DOI: 10.1002/anie.201404613

C–H Activation

C–H Bond Activation by f-Block Complexes

Polly L. Arnold, Max W. McMullon, Julia Rieb, and Fritz E. Kühn*

Keywords:
actinides · asymmetric catalysis · polarity reversal catalysis · radical addition · rare earths

Angewandte Chemie International Edition

Most homogeneous catalysis relies on the design of metal complexes to trap and convert substrates or small molecules to value-added products. Organometallic lanthanide compounds first gave a tantalizing glimpse of their potential for catalytic C–H bond transformations with the selective cleavage of one C–H bond in methane by bis(permethylcyclopentadienyl)lanthanide methyl [(η^5-C_5Me_5)$_2$Ln(CH_3)] complexes some 25 years ago. Since then, numerous metal complexes from across the periodic table have been shown to selectively activate hydrocarbon C–H bonds, but the challenges of closing catalytic cycles still remain; many f-block complexes show great potential in this important area of chemistry.

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1. Introduction

The selective oxidation of inert C–H bonds of hydrocarbons is a challenging topic in modern catalysis, but offers considerable benefits in the production of fine chemicals and pharmaceuticals. It also provides the opportunity to process hydrocarbons instead of generating energy solely by their combustion.[1]

The major processes for the direct conversion of alkanes into more valuable products are the energy-intensive cracking and thermal hydrogenation processes.[2] Consumption of methane, the main constituent of natural gas, as a fuel is rapidly growing, yet a direct conversion of methane to methanol would represent a much greater environmental and economic benefit.[3] The selective C–H bond functionalization of more exotic substrates is also highly desirable for fine chemicals and pharma production.[4] Controlled, metal-mediated C–H functionalization reactions remain difficult for the following reasons:

1. Lone pairs or low-lying empty orbitals on the hydrocarbon with which a metal could interact are absent.
2. Alkane hydrogens have a low acidity.
3. The C–H bond is thermodynamically more stable (90–110 kcal mol^{-1}) than the targeted C–M bond for the majority of metals.
4. A reaction with the C–H bond of an added substrate is entropically disfavored with respect to the nearby C–H bonds already present in the ligand framework.
5. The C–H bonds of alkanes are all very similar.
6. The initial product of C–H activation is often more reactive than the alkane itself, thus hampering chemoselectivity.

While no viable metal-catalyzed C–H functionalization system has yet been developed for alkanes, f-block metal complexes exhibit promising reactivity with regard to this goal. The lanthanide metals form a series of Ln^{III} cations that are large and Lewis acidic and offer the possibility to strongly activate more than one coordinated small molecule. Early actinides, which are also large and Lewis acidic, are less well understood. The use of carefully structured organic ligands that enable the solubilization of metal cations in the reaction medium (usually an organic solvent) and control substrate access (especially in an asymmetric manner) is significantly more complicated for these large cations.

It is notable that the earliest reactivity studies that are described below usually feature a bis(Cp*) (Cp* = pentamethylcyclopentadienyl, $C_5Me_5^-$) supporting ligand set to kinetically stabilize the complexes and intermediates. However, alternative supporting ligands are increasingly showing great utility. Improved characterization technologies, particularly paramagnetic NMR spectroscopy and single-crystal X-ray diffraction, are reducing the technical challenges associated with the study of paramagnetic complexes.

The principal mechanisms by which a C–H bond may be activated by a homogeneous metal catalyst are shown in Figure 1. Routes **A**–**C** can currently be envisioned for a rare-earth-metal or actinide complex. Oxidative addition (**D**) is also possible for uranium complexes with low oxidation states (+III or +IV), but no examples have yet been reported.

Currently, the best understood reactions of f-block elements in the context of hydrocarbon C–H bond activation is σ-bond metathesis (**A** in Figure 1). It relies on a four-center transition state with no change in the metal oxidation state; indeed it has been suggested that this can be a lower energy mechanistic pathway than oxidative addition, even when the latter is available.[5] The majority of cyclometalation-based ligand decomposition at f-block metal centers proceed through this mechanism.[6]

Activation through the addition of a C–H bond across an M=E bond (**B**) has been demonstrated for in situ generated

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[*] Prof. Dr. P. L. Arnold, M. Chem. M. W. McMullon
EaStCHEM School of Chemistry
University of Edinburgh, The King's Buildings
Edinburgh, EH9 3FJ (UK)
E-mail: Polly.Arnold@ed.ac.uk

M. Sc. J. Rieb, Prof. Dr. F. E. Kühn
Fakultät für Chemie, Zentralinstitut für Katalyseforschung
Technische Universität München (Germany)

Prof. Dr. P. L. Arnold, M. Chem. M. W. McMullon, M. Sc. J. Rieb, Prof. Dr. F. E. Kühn
Institute for Advanced Study, Technische Universität München
Lichtenbergstrasse 2a, 85748 Garching (Germany)

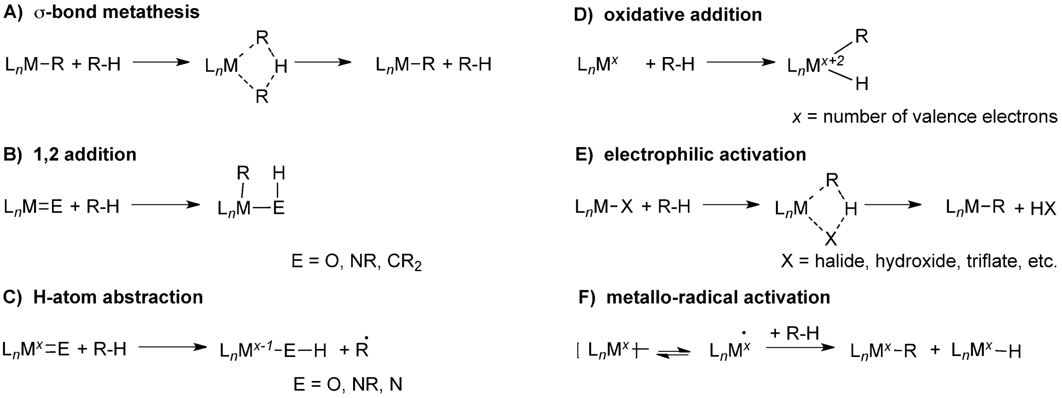


Figure 1. The types of C–H bond activation available to metal complexes.

Group 4 imido complexes. For example, $[(tBu_3SiO)_2Ti(=NSitBu_3)]$ reacts with methane to reform the $[Ti(CH_3)(HNSitBu_3)]$-containing complex from which it was originally derived.[7] This has encouraged the targeting of f-block complexes with metal–element double bonds either as terminal or bridging ligands, or as part of a ligand chelate.

Homolytic C–H bond scission by a metal oxo (**C**) group proceeds for d-block $L_nM(O)$ complexes when H-abstraction by the oxo group can form an intermediate $L_nM(OH)\cdot^-$ and the $\cdot CH_3$ radical. Depending on the local environment, the intermediates then normally collapse into metal hydroxide, alkoxide, or L_nM products and the alcohol if complete oxo transfer occurs. This mechanism is also available for uranium oxo groups.[8]

Uranium is the only potential candidate for organometallic C–H activation by oxidative addition (**D**) to a single metal center. Complexes of U^{III}, and potentially U^{IV}, could provide future entry points.

The final two reactions in Figure 1 (**E** and **F**) are currently not considered possible for these electropositive metals. However, the widespread use of simple Ce^{IV} salts to generate carbon-centered radicals has been used to form C–C bonds between a range of activated substrates, such as β-keto esters and diones, using an oxidative methodology.[9]

This review describes the first key results in the area, and surveys some of the most recent advances in C–H activation with f-block complexes. Although the selective functionalization of methane remains a fundamental goal in the field, pertinent information can be obtained by the study of its more reactive relatives, such as dihydrogen, silanes, strained or cyclic hydrocarbons, and heteroatom-containing molecules that contain either more acidic C–H bonds, or adjacent ligating atoms that can enhance reactivity.

Polly L. Arnold was born in London, UK, in 1972. She studied at the University of Oxford (BA 1994) and obtained her DPhil in 1997 at Sussex. After a Fulbright postdoctoral fellowship at MIT, she returned to the UK for a lectureship at the University of Nottingham. She has worked at the University of Edinburgh since 2007 where she currently holds the Crum Brown Chair of Chemistry. Her research interests are in small-molecule activation and its application in catalysis, and in the structure and bonding of actinide complexes.

Fritz E. Kühn studied chemistry at the Technische Universität München (TUM) and obtained his PhD in 1994. After a Humboldt postdoctoral fellowship at Texas A&M University, and a "Habilitation" in Munich, he became "Privatdozent" at the TUM in 2000. He was then appointed Principal Researcher at the Instituto Técnológico e Nuclear (ITN) in Sacavém (Portugal). Since 2006, he is Professor of Molecular Catalysis at TUM and since 2007 also Acting Chair of Inorganic Chemistry. His research areas are organometallic chemistry and catalysis.

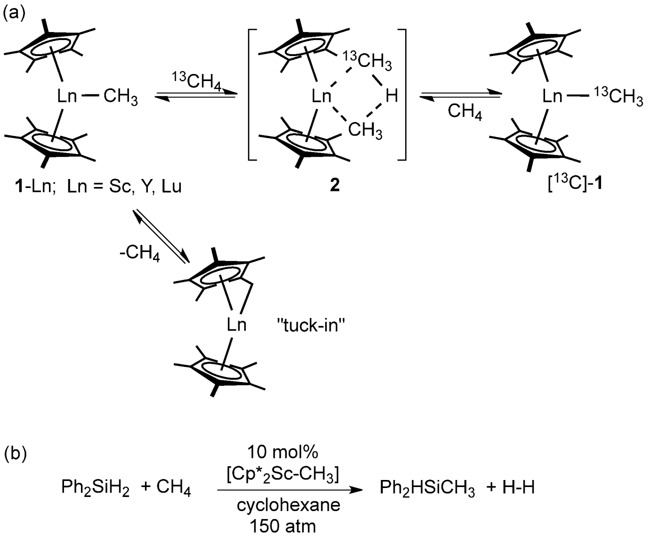
Max W. McMullon obtained his MChem at the University of Leeds in 2012 with his final year project on hafnium complexes for anti-cancer therapeutics under the supervision of Dr. Patrick McGowan. He is currently a PhD student at the University of Edinburgh, jointly supervised by Polly L. Arnold and Fritz E. Kühn. His research is focused on using heterobimetallic d/f systems for C–H activation.

Julia Rieb received her MSc in chemistry in 2013 from the Technische Universität München supported by the Studienstiftung des deutschen Volkes. She further studied and worked in the laboratories of Susannah L. Scott at the University of California at Santa Barbara as a Fulbright Scholar in 2012. Since 2013, she has been a PhD student jointly supervised by Fritz E. Kühn and Polly L. Arnold. Her PhD research is focused on the synthesis of lanthanide NHC complexes and their application for C–H activation.

2. σ-Bond Metathesis

2.1. [(Cp*)$_2$LnMe] and Related Complexes

The reaction in which [(Cp*)$_2$Ln(CH$_3$)] (M = Sc, Y, Lu, that is, smaller rare-earth metals) was demonstrated to activate methane (CH$_4$) for the first time is shown in Scheme 1 a.[10] Treatment with ^{13}C-labeled ^{13}CH$_4$ resulted in methane exchange via a σ-alkane complex, then the undetected four-center transition state **2**. This reactivity is notably different to other organometallic carbanions such as Grignard reagents, whose reactivity is strictly dominated by pK_a values. This is due to the accessibility of metal-based f and d orbitals and the suggested accessibility of the 4f^{n}5d^1 configuration for these metal ions.[11] While ethane and propane were also observed to react with **1**, no material was isolable and the metal products were assumed to decompose through β-hydrogen elimination. The absence of redox reactivity of the metal center, the strongly bound and sterically protecting Cp* ligands, and the strong M–C bond makes σ-bond metathesis a straightforward reaction in these rare-earth-metal complexes. As σ-bond metathesis plays a critical role in certain olefin polymerizations and reactions of dihydrogen and silane, these and related reactions were studied intensely in the following years.[12]



Scheme 1. Methane activation and silylation chemistry.

