

UCLA

UCLA Previously Published Works

Title

Aromatic C-F Bond Activation by Rare-Earth-Metal Complexes

Permalink

<https://escholarship.org/uc/item/3f58f533>

Journal

Organometallics, 36(1)

ISSN

0276-7333

Authors

Huang, Wenliang
Diaconescu, Paula L

Publication Date

2017-01-09

DOI

10.1021/acs.organomet.6b00661

Peer reviewed

Aromatic C–F Bond Activation by Rare-Earth Metal Complexes

Wenliang Huang[§] and Paula L. Diaconescu^{*†}

[†] Department of Chemistry & Biochemistry, University of California, Los Angeles, California 90095, United States

[§] Current Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02141, United States

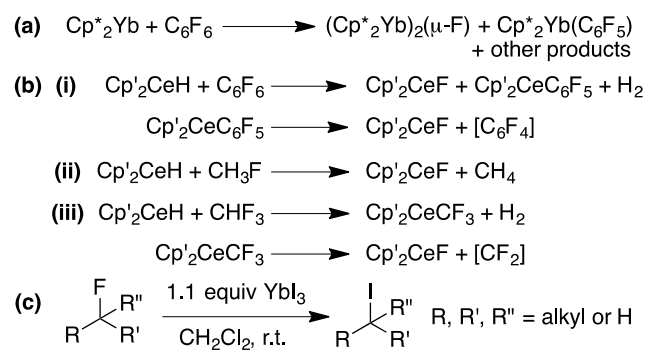
Supporting Information Placeholder

ABSTRACT: C–F bond activation is a challenging reaction with increasing importance in synthesis. The strength of the C–F bond and the shielding effect of the fluorine atom render its activation difficult. Rare-earth metals offer an exceptional opportunity for this process because the high dissociation energy of the M–F bond offsets the strength of the C–F bond. Herein we report a unique reaction for the C–F activation of aromatic bonds by rare-earth metal complexes. The strong C–F bond of perfluorobenzene is cleaved under reducing conditions in the presence of a rare-earth metal iodide to form initially an equimolar mixture of a metal fluoride and a metal perfluorophenyl complex; the latter eventually undergoes β -F elimination to a metal fluoride. A similar reactivity is observed when reacting inverse sandwich rare-earth metal arene complexes with perfluorobenzene. All compounds were characterized by X-ray crystallography, multi-nuclear NMR spectroscopy, and elemental analysis.

Introduction

When compared to hydrocarbons, fluorocarbons exhibit unique and advantageous chemical, physical, and physiological properties.^{1–4} Notable examples include the use of perfluorocarbons as blood substitutes⁵ or as solvents for biphasic reactions,⁶ both applications utilizing the chemical inertness and miscibility properties of perfluorocarbons. In order to exploit fluorocarbons, various methods have been developed to introduce C–F bonds in organic molecules.^{7–11} However, the high volatility and devastating environmental impacts of fluorocarbons demand the concurrent advancement of methods to relieve their negative effects on the planet.^{12–13} Since simple burning of fluorocarbons would only release global warming gases, more sophisticated methods are required to remove fluorine. C–F bond activation has thus become a subject with increasing importance. While C–H bond activations already present a great challenge for chemists due to the high bond dissociation energy (104.9(0.1) kcal/mol for CH₃–H)¹⁴ and chemical inertness, C–F bond activation is arguably an even greater challenge since it is the strongest single bond between carbon and any element (115(4) kcal/mol for CH₃–F),¹⁴ while the fluorine atom has a steric and electronic shielding effect.³ Despite the difficulty associated with C–F bond activation, metal mediated C–F bond transformations have been demonstrated and reviewed in the literature, including examples for both early and late transition metals.^{15–22} Albeit in most cases C–F bond activation was achieved in a stoichiometric fashion due to the high stability of the corresponding metal fluoride, a common product of metal mediated C–F bond transformations, it is possible to make the reaction catalytic through the use of a fluorine trapper such as a silane or aluminum hydride by taking advantage of the strength of the Si–F and Al–F bonds.^{23–27}

chometric fashion due to the high stability of the corresponding metal fluoride, a common product of metal mediated C–F bond transformations, it is possible to make the reaction catalytic through the use of a fluorine trapper such as a silane or aluminum hydride by taking advantage of the strength of the Si–F and Al–F bonds.^{23–27}



Scheme 1. Representative examples of C–F bond activation by rare-earth metal complexes: (a) Reaction of Cp^{*}₂Yb(II) (Cp^{*} = $\eta^5\text{-C}_5\text{Me}_5$) with perfluorobenzene;³⁶ (b) Activation of fluorocarbons by Cp'₂CeH (Cp' = $\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_3\text{-1,2,4}$);^{37–38} (c) F/I exchange between alkyl fluorides and YbI₃.³⁹

Rare-earth metals present unique opportunities for C–F bond activation. First, they form strong bonds with the most electronegative fluorine atom since rare-earth metal

ions are hard acids according to Pearson's acid/base concept.²⁸ For example, the average Ce–F bond enthalpy of CeF₃(g) is 153 kcal/mol,²⁹ comparable to the bond enthalpy of the C₆F₅–F bond at 154 kcal/mol.³⁰ Second, in spite of the fact that the fluorine atom is not a particularly good Lewis donor or hydrogen bond acceptor,³ lanthanides and actinides form significant interactions with C–F bonds either intermolecularly³¹ or intramolecularly.^{32–35} While the former guarantees that the C–F bond transformation is thermodynamically favorable, the latter allows a relatively low activation barrier for C–F activation.

Early reports of C–F bond activation mediated by lanthanides involved divalent complexes of Eu, Yb, and Sm. For example, Deacon et al. reported the *ortho*-fluorine atom abstraction from perfluorophenyl or its derivatives by Yb(II).^{40–41} Later, Andersen and Watson reported the defluorination of fluorocarbons, including perfluorobenzene and perfluoroolefins, by divalent lanthanide metallocenes (Scheme 1a).^{36, 42} In these cases, a trivalent lanthanide fluoride was the product and the reaction rate was well correlated to the redox potential of the corresponding divalent lanthanide reagent.⁴² Furthermore, Schwarz and co-workers reported a gas phase reaction between lanthanide cations and fluorocarbons and found that the C–F bond activation was applicable to all cationic lanthanide complexes studied and, in most cases, resulted in the formation of a Ln–F bond and an organic radical species.^{43–44} Deacon and co-workers gradually expanded the synthesis of lanthanide fluorides with different ancillary ligands by means of C–F bond activation.^{45–49} Andersen, Eisenstein, and Maron conducted experimental and computational studies on the C–F activation reaction by Cp'₂CeH (Cp' = η⁵-C₅H₂(CMe₃)_{3-1,2,4})^{36, 42} and showed that while the reaction outcome was hydrogen for fluorine exchange, it did not follow a simple σ-bond metathesis mechanism (Scheme 1b).³⁷ Follow-up studies suggested a more complicated mechanism might be in play due to the large difference in charge distribution between starting materials and products.^{50–51} Recently, Hilmersson et al. demonstrated an efficient halogen exchange reaction between LnI₃ and unactivated alkyl fluorides (Scheme 1c).³⁹ It was initially discovered when the same group studied the reductive defluorination of alkyl fluorides using iodide contaminated Sm[N(SiMe₃)₂]₂.⁵² Subsequent optimizations showed that the reactivity followed a simple trend: the smaller the lanthanide ion, the higher the yield of halogen exchange. That rendered YbI₃ the best reagent tested (the reactivity of LuI₃ or ScI₃ was not reported). The same group also published a C–N cross coupling reaction using an alkyl fluoride, a secondary amine, and a stoichiometric amount of La[N(SiMe₃)₂]₃.⁵³ Examples of C–F bond activation by actinides are rare. Andersen and Bergman reported that (η⁵-MeC₅H₄)₃U(*t*Bu) could activate the C–F bonds of both aromatic and aliphatic perfluorocarbons and proposed a radical cage mechanism.⁵⁴

