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Authors: Fang-Che Hsueh, Thayalan Rajeshkumar, Bastiaan Kooij, Rosario Scopelliti, Kay Severin, Laurent Maron, Marinella Mazzanti, and Ivica Zivkovic

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Bonding and Reactivity in Terminal versus Bridging Arenide Complexes of Thorium Acting as Th(II) Synthons

Fang-Che Hsueh,[§a] Thayalan Rajeshkumar,[b] Bastiaan Kooij,[c] Rosario Scopelliti,[a] Kay Severin,[c] Laurent Maron,*[b] Ivica Zivkovic,[d] and Marinella Mazzanti*[a]

[a]   F. C. Hsueh, R. Scopelliti, M. Mazzanti
        Group of Coordination Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland
        E-mail: marinella.mazzanti@epfl.ch
[b]   T. Rajeshkumar, L. Maron
        Laboratoire de Physique et Chimie des Nano-objets, Institut National des Sciences Appliquées, 31077, Toulouse, Cedex 4, France
[c]   B. Kooij, K. Severin
        Laboratory of Supramolecular Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland
[d]   I. Zivkovic
        Laboratory for Quantum Magnetism, Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland

Abstract: Thorium redox chemistry is extremely scarce due to the high stability of Th(IV). Here we report two unique examples of thorium arenide complexes prepared by reduction of a Th(IV)-siloxide complex in presence of naphthalene, the mononuclear arenide complex $[K(OSi(O^tBu)_3)_3Th(\eta^6-C_{10}H_8)]$ (**1**) and the inverse-sandwich complex $[K(OSi(O^tBu)_3)_3Th]_2(\mu-\eta^6,\eta^6-C_{10}H_8)]$ (**2**). The electrons stored in these complexes allow the reduction of a broad range of substrates (N_2O, AdN_3, CO_2, HBBN). Higher reactivity was found for the complex **1** which reacts with the diazoolefin $IDipp=CN_2$ to yield the unexpected Th(IV) amidoalkynyl complex **5** *via* a terminal N-heterocyclic vinylidene intermediate. This work showed that arenides can act as convenient redox-active ligands for implementing thorium-ligand cooperative multielectron transfer and that the reactivity can be tuned by the arenide binding mode.

Introduction

Compounds of f-elements containing metal-arene/arenide interactions have been increasingly studied because of their ability to stabilize low oxidation states and promote unusual properties and reactivity.[1]

In particular, uranium-arene δ-bonding interactions were shown to stabilize low oxidations states,[2] support U=C multiple bonding,[3] promote unusual magnetic properties and reactivity.[1a, 1f] Fortier and coworkers have also recently reported the synthesis of unsupported uranium arene metalates taking advantage of the Chatt salt metathesis route.[1h] Furthermore, stable inverse-sandwiches complexes of uranium in different oxidation states (+2 to +4) have been synthesized with several supporting ligands and involve different degree of arene reduction ranging from arene^{-1} to arene^{-4}.[1e] These complexes were shown to act as U(II) and U(I) synthons that can perform multielectron redox chemistry[4, 2c] and novel arene functionalization reactions,[1b] cycloadditions,[5] and metal-metal bond formation reactions[6] never observed in d-block chemistry.

In contrast, the thorium arene/arenide chemistry is much less developed with the only example of a Th inverse sandwich complex having been reported very recently by Huang and

Diaconescu.[1g] This unique arene-bridged dithorium complex was described as a Th(IV) arene tetraanion and was shown to act as a four-electron reductant towards cyclooctatetraene or azobenzene.

Examples of mononuclear thorium arenides are also limited to two Th(IV) complexes containing one[7] and two[8] terminally bound naphthalenide dianions reported 20 years ago by Gambarotta and coworkers. These complexes were shown to act as Th(II) synthons using the electrons stored in the naphtalenide ligand to promote the reduction of unreactive small molecules (N_2 and CO_2),[8, 7] providing a rare example of small molecule activation and redox reactivity by a thorium complex.[9]

Notably, while thorium(IV) compounds have found application in catalysis[10], reactivity studies of low valent thorium are confined to a handful of examples due to the paucity of crystallographically characterized Th(III) (less than a dozen) and Th(II) complexes (five complexes)[11] all based on the triscyclopentadienyl anion $[Cp''_3Th^{II}]^-$ $(cp''=C_5H_3(SiMe_3)_2)$. Due to the high stability of Th(IV)[12] and the tendency of low valent thorium to undergo decomposition[13] and disproportionation reactions[14] the redox reactivity of thorium remains poorly developed.

However, recent studies showed that redox-active ligands can be used to promote multielectron transfer reactions in thorium complexes,[15a-f, 9a, 9c] but studies involving arenides remained limited to three examples.[8, 16, 1g]

Having previously found that siloxides are versatile supporting ligands that promote the formation of inverse sandwiches of uranium and lanthanides ions[17] we set out to explore the possibility of accessing reactive Th arenide complexes. Here we report the molecular and electronic structure of a rare mononuclear naphthalenide Th complex and the second example of a thorium inverse sandwich which can be selectively prepared by controlling the Th: naphthalene ratio. A comparative reactivity study was performed for the two systems and we show that both complexes act as Th(II) synthon reducing a range of unsaturated substrates in a controlled manner, but no reactivity was observed for the Th-inverse sandwich with a diazoolefin. In contrast, the terminal mononuclear naphthalenide shows unprecedented

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reactivity leading to an amido-alkynyl complex through a transient thorium vinylidene complex.

Results and Discussion

Synthesis and Characterization of Thorium-Arene Complexes
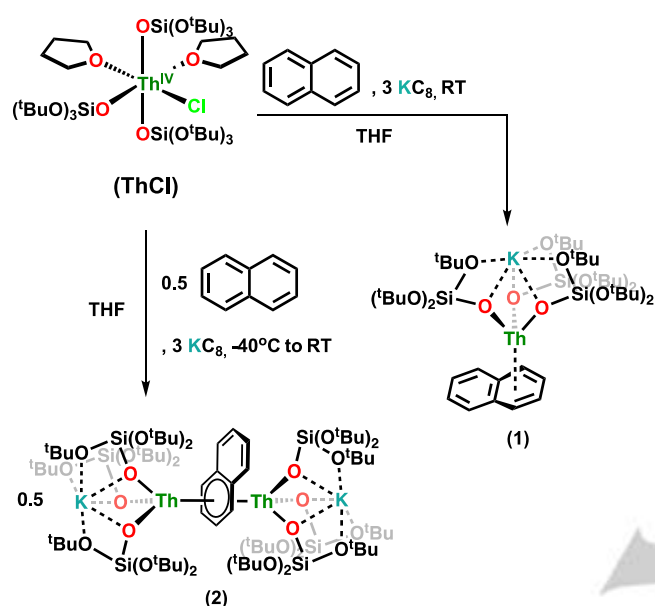
Scheme 1. Synthesis of complex **1** and **2**

