Formation of Tetrafluorobenzyne by β-Fluoride Elimination in Zirconium-Perfluorophenyl Complexes

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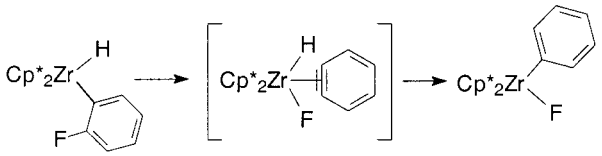
Received October 10, 2001

$Cp^*_2ZrH_2$ (Cp^* = pentamethylcyclopentadienyl) and $Hg(C_6F_5)_2$ react in pentane to form $Cp^*_2Zr(C_6F_5)H$ in high yield at room temperature. $Cp^*_2Zr(C_6F_5)H$ reacts intramolecularly at 120 °C under an atmosphere of H_2 to give $Cp^*_2Zr(o\text{-}C_6F_4H)F$ quantitatively by β-fluoride elimination and subsequent insertion of tetrafluorobenzyne into the Zr−H bond. Under vacuum, $Cp^*_2Zr(C_6F_5)H$ decomposes into a mixture of $Cp^*_2Zr(o\text{-}C_6F_4H)F$ and the ring methyl C−H activated product, $Cp^*(Fv)Zr(C_6F_5)$ (Fv = tetramethylfulvene). Upon further heating, $Cp^*(Fv)Zr(C_6F_5)$ reacts to form the novel complex $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$, formed by β-fluoride elimination and subsequent insertion of tetrafluorobenzyne into the $Zr-CH_2$ bond.

Introduction

The coordination and activation of fluorocarbons by metal reagents has been a subject of interest for many decades.[1] The high electronegativity of fluorine imparts low polarizability and weak σ-basicity to the lone pairs, making saturated fluorocarbons unable to coordinate strongly to metal centers. However, the presence of fluorine on a coordinated ligand in close proximity to a metal center may facilitate its coordination, making the C−F bond more reactive and susceptible to chemical attack. Ortho-substituted aryl fluorides are one class of compounds that have been shown, in several cases, to undergo C−F bond activation with release of benzyne. We have recently observed such reactivity in the reaction of $Cp^*_2ZrH_2$ and fluorobenzene, forming a mixture of Cp^*_2ZrHF, benzene, and $Cp^*_2Zr(C_6H_5)F$ by competing dual pathways.[2] In one pathway, Cp^*_2ZrHF and benzene form concurrently by hydride attack on the aromatic ring and fluoride abstraction by zirconium. In the second pathway, $Cp^*_2Zr(o\text{-}C_6H_4F)H$ forms by ortho C−H activation of fluorobenzene, β-fluoride elimination to form a zirconium-benzyne complex, and finally, insertion of benzyne into the Zr−H bond to give $Cp^*_2Zr(C_6H_5)F$ (eq 1).



(1)

The lanthanide complex $Sm(C_6F_5)_2$ was shown to decompose into a complex mixture of products including $Sm(C_6F_5)F$, SmF_2, $Sm(C_6F_5)F_2$, $Sm(C_6F_4\text{-}C_6F_5)F$, and organic 1H-perfluorobiphenyls and 1H-perfluoroterphenyls. The observed products were explained by β-fluoride elimination and subsequent insertion of tetrafluorobenzyne into the Sm−aryl bonds.[3] Similarly, the metallocene complexes $Cp_2M(C_6F_5)_2$ (M = Ti, Zr) have been shown to decompose with release of tetrafluorobenzyne and concomitant formation of $Cp_2M(C_6F_5)F$.[4,5] In the zirconium system, some of the tetrafluorobenzyne was trapped using durene to give a Diels−Alder adduct. In the absence of durene, tetrafluorobenzyne formed adducts with the THF solvent.[5]

Interestingly, neither Cp_2ZrHF nor $Cp_2Zr(C_6F_5)H$ has been reported in the literature, and our attempts to prepare these apparently unstable compounds by a number of methods have been unsuccessful. However, the pentamethylcyclopentadienyl analogues Cp^*_2ZrHF and $Cp^*_2Zr(C_6F_5)H$ are both stable. In this study, we describe the synthesis and intramolecular reaction modes of $Cp^*_2Zr(C_6F_5)H$.