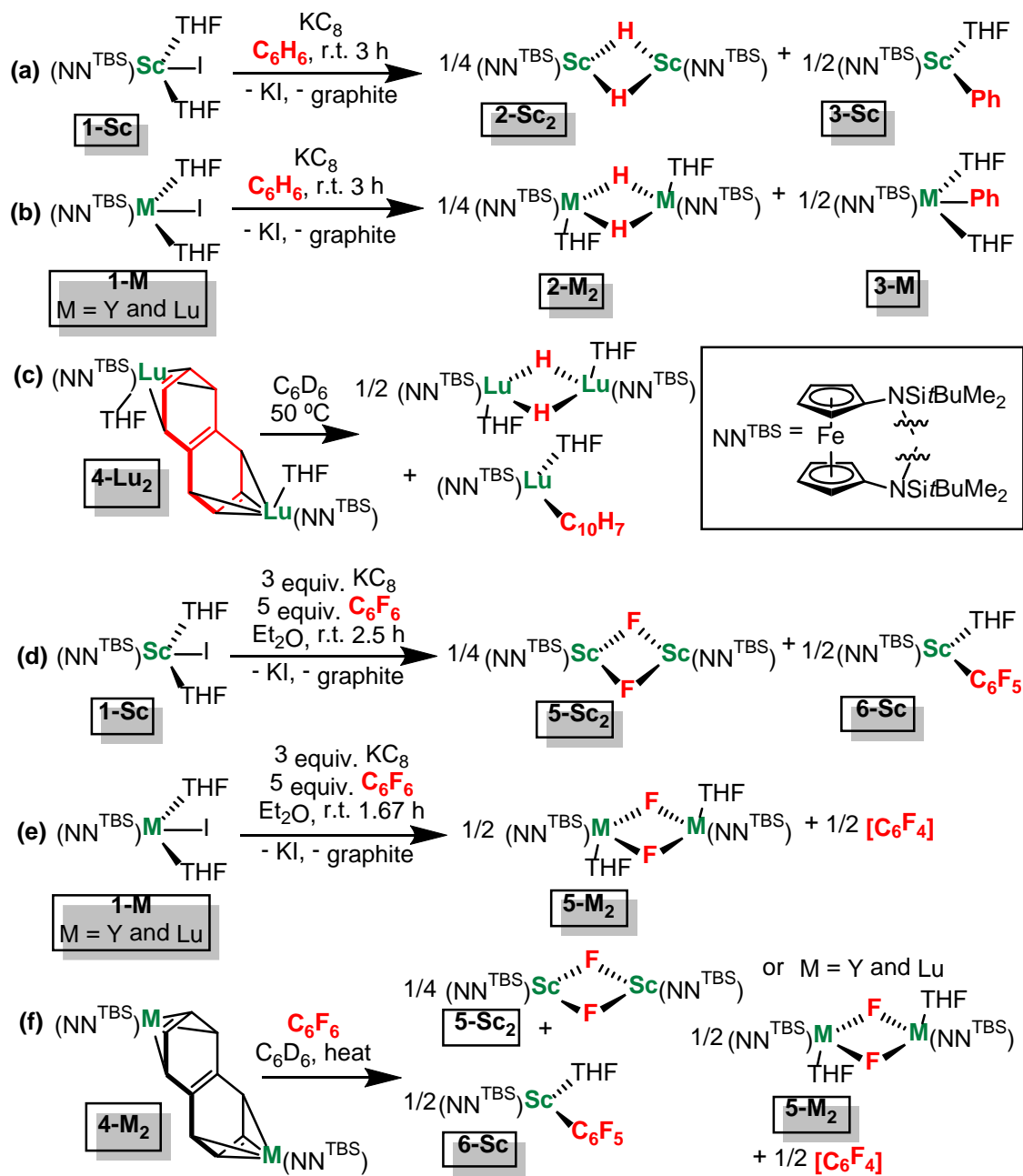
Results and discussion

As part of our group's continuing efforts to explore the chemistry of rare-earth metals and actinides supported by ferrocene-derived ligands,^{55–62} especially redox reactions in the presence of arenes,^{63–71} we discovered a bimetallic cleavage of the C–H bond of benzene by (NN^{TBS})MI(THF)₂ (**1-M**, H₂(NN^{TBS}) = fc(NHSitBuMe₂)₂, fc = 1,1'-ferrocenediyl; M = Sc, Y, and Lu) and potassium graphite (KC₈) to form an equimolar mixture of [(NN^{TBS})M(μ-H)₂(THF)_x]₂ (**2-M₂**, M = Sc, x = 0 or 1; M = Y or Lu, x = 1) and (NN^{TBS})MPh(THF) (**3-M**, Scheme 2a, b). In addition, the C–H bond activation of a naphthalene dianion sandwiched between two lutetium ions in the previously isolated [(NN^{TBS})Lu(THF)]₂(μ-C₁₀H₈) (**4-Lu₂**) was observed upon moderate heating (Scheme 2c).⁶⁹ Based on experimental and computational studies, we proposed that the reaction proceeds through an inverse sandwich metal benzene intermediate followed by an asymmetric bimetallic transition state for C–H bond cleavage that involves metal based orbitals, the π* orbital of benzene, and the σ* orbital of the C–H bond. This mechanism is fundamentally different from previously established C–H bond activation mechanisms, such as σ-bond metathesis and 1,2-addition.^{72–73} Inspired by this C–H bond activation reactivity, we turned to investigate whether the **1-M**/KC₈ system is capable of C–F bond activation. Herein, we report the C–F bond activation of C₆F₆ by **1-M**/KC₈ to give metal fluoride and metal perfluorophenyl products. Moreover, the previously reported [(NN^{TBS})M(THF)_x]₂(μ-C₁₀H₈) (**4-M₂**, M = Sc, x = 0; M = Y or Lu, x = 1)^{63–64, 66} was able to activate C₆F₆ to give the same products.

C₆F₆ is easier to reduce than C₆H₆ because of the substitution of the less electronegative hydrogen atoms by fluorine atoms (Pauling scale, H 2.20, F 3.98).⁷⁴ In the case of C–H bond activation, benzene was used as a solvent initially. Subsequent experiments showed that the reaction could proceed in hexanes with excess benzene (ca. 50 equivalents) but at a slower rate. Since KC₈ is incompatible with neat C₆F₆ (a small scale test resulted in a flash fire in a dinitrogen filled glove-box and left behind a black solid), it is necessary to use C₆F₆ in a low concentration in a compatible solvent to minimize the nonproductive side reaction between KC₈ and C₆F₆. After optimization, we found that using 3 equivalents of KC₈, 5 equivalents of C₆F₆, and diethyl ether (Et₂O) as the solvent led to the best results. Addition of 3 equivalents of KC₈ into a Et₂O solution of pre-dissolved 1 equivalent of **1-Sc** and 5 equivalents of C₆F₆ at room temperature led to no immediate color change. After 2.5 hours of stirring at room temperature (the reaction was monitored by ¹H NMR spectra of aliquots taken at various intervals, Figures S13–S16), the reaction went to completion. The crude product contained [(NN^{TBS})Sc(μ-F)]₂ (**5-Sc₂**) and (NN^{TBS})Sc(C₆F₅)(THF) (**6-Sc**) in a close to equimolar ratio as determined by ¹H NMR spectroscopy (Scheme 2d). Compounds **5-Sc₂** and **6-Sc** were separated based on their solubility properties: **6-Sc** could be extracted into hexanes, while **5-Sc₂** was barely soluble in hexanes and, therefore, could be subsequently extracted into toluene. Analytically pure compounds were obtained after crystallization: **6-Sc** could be isolated from hexanes in a 28% yield and **5-Sc₂** from toluene/hexanes in a 27% yield (yields are