To prepare thorium-arene complexes, supported by $-OSi(O^tBu)_3$ ligands, we pursued the reduction of the heteroleptic Th(IV) complex, $[Th(OSi(O^tBu)_3)_3Cl(THF)_2]$ precursor in the presence of of naphthalene (Scheme 1).[18] Addition of excess (3 equiv.) KC_8 to a THF solution of $[Th(OSi(O^tBu)_3)_3Cl(THF)_2]$ and naphthalene (1 equiv.) at room temperature resulted in a black reaction mixture. After 2 hours, formation of a new species and full consumption of the starting material was observed by ^1H NMR spectroscopy (Figure S1). Black crystals of the complex $[K(OSi(O^tBu)_3)_3Th(\eta^6-C_{10}H_8)]$ (**1**) were isolated in 80% yield from a concentrated hexane solution of the reaction mixture at −40 °C. Similarly, addition of excess (3 equiv.) KC_8 to a THF solution of $[Th(OSi(O^tBu)_3)_3Cl(THF)_2]$ (1 equiv.) and 0.5 equiv. of naphthalene at −40°C led to a dark reaction mixture. The ^1H NMR spectrum showed that a new species was formed (Figure S12). Black crystals of the complex $[K(OSi(O^tBu)_3)_3Th]_2(\mu-\eta^6,\eta^6-C_{10}H_8)]$ (**2**) were isolated in 67% yield from a concentrated hexane/Et$_2$O reaction mixture at −40 °C. Interestingly, the reduction of $[Th(OSi(O^tBu)_3)_3Cl(THF)_2]$ in the presence of 1 equiv. of naphthalene resulted in a mononuclear thorium complex with a terminally bound naphthalene, while the reduction in the presence of 0.5 equiv. of naphthalene led to an inverse-sandwich complex where the naphthalene bridges two thorium centers. Only one example of thorium monoarene complex was isolated previously by Gambarotta[7] from the reduction of the Th(IV) complex {[(Et$_8$-calix[4]tetrapyrrole)Th(Cl)]$_2$K$_2$} ligand with potassium naphthalenide. More recently, the first example a of thorium

inverse-sandwich complex was obtained by Huang[1g] with the fc-(NSi^{t}BuMe$_2$)$_2$ (fc = 1,1′-ferrocenediyl) supporting ligand.

The UV−vis absorption spectra of **1** and **2** showed a broad band between 300 and 600 nm (Figure S57), but no characteristic absorption above 600 was observed that could be assigned to a Th(III) complex (700 - 800 nm).[11b] The band at 470 nm observed for **1** could be tentatively assigned to the naphthalenide radical.[19] The observed chemical shifts of the signals assigned to the terminal and bridging naphthalenides in the ^1H NMR spectra of complexes **1** (resonances at 2.82, 5.03, 5.29, 5.92 ppm Figure S2) and **2** (resonances at 3.46, 3.91, 5.44, 6.77 ppm S13) are similar to those reported for arene compounds containing thorium in a formal +IV oxidation state[1g] and are consistent with the dearomatization of the ring. A similar dearomatization was observed in the analogous terminal naphthalene complexes,[1d] and in diuranium and dithorium naphthalene inverse-sandwich complexes.[20a, 6a, 20b, 1g]

In order to further investigate the electronic structure of complexes **1** and **2**, X-band EPR spectra were measured. Complex **1** (Figure S64) and complex **2** (Figure S65) both exhibit an isotropic EPR signal in solid-state at 6 K with g_{iso}= 2.006 which decreases significantly in intensity at 298 K. The assignment of the observed signal remains ambiguous. EPR signals at g_{iso}= 1.84-1.916 were previously measured at 298 and 77 K for Th(III) complexes displaying a different geometry (pseudo-trigonal planar or square planar geometry) and in a 6d^1 ground state.[11b] In contrast the presence of an EPR signal was not observed in the only other reported inverse-sandwich complex of Th which was identified as a Th(IV)- napthalene^{4-} complex.[1g] Preliminary variable temperature magnetic susceptibility data (2 K - 290 K) also show the presence of a paramagnetic component with a magnetic moment increasing from 0.054 at 2 K to 1.07 µB at 290 K or **1** (Figure S67) and from 0.084 at 2K to 1.05 µB at 290 K for **2** (Figure S69). The observed behavior could be due to mixing of the singlet ground-state magnetic component with low-lying excited states.

Structural Characterization of Thorium-Arene Complexes

The solid-state structures of complexes **1** and **2** were determined by X-ray diffraction studies. The molecular structures of complexes **1** and **2** are presented in Fig. 1 and Fig. 2, respectively. Complex **1** shows a mononuclear structure with a naphthalene ligand terminally bound in a η^6-fashion. Conversely, complex **2** presents a dinuclear structure with a naphthalene ligand bridging two thorium centers in a μ-η^6, η^6-fashion.

In complex **1**, the Th-C bond distances reveal three sets of bond lengths, two shorter (Th1- η^6C_{napt} = 2.575(4)-2.600(4) Å), two intermediate (Th1- η^6C_{napt} = 2.782(4)-2.786(4) Å), and two longer (Th1- η^6C_{napt} = 2.926(5)-2.952(4) Å) that differ by approximately 0.2-0.4 Å, a consequence of the observed ring puckering of the naphthalene ligand. Such a binding mode was already observed in a U-anthracenide complex recently reported by Fortier and coworkers.[1h] The average Th-C distance of 2.77(10) Å is slightly longer than the one found in the only reported thorium monoarene complex, $[{(Et_8-calix[4]tetrapyrrole)Th}{K(dme)}(\eta^4-C_{10}H_8)[Li(dme)_3]$,[7] where the naphthalene is bound in a η^4-fashion (average Th-C = 2.72 (4) Å).

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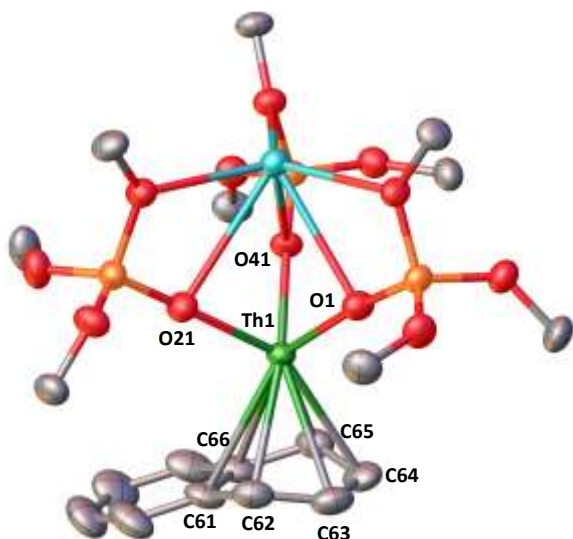**Figure 1.** Molecular structure of complex [K(OSi(OᵗBu)₃)₃Th(η⁶-C₁₀H₈)], **1**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the −OSi(OᵗBu)₃ ligands have been omitted for clarity.

The C-C bond lengths in the Th-bound ring of the naphthalene ligand (1.373 (10), 1.435(6), 1,447(8), 1.450(8), 1.475(7) and 1.476 (7) Å) in **1** are consistent with the presence of a cycloalkene fragment and are similar to those found in the thorium monoarene complex [{(Et₈-calix[4]tetrapyrrole)Th}{[K(dme)}(η⁴-C₁₀H₈)[Li(dme)₃].[7] The observed bonding scheme is consistent with the presence of a reduced naphthalene ligand and indicates that the reduction has occurred, at least to some extent, on the ligand. The Th-C_centroid distance (2.379(18) Å) is shorter than those found in Th(IV) neutral arene complexes (2.655 to 2.95 Å) [21] and in the Th(IV) naphthalenide complex in the [{(Et₈-calix[4]tetrapyrrole)Th}{[K(dme)}(η⁴-C₁₀H₈)[Li(dme)₃] (2.423 Å), [7].

