

Concomitant Carboxylate and Oxalate Formation From the Activation of CO₂ by a Thorium(III) Complex

Alasdair Formanuik,^[a] Fabrizio Ortu,^[a] Christopher J. Inman,^[b] Andrew Kerridge,^[c] Ludovic Castro,^[d] Laurent Maron,^{*[d]} and David P. Mills^{*[a]}

Abstract: Improving our comprehension of diverse CO₂ activation pathways is of vital importance for the widespread future utilization of an abundant greenhouse gas. CO₂ activation by uranium(III) complexes is now relatively well understood, with oxo/carbonate formation predominating as CO₂ is readily reduced to CO, but isolated thorium(III) CO₂ activation is unprecedented. We show that the thorium(III) complex, [Th(Cp'')₃] (**1**, Cp'' = {C₅H₃(SiMe₃)_{2-1,3}}), reacts with CO₂ to give the mixed oxalate-carboxylate thorium(IV) complex $[\{\text{Th}(\text{Cp}'')_2[\kappa^2\text{-O}_2\text{C}\{\text{C}_5\text{H}_3\text{-}3,3'\text{-(SiMe}_3)_2\}]\}_2(\mu\text{-}\kappa^2\text{-}\kappa^2\text{-C}_2\text{O}_4)]$ (**3**). The concomitant formation of oxalate and carboxylate is unique for CO₂ activation, as in previous examples either reduction or insertion is favored to yield a single product. Therefore, thorium(III) CO₂ activation can differ from better understood uranium(III) chemistry.

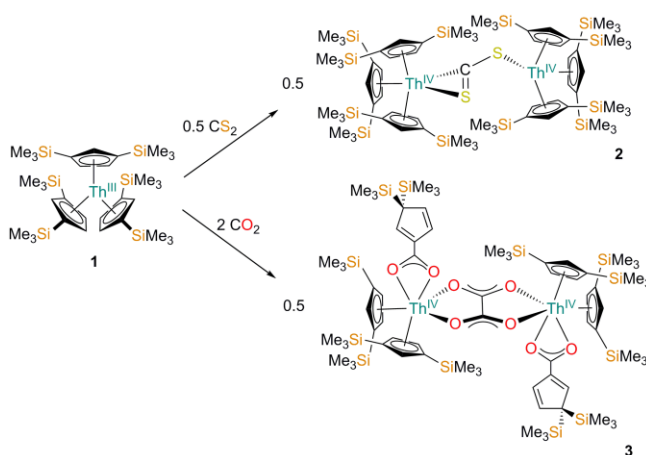
There has been an international drive to reduce emissions of CO₂ through cleaner energy generation since its identification as a key contributor to global warming.^[1] In tandem the employment of CO₂ as a C₁ feedstock for fine chemical (by direct insertion into organic molecules)^[2] and liquid fuel (*via* reduction to CO for Fischer-Tropsch processes)^[3] synthesis have rapidly expanded to complement the optimized photosynthetic pathways employed by Nature.^[4] Early d-transition metal complexes have received most attention for CO₂ activation as their inherent oxophilicity is advantageous in overcoming the considerable thermodynamic and kinetic barriers in this process.^[5] Similarly, actinides are highly oxophilic, so CO₂ activation by U^{III} complexes is also developing rapidly^[6] and proof of concept catalytic processes have been disclosed.^[7] The mapping of U^{III}-mediated CO₂ activation by DFT calculations has provided key insights into possible mechanistic pathways.^[8] In contrast, Cloke reported the only example of CO₂ activation by a putative Th^{III} intermediate^[9] as Th^{III} small molecule activation is in its infancy.^[10,11] Herein we report the first reaction of an isolated Th^{III} complex with CO₂, and CS₂ for comparative studies.

[Th(Cp'')₃] (**1**, Cp'' = {C₅H₃(SiMe₃)_{2-1,3}}) reacts with 0.5 to 10 equivalents of CS₂ to give $[\{\text{Th}(\text{Cp}'')_3\}_2(\mu\text{-}\kappa^1\text{-}\kappa^2\text{-CS}_2)]$ (**2**) as the only isolable product in 45 % yield (Scheme 1; see ESI for full details). This reaction is consistent with U^{III} chemistry as the

