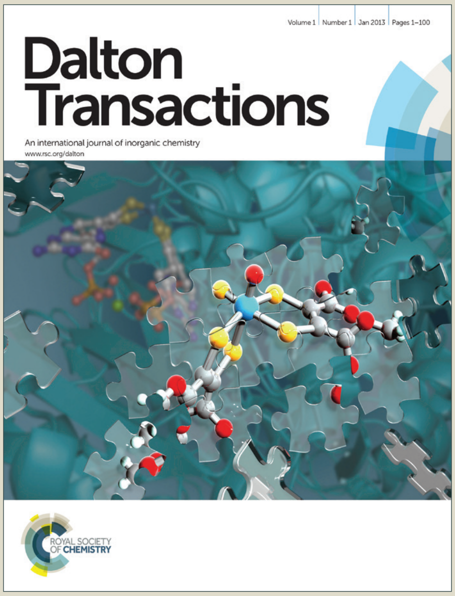
Dalton Transactions

Accepted Manuscript



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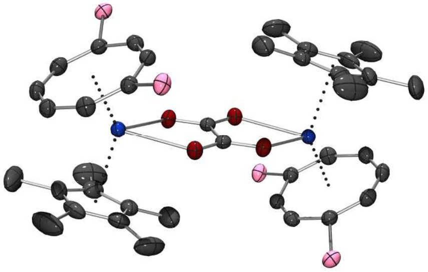
The synthesis of thorium complexes of the type Th(COT^{TIPS2})Cp*X (X= Cl, I, CH_2Ph, H) and their reactivity towards CO_2, including reductive coupling to form an oxalate complex, are reported.



Mixed Sandwich Thorium Complexes Incorporating Bis(tri-isopropylsilyl)cyclooctatetraenyl and Pentamethylcyclopentadienyl Ligands: Synthesis, Structure and Reactivity

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Abstract

The Th(IV) mixed-sandwich halide complexes Th(COT^{TIPS2})Cp*X (where COT^{TIPS2} = 1,4-{Si^{i}Pr$_3$}$_2$C$_8$H$_6$, X = Cl, I) have been synthesised, and structurally characterised. When Th(COT^{TIPS2})Cp*I is reduced *in-situ* in the presence of CO$_2$, a mixture of dimeric carboxylate and oxalate complexes {Th(COT^{TIPS2})Cp*}$_2$(μ-κ^1:κ^2-CO$_3$) and {Th(COT^{TIPS2})Cp*}$_2$(μ-κ^2:κ^2-C$_2$O$_4$)are formed, possibly *via* a transient Th(III) species. Th(COT^{TIPS2})Cp*Cl is readily alkylated to yield the benzyl complex Th(COT^{TIPS2})Cp*CH$_2$Ph, which reacts with CO$_2$ to form a carboxylate and with H$_2$ to form a hydride; the latter inserts CO$_2$, giving the bridging formate complex {Th(COT^{TIPS2})Cp*(μ-κ^1:κ^1-O$_2$CH)}$_2$.

Introduction

The activation of small molecules by uranium(III) complexes is currently an area of considerable interest, and we and others have reported a number of novel reductive transformations of, for example, CO, CO$_2$ and N$_2$ by molecular U(III) compounds.[1] Extension of this reduction chemistry to thorium is potentially of considerable interest, especially in view of the Th(IV)/Th(III) redox couple which is expected to be considerably more negative than that of uranium. However, unlike uranium, access to the trivalent oxidation state of thorium is not straightforward. Indeed, only a handful of unambiguously characterised Th(III) complexes have been reported in the literature: Th(Cp")$_3$ (where Cp" = C$_5$H$_3${SiMe$_3$}$_2$, C$_5$H$_3${SiMe$_2{}^t$Bu}$_2$), [Th(COT")$_2$][K.(DME)$_2$] (where COT" = 1,4-{Si^{t}BuMe$_2$}$_2$C$_8$H$_6$), and ThCp*$_2$(^{i}PrNC(Me)N^{i}Pr).[2-5] It was envisaged that the mixed-sandwich ligand system consisting of dianionic COT^{TIPS2} (where COT^{TIPS2} = 1,4-{Si^{i}Pr$_3$}$_2$C$_8$H$_6$) and monoanionic Cp* ligands may provide sufficient steric and electronic stabilisation to isolate a Th(III) compound, which would be expected to display high reactivity towards CO or CO$_2$ in a manner similar to the analogous trivalent uranium system U(COT^{TIPS2})Cp*.[6,7] Alternatively, the *in-situ* reduction of a mixed sandwich Th(IV) halide precursor in the presence of a small molecule may produce a transient Th(III) intermediate, which could induce reductive transformations.

In addition to the reduction chemistry, the reactivity of Th-C and Th-H bonds in thorium(IV) systems towards small molecules such as CO$_2$ is also of interest. This was first reported by Marks and Moloy in 1985, who demonstrated the ability of Th(Cp*)$_2$(Me)$_2$ to insert 2 equivalents of CO$_2$ to form a bis-acetate, Th(Cp*)$_2$(OAc)$_2$, and that Th(Cp*)$_2$(OCH^{t}Bu$_2$)(H) will insert 1 equivalent of CO$_2$ to yield a formate complex, $Th(Cp^*)_2(OCH^tBu_2)(\kappa^2\text{-}O_2CH)$.[8] Subsequently, a number of Th(IV) alkyl complexes have been synthesised, both in metallocene[9-16] and non-metallocene[17-20] ligand frameworks, and a small number of these have shown insertion reactivity towards CO_2.[20-22] Th(IV) hydride complexes have also been synthesised, mainly supported by cyclopentadienyl-based ligands, and containing both bridging and terminal hydride ligands, however their CO_2 insertion chemistry has not been extensively explored.[10,13-16,23-29] Alkyl and hydride compounds of the mixed-sandwich thorium system containing an unsubstituted COT ring and a Cp* ligand have been described by Sattelberger *et al.*; the crystal structure of $Th(COT)Cp^*(CH\{TMS\}_2)$ was reported, along with some evidence for the formation of an oligomeric hydride, $[Th(COT)Cp^*H]_x$.[14] It was anticipated that the increased solubility and greater steric shielding provided by use of the silyl-substituted COT^{TIPS2} ligand might allow the stabilisation and structural characterisation of such a hydride complex.