calculated based on 100% **1-M**). Other rare-earth metal complexes, namely yttrium and lutetium, were also able to promote the C–F bond activation of C_6F_6 . When **1-Y** or **1-Lu** was used instead of **1-Sc**, $[(NN^{TBS})Y(\mu-F)(THF)]_2$ (**5-Y₂**) or $[(NN^{TBS})Lu(\mu-F)(THF)]_2$ (**5-Lu₂**) was the only identified product with an isolated yield of 50% or 38%, respectively (Scheme 2e). The absence of $(NN^{TBS})Y(C_6F_5)(THF)$ (**6-Y**) or $(NN^{TBS})Lu(C_6F_5)(THF)$ (**6-Lu**) was attributed to a rapid β -F abstraction reaction. In agreement, a set of two ^{19}F NMR peaks with an AA'BB' pattern was observed in the crude reaction mixture and assigned as the [2+4] cycloaddition product of perfluorobenzynes and cyclopentadiene (Figure S17). Similar products were observed in cases involving the decomposition of lanthanide perfluorophenyl complexes.³⁷

We repeated the reaction using C_6D_6 as a solvent instead of Et_2O in order to monitor it directly by 1H and ^{19}F NMR spectroscopy and to determine whether the C–F bond activation reaction is selective in the presence of C–D bonds. Despite the fact that **1-Sc**/KC₈ activates the C–D bond of C_6D_6 , a C–D activation product was not observed in the presence of C_6F_6 . Instead, **5-Sc₂** and **6-Sc** were the only observed products (Figure S18); no reaction intermediate was identified by 1H and ^{19}F NMR spectroscopy.



Scheme 2. Reductive cleavage of C–H/F bonds: (a, b) of benzene to form **2-M₂** and **3-M** using the **1-M/KC₈** system; (c) of naphthalene from **4-M₂**; (d, e) of perfluorobenzene to form **5-M₂** and **6-M** using the **1-M/KC₈** system; (f) of perfluorobenzene by **4-M₂** (M = Sc, Y, Lu).

The fact that C–F bond activation could proceed without the interference of C–D activation led us to explore whether **4-M₂** could act as a sole reagent to facilitate the activation of C₆F₆ (Scheme 2f). Compounds **4-M₂** are known to undergo intramolecular C–H bond activation of the naphthalene dianionic ligand;⁶⁹ however, when heating a solution of **4-Sc₂** in the presence of excess C₆F₆, we only observed the C–F bond activation products, **5-Sc₂** and **6-Sc** (Figure S19). The absence of C–H bond activation products, **2-Sc₂** and **3-Sc**, is likely a consequence of the following: (1) C–H bond activation of naphthalene in **4-Sc₂** requires a higher temperature (85 °C) than C–F bond activation (50 °C); (2) C₆F₆ is more readily reducible than naphthalene,⁷⁵ so the arene exchange reaction occurs before either C–F or C–H bond activation. In the case of **4-Y₂** or **4-Lu₂**, **5-Y₂** or **5-Lu₂** was the single product identified (Figure S20, S21); an organic fluorine containing byproduct that is probably the cycloaddition product of perfluorobenzene, since it had a similar AA'BB' pattern to the one observed in the reaction of **1-M/KC₈** (M = Y or Lu) and C₆F₆, was also observed (Figure S17). It is noteworthy to mention that a set of three ¹⁹F NMR peaks in a 1:2:2 ratio, similar to the fluorine signals of **6-Sc**, were initially observed in the reaction of **4-Lu₂** and C₆F₆ implying the formation of **6-Lu** (Figure S22); however, those peaks quickly diminished as the reaction progressed. No ¹⁹F NMR signals attributed to **6-Y** could be detected even in the beginning of the reaction of **4-Y₂** and C₆F₆ (Figure S23).

All products, **5-M₂** and **6-Sc** were characterized by X-ray crystallography, elemental analysis, and ¹H, ¹³C, and ¹⁹F NMR spectroscopy. For **5-M₂**, the ¹⁹F chemical shift was observed as a broad singlet at -31.2, -32.8, and -49.0 ppm for the Sc, Y, and Lu complexes, respectively (Figure S3, S9, S12). The ¹⁹F chemical shift of fluoride in [Cp₂Sc(μ-F)]₃ was reported at -66.8 ppm as a singlet,⁷⁶ while the ¹⁹F NMR signal for [LaF(DippForm)₂(THF)] (DippForm is the anion of *N,N'*-bis(2,6-di-*iso*-propylphenyl)formamidine) was observed at +150.2 ppm.⁴⁷ The broad nature of the ¹⁹F signal is probably due to the fast exchange between two bridging fluorides as well as to coupling with the metal ions. Because of the line broadening, we were not able to determine the coupling constant between the ¹⁹F and ⁸⁹Y nuclei. The ¹⁹F NMR spectrum of **6-Sc** (Figure S6) showed three multiplets centered at -119.4, -155.5, and -160.7 ppm in a 2:1:2 ratio, comparable to those of Cp^{*}Yb(C₆F₅)(THF)₃ at -109.8, -162.4, and -162.9 in THF-*d*₈.⁷⁷ The sharp nature of the ¹⁹F NMR signals for **6-Sc** suggested that no coalescence is present at room temperature, implying the absence of an *ortho*-C–F→Ln interaction in solution.^{35, 78}

Single crystals of **5-Sc₂** were grown from a concentrated hexanes solution with a formula of [(NN^{TBS})Sc][[(NN^{TBS})Sc(THF)](μ-F)₂] (Figure 1). Compound **5-Sc₂** crystallized in an asymmetric dinuclear structure with only Sc1 coordinated by a THF molecule. The average Sc–F distance of 2.064(5) Å is within error to that of 2.046(8) Å in

[Cp₂Sc(μ-F)]₃.⁷⁶ The absence of a coordinating THF molecule in the other scandium fragment not only led to a shorter Sc₂–F distance of 2.040(5) Å than the Sc₁–F distance of 2.086(5) Å but also resulted in a significant difference between the two Sc–Fe distances. Furthermore, although the Sc₁–Fe₁ distance of 3.377(1) Å is much longer than the sum of the iron and scandium covalent radii (3.02 Å),⁷⁹ the Sc₂–Fe₂ distance of 2.840(2) Å is about 0.18 Å shorter than the sum of metal covalent radii, indicating a donor-acceptor type interaction between the electron-rich ferrocene backbone and the electrophilic scandium ion.^{62, 80–88} Different metal-iron distances in asymmetric dinuclear compounds were previously observed also in **4-Sc₂**.⁶⁹ The Sc–F–Sc angles are essentially the same, 106.7(2)° and 106.6(2)°, and both are much sharper than the corresponding angle in [Cp₂Sc(μ-F)]₃ at 153.4(5)°.⁷⁶

