Double Reduction of 4,4′-Bipyridine and Reductive Coupling of Pyridine by Two Thorium(III) Single-Electron Transfers


Abstract: The redox chemistry of uranium is burgeoning and uranium(III) complexes have been shown to promote many interesting synthetic transformations. However, their utility is limited by their reduction potentials, which are smaller than many non-traditional lanthanide(II) complexes. Thorium(III) has a greater redox potential so it should present unprecedented opportunities for actinide reactivity but as with uranium(II) and thorium(II) chemistry these have not yet been fully realized. Here we present reactivity studies of two equivalents of [Th(Cp′)2]1 (Cp′ = {C5H5(SiMe3)2-1,3}) with 4,4′-bipyridine or two equivalents of pyridine to give [Th(Cp′)2]1[µ-(NC2H4)]2 (2) and [Th(Cp′)2]1[µ-(NC3H5)]2 (3), respectively, which contain doubly reduced substrates. As relatively large reduction potentials are required to effect these transformations we have shown that thorium(III) can promote reactions that uranium(III) cannot, opening up promising new reductive chemistry for the actinides.

Deepening our understanding of the actinides is crucial for the future development of bulk processes associated with nuclear fuel cycles.[1] For example, improved knowledge of reduction potentials developed during the Manhattan project led to the patenting of the PUREX (Plutonium Uranium Redox Extraction) process for selective plutonium extraction.[2] Whilst the reduction potentials of actinides in acidified aqueous solution are well established,[3] these differ markedly for molecular systems and this area is poorly developed for ThIII[4] compared to UIII complexes, which have been shown to promote many interesting synthetic transformations.[5] This disparity needs to be addressed as the pace of development of thorium nuclear power continues to intensify.[6] Molecular thorium chemistry is dominated by the +4 oxidation state and there are few examples of structurally characterized ThIV:[7] and ThIII:[7a,8] complexes. As with ThIII chemistry, the reactivity of UIII and ThIII complexes is currently limited to only a handful of examples.[7a,7b] Standard reduction potential data indicates that ThIII should be far more reducing than UIII [E0 ThiV → ThiII = −3.7 V, cf. UIV → UIII = −0.6 V][7a] but the enhanced reducing power of a ThIII complex over a comparable UIII complex in non-aqueous conditions has not been proven experimentally to date.[7b,8] Therefore, we envisaged that the treatment of [Th(Cp′)2]1 (Cp′ = {C5H5(SiMe3)2-1,3})[8a] with pyridine and 4,4′-bipyridine (4,4′-bipy) would define its reducing capability as the reduction potentials of these N-heterocycles are well-established (E1/2 in DMF/0.1 M N’Bu4Cl vs. Ag/AgCl: py = −2.76 V; 4,4′-bipy = −1.91 and −2.47 V)[10] and the reduction of these substrates has not previously been mediated by any UIII complex.[9] However, LnIII (Ln = lanthanide) chemistry is now blossoming[11] and the reducing couple of N-heterocycles by LnIII (Ln = Sm, Tb, Yb) complexes has been studied in depth previously.[12] It is noteworthy that Berthet, Ephrakhine and co-workers have shown that UIII can reduce 2,4,6-tris(2-pyridyl)-1,3,5-triazine[13] and [U(Cp’)]2 (Cp’ = {C5H5SiMe3}) can reduce pyrazine.[14] Germane to this study ThIV complexes containing direduced 2,2′-bipy have been reported by Walter and Zic[15-17] and Arnold,[18] and uranium complexes containing mono-reduced 2,2′-bipy have been reported by Bart[19] and Cummins.[20]

Two equivalents of 1 doubly reduce 4,4′-bipy and redox couple two equivalents of pyridine to yield [Th(Cp′)2][µ-(NC2H4)]2 (2) and [Th(Cp′)2][µ-(NC3H5)]2 (3), respectively (Scheme 1). Although selected LnIII (Ln = Sm, Tb, Yb)[22a-c] and ScIII arene[25] complexes can redox-couple pyridine, Ephrakhine and co-workers have shown by single crystal XRD studies that the comparable UIII complexes [U(Cp’)]2 and [U(Cp’)]2 (Cp’ = {C5H5SiMe3}) do not reduce pyridine[14,22] or 4,4′-bipy.[23] The formulations of 2 and 3 were confirmed by single crystal XRD (Figures 1-2), 1H, 13C{1H} and 29Si{1H} NMR spectroscopy and elemental analysis (see Supporting Information). The only structurally authenticated thorium complexes containing 4,4′-bipy are [Th(C5H5)2(4,4′-bipy)],[21] [Th[OTerMS]2(µ3-BH4)][21] and [Th[OTerMS]2(µ3-BH4)][21] and [Th[OTerMS]2(BH4)[21] have which neutral 4,4′-bipy units. It is noteworthy that ThIV complexes containing direduced 2,2′-bipy previously reported in the literature[15-18] have to date exclusively been prepared by reduction of ThIV precursors with KNC (E1/2 in DMF/0.1 M N’Bu4Cl vs. Ag/AgCl: 2,2′-bipy = −2.19 and −2.76 V)[10] Complex 1 does not react with polyaromatics with smaller reduction potentials such as anthracene (E1/2 = −1.98 V) or naphthalene (E1/2 = −2.60 V)[26] indicating that coordination is necessary for electron transfer.