In complex **2**, the bound naphthalene ligand is significantly more planar (deviation 3.4º from plane) than in **1** (deviation 12.1º from plane) resulting in a smaller range of the Th-C bond distances (2.539(4)-2.764(4) Å) compared to **1**. The value of Th-C distances and the average Th-C_centroid distance (2.233(4) Å) are comparable to the only reported thorium inverse-sandwich [(NNᵀᴮˢ)Th-(THF)]₂(μ-η⁶,η⁶-C₁₀H₈)(NNᵀᴮˢ = fc-(NSiᵗBuMe₂)₂, fc = 1,1′-ferrocenediyl))(Th-C = 2.566(9)-2.763(9) Å, average Th-C_centroid = 2.227(14) Å).[19] The C-C bond lengths in the bound ring range from 1.455 (6) to 1.476 (6) Å with an average value of 1.465 (14) Å. These values are close to those reported for the complex [(NNᵀᴮˢ)Th-(THF)]₂(μ-η⁶,η⁶-C₁₀H₈)] (1.441(7)-1.459(7) Å)[19] and are consistent with the aromatic character of the ring. In the pendant ring a diene-like character is suggested by the observed bond alternation (1.462(6), 1.349(7), 1.444(8) 1.349(7), and 1.449(6) Å). A similar dearomatization was reported in the only other example of thorium inverse sandwich[19] and in inverse-sandwich diuranium naphthalene complexes.[20a] The average Th−C distance of 2.666(14) Å and the average Th-C_centroid distance of 2.233(4) Å in **2** are significantly shorter than the average Th−C distances (2.77 (10) Å) and Th-C_centroid distance (2.379(18) Å) in **1** suggesting that the Th-arene interaction is stronger. Noteworthy, the average value of the Th-O_sil distances in both thorium arene complexes (2.238(5) Å in **1**, 2.277(7) Å in **2**) are significantly longer than in the [Th(OSi(OᵗBu)₃)₃Cl(THF)₂] precursor (2.19(1) Å).[18]

Overall, the metrical parameters are consistent with the presence of a reduced naphthalene, but the degree of reduction cannot be unambiguously established.
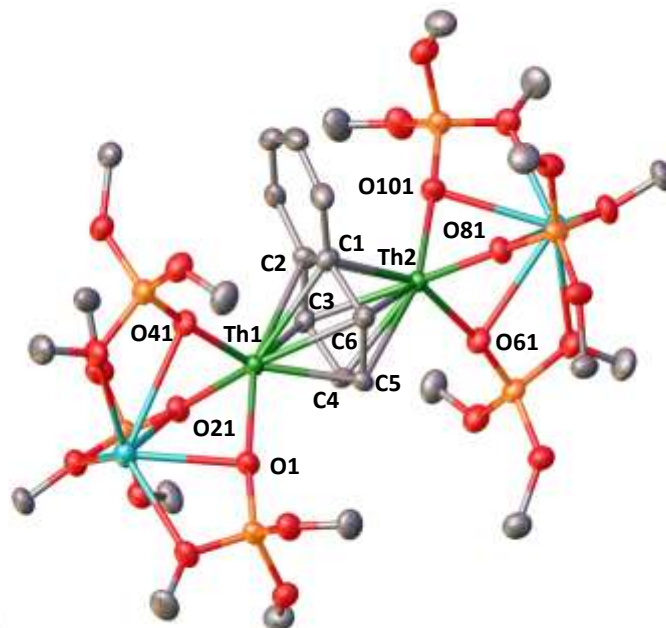

Figure 2. Molecular structure of [K(OSi(OᵗBu)₃)₃Th]₂(μ-η⁶,η⁶-C₁₀H₈)], **2**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the −OSi(OᵗBu)₃ ligands have been omitted for clarity.

Electronic structure of Thorium-Arene Complexes

To gain some insights onto the thorium oxidation states in complexes **1** and **2**, DFT calculations (B3PW91) have been performed. The geometry optimizations were carried out on two different spin states, namely a singlet and a triplet. For complex **1**, the singlet associated to the +IV oxidation state of Th and a doubly-reduced arene (in line with the Natural Charges, Table S6) is computed to be the ground state, while the triplet, that corresponds to a +III oxidation state, being higher in energy by only 5.1 kcal.mol⁻¹ (that is 0.18 eV) (Fig.3). The DFT-calculated electronic structure shows that the excited state has an electron localized in an orbital that mixes 6d and 5f but that is mainly 5f (69%). Therefore, the triplet spin state could be thermally populated even at low temperature in line with the magnetic data measured for complex **1**. It is noteworthy that the optimized geometry of the singlet spin state is in line with the experimental one (Table S4). The bonding of this complex was thus analyzed using Molecular Orbitals (MO) and Natural Bonding Orbitals (NBO) methods. The interaction between the arene and the thorium centre is only observed at the second-order donor acceptor level with donation from the C-C π orbitals to empty *df* orbital on Th (Table S8). The associated Wiberg Bond Indexes (Table S5) are in the range of 0.1-0.5 which is in line with what reported by Huang and Diaconescu for an amide supported inverse-sandwich complex of thorium.[19] Similarly, the HOMO of the system (Table S9) is δ-bond that implies overlap between the arene π* and a *df* orbital on Th. The situation is similar for complex **2** where the optimized geometry of the singlet compares better than the triplet geometry with the experimental one (Table S10). However, energetically, the triplet is found to be very close in

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energy (2.1 kcal.mol^{-1} or 0.09 eV) and therefore the possibility of a multireference ground state for complex **2** has been envisioned.
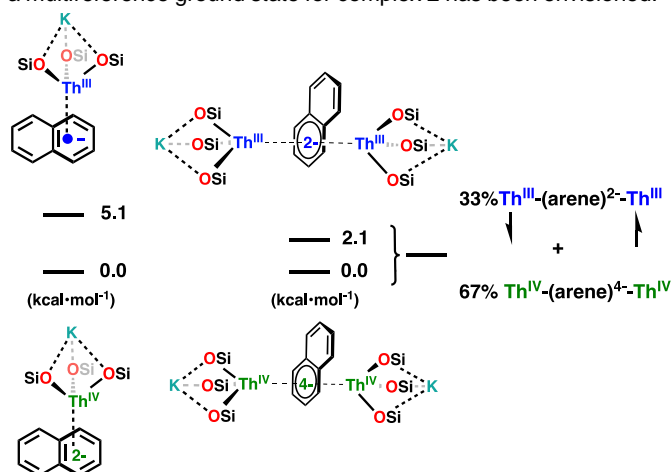

Figure 3. Different spin states of complex **1** and **2**. The siloxide ligand is written as OSi in **1** and **2**.

