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Mechanism of Vinylic and Allylic Carbon−Fluorine Bond Activation of Non-Perfluorinated Olefins Using $Cp^*_2ZrH_2$

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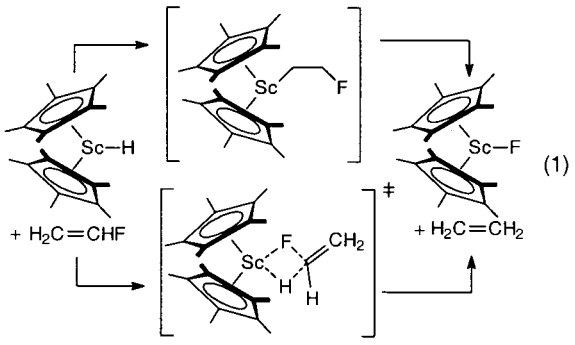
Abstract: $Cp^*_2ZrH_2$ (**1**) (Cp^* = pentamethylcyclopentadienyl) reacts with vinylic carbon−fluorine bonds of $CF_2{=}CH_2$ and 1,1-difluoromethylenecyclohexane ($CF_2{=}C_6H_{10}$) to afford Cp^*_2ZrHF (**2**) and hydrodefluorinated products. Experimental evidence suggests that an insertion/β-fluoride elimination mechanism is occurring. Complex **1** reacts with allylic C−F bonds of the olefins, $CH_2{=}CHCF_3$, $CH_2{=}CHCF_2CF_2CF_2CF_3$, and $CH_2{=}C(CF_3)_2$ to give preferentially **2** and $CH_3{-}CH{=}CF_2$, $CH_3{-}CH{=}CF{-}CF_2CF_2CF_3$, and $CF_2{=}C(CF_3)(CH_3)$, respectively, by insertion/β-fluoride elimination. In the reactions of **1** with $CH_2{=}CHCF_3$ and $CH_2{=}CHCF_2CF_2CF_2CF_3$, both primary and secondary alkylzirconium olefin insertion intermediates were observed in the ^1H and ^{19}F NMR spectra at low temperature. A deuterium labeling study revealed that more than one olefin-dihydride complex is likely to exist prior to olefin insertion. In the presence of excess **1** and H_2, $CH_2{=}CHCF_3$ and $CH_2{=}CHCF_2CF_2CF_2CF_3$ are reduced to propane and (*E*)-$CH_3CH_2CF{=}CFCF_2CF_3$, respectively.

Introduction

The cleavage of highly inert carbon−fluorine bonds by transition-metal complexes has received considerably little attention in the past few decades.[1] Activation of C−F bonds often requires forcing conditions and, in many cases, results in loss of selectivity and/or overreduction of the fluorocarbon to form undesirable products. However, transition-metal complexes have been shown to activate strong C−F bonds under very mild conditions and therefore offer potential for selective C−F activation and elimination of overreduction products. Overcoming these hurdles will no doubt assist in the manufacture of valuable products for the chemical industry and could find applications in chlorofluorocarbon (CFC) interconversions.

Most C−F activation reactions by transition-metal complexes involve aromatic or olefinic fluorocarbons,[2] while relatively few examples are reported for aliphatic fluorocarbons.[3] This is, in part, attributed to the weak σ-basicity of the fluorine lone pairs and the absence of a π-framework resulting in weak coordinating ability of saturated fluorocarbons. Fluorinated olefins are generally much more reactive. The highly electronegative fluorine atom prefers to bond to carbon orbitals of minimal "s" character, favoring sp^3 versus sp^2 orbitals. In addition, repulsion between lone pairs on fluorine and π-electrons destabilizes the unsaturated site.[4]

A few examples of apparent β-F elimination processes have been reported in reactions of transition-metal complexes with fluorinated olefins. For example, in a study by Burger,[5] Cp^*_2ScH and fluoroethylene reacted at −80 °C to give Cp^*_2ScF and $Cp^*_2ScCH_2CH_3$ (eq 1). Because no intermediates were observed, two possible mechanisms were proposed and unresolved: (1) an olefin insertion followed by β-fluoride elimination to give ethylene, and (2) a direct four-centered metathesis, exchanging hydrogen for fluorine. Free ethylene was not observed, as fast insertion into another Cp^*_2ScH occurs to form $Cp^*_2ScCH_2CH_3$.



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* To whom correspondence should be addressed. E-mail: jones@chem.rochester.edu.

(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*, 373. (b) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber.* **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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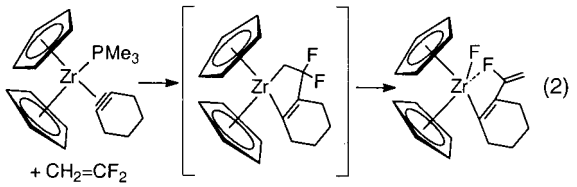
10.1021/ja0125568 CCC: $22.00

Very recently, Caulton et al. showed that Cp_2ZrHCl reacts with fluoroethylene to give Cp_2ZrFCl, $Cp_2Zr(CH_2CH_3)Cl$, and Cp_2ZrF_2.[6] Again, no intermediates were observed in this reaction, but DFT calculations suggested that a metathesis mechanism was energetically disfavored over an insertion/elimination pathway. The calculations also predicted a transition state leading to the insertion product rather than an η^2-olefin complex as a stable intermediate.

Buchwald has presented an interesting example of C−F bond activation of a fluorinated olefin involving the zirconium cyclohexyne complex, $Cp_2Zr(PMe_3)(C_6H_8)$ (eq 2).[7] A mechanism was proposed involving an initial insertion of the olefin followed by β-fluoride elimination to form the strong Zr−F bond.



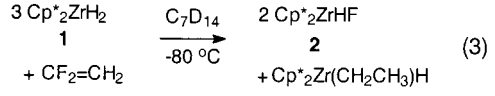
(2)

β-X elimination processes are also believed to be responsible for the inability of early transition-metal complexes to polymerize vinyl halides by a coordination/insertion mechanism. Jordan has recently shown that [*rac*-(EBI)ZrMe][$MeB(C_6F_5)_3$] (EBI = 1,2-bis(indenyl)ethylene) reacts stoichiometrically with 2 equiv of vinyl chloride to give $Cp^*_2ZrCl_2$, $B(C_6F_5)_3$, and atactic polypropylene.[8] The observed products were explained by a mechanism involving an initial vinyl chloride insertion into the Zr−Me bond followed by β-Cl elimination to release propene, although these processes were not directly observed.

In this manuscript, the mechanism of hydrodefluorination reactions of $Cp^*_2ZrH_2$ with polyfluorinated olefins is described in detail. Nonperfluorinated olefins containing vinylic and allylic C−F bonds react by an insertion/β-fluoride elimination mechanism. The insertion/β-fluoride elimination step has been evidenced by the characterization of insertion intermediates at low temperature. Further studies using deuterium labeling suggest that insertion to form the secondary alkylzirconium hydride intermediate involves olefin coordination exclusively in the lateral positions of the metallocene.

Results and Discussion

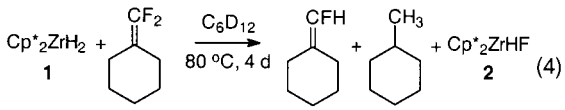
Reaction of 1,1-Difluoroethylene and $Cp^*_2ZrH_2$. Reaction of $Cp^*_2ZrH_2$ (**1**) with 1 equiv of 1,1-difluoroethylene in cyclohexane-d_{12} at room temperature affords a 2:1 mixture of Cp^*_2ZrHF (**2**) and $Cp^*_2Zr(CH_2CH_3)H$, along with excess starting olefin (eq 3). Using low-temperature NMR spectroscopy in methylcyclohexane-d_{14} solvent, we found that the reaction proceeded at −80 °C with no intermediates or intermediate fluorocarbons observed.



(3)

Similar reactions have been observed with Cp^*_2ScH, Cp_2ZrHCl, and B_2H_6, and in all cases no intermediates were observed.[5,6,9] An insertion/β-fluoride elimination or a direct four-center metathesis mechanism has been proposed to explain these H/F exchanges. Another example of apparent insertion/β-fluoride elimination was reported in the reaction of diborane with 3,3,3-trifluoropropene.[10] The reaction products consisted of a complex mixture of 1,1-difluoropropene, 1-fluoropropene, *n*-propylboron difluoride, boron trifluoride, and 3,3,3-trifluoropropyl boron difluoride.

