

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

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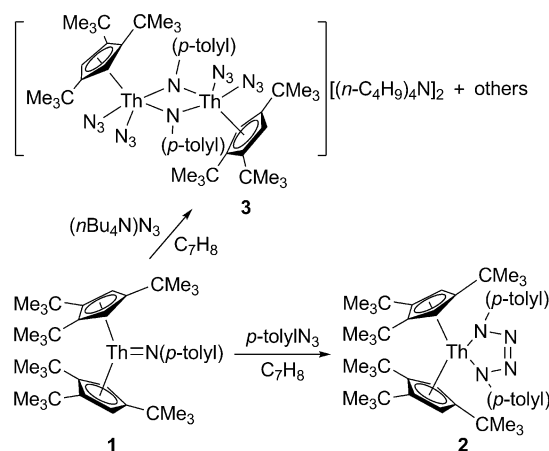
Dedicated to Professor Changtao Qian on the occasion of his 80th birthday

Abstract: The reaction of the base-free terminal thorium imido complex $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th=N(p-tolyl)}]$ (**1**) with *p*-azidotoluene yielded irreversibly the tetraazametallacyclopentene $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th(N(p-tolyl)N=N-N(p-tolyl))}]$ (**2**), whereas the bridging imido complex $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th(N}_3)_2\{\mu\text{-N(p-tolyl)}\}_2\{[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\}]$ (**3**) was isolated from the reaction of **1** with $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{N}_3$. Unexpectedly, upon the treatment of **1** with 9-diazafluorene, the NN bond was cleaved, an N atom was transferred, and the η^2 -diazenido iminato complex $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th}\{\eta^2\text{-[N=N(p-tolyl)]}\}\{\text{N=(9-C}_{13}\text{H}_8)\}\}]$ (**4**) was formed. In contrast, the reaction of **1** with $\text{Me}_3\text{SiCHN}_2$ gave the nitrilimido complex $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th}\{\text{NH(p-tolyl)}\}\{\text{N}_2\text{CSiMe}_3\}]$ (**5**), which slowly converted into $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}\{\eta^5\text{-}\kappa\text{-N-}1,2\text{-(Me}_3\text{C)}_2\text{-4-CMe}_2\text{(CH}_2\text{NN=CHSiMe}_3\text{C}_5\text{H}_2\text{)}\}\text{Th}\{\text{NH(p-tolyl)}\}]\}$ (**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,^[3],4] and therefore the exploration of their intrinsic reactivity is still in its infancy.^[4] Thorium possesses the electronic ground state $[\text{Rn}] 6\text{d}^2 7\text{s}^2$, 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 $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th=N(p-tolyl)}]$ (**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 $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th=E}]$ ($\text{E} = \text{O}, \text{S}$) by cycloaddition–elimination reactions with $\text{Ph}_2\text{C=E}$ ($\text{E} = \text{O}, \text{S}$) 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 $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th}\{\text{N(p-tolyl)N=N-N(p-tolyl)}\}]$ (**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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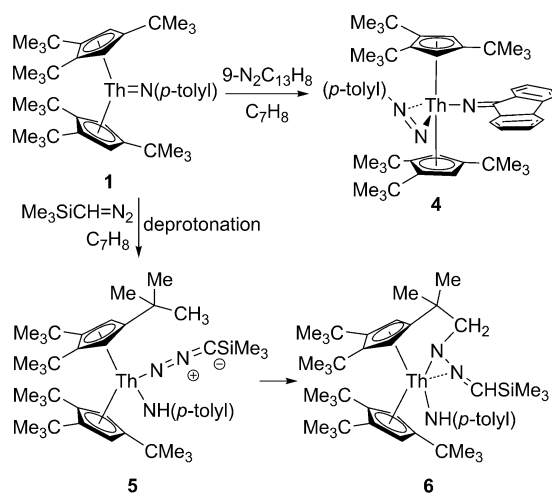
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imido compounds. However, in contrast to those of zirconium^[6e] and niobium^[7c] imido complexes, the reaction of **1** with organic azides is irreversible, as demonstrated by variable-temperature ¹H NMR spectroscopic investigations (20–100 °C). This 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*-C₄H₉)₄N]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 $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}(\text{N}_3)_2\{\mu\text{-N}(p\text{-tolyl})\}_2][(\text{n-C}_4\text{H}_9)_4\text{N}]_2$ (**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-diazo fluorene yielded the η^2 -diazenido iminato metallocene $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}\{\eta^2\text{-[N=N}(p\text{-tolyl})]\}\{\text{N}=(9\text{-C}_{13}\text{H}_8)\}]$ (**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 Me₃SiCHN₂, which contains an α -H atom, was used as the diazoalkane, the nitrilimido complex $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}\{\text{NH}(p\text{-tolyl})\}\{\text{N}_2\text{CSiMe}_3\}]$ (**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.^[5c] Although complex **5** was stable at 100 °C for 1 week, a small amount (5 %) of $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\{\eta^5\text{-}\kappa\text{-N-}1,2\text{-(Me}_3\text{C)}_2\text{-4-CMe}_2\text{(CH}_2\text{NN=CHSiMe}_3\text{)}_2\}\text{Th}\{\text{NH}(p\text{-tolyl})\}]$ (**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).

