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Reactivity of a dithorium oxo complex from adventitious water†

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The presence of adventitious water in the treatment of $[\text{ThCl}_4(\text{DME})_2]$ with two equivalents of $[\text{K}(\text{C}_5\text{Me}_5)]$ results in the formation of the title bridging oxo complex, $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}\}_2(\mu\text{-O})]$ (**1**). This complex can also be formed from the reaction of $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}_2\}]$ with one equivalent of degassed water. The reactivity of the oxo complex was probed with Me_3SiCl and AlCl_3 , resulting in the quantitative formation of $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}_2\}]$. Treatment of $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}\}_2(\mu\text{-O})]$ with two equivalents of MeMgCl leads to $[\{(\text{C}_5\text{Me}_5)_2\text{ThMe}\}_2(\mu\text{-O})]$ (**2**) which can be further treated with $\text{PhN}(\text{H})\text{N}(\text{H})\text{Ph}$, yielding $[\{(\text{C}_5\text{Me}_5)_2\text{Th}(\text{PhNN}(\text{H})\text{Ph})\}_2(\mu\text{-O})]$ (**3**). Each complex has been characterized by spectroscopic and structural methods.

Introduction

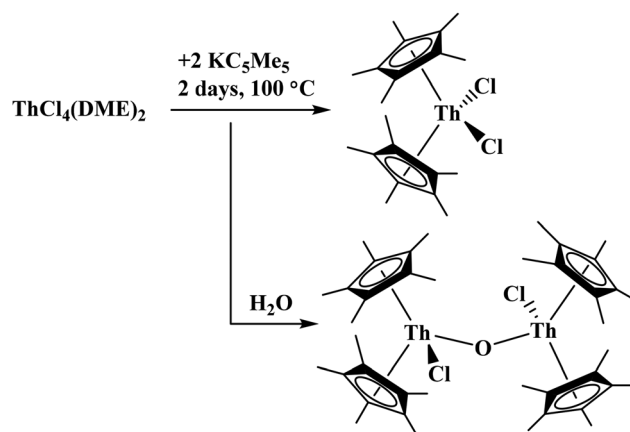
Bridging oxo complexes are ubiquitous in the coordination chemistry of actinides due to their oxophilic nature.^{1–3} At times, oxo compounds, particularly in Group 4 and f element organometallic chemistry, are not well characterized because they are often unwanted byproducts of reactions that form in the presence of adventitious water and other substrates.^{4–7} For example, the catalytic activity of $[\{(\text{C}_5\text{H}_5)_2\text{Zr}(\text{H})(\text{Cl})\}]$ diminishes with the formation of the oxo, $[\{(\text{C}_5\text{H}_5)_2\text{Zr}(\text{Cl})\}_2(\mu\text{-O})]$.⁸ There are relatively few examples of organometallic reactivity with water in the literature since the exclusion of air and water is desired.^{9–15} While the Group 4 complexes, $[\{(\text{C}_5\text{Me}_5)_2\text{M}(\text{Cl})\}_2(\mu\text{-O})]$, $\text{M} = \text{Ti}, \text{Zr}$, are known, the analogous thorium complex has not been reported.¹⁶

To synthesize $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}_2\}]$, $[\text{ThCl}_4(\text{H}_2\text{O})_4]$ is dehydrated using Me_3SiCl in the presence of DME as solvent to form $[\text{ThCl}_4(\text{DME})_2]$ followed by treatment with two equivalents of $[\text{K}(\text{C}_5\text{Me}_5)]$ (Scheme 1).^{17,18} Herein, we report that water left over from using a sub-stoichiometric amount of Me_3SiCl leads to the clean formation of the bridging oxo complex, $[\{(\text{C}_5\text{Me}_5)_2\text{Th}(\text{Cl})\}_2(\mu\text{-O})]$ (**1**). We surmised that this compound could have been previously seen or potentially seen by groups doing $(\text{C}_5\text{Me}_5)^{1-}$ based thorium chemistry. However, instead of moving on, we have used this bridging oxo complex to show that the desired dichloride complex can be reproduced and used as a starting material to produce a rare oxo/alkyl compound.

