Insertion, protonolysis and photolysis reactivity of a thorium monoalkyl amidinate complex

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Results and discussion

Having previously established the ability of 1 to undergo chalcogen atom insertion and generate unique thorium chalcogenolates,35 we next sought to examine potential insertion chemistry of this monoalkyl system with various small molecules. Evans has described the insertion of carbodiimides and organic azides into one alkyl moiety of Cp,ThMe₂.16 With this in mind, we targeted the synthesis of a tetrakis(amidinate) complex through the reaction of 1 with N,N'-disisopropylcarbodiimide (Scheme 1). However, despite forcing conditions (100 °C), carbodiimide insertion into the Th–C bond was not observed, most likely a result of steric saturation around the metal center. Regardless, the alternative salt metathesis route observed was likely a result of steric saturation around the metal center. The molecular structure of 2, determined by single-crystal X-ray diffraction studies, shows a pseudo-tetrahedral geometry of the amidinate ligands around the thorium center (Fig. 1). The Th–N₃ bond lengths vary between 2.49 and 2.62 Å, indicating the significant steric congestion imposed by the isopropyl groups of the amidinate ligands. The structural parameters of 2 combined with the reaction conditions necessary to form 2 support the notion that insertion of carbodiimide into the Th–C bond was hindered by steric crowding, and indicate that related insertion reactions might be subject to this constraint. Due to the steric protection afforded by the tetrakis(amidinate) framework, and inspired by the work of Evans regarding low-valent thorium chemistry,16 we attempted the reduction of 2 with KC₈ in the presence of 18-crown-6; nevertheless, no colour change was observed and only starting material was isolated.

Reaction of 1 with an equivalent of p-tolyl azide resulted in insertion to form the triazenido complex Th[(p-tolyl)

Scheme 2 Synthesis of 3 and thermal decomposition to 4.

NNN(CH₂SiMe₃)₂κ²N₁₂(BIMA)₃ (3) in 83% yield (Scheme 2). The ¹H NMR spectrum displayed the diagnostic downfield shift of the methylene resonance which was also observed to result from chalcogen insertion.15 In the present case, we observed a shift from δ = −0.08 in 1 to δ = 3.99 in 3, alongside shifted amidinate resonances and the appearance of resonances attributable to the p-tolyl group. X-ray diffraction studies revealed a κ²N₁₂ coordination mode of the triazenido moiety (Fig. 2), similar to that observed by Evans in the thorium metallocene system.16 The metrical parameters relating to the N₃ fragment show the effect of delocalization, with bond lengths of 1.314(6) and 1.285(6) Å for N(7)−N(8) and N(8)−N(9), respectively, a difference of only ~0.03 Å. In contrast, Evans’ system that utilized adamantyl azide exhibited a more localized bonding for the analogous nitrogens, with bond lengths of 1.360(3) and 1.243(3) Å, a difference of ~0.12 Å.16 The Th(1)−N(7) distance of 2.474(4) Å is ~0.1 Å longer than that seen in the thorium metallocene system, while the Th(1)−N(8) distance of 2.597(4) Å is...
Close inspection of the $^1$H NMR spectrum revealed a resonance attributable to ethylene. With this information we envisioned that 3 was losing diazomethane ($N_2CH_2$), which then decomposed to dinitrogen and ethylene,$^{39}$ resulting in the thorium amido species $\text{Th}[\{p$-\text{tolyl}$\}{\text{N(SiMe}_3\}_2}][\text{BIMA}]_3$ (4, Scheme 2). Ethylene formation may be the result of singlet methylene$^{40}$ generation and coupling upon $N_2CH_2$ decomposition. In order to try and trap the transient singlet methylene, similar heating experiments were conducted in the presence of 2-butyne and 1,1-diphenylethylene and monitored by $^1$H NMR spectroscopy. Although it was difficult to unambiguously identify the trapped products (1,2-dimethylcyclopropene and 1,1-diphenylecyclopane, respectively), the formation of ethylene was not seen with either trapping reagent, and a singlet at δ 1.13 was observed in the 1,1-diphenylethylene experiment, which we tentatively assign to 1,1-diphenylecyclopane.$^{41}$ We were able to confirm the identity of 4 as the thorium amido complex by X-ray diffraction studies (Fig. 2). To the best of our knowledge, this is the first example of clean thermal decomposition of an actinide triazenido complex to the corresponding amido species. Bart and co-workers have observed thermal instability in certain uranium triazenido species, which has led to intractable mixtures of products.$^{42}$ However, the thermal decomposition of $\text{L}^{\text{Bu}}\text{Fe}[\text{η}^1\text{-HNNNAd}]$ (where $\text{L}^{\text{Bu}} = \text{tert}-\text{butyl}$ substituted-$\text{N}^2\text{N}^2$-diaryl-$\beta$-diketiminate, aryl = 2,6$^3\text{-Pr}_2\text{-C}_6\text{H}_3$) to the corresponding primary amido species $\text{L}^{\text{Bu}}\text{FeNHAd}$ has been observed.$^{43}$ This was rationalized based on the instability of free $\text{H}_2\text{NNNR}$ compounds with respect to loss of dinitrogen. The $\text{Th}(1)$-$\text{N}(7)$ bond distance of 2.399(2) Å in 4 is very close to the $\text{Th}$-$\text{N}$ bond distance of 2.389(2) Å observed by Walter and co-workers in $[\eta^5$-$1,2,4\{\text{Me}_2\text{C}_5\}_2\text{C}_6\text{H}_3\text{H}_2\text{];Th(Cl)}\text{[N(p-tolyl)]SiH}_2\text{Ph}$, which has a similar silyl amide environment.$^{44}$ The nitrogen atom of the amido exhibits a trigonal planar geometry ($\Sigma \angle \approx 360^\circ$), also consistent with Walter’s complex. A series of NMR scale experiments revealed the thermal decomposition to be concentration dependent, with higher concentrations of 3 leading to the generation of the silyl amine ($p$-tolyl)$\text{NH(SiMe}_3\}_2$ (as determined by $^1$H NMR spectroscopy) and a mixture of unknown species (see Fig. 57 in ESI†). The identity of these products, along with mechanistic studies regarding the formation of 4 from 3, is currently under investigation.

