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Experimental and Computational Studies on the Reactivity of a Terminal Thorium Imidometallocene towards Organic Azides and Diazoalkanes**

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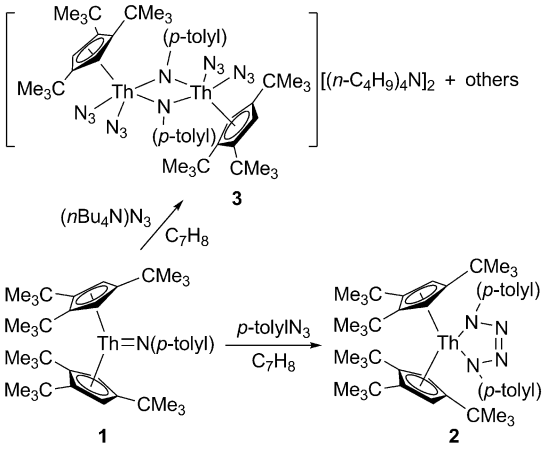
Dedicated to Professor Changtao Qian on the occasion of his 80th birthday

Abstract: *The reaction of the base-free terminal thorium imido complex [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th=N(p-tolyl)] (**1**) with p-azidotoluene yielded irreversibly the tetraazametallacyclopentene [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th{N(p-tolyl)N=N−N(p-tolyl)}] (**2**), whereas the bridging imido complex [{[η⁵-1,2,4-(Me₃C)₃C₅H₂]Th(N₃)₂}₂{μ-N(p-tolyl)}₂][(n-C₄H₉)₄N]₂ (**3**) was isolated from the reaction of **1** with [(n-C₄H₉)₄N]N₃. Unexpectedly, upon the treatment of **1** with 9-diazofluorene, the NN bond was cleaved, an N atom was transferred, and the η²-diazenido iminato complex [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th{η²-[N=N(p-tolyl)]}{N=(9-C₁₃H₈)}] (**4**) was formed. In contrast, the reaction of **1** with Me₃SiCHN₂ gave the nitrilimido complex [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th{NH(p-tolyl)}{N₂CSiMe₃}] (**5**), which slowly converted into [{η⁵-1,2,4-(Me₃C)₃C₅H₂}{η⁵:κ-N-1,2-(Me₃C)₂-4-CMe₂(CH₂NN=CHSiMe₃)C₅H₂}Th{NH(p-tolyl)}] (**6**) by intramolecular C−H bond activation. The experimental results are complemented by density functional theory (DFT) studies.*

In contrast to well-established uranium imido chemistry,[1–3] examples of well-defined thorium imido complexes are still limited,[3j,4] and therefore the exploration of their intrinsic reactivity is still in its infancy.[4] Thorium possesses the electronic ground state [Rn] $6d^2 7s^2$, and therefore one might expect a similar reactivity to that of early transition metals, for which several complexes with M=NR bonds have been prepared.[5–7] Nevertheless, more recent studies indicate that 5f orbitals indeed contribute to the bonding in thorium organometallic complexes, thus leading to distinctively different reactivity as compared to that of Group 4 complexes.[8] In this context, the base-free terminal thorium imido complex [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th=N(*p*-tolyl)] (**1**) was prepared.[9,10] This complex shows rich reactivity in the activation of elemental sulfur (S_8)[9] and Si−H bonds.[11] Furthermore, complex **1** is an efficient catalyst for the trimerization of PhCN and acts as an important intermediate in the catalytic hydroamination of internal acetylenes.[9] Moreover, it is also a useful precursor for the preparation of oxido and sulfido thorium metallocenes [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th=E] (E = O, S) by cycloaddition–elimination reactions with Ph_2C=E (E = O, S) or CS_2.[12] Encouraged by the latter aspect, we are now investigating the scope of these cycloaddition reactions with unsaturated molecules. As part of these studies, the first examples of [2+3] and [2+2] cycloaddition reactions promoted by **1** and organic azides and diazoalkanes are presented herein.

Complex **1** reacted in a [2+3] cycloaddition reaction with *p*-azidotoluene to give the tetraazametallacyclopentene [{η⁵-1,2,4-(Me₃C)₃C₅H₂}₂Th{N(*p*-tolyl)N=N−N(*p*-tolyl)}] (**2**) with quantitative conversion (Scheme 1). Similar reactivity was observed for aluminum,[13] germanium,[14] and osmium[15]



Scheme 1. Synthesis of complexes **2** and **3**.

