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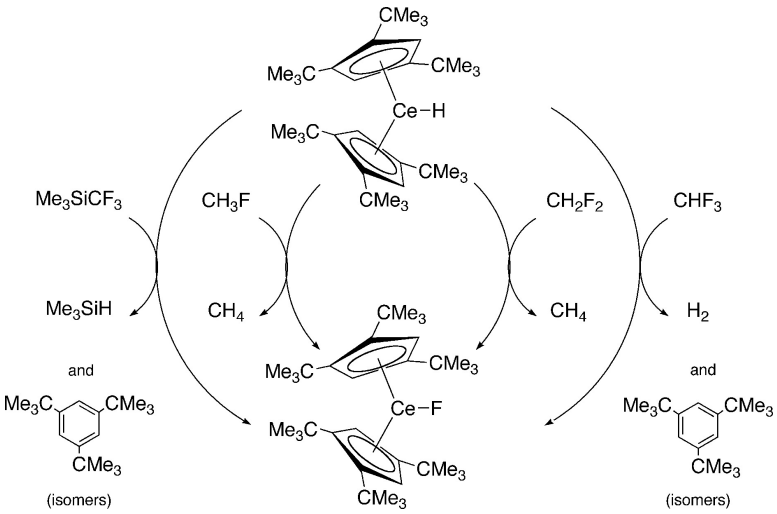
*J. Am. Chem. Soc.*, **2005**, 127 (21), 7781-7795• DOI: 10.1021/ja0504800 • Publication Date (Web): 07 May 2005



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# Hydrogen for Fluorine Exchange in $CH_{4-x}F_x$ by Monomeric $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2CeH$: Experimental and Computational Studies

Evan L. Werkema,[†] Elsa Messines,[‡] Lionel Perrin,[§] Laurent Maron,*[,‡] Odile Eisenstein,*[,§] and Richard A. Andersen*[,†]

*Contribution from the Chemistry Department and Chemical Sciences Division of Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, Laboratoire de Physique Quantique, UMR 5626-CNRS, IRSAMC, Université Paul Sabatier, 118 Route de Narbonne, 31064 Toulouse Cedex 04, France, and LSDSMS, (UMR 5636-CNRS), Institut Gerhardt, cc14, Université Montpellier 2, 34095 Montpellier Cedex 5, France*

Received January 24, 2005; E-mail: laurent.maron@irsamc.ups-tlse.fr; odile.eisenstein@univ-montp2.fr; raandersen@lbl.gov

***Abstract:*** The monomeric metallocenecerium hydride, $Cp'_2CeH$ ($Cp' = 1,2,4$-tri-*tert*-butylcyclopentadienyl), reacts instantaneously with $CH_3F$, but slower with $CH_2F_2$, to give $Cp'_2CeF$ and $CH_4$ in each case, a net H for F exchange reaction. The hydride reacts very slowly with $CHF_3$, and not at all with $CF_4$, to give $Cp'_2CeF$, $H_2$, and 1,2,4- and 1,3,5-tri-*tert*-butylbenzene. The substituted benzenes are postulated to result from trapping of a fluorocarbene fragment derived by α-fluoride abstraction from $Cp'_2CeCF_3$. The fluoroalkyl, $Cp'_2CeCF_3$, is generated by reaction of $Cp'_2CeH$ and $Me_3SiCF_3$ or by reaction of the metallacycle, $[(Cp')(Me_3C)_2C_5H_2C(Me_2)CH_2]Ce$, with $CHF_3$, and its existence is inferred from the products of decomposition, which are $Cp'_2CeF$, the isomeric tri-*tert*-butylbenzenes and in the case of $Me_3SiCF_3$, $Me_3SiH$. The fluoroalkyls, $Cp'_2CeCH_2F$ and $Cp'_2CeCHF_2$, generated from the metallacycle and $CH_3F$ and $CH_2F_2$, respectively, are also inferred by their decomposition products, which are $Cp'_2CeF$, $CH_2$, and CHF, respectively, which are trapped. DFT(B3PW91) calculations have been carried out to examine several reaction paths that involve CH and CF bond activation. The calculations show that the CH activation by $Cp_2CeH$ proceeds with a low barrier. The carbene ejection and trapping by $H_2$ is the rate-determining step, and the barrier parallels that found for reaction of $H_2$ with $CH_2$, CHF, and $CF_2$. The barrier of the rate-determining step is raised as the number of fluorines increases, while that of the CH activation path is lowered as the number of fluorines increases, which parallels the acidity.

## Introduction

The hydrogen for fluorine exchange reaction in fluoromethanes is a thermodynamically favorable transformation. The exchange reaction is exothermic by 20−30 kcal mol$^{-1}$ because the exchange results in formation of HF, eq 1, in which the bond disruption enthalpy of 135 kcal mol$^{-1}$ is 30 kcal mol$^{-1}$ larger than that of $H_2$ (105 kcal mol$^{-1}$). The C−F bond dissociation enthalpy (BDE) monotonically decreases on going from $CF_4$ to $CH_3F$, the average BDE values of $CF_4$, $CHF_3$, $CH_2F_2$, and $CH_3F$ are 130, 129, 120, and 108 kcal mol$^{-1}$, respectively, making the reaction more exothermic as the fluorine content decreases. The C−H BDE in the fluoromethanes decreases from 107 to 100 kcal mol$^{-1}$ in the above series.[1]

$$CH_{4-x}F_x + {}^1/_2H_2 \rightarrow CH_{5-x}F_{x-1} + HF \qquad x = 1-4 \quad (1)$$

The exchange does not occur, however, without a catalyst. For example, passing a mixture of $CH_3F$ and $H_2$ over Pd/C at 240 °C results in a 10% conversion to methane.[2] The favorable thermodynamics of eq 1 are clearly due to the bond enthalpy of H−F being greater than either the H−H or the C−F bond. Lanthanide fluorides, in general, have average bond enthalpies larger than that of HF, for example, the average bond enthalpy of $CeF_3$(g) is 153 kcal mol$^{-1}$.[3] Although the Ce−H bond enthalpy in $CeH_3$ is unknown, it is likely to be less than that of H−H, as is the case for the metallocenes, $Cp'_2MH$; the M−H bond enthalpy is 67 kcal mol$^{-1}$ in $(Me_5C_5)_2LaH$ or $(Me_5C_5)_2LuH$ and 80 kcal mol$^{-1}$ in $(Me_5C_5)_2ZrH_2$,[4] and the H/F exchange reaction will be exothermic. Bare cationic metal atoms in the gas-phase defluorinate some fluoromethanes. For example, $Ce^+$(g) forms $CeF_2^+$(g) from $CH_3F$, but no abstraction is observed from $CHF_3$ or $CF_4$, bracketing the $CeF^+$(g) bond enthalpy between 110 and 130 kcal mol$^{-1}$.[5]

The H/F exchange reactions in halofluoromethanes are of some interest in the biological community because the cobal-

[†] University of California, Berkeley.
[‡] Université Paul Sabatier.
[§] Université Montpellier 2.

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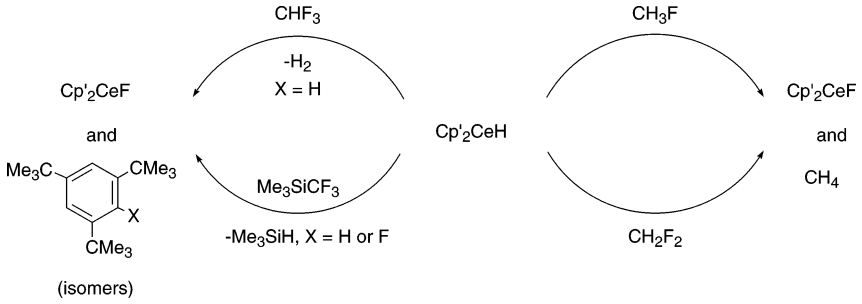
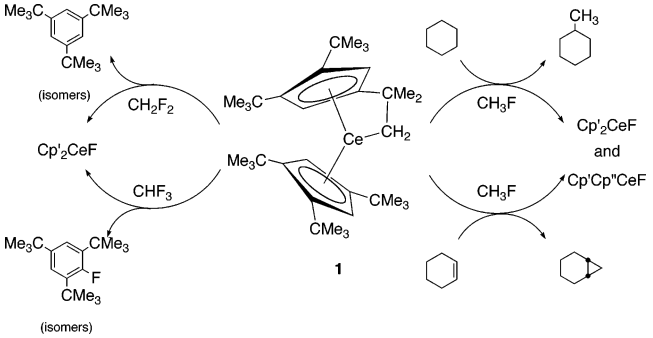
***Scheme 1.*** Reactions of $Cp'_2CeH$ ($Cp' = 1,2,4\text{-}(Me_3C)_3C_5H_2$) with Fluorocarbons




amines defluorinate them. For example, photolysis of cobalamines in the presence of $CHF_2Cl$ and $H_2$ yields methane. The mechanism of this reaction is unknown, but a mechanism in which α-F abstraction from a $(L)CoCHF_2$ species followed by trapping of the resulting carbene with $H_2$ has been suggested.[6] In related experiments, corrinoids catalyze the reduction of, for example, $CF_3Cl$ to CO in the presence of $Ti^{III}$ citrate in water. The mechanism is suggested to involve formation of carbenes that are trapped by water to give CO and HX.[7] The organometallic chemistry literature contains examples of model systems that relate, in a general way, to the biological ones mentioned. The iridium cation, $(Me_5C_5)Ir(PMe_3)(H_2O)(C_2F_5)^+$, undergoes hydrogenolysis to give $CH_2FCF_3$ and $CH_3CF_3$ by a mechanism proposed to proceed by way of an iridium carbene species.[8] The aqueous acid hydrolysis of $[CF_3Cr(OH_2)_5]^{2+}$ gives $[FCr(OH_2)_5]^{2+}$ and CO, a reaction also suggested to involve hydrolysis of a carbene.[9] Experimental and computational studies of the carbene transfer to various traps have been carried out for $RCH_2LiX$ where X is chloride, bromide, or iodide, the Simmons−Smith reagent RCHIZnI, and with $ISmCH_2I$.[10]

Thus, reactions of organometallic compounds can provide model systems that illuminate pathways followed by much more complex molecules. Recently, we developed the synthesis of the monomeric metallocene hydride of cerium, $Cp'_2CeH$ where Cp′ is 1,2,4-tri-*tert*-butylcyclopentadienyl, and showed that it undergoes H/F exchange reactions with $C_6F_6$ and $C_6F_5H$.[11] The general subject of intermolecular C−F activation has been extensively studied, and several reviews are available, largely within the framework of oxidative addition reactions.[12] Computational studies have shown that the C−F activation may be exothermic but that a high activation barrier is usually observed with late transition metal systems.[13] In the case of early transition metals, the activation barrier is generally lower and several cases of H/F exchange have been observed; it appears that the $C(sp^2)-F$ bond is activated more easily than the $C(sp^3)-F$ bond.[14] The reactions of bare metal centers have been analyzed by computational methods, showing that electron transfer as well as oxidative insertion paths are possible.[15] In this paper, we show that $Cp'_2CeH$ reacts with hydrofluoromethanes, and we explore the mechanistic pathways by DFT calculations on the model metallocene hydride, $Cp_2CeH$.