A CASSCF calculation was thus carried out by distributing 2 electrons into 3 orbitals, which is the smallest active space needed to describe this state (other larger active spaces were also used and led to the same result), and the ground state is found to be an open shell singlet that is a mixture of the Th(IV)-(arene)$^{4-}$-Th(IV) (67%) configuration and of the Th(III)-(arene)$^{2-}$-Th(III) (33%) one (Fig.3) while the first excited state is a pure triplet (at 0.09 eV so that it could be also thermally populated). This multireference ground state is in line with the experimental observation of a Th(IV) NMR and of a paramagnetic component

in the variable temperature magnetic susceptibility data. Since the ground state is multireference, the bonding in the complex implies the presence of both Th(IV) and Th(III) and therefore doubly-reduced and tetra-reduced arene. However, since the Th(IV) contributes more than Th(III) to the multiconfiguration, the bonding and the geometry of complex **2** are better represented by the singlet. The bonding is quite similar to that described for complex **1** with donation from the C-C π to empty df on Th with WBI in the 0.2-0.4 range (Tables S11 and S13). The HOMO and HOMO-1 (Table S14) display two δ-bonds in line with a primarily tetra-reduced arene and two Th(IV) as found in the only previously reported Th-inverse-sandwich complex.[1g]

Reactivity of Thorium-Arene Complexes

With the terminal and bridging naphthalene complexes on hand, we set out to investigate if the electrons stored in the complexes **1** and **2** could become available for the reduction of substrates.

Reaction with N$_2$O
At first, we investigated the reaction with the strong oxidizing agent N$_2$O.[22] Addition of excess N$_2$O (1 atm) to a THF solution of **1** led immediately to a color change from black to colorless, full consumption of the starting material and the formation of a new species as indicated by ^{1}H NMR studies (Figure S22). Colorless crystals of the complex [K$_2${(Th(OSi(O^{t}Bu)$_3$)$_3$)$_2$(μ-O)$_2$}], **3** were isolated from concentrated hexane at −40 °C.

The solid-state structure of **3** (Fig. 4), determined by X-ray diffraction studies, shows the presence of a dinuclear complex consisting of two equivalent Th(IV) ions, bridged by two oxide ligands.
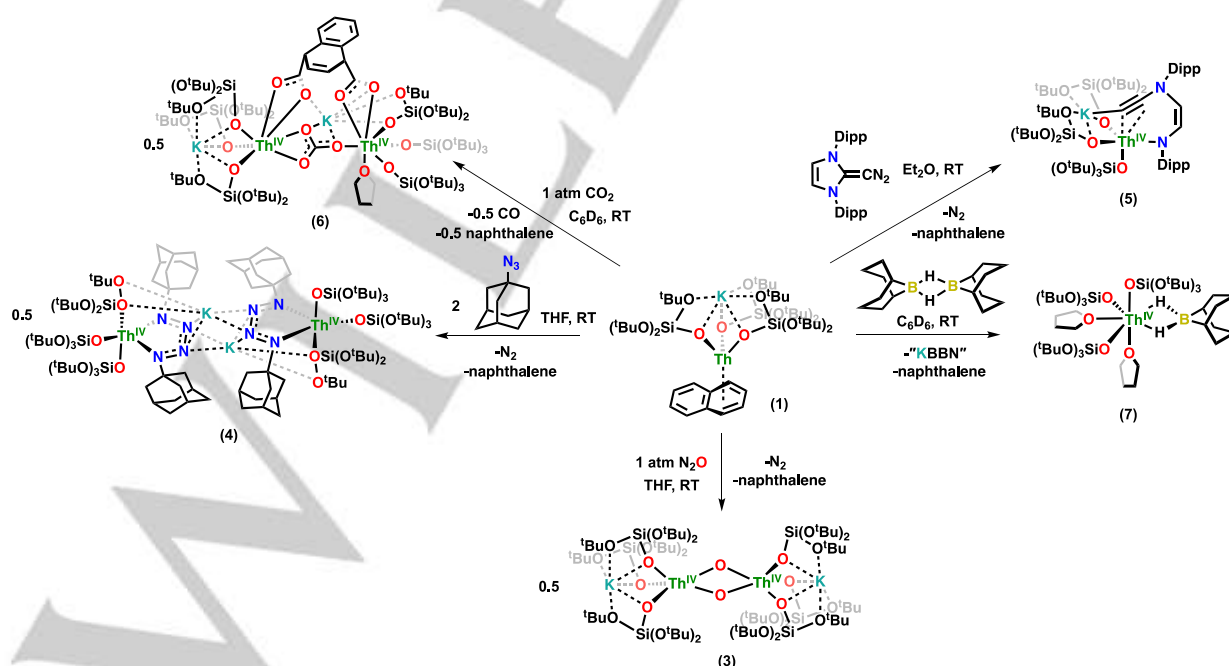
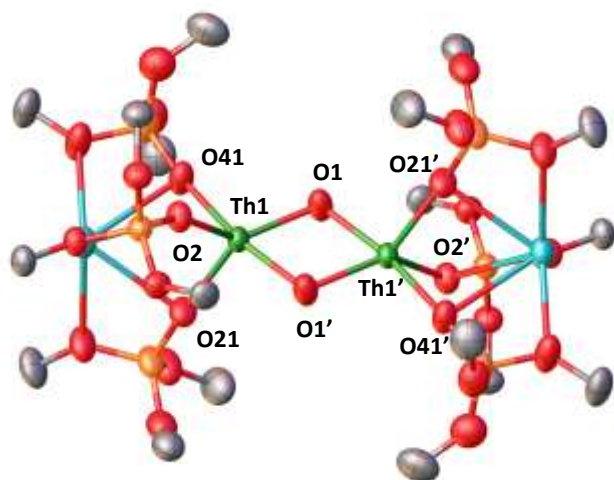**Scheme 2.** Reactivity of complex **1** towards small molecules.

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Figure 4. Molecular structure of [K$_2$\{(Th(OSi(O^{t}Bu)$_3$)$_3$)$_2$(μ-O)$_2$\}], **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the −OSi(O^{t}Bu)$_3$ ligands have been omitted for clarity.

Each Th(IV) center is pentacoordinated in a distorted square-pyramidal geometry and is bound by three -OSi(O^{t}Bu)$_3$ ligands and the two bridging oxides. Two K$^+$ cations are bound in the pockets formed by each set of three siloxide ligands .

The Th-O$_{oxo}$ (2.187 (6) Å) distances are similar to those found in the previously reported bis-oxo-bridged dithorium(IV) complexes (2.135(9)-2.195(8) Å).[23] The Th1O1Th1' and Th1O1'Th1' angles are equivalent, with values of 106.8(2)°. These values are in line with those reported for the bis-oxide Th(IV) complexes supported by Cp ligands, \{[η^5-1,2,4-(Me$_3$C)$_3$-C$_5$H$_2$]2Th\}$_2$(μ-O)$_2$, and \{[η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th\}$_2$(μ-O)$_2$, (106.1(4)°-108.9(2)°)).[23] Complex **2** also reacted with excess N$_2$O (1 atm), leading immediately to a color change from black to colorless. The ^{1}H NMR spectrum of the reaction mixture revealed the clean formation of **3** (Figure S26). The reactions of **1** and **2** with N$_2$O probably proceed with the two-electron reduction of N$_2$O and formation of terminal Th(IV) oxo that rapidly dimerizes. Dimerization of Th(IV) oxo due to its high basicity has been reported[23a] and is only prevented by tuning the sterics of supporting ligands.[9c] [23a, 24, 23b] The observed reactivity shows that the two/four electrons stored in the naphthalenide ring can be transferred to strongly oxidizing substrates. Only very recently, the first example of the formation of a terminal thorium oxo complex supported by a redox-active ligand was reported.[9c]

Reaction with AdN$_3$

We then explored the possibility of isolating a terminal imido complex by reacting **1** with a bulky organic azide.[23]

^{1}H NMR studies showed that the addition of 1 equiv. of 1-azidoadamantane to a THF solution of **1** at room temperature resulted in the formation of a new species and unreacted complex **1** (Figure S30). Addition of 2 equiv. of 1-azidoadamantane to a THF solution of **1** at room temperature resulted immediately in a color change from dark to colorless and full consumption of the starting material to yield a new species as indicated by ^{1}H NMR studies (Figure S30). Colorless crystals of complex **4**,

[K(OSi(O^{t}Bu)$_3$)$_3$Th(η^2-1,4-R$_2$N4)]$_2$ (R= adamantyl) were isolated in 73% yield from a concentrated hexane solution at −40 °C.

