Aliphatic and Aromatic Carbon−Fluorine Bond Activation with $Cp^*_2ZrH_2$: Mechanisms of Hydrodefluorination

Bradley M. Kraft, Rene J. Lachicotte, and William D. Jones*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627

Received April 26, 2001

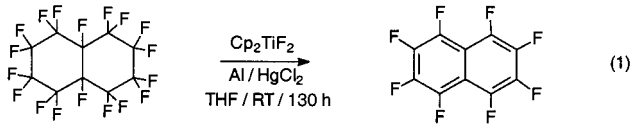
Abstract: $Cp^*_2ZrH_2$ (**1**) (Cp^* = pentamethylcyclopentadienyl) reacts with primary, secondary, and tertiary monofluorinated aliphatic hydrocarbons to give Cp^*_2ZrHF (**2**) and/or $Cp^*_2ZrF_2$ and alkane quantitatively through a radical chain mechanism. The reactivity of monofluorinated aliphatic C−F bonds decreases in the order 1° > 2° > 3°. The rate of hydrodefluorination was also greatly reduced with $-CF_2H$ and $-CF_3$ groups attached to the hydrocarbon. An atmosphere of H_2 is required to stabilize **1** against C−H activation of the Cp*-methyl groups and subsequent dimerization under the thermal conditions employed in these reactions. Reaction of **1** with fluorobenzene cleanly forms a mixture of Cp^*_2ZrHF, benzene, and $Cp^*_2Zr(C_6H_5)F$. Detailed studies indicate that radicals are not involved in this aromatic C−F activation reaction and that dual hydrodefluorination pathways are operative. In one mechanism, hydridic attack by $Cp^*_2ZrH_2$ on the aromatic ring and fluoride abstraction is involved. In the second mechanism, an initial ortho C−H activation occurs, followed by β-fluoride elimination to generate a benzyne complex, which then inserts into the zirconium−hydride bond.

Introduction

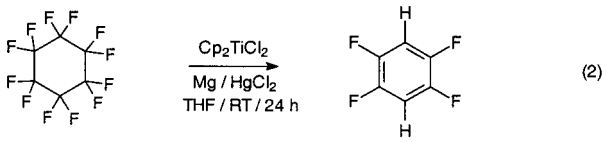
Of all types of bonds in organic chemistry, the carbon−fluorine bond is the most inert and resistant to oxidative degradation.[1] In addition, fluorocarbons have exceptional and unique physical and chemical properties, and have found widespread use in practical applications such as refrigerants, aerosol propellants, plastics, pharmaceuticals, oils, pesticides, and others. Given the chemical inertness and long environmental lifetimes of fluorocarbons, their distribution and accumulation in the environment has raised concern of their effects and ultimate fate in the biosphere. Recently, 3M company has discontinued their Scotchguard products containing perfluorooctane sulfonate, as trace amounts of this substance were found to linger in animal and human tissue samples from all across the globe.[2]

Some of the research in fluorocarbon chemistry is aimed at the development of non-ozone-depleting substitutes for CFCs (chlorofluorocarbons) as well as effective methods for disposal of the existing CFC stockpiles by conversion of CFCs to HFCs (hydrofluorocarbons) or other non-ozone-depleting substances.[3] In general, hydrodehalogenation reactions of fluorocarbons and CFCs require strongly reducing conditions and formation of a halide salt as necessary driving forces. In fact, the current commercial method of CFC disposal is a slow process, using sodium in liquid ammonia.[3b] An alternative route to dehalogenation and C−F activation reactions involves the use of organometallic complexes in homogeneous solution. Although rare, organometallic systems serve as catalytic models which can circumvent conventional hydrodehalogenation reaction requirements.[4]

Kiplinger and Richmond have demonstrated the catalytic aromatization of cyclic perfluorocarbons using Cp_2MF_2 (M = Ti, Zr) and activated magnesium or aluminum as the reductant and fluoride sink (eqs 1 and 2).[5] This study demonstrated for



(1)



(2)

the first time that early transition-metal complexes are capable of catalytic activity in C−F activation, as formation of strong metal−fluoride bonds is generally limiting to catalysis. The authors were uncertain whether M^{II} or M^{III} species were involved in the reduction, but believed the metallocene fragment served as an "electron shuttle" to transfer electrons from the terminal reductant to the fluorinated organic substrate. Interestingly, the reduction of perfluorocyclohexane to tetrafluorobenzene involved hydrogen abstraction from the THF solvent.

We have recently reported that $Cp_2Zr(C_6F_5)_2$ decomposes intramolecularly to form $Cp_2Zr(C_6F_5)F$ to release tetrafluorobenzyne. In the presence of C_6F_6, a competing reaction to form perfluorophenylene oligomers was observed. The oligomers were believed to form by a radical chain mechanism with $Cp_2Zr^{III}(C_6F_5)$ proposed as the reactive species toward the C−F bonds of C_6F_6.[6]

(1) Smart, B. E. In *The Chemistry of Functional Groups, Supplement D*; Patai S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Chapter 14.

(2) Weber, J. *Business Week* **2000**, *June 5*, 96−98.

(3) 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*, 373. (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.

(4) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674.

(5) Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805−6.

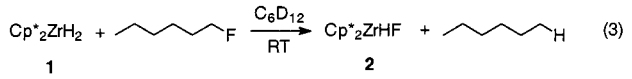
10.1021/ja016087l CCC: $20.00
Published on Web 10/06/2001

Bercaw has shown that $Cp^*_2HfH_2$ reacts with halogenated hydrocarbons, such as CH_3X (X = Cl, Br, I), to give Cp^*_2HfHX and $Cp^*_2HfX_2$.[7] Similarly, the neutral tungstenocene dihydride, Cp_2WH_2, also reacts with a variety of aliphatic and olefinic chloro- and bromocarbons to give hydrogenated products.[8] Other early metal C−F activation has been observed in reactions of fluoroethylene with complexes Cp_2ZrHCl and $(^tBu_3SiO)_3TaH_2$ by a β-F elimination mechanism.[9,10] The reduction of organic halides by the anionic complexes, $[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$, $[HW(CO)_5]^-$, $[HW(CO)_4P(OMe_3)]^-$, $[HCr(CO)_5]^-$, and $[CpFe(CO)_2]^-$, has been shown to occur by S_N2 and/or single electron-transfer processes.[11,12]

In the present study, it is demonstrated that reactions of $Cp^*_2ZrH_2$ with aliphatic fluorocarbons occur via a radical pathway with $Cp^*_2Zr^{III}H$ as the reactive species toward aliphatic C−F bonds. In contrast, reactions of $Cp^*_2ZrH_2$ with aromatic C−F bonds, such as in fluorobenzene and 1-fluoronaphthalene, do not show evidence for radicals, and are believed to occur through a nucleophilic displacement mechanism.

