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Carbon–fluorine bond activation of perfluorinated arenes with $Cp^*_2ZrH_2$

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Abstract

Reaction of $Cp^*_2ZrH_2$ (Cp*, pentamethylcyclopentadienyl) with excess hexafluorobenzene produces a mixture of Cp^*_2ZrHF, C_6F_5H and $Cp^*_2Zr(C_6F_5)H$ in ca. 2:1:1 ratio. Reaction of $Cp^*_2ZrH_2$ with excess C_6F_5H produces a mixture of Cp^*_2ZrHF, $Cp^*_2Zr(C_6F_5)H$, $Cp^*_2Zr(o\text{-}C_6F_4H)H$, $p\text{-}C_6F_4H_2$, and $o\text{-}C_6F_4H_2$ with preferred *ortho* aromatic C–F activation. Dual mechanisms are proposed for the formation of Ar^FH and $Cp^*_2Zr(Ar^F)H$ species.

Keywords: Bond activation; Perfluorinated arenes; Pentamethylcyclopentadienyl

1. Introduction

The carbon–fluorine bond is the strongest and most unreactive bond found in organic molecules and its use as an active functional group is a significant chemical challenge. Some of the major goals in carbon–fluorine bond activation studies include the functionalization of saturated fluorocarbons and the conversions of chlorofluorocarbons (CFCs) into non-ozone-depleting substances [1]. Transition-metal complexes are one class of compounds that have been shown to cleave strong C–F bonds either stoichiometrically or catalytically [1]. In most examples of C–F activation reactions by transition metals, the reactions are thermodynamically driven by formation of a strong metal–fluorine bond, and this result generally precludes the use of the metal as a defluorination catalyst. The addition of a second reductant and/or fluoride acceptor, however, can sometimes regenerate the reactive metal complex, and allow the facile catalytic cleavage of C–F bonds [2].

Perfluorinated unsaturated compounds are generally more reactive than their less-fluorinated counterparts. This is due to the high electronegativity of fluorine, which imparts an increase in electrophilicity of the adjacent double bonds. The effect is prominently observed by comparison of the reactions of hexafluorobenzene and monofluorobenzene. Monofluorobenzene (without additional activating groups) is virtually inert toward nucleophiles [1]. Hexafluorobenzene has an estimated C–F bond dissociation energy of 154 kcal mol^{-1} [3], the highest of the fluorobenzenes, yet it is significantly more reactive toward nucleophiles and electron-rich metal complexes.

In several cases, transition-metal hydride complexes have been shown to react with C_6F_6 to form pentafluorophenyl hydride complexes. For example, $Cp^*Rh(PMe_3)H_2$ reacts to form $Cp^*Rh(PMe_3)(C_6F_5)H$ by a base-catalyzed process involving nucleophilic displacement of fluoride ion by the anion, $[Cp^*Rh(PMe_3)H]^-$ [4]. Similarly, $Cp^*Ir(PMe_3)(H)(Li)$ reacts with C_6F_6 to form LiF and $Cp^*Ir(PMe_3)(C_6F_5)H$ [5]. In contrast, an electron transfer mechanism was proposed in the reaction of $Ru(dmpe)_2H_2$ with C_6F_6 to give *trans*-$Ru(dmpe)_2(C_6F_5)H$ [6]. In other cases, metal complexes react with C_6F_6 to give pentafluorophenyl fluoride complexes. For example, $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) reacts with C_6F_6 in the presence of PEt_3 or $Ni(PEt_3)_4$ to give *trans*-$Ni(PEt_3)_2(C_6F_5)F$ [7]. [(dtbpm)Pt(neopentyl)H] (dtbpm = di(*t*-butyl)phosphinomethane) reacts thermally with C_6F_6 to give $(dtbpm)Pt(C_6F_5)F$ quantitatively [8]. Low temperature

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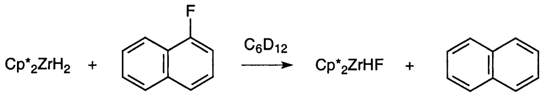
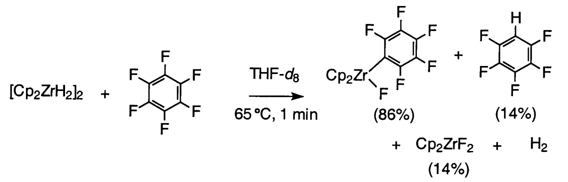
photolysis of $Cp^*Rh(PMe_3)(\eta^2\text{-}C_6F_6)$ produced $Cp^*Rh(PMe_3)(C_6F_5)F$ in low yield [9].

We have recently reported the reactions of $Cp_2^*ZrH_2$ with monofluorobenzene and 1-fluoronaphthalene to give Cp_2^*ZrHF and free arene [10]. Fluorobenzene reacts slowly over 40 days at 85 °C to give a mixture of Cp_2^*ZrHF, benzene, and $Cp_2^*Zr(C_6H_5)F$ in 1:1:0.75 ratio. Reaction of $Cp_2^*ZrH_2$ with 1-fluoronaphthalene, however, gives only Cp_2^*ZrHF and naphthalene within 4 days at 85 °C, according to Eq. (1). There was no evidence for free radicals in these reactions, as the rate of reaction with fluoronaphthalene was unaffected by added radical initiators or inhibitors, and otherwise followed clean bimolecular reaction kinetics. We, therefore, proposed a mechanism involving nucleophilic hydride attack on the ring and fluoride elimination involving a carbanionic intermediate-transition state. The decreased loss in resonance energy in the transition state was believed to be responsible for the increased reactivity of fluoronaphthalene in comparison with fluorobenzene. In the reaction of $Cp_2^*ZrH_2$ with fluorobenzene, the secondary product, $Cp_2^*Zr(C_6H_5)F$, was shown to form by an initial ortho aryl C–H activation, β-fluoride elimination to give a benzyne complex, and finally, insertion of benzyne into the Zr–H bond [10].



(1)

Recently reported from our laboratory is the reaction of $[Cp_2ZrH_2]_2$ with C_6F_6 to produce a mixture of $Cp_2Zr(C_6F_5)F$, C_6F_5H, and Cp_2ZrF_2, according to Eq. (2) [11]. An oxidative addition to 'Cp_2Zr' was proposed to account for $Cp_2Zr(C_6F_5)F$. The *ansa*-derivative, $(Me_2Si(C_5H_4)_2ZrH_2)_2$, also reacts with C_6F_6 to give the apparent oxidative addition product, $Me_2Si(C_5H_4)_2Zr(C_6F_5)F$ [12].



(2)

Due to the low solubility of these zirconium hydride complexes, a thorough kinetic and mechanistic study was not possible, and, therefore, the soluble and monomeric $Cp_2^*ZrH_2$ was chosen as a suitable substrate to continue this investigation. Surprisingly, reaction of $Cp_2^*ZrH_2$ with C_6F_6 did not give the analogous pentafluorophenyl fluoride complex, but rather a pentafluorophenyl hydride complex as a major reaction product. The results of this study are presented in this paper.