Results and Discussion

Synthesis and Characterization of $Cp^*_2Zr(C_6F_5)H$. The reaction of $Cp^*_2ZrH_2$ with $Hg(C_6F_5)_2$ (2:1 mole ratio) at room temperature in pentane afforded $Cp^*_2Zr(C_6F_5)H$ (**1**), H_2, and elemental mercury (eq 2).

$$2\ Cp^*_2ZrH_2 + Hg(C_6F_5)_2 \xrightarrow{\text{pentane}} \underset{\mathbf{1}}{Cp^*_2Zr(C_6F_5)H} + H_2 + Hg^0 \quad (2)$$

1 is isolated as an orange solid in 95% yield by filtration of mercury and removal of the solvent. Crystallization in pentane at −30 °C yields X-ray quality crystals. The X-ray structure is shown in Figure 1,

(1) There are several recent reviews on C−F activation by metal reagents, see: (a) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 313. (b) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recl.* **1997**, *130*, 145. (c) Richmond, T. G. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer: New York, 1999; Vol. 3, p 243.

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(4) (a) Treichel, P. M.; Chaudhari, M. A. Stone, F. G. A. *J. Organomet. Chem.* **1963**, *1*, 98. (b) Chaudhari, M. A.; Treichel, P. M.; Stone, F. G. A. *J. Organomet. Chem.* **1964**, *2*, 206.

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Publication on Web 01/18/2002

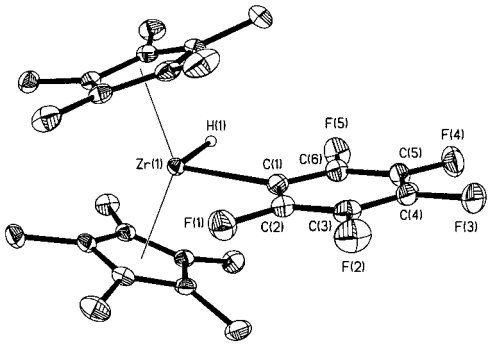


Figure 1. ORTEP drawing of $Cp^*_2Zr(C_6F_5)H$, **1**, showing 30% probability ellipsoids. The hydride ligand was located and refined.

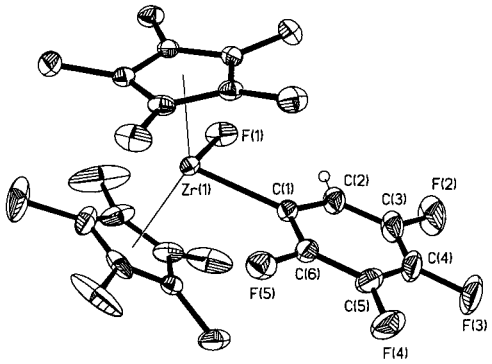
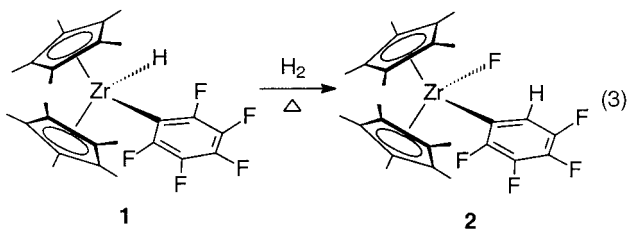


Figure 2. ORTEP drawing of $Cp^*_2Zr(o\text{-}C_6F_4H)F$, **2**, showing 30% probability ellipsoids.

showing the perfluoroaryl group lying in the wedge of the Cp^*_2Zr moiety (twist = 6.8°). The ^{19}F NMR spectrum in cyclohexane-d_{12} for **1** shows five distinct fluorine resonances, indicating hindered rotation about the Zr−aryl bond. In the ^1H NMR spectrum, the hydride resonance at δ 7.71 is a doublet of doublets, arising from coupling of the magnetically inequivalent ortho-substituted aryl fluorines. The rate of rotation of the Zr−aryl bond could not be determined, as heating **1** at 105 °C in the NMR probe in toluene-d_8 did not result in coalescense of the ^{19}F NMR resonances. Perfluoroaryl ligands attached to sufficiently bulky substituted zirconocenes generally show hindered rotation at room temperature.[6]

