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Arene-ligated Heteroleptic Terphenolate Complexes of Thorium

Jamie McKinven, Gary S. Nichol, and Polly L. Arnold

Bulky terphenolate ligands allow the synthesis of rare heteroleptic thorium chloride, and borohydride complexes; in the absence of donor solvents, the terphenolate ligands protect the metal ions through neutral Th-η^6^-arene interactions in a thorium bis (arene) sandwich motif.

Introduction

Homoleptic aryloxide complexes of the actinides have good literature precedent, and have facilitated recent advances in actinide-mediated catalysis and the isolation of actinide compounds in which the metal has a rare assigned oxidation state. However, studies on the synthesis and reactivity of heteroleptic aryloxide complexes of actinides are scant, primarily due to difficulties associated with the ready ligand redistribution processes available to these large metal cations. Terphenolates were developed as particularly bulky ligands over a decade ago to support unusual chemistries and formal oxidation states in d- and p-block elements, whilst the terphenyl substituent has been incorporated as ligand substituents to enhance reactivity, for example enabling the catalytic conversion of dinitrogen to ammonia by molybdenum imido-alkylidene derivatives of the form [Mo(NR)(CHR')(OAr)(Pyr)] (where OAr is a terphenolate and Pyr is a pyrrolide). There are a few examples of their use with actinides: Heteroleptic uranyl \([\text{UO}_2\text{(O}2,6\text{NPh}_2\text{C}_6\text{H}_3)\text{Cl}_2}\text{(THF)}_2]\) or uranium(IV) iodides \([\text{UI}_3\text{(O}2,6\text{NPh}_2\text{C}_6\text{H}_3)\text{(THF)}_2]\) have been reported, but only a homoleptic, unsubstituted tetrakis(terphenolate) Th^IV complex \([\text{Th(O}2,6\text{NPh}_2\text{C}_6\text{H}_3)_4]\) is known. We were interested in the potential for terphenolate ligands to sterically protect a reaction space at a Th^IV centre in which the reactivity of small substrates could be explored. Herein, we describe the first synthesis and characterisation of heteroleptic substituted terphenolate complexes of thorium, and the ability of the ligand ortho-aryl substituents to provide a flexible, additional protection to the Th^IV cation.

Results and Discussion

Synthesis of \([\text{Th(OTerMes}_2\text{Cl}_2\text{(DME)}]\), 1a

The reaction of \(\text{ThCl}_4\text{DME}_2\) and two equivalents of KOTerMes, generated \textit{in situ} by reaction of HOTerMes (C_{24}H_{25}OH) with KH, affords \([\text{Th(OTerMes}_2\text{Cl}_2\text{(DME)}]\), 1a, as an off-white solid in 66 % yield after workup (Equation 1). Single crystals suitable for X-ray diffraction of 1 were grown from a saturated solution of toluene at -30°C; the solid state structure is shown in Figure 1a.

Synthesis of \([\text{Th(OTerMes}_2(\eta^3\text{-BH}_4)_2\text{(DME)}]\), 1b

A salt elimination reaction between 1a and Ca(BH_4)_2(THF)_2 in toluene generates \([\text{Th(OTerMes}_2(\text{H}_3\text{BH}_2)\text{(DME)}]\), 1b as colourless crystals in 63 % yield after workup (Equation 1). The use of Ca(BH_4)_2(THF)_2 as a metathesis precursor for forming thorium borohydride complexes has precedent.
Characterisation of 1a and 1b

Heteroleptic thorium borohydride complexes are rare, with only two other crystallographically characterised examples, [Th(N(SiMe₃)₂)₂(η⁶-BH₄)₃] and [Th(Ind*)₂(η⁶-BH₄)₂] (Ind* = permethylated indenyl) previously reported.¹⁰ ¹⁶ The BH₄ groups are readily identified in the NMR spectra as a broad shoulder under one of the DME proton resonances at 3.03 ppm in the ¹H NMR spectrum, and a poorly resolved pentet at -12.4 ppm in the ¹³B NMR spectrum, which is resolved as a singlet upon proton decoupling. This is consistent with an averaged BH₄ proton environment on the NMR time scale. No boron NMR spectroscopic data were reported for other heteroleptic thorium borohydrides; for comparison the homoleptic thorium borohydrides; for comparison the homoleptic [Th(H₂BH₄)₂]₃ has a ¹³B NMR spectral chemical shift at -19.3 ppm (also a quartet).²¹ The FTIR spectrum of 1b displays weak absorptions consistent with 4-BH₄ binding;²² ν(B–H₃) 2473 and 2455 cm⁻¹ and ν(B–H₅) 2225 and 2164 cm⁻¹. Single crystals suitable for X-ray diffraction of 1b were grown from a saturated solution in toluene at -30°C.

