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Authors

Huang, Wenliang
Diaconescu, Paula L

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C-H Bond Activation of Hydrocarbons Mediated by Rare-Earth Metals and Actinides: Beyond σ-Bond Metathesis and 1,2-Addition

Wenliang Huang and Paula L. Diaconescu*
Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles
E Young Drive East, Los Angeles, CA 90095

Abstract: The present review discusses C-H bond activation of hydrocarbons mediated by rare-earth metal complexes with an emphasis on type of mechanisms. The review is organized as follows: in the first part, C-H bond activations mediated by rare-earth metals and actinides following traditional reaction pathways, such as σ-bond metathesis and 1,2-addition, are summarized; in the second part, non-traditional C-H bond activation examples are discussed in detail in order to understand the underlying mechanisms. The scope of the review is limited to rare-earth metals and actinides, but, in some cases, closely related reactivity of group 4 metals will be included for comparison. The purpose of the review is not only to provide a brief overview of C-H bond activation by *f*-elements but also to bring to attention unusual C-H bond cleavage reactivity following mechanisms different than σ-bond metathesis and 1,2-addition.

1. Introduction

C-H activation has been one of the most important research areas in chemistry in the last several decades because it holds the key to some of the most promising processes for an energy-sustainable and carbon-neutral human future, such as the selective oxidation of methane to methanol[1, 2] and alkane metathesis to produce higher *n*-alkanes as transportation fuels from the abundant lower linear alkanes.[3, 4] The fact that the C-H bond is ubiquitous in organic molecules is both a blessing and a curse. On the pro side, it provides an entry to utilize abundant hydrocarbon feedstock efficiently in order to produce fine chemicals and to enable late-stage synthetic methodology in medicinal chemistry. On the con side, it demands high chemo- and stereoselectivity to become useful in introducing a certain functional group at a specific position. Because of its high bond dissociation energy and lack of polarity, the C-H bond of hydrocarbons is amongst the most inert chemical bonds. The strong and non-polar nature of C-H bonds makes their selective C-H activation one of the most challenging tasks that chemists face today.[1, 5-8]

Through evolution over billions of years, nature has come up with its own ways to functionalize C-H bonds selectively by using specific enzymes. Cytochrome P450 oxidases are a well-known family of enzymes that can activate C-H bonds of organic substrates.[9] Furthermore, methane monooxygenase can even activate the arguably most difficult substrate, methane, at ambient conditions.[10] On the other hand, the first example of a metal mediated C-H bond activation was reported by Chatt and Davidson in 1965: arenes, such as benzene and naphthalene, were found to form Ru(0) complexes and then undergo C-H activation to give a Ru(II) hydride/alkyl product.[11] Notable early milestones in metal catalyzed C-H activation include the discovery of methane exchange at Cp^*_2LuMe ($Cp^* = \eta^5\text{-}C_5Me_5$) (σ-bond metathesis mechanism, Chart 1a)[12] and the reactivity of $Cp^*Ir(PMe_3)$ toward various hydrocarbons (oxidative addition mechanism, Chart 1b).[5] New mechanisms, such as 1,2-addition (Chart 1c)[13, 14] and σ-complex assisted mechanism (σ-CAM) metathesis (Chart 1d),[15] were unveiled later, together

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with the successful catalytic applications in C-H bond functionalization using either early or late transition metal complexes.[16-18] In order to discover new types of reactivity and design efficient and selective catalysts for existing transformations, it is imperative to understand reaction mechanisms by both experimental[19-21] and theoretical means.[7, 15, 22, 23]
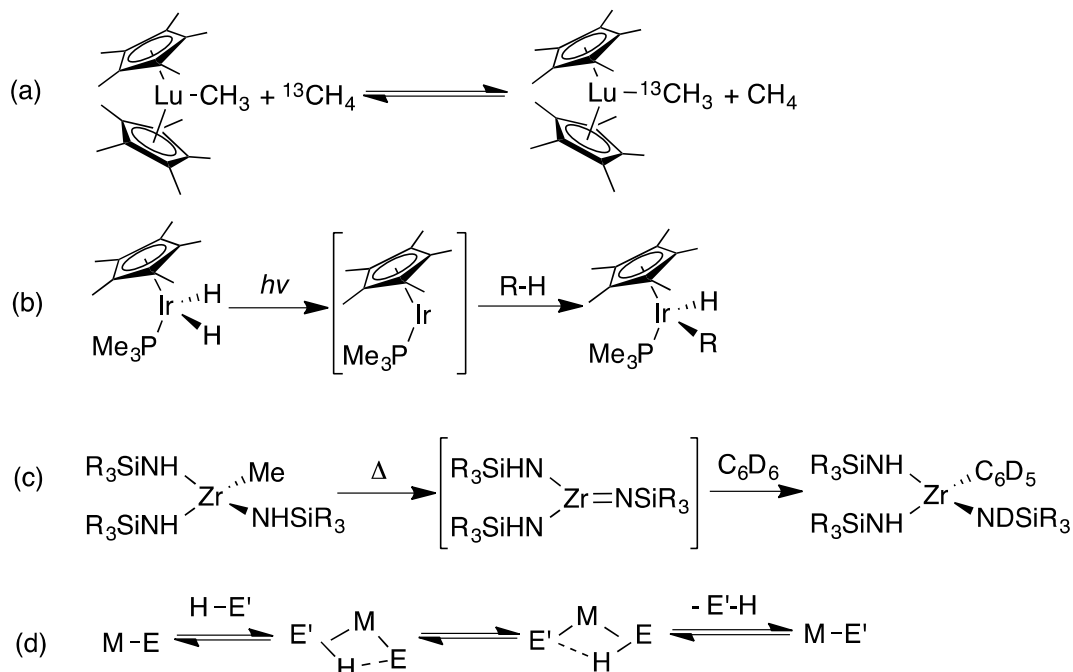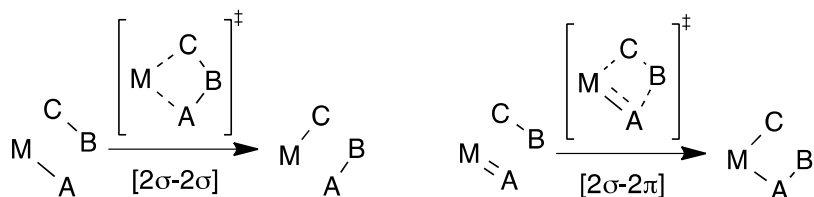
(a) $Lu-CH_3 + {}^{13}CH_4 \rightleftharpoons Lu-{}^{13}CH_3 + CH_4$

(b)

(c) R_3SiNH, R_3SiNH Zr Me, $NHSiR_3$ $\xrightarrow{\Delta}$ $\left[R_3SiHN, R_3SiHN \ Zr=NSiR_3 \right]$ $\xrightarrow{C_6D_6}$ $R_3SiNH, R_3SiNH \ Zr \ C_6D_5, NDSiR_3$

(d) $M-E \rightleftharpoons$ E' $\overset{H-E'}{\diamond}$ $\overset{M}{\diamond}$ E $\rightleftharpoons$ E' $\overset{M}{\diamond}$ E $\overset{-E'-H}{\rightleftharpoons}$ $M-E'$

Chart 1. Four representative mechanisms for C-H bond activation: (a) σ-bond metathesis; (b) oxidative addition; (c) 1,2-addition; (d) σ-CAM metathesis.

Scheme 1. [2σ-2σ] σ-Bond metathesis *vs.* [2σ-2π] 1,2-addition.

Metals with a d^0f^n configuration, group 3 metals, lanthanides, and actinides, are usually classified as *f*-elements. Because they are highly electropositive, they form polarized bonds with *p*-block elements, including carbon and nitrogen. So far, two reaction mechanisms have been established for d^0f^n metals: σ-bond metathesis, a [2σ-2σ] process,[12] and 1,2-addition, a [2σ-2π] process (2σ stands for the two electrons involved in the transition state that come from a σ bond and 2π indicates the two electrons involved in the transition state that come from a π bond) (Scheme 1).[13, 14] Oxidative addition, another type of reaction mechanism that is common for late transition metals,[5, 7] is absent from the chemistry of rare-earth metals or actinides. This is partly because of the lack of valence electrons, i.e., a d^0 electronic configuration; however, even for uranium, which has multiple accessible oxidation states, no genuine oxidative addition reactivity has been reported. The subject of C-H bond activation mediated by *f*-elements has been discussed by several recent reviews.[8, 18, 24-27]

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Most examples of C-H bond activation mediated by rare-earth metals and actinides follow a σ-bond metathesis mechanism. This is because these highly electropositive metal centers and the corresponding polarized M-C bonds are poised to cleave the strong and non-polar C-H bond. Recently, 1,2-addition has emerged as an important pathway for C-H bond activation for *f*-block elements, after the successful preparation of intermediates[28-31] or isolated complexes[32-35] containing metal-element multiple bonds. However, some examples of C-H bond activation cannot be explained either by a σ-bond metathesis or a 1,2-addition mechanism. Such unusual reactivity is overlooked in comprehensive reviews and usually grouped with reactions generating similar products. However, an abnormal reactivity may suggest a fundamentally different reaction mechanism that can open up new avenues for C-H bond activation and functionalization. Therefore, the current review will emphasize those examples of C-H bond activation of hydrocarbons that cannot be rationalized by traditional reaction pathways (σ-bond metathesis and 1,2-addition).

The present review is organized in the following way: in the first part, C-H bond activation mediated by rare-earth metals and actinides following traditional reaction pathways is summarized; in the second part, non-traditional C-H bond activation reactivity will be discussed in detail in order to understand the underlying mechanisms. The scope of the review is limited to rare-earth metals and actinides, but, in some cases, closely related reactivity of group 4 metals will be included for comparison. The purpose of the review is to provide not only an overview of C-H bond activation by *f*-elements but also to bring to attention unusual reactivity following mechanisms different than σ-bond metathesis and 1,2-addition.

2. Traditional reaction pathways

In 1965, Chatt reported the first example of ruthenium mediated C-H bond activation of arenes.[11] By treating *trans*-[RuCl$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)] with excess freshly prepared sodium-naphthalene in tetrahydrofuran, a compound with the formula Ru(C$_{10}$H$_8$)(Me$_2$PCH$_2$CH$_2$PMe$_2$) was obtained and later confirmed to be *cis*-[Ru(H)(2-naphtyl)(Me$_2$PCH$_2$CH$_2$PMe$_2$)] (Scheme 2). Similar reactivity was observed when benzene or anthracene was used instead of naphthalene. The activation of arenes by ruthenium complexes followed the oxidative addition mechanism: first, the ruthenium center was reduced to Ru(0), with the arene coordinated to the electron rich metal center, to form the intermediate Ru(arene)(Me$_2$PCH$_2$CH$_2$PMe$_2$); second, the C-H bond of the arene was cleaved to form a hydride and an aryl ligand with the concomitant two-electron oxidation of the metal center. Later, this mechanism was found to be common to late transition metal complexes, especially noble metals in their low oxidation states.[5, 7, 36]
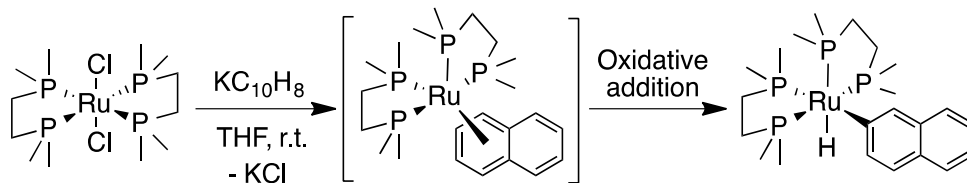
Scheme 2. The first example of metal mediated C-H bond activation.