***Scheme 2.*** Reactions of the Metallacycle **1**, Where Cp′ = 1,2,4-$(Me_3C)_3C_5H_2$ and Cp″ = $(Me_2Et)(Me_3C)_2C_5H_2$, with Fluorocarbons




## Results and Their Interpretation

**General.** The reactions of $Cp'_2CeH$ or the metallacycle, **1**, and the fluoromethanes $CH_{4-x}F_x$ ($x = 0-4$), Schemes 1 and 2, are studied by monitoring the changes that occur in the $^1H$ NMR spectrum in $C_6D_6$ or $C_6D_{12}$ over time; the *tert*-butyl resonances of the paramagnetic hydride disappear and those of $Cp'_2CeF$ appear. The identity of the non-cerium containing products is deduced by the characteristic resonances in their $^1H$ and $^{19}F$ NMR spectra. At the end of the reactions, the samples are hydrolyzed ($H_2O$ or $D_2O$) and examined by GCMS to deduce their identity. In those cases where the reaction is rapid, the

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reactions are clean and excellent mass balance is observed. In those cases where the reactions are slow, the identity of the major compounds is established, but minor products are not always identified. When feasible, labeling and trapping experiments are used to confirm the spectroscopic results. The synthesis, solution spectroscopy, and solid-state structures of $Cp'_2CeH$, the starting metallocene, and $Cp'_2CeF$, the ending metallocene, are known.[11]

**Reactions of $Cp'_2CeH$ and $CH_{4-x}F_x$; Scheme 1.** Exposure of $Cp'_2CeH$ to $CH_4$ in $C_6D_{12}$ does not change the appearance of the $^1H$ NMR spectrum relative to the individual resonances over a month at room temperature. The lack of exchange is not surprising because the Ce−Me bond enthalpy is likely to be less than that of Ce−H, a trend found in f-block and early d-transition metal metallocenes.[16] The reluctance of methane to react with the hydride is fortunate, because exposure of the hydride to $CH_3F$ results in a rapid color change from purple to orange, disappearance of the hydride resonances, and appearance of those due to the fluoride and methane, eq 2.

$$Cp'_2CeH + CH_3F \rightarrow Cp'_2CeF + CH_4 \qquad (2)$$

Methane does not react with the hydride, so the net reaction is a simple H/F exchange. To be certain that the hydride in the methane originates from the cerium hydride, repeating the reaction under an atmosphere of $D_2$ gives the fluoride and a mixture of $CH_4$ and $CH_3D$ in approximately equal amounts. This experiment implies that the exchanges symbolized in eqs 3a,b are occurring. No multiple H/D exchange in methane is observed, consistent with the lack of reaction between $Cp'_2CeD$ and methane.

$$Cp'_2CeH + D_2 \rightarrow Cp'_2CeD + HD \qquad (3a)$$

$$Cp'_2CeD + CH_3F \rightarrow Cp'_2CeF + CH_3D \qquad (3b)$$

Exposure of $Cp'_2CeH$ to an excess of $CH_2F_2$ in $C_6D_{12}$ ultimately gives the same products shown in eq 2, but the rate is much slower, hours rather than seconds. Repeating the reaction in the presence of $D_2$ gives $CH_3D$ and $CH_2D_2$ in approximately equal amounts. The HD was not detected presumably because of its low solubility in $C_6D_{12}$. The labeling result may be rationalized by the net reactions shown in eqs 2 and 4, in which the rate of H/F exchange in eq 4 is slower than that of eq 2. No $CH_3F$ is detected in the $^1H$ or the $^{19}F$ NMR spectrum, consistent with these deductions about the relative rates.

$$Cp'_2CeH + CH_2F_2 \rightarrow Cp'_2CeF + CH_3F \qquad (4)$$

The reaction of $CHF_3$ is much slower than the other two reactions (eqs 2, 4); weeks rather than hours are required. Although all of the CeH resonances ultimately disappear and $Cp'_2CeF$ is the ultimate cerium containing product formed, no methane is observed in the $^1H$ NMR spectrum, although a resonance due to dihydrogen appears. Under an atmosphere of either $D_2$ or $CH_4$, no deuterated methane or ethane was detected. Several $Me_3C$-resonances appear in the diamagnetic region of the $^1H$ NMR spectrum; these resonances are not due to the isomeric dienes of general formula $(Me_3C)_3C_5H_3$ formed by hydrolysis from traces of water over the long reaction time, but they were ultimately identified as due to two isomers of tri-*tert*-butylbenzene in the following way. At the end of the reaction, the mixture was hydrolyzed with $H_2O$ (or $D_2O$) and the hydrolyzate was analyzed by GCMS, which showed two isomers with identical molecular ions whose fragmentation patterns were identified as being those of the isomeric benzenes 1,3,5-$(Me_3C)_3C_6H_3$ and 1,2,4-$(Me_3C)_3C_6H_3$. Once the isomers were identified, the resonances due to 1,3,5-$(Me_3C)_3C_6H_3$ in the $^1H$ NMR spectrum were compared with those of an authentic specimen. The relative intensity showed that the isomers are present in comparable amounts. The only source of the three *tert*-butyl fragments is the $(Me_3C)_3C_5H_2^-$ ring, and the only source of the $C_1$ fragment is $CHF_3$. Clearly, the net reaction of $CHF_3$ is different from that of either $CH_2F_2$ or $CH_3F$. The reactions, illustrated in eq 5, may be used to rationalize the identified products. Equation 5a is consistent with the detection of dihydrogen, and eq 5b is consistent with formation of $Cp'_2CeF$ by way of $Cp'_2CeCF_3$ that is not detected and difluorocarbene that is trapped by a Cp′-ring bound to either $Cp'_2CeF$ or $Cp'_2CeH$, as illustrated in eqs 5c and 5d. These four equations rationalize the products identified, and they are suggested as a guide to our thinking about the net reaction.

$$Cp'_2CeH + CHF_3 \rightarrow Cp'_2CeCF_3 + H_2 \qquad (5a)$$

$$Cp'_2CeCF_3 \rightarrow Cp'_2CeF + \text{“}CF_2\text{”} \qquad (5b)$$

$$Cp'_2CeF + \text{“}CF_2\text{”} \rightarrow Cp'CeF_2 + \text{“}Cp'CF\text{”} \qquad (5c)$$

$$Cp'_2CeH + \text{“}Cp'CF\text{”} \rightarrow Cp'_2CeF + \text{“}Cp'CH\text{”} \qquad (5d)$$

There is literature precedent for carbene insertion into the $(Me_3C)_3C_5H_2^-$ ring. Reaction of $(Me_3C)_3C_5H_3$ and a dihalocarbene generated from $CHCl_3$ or $CHBr_3$ and strong base yields the 1,2,4-tri-*tert*-butyl-5-halobenzenes.[17] Although no resonances for $Cp'_2CeCF_3$ are detected, see later, trifluoromethylmetal species decompose by α-F abstraction to yield $CF_2$ fragments that are subsequently trapped.[18] Thus, the reaction shown in eq 5b is reasonable, the difluorocarbene is an electrophile and it can add to the different double bonds of the Cp′-ring, and the resulting cerium compounds decompose to isomeric tri-*tert*-butylfluorobenzenes, as illustrated in eq 5c. However, the tri-*tert*-butylfluorobenzenes are not observed; only isomeric tri-*tert*-butylbenzenes are observed. Mixing $Cp'_2CeH$ and the isomeric tri-*tert*-butylfluorobenzenes does not give H/F exchange products; that is, the reaction symbolized in eq 5d does not occur. A possible reason for the absence of tri-*tert*-butylfluorobenzenes is suggested by the following experiments. Mixing $Cp'_2CeH$ and $Cp'_2Ce(OSO_2CF_3)$ instantaneously gives $Cp'_2CeF$ and a new paramagnetic cerium metallocene, thought to be $Cp'_2Ce(OSO_2CHF_2)$, the result of intermolecular H/F exchange analogous to the reaction symbolized in eqs 2 and 4. Mixing $Cp'_2CeH$ with $(Cp'\text{-}d_{27})_2CeF$ in $C_6D_{12}$ instantaneously gives an equilibrium mixture with $Cp'_2CeF$ and $(Cp'\text{-}d_{27})_2CeH$, the net result of intermolecular H/F exchange. Thus, it is reasonable to suggest

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that when $Cp'_2CeCF_3$ forms (eq 5a), in the presence of $Cp'_2CeH$, rapid intermolecular H/F exchange generates $Cp'_2CeF$ and $Cp'_2CeCHF_2$, which forms $Cp'_2CeF$ and Cp′CH, the net products observed. Evidence for the decomposition of hypothetical $Cp'_2CeCHF_2$ is provided in the next section.

The sequence of events just outlined demands that $Cp'_2CeCF_3$ is formed. Generating or perhaps isolating $Cp'_2CeCF_3$ and allowing it to decompose is a crucial experiment, because in absence of this datum, the reactions in eq 5 are without experimental foundation. Generating $Cp'_2CeCF_3$ is done in the following manner. Addition of $Me_3SiCF_3$ to $Cp'_2CeH$ in an NMR tube instantly gives resonances due to $Cp'_2CeF$, the isomeric tri-*tert*-butylbenzenes and tri-*tert*-butylfluorobenzenes, as well as a resonance due to $Me_3SiH$. Repeating the experiment with the $[Cp'\text{-}d_{27}]_2CeD$ gives $Me_3SiD$ and the isomers of $[(CD_3)_3C]_3C_6H_2D$. Trifluoromethyltrimethylsilane in the presence of CsF is a $CF_3$ transfer reagent for synthesis of $Cp_2Ti(CF_3)(F)$.[19] The net reaction may be written as in eq 6, where the difluorocarbenes are trapped as described above. This set of reactions justifies the speculation about the formation of a trifluoromethyl cerium intermediate, but they just describe the net reaction without mechanistic information.

$$Cp'_2CeH + Me_3SiCF_3 \rightarrow Cp'_2CeCF_3 + Me_3SiH \quad (6a)$$

$$Cp'_2CeCF_3 \rightarrow Cp'_2CeF + \text{“}CF_2\text{”} \quad (6b)$$

Exposure of $Cp'_2CeH$ to $CF_4$ in $C_6D_{12}$ for a time period of up to a month does not produce any change in the $^1H$ NMR spectrum. Thus, $CF_4$ does not undergo H/F exchange. Although $CF_4$ is the most stable fluorocarbon known,[20] the lack of reaction is kinetic rather than thermodynamic. A very high barrier to H/F exchange of $Cp_2LaH$ and $CF_4$ is obtained from DFT calculations.[21] Support for the kinetic stability of $CF_4$ is derived by noting that the averaged bond dissociation enthalpy of $CF_4$ is 130 kcal $mol^{-1}$ while that of $SiF_4(g)$ is 142 kcal $mol^{-1}$.[3] Mixing $Cp'_2CeH$ and $SiF_4$ generates $Cp'_2CeF$ and other unidentified compounds instantaneously, showing that the stronger (Si−F) bond reacts more rapidly than the weaker one (C−F). It is noteworthy that perfluoromethylcyclohexane and $Cp'_2CeH$ does indeed produce $Cp'_2CeF$, but the reaction time is on the order of a month. Similarly, the $PhCF_3$ and $Cp'_2CeH$ yield resonances due to $Cp'_2CeF$ over 3 days; several other cerium containing species were observed in the $^1H$ NMR spectrum, and these reactions were not studied further.

Summarizing this part, the qualitative results show a large variation in rates of reaction as the H to F ratio changes in the reaction of $Cp'_2CeH$ with hydrofluoromethanes. The reactions of $Cp'_2CeH$ and $CH_3F$ and $CH_2F_2$ are clean as only two products are formed, eqs 2 and 4. The reaction of $CHF_3$, however, is very slow and produces several products; no methane is detected, but products resulting from difluorocarbene are observed. No mechanistic information is available from these experiments because no intermediates are detected in the NMR experiments. Insight into the mechanisms is explored by DFT calculations described later.

**Reaction of the Metallacycle with Hydrofluorocarbons, Scheme 2.** The implication of the reaction symbolized by eq 6 is that $Cp'_2CeCH_{3-x}F_x$, $x = 0-3$, in general and $Cp'_2CeCF_3$ in particular are unstable relative to $Cp'_2CeF$ and a carbene fragment. To learn more about these hypothetical fluoroalkyls and their decomposition pathway, their synthesis was desired. In our previous H/F exchange studies, the metallacycle **1**, in Scheme 2, was shown to react with $HC_6F_5$, but not with $C_6F_6$, to give the isolable perfluorophenyl derivative, $Cp'_2Ce(C_6F_5)$. Thus, reactions of the metallacycle with $CH_{4-x}F_x$, $x = 0-4$, were explored.