2. Results and discussion

2.1. Reaction of $Cp_2^*ZrH_2$ with hexafluorobenzene

Reaction of $Cp_2^*ZrH_2$ with 20 equivalents of C_6F_6 in cyclohexane-d_{12} over ~6 h at 85 °C affords a clean mixture of Cp_2^*ZrHF, $Cp_2^*Zr(C_6F_5)H$, and C_6F_5H in 2:1:1 ratio, according to Scheme 1. These species grow in together, and no intermediates were detected. A small amount (< 5%) of $Cp_2^*ZrF_2$ is also observed [13]. The ratio of C_6F_5H to $Cp_2^*Zr(C_6F_5)H$ remained unchanged under conditions employing one equivalent of C_6F_6 or neat C_6F_6 solvent. All products were characterized by ^1H and ^{19}F-NMR spectroscopy and GC–MS, and independent synthesis of $Cp_2^*Zr(C_6F_5)H$ [14]. When the reaction of $Cp_2^*ZrH_2$ and excess C_6F_6 was performed in THF-d_8 solvent, many other unidentified C–F activated products along with Cp_2^*ZrHF, C_6F_5H, and $Cp_2^*Zr(C_6F_5)H$ were observed. In contrast to the reaction of C_6F_6 with $[Cp_2ZrH_2]_2$, the 'oxidative addition' product, $Cp_2^*Zr(C_6F_5)F$, was not detected under any conditions. $Cp_2^*Zr(C_6F_5)F$ was prepared independently by reaction of $Cp_2^*Zr(C_6F_5)H$ with 70/30 HF–pyridine in pentane. The X-ray structure of this compound is shown in Fig. 1. Although required for mass balance, H_2 was not observed in the ^1H-NMR spectrum in this reaction.

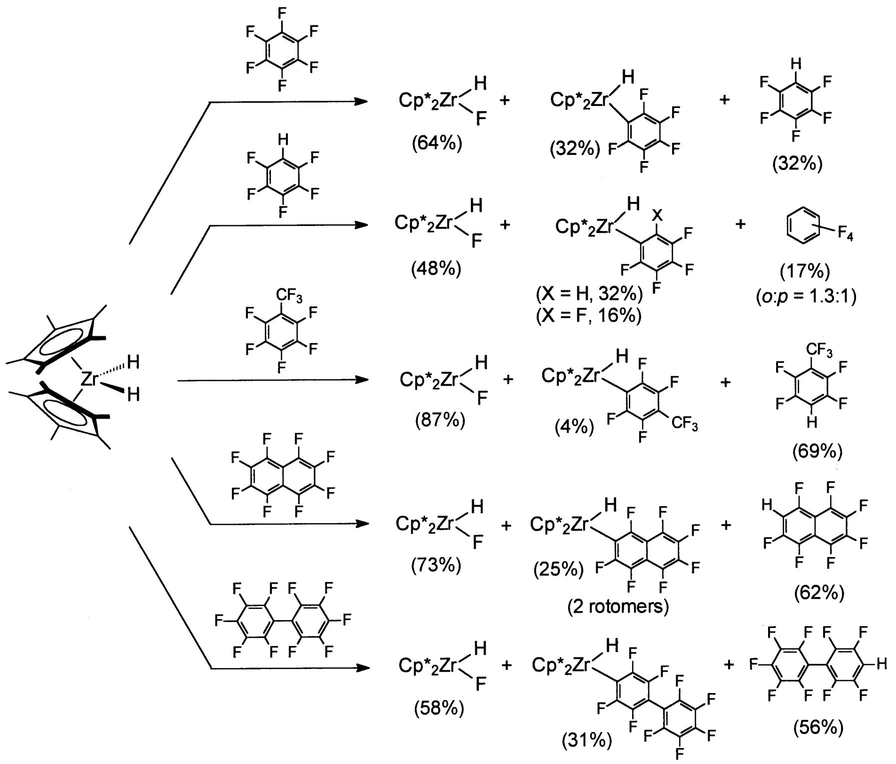
2.2. Reaction of $Cp_2^*ZrH_2$ with pentafluorobenzene

Reaction of $Cp_2^*ZrH_2$ with 20 equivalents of C_6F_5H in cyclohexane-d_{12} over 6 h at 85 °C afforded a clean mixture of C–H and C–F activated products consisting of Cp_2^*ZrHF, $Cp_2^*Zr(C_6F_5)H$, $Cp_2^*Zr(o\text{-}C_6F_4H)H$, $o\text{-}C_6F_4H_2$, $p\text{-}C_6F_4H_2$, and $Cp_2^*ZrF_2$, according to Scheme 1. Overall, *ortho* C–F activation was preferred to give $o\text{-}C_6F_4H_2$ and $p\text{-}C_6F_4H_2$ in 0.60:0.46 ratio [15]. No $Cp_2^*Zr(p\text{-}C_6F_4H)$ was observed. The identity of $Cp_2^*Zr(o\text{-}C_6F_4H)H$ was confirmed by independent synthesis [14], and $o\text{-}C_6F_4H_2$ and $p\text{-}C_6F_4H_2$ were verified by GC–MS and comparison with authentic samples.

2.3. Reaction of $Cp_2^*ZrH_2$ with perfluorotoluene, perfluoronaphthalene, and perfluorobiphenyl

$Cp_2^*ZrH_2$ reacts with perfluorotoluene (one equivalent) in cyclohexane-d_{12} at room temperature over 3 days to give Cp_2^*ZrHF and $p\text{-}CF_3C_6F_4H$ in 1.3:1 ratio. Only small amounts of $Cp_2^*Zr(p\text{-}C_6F_4CF_3)H$ (~4%) and $Cp_2^*ZrF_2$ (~4%) were observed (Scheme 1).

Reaction of perfluoronaphthalene (five equivalents) with $Cp_2^*ZrH_2$ at 85 °C over 1.5 h affords a mixture of $Cp_2^*Zr(C_{10}F_7)H$ [16], heptafluoronaphthalene, Cp_2^*ZrHF, and a small amount (< 10%) of $Cp_2^*ZrF_2$. Formation of free arene was favored in this case to



Scheme 1. Distribution of products in reactions of $Cp^*_2ZrH_2$ with fluorinated arenes. Percents given in parenthesis are based on total zirconium. Small amounts (1–10%) of $Cp^*_2ZrF_2$ are also formed in these reactions (not shown).