Results and Discussion

Reactions of Monofluorinated Hydrocarbons and CFCs with $Cp^*_2ZrH_2$. Reaction of 1 equiv of $Cp^*_2ZrH_2$ (**1**) with 1-fluorohexane in cyclohexane-d_{12} at 23 °C over a period of ~2 days produces Cp^*_2ZrHF (**2**) and hexane quantitatively (eq 3). Subsequent addition of 1 equiv of 1-fluorohexane and heating to 120 °C over 10 days produces $Cp^*_2ZrF_2$ and hexane quantitatively.



No deuterium was incorporated into the hexane as verified by MS. **2** has been prepared previously by conproportionation of $Cp^*_2ZrH_2$ and $Cp^*_2ZrF_2$.[13] Fluorocyclohexane reacts similarly to give a mixture of Cp^*_2ZrHF and $Cp^*_2ZrF_2$, but elevated temperatures were required (120 °C) and the reaction time must be increased. At these temperatures, an atmosphere of H_2 must be present to stabilize **1** against loss of H_2 and subsequent dimerization (vide infra). Tertiary fluorine-substituted carbon centers, such as in 1-fluoroadamantane, also react with **1**, but proceed only very slowly at 120 °C reaching ~25% completion after 1 week.

In competitive reactions, a 5:5:1 mixture of fluorohexane, fluorocyclohexane, and **1** reacted at 40 °C to give a 2.1:1 ratio of hexane:cyclohexane. In comparison, when two separate but parallel reactions were conducted at 40 °C with a stock solution of **1** to which each fluorocarbon was added, a 2.3:1 ratio of yields of hexane:cyclohexane reduction products was observed. In a competition involving a 5:5:1 ratio of fluorocyclohexane: 1-fluoroadamantane:**1**, a 33:1 ratio of cyclohexane:adamantane was observed, underscoring the lower reactivity of the tertiary C−F bond.

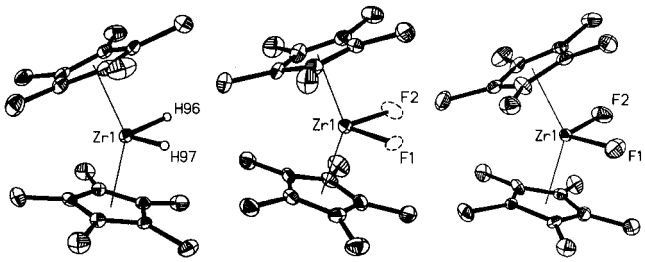


Figure 1. ORTEP drawings of $Cp^*_2ZrH_2$, Cp^*_2ZrHF, and $Cp^*_2ZrF_2$ showing 30% probability ellipsoids. The hydrides in $Cp^*_2ZrH_2$ were located and refined. The fluorine in Cp^*_2ZrHF is disordered over the two equatorial sites ($^1/_2$ F each), and the hydride was not located. For $Cp^*_2ZrH_2$: ∠Cp*−Zr−Cp* = 144.2°, ∠H−Zr−H = 99(2)°, $P2_12_12$. For Cp^*_2ZrHF: ∠Cp*−Zr−Cp* = 141.4°, ∠'F'−Zr−'F' = 93.9(4)°, $P2_12_12$. For $Cp^*_2ZrF_2$: ∠Cp*−Zr−Cp* = 138.7°, ∠F−Zr−F = 99.6(3)°, *C*2/*c*. Note the increase in metallocene bending with increased fluorine substitution.

Increasing geminal fluorine substitution also decreases the reactivity toward hydrodefluorination. For example, 1,1-difluoroethane reacts with **1** under H_2 to ~90% completion after 1 day to produce ethane and Cp^*_2ZrHF upon heating to 150 °C. 1,1,1-Trifluoropropane was even more unreactive, reacting over 2 weeks at 150 °C to form Cp^*_2ZrHF in ~57% yield by NMR integration. Propane was not identified in the ^1H NMR spectrum and other unidentified decomposition products were observed. $Cp^*_2ZrH_2$ is unreactive with perfluorocarbons such as perfluorohexane and perfluoroisobutane even with prolonged heating at 150 °C. However, a reaction with perfluorocyclohexane to give Cp^*_2ZrHF did occur, but the organic product(s) could not be identified.

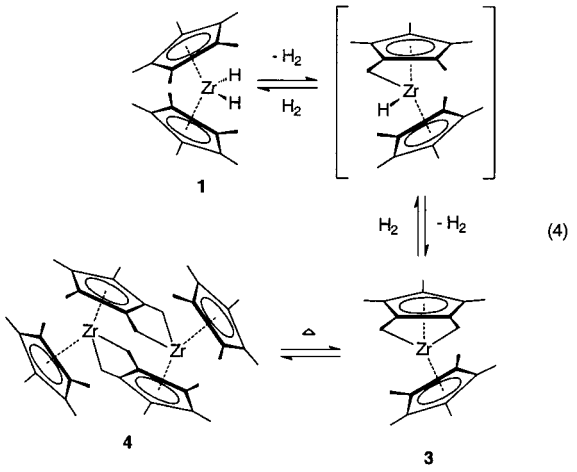
CFCs also react with **1** to give HFCs and subsequent hydrogenated products. Dichlorofluoromethane reacted readily at room temperature with 3 equiv of **1** to give fluoromethane, Cp^*_2ZrHCl, and a small amount of $Cp^*_2ZrCl_2$. Methane forms when the sample is allowed to stand for 1 day at ambient temperature, with **2**, $Cp^*_2ZrF_2$, and Cp^*_2ZrFCl also being observed. Difluorodichloromethane and difluorochloromethane were also found to give initially the dechlorinated organic product, difluoromethane, upon reaction with 4 equiv of **1**. As with CF_2HCH_3, subsequent defluorination of CF_2H_2 was slow, requiring heating to 120 °C under H_2 over a period of >10 days for complete dehalogenation to occur, giving methane.

The crystal structures of $Cp^*_2ZrH_2$, Cp^*_2ZrHF, and $Cp^*_2ZrF_2$ have been characterized by single-crystal X-ray crystallography (Figure 1). The structural data indicate that increasing fluorine substitution on zirconium decreases the Cp*−Zr−Cp* angle.

