

Gas-Phase Reactivity of Lanthanide Cations with Fluorocarbons: C–F versus C–H and C–C Bond Activation

Hans H. Cornehl, Georg Hornung, and Helmut Schwarz*

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, D-10623 Berlin, FRG

Received April 23, 1996[⊗]

Abstract: The gas-phase reactivity of the fluorinated hydrocarbons CF₄, CHF₃, CH₃F, C₂F₆, 1,1-C₂H₄F₂, and C₆F₆ with the lanthanide cations Ce⁺, Pr⁺, Sm⁺, Ho⁺, Tm⁺, and Yb⁺ and the reactivity of C₆H₅F with all lanthanide cations Ln⁺ (Ln = La–Lu, with the exception of Pm⁺) have been examined by *Fourier-transform* ion cyclotron resonance mass spectrometry. The perfluorinated compounds tetrafluoromethane and hexafluoroethane as well as trifluoromethane do not react with any lanthanide cation. Selective activation of the strong C–F bonds in fluoromethane, 1,1-difluoroethane, hexafluorobenzene, and fluorobenzene appears as a general reaction scheme along the 4f row. Experimental evidence is given for a “harpoon”-like mechanism for the F atom abstraction process which operates via an initial electron transfer from the lanthanide cation to the fluorinated substrate in the encounter complex Ln⁺RF. The most reactive lanthanides La⁺, Ce⁺, Gd⁺, and Tb⁺ and also the formal closed-shell species Lu⁺ exhibit additional C–H and C–C bond activation pathways in the reaction with fluorobenzene, namely dehydrohalogenation as well as loss of a neutral acetylene molecule. In the case of Tm⁺ and Yb⁺ the formation of neutral LnF₃ is observed in a multistep process via C–C coupling and charge transfer.

Introduction

Selective metal-mediated activation of the carbon–fluorine bond is still a formidable task in organometallic chemistry.¹ In general, C–F bonds are known to be significantly stronger than the corresponding C–H and C–C bonds. Further, low polarizabilities as well as an overall chemical “inertness” distinguish perfluorinated compounds from other organic molecules. Although numerous gas-phase investigations have led to a remarkable knowledge on intrinsic properties and reactivities of “bare” and ligated transition metals,² so far, little is known about the activity of “bare” lanthanide monocations Ln⁺ (Ln = La–Lu) toward fluorinated hydrocarbons.³ In the course of systematic investigations on trends in chemical reactivity of the cationic elements along the 4f row,^{4,5} in this paper we report a comparative study of the whole series Ln⁺ (except for Pm⁺, which does not have any stable isotopes) with fluorobenzene, complemented by the gas-phase reactions of selected lanthanide

cations Ln⁺ (Ln = Ce, Sm, Ho, Tm, and Yb) with several fluorinated hydrocarbons. In recent systematic studies on the chemical reactivity of all “bare” lanthanide cations toward 1,3,5-tri-*tert*-butylbenzene^{4e} and toward small alkanes and alkenes,^{4f} the ability of the 4f-block elements to activate C–H or C–C bonds of hydrocarbons could be related to the metal’s electronic ground state and the excitation energies to the lowest electronic states with two non-f electrons in the valence configurations. Thus, distinct differences in reaction kinetics, mechanisms, and product distributions are observed along the element cations of the 4f row, although these are often considered to exhibit similar chemical behavior in the condensed phase. This result, in connection with the observation that only neutral closed-shell molecules are lost during the activation processes, strongly supports insertion/elimination mechanisms. On the other hand, in a recent case study of the CeO₂⁺ species⁶ activation of hydrocarbons via direct H-atom abstraction was observed, and also in the systems Pr⁺/fluorinated hydrocarbons^{3b} a “harpoon”-like activation mechanism has been discussed. This paper focuses on the question whether the results obtained for activation of unfunctionalized hydrocarbons can be transferred to partially and totally fluorinated ones. In this context, special emphasis will be given to a discussion of the mechanistic alternatives insertion/elimination vs direct atom-abstraction, and experimental evidence will be presented in favor of the latter as far as C–F bond activation is concerned.

Experimental Section

The experiments were performed using a Spectrospin-CMS-47X Fourier-transform ion cyclotron resonance mass spectrometer; the instrument and its operational details have been described elsewhere.⁷ Lanthanide ions, Ln⁺, were generated by laser desorption/laser ionization in the external ion source by focusing the beam of a Nd:YAG laser (Spectron Systems; λ_{max} = 1064 nm) onto pure metal pieces

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

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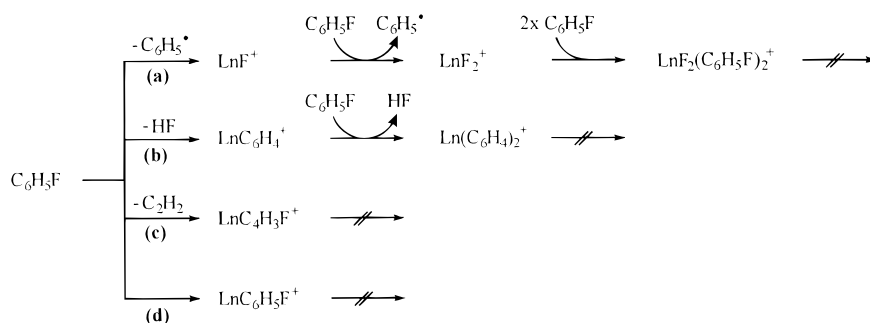
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(5) For a recent review on condensed phase organolanthanide chemistry, see: Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