Although achieved with both transition metal$^{45-48}$ and uranium$^{49-52}$ species, isocyanide insertion into thorium alkyl bonds to form the corresponding $\eta^2$-iminoacyl complexes has not yet been reported. While sterics precluded the insertion of $\text{N}^2\text{N}^2$-disopropylcarbodiimide, isocyanide insertion was realized with one equivalent of 2,6-dimethylphenylisocyanide and moderate heating, resulting in $\text{Th}[\text{η}^5\text{-C(C=N)}\text{-2,6-Me}_2\text{-C}_6\text{H}_3\text{-}(\text{CH}_2\text{SiMe}_3\}_2][\text{BIMA}]_3$ (5) as a colourless, crystalline solid in 81% yield (Scheme 3). To the best of our knowledge this is the first thorium $\eta^2$-iminoacyl complex. Monitoring the reaction by $^1$H NMR spectroscopy confirms that this insertion proceeds slowly at room temperature (~95% conversion after 96 h), presumably due to the steric clash between the xylyl moiety and amido ligands. As expected, the diagnostic downfield shift of the methylene singlet to δ 2.85 indicated successful isocyanide insertion, along with new methyl and aromatic resonances.
corresponding to the xylyl group. X-ray diffraction studies revealed the $n^2$-coordination mode of the imine moiety, with the N(7)–C(29) bond length of 1.299(4) Å falling in the range seen for other transition metal iminoacyl species (Fig. 3). The Th(1)–N(7) distance of 2.469(2) Å is noticeably shorter than that typically observed for a dative Th–N bond, while the Th(1)–C(29) bond length of 2.529(3) Å is in the range observed for other σ-bonded alkyl moieties. This insertion differs from that observed by Andersen and co-workers in their Th(CH$_2$SiMe$_3$)$_2$N(SiMe$_3$)$_2$(NR$_2$)$_2$ complex, which undergoes insertion of tert-butyl isocyanide into the C–Si bond of the metallacycle to produce Th([tBuNC(CH$_2$)SiMe$_3$]$_2$N(SiMe$_3$)$_2$(NR$_2$)$_2$. Similar reactivity was observed with CO in Andersen’s system, resulting in Th[[OC(==CH$_2$)SiMe$_3$]$_2$N(SiMe$_3$)$_2$(BIMA)$_2$ (4)]. Complex 6 crystallized with two independent molecules in the asymmetric unit due to disorder in the enolate moiety; thus, the metrical parameters of only the nondisordered molecule will be discussed. The Th(1)–O(1) bond