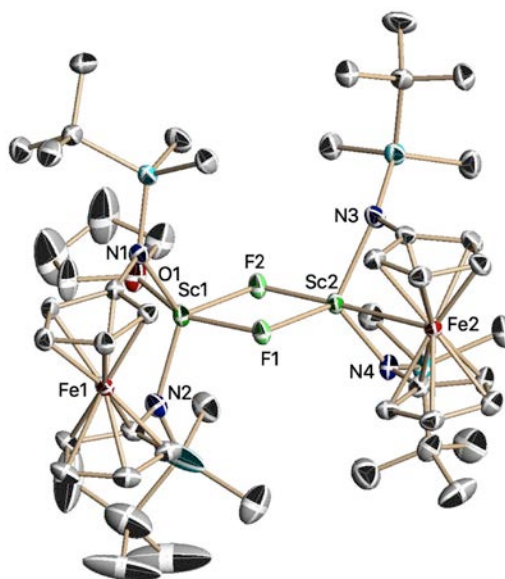


Figure 1. Molecular structure of **5-Sc₂** with thermal ellipsoids drawn at the 50% probability level. Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Sc₁–F₁ 2.090(4), Sc₁–F₂ 2.083(5), Sc₂–F₁ 2.036(5), Sc₂–F₂ 2.045(5), Sc₁–N₁ 2.055(7), Sc₁–N₂ 2.050(8), Sc₁–O₁ 2.200(6), Sc₂–N₃ 2.058(8), Sc₂–N₄ 2.065(8), Sc₁–Sc₂ 3.310(2), Sc₁–Fe₁ 3.377(1), Sc₂–Fe₂ 2.840(2), Sc₁–F₁–Sc₂ 106.7(2), Sc₁–F₂–Sc₂ 106.6(2), N₁–Sc₁–N₂ 127.7(3), N₃–Sc₂–N₄ 114.5(3).

Single crystals of **5-Y₂** and **5-Lu₂** were grown from toluene solutions layered with hexanes with a general formula of [(NN^{TBS})M(μ-F)(THF)]₂ (M = Y and Lu). The Y–F and Lu–F distance is 2.214(4) and 2.182(6) Å in **5-Y₂** and **5-Lu₂**, respectively, and is comparable to the average Sc–F distance in **5-Sc₂** when taking into account the ionic radii of different metal ions. However, the Y–F–Y and Lu–F–Lu angles are 68.8(2)° and 69.6(2)°, significantly sharper than that of Sc–F–Sc. Since the electrophilicity of metal ions is offset by the coordination of one THF molecule per metal ion, the

distances of Y–Fe and Lu–Fe are 3.333(1) and 3.363(2) Å, respectively, comparable to the Sc1–Fe1 distance of 3.377(1) Å and longer than the sum of the covalent radii of 3.22 Å for Y and Fe and 3.19 Å for Lu and Fe.⁷⁹

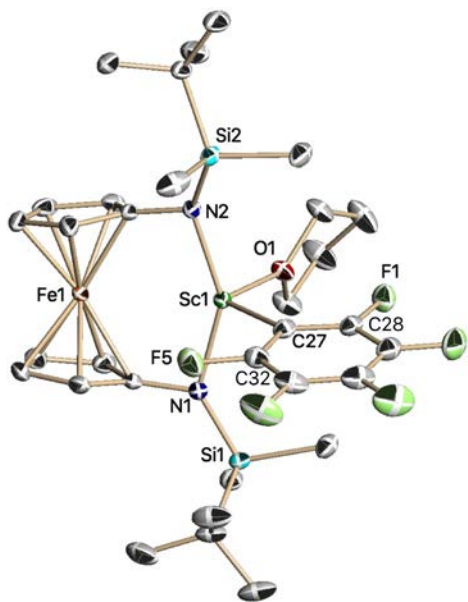
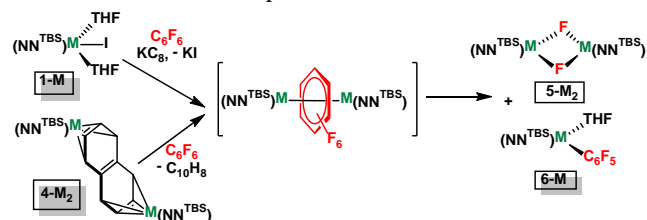


Figure 2. Molecular structure of **6-Sc** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Sc1–C27 2.308(1), Sc1–N1 2.046(1), Sc1–N2 2.059(1), Sc1–O1 2.145(1), Sc1–Fe1 3.027(1), Sc1–F1 3.429(1), Sc1–F5 3.335(1), F1–C28 1.366(2), F5–C32 1.370(2), C27–Sc1–O1 110.94(4), N1–Sc1–N2 148.08(4).

Single crystals of **6-Sc** were grown from a hexanes solution with a formula of (NN^{TBS})Sc(C₆F₅)(THF) (Figure 2). The Sc–C₆F₅ distance is 2.308(1) Å, slightly longer than the Sc–C₆H₄Me-*p* distance of 2.250(3) Å and Sc–C₆H₄Me-*o* distance of 2.247(5) Å, but much shorter than the Yb–C₆F₅ distance in Cp^{*}Yb(C₆F₅)(THF)₃ (2.597(5) Å) or in Yb(C₆F₅)₂(THF)₄ (2.649(3) Å).⁷⁷ However, if accounting for the difference between the effective ionic radii of Sc(III) (0.745 Å) and Yb(II) (1.02 Å),⁸⁹ the Sc–C₆F₅ distance in **6-Sc** is comparable to the Yb–C₆F₅ distance in Cp^{*}Yb(C₆F₅)(THF)₃. The two Sc–F_{ortho} distances are 3.429(1) and 3.335(1) Å, both being much longer than the Yb–F_{ortho} distance of 3.162(4) Å in Cp^{*}Yb(C₆F₅)(THF)₃, precluding any possible agostic interaction between scandium and the ortho fluorine atom. The lack of such an interaction may contribute to the relative stability of **6-Sc**. **6-Sc** slowly decomposed to **5-Sc**₂ and perfluorobenzene [C₆F₄] upon heating (a 78:22 ratio of **5-Sc**₂ and **6-Sc** was observed after 2 d at room temperature based on ¹H NMR spectroscopy, Figure S24). It is known that the C–F→Ln distances do not follow the trend of ionic radii of the lanthanides; for example, in the series of [(DME)₃Ln(SC₆F₅)₂][Hg₂(μ-SC₆F₅)₂(SC₆F₅)₄] (DME = 1,2-dimethoxyethane, Ln = La, Ce, Pr, Nd, Sm, Gd), the C–F→Ln distances remain in the range of 2.80 to 2.82 Å, except for the smaller Gd(III) (2.84 Å), in spite of the gradually decrease of the Ln(III) ionic radii from La to Gd.⁹⁰

In another case, while the C–F→Ln interaction exists in the solid state structure of (py)₄Sm(SC₆F₅)₃ (py = pyridine), no such interaction is present in (py)₄Yb(SC₆F₅)₃ despite the fact that Yb(III) is more Lewis acidic than Sm(III).⁹¹ This discrepancy in the lanthanide series suggests a complicated nature of the C–F→Ln interaction that has been discussed in a recent perspective article.³⁵

Although we were unable to isolate **6-Y** and **6-Lu** from the reaction of **1-M**, C₆F₆, and KC₈, the observation of a small amount of **6-Lu** at the beginning of the reaction between **4-Lu**₂ and C₆F₆ suggested that all three metals (Sc, Y and Lu) should follow a similar mechanism involving the initial formation of equimolar amounts of **5-M**₂ and **6-M**. While **6-Sc** is relatively stable under the reaction conditions, **6-Y** and **6-Lu** immediately decomposed to **5-Y**₂ and **5-Lu**₂ with the concomitant generation of perfluorobenzene. The formation of both **5-M**₂ and **6-M** resembles the reaction of Cp^{*}₂Yb and C₆F₆, in which both [Cp^{*}₂Yb(μ-F)]₂ and Cp^{*}₂Yb(C₆F₅) were identified as products (Scheme 1a).³⁶ However, in the latter, the product ratio was not quantified. Based on the product ratio and literature precedence, we propose that the C–F bond activation described herein might proceed by the following mechanism: hexafluorobenzene was first reduced by KC₈ or **4-M**₂ to form a bimetallic intermediate with a doubly reduced (C₆F₆)²⁻ ring sandwiched between the two metal centers, followed by a cleavage of the C–F bond to form the observed products, **5-M**₂ and **6-M** (Scheme 3). This mechanism is analogous to that proposed for the C–H bond activation of benzene by the **1-M**/KC₈ system.⁶⁹ Since C₆F₆ is easier to reduce than C₆H₆ or C₁₀H₈,⁷⁵ the competition experiment between the C–F bond activation of C₆F₆ and the C–D bond activation of C₆D₆ by **1-Sc**/KC₈ system yielded only C–F bond activation products; the reaction between **4-M**₂ and C₆F₆ resulted in C–F bond activation products as well.