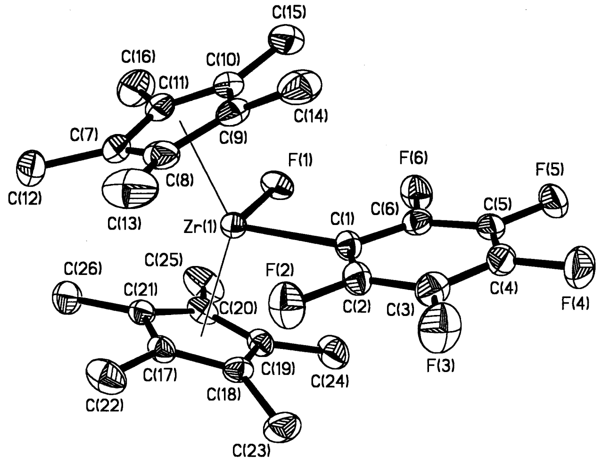


Fig. 1. ORTEP drawing of $Cp^*_2Zr(C_6F_5)F$ showing the perfluoroaryl group lying in the wedge of the Cp^*_2Zr moiety (twist = 4.5°), thermal ellipsoids are shown at the 30% level; $d_{Zr\text{-}F(1)} = 1.95$ Å; $d_{Zr\text{-}C(1)} = 2.35$ Å; $d_{Zr\text{-}F(2)} = 3.47$ Å; $\angle$ Cp*–Zr–Cp* = 139.6°.

produce heptafluoronaphthalene and $Cp^*_2Zr(C_{10}F_7)H$ in ~2.3:1 ratio (Scheme 1).

Reaction of perfluorobiphenyl (ten equivalents) with $Cp^*_2ZrH_2$ at 85 °C over 20 h affords a mixture of Cp^*_2ZrHF, $Cp^*_2Zr(p\text{-}C_6F_4\text{-}C_6F_5)H$, $p\text{-}C_6F_5\text{-}C_6F_4H$, and a small amount (< 10%) of $Cp^*_2ZrF_2$. For this substrate, free fluoroarene was favored to produce nonafluorobiphenyl and $Cp^*_2Zr(p\text{-}C_6F_4\text{-}C_6F_5)H$ in ~1.8:1 ratio (Scheme 1).

2.4. Reaction profile and kinetic studies

The reaction of $Cp^*_2ZrH_2$ with C_6F_6 was monitored by ^{19}F-NMR spectroscopy over the course of the reaction at 85 °C [17]. As shown in Fig. 2, C_6F_5H and $Cp^*_2Zr(C_6F_5)H$ are formed at approximately the same rate throughout the course of the reaction with concomitant formation of two equivalents of Cp^*_2ZrHF. It, therefore, appeared that C_6F_5H and $Cp^*_2Zr(C_6F_5)H$ could be formed together from a common intermediate. The reactions of $Cp^*_2ZrH_2$ with perfluorotoluene, per-

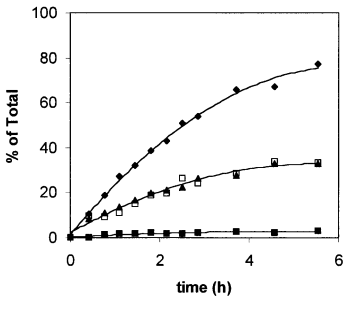


Fig. 2. Reaction profile for reaction of $Cp^*_2ZrH_2$ (0.06 M) and C_6F_6 (1.2 M) at 85 °C in C_6D_{12} solvent; ◆ = Cp^*_2ZrHF; ▲ = $Cp^*_2Zr(C_6F_5)H$; □ = C_6F_5H; ■ = $Cp^*_2ZrF_2$.

fluoronaphthalene, and perfluorobiphenyl, however, give preferentially free arene and less $Cp^*_2Zr(Ar^F)H$, suggesting that dual mechanisms are involved in the formation of these two types of products rather than a mechanism that requires a 1:1 stoichiometry. In the reaction with C_6F_6, the identical rates of formation of these two products could, therefore, be mere coincidence.

The reaction profile with C_6F_6 also implies that $Cp^*_2Zr(C_6F_5)H$ is not formed from a secondary reaction of $Cp^*_2ZrH_2$ with C_6F_5H. Additional support for this conclusion is seen in the loss of selectivity in the reaction of $Cp^*_2ZrH_2$ with C_6F_5H to give several doubly hydrodefluorinated aromatic products along with $Cp^*_2Zr(C_6F_5)H$ (Scheme 1). None of these $C_6F_4H_2$ products are observed in the reaction with C_6F_6 (vide supra).

Kinetic studies were performed to measure the concentration dependence and order of the rate of the reaction on $[C_6F_6]$. For a solution containing 0.055 M $Cp^*_2ZrH_2$ and excess C_6F_6 (0.55–2.20 M), plots of $\ln[Cp^*_2ZrH_2]$ versus time were linear (Fig. 3) and the pseudo-first order rate constants (k_{obs}) were obtained from the slopes (Table 1) [17]. The C_6F_6 concentration dependence is not quite first order, as doubling the concentration of C_6F_6 did not cause a doubling of the rate. The order with respect to $[C_6F_6]$ was determined by plotting a graph of $\ln k_{obs}$ versus $\ln[C_6F_6]$, where $k_{obs} = k \cdot [C_6F_6]^n$ (Fig. 4). The slope of the line, n, equals the kinetic order, and was calculated to be ~ 0.7, giving the overall rate equation, rate $= k[Cp^*_2ZrH_2][C_6F_6]^{0.7}$.

The apparent first order dependence of the rate on $[Cp^*_2ZrH_2]$ was verified. For solutions containing 1.24 M C_6F_6, three separate reactions were run with different $Cp^*_2ZrH_2$ concentrations (0.031–0.126 M). First-order plots of $\ln[Cp^*_2ZrH_2]$ versus time are linear (Fig. 5), and give observed rate constants of 0.011 ± 0.002 min^{-1} [17].

The results of the kinetic studies are almost but not exactly consistent with a bimolecular reaction between $Cp^*_2ZrH_2$ and C_6F_6. It is quite possible that the true order in $[C_6F_6]$ is 1.0, and that the apparent deviation from unity is due to the fact that the nature of the solvent changes considerably as C_6F_6 concentration increases (2.20 M = 25% C_6F_6 by volume). It is possible that the activity of C_6F_6 does not double as its concentration is doubled, giving rise to the fractional order in $[C_6F_6]$.

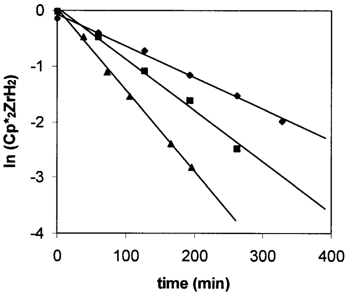


Fig. 3. Graph of $\ln[Cp^*_2ZrH_2]$ vs. time for 0.055 M $Cp^*_2ZrH_2$ and ◆ = 0.55 M C_6F_6; ■ = 1.10 M C_6F_6; ▲ = 2.20 M C_6F_6 in C_6D_{12} at 85 °C.

Table 1
Pseudo-first order rate constants for the reaction of $Cp^*_2ZrH_2$ (0.055 M) with excess C_6F_6 at 85 °C

$[C_6F_6]$ (M)	k_{obs} (s^{-1})
0.55	$9.5(4) \times 10^{-5}$
1.10	$1.5(1) \times 10^{-4}$
2.20	$2.4(1) \times 10^{-4}$

Errors are shown as standard deviations (S.D.).