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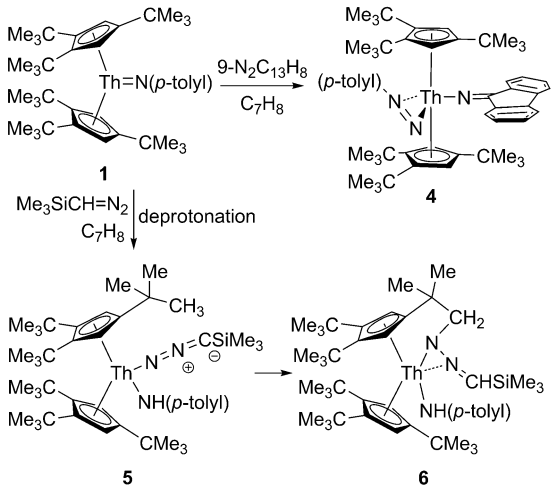
imido compounds. However, in contrast to those of zirconium[6e] and niobium[7c] imido complexes, the reaction of **1** with organic azides is irreversible, as demonstrated by variable-temperature ^{1}H NMR spectroscopic investigations (20–100 °C). This difference in reactivity might be ascribed to the more polarized actinide imido bond[11] as a direct consequence of the involvement of the 5f orbitals in the bonding of these complexes; this more polarized bond is the major difference with respect to Group 4 metal compounds with their more covalent bonds.[8c,11] Under similar reaction conditions, the treatment of **1** with $[(n\text{-}C_4H_9)_4N]N_3$ did not give the desired cycloaddition product; instead, one cyclopentadienyl ligand was replaced by two azido ligands. However, the steric demand in this new complex was no longer sufficient to prevent dimerization, and therefore the μ-imido-bridged complex $[\{[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]Th(N_3)_2\}_2\{\mu\text{-}N(p\text{-tolyl})\}_2][(n\text{-}C_4H_9)_4N]_2$ (**3**) was isolated in 40 % yield (as based on **1**; Scheme 1).

The reaction of **1** with diazo compounds proceeds through two distinct pathways, depending on the diazoalkane. The treatment of **1** with 9-diazofluorene yielded the η^2-diazenido iminato metallocene $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2Th\{\eta^2\text{-}[N{=}N(p\text{-tolyl})]\}\{N{=}(9\text{-}C_{13}H_8)\}]$ (**4**) with quantitative conversion (Scheme 2). In this reaction, the NN bond in 9-diazafluorene



Scheme 2. Synthesis of complexes **4**–**6**.

was broken, and a nitrogen atom was transferred to the thorium imido moiety. However, when Me_3SiCHN_2, which contains an α-H atom, was used as the diazoalkane, the nitrilimido complex $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2Th\{NH(p\text{-tolyl})\}\{N_2CSiMe_3\}]$ (**5**) was isolated as a pale-yellow oil in quantitative yield. This reaction can be rationalized by the deprotonation of the diazoalkane by the strongly polarized Th=N(*p*-tolyl) group. Similar reactivity was recently reported for a scandium complex.[5e] Although complex **5** was stable at 100 °C for 1 week, a small amount (5 %) of $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}\{\eta^5{:}\kappa\text{-}N\text{-}1,2\text{-}(Me_3C)_2\text{-}4\text{-}CMe_2(CH_2NN{=}CHSiMe_3)C_5H_2\}Th\{NH(p\text{-tolyl})\}]$ (**6**) was formed by intramolecular C–H bond activation when the pale-yellow oil **5** was stored at room temperature for 3 months (Scheme 2).

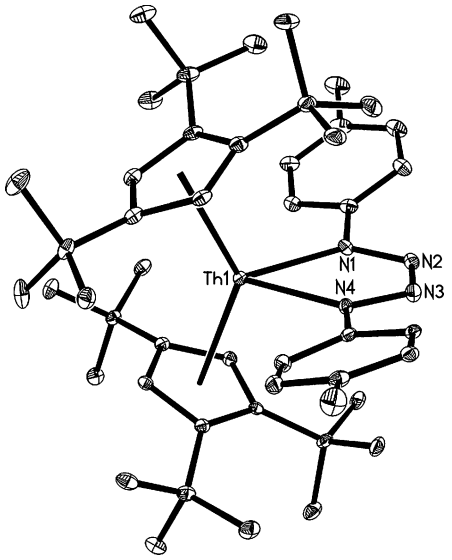


Figure 1. Molecular structure of **2** (with thermal ellipsoids drawn at the 35 % probability level).

