

Activation of Aromatic, Aliphatic, and Olefinic Carbon–Fluorine Bonds Using $\text{Cp}^*_2\text{HfH}_2$

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The hafnium hydride $\text{Cp}^*_2\text{HfH}_2$ is reacted with a series of fluorocarbons to examine the scope of C–F bond activation. Aromatic, vinylic, and aliphatic C–F bonds all show some degree of reactivity, and possible mechanisms are discussed.

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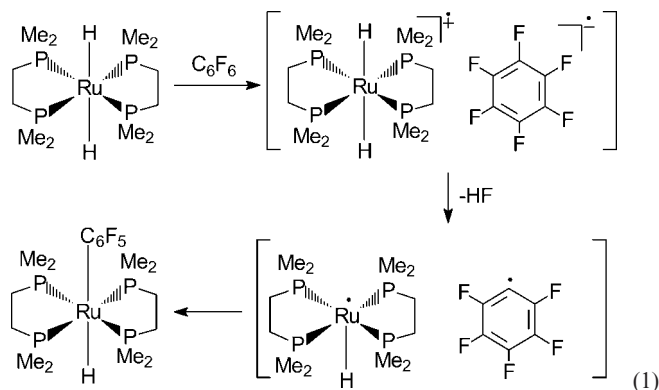
Introduction

Organometallic chemists have long been interested in the activation of typically inert C–F bonds using transition-metal complexes. The advantages of promoting C–F bond cleavage are both academic and practical. In one sense, the selective and predictable disruption of these interactions may result in greater synthetic utility of readily available fluorocarbons. In addition, such knowledge could have environmental ramifications, eventually leading to the destruction of harmful chlorofluorocarbons (CFCs) in the upper atmosphere. While both stoichiometric^[1] and catalytic^[2] C–F activation reactions have been reported using transition metals, significant efforts continue to be made to improve known methodologies and to discover new ways to cleave these strong bonds selectively with an important goal being an understanding of the mechanisms by which these transformations take place.

To date, a variety of mechanisms for C–F bond activation by transition metals have been suggested. Some of the more notable strategies involve electron transfer, electrophilic pathways, homolytic cleavage, oxidative addition, and nucleophilic routes.^[3–4] While many of these mechanisms feature intermolecular interactions, several examples involve intramolecular activation,^[5–6] which is oftentimes accompanied by the liberation of a small molecule such as HF.

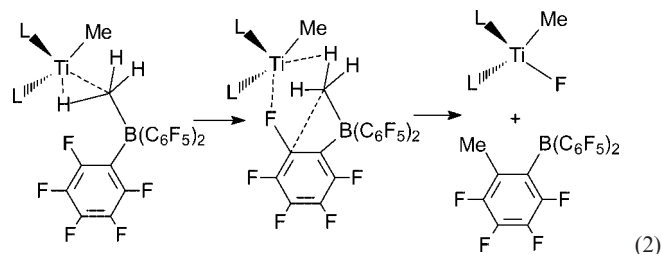
As an example of the electron-transfer mechanism, Perutz and co-workers have suggested that an electron-rich dihydride, $\text{Ru}(\text{dmpe})_2\text{H}_2$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$), is capable of donating an electron to a heavily fluorinated aromatic compound, eventually leading to the formation of the

observed product by the route depicted in Equation (1).^[7] Similar considerations have been implicated in reactions involving Ni and Rh.^[8–9]



Electrophilic C–F bond activation has been suggested to occur by fluoride transfer, especially when strong Lewis acids are employed. For example, fluoride transfer from an aromatic fluorocarbon to an open coordination site in $[\text{L}_2\text{TiMe}]^+$ systems has recently been proposed by Ziegler and co-workers.^[10] Rosenthal et al. have shown that cationic zirconocene complexes can abstract fluoride from perfluorophenyl groups to give Zr–F species.^[11] In most cases where suggested, fluoride transfer is thought to likely occur through a cyclic transition state [Equation (2)]. Furthermore, olefinic fluorocarbons have been shown to participate in β -fluoride elimination following insertion into metal-hydride bonds, leading to the generation of a new fluorocarbon or small fluorine-containing molecule.^[12–15] For perfluoroalkyl–metal complexes, α -fluoride elimination has been shown to be operative in several systems, many of which feature the use of Group 9 metals.^[16] A titanium perfluoromethyl complex has also been reported, indicating that such species can be stable.^[17]

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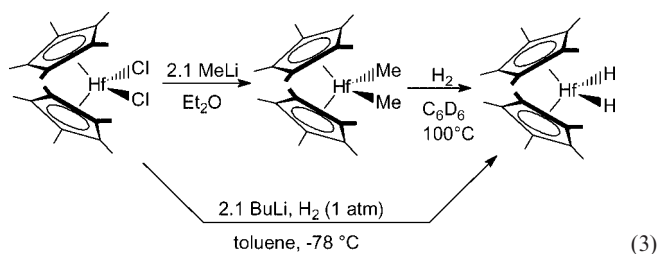
In addition to mechanisms involving the transfer of electrons or fluoride, other mechanisms that have been identified include the involvement of radical-based species in the C–F bond cleavage reactions of aliphatic fluorocarbons using $\text{Cp}^*_2\text{ZrH}_2$,^[18] the oxidative addition of an aromatic C–F bond to phosphane Ni^0 complexes,^[9,19] and the nucleophilic aromatic substitution on fluorinated aromatic species using early transition-metal complexes.^[1(d),6]

As an addition to the variety of metal-based systems known to cleave C–F bonds,^[3,20] the following account summarizes C–F bond activation research done using bis(pentamethylcyclopentadienyl)hafnium dihydride, $\text{Cp}^*_2\text{HfH}_2$ (**1**). The substrate scope includes aromatic, aliphatic, and olefinic compounds featuring varying steric properties and degrees of fluorination. Heterocyclic substrates are also briefly considered, and mechanistic insight into the reaction of **1** with several fluorinated alkenes is presented.