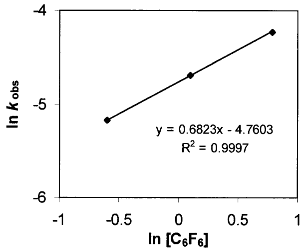


Fig. 4. Graph of $\ln k_{obs}$ vs. $\ln[C_6F_6]$ for reactions in C_6D_{12} at 85 °C.

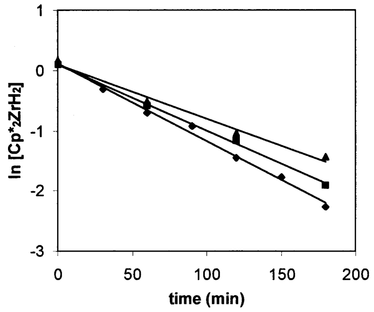


Fig. 5. Graph of $\ln[Cp^*_2ZrH_2]$ vs. time for 1.24 M C_6F_6 and ■ = 0.031 M; ▲ = 0.063 M; ◆ = 0.126 M $Cp^*_2ZrH_2$ in C_6D_{12} at 85 °C.

The reaction of $Cp^*_2ZrH_2$ with C_6F_6 was performed in the presence of radical traps, 9,10-dihydroanthracene and triphenylmethane to test for the possibility of a radical chain mechanism. In all cases, no decrease in rate was observed (Fig. 6), no change in the ratios of the products was observed, and no other products were detected [17]. Also, no decrease in rate was observed when the reaction was performed in cumene solvent. These observations suggest that free $Ar^{F\bullet}$ radicals are not involved in this chemistry. When the reaction was performed in the presence of sodium and naphthalene (a radical initiator), no increase in rate was observed. Addition of a small amount of 1-fluorohexane to the reaction mixture was also ineffective for initiation of the reaction [10]. Finally, addition of H_2 (1.3 atm) to the reaction mixture had no effect on the rate.

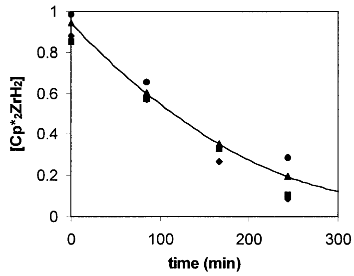


Fig. 6. Graph of [$Cp^*_2ZrH_2$] vs. time for 0.037 M $Cp^*_2ZrH_2$ and 0.73 M C_6F_6 in C_6D_{12} at 85 °C in the presence of radical inhibitors and sodium naphthalene. ◆ = C_6F_6 only; ▲ = 0.19 M triphenylmethane; ■ = 0.19 M 9,10-dihydroanthracene; ● = 5 mol% sodium and naphthalene.

2.5. *Mechanism of C_6F_5H formation*

A possible mechanism to explain the formation of C_6F_5H in the reaction with C_6F_6 involves nucleophilic hydridic attack on the arene followed by fluoride elimination to form Cp^*_2ZrHF (Fig. 7). This S_NAr2 pathway is supported by the known hydridic nature of $Cp^*_2ZrH_2$ [18] and the reactivity of C_6F_6 toward nucleophilic attack [1]. This pathway is also supported by the observation of increased reactivity with perfluoronaphthalene in comparison with C_6F_6. As in the reactions of $Cp^*_2ZrH_2$ with monofluorobenzene and monofluoronaphthalene [10], the decreased loss in resonance energy in the carbanionic intermediate-transition state may account for the increased reactivity for the fused-ring system. Similarly, the reaction of $Cp^*_2ZrH_2$ and C_6F_5H to give *o*-$C_6F_4H_2$ and *p*-$C_6F_4H_2$ could also occur by the hydridic attack mechanism.

Several other mechanisms for the formation of C_6F_5H were discounted. First, a radical chain mechanism is inconsistent with the observation that there is no effect on the rate or distribution of products by radical inhibitors or initiators. Second, the reaction of $Cp^*_2Zr(C_6F_5)F$ or $Cp^*_2Zr(C_6F_5)H$ with H_2 does not occur to give C_6F_5H under the same reaction conditions. Third, the possibility of a [$Cp^*_2Zr^{II}$] intermediate in the formation of C_6F_5H is also unlikely as no reaction was observed with $[Cp^*_2Zr]_2(N_2)_3$ and C_6F_6 at room temperature. Heating this mixture to 85 °C did not give C–F activated products, but rather formed $Cp^*_2ZrH_2$ and other unidentified species by an undetermined mechanism.

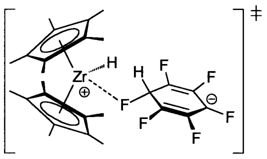
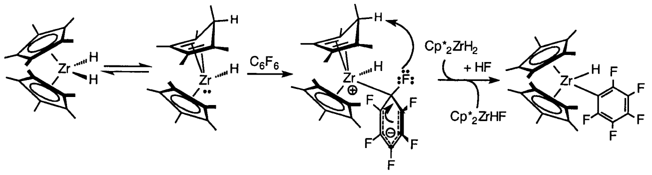


Fig. 7. Possible intermediate-transition state leading to formation of C_6F_5H and Cp^*_2ZrHF.

2.6. *Mechanism of $Cp^*_2Zr(C_6F_5)H$ formation*

Several mechanisms for the formation of $Cp^*_2Zr(C_6F_5)H$ can be immediately ruled out. First, conproportionation of $Cp^*_2Zr(C_6F_5)F$ and $Cp^*_2ZrH_2$ at 85 °C did not produce $Cp^*_2Zr(C_6F_5)H$. Second, a radical mechanism is unlikely as no effect was observed by the radical inhibitors or initiators. Third, a 'metathesis' of $Cp^*_2ZrH_2$ and C_6F_6 to form Zr–Aryl^F and H–F bonds via a 4-centered transition state is unlikely as the polarizations of the bonds, $^{\delta+}Zr\text{–}H^{\delta-}$ and $^{\delta+}C\text{–}F^{\delta-}$, are incompatible.

One mechanism which could lead to formation of $Cp^*_2Zr(C_6F_5)H$ involves an initial reversible metal-to-ring hydride transfer to form the Zr^{II} intermediate, $Cp^*(C_5Me_5H)ZrH$ (Eq. (3)). This Zr^{II} intermediate could quickly undergo nucleophilic attack on C_6F_6 to displace fluoride ion and form the Zr–Aryl^F bond. The fluoride ion could then deprotonate the diene ligand to form $Cp^*_2Zr(C_6F_5)H$ and HF. HF would quickly react with $Cp^*_2ZrH_2$ to give Cp^*_2ZrHF and H_2. This mechanism accounts for the observed products, although it is not clear why a C–F activation reaction with $[Cp^*_2Zr]_2(N_2)_3$ is not observed if a Zr^{II} intermediate is involved (vide supra).