Reaction of 1,1-Difluoromethylenecyclohexane and $Cp^*_2ZrH_2$. In contrast to $CF_2{=}CH_2$, $Cp^*_2ZrH_2$ (1 equiv) is unreactive with 1,1-difluoromethylenecyclohexane ($CF_2{=}C_6H_{10}$) at room temperature. Consumption of **1** required heating the reaction mixture at 80 °C for 4 days to produce a mixture of **2**, 1-fluoromethylenecyclohexane, and methylcyclohexane in approximately a 5:1:2 ratio (eq 4). The extreme difference in reactivity relative to $CF_2{=}CH_2$ argues against a four-center metathesis pathway on steric grounds and suggests that insertion/β-fluoride elimination is highly likely for these vinylic C−F activation reactions. The insertion reaction with $CF_2{=}C_6H_{10}$ leading to a tertiary alkyl hydride complex is extremely difficult sterically and would be expected to require more harsh conditions, as observed. Tertiary alkylzirconium complexes, such as $Cp_2Zr(CMe_3)Cl$, have not been accessible for characterization even as intermediates.[11]



(4)

While an insertion to give an intermediate alkylzirconium complex with α-fluorine substitution might be considered, this process is electronically disfavored. The site of attack by nucleophiles (H^-) on fluorinated olefins is largely influenced by inductive effects and the stability of the carbanion formed in the transition state. In this case, hydride attack at the internal carbon of the olefin, $CF_2{=}C_6H_{10}$, leads to the destabilization of the developing negative charge on $-CF_2$. Although carbanions are inductively stabilized by α-substituted electron-withdrawing groups (i.e., fluorine), destabilizing fluorine lone pair repulsion with the carbanion is the dominant factor.[12] In addition, Caulton's theoretical calculations for the reaction of Cp_2ZrHCl with fluoroethylene predict regioselective insertion leading to fluorine substitution on C_β of the resulting fluoroalkyl ligand. The calculations also show that the transition-state energy for a four-center metathesis pathway is significantly higher than that for insertion/β-F elimination.[6]

The formation of methylcyclohexane can be explained by formation of methylenecyclohexane by subsequent defluorination of 1-fluoromethylenecyclohexane, fast insertion by **1** to form the methylcyclohexyl hydride complex, and finally decomposition of the alkylzirconium hydride to release the alkane.[13]

Reaction of 3,3,3-Trifluoropropene and $Cp^*_2ZrH_2$: Observation of Insertion Intermediates at Low Temperature. Reaction of 1 equiv of 3,3,3-trifluoropropene with **1** in cyclo-

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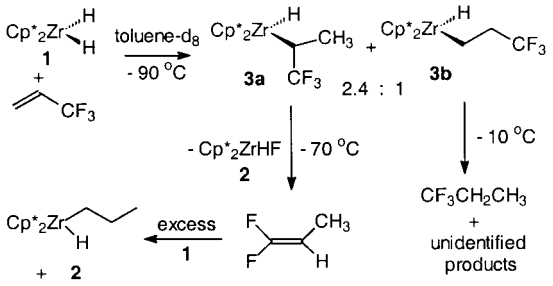
(13) For a study of decomposition of Cp^*_2ZrRH complexes, see: Miller, F. D. Ph.D. Dissertation, Arizona State University, 1986.

Scheme 1



hexane-d_{12} at room temperature affords a mixture of **2**, the intermediate olefin, $CF_2{=}CHCH_3$, $Cp^*_2Zr(CH_2CH_2CH_3)H$, $Cp^*_2ZrF_2$, and $CF_3CH_2CH_3$ in an ~23:12:4:2:1 ratio. Under similar conditions when excess **1** is present, only **2**, $Cp^*_2ZrF_2$, and $Cp^*_2Zr(CH_2CH_2CH_3)H$ are observed in an ~18:5:1 ratio. The ratio of the products was found to be dependent on temperature and effective mixing of the sample. For example, mixing the sample at −65 °C in toluene-d_8 and warming slowly consistently produces $CF_3CH_2CH_3$ in the product mixture. $CF_3CH_2CH_3$ was confirmed by independent preparation by hydrogenation of 3,3,3-trifluoropropene.

Using low temperature NMR spectroscopy in toluene-d_8 solvent, we observed both the internal and the terminal insertion products, $Cp^*_2Zr(CH(CF_3)CH_3)H$ (**3a**) and $Cp^*_2Zr(CH_2CH_2CF_3)H$ (**3b**), exclusively in a 2.4:1 ratio at −90 °C (Scheme 1). These complexes have been characterized by ^{1}H, ^{19}F, and ^{1}H COSY NMR spectroscopy at low-temperature only, as these intermediates are unstable upon warming. The internal insertion product **3a** displays a doublet in the ^{19}F NMR spectrum at δ −49.1, with coupling (J_{H-F} = 16.6 Hz) to the adjacent methine proton. The downfield shift of the $-CF_3$ resonance indicates strong deshielding by the Cp^*_2Zr fragment or possible transient interactions of the β-fluorines with the metal. The Cp* resonance was found to couple weakly with the zirconium-hydride resonance located at δ 5.84 as evidenced in the ^{1}H COSY spectrum. The *i*-propyl methyl resonance is a doublet with J_{H-H} = 7.3 Hz and is shifted upfield to δ −0.49 because of shielding by zirconium. The methine resonance was also located from the ^{1}H COSY spectrum as a broad multiplet. The terminal insertion complex **3b** was characterized by a triplet in the ^{19}F NMR spectrum showing a coupling constant, J_{H-F} = 10.2 Hz, typical for vicinal aliphatic H/F coupling.[14] The ^{1}H COSY spectrum of this species also shows weak coupling between the Cp* methyl and hydride resonances.

Complex **3a** reacts at −70 °C to form $CF_2{=}CHCH_3$ and **2** quantitatively by β-fluoride elimination. Isomerization of **3a** to **3b** was not observed at any time and was verified using an internal standard as an integration reference. Complex **3b** decomposes at −10 °C to give $Cp^*_2ZrF_2$, some $CF_3CH_2CH_3$, and unidentified product(s), evidenced by very broad peaks in the ^{19}F NMR spectrum. No other intermediate olefins were observed after the disappearance of $CF_2{=}CHCH_3$ even at low temperature. The formation of $Cp^*_2Zr(CH_2CH_2CH_3)H$ can be explained by a series of fast insertion/β-fluoride elimination steps and finally insertion of propene into the Zr−H bond of **1**.

The observed kinetic preference for internal alkyl insertion with $CH_2{=}CHCF_3$ appears unusual based on sterics, but is not unexpected based on electronics. By induction, the $-CF_3$ group may destabilize the developing positive charge on the internal carbon in the transition state of insertion and would prefer

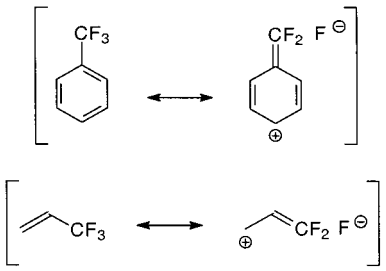
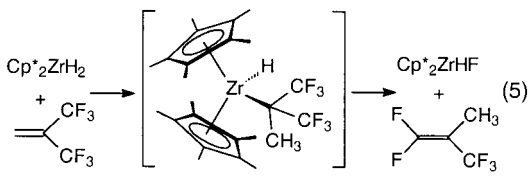


Figure 1. "Negative" hyperconjugation can be used to explain the reactivity of fluorinated olefins.

hydride attack on the terminal carbon to give the internal insertion product **3a**. Alternatively, C−F no-bond resonance, or "negative" hyperconjugation, can be invoked to explain the nature of the electronic effects of a perfluoroalkyl group.[15] A resonance form for α,α,α-trifluorotoluene has been proposed previously and can be extended to $CH_2{=}CHCF_3$ (Figure 1). The resonance form designates the terminal carbon as electron-deficient, the opposite of what would be expected by pure inductive effects. Negative hyperconjugation may also be responsible for weakening of the C−F bond. We have recently reported that 1,1,1-trifluoropropane is unreactive with $Cp^*_2ZrH_2$ at 85 °C, that α,α,α-trifluorotoluene is reduced to toluene at 85 °C over 30 d, and that 3,3,3-trifluoropropene is reactive at −70 °C to give hydrodefluorinated products.[3b] The presence of adjacent sp^2 orbitals capable of stabilizing "no-bond" resonance structures appears to increase significantly the rate of hydrodefluorination by $Cp^*_2ZrH_2$.

