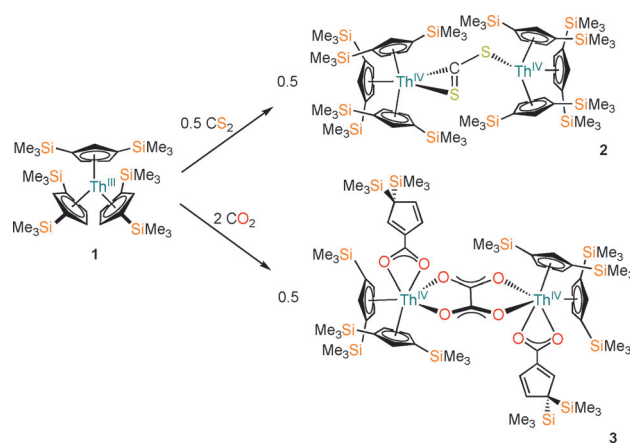**■ Subvalent Compounds**

Concomitant Carboxylate and Oxalate Formation From the Activation of CO_2 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 CO_2 activation pathways is of vital importance for the widespread future utilization of this abundant greenhouse gas. CO_2 activation by uranium(III) complexes is now relatively well understood, with oxo/carbonate formation predominating as CO_2 is readily reduced to CO, but isolated thorium(III) CO_2 activation is unprecedented. We show that the thorium(III) complex, $[Th(Cp'')_3]$ (1, $Cp'' = \{C_5H_3(SiMe_3)_2$-1,3\}), reacts with CO_2 to give the mixed oxalate-carboxylate thorium(IV) complex $[\{Th(Cp'')_2[\kappa^2\text{-}O_2C\{C_5H_3\text{-}3,3'\text{-}(SiMe_3)_2\}]\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2O_4)]$ (3). The concomitant formation of oxalate and carboxylate is unique for CO_2 activation, as in previous examples either reduction or insertion is favored to yield a single product. Therefore, thorium(III) CO_2 activation can differ from better understood uranium(III) chemistry.

There has been an international drive to reduce emissions of CO_2 through cleaner energy generation since its identification as a key contributor to global warming.[1] In tandem the employment of CO_2 as a C_1 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 CO_2 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 CO_2 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 CO_2 activation by DFT calculations has provided key insights into possible mechanistic pathways.[8] In contrast, Cloke reported the only example of CO_2 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 CO_2, and CS_2 for comparative studies.

$[Th(Cp'')_3]$ (1, $Cp'' = \{C_5H_3(SiMe_3)_2$-1,3\}) reacts with 0.5 to 10 equivalents of CS_2 to give $[\{Th(Cp'')_3\}_2(\mu\text{-}\kappa^1{:}\kappa^2\text{-}CS_2)]$ (2) as the only isolable product in 45% yield (Scheme 1; see the Supporting Information for full details). This reaction is consistent with

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

[a] A. Formanuik, Dr. F. Ortu, Dr. D. P. Mills
School of Chemistry, The University of Manchester
Manchester, M13 9PL (UK)
E-mail: david.mills@manchester.ac.uk

[b] C. J. Inman
Department of Chemistry and Biochemistry, School of Life Sciences
University of Sussex, Brighton, BN1 9QL (UK)

[c] Dr. A. Kerridge
Department of Chemistry, Lancaster University, Lancaster,
LA1 4YB (UK)

[d] Dr. L. Castro, Prof. L. Maron
LPCNO, CNRA and INSA, Université Paul Sabatier,
135 Avenue de Rangueil, Toulouse 31077 (France)
E-mail: laurent.maron@irsamc.ups-tlse.fr

U^{III} chemistry as the double reduction of CS_2 by $[U(Cp')_3]$ ($Cp' = C_5H_4SiMe_3$) yields $[\{U(Cp')_3\}_2(\mu\text{-}\kappa^1{:}\kappa^2\text{-}CS_2)]$.[12] However, **1** reacts with excess CO_2 to give $[\{Th(Cp'')_2[\eta^2\text{-}O_2C\{C_5H_3\text{-}3,3'\text{-}(SiMe_3)_2\}]\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2O_4)]$ (3) in 65% yield (Scheme 1), in contrast to the U^{III} reduction of CO_2 by $[U(Cp')_3]$ to afford $[\{U(Cp')_3\}_2(\mu\text{-}O)]$ 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 CO_2 gave a mixture of products including carboxylate (see the Supporting Information).
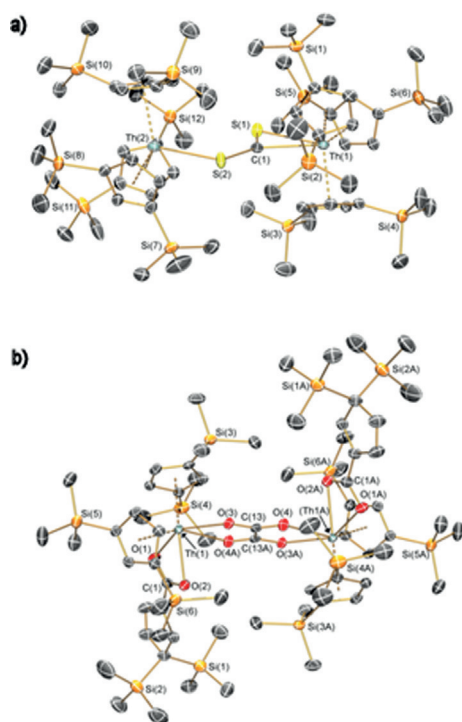
Figure 1. Molecular structure of a) **2** and b) **3**·2C_7H_8 with selected atom labelling and displacement ellipsoids set to 30% probability level. Hydrogen atoms, minor disorder components and lattice solvent omitted for clarity.