Scheme 3. Proposed mechanism for the C–F bond activation of C₆F₆ by **1-M**/KC₈ or **4-M**₂.

Conclusions

Rare-earth metal iodides supported by a ferrocene diamide ligand were capable to activate the strong aromatic C–F bond of hexafluorobenzene in the presence of the reducing agent potassium graphite. Equimolar formation of scandium fluoride and scandium perfluorophenyl complexes echoed our previous report on bimetallic cleavage of aromatic C–H bonds. Moreover, well-defined inverse sandwich rare-earth metal naphthalene complexes can also activate hexafluorobenzene to form the same products. The C–F bond activation described here complements previous literature reports of lanthanide facilitated C–F

bond activation and may shine light on future developments of stoichiometric and catalytic C-F bond transformations mediated by rare-earth metals.

Experimental details

General Considerations: All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun nitrogen glove box unless otherwise specified. Solvents, including toluene, hexanes, diethyl ether (Et₂O), tetrahydrofuran (THF), and dichloromethane, were purified using a two-column solid-state purification system by the method of Grubbs⁹² and transferred to the glove box without exposure to air. *n*-Pentane was distilled over calcium hydride under dinitrogen atmosphere. Methanol was distilled over calcium oxide under a dinitrogen atmosphere. All solvents were stored on activated molecular sieves for at least a day prior to use. NMR solvents, benzene-*d*₆, were obtained from Cambridge Isotope Laboratories, degassed three times, and stored over activated molecular sieves for one week prior to use. Rare-earth metal oxides (scandium, yttrium, and lutetium) were purchased from Stanford Materials Corporation, 4 Meadowpoint, Aliso Viejo, CA 92656, and used as received. Trimethylsilyl iodide (Me₃SiI) was purchased from Alfa Aesar, directly brought into a glove box, and stored over activated molecular sieves in a -35 °C freezer prior to use. Hexafluorobenzene was purchased from Sigma-Aldrich, degassed three times, and stored over activated molecular sieves for one week prior to use. KO^tBu was purchased from Strem Chemicals Inc. and directly brought into a glove box without exposure to air or moisture. Potassium graphite (KC₈) was synthesized by Professor Richard B. Kaner's group (UCLA) and received as a gift. Other solid chemicals were purified by crystallization; while liquid chemicals were degassed three times and stored over activated molecular sieves for one week prior to use. (NN^{TBS})MI(THF)₂, **1-M** (M = Sc, Y and Lu) and [(NN^{TBS})M(THF)_x]₂(μ-C₁₀H₈) (**4-M**₂, M = Sc, x = 0; M = Y or Lu, x = 1) were synthesized according to published protocols.^{63-64, 66, 93-94} Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AV300, Bruker DRX500, Bruker AV500, or Bruker AV600 spectrometers at 25 °C in C₆D₆ unless otherwise specified. Chemical shifts are reported with respect to internal solvent (C₆D₆ at 7.16 ppm). CHN analyses were performed in house on a CE-440 Elemental Analyzer manufactured by EXETER ANALYTICAL, INC. *Note:* The perfluorophenyl complex **6-Sc** could be potentially shock sensitive. However, we did not observe any instability for the preparative scale reported herein.

C-F Bond Activation of Hexafluorobenzene (C₆F₆) by the **1-M**/KC₈ (M = Sc, Y and Lu) system and product characterization

M = Sc: 1 equiv **1-Sc** (0.203 g, 0.268 mmol) and 5 equiv C₆F₆ (0.248 g, 1.333 mmol) were weighed in a 20 mL scintillation vial and dissolved in Et₂O (6 mL). 3 equiv KC₈ (0.107 g, 0.788 mmol) was added to the solution and the reaction

mixture was stirred at 25 °C. Aliquots were taken at 0.5, 1.0, 2.0, and 2.5 h and the reaction was monitored by ¹H NMR spectroscopy. The reaction went to completion after stirring at 25 °C for 2.5 h. The solution was filtered through Celite to remove graphite and potassium iodide (KI). The volatiles were removed under reduced pressure. The resulting yellow solid was dispersed in 10 mL hexanes, followed by vacuum for removing the volatiles. This process was repeated one more time. Then the solid was extracted into hexanes and toluene. After removing the volatiles, the hexanes extraction weighed 0.0950 g and contained mostly **6-Sc**, while the toluene extraction weighed 0.0570 g and contained purely **5-Sc**₂. Analytically pure compounds were obtained after crystallization: **6-Sc** from hexanes, yield: 0.0535 g, 27.5%; **5-Sc**₂ from toluene/hexanes, yield: 0.0372 g, 27.4%. Single crystals of **6-Sc** were grown from a hexanes solution. Single crystals of **5-Sc**₂ were grown from a concentrated hexanes solution with an extra THF molecule coordinating to one of the scandium centers. Characterization for **6-Sc**: ¹H NMR (500 MHz, C₆D₆, 25 °C) δ, ppm: 4.11, 4.00, 3.56, and 2.90 (s, 2H each, all belong to CH on Cp), 4.00 (m, 4H, OCH₂CH₂), 1.26 (m, 4H, OCH₂CH₂), 0.88 (s, 18H, C(CH₃)₃), and 0.09 and 0.04 (s, 6H each, SiCH₃); ¹³C NMR (126 MHz, C₆D₆, 25 °C) δ, ppm: multiplets from 147 to 135 (CF on C₆F₅, the *ipso*-C is missing due to complicated ¹³C-¹⁹F coupling), 103.2 (CN), 73.2, 70.5, 68.6, and 67.5 (CH on Cp and OCH₂CH₂), 27.4 (C(CH₃)₃), 24.9 (OCH₂CH₂), 20.2 (C(CH₃)₃), and -2.8 (SiCH₃); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C) δ, ppm: -119.4 (m, 2F, *ortho*-CF), -155.5 (t, ³J_{FF} = 19.7 Hz, 1F, *para*-CF), and -160.7 (m, 2F, *meta*-CF). Anal. (%): Calcd. for C₃₂H₄₆N₂F₅FeOScSi₂, M_w = 726.696: C, 52.89; H, 6.38; N, 3.85. Found: C, 53.35; H, 6.60; N, 3.48. Characterization for **5-Sc**₂: ¹H NMR (500 MHz, C₆D₆, 25 °C) δ, ppm: 4.18, 4.01, 3.98, and 3.74 (s, 2H each, all belong to CH on Cp), 1.07 (s, 18H, C(CH₃)₃), and 0.42 and 0.36 (s, 6H each, SiCH₃); ¹³C NMR (126 MHz, C₆D₆, 25 °C) δ, ppm: 107.6 (CN), 71.4, 70.2, 68.7, and 63.5 (CH on Cp), 27.6 (C(CH₃)₃), 19.8 (C(CH₃)₃), and -1.3 and -3.1 (SiCH₃); ¹⁹F NMR (470 MHz, C₆D₆, 25 °C) δ, ppm: -31.2 (br s, *fluoride*). Anal. (%): Calcd. for C₄₄H₇₆N₄Fe₂F₂Sc₂Si₄, M_w = 1013.062: C, 52.17; H, 7.56; N, 5.53. Found: C, 50.92; H, 7.08; N, 4.96.