precluding their clean isolation and characterization, despite yields of ~80% for the bulk mixture. The major species, as identified by $^1$H NMR spectroscopy, exhibited inequivalent methylene protons that are consistent with those observed in Th[[OC(==CH$_2$)SiMe$_3$]$_2$N(SiMe$_3$)$_2$(NR$_2$)$_2$] (see Fig. S10 in ESI†). This inequivalency would not be seen in the $^1$H NMR spectrum of the thorium acyl species generated by simple CO insertion into the Th–C bond; thus, we postulated that it was likely a similar insertion into the C–Si bond of 1 occurred (Scheme 3). This hypothesis was proven by X-ray diffraction studies, as a few X-ray quality crystals were isolated from a very concentrated pentane solution stored at −35 °C for 3 days, confirming the identity of the CO insertion as the enolate complex Th[OC(==CH$_2$)SiMe$_3$]$_2$N(SiMe$_3$)$_2$(BIMA)$_2$ (6) (Fig. 4). Complex 6 crystallized with two independent molecules in the asymmetric unit due to disorder in the enolate moiety; thus, the metrical parameters of only the nondisordered molecule will be discussed. The Th(1)–O(1) bond
length of 2.216(2) Å is slightly longer than the Th–O bond length of 2.166(2) Å seen in Th(OCH2NMe2)(BIMA)3, while the C(25)–C(26) bond length of 1.338(5) Å is consistent with a carbon–carbon double bond, and the trigonal planar geometry of C25 (Σ ≈ 360°) indicates sp2 hybridization. This type of reactivity has preceded in both uranium and thorium systems, and has been explained by initial CO insertion into the M–C bond to form the metal acyl, which then isomerizes to form a carbene-like intermediate that can then insert into the Si–C bond (Scheme 4). Alongside crystals of 6 were crystals of a different product, which we have tentatively assigned to the other resonances observed in the 1H NMR spectrum of the bulk material (see Fig. S10 in ESI†). X-ray diffraction studies revealed this product to be Th[OC(NiPr)C(CH2SiMe3)(C(Me)N(iPr))O–κ2O,O'](BIMA)2 (7), the result of reductive CO coupling and insertion into an amidinate ligand (Fig. 4). The Th(1)–O(1) and Th(1)–O(2) bond lengths of 2.220(2) and 2.290(2) Å, respectively, are slightly longer than that seen in 6 and Th(OCH2NMe2)2(BIMA)3, while the bond length of 2.764(3) Å for Th(1)–N(5) is indicative of a dative interaction. A single bond length of 1.558(5) Å is observed for C(22)–C(23), whereas imine bonds are seen for C(23)–N(6) and C(20)–N(5) (1.266(4) and 1.282(4) Å, respectively). This type of CO coupling mimics the enediolate formation observed with various actinide bis-alkyl systems.

Regarding the formation of 7, it seems unlikely that this product is obtained from the interaction of a molecule of CO with 6, due to the intact nature of the trimethylsilylmethyl alkyl fragment. Instead, it is likely that 7 results from “trapping” of the carbene-like intermediate, which precedes formation of 6, by another molecule of CO to form a transient ketene, and subsequent insertion and rearrangement steps lead to 7 as the final product (Scheme 4). Kinetically this intermolecular process is slower than the intramolecular attack by the carbene intermediate on the C–Si bond, producing 6 as the major product. Exposing a mixture of 6 and 7 to additional CO did not change the ratio of products observed, confirming that 7 is not generated from 6. In an attempt to avoid the formation of 7, the slow addition of 1 eq. of CO to a stirred hexanes solution of 1 was conducted, resulting in clean formation of 6 in 64% yield. Development of a synthetic strategy to produce 7 is currently underway. Looking to other small molecules, insertion reactivity with CO2 and CS2 did not proceed cleanly, yielding intractable mixtures.