Thermolysis of $Cp^*_2Zr(C_6F_5)H$. Thermolysis of **1** at 100 °C for 20 days under 1.3 atm H_2 in cyclohexane-d_{12} afforded $Cp^*_2Zr(o\text{-}C_6F_4H)F$ (**2**) quantitatively (eq 3).



2 was characterized by ^1H and ^{19}F NMR spectroscopy, elemental analysis, and X-ray crystallography (Figure 2). Relevant structural details are summarized in Table 1, and the aryl group lies in the wedge of the Cp^*_2Zr moiety (twist = 0.7°). **2** was also prepared independently

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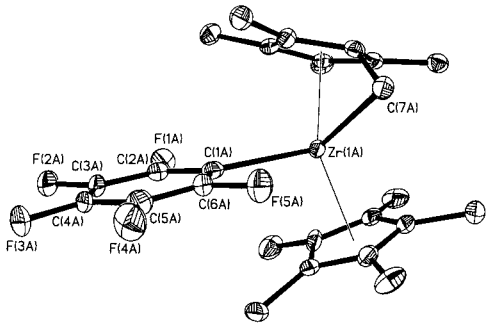


Figure 3. ORTEP drawing of $Cp^*(Fv)Zr(C_6F_5)$, **3**, showing 30% probability ellipsoids.

Table 1. Structural Parameters for Cp^*_2ZrXY Compounds

compound	∠Cp*−Zr−Cp*, deg	d_{Zr-X}, Å	d_{Zr-Y}, Å
1 X = H, Y = C_6F_5	141.4	1.90(2)	2.355(2)
2 X = F, Y = *o*-C_6F_4H	140.7	1.959(2)	2.306(3)
2a X = H, Y = *o*-C_6F_4H	142.2	2.00(5)	2.294(5)
3 X = CH_2-Cp*, Y = C_6F_5	142.8	2.371(5)	2.348(6)
4a X = Cl, Y = *o*-$C_6F_4CH_2$-Cp*	137.5	2.343(3)	2.339(6)

by reaction of $Cp^*_2Zr(o\text{-}C_6F_4H)H$ (**2a**)[7] with 70% HF in pyridine in 40% yield. The ^{19}F NMR spectrum of **2** shows four multiplets for the fluorines of the aryl group, consistent with the presence of only one rotamer or with rapid rotation around the Zr−aryl bond.

Thermolysis of **1** at 80 °C for 28 days in cyclohexane-d_{12} under vacuum produced mainly **2**, but also produced $Cp^*(Fv)Zr(C_6F_5)$ (**3**) (Fv = tetramethylfulvene), $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$ (**4**), and $Cp^*_2ZrF_2$ in ∼14:36:3:1 ratio by NMR integration. **3** was prepared independently in 56% yield by reaction of $Cp^*(Fv)ZrCl$[8] with LiC_6F_5 in diethyl ether at low temperature and is isolated as dark red crystals by crystallization from pentane at −78 °C. The X-ray structure is shown in Figure 3, with the aryl group once again lying in the Cp^*_2Zr wedge (twist = 1.0°). The ^{19}F NMR spectrum of **3** shows five magnetically inequivalent fluorine resonances, again caused by hindered rotation about the Zr−aryl bond. As before, determination of the rate of rotation could not be determined, as no indication of coalescence was observed upon heating to 105 °C in toluene-d_8. The ^1H NMR spectrum of **3** in toluene-d_8 shows seven resonances at δ 2.21, 1.87, 1.71, 1.66, 1.56, 1.33, and 1.15 in 1:1:3:15:3:3:3 ratio. The separate doublet of doublet resonances at δ 2.21 and 1.87 represent the magnetically inequivalent methylene protons. Decoupling experiments show that only one of the ortho fluorine atoms of the aryl group is coupled to the methylene protons.