A transition state in which H$^{\delta+}$ is transferred between two metal-coordinated methyl groups [M$^{\delta+}$-CH$_3$$^{\delta-}$] was described by Bercaw and co-workers for the heterolytic cleavage of the C–H bond by the electrophilic metal center, in wide ranging studies of [Cp*$_2$ScR] complexes (R = H, hydrocarbyl).[13] Backed up by DFT calculations,[14] these studies explain why the methyl group cannot take the central position in the four-center-four-electron intermediate, and no C–C bond formation should be possible. However, using the same [Cp*$_2$Sc–CH$_3$] (**1**-Sc), Tilley and Sadow showed that the silicon atom of a silane can occupy this β-position. They also demonstrated a catalytic conversion of methane to methylsilane (Scheme 1 b) using 150 atm pressure of methane and achieved five turnovers after one week. The formation of a stronger Si–C bond makes this reaction possible. The rate limiting step is the C–H bond activation.[15] The traditional description of the d^0 Sc^{III} center as "electrophilic" has been revisited more recently by Periana et al. in a computational study of the charge-transfer stabilization energies (HOMO to LUMO) between the metal–ligand fragment and the coordinated C–H bond in the transition state of the C–H bond cleavage reaction. They suggested a nucleophilic classification for the C–H activation by [Cp*$_2$ScCH$_3$] and a nucleophilic attack from the negatively polarized carbon atom of the highly polarized Sc–CH$_3$ bond.[16]

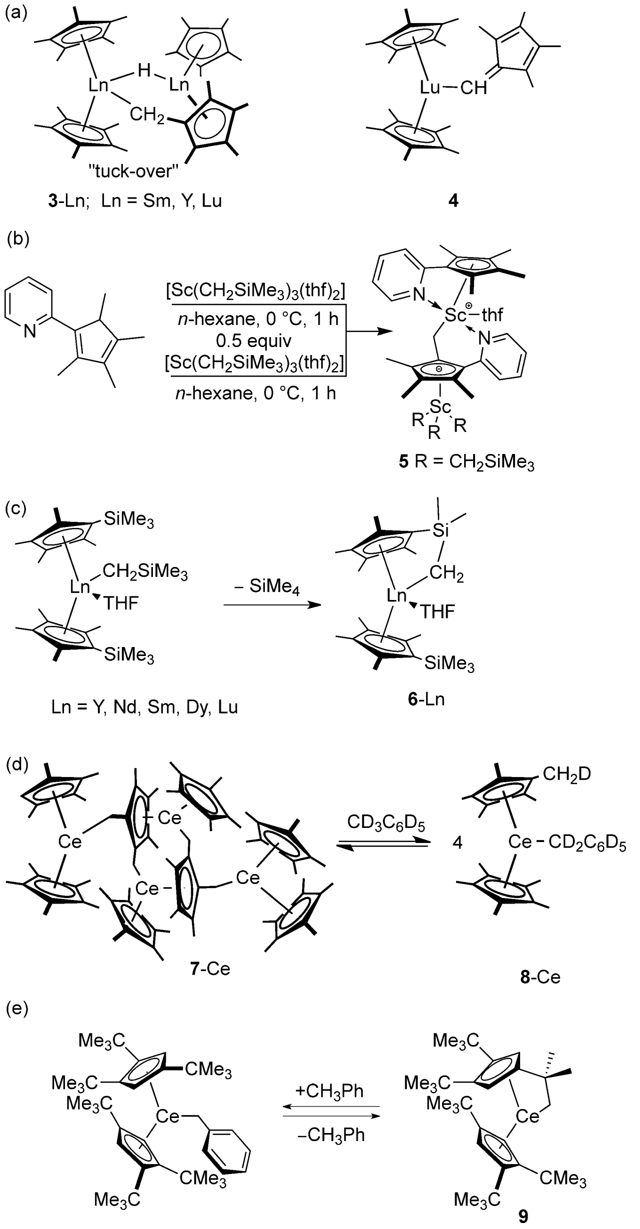
Scheme 1 a also shows the potential, undesired (but often reversible) C–H activation of the ligand, namely the formation of a "tuck-in" metallacycle. Despite the repeated invocation of "tuck-in" complexes in mechanistic schemes involving f-block elements, they have only recently been spectroscopically and crystallographically confirmed for f-block complexes. Evans reported the crystal structure of a "tuck-over" complex **3** and a vinyl complex **4** of Lu^{III}, which was unexpectedly obtained through C–H activation of tetramethylfulvene (Scheme 2 a).[17]

Many Cp-supported f-block "tuck-in" and "tuck-over" complexes have now been reported. Other interesting examples (shown in Scheme 2) are the "tuck-over" zwitterionic complex [(η^5:κ-C$_5$Me$_4$-C$_5$H$_4$N)Sc(thf){μ-η^5:η^1:κ-C$_5$Me$_3$(CH$_2$)-C$_5$H$_4$N}Sc(CH$_2$SiMe$_3$)$_3$] (**5**) formed through spontaneous C–H activation of a pyridyl-functionalized Cp ligand,[18] and a "tuck-in" [(η^5:η^1-C$_5$Me$_4$SiMe$_2$CH$_2$)Ln(C$_5$Me$_4$SiMe$_3$)(thf)] (**6**; Ln = Y, Nd, Sm, Dy, Lu).[19]

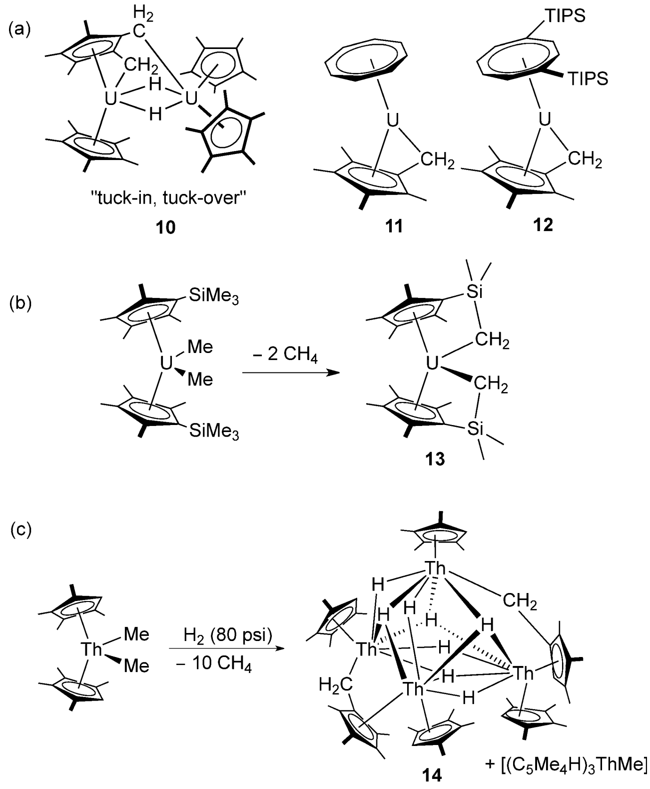
Many of these molecules show interesting C–H activation chemistry. For example, storage of a solution of [(Cp*$_2$MH)$_2$] (M = Sm, Y) in benzene/alkane results in H$_2$ elimination to give the "tuck-over" complex [(Cp*$_2$M(μ-H)(μ-CH$_2$C$_5$Me$_4$)MCp*)] (Scheme 2 a) significantly more rapidly for Y.[20,21] Analogously when the complex (Cp*$_2$MR) (M = Ce, La; R = CH(SiMe$_3$)$_2$) was left in a solution of cyclohexane or methylcyclohexane, RH was eliminated to give the doubly metalated complexes **7**-Ce (Scheme 2 d). Compound **7**-Ce reacted with deuterated toluene to give [Cp*(C$_5$Me$_4$CH$_2$D)Ce(CD$_2$C$_6$D$_5$)] (**8**-Ce),[22] but in situ studies showed no generation of CHD(SiMe$_3$)$_2$, which suggested that the reaction proceeds not by a direct σ-bond metathesis mechanism, but via the doubly metalated product.

Solutions of the cerium complex [(η^5-C$_5$H$_2$(C(CH$_3$)$_3$)$_3$)Ce-(CH$_2$Ph)] in cyclohexane were reported by Andersen et al. to form a "tuck-in" complex **9** (Scheme 2 e) through the elimination of toluene. They also found that **9** shows further reactivity with MeX (X = halide) to give [(η^5-C$_5$H$_2$(C-(CH$_3$)$_3$)$_3$)Ce(R)]X. The alkyl groups in the compound were found to be readily exchangeable, allowing deuteration studies to confirm the nature of the C–H bond activation reactions.[23]

Examples of the many actinide "tuck-in" and "tuck-over" complexes (Scheme 3) include: a bimetallic uranium complex that exhibits both "tuck-in" and "tuck-over" Cp* metalation; [Cp*U(μ-η^5:η^1:η^1-C$_5$Me$_3${CH$_2$}$_2$)(μ-H)$_2$UCp*$_2$] (**10**) formed by



Scheme 2. Rare-earth-metal “tuck-in” and “tuck-over” complexes.



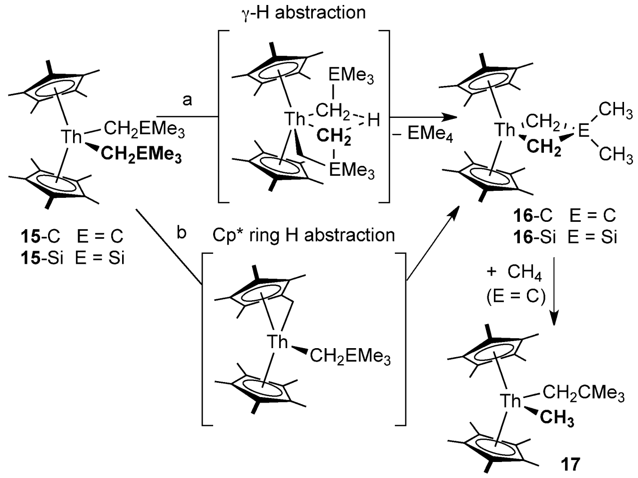
Scheme 3. Actinide “tuck-in” and “tuck-over” complexes.

heating a mixture of the uranium hydrides [{Cp*$_2$UH$_2$}$_2$] and [{Cp*$_2$UH}$_2$] to 110 °C in toluene;[24] [(η^5:η^1-C$_5$Me$_4$CH$_2$)U(C$_8$H$_8$)] (**11**) formed by σ-bond metathesis elimination of C$_6$H$_6$ by heating [(C$_5$Me$_5$)(C$_8$H$_8$)UPh] in toluene;[25] “tuck-in” [(η^5:η^1-C$_5$Me$_4$CH$_2$)U(C$_8$H$_6$$^{\mathrm{TIPS2}}$)] (**12**; TIPS = triisopropylsilyl) formed by a loss of RH through σ-bond metathesis at 70 °C (RH = CH$_4$, CH$_3$Ph, SiMe$_4$, CH$_2$(SiMe$_3$)$_2$);[26] the double alkylsilyl “tuck-in” U$^{\mathrm{IV}}$ complex [(η^5:η^1-C$_5$Me$_4$SiMe$_2$CH$_2$)$_2$U] (**13**) was formed from methane elimination in refluxing toluene (Scheme 3b);[27] and polyhydride **14** formed from [(C$_5$Me$_4$H)$_2$Th(Me)$_2$] under an 80 psi hydrogen overpressure (Scheme 3c).[28]

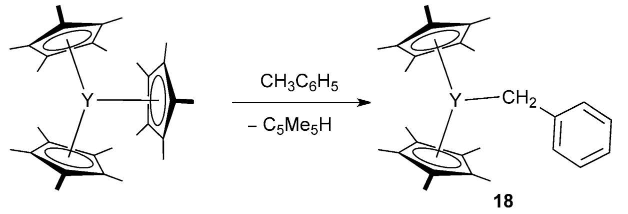
A thorium “tuck in” complex [(η^5:η^1-C$_5$Me$_4$CH$_2$)(η^5-C$_5$Me$_5$)Th{*i*PrNC(Me)N*i*Pr-κ^2-*N*,*N′*}] has recently been made from the ion pair [(C$_5$Me$_5$)$_2$Th{*i*PrNC(Me)N*i*Pr-κ^2-*N*,*N′*}][BPh$_3$Me]. Interestingly, the analogous reaction with uranium did not give the anticipated U analogue.