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Scheme 1



(>99%; Tb, Dy, Tm, and Yb from Heraeus; La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Er, and Lu from Strem Chemicals). Most of the targets need not be stored under protective conditions, since the surface oxide layer is easily removed in the laser ablation process under the conditions of ion generation. However, La, Ce, Pr, and Eu suffer from fast oxidation upon exposure to air. Therefore, the respective targets were permanently stored under mineral oil. After being generated the ions were extracted from the external ion source and via a system of electrostatic potentials and lenses transferred into the cylindrical ICR-cell, which is located in the field of a superconducting magnet (Oxford Instruments, maximum field strength 7.05 T). Then, the respective element's most abundant isotope was isolated using FERETS,⁸ a computer-controlled ion ejection protocol which combines frequency sweeps and single-frequency pulses to optimize ejection of all undesired ions by resonant excitation. Prior to any chemical reaction, Ln^+ ions were thermalized by allowing them to collide with repeatedly pulsed-in argon (maximum pressure ca. 5×10^{-5} mbar, 100 collisions per ion). Reactants were admitted to the cell via a leak valve at a stationary pressure of $(1-15) \times 10^{-8}$ mbar, as measured by a calibrated ion gauge (BALZERS IMG070). Rate constants were determined from the pseudo-first-order decay of the reactant ions and are reported as percentage of the theoretical collision rate according to the average dipole orientation approximation⁹ (k_{ADO}) with an estimated error of $\pm 30\%$. Thorough thermalization of the ions was evaluated by the reproducibility of the reaction kinetics as well as the strict first-order behavior of the reactant-ion decay. Reaction products were identified using high-resolution mass spectra, and the consecutive reactions were investigated by MS/MS and double resonance techniques. Since we cannot exclude that some electronically excited Ln^{+*} ions are not completely quenched by multiple collisions with argon, each reaction was followed until the reactant ion intensity accounted for less than 20% of the sum of all ion intensities in order to assure that mainly ground state Ln^+ were involved in the process of interest. All functions of the mass spectrometer were controlled by a Bruker Aspect 3000 minicomputer.

Unfortunately, most of the Ln^+ ions ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{and Er}$) undergo fast side reactions with oxygen sources present as contaminants in the background of the machine (i.e. mainly H_2O and O_2). In those cases where the undesired processes accounted for more than 5% of the products, the overall reaction rates were multiplied by the sum of the initial ratios of C–F, C–H, and C–C bond activation to obtain corrected rate constants for these processes. If reactions of interest were not observed, an upper bound for the overall reaction rate is derived from the pressure of the reactant gas, the reaction time, and the signal-to-noise ratio. Branching ratios are calculated from the initial slopes of the primary product-ion intensities and are reported with an estimated error of $\pm 50\%$.

Results and Discussion

In the first section of this paper we present the reactions of all lanthanide cations Ln^+ ($\text{Ln} = \text{La-Lu}$, except Pm) with

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Table 1. Primary Product Branching Ratios (%) and Rate Constants Relative to the Theoretical Collision Rate Constant k_{ADO} for Reactions of Lanthanide Cations with Fluorobenzene (see also Scheme 1)

	LnF^+	LnC_6H_4^+	$\text{LnC}_4\text{H}_3\text{F}^+$	$\text{LnC}_6\text{H}_5\text{F}^+$	k/k_{ADO}
La^+	70	20	10		1.00
Ce^+	50	25	25		1.00
Pr^+	100				0.80
Nd^+	100				1.00
Sm^+	100				0.70
Eu^+	100				0.70
Gd^+	25	50	25		1.00
Tb^+	20	60	20		1.00
Dy^+	100				0.45
Ho^+	100				0.40
Er^+	30			70	0.30
Tm^+	70			30	0.20
Yb^+	50			50	0.02
Lu^+	20	10	5	65	0.85

fluorobenzene. This substrate was chosen for several reasons: (i) Even the most unreactive lanthanide cations are able to activate fluorobenzene. (ii) Furthermore, fluorobenzene represents a suitable model to probe selectivity with respect to C–F vs C–H and C–C bond activation. (iii) The reactions of M^+ ($\text{M} = \text{Sc-Zn}$) with $\text{C}_6\text{H}_5\text{F}$ ¹⁰ form the subject of earlier studies thus providing reference for comparison between lanthanides and the first-row transition metals. In the second part, the behavior of several selected Ln^+ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Sm}, \text{Ho}, \text{Tm}, \text{and Yb}$) toward additional perfluorinated (tetrafluoromethane, hexafluoroethane, and hexafluorobenzene) as well as partially fluorinated (trifluoromethane, fluoromethane, and 1,1-difluoroethane) hydrocarbon compounds is discussed.