In this paper we describe the synthesis and characterisation of two Th(IV) halide complexes, $Th(COT^{TIPS2})Cp^*X$ (where X = Cl, I), attempted reduction of the latter, and the formation of dimeric carbonate and oxalate complexes, $\{Th(COT^{TIPS2})Cp^*\}_2(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3)$ and $\{Th(COT^{TIPS2})Cp^*\}_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}C_2O_4)$, from the *in situ* reduction of the iodide with NaK_3 under an atmosphere of CO_2. Furthermore, we also present the synthesis of a Th(IV) alkyl and a hydride complex, and the results of their reactivity towards CO_2, and a comparison with the related U(IV) chemistry using the same mixed-sandwich ligand system.[30]

Results and discussion

Synthesis and characterisation of halide complexes

The thorium mixed-sandwich chloride complex, $Th(COT^{TIPS2})Cp^*Cl$ (**1**), was prepared from the reaction of $ThCl_4$ and $MgClCp^*(THF)(PhMe)_{0.5}$, forming the intermediate $ThCp^*Cl_3(THF)_2$ without isolation, followed by the addition of $K_2(COT^{TIPS2})$ to yield **1** as light yellow crystals after workup. A sub-stoichiometric quantity of $K_2(COT^{TIPS2})$ was used to inhibit the very favourable formation of the 'thorocene' complex, $Th(COT^{TIPS2})_2$. The related iodide complex, $Th(COT^{TIPS2})Cp^*I$ (**2**), can be synthesised by stirring a toluene solution of **1** with an excess of TMSI for three days. After removal of volatiles, **2** can be isolated as light yellow crystals from toluene, slow-cooled to -35 °C. Attempts to synthesise **2** *via* the analogous mono-Cp* iodide complex, $ThCp^*I_3(THF)_x$, from $ThI_4(THF)_4$ and $MgClCp(THF)(PhMe)_{0.5}$ and subsequent reaction with $K_2(COT^{TIPS2})$ were unsuccessful due to the apparent instability of $ThCp^*I_3(THF)_x$.

Both **1** and **2** were characterised by mass spectrometry, displaying the anticipated M^+ parent ions at m/z = 818 and 910 respectively. The ^1H and $^{13}C\{^1H\}$ NMR data is consistent with the expected η^5- and η^8-coordination of the Cp* and COT^{TIPS2} ligands, and the elemental analyses returned the expected values. The molecular structures of **1** and **2** are shown in Figures 1 and 2, and geometric parameters are summarised in Table 1. Both **1** and **2** crystallise in the triclinic P-1 space group, containing two independent molecules in the unit cell, and are structurally similar; the Th-halide bond distance in **2** is, as anticipated, longer than in **1** (2.6865(16) v. 3.1104(5) Å), and the Ct1-Th1-Ct2 angle in **2** is marginally smaller than in **1**, due to the larger size of the iodide ligand. The Th-X (where X = Cl, I) bond distances in **1** and **2** are consistent with those previously reported for other terminal thorium halide complexes (averages: 2.70(6) Å for Th-Cl, 3.09(9) Å for Th-I).[31]

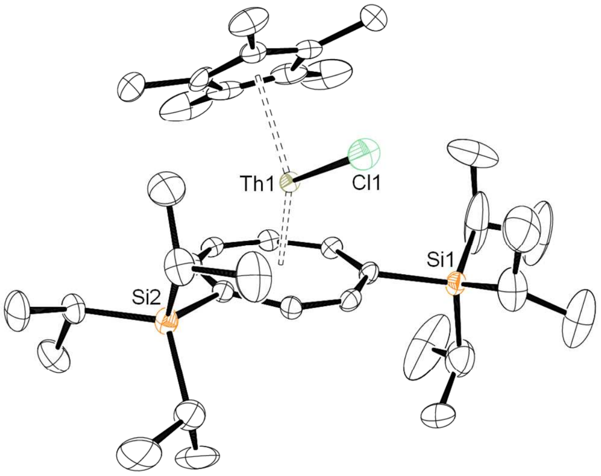


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity.

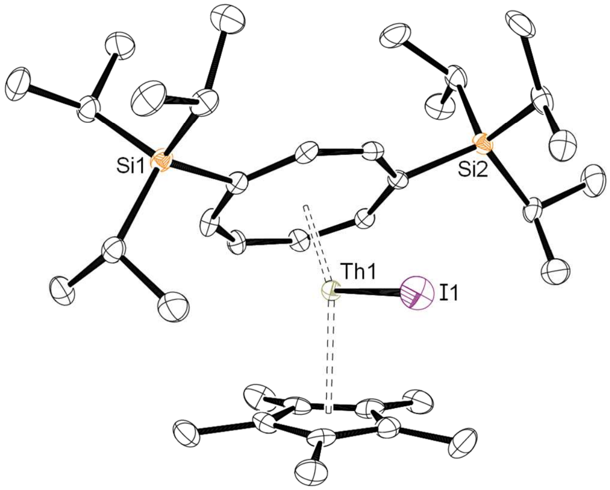


Figure 2. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity.

Table 1. Selected bond distances (Å) and angles (°) for **1** and **2**. Ct1 is the Th-COT centroid, Ct2 is the Th-Cp* centroid, X is the halide ligand.

	1	**2**
Th-X	2.6865(16)	3.1104(5)
Th-Ct1	1.9846(3)	1.980(18)
Th-Ct2	2.5292(3)	2.530(7)
Ct1-Th-Ct2	140.531(15)	140.2(4)

Attempted synthesis of Th(III) mixed-sandwich complexes and *in-situ* reductive reactions with small molecules

Since the synthesis of a Th(III) mixed sandwich complex was one of the principle aims of this work, reaction of both halides **1** and **2** with reducing agents was investigated. Initial cyclic voltammetry studies showed irreversible reduction waves for **1** and **2** at -3.33 and -3.32 V (with respect to the ferrocene/ferrocenium couple), respectively, presumably corresponding to a one-electron reduction of the metal centre (see ESI for voltammograms and full details). Shortly after this event was detected, decomposition of the thorium complexes ensued, apparent from diminishing current response over successive cycles and from deposition of material on the working electrode surface, and eventual discolouration of the solution after many cycles. Attempted chemical reduction of **1** or **2** with KC_8 resulted in no reaction, even after sonication; reacting **1** or **2** with NaK_3 yielded the substituted 'thorocene' $Th(COT^{TIPS2})_2$ and a dark precipitate, presumably thorium metal, both at ambient and elevated temperatures. Thus it would appear that any Th(III) mixed sandwich species disproportionates to Th(IV) and "Th(0)".

In view of the above results, *in-situ* reactions of toluene solutions of **1** or **2** with NaK_3 under an atmosphere of either ^{13}CO or $^{13}CO_2$ were performed. The chloride **1** showed no reactivity towards either gas, while **2** did not react with ^{13}CO, instead yielding $Th(COT^{TIPS2})_2$ and elemental thorium after 14 days. However stirring **2** with an excess of $^{13}CO_2$ and NaK_3 for a period of 12 days resulted in the appearance of two new resonances, at δ 167 and 172 ppm, in the $^{13}C\{^1H\}$ NMR spectrum of a reaction aliquot. Workup and selective crystallisation yielded two new dinuclear thorium species: a Th(IV) carbonate (**3**), and a Th(IV) oxalate (**4**) in low yields (12 and 2% respectively), the molecular structures of which are shown in Figures 3 and 4.

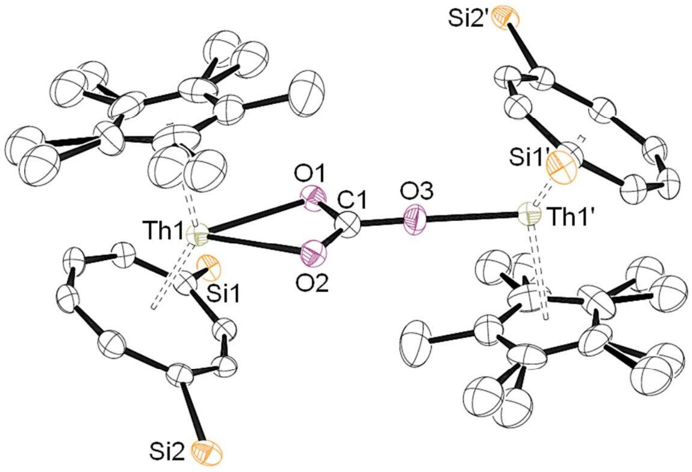


Figure 3. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Carbonate core shown is one of two overlapping positions – for alternative views of the structure, see ESI. Hydrogen atoms and ^{i}Pr groups omitted for clarity.