Thermolysis of $Cp^*(Fv)Zr(C_6F_5)$. Thermolysis of **3** in cyclohexane-d_{12} at 120 °C for 4 days afforded $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$ (**4**) in 58% yield (by NMR integration against an internal standard) along with other

(7) $Cp^*_2Zr(o\text{-}C_6F_4H)H$ (**2a**) is prepared by reaction of $Cp^*_2ZrH_2$ with $Hg(o\text{-}C_6F_4H)_2$. See Experimental Section and Supporting Information for details and the X-ray structure.

(8) Pattiasina, J. W. Ph.D. Dissertation, University of Groningen, 1988.

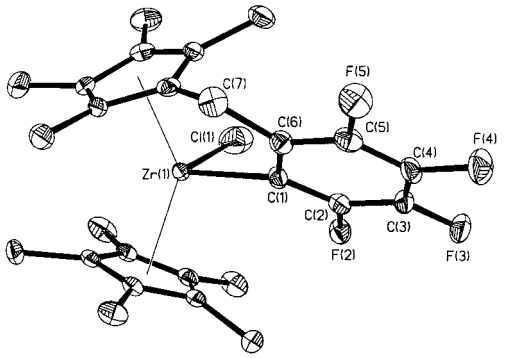
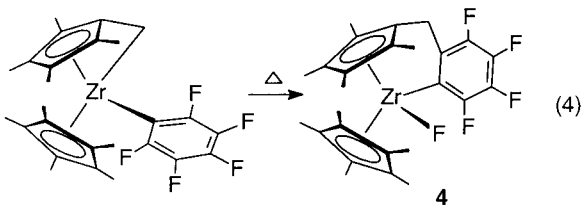


Figure 4. ORTEP drawing of Cp*($C_5Me_4CH_2(C_6F_4)$)ZrCl, **4a**, showing 30% probability ellipsoids.

unidentified products (eq 4). The unidentified products are decomposition products of **4**, as prolonged heating of the reaction mixture at 120 °C resulted in decreased yield.



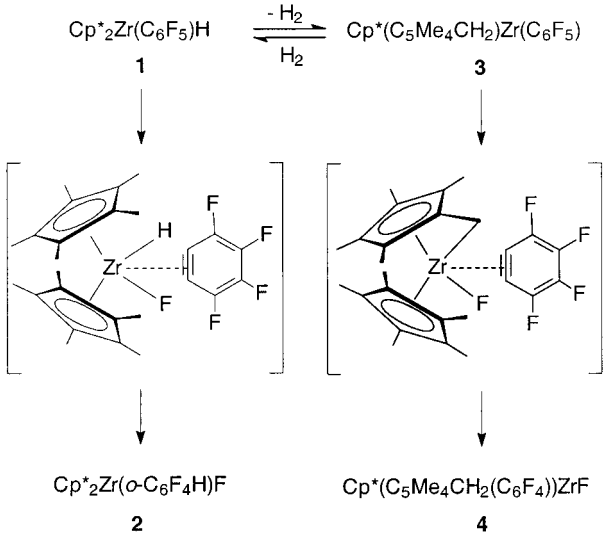
3 **4**

The ^{1}H NMR spectrum shows a Cp* resonance, four singlet methyl resonances, and two doublets for the inequivalent methylene protons. The ^{19}F NMR spectrum shows four aromatic fluorine resonances and one Zr-F resonance shifted far downfield. **4** could not be effectively separated from the other unidentified reaction products, but could be derivatized into Cp*($C_5Me_4CH_2$-(C_6F_4))ZrCl (**4a**) by heating the product mixture containing **4** with LiCl. A single crystal of **4a** was isolated for characterization by X-ray crystallography (Figure 4), showing the formation of the C−C bond between the aryl group and the fulvene. The aryl group now lies at an angle of 28.5° to the plane of the Cp*$_2$Zr wedge.