M = Y: Scale: **1-Y** (0.305 g, 0.380 mmol), 5 equiv C₆F₆ (0.357 g, 1.92 mmol), and 3.5 equiv KC₈ (0.185 g, 1.37 mmol) in Et₂O (10 mL). The reaction was monitored by taking aliquots (checked by ¹H NMR spectroscopy) and went to completion after stirring at 25 °C for 1 h 40 min. The ¹H NMR of all the aliquots and the crude product (after filtering through Celite and removing volatiles) showed a single product, **5-Y**₂. The crude product was washed with hexanes to yield a yellow solid that was collected on a medium frit, yield: 0.118 g, 49.7%. Single crystals of **5-Y**₂ were grown from a toluene solution layered with hexanes. Characterization of **5-Y**₂: ¹H NMR (500 MHz, C₆D₆, 25 °C) δ, ppm: 4.02 and 3.74 (br s, 4H each, both belong to CH on Cp), 4.02 (br s, 4H, OCH₂CH₂), 1.45 (m, 4H, OCH₂CH₂), 1.07 (s, 18H, C(CH₃)₃), and 0.32 (s, 12H each, SiCH₃); ¹³C NMR (126 MHz, C₆D₆, 25 °C) δ, ppm: 106.7 (CN), 70.4 and 66.7 (CH on Cp), 66.7 (OCH₂CH₂), 28.1 (C(CH₃)₃), 25.4 (OCH₂CH₂), 20.4 (C(CH₃)₃), and -1.4 (SiCH₃); ¹⁹F NMR (282 MHz, C₆D₆, 25

°C) δ , ppm: -32.8 (br s, fluoride). Anal. (%): Calcd. for $C_{52}H_{92}N_4Fe_2F_2O_2Si_4Y_2$, $M_w = 1245.176$: C, 50.16; H, 7.45; N, 4.50. Found: C, 50.27; H, 7.55; N, 4.32.

M = Lu: Scale: **1-Lu** (0.304 g, 0.342 mmol), 5 equiv C_6F_6 (0.344 g, 1.85 mmol), and 3.5 equiv KC_8 (0.170 g, 1.26 mmol) in Et_2O (10 mL). The reaction was monitored by taking aliquots (checked by 1H NMR spectroscopy) and went to completion after stirring at 25 °C for 1 h 40 min. The 1H NMR of all the aliquots and the crude product (after filtering through Celite and removing volatiles) showed a single product, **5-Lu₂**. The crude product was washed with hexanes to yield a yellow solid that was collected on a medium frit, yield: 0.0920 g, 38.0%. Single crystals of **5-Lu₂** were grown from a toluene solution layered with hexanes. Characterization of **5-Lu₂**: 1H NMR (500 MHz, C_6D_6 , 25 °C) δ , ppm: 3.99 and 3.84 (br s, 4H each, both belong to CH on Cp), 3.99 (br s, 4H, OCH_2CH_2), 1.43 (m, 4H, OCH_2CH_2), 1.07 (s, 18H, $C(CH_3)_3$), and 0.34 (s, 12H each, $SiCH_3$); ^{13}C NMR (126 MHz, C_6D_6 , 25 °C) δ , ppm: 105.9 (CN), 70.5 and 67.0 (CH on Cp), 67.0 (OCH_2CH_2), 28.1 ($C(CH_3)_3$), 25.5 (OCH_2CH_2), 20.5 ($C(CH_3)_3$), and -1.4 ($SiCH_3$); ^{19}F NMR (282 MHz, C_6D_6 , 25 °C) δ , ppm: -49.0 (br s, fluoride). Anal. (%): Calcd. for $C_{52}H_{92}N_4Fe_2F_2Lu_2O_2Si_4$, $M_w = 1417.298$: C, 44.07; H, 6.54; N, 3.95. Found: C, 43.81; H, 6.46; N, 3.77.

C-F Bond Activation of Hexafluorobenzene (C_6F_6) by M_2 -naph (M = Sc, Y and Lu)

Sc: **4-Sc₂** (0.012 g, 0.011 mmol) and C_6F_6 (0.0020 g as a stock solution in C_6D_6 , 0.011 mmol) were dissolved in C_6D_6 (0.7 mL). The reaction was monitored by 1H and ^{19}F NMR spectroscopy. The reaction went to completion (no **4-Sc₂** left) after heating at 50 °C (1 d), 70 °C (3 d), and 85 °C (10 d). Upon the consumption of **4-Sc₂**, **5-Sc₂** and **6-Sc** were gradually formed in a 1:1 ratio initially; the ratio increased due to the decomposition of **6-Sc** into **5-Sc₂** and the benzyne (C_6F_4) derived by-product as implied by 1H and ^{19}F NMR spectroscopy.

Y: **4-Y₂** (0.009 g, 0.007 mmol) and C_6F_6 (0.0013 g as a stock solution in C_6D_6 , 0.007 mmol) were dissolved in C_6D_6 (0.7 mL). The reaction was monitored by 1H and ^{19}F NMR spectroscopy. The reaction went to completion (no **4-Y₂** left) after room temperature (1 d) and then heating at 50 °C (2 d). Upon the consumption of **4-Y₂**, **5-Y₂** and the benzyne (C_6F_4) derived by-product were formed gradually as implied by 1H and ^{19}F NMR spectroscopy.

Lu: **4-Lu₂** (0.010 g, 0.007 mmol) and C_6F_6 (0.0013 g as a stock solution in C_6D_6 , 0.007 mmol) were dissolved in C_6D_6 (0.7 mL). The reaction was monitored by 1H and ^{19}F NMR spectroscopy. The reaction went to completion (no **4-Lu₂** left) after room temperature (1 h) and then heating at 50 °C (1 d). Upon the consumption of **4-Lu₂**, **5-Lu₂** and **6-Lu** were initially formed; however, **6-Lu** quickly decomposed to **5-Lu₂** and the benzyne (C_6F_4) derived by-product as implied by 1H and ^{19}F NMR spectroscopy.

Competition Experiment between C-F Bond Activation of C_6F_6 and C-D Bond Activation of C_6D_6 by the 1-Sc/ KC_8 system

In a J-Young tube (NMR tube with a Teflon screw cap), **1-Sc** (0.021 g, 0.028 mmol) and 8 equiv C_6F_6 (0.040 g, 0.306

mmol) were dissolved in C_6D_6 (0.5 mL, 5.611 mmol). 5 equiv KC_8 (0.023 g, 0.170 mmol) was added to the solution. The reaction was monitored by 1H NMR spectroscopy. **5-Sc₂** and **6-Sc** were observed as the products, while neither **2-Sc₂-d₂** nor **3-Sc-d₂** was observed as implied by 1H and ^{19}F NMR spectra.

X-ray Crystallography. X-ray quality crystals were obtained from various concentrated solutions placed in a -40 °C freezer in the glovebox unless otherwise specified. Inside the glovebox, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker SMART 1000 single crystal X-ray diffractometer using Mo $K\alpha$ radiation and a SMART APEX CCD detector. The data was reduced by SAINTPLUS and an empirical absorption correction was applied using the package SADABS. The structure was solved and refined using SHELXTL (Bruker 1998, SMART, SAINT, XPREP AND SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA). Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the distances and angles and with anisotropic displacement parameters are listed in the cif.

ASSOCIATED CONTENT

Supporting Information

Experimental details, NMR spectra and X-ray crystallographic data are included in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* pld@chem.ucla.edu

Notes

The authors declare no conflict of interest.