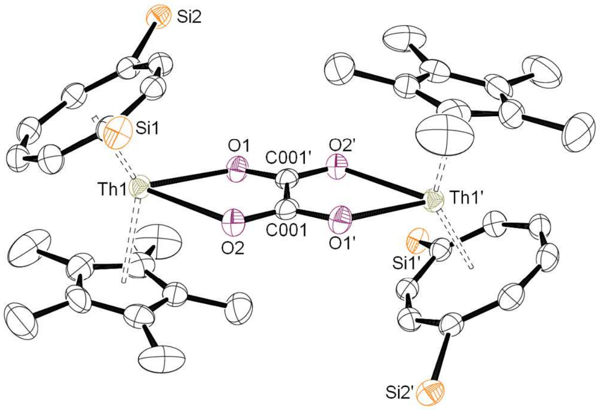


Figure 4. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, ^{i}Pr groups and co-crystallising molecule of toluene omitted for clarity. Th1-O1 = 2.473(2) Å, Th1-O2 = 2.475(3) Å, O1-C001 = 1.264(4) Å, O2-C001 = 1.260(4) Å, C001-C001' = 1.518(7) Å.

Table 2. Selected bond distances (Å) and angles (°) for **3** and **4**. Ct1 is the Th-COT centroid, Ct2 is the Th-Cp* centroid, X is the halide ligand.

	3	**4**
Th-Ct1	2.0226(9)	2.02932(17)
Th-Ct2	2.5388(11)	2.54142(17)
Ct1-Th-Ct2	138.88(3)	139.402(7)

The carbonate **3** crystallises in the triclinic space group P-1, containing half of the dimeric structure in the asymmetric unit, with the carbonate moiety bound in an κ^1:κ^2 fashion to two thorium centres, modelled in this structure as a 50:50 mixture of superimposed κ^1:κ^2 and κ^2:κ^1 moieties, similar to the U(IV) carbonate previously reported in this mixed-sandwich system (for more detail, see ESI).[7] As a result of this superimposition, metrical parameters describing the carbonate unit cannot be reliably reported, however, the rest of the structure can be accurately described. The oxalate **4** also crystallises in P-1 with half the molecule in the asymmetric unit, and does not contain disorder around the central oxalate moiety. The Th1-O1 and Th1-O2 bond distances are virtually identical (2.473(2) and 2.475(3) Å respectively), as are the O1-C001 and O2-C001 bond distances (1.264(4) and 1.260(4) Å respectively). The bond between C001 and C001' (symmetry generated) is single in nature, at 1.518(7) Å. There are no other Th(IV) oxalates supported by metallocene frameworks reported in the literature, however, several inorganic thorium oxalates have been reported containing bridging oxalate moieties as part of larger structural frameworks, *i.e.* $Th(C_2O_4)_2(H_2O)_2.2H_2O$.[32-36] The Th-$O_{oxalate}$ bond distances in **4** lie just outside the lower range of those found in the latter (2.481(2) – 2.578(7) Å), whilst the O-$C_{oxalate}$ bond distances in **4** are above the upper range of those found in the inorganic oxalates (1.242(3) – 1.261(4) Å). The difference in oxalate bond distances in **4** as compared to those in the purely inorganic oxalates is likely due to the supporting ligands: the oxophilic thorium centre in **4** is only bound to soft carbocylic ligands, rather than to other, hard oxygen donors. The C-$C_{oxalate}$ bond distance in **4** is, however, comparable to those in the other inorganic oxalate structures (range 1.50(2) – 1.545(7) Å).

The Th-centroid bond distances for both Th-Ct1 and Th-Ct2 (COT^{TIPS2} centroid and Cp* centroid respectively) in **3** and **4** are greater than in the halides **1** and **2**: the bridging nature of the former structures, together with the bidentate bonding mode of the oxalate and carbonate ligands, introduces steric repulsion between the COT^{TIPS2} and Cp* ligands, in contrast to the monomeric η^1-coordinated halide ligands in **1** and **2**. The Ct1-Th-Ct2 angles are similarly smaller in **3** and **4** than in **1** and **2**.

The formation of **3** and **4** could be ascribed to the reduction of CO_2 by a transient Th(III) species generated by the reaction of **2** with NaK_3, but which rapidly disproportionates in the absence of CO_2. However, other pathways cannot be excluded: for example, alkali metals alone will reduce CO_2 to oxalate and carbonate salts,[37] so it is possible that **3** and **4** result from a transmetallation reaction between sodium/potassium carbonate and oxalate and the iodo-complex **2**. However two factors mitigate against the latter pathway: (i) the reaction to form **3** and **4** does not occur with the chloro-complex **1** which would be expected to undergo such a transmetallation reaction with equal facility; (ii) attempts at recreating the transmetallation reaction by treatment of a toluene solution of **2** with a mixture of excess Na_2CO_3 and K_2CO_3 or excess of $Na_2C_2O_4$ for an extended period (11 days) failed to produce either **3** or **4**.

Synthesis and reactivity of Th(IV) alkyl and hydride complexes

The previously reported U(IV) mixed-sandwich alkyls, $U(COT^{TIPS2})Cp^*(R)$ (where R = CH_3, CH_2Ph, CH_2TMS, $CH\{TMS\}_2$), and hydride, $U(COT^{TIPS2})Cp^*(H)$, are reactive towards CO_2 and will undergo insertion reactions to form the corresponding monomeric carboxylate and formate products, $U(COT^{TIPS2})Cp^*(\kappa^2\text{-}O_2CR)$ (where R = CH_3, CH_2Ph, CH_2TMS, H).[30] The thorium benzyl alkyl, $Th(COT^{TIPS2})Cp^*(CH_2Ph)$ (**5**), was synthesised *via* salt metathesis between **1** and KCH_2Ph, yielding yellow crystalline **5** in a 60 % yield. The molecular structure of **5** (Figure 5) shows the benzyl ligand in the expected η^1-coordination mode. In comparison to the uranium analogue, the metal-centroid and metal-CH_2Ph bond distances are longer in **5**, in accordance with the larger ionic radius of Th(IV) *v.* U(IV) (Table 3). In comparison to other Th(IV) benzyl complexes, the Th-C bond length is greater than any previously reported (range: 2.53(2) – 5.581(19) Å),[31] likely due to the steric demands imposed by the bulky TIPS groups on the COT ring. Unlike its uranium analogue, **5** appears to be stable in solution and in the solid state at ambient temperature. No evidence has been seen for the existence of a 'tucked-in' species – formed *via* activation of a Cp* methyl group and loss of toluene – as occurs in the uranium system.