Decomposition of $Cp^*_2ZrH_2$. As mentioned above, H_2 is required to stabilize **1** in reactions carried out at temperatures above 85 °C. In the absence of H_2, $Cp^*_2ZrH_2$ decomposes in solution above 85 °C to produce an extremely insoluble yellow material. In the presence of 1.3 atm of H_2, little or none of this precipitate is observed. At 120 °C, a solution of **1** under vacuum develops a red color within a few minutes followed by precipitation of a substantial amount of the insoluble yellow material within 30 min. A single crystal of this material was mounted on the diffractometer and the unit cell constants were obtained, matching those found for the dimeric species, $\{Cp^*(C_5Me_3(CH_2)_2Zr\}_2$ (**4**), previously prepared by Pattiasina by thermolysis (180 °C) of the allyl−diene complex, $Cp^*(C_5Me_3(CH_2)_2)Zr$ (**3**), in benzene solution.[14]

(6) Edelbach, B. L.; Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 10327−31.
(7) Roddick, D. M.; Fryzuk, M. D.; Deidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97−104.
(8) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, *10*, 989−91.
(9) Watson, L. A.; Yandulov, D. V.; Caulton, K. G. *J. Am. Chem. Soc.* **2001**, *123*, 603.
(10) Strazisar, S. A.; Wolczanski, P. T. *J. Am. Chem. Soc.* **2001**, *123*, 4728.
(11) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.
(12) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83.
(13) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

The decomposition pathway is likely to involve a series of reversible ring-metalation reactions of the Cp* methyl groups. All 30 methyl protons are known to undergo intramolecular exchange with the hydride positions of **1**.[15] In the absence of H_2, the intermediate fulvene or "tuck-in" complex may form readily at higher temperatures, and could lead to a subsequent C−H activation of a second methyl group to form **3**. The presence of **3** was confirmed by heating solid **1** for 19 h at 85 °C under dynamic vacuum to give a mixture of red and yellow solid. The ^1H NMR spectrum of a C_6D_{12} solution of the solid residue revealed ∼20% conversion to **3** and unreacted **1** only. Addition of H_2 to this solution formed **1** quantitatively. Once **3** is formed, a competing reaction to form the insoluble dimer, **4**, occurs (eq 4). Isolation of **4** and treatment with 1.3 atm of H_2



in toluene at 95 °C for 1 day led to quantitative reformation of $Cp^*_2ZrH_2$. The reversibility of this decomposition pathway explains why addition of H_2 is required to stabilize **1** in reactions at temperatures above 85 °C. However, because the reaction of **1** and 1-fluorohexane proceeds in the absence of H_2, it is concluded that H_2 is not directly involved in the hydrodefluorination process.

Mechanism of Aliphatic Hydrodefluorination. The kinetics of the reaction of **1** with fluorohexane were first examined as a means of probing the mechanism of hydrodefluorination. The reactions were performed in cyclohexane-d_{12} solvent at 45 °C. The overall reaction does not follow a clean first-order rate law, showing a decrease in rate after ∼80−90% of $Cp^*_2ZrH_2$ is consumed. However, with use of initial rate data, the rate constant for reaction of **1** with fluorohexane was found to be dependent on [fluorohexane]. A plot of k_{obs} vs fluorohexane concentration generated a second-order rate constant of 1.6×10^{-6} M^{-1} s^{-1} (Figure 2).

When a freshly prepared batch of $Cp^*_2ZrH_2$ was prepared and used for kinetic studies, the rate of the reaction was found to be significantly slower under similar conditions. This was the first indication that a radical mechanism may be operative and could be initiated by a trace impurity in $Cp^*_2ZrH_2$. In the presence of the radical inhibitor isopropylbenzene (10 equiv), no change in the rate of reaction was observed. However, in the presence of radical inhibitors with weaker homolytic C−H bond strengths, such as 9,10-dihydroanthracene or triphenylmethane, severe inhibition was observed, suggesting again that radicals are involved in the mechanism (Figure 3). Addition of *n*-propyl bromide (5 mol %) had essentially no effect on the rate of the reaction. The possibility of a radical mechanism stands in contrast to a concerted H/F exchange as was suggested in our recent communication.[16]

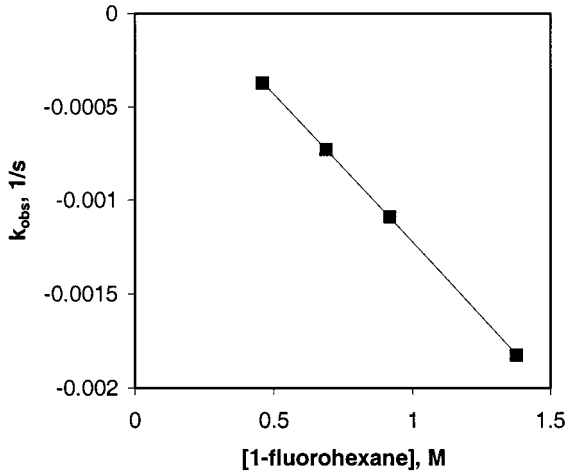


Figure 2. Graph of k_{obs} vs [1-fluorohexane] for reaction of **1** with 1-fluorohexane using initial rate data only.

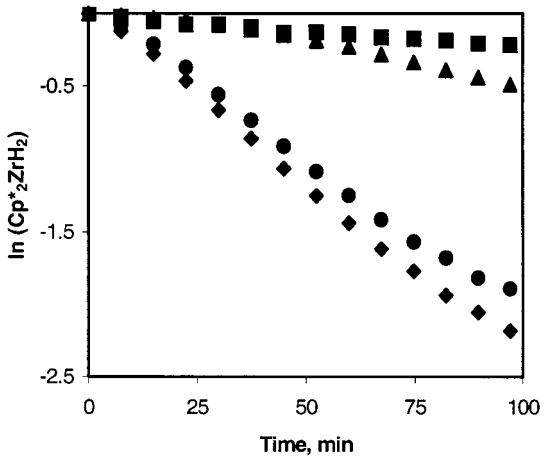


Figure 3. Graph of ln($Cp^*_2ZrH_2$ Area) vs time showing the effect of radical inhibitors: (◆) 0.046 M 1-fluorohexane only; (■) 0.458 M 9,10-dihydroanthracene; (▲) 0.458 M triphenylmethane; and (●) 5 mol % *n*-propyl bromide.

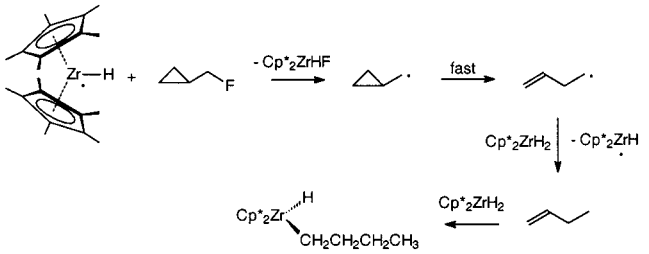
The addition of sodium and naphthalene was effective for initiation of the reaction, reaching completion within 45 min, approximately 3 times faster than the control experiment. **2** was formed in quantitative yield based on NMR integration and formation of hexane was verified by GC/MS. The reaction also proceeded at a more rapid rate in the presence of sodium only. Na/naphthalene and fluorohexane were found to react in the absence of added $Cp^*_2ZrH_2$ under the same conditions but gave only ∼5% conversion to hexane based on NMR integration. In the beginning of the reactions initiated by a reducing agent, severe broadening of the ^1H NMR resonances was observed, but at the end of the reaction, the resonances had become sharp, suggesting the presence of a transient paramagnetic Zr^{II} or Zr^{III} species early in the reaction. When the reaction was performed in the presence of another potential radical initiator, $TiCl_3$, similar broadening of the resonances was observed, but no apparent increase in the rate was observed and only a trace of Cp^*_2ZrHCl was observed. Other initiators such as TEMPO and VAZO were not suitable initiators as reaction with $Cp^*_2ZrH_2$ occurred.

