

Cyclometalative C–H bond activation in rare earth and actinide metal complexes

Cite this: *Chem. Soc. Rev.*, 2013, **42**, 1947

Kevin R. D. Johnson and Paul G. Hayes*

Cyclometalative C–H bond activation is a process that is commonly encountered in the field of organometallic chemistry. In rare earth and actinide complexes, ligand cyclometalation is most prevalent in highly reactive alkyl and hydrido species. Numerous factors promote ligand cyclometalation and influence the rate at which it occurs. This tutorial review discusses key issues relevant to ligand cyclometalation in rare earth and actinide complexes, including kinetic and mechanistic considerations. A variety of examples is presented for a wide range of ligand types and metals, the scope of which is intended to include routine cases, while also highlighting exceptional cyclometalation reactions that lead to unusual bonding modes. The reaction chemistry of cyclometalated rare earth and actinide complexes with various small molecule substrates (e.g. phenol, anilines, triethylammonium salts, alkynes, olefins, hydrogen and hydrocarbons) is also outlined.

Received 28th August 2012

DOI: 10.1039/c2cs35356c

www.rsc.org/csr

Department of Chemistry and Biochemistry, University of Lethbridge,
4401 University Drive, Lethbridge, AB, Canada T1K 3M4. E-mail: p.hayes@uleth.ca;
Fax: +1 403 329 2057; Tel: +1 403 329 2313

1. Introduction

In the rapidly developing field of rare earth and actinide organometallic chemistry, the use of ancillary ligands is



Kevin R. D. Johnson

Kevin R. D. Johnson attended the University of Victoria where he obtained a BSc degree in 2007 while conducting research in the laboratory of Prof. David Berg. In 2012, he received a PhD degree at the University of Lethbridge under the supervision of Prof. Paul G. Hayes, studying organolanthanide chemistry. His research interests include ligand design and the activation of small molecules using organometallic f-element complexes.



Paul G. Hayes

Paul G. Hayes received a BSc (Honours) from Mount Allison University in 1999. In 2004, he completed his PhD degree at the University of Calgary under the tutelage of Prof. Warren Piers, studying cationic organoscandium complexes. During his time in Calgary, he was awarded NSERC and Sir Izaak Walton Killam Doctoral Fellowships as well as a Ralph Steinhauer Award of Distinction. In 2004, he undertook an NSERC

Postdoctoral Fellowship in the laboratories of Prof. T. Don Tilley where he developed new routes to transition metal silylene and stannylenes complexes. In 2006, Hayes accepted a faculty position at the University of Lethbridge; he was promoted to Associate Professor in 2010. He received an Alberta Ingenuity New Faculty award in 2009 and was recognized with a Confederation of Alberta Faculty Associations Distinguished Academic Early Career Award in 2010. His current research interests include synthetic and mechanistic organometallic chemistry with a particular focus on the development of new chemical transformations and catalysis.

essential for stabilizing highly reactive metal complexes. Typically, sterically bulky ligands are utilized for the purpose of saturating the large coordination sphere of these metals. The development of crowded f-element complexes has led to the formation of remarkably stable compounds, and also new forms of reactivity, such as sterically induced reduction.¹ In other cases, however, such crowding is a contributing factor to ligand cyclometalative C–H bond activation pathways.

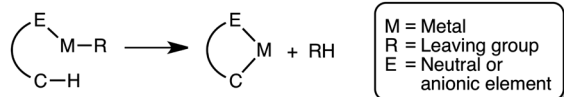
This tutorial review discusses the major factors leading to ligand cyclometalation in rare earth and actinide complexes, including kinetic and mechanistic considerations. It is not intended to be fully comprehensive, but rather, to highlight noteworthy and representative examples of cyclometalative reactivity in complexes of these metals. Cyclometalation reactions involving main group,² late transition,^{3–5} and early transition⁶ metal complexes have been previously reviewed and for this reason will not be addressed. The reactivity discussed herein is relevant to the development of new types of catalysts for various small molecule transformations and of fundamental interest from a perspective of studying unique bonding and reactivity patterns.

2. Cyclometalative C–H bond activation

Cyclometalative C–H bond activation is a process that is frequently observed in the field of organometallic chemistry. It is defined as a transformation whereby a ligand undergoes an intra- or intermolecular metalation reaction to afford a chelate ring that contains a new M–C bond (Scheme 1).⁵

Ligand cyclometalation has a propensity to occur in highly reactive alkyl or hydrido complexes and typically occurs *via* an ordered four-centre $[2\sigma + 2\sigma]$ transition state. The process is entropically driven (*vide infra*), although steric factors can also significantly influence ligand metalation.⁵

With regard to thermodynamic considerations, cyclometalation is usually slightly endothermic in nature, *i.e.*, it exhibits a positive ΔH . However, as the reaction involves the formation of a metalated chelate ring and liberation of a free molecule (*e.g.* an alkane or hydrogen gas) as a by-product, the entropy of the system is increased. Hence, cyclometalation reactions typically exhibit a large positive ΔS . At sufficiently high temperatures, the Gibbs free energy change in the reaction becomes negative, and thus, thermodynamically favourable.⁷ In general terms, complexes of the form L_xMR_y (L = ancillary ligand; R = alkyl or hydride; x, y = coordination numbers) are entropically susceptible to metalative alkane elimination reactions that produce cyclometalated complexes and RH.



Scheme 1 Ligand cyclometalation.

3. Rare earth cyclometalation

3.1 Tuck-in and tuck-over rare earth complexes

As one of the most ubiquitous ligands in organolanthanide chemistry, Cp* (Cp* = $\eta^5\text{-C}_5\text{Me}_5$) has been utilized to stabilize a wide range of rare earth complexes.⁸ Compared to other common carbocyclic ligands, such as $\eta^5\text{-C}_5\text{H}_5$ (Cp), Cp* has proven popular for use in lanthanide chemistry due to its large size and enhanced solubilizing ability. To a considerable extent, the C–H bonds of the Cp* ligand are resilient to cyclometalative C–H bond activation; however, cyclometalation of the ligand has been observed in various highly reactive species. In such cases the C–H bond activation of a methyl group results in a complex containing a tetramethylfulvene moiety, and is commonly referred to as a “tuck-in” complex. Several resonance structures can be drawn for tetramethylfulvene whereby the ligand can coordinate to a metal in a $\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1$ fashion with a formal charge of -2 (i, Chart 1) or in a $\pi\text{-}\eta^6$ mode with a formal charge of 0 (ii, Chart 1). The relative contribution of these two resonance structures has been previously discussed with respect to high and low valent transition metal tuck-in complexes.^{9,10} In terms of f-element tuck-in complexes, the $\pi\text{-}\eta^6$ mode is not normally considered probable because of the limited number of available oxidation states for these metals. Thus, the best bonding description is generally accepted to be the $\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1$ mode.¹¹

Rare earth tuck-in complexes have been proposed since the early 1980's. For example, an investigation by Watson regarding the activation of methane and benzene by a methyl lutetium complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{LuCH}_3]_n$ (**1**, $n = 1$ or 2) implicated the formation of a tucked-in lutetium intermediate $(\eta^5\text{-C}_5\text{Me}_5)\text{Lu}\{\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)\}$ (**2**) (Scheme 2).¹² Despite the reactivity and kinetic data supporting the identity of complex **2** as a cyclometalated tuck-in complex, no structural data has been obtained to date. However, a variety of transition and actinide metal tuck-in complexes have been structurally characterized, thus supporting the expected connectivity of the lutetium derivative.⁹

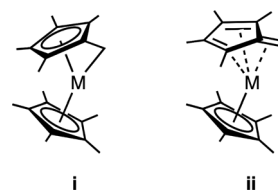
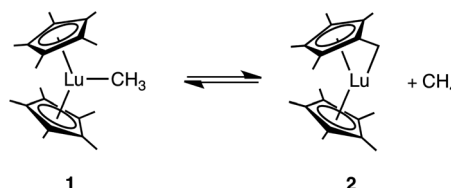


Chart 1 Tetramethylfulvene bonding modes.



Scheme 2 Postulated lutetium tuck-in complex.

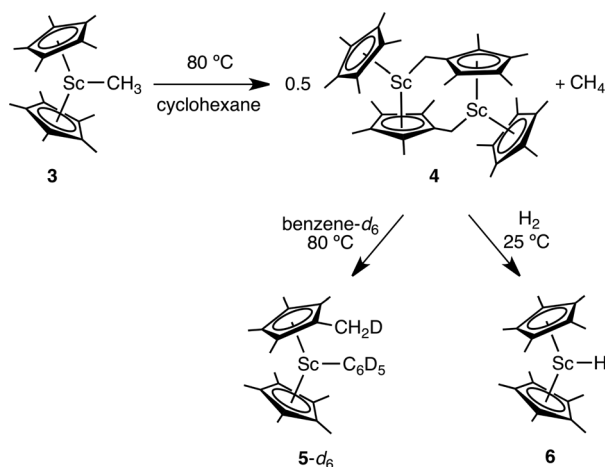
A related scandium complex was developed by Bercaw and co-workers,¹³ whereby $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$ (**3**) was heated in cyclohexane at 80 °C for several days to afford $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}\{\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)\}]_2$ (**4**) and methane. The postulated structure, which contains one unperturbed $\eta^5\text{-C}_5\text{Me}_5$ ring and one metalated $\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)$ ring per scandium centre, is supported by the ^1H NMR spectrum (benzene- d_6) which exhibits four singlets at δ 2.08, 1.96, 1.54 and 1.39 with relative integrations of 6 : 15 : 6 : 2. Early studies initially assigned **4** as a dimeric complex featuring bridging methylene groups because of its low solubility.¹⁴ The solid-state structure was later obtained, indeed confirming complex **4** is a dimer.¹⁵ The fully deuterated analogue of **4** can be prepared by the thermolysis reaction of perdeuterated complex $(\text{Cp}^*\text{-}d_{15})_2\text{ScCH}_3$ (**3- d_{30}**) in cyclohexane at 80 °C with loss of CH_3D . A measurable kinetic isotope effect for this reaction ($k_{\text{H}}/k_{\text{D}} = 1.6(2)$) supported the notion that ligand cyclometalation was the rate limiting step.

Complex **4** reacts cleanly with either benzene- d_6 or H_2 (1 atm) to afford $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{D})\text{Sc}(\text{C}_6\text{D}_5)$ (**5- d_6**) or $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScH}$ (**6**), respectively as the sole products (Scheme 3).