The molecular structure of **2** is shown in Figure 1. To the best of our knowledge, **2** is the first structurally characterized actinide tetraazametallacyclopentene. The Th^{4+} ion is η^5-bound to two eclipsed Cp rings and σ-coordinated to two nitrogen atoms from the group {N(*p*-tolyl)N=N–N(*p*-tolyl)} in a distorted-tetrahedral geometry with an average Th–C(ring) distance of 2.879(3) Å, a Cp(cent)-Th-Cp(cent) angle of 110(1)°, and a N(1)-Th-N(4) angle of 61.4(1)°. The Th–N(1) distance is 2.366(3) Å, and the Th–N(4) distance is 2.354(3) Å, which are in the same range as those found in $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2Th\{N(p\text{-tolyl})C(S){-}S\}]$ (2.347(6) Å)[12] and $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2Th\{N(p\text{-tolyl})C(NPh){-}S\}]$ (2.328(3) Å).[12] Furthermore, the N(2)–N(3) distance (1.264(4) Å) is consistent with an N=N double bond,[13] whereas the N(1)–N(2) (1.394(4) Å) and N(3)–N(4) (1.389(4) Å) distances are shorter than a N–N single bond (ca. 1.50 Å).[13] Interestingly, the five-membered ThN_4 ring is essentially planar, and the coordination environment at N(1) and N(4) is trigonal-planar (sum of the angles: 359.6°). This ThN_4 metallacycle may be compared to the C_2N_2Th moiety in the diazabutadiene complex $[\{(2,4,6\text{-}Me_3C_6H_2)NC(Me){=}C(Me)N(2,4,6\text{-}Me_3C_6H_2)\}Th(thf)]$.[16]

Single-crystal X-ray diffraction analysis of **3** showed well-separated, alternating layers of discrete tetrahedral $[(n\text{-}C_4H_9)_4N]^+$ cations and $[\{[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]Th(N_3)_2\}_2\{\mu\text{-}N(p\text{-tolyl})\}_2]^{2-}$ anions. The anion is centrosymmetric, and the Th^{4+} ions adopt a distorted-trigonal-bipyramidal structure (Figure 2) with an average Th–C(Cp) distance of 2.892(4) Å. The average Th–N(μ-N) distance of 2.301(3) Å is shorter than the Th–N(N_3) distance of 2.411(3) Å. Overall, these metric parameters can be compared to those found in **2**. The separation of the two Th^{4+} cations is 3.697(1) Å, which is longer than the distance found in $[\{[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th\}_2(\mu\text{-}O)_2]$ (3.546(1) Å).[12]

The molecular structure of **4** is shown in Figure 3. The Th^{4+} ion also adopts a distorted-trigonal-bipyramidal geometry, with coordination by two η^5-bound Cp rings, a σ-

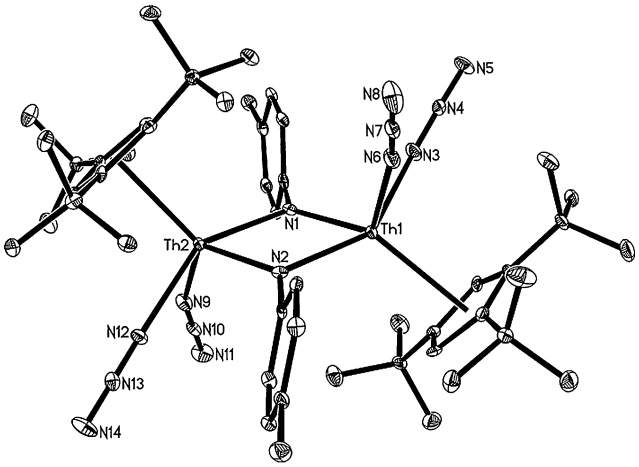


Figure 2. Molecular structure of the anion in **3** (with thermal ellipsoids drawn at the 35% probability level).