Compound 1a displays pseudo-octahedral geometry around the thorium cation, with two trans-oriented Ter⁶⁺O ligands and a nearly linear O1-Th1-O2 bond angle (179.1(2)°). This is atypical, and presumably a result of the steric bulk of the aryloxides as it is the most linear O-Th-O observed in six-coordinate thorium aryloxide complexes.²³ The Th-O1,2 bonds are 2.180(3) Å, amongst the shortest reported Th-O single bonds, although they are significantly longer than the Th–O bond length of the thorium oxo-complex of 1.929(4) Å (molecular single Th-O bonds in the CSD range from 1.929 to 3.051 Å).²³,²⁴ The solid-state molecular structure of 1b, Figure 1b, is essentially the same as that of 1a, although the O1-Th1-O2 angle of 158.5(2)° is now significantly more bent than in 1a. There is a notable difference between the C11-Th1-C11 angle in 1a, 127.28(7)°, and the B1-Th1-B2 bond angle in 1b, 96.00(2)°, presumably due the greater steric demand of the tridentate borohydride ligand and perhaps due to the greater π-bonding character of BH₄⁻ ligand compared to the Cl⁻ ligand, and its capacity for different bonding modes.²⁵ The Th-O1 bond distance of 2.191(4) Å in 1b, is identical within s.u.s to the analogous bond distance in 1 of 2.180(3) Å.

A variety of experiments were undertaken with the target of removing the coordinated DME solvent from 1. The application of dynamic vacuum (10⁻³ mbar over 12 hours) or heating in non-coordinating solvents (benzene, toluene, hexane) had no effect.

Synthesis of Th(OTerMes)₂(η⁶-BH₄)₂, 2

The treatment of 1a with trimethyl aluminium in toluene also yielded no reaction, but in the case of 1b resulted in the abstraction of DME to afford AlMe₃ and DME and the unusually low-coordinate Th(OTerMes)₂(H₂BH₄)₂, 2, as colourless needles in a 50 % yield after workup (Equation 2). We attribute this surprising contrast in reactivity to a very similar Lewis acidity of the two metal cations which are competing for the DME molecule. The [Th(IV)Cl₂] is a slightly harder, more strongly Lewis acid unit than the [Th(IV)(BH₄)₂] fragment, enabling the Al(III) centre to out-compete the Th(IV) centre for the O donor solvent in just the latter case.