Addition of an excess of $CH_4$ to the metallacycle in $C_6D_{12}$ does not result in change of appearance of the $^1H$ NMR spectrum over the period of a month. However, reaction of the metallacycle, in which all of the hydrogens in the $CMe_3$ groups were exchanged by deuterium, with methane in $C_6D_{12}$ over the course of a week produced some $CH_3D$. Prolonged exposure gives $CH_2D_2$, $CHD_3$, and presumably $CD_4$. This result implies that the C−H bond of methane can reversibly insert into the Ce−C bond of the metallacycle, a process that is essentially thermoneutral. It is revealing, in this regard, to mention an experiment aimed at the synthesis of $Cp'_2CeMe$ from $Cp'_2CeX$ (X = I or $O_3SOCF_3$) and MeLi in hexanes−ether. Conducting the reaction and workup at room temperature gives a material whose $^1H$ NMR spectrum ($C_6D_6$) is identical to that of the metallacycle **1**. When the reaction and workup was repeated at low temperature, the $^1H$ NMR spectrum showed resonances due to the metallacycle and a pair of $Me_3C$-resonances in a 2:1 area ratio (see Experimental Section for details). The latter resonances disappear with time as the metallacycle resonances increase in intensity and a resonance due to methane appears. This result is understandable if the Ce−C bonds are assumed to be of comparable strength and the increase of entropy drives the methane elimination reaction. The only alkyl so far isolated is the benzyl, $Cp'_2CeCH_2Ph$, which slowly yields the metallacycle and toluene at room temperature.[11]

Addition of $CH_3F$ to a solution of the metallacycle in $C_6D_{12}$ in a NMR tube and heating at 60 °C over a period of 12 h results in the appearance of resonances due to $Cp'_2CeF$ and a set of resonances due to a new cerium metallocene (X) in a 5:1 ratio. The identity of X is established by the following experiments. Repeating the reaction in the presence of cyclohexene showed resonances in the $^1H$ NMR spectrum due to $Cp'_2CeF$, X, and norcarane (Scheme 2), although the ratio of X to $Cp'_2CeF$ is less than in the absence of cyclohexene.[22] Repeating the reaction of the metallacycle with $CH_3F$ in $C_6D_{12}$, without cyclohexene, followed by hydrolysis ($H_2O$) and analysis of the organic fraction by GCMS shows cyclohexane-$d_{12}$ (solvent), methylcyclohexane-$d_{12}$, Cp′H, and a new cyclopentadiene whose *m*/*z* value is 14 amu higher than Cp′H, that is, Cp′$(CH_2)$H. Repeating the above reaction in $C_6H_{12}$, rather than $C_6D_{12}$, gives methylcyclohexane in addition to cyclohexane, the solvent. These experiments show that $CH_2$ is trapped by C=C or C−H

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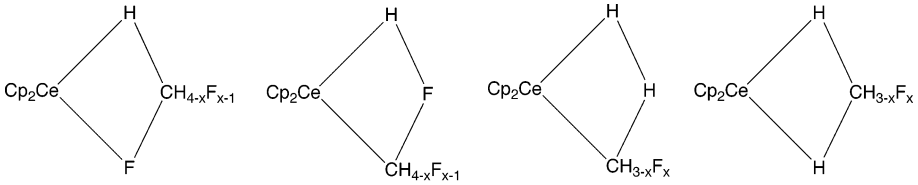
(22) To be sure that cyclohexene does not change the course of the reaction, the perdeuteriometallacycle was exposed to a large excess of cyclohexene in $C_6D_{12}$. Over the course of a week, 1,2-dideuteriocyclohexene was the only product observed by $^2H$ NMR spectroscopy. This experiment shows that cyclohexene inserts into the metallacycle to give the metallocene cerium cyclohexenyl derivative and this eliminates cyclohexene-$d_1$. Because both olefinic C−H bonds undergo H/D exchange, the process is reversible. The rate of addition is slow, and therefore cyclohexene is present in sufficient excess to act as a trapping reagent. Cyclohexene reacts rapidly with $Cp'_2CeH$ generating the cyclohexyl derivative that yields the metallacycle and cyclohexane. Under dihydrogen, the metallacycle or $Cp'_2CeH$ is a hydrogenation catalyst for cyclohexene. Thus, cyclohexene cannot be used as a carbene trap in reactions of $Cp'_2CeH$.

***Scheme 3.*** Schematic 4c-4e Transition States ($x = 1-4$ for **2** and **3**; $x = 0-3$ for **4** and **5**)




bonds and provides a clue as to the identity of X, because the metallocene rings have C−H bonds. Exposing the perdeuteriometallacycle to $CH_3F$ in $C_6D_{12}$ showed resonances in the $^2H$ NMR spectrum due to (Cp′-$d_{27}$)(Cp′-$d_{26}$)CeF, while the $^1H$ NMR spectrum contained three new resonances with chemical shifts in the region found for the $Me_3C$ groups in $Cp'_2CeF$. Hydrolysis ($H_2O$) and examination of the hydrolysate by GCMS showed that two cyclopentadienes were present, which were a mixture of the isotopomers (Cp′-$d_{26}$)H, (Cp′-$d_{27}$)H, and (Cp′-$d_{26}$)($CH_2$)(H), (Cp′-$d_{27}$)($CH_2$)(H), that is, the isotopomers of {[$(CD_3)_2$($CD_2$-$CH_2$D)C][$(CD_3)_3$C][$(CD_3)_2$($CD_2$H)C]$C_5H_3$}. Examination of the $^1H$ NMR spectrum of the diene shows three single resonances in the $Me_3C-$ region for the three possible isotopomers of this diene. This is sufficient evidence to identify X as [($Me_2$EtC)-($Me_3$C)$_2C_5H_2$]$_2$CeF, the result of insertion of $CH_2$ into a C−H bond of the ring substituted $CMe_3$ group. Thus, C−H bonds of the solvent and the ring substituents trap the $CH_2$ fragment. However, there is still an unsettling question: photochemical decomposition of $CH_2N_2$ in the presence of cyclohexene gives norcarane and the three isomeric methylcyclohexenes in a ratio of about 2:3.[23] In a later study, singlet $CH_2$ was found to react with all substrates including C−H bonds of saturated hydrocarbons at diffusion-controlled rates.[24] Norcarane is the expected reaction product of singlet methylene, but no evidence of insertion into the C−H bonds of cyclohexene is observed in our experiments. A way around the selectivity issue is to postulate that the carbene generated in our studies is not a free carbene, but a carbenoid, that is a methylene, in which the metal and leaving group (F) are still attached to the $CH_2$ fragment. Carbenoid fragments are electrophiles that react much like free carbenes but show greater selectivity.[25] The cerium reaction is therefore related to that observed for various carbenoid precursors such as RHCLiX, the Simmons−Smith reagent, RCHIZnI, and $ISmCH_2I$.[10] A similar set of experiments with the metallacycle and $CH_2F_2$ gives $Cp'_2CeF$ and the two isomers of tri-*tert*-butylbenzene, or with $CHF_3$ that gives the isomeric tri-*tert*-butylfluorobenzenes, in the absence of a trapping reagent, Scheme 2. In the presence of cyclohexene, similar results are obtained indicating that cyclohexene is not as good a trap as the substituted-cyclopentadienyl ring. This set of experiments is consistent with the idea that the C−H bond in hydrofluoromethanes inserts into the Ce−C bond of the metallacycle generating a metallocenecerium-fluoroalkyl that is not observed by $^1H$ NMR spectroscopy, but whose identity is inferred by the products of decomposition. The mechanism of the net reaction shown in Schemes 1 and 2 is explored by DFT calculations in the next section.

## Computational Studies

**General Considerations.** In the calculations, $Cp'_2CeH$ is modeled by $Cp_2CeH$, which changes the steric effects of the metallocene fragment. Because the fluoroalkanes are small molecules, steric effects are not likely to play an important role in the relative activation barriers. This approach has been used successfully in a number of previous studies.[11,21,26]

The reactions have a very large thermodynamic driving force because the calculated change in free energies for the net H/F exchange reaction is −77, −64, and −57 kcal mol$^{-1}$ for $CH_3F$, $CH_2F_2$, and $CHF_3$, respectively, in agreement with the trend in the relative experimental C−F BDE's in the fluoroalkanes. The kinetic barriers and therefore the potential energy surfaces determine the relative rates of reaction and product distribution. $Cp_2CeH$ has a choice of reacting with either a C−F bond or C−H bond of the fluoroalkane $CH_{4-x}F_x$, which leads to four types of transition states represented in Scheme 3. The transition state **2** corresponds to C−F activation with the carbon atom at the $\beta$ position in a 4c-4e metathesis transition state and gives $Cp_2CeF$ and $CH_{(4-x)+1}F_{x-1}$ by way of direct H/F exchange. The transition state **3** corresponds to a C−F activation but has the carbon atom located at the α position of the 4c-4e metathesis transition state. It gives an alkyl complex and HF, which form $Cp_2CeF$ and $CH_{(4-x)+1}F_{x-1}$ by HF addition to the Ce−C bond. This path is an indirect H/F exchange reaction. The transition state **4** corresponds to C−H activation. Further reaction is required for formation $Cp_2CeF$ and $CH_{(4-x)+1}F_{x-1}$. The transition state **5** is a degenerate H/H exchange. The calculated intermediates and transition states will be labeled with *x* where *x* is the number of fluorine atoms in the reactant. Many studies of reactivity are discussed on the basis of changes in energy (*E*) and not of free energy (*G*), but it is not reasonable to ignore the entropic factor in a bimolecular reaction. There is some discussion about the validity of using entropic values calculated in the gas phase for describing reactions in solution.[27] For these reasons, two energy values are given in this paper for all extrema as $\Delta G/\Delta E$ in units of kcal mol$^{-1}$, where $\Delta G$ is the Gibbs energy change relative to a reference and $\Delta E$ is the relative energy change with respect to the same reference. In discussing the results, only changes in the free energy are used because $\Delta G$ and $\Delta E$ values give the same qualitative conclusions.

**Reactions with $CH_3F$.** The calculated transition states and intermediates are shown in Figure 1, and the free energy profile is shown in Figure 2.

**C−F Activation.** A change in free energy of 55.2/47.2 kcal mol$^{-1}$ is required for crossing transition state $\mathbf{3_{1F}}$. This high

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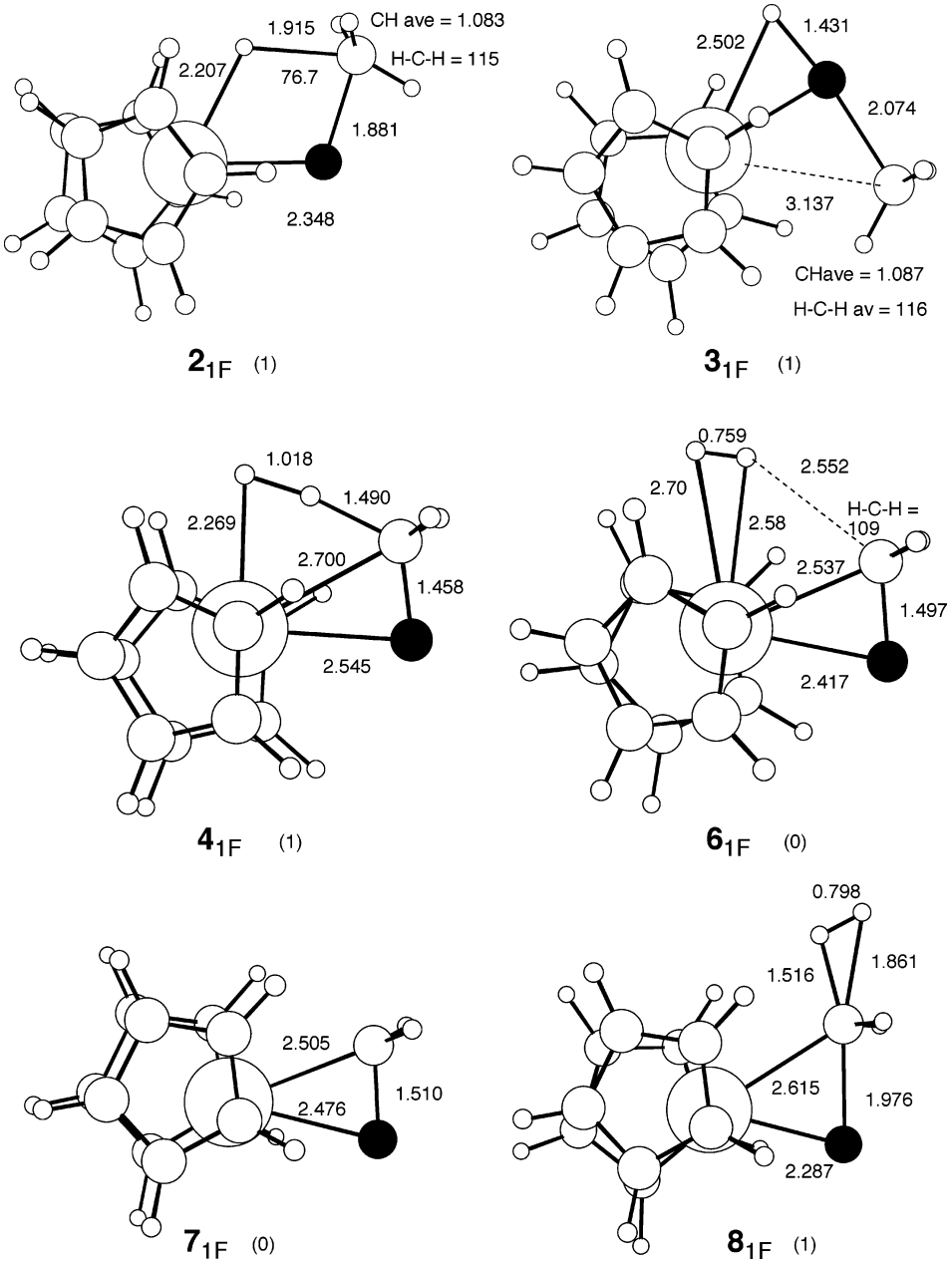


$\mathbf{2}_{1F}$ (1) $\mathbf{3}_{1F}$ (1) $\mathbf{4}_{1F}$ (1) $\mathbf{6}_{1F}$ (0) $\mathbf{7}_{1F}$ (0) $\mathbf{8}_{1F}$ (1)

***Figure 1.*** Optimized (B3PW91) structures for the reaction of $Cp_2CeH$ with $CH_3F$. Distances in angstroms and angles in degrees. The number in parentheses is the number of imaginary frequencies, 0 for a minimum and 1 for a transition state.

value indicates that $\mathbf{3}_{1F}$ is an unlikely transition state for the reaction. The transition state has an unusual geometry: HF is almost formed, while the $CH_3$ group is far from the metal center. It has been noted that a metathesis transition state in which the electronegative atom is located at the $\beta$ position in the metathesis transition state is unfavorable because the charge distribution in the 4c-4e transition state accumulates positive charge on the atoms in that position.[21] Thus, the electronegative fluorine atom will avoid the $\beta$-position.