(14) (a) Pattiasina, J. W. Ph.D. Dissertation, University of Groningen, 1988. (b) Spek, A. L.; Pattiasina, J. W.; Teuben, J. H. *Z. Kristallogr.* **1996**, *211*, 643.

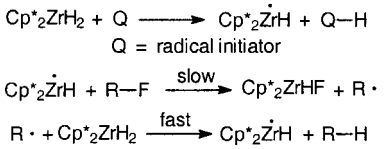
(15) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *167*, 136.

(16) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2000**, *122*, 8559.

Scheme 1



Scheme 2



Definitive evidence for radical formation was obtained by reaction of **1** with cyclopropylcarbinyl fluoride. The cyclopropylcarbinyl radical is known to ring-open irreversibly to give the butenyl radical at a rate of 2.70×10^8 s^{-1} at 30 °C.[17] Cyclopropylcarbinyl fluoride reacted with **1** within 15 min to give a clean 1:1 mixture of $Cp^*_2Zr(n\text{-butyl})H$ and **2**. No methylcyclopropane was observed in the ^1H NMR spectrum. These products can be accounted for by a mechanism in which a fluorine radical abstraction by a small amount of $Cp^*_2Zr^{III}H$ gives the cyclopropylcarbinyl radical. This radical quickly ring opens to form the butenyl radical, which then abstracts a hydrogen atom from **1** to continue the radical chain. Butene undergoes insertion with another equivalent of **1** to give the observed butyl hydride complex (Scheme 1). $Cp^*_2Zr(n\text{-butyl})H$ was characterized by ^1H NMR spectroscopy and reacted with H_2 to form **1** and butane, which was confirmed by ^1H NMR and GC/MS. Full characterization of $Cp^*_2Zr(n\text{-butyl})H$ was not possible due to the inherent instability of these types of alkyl hydride derivatives.[18] In a control experiment, **1** was found to be unreactive with methylcyclopropane at room temperature.

The reactivity trends observed with increasing geminal fluorine substitution on carbon are consistent with known characteristics of fluorocarbons. Increasing geminal fluorination is known to greatly increase the C−F bond strength. For example, the C−F bond dissociation energies for the fluoromethanes (CH_3F, CH_2F_2, CHF_3, and CF_4) increase from 109, 122, 128, to 130 kcal/mol, respectively.[1] However, based on radical stability, the C−F bond dissociation energy for monofluorinated substrates should decrease with increasing substitution at carbon (1°, 2°, 3°), but the opposite reactivity trend is observed. It is likely but unsubstantiated that steric repulsion with the Cp* ligands governs the ease of fluorine abstraction.

The mechanism in Scheme 2 best fits the observations. The reaction could be initiated by a trace unidentified impurity in $Cp^*_2ZrH_2$. As shown above, the initial rate is proportional to the fluorohexane concentration. The rate-determining step therefore involves fluorohexane and a steady-state concentration of the $Cp^*_2Zr^{III}H$ radical. The chain is continued by hydrogen abstraction by the alkyl radical from another $Cp^*_2ZrH_2$ molecule rather than from the deuterated NMR solvent, as no deuterium was incorporated into the hexane. Similarly, the reactions with other fluorocarbons and CFCs are likely to occur by the same mechanism. Radical chains of this type involving metal hydrides and alkyl halides are well-known.[11,12]

Effect of H_2 and THF. Addition of 1.3 atm of H_2 to the reaction of 1-fluorohexane significantly inhibited the reaction by ∼11-fold. It is well-known that H_2 exchanges with the hydride positions of $Cp^*_2ZrH_2$ below −80 °C.[15] When **1** is in the presence of H_2, severe broadening of the zirconium−hydride resonance is observed in the ^1H NMR spectrum. Free H_2 is never observed in the presence of **1** even when excess H_2 (∼5 equiv) is present. Attempts to observe an H_2 complex with use of low-temperature NMR spectroscopy in methylcyclohexane-d_{14} showed no evidence for a static H_2 complex even at −125 °C, as very little change in the ^1H NMR spectrum was observed. Although an H_2 complex could not be observed, it may still exist transiently and defluorination could be inhibited by H_2 coordination. Another possibility is that H_2 forms a complex with the $Cp^*_2Zr^{III}H$ radical to inhibit the fluorine abstraction step.

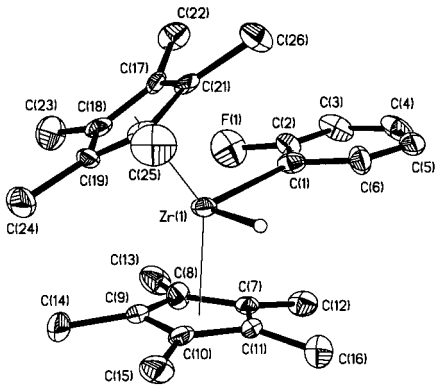
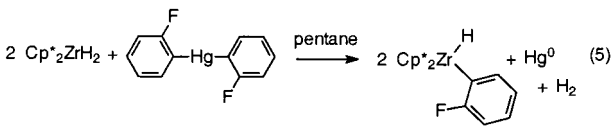


Figure 4. ORTEP drawing of $Cp^*_2Zr(o\text{-}C_6H_4F)H$ showing 30% probability ellipsoids.

A similar decrease in rate (∼8-fold) was also observed when the reaction of 1-fluorohexane was performed in THF-d_8 solvent. Again, this inhibition is attributed to occupation of the vacant coordination site of $Cp^*_2ZrH_2$.

Reaction of 1 with Fluorobenzene. Reaction of **1** with 1 equiv of fluorobenzene and 1.3 atm of H_2 in cyclohexane-d_{12} at 85 °C over 40 days resulted in a clean mixture of Cp^*_2ZrHF, benzene, and $Cp^*_2Zr(C_6H_5)F$ in 1:1:0.75 ratio. When the reaction was performed in THF-d_8 solvent, only traces of **2** were observed in addition to small amounts of other unidentified product(s) after 7 days at 85 °C. A similar reaction involving $(Cp^*_2YH)_2$ with halobenzenes was reported. In a reaction with fluorobenzene, a complex mixture of products formed instantly, two of which were identified as 2-fluorobiphenyl and $Cp^*_2Y(\text{-}C_6H_4\text{-}C_6H_4F)$.[19] The observed products were suggestive of benzyne formation. In the present study with fluorobenzene, an intermediate species was observed during the course of the reaction and has been assigned to the ortho C−H activated product, $Cp^*_2Zr(o\text{-}C_6H_4F)H$. Although this species could not be isolated directly from the reaction mixture, independent synthesis of this compound confirmed its identity. $Cp^*_2Zr(o\text{-}C_6H_4F)H$ was prepared in nearly quantitative yield by reaction of **1** with $Hg(o\text{-}C_6H_4F)_2$ in pentane (eq 5). The reaction is



complete within minutes and elemental mercury and H_2 gas are observed. The product was characterized by ^{19}F and ^1H NMR, X-ray, and elemental analysis. The X-ray structure is shown in Figure 4. Heating $Cp^*_2Zr(o\text{-}C_6H_4F)H$ in the presence of H_2 led

(17) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981.
(18) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818.
(19) Booij, M.; Deelman, B.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 331−40.