ACKNOWLEDGMENT

This work was supported by the NSF (CAREER Grant 0847735 and 1362999 to PLD and CHE-1048804 for NMR spectroscopy). We thank Professor Richard B. Kaner's group (UCLA) for samples of KC_8 .

REFERENCES

1. Smart, B. E., In *Organofluorine Chemistry: Principles and Commercial Applications*, Banks, R. E.; Smart, B. E.; Tatlow, J. C., Eds. Plenum Press: New York, 1994; p 57.
2. Hiyama, T., Ed., *Organofluorine Compounds Chemistry and Applications*. Springer: New York, 2000.
3. O'Hagan, D., *Chem. Soc. Rev.* **2008**, 37 (2), 308-319.
4. Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V., *Chem. Soc. Rev.* **2008**, 37 (2), 320-330.
5. Riess, J. G.; Le Blanc, M., *Angew. Chem. Int. Ed. Engl.* **1978**, 17 (9), 621-634.
6. Horváth, I. T.; Rábai, J., *Science* **1994**, 266 (5182), 72-75.
7. Gerstenberger, M. R. C.; Haas, A., *Angew. Chem. Int. Ed. Engl.* **1981**, 20 (8), 647-667.
8. J. Adams, D.; H. Clark, J., *Chem. Soc. Rev.* **1999**, 28 (4), 225-231.

9. Hollingworth, C.; Gouverneur, V., CHAPTER 7 Strategies Towards Challenging Fluorination Reactions. In *C-H and C-X Bond Functionalization: Transition Metal Mediation*, The Royal Society of Chemistry: 2013; pp 193-261.
10. Liang, T.; Neumann, C. N.; Ritter, T., *Angew. Chem. Int. Ed.* **2013**, *52* (32), 8214-8264.
11. Campbell, M. G.; Ritter, T., *Chem. Rev.* **2015**, *115* (2), 612-633.
12. Shine, K. P.; Sturges, W. T., *Science* **2007**, *315* (5820), 1804-1805.
13. Perutz, R. N., *Science* **2008**, *321* (5893), 1168-1169.
14. Blanksby, S. J.; Ellison, G. B., *Acc. Chem. Res.* **2003**, *36* (4), 255-263.
15. Burdeniuc, J.; Jedicka, B.; Crabtree, R. H., *Chem. Ber.* **1997**, *130* (2), 145-154.
16. Braun, T.; Perutz, R. N., In *Comprehensive Organometallic Chemistry III*, Crabtree, R. H.; Mingos, D. M. P., Eds. Elsevier: Oxford, U.K., 2007.
17. Amii, H.; Uneyama, K., *Chem. Rev.* **2009**, *109* (5), 2119-2183.
18. Sun, A. D.; Love, J. A., *Dalton Trans.* **2010**, *39* (43), 10362-10374.
19. Clot, E.; Eisenstein, O.; Jasim, N.; Macgregor, S. A.; McGrady, J. E.; Perutz, R. N., *Acc. Chem. Res.* **2011**, *44* (5), 333-348.
20. Klahn, M.; Rosenthal, U., *Organometallics* **2012**, *31* (4), 1235-1244.
21. Kuehnle, M. F.; Lentz, D.; Braun, T., *Angew. Chem. Int. Ed.* **2013**, *52* (12), 3328-3348.
22. Ahrens, T.; Kohlmann, J.; Ahrens, M.; Braun, T., *Chem. Rev.* **2015**, *115* (2), 931-972.
23. Scott, V. J.; Çelenligil-Çetin, R.; Ozerov, O. V., *J. Am. Chem. Soc.* **2005**, *127* (9), 2852-2853.
24. Yow, S.; Gates, S. J.; White, A. J. P.; Crimmin, M. R., *Angew. Chem. Int. Ed.* **2012**, *51* (50), 12559-12563.
25. Aizenberg, M.; Milstein, D., *Science* **1994**, *265* (5170), 359-361.
26. Aizenberg, M.; Milstein, D., *J. Am. Chem. Soc.* **1995**, *117* (33), 8674-8675.
27. Chen, Z.; He, C.-Y.; Yin, Z.; Chen, L.; He, Y.; Zhang, X., *Angew. Chem. Int. Ed.* **2013**, *52* (22), 5813-5817.
28. Pearson, R. G., *J. Am. Chem. Soc.* **1963**, *85* (22), 3533-3539.
29. Pankratz, L. B., *Thermodynamic Properties of Halides: Bulletin 674*. Bureau of Mines: 1984.
30. Smart, B. E., In *Chemistry of Functional Groups*, Patai, S.; Rappoport, Z., Eds. Wiley: New York, 1983.
31. San Filippo, J.; Nuzzo, R. G.; Romano, L. J., *J. Am. Chem. Soc.* **1975**, *97* (9), 2546-2546.
32. Yin, H.; Lewis, A. J.; Carroll, P.; Schelter, E. J., *Inorg. Chem.* **2013**, *52* (14), 8234-8243.
33. Yin, H.; Lewis, A. J.; Williams, U. J.; Carroll, P. J.; Schelter, E. J., *Chem. Sci.* **2013**, *4* (2), 798-805.
34. Alvarez, S.; Menjón, B., *Angew. Chem. Int. Ed.* **2014**, *53* (11), 2810-2811.
35. Yin, H.; Zabula, A. V.; Schelter, E. J., *Dalton Trans.* **2016**, *45* (15), 6313-6323.
36. Burns, C. J.; Andersen, R. A., *Journal of the Chemical Society, Chemical Communications* **1989**, (2), 136-137.
37. Maron, L.; Werkema, E. L.; Perrin, L.; Eisenstein, O.; Andersen, R. A., *J. Am. Chem. Soc.* **2005**, *127* (1), 279-292.
38. Werkema, E. L.; Messines, E.; Perrin, L.; Maron, L.; Eisenstein, O.; Andersen, R. A., *J. Am. Chem. Soc.* **2005**, *127* (21), 7781-7795.
39. Träff, A. M.; Janjetovic, M.; Ta, L.; Hilmersson, G., *Angew. Chem. Int. Ed.* **2013**, *52* (46), 12073-12076.
40. Deacon, G.; Mackinnon, P.; Tuong, T., *Aust. J. Chem.* **1983**, *36* (1), 43-53.
41. Deacon, G. B.; MacKinnon, P. I., *Tetrahedron Lett.* **1984**, *25* (7), 783-784.
42. Watson, P. L.; Tulip, T. H.; Williams, I., *Organometallics* **1990**, *9* (7), 1999-2009.
43. Heinemann, C.; Goldberg, N.; Tornieporth-Oetting, I. C.; Klapötke, T. M.; Schwarz, H., *Angew. Chem. Int. Ed. Engl.* **1995**, *34* (2), 213-217.
44. Cornehl, H. H.; Hornung, G.; Schwarz, H., *J. Am. Chem. Soc.* **1996**, *118* (41), 9960-9965.
45. Deacon, G. B.; Harris, S. C.; Meyer, G.; Stellfeldt, D.; Wilkinson, D. L.; Zelesny, G., *J. Organomet. Chem.* **1998**, *552* (1-2), 165-170.
46. Deacon, G. B.; Meyer, G.; Stellfeldt, D., *Eur. J. Inorg. Chem.* **2000**, *2000* (5), 1061-1071.
47. Cole, M. L.; Deacon, G. B.; Junk, P. C.; Konstas, K., *Chem. Commun.* **2005**, (12), 1581-1583.
48. Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Konstas, K.; Wang, J., *Chem. Eur. J.* **2007**, *13* (29), 8092-8110.
49. Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Wang, J., *Chem. Eur. J.* **2009**, *15* (13), 3082-3092.
50. Werkema, E. L.; Andersen, R. A., *J. Am. Chem. Soc.* **2008**, *130* (22), 7153-7165.
51. Werkema, E. L.; Andersen, R. A.; Maron, L.; Eisenstein, O., *Dalton Trans.* **2010**, *39* (29), 6648-6660.
52. Janjetovic, M.; Träff, A. M.; Ankner, T.; Wettergren, J.; Hilmersson, G., *Chem. Commun.* **2013**, *49* (18), 1826-1828.
53. Janjetovic, M.; Träff, A. M.; Hilmersson, G., *Chem. Eur. J.* **2015**, *21* (9), 3772-3777.
54. Weydert, M.; Andersen, R. A.; Bergman, R. G., *J. Am. Chem. Soc.* **1993**, *115* (19), 8837-8838.
55. Duhović, S.; Monreal, M. J.; Diaconescu, P. L., *J. Organomet. Chem.* **2010**, *695* (25), 2822-2826.
56. Duhović, S.; Monreal, M. J.; Diaconescu, P. L., *Inorg. Chem.* **2010**, *49* (15), 7165-7169.
57. Huang, W.; Carver, C. T.; Diaconescu, P. L., *Inorg. Chem.* **2011**, *50* (3), 978-984.
58. Wong, A. W.; Miller, K. L.; Diaconescu, P. L., *Dalton Trans.* **2010**, *39* (29 (New Horizons in Organo-f-element Chemistry)), 6726-6731.
59. Williams, B. N.; Huang, W.; Miller, K. L.; Diaconescu, P. L., *Inorg. Chem.* **2010**, *49* (24), 11493-11498.
60. Miller, K. L.; Carver, C. T.; Williams, B. N.; Diaconescu, P. L., *Organometallics* **2010**, *29* (10), 2272-2281.
61. Carver, C. T.; Diaconescu, P. L., *J. Alloys Compd.* **2009**, *488* (2), 518-523.
62. Huang, W.; Diaconescu, P. L., *Inorg. Chem.* **2016**, DOI: 10.1021/acs.inorgchem.6b01118.
63. Huang, W.; Khan, S. I.; Diaconescu, P. L., *J. Am. Chem. Soc.* **2011**, *133* (27), 10410-10413.
64. Huang, W.; Diaconescu, P. L., *Chem. Commun.* **2012**, *48* (16), 2216-2218.
65. Huang, W.; Dulong, F.; Wu, T.; Khan, S. I.; Miller, J. T.; Cantat, T.; Diaconescu, P. L., *Nat. Commun.* **2013**, *4*, 1448.
66. Huang, W.; Diaconescu, P. L., *Eur. J. Inorg. Chem.* **2013**, *2013* (22-23), 4090-4096.
67. Huang, W.; Abukhalil, P. M.; Khan, S. I.; Diaconescu, P. L., *Chem. Commun.* **2014**, *50* (40), 5221-5223.
68. Huang, W.; Diaconescu, P. L., Chapter 266 - Rare Earth Arene-Bridged Complexes Obtained by Reduction of Organometallic Precursors. In *Handbook on the Physics and Chemistry of Rare Earths*, Jean-Claude, G. B.; Vitalij, K. P., Eds. Elsevier: 2014; Vol. Volume 45, pp 261-329.
69. Huang, W.; Dulong, F.; Khan, S. I.; Cantat, T.; Diaconescu, P. L., *J. Am. Chem. Soc.* **2014**, *136* (50), 17410-17413.
70. Huang, W.; Diaconescu, P. L., *Dalton Trans.* **2015**, *44* (35), 15360-15371.
71. Huang, W.; Le Roy, J. J.; Khan, S. I.; Ungur, L.; Murugesu, M.; Diaconescu, P. L., *Inorg. Chem.* **2015**, *54* (5), 2374-2382.
72. Balcells, D.; Clot, E.; Eisenstein, O., *Chem. Rev.* **2010**, *110* (2), 749-823.
73. Huang, W.; Diaconescu, P. L., Chapter Two - CH Bond Activation of Hydrocarbons Mediated by Rare-Earth Metals and Actinides: Beyond σ -Bond Metathesis and 1,2-Addition. In *Advances in Organometallic Chemistry*, Pedro, J. P., Ed. Academic Press: 2015; Vol. Volume 64, pp 41-75.
74. Pauling, L., *J. Am. Chem. Soc.* **1932**, *54* (9), 3570-3582.
75. Marsella, J. A.; Gilicinski, A. G.; Coughlin, A. M.; Pez, G. P., *J. Org. Chem.* **1992**, *57* (10), 2856-2860.
76. Bottomley, F.; Paez, D. E.; White, P. S., *J. Organomet. Chem.* **1985**, *291* (1), 35-41.
77. Deacon, G. B.; Forsyth, C. M., *Organometallics* **2003**, *22* (7), 1349-1352.
78. Takemura, H.; Nakashima, S.; Kon, N.; Yasutake, M.; Shinmyozu, T.; Inazu, T., *J. Am. Chem. Soc.* **2001**, *123* (38), 9293-9298.
79. Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reyes, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S., *Dalton Trans.* **2008**, (21), 2832-2838.
80. Diaconescu, P. L., *Comment. Inorg. Chem.* **2010**, *31* (5-6), 196-241.
81. Diaconescu, P. L., *Acc. Chem. Res.* **2010**, *43* (10), 1352-1363.
82. Green, A. G.; Kiesz, M. D.; Oria, J. V.; Elliott, A. G.; Buechler, A. K.; Hohenberger, J.; Meyer, K.; Zink, J. I.; Diaconescu, P. L., *Inorg. Chem.* **2013**, *52* (9), 5603-5610.
83. Blass, B. L.; Hernández Sánchez, R.; Decker, V. A.; Robinson, M. J.; Piro, N. A.; Kassel, W. S.; Diaconescu, P. L.; Nataro, C., *Organometallics* **2016**, *35* (4), 462-470.
84. Gramigna, K. M.; Oria, J. V.; Mandell, C. L.; Tiedemann, M. A.; Dougherty, W. G.; Piro, N. A.; Kassel, W. S.; Chan, B. C.; Diaconescu, P.