Nitrile insertion was examined by the NMR-scale reaction of 1 and benzonitrile. The reaction was sufficiently complete (~95% conversion by 1H NMR spectroscopy) upon heating to 100 °C for 72 h, resulting in the ketimide complex Th[–N≡C(Ph)(CH2SiMe3)]3(BIMA)3 (Scheme 3). The methylene singlet is seen downfield at δ 2.73, along with new resonances corresponding to the aromatic protons of the phenyl ring, as well as aromatic resonances corresponding to the cyclotrimerization product of benzonitrile, 2,4,6-triphenyl-1,3,5-triazine (see Fig. S13 in ESI†). The Lewis acid-catalysed cyclotrimerization of benzonitrile has been previously reported for lanthanide-imido species, although the active species in this transformation has not been identified.

Looking to exploit the basic nature of the alkyl moiety of 1, protonolysis reactivity was explored with a variety of protic substrates, the results of which are summarized in Scheme 5. NMR-scale experiments were carried out with 1 and 2,6-diisopropylaniline, resulting in the primary amido species Th(NH-2,6-iPr2-C6H3)(BIMA)3 (9), as well as 1 and 2,6-di-tert-butylphenol, resulting in the aryloxide complex Th(O-2,6-Bu2-C6H3)(BIMA)3 (10), as determined by 1H NMR spectroscopy. While phenol addition and subsequent elimination of SiMe4 occurred within 12 h at room temperature, deprotonation of the aniline required extended reaction times at elevated temperatures before conversion to 9 was achieved. This can be rationalized on the basis of the higher pKa of the aniline (~30 vs. 16.8 in
DMSO)\textsubscript{2},\textsuperscript{65,66} as the sterics imposed by the 2,6-di-tert-butylphenol are greater than that of 2,6-diisopropylaniline.

Similar NMR experiments were also performed with primary and secondary phosphines, namely mesitylphosphine and diphenylphosphine, resulting in the thoriium phosphido complexes Th[PHMes]\textsubscript{2}(BIMA)\textsubscript{3} (11a) (Mes = 2,4,6-trimethylphenyl) and Th[PPh\textsubscript{3}](BIMA)\textsubscript{3} (11b), respectively, as determined by \textsuperscript{1}H and \textsuperscript{31}P NMR spectroscopy. Complex 11a exhibits a doublet at \( \delta \) = 45.4 in the \textsuperscript{31}P NMR spectrum with a \( J_{P,H} \) coupling constant of 195 Hz; the corresponding doublet in the \textsuperscript{1}H NMR is observed at \( \delta \) 89.5 corresponding to the thorium phosphido, alongside peaks consistent with the dehydrocoupled product Ph\textsubscript{2}P–PPh\textsubscript{3} (\( \delta \) = 14.9)\textsuperscript{67} and an unidentified phosphorus-containing species (\( \delta \) 106). These \textsuperscript{31}P chemical shifts are in the range reported for other primary and secondary thorium phosphido species.\textsuperscript{68–70} The dehydrocoupling of phosphines has been reported with zirconium phosphido complexes under similar reaction conditions.\textsuperscript{71} Both complexes 11a and 11b required elevated temperatures and prolonged reaction times to reach completion. We sought a more scalable strategy to synthesize 11a without the need for harsh reaction conditions, as complex 11a has the potential to form a thorium phosphinidene via deprotonation of the phosphido ligand. With few examples of thorium phosphinidenes available, this would provide valuable information regarding metal–ligand multiple bonding between thorium and the heavier pnicotgens.\textsuperscript{72–74} Salt metathesis between the previously reported ThCl(BIMA)\textsubscript{3} (ref. 35) and KPHMes\textsuperscript{75} provided a more direct route to 11a as bright yellow crystals in 58% yield. The \textsuperscript{13}C\textsuperscript{1}H NMR spectrum of 11a exhibits rare through-space coupling of the phosphorus atom and the isopropyl methyl carbons of the BIMA ligand (\( \delta_{P,C} \) = 2.1 Hz), as well as the ortho-methyls of the mesitylene ring (\( \delta_{P,C} \) = 9.6 Hz).\textsuperscript{75–78} This coupling is supported by the X-ray crystal structure of 11a, which displays a close proximity of the phosphorus atom to one of the BIMA isopropyl methyls (3.746(4) and 3.779(4) \( \AA \)), along with significant pyramidalization at P (\( \Sigma_{\text{P}} \approx 311^\circ \)) in the two independent molecules found in the asymmetric unit (Fig. 5). The orientation of the phosphorus lone pair toward these carbon atoms facilitates this spin–spin interaction. This is the first crystallographically characterized example of a thorium monophosphido species bearing a primary phosphido ligand; to date, only a handful of primary bis(phosphido)-thorium species have been isolated and characterized.\textsuperscript{78–79} The Th–P bond lengths seen in the two molecules in the asymmetric unit (3.0497(8) and 3.0404(8) \( \AA \)) are ~0.15 \( \AA \) longer than those observed in the previously reported bis(phosphido)-thorium complexes. Attempts to deprotonate 11a to form the corresponding thorium phosphinidene have thus far proven unsuccessful.