Mechanistic Considerations. The mechanism for formation of **2** from **1** can be explained by initial β-fluoride elimination to generate tetrafluorobenzyne or a tetrafluorobenzyne complex followed by insertion of tetrafluorobenzyne into the Zr−H bond. Evidence for free tetrafluorobenzyne was confirmed by independent thermolysis of **1** in the presence of 10 equiv of durene, a benzyne trap,[5] which formed the durene-tetrafluorobenzyne adduct in 20% yield by NMR integration. Very recently, the first transition-metal complex of tetrafluorobenzyne, Ir(η^5-C_5Me_5)(PMe_3)(η^2-C_6F_4), has been isolated and structurally characterized.[9] However, in the current system, no intermediate tetrafluorobenzyne complex could be detected by NMR spectroscopy.

The mechanism for formation of **4** from **1** can be explained by an initial ring methyl C−H activation to give **3** and H_2, followed by β-fluoride elimination to release tetrafluorobenzyne followed by insertion of tetafluorobenzyne into the Zr−CH_2 bond (Scheme 1). This mechanism is supported by independent thermolysis of **3** to form **4** and also the observation of the durene-tetrafluorobenzyne adduct in 36% yield upon thermolysis of **3** in the presence of 10 equiv of durene. As before, an intermediate tetrafluorobenzyne complex could not be detected by NMR spectroscopy.

Scheme 1. Intramolecular Reaction Modes of Cp*$_2$Zr(C_6F_5)H Involving Tetrafluorobenzyne Intermediates



In several systems involving the formation of nonfluorinated benzyne complexes, both ortho C−H activation and elimination of arene or alkane occur.[10,11] In a relevant system involving benzyne formation and ring methyl C−H activation, Cp*$_2$Zr(C_6H_5)$_2$ reacts to give Cp*(Fv)Zr(C_6H_5) and benzene quantitatively.[12] Strong evidence was presented in support of aryl C−H activation to give the Zr^{II} benzyne intermediate Cp*$_2$Zr(C_6H_4) prior to ring methyl hydrogen atom transfer. A similar reaction sequence involving initial aryl C−F activation in the reaction of **1** to form **4** is highly unlikely. Independent experiments show that **3** forms **4** directly, and therefore ring methyl hydrogen atom transfer occurs prior to β-fluoride elimination. For the ring methyl C−H activation of **1**, a ring methyl hydrogen atom transfer to give H_2 and **3** is proposed followed by subsequent reaction to form **4**. Addition of 1.3 atm H_2 to **3** gave **1** cleanly and quantitatively. This observation clearly illustrates the equilibrium between **1** and **3** and explains why **2** is formed exclusively in the thermolysis of **1** in the presence of added H_2.

An alternative mechanism to explain the formation of **4** from **1** involves β-fluoride elimination to give free tetrafluorobenzyne and Cp*$_2$ZrHF. Cp*$_2$ZrHF could then undergo fast ring methyl C−H activation to give Cp*(Fv)ZrF followed by insertion of tetrafluorobenzyne into the Zr−CH_2 bond. This mechanism was ruled out with independent experiments showing that **3** reacts to give **4** in the absence of H_2, Cp*(Fv)ZrF is not observed at any time during the reaction, and last, Cp*$_2$ZrHF remains stable against ring methyl C−H activation under the same reaction conditions. A pathway involv-

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(10) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(11) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

(12) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232.

ing reductive elimination of an aryl−methylene bond in **3** followed by C−F activation is also inconsistent with the formation of benzyne-trapped products.

Conclusions

The thermal decomposition of $Cp^*_2Zr(C_6F_5)H$ occurs by dual pathways to give $Cp^*_2Zr(o\text{-}C_6F_4H)F$ and $Cp^*(Fv)Zr(C_6F_5)$ by competing C−F and C−H bond activation pathways. Further reaction with $Cp^*(Fv)Zr(C_6F_5)$ leads to formation of $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$, formed by insertion of tetrafluorobenzyne into the $Zr-CH_2$ bond of the fulvene complex. In both C−F bond activation reactions, tetrafluorobenzyne was trapped with durene to form the Diels−Alder adduct.