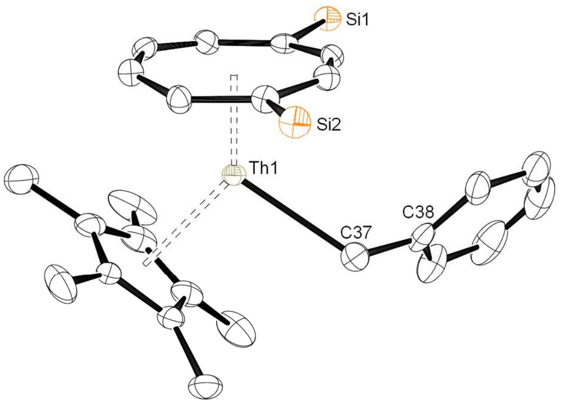


Figure 5. Molecular structure of one crystallographically independent molecule of **5** in the asymmetric unit, with thermal ellipsoids at the 50% probability level. Hydrogen atoms and ^{i}Pr groups omitted for clarity.

Table 3. Bond distances (Å) and angles (deg) in **5** (An = Th) and in U(COT^{TIPS2})Cp*CH$_2$Ph (An = U). Ct1 is the COT-ring centroid, Ct2 is the Cp*-ring centroid. Two values quoted for each compound equate to the two crystallographically independent molecules in the asymmetric units.

	An = Th	An = U
An-Ct1(Ct3)	2.0025(14)	1.9297(3)
	2.0056(14)	1.9304(3)
An-Ct2(Ct4)	2.538(2)	2.4899(3)
	2.539(2)	2.4836(3)
Ct1(Ct3)-An-Ct2(Ct4)	138.13(6)	137.217(13)
	137.07(7)	137.977(13)
An-C37(C87)	2.597(5)	2.532(4)
	2.598(4)	2.543(4)

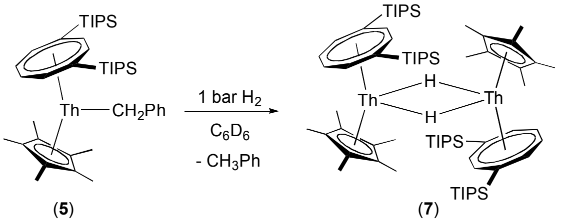
Exposure of **5** to either 1 equivalent or 1 bar of CO$_2$ yields the expected κ^2 phenyl carboxylate complex, Th(COT^{TIPS2})Cp*(κ^2-O$_2$C-CH$_2$Ph) (**6**). Performing the reaction with 1 equivalent of ^{13}CO$_2$ affords the corresponding labelled product, $^{13-}$**6**, and results in a prominent resonance at δ 188 ppm in the ^{13}C{^{1}H} NMR spectrum assigned to the inserted ^{13}C-labelled carboxylate carbon. This is in agreement with data reported by Mora *et al.* for a related Th(IV) carboxylate complex which includes a ^{13}C NMR resonance at δ 190.3 ppm assigned to the carboxylate carbon.[20] The ^{1}H NMR spectrum of ^{13}**-C** contains a doublet at 3.3 ppm (J_{CH} = 7.6 Hz) of integration 2H corresponding to the two $O_2{}^{13}C\text{-}CH_2Ph$ protons, which weakly couple to the ^{13}C atom. IR spectroscopic analysis of $^{13-}$**6** shows stretching frequencies at 1536 and 1383 cm^{-1}, corresponding to C-O asymmetric and symmetric stretches respectively. The mass spectrum of **6** shows the expected parent ion at m/z = 919, and the M$^+$ -Cp* fragment at m/z = 785. Whilst X-ray diffraction data was collected from several crystalline samples of **6**, the data could not be sufficiently refined: persistent electron density positioned above the COT-ring, and attributed to twinning in the crystal samples that could not be modelled, prevented satisfactory refinement of the data. However, connectivity could be established and the phenyl carboxylate ligand is bound κ^2 to the metal centre, and the structure is virtually identical to that of the uranium analogue (see ESI for the unrefined structure).

With the alkyl complex **5** in hand, the synthesis of a hydride complex was explored. Exposure of a d_6-benzene or pentane solution of **5** to 1 bar of H_2 resulted in a colour change from bright yellow to paler yellow over the course of several hours. The addition of 1 equivalent of H_2 yields the same colour change over a period of 48 hours, during which time some decomposition occurs, with free ligand and a small quantity of $Th(COT^{TIPS2})_2$ observed by ^1H NMR spectroscopy. The ^1H NMR spectrum of the product of the reaction between **5** and 1 bar of H_2 exhibits resonances attributable to free CH_3Ph, and a new resonance at 23.3 ppm of integration 1H relative to the other ligand signals, corresponding to a hydride ligand. Previously reported examples of Th(IV) metallocene hydride complexes reveal that ^1H NMR spectroscopic shifts of the hydride ligands are at notably low-field ppm values (between 17.1 – 20.5 ppm, Table 4). The IR spectrum of the reaction mixture contained intense vibrational bands at 1260, 1089, and 802 cm^{-1}, typical for bridging rather than terminal hydride complexes, as determined by comparison with previously reported Th(IV) hydride IR data (Table 4). It is hence proposed that, unlike the U(IV) analogue, the Th(IV) mixed-sandwich hydride is bridging, not terminal, in structure, giving $\{Th(COT^{TIPS2})Cp^*H\}_2$ (**7**, Figure 6). As previously noted, the larger ionic radius of Th(IV) *vs.* U(IV) is presumably responsible for this difference in structure.

Table 4. IR spectroscopic data and ^1H NMR spectroscopic shifts of hydride ligands in reported Th(IV) hydride metallocene complexes (where available). IR data in cm^{-1}, ^1H NMR data in ppm.

Complex	IR data	^1H NMR data	Ref.
$\{Cp^*{}_2Th(H)Cl\}_2$(b)	1229, 1152, 829, 672	19.0	24
$\{Cp^*{}_2Th(H)Me\}_2$ (b)		18.6	27
$\{Me_2Si(Cp^{Me4})_2ThH_2\}_2$ (b)	1285, 1155, 654, 481	18.36	13
$\{Cp^*Th(O\text{-}2,6\text{-}{}^tBu\text{-}C_6H_3)H_2\}_3$ (b)		18.54	16
$\{(COT)Cp^*Th(H)\}_x$ (b)	1147		14
$\{Th(O\text{-}2,6\text{-}{}^tBu\text{-}C_6H_3)_2H_2\}_3$ (b)	1336, 975, 795	20.54	15
$\{Cp^*{}_2Th(H_2)\}$ (b/t)	1404, 1370 (t) 1215, 1114, 844, 650 (b)	19.2	24
$Cp^*{}_2Th(H)(OTf)$ (t)		20.0	27
$Cp^*{}_2Th(H)(OSiMe_2{}^tBu)$ (t)		18.1	27
$Cp^*{}_2Th(H)(OCMe_3)$ (t)	1359	17.4	24
$Cp^*{}_2Th(H)(OCH^tBu_2)$ (t)		18.0	28
$Cp^*{}_2Th(H)(O\text{-}2,6\text{-}{}^tBu\text{-}C_6H_3)$ (t)	1365	19.1	28
$Cp^*{}_2Th(H)$(1*S*-endo-bornoxide) (t)	1348	17.7	29
$(C_5Me_4SiMe_3)_3Th(H)$ (t)	1460	12.94	25
$(C_9H_6SiMe_3)_3Th(H)$ (t)	1485	14.73	25
$(N\{TMS\}_2)_3ThH$ (t)	1480	0.63	17

(b) denotes bridging hydride ligand, (t) denotes terminal hydride ligand, (b/t) denotes both bridging and terminal hydride ligands.