Experimental section

General considerations

Unless specified, all reactions were performed under an inert atmosphere of nitrogen (N_2) using standard glovebox and Schlenk techniques. All solvents used in the synthesis were dried over molecular sieves and alumina in the MBRAUN solvent purification system. Toluene was further dried over sodium benzophenone ketyl radical and vacuum distillation. $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}_2\}]$ was prepared according to the literature procedure.^{17,18} 1,2-Diphenylhydrazine, trimethylsilyl chloride, and methyl magnesium bromide were used as received from Sigma Aldrich. All NMR spectra were recorded in deuterated benzene (C_6D_6) on either a 600 MHz, 500 MHz, or 400 MHz Bruker Avance spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR shifts are reported in part per million referenced internally to residue



Scheme 1 Synthesis of $[\{(\text{C}_5\text{Me}_5)_2\text{ThCl}_2\}]$ as well as $[\{(\text{C}_5\text{Me}_5)_2\text{Th}(\text{Cl})\}_2(\mu\text{-O})]$ when adventitious water is present.

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solvent impurities. Deuterated benzene was degassed with a three-cycle freeze–pump–thaw and dried over 4 Å molecular sieves for at least 48 hours before use. All infrared spectra were recorded as potassium bromide (KBr) pellets on a Nicolet Summit Pro FT-IR spectrometer.

Synthesis of $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (1)

To a 25 mL Schlenk flask charged with 2 mL toluene solution of $[(C_5Me_5)_2ThCl_2]$ (200 mg, 0.348 mmol) was added degassed water (6 μ L, 0.348 mmol) at room temperature. The mixture was allowed to stir for 2 h, at 110 °C, under reflux conditions. After the completion of the reaction, all volatiles were removed under vacuum, leaving a crude colourless solid. The Schlenk flask was taken inside the glovebox and filtered in toluene using an M-porosity-fitted glass funnel. All volatiles were removed again to obtain compound 1 as a colourless powder. To obtain an analytically pure sample, the crude product underwent two recrystallization cycles from a pentane-layered concentrated diethyl ether solution at –20 °C (85 mg, 45%). 1H NMR (C_6D_6 , 400 MHz, 25 °C): δ 2.14 (s, 30H, C_5Me_5), 2.24 (s, 30H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6 , 101 MHz): δ 112.35 (C_5Me_5), 112.38 (C_5Me_5), 126.05 (C_5Me_5), 126.57 (C_5Me_5). FTIR (KBr, cm^{-1}): 1438, 1084, 1017, 734.

Reaction of 1 with Me_3SiCl

A J. Young NMR tube was charged with $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (1) (50 mg, 0.045 mmol), and dissolved in 0.6 mL of C_6D_6 . To the resulting solution was added dropwise an excess amount of Me_3SiCl (24.4 mg, 0.229 mmol) at room temperature. The reaction mixture was then heated to 60 °C for 2 h, and the progress of the reaction was monitored using 1H NMR spectroscopy. The product was identified as $[(C_5Me_5)_2ThCl_2]$ by comparison to the 1H NMR spectrum of the pure compound.¹⁸ After the completion of the reaction, the J. Young NMR tube was taken inside the glove box, and the reaction mixture was filtered using an M-porosity-fitted glass funnel, and all volatiles were removed under vacuum. The resulting white solid was again dissolved in a minimum amount of toluene, concentrated, and kept in the freezer at –20 °C to obtain compound A as a colourless block crystal (42 mg, 80%). 1H NMR (C_6D_6 , 600 MHz, 25 °C): δ 1.98 (s, 30H, C_5Me_5). FTIR (KBr, cm^{-1}): 1438, 1084, 1017, 734.