In parallel, C-H bond activation by early transition metals was discovered soon thereafter. In 1981, Marks and co-workers reported the synthesis and reactivity of Cp$^*_2$MR$_2$ compounds (M = Th: R = CH$_3$, CH$_2$Si(CH$_3$)$_3$, CH$_2$C(CH$_3$)$_3$, CH$_2$C$_6$H$_5$, and C$_6$H$_5$; M = U: R = CH$_3$, CH$_2$Si(CH$_3$)$_3$, CH$_2$C$_6$H$_5$, and C$_6$H$_5$) and found that thorium dialkyl complexes could react with H$_2$ to generate [Cp$^*_2$Th(μ-H)(H)]$_2$ or with C$_6$D$_6$ to afford Cp$^*_2$Th(C$_6$D$_5$)$_2$ (Scheme 3).[37] The reaction with H$_2$

was proposed to proceed by a four-center transition state, which had been suggested earlier by Bercaw and co-workers in a related $Cp^*_2ZrR_2$ system.[38]
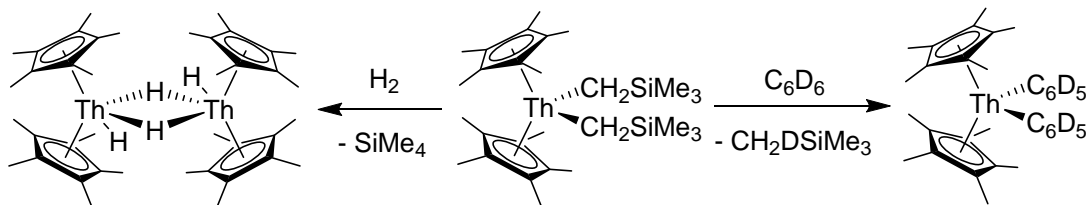
Scheme 3. Reactivity of dialkyl compounds of thorium and uranium supported by a pentamethylcyclopentadienyl ligand.

Two years later, Watson published a seminal paper on a methane exchange reaction between Cp^*_2MMe (M = Lu and Y) and $^{13}CH_4$ (see Chart 1a).[12] The kinetics study showed that the reaction was bimolecular and that the most probable mechanism involved a four-center transition state that was later named σ-bond metathesis.[19, 39] Today, σ-bond metathesis remains the dominant reaction pathway for early transition metals, rare-earth metals, and actinides, albeit 1,2-addition has emerged as a noticeable mechanism once metal-element multiple bonds of group 4 metals,[13, 14, 40-43] rare-earth metals,[29, 30, 32, 33] and actinides[31, 35, 44] could be isolated or characterized as intermediates. In addition, the concept of σ-bond metathesis has been extended to high valent late transition metal complexes and a new term, σ-CAM, σ-complex-assisted mechanism, was coined to describe this process (see Chart 1d).[15] σ-CAM differs from the familiar σ-bond metathesis mechanism by the fact that a stable (though not always isolable) σ-complex is formed prior to C-H bond cleavage, while in σ-bond metathesis a concerted bimolecular process is taking place without the formation of a σ-complex. Although σ-bond metathesis and the similar process σ-CAM are now known for both early and late transition metals, oxidative addition remains elusive to *f*-elements.[7, 8] This can be explained because *f*-elements usually have a d^0 electron configuration in their complexes and, therefore, lack the valence electrons to promote the oxidative addition process. This is true for lanthanides and even for uranium (either $U^{III/V}$ or $U^{IV/VI}$ cycle). In the following two sections, σ-bond metathesis and 1,2-addition reactions will be discussed in a chronological order.
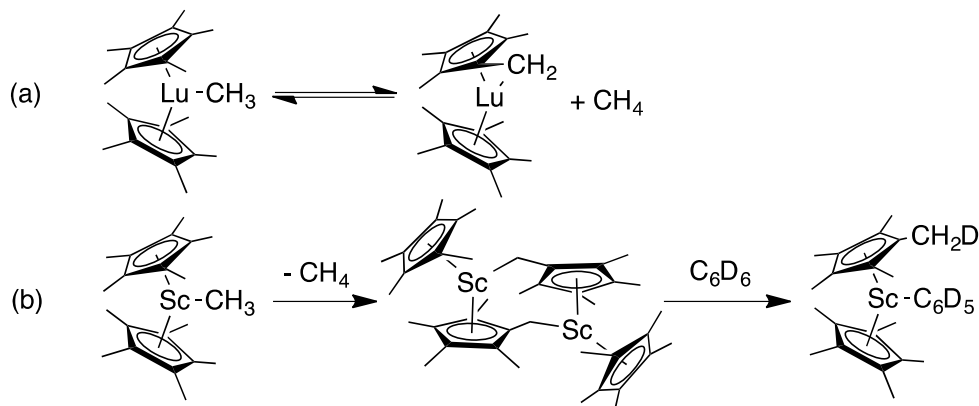
2.1. σ-Bond metathesis

σ-Bond metathesis, as its name implies, is the process involving σ bonds: two bonds are broken and two other bonds are formed simultaneously. It is a concerted mechanism and has a single transition state, commonly referred to as the four-center state. The four-center transition state looks similar to that of olefin metathesis; however, the two differ by the order of the chemical bonds: in σ-bond metathesis, only single bonds are broken and formed; while in olefin metathesis, double bonds are involved.[45] The first examples of σ-bond metathesis, a term coined much later for the sake of clarity,[18] were reported for $Cp_2Zr(IV)R_2$ and $Cp^*_2Zr(IV)R_2$ systems (R = alkyl or hydride) by Schwartz[46] and Bercaw,[38] respectively, both in 1978. The four-center transition state was suggested afterward based on mechanistic studies. As mentioned earlier, in 1981, Marks and co-workers reported the synthesis and reactivity of analogous actinide $Cp^*_2MR_2$ compounds (M = Th or U; R = alkyl, aryl, or hydride) and proposed a similar four-center mechanism.[37] It was not until 1983, when Watson published the seminal paper on $Cp^*_2M(CH_3)$ (M = Y or Lu)

mediated methane exchange between $Cp^*_2Lu(^{12}CH_3)$ and $^{13}CH_4$,[12] that this kind of reactivity started to draw attention, and studies inspired by Watson's work blossomed in the coming decades.[18] The significant impact of this work partially rested on an enthusiasm for the field of methane activation.[5, 6] A year later, Goddard and co-workers investigated by theoretical methods the [2σ-2σ] process using simple model complexes for early transition metals (titanium and scandium) and suggested a concerted four-center mechanism.[39] Four years later, in 1987, Bercaw and co-workers first used the term σ-bond metathesis to describe this reactivity, which was later adopted by others.[19] σ-Bond metathesis is not limited to C-H bond activation: other heteroatoms can undergo the four-center process to break and form new σ-bonds, for instance, E-H bonds, where E = heavy group 14 or group 15 elements, can be activated in a similar fashion.[18]

Examples of C-H bond activation by a σ-bond metathesis mechanism are numerous and an exhaustive review to include all of them is beyond the scope of this perspective. In order to lay the ground for a later presentation on reactivity beyond traditional mechanisms (σ-bond metathesis and 1,2-addition), representative examples in two sub-classes, intramolecular and intermolecular C-H bond activation, will be discussed. The former usually results in cyclometalation,[24] while the latter involves organic substrates bearing the to-be-activated C-H bond, which can be either an *sp*, an *sp²*, or an *sp³* C-H bond.

2.1.1. Intramolecular C-H bond activation

Scheme 4. (a) Postulated lutetium "tuck-in" complex; (b) Formation of scandium "tuck-over" complex and its reactivity.

Intramolecular C-H bond activation by σ-bond metathesis is common in highly reactive alkyl or hydride complexes of rare-earth metals and actinides. Typically, the product of the reaction is a cyclometalated compound with a concomitant loss of a small molecule, usually an alkane or H_2. The reaction is slightly endothermic but driven by a significant entropy gain derived from the loss of a small molecule. Therefore, the intramolecular C-H bond activation commonly occurs at a somewhat high temperature by heating the metal alkyl or hydride precursors in a relatively inert solvent, such as cyclohexane. The weakest and most sterically available C-H bond of the ancillary ligand is the obvious target. Since the C-H bond activation takes place on the supporting ligand, this is usually an undesired process and usually avoided in ligand design. Because pentamethylcyclopentadienyl (Cp*) has been commonly used as an ancillary ligand for *f*-elements, many instances in which the methyl group of the Cp* ligand is subjected to intramolecular C-H bond activation to form a cyclometalated product, usually called "tuck-in" complex, are known.[24]

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The "tuck-in" complexes bear ring strain so the cyclometalative reaction is usually reversible: in the presence of excess hydrocarbons or H_2, the equilibrium usually favors the metal alkyl or hydride complexes (Scheme 4).
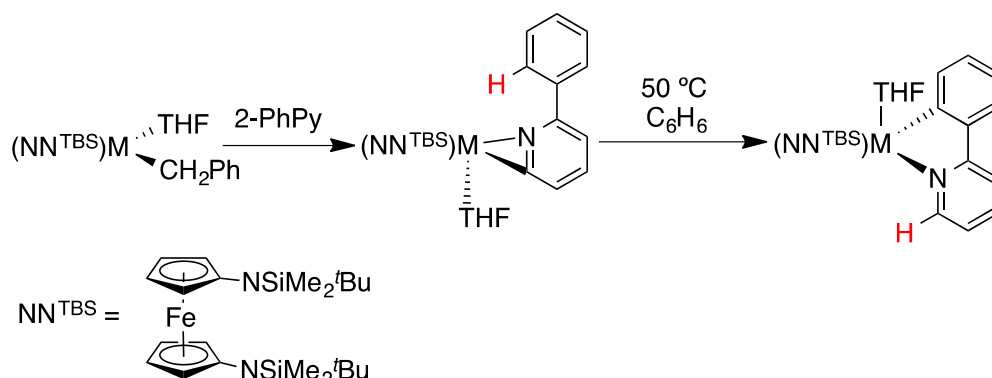
Scheme 5. Unusual hydrogen migration/C-H bond activation cascade reactivity of *ortho*-metalated 2-phenylpyridine complexes of yttrium and lutetium.

Other ancillary ligands such as silylamido ligands, β-diketiminato ligands, and phosphinimine ligands can also undergo intramolecular C-H bond activation to form cyclometalated products.[24] Besides ancillary ligands, heterocycles can also lead to such products. First, the heterocycle coordinates to the metal through σ-donation of the heteroatom. That brings the C-H bond that is *ortho* to the heteroatom in close proximity to the metal center and facile C-H activation occurs to form an η^2-heterocycle metal complex.[25-27, 47-67] In rare cases, cyclometalation can take place in a position other than *ortho*:[62, 68] Diaconescu and co-workers reported an unusual hydrogen migration/C-H bond activation that resulted in the formation of a metalacycle at the 2′-position of 2-phenylpyridine (Scheme 5).[69] The driving force for the reaction is the higher thermostability of the five-membered metallacycle than that of the three-membered metallacycle that usually results from *ortho*-C-H bond activation.

