Actinide-mediated coupling of 4-fluorobenzonitrile: synthesis of an eight-membered thorium(IV) tetraazametallacycle†

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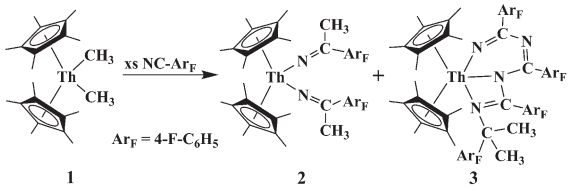
An eight-membered thorium(IV) tetraazamacrocycle is produced by the sequential, metal-mediated coupling of four equivalents of 4-fluorobenzonitrile; its formation is consistent with the involvement of an imido intermediate, generated from a thorium ketimide complex.

Over the past decade, there has been a growing interest in actinide molecular chemistry as 5f systems continue to generate a variety of novel structural motifs, and demonstrate unusual and fascinating reactivity patterns, including the activation and coupling of small molecules.[1] Recently, we reported that benzonitrile inserts into actinide–carbon bonds in complexes of the type $(C_5Me_5)_2AnR_2$ to afford bis(ketimide) complexes $(C_5Me_5)_2An[–N{=}C(Ph)(R)]_2$ (where An = Th, U; R = CH_3, CH_2Ph, Ph), which exhibit interesting physicochemical properties, consistent with enhanced covalency in the actinide–ketimide linkages.[2] Intrigued by the prospect of tuning the relative energies of the metal 5f- and 6d-orbitals by varying the electronic profile of the ketimide ligands, we extended this chemistry to include fluorinated nitriles, and discovered a new thorium-mediated reaction sequence that involves the coupling of four equivalents of 4-fluorobenzonitrile to yield an unusual eight-membered Th(IV) tetraazametallacycle.

Actinide complexes possessing fluorinated ligands are rare. This is based chiefly upon the perception that the fluorophilic actinide metal centers will engage in fluoride abstraction, which will shut down any productive chemistry.[3] However, as illustrated in eqn. (1), treatment of $(C_5Me_5)_2Th(CH_3)_2$ (**1**) with excess 4-fluorobenzonitrile yielded the expected bright yellow bis(ketimide) complex $(C_5Me_5)_2Th[–N{=}C(CH_3)(4\text{-}F–C_6H_4)]_2$ (**2**) as the major product (48% isolated), in addition to the novel orange-red Th(IV) tetraazamacrocycle (**3**) (3% isolated). Following work-up and crystallization from cold pentane solution, both complexes were reproducibly isolated in an analytically pure form, and were characterized by a combination of $^1H/^{13}C/^{19}F$ NMR and UV-vis/NIR spectroscopy, electrochemistry, elemental analysis and X-ray crystallography.‡



(1)

The molecular structure of **2** is shown in Fig. 1. The salient metrical parameters for this complex, namely the Th(1)–N(1) distance of 2.250(2) Å, the N(1)–C(11) distance of 1.260(3) Å and the Th(1)–N(1)–C(11) angle of 175.29(19)°, all compare well to those presented by the other two previously reported Th(IV) ketimide structures.[2c] The isolation of complex **2** further demonstrates the generality of this nitrile insertion chemistry for the preparation of actinide ketimide complexes.

Confirmation that the Th(IV) metal center had coupled together four equivalents of 4-fluorobenzonitrile and formed the eight-membered tetraazametallacycle **3** was obtained by a single-crystal X-ray crystallography study (Fig. 2). The molecular structure reveals that the thorium atom is 9-coordinate, adopting a characteristic bent-metallocene geometry, with Th–C_5Me_5 bond lengths of 2.598(5) and 2.577(5) Å and a C_5Me_5(centroid)–Th–C_5Me_5(centroid) bond angle of 133.7(5)°. These values are well within the range typically found for $(C_5Me_5)_2$Th(IV) complexes.[2c,4] The dianionic tetraaza ligand is contained within the metallocene wedge and consists of alternating C–N units, originating from the four 4-fluorobenzonitrile molecules. The ligand is bound to the thorium metal center in an η^3-(*N*,*N′*,*N″*)-fashion through two Th–N σ-bonds (Th(1)–N(2) and Th(1)–N(4)) and one Th–N dative interaction (Th(1)–N(1)).