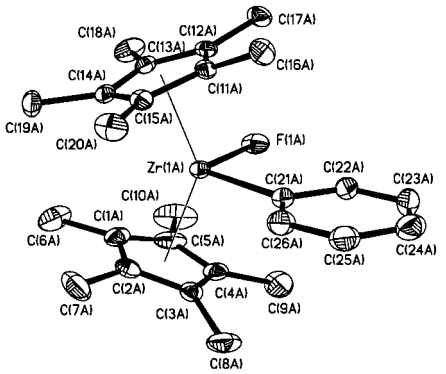
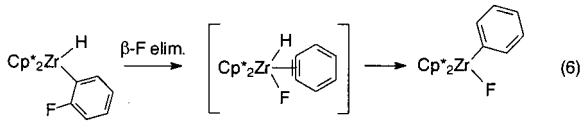


Figure 5. ORTEP drawing of $Cp^*_2Zr(C_6H_5)F$ showing 30% probability ellipsoids.

to a mixture of fluorobenzene, $Cp^*_2ZrH_2$, and $Cp^*_2Zr(C_6H_5)F$, indicating that the ortho C−H activation step is reversible. However, heating $Cp^*_2Zr(o\text{-}C_6H_4F)H$ in the absence of H_2 formed $Cp^*_2Zr(C_6H_5)F$ quantitatively. $Cp^*_2Zr(C_6H_5)F$ was characterized by ^{19}F and ^1H NMR, X-ray, and elemental analysis. The X-ray structure is shown in Figure 5. Regarding this reaction, it is likely that a β-fluoride elimination occurs to generate a benzyne complex that quickly inserts into the Zr−H bond to give $Cp^*_2Zr(C_6H_5)F$ (eq 6). The reaction was performed

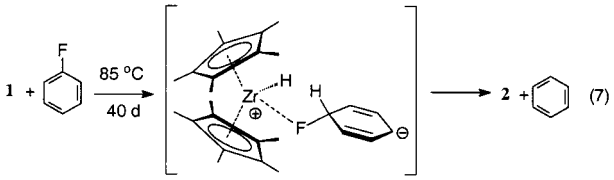


(6)

in the presence of 10 equiv of 1,2,4,5-tetramethylbenzene, a benzyne trap, but no benzyne adduct was observed in this reaction. Unlike the decomposition of $Cp_2Zr(C_6F_5)_2$ to release tetrafluorobenzyne,[6] it is possible that the nonfluorinated benzyne remains fully coordinated to zirconium as in the decomposition of Cp_2ZrPh_2.[20]

Several other mechanisms to explain the formation of $Cp^*_2Zr(C_6H_5)F$ were discounted: (1) Reaction of Cp^*_2ZrHF and benzene did not produce $Cp^*_2Zr(C_6H_5)F$ after 12 h at 120 °C. (2) $[Cp^*_2Zr]_2(N_2)_3$ did not react with 2 equiv of fluorobenzene at 77 °C to give $Cp^*_2Zr(C_6H_5)F$, suggesting that an oxidative addition to "$Cp^*_2Zr^{II}$" does not occur. (3) Cp^*_2ZrHF and $Cp^*_2Zr(C_6H_5)H$ do not conproportionate after 3 days at 120 °C. $Cp^*_2Zr(C_6H_5)F$ was prepared independently in 41% yield by addition of 1 equiv of phenyllithium to $Cp^*_2ZrF_2$ and subsequent recrystallization. $Cp^*_2Zr(C_6H_5)F$ was treated with 1.3 atm of H_2 and heated to 120 °C for 3 days, but resulted in no reaction. This observation eliminated the possibility that benzene and Cp^*_2ZrHF were formed by this pathway.

The reaction of **1** with 1-fluoronaphthalene proceeded much faster than that with fluorobenzene, and produced naphthalene and Cp^*_2ZrHF over 4 days at 85 °C with no Cp^*_2Zr(naphthyl)F being observed. Unlike the reactions with aliphatic fluorocarbons, this reaction showed no inhibition by 9,10-dihydroanthracene or triphenylmethane. Also, no increase in rate was observed when the reaction was performed in the presence of sodium/naphthalene initiator, suggesting that a radical mechanism is not involved for these aromatic C−F bond-activation reactions. The formation of Cp^*_2ZrHF and arene in the reactions with fluorobenzene and fluoronaphthalene is therefore best explained by a direct nucleophilic attack by hydride on the aromatic ring (S_NAr2) and fluoride abstraction by zirconium (eq 7). Sterically, 1-fluoronaphthalene might be expected to react



(7)

more slowly than fluorobenzene, but the opposite is observed. The increased reactivity with 1-fluoronaphthalene over fluorobenzene can be explained by the decreased loss of resonance energy in fluoronaphthalene in the intermediate/transition state. Further support for this mechanism is derived from the X-ray structure of a cationic Ti^{III} fluorobenzene complex, $Cp^*_2Ti(FC_6H_5)^+$, recently reported by Teuben et al.[21] The structure illustrates the effects of a neutral fluorocarbon ligand coordinated to a cationic center. In comparison with free fluorobenzene, lengthening of the C−F bond was observed that provides good evidence that coordination to a cationic center may cause a weakening of the C−F bond. In fact, heating $Cp^*_2Ti(FC_6H_5)^+$ was shown to cause C−F activation of the coordinated fluorobenzene.

Conclusions

A series of fluorocarbons react with $Cp^*_2ZrH_2$ to give primarily Cp^*_2ZrHF and alkane by a radical chain mechanism involving $Cp^*_2Zr^{III}H$ as the reactive species toward C−F bonds. Radical inhibitors and initiators are shown to severely affect the rate of reaction. Last, the reaction with cyclopropylcarbinyl fluoride to produce $Cp^*_2Zr(n\text{-butyl})H$ provides good evidence that alkyl radicals are generated in the reactions with aliphatic fluorocarbons. However, $Cp^*_2ZrH_2$ reacts with monofluoroarenes by a different mechanism involving hydridic attack on the aromatic ring and subsequent fluoride abstraction to yield Cp^*_2ZrHF and hydrogenated arene. In the reaction with fluorobenzene, an additional pathway occurs to form $Cp^*_2Zr(C_6H_5)F$. The complex was shown to form by an initial ortho C−H activation, subsequent fluoride elimination to generate a benzyne complex, and finally, insertion of benzyne into the zirconium−hydride bond.