For actinides, due to their high valence and capability to bind more ligands, a more diverse reactivity is observed compared to lanthanides. For example, the thorium dialkyl complex (η^5-$C_5Me_5)_2$Th(CH$_2$CMe$_3$)$_2$ was shown to be susceptible to γ-metalation of an alkyl group with loss of *neo*-pentane to generate the metalacyclobutane compound (η^5-C$_5$Me$_5$)$_2$Th[(CH$_2$)$_2$CMe$_2$], which was capable to active hydrocarbons, including methane, to give the mixed methyl/neopentyl product (η^5-C$_5$Me$_5$)$_2$Th(Me)(CH$_2$CMe$_3$) (Scheme 6a).[70, 71] Recently, Walter and co-workers synthesized the first *f*-element metalacyclopropene complex, [η^5-C$_5$H$_2$(CMe$_3$)$_3$-1,2,4]$_2$Th(η^2-C$_2$Ph$_2$),[72] and when the chemistry was expanded to other alkynes, such as PhCC^{i}Pr, the resulting metalacyclopropene, [η^5-C$_5$H$_2$(CMe$_3$)$_3$-1,2,4]$_2$Th(η^2-PhCC^{i}Pr), was not stable and underwent intramolecular C-H bond activation of the cyclopentadienyl *tert*-butyl group to afford a "tuck-in" type cyclometalation product (Scheme 6b).[73]
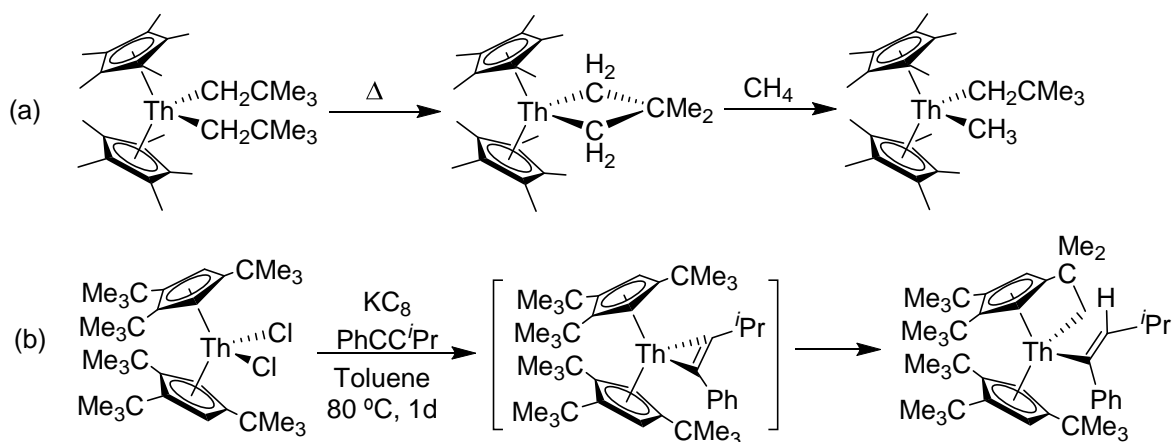
Scheme 6. (a) γ-Metalation of (η^5-C$_5$Me$_5$)$_2$Th(CH$_2$CMe$_3$)$_2$ and activation of methane by (η^5-C$_5$Me$_5$)$_2$Th[(CH$_2$)$_2$CMe$_2$]; (b) Intramolecular C-H bond activation from a thorium metallacyclopropene complex.

2.1.2. Intermolecular C-H bond activation

In a σ-bond metathesis mechanism, the hydrogen of the to-be-activated C-H bond always occupies the position diagonal to the metal center in the four-center transition state (Figure 1). The metal-element bond (typically M-C or M-H bond) is polarized and the element carries a partially negative charge. For C-H bonds, carbon is more electronegative than hydrogen, therefore, in the polarized transition state, carbon carries a partially negative charge while hydrogen carries a partially positive charge. Thus, the partially positive charged hydrogen is suitably positioned between two negatively charged atoms. Besides this favorable electrostatic interaction, a molecular orbital match also favors this conformation: the spherical 1s orbital of hydrogen fits well between the two electronegative atoms. If carbon occupied the same position as hydrogen, it would have a coordination number of five, which is energetically highly unfavorable.[74] The polarized four-center transition state can be viewed as a concerted proton transfer between two negatively charged atoms.[75] For carbon atoms with different hybridizations, their relative electronegativity follows the order $sp > sp^2 > sp^3$; therefore, the reactivity of C-H bonds in the σ-bond metathesis mechanism should follow the same trend, spC-H > sp^2C-H > sp^3C-H.[19] This is in contrast to radical processes, which will favor the activation of the weakest, sp^3 C-H bond. Within the category of sp^3 C-H bonds, the less sterically hindered are usually more reactive: for instance, a primary C-H bond is favored over secondary and tertiary C-H bonds, while methane, with a high bond dissociation energy of 105 kcal/mol,[76] is readily activated by Cp*$_2$MR (M = lanthanides and group 3 metals, R = alkyl or hydride)[12] or Cp*$_2$MR$_2$ (M = actinides, R = alkyl or hydride).[37]
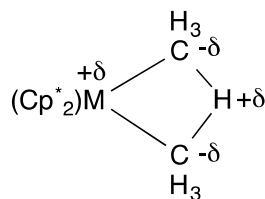

Figure 1. Transition state of the methane exchange reaction mediated by Cp*$_2$MMe.

2.1.2.1. *sp* C-H bonds

Despite their high dissociation energy of 133 kcal/mol,[76] *sp* C-H bonds are prone to C-H bond activation. Indeed, the simplest alkyne, acetylene, has a rather small pKa value of 25-26, which makes it a weak acid in organometallic chemistry, and can be deprotonated by a strong base such as a nitrogen or carbon based anion. Therefore, the reaction between a metal alkyl complex and a primary alkyne is usually thermodynamically favorable and resembles a classical acid-base metathesis reaction.
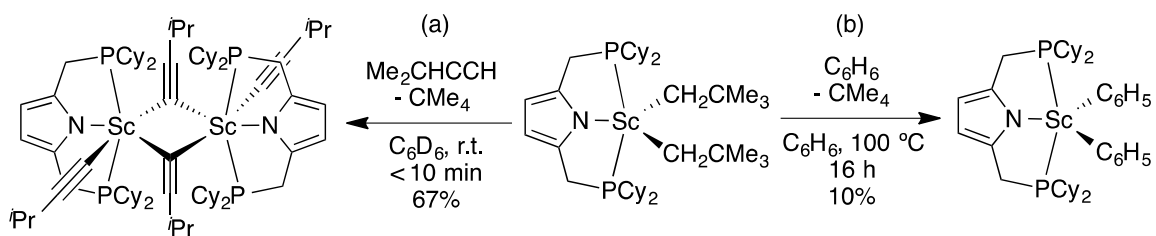

Scheme 7. *sp* C-H bond activation of *iso*-propylacetylene (a) and sp^2 C-H bond activation of benzene (b) by (PNP-Cy)Sc(CH$_2$CMe$_3$)$_2$.

Tilley and Andersen recently reported an intermolecular *sp* C-H bond activation by a scandium dialkyl complex supported by a monoanionic chelating PNP ligand (PNP = 2,5-bis(dialkylphosphinomethyl)-pyrrolide; alkyl = cyclohexyl, PNP-Cy; alkyl = *tert*-butyl, PNP-^{t}Bu).[77] (PNP-Cy)Sc(CH$_2$CMe$_3$)$_2$ reacted readily with *iso*-propylacetylene in C$_6$D$_6$ at ambient conditions to afford the dinuclear complex [(PNP-Cy)Sc(CC^{i}Pr)(μ-CC^{i}Pr)]$_2$ in a good isolated yield (67%, Scheme 7a). The authors also studied the reactivity of the scandium dialkyl complex toward other hydrocarbons, including benzene and methane, and found that the reaction of (PNP-Cy)Sc(CH$_2$CMe$_3$)$_2$ with benzene was much slower than with *iso*-propylacetylene and required a high temperature (100 ºC) to form (PNP-Cy)ScPh$_2$ in low yield (ca. 10%, Scheme 7b), while no reaction between (PNP-Cy)Sc(CH$_2$CMe$_3$)$_2$ and tetramethylsilane or methane was observed at 100 ºC in toluene-d_8. This systematic study supports the trend of C-H bond activation reactivity mentioned above, *sp* C-H > sp^2 C-H > sp^3 C-H.

2.1.2.2. sp^2 C-H bonds

Metal vinyl and aryl complexes are two typical classes of products resulting from sp^2 C-H bond activation from alkene and arene substrates, respectively. Bercaw and co-workers conducted a systematic study of the reactions between Cp$^*_2$ScR (R = alkyl or hydride) and various hydrocarbons, and found that while ethylene underwent rapid polymerization with Cp$^*_2$ScMe, substituted alkenes, such as styrene and isobutene, were readily activated through σ-bond metathesis to result in scandium vinyl compounds (Scheme 8a).[19] One interesting case was with propene: propene insertion into the Sc-Me bond occurs first; however, before a further insertion takes place, fast σ-bond metathesis with excess propene forms the corresponding scandium vinyl compound (Scheme 8b). Noteworthy, all scandium vinyl compounds are in a *trans* arrangement, probably due to steric reasons. The kinetics study of substituted styrenes showed no difference between electron-rich (*para*-OMe) and electron-poor (*pare*-CF$_3$) substrates. The authors also investigated the aromatic C-H bond activation of arenes by Cp$^*_2$ScMe (Scheme 8c). Both electrophilic aromatic substitution and σ-bond metathesis were considered as mechanisms for the reaction; however, the similar reaction rates when using electron-rich, electron-neutral, or

electron-poor benzene derivatives suggest that σ-bond metathesis is the operating mechanism for aromatic C-H bond activation. Another interesting study from the same work is the regioselectivity of toluene activation. It was found that while an appreciable amount of benzylic C-H bond activation was observed at the early stages of the reaction, the lack of preference for *ortho/para* over *meta*-C-H bond activation indicated no involvement of the π system in the reaction. The nearly statistical ratio between *meta* and *para*-tolyl products and the lower yield of *ortho*-tolyl product indicate that the selectivity of the reaction is a result of mainly steric factors (Scheme 8d).