Reactions of Lanthanide Cations with Fluorobenzene

Four primary product channels are observed upon collision of a “bare” lanthanide cation with a molecule of fluorobenzene (see Scheme 1). The corresponding branching ratios as well as the relative reaction rates are listed in Table 1: (a) abstraction of a fluorine atom with concomitant loss of a neutral phenyl radical appears to be a general process which occurs for all Ln^+ cations. However, in several cases this reaction has to compete with other similarly efficient pathways; (b) loss of neutral hydrogen fluoride and formation of a species with the formal composition LnC_6H_4^+ which most probably corresponds to a benzyne complex or a metallabenzocyclopropane; (c) formation of $\text{LnC}_4\text{H}_3\text{F}^+$ with concomitant loss of neutral acetylene, and (d) formation of the adduct complex $\text{LnC}_6\text{H}_5\text{F}^+$. Interestingly, pathway b is the only primary reaction observed in the cases of $\text{M}^+/\text{C}_6\text{H}_5\text{F}$ for $\text{M} = \text{Sc}, \text{Ti}, \text{V}, \text{Fe}$.¹⁰ As far as the other 3d

(10) (a) Bjanarson, A.; Taylor, J. W. *Organometallics* **1989**, 9, 2020. (b) Bjanarson, A. *Organometallics* **1991**, 10, 1244. (c) Further investigations on the reactions of 3d metals with 1-fluoronaphthalene are given in: Bjanarson, A. *Rapid Commun. Mass Spectrom.* **1994**, 8, 366. (d) Also see: Bjanarson, A. *Organometallics* **1996**, 15, 3275.

metals are concerned, only formation of an adduct complex or charge transfer from the metal to the organic substrate is observed.¹⁰ Formation of the fluoro complexes MF^+ cannot occur for instance in the case of iron since at least 125.3 ± 2.3 kcal/mol¹¹ are required to break the $\text{C}_6\text{H}_5\text{-F}$ bond whereas the energy gained in the formation of the $\text{Fe}^+\text{-F}$ bond only amounts to 96 kcal/mol.¹²

Fully in line with the findings for the reactions with alkanes and alkenes,^{4f} only those lanthanide cations which have two non-f electrons in their electronic ground state (La^+ , Ce^+ , Ge^+ , and Lu^+) as well as Tb^+ , which is the Ln^+ cation with the lowest excitation energy to a state with a $6s^15d^14f^m$ valence configuration,¹³ give rise to C–H and C–C bond activation (pathways b and c). The overall reaction rates in these cases are at the collisional limit, except for Lu^+ where k/k_{ADO} amounts to 0.85. The branching ratios for La^+ and Ce^+ on the one hand and Gd^+ and Tb^+ on the other hand are identical within the experimental error. The higher probability of F-atom abstraction for La^+ and Ce^+ (70% and 50%) as compared to Gd^+ and Tb^+ (25% and 20%) is not directly related to differences in the bond dissociation energy (BDE) of the newly formed $\text{Ln}^+\text{-F}$ bonds. This finding can rather be rationalized in terms of the “harpoon”-like mechanism proposed in an earlier work^{3b} and will be discussed in detail further below. The amount of C–C bond activation indicated by the loss of a neutral acetylene molecule, a process which is definitely not observed for the 3d transition metals, is of the same order of magnitude in all four cases (La^+ , 10%; Ce^+ , 25%; Gd^+ , 25%; Tb^+ , 20%). Besides its ability to activate all three different types of bonds in fluorobenzene (pathways a–c), Lu^+ mainly (65%) forms an adduct complex upon collision with the substrate (pathway d).

All the other Ln^+ ($\text{Ln} = \text{Pr–Eu}$, Dy–Yb) undergo abstraction of a fluorine atom to form LnF^+ as the only genuine bond activation process. However, the overall reactivity changes dramatically along the 4f row. Lanthanides of the first half of the 4f row including Tb^+ do activate fluorobenzene close to the collisional limit whereas the reaction efficiency drops gradually from Dy^+ ($0.45k_{\text{ADO}}$) to Tm^+ ($0.20k_{\text{ADO}}$). Not unexpectedly, the reactivity of Yb^+ , the only lanthanide cation which was found to be unreactive toward a variety of hydrocarbons,^{4f} is even an order of magnitude slower ($0.02k_{\text{ADO}}$) than that of Tm^+ . Moreover, a substantial fraction of the reactivity of fluorobenzene with the late lanthanides Yb^+ , Tm^+ , Er^+ , and also Lu^+ does correspond to simple adduct formation (see Table 1). We suggest that with decreasing reactivity toward the end of the 4f row the probability to form a simple adduct complex rises. In this context the strong tendency for adduct formation exhibited by Lu^+ appears exceptional and points toward its special position along the 4f elements (see below). Considering the fact that only exothermic or thermoneutral reactions are observed within the experimental setup, the above-mentioned observations lead to a lower bound for $\text{BDE}(\text{Ln}^+\text{-F})$ ($\text{Ln} = \text{La–Lu}$) of 123 kcal/mol.¹⁴

As far as further reaction steps are concerned (see Scheme 1), (a) all lanthanide–fluoro cations, except for SmF^+ and EuF^+ , selectively abstract another fluorine atom from fluorobenzene

(11) All thermochemical data of the organic compounds are taken from: (a) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Standard Reference Database, Positive Ion Energetics*, Version 2.01; Gaithersburg, MD, Jan 1994. (b) Lias, S. G.; Bartness, J. E.; Liebman, J. F.; Holmes, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data*, 17 **1988**, Suppl. 1.