The reaction of 1 with p-tolylacetylene proceeds cleanly, providing the thorium acetylide complex Th(C\textequiv=C–p-tolyl)(BIMA)\textsubscript{3} (12) as colourless crystals in 95% yield. This new alkyne species may serve as a useful starting material for future chemistry, as other thorium acetylide complexes have been shown to be active catalysts for the linear oligomerization of terminal alkynes.\textsuperscript{88} The \textsuperscript{1}H NMR spectrum displays a \( C_3 \)-symmetric amidinate environment along with resonances attributable to the \( p \)-toly group, while the \( ^{13}C\textsuperscript{1}H \) NMR spectrum features a downfield resonance of \( \delta \) 189.2 corresponding to the thorium-bound carbon atom of the alkyne, consistent with other thorium and group IV acetylenes.\textsuperscript{81–84} The IR spectrum exhibits a characteristic signal at 2061 cm\textsuperscript{–1} assigned to the \( C=\text{C} \) stretch. X-ray diffraction studies revealed a near-linear Th–C=\text{C} bond angle of 175.7(2)\textsuperscript{3} and bond lengths of 2.542(2) and 1.219(3) \( \AA \) for Th(1)–C(25) and C(25)–C(26), respectively (Fig. 6). The Th–C bond length in 12 is ~0.05 \( \AA \) longer than that of the few other thorium acetylide species to have been characterized crystallographically, namely [L][Th(C=CSiMe\textsubscript{3})\textsubscript{3}] and [(L)Th(C=CSi\textsubscript{2}Pr\textsubscript{3})\textsubscript{2}] (where L = trans-calix[2]benzene[2]pyrroloidine, and Th(Be\textsubscript{Mes}\textsubscript{2})(C=CP\textsubscript{3}toly)\textsubscript{2} (where Be\textsubscript{Mes} = mesitylstabilized bis[NHC]borate, NHC = N-heterocyclic carbene), which were only recently reported.\textsuperscript{27,75} A cationic species was targeted as a potential precursor to a Th(\textit{iii}) amidinate complex, as Evans has shown that reduction of a mixed cyclopentadienyl amidinate thorium cation, namely [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}PrNC(Me)NPr][Th(μ-BPh\textsubscript{3})\textsubscript{Me}], can be achieved with KC\textsubscript{8}.\textsuperscript{85} Treatment of 1 with [Et\textsubscript{3}NH][BPh\textsubscript{4}]\textsuperscript{86} in THF led to the isolation of [Th(THF)(BIMA)\textsubscript{3}]\textsubscript{2}[BPh\textsubscript{4}] (13) as colourless crystals in 81% yield. The NH\textsubscript{3} and SiMe\textsubscript{4} byproducts were easily removed under vacuum upon workup, and X-ray diffraction studies show a well separated ion pair with one THF molecule coordinated to the thorium center and another co-crystallized in the lattice (Fig. 7). The Th–Namid bond lengths are noticeably shorter (2.45–2.48 \( \AA \)) than that of 1 or 2, likely due to reduced steric congestion and higher electrophilicity of the metal center. The Th(1)–O(1) distance of 2.504(2) \( \AA \) is in the range observed for other THF-bound thorium complexes.\textsuperscript{87–89} The second equivalent of THF can be removed under high vacuum. The \textsuperscript{1}H NMR spectrum of dried 13 in CDCl\textsubscript{3} displays equivalent amidinate resonances, the...
aromatic peaks of the BPh₄ anion, and one set of resonances corresponding to coordinated THF. The complex displays appreciable stability in CDCl₃, but begins to decompose after ~24 h at room temperature. Attempted reduction of 13 with KC₈ in THF led to the isolation of 2. No colour change was observed throughout the reaction. Increasing the steric of the R groups on the amidinate nitrogens may help stabilize a tris-amidinate Th(III) complex, and work is currently ongoing to test this hypothesis. Attempts to utilize H₂ as a protic substrate and form a thorium hydride complex were not successful.