Experimental Section

General Considerations. All manipulations were performed inside a 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. ^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 downfield 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 i.d., 0.25 μm, 13 m) and a HP 5970 series mass selective detector. $Cp^*_2ZrH_2$, $Hg(C_6F_5)_2$, $Hg(o\text{-}C_6F_4H)_2$, and $Cp^*(C_5Me_4CH_2)ZrCl$ were prepared according to the literature procedures.[8,13−15] **Caution: Organomercury derivatives are highly poisonous and should be handled with great care.**[14,16]

Synthesis of $Cp^*_2Zr(C_6F_5)H$, 1. In the drybox, a solution of 200 mg (0.55 mmol) of $Cp^*_2ZrH_2$ in ∼5 mL of pentane was added dropwise to a slurry of 147 mg (0.275 mmol) of $Hg(C_6F_5)_2$ in ∼5 mL of pentane at room temperature. Vigorous evolution of H_2 occurred, and elemental mercury was formed. The mixture was stirred for 30 min, filtered over Celite, and stripped to dryness, giving an orange crystalline mass of $Cp^*_2Zr(C_6F_5)H$ (415 mg, 95%). $Cp^*_2Zr(C_6F_5)H$ was recrystallized from pentane at −30 °C to yield X-ray quality crystals. ^1H NMR (C_6D_{12}): δ 1.88 (s, 30 H, Cp*), 7.71 (dd, 1H, $Zr(C_6F_5)H$). ^{19}F NMR (C_6D_{12}): δ −116.3 (m, 1 F), −117.7 (m, 1 F), −155.2 (t, 1 F), −160.2 (m, 1 F), −161.9 (m, 1 F). Anal. Calcd for $C_{26}H_{31}ZrF_5$: C, 58.95; H, 5.90. Found: C, 59.04; H, 5.76.

Preparation of $Cp^*_2Zr(o\text{-}C_6F_4H)H$. A solution of 200 mg (0.55 mmol) of $Cp^*_2ZrH_2$ in ∼5 mL of pentane was added dropwise to a slurry of 137 mg (0.275 mmol) of $Hg(o\text{-}C_6F_4H)_2$ in ∼5 mL of pentane at room temperature. Vigorous evolution of H_2 and elemental mercury was observed. The mixture was stirred for 30 min, filtered over Celite, and stripped to dryness. The orange crystalline mass was dissolved in a minimum of pentane and crystallized at −30 °C to yield X-ray quality crystals of $Cp^*_2Zr(o\text{-}C_6F_4H)H$ (177 mg, 63%). The X-ray structure is included in the Supporting Information. For $Cp^*_2Zr(o\text{-}C_6F_4H)H$, ^1H NMR (C_6D_{12}): δ 1.847 (s, 30 H, Cp*), 5.98 (m, 1 H, Zr-C_6F_4H), 6.83 (br, 1 H, Zr*H*). ^{19}F NMR (C_6D_{12}): δ −118.1 (m, 1 F), −139.8 (m, 1 F), −157.4 (m, 1 F), −159.0 (m, 1 F). Anal. Calcd for $C_{26}H_{32}ZrF_4$: C, 61.02; H, 6.30. Found: C, 60.84; H, 6.08.

Synthesis of $Cp^*_2Zr(o\text{-}C_6F_4H)F$, 2. In the drybox, a solution of 60 mg (0.117 mmol) of $Cp^*_2Zr(o\text{-}C_6F_4H)H$ in ∼1 mL of pentane was prepared in a polyethylene reaction vessel. With stirring, HF-pyridine (70% HF, 30% pyridine) (∼0.1 mL) was added via syringe and vigorous H_2 evolution occurred. The solution was transferred to a glass vial to neutralize excess HF and stripped to dryness. The residue was redissolved in pentane, filtered, and stripped to dryness, yielding analytically pure $Cp^*_2Zr(o\text{-}C_6F_4H)F$ (25 mg, 40%). Anal. Calcd for $C_{26}H_{31}ZrF_5$: C, 58.95; H, 5.90. Found: C, 58.70; H, 6.18.