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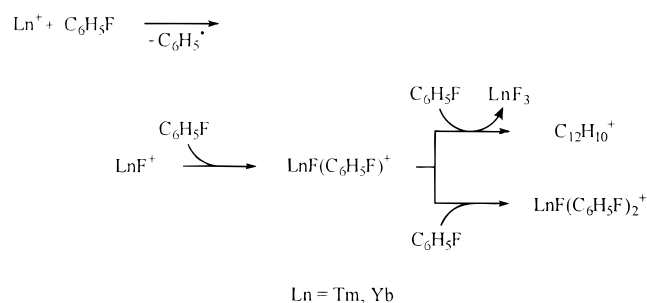
(13) Martin, W. C.; Zalubas, R.; Hagan, L. *Atomic Energy Levels—The Rare Earth Elements*; NSRDS-NBS 60; National Bureau of Standards: Washington, DC, 1978.

to yield LnF_2^+ with an efficiency comparable to that of the primary step. This result implies that also the second bond dissociation energy, $\text{BDE}(\text{FLn}^+\text{-F})$, is greater than 123 kcal/mol for $\text{Ln} = \text{La–Nd}$, Gd–Lu .¹⁴ In the monofluoro cations the metal center has a formal oxidation state of +II. Thus, the absence of the difluorides SmF_2^+ and EuF_2^+ compares to results from the condensed phase where those two lanthanides exhibit a particular stability of the +II oxidation state. However, in the case of Yb for which the +II oxidation state is also known to be stable, very slow formation of YbF_2^+ can be observed. We note in passing that for the late lanthanides Dy–Lu the species LnF_2^+ undergo subsequent addition of two more molecules of $\text{C}_6\text{H}_5\text{F}$. (b) The initially formed dehydrohalogenation products ($\text{Ln} = \text{La}$, Ce , Gd , and Tb) induce again loss of HF from $\text{C}_6\text{H}_5\text{F}$ to yield $\text{Ln}(\text{C}_6\text{H}_4)_2^+$. The corresponding products in the case of 3d metals have been described earlier as metalladibenzocyclopentane structures.^{10a,b} As already observed for Sc^+ , Ti^+ , V^+ , and Fe^+ , no further dehydrohalogenation step follows the second one. Besides addition of a water molecule from the background of the machine, which is not the subject of the present investigation, reaction pathway b stops at this stage for all lanthanide cations. Fully in line with the much lower ionization energy (IE) of the lanthanides in question as compared to, for example, iron (IEs [eV]: La , 5.58; Ce , 5.53; Gd , 6.15; Tb , 5.86; Fe , 7.90^{11,13}), no charge transfer reaction upon collision with a third $\text{C}_6\text{H}_5\text{F}$ molecule to form the biphenylene cation $\text{C}_{12}\text{H}_8^+$ and neutral $\text{LnC}_6\text{H}_5\text{F}$ takes place, while this process has been observed in the reaction of $\text{Fe}(\text{C}_6\text{H}_4)_2^+$ with fluorobenzene.^{10a} The LuC_6H_4^+ complex, however, does not react via bond activation with fluorobenzene; rather, it exclusively forms the adduct $\text{Lu}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5\text{F})^+$. This behavior can be rationalized under the assumption of a metallabenzocyclopropane structure, since in this case LuC_6H_4^+ exhibits a closed-shell $4f^{14}$ valence electron configuration at the metal center, which disfavors an insertion into a C–F, C–H, or C–C bond. (c) The primary ions $\text{LnC}_4\text{H}_3\text{F}^+$ do not undergo any further process, neither with fluorobenzene nor with background water. (d) The same applies for the adduct complexes $\text{LnC}_6\text{H}_5\text{F}^+$.