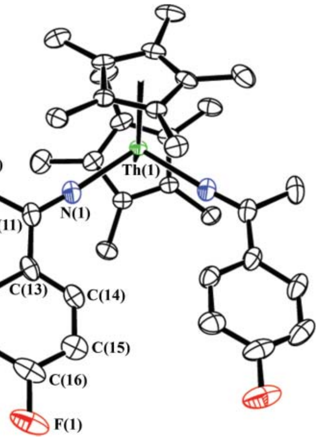


Fig. 1 Molecular structure of complex **2**, with thermal ellipsoids at the 50% probability level. The molecule has crystallographically imposed two-fold symmetry, with atom Th(1) lying on the two-fold rotation axis. Selected bond distances (Å) and angles (°): Th(1)–N(1) 2.250(2), N(1)–C(11) 1.260(3), N(1)–Th(1)–N(1#) 108.67(11), Th(1)–N(1)–C(11) 175.29(19), Th(1)–C_5Me_5(centroid) 2.543(3), C_5Me_5(centroid)–Th(1)–C_5Me_5(centroid) 143.4(2).†

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† Electronic supplementary information (ESI) available: Full experimental details, crystallographic details, and tables of bond distances and angles for **2** and **3**. See DOI: 10.1039/b614050e

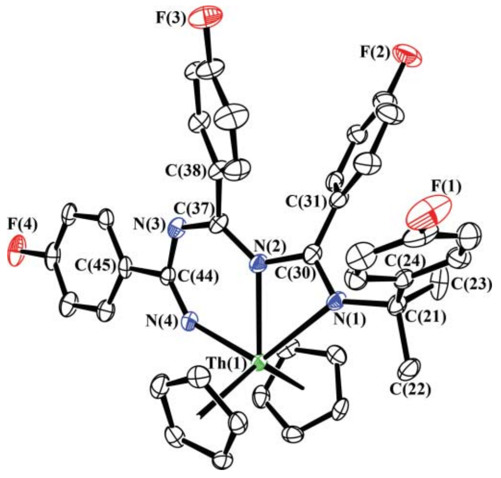
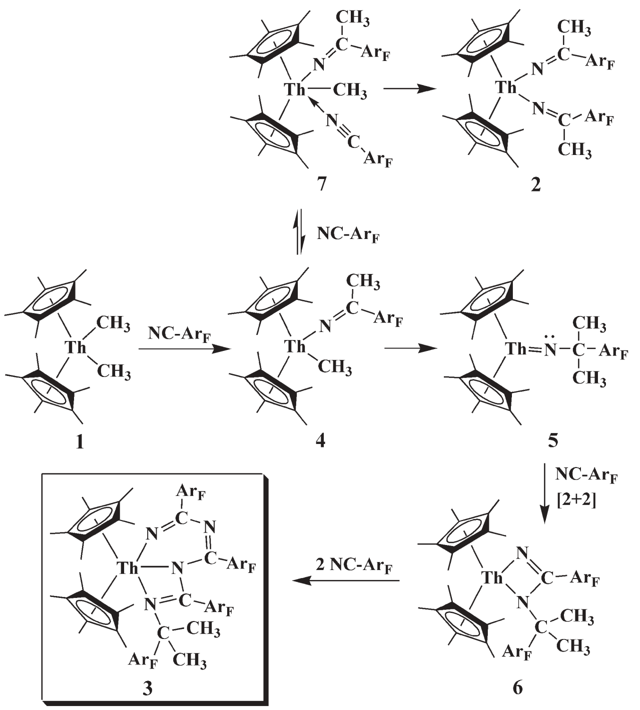