Further evidence for this powerful electronic effect is observed in the reaction of **1** with 3,3,3-trifluoro-2-(trifluoromethyl)propene. *For this substrate, internal olefin insertion requires zirconium to bond to a tertiary carbon*—an extremely sterically disfavored process. In fact, alkyl isomerization involving migration to a tertiary carbon with a nonfluorinated alkyl hydride complex, such as $Cp^*_2Zr(CH_2CH(CH_3)_2(H)$, is extremely slow ($t_{1/2}$ (23 °C) = 2.2 years)![11] However, the reaction with $CH_2{=}C(CF_3)_2$ occurs readily below −85 °C producing $CH_3(CF_3)C{=}CF_2$ and **2** *exclusively* with no formation of products derived from terminal insertion as observed in the reaction with $CH_2{=}CHCF_3$ (eq 5). Notably, this reaction occurs under even milder conditions than the reaction with $CH_2{=}CHCF_3$, possibly because of negative hyperconjugation with electronic delocalization over two $-CF_3$ groups. The tertiary alkyl hydride intermediate could not be observed at low temperature. The product olefin, 1,1-difluoro-(2-trifluoromethyl)propene, is unreactive with **1** at room temperature, following the similar lack of reactivity of 1,1-difluoromethylenecyclohexane.



(5)

Insertion/β-F elimination is also seen in the reaction of **1** with 3-trifluoromethyl-3,4,4,4-tetrafluoro-1-butene. Reaction of 1

(14) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972.
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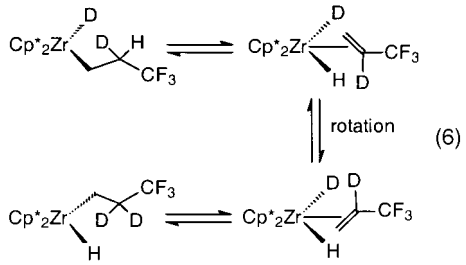
equiv of $CH_2{=}CHCF(CF_3)_2$ with **1** at room temperature gave a mixture of Cp^*_2ZrHF, $CH_3CH{=}C(CF_3)_2$, $Cp^*_2ZrF_2$, and $CH_3CH_2CF(CF_3)_2$ in a 1:1:0.25:2 ratio along with about 5% of an unidentified nonvolatile product.

Deuterium Labeling Studies. The reaction with $CH_2{=}CHCF_3$ was repeated using the deuterium-labeled complex, $Cp^*_2ZrD_2$. At −70 °C, the terminal deuteride insertion product, $Cp^*_2Zr(CH_2CHDCF_3)D$, $CF_2{=}CH{-}CH_2D$, and Cp^*_2ZrDF are observed as expected, the latter two products arising from β-F elimination in the internal deuteride insertion product. As the sample is warmed to −20 °C, the terminal insertion product exchanges deuterium between the hydride and β-position of the alkyl to give a 1.6:1 equilibrium mixture of $Cp^*_2Zr(CH_2CD_2CF_3)H$ and $Cp^*_2Zr(CH_2CHDCF_3)D$ (eq 6). This H/D exchange is clearly evidenced by the $-CF_3$ resonance in the ^{19}F NMR spectrum (Figure 2). The spectrum at −70 °C shows predominantly $Cp^*_2Zr(CH_2CHDCF_3)D$ (**A**) and a small amount of $Cp^*_2Zr(CH_2CD_2CF_3)H$ (**B**) as evidenced by the stepwise decrease in multiplicity of the $-CF_3$ resonance and upfield shifts. As the mixture is warmed to −20 °C, $Cp^*_2Zr(CH_2CD_2CF_3)H$ becomes the major isomer. Excess trifluoropropene is seen at −66.4 ppm. Notably, no incorporation of deuterium into trifluoropropene is observed as no additional upfield peak is observed. This observation indicates unequivocally that the H/D exchange is an intramolecular process. Nonfluorinated olefins were also found to undergo this type of exchange. For example, propene reacts with $Cp^*_2ZrD_2$ to give a 2:1 mixture of $Cp^*_2Zr(CH_2CD_2CH_3)H$ and $Cp^*_2Zr(CH_2CH(D)CH_3)D$, although the H/D exchange process occurred at a slightly higher temperature (0 °C).



(6)

An intermediate olefin-dihydride complex formed by β-hydride elimination is proposed to explain this H/D exchange process. Noting that the olefin is not labile, we found that both β positions cannot be substituted by deuterium unless the intermediate involves olefin coordination in the central equatorial position (eq 6). During the H/D exchange, no changes in the ratios of any other species are observed in the NMR spectra, indicating that no internal insertion product **3a** is formed, as β-fluoride elimination would rapidly occur in this species. Therefore, if an olefin complex is formed prior to formation of the internal insertion product **3a** during the initial zirconium-olefin encounter, we conclude that *it is not an olefin complex coordinated in the central equatorial site*.

Theoretical calculations for the reaction of fluoroethylene and Cp_2ZrHCl to give ethylene and Cp_2ZrFCl indicate that there is no η^2-olefin intermediate on the reaction path, but rather only a transition state.[6] The authors reason that the absence of electrons at the d^0 metal prevents stabilization by back-bonding, as may be the case for the Cp_2ZrHCl system and olefins with vinylic C−F bonds. Although $Cp^*_2ZrH_2$ is formally d^0, an intermediate olefin complex could be stabilized by electron density from the filled b_2 metal hydride bonding orbital and back-donation into the empty π^* olefin orbital of appropriate symmetry. Similar arguments have been proposed to explain the central coordination of CO in $Cp^*_2ZrH_2(CO)$ and potential dihydrogen adducts with $Cp^*_2ZrH_2$.[16,17]

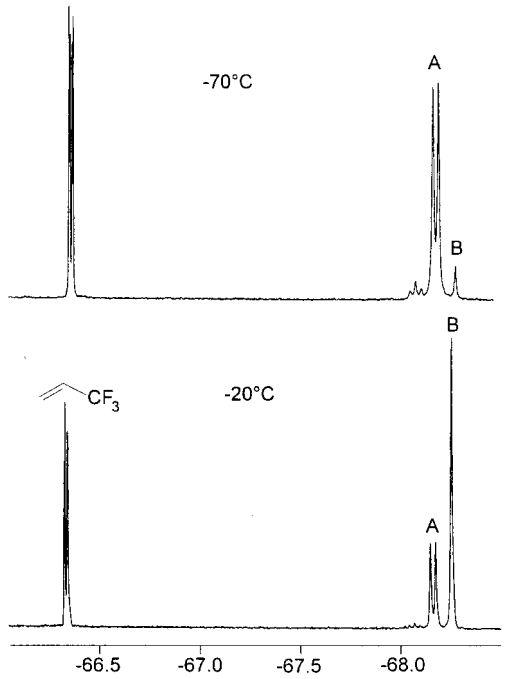


Figure 2. ^{19}F NMR spectra illustrating intramolecular deuterium exchange at the β-position of $Cp^*_2Zr(CH_2CH(D)CF_3)D$ (**A**) to give $Cp^*_2Zr(CH_2CD_2CF_3)H$ (**B**). A trace amount of $Cp^*_2Zr(CH_2CH_2CF_3)D$ can be seen at δ −68.1 (t).

In a recent study, intramolecular alkyl isomerization with $Cp^*_2Zr(CH_2CD(CH_3)_2)D$ was examined.[11] The deuterium-scrambled products, $Cp^*_2Zr(CHDCH(CH_3)_2)D$ and $Cp^*_2Zr(CH_2CH(CH_2D)(CH_3))D$, were believed to form via intermediate tertiary alkylzirconium hydride complexes formed by β-hydride elimination, olefin rotation and/or dissociation/reassociation, and reinsertion. In the present study, it appears consistent that alkyl isomerization (i.e., **3a** → **3b**) may require formation of an olefin complex in a lateral coordination site versus coordination in the central site, as no secondary alkylzirconium species are formed upon deuterium exchange involving the central-bound olefin-dihydride complex. Therefore, *at least two different olefin complexes are likely to be involved during the initial Zr-olefin encounter*. Scheme 2 illustrates two rotational isomers of the olefin complex with $CH_2{=}CHCF_3$ coordinated in a lateral site prior to formation of both terminal and internal insertion products. The olefin-dihydride complex with $CH_2{=}CHCF_3$ coordinated in the central equatorial site may also be involved in the initial Zr-olefin encounter, but would lead only to the terminal insertion product. The internal insertion product **3a** does not undergo reversible β-hydride elimination, as β-fluoride elimination rapidly takes place above −70 °C. Reversible β-hydride elimination from the terminal insertion product **3b** to give the laterally coordinated olefin complex may occur at higher temperatures (>−10 °C) upon its decomposition, but this possibility could not be studied in detail in this system.