Scheme 1. Synthesis of 2 and 3 from 1: i) 0.5 eq 4,4′-bipy, toluene, 18 h; ii) pyridine, toluene, 5 d.

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Supporting information for this article is available on the WWW.
The UV-Visible spectra of 2 and 3 (0.1 mM in toluene) were collected between 200-1400 nm (see Supporting Information). Complex 2 exhibits a strong broad absorbance centered at 444 nm (ε = 19,400 M⁻¹ cm⁻¹), assigned as a π-π* transition in the conjugated π-system, which is absent in 3. A sample of 3 (0.5 mM in toluene) was left to stand for four days at ambient temperature to develop an intense blue colour. The UV-vis spectrum of this sample was collected and the absorptions are comparable with an authentic sample of 1.[8b]

Powder X-band and Q-band EPR spectra of 3 were collected at 298 K (see Supporting Information). These spectra are consistent with an organic radical (g = 2), which we tentatively attribute to the presence of \([\text{Th}(_{2}\text{Cp})_{2}(\text{py})])\). No additional features could be modelled when the X-band spectrum was collected at 5 K. In contrast, the frozen solution X-band EPR of 3 in toluene at 40 K gave a spectrum with axially symmetric g values (g axial = 1.975; g perpendicular = 1.877) (see Supporting Information). These values correspond well with data previously reported for frozen solution EPR spectra of 1 in methylcyclohexane collected from 10–100 K [g axial = 1.9725(10); g perpendicular = 1.879(1)][6b].

As an equilibrium mixture of compounds forms almost immediately (<10 mins) when 3 is dissolved in [D₆]toluene, we could not extract kinetic parameters for the reverse reaction by ¹H NMR spectroscopy. However, an equilibrium constant, Kₑ, at 298 K was determined after the solution was left for five days at room temperature to equilibrate by comparing the ¹H NMR integrals of pyridine with those attributed to arise from 3 (Kₑ = 0.5 mol dm⁻³). The value of this constant did not change when the ¹H NMR spectrum was collected at 303 K or 313 K. In an attempt to show that \([\text{Th}(_{2}\text{Cp})_{2}(\text{py})])\) is an intermediate in the formation of 3 a [D₆]benzene solution of 1 containing 2 eq. pyridine was treated with excess 1,4-cyclohexadiene. No benzene or H₂ was observed in the ¹H NMR spectra of the reaction mixture and after several days crystals of 3 formed, so an organic radical intermediate could not be unequivocally proven (see Supporting Information). Finally, no products could be identified from the treatment of 1 with 2 eq. 4-tert-butylypyridine in [D₆]benzene using ¹H NMR spectroscopy. This reaction mixture retained the intense blue colour associated with solutions of 1, even upon heating to 323 K for 16 hours (see Supporting Information).

The reversible C–C bond formation in 3 is analogous to the reactions of the Fe³⁺ complexes [Fe₃(µ₂-NC₃H₄)][(C₆H₅)] (Ar = C₆H₅Pr₂-2,6) or [Fe₃(µ₂-(ArNC(Me))₂)][(µ₂-N₂)] with pyridine. Both reactions gave an Fe⁶⁺ product containing 4,4'-dihydrobis(4,4'-pyridine)-1,1'-diyl, \([\text{Fe}((\text{ArNC}(\text{Me}))_2)_2][\text{µ}_2-\text{N}_2])\), which exhibits a monomer-dimer equilibrium in solution.[27] Pyridine reduction by highly reducing Ln⁴⁺ systems is well-established[9b] but reversible C–C bond formation of an f-element complex containing a reduced unsubstituted pyridine ligand has not previously been observed to the best of our knowledge, although this has been seen for other N-heterocycles.[28] Unsurprisingly, 2 does not react with pyridine to give 3 as the reduction potential of 4,4'-bipy is less negative than that of pyridine and 1.[10a] In contrast, we found that a [D₆]benzene solution of 3 reacts sluggishly with 4,4'-bipy to give 2 and pyridine. The slow rate of this reaction can be attributed to the equilibrium of 3 with 1 and
pyridine, with competitive binding of pyridine and 4,4′-bipy to the single vacant coordination site of 1 (see Supporting Information).