Fig. 2 Molecular structure of complex **3**, with thermal ellipsoids at the 33% probability level. The C_5Me_5 methyl groups have been removed for clarity. Selected bond distances (Å) and angles (°): Th(1)–N(1) 2.727(4), Th(1)–N(2) 2.451(4), Th(1)–N(3) 3.879(4), Th(1)–N(4) 2.234(4), N(1)–C(21) 1.518(6), N(1)–C(30) 1.313(6), C(30)–N(2) 1.378(6), N(2)–C(37) 1.383(6), C(37)–N(3) 1.285(6), N(3)–C(44) 1.406(6), C(44)–N(4) 1.268(6), Th(1)–$C_5Me_{5(cent)}$ 2.598(5), 2.577(5), $C_5Me_{5(cent)}$–Th(1)–$C_5Me_{5(cent)}$ 133.7(5).†

The strong interaction between the anionic sp^2 N(2) and the Th metal center subdivides the eight-membered metallamacrocycle into two smaller ring systems. The six-membered unit is defined by Th(1)–N(4)–C(44)–N(3)–C(37)–N(2). The Th–N(4) distance in **3** is 2.234(4) Å and is in the usual range for a thorium–nitrogen ketimide bond.[2c] The next four contiguous bonds in the ring have distances of 1.268(6) (N(4)–C(44)), 1.406(6) (C(44)–N(3)), 1.285(6) (N(3)–C(37)) and 1.383(6) Å (C(37)–N(2)), showing a pattern of alternating N=C double and C–N single bonds.[5]

The four-membered Th(1)–N(1)–C(30)–N(2) moiety in **3** is best described as a thorium 1,3-diazaallyl. The Th(1)–N(2) bond distance of 2.451(4) Å lies at the high end of the range of Th–N bond lengths reported for other Th(IV) amide complexes,[2c,4b,6] and the Th(1)–N(1) bond distance of 2.727(4) Å is consistent with a Th–N dative interaction.[7] The N(1)–C(30) and C(30)–N(2) distances, of 1.313(6) and 1.378(6) Å, respectively, are intermediate between N–C single and N=C double bonds, implying some electronic delocalization over the 1,3-diazallyl N–C–N fragment.[5] Additional evidence for this is provided by the observation that the angles around N(2) sum to 360°, consistent with a planar sp^2-hybridized nitrogen atom. The sum of this structural evidence allows for the representation of the macrocyclic ligand shown in Scheme 1.

As expected for Th(IV) systems, the electrochemistry observed for complexes **2** and **3** are strictly due to ligand-based processes (Fig. 3).[2b] For the metallacycle **3**, two reversible reduction waves are observed at $E_{1/2} = -2.22$ and -2.56 V, and an irreversible reduction step is found at $E_{p,c} = -3.05$ V (all *vs.* $[(C_5H_5)_2Fe]^{+/0}$). This contrasts with the electrochemistry seen for complex **2**, which is dominated by an irreversible reduction process ($E_{p,c} = -2.53$ V), and with previously characterized non-fluorinated thorium bis(ketimide) complexes, having comparable reductions at more negative potentials (~ -2.8 to -3.0 V).[2] The additional reversible reductions observed for complex **3** are attributed to the ability of the conjugated tetraaza ligand framework to stabilize negative charge by means of new low-lying π^* orbitals.



Scheme 1 Proposed reaction pathway for the formation of the thorium metallamacrocycle **3**. Ar_F = 4-F–C_6H_4.

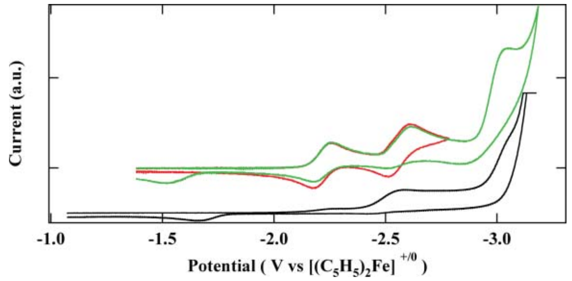


Fig. 3 Cyclic voltammograms for **2** (black) and **3** (green/red) in ~0.1 M $[Bu_4N][B(C_6F_5)_4]$/THF at a Pt disk electrode. The scan rates are all 200 mV s^{-1}.