The solid-state molecular structure of **4** was determined by X-ray diffraction (Fig. 5 and Figure S70) and showed the presence of a dimeric complex where two [K(OSi(O^{t}Bu)$_3$)$_3$Th(η^2-1,4-R$_2$N4)] moieties are held together by the potassium cations bridging the tetraazabutadiene and siloxides ligands bound to different Th(IV) ions. Each monomeric unit in **4** contains a Th(IV) ion bound by three -Si(O^{t}Bu)$_3$ ligands and one tetraazabutadiene η^2-1,4-R$_2$N$_4$ (R= adamantyl) ligand in a distorted trigonal bipyramid geometry. The average value of the Th-N distances (2.411(12) Å) is noticeably shorter than that typically observed for a dative Th–N bond, but longer than the Th-N bond distance found in the previously reported tetraazabutadiene analogue, [\{η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$\}$_2$Th\{N(p-tolyl)N=N-N(p-tolyl)\}](2.354(3)-2.366(3) Å).[15c]
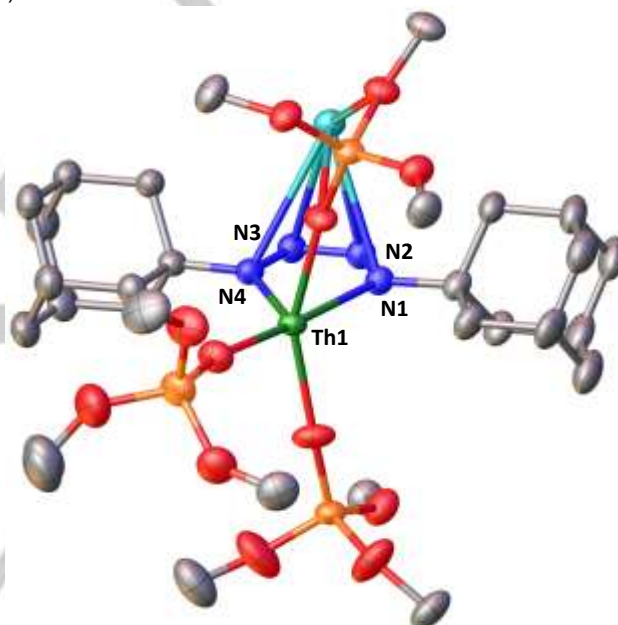

Figure 5. Molecular structure of the monomeric unit [K(OSi(O^{t}Bu)$_3$)$_3$Th(η^2-1,4-R$_2$N$_4$)] (R= adamantyl) in **4**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the −OSi(O^{t}Bu)$_3$ ligands have been omitted for clarity.

In the tetraazabutadiene ligand, the central N2–N3 bond (1.292(9) Å) is consistent with the presence of a N=N double bond. Additionally, the N1-N2 and N3-N4 distances (1.347(8) and 1.382(8) Å) are significantly shorter than a N-N single bond, suggesting the presence of delocalized electron density. These bond length differences were also observed in the only other reported thorium tetraazabutadiene complexes \{η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$\}$_2$Th\{N(p-tolyl)N=N-N(p-tolyl)\}], (η^5-C$_5$Me$_5$)$_2$Th-[N(p-tolyl)N=N-N (p-tolyl)] [15c, 15f] and in early transition metal complexes of tetraazabutadiene[25] and are in agreement with the presence of a dianionic tetraazene-1,4-diimido ligand with an isolated N=N double bond. Tetraazadiene complexes have been isolated for d-block metals and are most commonly prepared by the cycloaddition of organic azides with imido complexes. The imido complexes may be isolated or generated in situ by thermal fragmentation of azides at low-valent metal centers. An example

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of cycloaddition of organic azides to an isolated Th-imido complex to yield tetraazametallacyclopentene has also been reported.[15f] Thus the formation of **4** is most likely the result of the reaction of an intermediate terminal imido complex with excess azide to give the tetraazabutadiene cycloaddition product. The formation of a putative imido intermediate could be observed (together with signals of complex **4**) in the ^{1}H NMR spectrum of the reaction mixture obtained by reacting **1** with azide in 1:1 ratio at low temperature (Figure S31). The intermediate converts rapidly into **4** upon addition of a second equiv. of azide. These results indicate a high reactivity of the terminal imido intermediate which is due to the high basicity of the Th(IV) imido group.[26] The reaction profile of this reaction was computed at the DFT level and is reported in the ESI (Figure S72). Interestingly, the potassium cation participates in the formation of the imido intermediate.

The formation of **4** clearly indicates that complex **1** acts as a two-electron reductant. Complex **2** showed exactly the same reactivity as **1** also resulting in the formation of complex **4**, but it required 4 equiv. of 1-azidoadamantane to consume all the starting material as indicated by ^{1}H NMR studies (Figure S32). These results confirm that four electrons are stored in complex **4** and these electrons can become available for redox transformations. The observed reactivity differs significantly from that reported by Gambarotta and coworkers where the Th(IV) naphthalenide also transfer two electrons to the organic azide Me_3SiN_3 but further reactivity of the putative imido intermediate with a second azide resulted in the transfer of the Me_3Si group to the imide N atom to form a silazanate and KN_3.

Different reactivity with organic azides was also reported for U(III) inverse sandwich complexes supported by cyclopentadienyl ligands, resulting in the formation of a U(VI) bis-imido complex.[27]

Reaction with an imidazole-based diazoolefin

Despite the significant advancements made in actinide–carbene chemistry in the past decade, all but one examples reported thus far are based on chelating heteroatom-containing ligands to stabilize actinide carbenes.[28] In the absence of heteroatom substituents alkylidenes or even the more stable vinylidene were not isolated and only one example of actinide allenylidene was reported recently by Kent and Hayton.[29] [28e] In an effort to find new routes to actinide alkylidenes, Hayton and coworkers explored the reactivity of diphenylcyclopropene with actinides and reported that ring opening of a thorium cyclopropenyl complex generates a transient thorium carbene that could not be isolated.[28e]

Inspired by the reaction of the imidazole-based diazoolefin $IDipp=CN_2$[30] with $VCl_3(THF)_3$ which resulted in the formation of a vinylidene complex,[31] we investigated the reaction of complex **1** with $IDipp=CN_2$ targeting the synthesis of a thorium vinylidene. Addition of one equivalent $IDipp=CN_2$ to a Et_2O solution of **1** at −40 °C for 3 h resulted in an orange reaction mixture and full consumption of the starting material (Figure S33). The unexpected Th(IV) amido acetylido complex $[(OSi(O^tBu)_3)_3Th(\eta^2-C\equiv CNRCH=CHNR)K]$ (R= Dipp), **5** was isolated from concentrated hexane reaction mixture at −40 °C.