Results and Discussion

Synthesis of $\text{Cp}^*_2\text{HfH}_2$ and its Fluoro Derivatives

The synthesis of **1** was achieved by conversion of commercially available $\text{Cp}^*_2\text{HfCl}_2$ to $\text{Cp}^*_2\text{HfMe}_2$ ^[21] followed by reaction with hydrogen at elevated temperature [Equation (3)]. Comparison of ^1H NMR spectroscopic data to known literature values for **1** confirmed that it was indeed the expected product.^[22]



The long reaction time required for a reasonable degree of conversion can be avoided using the method reported by Bercaw, in which **1** was made directly from $\text{Cp}^*_2\text{HfCl}_2$ using *n*-butyllithium under hydrogen, a process that afforded the dried, isolated product in roughly 3 d.^[22] Due to the sensitive nature of the starting hafnium complex,^[23] great care was taken to prevent air and moisture from being present in any reaction using **1** as a starting material. To this end,

all solvents must first be dried with purple sodium/benzophenone ketyl and then over green titanocene, formed from the reaction of Cp_2TiCl_2 and zinc dust in the solvent of interest.^[24]

In order to obtain a general idea of how **1** reacts with fluorinated organic compounds, the starting hafnium complex was treated with several substrates, including fluorinated aromatics and olefinic compounds, aliphatic C–F bonds, and fluorinated heterocycles.

In most of the reactions, two primary metal-based products formed, Cp^*_2HfHF (**2**) and $\text{Cp}^*_2\text{HfF}_2$ (**3**), as a result of either mono- or di-hydrodefluorination, respectively. Their presence in the reaction mixtures was determined by

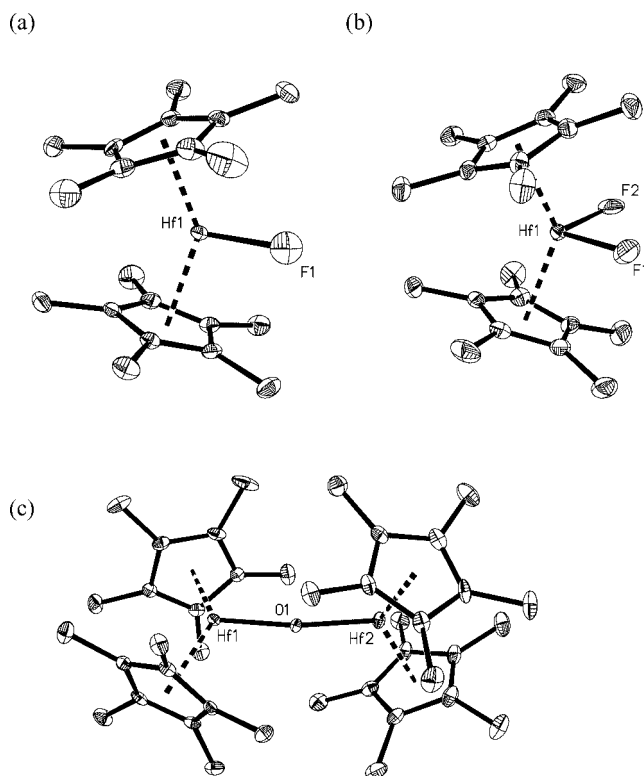


Figure 1. ORTEP diagrams of: a) **2**; b) **3**; and c) **4**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The fluoride ligand in **2** is disordered over two sites.

Table 1. Selected X-ray data for **2**, **3**, and **4**.

	Cp^*_2HfHF (2)	$\text{Cp}^*_2\text{HfF}_2$ (3)	$[\text{Cp}^*_2\text{Hf}]_2\text{O}$ (4)
Space group	$P2_1/c$	$P2_1/n$	Pn
$R(\text{int.})$	1.65%	3.25%	3.02%
$R(\sigma)$	3.16%	3.52%	4.06%
R_1	4.32%	5.02%	2.41%
Cp*–Hf–Cp*	141.7°	137.2°	130.9°
Angle ^[a,b,c]	140.3°	139.0°	133.0°
Hf–O–Hf angle	N/A	N/A	172.2(2)°
Hf–F or Hf–O	1.978(6)	2.017(4)	1.991(3)
bond length ^[b] [Å]	1.998(8)	2.126(4)	1.985(3)

[a] Cp* represents the cyclopentadienyl centroid. [b] For the structures of **2** and **3**, two molecules were present in the asymmetric unit. Values for both structures are presented. [c] For purposes of comparison, the Cp*–Hf–Cp* angle has been reported to be 144.1° for **1**.^[28]

Table 2. Summary of crystallographic data for **2**, **3**, and **4**.