double reduction of CS₂ by [U(Cp')₃] (Cp' = C₅H₄SiMe₃) yields $[\{\text{U}(\text{Cp}')_3\}_2(\mu\text{-}\kappa^1\text{-}\kappa^2\text{-CS}_2)]$.^[12] However, **1** reacts with excess CO₂ to give $[\{\text{Th}(\text{Cp}'')_2[\eta^2\text{-O}_2\text{C}\{\text{C}_5\text{H}_3\text{-}3,3'\text{-(SiMe}_3)_2\}]\}_2(\mu\text{-}\kappa^2\text{-}\kappa^2\text{-C}_2\text{O}_4)]$ (**3**) in 65 % yield (Scheme 1), in contrast to the U^{III} reduction of CO₂ by [U(Cp')₃] to afford $[\{\text{U}(\text{Cp}')_3\}_2(\mu\text{-O})]$ and CO.^[13] The FTIR spectrum of **3** has absorptions at 1653 cm⁻¹ and 1560 cm⁻¹ that can be attributed to asymmetric C–O stretches of the oxalate and carboxylate groups respectively.^[14] The reaction of **2** with CO₂ gave a mixture of products including carboxylate (see ESI).

The solid state structures of **2** and **3**·2C₇H₈ were determined by single crystal XRD (Figure 1. A polymorph **2b**·2C₆H₁₄ was also obtained; see ESI). The (μ-CS₂)²⁻ unit in **2** was disordered over two positions so only the major component is discussed here. This fragment binds in an asymmetrical μ-κ¹:κ²-fashion [S–C: 1.644(11) and 1.717(10) Å; S–C–S: 124.4(7)°], in common with the motif seen for $[\{\text{U}(\text{Cp}')_3\}_2(\mu\text{-}\kappa^1\text{-}\kappa^2\text{-CS}_2)]$ [S–C: 1.464(19) and 1.831(19) Å; S–C–S: 131.7(13)°]^[12] and similar to that seen for $[\{\text{U}(\text{OSi}(\text{O}^i\text{Bu})_3)_3\}_2(\mu\text{-}\kappa^2\text{-}\kappa^2\text{-CS}_2)]$ [S–C: 1.594(12) and 1.748(11) Å; S–C–S: 131.6(8)°].^[15] The oxalate of **3** has similar metrical parameters to those seen in $[\{\text{Th}(\text{COT}^{\text{TIPS}2})_2(\text{Cp}^*)\}_2(\mu\text{-}\kappa^2\text{-}\kappa^2\text{-C}_2\text{O}_4)]$.^[9] The carboxylate ligand exhibits both C–C and C=C distances in the C₅ ring and a geminal 3,3'-disilane. The statistically identical C–O_{carboxylate} [1.284(5) and 1.263(5) Å] distances evidence the complete delocalization about the carboxylate framework, although the binding is asymmetric due to sterics [Th–O_{carboxylate} 2.400(3) and 2.484(2) Å]. The electronic structures of **2** and **3** were characterized at the density functional theory (DFT) level, employing the B3LYP exchange-correlation functional and a polarized split-valence basis set for structural optimizations. Structural parameters of **3** were in good agreement with experiment (see ESI for full details).

We postulated that **3** forms *via* a $[\{\text{Th}(\text{Cp}'')_3\}_2(\mu\text{-CO}_2)]$ intermediate that is analogous to **2**. The bulky Cp'' ligands hinder the elimination of CO and the formation of $[\{\text{Th}(\text{Cp}'')_3\}_2(\mu\text{-O})]$,^[16] so a second molecule of CO₂ reacts with the (μ-CO₂)²⁻ fragment to give an oxalate. There are many examples of sterically



Scheme 1. Synthesis of **2** and **3** from **1**.

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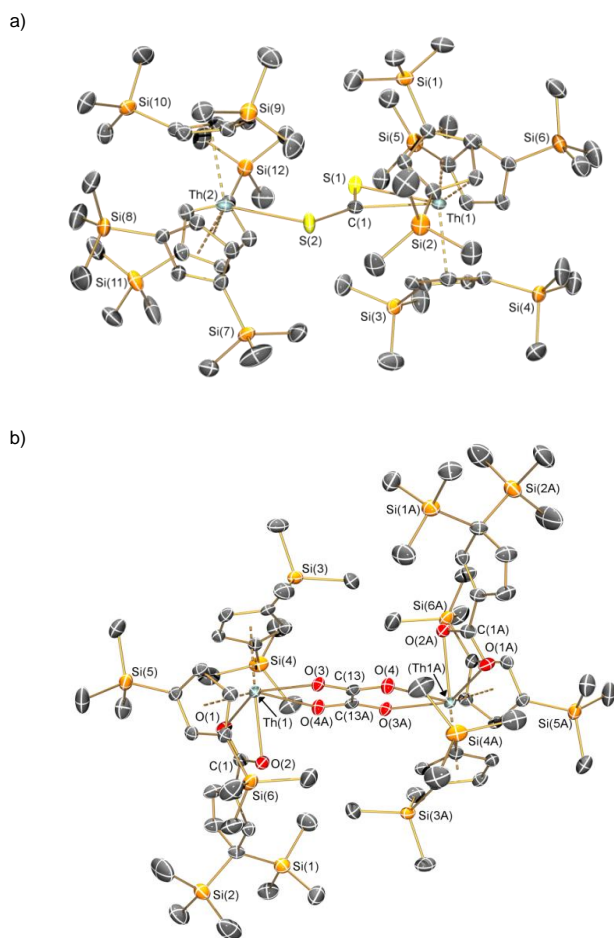