Reaction of 1 with $AlCl_3$

To a J. Young NMR tube initially charged with $AlCl_3$ (12.2 mg, 0.091 mmol), was added 0.6 mL C_6D_6 solution of $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (1) (50 mg, 0.045 mmol), at room temperature. The reaction mixture was then heated to 60 °C for 12 h, and the progress of the reaction was monitored using 1H NMR spectroscopy. The product was identified as $[(C_5Me_5)_2ThCl_2]$, by comparison to the 1H NMR spectrum of the pure compound.¹⁸

Synthesis of $[(C_5Me_5)_2Th(Me)]_2(\mu-O)$ (2)

To a 25 mL Schlenk flask charged with colourless 5 mL diethyl ether solution of $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (1) (200 mg, 0.183 mmol), was added dropwise an excess amount of methyl

magnesium chloride (0.420 mmol) at room temperature, forming a visibly cloudy reaction mixture. After 5 min of stirring an excess amount of dioxane was added, which resulted in the formation of a white ppt of presumably a dioxane- $MgCl_2$ complex. The reaction mixture was then stirred for 7 h at room temperature, after which time all volatiles were removed under a vacuum first at room temperature and then at 50 °C to ensure the complete removal of excess dioxane. The off-white solid obtained was further extracted with toluene 2 \times 5 mL, filtered using an M-porosity-fitted glass funnel, concentrated, and kept in the freezer at –20 °C to obtain compound 2 as a colourless block crystal. An analytically pure sample of compound 2 was obtained upon further recrystallization using pentane-layered concentrated diethyl ether solution at –20 °C (154 mg, 80%). 1H NMR (C_6D_6 , 600 MHz, 25 °C): δ 0.33 (s, 6H, CH_3), 2.08 (s, 60H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6 , 150 MHz): δ 11.9 (C_5Me_5), 12.1 (C_5Me_5), 57.7 (CH_3), 122.7 (C_5Me_5), 122.8 (C_5Me_5). FTIR (KBr, cm^{-1}): 1107, 1023, 875, 805.

Synthesis of $[(C_5Me_5)_2Th(\eta^2-PhNNHPh)]_2(\mu-O)$ (3)

To a 25 mL Strauss flask initially charged with a colourless 5 mL toluene solution of $[(C_5Me_5)_2Th(Me)]_2(\mu-O)$ (2) (100 mg, 0.095 mmol) was added dropwise a toluene solution of 1,2-diphenyl hydrazine (36.8 mg, 0.199 mmol) at room temperature, with instant gas evolution observed. The reaction mixture was then stirred for 8 h at 70 °C. The colour of the reaction mixture eventually changed from colourless to green. After the completion of the reaction, all volatiles were removed under vacuum. The obtained dark green solid was extracted with diethyl ether 2 \times 5 mL, filtered using an M-porosity-fitted glass funnel, concentrated, and kept in the freezer at –20 °C to obtain compound 3 as a needle green crystal (79 mg, 60%). 1H NMR (C_6D_6 , 400 MHz, 25 °C): δ 1.82 (bs, 60H, C_5Me_5), 5.34 (s, 2H, NH), 6.75 (s, 8H, Ph), 7.35 (bs, 12H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6 , 101 MHz): δ 11.2 (C_5Me_5), 109.9, 116.3, 121.6 (Ph), 126.2 (C_5Me_5), 138.7, 154.5 (Ph). IR (KBr, cm^{-1}): 3334 (ν N–H), 1103, 752.

Results and discussion

To isolate $[(C_5Me_5)_2ThCl_2]$, we followed the traditional method developed by Kiplinger *et al.*¹⁷ The reaction of $[ThCl_4(DME)_2]$ was carried out with 2.3 equivalents of $K(C_5Me_5)_2$ in toluene at 110 °C for 2 days. However, instead of the desired $[(C_5Me_5)_2ThCl_2]$, the formation of the bridging oxo complex, $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (1), was observed in 55% yield as a white solid. It was anticipated that some adventitious water molecules might have caused the formation of the bridging oxo complex. Using a sub-stoichiometric amount of Me_3SiCl in the synthesis of $[ThCl_4(DME)_2]$ from $[ThCl_4(H_2O)_4]$ might have resulted in some leftover water, causing the formation of $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$.