	Benzyl	o-	m-	p-
product ratios after 2 h at 80 ºC (sum = 100)	14	6	57	23
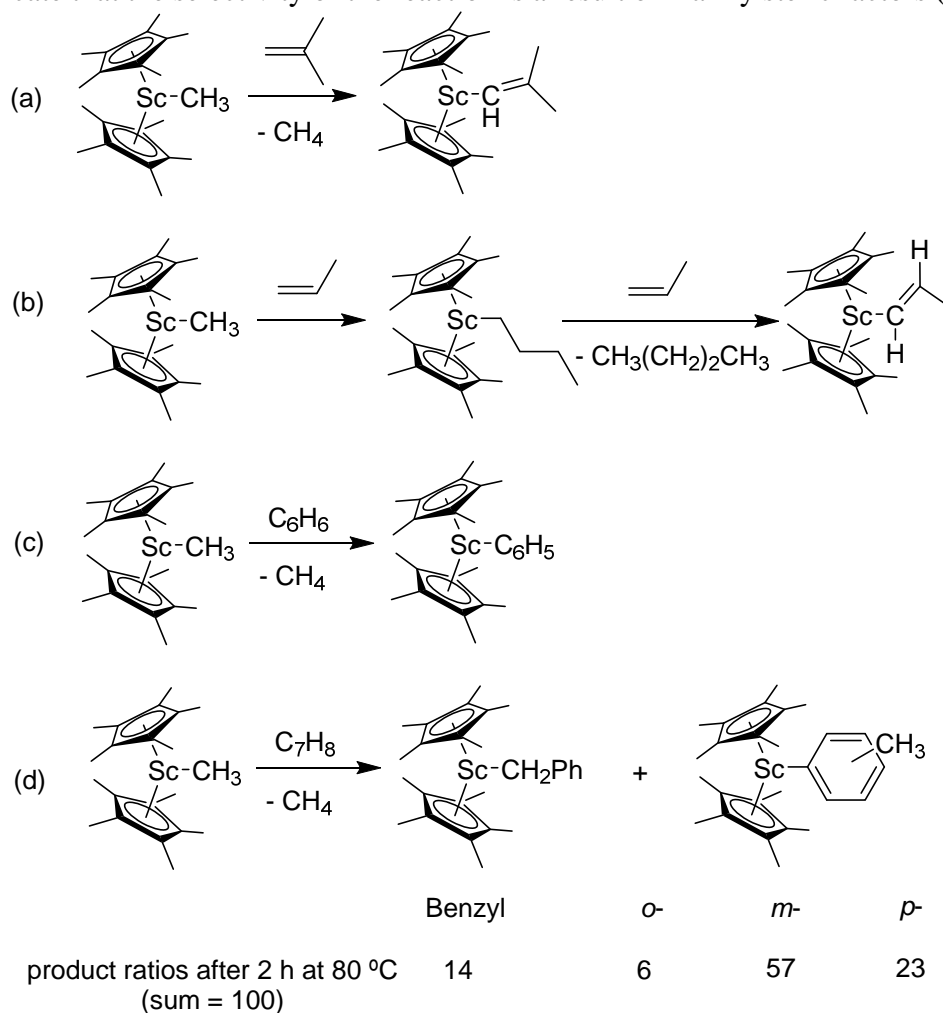
Scheme 8. *sp²* C-H bond activation by Cp*$_2$ScMe: (a) vinylic C-H bond activation of *iso*-butene; (b) insertion of propene followed by vinylic C-H bond activation; (c) aromatic C-H bond activation of benzene; (d) regioselectivity of C-H bond activation of toluene by Cp*$_2$ScMe.

2.1.2.3. *sp³* C-H bonds

The relative reaction rates of *sp³* C-H bond activation by *f*-elements through σ-bond metathesis are methane ~ primary > secondary > tertiary.[19] This is evidenced by the intermolecular H/D exchange catalyzed by Cp*$_2$ScH: methane and other primary C-H bonds in SiMe$_4$, PMe$_3$, and even propane at the primary positions lead to a moderate yield, while substrates containing only secondary C-H bonds such as cyclopentane show a much slower rate (0.06 turnovers/h at 120 ºC). This phenomenon is rationalized on the basis of the four-center transition

state: the steric interactions of the substrate substituents with the bulky Cp* ligand are dominating. For secondary and tertiary C-H bonds, the unfavorable interaction between the Cp* ligand and the alkyl substituents increase the energy of the four-center transition state.[19] Due to the low reactivity of secondary C-H bonds, cyclohexane-d_{12} is commonly used as a solvent for mechanistic studies of C-H bond activation.
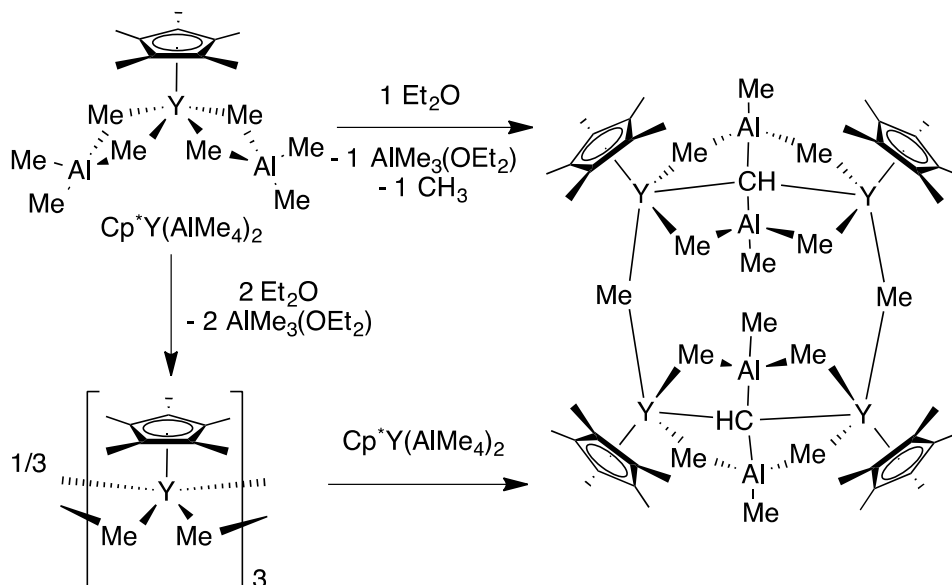

Scheme 9. Multiple C-H bond activations of a methyl group by treating a yttrium aluminate complex with a Lewis base.

The most noteworthy example of sp^3 C-H bond activation is Watson's milestone study on methane exchange mediated by Cp*$_2$MMe (M = Y or Lu).[12] As mentioned, Bercaw and co-workers published a thorough report on C-H bond activation of various hydrocarbon substrates with a detailed mechanistic study.[19] For actinides, similar reactivity of Cp*$_2$MR$_2$ (R = Th or U, R = alkyl, aryl, or hydride) toward hydrocarbons, including methane and benzene, was reported by Marks and co-workers even prior to Watson's discovery in lanthanide chemistry.[37] However, after three decades of Watson and Marks' breakthrough reports, examples of C-H bond activation of hydrocarbons by f-element complexes supported by cyclopentadienyl or its derivative ligands are still limited.[24]

An example worth mentioning is the multiple C-H bond activation of a methyl ligand to form a multinuclear cluster. Anwander and co-workers reported the formation of an Y$_4$Al$_4$ cluster containing two bridging methine (CH^{3-}) ligands by treating the yttrium aluminate Cp*Y(AlMe$_4$)$_2$ with a stoichiometric amount of Et$_2$O (Scheme 9).[78] The authors proposed that the C-H bond activation of the coordinating methyl group was triggered by the highly reactive "free" Cp*YMe$_2$ species upon removal of AlMe$_3$ by Et$_2$O, since the reaction of an equivalent of Cp*Y(AlMe$_4$)$_2$ and one-third equivalent of pre-formed [Cp*YMe$_2$]$_3$ resulted in the formation of the Y$_4$Al$_4$ cluster (Scheme 9). The striking feature of the Y$_4$Al$_4$ cluster is the presence of the methine ligand bridging two yttrium(III) and two aluminum(III) ions. The multiple C-H bond activations of a methyl ligand is a topic of great interest since such processes can provide a synthetic entry to carbide ligands within a metal cluster, and, therefore, shed light on living enzymes such as nitrogenase.[79-81]