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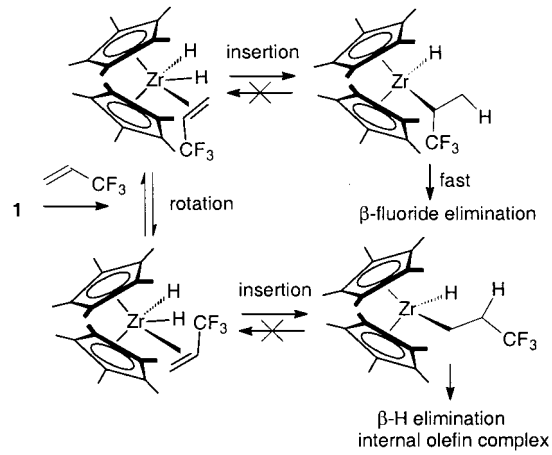
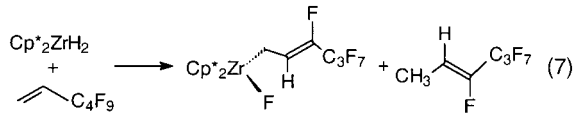
Scheme 2



Further details of this process are elucidated in the reaction of $Cp^*_2ZrH_2$ with nonafluoro-1-hexene.

Reaction of CH_2═$CHCF_2CF_2CF_2CF_3$ and $Cp^*_2ZrH_2$. Reaction of 1 equiv of **1** with 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene at room temperature in cyclohexane-d_{12} instantly produces a 2.3:2.3:1 mixture of **2**, (*Z*)-CH_3CH═CFC_3F_7, and (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ only (eq 7). H_2 was also observed in the ^1H NMR spectrum. When the reaction is performed at −70 °C in toluene-d_8 and warmed slowly to room temperature, the ratio observed was 7.3:7.3:1. Under these conditions, the fluoroalkane $CH_3CH_2C_4F_9$ is also observed with a respective integration of 0.6.



The products of the reaction were characterized by ^1H, ^{19}F, ^1H COSY, and ^{19}F COSY NMR spectroscopy and GC/MS. The identity of $CH_3CH_2C_4F_9$ was confirmed by independent preparation by hydrogenation of nonafluorohexene over Pd on carbon. The complex $Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ was elusive to separation, and further characterization by X-ray crystallography or elemental analysis was not possible. The stereochemistry of (*Z*)-CH_3CH═CFC_3F_7 and (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ was determined from typical magnitudes for vinylic *trans*-H/F coupling.[14]

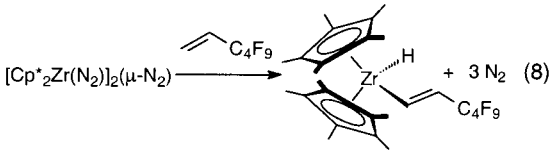
Like the reaction with trifluoropropene, both terminal and internal insertion intermediates in the reaction with nonafluorohexene are observed at −90 °C in methylcyclohexane-d_{14} solvent. The internal insertion complex is more reactive than the analogous intermediate observed in the trifluoropropene reaction and was observed only transiently, undergoing β-fluoride elimination even at −90 °C to give exclusively (*Z*)-CH_3CH═CFC_3F_7. This intermediate was characterized by ^{19}F NMR spectroscopy only, as the ^1H NMR resonances could not be assigned unambiguously. The terminal insertion intermediate, $Cp^*_2Zr(CH_2CH_2C_4F_9)H$, decomposes at −10 °C into (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ with concomitant formation of $CH_3CH_2C_4F_9$ and H_2. Very small increases (2−5%) in both Cp^*_2ZrHF and CH_3CH═CFC_3F_7 were also observed when the reaction was performed with an internal standard.

The ratio of **2**, (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$, and $CH_3CH_2C_4F_9$ is dependent on at least two factors. First, the temperature of mixing was also found to affect the ratio of (*Z*)-CH_3CH═CFC_3F_7 and $Cp^*_2Zr(CH_2CH_2C_4F_9)H$. The lower the temperature of mixing, the more internal insertion product is formed which in turn generates more of the *Z*-olefin. This observation is interpreted as a temperature dependence on the orientation of the olefin in the olefin-dihydride complexes prior to formation of the terminal or internal insertion product, as shown in Scheme 2 for the analogous reaction with trifluoropropene. Second, the rate of warming of the terminal insertion intermediate affects the ratio of $Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ and $CH_3CH_2C_4F_9$. The faster the solution is warmed above −10 °C, the less fluoroalkane is produced. Because H_2 was observed, it is likely that the formation of fluoroalkane is a product of hydrogenolysis of $Cp^*_2Zr(CH_2CH_2C_4F_9)H$, as is typical for Cp* zirconium alkyl hydride derivatives.[18] When the reactants are mixed and stirred at −78 °C under an atmosphere of added H_2 and allowed to warm slowly to room temperature, the amount of fluoroalkane is substantially increased, forming $Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ and $CH_3CH_2C_4F_9$ in a 0.2:1 ratio. The terminal insertion product is therefore believed to react with H_2 to give fluoroalkane in competition with intramolecular decomposition giving $Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$.

In a recent paper, reductive elimination of propane from $Cp^*_2Zr(CH_2CH_2CH_3)H$ was reported to be induced by added α-olefins.[11] The formation of fluoroalkane by a similar mechanism was considered for this reaction. However, in the absence or presence of excess olefin, the disappearance of $Cp^*_2Zr(CH_2CH_2C_4F_9)H$ was found to occur at the same rate with no change in the product ratios and with no other products observed.[19] The reaction of $Cp^*_2Zr(CH_2CH_2C_4F_9)H$ to form $Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ is therefore likely to be intramolecular and does not involve olefin-induced reductive elimination of alkane.

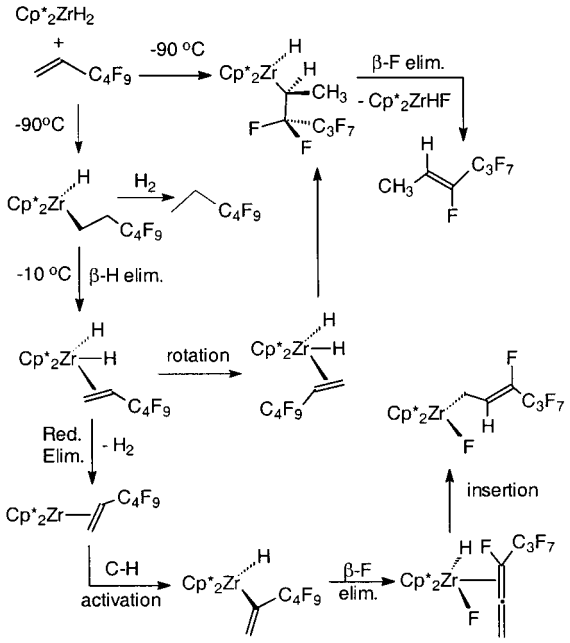
The deuterium-labeled complex, $Cp^*_2Zr(CH_2CH(D)C_4F_9)D$, was prepared by reaction of $Cp^*_2ZrD_2$ with the fluoroolefin in an attempt to probe the mechanism of decomposition and source of H_2. H/D exchange was again observed at −20 °C to give a 1:1.5 mixture of $Cp^*_2Zr(CH_2CH(D)C_4F_9)D$ and $Cp^*_2Zr(CH_2CD_2C_4F_9)H$. Upon warming to −10 °C, both H_2 and HD were observed in the ^1H NMR spectrum. Because of the H/D exchange process at the β position and the uncertainty of other possible hydride exchanges with H_2, the source of H_2 could not be determined unambiguously.

The reaction of nonafluorohexene with the known dinitrogen complex, $[Cp^*_2Zr]_2(N_2)_3$, was carried out to probe reactivity of a potential $[Cp^*_2Zr^{II}]$ intermediate.[20] Reaction of a 0.5:1 mixture of $[Cp^*_2Zr]_2(N_2)_3$ and nonafluorohexene at room temperature over ∼5 min produced a clean mixture of the C−H activated product, (*E*)-$Cp^*_2Zr(CH$═$CHC_4F_9)H$ (97%), and a small amount of (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFC_3F_7)F$ (3%), the latter also observed in the reaction with $Cp^*_2ZrH_2$ (eq 8). Both components of this mixture were unreactive with 1.3 atm of added H_2.