The direct H/F exchange pathway by way of transition state $\mathbf{2}_{1F}$ requires a free energy of activation of 31.1/21.1 kcal mol$^{-1}$. The direct H/F exchange barrier is considerably lower than $\mathbf{3}_{1F}$ and also lower than the H/H exchange in methane (71.6/62.0 kcal mol$^{-1}$). The geometry of $\mathbf{2}_{1F}$ shows a slightly pyramidal $CH_3$ group interacting with H and F. The geometry of the $CH_4F^-$ fragment is similar to that of a trigonal bipyramid in which the $CH_3$ group can behave as a turnstyle.

**C−H Activation.** The nonproductive H/H exchange proceeds by way of a transition state $\mathbf{5}_{1F}$ in which the carbon is at the $\beta$ position in the 4c-4e metathesis transition state; it has a high free energy of activation of 58.7/48.3 kcal mol$^{-1}$. This calculated barrier is however significantly lower than that calculated for $CH_4$ (71.6/62.0 kcal mol$^{-1}$). The C−H activation in which the carbon atom is at the $\alpha$ position proceeds by way of transition state $\mathbf{4}_{1F}$ with a low free energy of activation of 18.0/7.5 kcal mol$^{-1}$. In $\mathbf{4}_{1F}$, the carbon atom, the hydrogen atom that is transferred, and the hydride on cerium are essentially collinear (170°) implying that this elementary step is a proton transfer between an anionic alkyl and a hydride, as was previously found in the reaction of $Cp_2LnH$ with $H_2$ or $CH_4$.[26a,b] In $\mathbf{4}_{1F}$, the $CH_2F$

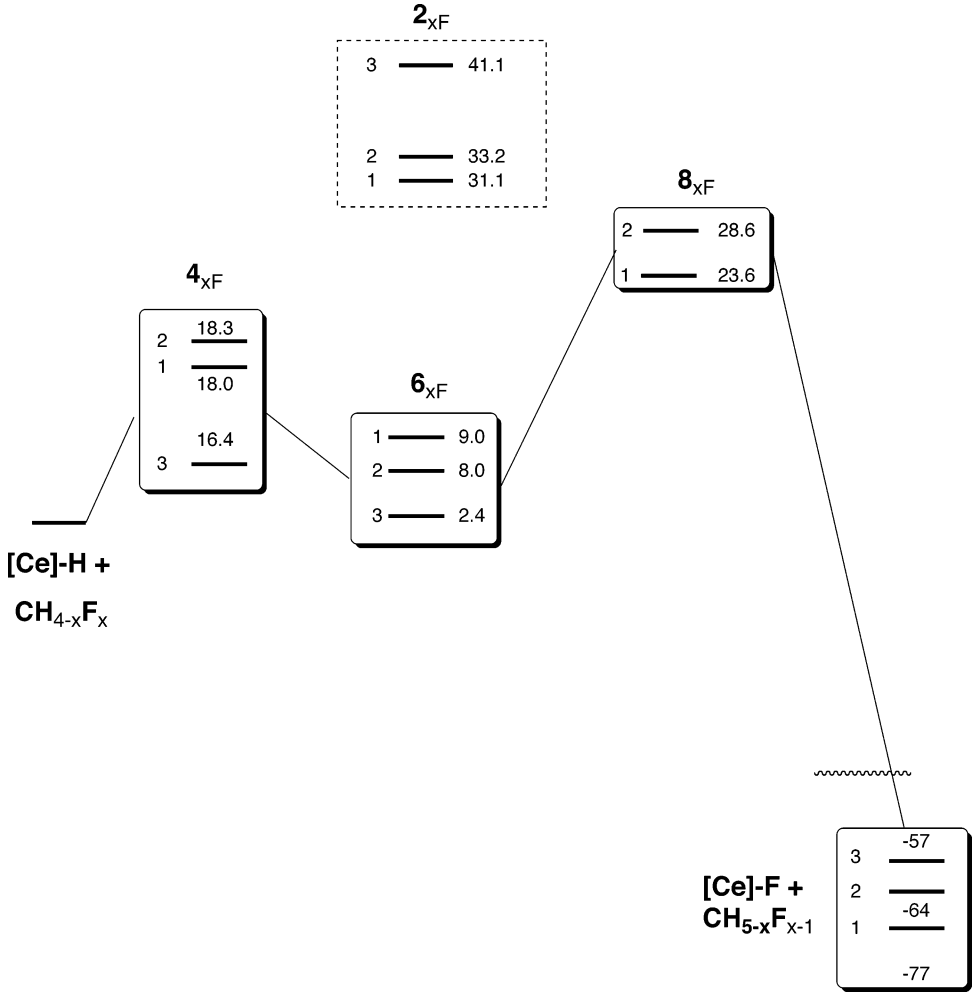


***Figure 2.*** Free energy profile in kcal mol$^{-1}$ for the reactions of $Cp_2CeH$ and $CH_{4-x}F_x$ ($x = 1-3$). The value of $x$ is shown on the left at each energy level. The energies in solid boxes correspond to the CH activation, via transition state $\mathbf{4}_{xF}$, followed by insertion of the carbene into $H_2$ via transition state $\mathbf{8}_{xF}$ ($\mathbf{8}_{3F}$ could not be located). The energies in the dash box correspond to the direct H/F exchange via transition state $\mathbf{2}_{xF}$.

group is $\eta^2$-bonded to Ce via the C−F bond that is elongated from 1.38 Å in free $CH_3F$ to 1.46 Å in $\mathbf{4}_{1F}$. Transition state $\mathbf{4}_{1F}$ leads to an adduct, $\mathbf{6}_{1F}$, between $Cp_2CeCH_2F$ ($\mathbf{7}_{1F}$) and $H_2$, which has a free energy of 9.0/−0.2 kcal mol$^{-1}$ relative to separated $Cp_2CeH$ and $CH_3F$. Dihydrogen is weakly bonded in $\mathbf{6}_{1F}$ ($\Delta E = 0.6$ kcal mol$^{-1}$), and loss of $H_2$ is entropically driven, $\Delta G = -8.6$ kcal mol$^{-1}$. In $Cp_2CeCH_2F$, $\mathbf{7}_{1F}$, the C−F bond is stretched to 1.51 Å as Ce−F forms. The Ce−F distance of 2.47 Å compares with 2.16 Å in $Cp_2CeF$.

The fluoroalkyl is not the final product, so another transformation of the fluoroalkyl is required to account for the end products. Formation of free $CH_2$ and $Cp_2CeF$ is not possible because the activation energy for this reaction is very high and unfavorable. For example, a separated singlet $CH_2$ and $Cp_2CeF$ is calculated to be 43.1/59.7 kcal mol$^{-1}$ above the energy of $Cp_2CeCH_2F$. In contrast, insertion of $CH_2$ into $H_2$, with concomitant cleavage of the C−F bond and formation of $CH_4$ and $Cp_2CeF$ via a transition state shown as $\mathbf{8}_{1F}$, is only 23.6/14.5 kcal mol$^{-1}$ above the energy of separated reactants $Cp_2CeH$ and $CH_3F$. At the transition state $\mathbf{8}_{1F}$, the C−F bond is significantly elongated (1.98 Å) and the shorter distance between C and $H_2$ is 1.52 Å. The midpoint of $H_2$, C, and F are essentially aligned, showing that the p-orbital of $CH_2$ points toward the leaving fluoride and the incoming $H_2$. The interaction between $CH_2$ and the metal occurs via the $\sigma$ orbital of the $CH_2$ fragment with a relatively short Ce−C distance of 2.6 Å. The $H_2$ ligand is tilted with respect to the carbene such that the hydrogen atom that is close to the metal is also close to the C atom. This geometry shows that the $CH_2$ fragment still interacts with the metal and the fluorine atom; that is, it is a carbenoid fragment that behaves as an electrophile.

In the case of $CH_3F$, two paths with comparable barriers can lead to the observed products as shown by the free energy profile shown in Figure 2. In one path, C−H activation precedes formation of $Cp_2CeCH_2F$ and $H_2$. This is followed by a step in which the C−F bond is cleaved and the $CH_2$ inserts into $H_2$. The other path, a direct H/F exchange, has a slightly higher barrier.

**Reaction of $CH_2F_2$.** The replacement of a hydrogen atom by a fluorine in the fluoromethane modifies only slightly the energy pattern calculated for $CH_3F$ (Figure 2). The transition state $\mathbf{3}_{2F}$ for the transfer of F has a free energy of 54.2/45.0 kcal mol$^{-1}$, which is unfavorable. The free energy (33.2/23.0 kcal mol$^{-1}$) of the transition state $\mathbf{2}_{2F}$ for the direct H/F exchange is just a little higher than $\mathbf{2}_{1F}$. The transition state $\mathbf{4}_{2F}$ via C−H activation, forming $Cp_2CeCF_2H$, $\mathbf{7}_{2F}$, and eliminating $H_2$ has the lowest activation energy barrier (18.3/8.4 kcal mol$^{-1}$) for all of the processes considered. The adduct $\mathbf{6}_{2F}$ of $H_2$ and $Cp_2$-

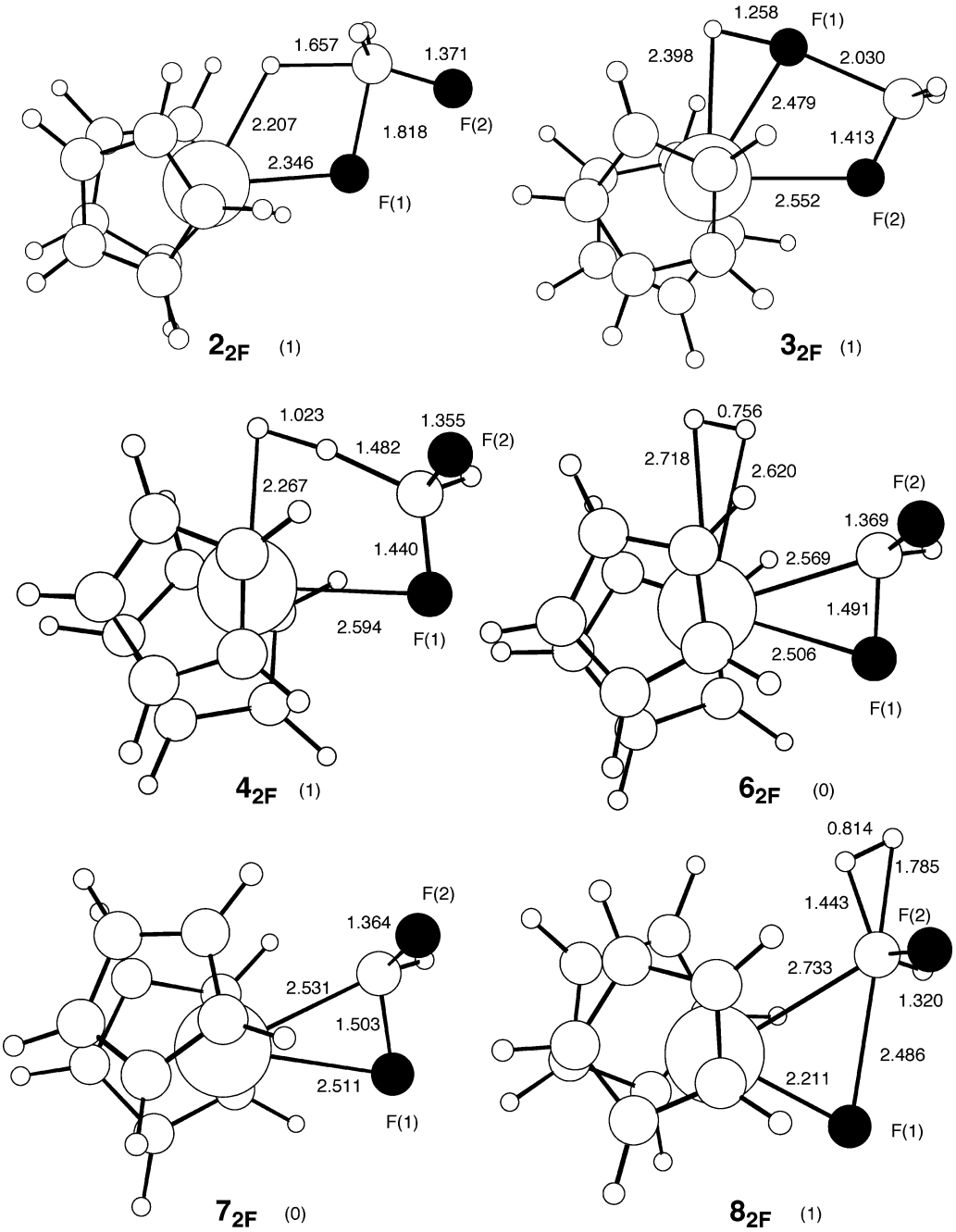


***Figure 3.*** Optimized (B3PW91) structures for the reaction of $Cp_2CeH$ with $CH_2F_2$. Distances in angstroms. The number in parentheses is the number of imaginary frequencies, 0 for a minimum and 1 for a transition state.