2.2. 1,2-Addition

Distinct from σ-bond metathesis, 1,2-addition involves the participation of a π-bond of a M=E fragment that is usually highly polarized.[7] However, 1,2-addition and σ-bond metathesis share common features such as the four-center transition state and the proton-type hydrogen transfer. Since 1,2-addition requires the presence of a metal-element multiple bond, its discovery and development accompany the synthesis of metal complexes containing such moieties. In some cases, the products of a 1,2-addition process were used as evidence for the formation of transient metal-element multiple bonds.[28, 29, 31] The groups of Wolczanski and Bergman simultaneously reported the first examples of C-H bond activation by 1,2-addition, employing various hydrocarbon substrates in the presence of transient zirconium imide species.[13, 14] The transient zirconium imide intermediate could be trapped by a strong Lewis base such as tetrahydrofuran (THF) and was able to activate the C-H bond in methane and benzene. By using a bulky amide ligand, Wolczanski and co-workers could study the 1,2-addition reaction in detail (Scheme 10).[13] Later, Mindiola and co-workers published a series of reports on the generation of a transient titanium alkylidyne from a titanium alkylidene precursor and its ability to promote the C-H bond activation of benzene,[40] mesitylene (benzylic position), tetramethylsilane,[41] linear alkanes (C2-C8), and some cyclic alkanes such as cyclohexane (Scheme 11).[43] It is worth mentioning that the transient titanium alkylidyne could even activate strong bonds like (Ar)C-OMe and (Ar)C-F when no C-H bond is present in the substrates (Scheme 11).[42] All bond activation reactions were proposed to go through a 1,2-addition mechanism mediated by the intermediate containing a titanium-carbon triple bond. The proposed mechanism was supported by both experimental and theoretical studies.[41, 43]
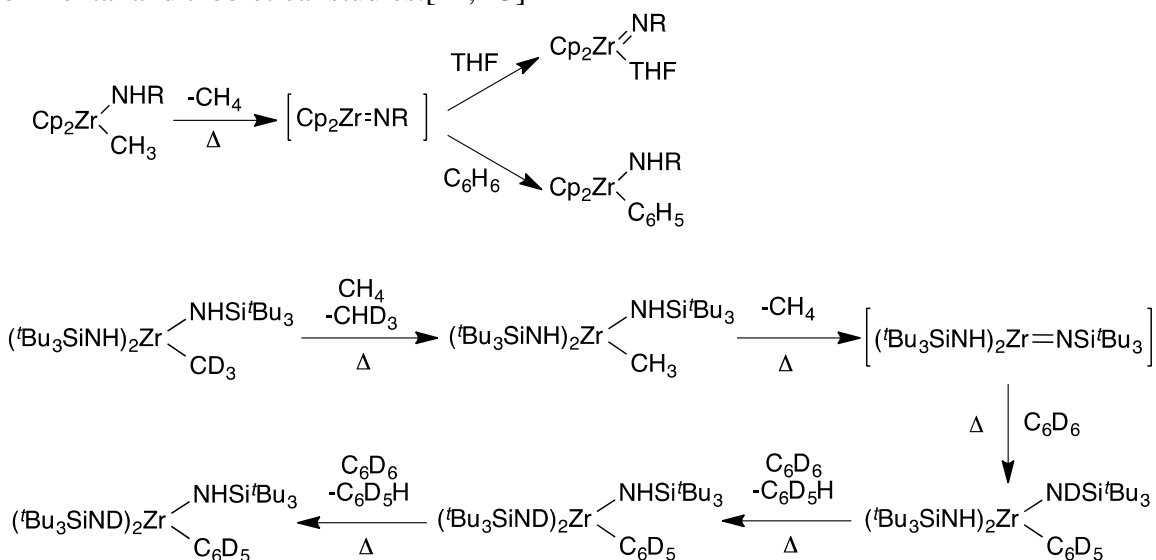
Scheme 10. Generation of transient zirconium imido species and their C-H bond activation reactivity.
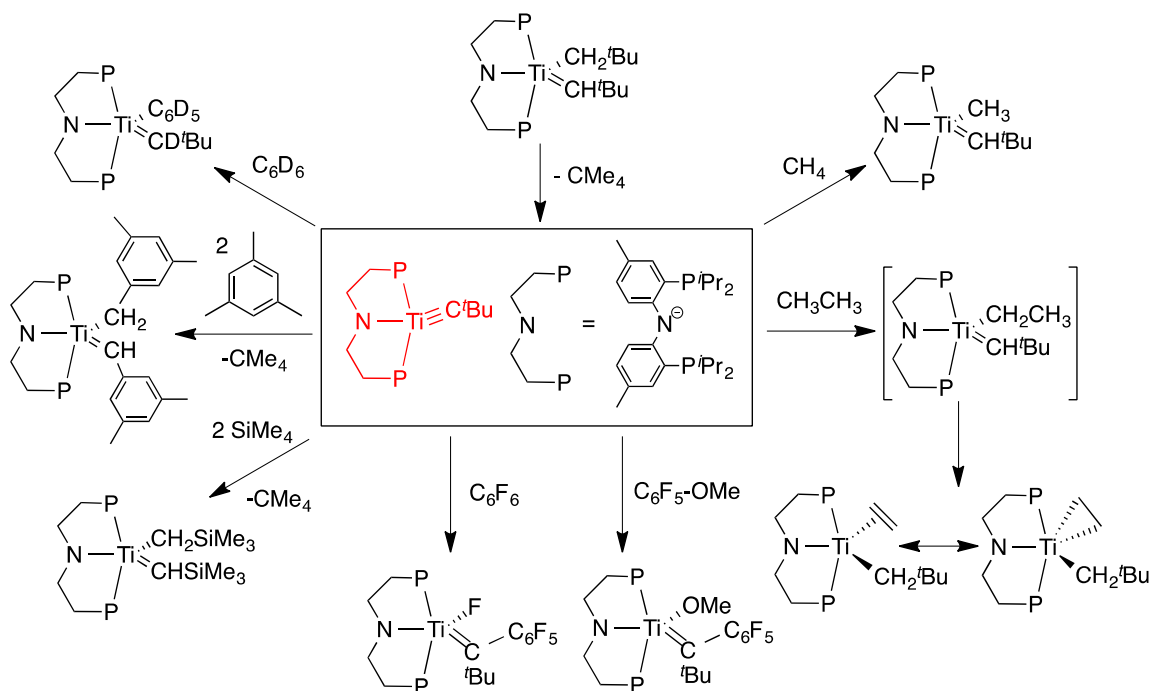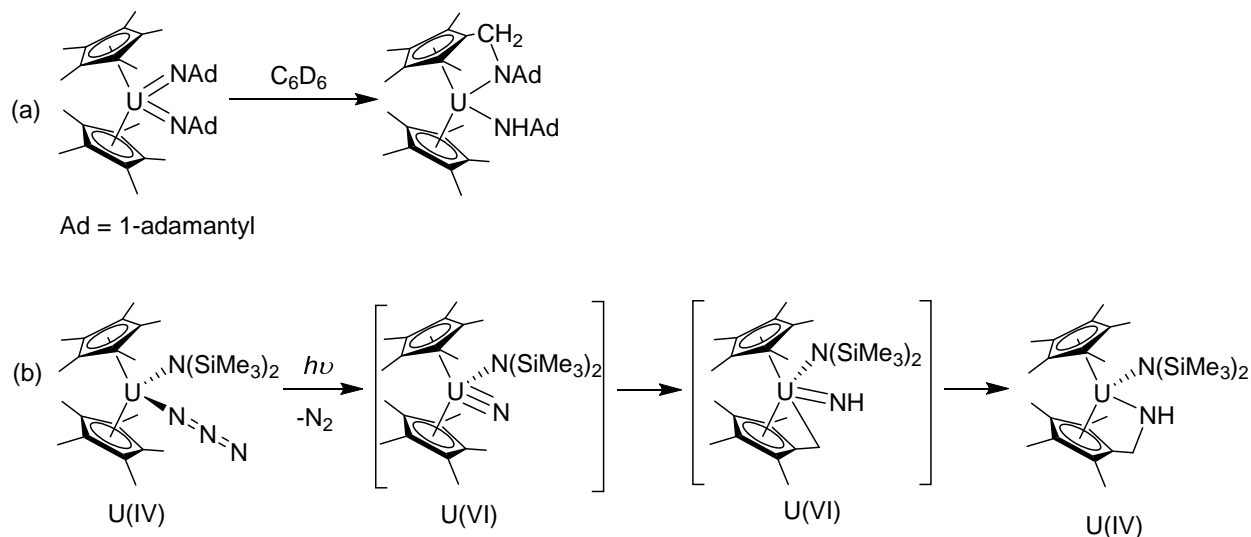
Scheme 11. C-H bond activation promoted by a transient titanium alkylidyne.
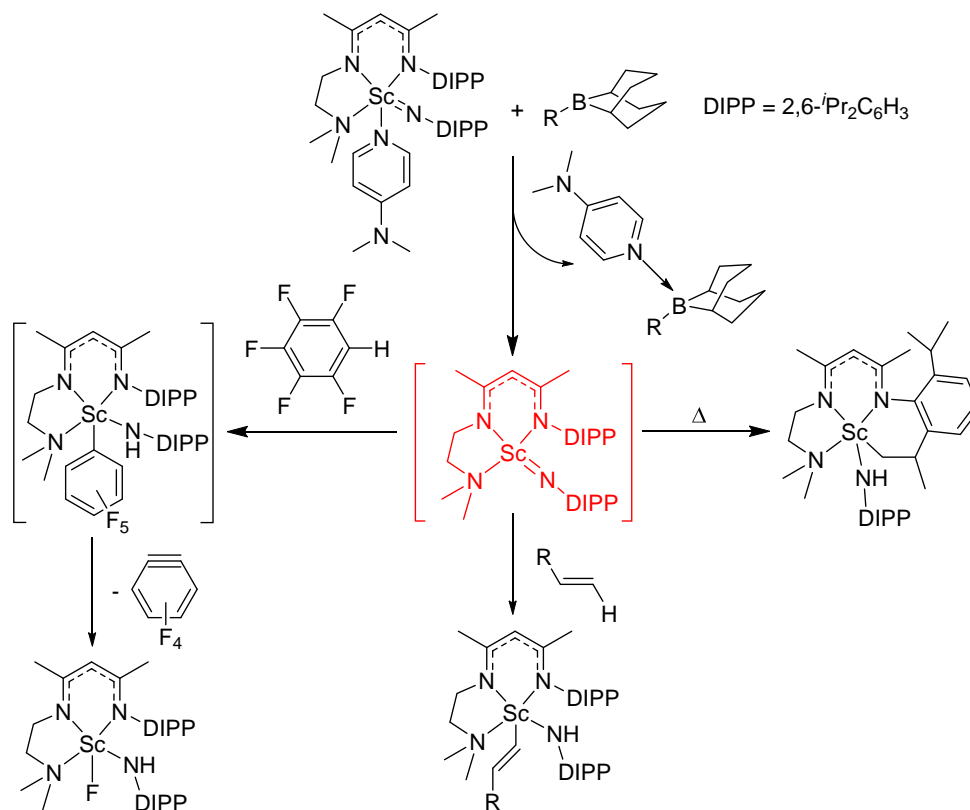
Scheme 12. Inter- and intramolecular C-H bond activation promoted by an *in situ* generated base-free scandium imido complex.

Despite the early discovery and advancement of 1,2-addition type C-H bond activation enabled by transient group 4 metal imide or alkylidyne species, such reactions were absent from the *f*-element chemistry until recently. Compared to *f*-elements, group 4 metals are less electropositive and tend to form bonds with a more covalent character with *p*-block elements such as carbon, nitrogen, and oxygen.[82, 83] The first example of a structurally characterized rare-earth metal terminal imido complex was reported in 2010 by Chen and co-workers as a scandium complex.[32] Albeit the incorporation of a Lewis base was found necessary to stabilize the terminal scandium imido complex and thus inhibits its reactivity, the same group reported later that a base-free scandium imido species could be generated *in situ* by treating the isolated Lewis base adduct with a strong Lewis acid such as 9-BBN (9-borabicyclononane); this species undergoes inter- and intramolecular C-H bond activation, presumably through a 1,2-addition mechanism (Scheme 12).[34] Other examples of transient scandium imido intermediates that could activate C-H bonds either intra-[30] or intermolecularly[28, 29] were also reported (Scheme 13).

Scheme 13. Intra- and intermolecular C-H bond activation promoted by transient scandium imido complexes.

For actinides, especially uranium, U-E multiple bonds have been known for a long time. Uranyl, $[O=U=O]^{2+}$, has two extremely strong uranium-oxygen bonds with a calculated bond order of 3 (each).[84] Other than oxygen, uranium can form multiple bonds with nitrogen, carbon, sulfur, phosphorus,[85] and, most recently, arsenic.[86] Among them, uranium terminal imido[87, 88]

and terminal nitrido[35] complexes were studied most intensely. Both an isolated U(VI) bisimido complex[89] and a transient U(VI) nitrido species[31] were found to activate C-H bonds intramolecularly (Scheme 14). However, unlike 1,2-addition in group 4 and rare-earth metal chemistry, the uranium centers were reduced by two electrons to U(IV) in both products. Kiplinger and co-workers studied such a reaction computationally and concluded that a two-step mechanism operates, in which a 1,2-addition by a transient nitrido is followed by a 1,2-migration of an alkyl from uranium to the imido fragment (Scheme 14b).[90] The overall reaction can be described as the insertion of a transient nitride ligand into a C-H bond in a 1,1-fashion. This type of reactivity is directly related to the fact that uranium has multiple accessible oxidation states.


Scheme 14. (a) Intramolecular C-H bond activation promoted by U(VI) bisimido complex; (b) 1,1-Insertion of a transient U(VI) nitrido species into an intramolecular C-H bond and proposed mechanism.

3. C-H Bond activation beyond traditional reaction pathways

Transition metals usually have multiple accessible oxidation states and a relatively large number of valence electrons. For instance, iron can be in any of the oxidation states from -2 to +6. This gives them the capacity to undergo redox processes at the metal center. Especially for the second and third row transition metals, two-electron redox processes, namely oxidative addition (+2 change of the metal oxidation state) and reductive elimination (-2 change of the metal oxidation state), are common. For example, Pd(0)/Pd(II) cycles make palladium especially prominent in C-X cross-coupling reactions (X = carbon, nitrogen, or other heteroatoms).[91] However, when moving to the left of the periodic table, the number of available oxidation states becomes limited. For example, for group 4 metals, the most common oxidation state is +4; lower oxidation states are known but rare. For group 3 metals and lanthanides, the +3 oxidation state dominates their chemistry and only few metals have other accessible oxidation states (+4 for Ce, +2 for Eu, Yb, and Sm). Despite recent advances in the synthesis and characterization of low valent molecular rare-earth metal complexes,[92-94] their chemistry remains limited.[95] For actinides, while thorium behaves similarly to lanthanides and its chemistry is dominated by the +4 oxidation state, uranium can access multiple oxidation states. Indeed, uranium has been shown to support redox chemistry at the metal center and the addition of E-E bonds (E = electronegative element