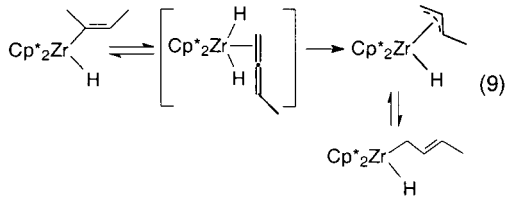


(18) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.
(19) The decomposition of $Cp^*_2Zr(CH_2CH_2CF_3)H$ was also found to occur even in the absence of all olefins at low temperature. See Experimental Section.

Scheme 3



$[Cp^*_2Zr]_2(N_2)_3$ is known to activate both internal and terminal vinylic C−H bonds.[21] 1-Butene, *cis*-, and *trans*-2-butene all react to give the crotyl-hydride complex, *syn*-$Cp^*_2Zr(\eta^3\text{-}C_4H_7)H$, at 40 °C. $Cp^*_2Zr(\eta^3\text{-}C_4H_7)H$ is also formed upon rearrangement of the 2-butenyl-hydride complex via a β-hydride elimination and reinsertion into the coordinated methylallene intermediate (eq 9).[22] Finally, NMR studies have shown that the crotyl-hydride complex is in equilibrium with the η^1-rearranged product.[21]



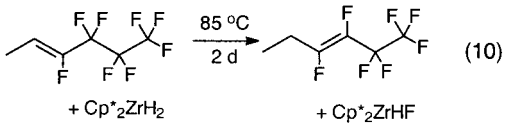
Similarly, activation of both internal and terminal C−H bonds could be occurring in the reaction with nonafluorohexene and $[Cp^*_2Zr]_2(N_2)_3$. The major product observed, $Cp^*_2Zr(CH{=}CH\text{-}C_4F_9)H$, can be explained by direct oxidative addition of the terminal C−H bond, whereas evidence for the internal C−H activation product could manifest itself as the rearranged product, $Cp^*_2Zr(CH_2CH{=}CFC_3F_7)F$.

The decomposition of $Cp^*_2Zr(CH_2CH_2C_4F_9)H$ can be explained by an initial β-hydride elimination to give an olefin-dihydride complex with the olefin coordinated in a lateral position (Scheme 3). The small increase in Cp^*_2ZrHF and $CH_3CH{=}CFC_3F_7$ upon disappearance of $Cp^*_2Zr(CH_2CH_2C_4F_9)H$ is consistent with a small amount of olefin rotation and reinsertion to give the internal insertion intermediate followed by β-fluoride elimination. The remainder of the olefin-dihydride complex undergoes reductive elimination of H_2 to give the Zr^{II} olefin complex. Internal vinylic C−H activation could then occur. The allene intermediate is then formed by fast β-fluoride elimination, followed by insertion to give the observed product, $(Z)\text{-}Cp^*_2Zr(CH_2CH{=}CFC_3F_7)F$.

Notably, no terminal vinylic C−H activation product is observed in the reaction with $Cp^*_2ZrH_2$ and nonafluorohexene, indicating that the predominant Zr^{II} intermediate is not the same as that involved in the reaction with $[Cp^*_2Zr]_2(N_2)_3$. A possible explanation is that the reactive species in the reaction with the dinitrogen complex is dimeric, retaining the bridging coordinated N_2, and disfavors internal C−H activation for steric reasons. By the same argument, the reaction with monomeric "Cp^*_2Zr" is less crowded, allowing access to cleave the internal C−H bond. The formation of both C−H activated products appears to be irreversible, as no $Cp^*_2Zr(CH{=}CHC_4F_9)H$ is formed in the reaction with $Cp^*_2ZrH_2$, $Cp^*_2Zr(CH_2CH{=}CFC_3F_7)F$ does not react with H_2, and, last, $Cp^*_2Zr(CH{=}CHC_4F_9)H$ does not rearrange to form $Cp^*_2Zr(CH_2CH{=}CFC_3F_7)F$ upon thermolysis in the presence of H_2.

The exclusive stereoselectivity of the product olefin, $(Z)\text{-}CH_3CH{=}CFC_3F_7$, is derived thermodynamically from β-fluoride elimination with the alkyl groups oriented trans. The ^{19}F NMR spectrum of the internal insertion intermediate, $Cp^*_2Zr(CH(CH_3)C_4F_9)H$, shows two distinct resonances for the $\beta\text{-}CF_2$ unit, indicating a single set of diastereotopic fluorine atoms. Very strong geminal F−F coupling (J_{F-F} = 248 Hz) is observed in a magnitude similar to that observed for 1,1-difluorocyclohexane.[23]

The product olefin, $(Z)\text{-}CH_3{-}CH{=}CFC_3F_7$, was heated in the presence of excess **1** at 85 °C for 2 d in cyclohexane-d_{12} to afford a new selectively defluorinated olefin, $(E)\text{-}CH_3CH_2CF{=}CFCF_2CF_3$, along with Cp^*_2ZrHF and $Cp^*_2ZrF_2$ (eq 10). The large F−F coupling (J_{F-F} = 133 Hz) identifies the trans stereochemistry of the double bond. The stereochemistry of the product can again be explained by insertion and β-fluoride elimination with the alkyl groups oriented trans. Further reaction with the olefin does not occur even in the presence of excess **1** and prolonged heating at 85 °C.



Reactions of Cp^*_2ZrHF with Olefins. Cp^*_2ZrHF is unreactive with 3,3,3-trifluoropropene, 1,1-difluoroethylene, and 1,1-difluoropropene in cyclohexane-d_{12}, even with heating at 85 °C. Even reaction of Cp^*_2ZrHF with propene does not lead to $Cp^*_2Zr(CH_2CH_2CH_3)F$. This is in direct contrast to reactivity of olefins observed with Schwartz's reagent, Cp_2ZrHCl, and $Cp^*CpZrHCl$.[24,25] Disproportionation of Cp^*_2ZrHF to form $Cp^*_2ZrH_2$ and $Cp^*_2ZrF_2$ does not occur, while the reverse reaction goes to completion.[26] $Cp^*_2ZrH_2$, if formed in even trace amounts in the reaction of **2** with trifluoropropene, for example, would react quickly to form Cp^*_2ZrHF especially at elevated temperatures.

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Conclusions

$Cp^*_2ZrH_2$ reacts with both allylic and vinylic C−F bonds of nonperfluorinated olefins by an insertion/β-fluoride elimination mechanism. The observation of decreased reactivity with 1,1-difluoromethylenecyclohexane provides solid experimental evidence against a σ-bond metathesis mechanism. Good selectivity for C−F activation is observed for a few olefinic substrates. Evidence is presented for kinetically preferred internal insertion with olefins containing allylic C−F bonds. A mechanistic investigation using deuterium labeling offers good evidence for the existence of several olefin-dihydride complexes prior to olefin insertion.

Experimental Section

General Considerations. All manipulations were performed inside a N_2-filled Vacuum Atmospheres glovebox or on a high vacuum line. Cyclohexane, cyclohexane-d_{12}, toluene-d_8, and methylcyclohexane-d_{14} (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.[27] D_2 (Cambridge) was used as received. 3,3,3-Trifluoropropene (Aldrich), 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (Aldrich), 3-trifluoromethyl-3,4,4,4-tetrafluoro-1-butene (Matrix), 1,1-difluoroethylene (Flura), and 3,3,3-trifluoro-2-(trifluoromethyl)propene (Matrix) were used as received. All liquids were degassed by the freeze−pump−thaw method. ^{1}H and ^{19}F NMR spectra were recorded using a Bruker Avance 400 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). ^{19}F NMR spectra were recorded at a minimum resolution of 0.5 Hz. GC/MS analyses were conducted using a 5890A Series GC equipped with a Restek RTX-5 column (0.25 mm i.d., 0.25 μ, 13 m) and a HP 5970 series mass selective detector. $Cp^*_2ZrH_2$, $Cp^*_2Zr(CH_2CH_2CH_3)H$, 1,1-difluoromethylenecyclohexane, and 1-fluoroadamantane were prepared according to the literature procedures.[11,28−30]

Reaction of 1 with 1,1-Difluoroethylene. A resealable NMR tube was charged with 13 mg (0.036 mmol) of $Cp^*_2ZrH_2$ and dissolved in cyclohexane-d_{12}. The solution was freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 82 Torr (0.036 mmol) of 1,1-difluoroethylene was condensed in at −196 °C. The tube was quickly warmed to room temperature, shaken, and analyzed. For $Cp^*_2Zr(CH_2CH_3)H$, ^{1}H NMR (C_6D_{12}): δ 1.81 (s, 30H, Cp*), −0.93 (t, 3H, J_{H-H} = 8.6 Hz, $ZrCH_2CH_3$), −0.17 (q, 2H, J_{H-H} = 8.7 Hz, $ZrCH_2CH_3$), 3.17 (s, 1H, Zr*H*). For **2**, ^{1}H NMR (C_6D_{12}): δ 1.92 (s, 30H, Cp*), 6.23 (s, 1H, Zr*H*F). ^{19}F NMR (C_6D_{12}): δ 77.67 (s, 1F).