$CeCF_2H$ has a free energy of 8.0/−1.1 kcal mol$^{-1}$ relative to the separated reactants $Cp_2CeH$ and $CH_2F_2$. Dissociation of $H_2$ from $\mathbf{6_{2F}}$ lowers the free energy by 8.0/0.0 kcal mol$^{-1}$. $Cp_2CeCF_2H$, $\mathbf{7_{2F}}$, does not produce free CHF and $Cp_2CeF$ because this transformation is very endoergic (25.2/41.4 kcal mol$^{-1}$). Insertion of CHF into $H_2$ and the associated formation of $Cp_2CeF$ occurs via transition state $\mathbf{8_{2F}}$, which is 28.6/20.0 kcal mol$^{-1}$ above the separated reactants $Cp_2CeH$ and $CH_2F_2$. Finally, the activation barrier for the degenerate H/H exchange reaction via transition state $\mathbf{5_{2F}}$ is 62.8/53.4 kcal mol$^{-1}$, which is slightly higher than that for $CH_3F$.

The geometry of the stationary points on the $CH_2F_2$ potential energy surface is similar to that found for $CH_3F$ as is observed by comparing the structural parameters in Figures 1 and 3. One of the fluorine atoms of $CH_2F_2$, F(1), occupies the site of the unique F of $CH_3F$ in the various stationary points. The other fluorine, F(2), largely influences the electronic environment of the carbon fragment. In $\mathbf{2_{2F}}$, F(2) is located on the apical site of a trigonal-based bipyramid formed by $CF_2H_3$. The C−F(1) distance is slightly shorter in $\mathbf{7_{2F}}$ than in $\mathbf{7_{1F}}$. In $\mathbf{8_{2F}}$, the transition state for insertion of CHF into the $H_2$ and formation of $Cp_2CeF$, F(2) stabilizes the native carbene CHF(2) fragment, which results in a longer C−F(1) distance for the bond being cleaved.

**Reaction of $CHF_3$.** The trends in activation energies found in the case of $CH_3F$ and $CH_2F_2$ are maintained in $CHF_3$. The net result of the additional fluorine atoms increases the barrier for all of the transformations except for C−H activation. The transfer of F, via transition state $\mathbf{3_{3F}}$, remains high in energy

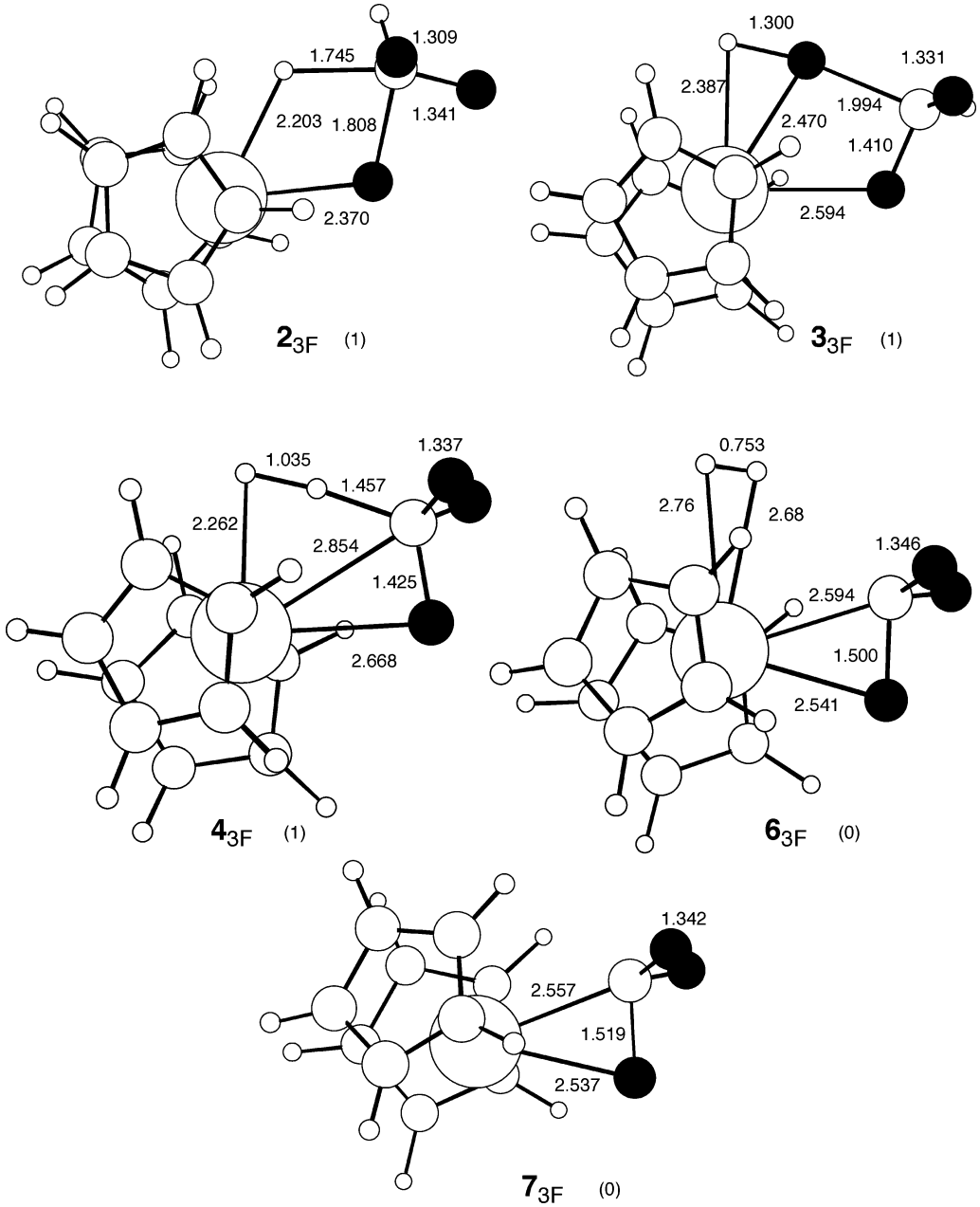


***Figure 4.*** Optimized (B3PW91) structures for the reaction of $Cp_2CeH$ with $CHF_3$. Distances in angstroms. The number in parentheses is the number of imaginary frequencies, 0 for a minimum and 1 for a transition state.

(60.0/49.0 kcal mol$^{-1}$). The activation energy barrier for direct H/F exchange, via transition state $\mathbf{2}_{3F}$, is 41.1/30.0 kcal mol$^{-1}$. The C−H activation process via transition state $\mathbf{4}_{3F}$ benefits from the increased number of fluorine atoms because the activation energy barrier is only 16.4/6.7 kcal mol$^{-1}$. The three fluorine atoms increase the acidity of the hydrogen that in turn lowers the barrier for the proton transfer as the hydride forms $H_2$. This transition state leads to the formation of an adduct $\mathbf{6}_{3F}$ of $H_2$ and $Cp_2CeCF_3$, whose free energy is 2.4/−6.0 kcal mol$^{-1}$ relative to separated reactant $Cp_2CeH$ and $CHF_3$. Loss of $H_2$ from $\mathbf{6}_{3F}$ lowers the free energy by 7.7/0.0 kcal mol$^{-1}$. $Cp_2CeCF_3$, $\mathbf{7}_{3F}$, expels $CF_2$ and forms $Cp_2CeF$ with a change of free energy of 6.3/16.0 kcal mol$^{-1}$ relative to $\mathbf{7}_{3F}$. The activation energy barrier for the H/H exchange via transition state $\mathbf{5}_{3F}$ is 63.6/51.4 kcal mol$^{-1}$. The transition state $\mathbf{8}_{3F}$ for insertion of $CF_2$ into $H_2$ and associated cleavage of the C−F bond to form $Cp_2CeF$ and $CH_2CF_2$, starting from intermediate $\mathbf{6}_{3F}$, could not be located.

There is no major difference in the geometry of the stationary points as the fluoroalkane is changed from $CH_3F$ to $CH_2F_2$ to $CHF_3$ (Figures 1, 3, and 4, respectively). For example, in the transition state $\mathbf{2}_{3F}$, the trigonal bipyramidal fragment $CF_3H_2^-$ has one F near the metal as in $CH_3F$, one F at the apical site as in $CH_2F$, and the remaining F is on the equatorial site.

**Reaction of $CF_4$.** The calculated activation barriers for reaction of $CF_4$ with $Cp_2MH$ have been published,[21] and some key points that are relevant to the present studies are mentioned here. Only C−F activation is possible, and the activation energies via the transition states $\mathbf{2}_{4F}$ and $\mathbf{3}_{4F}$ are 47.5/32.7 and 57.3/44.5 kcal mol$^{-1}$, respectively. In accord with the results

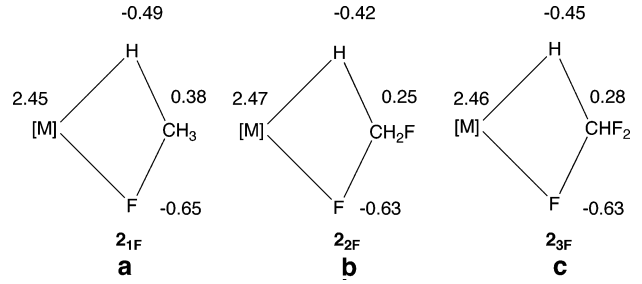


***Figure 5.*** NBO charges on M, H, F, and on the entire group at the $\beta$ position in the kite-shaped transition state $\mathbf{2_{xF}}$.

on the other fluorinated alkanes described here, $\mathbf{2_{4F}}$ is lower in energy than $\mathbf{3_{4F}}$.

**Discussion of the Computational Results.** The energy and free energy profiles for the paths going via $\mathbf{2_{xF}}$ (direct H/F exchange) and via $\mathbf{4_{xF}}$ (CH activation) and $\mathbf{8_{xF}}$ (carbene insertion into $H_2$) are shown in Figure 2. Earlier work has shown that the 4c-4e kite-shaped transition state has a high energy barrier when a carbon atom is located at the site $\beta$ to the metal center.[26b,28] The H/H exchange in the reaction of $Cp_2CeH$ with $CH_4$ has a very high activation energy barrier of 71.6/62.0 kcal mol$^{-1}$. Introducing one fluorine atom, as in the reaction of $Cp_2$-CeH with $CH_3F$, lowers the activation energy barrier for the H/F exchange via transition state $\mathbf{2_{1F}}$ by about 40 kcal mol$^{-1}$ and also lowers the activation energy for H/H exchange via transition state $\mathbf{5_{1F}}$, by around 20 kcal mol$^{-1}$. Introducing more fluorine atoms, as in the reactions of $Cp_2CeH$ with $CH_2F_2$ or $CHF_3$, raises the activation barriers for the H/F and H/H exchanges as compared to the reaction with $CH_3F$. It appears that the 4c-4e kite-shaped transition state with a carbon atom at the $\beta$ site has the lowest energy when only one fluorine is on the carbon center, the H/F exchange being preferred over the H/H exchange. It has been shown that the 4c-4e transition state in the metathesis reaction of the M−H from a metallocene hydride and the C−H bonds of an alkane could be conveniently viewed as the interaction of a $Cp_2M^+$ cation with an anionic organic fragment formed from the nucleophilic addition of the hydride to the alkane.[21,26b] Positive and negative charges alternate in the kite-shaped transition state. The NBO analysis at the three transition states $\mathbf{2_{xF}}$ shows that $\mathbf{2_{1F}}$ has the highest negative charge on the hydride and the fluoride and the highest positive charge on the group at the $\beta$ position (compare **a**, b, and c in Figure 5).