from group 15, 16, or 17).[96] However, this chemistry is still limited and genuine oxidative additions of relatively inert C-H bonds remain rare.[8, 97] One reason for the lack of two-electron transfer processes with *f*-elements is their high tendency to undergo one-electron redox processes. Therefore, it might be necessary to bring two metal centers in close proximity in order to enable a bimetallic two-electron transformation, in a similar fashion to the recently established bimetallic Pd(II)/Pd(III) cycle.[98]
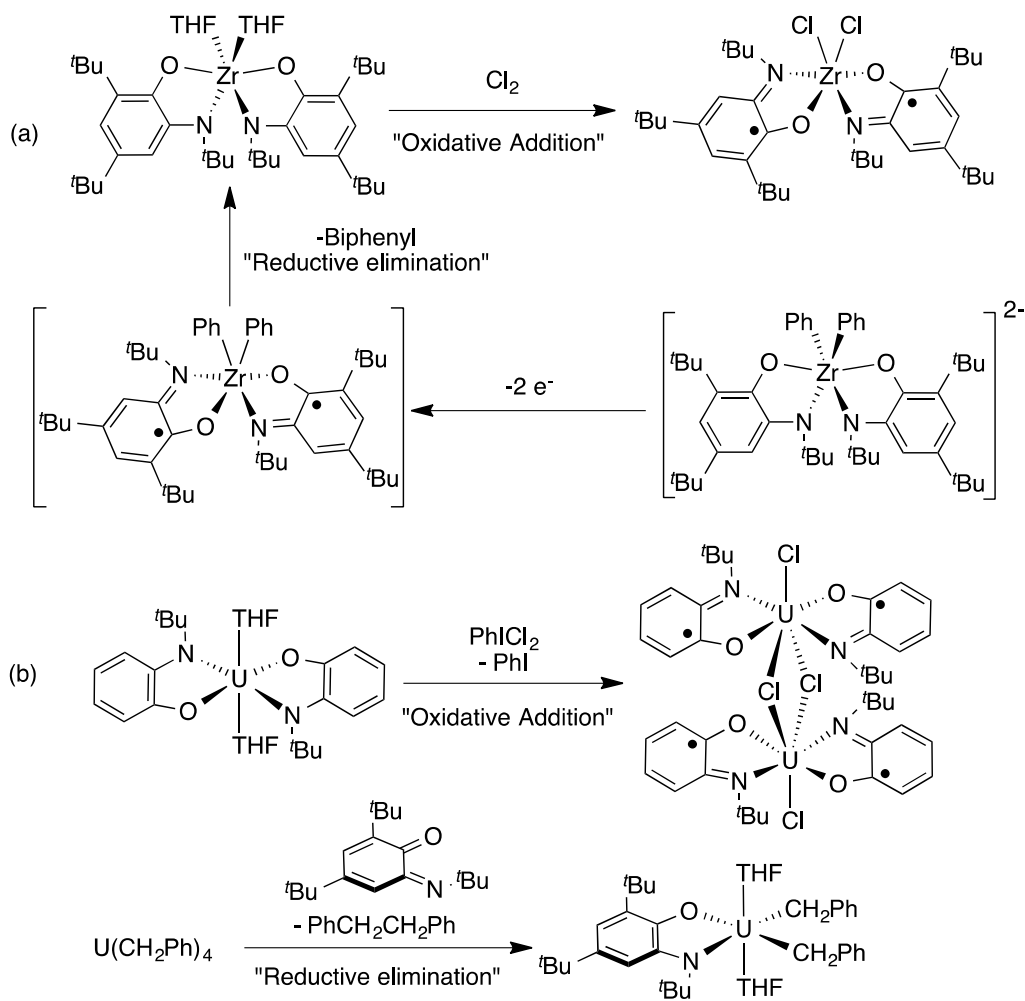
Scheme 15. Pseudo oxidative addition / reductive elimination at Zr(IV) (a) and U(IV) (b) centers utilizing redox active amidophenolate ligands.

Another approach to achieve a two-electron transformation such as oxidative addition or reductive elimination for $d^0 f^n$ metals is to introduce redox non-innocent ligands. Instead of changing the oxidation state of the metal center, the electrons stored in the ligand fragment become involved in substrate activation. Heyduk and co-workers were the first to apply this principle to zirconium by using a redox non-innocent amidophenolate ligand with two accessible oxidation states, dianion or radical monoanion. When treating a bisamidophenolate(2-) zirconium(IV) complex with a strong oxidant such as Cl_2, the halogen added oxidatively to the zirconium center;[99] on the other hand, when a diphenyl bisamidophenolate(2-) zirconium(IV) dianion was oxidized by two electrons, the resulting neutral diphenyl bisamidophenolate(1-) zirconium intermediate could reductively eliminate the two phenyl groups to form biphenyl with the

concomitant reduction of the bisamidophenolate(1-) ligand to bisamidophenolate(2-) (Scheme 15a).[100] Recently, Bart and co-workers reported similar chemistry for uranium: a bisamidophenolate(2-) uranium(IV) complex could undergo oxidative addition at a single uranium center assisted by the oxidation of the amidophenolate ligand from a dianion to a radical monoanion;[101] reversely, addition of iminoquinone, the neutral version of the amidophenolate ligand, to uranium(IV) tetrabenzyl resulted in extrusion of two benzyl radicals to form 1,2-diphenylethane and an amidophenolate dibenzyl uranium(IV) complex[102] (Scheme 15b).

In spite of the absence of C-H bond activation by an oxidative addition mechanism mediated by *f*-elements, these two approaches, use of a bimetallic system or a redox non-innocent ligand, bring new opportunities to discover novel types of C-H bond activation utilizing *f*-element metal complexes, as discussed below. It is interesting to note that, in most cases, strong reducing conditions are applied.

3.1. Rare-earth metal mediated bimetallic cleavage of aromatic C-H bonds

Recently, Diaconescu and co-workers reported the bimetallic cleavage of aromatic C-H bonds by rare-earth metal complexes[103] supported by a 1,1′-ferrocenediamide ligand.[25, 26, 47-49, 51-53, 55-60, 104-120] When reacting $(NN^{fc})ScI(THF)_2$ ($NN^{fc} = 1,1'$-fc(NSi^{t}BuMe$_2$)$_2$) and potassium graphite (KC_8) in benzene, two products containing a $(NN^{TBS})Sc$ fragment were obtained in an equimolar ratio.[103] The two products were $[(NN^{fc})Sc(\mu\text{-}H)]_2$ and $(NN^{fc})ScPh(THF)$ as confirmed by X-ray crystallography, ^1H and ^{13}C NMR spectroscopy, and independent synthesis (Scheme 16a). This reactivity is not limited to scandium: other rare-earth metal complexes, $(NN^{fc})YI(THF)_2$ and $(NN^{fc})LuI(THF)_2$, gave analogous products (Scheme 16b). The same products were obtained under an N_2, argon, *vacuo*, and H_2 atmosphere under similar reaction times. Different reducing agents were also investigated: although sodium mirror promoted the reaction similarly to KC_8, sodium amalgam (up to 2.5% sodium wt%) did not lead to the expected products even after a prolonged reaction time.
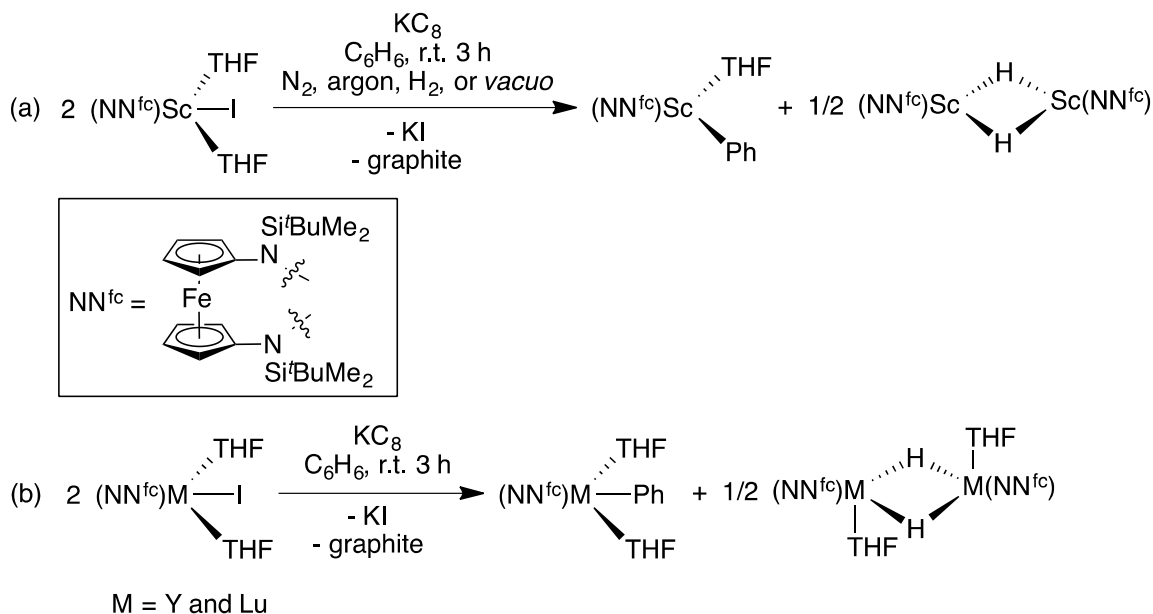
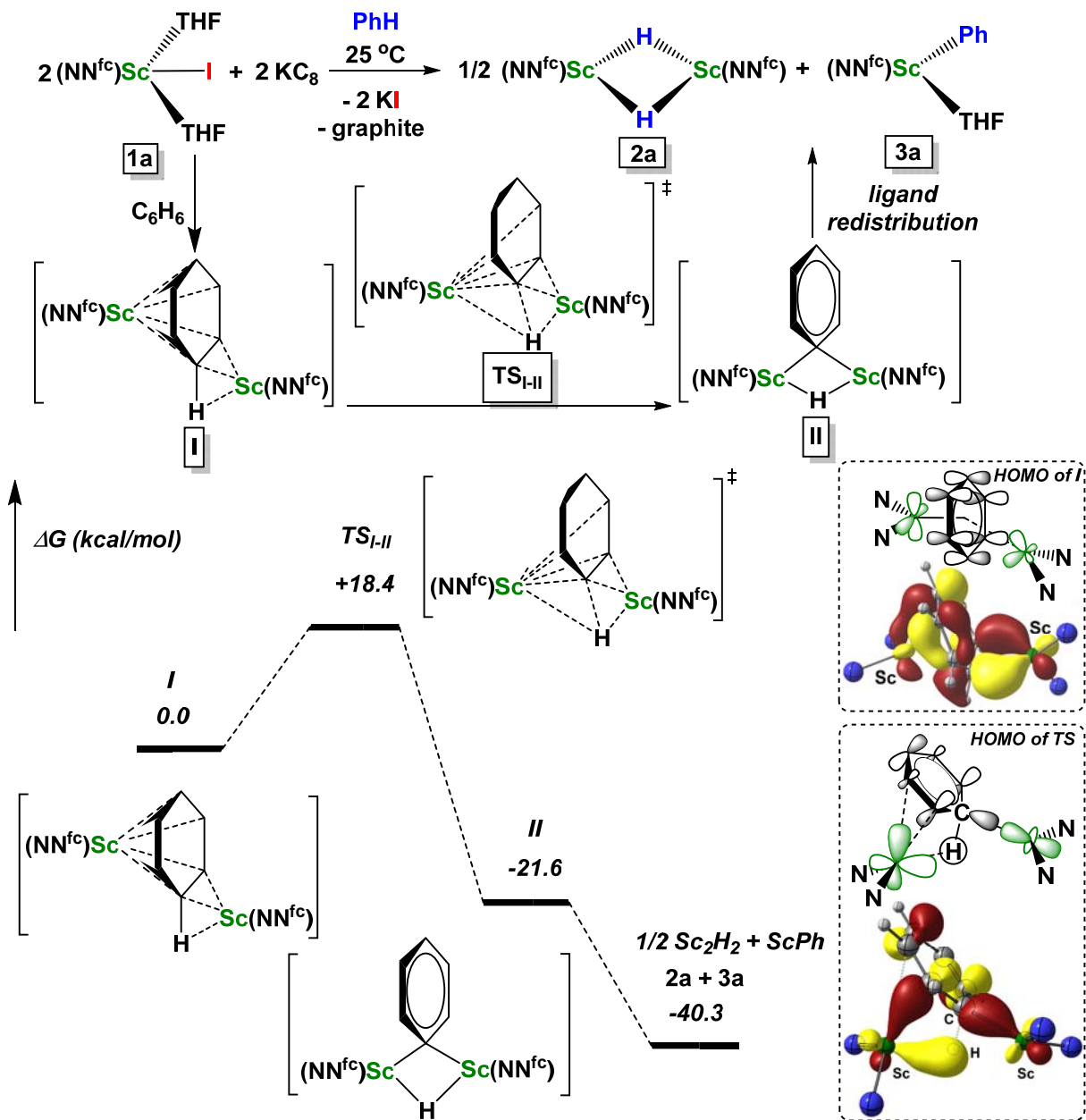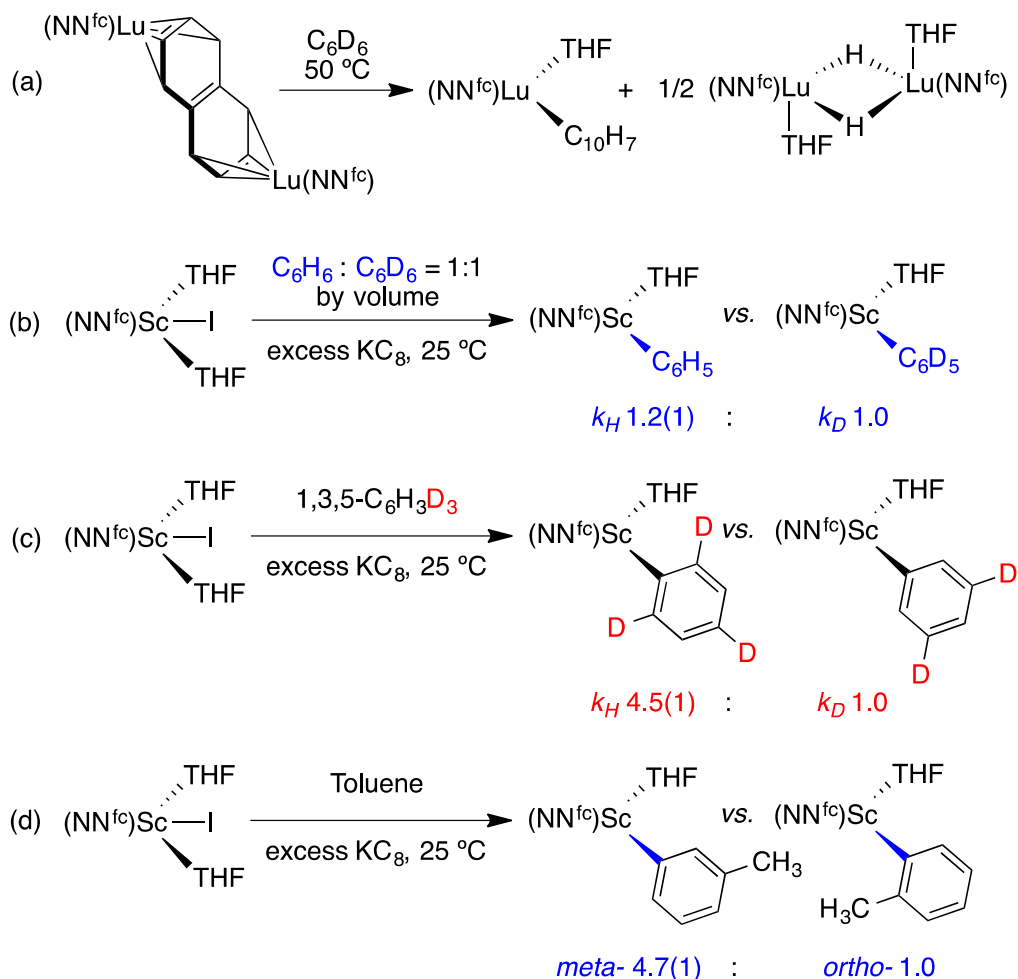**Scheme 16.** C-H bond activation of benzene by $(NN^{TBS})MI(THF)_2$ and KC_8.