	2	3	4
Chemical formula	C ₂₀ H ₃₁ FHf	C ₂₀ H ₃₀ F ₂ Hf	C ₄₀ H ₆₂ Hf ₂ O
Formula weight	468.94	486.93	915.88
Crystal system	monoclinic	monoclinic	monoclinic
Space group (<i>Z</i>)	<i>P</i> 2 ₁ / <i>c</i> (8)	<i>P</i> 2 ₁ / <i>n</i> (8)	<i>P</i> <i>n</i> (2)
<i>a</i> [Å]	15.7895(8)	13.0151(5)	11.0534(7)
<i>b</i> [Å]	15.4046(8)	19.0896(8)	10.1633(6)
<i>c</i> [Å]	16.3652(8)	15.8115(7)	16.5842(10)
β [deg]	109.232(1)	107.969(1)	103.449(1)
<i>V</i> [Å ³]	3758.4(3)	3736.8(3)	1811.96(19)
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.658	1.731	1.679
Crystal dimensions [mm]	0.24 × 0.20 × 0.10	0.47 × 0.45 × 0.22	0.50 × 0.50 × 0.41
Temperature [K]	100	100	100
2 θ Range [deg]	4–60	4–60	4–60
Data collected	–19 ≤ <i>h</i> ≤ 30, –15 ≤ <i>k</i> ≤ 15, –15 ≤ <i>l</i> ≤ 16	–18 ≤ <i>h</i> ≤ 18 –26 ≤ <i>k</i> ≤ 26 –22 ≤ <i>l</i> ≤ 22	–15 ≤ <i>h</i> ≤ 15 –14 ≤ <i>k</i> ≤ 14 –23 ≤ <i>l</i> ≤ 23
No. of data collected	55625	55828	25483
No. of unique data	10862	10819	10302
Agreement between equiv. data	0.0339	0.0222	0.0302
No. of observed data [<i>I</i> > 2 σ (<i>I</i>)]	9891	10035	10164
No. of parameters varied	417	435	414
μ [mm ⁻¹]	5.556	5.599	5.754
Absorption correction	empirical (SADABS)	differential (DIRDIF)	empirical (SADABS)
Range of transmission factors	0.279–0.576	0.0983–0.292	0.71–0.91
<i>R</i> ₁ (<i>F</i> _o), <i>wR</i> ₂ (<i>F</i> _o ²), all data	0.0409, 0.0844	0.0235, 0.0519	0.0236, 0.0579
<i>R</i> ₁ (<i>F</i> _o), <i>wR</i> ₂ (<i>F</i> _o ²), [<i>I</i> > 2 σ (<i>I</i>)]	0.0363, 0.0825	0.0209, 0.0508	0.0233, 0.0578
Goodness of fit	1.076	1.023	1.014

their characteristic NMR spectroscopic data. Characterization of **2** was accomplished by ¹H and ¹⁹F NMR, as well as by ¹H–¹⁹F heteronuclear correlation spectroscopy. The structure of **2** was confirmed by X-ray crystallography (Figure 1).^[25] Complex **3** was characterized by ¹⁹F NMR spectroscopic data, which was later confirmed through independent synthesis of the complex.^[26] Further characterization was achieved through ¹H NMR spectroscopic data^[26] and X-ray crystallography (Figure 1).^[25] An additional hafnium complex, (Cp*₂HfH)₂O (**4**), was isolated from a crystallization attempt of **1** and was characterized by X-ray crystallography (Figure 1) and ¹H NMR spectroscopic data.^[23,27] This compound likely arises from side reaction with adventitious water. Selected distances and angles for complexes **2**, **3**, and **4** are summarized in Table 1. Selected crystallographic data are compared in Table 2.

Reactions of **1** with Fluoroaromatics and Fluoroaliphatics

The compounds 2- and 3-fluoropyridine both were observed to react with **1** at room temperature over the course of several hours. NMR analysis of the reaction mixtures revealed the presence of **2** and small amounts of **3** in both reactions but no free pyridine in either. In both reactions, **2** forms prior to the formation of **3**, indicating a sequential reaction of the Hf–H bond. In addition, pyridine was not observed by GC–MS analysis of the volatile materials from the reactions, suggesting that it forms strong adducts with hafnium-containing moieties in the reaction mixture. While 2-fluoropyridine reacts within a few hours, 3-fluoropyridine reacts relatively sluggishly over the course of several days.

Additional reactions using monofluorinated aromatic compounds were briefly pursued, but these experiments did not reveal the expected evidence of C–F bond cleavage. Specifically, 2- and 4-fluorobiphenyl were allowed to react with **1** for over 3 d at 120 °C without displaying C–F reactivity. In addition to reactions with monofluorinated aromatic substrates, the activation of aliphatic C–F bonds was studied using 1-fluorohexane. Initial conversion of **1** to **2** was not observed by ¹⁹F NMR until the reaction mixture was monitored after being heated to 60 °C for 44 h. The reaction was nearly complete after 20 d at 120 °C. Furthermore, hexane was also detected by ¹H NMR spectroscopy^[18] with the observed ratio of **2**:hexane being 0.4:1.0. Small amounts of **3** (5%) were also observed.

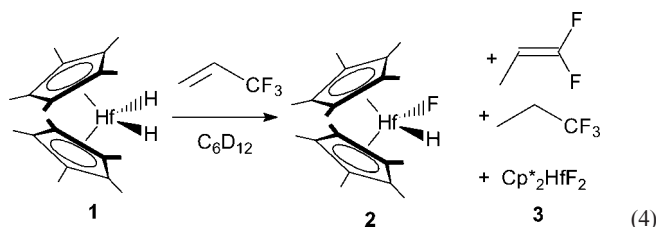
Several polyfluorinated aromatic compounds were examined. Highly symmetric substrates 1,2,4,5-tetrafluorobenzene and 2,2',3,3',5,5',6,6'-octafluorobiphenyl did not participate in C–F bond cleavage after days at 120 °C. However, heating for 120 h at 100 °C produced traces of **2** or **3** in reactions involving 1,2,3,4-tetrafluorobenzene and 2,3,4,5,6-pentafluoro(allyl)benzene, respectively. While longer reaction times at elevated temperatures reduced the amount of substrate relative to metal-based products, the products generated do not display NMR spectroscopic data that matches that of the expected organic products.^[29]

Several perfluorinated aromatic compounds were also examined: hexafluorobenzene, octafluoronaphthalene, and decafluorobiphenyl. NMR analysis of the reactions showed that each reaction generated **2** upon heating, but that weeks at 100–120 °C are required. The observed ¹⁹F NMR chemical shift values of the organic products match known values

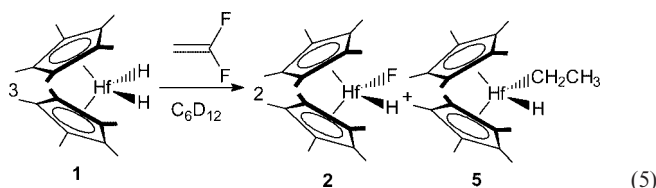
for pentafluorobenzene, 2H-heptafluoronaphthalene, and 4H-nonafluorobiphenyl.^[1(d)] Additionally, 2H-heptafluoronaphthalene was observed by GC-MS analysis of the volatile materials from its respective reaction and the potential presence of 2H-nonafluorobiphenyl as the major product from its respective reaction was discounted based on previously published NMR spectroscopic data.^[30] Note that C_6F_6 is substantially less reactive than the other perfluoroarenes.