Reaction of 1 with 1,1-Difluoromethylenecyclohexane. Fifteen milligrams (0.041 mmol) of $Cp^*_2ZrH_2$ was added to a resealable NMR tube and dissolved in cyclohexane-d_{12}. Next, 4.9 μL (0.041 mmol; d = 1.12 g/mL) of 1,1-difluoromethylenecyclohexane was added via microliter syringe, and the tube was immersed in a thermostated 80 °C oil bath for 4 d. A mixture of **2**, 1-fluoromethylenecyclohexane, and methylcyclohexane was formed in a 5.3:1:2.1 ratio along with starting olefin. The volatiles of the reaction mixture were vacuum transferred from the NMR tube for GC/MS analysis. For C_6H_{10}=CHF, ^{1}H NMR (C_6D_{12}): δ 6.26 (dm, J_{H-F} = 86.4 Hz, 1H, =C*H*F), 2.21 (br, 2H), 1.90 (br, 2H), 1.50 (m, 4H). The additional peak integrating for 2H is obscured. ^{19}F NMR (C_6D_{12}): δ −139.5 (d, J_{H-F} = 86.5 Hz, 1F, =CH*F*). MS (*m*/*z*): 114 (M^+). For $C_6H_{11}CH_3$, ^{1}H NMR (C_6D_{12}): δ 1.66 (m, 5H), 1.25 (m, 4H), 0.86 (m, 5H). GC/MS (*m*/*z*): 98 (M^+).

Reaction of 1 with 1 equiv of 3,3,3-Trifluoropropene. A resealable NMR tube was charged with 14 mg (0.038 mmol) of $Cp^*_2ZrH_2$ and dissolved in cyclohexane-d_{12}. The solution was freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 89 Torr (0.038 mmol) of trifluoropropene was condensed in at −196 °C. The solution was warmed to room temperature, shaken, and analyzed by ^{19}F and ^{1}H NMR. **2**, CF_2=$CHCH_3$, $Cp^*_2Zr(CH_2CH_2CH_3)H$, $Cp^*_2ZrF_2$, and $CF_3CH_2CH_3$ were observed in approximately a 23:12:4:2:1 ratio. For CF_2=$CHCH_3$, ^{1}H NMR (C_6D_{12}): δ 3.99 (m, 1H), 1.49 (m, 3H). ^{19}F NMR (C_6D_{12}): δ −88.9 (dquin, J_{F-F} = 47.8 Hz, 1F), −92.6 (ddq, J_{F-F} = 47.8 Hz, 1F). GC/MS (*m*/*z*): 78 (M^+). For $Cp^*_2Zr(CH_2CH_2CH_3)H$, ^{1}H NMR (C_6D_{12}): δ 1.91 (s, 30H, Cp*), 0.85 (t, 3H, $ZrCH_2CH_2CH_3$), 0.24 (sex, 2H, $ZrCH_2CH_2CH_3$), −0.026 (m, 2H, $ZrCH_2CH_2CH_3$), 5.32 (s, 1H, Zr*H*). For $Cp^*_2ZrF_2$, ^{1}H NMR (C_6D_{12}): δ 1.86 (s, 30H). ^{19}F NMR (C_6D_{12}): δ 34.1 (s, 2F). For $CF_3CH_2CH_3$, ^{1}H NMR (C_6D_{12}): δ 1.064 (t, 3H), 1.97 (m, 2H). ^{19}F NMR (C_6D_{12}): δ −69.21 (t, 3F).

Preparation of 1,1,1-Trifluoropropane. Cyclohexane-d_{12} and ~12 mg of 10% Pd on carbon were added to a resealable NMR tube. The mixture was freeze−pump−thaw degassed three times, and with an 8 mL calibrated glass bulb, 55 Torr (0.024 mmol) of 3,3,3-trifluoropropene was condensed in followed by admission of 1.3 atm of H_2. The tube was thawed and stirred for 1 h at room temperature, at which time, 1,1,1-trifluoropropane formed quantitatively. (See above for NMR data.)

Reaction of 4 equiv of 1 with 3,3,3-Trifluoropropene. A resealable NMR tube was charged with 16 mg (0.044 mmol) of $Cp^*_2ZrH_2$ and dissolved in cyclohexane-d_{12}. The solution was freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 25 Torr (0.011 mmol) of trifluoropropene was condensed in at −196 °C. The solution was warmed to room temperature, shaken, and analyzed by ^{19}F and ^{1}H NMR. **2**, $Cp^*_2ZrF_2$, and $Cp^*_2Zr(CH_2CH_2CH_3)H$ were observed in approximately a 18.3:5.4:1 ratio. No $CF_3CH_2CH_3$ or CF_2=$CHCF_3$ was observed.

Reaction of 1 with 3,3,3-Trifluoropropene at Low Temperature. A sealable NMR tube was charged with 14 mg (0.038 mmol) of $Cp^*_2ZrH_2$ and 5 mg (0.032 mmol) of 1-fluoroadamantane and dissolved in toluene-d_8. The solution was cooled to −94 °C with an acetone/N_2 slush bath and freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 76 Torr (0.032 mmol) of trifluoropropene was condensed in at −94 °C. The tube was flame sealed under vacuum. Effective mixing of the contents at −94 °C was accomplished by immersing the tube completely in the slush bath Dewar, covering with a cork, and inverting several times. The tube was then quickly placed into the thermostated −90 °C NMR probe. Two insertion products, $Cp^*_2Zr(CH(CF_3)CH_3)H$ and $Cp^*_2Zr(CH_2CH_2CF_3)H$, were observed in a 2.4:1 ratio, respectively, and characterized by ^{1}H, ^{19}F NMR, and ^{1}H COSY. **2** was not observed at this point in the reaction. For $Cp^*_2Zr(CH(CF_3)CH_3)H$, ^{1}H NMR (toluene-d_8, −80 °C): δ 1.606 (s, 30H, Cp*), −0.49 (d, J_{H-H} = 7.3 Hz, 3H, CH−C*H*$_3$), 0.92 (br, 1H, C*H*-CH$_3$), 5.84 (s, 1H, Zr*H*). ^{19}F NMR (toluene-d_8, −80 °C): δ −49.15 (d, J_{H-F} = 16.6 Hz, 3F). For $Cp^*_2Zr(CH_2CH_2CF_3)H$, ^{1}H NMR (toluene-d_8, −80 °C): δ 1.69 (s, 30H, Cp*), 0.05 (m, 2H, $ZrCH_2CH_2CF_3$), 1.5−2.0 (obscured by Cp* resonances, (2H), $ZrCH_2CH_2CF_3$), 6.08 (s, 1H, Zr*H*). ^{19}F NMR (toluene-d_8, −80 °C): δ −66.5 (t, 3F). Unambiguous assignment of the hydrides was possible by the observation of coupling between all Zr−H and corresponding Cp* methyl protons in the ^{1}H COSY spectrum. The sample was warmed to −70 °C. At this temperature, $Cp^*_2Zr(CH(CF_3)CH_3)H$ was converted into a 1:1 mixture of **2** and CF_2=$CHCH_3$ using 1-fluoroadamantane as an internal standard. The peak intensity of $Cp^*_2Zr(CH_2CH_2CF_3)H$ remained unchanged. For **2**, ^{1}H NMR (toluene-d_8, −70 °C): δ 1.89 (s, 30H, Cp*), 6.50 (s, 1H, Zr*H*F). ^{19}F NMR (toluene-d_8, −70 °C): δ 71.6 (s). For CF_2=$CHCH_3$, ^{1}H NMR (toluene-d_8, −70 °C): δ 3.67 (dqd, $J_{trans-H-F}$ = 25.4 Hz, J_{H-CH3} = 7.1 Hz, $J_{cis-H-F}$ = 2.4 Hz, 1H), 1.12 (m, 3H). ^{19}F NMR (toluene-d_8, −70 °C): δ −88.0 (dm, J_{F-F} = 49.8 Hz, 1F), −92.35 (ddq, J_{F-F} = 49.8 Hz, $J_{trans-H-F}$ = 25.4 Hz, J_{F-CH3} = 2.9 Hz, 1F). The chemical shifts and coupling constants of CF_2=$CHCH_3$ closely match those found previously.[31]