In a similar manner, Lappert *et al.* reported the formation of $[(Th\{C_5H_3(SiMe_3)_{2-1,3}\}_2(\mu-O)]$ by stirring the (di-substituted-cyclopentadienyl)thorium(III) complexes $[Th\{\eta^5-$



$C_5H_3(SiMe_3)_2-1,3\}_3]$ in wet toluene.^{19,20} To probe this hypothesis of oxo formation coming from water, the reaction of degassed water was added to a toluene solution of $[(C_5Me_5)_2ThCl_2]$ at room temperature. The reaction was allowed to stir at 110 °C for 2 h to result in $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$, **1** (Scheme 2). While the 1H NMR spectrum showed quantitative conversion to **1**, recrystallization from an ether/pentane solvent mixture resulted in a 45% yield. Adding an exact equivalent amount of degassed water is vital for product formation, as an excess amount of H_2O results in the decomposition of the product with the formation of Cp^*H . Compound **1** is stable at room temperature under an inert atmosphere of nitrogen and is soluble in toluene, tetrahydrofuran, and ether. While similar Group IV complexes are known,^{21–23} **1** represents the first example of a thorium μ -oxo dimer featuring chloro functionalization.^{19,20,24–27}

Compound **1** was characterized in solution by multi-nuclear (1H , ^{13}C) NMR spectroscopy. The methyl proton of the Cp^* ligand resonates as two singlets at 2.14 and 2.24 ppm, spanning the typical diamagnetic region, as expected for a thorium(IV) complex. This separate Cp^* resonance for both the thorium centers highlights the unsymmetrical Cp^* ligand environment attributed to the restricted rotation along the Th–O–Th axis in solution. The variable-temperature NMR spectroscopy conducted in C_6D_6 solvent revealed no coalescence of the methyl peak signals of C_5Me_5 between 25 °C and 60 °C (see ESI† for details).

The solid-state characterization of **1** was performed using single-crystal XRD studies (Fig. 1). Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of the main moiety and two half-toluene molecules per asymmetric unit. The complex has C_2 point symmetry with the 2-fold axis passing through the O atom at a roughly 30° angle to the Th–Cl bonds. The geometry around both the thorium centres is pseudo-tetrahedral, having two η^5-Cp^* , one chloro, and one bridging oxide ligand in the coordination sphere. The average Th–O bond distance (2.1725 Å) is similar to other reported thorium μ -oxo dimers $\{[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2Th\}_2(\mu-O)_2$ (2.1796 Å) and $\{[\eta^5-1,3(Me_3C)_2C_5H_3]_2Th\}_2(\mu-O)_2$ (2.135(9) and 2.195(8) Å).^{24,25} The Th–Cl bond distances are 2.653(3) and 2.665(3) Å which is comparable to 2.601(4) Å in $[(C_5Me_5)_2ThCl_2]$. The Th–O–Th bond angle in **1** is slightly bent (164.4(4)°) compared to the Zr–O–Zr (168.9(8)°) and Ti–O–Ti (173.8°) bond angles in analogous $[(C_5H_5)_2Zr(Cl)]_2(\mu-O)$ and $[(C_5H_5)_2Ti(Cl)]_2(\mu-O)$ group (IV) μ -oxo dimers.^{21,23} The pres-

