Applications of boroxide ligands in supporting small molecule activation by U(III) and U(IV) complexes†

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The boroxide ligand [OBAr₂]⁻ (Ar = Mes, Trip) is shown to be able to support both U(III) and U(IV) centres for the first time. The synthesis and structures of homoleptic and heteroleptic U(III) and U(IV) complexes are reported. The UX₃ complex with larger substituents, [U(OBTrip)₃]₂, exhibits greater thermal stability compared to less encumbered [U(OBMes)₂]₂ but reacts with a smaller range of the small molecules tested to date. Initial studies on their capacity to participate in small molecule chemistry show that dark purple [U(OBMes)₂]₁₂ binds and/or reductively activates a variety of small molecules such as pyridine-oxo, triphenylphosphineoxide, sulfur, and dicyclohexylcarbodiimide. While [U(OBMes)₂]₁₂ shows no reaction with CO or CO₂, [U(OBTrip)₂]₁₂ is oxidised by both, in the former case forming [U(OBTrip)₄]⁻, and in the latter case forming a small quantity of the structurally characterised μ-carbonate product ([μ- CO₃][U(OBTrip)₂]₁₂).

Introduction

Complexes of the form UX₃ where X is a large, monooanionic ligand such as an amide or aryloxide have shown great utility in the binding and reductive activation of small molecules. The choice of X provides great control over the space at the Lewis acidic metal, and the strength of the reducing capacity of the U(III) centre. For example, the common silylamine and aryloxide complexes [UN⁺] and [U(Odtbp)].[N⁺ = N(SiMe₃)₂, Odtbp = O-2,6-Bu₂C₆H₃] reductively couple carbon monoxide gas at room temperature and pressure to form the [OCCO]²⁻ fragment as the sole product in [X₂UOCOUCX₂].[1,2] The dinuclear tren derivative [U(tren)₂][μ-η²:η¹:N₂] (tren = N(NCH₂CH₂NSiMe₃)) and [U(Odtbp)]₂ show ready but reversible side-on N₂ coordination,[3] but the Odtbp analogue (Odtbp = O-2,4,6-Bu₃C₆H₂) [[U(Odtbp)]₂][μ-η²:η²:N₂] releases N₂ only upon heating a solution to 80 °C, even in the presence of small O-containing reagents such as CO₂ and CO.[2]

We showed that bulky trimesitylsiloxide complexes bind N₂ even more strongly in [[U(OSiMes)₃]₂][μ-η²:η¹:N₂]] and others have shown that further functionalisation of the trapped and reduced N₂ in polymeric nitrido complexes supported by tertbutylsiloxides is possible.[4] Flexible uranium siloxides have also allowed reactions such as CO₂ deoxygenation and carbonate formation in [[U(OSi(O'Bu)₃)]₂][μ-η²:η¹:CO₃]⁻.[5]

The capacity to transfer one X ligand has also provided significant advantages for new reactivity. For example, storage of arene solutions of [UX₃] (X = N⁺, Odtbp) results in the spontaneous reductive activation of the arene (over 90 h at 90 °C, or 30 days at 25 °C) through the formation of [[X₃U]₂][μ-η²:η⁶:C₆H₆] and elimination of two equivalents of UX₃ by-product.[6] The trapped arenes are also sufficiently reduced that a mild, homogeneous borylation of one C–H group is possible.

Boroxides provide an interesting alternative to alkoxides and aryloxides as these can provide greater delocalisation of the electron density across the OBM bond, and even a distant Lewis acidity via an empty orbital on the boron atom, thus allowing the electron density to be tuned at the metal centre.[7] The aryl functionalisation can also provide a larger protected pocket at the metal as the bulk of the aryl groups is maintained at a greater distance from the metal binding site.[8]

We have studied the capacity of the boroxide ligand [OBAr₂]⁻ (Ar = Mes, Trip) to bind U(III) for the first time. Here we show the synthesis and structures of new U(III) and U(IV) comp-
plexes and initial studies on their capacity to participate in small molecule chemistry.