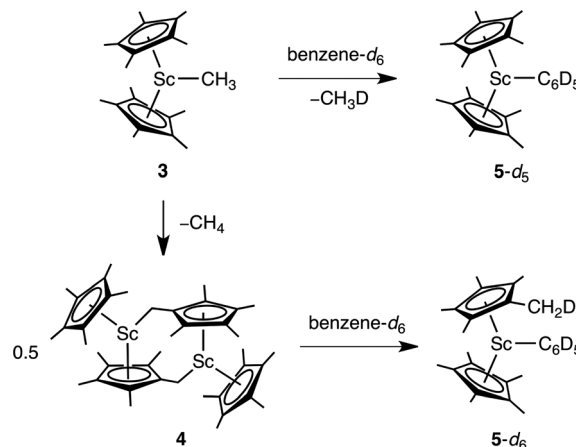
Interestingly, if complex **3** is reacted with benzene- d_6 at elevated temperature a competitive process is observed, involving (i) the bimolecular reaction of **3** with benzene- d_6 to afford **5- d_5** and CH_3D ; and (ii) the unimolecular cyclometalation reaction to **4** (possibly a tuck-in species of similar form to that depicted for lutetium complex **2**) with concomitant loss of CH_4 , followed by rapid reaction with benzene- d_6 to give **5- d_6** (Scheme 4). The bimolecular pathway is favoured at low temperature (60 °C) relative to unimolecular metalation by a ratio of 76 : 24. However, at 125 °C equal (50 : 50) preference for both pathways was reported.

For comparison to the scandium methyl complex **3**, the neopentyl derivative was prepared. This complex could also be used to activate hydrocarbons, but notably, was not susceptible to cyclometalative reactivity. Instead, hydrocarbon intermolecular C–H bond activation occurred exclusively.¹⁶

The term “tuck-over” complex is commonly used to describe the class of Cp^* metalated species that are formed by an intermolecular metalative C–H bond activation pathway.



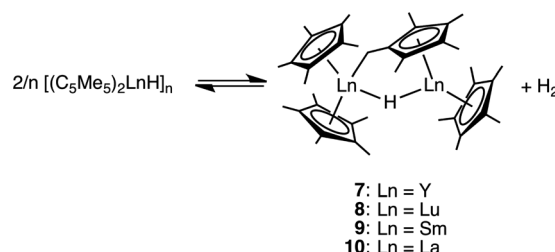
Scheme 3 Synthesis and reactivity of a cyclometalated scandium complex.



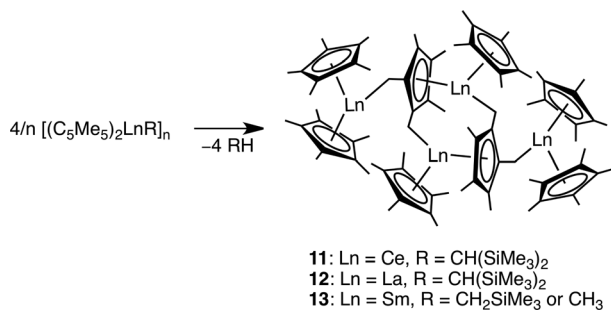
Scheme 4 Competitive reactivity of complex **3**.

The dimeric scandium complex **4** discussed above, can thus, be referred to as a tuck-over complex. An array of other rare earth tuck-over variants has also been outlined in the scientific literature. For example, thermolysis of lanthanide hydride complexes $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{LnH}]_n$ was found to result in intermolecular C–H bond activation of a Cp^* methyl group to generate complexes of the form $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ln}(\mu\text{-}\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)(\mu\text{-H})\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2]$ ($\text{Ln} = \text{Y}$, **7**;¹⁷ Lu , **8**;¹⁸ Sm , **9**;¹⁹ La , **10**²⁰) with simultaneous production of hydrogen gas (Scheme 5). The final complexes of this transformation were binuclear species with bridging hydride and tetramethylfulvene ligands. The reaction itself is reversible in closed systems; accordingly, formation of the tuck-over complexes can be inhibited by an atmosphere of dihydrogen.¹⁹ The structures of these lanthanide tuck-over species have been unambiguously established by single crystal X-ray diffraction experiments. Additional characterization of the complexes was performed by NMR spectroscopy, IR spectroscopy and elemental analyses, and in the case of **9**, magnetic susceptibility measurements. Furthermore, Toepler pump collection of the gases liberated during the formation of **9** revealed 1 mol of H_2 was released, rather than 2 mol. This analysis was consistent with the proposed dimeric structure containing one hydride ligand.

Intermolecular double metalation of a Cp^* ligand was reported in cerium²¹ lanthanum²¹ and samarium²² alkyl complexes. In cyclohexane or methylcyclohexane solutions, complexes of the form $(\eta^5\text{-C}_5\text{Me}_5)_2\text{LnR}$ ($\text{Ln} = \text{Ce}$, $\text{R} = \text{CH}(\text{SiMe}_3)_2$, **11**; $\text{Ln} = \text{La}$, $\text{R} = \text{CH}(\text{SiMe}_3)_2$, **12**; $\text{Ln} = \text{Sm}$, $\text{R} = \text{CH}_2\text{SiMe}_3$ or CH_3 , **13**) underwent



Scheme 5 Preparation of rare earth tuck-over complexes via loss of H_2 .



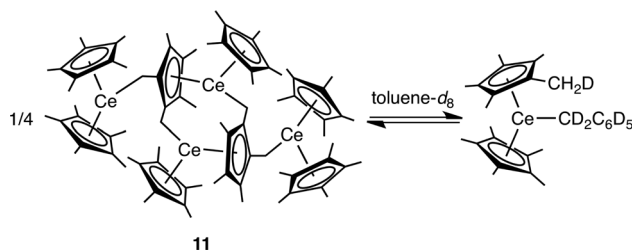
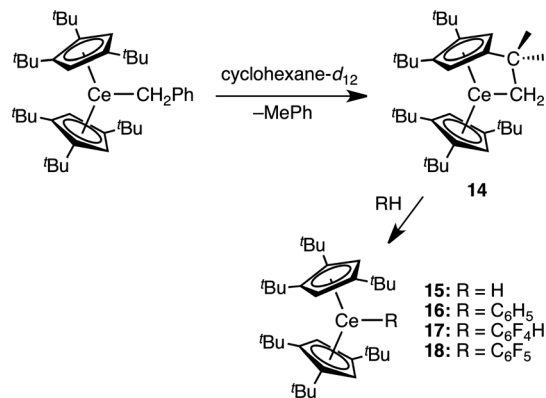
Scheme 6 Double metalation of Cp* ligands.

ligand metalation with loss of alkane to afford the polymetallic cluster compounds $(\eta^5\text{-C}_5\text{Me}_5)_6\text{Ln}_4(\mu_3\text{-}\eta^5\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{Me}_3(\text{CH}_2)_2)_2$ (Scheme 6). The products of these thermolysis reactions contained two trianionic $[\text{C}_5\text{Me}_3(\text{CH}_2)_2]^{3-}$ ligands whereby two methyl groups of the Cp* ring had undergone C–H bond activation. The cerium and samarium complexes were both characterized by X-ray diffraction. The solid-state structures of complexes **11** and **13** exhibited similar bonding motifs; however, the crystal structures were not isomorphous due to the presence of cyclohexane in the lattice of the cerium derivative. The samarium complex was unsolvated.

Related reactivity involving the thermolysis of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{-LnCH}(\text{SiMe}_3)_2$ (Ln = Ce, La) in toluene solution rather than cyclohexane afforded the corresponding benzyl derivatives $(\eta^5\text{-C}_5\text{Me}_5)_2\text{LnCH}_2\text{Ph}$. When this reaction was performed in toluene-*d*₈ and monitored *in situ*, formation of a deuterated benzyl complex ensued with initial generation of only $\text{CH}_2(\text{SiMe}_3)_2$ (CHD(SiMe₃)₂ was not observed). This result indicated that the reaction proceeds *via* the metalated derivatives **11** and **12** rather than by direct σ -bond metathesis of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{LnCH}(\text{SiMe}_3)_2$ with toluene. Interestingly, thermolysis of **11** in toluene-*d*₈ at 80 °C, demonstrated that the reaction is reversible, as scrambling of deuterium atoms into the Cp* rings was observed over time (Scheme 7).

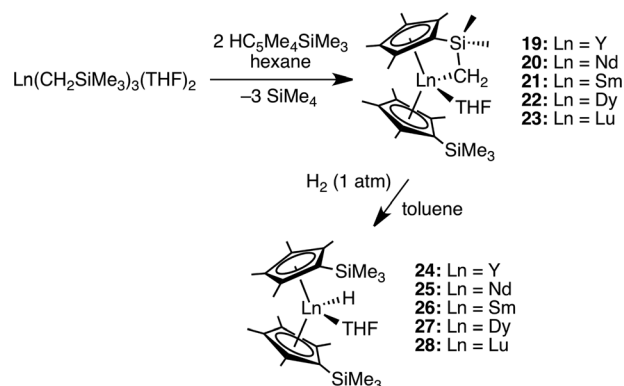
The doubly metalated Ce, La and Sm complexes act as complementary C–H bond activation products to the tuck-in and tuck-over complexes discussed above. Clearly, the Cp* ligand is not fully resistant to metalative C–H bond activation and a diverse collection of products can be generated as a result of these processes.

Related to the Cp* ligand are the carbocyclic ligands $\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_3$ and $\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3$. Both ligands exhibit different steric properties from Cp* and thus, their use in supporting rare earth metals often results in different reaction chemistry.

Scheme 7 Activation of toluene-*d*₈ by complex **11**.Scheme 8 Cyclometalation in a C₅H₂(CMe₃)₃ ligand.

In a cerium benzyl complex of the $\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_3$ ligand, cyclometalative C–H bond activation was reported by the groups of Maron, Eisenstein and Andersen.²³ Thermolysis of $[(\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_3)_2\text{CeCH}_2\text{Ph}]$ in alkane solvent over 12 hours afforded the metallacyclic compound $[(\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_3)\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_2(\text{CMe}_3)_2(\text{CMe}_2\text{CH}_2)\}\text{Ce}]$, **14** with loss of toluene. Cyclometalated species **14** was found to be reactive towards a variety of substrates, such as H₂, benzene, 1,2,4,5-tetrafluorobenzene and pentafluorobenzene, to give the corresponding cerium hydrido, phenyl and fluorophenyl derivatives, respectively (Complexes **15**–**18**, Scheme 8).

In a comparable manner to that observed for the $\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_3$ ligand, lanthanide complexes of the $\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3$ ligand have been shown to undergo cyclometalative alkane elimination reactions. Hou and co-workers have described the reaction of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with $\text{HC}_5\text{Me}_4\text{SiMe}_3$ to give complexes $(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)(\text{THF})$ (Ln = Y, **19**; Nd, **20**; Sm, **21**; Dy, **22**; Lu, **23**) with loss of tetramethylsilane (Scheme 9).²⁴ These complexes were generated *via* a transient alkyl intermediate, $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{CH}_2\text{SiMe}_3)(\text{THF})]$, which underwent cyclometalation of a SiMe₃ group and liberation of tetramethylsilane. Notably, subsequent reaction of the metalated complexes with hydrogen gas afforded terminal lanthanide hydride complexes stabilized by the two sterically demanding $\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3$ ligands, $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{LnH}(\text{THF})]$

Scheme 9 Cyclometalation in a C₅Me₄SiMe₃ ligand.

