Aliphatic Carbon–Fluorine Bond Activation Using (C₅Me₅)₂ZrH₂

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Received March 21, 2000

Carbone–fluorine bonds are among the strongest and most inert single bonds found in organic compounds. 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.

A variety of early transition metal complexes have been shown to be reactive toward aromatic C–F bonds such as those in perfluorobenzene, while only a few metal complexes show well characterized reactions with aliphatic fluorocarbons. The use of early transition metal hydrides in C–F activation remains a challenging task.

The reaction proceeds to completion within 2 days, and no intermediates are observed. Both Cp*₂ZrH₂ and Cp*₂ZrHF have been characterized by X-ray crystallography, and show the expected bent metalloocene geometries. Independent experiments employing isolated Cp*₂ZrHF show that this species does not disproportionate to give Cp*₂ZrF₂ and Cp*₂ZrH₂, as is believed to occur with Cp*₂ZrHF. Reaction of Cp*₂ZrHF with an additional equivalent of 1-fluorohexane leads to quantitative formation of Cp*₂ZrF₂, but elevated temperatures (120 °C) and extended reaction times (10 days) are required. When the reaction with I 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*₂ZrH₂. Florocyclohexane (1 equiv) reacts under H₂ to give cyclohexane in quantitative yield over a period of 4 days at 120 °C (eq 2). 1-Fluoroadamantane reacts with I (1 equiv) under H₂ to give adamantane and 2, but longer reaction times are required. The reaction was approximately 25% complete after 1 week at 120 °C.

Aliphatic fluorocarbons containing –CF₃H and –CF₂ groups also undergo defluorination, although with more difficulty. Reaction with 1,1-difluoroethane under H₂ 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 H₂ proceeds even more slowly (150 °C, >2 weeks). Again, no intermediate fluorocarbons (1,1-difluoropropane or 1-fluoro propane) are observed.

Under these conditions, slow decomposition of Cp*₂ZrH₂ occurs to give a yellow polymeric material of empirical formula believed to be \((\text{C}_n\text{Me}_{2n})\text{Zr}\). Although formation of Cp*₂ZrHF was observed, propane could not be cleanly identified in the 'H NMR spectrum.

CFCs also react to give HFCs and subsequent hydrogenated products. Dichlorofluoromethane reacts readily at room temperature with 3 equiv of I to give fluoromethane, Cp*₂ZrCl₂, and a small amount of Cp*₂ZrF₂. Methane forms if the sample is allowed to stand for 1 day at ambient temperature, with Cp*₂ZrHF, Cp*₂ZrF₂, and Cp*₂ZrFCl also being observed. Diluorodichloromethane and difluorochloromethane were also found to give initially the dechlorinated organic product, difluoromethane, upon reaction with 4 equiv of I. As with other geminal polyfluorinated substrates, subsequent defluorination is more difficult, requiring heating to 120 °C under H₂ over period of >10 days.

 Allylic and olefinic fluorinated substrates react much more quickly with I. 3,3,3-trifluoropropene reacts with 4 equiv of Cp*₂ZrH₂ to give propane and Cp*₂ZrHF (eq 3). Complete defluorination occurs within 10 min at room temperature! The intermediate fluorocarbon CF₂=CH₂ was identified by GC/MS and its characteristic 'H and 'F NMR spectra when the reaction was

10.1021/ja001006r CCC: $19.00 © 2000 American Chemical Society
Published on Web 08/18/2000
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 $\text{Cp}^*\text{Zr}(\text{n-propyl})\text{H}$ is seen prior to its decomposition to give propane.\textsuperscript{11} Formation of propane is facilitated by addition of $\text{H}_2$ to the propyl hydride complex.

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

\[
\text{7 Cp}^*\text{ZrH}_2 + \text{F}_3\text{C} = \text{CF}_3 \rightarrow \text{6 Cp}^*\text{ZrHF} + \text{Cp}^*\text{Zr}(\text{n-propyl})\text{H}
\]

(4)

Again, propene is not observed, but rather $\text{Cp}^*\text{Zr}(\text{n-propyl})\text{H}$ as an intermediate prior to its hydrogenolysis to give propane. Reaction with only 1 equiv of 1 gives mainly the selectively defluorinated product, $(E)$-$\text{CF}_3\text{-CF}=$CHF.

Benzyllic activation of a CF$_3$ group proved more difficult. $\alpha,\alpha,\alpha$-Trifluorotoluene reacts with 3 equiv of 1 under $\text{H}_2$ 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 tertiary mono-fluoroalkanes, suggests that the F/H exchange does not occur via a radical chain process.

Cp*-ZrH$_2$ also reacts with 1 equiv of perfluorobenzene after 1 day at 85 °C to give a mixture of $\text{Cp}^*\text{ZrHF}$, $\text{Cp}^*\text{Zr}(\text{CF}_3)\text{H}$, $\text{C}_6\text{F}_5\text{H}$, and $\text{Cp}^*\text{ZrF}_2$ (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 $[\text{Cp}_2\text{ZrH}_2]$, no $\text{Cp}^*\text{Zr}(\text{CF}_3)\text{F}$ was observed.\textsuperscript{3c} In comparison, 1-fluoro-naphthalene (1 equiv) reacts cleanly under $\text{H}_2$ over a period of 4 days at 85 °C to give naphthalene and $\text{Cp}^*\text{ZrHF}$ (eq 5).

\[
\text{Cp}^*\text{ZrH}_2 + \text{naphthalene} \rightarrow \text{Cp}^*\text{ZrHF} + \text{naphthalene}
\]

(5)

The formation of a strong Zr−F bond is no doubt a main driving force for all of these reactions. Surprisingly, reaction of $[\text{Cp}_2\text{ZrH}_2]$ 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.

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

JA001006R

(8) Details of the structures will be reported elsewhere. For $\text{Cp}^*\text{ZrH}_2$, the rings are oriented at an angle of 144.6°, whereas for $\text{Cp}^*\text{ZrHF}$, the $\text{Cp}^*\text{ZrZrCp}^*$ 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 $\text{H}_2$ is omitted from these reactions.

(10) CFC = chlorofluorocarbon. HFC = hydrofluorocarbon.