L.; Nataro, C., *Organometallics* **2013**, *32* (20 (SI: Ferrocene: Beauty and Function)), 5966–5979.
 85. Duhović, S.; Oria, J. V.; Odoh, S. O.; Schreckenbach, G.; Batista, E. R.; Diaconescu, P. L., *Organometallics* **2013**, *32* (20 (SI: Ferrocene: Beauty and Function)), 6012–6021.
 86. Monreal, M. J.; Diaconescu, P. L., *Organometallics* **2008**, *27*, 1702–1706.
 87. Carver, C. T.; Monreal, M. J.; Diaconescu, P. L., *Organometallics* **2008**, *27*, 363–370.
 88. Monreal, M. J.; Carver, C. T.; Diaconescu, P. L., *Inorg. Chem.* **2007**, *46*, 7226–7228.

89. Shannon, R., *Acta Crystallogr. Sect. A* **1976**, *32* (5), 751–767.
 90. Banerjee, S.; Emge, T. J.; Brennan, J. G., *Inorg. Chem.* **2004**, *43* (20), 6307–6312.
 91. Melman, J. H.; Rohde, C.; Emge, T. J.; Brennan, J. G., *Inorg. Chem.* **2002**, *41* (1), 28–33.
 92. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, *15* (5), 1518–1520.
 93. Huang, W.; Upton, B. M.; Khan, S. I.; Diaconescu, P. L., *Organometallics* **2013**, *32* (5), 1379–1386.
 94. Huang, W.; Brosmer, J. L.; Diaconescu, P. L., *New. J. Chem.* **2015**, *39* (10), 7696–7702.

TOC Graphic