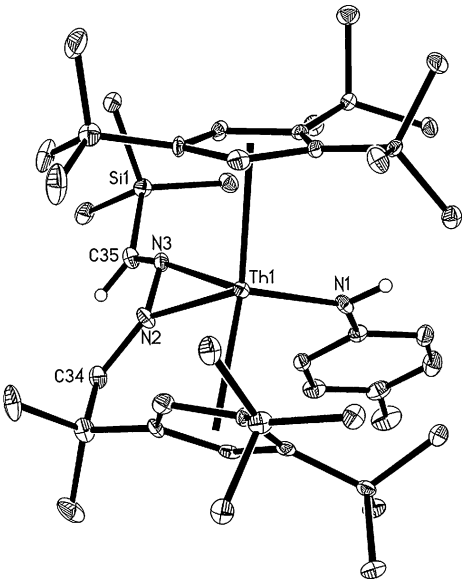


Figure 4. Molecular structure of **6** (with thermal ellipsoids drawn at the 35% probability level).

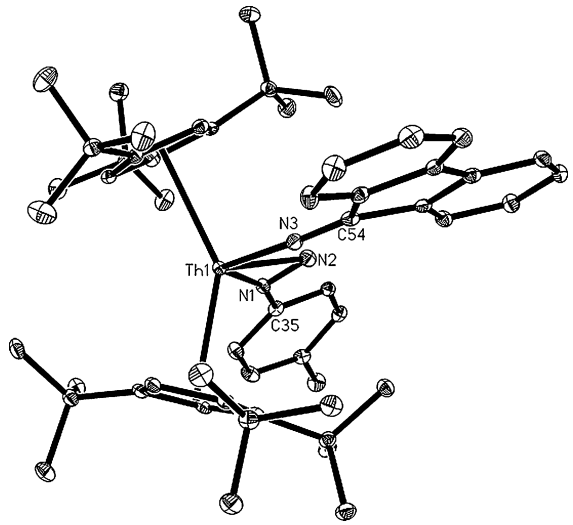


Figure 3. Molecular structure of **4** (with thermal ellipsoids drawn at the 35% probability level).

coordinated nitrogen atom from the iminato group {N=(9-$C_{13}H_8$)}, and two nitrogen atoms of the η^2-bound diazenido group {N=N(*p*-tolyl)}. The average Th–C(ring) distance is 2.880(3) Å, and the Cp(cent)-Th-Cp(cent) angle is 143.9(1)°. Nevertheless, more relevant is that the formation of complex **4** is the first example of the NN bond cleavage of a diazoalkane as induced by an actinide imido complex. The short Th–N(3) distance of 2.275(2) Å and the Th-N(3)-C(54) angle of 161.6(2)° suggest nitrogen π-donation to the thorium atom.[9] The N(1)–N(2) distance of 1.240(3) Å is close to that found in $[(\eta^5\text{-}C_5H_5)_2Ti\{N_2C(CO_2Et)_2\}]$ (1.214(7) Å);[17] it is consistent with an N=N double bond[13] and comparable to that (N(2)–N(3) 1.264(4) Å) in **2**. The Th–N(1) and Th–N(2) distances are 2.478(2) and 2.437(2) Å, respectively, and thus slightly longer than the Th–N(3) distance (2.275(2) Å), but comparable to those found in **2** and **3**.

Figure 4 depicts the molecular structure of **6**, in which the Th^{4+} ion is η^5-bound to two Cp rings, σ-coordinated to the nitrogen atom of the {NH(*p*-tolyl)} group, and coordinated to the two nitrogen atoms of the {1,2-$(Me_3C)_2$-4-$CMe_2(CH_2NN{=}CHSiMe_3)C_5H_2$} group in a distorted-trigonal-bipyramidal fashion. The N(2)–N(3) distance of 1.366(8) Å is comparable to those (N(1)–N(2) 1.394(4) Å and N(3)–N(4) 1.389(4) Å) found in **2**, whereas the relatively long Th–N(3) distance of 2.758(6) Å is again indicative of a datively coordinated nitrogen atom.[18] The Th–N(2) distance of 2.274(6) Å is shorter than Th–N(3) (2.758(6) Å), but close to the values found for the Th–N(1) distance (2.305(6) Å) and those in **2**, **3**, and **4**. Whereas complex **4** contains a η^2-diazenido moiety, the {1,2-$(Me_3C)_2$-4-$CMe_2(CH_2NN{=}CHSiMe_3)C_5H_2$]} group can be considered as a η^2-hydrazido fragment.