(**5**) (**7**)

Figure 6. Formation of proposed bridging hydride complex, **7,** from the reaction of **5** with 1 bar of H_2.

Despite our best efforts, the isolation of **7** as a pure crystalline material has not been successful, hence elemental analysis has not been possible. Mass spectral analysis does not show the expected parent ion for a bridging hydride, however, an ion at m/z = 784 is observed, corresponding to the fragment 'ThCOT^{TIPS2}Cp*', along with an ion at m/z = 1065, indicating the fragmentation and rearrangement product, Th(COT^{TIPS2})$_2$. **7** appears to be noticeably more stable than the uranium analogue, U(COT^{TIPS2})Cp*(H) and does not decompose to any significant extent to either a trivalent mixed-sandwich product or to a 'tucked-in' product when subjected to reduced pressure. The lack of ready access to the Th(III) oxidation state may explain this observation, potentially also implying that the ubiquitous 'tucked-in' product in the uranium system, U(COT^{TIPS2})(η^5:η^1-$C_5Me_4CH_2$), may be formed *via* a U(III) intermediate, hence its absence in the Th(IV) reaction mixtures. This same marked contrast in stability of a Th(IV) hydride in comparison to the U(IV) analogue was also noted by Marks *et al.* in their studies on the actinide hydrides, {AnCp*$_2$H$_2$}$_2$.[24]

Further evidence for the formulation and hydride bridging conformation of **7** arises from reaction of the latter with CO_2. Upon the addition of 1 equivalent of $^{13}CO_2$ to a frozen d_6-benzene solution of **7**, a colour change to deeper yellow occurs whilst warming to ambient temperature. ^{1}H NMR spectroscopic analysis of the reaction mixture shows the formation of a single new product **8** and the disappearance of the hydride resonance at 23.4 ppm; the $^{13}C\{^1H\}$ NMR spectrum contains an intense singlet resonance at 177.2 ppm. The ^{1}H coupled ^{13}C NMR spectrum of **8** exhibits a doublet at 177.2 ppm with J_{CH} = 211 Hz which correlates to a doublet in the ^{1}H NMR spectrum at 9.0 ppm (J_{CH} = 211 Hz), consistent with the a single proton attached to the inserted ^{13}C atom. IR spectroscopic data shows a vibration at 1543 cm^{-1}, assigned to a formate ligand.

X-ray diffraction quality crystals of **8** were grown from a saturated toluene solution cooled to -35 °C, revealing the structure to be the bridging formate complex, {Th(COT^{TIPS2})Cp*(μ-κ^1:κ^1-$O_2{}^{13}CH$)}$_2$ (Figure 7). This supports the proposition that the parent hydride complex, **7**, is also bridging in nature. The dimeric structure of **8** is in contrast to that of the monomeric U(IV) formate complex, U(COT^{TIPS2})Cp*(κ^2-O_2CH), again due to the larger ionic radius of Th(IV) vs. U(IV).

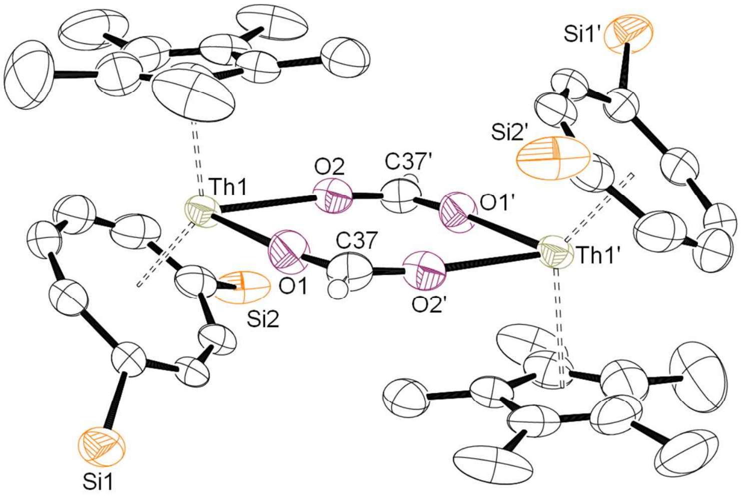


Figure 7. Molecular structure of **8** with thermal ellipsoids at the 50% probability level.

Table 5. Selected bond distances (Å) and angles (deg) for **8**.

Metric	Value
Th1-O1	2.408(5)
Th1-O2	2.394(4)
O1-C37	1.240(8)
O2-C37	1.231(7)
Th1-O1-C37	169.7(4)
Th1-O2-C37	166.9(5)
O1-C37-O2	126.8(6)
O1-Th1-O2	75.88(16)
Ct1-Th	2.045(3)
Ct2-Th	2.557(4)
Ct1-Th-Ct2	135.15(12)

Only two other crystallographically characterised Th(IV) formate complexes have been reported, both of which are hexanuclear: neutral $Th_6(OH)_4O_4(H_2O)_6(HCO_2)_{12}.nH_2O$, and $[Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(HCOO)_{12}(H_2O)_6]Na_3(ClO_4)_{3.5}(H_2O)_{5.5}(H_3O)_{0.5}$.[38,39] In each structure, the formate moieties bridge between two Th centres, as in **8**, but the Th atoms are also bound to either (μ_3-O) or (μ_3-OH) bridges, which dictate the overall geometry of the cluster. The Th-$O_{formate}$ bond lengths in the former complex range from 2.478(14) – 2.523(16) Å, and in the latter from 2.463 – 2.543 Å, both significantly longer than in **8**. The O-C-O angles of the bridging formate moieties range from 124(2) – 129.3(2) ° in both structures, comparable to the O_1-C_{37}-O_2 angle of 126.6(6) ° found in **8**. In comparison to the two other dimeric Th(IV) mixed-sandwich structures reported in this work, **3** and **4**, the Ct1-Th and Ct2-Th distances of 2.045(3) and 2.557(4) Å in **8** are marginally longer, and the Ct1-Th-Ct2 angle of 135.15(12) ° is also greater.

Conclusions

Attempts to prepare a stable Th(III) mixed sandwich complex of the type 'ThCOT^{TIPS2}Cp*' by reduction of Th(IV) halide precursors have been unsuccessful, although such a species may be implicated in reductions carried out under a CO_2 atmosphere which result in dimeric thorium carbonate and oxalate products. Synthesis of the benzyl derivative Th(COT^{TIPS2})Cp*CH_2Ph proceeds straightforwardly, and the former reacts readily with hydrogen to yield a hydride complex and hence a formate derivative *via* insertion of CO_2 into the Th-H bond. However, in contrast to the U(IV) chemistry reported for this mixed-sandwich system, the larger ionic radius of Th(IV) compared to U(IV) results in dimeric structures for both the hydride and formate complexes. In addition, no evidence has been seen for the existence of a 'tucked-in' Th(IV) complex, Th(COT^{TIPS2})(η^5:η^1-$C_5Me_4CH_2$), formed *via* the activation of a Cp* methyl group, a commonly observed degradation pathway for alkyls and hydrides in the U(IV) system.