A very unusual reaction pathway is observed in the case of TmF^+ and also YbF^+ ; in the latter, however, at the borderline of the detection limit: Both fluorides form an adduct with fluorobenzene which upon interaction with yet another $\text{C}_6\text{H}_5\text{F}$ molecule, on the one hand, yields the bisadduct complex $\text{LnF}(\text{C}_6\text{H}_5\text{F})_2^+$, and, on the other hand, gives rise to an unexpected C–C coupling reaction combined with a charge transfer reaction (in the following denoted as coupling/CT process) under formation of an ion with the composition $\text{C}_{12}\text{H}_{10}^{+}$, most probably the radical cation of biphenyl, concomitant with neutral LnF_3 (see Scheme 2). The fact that only the late lanthanides Tm and Yb exhibit this surprising reactivity merits further attention. As already mentioned, under the experimental conditions chosen, only exothermic reactions can be observed. Despite the lack of reliable data for $\text{BDE}(\text{Ln}^+\text{-F})$ and $\text{BDE}(\text{FLn}^+\text{-C}_6\text{H}_5\text{F})$ one can crudely estimate that the corresponding process would also be thermochemically feasible for other lanthanides than Tm and Yb . Therefore, we believe that the reaction does not proceed because of other, non-

(14) (a) In an earlier extensive mass spectrometric study on lanthanide fluorides, $\text{IE}(\text{LnF}_n)$ ($n = 1,2$) as well as $\text{BDE}(\text{F}_n\text{Ln-F})$ ($n = 0-2$) are reported with substantial error bars. However, they certainly serve to give orders of magnitude for these values and trends along the 4f row: Zmbov, K. F.; Margrave, J. L. In *Mass Spectrometry in Inorganic Chemistry*; Margrave, J. L., Ed. *Adv. Chem. Ser.* **1968**, 72, 267. (b) The following more recent values [kcal/mol] can be extracted from ref 11: (i) $\text{BDEL}(\text{Ln}^+\text{-F})$, Nd , 143 ± 7 ; Sm , 130 ± 7 ; Dy , 125 ± 7 ; Ho , 127 ± 7 ; Er , 131 ± 7 ; (ii) $\text{BDE}(\text{FLn}^+\text{-F})$, Nd , 129 ± 14 ; Er , 127 ± 14 .

Scheme 2



thermochemical reasons, which we suggest, in a qualitative way, are the following: The orders of magnitude for the IEs of the species Ln,¹¹ LnF, and LnF₂¹⁴ are 6.0, 6.5, and 7.0 eV, respectively, and thus too low to induce charge transfer from the organic ligand in question. Upon formation of the third lanthanide–fluorine bond in LnF₃, however, the Ln valence shell is saturated and ionization is expected to become energetically much more demanding. Therefore, one can estimate that only during transfer of a third fluorine atom to the lanthanide center within the rovibrationally excited encounter complex FLn-(C₆H₅F)₂⁺ does the IE of the metal centered fragment surpass that of the organic ligand. Consequently, only those lanthanides which are able to at least give rise to LnF₂⁺ in the reaction with two fluorobenzene molecules are expected to undergo the coupling/CT process. On the other hand, for those lanthanides whose cationic fluorides quickly form the triatomic LnF₂⁺, with concomitant loss of a phenyl radical, a stabilized adduct complex FLn⁺–C₆H₅F is not formed and thus the coupling/CT pathway is not accessible. These considerations obviously point toward strong kinetic restrictions in the coupling/CT process for all lanthanides except Tm and Yb.

Trends in Reactivity of Lanthanide Cations with Selected Fluorohydrocarbons

In light of the remarkable differences in chemical behavior of the “bare” lanthanide cations toward alkanes, alkenes,^{4f} *tert*-butylbenzene,^{4e} and fluorobenzene (this paper) six lanthanides, namely Ce⁺, Pr⁺,^{3b} Sm⁺, Ho⁺, Tm⁺, and Yb⁺, have been selected according to the reactivity patterns observed along the 4f row⁴ to get further insight into selectivity and thermochemistry of C–F bond activation of fluorinated hydrocarbons. Ce was chosen as a representative for the most reactive lanthanides and Pr and Sm as examples for a more and a less reactive element of the 4f-row’s first half, respectively. The same considerations apply for Ho and Tm for the second half, respectively. Finally, Yb serves as a probe for the general “onset” in reactivity of the hole series. Several perfluorinated (CF₄, C₂F₆, and C₆F₆) as well as partially fluorinated hydrocarbons (CHF₃, CH₃F, and 1,1-C₂H₄F₂) were chosen as substrates to investigate the role of polarizability and C–F bond strength, on the one hand, and trends in selectivity of the “bare” lanthanide cations, on the other hand.

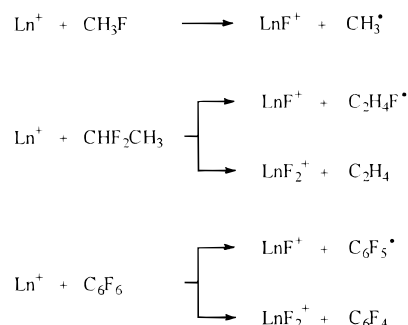
None of the lanthanide cations under investigation was found to react with tetrafluoromethane (BDE(CF₃–F) = 132.4 kcal/mol), trifluoromethane (BDE(F₂HC–F) = 128 ± 3 kcal/mol), or hexafluoroethane (BDE(C₂F₅–F) = 127 kcal/mol). Unfortunately, no precise thermochemical information is available for the bond strength in the diatomic species Ln⁺–F,¹⁴ the most probable product of an activation of those substrates (see above and ref 3b). Thus, it is difficult to decide whether the non-observance of a reaction is due to the endothermicity of the appropriate processes or whether too short lifetimes of the