The bond dissociation energy of $H_2$ in $\mathbf{6_{xF}}$ is very small, and dissociation of $H_2$ is favored by the increase in entropy. However, the bond dissociation energy is most likely to be significantly underestimated by the DFT calculations[29a] despite the fact that B3PW91 was found to perform better than other functionals.[29b] Calculations with elaborate methods adapted to the calculations of relatively weak interactions cannot be carried out because of the size of the system. It is important to note that $H_2$ is significantly perturbed by the presence of the $M^{\delta+}$−$C^{\delta-}$ bond because it is strongly positively charged (+0.2 e$^-$ on each H atom), which signals an interaction between the carbon fragment and $H_2$.

The transition state for insertion of the carbene into $H_2$ with synchronous cleavage of C−F(1), $\mathbf{8_{xF}}$, could only be located for the case of $CH_3F$ (insertion of $CH_2$) and $CH_2F_2$ (insertion of CHF). The geometry of the carbene···$H_2$ fragment in the transition state $\mathbf{8_{xF}}$ resembles the geometry of the insertion of the free carbenes into $H_2$. The energy barrier increases from $\mathbf{8_{1F}}$ to $\mathbf{8_{2F}}$, which parallels the barriers for insertion of the free carbenes into $H_2$.[30] The calculated energy barrier at the same level of theory for the reaction of singlet free $CH_2$ or CHF with $H_2$ is 4.5 and 8.5 kcal mol$^{-1}$, respectively. Although these calculations are only indicative of the trends, they mirror the qualitative facts; fluorine deactivates the carbene by stabilizing it. Because the fluoroalkyl cerium group is the source of the carbene, the energy profile for creating a free carbene was calculated. This is highly unfavorable for $CH_3F$ (formation of $CH_2$), but more favorable with the substituted carbenes. In the case of $CHF_3$, formation of $CF_2$ from $Cp_2Ce-CF_3$ is calculated to be essentially barrierless, and the formation of $CF_2$ is expected.

**Discussion of the Experimental Results.** The calculations suggest that the lowest energy pathway is formation of $Cp'_2CeCH_{3-x}F_x$, $x = 0-3$, in each case because the intermolecular C−H activation barrier is less than the C−F activation barrier for each of the hydrofluoromethanes studied. This pattern is consistent with the experimental and computational results found for the reaction of $Cp'_2CeH$ with $C_6F_6$ or $C_6F_5H$.[11] In the latter set of reactions, the intermediate fluoroaryl, $Cp'_2CeC_6F_5$, was isolated from the reaction of the metallacycle **1** and $C_6F_5H$, and a related strategy was employed for synthesis of the hypothetical $Cp'_2CeCF_3$, exposure of metallacycle **1** to $CHF_3$. The fluoroalkyl was not detected by $^1$H NMR spectroscopy, but $Cp'_2CeF$ and the isomeric tri-*tert*-butylfluorobenzenes were observed. The formation of tri-*tert*-butylfluorobenzenes can be rationalized as shown in Scheme 4, in which the $(Me_3C)_3C_5H_2^-$ ligand acts as a trap for $CF_2$.[17] An alternative method for generating $Cp'_2CeCF_3$ is addition of $Me_3SiCF_3$ to $Cp'_2CeH(D)$, which generates $Me_3SiH(D)$, the isomeric tri-*tert*-butylbenzenes, and a small amount of tri-*tert*-butylfluorobenzenes. Our original postulate was that the tri-*tert*-butylfluorobenzenes could undergo H/F exchange, but this is unreasonable because $Me_3SiCF_3$ reacts instantaneously with $Cp'_2CeH$ so the concentration of the hydride is tiny when the fluorobenzenes are formed. This negative inference is shown to be correct by the lack of reaction between the tri-*tert*-butylfluorobenzenes and $Cp'_2CeH$. The disappearance pathway was discovered by exposing $(Cp'\text{-}d_{27})_2$-CeD to $CHF_3$, which generates $(Cp'\text{-}d_{27})_2CeF$, and isomeric tri-*tert*-butylbenzenes $[(CD_3)_3C]_3C_6H_2D$. This implies that $Cp'_2$-$CeCF_3$, which forms slowly in this reaction, undergoes D/F exchange with $Cp'_2CeD$ to give $Cp'_2CeCDF_2$, and this yields $Cp'_2CeF$ and the isomeric deutero tri-*tert*-butylbenzenes.

The experimental outcome of the reaction of $CHF_3$ and metallacycle **1**, yielding $Cp'CeCF_3$, which decomposes to $Cp'_2$-

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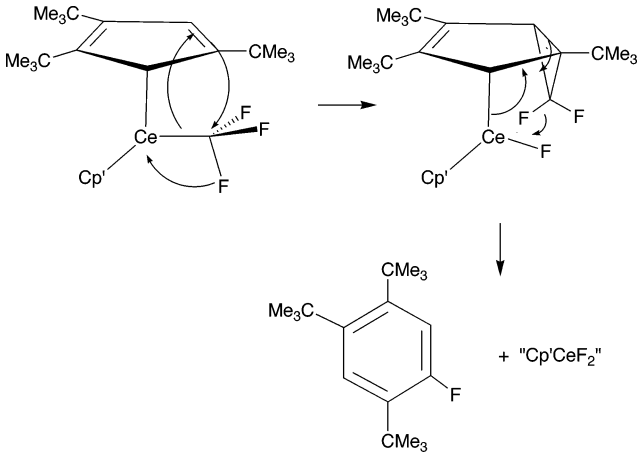
***Scheme 4.*** Formation of an Isomer of Tri-*tert*-butylfluorobenzene[a]




[a] Insertion of the carbene into the other double bond will generate the other isomer. In the case of CHF insertion, only isomeric tri-*tert*-butylbenzenes will form.

CeF and $CF_2$, is consistent with the calculated barrier. The products derived from the hypothetical intermediates $Cp'_2CeCHF_2$ or $Cp'_2CeCH_2F$, formed by reaction of **1** and $CH_2F_2$ or $CH_3F$, respectively, are the isomeric tri-*tert*-butylbenzenes and $Cp'_2CeF$ or $Cp'_2CeF$ and [Cp′Cp″]CeF, respectively (Scheme 2). These products may be rationalized by ejection of CHF from $Cp'_2CeCHF_2$ that is trapped by a C═C bond in the Cp′ ligand, but in the case of $Cp'_2CeCH_2F$, $CH_2$ is trapped by the C−H bond of the Cp′ ligand. However, the products resulting from the reaction of **1** with $CH_2F_2$ or $CH_3F$ are different from those formed in the reaction of $Cp'_2CeH$ with these two fluoromethanes implying either that $Cp'_2CeCH_{3-x}F_x$, where $x = 1$, 2, are not formed in the reaction with $Cp'_2CeH$ or that the ejected carbenes are trapped by dihydrogen. No products resulting from a carbene insertion into the Cp′ ring are detected in this case. Some circumstantial evidence for dihydrogen acting as a trapping reagent is derived from the products formed in the reaction of the metallacycle and $CH_3F$, where no dihydrogen is present, because the C−H bonds of solvent or the $Me_3C$-groups of the cyclopentadienyl ring are traps for the $CH_2$ fragment. This is consistent with the proposition that the $CH_2$-fragment rapidly inserts into the C−H or H−H bonds that are in the neighborhood.

## Epilogue

The key point that emerges from the calculational study of $Cp_2CeH$ and $CH_{4-x}F_x$ ($x = 1-3$) is that the lowest energy barrier is intermolecular C−H activation forming $Cp_2CeCH_{3-x}F_x$ and $H_2$. The relative barrier, $CH_3F > CH_2F_2 > CHF_3$, parallels the acidity because the transition state geometries (Figures 1, 3, and 4) resemble that of a proton-transfer transition state. The cerium alkyl intermediates traverse a higher energy transition state that is associated with large reorganizations of the atoms within the coordination sphere, breaking the C−F bond, making a Ce−F bond and trapping of the carbene fragment. The barrier of the rate-determining step is therefore traced to trapping of the carbenoid fragment, $CH_2$, CHF, or $CF_2$. The calculations on the metallocene show that the relative rates of reaction of the carbenoid fragment with $H_2$ parallel those calculated for insertion of free carbenes into $H_2$, $CH_2 > CHF \gg CF_2$. Thus, the lifetime of the carbene fragments is $CH_2 < CHF \ll CF_2$ implying that $CH_2$ and CHF are trapped by $H_2$, formed in the C−H activation event. Dihydrogen is therefore an efficient trap in the reaction of $Cp'_2CeH$ with $CH_3F$ and $CH_2F_2$, because it never leaves the coordination sphere as the products evolve. When $H_2$ is absent, in the reaction of metallacycle, the C−H and C═C bonds are the only traps that are available. As the lifetime of the $CF_2$ fragment is longer, it is therefore more selective and it is intramolecularly trapped by insertion into the C═C bond of the cyclopentadienyl ring.

The postulate that the intermolecular C−H activation with lanthanide hydrides precedes the rate-determining step of C−F activation in the fluoromethanes is in agreement with the experimental and calculated results observed in the reaction of aromatic fluorocarbons with the same metallocenes.[11] In the latter case, the intermediate $Cp'_2CeC_6F_5$ was isolated, whereas the analogous intermediate $Cp'_2CeCF_3$ is not, perhaps because the aromatic C−F bond is stronger than an aliphatic one and the interaction of the C−F bond in the Ce($\eta^2$-$CF_3$) group lowers the barrier to Ce−F formation in the latter case, that is, thermodynamic and kinetic differences, respectively. The general reactivity pattern that emerges in these two studies is (i) intermolecular C−H activation is a lower barrier process than C−F activation, (ii) the C−F bond activation is the rate-determining step, and (iii) the net reaction rate (global rate) constant depends on how the intermediates deal with the activation energy barrier on the way to the thermodynamically favored outcome, H/F exchange. Thus, fluorocarbons are inert or relatively inert because of kinetic not thermodynamic factors in f- and late d- transition metal complexes.[13] Kinetic factors are the reason for the lack of reaction between $Cp'_2CeH$ and $CF_4$, whereas $Cp'_2CeH$ does indeed react with $C_6F_6$ even though the C−F bond is stronger in the latter. Both processes begin by C−F activation, but the change in activation free energy is 30 kcal mol$^{-1}$ higher for $CF_4$ than $C_6F_6$, which is related to the greater ease with which an aromatic ring reorganizes the electronic charges.[11,21]

## Experimental Details

**General.** Manipulations were performed as previously reported[11] except that, unless otherwise noted, samples for GCMS were prepared from NMR reaction samples by adding a drop of $H_2O$ rather than $D_2O$. The principle elution peaks consisted of free Cp′H and other organic compounds that were identified by their molecular ions and fragmentation patterns, where possible, in concert with their $^1$H and $^{19}$F NMR spectra. Fluoromethane gases were obtained from Scott Specialty Gases in 99.99% purity and used as received. The abbreviation Cp′ is used for the 1,2,4-tri-*tert*-butylcyclopentadienyl ligand, Cp′-$d_{27}$ is used for the same ligand with all *tert*-butyl groups deuterated, and Cp″H is used for the $[Me_2EtC][Me_3C]_2C_5H_2$ ligand.