Acknowledgements

We thank the European Research Council for financial support of this work and Dr G. J. Tizzard (NCS Southampton) for assistance with X-ray crystallography.

Experimental

General experimental details

Air-sensitive compound manipulations were carried out under an inert atmosphere of N_2 or Ar using standard Schlenck techniques or in an MBraun glove box (N_2 or Ar, < 1 ppm H_2O and < 1 ppm O_2). Solvents were pre-dried over sodium wire (with the exception of DCM which was not pre-dried) before heating at reflux over the appropriate drying agent (NaK_3: pentane, Et_2O; K: THF, 1,4-dioxane; Na: toluene; CaH_2: DCM). Dried solvents were degassed and stored in potassium-mirrored ampoules after collection, with the exception of THF, which was stored in an ampoule containing flame-dried 4Å molecular sieves. Deuterated NMR solvents were purchased from GOSS Scientific Ltd. and purified by heating at reflux over the appropriate drying agent, vacuum transferred into ampoules and stored under nitrogen prior to use. NMR spectroscopic analysis was performed using a Varian VNMR 400 spectrometer: ^{1}H NMR was run at 399.5 MHz, ^{13}C NMR at 100.5 MHz. Chemical shifts are quoted in parts per million and are internally referenced to residual protic solvent (^{1}H) or deuterated solvent shifts (^{13}C). EI-MS was performed by Dr. A. K. Abdul-Sada at the University of Sussex using a VG Autospec Fissions instrument (EI at 70 eV). IR spectra were recorded using NaCl plates on a Perkin-Elmer Spectrum One FTIR machine. Elemental analyses were performed by Mr. Des Davis at the University of Bristol. All XRD data sets were collected on a Bruker-Nonius Kappa CCD area detector diffractometer with a sealed tube source (Mo or Cu α) and an Oxford Cryosystems low temperature device, operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. Structures were either determined using Olex2,40 solved with the Superflip structure solution program using Charge Flipping[41] and refined with ShelXL refinement program,[42] or solved using the WinGX package and all software within.[43] CCDC 1008139-1008144 contain the supplementary crystallographic data for compounds **1**-**5** and **8**. $ThCl_3Cp^*(THF)_x$,[44] KCH_2Ph,[45] and $K_2(COT^{TIPS2})$[6] were prepared using standard literature procedures. $^{13}CO_2$ (99%) was supplied by EuroIsotop and used as supplied. Gas transfer was *via* Toepler pump. Electrochemical studies (cyclic voltammetry) were carried in dry THF containing 0.1 M $[N^nBu_4][PF_6]$ as the supporting electrolyte using a BASi Epsilon-EC potentiostat under computer control, performed by A. Kilpatrick of the University of Sussex. Cyclic voltammetry experiments were performed using a three-electrode configuration with a glassy carbon disc having an area of 7.0 mm^2 as the working electrode, a platinum wire as the counter electrode and a silver wire as the pseudoreference electrode. The Ag wire pseudoreference electrode was calibrated to the ferrocene/ferrocenium couple in THF, relative to which all of the standard potentials are reported. Ferrocene (*ca.* 3 mg) was added to a 0.1 M solution of electrolyte in THF (5 cm^3) containing the dissolved metal complexes (5 – 8 mM).

Synthesis of Th(COT^{TIPS2})Cp*Cl (1)

A stirred solution of $ThCp^*Cl_3(THF)_2$ (492 mg, 0.797 mmol in 20 cm^3 of THF) was cooled to -78 °C, and to this was added a THF solution of K_2COT^{TIPS2} (355 mg, 0.717 mmol, 0.9 eq) dropwise over 20 minutes. The resulting off-white suspension was allowed to stir for a further 18 hours whilst warming to ambient temperature, during which time it became light yellow with white solids. Removal of volatiles gave yellow viscous solids, and extraction with pentane followed by filtration gave a yellow solution which, when slow-cooled to -50 °C, yielded yellow prisms of **1** suitable for X-ray diffraction studies. Yield = 382 mg (0.466 mmol), 59% w.r.t. $ThCp^*Cl_3(THF)_2$. ^{1}H NMR (C_6D_6, 399.5 MHz): δ_H 7.12 (s, 2H, COT-H), 6.70 (m, 2H, COT-H), 6.41 (m, 2H, COT-H), 1.95 (s, 15H, Cp*), 1.59 (septet, J_{HH} = 7.5 Hz, 6H, ^{i}Pr-CH), 1.32 (d, J_{HH} = 7.6 Hz, 18H, ^{i}Pr-CH$_3$), 1.22 (d, J_{HH} = 7.5 Hz, 18H, ^{i}Pr-CH$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.5 MHz, 303 K): δ_C 127.6 (Cp-*C*CH$_3$), 113.5 (COT-*C*H), 107.6 (COT-*C*H), 107.1 (COT-*C*Si), 105.0 (COT-*C*H), 20.1 (^{i}Pr-*C*H$_3$), 19.7 (^{i}Pr-*C*H$_3$), 12.8 (^{i}Pr-*C*H), 11.8 (Cp-*C*H$_3$). MS (E)$^+$: *m/z* 818 (M$^+$, 95%), 775 (M$^+$ -^{i}Pr, 33%), 683 (M$^+$ -Cp*, 100%). Anal. Found: C, 53.00; H, 8.00. $C_{36}H_{63}Si_2ClTh$ requires C, 52.76; H 7.75%.

Synthesis of Th(COT^{TIPS2})Cp*I (2)

An excess of trimethylsilyliodide (552 mg, 2.76 mmol) was added to a stirred toluene solution of **1** (420 mg, 0.513 mmol) at ambient temperature. After stirring for three days, all volatiles were removed from the yellow solution under reduced pressure, giving light yellow solids. Extraction in toluene (ca. 5 cm^3) and slow-cooling to -35 °C yielded light yellow prisms of **2** in good yield, suitable for X-ray diffraction studies. Yield = 277 mg (0.304 mmol), 59% w.r.t. **1**. ^{1}H NMR (C_6D_6, 399.5 MHz, 303 K): δ_H 7.18 (s, 2H, COT-H), 6.70 (m, 2H, COT-H), 6.38 (m, 2H, COT-H), 2.00 (s, 15H, Cp*), 1.62 (septet, J_{HH} = 7.6 Hz, 6H, ^{i}Pr-CH), 1.33 (d, J_{HH} = 7.5 Hz, 18H, ^{i}Pr-CH$_3$), 1.24 (d, J_{HH} = 7.5 Hz, 18H, ^{i}Pr-CH$_3$). $^{13}C\{^1H\}$

NMR (C_6D_6, 100.5 MHz, 303 K): δ_C 128.8 (Cp-*C*CH_3), 114.4 (COT-*C*H), 109.0 (COT-*C*Si), 107.6 (COT-*C*H), 104.7 (COT-*C*H), 20.3 (^{i}Pr-*C*H_3), 20.2 (^{i}Pr-*C*H_3), 13.0 (^{i}Pr-*C*H), 12.7 (Cp-*C*H_3). MS (EI)$^+$: *m/z* 910 (M^+, 13%), 867 (M^+ -^{i}Pr, 10%), 157 (Si^{i}Pr$_3$, 100%). Anal. Found: C, 47.64; H, 6.87. $C_{36}H_{63}Si_2ITh$ requires C, 47.46; H 6.97%.