Thermolysis of $Cp^*_2Zr(C_6F_5)H$ under H_2. In a resealable NMR tube, 12 mg (0.033 mmol) of $Cp^*_2Zr(C_6F_5)H$ was added, dissolved in cyclohexane-d_{12}, and freeze−pump−thaw degassed three times. H_2 (1.3 atm) was admitted into the tube, and the solution was heated in a thermostated 100 °C oil bath for 20 days, leading to quantitative conversion of $Cp^*_2Zr(o\text{-}C_6F_4H)F$. ^1H NMR (C_6D_{12}): δ 1.786 (s, 30 H, Cp*), 6.63 (m, 1 H, Ar_f-*H*). ^{19}F NMR (C_6D_{12}): δ 90.5 (s, 1 F, Zr-*F*), −113.9 (m, 1 F), −139.3 (m, 1 F), −157.9 (m, 1 F), −158.8 (m, 1 F).

Thermolysis of $Cp^*_2Zr(C_6F_5)H$ under Vacuum. In a sealable NMR tube, 29 mg of $Cp^*_2Zr(C_6F_5)H$ was added and dissolved in cyclohexane-d_{12}. The solution was freeze−pump−thaw degassed three times and sealed under vacuum. The tube was then heated in a 80 °C oil bath. After 28 days, the starting material was ∼92% depleted, yielding a 36:14:3:1 mixture of $Cp^*(C_5Me_4CH_2)Zr(C_6F_5)$, $Cp^*_2Zr(C_6F_4H)F$, $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$, and $Cp^*_2ZrF_2$, respectively. For $Cp^*(C_5Me_4CH_2)Zr(C_6F_5)$, ^1H NMR (toluene-d_8): δ 2.21 (dd, 1 H), 1.87 (dd, 1 H), 1.71 (d, 3 H), 1.66 (s, 15 H), 1.56 (s, 3 H), 1.33 (s, 3 H), 1.15 (d, 3 H). ^{19}F NMR (toluene-d_8): δ −114.6 (m, 1 F), −124.4 (d, 1 F), −156.0 (t, 1 F), −161.0 (quin, 1 F), −161.6 (quin, 1 F). For $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$, ^1H NMR (C_6D_{12}): δ 3.75 (d, J_{H-H} = 17.5 Hz, 1 H), 3.57 (d, J_{H-H} = 17.5 Hz, 1 H), 2.13 (s, 3 H), 2.12 (s, 3 H), 1.86 (s, 15 H), 1.73 (s, 3 H), 1.51 (s, 3 H). ^{19}F NMR (C_6D_{12}): δ 87.6 (br s, 1 F), −108.4 (m, 1 F), −140.6 (t, 1 F), −158.9 (m, 1 F), −160.1 (m, 1 F).

Thermolysis of $Cp^*_2Zr(C_6F_5)H$ in the Presence of Durene (1,2,4,5-tetramethylbenzene). In a resealable NMR tube, 18 mg (0.034 mmol) of $Cp^*_2Zr(C_6F_5)H$ and 46 mg (0.34 mmol) of durene were dissolved in cyclohexane-d_{12}. The tube was then placed in a 120 °C oil bath for 4 days. Both $Cp^*_2Zr(o\text{-}C_6F_4H)F$ and $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$ were formed along with the Diels−Alder adduct $C_6H_2(CH_3)_4(C_6F_4)$ in 20% yield by NMR integration. The solvent was replaced with THF-d_8 for direct comparison of known chemical shifts.[4] For $C_6H_2(CH_3)_4(C_6F_4)$, ^1H NMR (THF-d_8): δ 4.57 (t, 2 H), 1.80 (s, 12 H). ^{19}F NMR (THF-d_8): δ −151.1 (m, 2 F), −163.6 (m, 2 F). GC/MS (*m*/*z*): 282 (M^+).