Reactions of **1** with Fluoroolefins

Partially fluorinated olefins investigated include 3,3,3-trifluoropropene, 1,1-difluoroethylene, hexafluoroisobutene, 3,4,4,4-tetrafluoro-3-trifluoromethyl-1-butene, α -(trifluoromethyl)styrene, and difluoromethylenecyclohexane. Reaction with 3,3,3-trifluoropropene produced **2**, **3**, 1,1-difluoropropene, and 1,1,1-trifluoropropane in a 3.7:0.5:3.4:1.0 ratio after 43 h at room temperature [Equation (4)]. However, the bulk of the conversion was observed to have occurred by ^{19}F NMR spectroscopy after roughly 3 min had elapsed. NMR spectroscopic data from 1,1-difluoropropene and 1,1,1-trifluoropropane match previously reported data^[14] and 1,1-difluoropropene was identified by analyzing the volatile materials from the reaction by GC-MS.

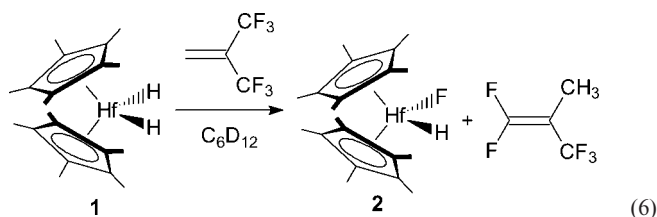


Reaction of **1** with 1,1-difluoroethylene produced **2** and a species assigned as $Cp^*_2Hf(CH_2CH_3)H$ (**5**) after 20 min at room temperature [Equation (5)]. The diagnostic 1H NMR signals for **5** [δ = 11.95 (s, $Hf-H$), 0.32 (t, $-CH_2CH_3$), -0.22 (q, $-CH_2CH_3$)] are close to those reported for this complex in C_6D_6 .^[22] Furthermore, because 1-fluoroethylene^[31] and free ethylene^[32] were not observed, the formation of this complex can be rationalized by subsequent insertions and eliminations of 1,1-difluoroethylene and fluoroethylene into a $Hf-H$ bond, a sequence of transformations which ultimately result in ethylene formation. This ethylene then undergoes $Hf-H$ insertion to finally arrive at **5**.

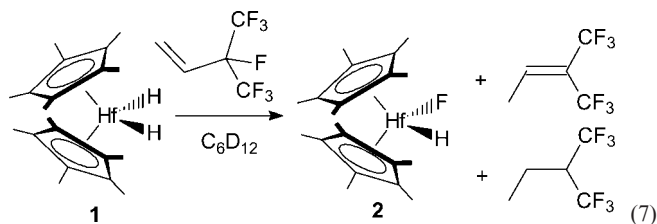


In order to alter the steric profile of the studied olefins, bulkier alkenes were then used to contrast their reactivity with that of the smaller compounds. The reaction of **1** and

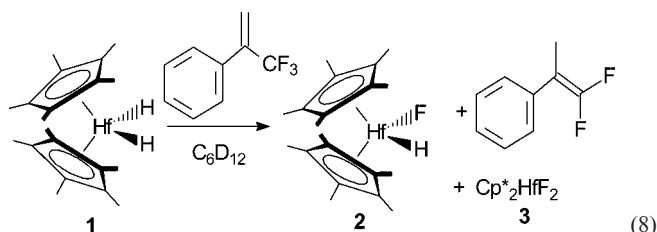
hexafluoroisobutene produced 1,1,3,3,3-pentafluoro-2-methyl-1-propene^[14] after 50 h at room temperature [Equation (6)]. The final ratio of **2**:1,1,3,3,3-pentafluoro-2-methyl-1-propene was 1.7:1.0, according to ^{19}F NMR spectroscopic data.



The analogous reaction using 3,4,4,4-tetrafluoro-3-trifluoromethyl-1-butene produced 1,1,1-trifluoro-2-trifluoromethyl-2-butene and 1,1,1-trifluoro-2-trifluoromethyl-2-butane, both of which could be confirmed by literature precedent [Equation (7)].^[14] The reaction was allowed to proceed for 146 h at room temperature, although this time was not sufficient to completely consume **1**. The final ratio of **2**:1,1-trifluoro-2-trifluoromethyl-2-butene: 1,1,1-trifluoro-2-trifluoromethyl-2-butane obtained from ^{19}F NMR spectroscopic data was 11.3:7.9:1.0. The olefinic organic product was also identified by GC-MS.

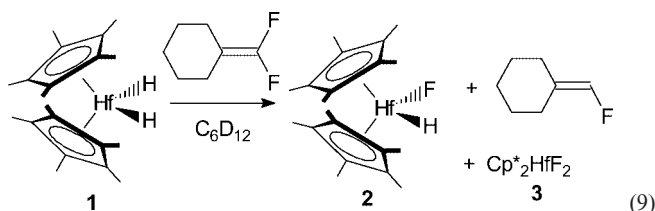


The reaction of **1** with α -(trifluoromethyl)styrene produced β,β -difluoro- α -methylstyrene, the presence of which was confirmed from previous NMR spectroscopic data [Equation (8)].^[33] First evidence of the formation of **2** was observed after heating the reaction mixture for 18 h at 80 °C. **3** was first observed following 92 h of heating at 80 °C. The reaction was terminated after 163.5 h at 160 °C. On the basis of ^{19}F NMR spectroscopic data, the final ratio of **2**:**3**: β,β -difluoro- α -methylstyrene was 0.8:1.0: 1.5.