(3)

It is known that all of the Cp*-methyl protons of $Cp^*_2ZrH_2$ are exchanged in the presence of H_2 [18]. The proposed mechanism for this exchange involves a metal-to-ring hydride transfer to form the Zr^{II} intermediate, $Cp^*(C_5Me_5H)ZrH$, as proposed in the mechanism above. It might be expected, however, that HF would not react selectively with $Cp^*_2ZrH_2$ to form Cp^*_2ZrHF, as formation of some $Cp^*_2Zr(C_6F_5)F$ might be expected by reaction of HF with $Cp^*_2Zr(C_6F_5)H$. In an independent experiment, a limiting amount of 0.12 M HF (70:30 w/w HF:pyridine) in pentane was added to a dilute solution of $Cp^*_2ZrH_2$ (0.002 M) and $Cp^*_2Zr(C_6F_5)H$ (0.002 M) in pentane in a polyethylene reaction vessel. A mixture of products including $Cp^*_2Zr(C_6F_5)F$, Cp^*_2ZrHF, $Cp^*_2ZrF_2$, and small amounts of other unidentified species were observed, suggesting that HF does not react selectively with $Cp^*_2ZrH_2$. This distribution of products, however, may be due to the fact that HF–pyridine is different than free HF, and it was found in an independent experiment that pyridine itself reacts with $Cp^*_2ZrH_2$ to give unidentified products. High local concentrations of HF are also undoubtedly present during the addition of HF–pyridine to the independently prepared mixture of $Cp^*_2ZrH_2$ and $Cp^*_2Zr(C_6F_5)H$, and this might also account for the loss in selectivity that might otherwise be observed.

An alternative mechanism which leads to $Cp^*_2Zr(C_6F_5)H$ is homolytic C–F cleavage of C_6F_6 by a 'hydrogen-depleted' dimer, such as the Zr^{III} diradical, $[Cp^*_2Zr]_2(H)(\mu\text{-}H)$ or $[Cp^*_2Zr(\mu\text{-}H)]_2$ (Fig. 8). This mechanism would also account for the inability to trap free $C_6F_5^\bullet$ radicals. The involvement of a dimeric species has been proposed in the reaction of $[Cp_2ZrH_2]_2$ with diphenylacetylene, primarily because the dominant form of the Cp analog is the dimer [19]. The dimeric form of $Cp^*_2ZrH_2$, however, has not been observed. It might be possible that loss of H_2 from the dimer is induced by C_6F_6 in a fast termolecular step prior to homolysis of the C–F bond, although the kinetic studies appear inconsistent with this proposal.

Other zirconocene complexes, $(C_5Me_4H)_2ZrH_2$ [20] and $Me_2Si(C_5Me_4)_2ZrH_2$ [21], which exist as a monomer–dimer equilibrium in solution at room temperature were examined to broaden the scope of this reaction and to test the possibility of a reactive dimeric intermediate. Both of these complexes reacted with C_6F_6 under more mild conditions to give analogous products. Specifically, reaction of $(C_5Me_4H)_2ZrH_2$ with C_6F_6 (20 equivalents) at room temperature afforded $(C_5Me_4H)_2Zr(C_6F_5)H$, C_6F_5H, $(C_5Me_4H)_2Zr(o\text{-}C_6F_4H)H$, $(C_5Me_4H)_2ZrHF$ and $(C_5Me_4H)_2ZrF_2$ in 1:1.1:0.6:3.1:0.3 ratio. Reaction of $(C_5Me_4H)_2ZrH_2$ with C_6F_5H (ten equivalents) produced $(C_5Me_4H)_2ZrHF$, $(C_5Me_4H)_2Zr(o\text{-}C_6F_4H)H$ in ~1.4:2.6 ratio and ~10% $(C_5Me_4H)_2Zr(C_6F_5)H$.

The reaction of $Me_2Si(C_5Me_4)_2ZrH_2$ with C_6F_6 (ten equivalents) also occurred at room temperature to afford $Me_2Si(C_5Me_4)_2ZrHF$, $Me_2Si(C_5Me_4)_2Zr(C_6F_5)H$, and $Me_2Si(C_5Me_4)_2Zr(o\text{-}C_6F_4H)H$ in 4.5:1.8:1 ratio along with H_2 and a small amount ($<$ 10%) of other unidentified species. Only traces of C_6F_5H could be detected in this reaction. Although an increase in the rate of reaction of $(C_5Me_4H)_2ZrH_2$ and $Me_2Si(C_5Me_4)_2ZrH_2$ with C_6F_6 might suggest the involvement of a dimeric species, the increased electrophilicity of both of these substrates in comparison with $Cp^*_2ZrH_2$ might also explain the increased reactivity.

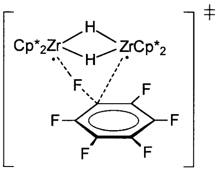


Fig. 8. Possible transition state leading to formation of Cp^*_2ZrHF and $Cp^*_2Zr(Ar^F)H$.

3. Conclusion

Reaction of $Cp^*_2ZrH_2$ with hexafluorobenzene produces a mixture of Cp^*_2ZrHF, C_6F_5H, and $Cp^*_2Zr(C_6F_5)H$ by dual mechanisms. Radical initiators and inhibitors had no effect on the rate of reaction or distribution of products. A nucleophilic hydride attack on C_6F_6 followed by fluoride elimination is proposed to explain the formation of C_6F_5H and one equivalent of Cp^*_2ZrHF. The formation of $Cp^*_2Zr(C_6F_5)H$ and the second equivalent of Cp^*_2ZrHF is difficult to explain. A metal-to-ring hydride transfer followed by attack on the $Aryl^F$ ring by the zirconium nucleophile would generate a zwitterionic intermediate. Elimination of fluoride ion and subsequent deprotonation of the diene ligand produces $Cp^*_2Zr(C_6F_5)H$ and HF. HF could then react with an additional equivalent of $Cp^*_2ZrH_2$ to give Cp^*_2ZrHF and H_2. An alternative mechanism proposed for formation of $Cp^*_2Zr(C_6F_5)H$ involves homolytic cleavage of a C–F bond of C_6F_6 by a hydrogen-depleted dimer such as $(Cp^*_2ZrH)_2$.

4. Experimental

All manipulations were performed inside an N_2-filled Vacuum Atmospheres glovebox or on a high vacuum line. Cyclohexane and cyclohexane-d_{12} were dried and vacuum distilled from purple solutions of benzophenone ketyl. UHP grade H_2 (air products) was purified by passage over activated 4 Å molecular sieves and MnO on vermiculite. Hexafluorobenzene, pentafluorobenzene, perfluorotoluene, perfluoronaphthalene, and perfluorobiphenyl were purchased from Aldrich and used as received. ^1H and ^{19}F-NMR spectra were recorded using a Bruker Avance400 spectrometer. ^{19}F-NMR spectra were referenced to α,α,α-trifluorotoluene (taken as δ −63.73 relative to $CFCl_3$ with down-field chemical shifts taken to be positive). GC–MS analyses were conducted using a 5890A Series GC equipped with a Restek RTX-5 column (0.25 mm ID, 0.25 μm, 13 m) and a HP 5970 series mass selective detector. $Cp^*_2ZrH_2$ [22], $Me_2Si(C_5Me_4)_2ZrH_2$ [21], and $(C_5Me_4H)_2ZrH_2$ [20] were prepared according to the literature procedures.