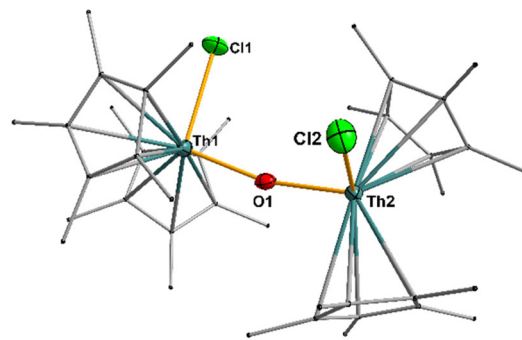
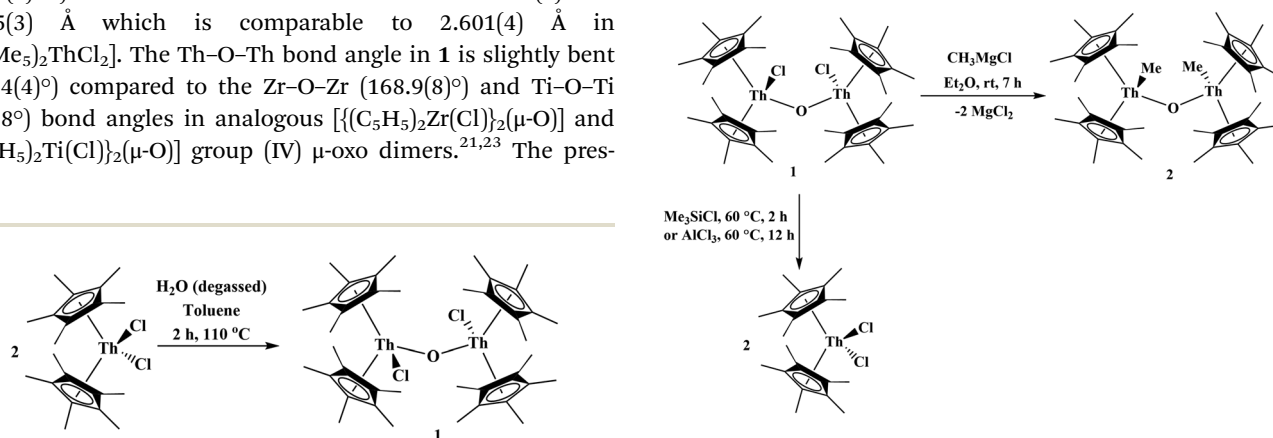


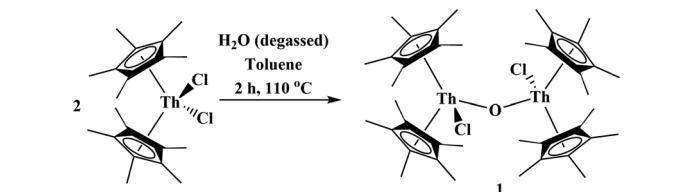
Fig. 1 Molecular structure of $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (**1**). All the hydrogen atoms are omitted for clarity. Displacement parameters are shown at 50% probability. Selected interatomic distances [Å] and angles [°]: Th1–O 2.165(9), Th2–O 2.180(9), Th1–Cl1 2.653(3), Th2–Cl2 2.665(3); Cl1–Th1–O 100.2(2), Cl2–Th2–O 100.7(2), Th1–O–Th2 164.4(4).

ence of chlorides, combined with the bridging μ -oxide ligand in the thorium μ -oxo dimer complex, makes it an ideal precursor for further derivatization to form bimetallic thorium compounds.

To probe its reactivity, **1** was treated with CH_3MgCl , Me_3SiCl , and $AlCl_3$. Thorium oxide complexes exhibit significantly lower reactivity compared to their uranium counterparts. This is evident from the sluggish and highly energy-intensive reaction of ThO_2 with CCl_4 , which requires elevated temperatures of 450–500 °C,²⁸ whereas U_3O_8 undergoes similar reactions with chlorocarbons at much milder conditions.²⁹ Walter *et al.* also observed that thorium μ -oxo dimers $\{[1,2,4-(Me_3C)_3C_5H_2]_2Th(\mu-O)\}_2$ remained unreactive towards Me_3SiCl , even at elevated temperatures.²⁵ Interestingly, despite their thermodynamic stability, **1** can be converted back to the parent $[(C_5Me_5)_2ThCl_2]$ complex upon reaction with excess Me_3SiCl in toluene at 60 °C within 2 hours, yielding 80% of the product along with $Me_3SiOSiMe_3$ formation (Scheme 3). This transformation was successfully monitored and confirmed *via* 1H NMR spectroscopy. Heating



Scheme 3 Reactivity of bridging oxo complex $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (**1**), with CH_3MgCl $Me_3SiCl/AlCl_3$ to deliver $[(C_5Me_5)_2Th(Me)]_2(\mu-O)$ (**2**), and $[(C_5Me_5)_2ThCl_2]$.