Marks and co-workers undertook a detailed mechanistic study on the highly regioselective thermally induced cyclometalation of sterically congested thorium dialkyl complexes [Cp*$_2$Th(CH$_2$EMe$_3$)$_2$] (**15**-E) (E = C, Si), the driving force of which is the production of the unreactive small organic molecules EMe$_4$.[29] Two competing concerted mechanisms were identified for **15**-E, proceeding through a transition state similar to that observed in σ-bond metathesis. The first involves γ-hydrogen abstraction from the dialkyl group (Scheme 4a) and the second involves hydrogen abstraction from the Cp* ring to afford a “tuck-in” complex (Scheme 4b). The use of CD$_4$ shows a large kinetic isotope effect (k_H/k_D = 6.6(2) at 85 °C), which suggests that the activation of methane is the rate-determining step for the overall reaction. The most interesting reactivity in this system comes from the metallacyclobutane **16**-C, which combines non-negligible ring strain (ca. 15 kcal mol^{-1}), steric interactions, and/or weak Th–C σ-bonds, to give a negative Δ*G* for the reaction with methane, affording **17** in cyclohexane as solvent.[30] Further, once deposited onto dehydroxylated alumina, these organothorium complexes are catalysts for the deuteration of C–H bonds with D$_2$ in a range of alkanes.[31]

A more unusual route to C–H activation is accessible from [Y(Cp*)$_3$], which was traditionally considered too sterically congested to be isolable. [Y(Cp*)$_3$] has long Ln–C bonds and the ligand is sufficiently weakly bound that it can metalate the solvent, toluene (Scheme 5), affording **18** and C$_5$Me$_5$H. The analogue [Sm(Cp*)$_3$] reacts through the homol-



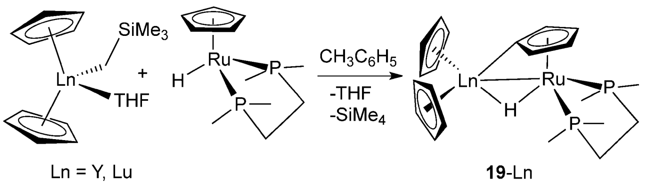
Scheme 4. Use of ring strain to enhance the C–H activation reactivity of thorium complexes.



Scheme 5. Toluene activation by a sterically crowded Y complex.

ysis of one Sm–Cp* bond (in a sterically induced reduction mechanism) to afford the isolable Sm^{II} complex $[Sm(Cp^*)_2]$ and the reactive hydrocarbyl radical.[32]

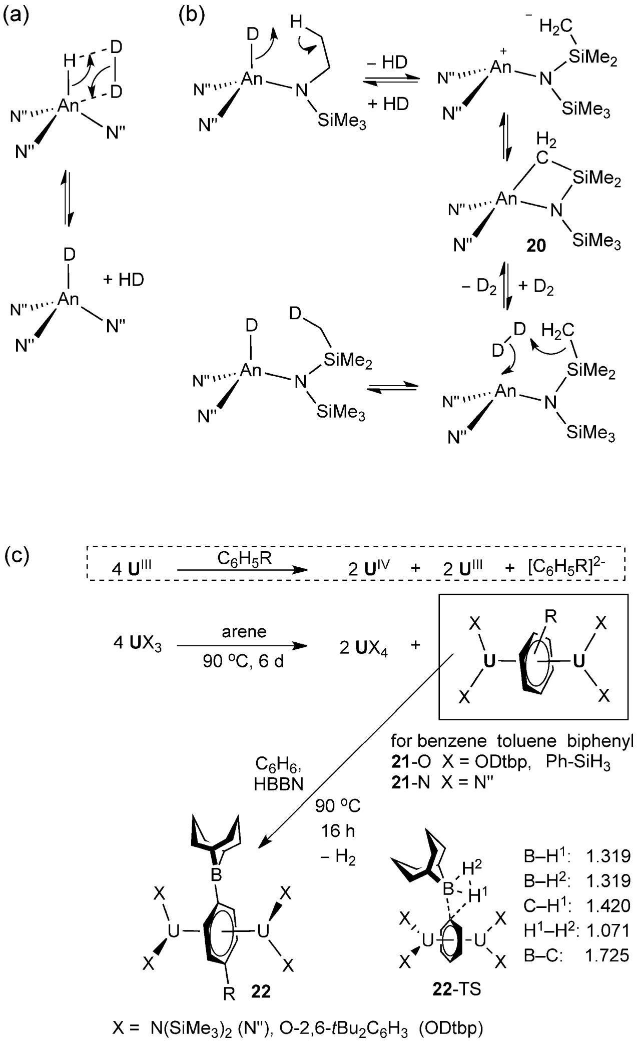
The unusual heterobimetallic "tuck-over" complex **19** is formed from $[Cp_2Ln(CH_2SiMe_3)(thf)]$ (Ln = Y, Lu) and [HRu(dmpe)Cp] in toluene at −40 °C with the loss of tetramethylsilane (Scheme 6). Complex **19**-Y undergoes further Y–C bond insertion.[33]



Scheme 6. Formation of a "tuck-over" complex with a metal–metal bond.

2.2. Post-Metallocene Complexes with C–H Interactions and Their Reactions

The Cp* complexes show a variety of "bitten-in" forms, highlighting a major potential problem for the design of supporting ligands for these reactive metals, although often the reversibility allows for intermolecular C–H activation processes to take place. The development of "post-metallocene" ligands, polydentate, anionic ligands that are sufficiently large, soluble, and robust to support new C–H bond activation chemistry, has increasingly focused on nitrogen-donor ligands. While many are excellent supporting scaffolds, examples of unanticipated metalation, albeit sometimes reversible, are still a major factor in their reactivity.[34]



Scheme 7. Actinide amides and aryloxides that undergo reversible deuteration (An = U, Th) and spontaneously reductively activate and C–H functionalize arenes.

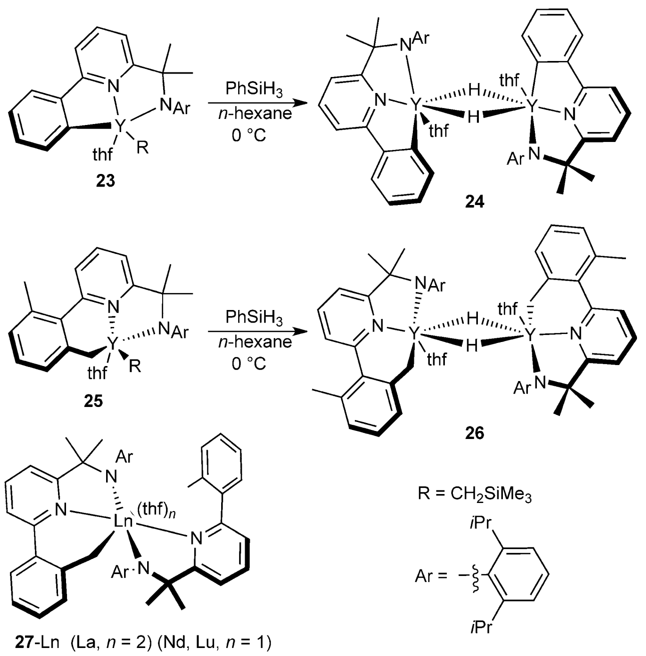
The thermal decomposition of $[\{(Me_3Si)_2N\}_3AnX]$ (An = U, Th; X = H, Me, Et, or CH_2SiMe_3) results in the formation of the metallacycle $[\{(Me_3Si)_2N\}_2An\{(CH_2SiMe_2)N(SiMe_3)\}]$ (**20**; Scheme 7b), without a change in oxidation state, as a result of the metalation of one $SiMe_3$ CH group. This metallacycle reversibly reacts with dihydrogen or deuterium (as does the hydride $[\{(Me_3Si)_2N\}_3AnH]$), and the molecule can be perdeuteriated, most likely through sequential σ-bond metathesis steps (Scheme 7b).[35]

We recently developed a new in situ arene C–H bond functionalization methodology to convert C–H to C–B bonds (Scheme 7c). When stored at elevated temperatures for a few days, or ambient temperature for up to a month, arene solutions of simple uranium complexes UX_3 (X = bulky aryloxide, amide) spontaneously disproportionate, transferring an electron and X ligand and generating a “UX_2” unit that binds and reduces the arenes. The two products are “inverse sandwich” compounds $[X_2U(\mu\text{-}\eta^6{:}\eta^6\text{-arene})UX_2]$ (**21**) and UX_4. Calculations and kinetic studies suggest a mechanism of cooperative small-molecule activation involving spontaneous arene reduction, which allows functionalized arenes to be incorporated, and reagents such as boranes to be introduced, for example affording **22**. An unusual mechanism is also suggested from calculations in which the strongly reduced arene undergoes a form of electrophilic aromatic substitution in which the C–B and H–H bonds form at the transition state **22**-TS with very little perturbation of the U-bound arene. This behaviour differs substantially from previously found mechanisms for both main group and transition-metal reagents.

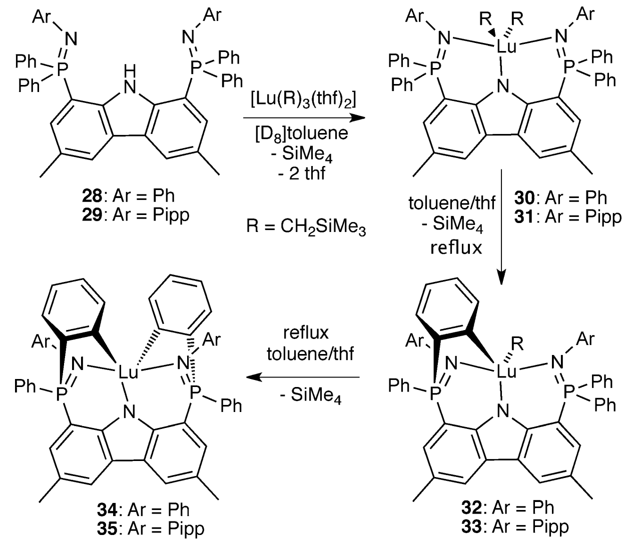
A comparison with related 4f-arene complexes is of value: Lappert and co-workers observed no C–H bond activation in the benzene radical anion complexes such as $[K([18]crown\text{-}6)][Ln(Cp^t)_3(\mu_2\text{-}\eta^6{:}\eta^4\text{-}C_6H_6)]$ ($Cp^t = 1,3\text{-}(t\text{Bu})_2C_5H_3$),[36] but spontaneous C–C aryl coupling was observed by Fryzuk et al. from the intermediate $[\{(P_2N_2)Y\}_2(\mu\text{-}C_6H_4\text{-}p\text{Me})_2]$ ($P_2N_2 = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$), which forms during the dissolution of $[(P_2N_2)Y(CH_2SiMe_3)]$ in toluene, resulting in $[\{(P_2N_2)Y\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_4\text{-}p\text{Me-}C_6H_4\text{-}p\text{Me})_2]$.[37]

Giambastiani and Kempe and their respective co-workers used amidopyridinate ligands to stabilize hydrocarbyl complexes of rare-earth metals: **23, 25**, and **27** undergo reactions with $PhSiH_3$, which proceed through σ-bond metathesis to give hydrido complexes, including **24** and **26** (Scheme 8).[38,39]

Intramolecular C–H σ-bond metathesis of bis(phosphinimine)carbazole adducts $[L^{Ph}Lu(CH_2SiMe_3)_2]$ (**30**) and $[L^{Pipp}Lu(CH_2SiMe_3)_2]$ (**31**) ($L^{Ph} =$ **28**, $L^{Pipp} =$ **29**; Pipp = *para*-isopropylphenyl, Scheme 9) first affords singly metalated products **32** and **33**, then doubly metalated products **34** and **35** upon heating to reflux in toluene or THF.[40]



Scheme 8. Amidopyridinate complexes.



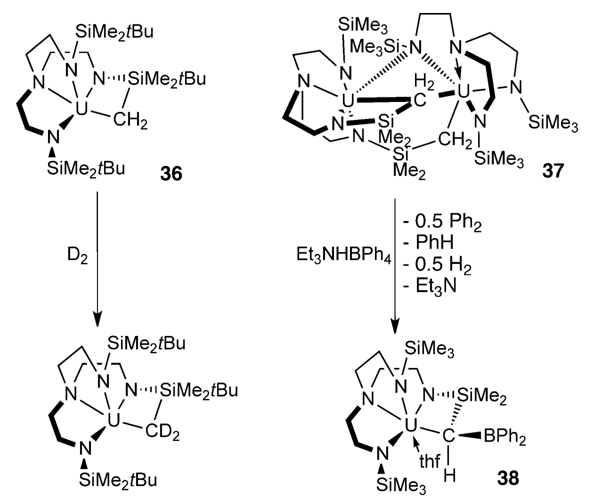
Scheme 9. Loss of $SiMe_4$ through complexation of $[Lu(R)_3(thf)_2]$ with a bis(phosphinimine)carbazolate ligand.