Characterisation of 2

Single crystals suitable for X-ray diffraction were grown by allowing a C₆D₆ solution of 2 to evaporate to dryness. The solid-state structure is displayed in Figure 2; one mesityl ring of each terphenolate ligand now participates in an η⁶-interaction with the thorium ion. The Th(IV) cation is pseudo-octahedral, with the two η⁶-aryl interactions mutually trans, forming a weakly sandwiched thorium bis(arene) fragment. The Th(IV)-arene centroid axis, Cᵗ-Cᵗ₁-Cᵗ₂ is close to linear, at 172.88°. The distance to one of the aranes is very long, and presumably a very weak interaction, characterised by a Th-Cᵗ₁ distance of 4.05(1) Å, whilst the other is short, with a Th-Cᵗ₂ distance of 2.815(3) Å, although still relatively long compared with the few other examples of Th-η⁶-arene interactions (A survey of the CSD found that neutral η⁶-Th-Cᵗ distances in the literature range from 2.706 to 2.950 Å).²³,²₆-²₈ These Th-Cᵗ distances are longer than the macrocyclic neutral phenyl interactions observed in [ThCl₂(κ⁶-NC₆H₄(CH₃)₂)(η⁶-C₆H₆)(Li[DME])₂] and [ThCl₂(κ⁶-NC₆H₄(CH₃)₂)(η⁶-C₆H₆)(μ-PhNNPh)(Li[DME])]+ by Gambarotta et al. The mesityl rings that participate in η⁶-aryl interactions deviate from the parallel by 24.49°. The two O atoms and two B atoms are approximately coplanar, with a deviation of O1TerMes (that which displays the weaker Th-arene interaction) of 28.54° out of the plane. The TerMesO⁻-ligands are cis-disposed as evidenced by the O1-Th1-O2 bond angle of 89.0(3)°, substantially smaller than the corresponding angle in 1b. The
B1-Th1-B2 bond angle of 2, 92.9(7)°, represents a contraction of this angle compared to 1b. The room-temperature $^1$H NMR spectrum of a benzene solution of 2 contains a single environment for the Ter$^{Mes}$O$^-$ protons, suggesting a dynamic equilibrium is present on the NMR timescale that interconverts the free and Th-bound Mes groups. Similarly to 2, the [BH$_4$]$^-$ groups appear as a broad resonance at -0.39 ppm in the $^1$H NMR spectrum and as a poorly resolved pentet at -10.08 ppm in the $^{11}$B NMR spectrum which resolves into a singlet upon proton decoupling. However, the FTIR spectrum of 2 displays weak absorptions characteristic of an $\eta^2$-BH$_4$ binding mode (2500–2200 cm$^{-1}$)$_{22}$ $\nu$(B–H) 2474 cm$^{-1}$ and $\nu$(B–H$_3$) 2216 and 2149 cm$^{-1}$. Hydrogen atoms were not located in the solid-state structure of 2 (Figure 2) but the Th-B distance has increased from 2.640(1) Å in 1b to 2.670(2) Å.

![Figure 2: Displacement ellipsoid drawing of the solid-state molecular structure of 2 (50 % probability ellipsoids). Hydrogen atoms are omitted for clarity.](image)

Synthesis of [Th(OTer$^{Mes}$)$_2$(H$_2$BH$_4$)$_2$(4,4-NC$_6$H$_4$C$_6$H$_4$N)$_2$]$_\infty$, 3

Treatment of 1a with two equivalents of 4,4-bipyridine successfully displaces the coordinated DME to afford a coordination polymer [Th(OTer$^{Mes}$)$_2$(H$_2$BH$_4$)$_2$(4,4-NC$_6$H$_4$C$_6$H$_4$N)$_2$]$_\infty$, 3, which crystallises readily and cleanly out of the reaction mixture as yellow crystals, equation 3. The solid state structure of a single repeat unit of 3 is displayed in Figure 3.

![Figure 3: Displacement ellipsoid drawing of the solid-state molecular structure of the monomeric unit of 3 (50 % probability ellipsoids). Hydrogen atoms and toluene solvent molecules are omitted for clarity.](image)

Characterisation of 3

In 3 the pseudo-octahedral Th$^{IV}$ centre still has two trans-disposed Ter$^{Mes}$ ligands with the same angle (179.00(6)$^\circ$) as in 1a (within s.u.s). In contrast, the two BH$_4$ ligands are also now mutually trans, as evidenced by a B1-Th1-B1 angle of 167.33(10)$^\circ$, allowing the trans-4,4-bipyridine ligation to generate nearly linear 1-D polymeric chains (see Figure 5) in the solid state; the complex crystallises directly from the reaction mixture. The Th1-Th1-Th1 angle of 152.40(5)$^\circ$ shows that there is a significant undulation in the polymeric chain. The two OTer$^{Mes}$ central aryloxide C$_6$ planes are now orthogonal, whereas in 1a, 1b and 2 they are parallel, presumably due to avoid interactions with the coordinated bipyridine. The Th-O bonds are both short, 2.168(2) and 2.210(2) Å, with Th-O1 being shorter, perhaps due to a π-stacking between one of the mesityl rings on OtTer$^{Mes}$ and the 4,4-bipyridyl ligand (Ct1-Ct2 distance 3.74(7) Å). Both Th-O bond lengths, as for 1a, 1b and 2 remain short for Th-O bonds. The Th-N bond distances in 3, of 2.626(2) and 2.644(2) Å, are typical. The [BH$_4$]$^-$ group is observed as a broad resonance at 3.28 ppm in the $^1$H NMR spectrum and as a broad singlet at -6.42 ppm in the $^{11}$B NMR spectrum, which sharpens upon proton decoupling, consistent with an averaged BH$_4^-$ proton environment on the NMR timescale. The FTIR spectrum of 3 contains weak absorptions in the 2500–2200 cm$^{-1}$ region consistent with a (µ-H)$_2$ binding mode.$^{22}$ $\nu$(B–H$_3$) 2454 cm$^{-1}$ and $\nu$(B–H$_3$) 2237 and 2171 cm$^{-1}$. The Th-B bond lengths in 3, of 2.666(3) and 2.673(3) Å, are comparable to those seen in 2 and slightly longer than those in 1b.