Scheme 2 Synthesis of bridging oxo complex $[(C_5Me_5)_2Th(Cl)]_2(\mu-O)$ (**1**).



at 60 °C is required to achieve a complete conversion of **1** to $[(C_5Me_5)_2ThCl_2]$. Stirring the reaction at room temperature leads to incomplete conversion. Similarly, the stoichiometric reaction of **1** with $AlCl_3$ also resulted in the formation of $[(C_5Me_5)_2ThCl_2]$ when performed in C_6D_6 at 60 °C for 12 h (see ESI† for details), although the fate of the oxo is unknown, but presumably alumina since a precipitate is observed.

Following the literature precedence for the synthesis of $[(C_5Me_5)_2ThMe_2]$ from $[(C_5Me_5)_2ThCl_2]$,^{17,18} the stoichiometric reaction of **1** with methyl Grignard reagent, CH_3MgCl , in diethyl ether at room temperature for 7 h resulted in methyl thorium μ -oxo dimer $\{[(C_5Me_5)_2Th(CH_3)_2(\mu-O)]\}_2$ (**2**), in 80% yield as an off-white solid (Scheme 3). Compound **2** is stable at room temperature under an inert atmosphere and is soluble in tetrahydrofuran, toluene, and ether. The formation of compound **2** was characterized both in solution and solid state using multinuclear NMR spectroscopy and single-crystal XRD, respectively. In contrast to compound **1**, all four pentamethylcyclopentadienyl methyl protons in compound **2** appear as a singlet at 2.14 ppm probably due to the fluxional rotation of the molecule along the Th–O–Th axis. The methyl protons appear as a singlet at 0.33 ppm. All the peaks are shifted downfield compared to the $[(C_5Me_5)_2ThMe_2]$ ¹⁸ due to the electronegative oxide bridge.

The molecular structure of compound **2**, Fig. 2, determined using a single-crystal XRD study, is analogous to compound **1**, with an average Th–O bond length of 2.175 Å, comparable to compound **1** (2.1725 Å). The coordination sphere of the pseudo-tetrahedral thorium centres is occupied by two η^5 -Cp*, one methyl, and one bridging oxide ligand. The Th–Me bond distances in compound **2** are 2.506(3) and 2.508(3) Å which are marginally longer than those compared to 2.471(8) and 2.478(9) Å in $[(C_5Me_5)_2ThMe_2]$.³⁰

Next, we probed the reactivity of the methyl complex as this could be further derivatized. Previously, we reported the synthesis of diphosphido complexes through the protonolysis of the $[(C_5Me_5)_2ThMe_2]$ with dimesityldiphosphane, $MesP(H)P(H)Mes$.³¹ In this case, we were interested to see if a bridging oxo/diphosphido complex would form. However, the stoichiometric reaction of **2** was performed with one equivalent of $MesP(H)P(H)Mes$ in toluene at 70 °C for one day which only led to the formation of an unidentified insoluble mixture. In addition, we reported the synthesis of a bridging oxo/arsinidide complex, $\{[(C_5Me_5)_2Th(\mu-O)(\mu-AsMes)]\}_2$, from the reaction of $\{[(C_5Me_5)_2Th(\mu-AsMes)]\}_2$ with $OPPh_3$.³¹ Therefore, we surmised that the reaction of **2** with mesitylarsine, $MesAsH_2$, would form the same compound through an alternate route. However, similar to the diphosphane reaction, no product could be identified from the reaction mixture. Perhaps the bulkiness of the mesityl group is large enough to prevent the interaction of Th(IV) with the pnictogen centre. However, when **2** was treated with diphenyl hydrazine, $PhN(H)N(H)Ph$, having less bulky phenyl groups, the reaction cleanly afforded the mono-deprotonated diamido thorium μ -oxo dimer $\{[(C_5Me_5)_2Th(\eta^5-PhN(H)NPh)]_2(\mu-O)]\}$ (**3**), in 60% yield as a green solid (Scheme 4). We also attempted to fully deprotonate the hydrazinide ligand employing a higher temperature (85 °C) and increased reaction time (24 h) to see the protonation of the oxo ligand, but it did not react further.