**NMR Tube Reaction of $CHF_3$ and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$[11] was dissolved in $C_6D_{12}$ in an NMR tube. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CHF_3$ (1 atm). The tube was warmed to 19 °C and allowed to stand. After 20 min, the ratio of $Cp'_2CeH$ to $Cp'_2CeF$ was 32:1, after 3 days it was 1:3.5, and after 6 days it was 1:18. After 26 days, the solution color had changed from purple to orange, all $Cp'_2CeH$ resonances had disappeared from the $^1$H NMR spectrum, and resonances of $Cp'_2CeF$ had appeared. Integration of the *tert*-butyl signal intensities relative to the residual solvent proton signal indicated that slightly less than half an equivalent of $Cp'_2CeF$ had formed relative to the starting material. Resonances due to the two isomers of tri-*tert*-butylbenzene also appeared. GCMS analysis showed two principle components in

addition to Cp′H, with $(M)^+$ *m*/*z* 246 and elution times and fragmentation patterns consistent with isomeric tri-*tert*-butylbenzenes. The isomers were present in approximately a 1:1 ratio and accounted for most of the remainder of the starting material.[31]

**NMR Tube Reaction of $CHF_3$ and $(Cp'\text{-}d_{27})_2CeD$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$[11] was dissolved in $C_6D_6$ in an NMR tube. The sample was heated at 60 °C for 13 days to perdeuterate the ring *t*-Bu groups; the sample was taken to dryness and the dark red solid residue redissolved in fresh $C_6D_6$ after 4 days and again after 8 days. After 13 days, the sample was then taken to dryness, and the dark red solid residue was redissolved in $C_6D_{12}$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $D_2$ (1 atm). The ratio of the unique *t*-$Bu_H$ to the ring hydrogen resonance in the $^1$H NMR spectrum was 1:42. In the $^2$H NMR spectrum, both *t*-$Bu_D$ resonances were observed, and the ring hydrogen resonance was absent. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CHF_3$ (1 atm). The sample was heated at 60 °C for 1 day, after which time the ring resonance of $(Cp'\text{-}d_{27})_2CeD$ had disappeared, the ring resonance of $(Cp'\text{-}d_{27})_2CeF$ had appeared in the $^1$H NMR spectrum, and resonances consistent with $(Cp'\text{-}d_{27})_2CeF$ had appeared in the $^2$H NMR spectrum. GCMS analysis showed two principal components in addition to $(Cp'\text{-}d_{27})H$, with envelopes centered around $(M)^+$ *m*/*z* 274 and elution times consistent with tri-*tert*-butylbenzene-$d_{28}$. The extra deuterium is presumed to come from a D for F exchange between $(Cp'\text{-}d_{27})_2CeD$ and an intermediate $(Cp'\text{-}d_{27})_2CeCF_3$; see below.

**NMR Tube Reaction of $Me_3SiCF_3$ and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube. A drop of $Me_3SiCF_3$ was added. Upon agitation, the purple solution turned orange. The $^1$H NMR spectrum showed the presence of $Cp'_2CeF$, $Me_3SiH$, and both isomers of tri-*tert*-butylbenzene. The $^{19}$F NMR spectrum contained two new resonances consistent with two isomers of tri-*tert*-butylfluorobenzene. GCMS analysis showed four principal components in addition to Cp′H, two with $(M)^+$ *m*/*z* 246 and elution times consistent with isomeric tri-*tert*-butylbenzenes, and two with $(M)^+$ *m*/*z* 264 consistent with isomeric tri-*tert*-butylfluorobenzenes. The ratio of tri-*tert*-butylbenzenes to tri-*tert*-butylfluorobenzenes was approximately 8:1. The symmetric and asymmetric isomers of tri-*tert*-butylbenzene were present in approximately equal amounts ($^1$H NMR), while those of tri-*tert*-butylfluorobenzene were present in a 1.5:1 ratio ($^{19}$F NMR). Characterization of tri-*tert*-butylfluorobenzene: symmetric isomer, $^{19}$F NMR ($C_6D_{12}$) $\delta$ −111.38 (1F, s), GCMS $(M)^+$ *m*/*z* (calcd, found) 264 (100,100) 265 (20,22) 266 (2,3); asymmetric isomer, $^{19}$F NMR ($C_6D_{12}$) $\delta$ −95.86 (1F, d, $J_{H-F} = 16$ Hz), GCMS $(M)^+$ *m*/*z* (calcd, found) 264 (100,100) 265 (20,34) 266 (2,7).

**NMR Tube Reaction of $Me_3SiCF_3$ and $(Cp'\text{-}d_{27})_2CeD$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_6$ in an NMR tube. The sample was heated at 60 °C to perdeuterate the ring *t*-Bu groups. After 4 days, the sample was taken to dryness, and the dark red solid residue was redissolved in $C_6D_6$. The sample was heated for an additional 4 days, then taken to dryness, and the dark red solid residue was dissolved in $C_6D_{12}$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $D_2$ (1 atm). The ratio of the unique *t*-$Bu_H$ to the ring hydrogen resonance in the $^1$H NMR spectrum was 1:4. In the $^2$H NMR spectrum, both *t*-$Bu_D$ resonances were observed, and the ring hydrogen resonance was absent. A drop of $Me_3SiCF_3$ was added, and upon agitation, the solution color changed from purple to orange. The ring resonance of $(Cp'\text{-}d_{27})_2CeD$ disappeared, and the ring resonance for $(Cp'\text{-}d_{27})_2CeF$ had appeared in the $^1$H NMR spectrum. Resonances due to $(Cp'\text{-}d_{27})_2CeF$ and $Me_3SiD$ appeared in the $^2$H NMR spectrum, and resonances due to the two isomers of tri-*tert*-butylfluorobenzene-$d_{27}$ appeared in the $^{19}$F NMR spectrum. The sample was twice taken to dryness, redissolved in $C_6H_6$, and a small amount of $Cp'_2CeH$ was added. After 30 min, the $^{19}$F NMR spectrum remained unchanged, but the $^2$H NMR spectrum contained resonances consistent with both $(Cp'\text{-}d_{27})_2CeF$ and $(Cp'\text{-}d_{27})_2CeH$ in a 2:1 ratio, implying that H for F exchange occurred. The $^1$H NMR spectrum likewise contained resonances of $Cp'_2CeF$ and $Cp'_2CeH$ in the same ratio. GCMS analysis showed four principal components, in addition to $Cp'H/(Cp'\text{-}d_{27})H$, two with envelopes centered around $(M)^+$ *m*/*z* 274, with elution times consistent with the isomeric tri-*tert*-butylbenzenes-$d_{28}$, and two with envelopes centered around $(M)^+$ *m*/*z* 291, with elution times consistent with the isomeric tri-*tert*-butylfluorobenzenes-$d_{27}$. The extra deuterium in the tri-*tert*-butylbenzene is presumed to come from a D−F exchange between the intermediate $(Cp'\text{-}d_{27})_2CeCF_3$ and $(Cp'\text{-}d_{27})_2CeD$, generating $(Cp'_2\text{-}d_{27})_2CeCDF_2$ and $(Cp'_2\text{-}d_{27})_2CeF$; see later experiments.

**NMR Tube Reaction of $CH_2F_2$ and $Cp'_2CeH$ in $C_6D_6$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_2F_2$ (1 atm). The tube was warmed to 19 °C and allowed to stand. After 10 min, the ratio of $Cp'_2CeH$ to $Cp'_2CeF$ by $^1$H NMR spectroscopy was 10:1, after 20 min it was 5:1, and after 1 h it was 2:1. After 1 day, all of the resonances due to $Cp'_2CeH$ had disappeared and an equivalent amount of $Cp'_2CeF$ had formed along with $CH_4$. Over the time period of the experiment, the color had turned from purple to orange.

**NMR Tube Reaction of $D_2$, $CH_2F_2$, and $Cp'_2CeD$ in $C_6D_6$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_6$ in an NMR tube. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $D_2$. The tube was warmed to 19 °C and shaken vigorously. Analysis by $^1$H NMR spectroscopy confirmed the presence of $Cp'_2CeD$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was partially evacuated and replaced with $CH_2F_2$. The sample was stored at 19 °C for 1 day, after which time the solution color had changed from purple to orange. Analysis by $^1$H NMR confirmed the absence of $Cp'_2CeD$ and the formation of $Cp'_2CeF$. In addition, the spectrum contained resonances characteristic of $CH_4$ and $CH_3D$ in an approximately 1:1 area ratio; a trace of $CH_2D_2$ but no $CHD_3$ was observed in the spectrum.

**NMR Tube Reaction of $D_2$, $CH_2F_2$, and $(Cp'\text{-}d_{27})CeD$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_6$ in an NMR tube. The sample was heated at 60 °C for 6 days to perdeuterate the ring *t*-Bu groups. The sample was taken to dryness, and the solid residue was redissolved in fresh $C_6D_6$ and heated at 60 °C for 2 more days to complete the perdeuteration. Analysis by $^1$H and $^2$H NMR confirmed the presence of $(Cp'\text{-}d_{27})CeC_6D_5$.[11] The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $D_2$ (1 atm). The tube was warmed to 19 °C and shaken vigorously. Analysis by $^1$H and $^2$H NMR spectroscopy confirmed the presence of $(Cp'\text{-}d_{27})CeD$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was partially evacuated and replaced with $CH_2F_2$. The sample was stored at 19 °C for 1 day, after which time the solution color had changed from purple to orange. Analysis by $^1$H and $^2$H NMR spectroscopy confirmed the absence of $(Cp'\text{-}d_{27})CeD$ and the appearance of $(Cp'\text{-}d_{27})CeF$. In addition, the $^1$H NMR spectrum contained resonances characteristic of $CH_4$, $CH_3D$, and $CH_2D_2$ in an approximately 1:29:60 area ratio; no $CHD_3$ was observed.

**NMR Tube Reaction of $CH_3F$ and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_3F$ (1 atm). Upon warming to room temperature with agitation, the color of the solution changed from purple to orange. The $^1$H NMR spectrum showed that the $Cp'_2CeH$ had been quantitatively converted to $Cp'_2CeF$. The resonance due to $CH_4$ was observed.

**NMR Tube Reaction of $CH_3F$, $D_2$, and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $D_2$ (approximately 0.5 atm) and $CH_3F$ (approximately 0.5 atm). Upon warming to room temperature and agitating the solution,

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the color changed from purple to orange. The $^1$H NMR spectrum showed that the $Cp'_2CeH$ had been quantitatively converted to $Cp'_2CeF$. Resonances characteristic of $CH_4$ and $CH_3D$ had also appeared in approximately equal amounts, but no resonances due to $CH_2D_2$ were observed.

**NMR Tube Reaction of $CH_3F$ and $(Cp'\text{-}d_{27})_2CeD$ in $C_6D_6$.** $Cp'_2CeH$ was dissolved in $C_6D_6$ in an NMR tube. The sample was heated at 60 °C to perdeuterate the ring *t*-Bu groups and exchange the hydride with deuterium. After 11 days, the ratio of the unique $t\text{-}Bu_H$ to the ring hydrogen resonance in the $^1$H NMR spectrum had changed from 9:1 to 1:4. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_3F$ (1 atm). Upon warming to room temperature with agitation, the color of the solution changed from purple to orange. The ring resonance of $(Cp'\text{-}d_{27})_2CeD$ had been replaced by that of $(Cp'\text{-}d_{27})_2CeF$ in the $^1$H NMR spectra, and resonances characteristic of $CH_4$ and $CH_3D$ had also appeared in an approximately 1:2 area ratio; no $CH_2D_2$ was observed.

**NMR Tube Reaction of $CH_4$ or $CF_4$ and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_4$ or $CF_4$ (1 atm). The sample was heated at 60 °C for 30 days. No change was observed in the $^1$H NMR spectrum.

**NMR Tube Reaction of $CHF_3$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h, yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CHF_3$ (1 atm). The sample was heated at 60 °C for 1 day, by which time the resonances for $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1$H NMR spectrum and resonances of $Cp'_2CeF$ and several new diamagnetic products had appeared. Addition of a small amount of $Cp'_2CeH$ to the solution did not change the $^{19}$F NMR spectrum. GCMS analysis showed two primary components in addition to Cp′H, both with $(M)^+$ *m*/*z* 264, consistent with two isomers of tri-*tert*-butylfluorobenzene, one symmetric and the other asymmetric. The $^{19}$F NMR spectrum shows that the isomers are present in an approximately 1.5:1 ratio.

**NMR Tube Reaction of $CHF_3$, Cyclohexene, and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h, yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. A drop of cyclohexene was added. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CHF_3$ (1 atm). The sample was heated at 60 °C for 1 day, by which time the resonances for $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1$H NMR spectrum and resonances from $Cp'_2CeF$ and several new diamagnetic products had appeared. The $^{19}$F NMR spectrum and GCMS analysis were essentially identical to those from the reaction without cyclohexene present.

**NMR Tube Reaction of $CHF_3$, 2-Methyl-2-heptene, and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h, yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. A drop of 2-methyl-2-heptene was added. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CHF_3$ (1 atm). The sample was heated at 60 °C for 1 day, by which time the resonances for $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1$H NMR spectrum and resonances from $Cp'_2CeF$ and several new diamagnetic products had appeared. The $^{19}$F NMR spectrum and GCMS analysis were essentially identical to those from the reaction without 2-methyl-2-heptene present.