Both the groups of Scott and Liddle synthesized interesting “tuck-in” and “tuck-in-tuck-over” uranium complexes **36** and **37**, using silylated tren ligands $tren^{TBDMS}$ ($R = SiMe_2t\text{Bu}$) or $tren^{TMS}$ ($R = SiMe_3$), respectively ($tren = N(CH_2CH_2NR)_3$; Scheme 10).[41] The former has a very long U–C bond (2.75 Å) and is selectively deuterated by deuterium gas at just the CH_2 position.[42] The unusual U^{III} analogue was also isolated as the potassium salt. The ligand in **37** is partially recovered by protonation with Et_3NHBPh_4, but also incorporates one BPh_2 group into the uranium metallacycle **38**.[43]

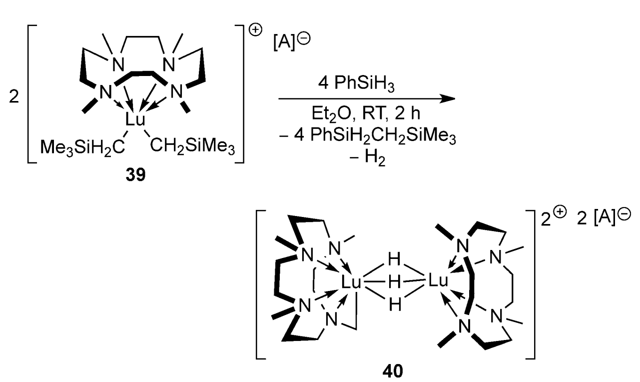
Okuda showed an interesting reversible H_2 activation in the Lu complex $[(Me_4TACD)Lu(CH_2SiMe_3)_2][A]$ (**39**; $A = B(3,5\text{-}C_6H_3(CF_3)_2)_4$; Me_4TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane). Treatment of **39** with four equivalents of $PhSiMe_3$ in diethyl ether eliminates $PhSiH_2CH_2SiMe_3$ and H_2 to form the dicationic trihydrido complex $[(Me_3TACD\text{-}CH_2)Lu(\mu\text{-}H)_3Lu(Me_4TACD)][A]_2$ (**40**; Scheme 11). Interestingly, and of potential synthetic use, is the reversible and controllable H_2 addition that is possible across the new Lu–CH_2 bond to give the tetrahydrido species $[(Me_4TACD)Lu(\mu\text{-}H)_4Lu(Me_4TACD)][A]_2$, as the reaction is reversed in vacuo at high temperatures. Reactions with D_2 and H_2 confirm the reversible C–H activation, with an inverse isotope effect suggesting a critical pre-equilibrium step in the reaction.[44]

2.3. Chelation-Assisted or Directed C–H Activation

The fact that C–H activation at the ligand is the entropically favored reaction has been used extensively to develop C–H bond functionalizations catalyzed by late transition metals. Substrates are chosen/designed such that prior coordination of a nearby heteroatom, often a pyridyl group, places the targeted C–H bond next to the metal, facilitating regiospecific *ortho* metalation.[45]



Scheme 10. "Tuck-in" and "tuck-in-tuck-over" complexes of uranium.



Scheme 11. Formation of a dicationic trihydrido lutetium complex.

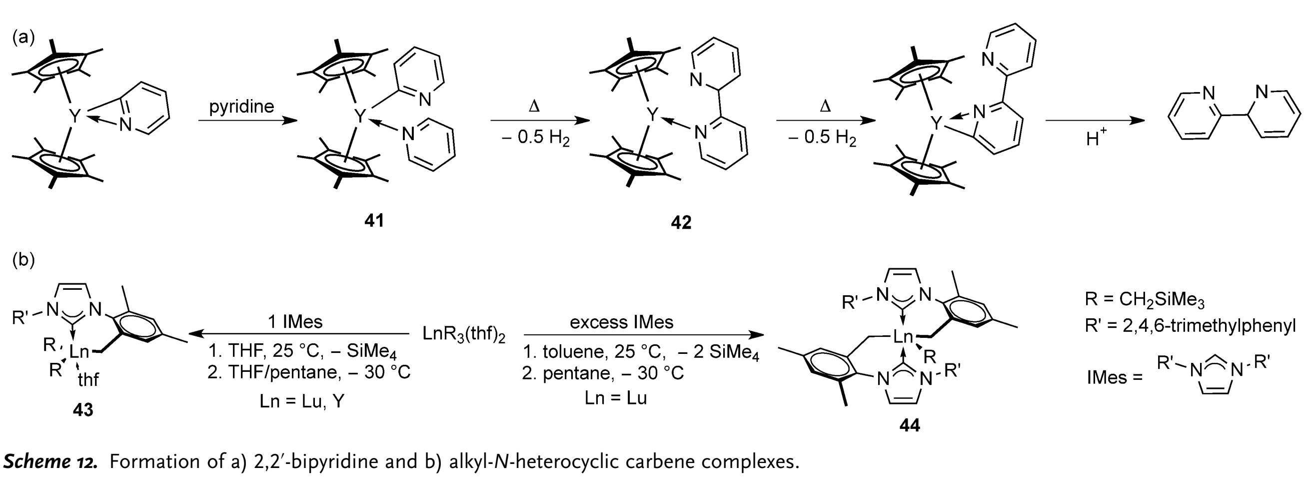
The pK_a value of the H atom in *ortho* position of pyridine is 43.6 in DMSO (44.7 in benzene),[46] and the H atom therefore less acidic than the other H atoms bound to the pyridine ring, thus stressing the fact that acidity is not generally an important issue in metalation reactions directed by d- or f-block metals, and that the pre-coordination of the heteroatom is the key step. Functionalization with catalytic turnover is usually achieved with cyclometalated palladium complexes through the addition of a stoichiometric amount of base, but this has been less widely explored for f-block systems so far. These coordination-directed reactions unfortunately exclude the simplest aliphatic hydrocarbons, but have led to a range of coupling and ring-opening reactions of pyridines and methylimidazoles.

Teuben's group reported that $[(Cp^*)_2Y(\kappa^2\text{-}C,N\text{-pyridyl})]$ is formed from the hydride $[(Cp^*)_2Y(H)]_2$ through the selective metalation of pyridine.[47] The addition of a further equivalent of pyridine gives the adduct $[(Cp^*)_2Y(\eta^2\text{-}C,N\text{-pyridyl})(NC_5H_5)]$ (**41**), which upon heating first forms the non-aromatic C–C coupled product $[(Cp^*)_2Y\{\kappa^1\text{-}2,2'\text{-}NC_5H_4\text{-}(2\text{-}NC_5H_5)\}]$ (**42**) by insertion, then eliminates hydrogen, and upon quenching 2,2′-bipyridine. This noncatalytic pyridine functionalization was extended to alkylated pyridines by the subsequent insertion of alkenes. The use of ethene at high pressure enabled a catalytic cycle with 44 % conversion of pyridine to 2-ethyl pyridine, although the original hydride complex was not a good intermediate in the catalytic cycle, as it can form other metalation products.

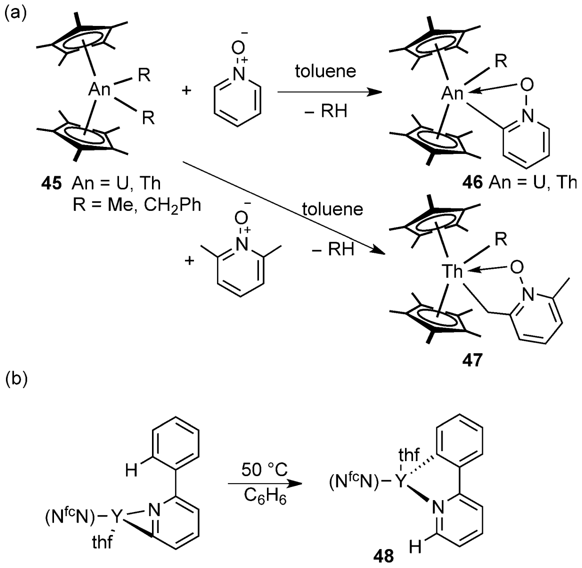
The Hou group extended this reaction of insertion into the C–H bond of alkenes with $[(Cp^*)_2LnR_2]/B(C_6F_5)_3$ (Ln = Sc, Y) to give over twenty functionalized examples,[48] and with $[(Cp^*)_2LnR_2]/(CPh_3)(B(C_6F_5)_4)$ (Ln = Sc, Y, Gd) to benzylic *ortho* groups of functionalized pyridines and anisoles.[49]

Both solvent and stoichiometry control the single or double metalation of the N-heterocyclic carbene to form **43** or **44**, respectively, when an NHC is coordinated to $[LuR_3(thf)_2]$ (R = CH_2SiMe_3, NHC = 1,3-dimesitylimidazole-2-ylidene; Scheme 12b). The faster metalation of the yttrium analogue was ascribed mainly to the electrophilicity of the metal center. The tricarbene analogue was not accessible, probably because of steric congestion.

One of the most surprising and interesting examples of directed C–H activation is shown in Scheme 13: Coordinatively unsaturated **45**-U binds pyridine-*N*-oxide as an O-donor in solution, rather than transferring the oxygen atom, which is the conventional mode of reactivity. Boiling the solution for four hours evolves methane and forms the η^2-*O*,*C*-pyridyl-*N*-oxide complex **46**. The thorium analogue **45**-Th reacts with 2,6-dimethylpyridine-*N*-oxide to readily form the C(sp^3)–H activation product **47**, but **46** is unreactive even after 12 h of boiling. It is very rare for Th^{IV} and U^{IV} complexes



Scheme 12. Formation of a) 2,2′-bipyridine and b) alkyl-*N*-heterocyclic carbene complexes.



Scheme 13. a) A new mode of reactivity for pyridine *N*-oxide, C–H activation. b) C–H activation of 2-phenylpyridine.

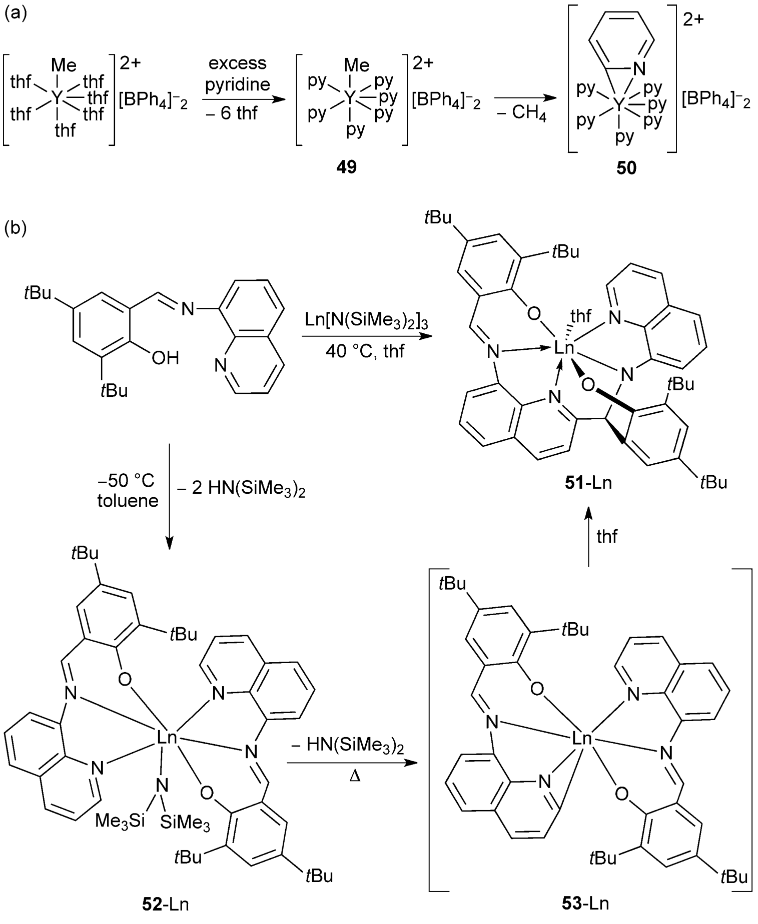
to show such different reactivities. According to studies of the mechanism, the C(sp^3)–H activation product is the kinetic product, and the C(sp^2)–H activation product is the thermodynamic product. Scrambling of the incorporated deuterium label was not observed, thus suggesting that no alkylidene intermediate was formed.[50] The Th/U differences are even more pronounced in the analogous reactions between **45** and pyridine/2,6-dimethylpyridine.[51]

Diaconescu and co-workers reported the formation of the *ortho*-metalated pyridyl adduct of the ferrocenyldiamido-supported Y complex [(NN^{fc})Y(η^2-*N,C*-6-phenylpyridyl)(thf)] (**48**, NN^{fc} = 1,10-fc(NSi*t*BuMe$_2$)$_2$; Scheme 13b), formed from a routine alkane elimination reaction between [(NN^{fc})Y(CH$_2$Ph)(thf)] and 2-phenylpyridine.[52] The product is however an isomer of the *ortho*-phenyl-metalated phenylpyridine ligands that are widely obtained from oxidative addition reactions of 2-phenylpyridine in Pd^{II}-catalyzed C–H functionalizations.[45] The reaction relies on the hemilability of the pyridine N atom. It proceeds very slowly (over 14 days) and exclusively in an intramolecular manner, through a stepwise pathway involving a proton transfer to the pyridyl N atom from the phenyl ring, then a 1,2-H shift, and recoordination of the pyridine N atom to the Y center. The five-membered metallacycle has not previously been observed in d^{0}f^n-complex C–H activation.[53]

The analogous pyridine C–C coupling is possible in scandium complexes of the 1,1′-ferrocenyldiamido ligand NN^{Fc}, but the reaction stops at the non-aromatic [(NN^{Fc})Sc{κ^1-2,2′-NC$_5$H$_4$(2-NC$_5$H$_5$)}]. N-Heterocycles with lower aromaticity than pyridine, such as methylpyrrole, are coupled, in some cases reversibly, after initial *ortho*-C–H metalation by the scandium methyl precursor.[54] Teuben had originally suggested that sterically less demanding complexes (e.g. of larger metals) might allow the development of better catalytic cycles. The use of yttrium or lanthanum analogues of the (NN^{Fc}) ligand generally show very little difference in the reactivity compared to the much smaller scandium complexes.