Results and discussion

Syntheses

The formation of dark purple $\text{[U(OBMes}_2\text{)]}_2 \, 1^\text{m}$ from HOBMes$_2$ and UN$_3^\text{″}$ occurs in less than 3 hours at room temperature in toluene solution, Scheme 1. Work-up from hexanes affords dark crystals in 46% yield, suitable for a single crystal X-ray diffraction study, Fig. 1. At room temperature the $^1\text{H}$ NMR spectrum of $1^\text{m}$ shows the retention of the dimeric structure in solution with two different sets of ligand resonances assignable to terminal and bridging ligands. The bulkier aryl groups on the boroxide still lead to similar reaction chemistry to afford $\text{[U(OBTrip}_2\text{)]}_2 \, 1^\text{t}$, although the major by-product in the synthesis is the tetrakis(ligand) complex $2^\text{t}$, and both UX$_3$ and UX$_4$ are isolated by fractional crystallisation in similar ($ca. 30\%$) yields. The disproportionation of uranium(III) to uranium(IV) and uranium metal is a known oxidative pathway.$^6,9,10$ Dark red crystals of the mononuclear diethylether adduct $\text{[Et}_2\text{O]U(OBTrip}_2\text{)]}_2 \, 1^\text{Et}_2\text{O}$ are formed from reactions in diethyl ether and have also been structurally characterised by a single crystal X-ray diffraction study, Fig. 1. The $^1\text{H}$ NMR spectrum of $1^\text{m}$ suggests exchange between unbound and bound Ar groups on bridging OBMes$_2$ at ambient temperature and support the dimeric conformation. The resonances assigned to the bridging ligands are strongly paramagnetically shifted out of the diamagnetic region (from $−3.71$ to $−15.13$ ppm) due to proximity to the uranium centres, whereas the resonances corresponding to the terminal ligands (double the relative intensity) are between $8.29$ to $2.53$ ppm. The $^{11}$B NMR spectrum contains a resonance at $73.7$ ppm that is tentatively assigned to one of

Scheme 1  Synthesis of complexes 1 showing common by-products and decomposition products.

Fig. 1  Displacement ellipsoid drawing of the molecular structure of (a) $1^\text{m}$ and (b) $1^\text{t}$-$\text{Et}_2\text{O}$. The hydrogen atoms are omitted and the mesityl and trisopropylphenyl groups are depicted as wireframe and capped sticks for clarity. The thermal ellipsoids are displayed at 50% probability.
what should be two different boron environments, but only one
other signal attributed to trace free ligand (50.8 ppm) is
observed over an extended frequency range.

Clean starting materials and precise control of the stoichio-
metry is key to the formation of pure samples, as both deriv-
atives of 1 are very air sensitive. The homoleptic UIV complexes
[U(OBAr2)4]2 are significantly more stable, and can be formed
as minor side products in syntheses of 1, and from indepen-
dent metathetical routes from the reaction between uranium
tetraoxide and the salt NaOBAr5. Scheme 1. A high-yielding
route to 2m is available from the reaction of NaOBMes2 with
[UI4(1,4-dioxane)3] in toluene, affording [U(OBMes2)4
(dioxane)0.5]2 (2m-diox). Colourless crystals of 2m-diox and
2m-C2H6 suitable for XRD analysis were obtained from slow
diffusion of hexanes into the reaction mixture, and standing of
a concentrated toluene solution, respectively, see below. Complex 2m-diox was characterised by 1H NMR spectroscopy,
mass spectrometry (APPI-MS) and single crystal XRD analysis.
The 1H NMR spectrum show the corresponding signals of one
boroxide ligand environment. Mass spectrometric analysis
showed the molecular ion at m/z = 1298.76 that corresponds to
[M]+ fragment [U(OBMes2)3]3+. The 1H NMR spectrum of 2m
contains many more resonances than that of 1 due to the con-
gestion around metal centre; twelve magnetically different
methyl group resonances are measured in the range of
4.13–18.40 ppm and five different methine groups are discern-
able in the range 8.86–4.78 ppm.

\[
[U(OBMes2)3]_{1/2} \text{N}_{0.0} \text{Cu}_{0.9} \left[ \text{OU(OBMes2)}_{3/2} \right]_{n} \text{[1m]}
\]