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Reaction of $Cp^*_2ZrD_2$ with 3,3,3-Trifluoropropene at Low Temperature. A resealable NMR tube was charged with 20 mg (0.055 mmol) of $Cp^*_2ZrH_2$ and dissolved in toluene-d_8. The solution was freeze−pump−thaw degassed three times, and 1 atm of D_2 was admitted into the tube. The tube was thawed, stirred for 5 min at room temperature, and brought into the drybox. The solution was transferred via pipet into a sealable NMR tube and attached to the vacuum line. The tube was then freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 127 Torr (0.055 mmol) of trifluoropropene was condensed in at −83 °C (ethyl acetate/N_2 slush). The tube was flame sealed under vacuum, mixed at −83 °C as described above, and placed into a −65 °C NMR probe. At this point, only the terminal insertion product, $Cp^*_2Zr(CH_2CH(D)CF_3)D$, is observed along with CF_2═$CHCH_2D$ and Cp^*_2ZrDF. For Cp^*_2ZrDF, ^{1}H NMR (toluene-d_8, −65 °C): δ 1.91 (s, 30H, Cp*). ^{19}F NMR (toluene-d_8, −65 °C): 71.2 (s). For CF_2═$CHCH_2D$, ^{1}H NMR (toluene-d_8): δ 3.64 (dt, J_{H-F} = 25.6 Hz, CF_2═C*H*−CH_2D), 1.06 (m, CF_2═CH−C*H*$_2$D). ^{19}F NMR (toluene-d_8, −65 °C): δ −93.8 (ddt, J_{F-F} = 49.9 Hz, 1F), −90.05 (dq, J_{F-F} = 49.9 Hz, 1F). Upon warming the solution to −20 °C, deuterium scrambling is observed to give $Cp^*_2Zr(CH_2CD_2CF_3)H$ and $Cp^*_2Zr(CH_2CH(D)CF_3)D$ in a 1.6:1 equilibrium ratio. For $Cp^*_2Zr(CH_2CH(D)CF_3)D$, ^{1}H NMR (toluene-d_8, −20 °C): δ 1.77 (s, 30H, Cp*), 0.05 (m, 2H, ZrC*H*$_2$CH(D)CF_3), C*H*(D) is obscured. ^{19}F NMR (toluene-d_8, −20 °C): δ −68.4 (d, $ZrCH_2CH(D)CF_3$). For $Cp^*_2Zr(CH_2CD_2CF_3)H$, ^{1}H NMR (toluene-d_8, −20 °C): δ 1.77 (s, 30H, Cp*), 0.05 (m, 2H, ZrC*H*$_2$$CD_2CF_3$), 6.18 (s, 1H, Zr*H*). ^{19}F NMR (toluene-d_8, −20 °C): δ −68.5 (s, $ZrCH_2CD_2CF_3$).

Reaction of $Cp^*_2ZrD_2$ with Propene. A resealable NMR tube was charged with 8 mg (0.02 mmol) of $Cp^*_2ZrH_2$ and dissolved in toluene-d_8. The solution was freeze−pump−thaw degassed three times, and 1 atm of D_2 was admitted into the tube. The tube was thawed and stirred for 5 min at room temperature and brought into the drybox. The solution was transferred via pipet into a sealable NMR tube and attached to the vacuum line. The tube was then freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 50 Torr (0.02 mmol) of propene was condensed in at −83 °C (ethyl acetate/N_2 slush). The tube was flame sealed under vacuum, mixed at −83 °C as described above, and placed into the −65 °C cooled NMR probe and warmed slowly to room temperature. At −30 °C, only $Cp^*_2Zr(CH_2CH(D)CH_3)D$ was observed by NMR integration. ^{1}H NMR (toluene-d_8): δ 1.81 (s, 30H, Cp*), 1.13 (d, 3H, $ZrCH_2CH(D)CH_3$), 0.36 (sex, 1H, C*H*D), 0.15 (d, 2H, ZrC*H*$_2$). After the mixture was warmed to 25 °C and stood for approximately 10 min, the zirconium-hydride resonance had increased, and the proton resonance at the β-position was observed to decrease to give approximately a 2:1 ratio of $Cp^*_2Zr(CH_2CD_2CH_3)H$:$Cp^*_2Zr(CH_2CH(D)CH_3)D$. For $Cp^*_2Zr(CH_2CD_2CH_3)H$, ^{1}H NMR: δ 1.81 (s, 30H), 1.02 (s, 3H, $Zr(CH_2CD_2CH_3)$), 0.07 (s, 2H, ZrC*H*$_2$), 5.57 (s, 1H, Zr*H*).

Reaction of 1 with 3,3,3-Trifluoropropene with Removal of Olefins Prior to $Cp^*_2Zr(CH_2CH_2CF_3)H$ Decomposition. A resealable NMR tube was charged with 20 mg (0.055 mmol) of $Cp^*_2ZrH_2$ and 5 mg of 1-fluoroadamantane as an integration standard. Approximately 0.7 mL of butane was vacuum transferred into the tube, warmed, and shaken to dissolve $Cp^*_2ZrH_2$. Much of the $Cp^*_2ZrH_2$ would not dissolve in butane at this temperature. With an 8 mL calibrated glass bulb, 127 Torr (0.055 mmol) of trifluoropropene was condensed at −116 °C. The tube was then placed in the NMR probe at −65 °C. After we saw the presence of the intermediate, $Cp^*_2Zr(CH_2CH_2CF_3)H$, the tube was removed from the probe and quickly placed in a −41 °C cold bath, attached to the vacuum line, and pumped to dryness. Toluene-d_8 was vacuum transferred into the tube at −116 °C to redissolve the contents, and the tube was placed into the NMR probe cooled to −55 °C. ^{19}F NMR indicated that CF_2═$CHCH_3$ and trifluoropropene were successfully removed. Upon warming to −5 °C, $Cp^*_2Zr(CH_2CH_2CF_3)H$ decreased with formation of $CF_3CH_2CH_3$ and unidentified product(s), evidenced by broad lumps in the baseline of the ^{19}F NMR spectrum. The decomposition occurred at a rate similar to that observed without the removal of olefins.

Reaction of 1 with 3,3,3-Trifluoro-2-(trifluoromethyl)propene. A sealable NMR tube was charged with 16 mg (0.044 mmol) of $Cp^*_2ZrH_2$ and dissolved in toluene-d_8. The solution was freeze−pump−thaw degassed three times. With an 8 mL calibrated glass bulb, 101 Torr (0.044 mmol) of 3,3,3-trifluoro-2-(trifluoromethyl)propene was condensed in at −94 °C. The tube was flame sealed, mixed at −94 °C, and dropped into the −85 °C cooled NMR probe. The reaction was nearly complete forming Cp^*_2ZrHF and 1,1-difluoro-2-(trifluoromethyl)propene exclusively. For $CH_3(CF_3)C$═CF_2, ^{19}F NMR (toluene-d_8): δ −60.5 (dd, 3F), −76.5 (m, 1F), −80.4 (m, 1F). ^{1}H NMR (toluene-d_8): δ 1.17. GC/MS (*m*/*z*): 146 (M^+).

Reaction of 1 with 3-Trifluoromethyl-3,4,4,4-tetrafluoro-1-butene. A resealable NMR tube was charged with 8 mg (0.022 mmol) of $Cp^*_2ZrH_2$ and dissolved in cyclohexane-d_{12}. The solution was freeze−pump−thaw degassed three times, and with an 8 mL calibrated glass bulb, 48 Torr (0.022 mmol) of 3-trifluoromethyl-3,4,4,4-tetrafluoro-1-butene was condensed in at −196 °C. The solution was warmed to room temperature, shaken, and analyzed by ^{19}F and ^{1}H NMR spectroscopy. A mixture of Cp^*_2ZrHF, CH_3CH═$C(CF_3)_2$, $Cp^*_2ZrF_2$, and $CH_3CH_2CF(CF_3)_2$ was observed in a 1:1:0.25:0.2 ratio. A small amount (<5%) of another nonvolatile species was observed but not identified. For CH_3CH═$C(CF_3)_2$, ^{19}F NMR (C_6D_{12}): δ −59.4 (s, 3F), −65.44 (s, 3F). ^{1}H NMR (C_6D_{12}): δ 6.71 (q, 1H), 1.96 (m, 3H). MS (*m*/*z*): 178 (M^+). For $CH_3CH_2CF(CF_3)_2$, ^{19}F NMR (C_6D_{12}): δ −76.9 (s, 6F), −185.53 (s, 1F). ^{1}H NMR (C_6D_{12}): δ 1.12 (t, 3H), 2.1 (m, 2H).