The use of the simple mono- and dicationic methyl complexes of lanthanides, [Ln(Me)$_2$(thf)$_6$]$^+$ and [Ln(Me)(thf)$_6$]$^{2+}$, offers an elegant new way to tune the reactivities of organolanthanides.[55] The complexes all metalate pyridine, the reaction proceeding after the initial coordination of the pyridine molecule, forming for example [Y(η^2-*C,N*-C$_5$H$_4$N)(NC$_5$H$_5$)$_6$]$^{2+}$[BPh$_4$]$_2^-$ (**50**), which retains the cationic charge (Scheme 14).[56] Calculations on the monocation [Y(η^2-*C,N*-C$_5$H$_4$N)$_2$(NC$_5$H$_5$)$_5$][BPh$_4$] suggest that a C–C bond-formation step that would convert the coordinated pyridyl ligands into neutral bipyridine could occur through a single-electron reductive C–C coupling; forming a bound bipyridyl radical anion.[57]

Shen and co-workers reported the activation of the quinoline ligand at the 2 position in yttrium and ytterbium bis(3,5-di-*tert*-butylsalicylidene)-8-aminoquinoline (L^{quin}) complexes. (L^{quin})Ln(N(SiMe$_3$)$_2$) (**52**-Ln: Ln = Y, Yb) was accessible at low temperatures, while higher temperatures afforded **51**-Ln and **53**-Ln, with **53**-Ln as the proposed intermediate.[58]



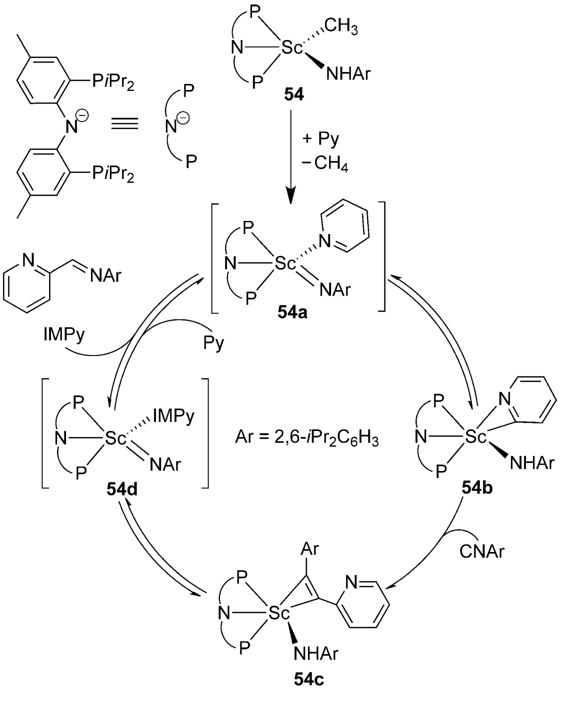
Scheme 14. a) Metalation of pyridine. b) Activation of quinoline-based ligands.

3. Addition of a C–H Bond Across an M=E Bond

Since Wolczanski's studies of the addition of a methane C–H bond across the M=N bond in early-transition-metal complexes, a number of groups have sought to isolate a rare-earth-metal complex containing a terminal, and thus reactive, metal–imido M=N bond or a metal–alkylidene M=C bond.[59] In contrast to the extensive number of reports on imido and carbene chemistry of d-block metals, such compounds with Group 3 metals and lanthanides still remain rare. Because of their increased Lewis acidity, f-block metal complexes should exhibit even more reactive M=E moieties compared to their d-block analogues. The lack of examples of isolated imido and alkylidene complexes is attributed to the mismatch in the ligand–metal orbital energy.[59] Most of the reported lanthanide–imido complexes exhibit bridging or capping amido or imido functionalities and accordingly lower reactivity.[60]

Convincing evidence of the transient existence of a terminal imidoscandium compound was presented in 2008.[61] [{PNP}Sc{NH(Ar)}(CH$_3$)] (**54**, PNP = N(2-*P*-(CHMe$_2$)$_2$-4-methylphenyl)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; Scheme 15) readily reacts with pyridine to afford a transmetalated pyridyl anilide complex [(PNP)Sc(NHAr)(η^2-NC$_5$H$_4$)]. Using a combination of isotopic labeling and reactivity studies with Al(CH$_3$)$_3$, the authors excluded a σ-bond metathesis mechanism and postulated a terminal imido intermediate **54a**, produced by α-hydrogen abstraction prior to the *ortho* metalation of pyridine by the 1,2 addition of a C–H bond across a Sc=N bond. The use of isotopically labeled C$_6$D$_6$ supported this hypothesis.[61]

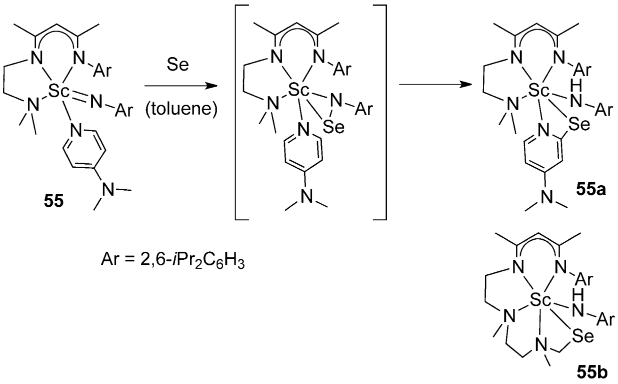
The postulated transient scandium imido complex **54a** can also functionalize pyridine with isonitriles C≡NAr (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ (DIPP) or 2,6-(CH$_3$)$_2$C$_6$H$_3$ (DMeP)) to afford mono- and disubstituted imino pyridines.[62] The proposed mechanism is shown in Scheme 15. A complete conversion to monosubstituted imido pyridines (IMPy) was achieved at 90 °C after 45 hours, that is, a TOF of 0.11 h (ca. 5.5 turnovers) was achieved.[62]



Scheme 15. Proposed catalytic cycle for C–H activation and functionalization of pyridines with isonitriles.

Extensive kinetic and mechanistic studies presented convincing evidence for the formation of the Sc^{III}–imido complex **54a**.[63] The results suggested that pyridine binding occurred prior to the formation of the imido species, and the enforced proximity of anilide and methyl ligands facilitates the proton transfer. The α-hydrogen abstraction is the rate-determining step. Notably, **54** can also activate the C(sp^3)–H bonds of 2-picoline and 2,6-lutidine.

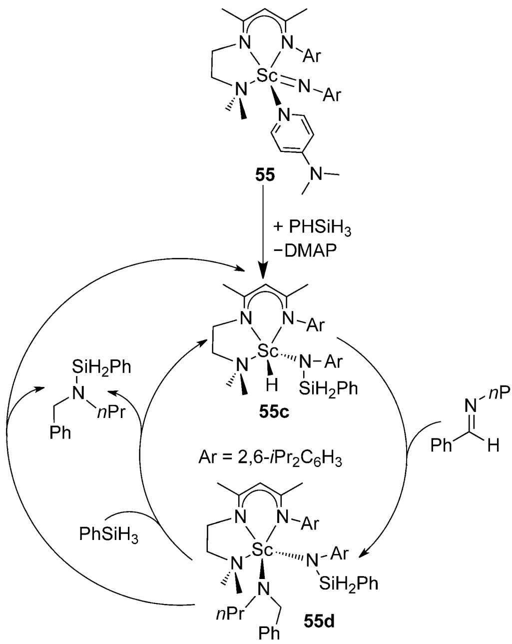
Chen and co-workers first isolated the terminal scandium–imido complex **55**.[64] Reactivity studies showed that elemental selenium formally undergoes an insertion into the Sc–C bond,[65] produced through prior C–H bond activation on Sc=N to afford **55a**.[65] A catalytic turnover for this system can be imagined through a Se–H bond formation by elimination of the aminoselenol to reform the Sc=N bond, but thermodynamic arguments may preclude such a reaction. The C(sp^3)–H bonds in related systems can also be metalated and functionalized with selenium to afford, for example, **55b**, but only at the side chains of the ligand. The authors suggest a mechanism that starts with a 1,2 cycloaddition of a selenium atom across the Sc=N bond (Scheme 16).



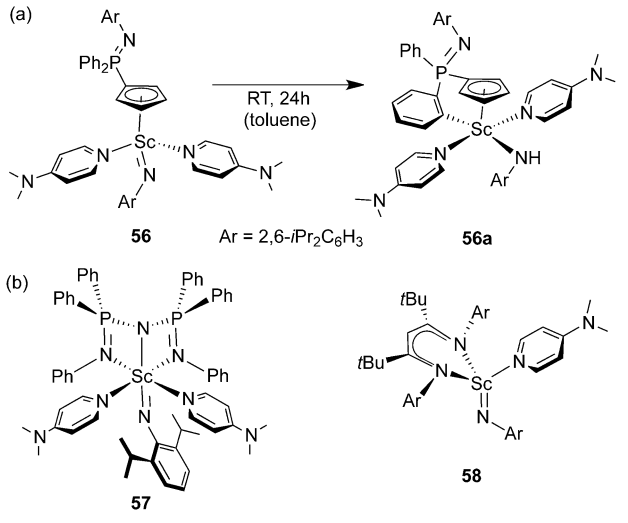
Scheme 16. The first terminal rare-earth-metal imido complex **53** and products of the formal selenium addition through C(sp^2)–H and C(sp^3)–H bond activation in the ligand.

Compound **55** can also activate Si–H bonds through a 1,2 addition to afford the scandium anilide hydride **55c**, which efficiently catalyzes the hydrosilylation of *N*-benzylidenepropan-1-amine with PhSiH$_3$.[66] With 5 mol% of the catalyst, the conversion of *N*-benzylidenepropan-1-amine was complete within 12 h at 20 °C; the proposed mechanism is shown in Scheme 17.

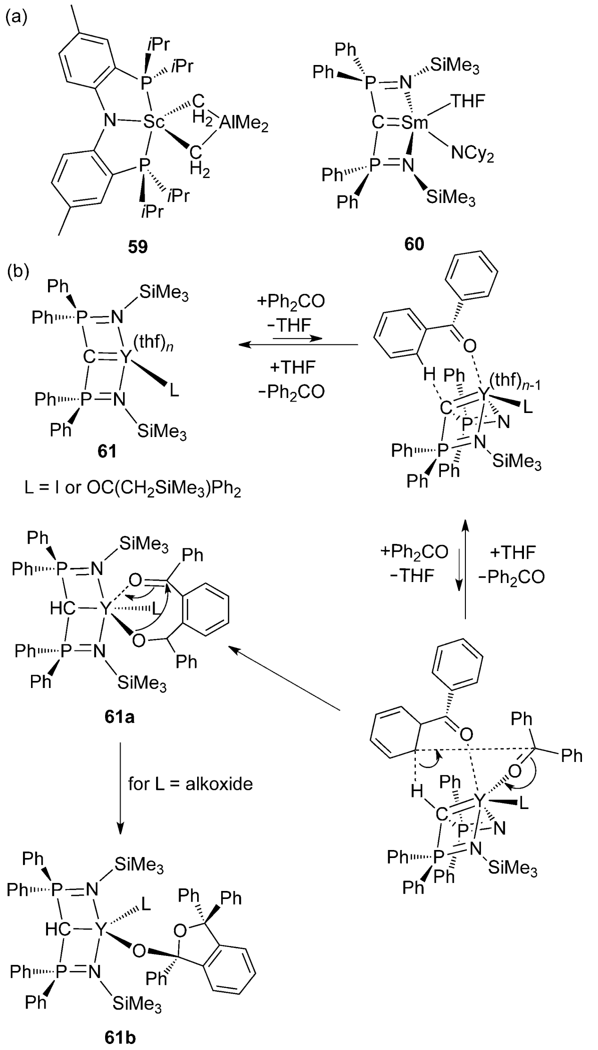
Cui and co-workers isolated the first cyclopentadienyl ligand supported scandium–imido complexes **56** and **57** using a phophazene ligand (Scheme 18 a,b).[67] Compound **56** is stable for a week at –30 °C, but undergoes intermolecular C–H activation to give the anilide complex **56a** at room temperature. Intermolecular hydrocarbon activation was not



Scheme 17. Proposed catalytic cycle for the conversion of *N*-benzylidenepropan-1-amine to its hydrosilylated derivatives.