Experimental Section

General Considerations. All manipulations were performed inside a N_2-filled Vacuum Atmospheres glovebox or on a high-vacuum line. NMR solvents, cyclohexane-d_{12}, and toluene-d_8 (Cambridge) 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. D_2 (Cambridge) was used as received. 1-Fluorohexane, fluorobenzene, and 1-fluoronaphthalene were purchased from Aldrich and used as received. Fluorocyclohexane was purchased from Matrix Scientific. CFCs were purchased from Matheson. All liquids were degassed by the freeze−pump−thaw method. ^1H and ^{19}F NMR spectra were recorded with a Bruker Avance400 spectrometer. ^{19}F NMR spectra were referenced to α,α,α-trifluorotoluene (δ 0.00 with downfield chemical shifts taken to be positive). GC/MS analyses were conducted with use of 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. $Cp^*_2ZrH_2$, 1-fluoroadamantane, and $Hg(o\text{-}C_6H_4F)_2$ were prepared according to the literature procedures.[22−24] **Caution:** Organomercury derivatives are highly poisonous and should be handled with great care.[25]

Reaction of 1-Fluorohexane with 1. A resealable NMR tube was charged with 20 mg (0.055 mmol) of **1** and dissolved in cyclohexane-d_{12}. 1-Fluorohexane (7.2 μL, 0.055 mmol, ρ = 0.80) was added via

(20) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

(21) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363. de Wolf, J. M.; Gercama, J.; del Hierro Morales, I.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H., submitted for publication.

syringe. The tube was allowed to stand for 2 days at room temperature. The reaction was ~93% complete with formation of Cp^*_2ZrHF and hexane. For Cp^*_2ZrHF: ^1H NMR (C_6D_{12}) δ 1.92 (s, 30 H, Cp*), 6.23 (s, 1 H, Zr*H*F); ^{19}F NMR δ 141.4 (s, 1 F). For C_6H_{14}: ^1H NMR δ 0.89 (t, 6 H), 1.28 (m, 8 H); MS (*m*/*z*) 86 (M^+). An additional equivalent of 1-fluorohexane (7.2 μL, 0.055 mmol) was added to the tube and heated at 120 °C for 10 days. The reaction mixture now consisted of a mixture of $Cp^*_2ZrF_2$ and hexane. For $Cp^*_2ZrF_2$: ^1H NMR (C_6D_{12}) δ 1.86 (s, 30 H, Cp*); ^{19}F NMR δ 97.8 (s, 2 F).

Kinetics for Reaction of 1-Fluorohexane with 1. In the drybox, 400 μL of a 0.0687 M stock cyclohexane-d_{12} solution of **1** containing 0.057 M of hexamethyldisilane standard was syringed into resealable NMR tubes. Fluorohexane was added with a microliter syringe and the total volume was brought to 0.600 mL. The reactions were monitored at 45 °C in the NMR probe. From initial rate data, the rate constants (k_{obs}) obtained for 458, 687, 916, and 1370 mM 1-fluorohexane were 3.7×10^{-4}, 7.3×10^{-4}, 1.1×10^{-3}, and 1.8×10^{-3} s^{-1}, respectively.

Reaction of 1-Fluorohexane and 1 in the Presence of Radical Inhibitors. A 160-μL aliquot (0.027 mmol) of a 0.172 M $Cp^*_2ZrH_2$ stock solution in cyclohexane-d_{12} was added to a resealable NMR tube followed by addition of 9,10-dihydroanthracene (50 mg, 0.27 mmol) or triphenylmethane (67 g, 0.27 mmol). Additional cyclohexane-d_{12} was added to bring the total volume to 0.60 mL. The reaction mixture was heated at 45 °C in the NMR probe and analyzed periodically over the course of the reaction.

Reaction of 1-Fluorohexane with 1 in the Presence of Sodium and Naphthalene. A 160-μL aliquot of a 0.137 M $Cp^*_2ZrH_2$ stock solution in cyclohexane-d_{12} was added to a resealable NMR tube containing ~3 mg of sodium metal and ~5 mg of naphthalene. 1-Fluorohexane (120 μL) was then added via syringe. The reaction mixture was heated at 45 °C in the NMR probe. The reaction was complete within 45 min, forming Cp^*_2ZrHF in nearly quantitative yield by ^1H NMR integration. Hexane was verified by GC/MS.

Reaction of Fluorocyclohexane with 1. A resealable NMR tube was charged with 20 mg (0.055 mmol) of **1** and dissolved in cyclohexane-d_{12}. Fluorocyclohexane (5.9 μL, 0.055 mmol, $\rho = 0.95$) was added via syringe. The tube was then freeze−pump−thaw degassed three times and 1.3 atm of H_2 was admitted into the tube. The tube was heated at 120 °C for 4 days. The reaction mixture consisted of a 12:1 mixture of Cp^*_2ZrHF and $Cp^*_2ZrF_2$, and cyclohexane. For C_6H_{12}: ^1H NMR (C_6D_{12}) δ 1.44 (s). C_6H_{12} was not distinguishable from C_6D_{12} solvent by GC/MS.

Reaction of 1-Fluoroadamantane with 1. A resealable NMR tube was charged with 20 mg (0.055 mmol) of **1** and 1-fluoroadamantane (8 mg, 0.052 mmol) and dissolved in cyclohexane-d_{12}. The tube was freeze−pump−thaw degassed three times and 1.3 atm of H_2 was admitted into the tube. The tube was heated to 120 °C for 6 days. The reaction was ~25% complete, producing Cp^*_2ZrHF and adamantane. For $C_{10}H_{16}$: ^1H NMR (C_6D_{12}) δ 1.86 (br, 4 H), 1.78 (br, 12 H); MS (*m*/*z*) 136 (M^+).

Reaction of 1,1-Difluoroethane with 1. Cyclohexane-d_{12} and ~10 mg of 10% palladium on carbon was added to a resealable NMR tube. In a 56-mL calibrated glass bulb, 13 Torr (0.039 mmol) of 1,1-difluoroethylene was condensed at −196 °C followed by admission of 1.3 atm of H_2. The mixture was thawed and stirred for 1 h at room temperature yielding 1,1-difluoroethane cleanly and quantitatively. For CF_2HCH_3: ^1H NMR (C_6D_{12}) δ 5.75 (tq, $J_{H-F} = 56.7$ Hz, 1 H), 1.43 (td, $J_{H-F} = 19.9$ Hz, 3 H); ^{19}F NMR (C_6D_{12}) δ −45.4 (m). The contents of the tube were vacuum transferred into another resealable NMR tube containing 28 mg of **1** (0.078 mmol). H_2 (1.3 atm) was admitted into the tube and the contents were heated at 150 °C for 24 h. At this point, $Cp^*_2ZrH_2$ was ~90% depleted with formation of Cp^*_2ZrHF, ethane, and a trace amount of $Cp^*_2ZrF_2$. For ethane: ^1H NMR (C_6D_{12}) δ 0.852 (s). The identity of ethane was further characterized by spiking with an authentic sample.