The molecular structure of complex **5** (Fig. 6) shows the presence of a mononuclear Th(IV) complex with a metal center bound by three -OSi(O^{t}Bu)$_3$ ligands, two carbon atoms and one amido group from the amido acetylide ligand. The structure is completed by one K$^+$ which is bound by two siloxides and a terminal alkynyl

(K1-C1= 2.785(7) Å). The Th-alkynyl distance (Th1-C1 = 2.538(7) Å, Th1-C2 = 3.099(6) Å) is longer than in terminal alkynyl complexes (Th-C$_{alkynyl}$ = 1.938(5)-2.642(5) Å)[32] The Th1-C1 and Th1-C2 distances compare well with previous η^2-alkynyl thorium complexes reported by Arnold (2.614(3)-3.029 Å).[32a] The triple bonds of the alkynyl ligands is slightly lengthened in comparison to the potassium alkynyl complex [K(2.2.2-cryptand)][C≡CPh] (1.215(3) Å) upon thorium binding (C1-C2 = 1.236(10) Å)[33] similar to what found in the reported η^2-alkynyl thorium complexes.[32a] The C-C distance remain much shorter than what found in thorium metallacyclopropene complexes.[34] Additionally, the Th-N bond distance (Th1-N1= 2.400(6) Å) is comparable to those found in previous thorium complexes containing DAB (diazabutadiene) ligands (2.279(9)-2.664(3) Å).[15a, 9a] The formation of complex **5** probably involves the two-electron reduction of the imidazole diazoolefin by complex **1** to yield a highly reactive transient thorium N-heterocyclic vinylidene complex followed by ring-opening of the imidazole ring to yield the final alkynyl complex. In order to trap this transient thorium vinylidene complex, we performed the reaction at −80 °C and −40 °C. At −80 °C, low temperature ^{1}H NMR studies showed almost no reaction (Figure S37). While at −40°C, low temperature ^{1}H NMR studies only showed the ring-opening species (Figure S38). This provides a synthetic route to an actinide vinylidene intermediate and evidence of the very high reactivity of the An=C multiple bonding.[35, 28e]

In contrast, complex **2** is stable in the chosen reaction conditions and did not react with two equivalents $IDipp=CN_2$ at room temperature or at 70 °C after 2 days, as shown by the ^{1}H NMR spectroscopy (Figure S39-S40). These results, suggest that the 6C, 10π-electron aromatic system in the bound naphthalene result in a higher stability and lower reactivity of the naphthalene ring.

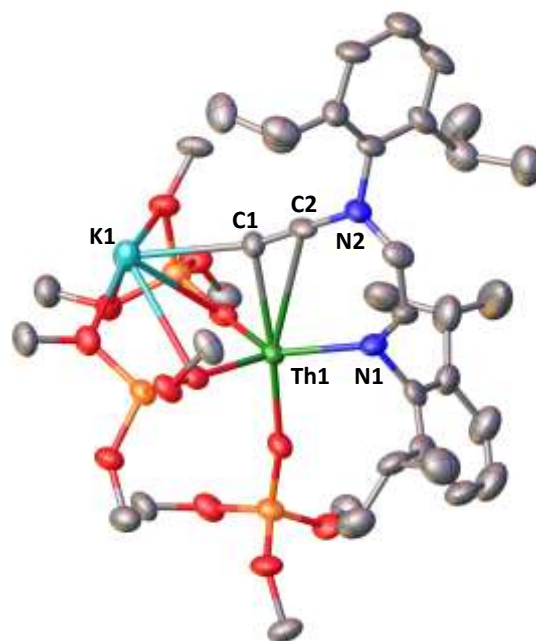**Figure 6.** Molecular structure of $[(OSi(O^tBu)_3)_3Th(\eta^2-C\equiv CNRCH=CHNR)K]$ (R= Dipp), **5**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the −OSi(O^{t}Bu)$_3$ ligands have been omitted for clarity.
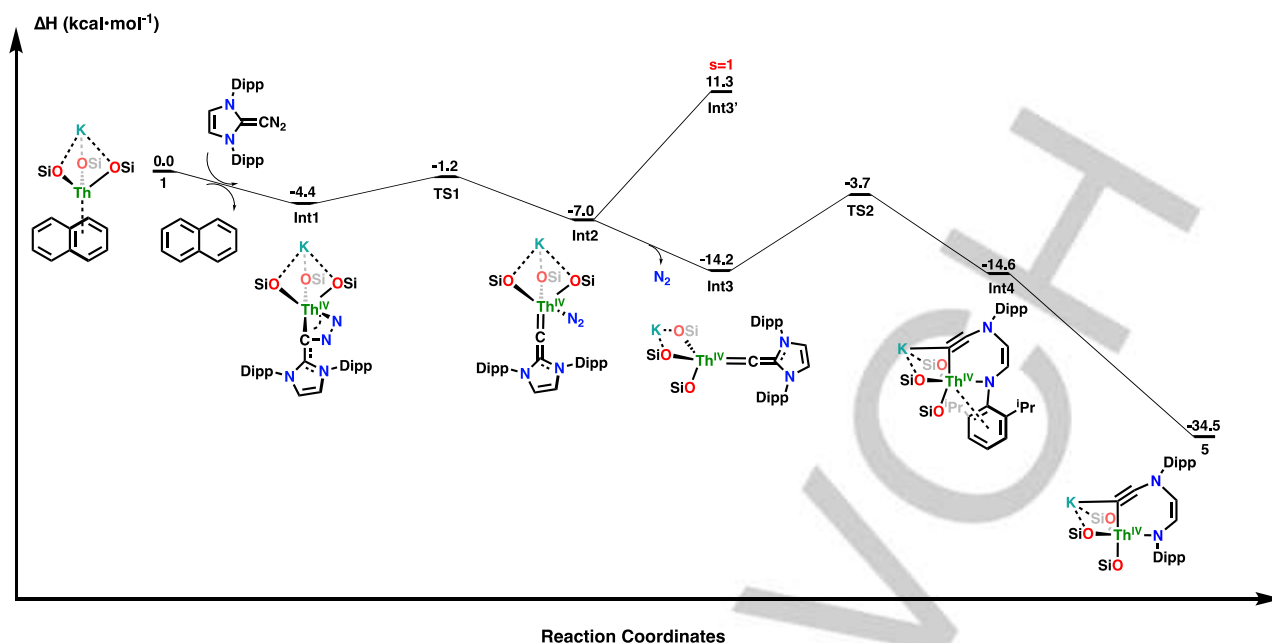
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Figure 7. Computed enthalpy profile at room temperature for the formation of **5** from the reaction of complex **1** with IDipp=CN$_2$. The enthalpy are given in kcal·mol^{-1}. The siloxide ligand is written as OSi.