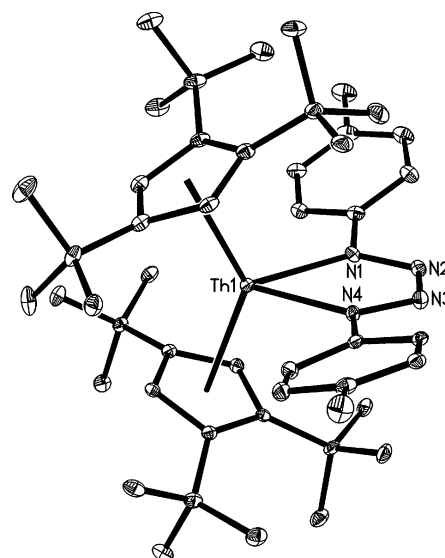


Figure 1. Molecular structure of **2** (with thermal ellipsoids drawn at the 35 % probability level).

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 Th⁴⁺ 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 $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}\{\text{N}(p\text{-tolyl})\text{C(S)–S}\}]$ (2.347(6) Å)^[12] and $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}\{\text{N}(p\text{-tolyl})\text{C–N(Ph)–S}\}]$ (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 ThN₄ ring is essentially planar, and the coordination environment at N(1) and N(4) is trigonal-planar (sum of the angles: 359.6°). This ThN₄ metallacycle may be compared to the C₂N₂Th moiety in the diazabutadiene complex $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NC(Me)=C(Me)N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)]\text{Th}(\text{thf})$.^[16]

Single-crystal X-ray diffraction analysis of **3** showed well-separated, alternating layers of discrete tetrahedral [(*n*-C₄H₉)₄N]⁺ cations and $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}(\text{N}_3)_2\{\mu\text{-N}(p\text{-tolyl})\}_2]^{2-}$ anions. The anion is centrosymmetric, and the Th⁴⁺ 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(N₃) distance of 2.411(3) Å. Overall, these metric parameters can be compared to those found in **2**. The separation of the two Th⁴⁺ cations is 3.697(1) Å, which is longer than the distance found in $[[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]\text{Th}_2(\mu\text{-O})_2]$ (3.546(1) Å).^[12]

The molecular structure of **4** is shown in Figure 3. The Th⁴⁺ ion also adopts a distorted-trigonal-bipyramidal geometry, with coordination by two η^5 -bound Cp rings, a σ -

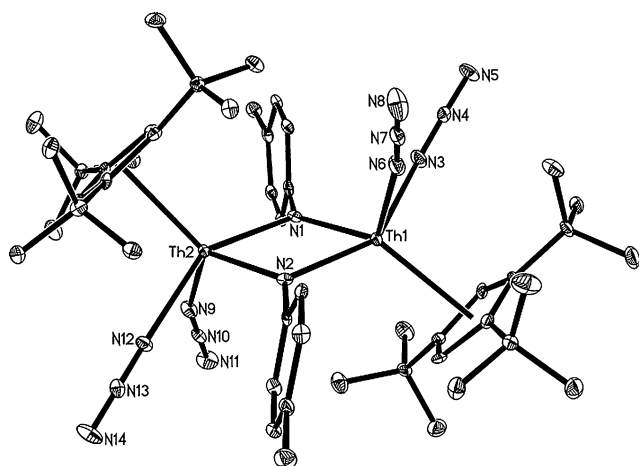


Figure 2. Molecular structure of the anion in **3** (with thermal ellipsoids drawn at the 35 % probability level).