Reaction of 1,1,1-Trifluoropropane with 1. Cyclohexane-d_{12} and ~13 mg of 10% palladium on carbon was added to a resealable NMR tube. In a 56-mL calibrated glass bulb, 55 Torr (0.17 mmol) of 3,3,3-trifluoropropene was condensed at −196 °C followed by admission of 1.3 atm of H_2. The mixture was thawed and stirred for 1 h at room temperature yielding 1,1,1-trifluoropropane cleanly and quantitatively. For $CF_3CH_2CH_3$: ^1H NMR (C_6D_{12}) δ 1.97 (m, 2 H), 1.06 (t, 3 H); ^{19}F NMR δ −5.48 (t, $J_{H-F} = 11.3$ Hz). The contents of the tube were vacuum transferred into another resealable NMR tube containing 17 mg of $Cp^*_2ZrH_2$ (0.047 mmol). H_2 (1.3 atm) was admitted into the tube and the contents were heated at 150 °C for 2 weeks. At this point, $Cp^*_2ZrH_2$ was ~80% consumed with formation of Cp^*_2ZrHF in ~57% yield by NMR integration. Other unidentified decomposition products of $Cp^*_2ZrH_2$ were also observed. Propane was not unambiguously identified in the ^1H NMR spectrum.

Reaction of Difluorodichloromethane with 1. In a resealable NMR tube, 27 mg (0.074 mmol) of **1** was dissolved in cyclohexane-d_{12}. On the vacuum line, the tube was freeze−pump−thaw degassed three times. In a 56-mL calibrated glass bulb, 7 Torr (0.021 mmol) of CF_2Cl_2 was condensed at −196 °C. Hydrogen (1.3 atm) was admitted into the tube. Upon thawing, a yellow precipitate formed. ^1H and ^{19}F NMR revealed formation of a mixture of $Cp^*_2ZrCl_2$, Cp^*_2ZrHCl, and CF_2H_2. For $Cp^*_2ZrCl_2$: ^1H NMR (C_6D_{12}) δ 1.94 (s). For Cp^*_2ZrHCl: ^1H NMR δ 1.97 (s, 30 H), 6.54 (s, 1 H). For CF_2H_2: ^1H NMR δ 5.44 (t, $J_{H-F} = 50.2$ Hz); ^{19}F NMR δ −77.8 (t, $J_{H-F} = 51.9$ Hz). The mixture was then heated at 120 °C for 11 days. The reaction mixture now consisted of a mixture of $Cp^*_2ZrCl_2$, Cp^*_2ZrHCl, Cp^*_2ZrHF, and methane. For CH_4: ^1H NMR δ 0.19 (s). The identity of methane was further characterized by spiking with an authentic sample.

Reaction of Difluorochloromethane with 1. In a resealable NMR tube, 25 mg (0.069 mmol) of **1** was dissolved in cyclohexane-d_{12}. On the vacuum line, the tube was freeze−pump−thaw degassed three times. In a 56-mL calibrated glass bulb, 8 Torr (0.024 mmol) of $CHClF_2$ was condensed at −196 °C. Hydrogen (1.3 atm) was admitted into the tube. Upon thawing, a yellow precipitate formed. ^1H and ^{19}F NMR revealed formation of a mixture of $Cp^*_2ZrCl_2$, Cp^*_2ZrHCl, and CF_2H_2. The mixture was then heated at 120 °C for 10 days. The reaction mixture now consisted of a mixture of $Cp^*_2ZrCl_2$, Cp^*_2ZrHCl, Cp^*_2ZrHF, and methane.

Reaction of Dichlorofluoromethane with 1. In a resealable NMR tube, 20 mg (0.055 mmol) of **1** was dissolved in cyclohexane-d_{12}. On the vacuum line, the tube was freeze−pump−thaw degassed three times. In a 56-mL calibrated glass bulb, 6 Torr (0.018 mmol) of $CHFCl_2$ was condensed at −196 °C. Hydrogen (1.3 atm) was admitted into the tube. Upon thawing, a yellow precipitate formed. ^1H and ^{19}F NMR revealed formation of a mixture of $Cp^*_2ZrCl_2$, Cp^*_2ZrHCl, CH_3F, and a trace amount of Cp^*_2ZrHF. The mixture was allowed to stand at room temperature for 1 day. The reaction mixture then consisted mostly of Cp^*_2ZrHCl and Cp^*_2ZrClF and methane. Only small amounts of Cp^*_2ZrHF and $Cp^*_2ZrF_2$ were present. For CH_3F: ^1H NMR (C_6D_{12}) δ 4.08 (d, $J_{H-F} = 46.4$ Hz); ^{19}F NMR δ −205.0 (q, $J_{H-F} = 45.2$ Hz). For Cp^*_2ZrClF: ^1H NMR δ 1.901 (s); ^{19}F NMR δ 129.5 (s).

Preparation of Cyclopropylcarbinyl Fluoride. Cyclopropylcarbinyltosylate (3.59 g, 0.0159 mmol) was added to "anhydrous" tetrabutylammonium fluoride[26] (prepared from 10 g [0.038 mmol] of TBAF·$3H_2O$), and the oily mixture was stirred for 2 h. The solution was freeze−pump−thawed three times on the vacuum line and the volatiles of the reaction were vacuum transferred into an empty ampule. About 1 mL of material was collected, consisting of an organic and aqueous layer. The organic layer was separated by removal with a syringe. ^1H NMR analysis of the organic layer showed ~50% cyclopropylcarbinyl fluoride along with olefin(s) and other unidentified impurities. Pure cyclopropylcarbinyl fluoride was obtained by treating 7 μL of the crude material with 50 mg of $Cp^*_2ZrH_2$ in cyclohexane-d_{12}. Immediately following mixing, the solution was freeze−pump−thawed three times and the volatiles were transferred to an empty NMR tube. This sample analyzed as >95% pure cyclopropylcarbinyl fluoride in C_6D_{12}. ^{19}F NMR

(22) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.
(23) Yoneda, N.; Fukuhara, T.; Nagata, S.; Suzuki, A. *Chem. Lett.* **1985**, 1693.
(24) Nesmeyanov, A. N.; Vanchikov, A. N.; Lisichkina, I. N.; Lazarev, V. V.; Tolstaya, T. P. *Dokl. Akad. Nauk SSSR Ser. Khim.* **1980**, *255*, 1136.
(25) Blayney, M. B.; Winn, J. S.; Nierenberg, D. W. *Chem. Eng. News* **1997**, *75* (19), 7.
(26) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(C_6D_{12}): δ −144.4 (td, J_{H-F} = 51 Hz); ^{1}H NMR δ 4.05 (dd, J_{H-F} = 49 Hz, 2 H), 1.10 (m, 1 H), 0.52 (m, 2 H), 0.23 (m, 2 H); MS (*m*/*z*) 74 (M^+). To this solution, 0.40 μL of $Me_3SiSiMe_3$ was added as a standard to determine the amount of cyclopropylcarbinyl fluoride present in solution.