The formation of complex **5** was investigated computationally and these studies supported the formation of a carbene intermediate (Fig. 7). The reaction begins by the exchange between the naphthalenide ligand and IDipp=CN$_2$. This exchange is computed to be favoured by 4.4 kcal mol^{-1}. In **Int1**, the IDipp=CN$_2$ molecule is doubly reduced so that the C-N bond is activated. Therefore, a C-N bond breaking TS is easily reached (barrier of 3.2 kcal·mol^{-1}). Following the intrinsic reaction coordinate, it leads to the formation of a N$_2$ molecule and of Th-carbene complex (**Int2**), whose formation is favourable by 7.0 kcal·mol^{-1}. The release of N$_2$ yields the carbene complex (**Int3**) and induces a further stabilization of 7.2 kcal·mol^{-1}. In this complex, the carbene is formally dianionic in line with a strongly nucleophilic Schrock-type carbene (as evidenced by the natural charge of -1.22 of the carbene carbon). The bonding in this complex, which is one of the first in the actinide chemistry, has been analysed using Natural Bonding Orbital (NBO) method. A Th=C double bond (Table S21) is found at the NBO level with two strongly polarized toward C (86%,80%), corroborated by the Th-C Wiberg Bond Index (WBI) of 1.16 (Table S19), further highlighting the nucleophilic character of the carbene. The strong nucleophilic character of this carbene allows the system to undergo an intramolecular Ring Opening (RO) reaction. The associated barrier is 10.5 kcal·mol^{-1}, allowing the formation of complex **5**. It is interesting to note that complex **5** is more stable than the carbene intermediate (**Int3**) by 20.3 kcal·mol^{-1}.

Reaction with CO$_2$

Since a mononuclear Th naphthalenide complex supported by a macrocyclic pyrrolide ligand was reported by Gambarotta and co-workers to react with CO$_2$ resulting in the addition of two reduced CO$_2$ molecules to the naphthalene arene ring,[16] we also set out to explore the reaction of complexes **1** and **2** with CO$_2$. Addition of excess (1 atm) CO$_2$ to a C$_6$D$_6$ solution of **1** at room temperature led to a color change from black to colorless immediately. Full consumption of the starting material and the formation of the

multiple species were observed in the ^{1}H NMR spectrum (Figure S41). Recrystallization of the reaction mixture from concentrated THF at −40 °C afforded few colorless crystals of the complex [K$_2${(Th(OSi(O^{t}Bu)$_3$)$_3$)$_2$(μ-CO$_3$)(μ-m-cis-1,4-(CO$_2$)$_2$C$_{10}$H$_6$)}], **6**.
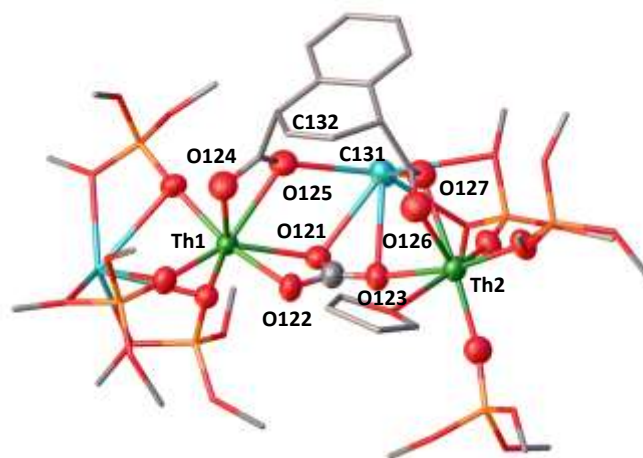
Figure 8. Molecular structure of [K$_2${(Th(OSi(O^{t}Bu)$_3$)$_3$)$_2$(μ-CO$_3$)(μ-m-cis-1,4-(CO$_2$)$_2$C$_{10}$H$_6$)}], **6**, with thermal ellipsoids drawn at the 40% probability level. Siloxide ligands depicted as sticks for clarity. Hydrogen atoms and methyl groups on the –OSi(O^{t}Bu)$_3$ ligands have been omitted for clarity.

Attempts to isolate analytically pure complex **6** proved unsuccessful due to the formation of multiple unidentified products. Next, we investigated the reaction with ^{13}C labelled CO$_2$. Addition of excess ^{13}CO$_2$ (4 equiv.) to a C$_6$D$_6$ solution of **1** led to the same results as the 1 atm reaction as indicated by the ^{1}H NMR spectrum (Figure S42) showing the presence of multiple species. After removal of the volatiles and hydrolysis with D$_2$O (pD = 13) of the reaction residue, ^{13}CO$_3^{2-}$ was observed by quantitative ^{13}C NMR spectroscopy in 21% yield (Figure S44). When the reaction is carried with stoichiometric (2 equiv.) amounts of ^{13}CO$_2$, the ^{1}H NMR spectrum is not significantly

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modified and it shows the presence of multiple species (Figure S45). After removal of the volatiles and hydrolysis with D_2O (pD = 13) of the reaction residue, $^{13}CO_3^{2-}$ was observed by quantitative ^{13}C NMR spectroscopy in 16% yield (Figure S46).

The solid-state molecular structure of **6** (Fig. 8) shows the presence of a dinuclear Th(IV) complex where two Th centers are bridged by the three oxygen atoms of a carbonate ligand and by the *cis*-1,4-dihydronaphthalene-1,4-dicarboxylate dianions with each carboxylate group binding a different thorium atom in a bidentate fashion. The Th2 center is heptacoordinated in a distorted capped octahedral geometry by a monodentate carbonate, three monodentate siloxide, a bidentate carboxylate, and a THF molecule, while the second thorium atom (Th1) is heptacoordinated in a distorted capped octahedral geometry by a bidentate carbonate, three monodentate siloxide, and a bidentate carboxylate. One K^+ cation is bound in the pocket formed by the three siloxide binding Th1 while a second K^+ cation is held by the oxygen atoms of a carboxylate, the carbonate and two siloxes. The $Th\text{-}O_{carbonate}$ distances range from 2.32(2) to 2.46(2) Å and the $Th\text{-}O_{carboxylate}$ distances range from 2.52(2) to 2.60(2) Å. The metrical parameters of one ring from the dihydronaphthalene residue remain unchanged while the ring which has undergone addition of two carboxylates shows a shorter C-C bond (C131-C132 =1.26(6) Å) for the two carbon atoms between the carboxylate groups, indicative of the double-bond localization.

The formation of complex **6** results formally from the reduction of four molecules of CO_2 by two molecules of complex **1**. Notably, two reduced CO_2 molecules are added to one naphthalene ligand while the bridging carbonate formed from the reductive disproportionation of two CO_2 molecules. The *cis* addition of two reduced CO_2 molecules to the naphthalenide ligand was also reported for the reaction of {[(Et$_8$-calyx-[4]-tetrapyrrole)ThK(DME)](μ,μ'-η^4:η^6-$C_{10}H_8$)(μ-K)}$_n$ with CO_2, but in the work of Gambarotta[16] the formation of carbonate was not detected.

