Communications to the Editor

Aliphatic Carbon−Fluorine Bond Activation Using $(C_5Me_5)_2ZrH_2$

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

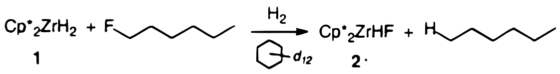
Department of Chemistry, University of Rochester
Rochester, New York 14627

Received March 21, 2000

Carbon−fluorine bonds are among the strongest and most inert single bonds found in organic compounds.[1] The extraordinary properties of fluorocarbons have led to their increased use commercially and, in turn, to an increased interest in the study of C−F activation. In particular, the development of CFC disposal methods remains a challenging task.[2]

A variety of early transition metal complexes have been shown to be reactive toward aromatic C−F bonds such as those in perfluorobenzene,[2−4] while only a few metal complexes show well characterized reactions with aliphatic fluorocarbons.[5] The use of early transition metal hydride reagents in C−F activation remains largely unexplored. In fact, only two examples of C−F activation by early transition metal hydrides have been documented.[6] The dihydride complex $Cp^*_2ZrH_2$ is known to react with a variety of unsaturated small molecules through what are commonly classified as electrophilic concerted addition reactions.[7] We have found that $Cp^*_2ZrH_2$ reacts with many types of fluorinated substrates to give hydrogenated organic products and Cp^*_2ZrHF.

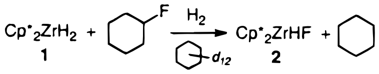
Reaction of $Cp^*_2ZrH_2$ (**1**) with 1-fluorohexane in cyclohexane-d_{12} at ambient temperature under 1.3 atm H_2 has been found to produce hexane and Cp^*_2ZrHF (**2**) in quantitative yield (eq 1).



(1)

The reaction proceeds to completion within 2 days, and no intermediates are observed. Both $Cp^*_2ZrH_2$ and Cp^*_2ZrHF have been characterized by X-ray crystallography, and show the expected bent metallocene geometries.[8] Independent experiments employing isolated Cp^*_2ZrHF show that this species does not disproportionate to give $Cp^*_2ZrF_2$ and $Cp^*_2ZrH_2$, as is believed to occur with Cp_2ZrHF.[4c] Reaction of Cp^*_2ZrHF with an additional equivalent of 1-fluorohexane leads to quantitative formation of $Cp^*_2ZrF_2$, but elevated temperatures (120 °C) and extended reaction times (10 days) are required. When the reaction with **1** was repeated in the presence of cumene, a radical trap, no change in the rate of reaction was observed.

Secondary and tertiary monofluorinated carbon centers also react with $Cp^*_2ZrH_2$. Fluorocyclohexane (1 equiv) reacts under H_2 to give cyclohexane in quantitative yield over a period of 4 days at 120 °C (eq 2). 1-Fluoroadamantane reacts with **1** (1 equiv) under H_2 to give adamantane and **2**, but longer reaction times are required. The reaction was approximately 25% complete after 1 week at 120 °C.

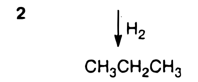


(2)

Aliphatic fluorocarbons containing $-CF_2H$ and $-CF_3$ groups also undergo defluorination, although with more difficulty. Reaction with 1,1-difluoroethane under H_2 affords ethane and Cp^*_2ZrHF. The reaction requires even higher temperatures (150 °C) reaching ∼90% completion after 1 day. The intermediate fluorocarbon, 1-fluoroethane, is not observed. Defluorination of 1,1,1-trifluoropropane under H_2 proceeds even more slowly (150 °C, >2 weeks). Again, no intermediate fluorocarbons (1,1-difluoropropane or 1-fluoropropane) are observed. Under these conditions, slow decomposition of $Cp^*_2ZrH_2$ occurs to give a yellow polymeric material of empirical formula believed to be $\{(C_5Me_5)(C_5(CH_3)_3(CH_2)_2)Zr\}_n$.[9] Although formation of Cp^*_2ZrHF was observed, propane could not be cleanly identified in the ^1H NMR spectrum.

CFCs also react to give HFCs and subsequent hydrogenated products.[10] Dichlorofluoromethane reacts readily at room temperature with 3 equiv of **1** to give fluoromethane, Cp^*_2ZrHCl, and a small amount of $Cp^*_2ZrCl_2$. Methane forms if the sample is allowed to stand for 1 day at ambient temperature, with Cp^*_2ZrHF, $Cp^*_2ZrF_2$, 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 other geminal polyfluorinated substrates, subsequent defluorination is more difficult, requiring heating to 120 °C under H_2 over period of >10 days.

Allylic and olefinic fluorinated substrates react much more quickly with **1**. 3,3,3-trifluoropropene reacts with 4 equiv of $Cp^*_2ZrH_2$ to give propane and Cp^*_2ZrHF (eq 3). Complete defluorination occurs within 10 min at room temperature! The intermediate fluorocarbon $CF_2{=}CH{-}CH_3$ was identified by GC/MS and its characteristic ^1H and ^{19}F NMR spectra when the reaction was



(3)

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(5) Aliphatic C−F references: (a) Kiplinger, J. L.; Richmond, *Chem. Commun.* **1996**, 1115. (b) Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805.