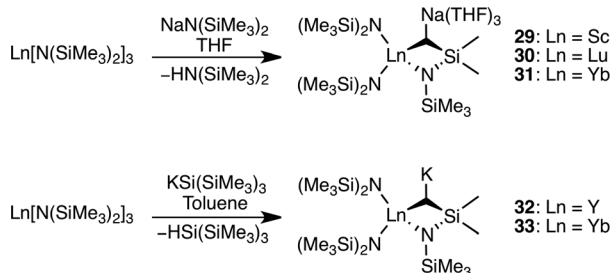
(Ln = Y, **24**; Nd, **25**; Sm, **26**; Dy, **27**; Lu, **28**), Scheme 9. More recently, similar cyclometalative reactivity was reported in a lutetium polyhydride cluster complex of the η^5 -C₅Me₄SiMe₃ ligand.²⁵

3.2 Rare earth γ -metalation of silylamido ligands

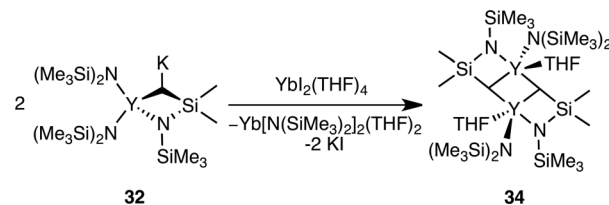
The bis(trimethylsilyl)amide ligand has proven popular for use in rare earth chemistry. The ligand lacks β -hydrogens, provides significant steric protection and is commercially available as the amine or as a variety of salts. This ligand is capable of interacting with metals *via* NSiCH₃...M C-H agostic interactions that can help stabilize coordinatively and electronically unsaturated metal complexes. While the ligand has been employed to support a wide array of metal complexes, deprotonation of the γ -methyl C-H group occasionally occurs.

Cyclometalation has been documented in some rare earth complexes as a result of γ -methyl deprotonation of the bis(trimethylsilyl)amide ligand by a strong base. For example, reaction of tris(silylamido) rare earth complexes (Ln = Sc, Lu, Yb) with NaN(SiMe₃)₂ resulted in deprotonation of the γ -carbon and formation of cyclometalated complexes (Scheme 10). Structural analysis of complexes **29** and **31** revealed planar four-membered metallacycles with Ln-C bond lengths of 2.271(5) Å and 2.386(11) Å for **29** and **31**, respectively. The Yb-C bond in **31** was found to be highly reactive towards insertion of 2,6-xylylisonitrile.²⁶

Niemeyer reported the reaction of Ln[N(SiMe₃)₂]₃ (Ln = Y, Yb) with hypersilyl potassium to afford complexes with the composition [N(SiMe₃)₂]₂LnN(SiMe₃)SiMe₂(CH₂)K (Ln = Y, **32**; Ln = Yb, **33**).²⁷ Recrystallization of **32** from a mixture of *n*-heptane and benzene (20 : 1) at -60 °C gave the corresponding benzene solvate [N(SiMe₃)₂]₂YN(SiMe₃)SiMe₂(CH₂)K(C₆H₆)₂, which was structurally characterized by X-ray crystallography. It has also been shown that the [N(SiMe₃)₂]₂YN(SiMe₃)SiMe₂(CH₂)⁻ anion can be generated through several other means. For example, reaction of Y[N(SiMe₃)₂]₃ with *n*-BuLi in the presence of tetramethylethylenediamine (TMEDA) afforded [N(SiMe₃)₂]₂YN(SiMe₃)SiMe₂(CH₂)Li(TMEDA) in good yield.²⁷ Alternatively, [N(SiMe₃)₂]₂YN(SiMe₃)SiMe₂(CH₂)K(THF)₂ and [N(SiMe₃)₂]₂YN(SiMe₃)SiMe₂(CH₂)]K(18-crown-6)(THF)(toluene)] were obtained from a Y[N(SiMe₃)₂]₃/K/C₈/N₂ reaction mixture in the presence of either THF or a combination of 18-crown-6, THF and toluene, respectively.²⁸ Interestingly two equivalents of complex **32** can be reacted with YbI₂(THF)₄ to generate the neutral dimer [N(SiMe₃)₂]₂YN(SiMe₃)SiMe₂(CH₂)(THF)₂, **34**, with loss of Yb[N(SiMe₃)₂]₂(THF)₂ and KI (Scheme 11).²⁷ Product **34** is notable as a cyclometalated rare earth compound of the



Scheme 10 γ -Deprotonation of the bis(trimethylsilyl)amide ligand.



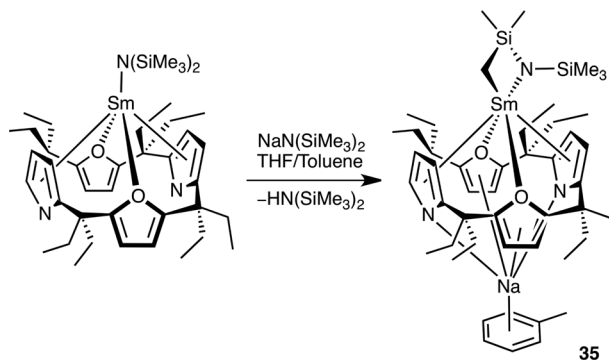
Scheme 11 Synthesis of a neutral γ -cyclometalated yttrium dimer.

bis(trimethylsilyl)amide ligand because unlike **29–33** it is not an “ate” complex. As such, it much more closely resembles the analogous cyclometalated transition metal^{29–31} and actinide^{32–34} complexes of the bis(trimethylsilyl)amide ligand.

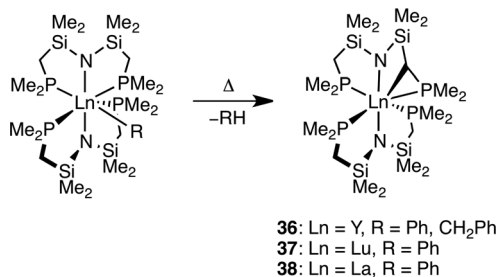
Reactivity involving γ -methyl deprotonation was also observed in a samarium bis(trimethylsilyl)amido complex of a *trans*-difuranyl substituted porphyrinogen ligand. Reaction with NaN(SiMe₃)₂ in THF, followed by recrystallization from toluene resulted in formation of the γ -cyclometalated derivative **35**, whereby one Na ion was retained in the product (Scheme 12). In complex **35**, the Sm(III) metal centre is bound to the cyclometalated γ -alkylamide moiety and to the porphyrinogen ligand in an η^5 : η^1 : η^5 : η^1 -bonding mode. The sodium cation is coordinated η^6 by a molecule of toluene and η^5 : η^1 : η^5 : η^1 by the porphyrinogen ligand. The four-membered metallacycle in **35** exhibited similar metrical parameters to the cyclometalated silylamido ligands in complexes **29** and **31**.

Many of the γ -cyclometalated rare earth complexes described above have been structurally characterized by X-ray crystallography. Similar structural features and metrical parameters of the Ln-C-Si-N metallacycles were reported in all cases.

Related to the bis(trimethylsilyl)amido ligand is the chelating amido-diphosphine framework [N(SiMe₂CH₂PMe₂)₂]⁻ developed by Fryzuk. This ancillary, which possesses a hard anionic nitrogen and two pendant phosphines as soft donors, has proven highly versatile in both early and late transition metal chemistry.³⁵ In group 3 and lanthanide chemistry, reaction of metal chloride complexes of the ligand, LnCl[N(SiMe₂CH₂PMe₂)₂]₂ (Ln = Y, Lu), with phenyllithium or benzyl potassium afforded the expected organometallic derivatives LnR[N(SiMe₂CH₂PMe₂)₂]₂ (Ln = Y, R = Ph, CH₂Ph; Ln = Lu, R = Ph). Intramolecular thermal decomposition of the



Scheme 12 γ -Cyclometalation in a samarium porphyrinogen complex.



Scheme 13 Cyclometalation of a hybrid amido-diphosphine ligand.

phenyl and benzyl complexes resulted in cyclometalation of the ligand methylene group with loss of a hydrocarbon molecule (**36**, Ln = Y; **37**, Ln = Lu). Reaction of the lanthanum chloride complex with phenyllithium afforded exclusively the cyclometalated product (**38**). Although the phenyl complex was not directly observed, it is likely that it existed as a transient intermediate (Scheme 13). The site of ligand cyclometalation in these complexes was inferred from ¹³C{¹H} NMR spectroscopy and ultimately confirmed by an X-ray crystal structure of **36**.³⁶

Kinetic analysis of the cyclometalation reaction that formed complex **36** revealed a first order process across a broad range of temperatures. From an Eyring analysis of the data, the activation parameters involving loss of benzene ($\Delta H^\ddagger = 20.5 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -4.1 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$) and toluene ($\Delta H^\ddagger = 20.6 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -3.3 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$) were determined to be highly comparable. Typically, a large and negative ΔS^\ddagger value is expected due to the formation of a highly ordered four-centred transition state; however, the small and negative ΔS^\ddagger value observed experimentally for this particular system was attributed to a transition state with a dissociated phosphine. The rate of cyclometalation at 73 °C was approximately one order of magnitude faster in the yttrium phenyl complex ($k = 1.65 \times 10^{-3} \text{ s}^{-1}$, half-life = 7.0 min) than the lutetium analogue ($k = 1.88 \times 10^{-4} \text{ s}^{-1}$, half-life = 61.3 min). The difference in rate was attributed to the larger size of yttrium *versus* lutetium, whereby the strained four-centred transition state was more difficult to access with a smaller metal. This notion was consistent with the fact that the lanthanum phenyl complex could not be isolated due to the larger size of the metal, and thus, higher reactivity.³⁶

Recently, the use of a bulky aryl/silylamide ligand [N(SiMe₃)-(2,6-ⁱPr₂C₆H₃)]⁻ to stabilize rare earth dialkyl complexes was reported by Hou and co-workers.³⁷ The alkane elimination reaction of Ln(CH₂SiMe₃)₃(THF)₂ with HN(SiMe₃)(2,6-ⁱPr₂C₆H₃) afforded the corresponding derivatives [N(SiMe₃)(2,6-ⁱPr₂C₆H₃)]Ln(CH₂SiMe₃)₂(THF) (Ln = Sc, **39**; Y, **40**; Ho, **41**; Lu, **42**) as well-defined four coordinate dialkyl complexes. In contrast, a similar reaction using the larger metal gadolinium led to the formation of a cyclometalated bimetallic species [Gd₂{N(2,6-ⁱPr₂C₆H₃)SiMe₂CH₂)}₃(THF)₃, **43**. It was presumed that the formation of **43** proceeded *via* the dialkyl [N(SiMe₃)(2,6-ⁱPr₂C₆H₃)]Gd(CH₂SiMe₃)₂(THF) as a transient intermediate, followed by γ -cyclometalation of a SiMe₃ group with loss of tetramethylsilane and subsequent ligand redistribution.