Figure 2. Proposed mechanism for benzene C-H bond activation mediated by $(NN^{fc})ScI(THF)_2$ (1a) and KC_8 to form $[(NN^{fc})Sc(\mu\text{-H})]_2$ (2a) and $(NN^{fc})ScPh(THF)$ (3a). Intermediates (I and II), transition state ($TS_{I\text{-}II}$), and final product 2a and 3a have been calculated by DFT methods. Reprinted with permission from W. Huang, F. Dulong, S. I. Khan, T. Cantat and P. L. Diaconescu, J. Am. Chem. Soc., 2014, 136, 17410-17413. Copyright (2014) American Chemical Society.

The C-H bond activation of benzene leading to equimolar amounts of metal hydride and metal phenyl products resembles the oxidative addition mechanism by late-transition metal complexes, in which a single, mixed metal hydride phenyl product forms. The intriguing reactivity and its generality for rare-earth metals prompted a detailed mechanistic study. Inspired by previous reports of inverse-sandwich rare-earth metal arene complexes[121-123] and taking into account the capacity of benzene to accept electrons under reducing conditions,[124, 125] the following

reaction mechanism was proposed (Figure 2): first, the reduction of (NN^{fc})ScI(THF)$_2$ and benzene by KC$_8$ leads to an inverse-sandwich discandium benzene intermediate (I); C-H bond cleavage takes place at I to form a discandium μ-phenyl μ-H intermediate (II), which then undergoes ligand disproportionation to the final observed products. It is interesting to mention that biphenyl behaves differently than benzene and forms tetranionic biphenyl inverse-sandwich dimetal complexes that feature a 6C, 10π-aromatic system localized on the phenyl ring coordinated to the two rare-earth metals.[104, 105]

Scheme 17. Mechanistic studies on bimetallic aromatic C-H bond activation: (a) C-H bond activation from an isolated lutetium naphthalene complex, [(NN^{fc})Lu(THF)]$_2$(μ-η^4:η^4-C$_{10}$H$_8$); (b) Determination of intermolecular KIE of benzene activation; (c) Determination of intramolecular KIE of benzene activation using 1,3,5-C$_6$H$_3$D$_3$; (d) Regioselectivity of toluene activation by (NN^{fc})ScI(THF)$_2$ and KC$_8$.

Experimental results support the proposed mechanism. (1) Although an intermediate species could not be observed by NMR spectroscopy, when heating [(NN^{fc})Lu(THF)]$_2$(μ-η^4:η^4-C$_{10}$H$_8$)[126-128] in C$_6$D$_6$ at 50 ℃, two products, [(NN^{fc})Lu(μ-H)(THF)]$_2$ and (NN^{fc})LuPh(THF), were formed (Scheme 17a). This result suggested that a metal arene inverse-sandwich complex could be a precursor in the C-H bond activation of arenes described above. (2) Inter- and

18

intramolecular kinetic isotope effects (KIEs) were determined to be 1.2(1) and 4.5(1) by using a 1:1 ratio of C_6H_6 vs. C_6D_6 and 1,3,5-$C_6H_3D_3$, respectively (Scheme 17b,c). These results were consistent with experimental observations that the rate-determining step occurs prior to the cleavage of the C-H bond, since no intermediates could be detected. The large difference between inter- and intramolecular KIEs indicates that benzene is bound to the metal center in an intermediate prior to the C-H bond activation step,[21] supporting the proposed metal arene inverse-sandwich complex I. (3) When using toluene as a substrate, the regioselectivity of C-H bond activation was intriguing: of the four possible products originating from the activation of the four chemically different C-H bonds (*ortho*, *meta*, *para*, and benzylic), only two of them, the scandium *ortho*-tolyl and *meta*-tolyl compounds, were observed in a 1:4.7(1) ratio (Scheme 17d). This regioselectivity is distinct from what has been observed for the σ-bond metathesis reaction between Cp^*_2ScMe and toluene, in which all four products were observed and the *meta* vs. *para*-tolyl product ratio was close to the statistical value (2:1). The observed selectivity in the present case resembles that of Birch reductions in the presence of an electron-donating substituent.[129]

DFT calculations were carried out to understand the mechanism of the C-H bond activation further. Due to the heterogeneous nature of KC_8, it was not possible to calculate the relative energy of the electron transfer step. However, according to literature values,[124, 130] either $(NN^{fc})ScI(THF)_2$ or benzene could be reduced by KC_8. A relative energy surface was calculated showing that the activation barrier for C-H bond activation is rather low, at 18.4 kcal/mol. The calculated inter- and intramolecular KIEs as well as regioselectivity of toluene activation were in excellent agreement with the experimental values. The highest occupied molecular orbitals (HOMOs) for intermediate I and TS$_{I-II}$ were informative: HOMO of I was mostly the π^* orbital of benzene showing a significant overlap with the *3d* orbitals of both scandium ions; HOMO of TS$_{I-II}$ reflects its asymmetric nature, with one scandium binding to the aryl carbon atom and the other binding to the hydride ligand and the π face of benzene. For all calculated species, the singlet state was found to be the most stable.

The unprecedented C-H bond activation products as well as the detailed mechanistic studies led to the discovery of a new fundamental mechanism for C-H bond activation mediated by rare-earth metal complexes. As mentioned earlier in this section, two key approaches, the presence of a bimetallic system and ligand participation in the redox process, played a major role: two scandium ions are required to stabilize the inverse-sandwich arene intermediate as well as the hydride and aryl ligands formed after the cleavage of the C-H bond; in addition, upon coordination to the metal center, the arene was reduced by two electrons, which were then used to activate the C-H bond. Unfortunately, this C-H bond activation requires strong reducing agents like KC_8 and is stoichiometric. Nonetheless, the discovery of the bimetallic activation of aromatic C-H bonds by rare-earth metal complexes opens up new avenues in *f*-element chemistry as well as C-H bond functionalization. Together with other recent advances in low valent rare-earth metal chemistry, it strongly suggests that the once considered redox irrelevant rare-earth metals have a versatile chemistry that is comparable to that of *d*-block transition metals.