Several new C–C and C–N bonds are formed in complex **3** at room temperature. A possible mechanism for the formation of **3** is given in Scheme 1. Nitrile insertion into the thorium–methyl bond of complex **1** would lead to the formation of the thorium ketimide complex **4**.[2,8] A 1,3-migration[9] of the thorium methyl group would generate thorium imido complex **5**, which undergoes a [2 + 2] cycloaddition with another equivalent of nitrile to give the diazathoracyclobutene **6**.[10] Subsequent insertion of two equivalents of nitrile into the thorium ketimide (Th–N=C) functional group[11] would afford the thorium macrocycle product **3**.

Clearly, the key step in this sequence is the ketimide to imido transformation, resulting from a 1,3-migration of the methyl group from the thorium metal center to the imino carbon on the ketimide ligand. Although this transformation has no precedent, it is reminiscent of the intramolecular 1,3-migrations of alkyl groups from Ti and Zr to the electrophilic imino carbon (M–N=C) in tetradentate Schiff base and dibenzotetramethyltetraazaannulene complexes.[12]

Unlike their uranium counterparts, thorium imido complexes remain exceedingly scarce but have been implicated as reactive intermediates in numerous catalytic cycles for the oligomerization and hydroamination of alkynes.[13] To date, efforts to stabilize the putative imido complex **5** have proven unsuccessful, since the insertion of two equivalents of nitrile to give the thermodynamically preferred bis(ketimide) complex **2** takes place, even with a deficiency of nitrile. Furthermore, attempts to increase the yield of **3** by using deficient or excess nitrile and a large dilution of reagents have not changed the observed ratio of products. We are currently exploring avenues to overcome the low yield of this interesting reaction, and are examining the synthetic versatility of this chemistry in the context of using actinide ketimide and imido complexes for the synthesis of new C–N bonds.

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Notes and references

‡ Reactions and manipulations were performed at 21 °C in a recirculating Vacuum Atmospheres Model HE-553-2 inert atmosphere (N_2) dry box with a MO-40-2 Dri-Train, or using standard Schlenk and high vacuum line techniques.