3.3 Rare earth cyclometalation in β -diketiminato ligands

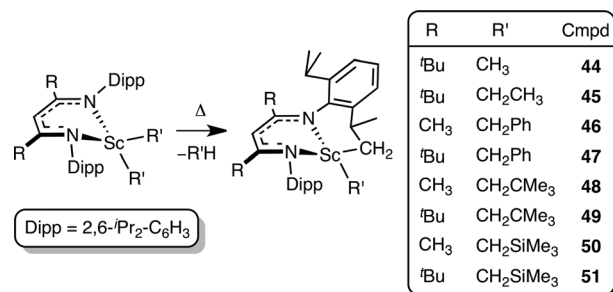
The β -diketiminato (nacnac) framework is a popular scaffold for use in rare earth metal chemistry.³⁸ It is commonly substituted at the *N*-aryl positions with bulky 2,6-diisopropylphenyl rings; a variety of organolanthanide complexes have been stabilized with this form of the ligand.^{38,39} In some cases, though, the sterically demanding nature of this ligand has also resulted in cyclometalation reactivity. Well-defined examples of this process were documented in four coordinate scandium dialkyl complexes. In these complexes, a thermally induced cyclometalative reaction involving the methyl C–H bond of a 2,6-diisopropylphenyl group transpired with extrusion of alkane (Scheme 14).⁴⁰ It was found that the less bulky nacnac derivatives (R = Me) resulted in initial cyclometalation with loss of alkane, but subsequent reaction progress led to ill-defined products. Incorporation of bulkier *tert*-butyl groups at the R site on the nacnac backbone allowed for clean formation of the cyclometalated products.

The NMR spectra of cyclometalated complexes of non-Cp ligands are often exceedingly complicated because of the low symmetry of the resultant products. The ¹H NMR spectrum of cyclometalated compound **51**, for example, exhibited seven doublets for the isopropyl methyl groups and four multiplets for the methine protons. The cyclometalation reaction also generated diastereotopic methylene Sc–CH₂ protons.

Kinetic analysis of the metalation process that generated **51**, revealed a first order reaction, as expected, across a wide temperature range from 30 °C to 70 °C. Activation parameters of $\Delta H^\ddagger = 19.7(6) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -17(2) \text{ cal mol}^{-1} \text{ K}^{-1}$ were obtained from an Eyring plot. The rate of cyclometalation in the formation of compounds **44**–**51** was found to be influenced by steric factors; the bulkier derivatives experienced a faster rate of cyclometalation. In addition, a substantially accelerated rate of ligand cyclometalation (approximately one order of magnitude) was observed in cationic scandium nacnac complexes compared to the neutral analogues.⁴¹

3.4 Rare earth cyclometalation of phosphinimine ligands

The phosphinimine functional group has recently received significant interest in organometallic chemistry of the rare earth metals. However, in certain sterically crowded alkyl complexes, ligands containing the phosphinimine functionality have proven prone to cyclometalative decomposition with loss



Scheme 14 Cyclometalation of a β -diketiminato framework.

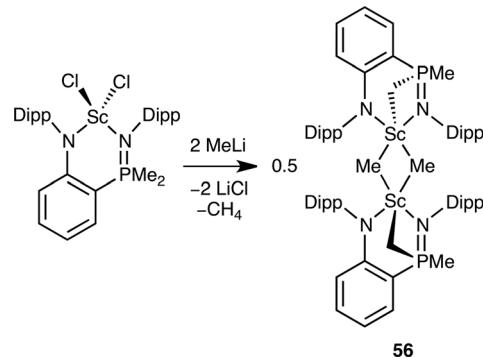
of alkane. For example, dialkyl rare earth complexes of *P*-phenyl substituted anilido-phosphinimine ligands were shown to readily degrade *via ortho*-metalation of a phosphinimine phenyl ring (Scheme 15) resulting in the formation of cyclometalated mixed aryl/alkyl rare earth products (Ln = Y, 52; Ln = Lu, 53).

Intriguing reactivity has been achieved from these species through reaction with various small molecules. Reaction of 52 with two equivalents of 2,6-diisopropylaniline resulted in alkane elimination and metallacycle ring opening to afford the bis(anilide) complex (54).⁴² Similar protonolysis chemistry was observed during the reaction of 53 with phenylacetylene, whereby a bis(alkynyl) lutetium complex was generated (Scheme 16).⁴³

Precedent for cyclometalation has also been demonstrated in a less sterically demanding *P*-methyl substituted derivative of the anilido-phosphinimine ligand. Reaction of a scandium chloride complex of the ligand with two equivalents of methyl-lithium gave a cyclometalated scandium complex (56) with release of methane. It was speculated that the reaction proceeded through a transient scandium dimethyl complex that was thermally susceptible to a cyclometalative alkane elimination reaction (Scheme 17).⁴⁴

We have developed a variety of *NNN* bis(phosphinimine) pincer ligands based on carbazole⁴⁵ and pyrrole⁴⁶ aromatic cores. Lutetium dialkyl complexes of both frameworks can readily be prepared *via* the alkane elimination reaction of the proteo ligands with $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (Chart 2).

The dialkyl lutetium complex of the pyrrole ligand was found to be thermally stable in solution (benzene-*d*₆) at elevated temperature (60 °C). Conversely, the analogous complex of the carbazole ancillary exhibited thermal degradation *via* a rapid intramolecular cyclometalation process. At temperatures above 0 °C the dialkyl lutetium complex of the



Scheme 17 Cyclometalation of a *P*-methyl substituted anilido-phosphinimine ligand.

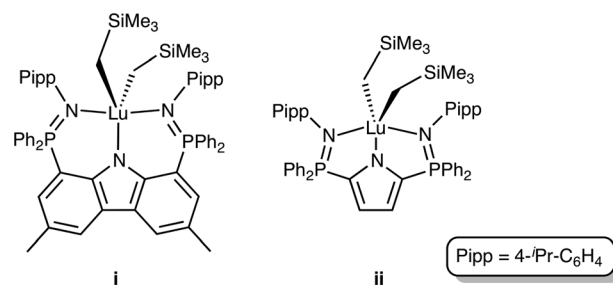
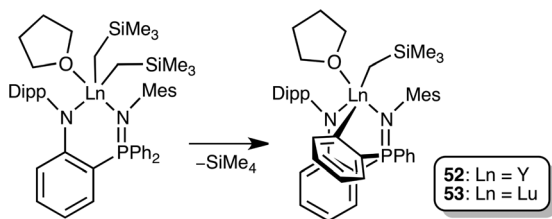


Chart 2 Dialkyl lutetium complexes of bis(phosphinimine)carbazole and pyrrole pincer ligands.

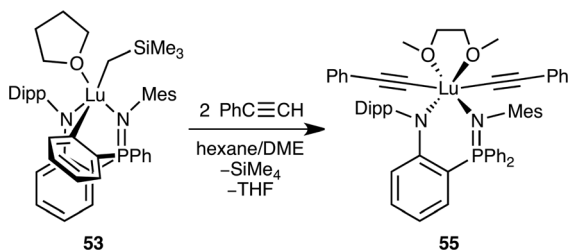
carbazole ligand rapidly undergoes two sequential *ortho*-metalation reactions with loss of two equivalents of tetramethylsilane to afford a doubly metalated derivative (57, Scheme 18). The rate of metalation across a broad range of temperatures was monitored, and the activation parameters ($\Delta H^\ddagger = 19.2(2)$ kcal mol⁻¹ and $\Delta S^\ddagger = -8.2(2)$ cal K⁻¹ mol⁻¹) were determined. These values correspond well to that expected for a highly ordered four-centred transition state and agree well with others reported for intramolecular σ -bond metathesis reactions.

Doubly *ortho*-metalated complex 57 can be readily reacted with various reagents in order to further functionalize the metal centre. For example, reaction of complex 57 with 2,4,6-tri-*tert*-butylaniline affords anilide complex 58 whereby the ligand is coordinated *via* three nitrogen atoms and one *ortho*-metalated *P*-phenyl ring. Interestingly, complex 58 was highly unstable toward a thermally induced intramolecular rearrangement to the structural isomer 59 in which the ligand is bound to the metal centre *via* three nitrogen atoms and one *ortho*-metalated *N*-aryl ring (Scheme 18). Kinetic and deuterium labeling studies revealed that this transformation proceeded by direct exchange of the cyclometalated aryl groups.⁴⁷

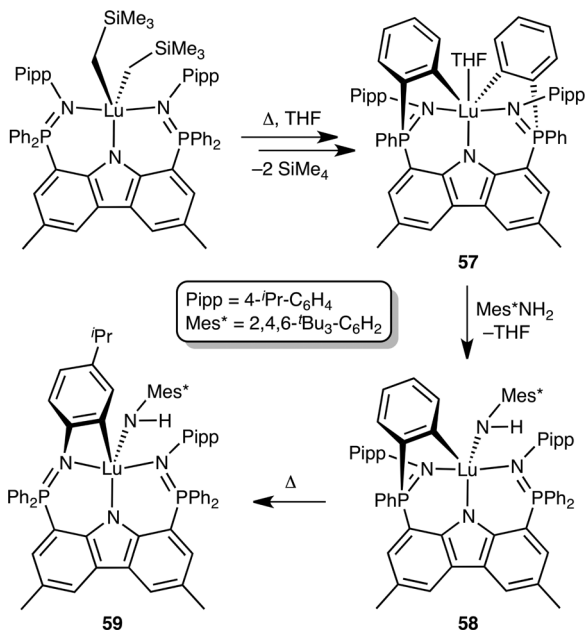
Alternatively, access to a lutetium diiodide derivative, 60, can be achieved through the acid–base reaction of 57 with $[\text{Et}_3\text{NH}]\text{I}$ in dichloromethane (Scheme 19).⁴⁸ This reaction afforded a six coordinate lutetium diiodide complex with two trans iodo ligands, one THF donor and the bis(phosphinimine)carbazole ligand κ^3 bound through three nitrogen atoms.



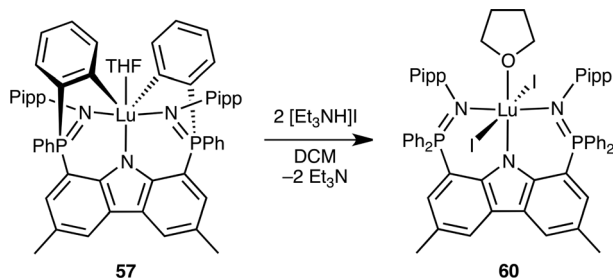
Scheme 15 *Ortho*-metalation of a *P*-phenyl substituted anilido-phosphinimine ligand.



Scheme 16 Synthesis of a bis(alkynyl) lutetium complex.