Table 2. Rate Constants Relative to the Theoretical Collision Rate Constant k_{ADO} for Reactions of Lanthanide Cations with Three Selected Fluorocarbon Compounds^a (Branching Ratios (%) for Abstraction of One vs Two Fluorine Atoms in the Primary Step Are Given in Parentheses)

	CH ₃ F	C ₂ H ₄ F ₂	C ₆ F ₆	
Ce ⁺	0.20	0.15 (80/20)	0.75	(30/70)
Pr ⁺	0.20	0.20 (80/20)	1.00	(35/65)
Sm ⁺	0.05	0.05 <i>b</i>	0.50	(30/70)
Ho ⁺	0.02	<0.002 <i>b</i>	0.05	(–/100)
Tm ⁺	<0.001	<0.001 <i>b</i>	0.01	(20/80)
Yb ⁺	<0.001	<0.001 <i>b</i>	<0.001	<i>b</i>

^a No reaction is observed with CF₄, CHF₃, and C₂F₆. ^b No primary product branching ratios can be given due to the low ion intensities.

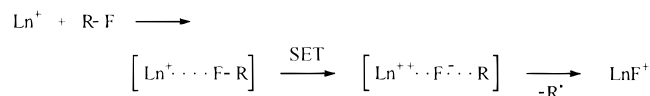
Scheme 3



rovibrationally excited ion/molecule encounter complexes or kinetic barriers along the activation cause the inertness. Table 2 summarizes the relative rate constants and, if applicable, the branching ratios for the corresponding ion/molecule reactions with fluoromethane, 1,1-difluoroethane, and hexafluorobenzene (see Scheme 3).

As representatives of the reactive lanthanide cations, Ce⁺ and Pr⁺ show similar reactivity. Both cations selectively activate the C–F bond in fluoromethane (BDE(CH₃–F) = 112 ± 0.3 kcal/mol) to yield CeF⁺ (0.20 k_{ADO}) and PrF⁺ (0.20 k_{ADO}), respectively. In the corresponding reaction with 1,1-difluoroethane (BDE(H₃CCHF–F) = 113 kcal/mol) besides the single defluorination an additional double defluorination pathway gives rise to CeF⁺, CeF₂⁺ (CeF⁺:CeF₂⁺ = 4:1, 0.15 k_{ADO}) and PrF⁺, PrF₂⁺ (PrF⁺:PrF₂⁺ = 4:1; 0.20 k_{ADO}) as primary products, respectively. Interestingly, notwithstanding the fact that cleavage of the corresponding C–F bonds in fluoromethane and 1,1-difluoroethane is by at least 11 kcal/mol (CH₃F) and 10 kcal/mol (1,1-C₂H₄F₂) favored as compared to fluorobenzene (see above), the reaction rates are significantly lower with the former two substrates—a clear indication that the lifetime of the initially formed ion/molecule complex is rate determining. With the less reactive lanthanide cations Sm⁺, Ho⁺, Tm⁺, and Yb⁺ the observed reaction rate constants drop, down to the detection limit. In contrast to the aliphatic 1,1-difluoroethane, in the reaction of the aromatic hexafluorobenzene (BDE(C₆F₅–F) = 117 kcal/mol) with Ce⁺ (0.75 k_{ADO}), Pr⁺ (1.00 k_{ADO}), and even Sm⁺ (0.50 k_{ADO}), the double defluorination pathway, resulting in the formation of CeF₂⁺, PrF₂⁺, and SmF₂⁺, respectively, and C₆F₄ loss predominates the abstraction of a single fluorine atom. This experiment supports earlier conjectures from solution chemistry¹⁵ that tetrafluorobenzene, the existence of which in the condensed phase is yet unproved, is an intermediate in the activation of hexafluorobenzene by electron-deficient lanthanide complexes. In the case of Ho⁺, Tm⁺, and Yb⁺ the activation

(15) Deacon, G. B.; Mackinnon, P. I.; Tuong, T. D. *Aust. J. Chem.* **1983**, *36*, 43.

Scheme 4

of hexafluorobenzene is very inefficient and reaction rates are at the detection limit.

With regard to the thermochemistry, the non-observation of C–F bond activation in CHF_3 suggests an upper bound $\text{BDE}(\text{Ln}^+-\text{F}) \leq 131$ kcal/mol for all the lanthanides. However, in the case of Ho^+ , for example, no C–F bond activation is observed in the reactions with fluoromethane or 1,1-difluoroethane in contrast to the case of fluorobenzene which has a significantly stronger C–F bond. Hence, the available experimental data do not allow for an estimation of the upper bound for $\text{BDE}(\text{Ln}^+-\text{F})$, because the observed reactivity is governed not only by thermochemistry but also by kinetic effects such as the lifetimes of the rovibrationally excited ion/molecule encounter complexes or kinetic barriers along the reaction pathway.