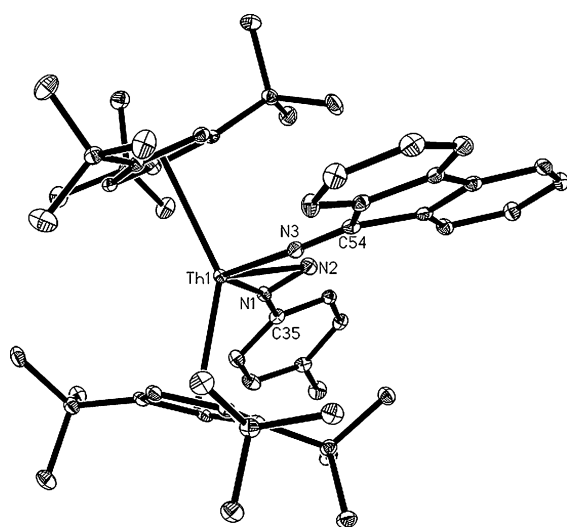


Figure 3. Molecular structure of **4** (with thermal ellipsoids drawn at the 35 % probability level).

coordinated nitrogen atom from the iminato group $\{N=(9-C_{13}H_8)\}$, and two nitrogen atoms of the η^2 -bound diazenido group $\{N=N(p\text{-tolyl})\}$. 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 $[(\eta^5-C_5H_5)_2Ti\{N_2C(CO_2Et)_2\}]$ (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 Th⁴⁺ ion is η^5 -bound to two Cp rings, σ -coordinated to the

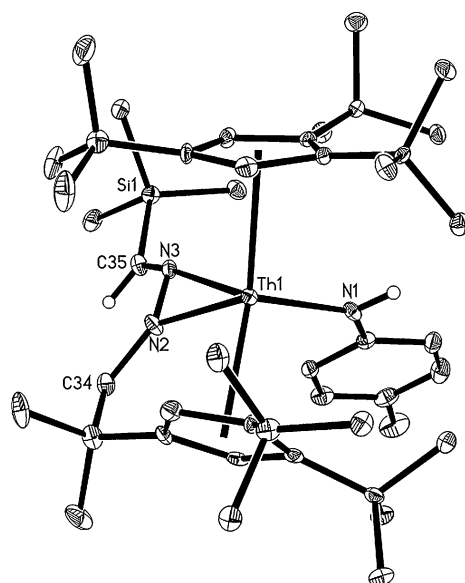


Figure 4. Molecular structure of **6** (with thermal ellipsoids drawn at the 35 % probability level).

nitrogen atom of the $\{NH(p\text{-tolyl})\}$ 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 $\Delta G(298\text{ K}) = -90.3\text{ kJ mol}^{-1}$ 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 $\Delta G^\ddagger = 31.8\text{ kJ mol}^{-1}$ (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 ($\Delta G(298\text{ K}) = -62.3\text{ kJ mol}^{-1}$) 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 ($-125.8\text{ kJ mol}^{-1}$) than the intermediate **INT** (-62.3 kJ mol^{-1} ; Figure 5). Moreover, the potential-energy profile suggests a short lifetime for **INT**,

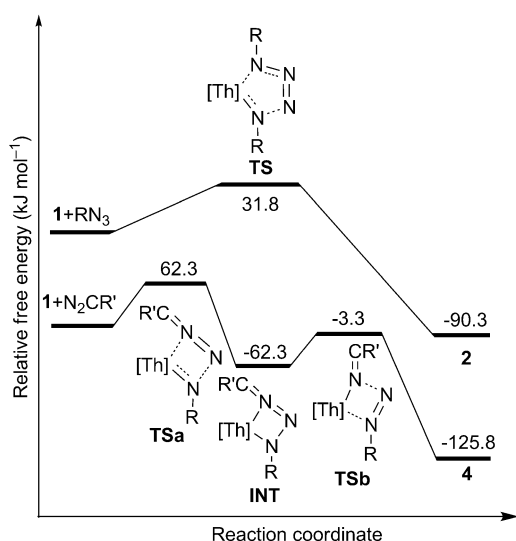


Figure 5. Free-energy profile (kJ mol^{-1}) obtained at the B3PW91-PCM + D3 level of theory for the reactions $1 + p\text{-N}_3\text{C}_6\text{H}_4\text{CH}_3$ and $1 + (\text{C}_{12}\text{H}_8)\text{CN}_2$. $[\text{Th}] = \{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th}$, $\text{R} = p\text{-tolyl}$, $\text{R}' = \text{C}_{12}\text{H}_8$.

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 $[\{\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\}_2\text{Th}=\text{N}(p\text{-tolyl})]$ (**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 $\text{Th}=\text{NR}$ 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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