Synthesis of {Th(COT^{TIPS2})Cp*}$_2$(μ-κ^1:κ^2-CO_3) (3)

To a pale yellow solution of **2** (0.090 g, 0.0989 mmol) in toluene (1 cm^3) was added an excess of NaK_3; the mixture was cooled to -78 °C and $^{13}CO_2$ (3 eq) was added. This mixture was allowed to stir for 16 days before filtration. Storage at -35 °C yielded pale yellow rectangular crystals of **3** in poor yield that were suitable for X-ray diffraction analysis. Yield = 0.010 g (0.00615 mmol), 12% w.r.t. **2**. ^{1}H NMR (C_7D_8, 399.5 MHz, 303K): δ_H 6.73 (m, 4H, COT-H), 6.53 (m, 2H, COT-H), 2.01 (s, 15H, Cp*), 1.62 (septet, J_{HH} = 7.45 Hz, 6H, ^{i}Pr-CH), 1.32 (d, J_{HH} = 7.38 Hz, 18H, ^{i}Pr-CH_3), 1.24 (d, J_{HH} = 7.75 Hz, 18H, ^{i}Pr-CH_3). ^{13}C{^{1}H} NMR (C_7D_8, 100.5 MHz, 303K): δ_C 177.5 (Cp-*C*CH_3), 167.8 (*C*O_3), 111.1 (COT-*C*H), 108.2 (COT-*C*H), 106.5 (COT-*C*H), 105.5 (COT-*C*H), 20.7 (^{i}Pr-*C*H_3), 20.5 (^{i}Pr-*C*H_3), 13.5 (^{i}Pr-*C*H), 11.9 (Cp-*C*H_3). MS (EI)$^+$: *m/z* 1494 (M^+ -Cp*, 1%), 1449 (M^+ -Cp*, -^{i}Pr, 2%), 784 (‘Th(COT^{TIPS2})Cp*’, 100%). Anal. Found: C 47.05, H 6.56. $C_{73}H_{126}O_3Si_4Th_2$ requires C 46.9, H 6.74%.

Synthesis of {Th(COT^{TIPS2})Cp*}$_2$(μ-κ^2:κ^2-C_2O_4) (4)

To a pale yellow solution of **2** (0.100 g, 0.110 mmol) in toluene (1 cm^3) was added an excess of NaK_3; the mixture was cooled to -78 °C and $^{13}CO_2$ (5 eq) was added. This mixture was allowed to stir for 5 days before filtration. Storage at -35 °C yielded pale yellow rectangular crystals of **4** in poor yield that were suitable for X-ray diffraction analysis. Yield = 0.002 g (0.00122 mmol), 2% w.r.t. **2**. ^{1}H NMR (C_6D_6, 399.5 MHz, 303K): δ_H 6.82 (m, 2H, COT-H), 6.70 (m, 4H, COT- H), 1.99 (s, 15H, Cp*), 1.63 (septet, J_{HH} = 7.59 Hz, 6H, ^{i}Pr-CH), 1.31 (d, J_{HH} = 7.51 Hz, 18H, ^{i}Pr-CH_3), 1.28 (d, J_{HH} = 7.51 Hz, 18H, ^{i}Pr-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125.72 MHz, 303K): δ_C 172.1 (*C_2*O_4), 128.4 (Cp*C*CH_3), 109.9 (COT-*C*H), 105.3 (COT-*C*H), 105.2 (COT-*C*H), 20.1 (^{i}Pr-*C*H_3), 19.8 (^{i}Pr-CH_3), 12.9 (^{i}Pr-CH), 11.7 (Cp-CH_3). MS (EI)$^+$: *m/z* 1657 (M^+, 1%), 1552 (M^+ -Cp*, 1%).

Synthesis of Th(COT^{TIPS2})Cp*CH_2Ph (5)

KCH_2Ph (9 mg, 0.072 mmol) and **1** (60 mg, 0.072 mmol) were dissolved in 10 cm^3 of toluene and stirred for 12 hours, during which time the solution changed colour from light yellow to a darker yellow. Removal of volatiles under reduced pressure and subsequent extraction and filtration in pentane afforded a yellow solution, from which yellow crystals of X-ray diffraction quality were isolated upon slow-cooling to -20 °C. Yield: 38 mg (0.043 mmol), 60% w.r.t. **1**. ^{1}H NMR (C_6D_6, 399.5 MHz, 303 K): δ_H 7.30 (t, J_{HH} = 7.6 Hz, 2H, *meta*-C_6H_5), 7.02 (s, 2H, COT-H), 7.01 (s, 2H, *ortho*-C_6H_5), 6.75 (t, J_{HH} = 7.5 Hz, *para*-C_6H_5), 6.63 (m, 2H, COT-H), 6.28 (m, 2H, COT-H), 1.90 (s, 15H, Cp*), 1.45 (septet, J_{HH} = 7.4 Hz, 6H, ^{i}Pr-CH), 1.27 (d, J_{HH} = 7.4 Hz, 18H, ^{i}Pr-CH_3), 1.21 (d, J_{HH} = 7.4 Hz, 18H, ^{i}Pr-CH_3), 1.13 (s, 2H, C_6H_5C*H_2*). ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 303 K): δ_C 128.4 (Cp-*C*CH_3), 127.7 (Ph-*C*H), 126.5 (Ph-*C*H), 124.8 (Ph-*C*H), 113.3 (COT-*C*H), 110.4 (COT-*C*H), 107.9 (COT-*C*Si), 104.4 (COT-*C*H), 95.6 (C_6H_5*C*H_2), 20.4 (^{i}Pr-*C*H_3), 20.3 (^{i}Pr-*C*H_3), 13.0 (^{i}Pr-*C*H), 11.8 (Cp-*C*H_3). Ph-*C* could not be definitively assigned. MS (EI)$^+$: *m/z* 783 (M$^+$, -CH$_2$Ph, 12%), 157 (Si^{i}Pr$_3$, 100 %). Anal. Found: C, 59.41; H, 8.25. C$_{43}$H$_{70}$Si$_2$Th requires C, 59.01; H 8.06%.