With the successful reaction of diphenyl hydrazine and unsuccessful reactions with substrates with the softer phosphorus and arsenic donor atoms, this reactivity is most likely electronic, and not steric, in nature. While the oxo/arsinidide complex has been reported, it was made in a different manner, so we surmise that it cannot be made using the bridging oxo moiety already installed. In the reaction chemistry of **2**, the electron density to satisfy the thorium centres is only accomplished with the most electronegative nitrogen-based ligand. Compound **3** is stable at room temperature under an inert atmosphere and is soluble in tetrahydrofuran, toluene, and ether. The formation of compound **3** was confirmed using multinuclear NMR spectroscopy in the solution state and with single crystal XRD studies in the solid state. The 1H NMR spectra obtained in benzene- d_6 show symmetry in the solution

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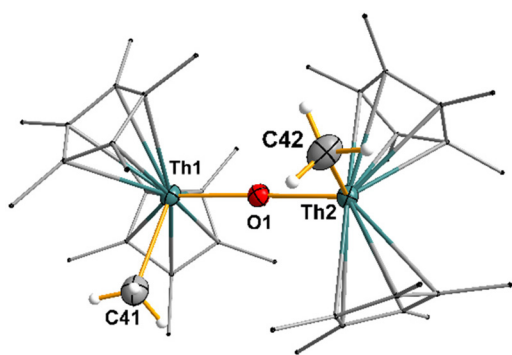
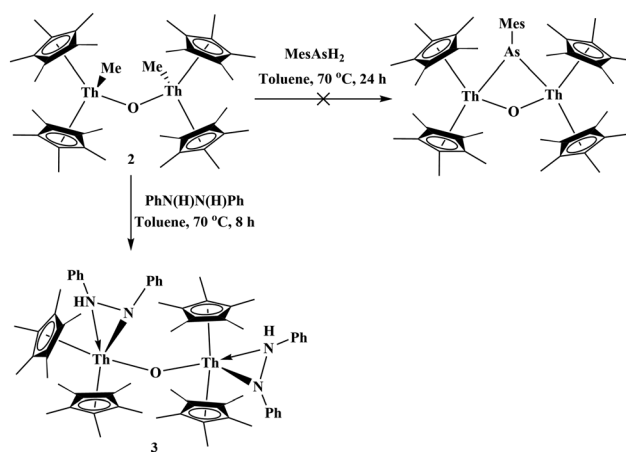


Fig. 2 Molecular structure of **2**. All the hydrogen atoms except for the methyl protons, as well as disorder, are omitted for clarity. Displacement parameters are shown at 50% probability. Selected interatomic distances [Å] and angles [°]: Th1–O1 2.171(5), Th2–O1 2.179(5), Th1–C41 2.509(9), Th2–C42 2.505(8); C41–Th1–O1 100.2(2), C42–Th2–O1 100.7(2), Th1–O1–Th2 164.4(4).



Scheme 4 Reaction of $\{[(C_5Me_5)_2Th(Me)]_2(\mu-O)\}$ (**2**), with 1,2-diphenylhydrazine for the synthesis of $\{[(C_5Me_5)_2Th(PhNN(H)Ph)]_2(\mu-O)\}$ (**3**).