Mechanistic Considerations

In a recent investigation on reactions of Pr^+ with fluorinated hydrocarbons (in the following denoted as R–F) two alternative reaction mechanisms have been proposed for the activation processes observed which lead to PrF^+ and loss of a neutral organic radical R^\cdot :^{3b} (i) After insertion into the R–F bond via an “avoided crossing” of two hypersurfaces corresponding to the Pr^+ ground state and an excited state of a valence configuration with two non-f electrons to yield $\text{F-Pr}^+-\text{R}$, the radical R^\cdot is eliminated. (ii) Upon coordination of R–F to Pr^+ through the electronegative fluorine atom, a single electron transfer (SET)¹⁷ from Pr^+ to the fluorine takes place which favors the homolytic cleavage of the C–F bond to form the PrF^+ species (see Scheme 4).

It has been shown elsewhere^{4f} that mechanism i is applicable in the case of hydrocarbon activation by Ln^+ . The dehydrohalogenation of fluorobenzene by La^+ , Ce^+ , Gd^+ , Tb^+ , and Lu^+ exactly parallels the results obtained in ref 4f and, most likely, proceeds in an insertion/elimination sequence. Therefore, if insertion into the C–F bond would also occur prior to F-atom abstraction, one would expect at least a small fraction of dehydrohalogenation products for all Ln^+ since consecutive β -H shift and elimination of HF should be easy after the strong C–F bond had already been activated. On the other hand, mechanism ii accounts for the dominant ionic character of the newly formed Ln^+-F bond, the strength of which should be partly reflected by the second ionization energy (second IE) of the lanthanides.¹⁶ As, according to mechanism ii, a SET from the lanthanide monocation has to take place prior to product formation, the second IE(Ln) should be related to the ability of Ln^+ to abstract a F atom from R–F. To test the applicability of model ii the relative reaction rates of Ln^+ with $\text{C}_6\text{H}_5\text{F}$ are plotted versus the second ionization energies (Figure 1). In those cases where several parallel primary reaction pathways are observed only the fraction for F-atom abstraction has been taken into account. However, this procedure implies a systematic error—depending on the relative weight of the competing processes—which finds

(16) Second IE [eV] according to ref 13: La, 11.1; Ce, 10.8; Pr, 10.6; Nd, 10.7; Pm, 10.9; Sm, 11.1; Eu, 11.2; Gd, 12.1; Tb, 11.5; Dy, 11.7; Ho, 11.8; Er, 11.9; Tm, 12.1; Yb, 12.2; Lu, 13.9.

(17) Electron transfer has been suggested earlier to account for C–F bond activation by rhodium and ruthenium complexes: (a) Blum, O.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1991**, 258. (b) Whittlesey, M. K.; Perutz, R. N.; Moore, M. M. *J. Chem. Soc., Chem. Commun.* **1996**, 787.

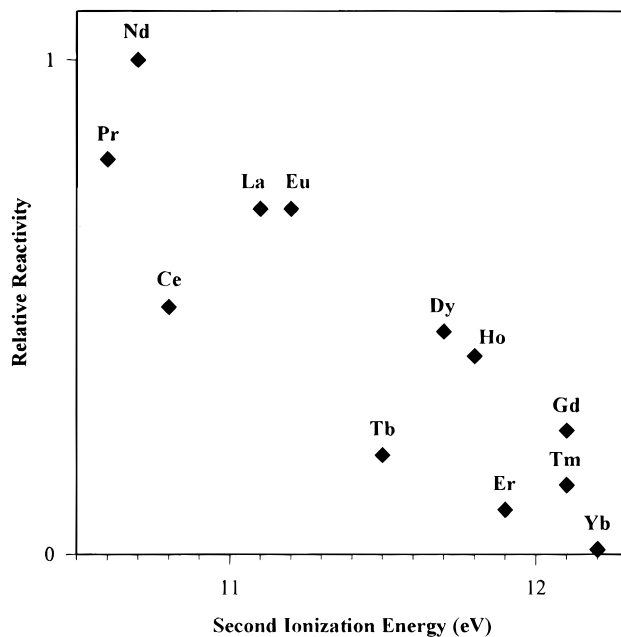


Figure 1. Relative reaction rates of Ln^+ with fluorobenzene, with regard to F-atom abstraction processes as a function of the second IE(Ln).

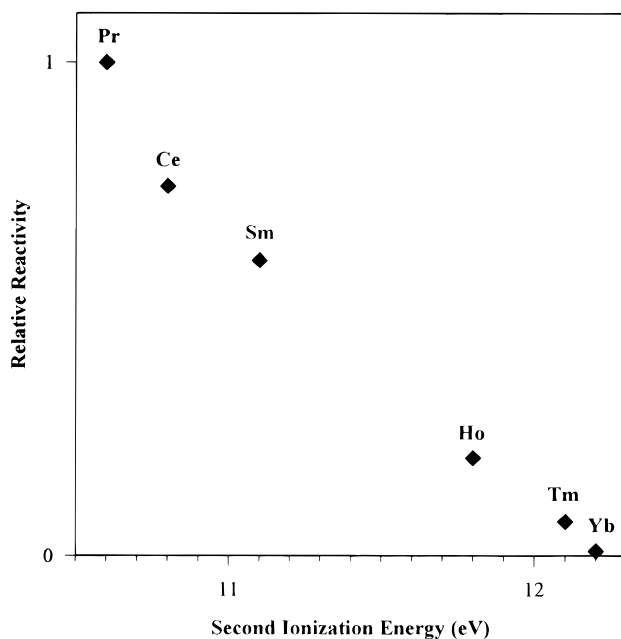


Figure 2. Sum of the relative reaction rates of Ln^+ with fluoromethane, 1,1-difluoroethane, hexafluorobenzene, and fluorobenzene, with regard to F-atom abstraction processes as a function of the second IE(Ln).