Reaction with HBBN

Finally, we investigated the reaction of the two thorium naphthalene complexes with the borylating agent, 9-borabicyclo[3.3.1]nonane (HBBN), which was reported to promote the arene C-H borylation of an uranium inverse-sandwich complex supported by aryloxide ligands.[1b]

The reaction of two equivalents of 9-borabicyclo[3.3.1]nonane (HBBN) with a benzene solution of complex **1** at room temperature for 16 h, resulted in the full consumption of the starting material and the formation of the complex [(OSi(O^{t}Bu)$_3$)$_3$(THF)$_2$Th(η^2-H$_2$BC$_8$H$_{14}$)], **7** (Figure S49). Colorless crystals were isolated from a concentrated THF/Et$_2$O reaction mixture at −40 °C. The ^1H NMR spectrum of isolated complex **7** displays a broad quartet resonance signal at δ 4.67 in THF-d$_8$ which can be assigned to boron-bound hydrides (Figure S52). Additionally, the ^{11}B NMR spectrum exhibits a triplet resonance at δ 2.89, which is in the range typically observed for boron hydrides (Figure S55).[36] The formation of **7** involves the reduction of two HBBN molecules to yield the H$_2$BBN anion. We propose the concomitant formation of a transient KBBN as byproducts that rapidly decompose, yielding unidentified species containing one proton on the boron. A doublet signal was observed in ^{11}B NMR spectroscopy in the reaction mixtures (Figure S50).

These byproducts could not be conclusively characterized and therefore they have been represented as "KBBN" in Scheme 2. In

the reaction of **1** with HBBN, the two electrons stored on the naphthalene ligand are transferred to two molecules of HBBN and neutral naphthalene is released.

The solid-state molecular structure of **7** as determined by X-ray diffraction studies (Fig. 9) shows a mononuclear Th(IV) complex. The Th center is seven-coordinated by two hydrides from the H$_2$BBN moiety, three -OSi(O^{t}Bu)$_3$ ligands and two THF ligands in a pseudo-octahedral geometry. The hydrides were located unambiguously in the Fourier difference map and refined isotropically and the η^2-binding mode of the H$_2$BBN moiety was confirmed by FTIR spectroscopy (Figure S63).[37] The Th-B distance (Th1-B1= 2.838(7) Å) is longer than those found in thorium complexes containing bidentate borohydrides (2.49(6)-2.670(2) Å),[38a, 21a, 38b] but is similar to the distances reported by Girolami[38a] and Arnold[38b] for the complexes [Th(H$_3$BNMe$_2$BH$_3$)$_4$] and [(BIMA)$_3$Th(μ-H)$_2$[B(C$_8$H$_{14}$)](BIMA= MeC(N^{i}Pr)$_2$) respectively which exhibit Th–B distances between 2.882(3) to 3.193(5) Å. The mean value of the Th-H distances (2.36(4) Å) is comparable to the previously reported thorium borohydrides complexes (2.37(2)-2.539(18) Å). [38a, 21a, 38b]
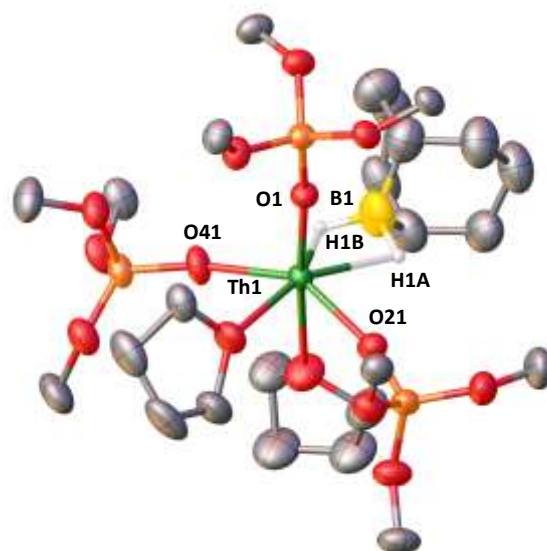

Figure 9. Molecular structure of [(OSi(O^{t}Bu)$_3$)$_3$(THF)$_2$Th(η^2-H$_2$BC$_8$H$_{14}$)], **7**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the −OSi(O^{t}Bu)$_3$ ligands have been omitted for clarity.

The reactivity of **2** with 9-borabicyclo[3.3.1]nonane (HBBN) was also examined. Addition of two equivalents of HBBN to a benzene solution of **2** at room temperature only led to slight changes in the ^1H NMR spectrum (Figure S56). Most of the **2** remained unreacted. Again, the high stability of complex **2** towards HBBN is probably explained by the aromatic character of the bound arene. Heating the reaction mixture at 80 °C for 24 h and monitoring by ^1H NMR spectroscopy showed unreacted **2**, [(OSi(O^{t}Bu)$_3$)$_3$(THF)$_2$Th(η^2-H$_2$BC$_8$H$_{14}$)], **7** and unidentified species (Figure S56). The formation of arene C-H Borylated product was not observed, suggesting a lower reactivity of the inverse-sandwich complex **2** compared to the uranium inverse-sandwich complex supported by aryloxide ligands reported by Arnold and coworkers.[1b]

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Conclusion

In summary, we synthesized and characterized two arene complexes of thorium by using siloxides as supporting ligands. By simply changing the naphthalene:thorium ratio, we isolated a mononuclear thorium complex with a terminally bound a naphthalene, which is the third example of its kind, or a naphthalene bridged inverse sandwich complex, which is only the second example reported so far. The structural data suggest the presence of a reduced naphthalene, but do not allow the unambiguous assignment of the thorium oxidation state. The computed electronic structure of complex **1** shows the presence of a Th^{IV}-naphthalenide^{2-} species as ground state but with an accessible triplet state corresponding to the Th^{III}-naphthalenide^{-} species. A multiconfigurational state is found for the electronic structure of **2** with a mixture of the Th(IV)-(arene)$^{4-}$-Th(IV) (67%) configuration and the Th(III)-(arene)$^{2-}$-Th(III) (33%). The reactivity studies carried out for the two complexes show that the 2 and 4 electrons stored in complexes **1** and **2** respectively can become available for the reduction of a range of substrates. Complexes **1** and **2** show similar reactivity towards N_2O, AdN_3 and CO_2. Both complexes **1** and **2** also reduce the borane HBBN but while the reaction of **1** proceeds rapidly at room temperature, the reaction of **2** with HBBN requires higher temperature. The lower reactivity of the inverse-sandwich complex **2** compared to the terminally bound naphthalenide complex **1** is confirmed by the lack of reactivity of **2** with the imidazole-based diazoolefin $IDipp=CN_2$ even at high temperatures. In contrast, complex **1** reacts immediately at -40°C to yield the unexpected Th(IV) amido-alkynyl complex **5**.

The computed mechanism indicated that the reaction proceeds *via* the formation of a highly reactive terminal N-heterocyclic vinylidene complex followed by ring-opening of the imidazole ring to yield the alkynyl species. Importantly, this reactivity provides a potential route to the isolation of a "Schrock-type" non-heteroatom-stabilized vinylidene and the first evidence of their formation. Finally, the reactivity presented indicated that arenides can act as convenient redox-active ligands for implementing thorium-ligand cooperative multielectron transfer.

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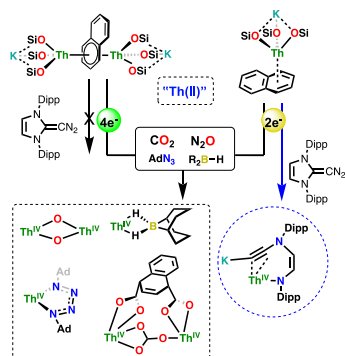
A mononuclear arenide complex and an inverse-sandwich complex of thorium can perform multielectron reductive chemistry with a range of substrates acting as Th(II) synthons. The mononuclear complex shows higher reactivity towards an azoolefine yielding a Th(IV) amidoacetylido complex *via* a vinylidene intermediate suggesting that the Th reactivity is tuned by the arenide binding mode.

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