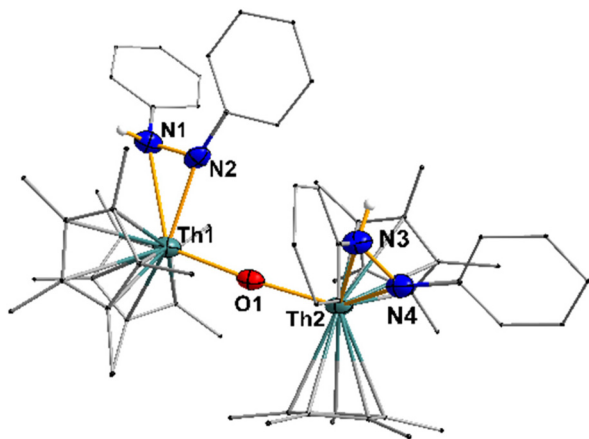


Fig. 3 Molecular structure of **3**. All the hydrogen atoms except for the N–H are omitted for clarity. Displacement parameters are shown at 50% probability; Selected interatomic distances [Å] and angles [°]: Th1–O1 2.236(4), Th2–O1 2.225(4), Th1–N1 2.364(5), Th1–N2 2.747(4), Th2–N3 2.324(3), Th2–N4 2.654(3); N1–Th1–N2 31.72(13), O1–Th1–N1 123.22(13), O1–Th1–N2 92.29(12), Th1–O1–Th2 175.24(16), N3–Th2–N4 31.90(14), O1–Th2–N3 91.09(13), O1–Th2–N4 122.10(13).

state with only one singlet corresponding to all the four C_5Me_5 rings at 1.82 ppm, while the aromatic peaks of the phenyl ring appear as two broad multiplets at 6.72 and 7.33 ppm. This upfield shift in the Cp* resonances in **3** compared to precursor **2** is due to the donation of electron density from one of the nitrogen atoms of the respective hydrazinide ligand attached, which eventually enhances the electron shielding around the Cp* methyl protons. The molecular structure of compound **3** was determined using single-crystal XRD studies that showed the anticipated dithorium molecular structure along with diethyl ether molecules of solvation. The coordination sphere of each Th centre is occupied by an η^2 -diphenylhydrazinide ligand, two η^5 -Cp* ligands, and a $(\mu_2-O)^{2-}$ ion which bridges the metal centres at a nearly linear Th–O–Th angle, 175.2(2)°, (Fig. 3). The Th–O distances are statistically identical (Th1–O1 = 2.236(4) Å, Th2–O1 = 2.225(4) Å). The hydrazinide ligand is singly deprotonated, resulting in the formation of one anionically charged and dative bond between the Th and N atoms. Hydrazanato ligands, or similar moieties, are rare with thorium, and **3** seems to be the first hydrazinide complex with thorium. The Th–N distances in **3** of Th1–N2 = 2.364(5) Å and Th1–N1 = 2.747(4) Å compare similarly to other η^2 -(N,N′)-three-membered metallocycles with thorium.^{32–41} The two metal centers differ from each other most significantly by the orientation of the Cp* rings, which are nearly eclipsed for one Th centre and staggered for the other. Compound **3** shows IR absorptions at 3324 cm^{-1} , attributed to the N–H bond stretching mode.

Conclusions

Despite the unintended presence of trace water during the synthesis of $[(C_5Me_5)_2ThCl_2]$, we successfully isolated a thorium μ -oxo complex, $[(C_5Me_5)_2ThCl_2](\mu-O)$ (**1**), and able to reproduce,

in high yield, through the direct reaction of $[(C_5Me_5)_2ThCl_2]$ with a half equivalent of deoxygenated water. This thorium μ -oxo dimer exhibits reversible conversion back to $[(C_5Me_5)_2ThCl_2]$ upon treatment with excess Me_3SiCl or a stoichiometric amount of $AlCl_3$. Mistakes occur in synthetic chemistry, but this does not mean that the compound must be thrown away, and we hope this report inspires others to examine alternative ways to get to a desired product or make use of their mistakes. The chloride compound, **1**, can be converted to the methyl analogue of complex **1**, $[(C_5Me_5)_2ThMe_2](\mu-O)$ (**2**), via a substitution reaction with two equivalents of $MeMgBr$. Further protonation of compound **2** with $PhN(H)N(H)Ph$ resulted in the formation of $[(C_5Me_5)_2Th(PhNN(H)Ph)_2](\mu-O)$ (**3**). This represents a rare, reproducible example of an organoactinide complex reactivity with water and its use as a starting material to produce further functionalities.

Data availability

The dataset supporting this article has been uploaded as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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