Synthesis of $(C_5Me_5)_2Th[–N{=}C(4\text{-}F–C_6H_4)–N{=}C(4\text{-}F–C_6H_4)–N–C(4\text{-}F–C_6H_4){=}N–C(4\text{-}F–C_6H_4)(CH_3)_2]$ (3): A toluene solution (10 mL) of 4-fluorobenzonitrile (0.54 g, 4.75 mmol) was slowly added to a toluene solution (30 mL) containing $(C_5Me_5)_2Th(CH_3)_2$ (**1**) (0.54 g, 1.02 mmol). The reaction mixture immediately changed color from clear and colorless to bright yellow. The solution was stirred for 14 h and the volatiles removed under reduced pressure. The resulting yellow residue was extracted with pentane (40 mL) and filtered through a Celite-packed coarse-porosity frit. The yellow filtrate was stored at −30 °C for 3 weeks, during which time the product deposited as orange-red crystals, accompanied by a yellow powder of (**2**). The macrocycle product (**3**) was isolated by removing the crystals by pipette, collecting them by vacuum filtration, washing with pentane (3 × 2 mL), and drying them under reduced pressure. Yield 0.030 g, 3%. ^1H NMR (toluene-d_8, 300 MHz): δ 8.63 (dd, J_{HH} = 8.4 Hz, J_{HF} = 6.0 Hz, 2 H, *meta*), 7.28 (dd, J_{HH} = 8.4 Hz, J_{HF} = 5.4 Hz, 2 H, *meta*), 7.18 (dd, J_{HH} = 8.1 Hz, J_{HF} = 5.7 Hz, 2 H, *meta*), 7.04 (m, 2 H, *meta*), 6.90 (t, J_{HH} = 8.4 Hz, 2 H, *ortho*), 6.49 (t, J_{HH} = 8.4, 2 H, *ortho*), 6.16 (t, J_{HH} = 7.5 Hz, 2H, *ortho*), 6.06 (t, J_{HH} = 8.4 Hz, 2 H, *ortho*), 2.13 (s, 30 H, $C_5(CH_3)_5$) and 1.33 (s, 6 H, CH_3). ^{13}C NMR (toluene-d_8, 75 MHz): δ 176.6 (s, N=*C*), 164.7 (d, Ar–*C*, J_{CF} = 248.3 Hz), 163.2 (d, Ar–*C*, J_{CF} = 248.3 Hz), 162.8 (d, Ar–*C*, J_{CF} = 251.3 Hz), 162.4 (d, Ar–*C*, J_{CF} = 246.8 Hz), 158.3 (s, N=*C*), 155.5 (s, N=*C*), 149.1 (d, Ar–*C*, J_{CF} = 3.8 Hz), 140.5 (d, Ar–*C*, J_{CF} = 3.8 Hz), 135.5 (d, Ar–*C*, J_{CF} = 3.8 Hz), 132.2 (d, Ar–*C*, J_{CF} = 8.3 Hz), 130.9 (d, Ar–*C*, J_{CF} = 8.3 Hz), 130.6 (d, Ar–*C*, J_{CF} = 7.5 Hz), 128.2 (s, Ar–*C*), 125.1 (s, $C_5(CH_3)_5$), 115.8 (s, Ar–*C*), 115.5 (s, Ar–*C*), 115.2 (s, Ar–*C*), 114.9 (s, Ar–*C*), 114.7 (s, Ar–*C*), 14.6 (s, CH_3), 23.2 (s, $C(CH_3)_2$) and 12.9 (s, $C_5(CH_3)_5$). ^{19}F NMR (toluene-d_8, 282 MHz): δ −111.61 (m, Ar–*F*), −113.79 (m, Ar–*F*), −114.22 (m, Ar–*F*) and −116.37 (m, Ar–*F*). Anal. calc. for $C_{55}H_{64}N_4F_4Th$: C, 60.65; H, 5.92; N, 5.14. Found: C, 60.46; H, 5.95; N, 5.07%.

Crystal structure data for 2: $C_{36}H_{44}F_2N_2Th$, M = 774.77, monoclinic, space group $C2/c$ (no. 15), a = 12.9201(6), b = 14.0054(7), c = 18.2113(9) Å, β = 98.677(1)°, V = 3257.6(3) Å^3, T = 141(2) K, Z = 4, μ(Mo-K$_\alpha$) = 4.615 mm^{-1}, λ = 0.71073 Å, 17967 reflections measured, 4014 unique (R_{int} = 0.0222), which were used in all calculations. Final R_1 = 0.0197, w$R(F^2)$ = 0.0488 (all data). CCDC 622496.

Crystal structure data for 3: $C_{50}H_{52}F_4N_4Th{\cdot}C_5H_{12}$, M = 1089.14, monoclinic, space group $C2/c$ (no. 15), a = 24.6845(13), b = 18.9028(10), c = 20.7781(11) Å, β = 95.014(1)°, V = 9658.1(9) Å^3, T = 141(2) K, Z = 8, μ(Mo-K$_\alpha$) = 3.144 mm^{-1}, λ = 0.71073 Å, 40160 reflections measured, 9059 unique (R_{int} = 0.0631), which were used in all calculations. Final R_1 = 0.0505, w$R(F^2)$ = 0.0985 (all data). Disordered solvent molecules were treated using PLATON/SQUEEZE.[14] CCDC 622495. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b614050e

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