Complex 1 undergoes ligand exchange with one equivalent of 9-borabicyclo[3.3.1]nonane (9-BBN), affording \((\text{BIMA})_3\text{Th}[\mu^2-\text{H}]_2\text{B}(\text{C}_8\text{H}_{14})\) \((14)\) alongside one equivalent of \((\text{C}_8\text{H}_{14})\text{B}(\text{CH}_2\text{-SiMe}_3)\), as determined by \(^{11}\text{B}\{^1\text{H}\}\) NMR spectroscopy (resonance observed at \(\delta 84.3\) in \(\text{C}_6\text{D}_6\)). Complex 14 was isolated in 66% crystalline yield after workup (Scheme 6). The thorium borohydride complex exhibits equivalent amidinate ligands in solution according to \(^1\text{H}\) NMR spectroscopy. Additionally, broad \(\mu\)-H resonances and several multiplets corresponding to the \(\text{C}_8\text{H}_{14}\) fragment are observed. The \(^{11}\text{B}\{^1\text{H}\}\) NMR spectrum exhibits a single resonance at \(\delta 4.90\), which is in the range typically observed for boron hydrides. FTIR spectroscopy reveals a broad B–H stretch centered at 2021 cm⁻¹. X-ray diffraction studies show an eight-coordinate thorium center bearing bridging hydrides bound to the 9-BBN moiety (Fig. 8). The hydrides were located in the Fourier difference map and refined isotropically. The Th(1)–B(1) distance of 2.952(9) Å is significantly longer than typically observed with other thorium complexes containing bridging borohydrides (2.49(6)–2.670(2) Å), but is within the range observed by Girolami and co-workers in the complexes \([\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)]\) and \([\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)](\text{BH}_4)_2\), which exhibit Th–B distances between 2.848(9) to 3.193(5) Å. Complex 14 is surprisingly stable both under photolytic and elevated temperature conditions, with no decomposition or elimination of H₂ observed.

Storage of 1 at room temperature under dry nitrogen for several weeks led to slight discoloration of the crystalline solid. While the \(^1\text{H}\) NMR spectrum of this material showed very little change from that of pure 1, we decided to investigate the stability of 1 under photolytic conditions. The UV-Vis spectrum of 1 features an absorption with \(\lambda_{\text{max}} = 295\) nm, likely a ligand-based \(\pi-\pi^*\) transition (see Fig. S31 in ESI†). Irradiation of 1 with UV-light centered at 253 nm in \(\text{C}_6\text{D}_6\) and monitoring by \(^1\text{H}\) NMR spectroscopy showed elimination of SiMe₄ alongside the...
production of a single new product, which displayed inequiva-

tent amidinate ligands. Reaction times ranged from 24 h to 10
days, depending on the concentration of 1 in the sample
(~0.02–0.45 M), with higher concentrations taking longer.
Optimization of the reaction conditions, by use of a quartz
reaction vessel, cyclohexane-d12 and a xenon arc lamp, resulted
in significantly reduced reaction times (~2 h for ~0.03 M
solution). Removal of SiMe4 under vacuum and crystallization
to toluene afforded Th[BIMA]2(BIMA*) (15) in 53% yield
[BIMA* = (iPr)NC(CH2)N(iPr)]. Heating a solution of 1 at 100 °C
for 24 h and monitoring by 1H NMR spectroscopy showed no
decomposition of 1 or production of 15, eliminating the possi-
bility that conversion of 1 to 15 was thermally-induced.