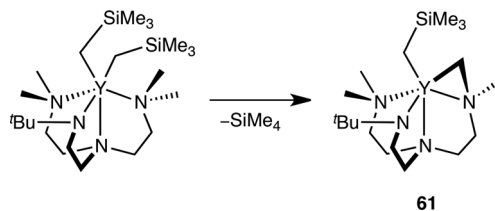
Scheme 18 Double *ortho*-metalation in a lutetium alkyl complex and subsequent reactivity with Mes^*NH_2 .



Scheme 19 Synthesis of a lutetium diiodide complex.

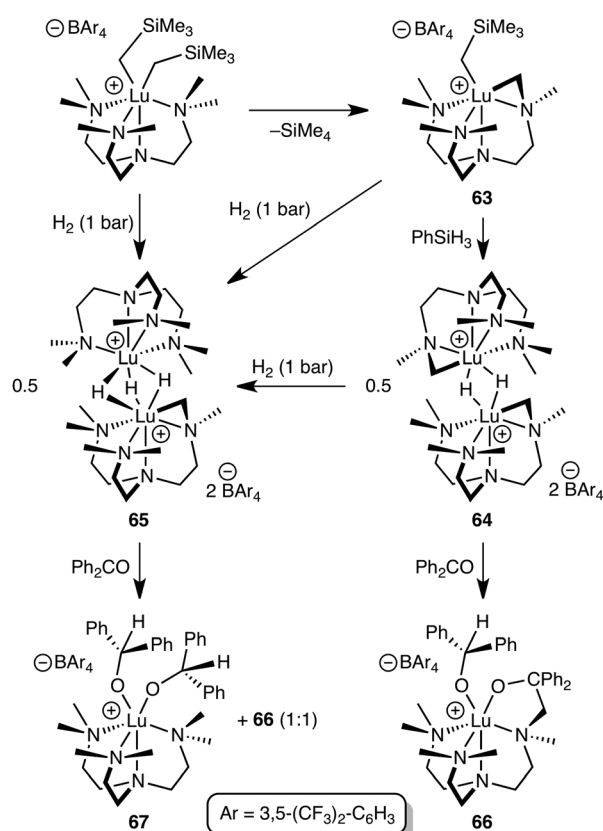
3.5 Rare earth cyclometalation involving other ancillary ligands

A variety of other ligand scaffolds have been shown to undergo cyclometalation reactions in rare earth alkyl complexes. For example an yttrium dialkyl complex of a triamino-amide ligand was found to quantitatively cyclometalate at ambient temperature *via* an NMe_2 group (Scheme 20). In aromatic solvent (benzene- d_6), full conversion to the cyclometalated product **61** occurred over 8 h. However, in Lewis basic solvent (THF- d_8), the transformation required substantially more time (2 days), implying a stabilizing effect of the dialkyl complex by the coordinating solvent. The metalated yttrium complex was determined to be monomeric by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, whereby the NCH_2Y and SiCH_2Y carbon resonances exhibited coupling to a single ^{89}Y nucleus ($^{89}\text{Y} = 100\%$, $I = 1/2$). In comparison, a cyclometalated lanthanum complex of a related TACN-amide ligand, $\{[(\mu\text{-CH}_2)\text{Me}(\text{TACN})\text{SiMe}_2\text{N}(\text{Bu})]\text{La}(\text{CH}_2\text{-SiMe}_3)_2\}$ (**62**, TACN = 1,4,7-triazacyclononane), was established to be a dimeric species, likely due to the larger ionic radius of lanthanum.⁴⁹



Scheme 20 Cyclometalation in an yttrium dialkyl complex of a triamino-amide ligand.

Cyclometalation of the neutral ligand tris{2-(dimethylamino)ethyl}amine, Me_6TREN , was recently reported in a cationic lutetium alkyl complex $[\text{Lu}(\text{Me}_6\text{TREN})(\text{CH}_2\text{SiMe}_3)_2][\text{BAR}_4]$ ($\text{Ar} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$).⁵⁰ In this transformation, metalation of a methyl group in Me_6TREN generated the monoanionic ligand $\text{Me}_5\text{TRENCH}_2^-$ with concomitant release of alkane. The cyclometalation reaction of the dialkyl lutetium complex proceeded at temperatures above 0°C , and resulted in exclusive formation of the cationic species $[\text{Lu}(\text{Me}_5\text{TRENCH}_2)(\text{CH}_2\text{SiMe}_3)][\text{BAR}_4]$, **63** (Scheme 21). Reaction of **63** with an excess of phenylsilane liberated a cationic lutetium hydride as a dimer, $[\text{Lu}_2(\text{Me}_5\text{TRENCH}_2)_2\text{H}_2][\text{BAR}_4]_2$, **64**. Interestingly, it was found that reaction of **64** with H_2 (1 bar) over 24 h converted one of the two $\text{Me}_5\text{TRENCH}_2^-$ ligands to Me_6TREN . This reaction resulted in the formation of a dicationic tri(μ_2 -hydride) complex, $[\text{Lu}(\text{Me}_5\text{TRENCH}_2)(\mu_2\text{-H})_3\text{Lu}(\text{Me}_6\text{TREN})][\text{BAR}_4]_2$, **65**.

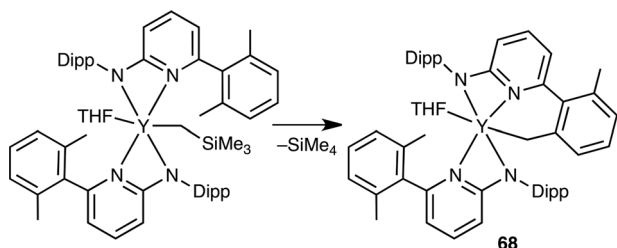


Scheme 21 Cyclometalation of Me_6TREN to $\text{Me}_5\text{TRENCH}_2^-$.

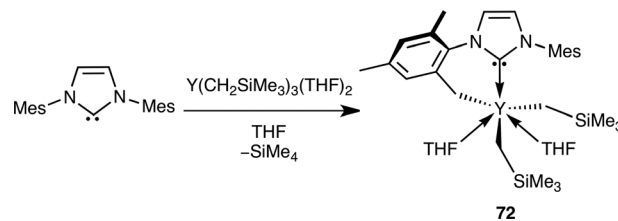
The conversion of complex **64** to **65** is comparable to the hydrogenolysis reactivity of cyclometalated species discussed in Section 3.1. In an effort to substantiate the nucleophilic nature of the hydride ligands in **64** and **65**, both complexes were reacted with benzophenone. In the case of **64**, reaction with four equivalents of benzophenone resulted in CO insertion into the two Lu–H and two cyclometalated Lu–CH₂N bonds to generate [Lu(Me₅TRENCH₂CPh₂O)(OCHPh₂)][BAR₄], **66**. The same reaction involving **65** resulted in the formation of a 1 : 1 mixture of **66** and the double Lu–H insertion product [Lu(Me₆TREN)(OCHPh₂)₂][BAR₄], **67**.

Intramolecular cyclometalation of an amidopyridinate ligand was reported in bis(amidopyridinate) yttrium alkyl and hydrido complexes.⁵¹ This transformation involved the methyl C–H bond of a 2,6-dimethylphenyl group and resulted in an yttrium complex with an amidopyridinate ligand κ³-bound to yttrium *via* two nitrogen atoms and one cyclometalated CH₂ group (**68**, Scheme 22). The effect that leaving group has on the rate of cyclometalation was reported, where R = CH₂Ph, CH₂SiMe₃ and H. While the bis(amidopyridinate) yttrium benzyl complex was found to be completely stable with no observable cyclometalation at ambient temperature, the corresponding trimethylsilylmethyl complex exhibited slow cyclometalative decomposition in toluene-*d*₈ at 296 K. Kinetic analysis of this transformation revealed a first-order dependence on the trimethylsilylmethyl yttrium complex ($k = 3.8 \times 10^{-3} \text{ h}^{-1}$, $t_{1/2} = 181 \text{ h}$). When the hydrido derivative was generated *in situ* (by reaction of the bis(amidopyridinate) yttrium trimethylsilylmethyl complex with PhSiH₃), a dramatic increase in the rate of cyclometalation (*ca.* 500 times faster than the trimethylsilylmethyl derivative) was observed.

The synthesis of *N*-heterocyclic carbene (NHC) complexes of rare earth metals was recently investigated by Okuda and co-workers. Reaction of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) with Ln(CH₂SiMe₃)₃(THF)₂, Ln = Y, Lu, resulted in formation of thermally robust trialkyl NHC complexes (IPr)Ln(CH₂SiMe₃)₃ (Ln = Y, **69**; Ln = Lu, **70**). When the analogous reaction was performed using the slightly less bulky NHC 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), only the lutetium derivative, (IMes)Lu(CH₂SiMe₃)₃, **71** could be isolated. The corresponding reaction between IMes and Y(CH₂SiMe₃)₃(THF)₂, resulted in cyclometalated dialkyl product **72**. Complex **72** formed by C–H activation of one of the *ortho*-methyl groups of the mesityl ring with elimination of tetramethylsilane (Scheme 23).⁵²



Scheme 22 Cyclometalation in an amidopyridinate yttrium complex.



Scheme 23 Cyclometalation of an IMes supported yttrium complex.

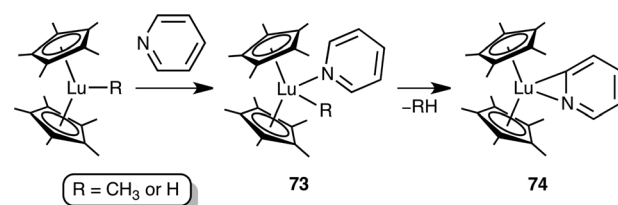
3.6 Rare earth cyclometalation of *N*-heterocycles

Heterocycles such as pyridine are frequently utilized in rare earth chemistry. Accordingly, it has been well-documented that such *N*-heterocycles are capable of cyclometalative C–H bond reactions involving lanthanide and actinide metals.⁵³ Notably, these cyclometalated species have proven useful for (i) generating functionalized heterocyclic derivatives by insertion of unsaturated substrates into the M–C bond; and (ii) the synthesis of metal-element multiple bonds *via* metallacycle ring opening.