![Figure 5](image)

Synthesis of [Th(OTer$^{Mes}$)$_2$(Cl)$_2$(4,4-bipyridyl)$_2$]$_\infty$, 4

Treatment of 1b with two equivalents of 4,4 bipyridine successfully displaces the coordinated DME to afford a coordination polymer [Th(OTer$^{Mes}$)$_2$(Cl)$_2$(4,4-bipyridyl)$_2$]$_\infty$, 4, which crystallises readily and easily out of the reaction mixture as colourless needles, Equation 4. The solid state structure of a single repeat unit of 4 is displayed in Figure 4.

Characterisation of 4

In 4 the Th$^{IV}$ centre has adopts a pseudo-pentagonal bipyramidal structure with 3 N-donor bipyridyl ligands and two chloride ligands in the equatorial plane whilst retaining the two trans disposed OTer$^{Mes}$ ligands at 177.78(11)$^\circ$. In 4 the Cl-Th-Cl angle of 159.24(4)$^\circ$ is wider when compared to 1a, presumably to enable the ligation of three donor ligands in the
equatorial plane. The equatorial ligands show significant deviations from the plane as evidenced by the angles $\angle O_1\text{-Th}_1\text{-X}$ (where X is the bonding atom in the plane.) The $\angle O_1\text{-Th}_1\text{-Cl}$ angles of 94.96(10) and 86.44(10)$^\circ$ are close to perpendicular but the $\angle O_1\text{-Th}_1\text{-N}$ angles of 103.94(12), 78.34(12) and 88.20(15)$^\circ$ indicate a substantial deviation from the plane. The increased number of donor ligands compared to 3. The increased number of donor ligands also results in three $\text{Th}_1\text{-N}_1\text{Th}_1\text{N}_3$ angles of 144.97(9), 150.32(9) and 64.66(9)$^\circ$. The first two of these angles are comparable to the analogous angle observed in 3, whilst the third generates a zig-zag shaped Th(bipy)Th(bipy)Th chains that build the overall 2-D polymer (Figure 6).

The two OTer$^{\text{Mes}}$ central aryl groups are, as seen in 3 orthogonal to each other; this is again likely to minimise the interactions with the bipyridine ligands. The Th-O bonds, 2.221(3) and 2.232(3) Å, are longer than those seen in 1-3, but remain short for Th-O bonds. This slight lengthening is to be expected from the increased electron donation that a third N donor ligand provides, increasing the electron density on thorium, and thus reducing the electrostatic interaction with the OTer$^{\text{Mes}}$ ligand. The Th-N bond distances in 4, of 2.695(4), 2.667(5) and 2.677(4) Å are typical. The Th-Cl bond distances in 4, of 2.698(2), 2.710(2) Å, are also typical.

As a donor, 4,4-bipyridine has been used extensively to bridge two metal centres to form co-ordination polymers, particularly for transition metals. There are few known actinide compounds containing 4,4-bipyridine as a bridging ligand and all involve uranium. The U-N bond distances are very similar to the Th-N distance in 3. To the best of our knowledge, 3 and 4 are the first compounds in which two thorium centres are bridged by 4,4-bipyridine, and only the second example of 4,4-bipyridine acting as a ligand towards thorium. Complexes 3 and 4 have shorter Th-N bond distances than the first reported example, [TH($\eta$-C$_8$H$_8$)(4,4-bipyridyl)](2.707(2) Å). The well-documented ability of bipyridyls to accept electrons may provide a route to reduced analogues of 3 or 4.