expression in the spread of the data points shown in Figure 1. The nevertheless obvious correlation appears even more compelling as one plots the sum of all relative reaction rates obtained in this study, with regard to C–F bond activation processes, versus the second ionization energies as depicted in Figure 2 (data only available for Ce, Pr, Sm, Ho, Tm, and Yb; see above). Despite its very high second IE of 13.9 eV, Lu^+ exhibits a substantial reactivity with regard to F-atom abstraction from fluorobenzene (see above) and does not fit in the plot drawn here. This behavior reflects its exceptional role in the lanthanide series which is partly based on its closed-shell ground state configuration ($6s^2 4f^{14}$) concomitant with the much higher second IE as compared to the other lanthanides. We conclude that the relationship between observed reactivity and second IE does certainly depend on further parameters which obviously are

constant along the 4f row from La to Yb but change when going to Lu. Finally, we note that within this model the bias toward F-atom abstraction in the systems La^+ , $\text{Ce}^+/\text{C}_6\text{H}_5\text{F}$ as compared to Gd^+ , $\text{Tb}^+/\text{C}_6\text{H}_5\text{F}$ can be rationalized with respect to the differences in the second IEs (La, 11.1; Ce, 10.8; Gd, 12.1; Tb, 11.5; all values in eV).

Summary and Conclusions

In this work we present a systematic study of the reactivity of "bare" Ln^+ cations ($\text{Ln}^+ = \text{La}^+ - \text{Lu}^+$, with the exception of Pm^+) with fluorobenzene. C–F bond activation of this substrate appears to be a general scheme observed in the reactions with Ln^+ cations. Additional reaction pathways, namely C–H and C–C bond activation, are only operative for those lanthanides which exhibit either an electronic ground state configuration with two non-f electrons (La^+ , Ce^+ , Gd^+ , and Lu^+) or a low excitation energy to such a state (Tb^+). Further investigations of Ce^+ , Pr^+ , Sm^+ , Ho^+ , Tm^+ , and Yb^+ with several fluorinated hydrocarbons (R–F) lead to the following picture: (i) None of the lanthanides were found to react with those R–F substrates where the carbon–fluorine BDE surpasses that of fluorobenzene (i.e. CF_4 , C_2F_6 , and CHF_3). (ii) On the other hand, selective homolytic C–F bond cleavage to form LnF^+ and neutral organic radicals R^{\bullet} is observed for the substrates fluoromethane, 1,1-difluoroethane, and hexafluorobenzene. In the latter two cases also direct formation of the LnF_2^+ species in the primary reaction step occurs.

As far as reaction rates are concerned, the efficiency for C–F bond activation drops dramatically along the 4f row and also with decreasing polarizabilities of the substrates. Thus, obviously not only a weaker $\text{BDE}(\text{Ln}^+ - \text{F})$ for the late lanthanides

but also lifetime effects in the initially formed rovibrationally excited ion/molecule complexes or barriers along the reaction pathway are responsible for the obtained reaction patterns. From the observation of $\text{Ln}^+ - \text{F}$ bond formation upon collision with fluorobenzene a lower bound for $\text{BDE}(\text{Ln}^+ - \text{F}) \geq 123$ kcal/mol can be derived for $\text{Ln} = \text{La} - \text{Lu}$.

As evidenced by the correlation of the second IE(Ln) with the overall observed ability of the "bare" lanthanide cations to activate a C–F bond in the substrates under investigation, a "harpoon" mechanism is postulated to be operative for the F-atom abstraction process. This mechanism is contrasted by the parallel C–H and C–C activation reactions observed for the most reactive lanthanides. This insertion/elimination mechanism is fully in line with earlier findings on C–H and C–C bond activation in hydrocarbons for which an "avoided curve-crossing" was found to be operative.

Finally, an unusual C–C coupling with concomitant electron transfer from the organic ligand to the metal-centered fragment to yield neutral LnF_3 and a $\text{C}_{12}\text{H}_{10}^+$ species (most probable the biphenyl radical cation) is observed. Although in a rough estimate this pathway should be thermochemically feasible for all lanthanides except Eu, it is only observed for Tm and Yb due to severe kinetic restrictions for the other 4f elements.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagen-Stiftung, and the Fonds der Chemischen Industrie. We are indebted to Dr. Christoph Heinemann for helpful discussions and Dr. Detlef Schröder for a critical review of the manuscript. We also thank the Reviewers for constructive comments.

JA961343T