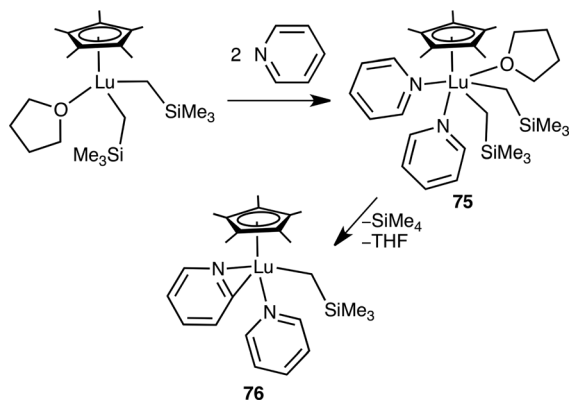
An early example of heterocycle metalation in rare earth chemistry involved the reaction of (η⁵-C₅Me₅)₂LuR (R = CH₃ or H) with pyridine. Coordination of pyridine to lutetium initially gave the anticipated adduct (**73**); however, subsequent C–H bond activation of the heterocycle at the 2-position led to cyclometalation and formation of **74** with loss of either methane or hydrogen gas (Scheme 24). Kinetic analysis revealed that the cyclometalation was first order in **73** with no dependence on the quantity of added pyridine, thus suggesting an intramolecular reaction with a rate determining C–H bond activation step. Notably, the metalated carbon atom in **74** exhibited a downfield shift of δ 234.26 in its ¹³C NMR spectrum (cyclohexane-*d*₁₂), which is typically diagnostic of a Ln–C_{aryl} bond in diamagnetic lanthanide complexes.⁵⁴

A similar pyridine activation process was observed in the half-metallocene complex (η⁵-C₅Me₅)Lu(CH₂SiMe₃)₂(THF). Reaction with two equivalents of pyridine in toluene solution generated the double adduct, **75**. Subsequent C–H bond activation of the *ortho* site of the pyridine ring led to formation of (η⁵-C₅Me₅)Lu[η²-(*N,C*)-NC₅H₄](CH₂SiMe₃)(NC₅H₅), **76** (Scheme 25).⁵⁵

Okuda reported reaction of the dicationic yttrium complex [YMe(THF)₆]²⁺[BPh₄]₂⁻ with excess pyridine, which resulted in rapid exchange of THF ligands for pyridine donors to afford [YMe(py)₆]²⁺[BPh₄]₂⁻. When left in a 2 : 1 solution of pyridine and pentane at ambient temperature this compound gradually



Scheme 24 Pyridine activation in a lutetium metallocene complex.

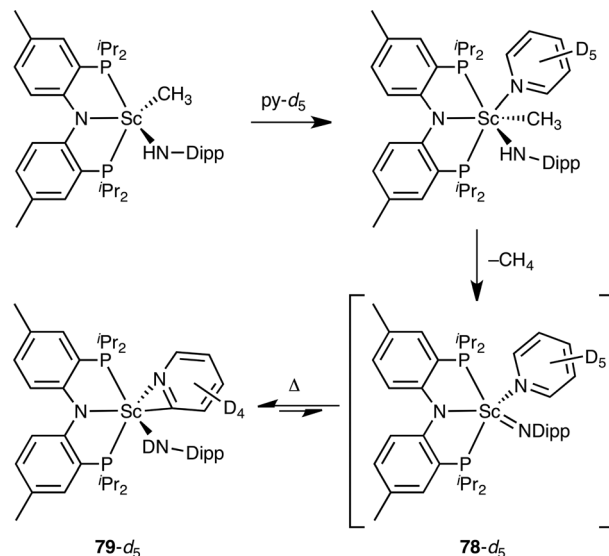


Scheme 25 Pyridine activation in a lutetium half-metallocene complex.

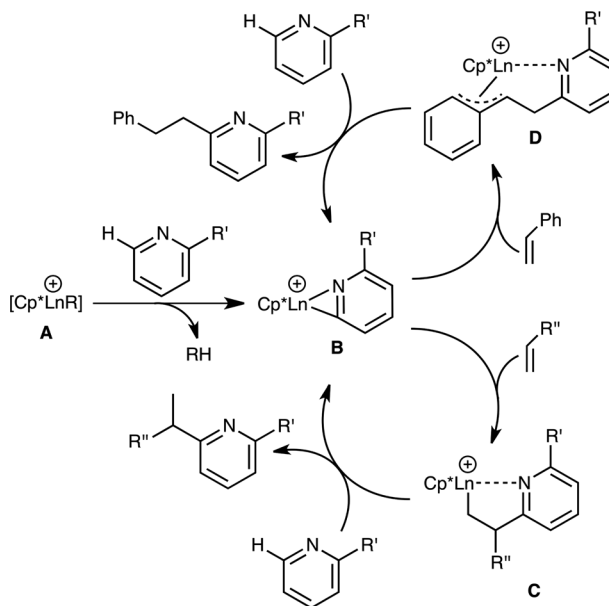
converted to the metalated species, $[\text{Y}(\eta^2\text{-}(N,C)\text{-NC}_5\text{H}_4)\text{-}(\text{NC}_5\text{H}_5)_6]^{2+}[\text{BPh}_4]_2^-$, **77**, over the course of 5 days.⁵⁶

A cyclometalated pyridine ligand was instrumental in the development of scandium imido chemistry by Mindiola and co-workers. It was found that the mixed alkyl/anilide complex $(\text{PNP})\text{Sc}(\text{CH}_3)\text{NHDipp}$, where $\text{PNP} = (2\text{-}^i\text{Pr}_2\text{P-4-Me-C}_6\text{H}_3)_2\text{N}^-$, reacts with pyridine to form cyclometalated product $(\text{PNP})\text{Sc}(\eta^2\text{-}(N,C)\text{-NC}_5\text{H}_4)\text{NHDipp}$ (**79**) with loss of methane. Various mechanisms were considered for this transformation, including (i) direct cyclometalation of pyridine with loss of methane; and (ii) α -NH abstraction to form a transient scandium imide and methane, followed by 1,2-addition of pyridine across the double bond. Deuterium labeling studies using pyridine- d_5 revealed the formation of $(\text{PNP})\text{Sc}(\eta^2\text{-}(N,C)\text{-NC}_5\text{D}_4)\text{NDDipp}$ (**79- d_5**), suggesting that α -hydrogen abstraction and loss of methane occurred prior to *ortho*-metalation of pyridine. Furthermore, loss of CH_4 , rather than CH_3D , and no deuterium incorporation into the anilide ring or PNP framework, was observed. Accordingly, the deuterium labeling study supported a mechanism that involved the formation of a transient scandium imide complex (**78**) and subsequent 1,2-C-H addition across the reactive $\text{Sc}=\text{NAr}$ bond (Scheme 26).⁵⁷ This work was notable because it provided the first experimental evidence for a terminal scandium imide. Shortly thereafter, a terminal scandium imide was in fact isolated and structurally characterized by Chen and co-workers.⁵⁸

Recently, Hou reported the catalytic addition of substituted pyridines to olefins using rare earth bis(benzyl) complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Ln}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$ ($\text{Ln} = \text{Sc}, \text{Y}$) in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$.⁵⁹ This process was selective to the *ortho* position of the pyridine ring and postulated to proceed *via* a half-sandwich rare earth cation coordinated to a cyclometalated pyridyl ligand. A variety of pyridine and olefin substrates, including α -olefins, styrenes, and 1,3-conjugated dienes, were reported to undergo the transformation with high functional group tolerance and selectivity. The proposed mechanism for this process is outlined in Scheme 27. Initial coordination of a pyridine substrate to a cationic half-sandwich rare earth alkyl cation (**A**), followed by cyclometalative C-H bond activation at the *ortho* site of the pyridine ring results in the pyridyl species **B**



Scheme 26 *Ortho*-metalation of pyridine *via* 1,2 addition across a transient $\text{Sc}=\text{N}$ double bond.



Scheme 27 Proposed mechanism for catalytic addition of pyridines to olefins by rare earth complexes.

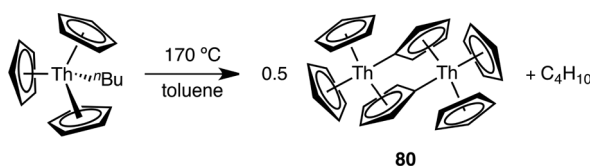
with loss of alkane. Subsequent 2,1-insertion of an α -olefin into the metal-pyridyl bond generates **C**, which can coordinate and cyclometalate a free pyridine molecule with release of the branched addition product and regeneration of **B**. The 2,1-insertion of an α -olefin is typically preferred so as to minimize steric hindrance; however, in the case of styrene, a 1,2-insertion into the metal-pyridyl bond can proceed to afford **D**, which is stabilized by a benzyllic interaction. Subsequent coordination and deprotonation by a free pyridine molecule liberates the linear addition product with regeneration of **B**.

4. Actinide cyclometalation

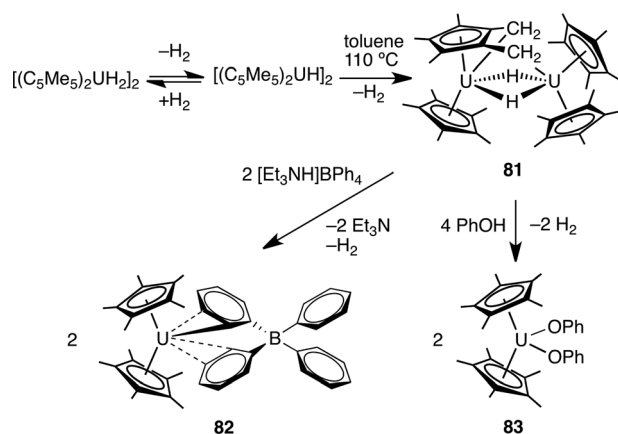
4.1 Tuck-in and tuck-over actinide complexes

An assortment of well-defined actinide tuck-in and tuck-over complexes of Cp and Cp* ligands have been reported in the literature. Marks published the thermolysis reaction of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Th}(\text{nBu})$ to form the metalated complex $(\eta^5\text{-C}_5\text{H}_5)_4\text{Th}_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4)_2$, **80** as a colourless crystalline solid with extrusion of alkane (Scheme 28). Characterization of the product by combustion analysis, mass spectrometry and infrared spectroscopy indicated the chemical composition of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Th}_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4)_2$; the connectivity was unambiguously established by a single crystal X-ray diffraction experiment. In the structure, each thorium centre is η^5 -bound to three Cp groups and σ -bonded to one bridging Cp ring. A similar transformation was also described for the uranium analogue.⁶⁰

Numerous structurally characterized actinide tuck-in and tuck-over complexes of the Cp* ligand have recently been reported by the Evans group. A uranium tuck-in/tuck-over complex was synthesized by heating an equilibrium mixture of tetravalent $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{UH}_2]_2$ and trivalent $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{UH}]_2$ in toluene solution at 110 °C (Scheme 29). Loss of hydrogen gas (measured by Toepler pump experiments) afforded the bimetallic complex **81**, whereby one doubly-metalated $[\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_3(\text{CH}_2)_2]^{3-}$ ligand is bound to uranium centres *via* both tuck-in and tuck-over coordination modes. The solid-state structure of **81** revealed long U–CH₂ bond lengths of 2.564(1) Å and 2.640(1) Å for the tuck-in and tuck-over interactions, respectively. Complex **81** can be reacted with various small molecules to derivatize the metal centre. For example, reaction with two equivalents of $[\text{Et}_3\text{NH}]\text{BPh}_4$ gave the ion pair



Scheme 28 Metalation of a Cp ligand by a thorium alkyl complex.