Irradiation of 1 results in C–H activation of a methyl group
on an amidinate ligand by the –CH2SiMe3 moiety, eliminating
SiMe4 and reducing the activated amidinate to a dianionic
ligand (Scheme 6). Heterolytic bond cleavage of the Th–C bond
resulting in a –CH2SiMe3 anion, which then attacks the methyl
backbone of an amidinate ligand, is a possible explanation for
the C–H activation and subsequent ligand reduction observed.
This is a rare example of an amidinate dianion, and the first

generated under photolytic conditions. The 1H NMR spectrum
of 15 exhibits a set of equivalent amidinate resonances, along-
side the resonances attributable to the amidinate dianion,
specifically a 2H septet at δ 4.24, a 2H singlet at δ 3.44, and a
12H doublet at δ 1.53. The 6H singlet corresponding to the
methyl groups of the monoanionic amidinates also appears at
δ 1.53 (see Fig. S29 in ESI†). In the 13C{1H} NMR spectrum
of 15, the terminal methylene carbon resonance is observed noticeably
downfield at δ 53.3, shifted by ~40 ppm from the amidinate methyls
seen at δ 12.2, but further upfield than that typically
seen with alkenes. The 1J(C,H) coupling constant of 157.6 Hz (as
measured from the 13C satellites observed in the 1H NMR
spectrum) is consistent with sp2 hybridization and similar to

that observed for ethylene. The ipso-carbon of the amidinate
dianion is shifted upfield to δ 154.2 from δ 172.8 as observed for
the monoanionic amidinates. X-ray diffraction studies revealed
a dimeric structure where the thorium centers are bridged by
the methylene carbon of the dianionic amidinate ligand (Fig. 9).
Complex 15 crystallizes in P1 with the asymmetric unit con-
taining only the monomer unit; the dimer is generated through
inversion symmetry. The Th(1)–C(21) bond distance of 2.749(3)
Å is significantly longer than the Th–C bond observed in 1
(2.557(3) Å), but shorter than the long Th–σ-alkyl bond distance
of 2.875(9) Å observed by Liddle and co-workers in [Th[N(CH2CH2-
NSiMe2Bu2][CH3CH2CH2SiMe3Bu2(µ-CH2)]]. The C(20)–
C(21) bond distance of 1.438(4) is longer by ~0.1 Å than typically
observed for C–C double bonds, but this lengthening may be
a result of delocalized electron density involved in the Th–C
contact, reminiscent of a three-center two-electron bond. This is
also manifested in the lack of planarity seen in the –N(CH2)CN–
unit of the amidinate dianion.

Conclusions

The amidinate-supported thorium monoalkyl complex 1
exhibits a variety of reactivity with small molecules, including
insertion, protonolysis and photolysis. The insertion of p-tolyl
azide lead to the thorium triazenido complex 3 which
undergoes clean thermal decomposition at low concentrations
to the corresponding amido complex 4, through the loss of the
unstable “N2CH2” fragment. This is the first example of an
actinide complex undergoing this rare transformation. Insertion
of xyllyl isocyanide results in the first crystallographically
characterized thorium iminoacyl complex. This insertion
reactivity differs from that observed with CO, which instead results
in the corresponding enolate species 6 upon CO insertion and
rearrangement, as well as the unique double CO insertion and
amidinate cleavage product 7. The utility of the alkyl moiety as
an internal base was demonstrated with a variety of protic

Fig. 8 Molecular structure of 14 (thermal ellipsoids drawn at the 50% probability level). Non-hydride hydrogen atoms omitted for clarity.

Fig. 9 Molecular structure of 15 (thermal ellipsoids drawn at the 50% probability level).
substrates, with the thorium phosphido complex 11a generated via both protonolysis and salt metathesis routes, the latter providing a more scalable option for the synthesis of 11a. The photolytic elimination of SiMe₄ concomitant with the reduction of an amidinate ligand to form complex 15 is unprecedented reactivity with amidinate-supported metal complexes, and a rare example of a complex bearing a dianionic amidinate ligand. Mechanistic and reactivity investigations of several of the complexes reported are currently ongoing.

Conflicts of interest

There are no conflicts to declare.

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