Figure 1. Molecular structure of a) **2** and b) $3 \cdot 2C_7H_8$ with selected atom labelling and displacement ellipsoids set to 30% probability level. Hydrogen atoms, minor disorder components and lattice solvent omitted for clarity.

demanding ligands promoting oxalate formation over a μ -oxo or carbonate in f-block CO_2 activation.^[8,17] Subsequent insertion of CO_2 into a Th-Cp* moiety and silyl/proton migration yields **3**. The insertion of CO_2 into lanthanide-Cp* bonds to form carboxylates has been postulated not to require steric strain to proceed.^[18] Additional experiments were performed to probe the mechanism of formation of **3** (see ESI). A Toepler pump was used to react **1** with 1 or 2 equivalents of CO_2 or $^{13}CO_2$ at $-78^\circ C$, and **3/3- ^{13}C** was the only identifiable product by 1H and $^{13}C\{^1H\}$ NMR spectroscopy in all cases. The reaction of **1** with supercritical CO_2 was monitored by 1H NMR spectroscopy, and comparison with an authentic sample showed the formation of **3**. Minor products in all reaction mixtures could not be identified. *In situ* FTIR spectroscopy was used to monitor the conversion of **1** to **3** at $-78^\circ C$ in methycyclohexane with stoichiometric CO_2 . No intermediates could be detected but the $CO_{2(g)}$ absorption at 2338 cm^{-1} diminished on slow warming to room temperature, coincident with the ingress of an oxalate absorption at 1653 cm^{-1} that is seen in the FTIR spectrum of crystalline **3**. The experiment was repeated with $^{13}CO_2$ and the oxalate absorbance of **3- ^{13}C** was observed at 1609 cm^{-1} , consistent with reduced mass considerations.

Given that no intermediates could be detected experimentally, we performed DFT studies to rationalize this unusual mechanism. Figure 2 shows the calculated enthalpy reaction profile for the formation of **3**, with the double reduction of CO_2 to give a μ - κ^1 : κ^2 - CO_2 dinuclear Th^{IV} complex the proposed first step based on the analogous CS_2 reaction as well as CO_2 reactivity reported with other actinide complexes.^[8,12,15,17] The oxalate formation invokes nucleophilic attack of a CO_2 molecule by a dimetalloxy-carbene intermediate $\{[Th(Cp^*)_3](\mu$ - κ^1 : κ^1 - $CO_2)\}$ (C2) in a carbenic fashion, which has previously only been seen in d-block CO_2 activation for Ti^{IV}.^[19] No pre-interaction is required between the Th^{IV} centers and the second CO_2 molecule, which is in contrast with all previous examples of

