 ppm corresponding to a time-averaged combination of bridging (H_b) and terminal (H_t) hydride resonances. Upon cooling, two decoalescence events are observed. The first (*T*_c = +10 °C) resolves H_t and H_b, and the second (*T*_c = –10 °C) resolves H_b into two independent resonances. In the lowest temperature regime, the magnetically non-equivalent bridging hydrides are observed at δ = –2.42 and –2.64 ppm. Although the terminal hydrides of **1b** could not be observed directly in the ¹H NMR data, ROESY and NOESY experiments conducted at –40 °C revealed chemical exchange of the bridging hydrides with two resonances at δ = +1.10 and +4.75 ppm,

which were assigned as the zirconium and aluminum terminal hydrides, respectively. These data are consistent with a “freezing-out” of the solid-state structure of **4b**, presumed by analogy to **4c**, in which the asymmetric environment at zirconium results in the magnetic non-equivalence of the bridging hydrides.

In the presence of 1.0 equivalent of **1b**, 5 mol% of **4b** proved kinetically competent for the hydrodefluorination of octafluorotoluene to *p*-CF₃C₆F₄H in 81% yield within 90 minutes at 25 °C (Table 1, entry 7).

In summary, we have discovered that four-coordinate diketiminate stabilized aluminum dihydrides are efficient terminal reductants for the zirconocene-catalyzed hydrodefluorination of fluoroarenes and drastically increased the scope of zirconocene hydrodefluorination catalysis. Initial data are consistent with catalyst turnover by fast ligand transfer between the catalyst and terminal reductant. While a heterobimetallic complex has been observed as a catalyst resting state it remains unclear whether such intermediates are involved in C–F bond cleavage.

Experimental Section

Preparative scale synthesis of **4c**: In a glovebox, **1c** (450 mg, 1.34 mmol, 1 equiv) and [(Cp₂ZrH₂)₂] (300 mg, 0.67 mmol, 0.5 equiv) were weighed and transferred to a Schlenk tube. The Schlenk was sealed and removed from the glovebox and attached to a vacuum line. Toluene (15 mL) was added by cannula and the mixture stirred for 24 h at 25 °C. The reaction mixture settled out and unreacted zirconocene dihydride removed by filtration. The solvent was removed from the filtrate under reduced pressure and *n*-hexane (20 mL) added to the crude mixture upon which point **4c** crystallized from solution. The product was isolated by filtration, dried under vacuum, and collected as colorless crystals (308 mg, 0.55 mmol, 41%). X-ray quality crystals were obtained from storage of a concentrated *n*-hexane solution at 5 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ = –0.71 (broad s, 1H, *MH* bridging), 1.48 (s, 6H, *CMe*), 2.30–2.32 (broad s, 12H, *o*-*ArMe*), 4.99 (s, 1H, *CH*), 5.19 (s, 10H, *CpH*), 7.01–7.03 ppm (m, 4H, *ArH*); ¹³C NMR (C₆D₆, 298 K, 125.7 MHz): δ = 19.5, 23.5, 97.8, 98.6, 125.9, 128.8, 134.4, 146.1, 168.7 ppm; Infrared (solid): $\tilde{\nu}$ = 2839, 1773 (wsh), 1527, 1376 cm^{–1}. Elemental analysis calc. for C₃₁H₃₉AlN₂Zr: C, 66.74; H, 7.05; N, 5.02 found C, 66.72; H, 7.18; N, 5.12.

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