Reaction of 1 with CH_2═$CHCF_2CF_2CF_2CF_3$ at Room Temperature. A resealable NMR tube was charged with 16 mg (0.044 mmol) of $Cp^*_2ZrH_2$ and dissolved in cyclohexane-d_{12}. Via syringe, 7.6 μL (0.044 mmol, d = 1.42) of CH_2═$CHCF_2CF_2CF_2CF_3$ was added. The solution was shaken and analyzed by ^{19}F, ^{19}F COSY, and ^{1}H NMR. A mixture of **2**, (*Z*)-CH_3CH═$CFCF_2CF_2CF_3$, and (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFCF_2CF_2CF_3)F$ was observed in approximately a 2.2:2.2:1 ratio. The volatiles were vacuum transferred from the NMR tube for GC/MS analysis. For (*Z*)-CH_3CH═$CFCF_2CF_2CF_3$, ^{19}F NMR (C_6D_{12}): δ −81.1 (m, 3F), −118.5 (m, 2F), −127.6 (m, 2F), −131.7 (m, 1F). ^{1}H NMR (C_6D_{12}): δ 5.02 (dq, J_{H-F} = 30.3 Hz, 1H), 1.72 (m, 3H). GC/MS (*m*/*z*): 228 (M^+). For (*Z*)-$Cp^*_2Zr(CH_2CH$═$CFCF_2CF_2CF_3)F$, ^{19}F NMR (C_6D_{12}): δ 87.0 (s, 1F, Zr*F*), −81.13 (t, 3F), −116.2 (m, 2F), −127.0 (m, 2F), −142.5 (br m, 1F). ^{1}H NMR (C_6D_{12}): δ 1.89 (s, 30H, Cp*), 5.79 (dt, J_{H-F} = 35.0 Hz, 1H), 1.28 (m, 2H).

Reaction of 1 with CH_2═$CHCF_2CF_2CF_2CF_3$ at Low Temperature. A resealable NMR tube was charged with 25 mg (0.069 mmol) of $Cp^*_2ZrH_2$ and dissolved in toluene-d_8. The solution was freeze−pump−thaw degassed three times at −78 °C, and 13 μL (0.076 mmol) of CH_2═$CHCF_2CF_2CF_2CF_3$ was vacuum transferred into the −78 °C cooled toluene-d_8 solution. The tube was then placed into a −70 °C cooled NMR probe. At this point, only **2**, (*Z*)-CH_3CH═$CFCF_2CF_2CF_3$, and the unstable intermediate, $Cp^*_2Zr(CH_2CH_2CF_2CF_2CF_2CF_3)H$, are observed. The sample was warmed to −40 °C, and the primary insertion product was characterized by ^{1}H COSY, observing coupling between Cp* methyl proton and hydride resonances. For $Cp^*_2Zr(CH_2CH_2CF_2CF_2CF_2CF_3)H$, ^{1}H NMR (toluene-$d_8$, −40 °C): δ 1.75 (s, 30H, Cp*), 6.20 (s, 1H, Zr*H*), 0.06 (m, 2H, ZrC*H*$_2$, $ZrCH_2CH_2$ is obscured). ^{19}F NMR (toluene-d_8, −40 °C): δ −80.0 (m, 3F), −115.5 (m, 2F), −123.6 (m, 2F), −125.2 (m, 2F). Repeating the same procedures above in methylcyclohexane-d_{14} solvent, we identified the secondary insertion product at −90 °C. For $Cp^*_2Zr(CH(CH_3)CF_2CF_2CF_2CF_3)H$, ^{19}F NMR (methylcyclohexane-d_{14}): δ −82.3 (m, 3F), −89.9 (dm, J_{F-F} = 248 Hz, 1F), −107.1 (dm, J_{F-F} = 248 Hz, 1F), −122.5 (m, 1F), −123.7 (m, 1F), −127.2 (m, 1F), −127.9 (m, 1F).

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Upon warming the solution above −10 °C, both $Cp^*_2Zr(CH_2CH{=}CFCF_2CF_2CF_3)F$ and the fluoroalkane, $CH_3CH_2C_4F_9$, were observed. For $CH_3CH_2C_4F_9$, ^{1}H NMR (C_6D_{12}): δ 2.03 (m, 2H), 1.11 (t, 3H). ^{19}F NMR (C_6D_{12}): δ −80.6 (m, 3F), −116.0 (m, 2F), −123.7 (m, 2F), −125.4 (m, 2F). GC/MS (*m*/*z*): 228 (M − 20). The parent ion (M^+ = 248) was not observed, but the overall spectrum was identical to that of the authentic sample (see below).

Preparation of $CF_3CF_2CF_2CF_2CH_2CH_3$. Approximately 20 μL of nonafluoro-1-hexene was added to a resealable NMR tube containing ∼10 mg of 10% Pd on carbon in cyclohexane-d_{12}. The solution was freeze−pump−thaw degassed, and 1.3 atm of H_2 was admitted into the tube. The tube was thawed and stirred for 20 min, after which all of the starting olefin was consumed producing 1,1,1,2,2,3,3,4,4-nonafluorohexane quantitatively. See above for NMR and MS data.

Reaction of $[Cp^*_2Zr]_2(N_2)_3$ with $CH_2{=}CHCF_2CF_2CF_2CF_3$. A resealable NMR tube was charged with 12 mg (0.015 mmol) of $[Cp^*_2Zr]_2(N_2)_3$ and suspended in cyclohexane-d_{12}. Nonafluoro-1-hexene (5.2 μL, 0.030 mmol, d = 1.42) was added via syringe. The tube was stirred for 5 min, upon which time the solution turned from dark purple to yellow. The reaction mixture contained ∼3% (*Z*)-$Cp^*_2Zr(CH_2CH{=}CFCF_2CF_2CF_3)F$ and 97% (*E*)-$Cp^*_2Zr(CH{=}CHCF_2CF_2CF_2CF_3)H$. For (*E*)-$Cp^*_2Zr(CH{=}CHCF_2CF_2CF_2CF_3)H$, ^{19}F NMR ($C_6D_{12}$): δ −81.3 (m, 3F), −109.6 (m, 2F), −122.8 (m, 2F), −125.7 (m, 2F). ^{1}H NMR (C_6D_{12}): δ 1.89 (s, 30H, Cp*), 7.04 (d, 1H, J_{H-H} = 20.4 Hz, Zr−C*H*), 6.58 (s, 1H, Zr*H*), 4.95 (dt, 1H, J_{H-H} = 20.4 Hz, ZrCH=C*H*).

Reaction of 1 with (*Z*)-$CH_3CH{=}CFCF_2CF_2CF_3$. A resealable NMR tube was charged with 30 mg (0.082 mmol) of $Cp^*_2ZrH_2$ and dissolved in C_6D_{12}. Nonafluoro-1-hexene (1.6 μL, 0.009 mmol) was added via syringe. The tube was immersed in an 85 °C oil bath for 2 d. NMR analysis revealed unreacted $Cp^*_2ZrH_2$, Cp^*_2ZrHF, $Cp^*_2ZrF_2$, and (*E*)-$CH_3CH_2CF{=}CFCF_2CF_3$. The volatiles were transferred to an empty NMR tube for further characterization by ^{19}F, ^{1}H, ^{1}H COSY and ^{19}F COSY NMR, and GC/MS analysis. For (*E*)-$CH_3CH_2CF{=}CFCF_2CF_3$, ^{1}H NMR (C_6D_{12}): δ 1.16 (t, 3H), 2.42 (m, 2H). ^{19}F NMR (C_6D_{12}): δ −85.1 (m, 3F), −120.3 (m, 2F), −139.1 (dm, $J_{trans-F-F}$ = 134 Hz, 1F), −172.7 (dm, $J_{trans-F-F}$ = 133 Hz, 1F). GC/MS (*m*/*z*): 210 (M^+).

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