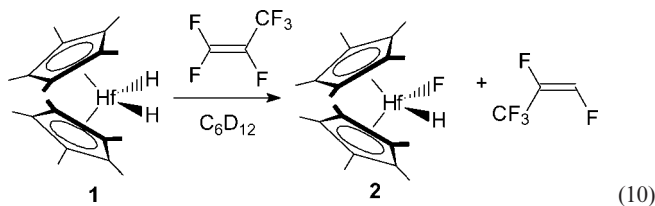
The reaction involving difluoromethylenecyclohexane was carried out in the same manner, producing **2**, **3**, and fluoromethylenecyclohexane in a 12.8:1.0: 38.0 ratio (by ^{19}F NMR) after 93 h of reaction at 160 °C [Equation (9)]. Initial formation of **2** was not observed until after 22 h had

elapsed at 120 °C. Literature values^[14] were used to match obtained NMR spectroscopic data with the corresponding organic product.



Reactions of **1** with Perfluoroolefins

Following the set of reactions using polyfluorinated alkenes, the perfluorinated olefins perfluoropropene and octafluorocyclopentene were used in reactions with **1**. The perfluoropropene reaction proceeded at room temperature and yielded **2** and (*E*)-1,2,3,3,3-pentafluoropropene in a 1.8:1.2 ratio (using ¹⁹F NMR spectroscopic data) after 41.5 h [Equation (10)]. The identity of the organic product was determined from previous NMR spectroscopic data^[15] and conflicted with the data available for the *Z* isomer.^[34]



On the basis of ¹⁹F NMR spectroscopic data, the analogous reaction using octafluorocyclopentene produced a mixture of **2**, **3**, and 1H-heptafluorocyclopentene in a 41:1.0:27.4 ratio after 47 h at room temperature. Identity of the organic product was confirmed by previously obtained NMR spectroscopic data^[34] and by GC-MS data obtained from the volatile materials from the reaction. Full consumption of **1** was achieved.

In an effort to understand the hydrodefluorination of octafluorocyclopentene in more detail, a stepwise C–F activation experiment was performed as follows: equimolar amounts of **1** and octafluorocyclopentene were reacted at room temperature, after which the volatile organic product (1H-heptafluorocyclopentene) was vacuum-transferred onto an additional equivalent of **1**. The first step of this reaction essentially proceeded as before, with the exception being that a small amount of a second product isomer, 4H-heptafluorocyclopentene, was observed by ¹⁹F NMR after 30 min of reaction at room temperature. The ratio of the major (expected) product to the new, minor product was 5.5:1.0. After 20 h of reaction, **1** was no longer present in the reaction mixture, and the volatile materials were vacuum-transferred to a second equivalent of **1**. The reaction was then periodically monitored by NMR spectroscopy over the course of several months (Figure 2). The reaction

at room temperature afforded 1H,2H-hexafluorocyclopentene as the initial major organic product. However, after an extended amount of time at room temperature, 1H,2H,3H-pentafluorocyclopentene could be observed. The identity of both fluorocyclopentene products was confirmed through comparison to available NMR spectroscopic data.^[34]

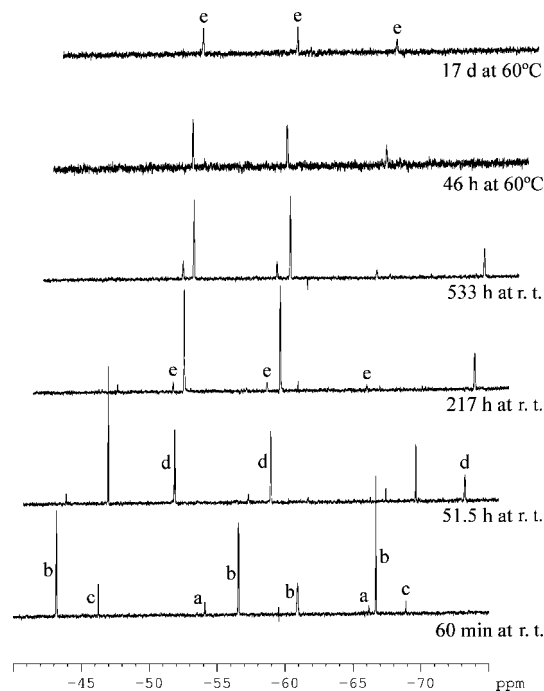
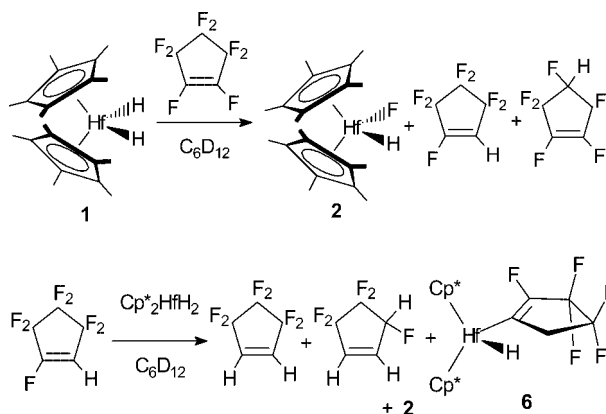


Figure 2. ¹⁹F NMR spectroscopic data for the stepwise hydrodefluorination of perfluorocyclopentene. Temperatures (°C) and allowed reaction times for the various spectra are listed in the right margin. (a = octafluorocyclopentene; b = 1H-heptafluorocyclopentene; c = 1H,2H-hexafluorocyclopentene; d = 1H,2H,3H-pentafluorocyclopentene; e = **6**).