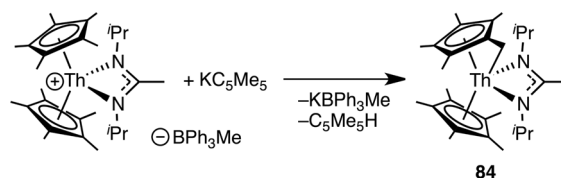
Scheme 29 Synthesis and reactivity of a uranium tuck-in/tuck-over complex.

$[(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}]\text{BPh}_4$, **82**, with loss of dihydrogen and two equivalents of triethylamine. Alternatively, treatment of **81** with four equivalents of phenol liberated the bis(phenoxide) complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{OPh})_2$, **83**, and two equivalents of hydrogen gas.¹¹

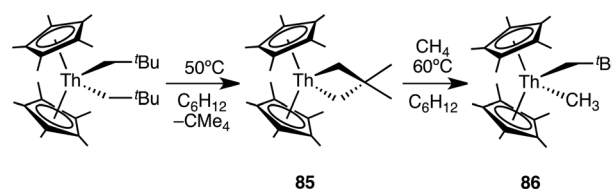
A monomeric thorium tuck-in complex was prepared by reaction of the mixed-ligand metallocene amidinate cation $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}\{\text{PrNC}(\text{Me})\text{N}^i\text{Pr-}\kappa^2\text{-N,N'}\}]^+$ with KC_5Me_5 (Scheme 30). The orange product $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)\text{Th}\{\text{PrNC}(\text{Me})\text{N}^i\text{Pr-}\kappa^2\text{-N,N'}\}]$, **84**, was fully characterized by spectroscopy (NMR and IR), combustion analysis, and its connectivity was confirmed by single-crystal X-ray diffraction. Notably, **84** was the first structurally characterized, unambiguously monomeric f-element tuck-in complex containing a cyclometalated $(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)^{2-}$ ligand. Attempts to perform the analogous reaction with uranium led to a different result, whereby a reduction of U^{4+} to U^{3+} occurred with formation of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}\{\text{PrNC}(\text{Me})\text{N}^i\text{Pr-}\kappa^2\text{-N,N'}\}]$ and loss of $(\text{C}_5\text{Me}_5)_2$ and KBPh_3Me .⁶¹

4.2 Actinide γ -metalation of alkyl and silylamido ligands

Several examples of γ -cyclometalation of alkyl and silylamido ligands have been published. This process was described by Marks and colleagues, wherein the dialkyl complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\text{CH}_2\text{CMe}_3)_2$ was shown to be susceptible to γ -metalation of an alkyl group with loss of neopentane (Scheme 31). An analogous transformation was also observed in the complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\text{CH}_2\text{SiMe}_3)_2$ with release of free tetramethylsilane; however, slightly higher temperatures were required. Notably, the thoracyclobutane compound $\text{Cp}^*_2\text{Th}(\text{CH}_2)_2\text{CMe}_2$, **85**, could be used to activate hydrocarbons. For example, $\text{Cp}^*_2\text{Th}(\text{CH}_2)_2\text{CMe}_2$ is capable of activating methane at the relatively mild temperature of 60 °C to give the mixed neopentyl/methyl product $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\text{CH}_2\text{CMe}_3)\text{Me}$, **86** (Scheme 31).^{62,63} Similar activation chemistry using the reagents tetramethylsilane or tetramethyltin led to the ring-opened products $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$, **87**, and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SnMe}_3)$, **88**, respectively (Chart 3).



Scheme 30 The first unambiguous example of a thorium tuck-in complex.



Scheme 31 Formation of a thoracyclobutane complex *via* γ -metalation and its subsequent application in methane activation.

Conversely, when complex **85** was reacted with trimethylphosphine, the product $\text{Cp}^*_2\text{Th}(\text{CH}_2)_2\text{PMe}$, **89**, was generated alongside neopentane (Chart 3). Olefins react with **85** by inserting into the thoracyclobutane ring. For instance, reaction with propylene afforded a thoracyclohexane product, **90** (Chart 3).⁶⁴

Cyclometalation of the bulky alkyl ligand $[\text{CH}(\text{SiMe}_3)_2]^-$ was reported by the Leznoff group in a uranium complex supported by a chelating diamido ether ancillary (${}^t\text{BuNON}$)²⁻.⁶⁵ Reaction of the dichloride uranium dimer $[({}^t\text{BuNON})\text{UCl}_2]_2$ with four equivalents of $\text{LiCH}(\text{SiMe}_3)_2$ in hexanes at ambient temperature afforded the cyclometalated alkyl-bridged uranium dimer $[({}^t\text{BuNON})\text{U}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)\}]_2$, **91**, with loss of alkane (Scheme 32). The γ -metalation of the bis(trimethylsilyl)methyl ligand in **91** was likely facilitated by significant steric crowding in the uranium complex. Interestingly, cyclometalated complex **91** is capable of catalyzing the polymerization of ethylene at 25 °C; however, it exhibited low catalyst activity compared to other related complexes.

Andersen and co-workers published a γ -metalation reaction in silylamide complexes of uranium and thorium.³² Pyrolysis of the actinide hydride compounds $\text{HAn}[\text{N}(\text{SiMe}_3)_2]_3$ (An = Th, **92**; U, **93**) led to the extrusion of hydrogen gas *via* γ -deprotonation of one silylamide ligand and cyclometalation (An = Th, **94**; An = U, **95**; Scheme 33). Under high pressures of H_2 , the process can be reversed to give the starting material $\text{HAn}[\text{N}(\text{SiMe}_3)_2]_3$. Likewise, under D_2 , the deuteride derivatives can be formed (An = Th, **92-d₂**; An = U, **93-d₂**; Scheme 33). If both cyclometalation and cyclometalation-reversal are allowed to repeat multiple times in the presence of excess D_2 , perdeuteration of complexes **92** and **93**, $\text{DAn}[\text{N}\{\text{Si}(\text{CD}_3)_3\}]_3$, can be achieved.

More recently, a variety of multi-metallic cyclometalated uranium complexes were isolated by Gambarotta and colleagues. The formation of one such product is outlined in Scheme 34; reaction of $[\text{U}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}[\mu\text{-Cl}]_2$ with $\text{LiCH}_2\text{SiMe}_3$ afforded trimetallic compound **96** in good yield. Interestingly, this complex features three singly γ -deprotonated silylamide ligands,

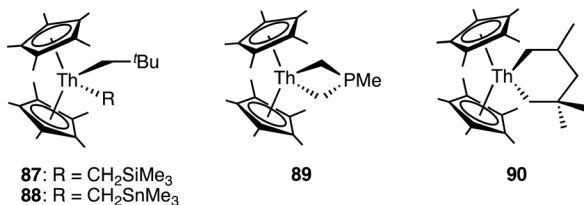
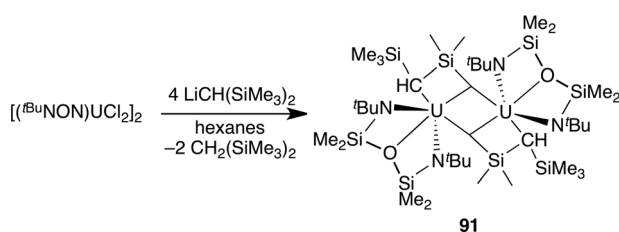
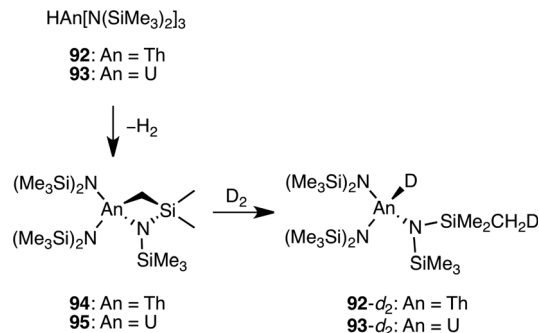


Chart 3 Small molecule reaction products from complex **85**.



Scheme 32 γ -Cyclometalation of a $[\text{CH}(\text{SiMe}_3)_2]^-$ ligand.



Scheme 33 γ -Cyclometalation of a silylamide ligand in actinide complexes.

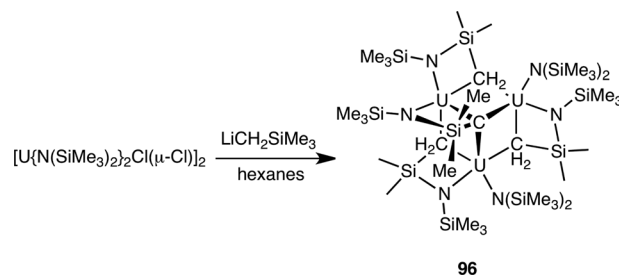
as well as one triply γ -deprotonated silylamide ligand. The triply deprotonated γ -carbon is best described as a tricapping carbyne ligand.³⁴

4.3 Actinide cyclometalation involving other ancillary ligands

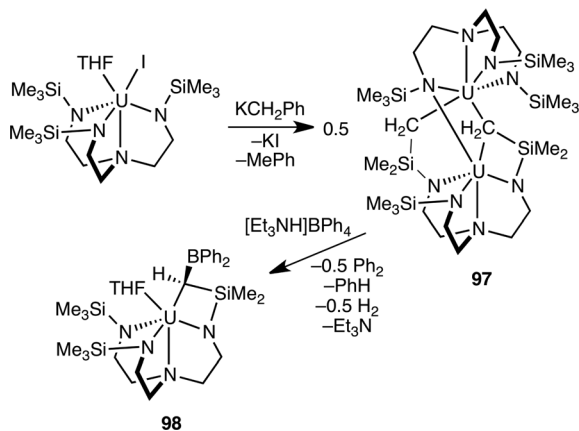
A uranium iodide complex of a triamidoamine ligand (Tren^{TMS}) was demonstrated to undergo cyclometalative reactivity when reacted with benzyl potassium (**97**, Scheme 35). Compound **97** is comparable to the tuck-in/tuck-over uranium complex **81** discussed above, in that one triamidoamine ligand has undergone both intra- and intermolecular metalation reactions to afford a bimetallic complex. In an attempt to generate the ion pair $[(\text{Tren}^{\text{TMS}})\text{U}(\text{THF})_2][\text{BPh}_4]$, complex **97** was reacted with $[\text{Et}_3\text{NH}]\text{BPh}_4$. However, the unexpected singly cyclometalated complex **98** was formed instead, whereby a BPh_2 moiety was bound to the metalated carbon atom of the ligand (Scheme 35). Significantly, the formation of **98** occurred *via* a double dearylation of the $[\text{BPh}_4]^-$ anion, marking the first time such reactivity had been observed for $[\text{BPh}_4]^-$.⁶⁶

4.4 Actinide cyclometalation of N-heterocycles

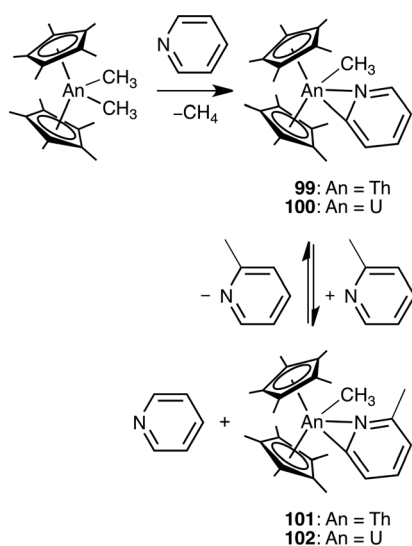
Much to the same extent as lanthanide alkyl complexes, actinide alkyls can undergo cyclometalation reactions with *N*-heterocycles. The dimethyl actinide complexes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{AnMe}_2$ (An = Th, U) react readily with pyridine at the 2-position to give the complexes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{An}[\eta^2\text{-}(N,C)\text{-NC}_5\text{H}_4]\text{Me}$ (An = Th, **99**; An = U, **100**; Scheme 36). It is believed that the reaction proceeds by initial coordination of pyridine to the metal, followed by cyclometalative C–H bond activation. Exchange of the cyclometalated pyridine ligand in **99** with 2-picoline proceeds at 90 °C to give the $\eta^2\text{-}(N,C)$ -picolyl complex



Scheme 34 Triple γ -deprotonation of a silylamide ligand by uranium.