Additionally, complex 1m is readily oxidised to the oxo UIV
product [OU(OBMes2)]3, 3m, due to the presence of traces of oxygen, which has been fully characterised from an indepen-
dent synthesis. Samples also decompose when heated to
100 °C in toluene or in the solid state (10−3 mbar, 115 °C, 6 h).
Upon exposure of a benzene solution of complex 1m to one
atmosphere of dry N2O, a rapid colour change from dark
purple to light brown is observed due to the formation of the
UV oxo complex 3m, which is assigned as containing bridging
oxo ligands by comparison with the literature and in consider-
ation of the size of the OBMes2 ligands, eqn (1). The 1H and
13C NMR spectra show resonances corresponding to one
mesityl environment, which is slightly shifted due to paramag-
netic contributions. The 11B NMR spectrum contains one reso-
nance at 89.29 ppm, which confirms the presence of only one
boron environment. The elemental analysis result is in agree-
ment with the formation of 3m. Reactions designed to reduce
complex 3m on a bulk scale have so far been unsuccessful; a
small quantity of a UIII product K2[(OBMes2)2U2(µ-O)] (10m)
that was isolated from a reaction with KC8 has been structu-
really characterised (see ESI† for details).

Any traces of the metallacycle [UN5–k2,N(SiMe3)C2H4] (N′ =
N(SiMe3), a common UIV contaminant in UN3+, forms
[UN′5(OMes2)] and [UN′3(OBTrip2)] (vide infra).

Crystallography

The solid-state structure of 1m confirms the formation of a
centrosymmetric binuclear UIII complex in which the two
uranium centres are bridged by two boroxide ligands (Fig. 1a)
in a distorted trigonal bipyramidal geometry due to the inter-
action of the uranium centres with the bridging mesityl
groups. The U--C distances for these interactions (U--Cavg
2.845 Å) are slightly longer than other n1 interactions with
uranium, such as the complexes bearing the ligand [1,3,2,5-
(Pr)2PhNC(=CH2)C6H4] reported by Gambaretta and co-
workers (2.678(12) Å).11 The U-O bond lengths for the boroxide
ligands are 2.548(10) Å and 2.372(10) Å for the bridging borox-
ides, and an average U–Oavg bond length of 2.196 Å for the
terminal boroxides. Both are in the same range as the U–O dis-
tances for the siloxide-bridged UIII dimer reported by Mazzanti
and co-workers, [U(Osi(O′Bu)3)]2(µ-O)2 reported by Gambarotta and co-
workers, [U(Osi(O′Bu)3)]2(µ-Osi(O′Bu)3)]2, which features two UIII centres with two bridging and two terminal silox-
ide ligands with U–O distances of 2.549(3) Å and 2.396(3) Å for
the bridging siloxides, and a U–Oavg of 2.193(4) Å for the termi-
nal ligands. Moreover, the U–U distance for complex 1m is
3.966 Å, which is similar to the UIII siloxide complex (U–U
3.9862(2) Å).5 The U–Oavg distance for the terminal ligands is
similar to that of [([Et2O)(UBTtrip2)]1 1m-Et2O (mean 2.183(7) Å) and
slightly longer than that of the uranium tris(aryloxide) complex,
[U(OiDbp)]3, with U–Oavg = 2.159 Å. The average B–O bond length of complex 1m is 1.351 Å. For both complexes the
B–Oavg fall within range for Ar2BO–M complexes reported in
the literature (1.295–1.405 Å, mean 1.350(1) Å for a fragment
search for Mes2BO–M in the Cambridge Structural Database).13

In the solid-state structure of 1m-Et2O the average U–Oboroxide Dis-
tance is 2.183 Å, slightly shorter in 1m but significantly longer
than in [U(OiDbp)]3 (2.159 Å). The U–Oether is 2.530(7) Å and
much shorter than in the seven-coordinate complex
([((NopAR)O)2(tacn)U(OTf)]2 (2.669(2) Å, NopAR = 2-neopentyl-
4-methylphenoxide, tacn = triazacyclononane), which is the
only other crystallographically characterised UIII diethyl-
 etherate.11 This is consistent with both the more electron-
deficient uranium centre engendered by the poor π donor prop-
erties of the boroxide ligand and the lower coordination
number in 1m-Et2O.