As described above, complex **1** irreversibly reacted with *p*-azidotoluene to yield the tetraazametallacyclopentene complex **2**, whereas the reaction of **1** with 9-diazofluorene induced a nitrogen-atom transfer to give a η^2-diazenido iminato metallocene **4**. To further understand these reactivity patterns, we performed dispersion-corrected DFT calculations at the B3PW91 level of theory. The reaction of **1** with *p*-azidotoluene to give **2** is exergonic with $\Delta G(298\,K) = -90.3\,kJ\,mol^{-1}$ and proceeds via the concerted [2+3] transition state **TS** formed by the Th=N and RN=N^+=N^- moieties (Figure 5). The barrier for this reaction is $\Delta G^{\neq} = 31.8\,kJ\,mol^{-1}$ (298 K), which is consistent with the rapid and irreversible formation of **2** at ambient temperature. In contrast, the formation of **4** from **1** + $(C_{12}H_8)CN_2$ is more complicated and involves a metallatriazacyclobutene intermediate **INT** and two transition states (**TSa** and **TSb**). The conversion of **1** + $(C_{12}H_8)CN_2$ into **INT** via transition state **TSa** for the [2+2] cycloaddition is energetically favorable ($\Delta G(298\,K) = -62.3\,kJ\,mol^{-1}$) with an activation barrier of 62.3 $kJ\,mol^{-1}$ at 298 K (Figure 5). However, the final product **4** is thermodynamically much more stable ($-125.8\,kJ\,mol^{-1}$) than the intermediate **INT** ($-62.3\,kJ\,mol^{-1}$; Figure 5). Moreover, the potential-energy profile suggests a short lifetime for **INT**,

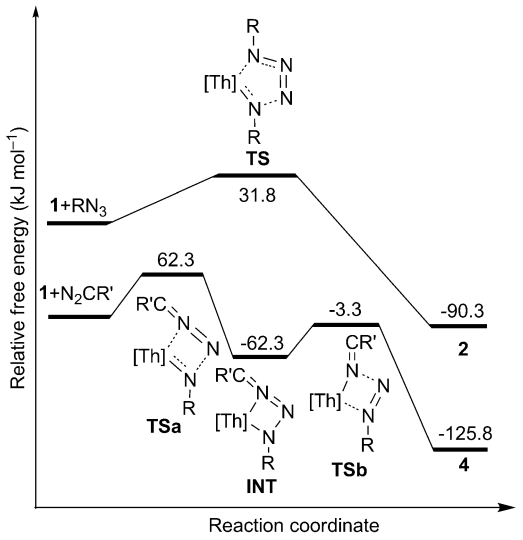


Figure 5. Free-energy profile (kJ mol^{-1}) obtained at the B3PW91-PCM + D3 level of theory for the reactions **1** + *p*-$N_3C_6H_4CH_3$ and **1** + $(C_{12}H_8)CN_2$. [Th] = {η^5-1,2,4-$(Me_3C)_3C_5H_2$}$_2$Th, R = *p*-tolyl, R′ = $C_{12}H_8$.

since the activation barrier for the formation of **4** from **INT** is only 59.0 kJ mol^{-1}. This result is also consistent with the experimental observation, since **INT** could not be isolated from the reaction mixture, and only **4** was observed by NMR spectroscopy.

In conclusion, the first examples of cycloaddition reactions between a terminal actinide imido complex and an organic azide or a diazoalkane were studied comprehensively. In contrast to the reactivity of zirconium[6e] and niobium[7c] imido complexes, organic azides, such as *p*-azidotoluene, were added irreversibly to the thorium imido complex [{η^5-1,2,4-$(Me_3C)_3C_5H_2$}$_2$Th=N(*p*-tolyl)] (**1**), thus supporting the notion that Th^{4+} behaves more like an actinide than a transition metal.[8c] However, the reaction of **1** with 9-diazofluorene resulted in nitrogen-atom transfer to the Th=NR moiety and the formation of a diazenido iminato metallocene **4**. DFT studies revealed that in the former case a [2+3] cycloaddition reaction takes place to give the tetraazametallacyclopentene **2**, whereas in the latter case the η^2-diazenido iminato **4** is formed in a [2+2] cycloaddition reaction. The development of new actinide imido complexes and the exploration of the thorium nitrilimido complex **5** in organic synthesis are ongoing projects in these laboratories.

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