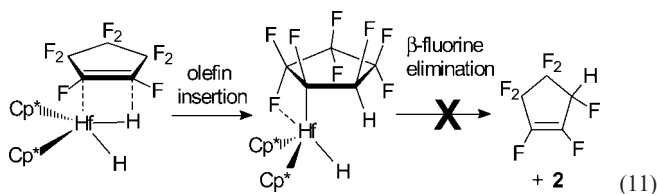
Following a period of decreased activity, the reaction mixture was heated first to 60 °C and then to 100 °C. The relatively high temperature drastically altered the observed product distribution and even resulted in the formation of a species tentatively assigned as **6** (Scheme 1). The assignment of **6** is based largely on NMR integration values and previous observation of a similar complex involving Zr.^[34]



Scheme 1.

There appeared to be no evidence of other fluorinated cyclopentene derivatives following prolonged heating at 100 °C.^[35] GC-MS analysis of the volatile materials from the reaction revealed the presence of 1H,2H,3H-pentafluorocyclopentene.

While the stepwise reaction of octafluorocyclopentene shows a preference for vinylic C–F activation over cleavage of neighboring C–F bonds, the mechanism by which the organic products are generated remains unclear. While an olefin insertion prior to β -fluoride elimination mechanism seems to be operative for other non-cyclic olefins,^[4,12–15] such a process cannot be responsible for the formation of observed products in this case, because the product predicted by the mechanism is not observed [Equation (11)]. Consequently, a new mechanism must be postulated for this facile olefinic hydrogenolysis. At this point, preliminary calculations suggest a 4-center metathesis pathway between the Hf–H and C–F bond for the reaction.



Low-Temperature Studies

Low-temperature NMR spectroscopy was used to look for intermediates that might provide mechanistic insight into the reaction of fluorinated olefins with **1**. In particular, reactions of **1** with 3,3,3-trifluoropropene, 1,1-difluoroethylene, and 1,1-difluoropropene were studied at low temperature. Reactions were initiated at –110 °C and samples monitored in the NMR probe as they warmed to room temperature. Of the substrates examined, the reactions involving 3,3,3-trifluoropropene provided the most insight. Figure 3 shows some of the ^{19}F NMR spectroscopic data obtained from this reaction.

The most striking aspect of the data presented in Figure 3 is the fact that some of the species observed, specifically the compounds corresponding to the peaks labeled **c** and **e**, seem to be present at low temperature but gradually vanish as the temperature is increased. One way to rationalize these observations is summarized in Equation (12) below. Assuming that insertion of the olefin into the metal-hydride bond of **1** is the initial step in the reaction, one could expect two different species – one with a branched fluoroalkyl ligand **7** and one featuring a straight-chain fluoroalkyl moiety **8** – to form. Because the NMR spectra taken from roughly –110 °C to –60 °C display only starting olefin, **1**, and two unidentified species, it seems reasonable to argue that the unassigned species may be the two insertion products, **7** and **8**. Strengthening that assertion is the fact that the signal assigned to **8** is a sharp triplet, as would be expected.

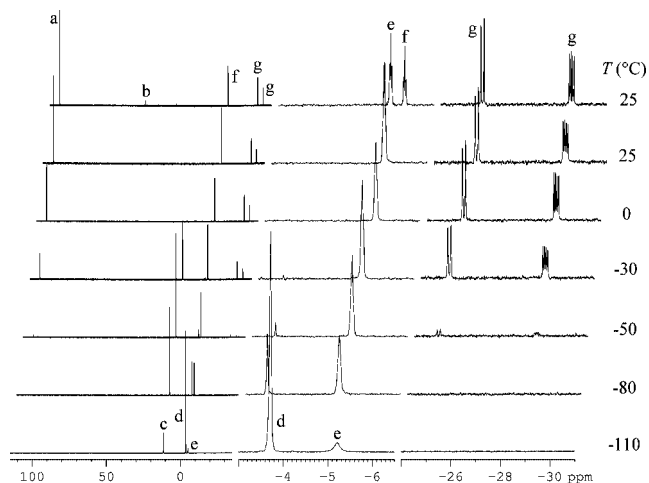
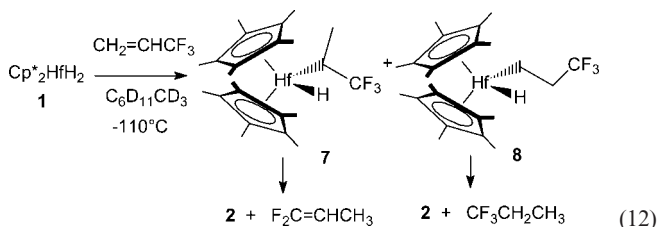


Figure 3. Variable-temperature ^{19}F NMR spectroscopic data for the reaction of 3,3,3-trifluoropropene with **1**. The temperatures (°C) corresponding to the various spectra are given in the right margin. Regions of interest are expanded for clarity. (a = **2**, b = **3**, c = **7**, d = 3,3,3-trifluoropropene, e = **8**, f = 1,1,1-trifluoropropane, g = 1,1-difluoropropene).



Subsequent warming of the reaction mixture results in relatively rapid disappearance of the NMR signal tentatively assigned to **7** accompanied by an appreciable increase in the signals corresponding to **2** and 1,1-difluoropropene. The β -fluoride elimination from the trifluoromethyl group is consistent with these observations. Moreover, prolonged storage of the reaction mixture at room temperature promotes the growth of the signal previously assigned to 1,1,1-trifluoropropane. Because the hydrogenated olefin signal intensity approaches that of the resonance assigned to **8**, it appears as though complex **8** may be the source of 1,1,1-trifluoropropane.