Together, the nearly linear U–O–B angle for the terminal
boroxide ligands (mean 171.6° in 1m 171.0° in 1m-Et2O) and the
elongation of the U–O bonds are a direct consequence of the
reduced π donating ability of the ligand compared with a carbo-
cyclic aryloxide, which is decreased by having a boron substitu-
et on the ligand. Electron density from the oxygen is accepted
by the boron, leading to a lower degree of π-donation from the
boroxide to the uranium centre.

The solid-state structure of 2m-diox reveals two UIV ions
both in a distorted trigonal bipyramidal coordination environ-
ment (Fig. 2a). Each uranium centre is ligated by one end of a
bridging dioxane molecule in an axial position with a U–O dis-
tance of 2.577(3) Å, which is considerably longer than in [UI4(1,4-
dioxane)3] or the [UI4(dioxane)3(aryl oxide)] previously reported by
our group (mean = 2.333(6) Å and 2.087 Å respectively).14–16 The

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boroxide ligands in the equatorial positions have a U–Oavg distance of 2.144(3) Å, which is shorter than in the uranium(III) complex 1m, consistent with a UIV centre, and similar to the U–O bond length for [U(OBTrip)4] with a U–O distance of 2.159(5) Å. The boroxide ligands in the axial positions have a U–O distance of 2.095(3) Å, which is much shorter than the equatorial boroxides. The B–Oavg distance is 1.356 Å, which is similar to complex 1m and falls within range for reported metal boroxide complexes. The U–O–Bavg angles are 167.1°, which is comparable to the U–O–B angles of the terminal boroxide ligands in 1m (mean 171.6°).

Single crystals of 2t·C7H8 suitable for X-ray diffraction analysis were obtained from concentrated toluene solution, and its solid-state structure is depicted in Fig. 2b. The solid-state structure shows an unsolvated four-coordinate uranium centre in tetrahedral geometry. The mean boroxide ligand U–O distance of 2.159(5) Å is shorter than in the uranium(III) complex 1t-Et2O, consistent with a uranium(IV) centre. The U–O bond lengths in 2t are longer than those in homoleptic uranium(IV) aryloxide [U(ODtbp)4] (2.135(4) Å), due to the greater steric demand of the boroxide ligand and poorer metal to ligand backbonding. The U–O–Bavg angles are comparable to those in 1t-Et2O (mean 171.0(5)°), despite the considerable bulk about the uranium centre. The average B–O bond length of 1.364(7) Å falls within range for reported metal boroxide complexes and is slightly longer than in 1t-Et2O. The longer B–O bond may be due to the more Lewis acidic uranium(IV) centre in 2t.

Reactions of 1m and 1t

Compound 1m has been treated with a wide range of small molecules, Scheme 2. Reactions with small, neutral N- or P-donor reagents that are readily visible by NMR spectroscopy were designed to identify whether the boron atoms in the ligands retain sufficient Lewis acidic character to participate in reactions. However, arene solutions of 1m showed no reaction with added Me3SiN3, PPh3, CH2(PPh2)2 (dppe), C2H4(PPh2)2 (dppe) or white phosphorus, P4. Normal, simple UX3 complexes with large monoanionic X ligands would be anticipated to react with these, readily forming oxidised uranium complexes or adducts, for example, [Me3SiN=UN″3],17,18 [Me3SiN=U(OSi(O′Bu)3)3],19 [U(BH4)3(PEt3)3].20

Pyridine N-oxide

The formation of oxo complexes with structures such as ULn=O,21–23 Ln=U=O13,24 or U=O–U15 have been reported from reactions with pyridine N-oxide. In this case, addition of benzene to a mixture of [U(OBMes2)3]2 and an excess of pyridine N-oxide provides a brown solution from which [U(OBMes2)4(py-O)2] (4m) can be isolated as dark orange solids after 72 hours, Scheme 2. The reaction proceeds through oxidation of complex 1m to mononuclear UIV complex 4m with ligand redistribution. Coordination of pyridine