A notable feature of the structure of 2 is the diagnostic interpyridyl C=C double bond length [1.376(10) Å], which is significantly shorter than those seen in 4,4′-bipy adducts such as [U(Cp)₃]₂[4,4′-bipy] [1.474(17) Å][23] or [Th(C₆H₆)₂(4,4′-bipy)] [1.478(4) Å][24] and is comparable to the distances in other diireduced 4,4′-dihydrbis(4,4′-pyridine)-1,1′-diyl complexes[24] and bis(trimethylsilyl)dihyro-4,4′-bipy [C=C; 1.381(3) Å].[25] The intra-pyridyl bond lengths are also diagnostic of di reduction. The inter-ring C–C distance in 3 [1.562(12) Å] is typical of a single bond and this, together with other heterocyclic ring metrics, is comparable with similar complexes in the literature.[12c–e,21,27] The Th–N distances in 2 [2.359(4) Å] and 3 [2.350(4) Å] are shorter than those in ThIV 4,4′-bipy adducts [range: 2.626(2)-2.707(2) Å][24,25] and are typical of ThIV–N amide bonds, e.g. [Th[N(SiMe₃)₂]₂(BH₄)] [2.32(2) Å].[30]

The electronic structures of 2 and 3 were characterized at the density functional theory (DFT) level, employing the PBE0 exchange-correlation functional and a polarized split-valence basis set for structural optimizations (see Supporting Information for full details). Electronic properties were derived from single-point energy calculations using a polarized valence triple-ζ basis set. Structural parameters were in excellent agreement with experiment, with bond lengths typically deviating from experimental values by less than 0.02 Å (see Supporting Information Table S4), justifying the model chemistry. Further confidence in these models was provided by the bulk features of the UV/visible spectrum of 2 and the IR spectra of 2 and 3 being reproduced with reasonable agreement by calculated values (see Supporting Information Tables S5-7). Inspection of the resultant molecular orbitals reveals the presence of both σ- and π-type Th–N bonding interactions (Figure 3), although the thorium contributions are, as would be expected, small.

The Th–N bond orders, obtained via the quantum theory of atoms in molecules (QTAIM)/Mayer approaches, were calculated to be 0.558/0.767 and 0.573/0.798 for 2 and 3, respectively. NBO analysis failed to identify any Th–N bonding orbitals, presumably due to Th contributions falling below the 5% default threshold, but Th contributions to the orbitals shown in Figure 3 were estimated via QTAIM and Hirshfeld partitioning of the molecular spaces. Both methods predicted small (~2-4%) Th contributions, and 3 was further investigated using QTAIM (See Supporting Information Table S9). All metrics indicate a predominantly ionic Th–N interaction with very similar covalent character. QTAIM metrics suggest a slightly more covalent interaction in 3. This is commensurate with the higher bond order and shorter Th–N bond: combined these measures indicate a stronger Th–N bond in 3. Th–N bond elipticities were calculated to be 0.29 and 0.27 for 2 and 3, respectively. When compared to those of benzene (0.23) and ethylene (0.45) these values indicate a degree of double bond character in the Th–N bonds of 2 and 3.

To conclude, we have demonstrated that two equivalents of the ThIV complex 1 promote the double reduction of 4,4′-bipyridine and the reductive coupling of pyridine. This work shows that ThIV complexes can exhibit reductive chemistry of the order of non-traditional LnIII systems, opening up new reductive chemistry for the actinides. The consequence is that the reductive small molecule activation chemistry of ThIV, thus far burgeoning only for UVI in the actinide series, should yield contrasting and fascinating results in future.

Experimental Section

Full synthetic details, characterization data and computational data for 2-3 is available in the Supporting Information. Additional research data supporting this publication are available from The University of Manchester eScholar repository at DOI:10.15127/1.302738.

Acknowledgements

We acknowledge the Engineering and Physical Sciences Research Council (grant numbers EP/K039547/1, EP/L014416/1 and EP/J002208/2), the Nuclear FIrST DTC, the EPSRC UK National Electron Paramagnetic Resonance Service and the University of Manchester for supporting this work.

Keywords: thorium • N ligand • subvalent compounds • reduction • electron transfer

Figure 3: Selected MOs of 2 and 3, exhibiting either Th–N σ- or σ-bonding character. All MOs rendered using an isosurface value of 0.015 a.u.


The Mighty Thorium: The reductive chemistry of the thorium(III) complex, \([\text{Th(C}_3\text{H}_5\text{SiMe}_3)_2\text{C}^\text{H}_3-1,3]_3\), is shown to be of the order of non-traditional lanthanide(II) complexes, opening up new reductive chemistry for the actinides.