The low-temperature experiment using 3,3,3-trifluoropropene was monitored by ^1H NMR in a separate trial and showed similar behavior to that observed by ^{19}F NMR spectroscopy. Specifically, two previously unobserved signals appeared between 12–14 ppm and were tentatively assigned as the Hf–H signals from **7** (δ = 13.80 ppm) and **8** (δ = 12.90 ppm). As expected, the signal from **7** decreased quickly upon warming and was completely absent by the time the reaction was warmed to –10 °C. In addition, another resonance at δ = 0.50 ppm exhibited the same behavior and was assigned as the methyl group of **7** based on integration. The Hf–H signal from **8** along with an additional signal at –0.03 ppm (assigned to the metal-bound

methylene of **8** based on integration) expectedly lingered at room temperature.

While the reaction of 3,3,3-trifluoropropene with **1** appeared to successfully demonstrate that the insertion/elimination mechanism accounts for the formation of observed products, the same could not be said for the reactions of 1,1-difluoroethylene and 1,1-difluoropropene with **1**. At the current time, it appears as though the reaction involving 1,1-difluoroethylene proceeds too rapidly at low temperature to observe intermediates. In contrast, the reaction of 1,1-difluoropropene has not provided results suitable for discussion of its mechanism of reaction.

Comparison with Reactions of Zirconium Dihydride

A comparison can be made here with the related reactivity of the zirconium analog $\text{Cp}^*_2\text{ZrH}_2$. This complex has been reported to reduce aliphatic,^[36] aromatic,^[1d–18] and olefinic^[14–15] C–F bonds under mild conditions. It can also undergo β -fluoride elimination in fluorophenyl derivatives to generate benzyne intermediates.^[37] In addition, reduction of sp^3 $\text{CF}_2\text{H–R}$ has been reported to occur slowly with this compound. The reaction mechanisms proposed vary from free radical chain for aliphatic C–F, to nucleophilic attack for monofluoroaromatics, to insertion/ β -fluoride elimination for fluoroolefins.^[4] Additionally, other electrophilic titanocene^[38] and zirconocene^[39] complexes have been seen to cleave C–F bonds in perfluoropyridine. In general, the reactivity patterns seen with $\text{Cp}^*_2\text{HfH}_2$ mimic those of $\text{Cp}^*_2\text{ZrH}_2$, except that the hafnium complex is less reactive. Reactions proceed to give similar products either slowly, or not at all. While fewer mechanistic studies have been undertaken with hafnium, it is likely that the substrates react by similar mechanisms as in the zirconium cases.

Experimental Section

All substrates were used as delivered without purification. Products have been characterized and unreacted starting materials have been identified primarily by comparing known ^{19}F NMR chemical shift values to those obtained during a given experiment (using external α,α,α -trifluorotoluene in $[\text{D}_{12}]\text{cyclohexane}$ as a reference). Reported NMR spectroscopic data not referenced to external α,α,α -trifluorotoluene in $[\text{D}_{12}]\text{cyclohexane}$ were converted accordingly. In some cases, ^1H NMR and GC-MS data were used to further confirm the identity of the organic products. NMR spectra were recorded with Bruker Avance instruments (400 or 500 MHz). GCMS data were recorded with a Shimadzu model QP2010 spectrometer. A Siemens SMART CCD area detector diffractometer equipped with an LT-2 low-temperature unit was used for X-ray crystal structure determination.

Preparation of $\text{Cp}^*_2\text{HfH}_2$: From dimethyl complex: $\text{Cp}^*_2\text{HfCl}_2$ (3.85 mmol; Strem) was dissolved in roughly 40 mL of diethyl ether (previously vacuum-transferred from purple sodium/benzophenone ketyl) in a nitrogen glovebox. On a Schlenk line, 2.1 equiv. of methylolithium (8.09 mmol; 1.4 M in Et_2O from Aldrich) were added to the reaction mixture by syringe under positive nitrogen pressure. The reaction mixture was stirred under static nitrogen for roughly 25 h before ca. 1 mL of ACS-grade methanol was added under pos-

itive nitrogen pressure to quench the reaction. The volatile materials were removed by vacuum. Isolation of the final product was achieved by filtering a hexane mixture of crude product through celite, cooling the filtrate to -78°C to induce crystallization, removing the mother liquor/washing the crystals with cold hexane via cannula transfer, and drying in vacuo (3.06 mmol, 80%). The second step involved placing a C_6D_6 solution of $\text{Cp}^*_2\text{HfMe}_2$ (0.06 mmol) under 15 psi of UHP-grade hydrogen gas (Airgas) at 100°C . The reaction was periodically monitored by ^1H NMR over the course of 6 weeks, with the hydrogen being replaced many times with fresh hydrogen following several freeze-pump-thaw degassing cycles ($\approx 97\%$ final conversion to **1**). The reaction was repeated on a preparative scale with the remaining $\text{Cp}^*_2\text{HfMe}_2$. **1** was also prepared in 33% yield from the reaction of $\text{Cp}^*_2\text{HfCl}_2$ and BuLi, as described in ref.^[22] ^1H NMR (C_6D_6): $\text{Cp}^*_2\text{HfCl}_2$, $\delta = 1.91$, s, $\text{Cp}^*_2\text{HfMe}_2$, $\delta = 1.80$, (s, 30 H), -0.70 (s, 6 H) $\text{Cp}^*_2\text{HfH}_2$ (**1**), $\delta = 2.05$, (s, 30 H), 15.63 (s, 2 H) ppm. ^1H NMR (C_6D_{12}): $\text{Cp}^*_2\text{HfH}_2$ (**1**), $\delta = 2.03$, (s, 30 H), 15.37 (s, 2 H) ppm.