Reaction of Cyclopropylcarbinyl Fluoride with 1. To a resealable NMR tube, **1** (10 mg, 0.027 mmol) was added and dissolved in a solution of cyclopropylcarbinyl fluoride (0.028 mmol) [see preparation of cyclopropylcarbinyl fluoride] in C_6D_{12}. After 15 min at room temperature, NMR analysis revealed a clean 1:1 mixture of Cp^*_2ZrHF, Cp^*_2Zr(*n*-butyl)H, and unreacted cyclopropylcarbinyl fluoride. No methylcyclopropane was observed. For Cp^*_2Zr(*n*-butyl)H: ^{1}H NMR (C_6D_{12}) δ 5.20 (s, Zr*H*, 1 H), 1.90 (s, Cp*, 30 H), 0.85 (t, $ZrCH_2CH_2CH_2CH_2CH_3$, 3 H), 1.17 (sex, $ZrCH_2CH_2CH_2CH_2CH_3$, 2 H), 0.10 (m, $ZrCH_2CH_2CH_2CH_2CH_3$, 2 H), −0.04 (m, $ZrCH_2CH_2CH_2CH_2CH_3$, 2 H). For further characterization of Cp^*_2Zr(*n*-butyl)H, the solution was freeze−pump−thawed three times and 1.3 atm of H_2 was admitted into the tube. After 5 min, Cp^*_2Zr(*n*-butyl)H had fully reacted to form butane and $Cp^*_2ZrH_2$. For butane: ^{1}H NMR (C_6D_{12}) δ 1.29 (m, 4 H), 0.89 (m, 6 H); MS (*m*/*z*) 58 (M^+).

Reaction of Fluorobenzene with $Cp^*_2ZrH_2$. A resealable NMR tube was charged with 21 mg (0.058 mmol) of **1** and dissolved in cyclohexane-d_{12}. Fluorobenzene (5.4 μL, 0.058 mmol, ρ = 1.02) was added via syringe. The tube was then freeze−pump−thaw degassed three times and 1.3 atm of H_2 was admitted into the tube. The tube was heated at 85 °C for 40 days, monitoring periodically over this time. At the end, the reaction mixture consisted of a 1:1:0.75 mixture of Cp^*_2ZrHF, benzene, and $Cp^*_2Zr(C_6H_5)F$. For $Cp^*_2Zr(C_6H_5)F$: ^{1}H NMR (C_6D_{12}) δ 1.72 (s, 30 H), 6.89 (m, 2 H), 7.00 (m, 3 H); ^{19}F NMR δ 139.7 (s). For C_6H_6: ^{1}H NMR δ 7.21 (s). $Cp^*_2Zr(o\text{-}C_6H_4F)H$ was observed as a transient species.

Synthesis of $Cp^*_2Zr(o\text{-}C_6H_4F)H$. In the drybox, 50 mg (0.137 mmol) of **1** and 27 mg (0.069 mmol) of $Hg(o\text{-}C_6H_4F)_2$ were added to a vial. Pentane (∼5 mL) was added and the mixture was stirred for 30 min at room temperature. Vigorous evolution of H_2 occurred and elemental mercury was formed. The product mixture was filtered over Celite and stripped to dryness leaving a yellow microcrystalline mass of >95% pure $Cp^*_2Zr(o\text{-}C_6H_4F)H$ (62 mg, 98%). X-ray quality crystals were obtained by crystallization from pentane at −30 °C. ^{1}H NMR (C_6D_{12}) δ 1.82 (s, 30 H), 6.34 (m, 1H), 6.59 (s, 1 H, Zr*H*), 6.61 (m, 1 H), 6.85 (m, 2H). ^{19}F NMR δ −28.0 (m). Anal. Calcd for $C_{26}H_{35}ZrF$: C, 68.22; H, 7.71. Found: C, 68.15; H, 7.91.

Thermolysis of $Cp^*_2Zr(o\text{-}C_6H_4F)H$. In the drybox, a resealable NMR tube was charged with 12 mg of $Cp^*_2Zr(o\text{-}C_6H_4F)H$, dissolved in cyclohexane-d_{12}. The tube was heated at 80 °C for 18 days producing $Cp^*_2Zr(C_6H_5)F$ cleanly and quantitatively. The volatiles were removed in vacuo and the residue was recrystallized in pentane at −30 °C to yield a single crystal that was sent for elemental analysis. Anal. Calcd for $C_{26}H_{35}ZrF$: C, 68.22; H, 7.71. Found: C, 67.91; H, 7.58.

Preparation of $Cp^*_2Zr(C_6H_5)F$. Into an ampule, 100 mg of $Cp^*_2ZrF_2$ (0.25 mmol) and 23 mg of phenyllithium (0.27 mmol) were added and suspended in ∼10 mL of toluene. The mixture was freeze−pump−thawed and heated to 85 °C for 5 h with stirring. The reaction mixture was stripped to dryness and ∼10 mL of pentane was added. Filtration over dried Celite, concentration, and crystallization at −30 °C yielded 47 mg (41%) of $Cp^*_2Zr(C_6H_5)F$. (See NMR data above.)

Reaction of 1-Fluoronaphthalene with $Cp^*_2ZrH_2$. A resealable NMR tube was charged with 15 mg (0.041 mmol) of **1** and dissolved in cyclohexane-d_{12}. 1-Fluoronaphthalene (4.52 μL, 0.041 mmol, ρ = 1.33) was added via syringe. The tube was freeze−pump−thaw degassed three times and 1.3 atm of H_2 was admitted into the tube. The tube was heated to 85 °C for 4 days producing Cp^*_2ZrHF and naphthalene in quantitative yield. For $C_{10}H_8$: ^{1}H NMR (C_6D_{12}) δ 7.33 (m, 4 H), 7.70 (m, 4 H); MS (*m*/*z*) 128 (M^+).

Thermal Decomposition of $Cp^*_2ZrH_2$. A resealable NMR tube was charged with 10 mg of $Cp^*_2ZrH_2$ and placed under high vacuum on the vacuum line. The tube was immersed in an 85 °C oil bath for 19 h over which time a small amount of red solid had formed. The solid residue was dissolved in C_6D_{12} and analyzed by ^{1}H NMR spectroscopy revealing a 5:1 ratio of $Cp^*_2ZrH_2$ and $Cp^*(C_5Me_3(CH_2)_2)Zr$. For $Cp^*(C_5Me_3(CH_2)_2)Zr$: ^{1}H NMR (C_6D_{12}) δ 2.01 (s, 15 H), 1.72 (s, 3 H), 1.31 (s, 6 H), 0.80 (d, 2 H, J = 6.2 Hz), 0.47 (d, 2 H, J = 6.2 Hz).

Acknowledgment. The authors thank the U.S. Department of Energy, Grant FG02-86ER13569 for support of this work.

Supporting Information Available: A description of the X-ray experimental procedures and tables giving crystallographic data, intramolecular distances and angles, and positional and thermal parameters for **1**, **2**, $Cp^*_2ZrF_2$, $Cp^*_2Zr(o\text{-}C_6H_4F)H$, and $Cp^*_2Zr(C_6H_5)F$ (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA016087L