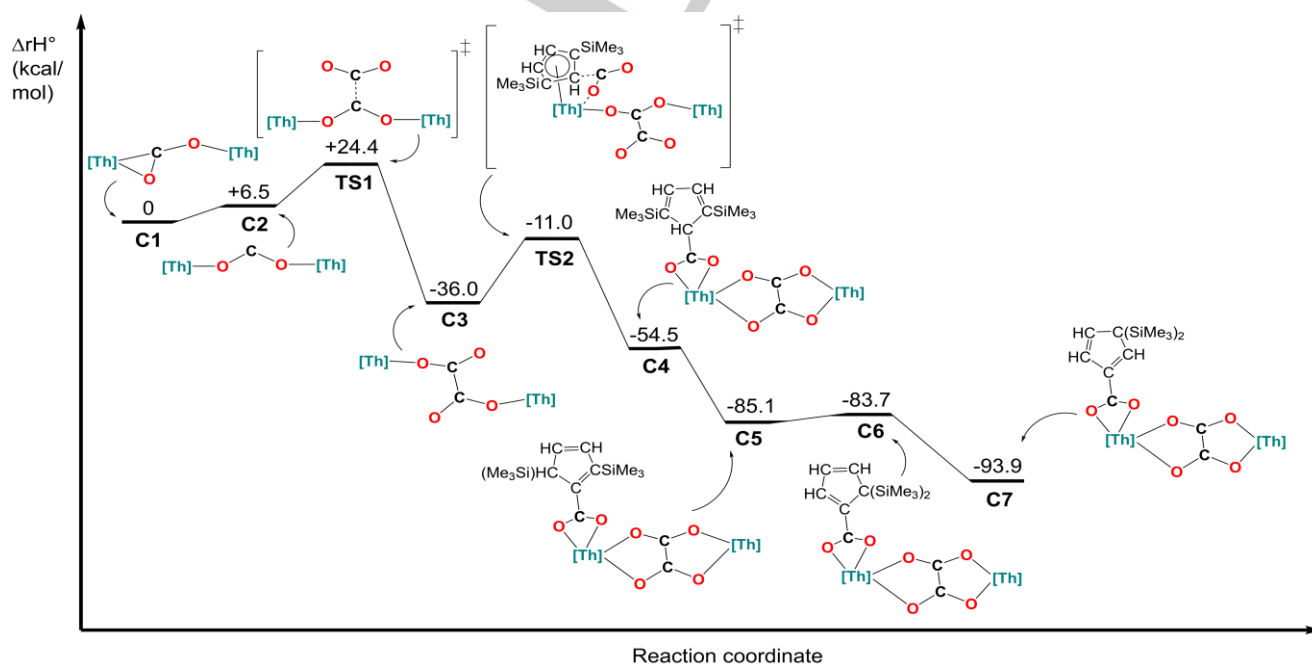


Figure 2. Computed enthalpy reaction profile for the formation of **3**.

Sm^{III} [17a-c] and U^{III} [17d] oxalate formation. The resultant *cis*- μ - κ^1 : κ^1 -C₂O₄ transition state (TS1) is one of several possible conformers that have $\Delta_r H^\circ$ values within the estimated error of the calculation (~3 kcal/mol) of each other, thus we do not comment on this further. Rearrangement of the oxalate to a *trans*- μ - κ^1 : κ^1 -binding mode increases the steric demands about the Th^{IV} centers (C3). The potential energy surface for these rearrangements is very flat and despite our efforts it was not possible to locate a transition state. This leads to insertion of CO₂ at a single position of a Th-Cp^{''} moiety at each Th^{IV} center (TS2) as the silicon centers stabilize negative charge at the beta position, allowing the best overlap with the empty orbital of CO₂. These insertions are accompanied by the rearrangement of the oxalate to a μ - κ^2 : κ^2 -binding mode. Subsequent proton and silyl group migrations in the dearomatized Cp^{''} rings give the observed product **3** at an energetic minimum.

To conclude we have shown that whilst CS₂ activation by [Th(Cp^{''})₃] is analogous to that seen for a similar U^{III} system, the mechanism by which it reacts with CO₂ to form a mixed oxalate/carboxylate product has no precedent in U^{III} chemistry, where CO₂ reduction (and subsequent carbonate formation depending on the supporting ligands) predominates. We probed this reaction to show that the oxalate is generated by a mechanism only seen previously in d-block chemistry, whereas the carboxylate forms *via* a route only seen before in f-element chemistry for lanthanide complexes. This shows that Th^{III} small molecule activation can furnish results that complement and contrast with uranium, lanthanide and d-transition metals. Future studies will target heteroallene activation by Th^{III} complexes supported by different ligand systems to test the generality or divergence of these processes.

Experimental Section

Full synthetic details, characterization data and computational data for **2-3** is available in the Supporting Information. Additional research data supporting this publication are available from The University of Manchester eScholar repository at DOI: 10.15127/1.302780.

Acknowledgements

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Keywords: actinides • thorium • subvalent compounds • reduction • small molecule activation

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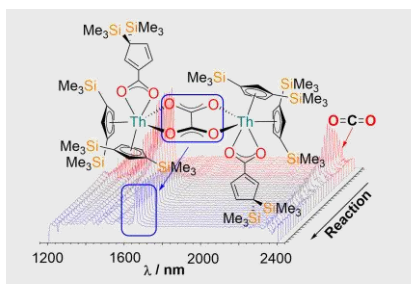
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