Isolation of **2 and **3**:** Samples of **2** and **3** were obtained from the non-volatile organometallic residue of the fluorocarbon reduction reactions. X-ray quality crystals were grown by allowing a pentane solution of the hafnium complex to evaporate into a small quantity of toluene at -30°C in a nitrogen glovebox. X-ray quality crystals of **4** were obtained by allowing pentane vapor to diffuse into a concentrated CH_2Cl_2 solution of **4** at room temperature in a nitrogen glovebox. For **2**, ^1H NMR (C_6D_{12}): $\delta = 1.95$ (s, 30 H), 10.90 (d, $J = 4.8$ Hz, 1 H) ppm. ^{19}F NMR: $\delta = 107.8$ (s) ppm. For **3**, ^1H NMR (C_6D_{12}): $\delta = 1.89$ (s) ppm. ^{19}F NMR: $\delta = 49.7$ (s) ppm. For **4**, ^1H NMR (C_6D_{12}): $\delta = 2.00$ (s, 30 H), 2.08 (s, 30 H), 9.79 (s, 2 H) ppm.

Reactions of **1 with Fluorocarbons:** All experiments were run in NMR tubes fitted with a Teflon™ stopper using equimolar amounts of **1** and substrate. Unless otherwise noted, twice-dried $[\text{D}_{12}]\text{cyclohexane}$ was used as solvent to dissolve mixtures of the starting hafnium complex and solid substrates in a nitrogen glovebox. In reactions involving liquid substrates, ca. 10 mg of **1** was first dissolved using C_6D_{12} in a nitrogen glovebox and the previously-degassed liquid substrate was added via syringe. Gaseous compounds were condensed into chilled reaction vessels using high vacuum techniques.

For reactions of 2- and 3-fluoropyridine, ^{19}F data^[40] showed the loss of fluorocarbon reactant and the formation of **2** and small amounts of **3** (2–4%) over the course of a week at room temperature. Pyridine was not seen by ^1H NMR spectroscopy.^[41] For reactions of 2- and 4-fluorobiphenyl, no reaction was observed at 120°C by ^{19}F NMR spectroscopy.^[42] Polyfluorinated aromatics showed only traces of reaction if any reaction at all after extended heating at 120°C , as determined by monitoring the ^{19}F NMR spectra of these reactions. Substrates examined were 1,2,4,5-tetrafluorobenzene,^[1(d)] 2,2',3,3',5,5',6,6'-octafluorobiphenyl,^[43] 1,2,3,4-tetrafluorobenzene,^[1(d)] and 2,3,4,5,6-pentafluoro(allyl)benzene.^[44] In contrast, perfluorinated aromatics showed some evidence for slow reaction. ^{19}F NMR spectroscopic examination of reactions of hexafluorobenzene,^[45] octafluoronaphthalene,^[46] and decafluorobiphenyl^[47] showed reduction to produce **2** after several days at 100 – 120°C . Reaction of **1** with 1-fluorohexane^[48] commenced only upon heating to 60°C , and approached completion after 20 d at 120°C .

^{19}F NMR spectroscopy was used to monitor reactivity of the partially fluorinated olefins 3,3,3-trifluoropropene,^[49] 1,1-difluoroethylene,^[50] hexafluoroisobutene,^[51] 3-trifluoromethyl-3,4,4,4-tetrafluoro-1-butene, α -(trifluoromethyl)styrene,^[52] and difluoromethyl-

enecyclohexane,^[53] as described in the text. Reactions of **1** with the perfluorinated olefins perfluoropropene^[54] and octafluorocyclopentene^[55] were also examined by ¹⁹F NMR spectroscopy, but no reaction occurred quickly at room temp.

Low-Temperature Reaction of 1 with Fluorocarbons: Compound **1** was dissolved in [D₁₄]methylcyclohexane in a nitrogen glovebox. The substrate of choice was measured by achieving the appropriate pressure in a pre-calibrated glass bulb. The substrate was then condensed into the reaction vessel following degassing of the solution of **1**. Special effort was directed at keeping the NMR tube cold following transfer of the substrate, which was achieved by thawing the frozen solution of **1** in a liquid nitrogen/ethanol slush bath (−116 °C). In most instances, the NMR probe was pre-cooled to −110 °C.

1,1-Difluoropropene was obtained through the previously mentioned reaction of **1** with 3,3,3-trifluoropropene, with the exception being that the reaction was run in C₆D₁₁CD₃ in instances where 1,1-difluoropropene was designed to serve as a starting material in a subsequent low-temperature experiment. The volatile materials from the reaction (primarily 1,1-difluoropropene, 1,1,1-trifluoropropane, and solvent) were vacuum-transferred from this reaction onto another equivalent of **1** before thawing the reaction mixture at −116 °C. Detailed descriptions of these reactions are given in the text.

X-ray Structure Determinations: Single crystals of **1**, **2**, and **3** were mounted under Exxon Paratone-8277TM on glass fibers and immediately placed in a cold nitrogen stream at 100 K on the X-ray diffractometer. The X-ray intensity data (1.3 hemispheres) were collected over 6 h with a standard Siemens SMART APEX II CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA).^[56] Data were corrected for absorption using the program SADABS.^[57] Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 97). The structures were solved by using direct methods and refined by full-matrix least-squares on *F*².^[58] For all of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters except for the fluoride ligand in **2**, which was disordered over two sites and refined isotropically. The Hf-bound hydride in **2** was not included in the final refinement model. There was nothing unusual about the solution or refinement of any of the structures, although the fluoride and hydride ligands in **2** were disordered (76/24 and 60/40). Compound **4** refined with a Flack parameter of 0.055(8). Further experimental details of the X-ray diffraction studies are provided in Table 2. CIF files for the structures **2–4** have been deposited with the CCDC.^[59]

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- [58] Using the SHELX95 package, $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_c^2) + (a \cdot P)^2 + b \cdot P]$ and $P = [f(\text{maximum of } 0 \text{ or } F_o^2) + (1 - f) \cdot F_c^2]$.
- [59] CCDC-618856 to -618858 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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