3.2. C-H Bond activation by low valent lanthanide and actinide complexes

Even prior to the bimetallic activation of aromatic C-H bonds by the $(NN^{fc})ScI(THF)_2/KC_8$ system, there were some isolated literature reports related to C-H bond activation under highly reducing conditions in the presence of rare-earth metals. In 2009, Nief, Junk, and co-workers observed an intramolecular C-H bond activation reaction from an isolated Nd(II) complex (Scheme 18a).[131] The product is a "tuck-in" type Nd(III) complex with the activation of one of

the methyl C-H bonds of a *tert*-butyl substituent. The authors attributed this C-H bond activation reactivity to the highly active Nd(II) center. Although no mechanism was proposed, these results could be the consequence of a radical process since neodymium was oxidized from the +2 to the +3 oxidation state with the likely loss of an H radical. Lappert and co-workers reported a similar example when studying the reactivity of KC_8 or K mirror in the presence of 18-crown-6 toward rare-earth metal cyclopentadienyl complexes.[132] When reacting $(Cp'')_3Y$ $(Cp'' = \eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3)$ with potassium mirror in the presence of 18-crown-6, a yttrium hydride, $[(Cp'')_2Y(\mu\text{-}H)]_2$, was observed in a small amount, in addition to $(Cp'')K(18\text{-crown-6})$ (Scheme 18b). It was proposed that the hydride originated from the solvent, benzene, since when using C_6D_6 as a solvent, the characteristic triplet of the hydride peak disappeared from the corresponding ^1H NMR spectrum. The authors suggested that a transient Y(II) species, presumably [K(18-crown-6)][(Cp'')_3Y], was responsible for hydride abstraction from benzene. That hypothesis was supported by the results of electrochemical reduction of $(Cp'')_3Y$[132] as well as the isolation and characterization of the analogous $[K(18\text{-crown-6})][(Cp')_3Y]$ $(Cp' = \eta^5\text{-}C_5H_4SiMe_3)$.[92]
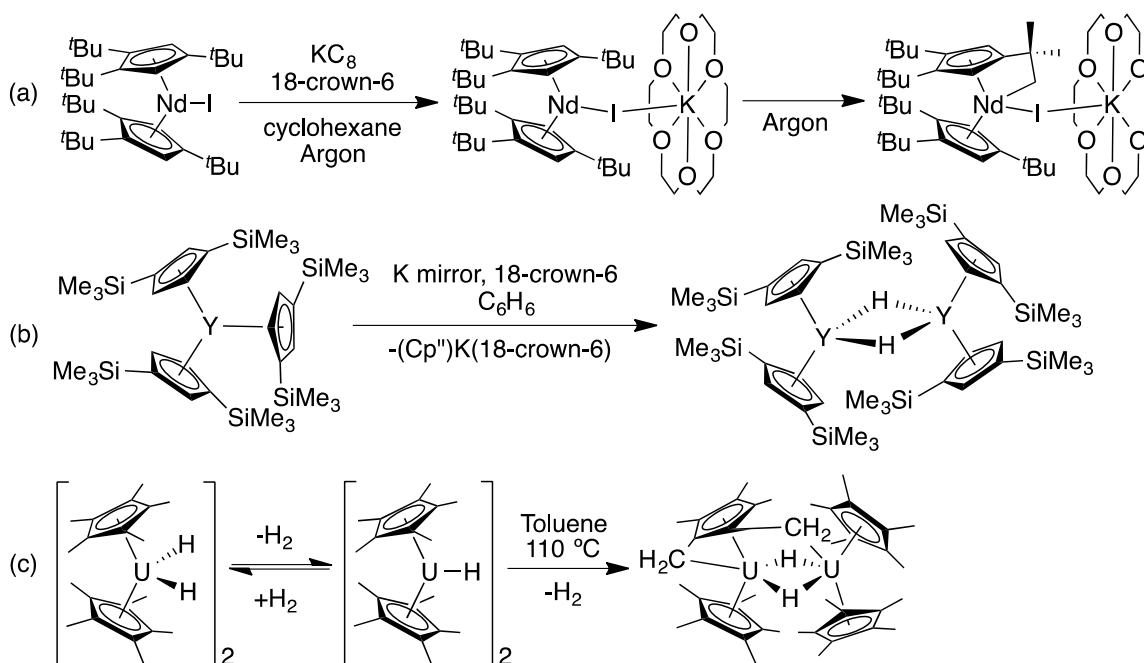

Scheme 18. C-H bond activation by low valent *f*-element complexes: (a) Intramolecular C-H bond activation in a neodymium(II) complex; (b) Hydride abstraction from benzene by in situ generated yttrium(II) species; (c) Formation of "tuck-in" and "tuck-over" diuranium complex through double cyclometalative C-H bond activation.

For actinides, Evans and co-workers have also shown an interesting case where a single diuranium complex containing both "tuck-in" and "tuck-over" features was formed through double intramolecular C-H bond activation of the Cp^* ligand (Scheme 19c).[97] The starting material was a U(III)/U(III) dihydride compound, which could reversibly bind one H_2 molecule to form a U(IV)/U(IV) tetrahydride complex. Upon heating in toluene at 110 °C, a U(IV)/U(IV) "tuck-in" and "tuck-over" complex was formed in good yield with the loss of one molecule of H_2. Albeit a mechanistic study was not conducted, the authors proposed that the formation of the "tuck-in" and "tuck-over" diuranium complex follows a double cyclometalative C-H bond activation by the U-

H bond followed by the trapping of H_2 generated in the process. If this proposal is correct, then the C-H bond activation here should still be cataloged in the σ-bond metathesis mechanism. However, since the net reaction result is a one electron oxidation at each uranium center, this reaction is worth mentioning in the present section.[96]

3.3. C-H Borylation of an inverse sandwich uranium arene complex
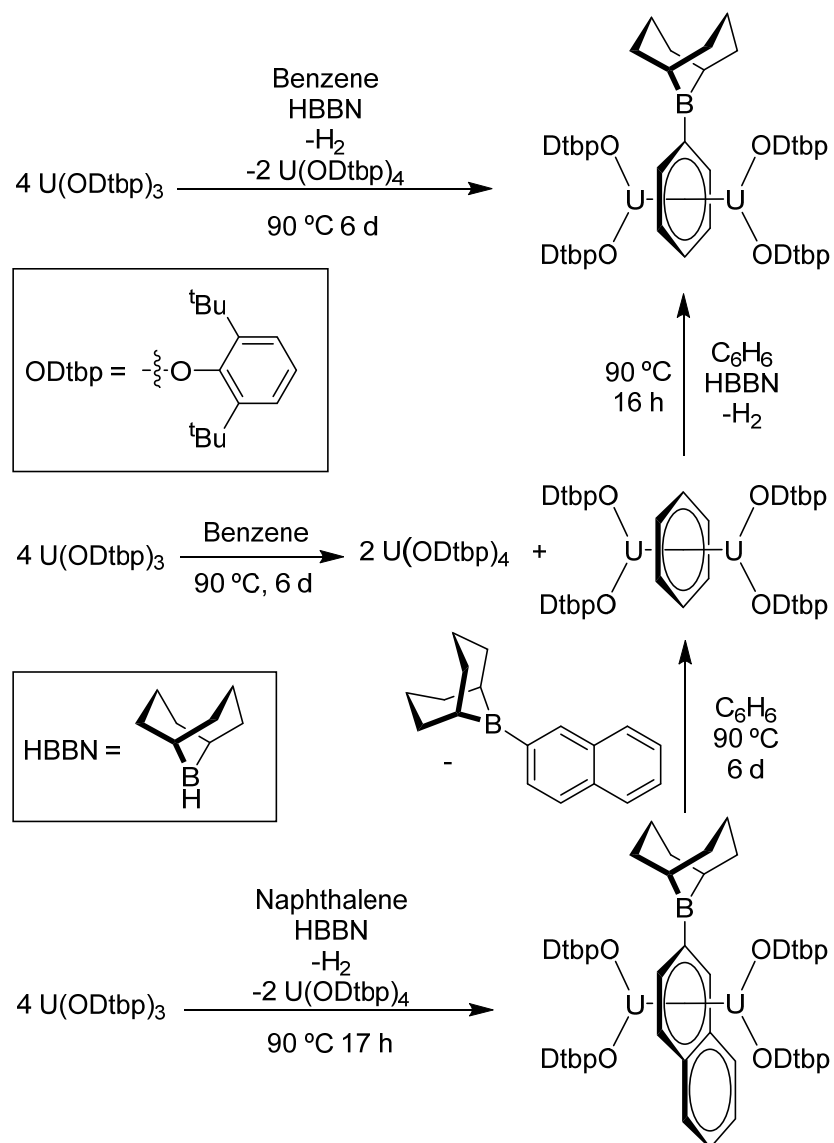
Scheme 19. Spontaneous reduction and C-H borylation of benzene and naphthalene by a U(III) complex.

Borylation of C-H bonds is an important avenue for C-H bond functionalization[133] since the borylated product plays an important role in cross-coupling reactions.[134] C-H bond borylation is mainly catalyzed by noble metals, such as rhodium. Rare-earth metal boryl complexes are rare.[135] However, in 2012, Arnold and co-workers reported an example of direct arene C-H borylation from an inverse-sandwich uranium arene complex.[136] In the presence of both U(ODtbp)₃ (ODtbp = O-2,6-^{t}Bu₂-C₆H₃) and the borane HBBN (9-bora-9-bicyclononane) in

benzene, the uranium borylated arene product [(DtbpO)$_2$U]$_2$(μ-C$_6$H$_5$BBN)] could be obtained together with the uranium disproportionation by-product U(ODtbp)$_4$ (Scheme 19). When the reaction was carried out in molten naphthalene instead of benzene, the uranium complex of borylated naphthalene (at the 2-position) could be obtained. Because of the higher thermal stability of the benzene complex, the borylated naphthalene fragment could be released by heating the respective uranium naphthalene complex in benzene (Scheme 19).

This result represents the first example of a synthetic cycle for arene borylation facilitated by an *f*-element. The authors investigated the reaction mechanism and proposed a concerted direct B-H attack on an aromatic C-H bond, which resulted in the formation of the B-C bond and the release of one molecule of H$_2$. This type of reactivity resembles σ-bond metathesis if boron is considered a metal center. Albeit uranium was not directly involved in the borylation of the arene C-H bond, the formation of the diuranium arene inverse-sandwich complex plays an important role. The arene, i.e. benzene or naphthalene, is partially reduced upon coordination to uranium,[137] which makes it more susceptible to attack by an electrophile such as borane. Therefore, although uranium is not directly involved in the C-H bond activation step, this example illustrates that *f*-elements can render arenes reactive in non-metal mediated transformations by forming activated arene metal complexes.

4. Summary

This year marks the 50th anniversary of Chatt's discovery of the first example of a metal mediated C-H bond activation. During this time, it has become a reality and is widely used in catalysis with high efficiency and selectivity.[138-140] However, most C-H bond functionalization reactions usually use late transition metals, especially noble metals, as catalysts. On the other hand, *f*-elements have been found to activate strong C-H bonds through a σ-bond metathesis pathway as shown by Marks's and Watson's seminal reports.[12, 70] Furthermore, with advances in synthesizing metal complexes containing metal-element multiple bonds, 1,2-addition has been established as an avenue to activate various hydrocarbons by transient metal imide or nitride species.[28-31, 34] In addition to these two non-redox processes, oxidative addition and reductive elimination enabled by the use of a redox non-innocent ligand have been shown possible for *f*-elements recently.[101, 102] Low valent lanthanide and actinide complexes have been shown to cleave C-H bonds either intramolecularly[97, 131] or from solvent molecules.[132] Another redox process, a bimetallic C-H bond activation, is the newest discovery in this area and its mechanism unveils the first example of *f*-element C-H bond activation resulting in the formation of an equimolar mixture of a metal hydride and metal phenyl products.[103] Other than the direct metal mediated C-H bond activation, a rare example of C-H bond borylation was established that involves a diuranium arene intermediate.[136] The coordination of the arene to the uranium center leads to some degree of reduction of the arene and makes it more active toward electrophilic substitution. Overall, the work surveyed in this review shows that rational ligand design, which has evolved from traditional ancillary Cp ligands to redox non-innocent ligands, has allowed rare-earth metals and actinides to play a larger role in the field of C-H bond activation and functionalization.

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