Scheme 35 Intra- and intermolecular cyclometalation in a uranium complex of a triamidoamine ligand.



Scheme 36 Cyclometalation of pyridine in actinide complexes.

($\eta^5\text{-C}_5\text{Me}_5$)₂Th[$\eta^2\text{-}(N,C)\text{-6-CH}_3\text{-NC}_5\text{H}_3$]Me (**101**). Notably, the uranium $\eta^2\text{-}(N,C)$ -picolyl analogue (**102**) can also be prepared; however, the exchange reaction is much more facile and proceeds at ambient temperature.⁶⁷

5. Conclusions

This tutorial review has summarized numerous diverse examples of cyclometalative C–H bond activation reactions in various ligands coordinated to rare earth and actinide complexes. The contributing factors toward this transformation have been highlighted; namely, high steric crowding and reduced electron density at a metal centre accelerate cyclometalation markedly. Rates for this process can also be influenced by metal ion size. Cyclometalated species often react with small molecules bearing acidic protons (e.g. phenol, anilines, alkynes and triethylammonium salts) to induce metallacycle ring opening and functionalization of the metal centre. Reactivity of hydrocarbon

substrates such as methane and olefins with cyclometalated f-element complexes has also been outlined. Clearly the potential for rare earth and actinide metal species to undergo both intra- and intermolecular C–H bond activation processes is a testament to the high reactivity of these metals, as well as their potential for applications relevant to the activation and functionalization of small molecules. It is anticipated that with further study and investigations into the constrained nature and potential reactivity of cyclometalated species, a wide range of applications may be realized, such as the use of cyclometalated complexes as resting states for various bond-forming catalytic transformations, or alternatively, the synthesis of metal–element multiple bonds *via* metallacycle ring opening reactions.

Notes and references

- W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435–3449.
- H.-P. Abicht and K. Issleib, *Z. Chem.*, 1977, **17**, 1–9.
- J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327–352.
- G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451–489.
- M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73–86.
- I. P. Rothwell, *Polyhedron*, 1985, **4**, 177–200.
- A. R. Dias, M. S. Salema, J. A. Martinho Simões, J. W. Pattiasina and J. H. Teuben, *J. Organomet. Chem.*, 1989, **364**, 97–103.
- W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119–2136.
- J. M. Fischer, W. E. Piers and V. G. Young Jr, *Organometallics*, 1996, **15**, 2410–2412, and references therein.
- H. Brunner, J. Wachter, G. Gehart, J.-C. Leblanc and C. Moise, *Organometallics*, 1996, **15**, 1327–1330.
- W. J. Evans, K. A. Miller, A. G. DiPasquale, A. L. Rheingold, T. J. Stewart and R. Bau, *Angew. Chem., Int. Ed.*, 2008, **47**, 5075–5078.
- P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491–6493.
- M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 203–219.
- M. E. Thompson and J. E. Bercaw, *Pure Appl. Chem.*, 1984, **56**, 1–11.
- S. Hajela, W. P. Schaefer and J. E. Bercaw, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **48**, 1771–1773.
- A. D. Sadow and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 7971–7977.
- M. Booi, B.-J. Deelman, R. Duchateau, D. S. Postma, A. Meetsma and J. H. Teuben, *Organometallics*, 1993, **12**, 3531–3540, and references therein.
- W. J. Evans, T. M. Champagne and J. W. Ziller, *J. Am. Chem. Soc.*, 2006, **128**, 14270–14271.
- W. J. Evans, T. A. Ulibarri and J. W. Ziller, *Organometallics*, 1991, **10**, 134–142.
- W. J. Evans, J. M. Perotti and J. W. Ziller, *Inorg. Chem.*, 2005, **44**, 5820–5825.
- M. Booi, A. Meetsma and J. H. Teuben, *Organometallics*, 1991, **10**, 3246–3252.
- W. J. Evans, J. M. Perotti and J. W. Ziller, *J. Am. Chem. Soc.*, 2005, **127**, 3894–3909.
- L. Maron, E. L. Werkema, L. Perrin, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2005, **127**, 279–292.
- Y. Takenaka and Z. Hou, *Organometallics*, 2009, **28**, 5196–5203.
- M. Nishiura, J. Baldamus, T. Shima, K. Mori and Z. Hou, *Chem.-Eur. J.*, 2011, **17**, 5033–5044.
- M. Karl, K. Harms, G. Seybert, W. Massa, S. Fau, G. Frenking and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1999, **625**, 2055–2063.
- M. Niemeyer, *Inorg. Chem.*, 2006, **45**, 9085–9095.
- M. Fang, J. E. Bates, S. E. Lorenz, D. S. Lee, D. B. Rego, J. W. Ziller, F. Furche and W. J. Evans, *Inorg. Chem.*, 2011, **50**, 1459–1469.
- P. Berno, R. Minhas, S. Hao and S. Gambarotta, *Organometallics*, 1994, **13**, 1052–1054.
- S. J. Simpson and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 3627–3629.
- X. Yu, S. Bi, I. A. Guzei, Z. Lin and Z.-L. Xue, *Inorg. Chem.*, 2004, **43**, 7111–7119.

- 32 S. J. Simpson, H. W. Turner and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 2991–2995.
- 33 A. Dormond, A. A. El Bouadili and C. Moïse, *J. Chem. Soc., Chem. Commun.*, 1985, 914–916.
- 34 I. Korobkov and S. Gambarotta, *Inorg. Chem.*, 2010, **49**, 3409–3418.
- 35 M. D. Fryzuk, *Can. J. Chem.*, 1992, **70**, 2839–2845.
- 36 M. D. Fryzuk, T. S. Haddad and S. J. Rettig, *Organometallics*, 1991, **10**, 2026–2036.
- 37 Y. Luo, M. Nishiura and Z. Hou, *J. Organomet. Chem.*, 2007, **692**, 536–544.
- 38 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031–3066.
- 39 K. R. D. Johnson, A. P. Côté and P. G. Hayes, *J. Organomet. Chem.*, 2010, **695**, 2747–2755.
- 40 P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2001, **20**, 2533–2544.
- 41 P. G. Hayes, W. E. Piers and M. Parvez, *Organometallics*, 2005, **24**, 1173–1183.
- 42 B. Liu, D. Cui, J. Ma, X. Chen and X. Jing, *Chem.–Eur. J.*, 2007, **13**, 834–845.
- 43 B. Liu, X. Liu, D. Cui and L. Liu, *Organometallics*, 2009, **28**, 1453–1460.
- 44 K. D. Conroy, W. E. Piers and M. Parvez, *J. Organomet. Chem.*, 2008, **693**, 834–846.
- 45 K. R. D. Johnson and P. G. Hayes, *Organometallics*, 2009, **28**, 6352–6361.
- 46 K. R. D. Johnson, M. A. Hannon, J. S. Ritch and P. G. Hayes, *Dalton Trans.*, 2012, **41**, 7873–7875.
- 47 K. R. D. Johnson and P. G. Hayes, *Organometallics*, 2011, **30**, 58–67.
- 48 K. R. D. Johnson, *Ph.D. Thesis*, University of Lethbridge, 2012.
- 49 S. Bambirra, S. J. Boot, D. van Leusen, A. Meetsma and B. Hessen, *Organometallics*, 2004, **23**, 1891–1898, and references therein.
- 50 A. Venugopal, W. Fegler, T. P. Spaniol, L. Maron and J. Okuda, *J. Am. Chem. Soc.*, 2011, **133**, 17574–17577.
- 51 G. G. Skvortsov, G. K. Fukin, A. A. Trifonov, A. Noor, C. Döring and R. Kempe, *Organometallics*, 2007, **26**, 5770–5773.
- 52 W. Fegler, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2010, **39**, 6774–6779.
- 53 P. L. Diaconescu, *Curr. Org. Chem.*, 2008, **12**, 1388–1405.
- 54 P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1983, 276–277.
- 55 K. C. Jantunen, B. L. Scott, J. C. Gordon and J. L. Kiplinger, *Organometallics*, 2007, **26**, 2777–2781.
- 56 S. Arndt, B. R. Elvidge, P. M. Zeimentz, T. P. Spaniol and J. Okuda, *Organometallics*, 2006, **25**, 793–795.
- 57 J. Scott, F. Basuli, A. R. Fout, J. C. Huffman and D. J. Mindiola, *Angew. Chem., Int. Ed.*, 2008, **47**, 8502–8505.
- 58 E. Lu, Y. Li and Y. Chen, *Chem. Commun.*, 2010, **46**, 4469–4471.
- 59 B.-T. Guan and Z. Hou, *J. Am. Chem. Soc.*, 2011, **133**, 18086–18089.
- 60 T. J. Marks, *Acc. Chem. Res.*, 1976, **9**, 223–230, and references therein.
- 61 W. J. Evans, J. R. Walensky and J. W. Ziller, *Chem.–Eur. J.*, 2009, **15**, 12204–12207.
- 62 J. W. Bruno, T. J. Marks and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 7357–7360.
- 63 C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 2214–2216.
- 64 C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 425–437.
- 65 C. E. Hayes and D. B. Leznoff, *Organometallics*, 2010, **29**, 767–774.
- 66 B. M. Gardner, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *J. Am. Chem. Soc.*, 2009, **131**, 10388–10389.
- 67 J. A. Pool, B. L. Scott and J. L. Kiplinger, *J. Alloys Compd.*, 2006, **418**, 178–183.

Downloaded by University of Lethbridge on 13 February 2013
Published on 30 November 2012 on http://pubs.rsc.org | doi:10.1039/C2CS35356C