Scheme 18. Isolable Sc=NR complexes that activate intramolecular C(sp^2)−H and intermolecular C(sp)−H bonds.

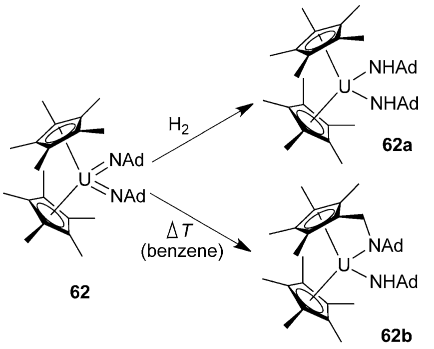


Scheme 19. A masked Sc=C bond, an ylid-stabilized Sm=C bond, and a proposed mechanism for Y=C-promoted rearrangement and C−H bond abstraction from benzophenone.

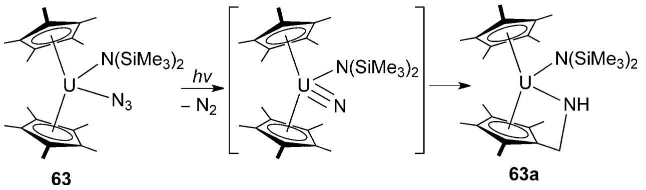
observed. No reactivity studies for **57** have been published to date. Piers and co-workers isolated the terminal imido β-diketiminato complex **58** (Scheme 18b), which activates the C−H bond of phenylacetylene.[68]

Nucleophilic carbene complexes have been stabilized by coordination of an additional Lewis acid, such as a rare-earth-metal cation,[34b] or Al^{III}[69] (see **59**, Scheme 19a). These stabilized complexes showed "Schrock-type" carbene character. A second series of rare-earth-metal complexes, in which a central CH$_2$ group of a bidentate N,N or S,S chelating ligand, H$_2$C(PPh$_2$NSiMe$_3$)$_2$ or H$_2$C(PPh$_2$S)$_2$, respectively, is doubly deprotonated to form a highly polar, formally doubly bonded M=C group. These complexes are exemplified by **60** in Scheme 19a.[70] The addition of Ph$_2$C=O to **61** leads to the reprotonation of the C^{2-} center through the selective *ortho*-metalation of one Ph group, directed by prior yttrium coordination of the O atom (Scheme 19b).[71] Subsequent C−C and C−O bond formations led to isobenzofurans and hydromethylbenzophenones.[71]

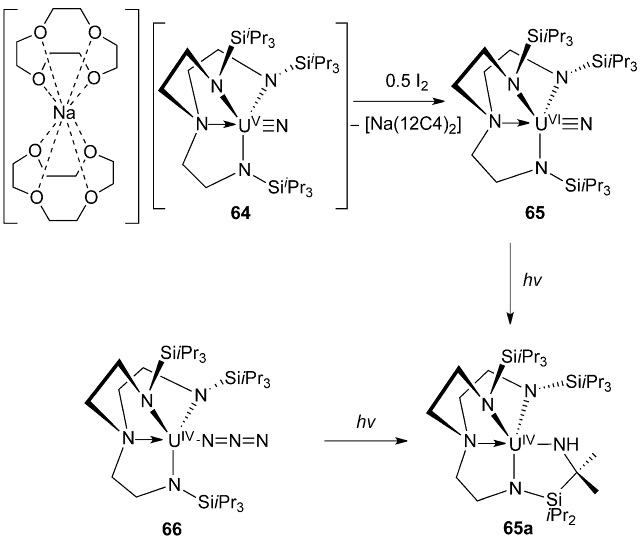
Many imido uranium complexes have been reported based on U^{IV}, U^{V} (most often), and U^{VI} complexes.[72] Although a few of them can show intramolecular [3+2] cycloaddition of ligand C−H bonds across M=N bonds to afford C−H bond cleavage,[73] none show reactivity toward intermolecular C−H bond activation. For example, thermolysis of **62** in benzene or hexane leads to intramolecular C−H bond activation of a Cp* methyl group across the two imido functional groups.[73a] The authors did not investigate the mechanism of this reaction, which presumably proceeds through the formation of an amine, which subsequently tautomerizes to **60b**. Complex [Cp*$_2$U(NAd)$_2$] (**62**) can also be reduced by H$_2$ to form the corresponding bis(amide)–U^{IV} complex (Scheme 20).[74]



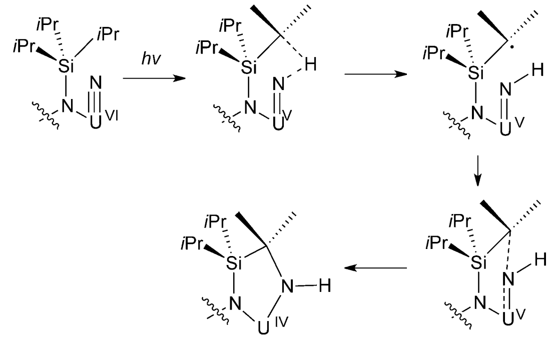
Scheme 20. Bis(imido)–U^{VI} complex **62** displaying reactivity toward H_2 and intramolecular C–H activation by thermolysis forming a new "tuck-in" compound.



Scheme 21. A proposed transient uranium nitride, which undergoes instantaneous intramolecular C–H bond activation.



Scheme 22. A terminal U^{VI}–nitride complex that undergoes an intramolecular ligand C–H activation.



Scheme 23. Proposed mechanism for the conversion of **65** into **65a**.

An unstable terminal uranium(VI) nitride complex was implicated as the product of N_2 release upon the photolysis of azide **63**.[75] The transient U≡N fragment (Scheme 21) was suggested to be so reactive that it undergoes rapid insertion into a C–H bond of the ligand to form an N–H bond and the "tuck-in" complex **63a**. DFT calculations on this proposed transient U≡N nitrido moiety reproduce the reactivity very well, including the requirement of photolysis, rather than thermolysis, to generate the reactive intermediate. Under photolytic conditions, both singlet and triplet configurations are accessible, and two potential energy surfaces were therefore computed for the reaction of the methyl group with the nucleophilic nitride unit, depending on the spin state. The calculated lowest energy pathway for C–H activation by the uranium nitride intermediate was deprotonation for the singlet surface, and H atom abstraction for the triplet surface. Subsequent 1,2 migration or radical recombination (for the singlet or triplet forms, respectively) lead to the observed CNH-containing product. This mechanism operates similarly to C–H bond oxidation by the Fe=O unit of the enzyme cytochrome P450.[76]

Liddle and co-workers isolated the first terminal U^V and U^{VI} nitrido complexes **64** and **65**, respectively (Scheme 22).[77] The photolysis of **65** leads to C–H activation of one isopropyl group in the Si(*i*Pr)$_3$ side chains and 1,1 insertion of the nitride to give amide **65a**. The proposed mechanism (Scheme 23) shows similarities to the H abstraction displayed by the uranyl ion,[78] and requires electron transfer to uranium followed by homolytic C–H and U≡N bond scissions. The authors agree with Kiplinger[75] that photolysis of uranium(VI)–azide generates a transient U^{VI}–nitride, which cannot be trapped in the photolysis reaction. Contrary to **65**, the photolysis of U^V–nitride **64** does not result in C–H activation, probably because of the inherently lower oxidizing and polarizing nature of U^V compared to U^{VI}.[77b]

In contrast to numerous reports on uranium–imido complexes, thorium–imido complexes are extremely scarce: the imido–metallocene complexes [$Cp_2Th{=}NR$] (Cp = η^5-1,2,4-$(Me_3C)_3C_5H_2$, R = *p*-tolyl **66** or Cp = Cp*, R = 2,6-dimethylphenyl **67**; Figure 2) undergo [2+2] cycloaddition reactions with nitriles[79] and alkynes[79–80] and concomitantly activate C–H bonds[80b] of alkynes to form mono(acetylide) thorium amido complexes.

Examples of actinide complexes with an M–C bond with multiple-bond character are limited to ligand systems with additional heteroatom stabilization. For example, the nucleophilic carbon atom in Gilje's phosphoylide compounds [$Cp_3U{=}CHP(Me)_2R$] (**68**; Scheme 24)[81] shows high reactivity toward nitriles,[82] isocyanates,[83] and CO.[84] The closely related complex [$U{=}CHPPh_3(NR_2)_3$] (**69**) is in equilibrium with free $Ph_3P{=}CH_2$ and the U^{IV} metallacycle [$U(CH_2SiMe_2NR)(NR_2)_2$] (**69a**). This reversible C–H activation is highly temperature dependent, because it is endothermic and entropically driven.[85]

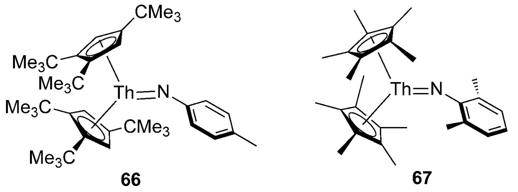
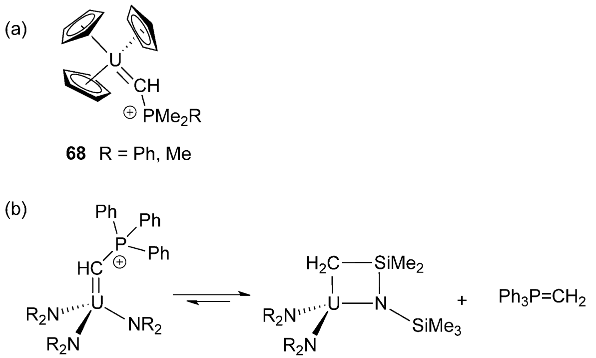
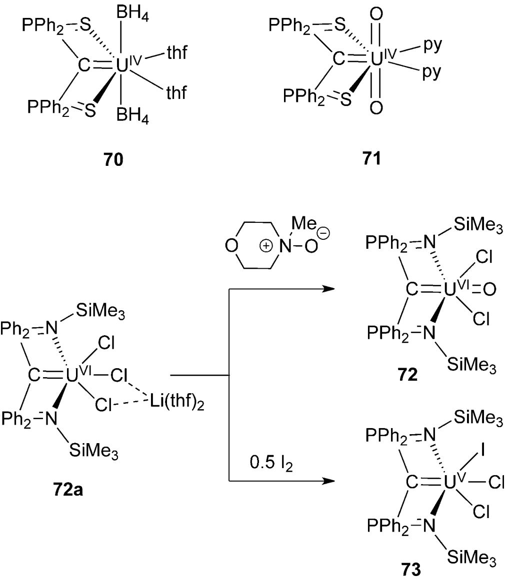


Figure 2. Examples of thorium imido complexes. **67** can activate C(sp)−H bonds of alkynes.



Scheme 24. Ylid complexes that contain a nucleophilic carbene unit: a) first reported, and b) in equilibrium with free $Ph_3P{=}CH_2$ and the U^{IV} metallacycle.

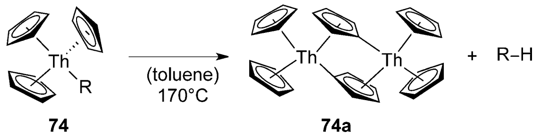
The most popular ligand systems used to stabilize the formal U=C and Th=C bonds with nucleophilic carbene atoms are bis(iminophosphorano)methandiide $(Ph_2P{=}NR)_2C^{2-}$ and bis(phosphorano)methandiide $(Ph_2P{=}S)_2C^{2-}$ pincer ligands described above. A wide range of these complexes are now known for U^{IV},[86] UO_2^{2+},[87] U^{V},[88] U^{VI}[88b] (Scheme 25), and Th^{IV}.[86c,89] However, reactivity studies of these complexes remain limited. Cavell's group described U^{IV} complexes that undergo [2+2] cycloaddition of nitriles to the carbon–metal bond,[86c] but to date no reports of C−H activation by these complexes have been observed.[88b]



Scheme 25. Uranium carbene complexes stabilized by heteroatom ligands.