**NMR Tube Reaction of $CH_2F_2$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_2F_2$ (1 atm). The sample was heated at 60 °C for 5 days after which time the resonances of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1$H NMR spectrum. Resonances due to $Cp'_2CeF$ and both isomers of tri-*tert*-butylbenzene had appeared in the spectrum. The presence of both isomers was confirmed by GCMS analysis.

**NMR Tube Reaction of $CH_3F$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_3F$ (1 atm). The sample was heated at 60 °C for 12 h after which time the resonances of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1$H NMR spectrum. Resonances for $Cp'_2CeF$ had appeared, as well as a set of new paramagnetic resonances, presumably due to a new metallocene cerium fluoride. GCMS analysis showed the formation of methylcyclohexane-$d_{12}$, Cp′H, and a new compound with $(M)^+$ *m*/*z* 248, Cp′H+$CH_2$. When the experiment was repeated and $D_2O$ was used to prepare the GCMS sample instead of $H_2O$, the molecular ion of the new species was *m*/*z* 249. The new metallocenes were further identified as described in the next experiment.

**NMR Tube Reaction of $CH_3F$ and $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_6$ and heated at 60 °C for 4 days to perdeuterate the ring *tert*-butyl groups. The sample was taken to dryness, and the solid residue was redissolved in fresh $C_6D_6$. The sample was heated for an additional 7 days, then taken to dryness, and the solid residue was redissolved in $C_6D_{12}$. The sample was heated at 60 °C for 1 day, yielding a solution of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_3F$(1 atm). The sample was heated at 60 °C for 2 days, after which time the resonances of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ had disappeared from the $^1$H and $^2$H NMR spectra. Resonances for $(Cp'\text{-}d_{27})_2CeF$ had appeared in the $^2$H NMR spectrum, as well as hints of the signals with chemical shifts similar those in the $^1$H NMR spectrum of the unlabeled, unknown metallocenes from the previous experiment. The $^1$H NMR spectrum contained three new resonances due to the three isotopomers arising from the insertion of $CH_2$ into a C−D bond in $(Cp'\text{-}d_{27})_2CeF$. A drop of $H_2O$ was added, and the sample was vigorously shaken. After 10 min, the solution was dried and filtered. The filtrate was added to a new NMR tube and heated at 60 °C for 1 day to isomerize the substituted cyclopentadienes. The $^1$H NMR spectrum contained three single resonances attributed to the three isotopomers of $(Cp''\text{-}d_{27})H$. GCMS analysis showed one major component in addition to $(Cp'\text{-}d_{27})H$ (envelope centered around $(M)^+$ *m*/*z* 260), with an envelope centered around $(M)^+$ *m*/*z* 274. Characterization of the new metallocenes: $^1$H NMR ($C_6D_{12}$) $\delta$ −0.100 (2H, $\nu_{1/2}$ = 20 Hz), −2.794 (2H, $\nu_{1/2}$ = 20 Hz), −6.129 (2H, $\nu_{1/2}$ = 20 Hz). Characterization of $Cp''H\text{-}d_{27}$: $^1$H NMR ($C_6D_{12}$) $\delta$ 1.19 (2H, s), 1.07 (2H, s), 1.00 (2H, s).

**NMR Tube Reaction of $CH_3F$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6H_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6H_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_3F$ (1 atm). The sample was heated at 60 °C for 12 h. GCMS analysis showed the formation of methylcyclohexane, Cp′H, and Cp″H in addition to solvent cyclohexane.

**NMR Tube Reaction of $CH_3F$, $CH_4$, and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_4$ (0.5 atm) and $CH_3F$ (0.5 atm). The sample was heated at 60 °C for 12 h after which time the resonances of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1$H NMR spectrum. The spectrum contained the same resonances as that of the reaction in the absence of $CH_4$.

**NMR Tube Reaction of $CH_3F$, Cyclohexene, and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C$-

$(Me_2)CH_2)Ce$. A drop of cyclohexene was added. The tube was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $CH_3F$ (1 atm). The sample was heated at 60 °C for 12 h after which time the resonances of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the $^1H$ NMR spectrum. Resonances due to $Cp'_2CeF$ had appeared in the $^1H$ NMR spectrum along with bicyclo[4.1.0]-heptane (norcarane) and a small amount of the unknown metallocene observed previously. GCMS analysis showed the presence of norcarane, Cp′H, and Cp″H; no methylcyclohexane or methylcyclohexenes were observed.

**NMR Tube Reaction of Cyclohexene and $Cp'_2CeH$ in $C_6D_6$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube, and a drop of cyclohexene (an excess) was added. Within 20 min, resonances due to $Cp'_2CeH$ had disappeared from the $^1H$ NMR spectrum and resonances of cyclohexane and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had appeared.

**NMR Tube Reaction of Cyclohexene and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. A drop of cyclohexene was added. After 1 h, a new pair of resonances in a 2:1 area ratio had appeared in the $^1H$ NMR spectrum. The new product was not further characterized, although it is presumably $Cp'_2Ce$(cyclohexenyl).

**NMR Tube Reaction of Cyclohexene and $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_6$ and heated at 60 °C for 4 days to perdeuterate the ring *tert*-butyl groups. The sample was taken to dryness, and the solid residue was redissolved in fresh $C_6D_6$. The sample was heated for an additional 4 days, then taken to dryness, and the solid residue was redissolved in $C_6D_{12}$. The sample was heated at 60 °C for 1 day, yielding a solution of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$. A drop of cyclohexene was added, and the sample was heated at 60 °C. After 1 day, a resonance at 5.63 ppm had appeared in the $^2H$ NMR spectrum, indicating that the protons on the $sp^2$-carbons of cyclohexene were being exchanged for deuterium. The sample was heated at 60 °C for 30 days, over which time this signal increased in intensity 10-fold. No resonances suggesting H for D exchange on the $sp^3$ carbons of cyclohexene could be distinguished from the $C_6D_{12}$ solvent signal. GCMS analysis showed that cyclohexene was present in large excess, as the molecular ion at $(M)^+$ $m/z$ 82 was present; in addition, the envelope for the $(Cp'\text{-}d_{27-x})H$ centered around $m/z$ 247 was also observed.

**NMR Tube Reaction of $C_7F_{14}$ and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube, and a drop of perfluoromethylcyclohexane was added. The sample was stored at ambient temperature for 5 days, by which time resonances of $Cp'_2CeF$ had appeared in the $^1H$ NMR spectrum. The ratio of $Cp'_2CeF$ to residual $Cp'_2CeH$ was 3:1. After 22 additional days at ambient temperature, only resonances due to $Cp'_2CeF$ were observed in the $^1H$ NMR spectrum. Identification of the other organic compounds was not pursued.

**NMR Tube Reaction of $C_6H_5CF_3$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)$ in $C_6D_{12}$.** $Cp'_2Ce(CH_2Ph)$ was dissolved in $C_6D_{12}$ and heated at 60 °C for 12 h yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. A drop of $C_6H_5CF_3$ was added, and the solution was stored at room temperature for 24 h, yielding a red solution. The $^1H$ NMR spectrum contained resonances for $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$, a small amount of $Cp'_2CeF$, and two new paramagnetic species with nearly coincident *tert*-butyl resonances in 2:1 ratios. The ratio of products was not significantly changed by heating the solution for 4 days at 60 °C. The new species were not characterized.

**NMR Tube Reaction of $C_6H_5CF_3$ and $Cp'_2CeH$ in $C_6D_{12}$.** $Cp'_2CeH$ was dissolved in $C_6D_{12}$ in an NMR tube, and a drop of $C_6H_5CF_3$ was added. The solution was stored at room temperature for 3 days, by which time the solution color had changed from purple to orange. The $^1H$ NMR spectrum contained resonances for $Cp'_2CeF$ and the same two new organometallic species observed in the reaction of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ and $C_6H_5CF_3$. The ratio of $Cp'_2CeF$ to the new species was 7:1.

**Reaction of $SiF_4$ and $Cp'_2CeH$.** $Cp'_2CeH$ (250 mg, 0.41 mmol) was dissolved in pentane (10 mL). The headspace was evacuated and replaced with $SiF_4$ (1 atm). The purple solution immediately turned orange, then cloudy and yellow as copious precipitate formed. The $^1H$ NMR spectrum of the crude product contained four resonances from paramagnetic compounds in a 1:2.5:3.5:3.5 area ratio. The suspension was taken to dryness, and the solid residue was dissolved in 15 mL of toluene. The volume of the solution was reduced until precipitation occurred, warmed to dissolve the precipitate, and then cooled to −15 °C, giving a yellow powder. The $^1H$ NMR spectrum revealed the same four resonances as the crude product and resonances due to $Cp'_2CeF$. In an NMR tube, a dilute solution of $Cp'_2CeF$ in $C_6D_6$ was cooled in a liquid nitrogen 2-propanol bath, and the headspace was evacuated and replaced with $SiF_4$ (1 atm). The tube was warmed to 19 °C and shaken vigorously. The orange solution turned yellow. The $^1H$ NMR spectrum was identical to that of the crude product of the reaction of $Cp'_2CeH$ and $SiF_4$.

**Reaction of $Cp'_2CeOSO_2CF_3$ and $CH_3Li$.** $Cp'_2CeOSO_2CF_3$ (1 g, 1.3 mmol) was dissolved in 20 mL of diethyl ether and chilled in a liquid nitrogen/2-propanol bath. $CH_3Li$ (1.8 mL of a 0.7 M solution in diethyl ether, 1.3 mmol) was added via syringe. The yellow solution immediately turned red and became cloudy after 10 min. An aliquot was removed and taken to dryness for quick analysis by $^1H$ NMR spectroscopy. The spectrum of the aliquot showed two new resonances [$^1H$ NMR ($C_6D_6$): $\delta$ −2.31 (36H, $\nu_{1/2}$ = 10 Hz), −12.7 (18H, $\nu_{1/2}$ = 16 Hz)], possibly due to $Cp'_2CeCH_3$, as well as resonances due to $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The latter resonances increased at the expense of the former over time.

**NMR Tube Reaction of $Cp'_2CeOSO_2CF_3$ and $Cp'_2CeH$ in $C_6D_6$.** Approximately equimolar amounts of $Cp'_2CeOSO_2CF_3$ and $Cp'_2CeH$ were dissolved in $C_6D_6$ in an NMR tube. The brown solution was stored at room temperature for 1 day. The $^1H$ NMR spectrum showed the presence of $Cp'_2CeF$, some residual $Cp'_2CeOSO_2CF_3$, and a new organocerium species with *tert*-butyl resonances in a 2:1 ratio. The ratio of $Cp'_2CeF$ to the new species was 1:1. The new species is presumed to be $Cp'_2CeOSO_2CHF_2$, but due to the unavailability of difluoromethanesulfonic acid, it was not possible to synthesize this material independently.

## Computational Studies

**Computational Details.** The Stuttgart−Dresden−Bonn Relativistic large Effective Core Potential (RECP)[32] has been used to represent the inner shells of Ce. The associated basis set augmented by an f polarization function ($\alpha$ = 1.000) has been used to represent the valence orbitals. F has also been represented by an RECP[33] with the associated basis set augmented by two contracted d polarization Gaussian functions ($\alpha_1$ = 3.3505(0.357851), $\alpha_2$ = 0.9924(0.795561)).[34] C and H have been represented by an all-electron 6-31G(d, p) basis set.[35] Calculations have been carried out at the DFT(B3PW91) level[36] with Gaussian 98.[37] The nature of the extrema (minimum or transition state) has been established with analytical frequencies calculations, and the intrinsic reaction coordinate (IRC) has been followed to confirm that transition states connect to reactants and products. The zero point energy (ZPE) and entropic contribution have been estimated within the harmonic potential

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approximation. The Gibbs free energy, $G$, was calculated for $T = 298.15$ K. The NBO analysis[38] was carried out replacing Ce by La because of the technical requirement to have even number of f electrons for the calculations. Following the tradition, we report geometrical parameters with an accuracy of $10^{-3}$ Å and angles with an accuracy of $10^{-1}$°, although we often discuss the geometrical parameters with lesser accuracy because of the many approximations made in the modeling and in the level of calculation.

**Acknowledgment.** This work was partially supported by the Director Office of Energy Research Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No DE-AC03-76SF00098. Calculations were in part carried out at the national computing center CINES and CALMIP (France). O.E. thanks the Miller Institute for a Visiting Miller Professorship at U.C. Berkeley. The French authors thank the CNRS and the Ministère of National Education for funding.

**Supporting Information Available:** Complete list of authors for the Gaussian 98 program in ref 37. List of energies, free energies in au, and coordinates of all calculated systems. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0504800

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