The main distinction between the polymeric structures of 3 and 4 lies in the type of polymer produced; 3 is a 1-D polymeric chain, whilst 4 forms 2-D polymeric sheets. This is a direct consequence of the number of bipyridine molecules that are ligated to the thorium centre, i.e. two trans-orientated molecules in 3 leads to a chain structure, whilst three molecules in a pentagonal equatorial plane leads to a 2D sheet structure. A further difference is that 4 contains voids of radius 1.2 Å (similar to the size of dihydrogen gas) which makes up 6.3% of the unit cell volume, whilst 3 does not contain any voids of this size.

Of note here is that 3 is soluble in benzene and non-coordinating solvents. This is not normally the case for coordination polymers which need, at the minimum, a suitable additional donor to terminate the oligomer ends or fully break up the polymer. We suggest that the demonstrated ability of the terphenolate arene groups to bind to the metal centres may allow 2 to form monomers in non-polar solvents, allowing for the ready dissolution of the polymeric structure.

### Experimental

#### General Methods

All manipulations were carried out using standard Schlenk line or glovebox techniques under an atmosphere of dinitrogen unless otherwise stated. DME was distilled from sodium under dinitrogen in a solvent still prior to use. Hexane, diethyl ether and toluene were degassed by sparging with dinitrogen and dried by passing through a column of activated sieves in Vacuum Atmospheres solvent towers. Solvents were stored over activated 4 Å molecular sieves. Deuterated solvents ($d$-toluene and C$_6$D$_6$) were boiled over potassium, vacuum-transferred and freeze-pump-thaw degassed three times prior to use.
1H NMR and 13C{1H} NMR spectra were recorded on a Bruker
PRO500 spectrometer operating at 499.90 and 125.76 MHz
respectively. 11B and 13B{1H} NMR spectra were recorded at
298 K on a Bruker PRO500 at 160.49 MHz and were
referenced to external BF2OEt2. Chemical shifts are reported in
parts per million and referenced to residual proton resonances
calibrated against external TMS (δ = 0 ppm). All spectra were
recorded at 298 K unless otherwise stated.

Elemental analyses were carried out by Mr. Stephen Boyer,
London Metropolitan University, Analytische Laboratorien
Germany and Medac Ltd UK. Infrared spectra were recorded
on a Jasco 410 spectrophotometer, w = weak, m = medium, s =
strong intensity on in a Nujol mull on BaF2 or NaCl plates.
BaF2 plates do not allow transmission below 1000 cm−1.

Synthetic Procedures

1a [Th(OTerMes)2Cl(DME)]

To a Schlenk charged with a stirrer bar and HOTerMes (1.3955g,
4.22 mmol), was added circa 40 ml of dry DME, forming a
brown solution. This solution was cannulated onto KH (169.3
mg, 4.22 mmol), causing vigorous effervescence and the
formation of a light brown suspension which was allowed to
stir for 2 hours. This suspension was then cannulated onto a
DME suspension of ThCl4(DME)2 causing the formation of a
dark brown suspension which was allowed to stir overnight.
The suspension was filtered to separate a red-brown solution
from a grey powder. Volatiles were removed from the filtrate in vacuo
and the resultant brown residue was extracted with
toluene, and then concentrated and cooled to −30°C, which
caused the formation of colourless crystals of 1a (1.4683g,
1.39 mmol, 66% yield). Single crystals suitable for X-ray
crystallography were grown from a saturated solution of
toluene held at a temperature of −30°C. Elemental analysis;
calculated: C 61.23%, H 5.93%; found: C 61.38%, H 6.04%.
1H NMR (500 MHz) δ 6.97 (t, J = 1.7 Hz, 1H, para C-H), 6.93 (d, J = 1.7 Hz, 2H, meta C-H), 6.87 (s, 4H, mesityl aromatic C-H),
3.15 (s, 3H, CH3OCH2CH2CH2OCH3), 2.27 (s, 12H, Ortho CH3),
2.26 (s, 6H, Para CH3), 2.02 (s, 2H, CH3OCH2CH2OCH3).
13C{1H} NMR (500 MHz) δ (ppm) 161.42 (q, C1), 137.36 (q,
C2, C6), 135.84 (q, C7, C16), 131.60 (q, C8, C12, C17, C21),
129.96 (s, C4), 129.33 (q, C10, C19), 128.71 (s, C9, C11, C18,
C20), 120.49 (s, C3, C5), 72.22 (s, CH3OCH2CH2OCH3
[C26,C27]), 63.49 (s, CH2OCH2CH2OCH2) [C25,C29], 21.54 (s,
C13, C15, C22, C24), 21.30 (s, C14, C23).