Synthesis of Th(COT$^{\text{TIPS2}}$)Cp*(κ^2-O$_2$^{13}C-CH$_2$Ph) (^{13}-6)

A C$_6$D$_6$ solution of **5** (12.6 mg, 0.014 mmol) was cooled to -78 °C, the ampoule headspace degassed, and a slight excess (0.024 mmol) of ^{13}CO$_2$ was delivered *via* Toepler pump. Upon warming to ambient temperature, a colour change to pale yellow was observed. Removal of volatiles under reduced pressure and extraction of the resulting yellow solids into pentane, followed by slow-cooling to -35 °C yielded pale yellow crystals of **^{13}-6**. Yield: 10.3 mg (0.011 mmol) 80 % w.r.t. **5**. ^{1}H NMR (C$_6$D$_6$, 399.5 MHz, 303 K) δ$_H$ 7.25-7.00 (overlapping signals, 5H, aromatic protons), 6.81 (m, 2H, COT-H), 6.57 (m, 2H, COT-H), 3.36 (d, ^{2}J$_{CH}$ = 7.6 Hz, 2H, C*H$_2$*-C$_6$H$_5$), 1.82 (s, 15H, Cp*), 1.61 (septet, J_{HH} = 7.5 Hz, 6H, ^{i}Pr-CH), 1.28 (d, J_{HH} = 7.4 Hz, 18H, ^{i}Pr-CH$_3$), 1.25 (d, J_{HH} = 7.5 Hz, 18H, ^{i}Pr-CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.5 MHz, 303 K): δ$_C$ 188.2 (O$_2$^{13}*C*), 130.4 (d, J_{CC} = 1.9 Hz, *C*H$_2$C$_6$H$_5$), 128.9 (*C*$_6$H$_5$), 128.7 (Cp-*C*CH$_3$), 127.5 (*C*$_6$H$_5$), 125.1 (*C*$_6$H$_5$), 111.0 (COT-*C*H), 107.6 (COT-*C*Si), 106.2 (COT-*C*H), 105.8 (COT-*C*H), 20.2 (^{i}Pr-*C*H$_3$), 19.8 (^{i}Pr-*C*H$_3$), 12.9 (^{i}Pr-*C*H), 11.6 (^{i}Pr-*C*H). MS (EI)$^+$: *m/z* 918 (M$^+$, 15%), 783 (M$^+$ -Cp*, 90%). IR (NaCl plates, cm^{-1}) 2942 s, 2864 s, 2342 w, 1536 br, 1462 m, 1383 m, 1260 w, 1015 w, 927 w, 881 m, 799 w. Anal. Found: C, 57.80; H, 7.80. (^{13}C)C$_{43}$H$_{70}$Si$_2$O$_2$Th requires C, 57.54; H 7.67%.

Synthesis of {Th(COT$^{\text{TIPS2}}$)Cp*H}$_x$ (where x = 1 or 2) (7)

A C$_6$D$_6$ solution of **5** (10.7 mg, 0.012 mmol) was frozen, the headspace evacuated, and 1 bar of H$_2$ was added to the J Young NMR tube. The reaction mixture was thawed, and a colour change to pale yellow was observed after 12 hours. Extraction into a variety of solvents (pentane, ether, TMS$_2$O) only yielded a viscous yellow-orange oil in all cases. Yield as determined by ^{1}H NMR spectroscopy: > 90 %. Crude isolated yield: *ca.* 7 mg (0.009 mmol), 75% w.r.t. **5**. ^{1}H NMR (C$_6$D$_6$, 399.5 MHz, 303 K): δ$_H$ 23.4 (s, 1H, Th-H) 7.14 (s, 2H, COT-H), 6.70 (m, 2H, COT-H), 6.37 (m, 2H, COT-H), 2.02 (s, 15H, Cp*), 1.59 (septet, J_{HH} = 7.5 Hz, 6H, ^{i}Pr-CH), 1.31 (d, J_{HH} = 7.5 Hz, 18H, ^{i}Pr-CH$_3$), 1.26 (d, J_{HH} = 7.4 Hz, 18H, ^{i}Pr-CH$_3$). Resonances attributed to CH$_3$Ph were also observed at 7.11-7.00 ppm, and at 2.11 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.5 MHz, 303 K): δ$_C$ 125.7 (Cp-*C*CH$_3$), 112.6 (COT-*C*H), 108.8 (COT-*C*Si), 105.3 (COT-*C*H), 20.0 (^{i}Pr-*C*H$_3$), 19.8 (^{i}Pr-*C*H$_3$), 12.7 (^{i}Pr-*C*H), 11.6 (Cp-*C*H$_3$). IR (NaCl plates, cm^{-1}) 2943 s, 2865 s, 1463 m, 1383 w, 1218 br, 1260 s, 1089 br s, 1030 s, 931 w, 882 s, 803 s, 758w, 624 s, 669s.

Synthesis of {Th(COT$^{\text{TIPS2}}$)Cp*(μ-κ^1:κ^1-O$_2$^{13}CH)}$_2$ (^{13}-8)

The *in-situ* reaction of a C$_6$D$_6$ solution of **5** (21 mg, 0.024 mmol) and H$_2$ was performed in a J Young NMR tube and left for 12 hours to form the hydride, **7**. Once frozen, the vessel headspace was evacuated and 1 equivalent of ^{13}CO$_2$ (0.024 mmol) was added *via* Toepler pump. A colour change to bright yellow was observed upon thawing and warming to ambient temperature. Removal of volatiles under reduced pressure and extraction in toluene, followed by slow-cooling to -35 °C yielded off-white crystals of **^{13}-8**. Yield: 14 mg (0.017 mmol), 71% w.r.t. **5**. ^{1}H NMR (C$_6$D$_6$, 399.5 MHz, 303 K) δ$_H$ 9.02 (d, J_{CH} = 211 Hz, 1H, O$_2$^{13}C-H), 6.91 (2H, COT-H), 6.76 (m, 2H, COT-H), 6.57 (m, 2H, COT-H), 1.84

(s, 15H, Cp*), 1.63 (septet, J_{HH} = 7.4 Hz, 6H, ^{i}Pr-CH), 1.29 (d, J_{HH} = 7.4 Hz, 18H, ^{i}Pr-CH_3), 1.24 (d, J_{HH} = 7.5 Hz, 18H, ^{i}Pr-CH_3). $^1H\{^{13}C\}$ NMR (C_6D_6, 399.5 MHz, 303 K, selected data) δ_H 9.02 (s, 1H, $O_2{}^{13}CH$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.5 MHz, 303 K): δ_C 177.2 ($O_2{}^{13}CH$), 124.8 (Cp*-CCH_3), 110.7 (COT-CH), 108.1 (COT-CH), 107.0 (COT-CSi), 19.8 (^{i}Pr-CH_3), 12.5 (^{i}Pr-CH_3), 12.5 (^{i}Pr-CH), 11.3 (^{i}Pr-CH). ^{13}C NMR (C_6D_6, 100.5 MHz, 303 K, selected data) δ_C 177.2 (d, J_{CH} = 211 Hz, $O_2{}^{13}CH$). MS (EI)$^+$: *m/z* 830 ('Th(COT^{TIPS2})Cp*($O_2{}^{13}CH$)', 10%), 694, ('Th(COT^{TIPS2})($O_2{}^{13}CH$)', 60%), 667, ('Th(COT^{TIPS2})(F)', 100%), the F is the result of abstraction from the mass spectrometer calibrant. IR (NaCl plates, cm^{-1}) 3583 w, 2943 s, 2865 s, 1543 br m, 1494 m, 1462 s, 1380 s, 1350 m, 1252 w, 1032 m, 1070 m, 1015 m, 930 w, 882 s, 752 m, 670 s. Anal. Found: C, 53.80; H, 7.81. $(^{13}C)_2C_{72}H_{128}Si_4O_4Th$ requires C, 53.65; H 7.77%.

Notes and references

† Electronic Supplementary Information (ESI) available: crystallographic data collection details for compounds **1-6** and **8**, along with the unrefined molecular structure of **6**, and cyclic voltammograms of **1** and **2** are given in the ESI. CCDC 1008139-1008144 contain the supplementary crystallographic data for compounds **1-5** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ca.ac.uk/data_request/cif. See DOI: 10.1039/b000000x/

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