4.1. *Reaction of hexafluorobenzene with $Cp^*_2ZrH_2$*

A sealable NMR tube was charged with 14 mg (0.038 mmol) of $Cp^*_2ZrH_2$ and dissolved in cyclohexane-d_{12}. Hexafluorobenzene (89 μl, 0.77 mmol, $d = 1.61$) was added via syringe. On the vacuum line, the solution was freeze–pump–thaw–degassed three times and sealed under vacuum. The tube was heated at 85 °C for 8 h upon which all $Cp^*_2ZrH_2$ had reacted. The reaction mixture consisted of a 2:1:1 mixture of Cp^*_2ZrHF, $Cp^*_2Zr(C_6F_5)H$, and C_6F_5H. No H_2 was observed in the ^{1}H-NMR spectrum. For $\mathrm{Cp^*_2ZrHF}$: ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 1.92 (s, 30H, Cp*), 6.23 (s, 1H, $\mathrm{Zr}\mathit{H}\mathrm{F}$). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ 77.67 (s, 1F). For $\mathrm{Cp^*_2Zr(C_6F_5)H}$: ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 1.88 (s, 30H, Cp*), 7.71 (dd, 1H, $\mathrm{Zr(C_6F_5)}\mathit{H}$). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −116.3 (m, 1F), −117.7 (m, 1F), −155.2 (t, 1F), −160.2 (m, 1F), −161.9 (m, 1F). For $\mathrm{C_6F_5H}$: ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 6.74 (m, 1H). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −140.3 (m, 2F), −155.3 (t, 1F), −163.8 (m, 2F).

4.2. Reaction of pentafluorobenzene with $\mathrm{Cp^*_2ZrH_2}$

In a resealable NMR tube, 15 mg (0.041 mmol) $\mathrm{Cp^*_2ZrH_2}$ was dissolved in cyclohexane-d_{12} followed by addition of 90 µl (0.81 mmol, $d = 1.514$) of pentafluorobenzene. Hydrogen (1.3 atm) was placed over the reaction mixture and the sample was heated at 85 °C for 6 h. A mixture of $\mathrm{Cp^*_2ZrHF}$, $\mathrm{Cp^*_2Zr(}o\mathrm{\text{-}C_6F_4H)H}$, $\mathrm{Cp^*_2Zr(C_6F_5)H}$, o-$\mathrm{C_6F_4H_2}$, p-$\mathrm{C_6F_4H_2}$, and $\mathrm{Cp^*_2ZrF_2}$ formed in 3:2:1:0.6:0.46:0.2 ratio. For $\mathrm{Cp^*_2Zr(}o\mathrm{\text{-}C_6F_4H)H}$, ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 1.847 (s, 30H, Cp*), 5.98 (m, 1H, $\mathrm{Zr{-}C_6F_4}\mathit{H}$), 6.83 (br, 1H, $\mathrm{Zr}\mathit{H}$). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −118.1 (m, 1F), −139.8 (m, 1F), −157.4 (m, 1F), −159.0 (m, 1F). For o-$\mathrm{C_6F_4H_2}$, ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 6.88 (m). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −139.0 (m, 2F), −155.5 (m, 2F). For p-$\mathrm{C_6F_4H_2}$: ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 6.89 (m). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −138.7 (m). The ^{1}H and ^{19}F-NMR resonances of o-$\mathrm{C_6F_4H_2}$, and p-$\mathrm{C_6F_4H_2}$ were verified by comparison with authentic samples.

4.3. Reaction of perfluorotoluene with $\mathrm{Cp^*_2ZrH_2}$

In a resealable NMR tube, 10 mg (0.027 mmol) $\mathrm{Cp^*_2ZrH_2}$ was dissolved in cyclohexane-d_{12} followed by addition of 3.90 µl (0.027 mmol, $d = 1.666$) of perfluorotoluene. The reaction mixture was allowed to stand at room temperature (r.t.) for 3 days consuming all $\mathrm{Cp^*_2ZrH_2}$. $\mathrm{Cp^*_2ZrHF}$, p-$\mathrm{CF_3C_6F_4H}$, $\mathrm{Cp^*_2Zr(}p\mathrm{\text{-}C_6F_4CF_3)H}$, $\mathrm{Cp^*_2ZrF_2}$ were observed in 14:11:1:1 ratio. For p-$\mathrm{CF_3C_6F_4H}$, ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 7.09 (m, 1H). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −56.77 (m, 3F), −136.3 (m, 2F), −139.6 (m, 2F). GC–MS (m/z): 218 [M$^+$]. For $\mathrm{Cp^*_2Zr(}p\mathrm{\text{-}C_6F_4CF_3)H}$: ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 1.88 (s, 30H), 7.55 (dd, 1H). ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −56.3 (m, 3F), −118.6 (m, 1F), −117.4 (m, 1F), −140.8 (m, 1F), −143.23 (m, 1F).

4.4. Reaction of perfluoronaphthalene with $\mathrm{Cp^*_2ZrH_2}$

In a resealable NMR tube, 12 mg (0.033 mmol) of $\mathrm{Cp^*_2ZrH_2}$ and 45 mg (0.16 mmol) of perfluoronaphthalene were dissolved in cyclohexane-d_{12}. The tube was heated in a thermostatted 85 °C oil bath for 1.5 h forming $\mathrm{Cp^*_2ZrHF}$, heptafluoronaphthalene, and $\mathrm{Cp^*_2Zr(C_{10}F_7)H}$ [16]. For $\mathrm{Cp^*_2Zr(C_{10}F_7)H}$ (two rotomers or isomers), ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 7.75 (dd, $\mathrm{Cp^*_2Zr(C_{10}F_7)}\mathit{H}$), 7.59 (dd, $\mathrm{Cp^*_2Zr(C_{10}F_7)}\mathit{H'}$). The Cp* methyl resonances were overlapping due to the presence of excess perfluoronaphthalene. ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −100.2 (dm, Zr-o-Ar$^\mathrm{F}$), −112.2 (dm, Zr-o-Ar$^\mathrm{F}$). Other ^{19}F resonances of could not be assigned unambiguously. For 2-H-heptafluoronaphthalene, ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 7.01 (m, $\mathrm{C_{10}F_7H}$). ^{19}F-NMR: δ −116.2 (dm, 1F), −134.1 (m, 1F), −144.3 (dt, 1F), −146.1 (dt, 1F), −149.3 (dtd, 1F), −153.6 (t, 1F), −156.5 (m, 1F). MS: 254 ([M$^+$], $\mathrm{C_{10}F_7H}$). The chemical shifts for 2-H-heptafluoronaphthalene match those previously reported [23].