Synthesis of $Cp^*(C_5Me_4CH_2)Zr(C_6F_5)$, 3. Into a 100 mL Schlenk flask, 800 mg (2.01 mmol) $Cp^*(C_5Me_4CH_2)ZrCl$ was added and dissolved in ∼40 mL of diethyl ether. Into a second round-bottomed flask, 246 μL (2.21 mmol, d = 1.514 g/mL) of pentafluorobenzene and ∼15 mL of diethyl ether were added and cooled to −78 °C. *n*-Butyllithium (1.41 mL, 2.26 mmol, 1.60 M in hexanes) was added dropwise with stirring and allowed to warm slowly to −20 °C followed by cooling to −78 °C. The resulting LiC_6F_5 solution was transferred via cannula into the $Cp^*(C_5Me_4CH_2)ZrCl$ solution at −78 °C, upon which the solution gradually turned from orange to deep red. The mixture was allowed to warm slowly to room temperature over 5 h. The solvent was replaced with pentane, filtered over Celite, and concentrated. Crystallization and filtration at −78 °C afforded dark red crystals of $Cp^*(C_5Me_4CH_2)Zr(C_6F_5)$ (600 mg, 56%). Anal. Calcd for $C_{26}H_{29}ZrF_5$: C, 59.17; H, 5.54. Found: C, 59.05; H, 5.71.

Thermolysis of $Cp^*(C_5Me_4CH_2)Zr(C_6F_5)$. Into a resealable NMR tube, 12 mg (0.023 mmol) of $Cp^*(C_5Me_4CH_2)Zr(C_6F_5)$ was dissolved in cyclohexane-d_{12}. α,α,α-Trifluorotoluene (1.0 μL) was added as an internal standard. The tube was immersed in a 120 °C oil bath for 4 days to give $Cp^*(C_5Me_4CH_2(C_6F_4))ZrF$ in 58% yield by NMR integration with other

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unidentified products. NMR data are given above. MS (*m*/*z*): 526 (M^+). The solution contents were transferred to an ampule along with dry LiCl (24 mg) and heated with stirring for 3 days at 100 °C for conversion of **4** into Cp*($C_5Me_4CH_2(C_6F_4)$)-ZrCl, **4a**. **4a** was isolated by repeating the reaction in an ampule using 190 mg of **3**. The resulting solution was filtered over Celite, stripped to dryness, and extracted with 4 mL of pentane. The extract was concentrated and cooled to −30 °C to give 10 mg of a yellow powder. Although the ^{19}F NMR spectrum showed the product cleanly, the ^1H NMR spectrum contained small impurities. ^1H NMR (C_6D_{12}): δ 1.89 (s, 15 H), 2.20 (s, 3 H), 1.99 (s, 3 H), 1.95 (s, 3 H), 1.63 (s, 3 H), 3.75 (d, $J_{H-H} = 17.5$ Hz, 1 H), 3.53 (d, $J_{H-H} = 17.5$ Hz, 1 H). ^{19}F NMR: δ −105.4 (m, 1 F), −140.6 (m, 1 F), −158.8 (m, 1 F), −159.9 (m, 1 F). MS (*m*/*z*): 542 (M^+). Anal. Calcd for $C_{26}H_{29}F_4ZrCl$: C, 57.38; H, 5.37. Found: C, 57.11; H, 5.63.

Thermolysis of Cp*($C_5Me_4CH_2$)Zr(C_6F_5) in the Presence of Durene. In a sealable NMR tube, 14 mg (0.027 mmol) of Cp*($C_5Me_4CH_2$)Zr(C_6F_5) and 36 mg (0.27 mmol) of durene were dissolved in cyclohexane-d_{12}. The mixture was freeze−pump−thawed three times and sealed with a torch. The tube was placed in a 125 °C oil bath for 2 days. Cp*($C_5Me_4CH_2$-(C_6F_4))ZrF was formed along with the Diels−Alder adduct, $C_6H_2(CH_3)_4(C_6F_4)$, in 36% yield by NMR integration.

Acknowledgment is made to the U.S. Department of Energy, Grant FG02-86ER13569, for their support of this work.

Supporting Information Available: Includes tables giving details of the crystallographic procedures along with intramolecular distances and angles, and positional and thermal parameters for **1**, **2**, **2a**, **3**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010888F