1b [Th(OTerMes)2]2[BH4]2(DME)]

To a Schlenk charged with a stirrer bar and 1a (150 mg, 0.142
mmol), was added circa 20 ml of dry toluene, forming an
orange-brown solution. To this solution was added a colourless
solution of Ca(BH4)2(THF)2 (30.5 mg, 0.142 mmol) in toluene
forming a pale yellow suspension upon addition. After 2 days of
stirring, this suspension had become colourless. The
suspension was filtered to give a colourless solution, and this
solution was concentrated and cooled to −30°C, to give
colourless crystals of 1b, (87.3 mg, 0.089 mmol, 63% yield.
Single crystals suitable for X-ray crystallography were grown from
a saturated solution of toluene held at a temperature of −30°C. Elemental analysis; calculated: C 61.79%, H 6.78%,
found: C 61.64%, H 6.82%. 1H NMR (500 MHz, C6D6) δ 6.88
(s, 2H), 6.85 (s, 1H), (overlapping aromatic para and ortho
protons of central phenyl ring), 6.81 (s, 4H) (meta C-H), 3.03
(s, 7H) (overlapping BHI and CH2(OCH2CH2OCH2), 2.25 (s,
6H) (para CH3), 2.18 (s, 12H) (ortho CH3), 2.12 (s, 2H)
(CH2OCH2CH2OCH3) 13B NMR (160 MHz, C6D6) δ -12.46
(pp). 11B{1H} NMR (160 MHz, C6D6) δ -12.42 (s). 13C NMR
(126 MHz, C6D6) δ 161.76 (s), 138.27 (s), 137.19 (s), 135.95
(s), 131.52 (s), 130.44 (s), 129.95 (s), 129.34 (s), 128.88 (s),
128.69 (s), 128.57 (s), 128.35 (s), 125.70 (s), 120.08 (s), 72.64
(s), 64.38 (s), 21.67 (s), 21.22 (s). FTIR Spectroscopy (Nujol
mull on BaF2 Plates) 2726 (m), 2474 (m), 2456 (m), 2226 (m),
2164 (m), 1460 (s), 1377 (s) cm−1.

2 Th(OTerMes)2[BH4]2

To a Schlenk charged with a stirrer bar and 1b (208.1 mg,
0.206 mmol), was added circa 20 ml of dry toluene, forming a
yellow-orange solution. To this solution was added via syringe a
solution of AlMe3 in hexanes (2.0M, 0.21ml, 0.41 mmol),
causing a lightening of the solution to yellow, and subsequent
formation of a fine suspension. After stirring overnight, the
suspension was filtered to yield a pale yellow solution. This
solution was concentrated and cooled to −30°C, to give white
needles of 2, (95.3 mg, 0.104 mmol, 50% yield). Single crystals
suitable for X-ray crystallography were grown from a saturated
solution of toluene stored at −30°C. Elemental analysis;
calculated: C 62.62%, H 6.36%; found: C 62.48%, H 6.44%.
1H NMR (500 MHz, C6D6) δ 6.88 (d, J = 2.9 Hz, 1H), 6.87 (s,
2H), 6.79 (s, 4H), 3.12 (s, 11H), 2.83 (s, 14H), 2.44 (s, 6H),
2.08 (s, 12H), -0.39 (s, 4H) (BH4). 13C NMR (126 MHz, C6D6)
δ 161.38 (s), 148.00 (s), 141.99 (s), 139.50 (s), 139.26 (s),
138.61 (s), 138.46 (s), 137.47 (s), 137.21 (s), 136.46 (s), 135.79
(s), 135.39 (s), 130.77 (s), 130.46 (s), 130.24 (s), 130.16 (s),
130.06 (s), 129.37 (s), 129.99 (s), 128.87 (s), 128.68 (s),
128.51 (s), 128.35 (s), 128.16 (s), 127.97 (s), 127.74 (s), 127.02 (s),
120.05 (s), 21.66 (s), 21.48 (s), 21.28 (s), 21.25 (s), 21.16 (s),
20.98 (s), 20.84 (s), 20.50 (s). 11B{1H} NMR (160 MHz, C6D6) δ -10.08 (p). 13B{1H} NMR (160 MHz, C6D6) δ -10.08 (s). FTIR
Spectroscopy (Nujol mull on NaCl plates) 2957 (s), 2922 (s),
2853 (s), 2474 (m), 2217 (m), 2149(m), 1611 (m), 1455 (m)
cm−1.