The solid state structures of **2** and **3**·2C_7H_8 were determined by single crystal XRD (Figure 1. A polymorph **2b**·2C_6H_{14} was also obtained; see the Supporting Information). The (μ-CS_2)$^{2-}$ unit in **2** was disordered over two positions so only the major component is discussed here. This fragment binds in an asymmetrical μ-κ^1:κ^2-fashion [S—C: 1.644(11) and 1.717(10) Å; S-C-S: 124.4(7)°], in common with the motif seen for [{U(Cp′$_3$)}$_2$(μ-κ^1:κ^2-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 [{U[OSi(OtBu)$_3$]$_3$}$_2$(μ-κ^2:κ^2-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 [{Th(COT^{TIPS2})(Cp*)}$_2$(μ-κ^2:κ^2-C_2O_4)].[9] The carboxylate ligand exhibits both C—C and C=C lengths in the C_5 ring and a geminal 3,3′-disilane. The C—O$_{carboxylate}$ [1.284(5) and 1.263(5) Å] lengths evidence 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 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 the Supporting Information for full details).

We postulated that **3** forms via a [{Th(Cp′′)$_3$}$_2$(μ-CO_2)] intermediate that is analogous to **2**. The bulky Cp′′ ligands hinder the elimination of CO and the formation of [{Th(Cp′)$_3$}$_2$(μ-O)],[16] so a second molecule of CO_2 reacts with the (μ-CO_2)$^{2-}$ fragment to give an oxalate. There are many examples of sterically 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^R 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 the Supporting Information for full details). A Toepler pump was used to react **1** with 1 or 2 equivalents of CO_2 or $^{13}CO_2$ at −78 °C, and **3**/**3**-^{13}C was the only identifiable product by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy in all cases. The reaction of **1** with supercritical CO_2 was monitored by ^{1}H 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 °C in methylcyclohexane 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 dimetalloxycarbene intermediate [{Th(Cp′′$_3$)}$_2$(μ-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 Sm$^{II[17a–c]}$ and U$^{III[17d]}$ oxalate formation. The resultant cis-μ-κ^1:κ^1-C_2O_4 transition state (TS1) is one of several possible conformers that have Δ_rH° values within the estimated error of the calculation (ca. 3 kcal mol^{-1}) 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 CO_2 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 CO_2. 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 although CS_2 activation by [Th(Cp′′)$_3$] is analogous to that seen for a similar U^{III} system, the mechanism by which it reacts with CO_2 to form a mixed oxalate/carboxylate product has no precedent in U^{III} chemistry, in which CO_2 reduction (and subsequent carbonate formation depending on the supporting ligands) predominates. We probed this reaction to show that the oxalate is generated by
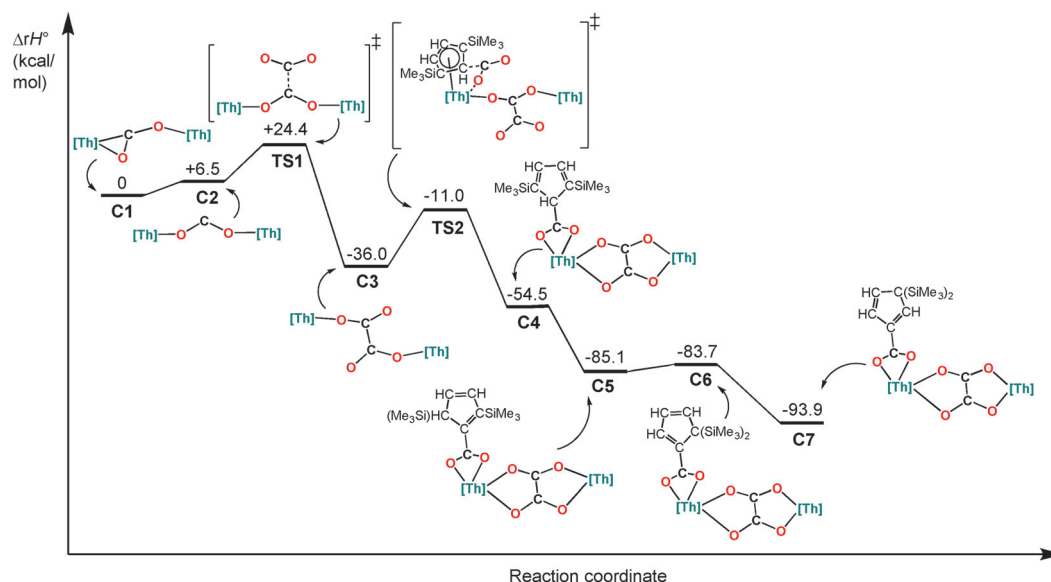
Figure 2. Computed enthalpy reaction profile for the formation of **3**.

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** and **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.

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