4.5. Reaction of perfluorobiphenyl with $\mathrm{Cp^*_2ZrH_2}$

In a resealable NMR tube, 10 mg (0.027 mmol) of $\mathrm{Cp^*_2ZrH_2}$ and 92 mg (0.27 mmol) of perfluorobiphenyl were dissolved in cyclohexane-d_{12}. The tube was heated in a thermostatted 85 °C oil bath for 20 h forming $\mathrm{Cp^*_2ZrHF}$, p-$\mathrm{C_6F_5{-}C_6F_4H}$, $\mathrm{Cp^*_2Zr(C_6F_4{-}C_6F_5)H}$, and $\mathrm{Cp^*_2ZrF_2}$. For $\mathrm{Cp^*_2Zr(C_6F_4{-}C_6F_5)H}$: ^{1}H-NMR ($\mathrm{C_6D_{12}}$): δ 7.75 (dd, $\mathrm{Cp^*_2Zr(C_{12}F_9)}\mathit{H}$), 1.91 (s, Cp*). The Cp* methyl resonances were overlapping due to the presence of excess perfluorobiphenyl. ^{19}F-NMR ($\mathrm{C_6D_{12}}$): δ −118.2 (m, 1F, Zr-o-Ar$^\mathrm{F}$), −118.8 (m, 1F, Zr-o-Ar$^\mathrm{F}$), −140.3 (m, 1F), −142.4 (m, 1F), −154.3 (t, 1F), −163.3 (m, 2F), −161.3 (2F, obscured). For p-$\mathrm{C_6F_5{-}C_6F_4H}$: ^{1}H-NMR: ($\mathrm{C_6D_{12}}$): δ 7.09 (m). ^{19}F-NMR: δ −137.9 (m, 2F), −138.7 (m, 2F), −138.8 (m, 2F), −151.5 (t, 1F), −161.6 (m, 2F), MS: 316 [M$^+$].

4.6. Kinetics for reaction of $\mathrm{Cp^*_2ZrH_2}$ with $\mathrm{C_6F_6}$

For [$\mathrm{C_6F_6}$] dependence: In the drybox, 240 µl of a 0.137 M stock cyclohexane-d_{12} solution of $\mathrm{Cp^*_2ZrH_2}$ containing 0.023 M α,α,α-trifluorotoluene standard was syringed into resealable NMR tubes. Hexafluorobenzene (38, 76, or 152 µl) was added with a microliter syringe and the total volume was brought to 0.600 ml. The tubes were heated side-by-side in a thermostatted 85 °C oil bath and analyzed periodically by ^{19}F-NMR spectroscopy. For [$\mathrm{Cp^*_2ZrH_2}$] dependence: Into resealable NMR tubes, 150, 300, and 600 µl of a 0.147 M stock cyclohexane-d_{12} solution of $\mathrm{Cp^*_2ZrH_2}$ containing 0.025 M α,α,α-trifluorotoluene standard was added with a syringe. Hexafluorobenzene (100 µl, 0.87 mmol) was added with a microliter syringe and the total volume was brought to 0.700 ml. The tubes were heated side-by-side in a thermostatted 85 °C oil bath and analyzed periodically by ^{19}F-NMR spectroscopy.

4.7. Reaction of $\mathrm{Cp^*_2ZrH_2}$ and $\mathrm{Cp^*_2Zr(C_6F_5)H}$ with HF–pyridine

Into a polyethylene reaction vessel, 15 mg $\mathrm{Cp^*_2ZrH_2}$ (0.041 mmol) and 22 mg $\mathrm{Cp^*_2Zr(C_6F_5)H}$ (0.041 mmol) were added and dissolved in 25 ml of pentane. A 0.12 M solution of HF was prepared by adding 0.085 g of 70:30 HF–pyridine solution to 24 ml of pentane in another polyethylene vessel. To the solution of zirconium complexes, 0.33 ml of the dilute HF–pyridine solution was added at r.t. with stirring. The pentane was removed under vacuum and the residue was analyzed by NMR spectroscopy in C_6D_{12}. A mixture of $Cp^*_2Zr(C_6F_5)F$, Cp^*_2ZrHF, $Cp^*_2ZrF_2$, and other species were detected.

4.8. Preparation of $Cp^*_2Zr(C_6F_5)F$

In a polyethylene vial, 60 mg $Cp^*_2Zr(C_6F_5)H$ was dissolved in 0.5 ml pentane and four drops of 70:30 HF–pyridine was added with stirring. Evolution of H_2 was observed and the solution became colorless. The solution was transferred to a glass vial to neutralize excess HF and the volatiles were removed in vacuo. Pentane was added, and the solution was filtered through a glass fiber filter. Concentration and cooling to −30 °C gave white crystals (40 mg, 64%). ^{1}H-NMR (C_6D_{12}): δ 1.806 (s, Cp*). ^{19}F-NMR (C_6D_{12}): δ 113.5 (d, $J = 44$ Hz, 1F, Zr–F), −111.6 (m, 1F), −111.1 (m, 1F), −155.3 (t, 1F), −160.1 (m, 1F), −162.5 (m, 1F). Anal. Calc. for $C_{26}H_{30}F_6Zr$: C, 57.01; H, 5.52. Found: C, 56.74; H, 5.39%.

4.9. Reaction of $(C_5Me_4H)_2ZrH_2$ with C_6F_6

A resealable NMR tube was charged with 10 mg (0.030 mmol) of $(C_5Me_4H)_2ZrH_2$ and dissolved in cyclohexane-d_{12}. Hexafluorobenzene (69 μl, 0.60 mmol, $d = 1.61$) was added via syringe and the tube was allowed to stand at r.t. for 2 days. The reaction mixture consisted of a mixture of $(C_5Me_4H)_2Zr(C_6F_5)H$, C_6F_5H, $(C_5Me_4H)_2Zr(o\text{-}C_6F_4H)H$, $(C_5Me_4H)_2ZrHF$ and $(C_5Me_4H)_2ZrF_2$ in 1:1.1:0.6:3.1:0.3 ratio. For $(C_5Me_4H)_2ZrHF$: ^{1}H-NMR (C_6D_{12}): δ 6.04 (s, 1H, Zr*H*F), 5.17 (s, 2H, C_5Me_4H), 2.11 (s, 6H), 1.99 (s, 6H), 1.96 (s, 6H), 1.81 (s, 6H). ^{19}F-NMR: δ 72.6 (s). For $(C_5Me_4H)_2Zr(C_6F_5)H$: ^{1}H-NMR (C_6D_{12}): δ 7.40 (dd, 1H, Zr*H*(C_6F_5), 5.25 (s, 2H, C_5Me_4H), 2.06 (s, 6H), 1.99 (s, 6H), 1.91 (s, 6H), 1.77 (s, 6H). ^{19}F-NMR: δ −118.0 (d, 1F), −120.3 (m, 1F), −155.9 (t, 1F), −161.2 (m, 1F), −162.4 (m, 1F). For $(C_5Me_4H)_2Zr(o\text{-}C_6F_4H)H$: ^{1}H-NMR ($C_6D_{12}$): δ 6.63 (s, 1H, Zr*H*), 6.04 (m, 1H, Ar^FH), 5.31 (s, 2H, C_5Me_4H), 2.00 (s, 6H), 1.97 (s, 6H), 1.91 (s, 6H), 1.65 (s, 6H). ^{19}F-NMR: δ −118.7 (m, 1F), −140.4 (t, 1F), −157.7 (m, 1F), −159.3 (m, 1F).