3 [Th(OTerMes)3]3[BH4](4,4NC6H4C6H4N)]

To a pale yellow solution of 1b (10 mg, 0.011 mmol) in d6-
toluene (0.6 mL) in a Teflon-valved valve NMR tube was added
as a white crystalline solid 4,4-bipyridine (3 mg, 0.020 mmol, 2
equiv) resulting in a yellow solution. Transfer of the solution to
a vial, and allowing this solution to stand resulted in the
formation of yellow crystals of 3, (7.0 mg, 0.006 mmol, 66% yield)
suitable for single crystal X-ray crystallography.

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Elemental analysis; calculated: C 64.69%, H 6.18%, N 2.60% found: C 64.44%, H 5.85%, N 2.72%.

1^H NMR (500 MHz, C$_6$D$_4$) δ 7.01 (s, 2H), 6.97 (s, 4H), 6.81 (s, 1H), 6.74 (s, 4H), 6.55 (s, 4H), 3.28 (s, 4H) (B$_2$H$_4$), 2.08 (s, 6H), 2.00 (s, 12H). 1^3C NMR (126 MHz, C$_6$D$_4$) δ 163.71 (s), 150.69 (s), 145.30 (s), 137.18 (s), 135.79 (s), 129.33 (s) 120.94 (s), 119.97 (s), 21.72 (s), 20.54 (s). 1^1B NMR (160 MHz, C$_6$D$_4$) δ -6.42 (s).

FTIR Spectroscopy (Nujol mull on NaCl Plates) 3011. 3007, 2991, 2901, 2831, 2237, 2171, 1610, 1454 cm$^{-1}$.

4[Th(OTMes$_3$)$_2$(Cl)$_2$(4,4-bipyridyl)$_2$]$_2$

To a brown solution of 1a (10 mg, 0.010 mmol) in C$_6$D$_4$ (0.6 mL) in a Teflon-valved valve NMR tube was added as a white crystalline solid 4,4-bipyridine (3 mg, 0.020 mmol, 2 equiv) resulting in a brown-orange solution. Allowing this solution to stand at room temperature resulted in the formation of colourless needles of 4, (5.0 mg, 0.005 mmol, 47% yield) suitable for single crystal X-ray crystallography.

Conclusions

To conclude, we have described the synthesis and characterisation of the first examples of heteroleptic terphenolate complexes of thorium. Complex 1a is a good precursor for rare, crystallographically characterised examples of thorium borohydride complexes. In contrast to the dichloride complex 1b, the borohydride ligands in 1b render the Th$^{IV}$ centre sufficiently ‘soft’ that the Lewis acidic centre Al$_{iii}$ is able to abstract the coordinated DME from only the latter, yielding complex 2 with two stabilising Th-$\eta$-arene interactions. The formation of reversible, neutral Th-$\eta$-arene interactions crystallographically characterised in 2, and suggested by the solubility of the rare one-dimensional co-ordination polymer 3, confirms the suitability of TerMesO$_3$ as a strongly binding $\sigma$-O-donor ancillary ligand for actinide cations with a flexible steric protection that can participate in $\pi$-stabilising interactions.

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Notes and references

‡ Electronic Supplementary Information (ESI) available: Full synthetic and crystallographic details for the complexes. See DOI: 10.1039/c000000x. CCDC codes for the structures are CCDC 1019326-1019329 and 1020471.