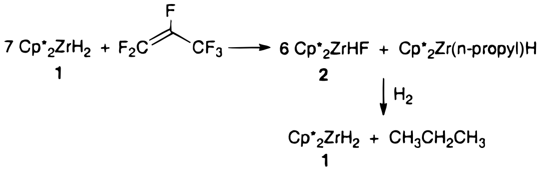
(6) (a) Burger, B. J. Ph.D. Thesis, California Institute of Technology, 1987. (b) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.

(7) (a) Bercaw, J. E. Advances in Chemistry Series, 167; American Chemical Society: Washington, DC, 1978; p 136. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (c) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

10.1021/ja001006r CCC: $19.00

repeated with 1 equiv of substrate. No other fluorocarbon species are seen in the ^{19}F NMR spectrum, where as little as a few percent could be detected. Although propene was not observed directly, the zirconium product Cp*$_2$Zr(*n*-propyl)H is seen prior to its decomposition to give propane.[11] Formation of propane is facilitated by addition of H_2 to the propyl hydride complex.

In an even more remarkable reaction, perfluoropropene was found to react with 7 equiv of Cp*$_2$ZrH$_2$ after 15 min at room temperature to give Cp*$_2$ZrHF and Cp*$_2$Zr(*n*-propyl)H (eq 4).

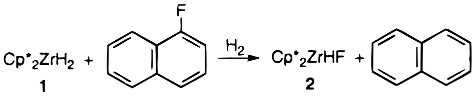


(4)

Again, propene is not observed, but rather Cp*$_2$Zr(*n*-propyl)H as an intermediate prior to its hydrogenolysis to give propane. Reaction with only 1 equiv of **1** gives mainly the selectively defluorinated product, (*E*)-$CF_3-CF{=}CHF$.

Benzylic activation of a CF_3 group proved more difficult. α,α,α-Trifluorotoluene reacts with 3 equiv of **1** under H_2 at 85 °C to give toluene and **2** only slowly over a period of >1 month, but reaches completion over 1 week at 120 °C. This observation, along with the trend observed with primary, secondary, and terteriary mono-fluoroalkanes, suggests that the F/H exchange does not occur via a radical chain process.

Cp*$_2$ZrH$_2$ also reacts with 1 equiv of perfluorobenzene after 1 day at 85 °C to give a mixture of Cp*$_2$ZrHF, Cp*$_2$Zr(C_6F_5)H, C_6F_5H, and Cp*$_2$ZrF$_2$ (2:1:1:0.1 ratio). Repetition of the reaction in the presence of cumene gives the same ratio of products at the same rate. Unlike the reaction with [Cp$_2$ZrH$_2$]$_2$, no Cp*$_2$Zr(C_6F_5)F was observed.[3c] In comparison, 1-fluoro-naphthalene (1 equiv) reacts cleanly under H_2 over a period of 4 days at 85 °C to give naphthalene and Cp*$_2$ZrHF (eq 5).



(5)

The formation of a strong Zr−F bond is no doubt a main driving force for all of these reactions. Surprisingly, reaction of [Cp$_2$ZrH$_2$]$_2$ with 1-fluorohexane does not lead to C−F activation, suggesting the enhanced hydridic character in the Cp* analog likely plays a major role in the mechanism. For the aliphatic systems, the order of reactivity 1° > 2° > 3° suggests that fluorine coordination to zirconium is necessary for hydrodefluorination. The reactivity trends together with experiments performed in the presence of a radical trap suggest that radical abstraction of fluorine is not involved. Consequently, many of these reactions are believed to proceed via a "bond metathesis pathway" involving simultaneous fluorine coordination to the 16-electron zirconium and hydridic attack on carbon. The olefins appear to react via an insertion/β-F-elimination pathway, building upon the well-established reactivity of the zirconium-hydride bond with olefins. These pathways are distinct from the common σ-bond metathesis reactions in that a lone pair on fluorine is likely to be involved in the 6-electron rearrangements. A full mechanistic investigation of these reactions is under study.

Acknowledgment is given to the U.S. Department of Energy (FG02-86ER13569) for their support of this work.

JA001006R

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[8] Details of the structures will be reported elsewhere. For Cp*$_2$ZrH$_2$, the rings are oriented at an angle of 144.6°, whereas for Cp*$_2$ZrHF, the Cp*−Zr−Cp* angle is 141.0°.

[9] Bercaw, J. E.; McAlister, D. R.; Erwin, D. K. *J. Am. Chem. Soc.* **1978**, *100* (18), 5966. This material also forms if H_2 is omitted from these reactions.

[10] CFC = chlorofluorocarbon. HFC = hydrofluorocarbon.

[11] Sanner, R. D.; Miller, F. D. *Organometallics* **1988**, *7*, 818.