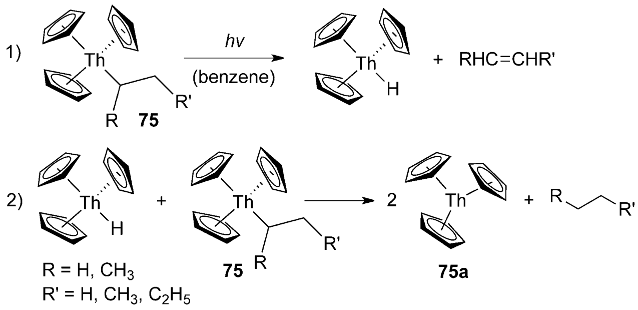
4. H-Atom Abstraction from Hydrocarbons

Lanthanide alkyl complexes show a much greater resistance toward β-hydrogen elimination reactions compared to transition-metal alkyl complexes, in spite of the fact that many of these organometallic compounds are coordinatively unsaturated and generally have highly polarized M−C bonds as a result of the combination of strongly Lewis acidic centers and strongly basic ligands. In comparison to organometallics of d-block elements, many organolanthanides require more forcing conditions to induce the elimination of the olefin.[90] For example, $[U(\eta^5\text{-}C_5H_5)_3R]$ and $[Th(\eta^5\text{-}C_5H_5)_3R]$ (**74**, R = hydrocarbon functionality) complexes strongly resist thermally induced β-hydrogen elimination. Instead, they undergo an intramolecular stereospecific hydrogen atom abstraction from cyclopentadienyl rings to produce the corresponding alkane and an organometallic product.[91] For thorium complexes, this compound could be identified as bimetallic $\eta^5{:}\eta^1$-cyclopentadienylthorium(IV) compound **74a** (Scheme 26).[91b] Thorium compounds are generally more thermally stable than their uranium analogues and the stability within one actinide series varies with the R substituent (primary > secondary > tertiary). Kinetic studies, deuterium labeling, and cross-over experiments strongly support the unimolecularity of the reaction. As nearly complete retention of configuration is observed at the σ-bonded carbon atom of the alkane, a radical mechanism can be ruled out. It is uncertain whether the hydrogen atom of cyclopentadienyl is transferred directly to the hydrocarbon ligand by a concerted, four-centered process, or whether it is first transferred to the actinide center and then to the R moiety.[91b]



Scheme 26. Thermal decomposition of cyclopentadienylthorium(IV) compounds.

In comparison to the thermally induced decomposition of cyclopentadienyl Th^{IV} complexes **75**, a photochemical excitation of the same compounds in benzene at wavelengths shorter than 350 nm results in a comparable mixture of alkane/alkene and complex $[Cp_3Th]$ (**75a**).[92] On the basis of deuterium-labeling experiments, a mechanism involving β-hydrogen elimination followed by the reaction of thorium hydride complex with another thorium alkyl complex could be postulated (Scheme 27).[93] This explains a nearly constant 1:1 mixture of alkene to alkane for most of the tested compounds. Interestingly, a slight excess of alkane for some hydrocarbyl ligands strongly correlates with the incorporation



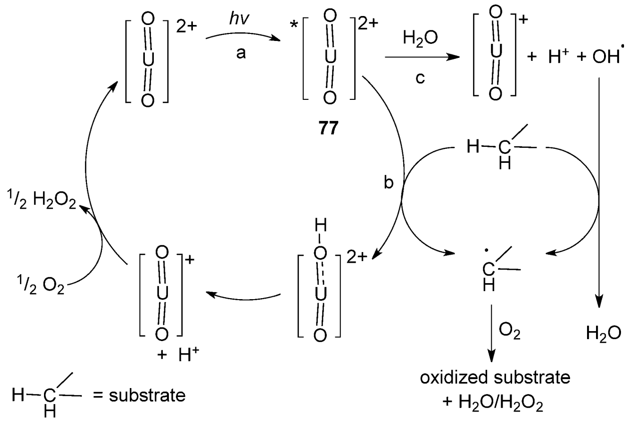
Scheme 27. Proposed two-step mechanism for the photochemical decomposition of tris(cyclopentadienyl)thorium(IV) hydrocarbyl complexes **75**.

of the deuterium atom from cyclopentadienyl or solvent molecules, thus suggesting that a minor C–H activation process, possibly radical in nature, may be operative.

For [Th(η^5-C_5H_5)$_3$$CH_3$], which does not have a β-hydrogen atom, the formation of methane proceeds much slower and the incorporation of deuterium from the Cp rings and solvent molecules occurs substantially more often. The substitution of cyclopentadienyl to indenyl ligands completely preclude the β-hydrogen elimination pathway, leading to the production of an alkane by intramolecular hydrogen abstraction. In comparison to the photochemistry of thorium alkyl compounds, analogous uranium complexes produce upon by photoexcitation predominantly the alkane with an incorporated hydrogen atom from cyclopentadienyl rings and solvent molecules, although a β-hydrogen elimination pathway certainly also exists. As the U^{III} oxidation state is more readily accessible than Th^{III}, the authors suggested a homolytic bond scission to alkyl radicals as a possible reaction mechanism for the photoinduced decomposition of uranium analogues.[93]

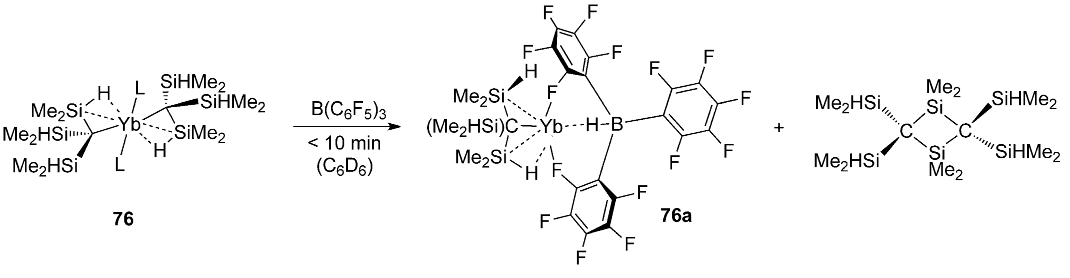
A prolonged thermolysis of [Y{C(SiHMe$_2$)$_3$}$_3$] and [Yb{C(SiHMe$_2$)$_3$}$_2$(thf)$_2$] (**76**) gives CH(SiHMe$_2$)$_3$ as the only product, probably as a result of the inhibition of a classical β-hydrogen elimination by the sterically hindered ligand.[94] However, the introduction of external Lewis acids results in the abstraction of the β-hydrogen and the extrusion of disilacyclobutane, a dimer of the silene $Me_2Si{=}C(SiHMe_2)_2$.[94a,95] Sadow and co-workers studied this reactivity with THF and TMEDA adducts of M{C(SiHMe$_2$)$_3$}$_2$ (M = Yb, Ca) and found two competing reaction pathways: ligand-group transfer and β-hydrogen abstraction. The followed pathway is strongly dependent on the identity of the metal, Lewis acid, and ancillary ligands. For example, the alkylation pathway is more likely to occur when the partners are less bulky, and the use of $B(C_6F_5)_3$ results exclusively in β-hydrogen abstraction (Scheme 28). Interestingly, the source of hydrogen in the thermally induced decomposition of the ytterbium complexes to CH(SiHMe$_2$)$_3$ is not clear, but labeling experiments with [Yb{C(SiDMe$_2$)$_3$}] rule out the Si–H group as a source.[95] An intermolecular C–H activation of one of the two methyl groups in the ligand and subsequent H atom abstraction could possibly explain these observations, but would require further isotopic labeling experiments.

The photochemistry of the uranyl ion has been studied since the beginning of the nineteenth century.[111] Irradiation by laser flash photolysis at wavelengths in the region of 350 to 490 nm is routinely used to generate the *[UO_2]$^{2+}$ ion (**77**, Scheme 29). This ion is strongly oxidizing ($E° = 2.6$ V) and can be considered a reactive oxygen-centered radical coordinated to U^V.[96] A range of different decay routes are available for the long-lived *[UO_2]$^{2+}$ ion, depending on the identity of nearby substrates. However, substrate activation reactions are generally carried out in water, so any hydrocarbon will have limited solubility, and be competing directly with the solvent water molecules in the reaction.



Scheme 29. Steps in the photocatalyzed H-atom abstraction from hydrocarbons by the uranyl dication.

Waltz et al. described the competition between water oxidation and the abstraction of an H atom from isobutene in an acidified aqueous uranyl perchlorate medium (Scheme 29) activated by a 347 nm laser (ca. 70 mJ of energy per flash).[97] The abstraction from the weakest, tertiary C–H bond (rather than from a primary C–H bond) by the uranyl species in its



Scheme 28. A Lewis acid mediated β-hydride abstraction reaction of [Yb{C(SiHMe$_2$)$_3$}$_2$(L)$_2$] (L = THF, TMEDA).

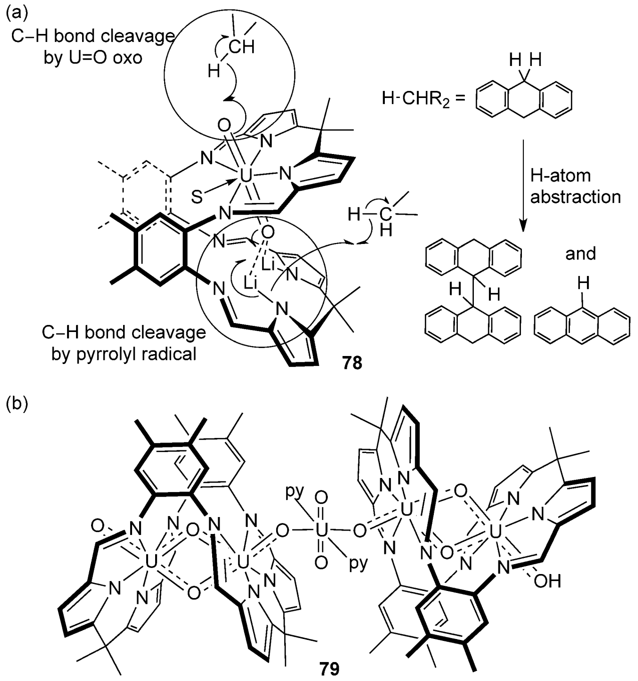
excited state is assumed; the resulting *tert*-butyl radical does not react further with the U^V uranyl $[UO_2]^+$ according to kinetic analyses. The $*[UO_2]^{2+}$ ion can also indirectly quench a substrate by reaction with water, forming the OH radical in a competitive reaction (Scheme 29c), and this radical can then also cleave the C–H bond of isobutane, thus forming the same products.

Bakac et al. surveyed a range of linear and cyclic hydrocarbons as quenchers for the $*[UO_2]^{2+}$ ion, finding the same mechanism for all, which involves H atom abstraction by the metal oxo species to form $[UO_2H]^{2+}$ (which transforms to $[UO_2]^+ + H^+$) and the alkyl radical.[98] In the presence of O_2, the latter rapidly forms an alkyl peroxyl radical, which is then transformed to the oxygenated complex, for example cyclopentane is converted to cyclopentanone. The $[UO_2]^+$ ion is automatically converted back to $[UO_2]^{2+}$ by dioxygen. The reaction is product specific, that is, only cyclopentanone and H_2O_2 and no cyclopentanol (which would quench faster than the alkane) are formed, which led the authors to suggest that the peroxyl radical $c\text{-}C_5H_9OO^{\bullet}$ behaves as a ligand for U in subsequent reactions.

With aqueous solutions of arenes, such as benzene or toluene, the oxidation to phenol or benzyl alcohol (and benzaldehyde) is catalytic in $*[UO_2]^{2+}$. Quantum yields of 70% for the conversion of benzene to phenol can be achieved under conditions in which the excited state $*[UO_2]^{2+}$ is quenched in equal measures by H_2O_2 and benzene. Kinetic isotope studies involving the deuteration of either benzene or water show only a pronounced decrease in the rate for water deuteration. This and other studies show that two pathways are available for the arenes: the productive one through H-atom abstraction, and the nonproductive one through the aromatic portion (which is the major path observed here).[99]

The lack of product specificity has recently led to an increased interest in the use of uranyl-based photocatalysis for the destruction of organic pollutants in the environment.[100] Ideally, catalysts with narrow band gaps that can use visible light and are photochemically stable in water would be employed. Current research efforts on catalytic systems are focused on methods to keep the ions away from the aqueous phase, for example through heterogenization.[101]

A thermally activated analogue of this oxo species has only recently been discovered. We reported asymmetric uranyl complexes with a polypyrrolic ligand. In these complexes, a uranyl species is held within a sterically protected environment ("Pacman" shape). Deprotonation of the two remaining pyrroles with two equivalents of base is suggested to disrupt the strong U–O bonding arrangement and results in oxo reactivity that is more reminiscent of dioxo catalysts of transition-metal complexes. Thus, H-atom abstraction from substrates containing weak C–H bonds, such as dihydroanthracene, is observed (Scheme 30).[102] However, mechanistic studies did not distinguish between reactions in which the intermediate $[U^{VI}O_2(Li_2L)]$ (**78**) can cleave a C–H bond. The uranyl oxo group either undergoes an intermolecular H-atom abstraction to form a U-OH species, or the C–H bond is cleaved by a pyrrolyl radical generated through an internal reduction process.