4.10. Reaction of $Me_2Si(C_5Me_4)_2ZrH_2$ with C_6F_6

A resealable NMR tube was charged with 5 mg (0.013 mmol) of $Me_2Si(C_5Me_4)_2ZrH_2$ and suspended in cyclohexane-d_{12}. Hexafluorobenzene (14.7 μl, 0.13 mmol, $d = 1.61$) was added via syringe and the tube was stirred at r.t. for 18 h. The reaction mixture consisted of a mixture of $Me_2Si(C_5Me_4)_2ZrHF$, $Me_2Si(C_5Me_4)_2Zr(C_6F_5)H$, and $Me_2Si(C_5Me_4)Zr(o\text{-}C_6F_4H)H$ in 4.5:1.8:1 ratio. A small amount of $Me_2Si(C_5Me_4)_2ZrF_2$ and other unidentified species were also detected. A total of eight Cp-methyl resonances were observed in the ^{1}H-NMR spectrum, but could not be assigned. For $Me_2Si(C_5Me_4)_2ZrHF$: ^{1}H-NMR (C_6D_{12}): δ 5.53 (s, 1H, Zr*H*), 0.72 (s, 6H, Me_2Si). ^{19}F-NMR: δ 75.6 (s). For $Me_2Si(C_5Me_4)_2Zr(C_6F_5)H$: ^{1}H-NMR ($C_6D_{12}$): δ 6.61 (dd, 1H, Zr*H*), 0.82 (s, 6H, Me_2Si). ^{19}F-NMR: δ −119.2 (m, 1F), −121.1 (m, 1F), −155.1 (t, 1F), −160.8 (m, 1F), −161.7 (m, 1F). For $Me_2Si(C_5Me_4)Zr(o\text{-}C_6F_4H)H$: ^{1}H-NMR ($C_6D_{12}$): δ 6.14 (tm, 1H, Ar^FH), 6.03 (s, 1H, Zr*H*), 0.77 (s, 6H, Me_2Si). ^{19}F-NMR: δ −118.8 (m, 1F), −139.7 (m, 1F), −156.6 (m, 1F), −158.2 (m, 1F).

4.11. Reaction of $(Me_2Si(C_5H_4)_2ZrH_2)_2$ with C_6F_6

A resealable NMR tube was charged with 12 mg (0.043 mmol) of $(Me_2Si(C_5H_4)_2ZrH_2)_2$ and suspended in THF-d_8. Hexafluorobenzene (119 μl, 1.03 mmol, $d = 1.61$) was added via syringe and the tube was heated at 85 °C for 10 min upon which the solution evolved H_2 and became homogeneous. The reaction mixture consisted of $Me_2Si(C_5H_4)_2Zr(C_6F_5)F$, C_6F_5H, and $Me_2Si(C_5H_4)_2ZrF_2$ in 3.5:1:1 ratio by NMR integration. For $Me_2Si(C_5H_4)_2Zr(C_6F_5)F$: ^{1}H-NMR (THF-$d_8$): δ 0.91 (s, 3H, Me_2Si), 0.78 (s, 3H, Me_2Si), 5.78 (m, 2H), 6.40 (m, 2H), 6.45 (m, 2H), 6.99 (m, 2H). ^{19}F-NMR (THF-d_8): δ 99.3 (brs, 1F), −114.4 (m, 2F), −158.8 (t, 1F), −164.2 (m, 2F). For $Me_2Si(C_5H_4)_2ZrF_2$: ^{1}H-NMR (THF-d_8): δ 0.82 (s, 6H, Me_2Si), 6.05 (m, 4H), 6.55 (m, 4H). ^{19}F-NMR: δ 30.4 (brs, 2F).

4.12. X-ray structural determination of $Cp^*_2Zr(C_6F_5)F$

A Siemens SMART CCD area detector diffractometer equipped with an LT-2 low temperature unit was used for X-ray crystal structure determination. A single crystal of $Cp^*_2Zr(C_6F_5)F$ was mounted under Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s per frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.54°) for both of the crystals. The unit cell parameters were based upon the least-squares refinement of three dimensional centroids of > 5000 reflections. Data were corrected for absorption using the

Table 2
Crystal data and structure refinement for $Cp^*_2Zr(C_6F_5)F$

Identification code	sad/jonbk17
Empirical formula	$C_{26}H_{30}F_6Zr$
Formula weight	547.72
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	15.3752(6)
b (Å)	15.6533(6)
c (Å)	20.0858(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4834.1(3)
Z	8
D_{calc} (Mg m^{-3})	1.505
Absorption coefficient (mm^{-1})	0.512
F(000)	2240
Crystal size (mm)	0.04 × 0.14 × 0.26
θ Range for data collection (°)	2.03–23.27
Limiting indices	$-17 \leq h \leq 13$, $-17 \leq k \leq 12$, $-21 \leq l \leq 22$
Reflections collected	21 054
Independent reflections	3470 [$R_{int} = 0.0634$]
Absorption correction	SADABS
Max/min transmission	0.928000, 0.799125
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3470/0/298
Goodness-of-fit on F^2	0.810
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0469$, $wR_2 = 0.1109$
R indices (all data)	$R_1 = 0.0786$, $wR_2 = 0.1298$
Largest difference peak and hole (e Å^{-3})	0.359 and −0.269

program SADABS. The space group assignment was made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structure was solved by using direct methods and refined by full-matrix least-squares on F^2. The non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions giving data:parameter ratios greater than 10:1. Table 2 contains crystallographic data.

5. Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 184938 for the compound $Cp^*_2Zr(C_6F_5)F$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[15] To our knowledge, the preference for *ortho* over *para* C–F activation of C_6F_5H is unprecedented.

[16] Two doublet of doublet resonances typical for $Cp^*_2Zr(Ar^F)H$ species were observed in the ^{1}H-NMR spectrum indicating either two geometrical isomers or two rotomers of $Cp^*_2Zr(C_{10}F_7)H$.

[17] The disappearance of $Cp^*_2ZrH_2$ could be determined only by monitoring the appearance of Cp^*_2ZrHF in the ^{19}F-NMR spectra. Overlap of the Cp* resonances in the ^{1}H-NMR spectrum prevented direct observation.

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