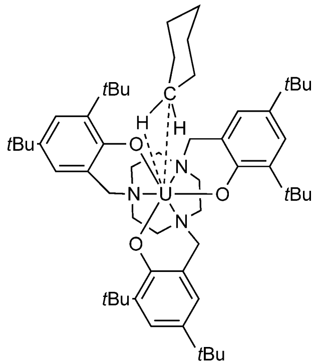
Scheme 30. a) Proposed mechanisms for C–H bond cleavage of a weak C–H bond-containing substrate by a doubly lithiated uranyl macrocyclic complex. b) Oligomers that contain U^V and U^{VI} uranyl ions formed as a result of a combination of H-abstraction from the solvent and $SiMe_3$ group abstraction from coordinated $N(SiMe_3)_2$ groups.

Previously reported reactions with potassium bases in the presence of E–SiR_3 compounds resulted in the silylation of the E-oxo group (E = N, C) and the formation of $O{=}U^V{-}OSiR_3$ complexes.[103] The similarities between these two systems might lend weight to the involvement of the uranium oxo group in the C–H bond activation. In reactions using the same Pacman macrocyclic ligand and an excess of uranyl silylamido reagent, that is, 2.5 equivalents of $[UO_2\{N(SiMe_3)_2\}_2(thf)]$ to every equivalent of H_2L, oligomers that contain a 2:1:1 ratio of $U^VO_2/U^{VI}O_2/L$ were formed as a result of a combination of H-abstraction from the solvent and $SiMe_3$ group abstraction from coordinated $N(SiMe_3)_2$ groups, **79**.[104] The symmetrical doubly silylated oxo-siloxy product $[(Me_3SiOUO)_2(L)]$ was the most soluble, and readily isolated component of the oligomer.

5. Oxidative Addition and Reductive Elimination

The few f-block elements that have more than one readily accessible oxidation state characteristically show single-electron redox processes, in contrast to the two-electron oxidative-addition pathways through which late transition-metal ions will insert into a C–H bond. Of the f-block elements, only uranium has suitably accessible redox couples as $U^{III/V}$ or $U^{IV/VI}$, although the latter couple would result in the formation of presumably highly unstable alkyl hydride complexes of U^{VI}. Much current research is focused on the incorporation of redox-active ligands to access multi-electron redox processes.

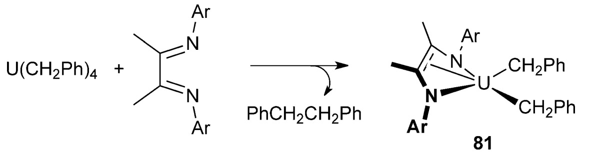
The formation of an agostic interaction between a C−H bond of a hydrocarbon and an f-block metal center in a low oxidation state is a good starting point in the study of oxidative additions. Even though metal–alkane complexes are presumed key intermediates in alkane σ-bond metathesis, only a handful of examples have been characterized. Meyer et al. used a ligand that is sufficiently resistant toward metalation to support the formation of the U^{III} complex **80** (Figure 3). A crystallographic characterization of **80** shows that a hydrocarbon molecule of the solvent was bound in the sterically protected pocket at the electron-rich metal cation. Precise location of the electron density was possible using ultralow temperature X-ray diffraction studies.[105] The disparity in electron density between H and U, the smallest and largest naturally occurring elements, precluded the location of the position of hydrogen atoms from the structural study. However, density functional theory (DFT) calculations suggested an η^2-*H*,*C* coordination of the alkane, as has been observed in transition-metal complexes, with a σ-based U–R interaction and the main orbital contribution coming from the $U(f_z{}^3)$ orbital. The U−C bond distances (3.731 Å–3.864 Å) are within the sum of the van der Waals radii for $U–CH_2/U–CH_3$ contacts. The complex is extremely reactive toward other small molecules, with immediate loss of the alkane.



80

Figure 3. A U^{III} complex that is kinetically robust enough to allow the isolation of **80** with an η^2-bound hydrocarbon.

The U^{IV} bis(benzyl) complex $[(dab)U(Bn)_2]$ (**81**, dab = ArN = C(Me)C(Me) = NAr, $Bn = CH_2Ph$; Scheme 31) was synthesized by Bart, in a process suggested to be akin to a formal C−C reductive elimination, and not seen previously for uranium. However, it must be stressed that this reaction does not occur with a change in oxidation state of uranium, but of the redox-active diazo ligand, which was originally used to great effect with Zr^{IV} by Abu-Omar et al.[106] The benzyl ligands were introduced through standard salt elimination procedures and are the only substrates reported so far.



81

Scheme 31. Extrusion of bibenzyl from the U^{IV} complex **81**, supported by the redox-active DAB ligand that can reversibly store up to two electrons.

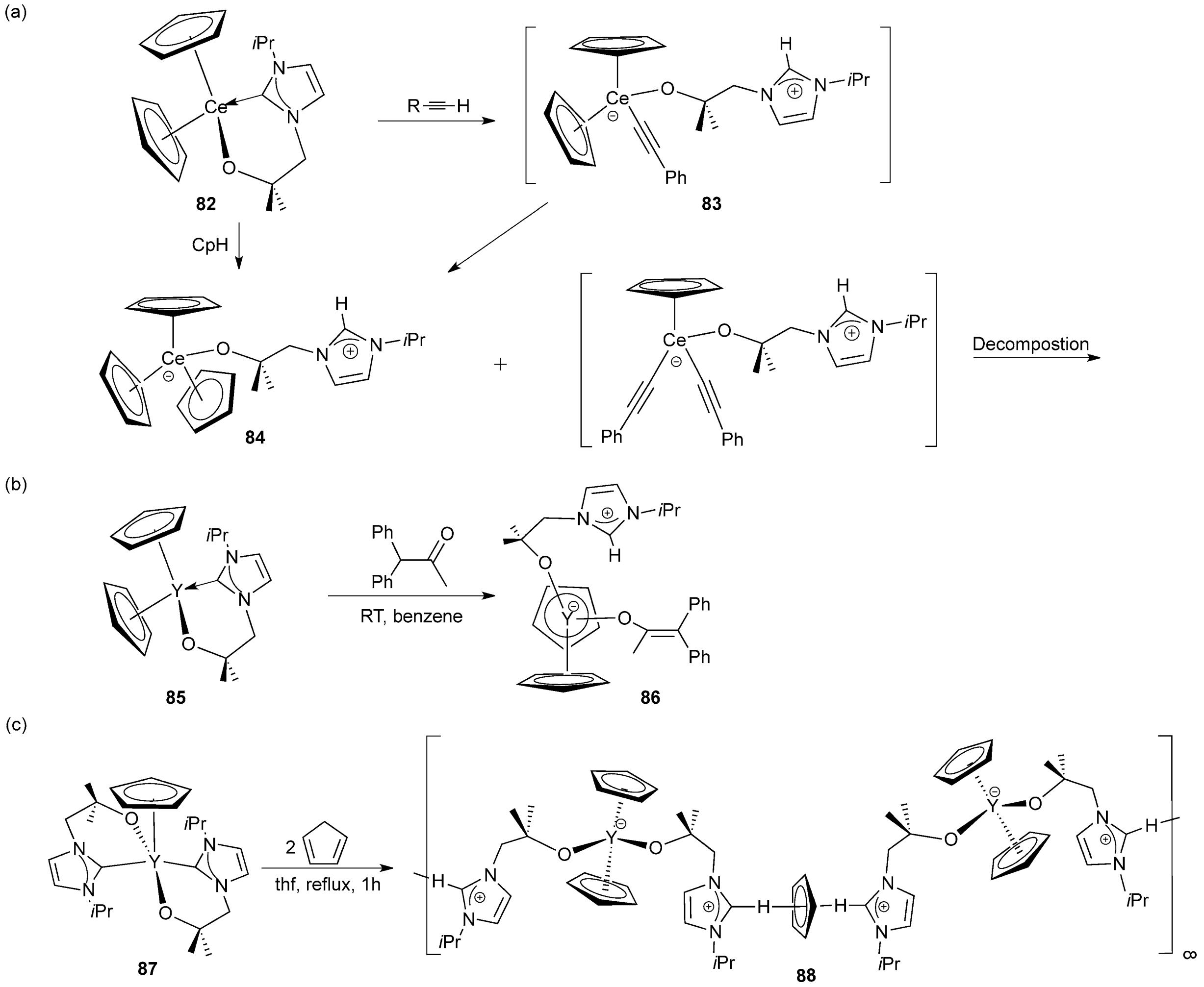
We recently showed that C−H activation of a range of substrates with relatively acidic C−H bonds was possible with cerium and yttrium complexes of N-heterocyclic carbenes (NHCs).[107] Terminal alkynes ($R = Me_3Si$, Ph) reacted with $[Cp_2Ce(L)]$ (**82**, L = ({1-C(N*i*Pr-CH_2CH_2N)}CH_2CMe_2O)) to give the zwitterionic intermediate $[Cp_2Ce(HL)(C{\equiv}CR)]$ (**83**), which then undergoes ligand rearrangement to afford $[Cp_3Ce(HL)]$ (**84**, HL = ({1-CH(N*i*Pr-CH_2CH_2N)}-CH_2CMe_2O); Scheme 32 a). The highly crystalline nature of $[Cp_3Ce(HL)]$ and the steric protection afforded by the Cp groups favor the isolation of this ligand redistribution product. The reaction of $[Cp_2Ce(L)]$ with cyclopentadiene gave the same C−H cleavage product $[Cp_3Ce(HL)]$. Neither the yttrium nor scandium analogues reacted with cyclopentadiene, possibly because of the smaller size of the metal cation. However, $[Cp_2Y(L)]$ (**85**) did react with diphenylacetone at 60 °C to give the C−H activation product $[Cp_2Y(HL)(OC(Me)C(Ph)_2)]$ (**86**, Scheme 32 b). The bis(NHC) complex $[CpY(L)_2]$ (**87**) also reacted with two equivalents of cyclopentadiene to afford an unusual C−H cleavage product, polymeric $[Cp_2Y(HL)_2(Cp)]_\infty$ (**88**) in which one of the newly formed cyclopentadienyl ions coordinates to the two imidazolium C−H groups rather than the Y cation (Scheme 32 c).

6. Summary and Outlook

In recent years, C−H bond activation with f-block metal complexes has moved well beyond C−H metalation, with complexes from across the rare-earth-metal series showing that a tunable size and Lewis acidity can deliver interesting new chemistry. The improved ability to handle the various oxidation states, particularly for uranium, and the use of non-innocent ligands suggests that there are many new C−H bond activation catalysts yet to be discovered.

There is still much scope for isolation and study of σ-alkane complexes, for example, the protonation of a metal-bound Rh^I–methyl complex, which recently allowed the retention of σ-bound methane to the metal for long enough for the product to be studied at low temperatures by NMR spectroscopy.[108] The identification of the first isolated terminal Sc=N complexes, and most recently, a Ce=O containing complex,[109] and uranium nitrides, and evidence of their reactivity should encourage further ligand design to support reactive polar Ln=E and An=E bonds. More work on the anaerobic chemistry of the uranyl oxo groups is already suggesting that a wider variety of bond activations may be accessible even in the absence of photolysis, for example, Lewis base assisted reduction, or activation with iodosilanes.[110]

Chemists are increasingly engaged in the design of supporting ligands with metalation-resistance in mind.[111] Finally, our ability to manipulate and analyze the catalytic reactivity of isolated metal complexes deposited onto surfaces is dramatically improving; it may be this heterogenization



Scheme 32. a) Activation of terminal alkynes and Cp using [$Cp_2Ce(L)$] (**82**) to form [$Cp_3Ce(HL)$] (**84**) via the intermediate [$Cp_2Ce(HL)(C{\equiv}CR)$] (**83**). b,c) Activation of Cp using [$Cp_2Ce(L)$] (**87**) to form polymer [$Cp_2Y(HL)_2(Cp)$]$_\infty$ (**88**).

that prevents new very reactive species from aggregation, avoiding the need for reactive solvents to interfere.[112] Another possibility is that new two-phase systems may help overcome overoxidation problems by selective removal into the secondary phase.

We are grateful for financial support from the Technische Universität München—Institute for Advanced Study, funded by the German Excellence Initiative, the EaStCHEM School of Chemistry, and the EPSRC.

Received: April 23, 2014

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