Scheme 2 Reactions of complex 1m investigated.
N-oxide to a metal is not unique, although relatively rare.\textsuperscript{13,26–29} The identity of complex \textsuperscript{4m} was confirmed by \textsuperscript{1}H NMR spectroscopy, APPI mass spectrometry and single crystal XRD analysis. Mass spectrometric data showed the expected molecular ion at \textit{m/z} = 1223.65, which corresponds to the [M]\textsuperscript{+} fragment, [U(\text{OBMes}_2)_2(\text{Py-O})]\textsuperscript{+}. Dark orange crystals of \textsuperscript{4m} suitable for XRD analysis were grown from a concentrated benzene solution. The data are of sufficient quality to discuss connectivity information but not for bond metrics. The solid-state structure reveals a U\textsuperscript{IV} complex with a distorted octahedral geometry with the boroxide ligands in the equatorial positions and the pyridine N-oxide ligands in the axial positions (Fig. 3).

**Triphenylphosphine oxide**

Phosphine oxides are widely used ligands in f-element chemistry. As a result of the oxophilic and Lewis acidic character of lanthanides and actinides, phosphine oxides coordinate readily, and are able to stabilise a variety of complexes in low oxidation states.\textsuperscript{30–35} Moreover, applications in catalysis and liquid–liquid extraction processes have been found.\textsuperscript{36} Therefore, the reaction of a benzene solution of the uranium boroxide complex \textsuperscript{1m} with two equivalents of OPPh\textsubscript{3} was carried out, Scheme 3. This co-crystallised together with a minor by-product [U(\text{κ}^2-\text{OB(Mes)}\text{O})(\text{OBMes}_2)_3] (\textsuperscript{6m}).\textsuperscript{7}

The \textsuperscript{1}H NMR spectrum of \textsuperscript{5m} in \textit{C}_6\textit{D}_6 contains six resonances which range from 6.9 to 1.87 ppm. The \textsuperscript{31}P NMR spectrum shows a single broad resonance at \textasciitilde17.83 ppm, and this is significantly shifted from the free OPPh\textsubscript{3} resonance (\textasciitilde25 ppm) as a result of its proximity to the metal centre. Mass spectrometric analysis (APPI-MS) showed a molecular ion peak at \textit{m/z} = 1589.77 that corresponds to fragment \textsuperscript{[5m]}\textsuperscript{+}. By-product [U(\text{κ}^2-\text{OB(Mes)}\text{O})(\text{OBMes}_2)_3] (\textsuperscript{6m}) contains a coordinated boroxinato ligand, a cyclic anhydride of borinic acid,\textsuperscript{37} which is formally a product of ligand condensation, but probably formed from a contaminant in the ligand. Boroxines are rigid bidentate ligands which have drawn attention recently, mostly by forming complexes of main group elements, \textit{e.g.} for Al,\textsuperscript{18–40} Sn, Sb and Bi;\textsuperscript{41–47} but also for transition metals such as Mn,\textsuperscript{48} Au\textsuperscript{37,49} and Pt.\textsuperscript{50}

Single crystals of \textsuperscript{5m} and \textsuperscript{6m} were obtained by slow diffusion of hexanes into a benzene solution. Complex \textsuperscript{5m} has an approximately trigonal bipyramidal coordination geometry (Fig. 4). The U–OPPh\textsubscript{3} bond lengths are 2.273(4) Å and 2.270(4) Å, which are \textasciitilde0.1 Å shorter than other U\textsuperscript{III}-OPPh\textsubscript{3} distances previously reported.\textsuperscript{16,51} The U–O–P angles for the phosphine oxide ligands are 170.4(3)° and 174.4(2)° respectively, and the O₄–U–O₅ angle is 176.62(13)°. These angles are similar to the angles in the known complex, \textsuperscript{[U(NPhArF)₃(OPPh₃)₂]}\textsuperscript{24}. The U–O\textsubscript{avg} distance for the boroxide ligands is 2.124 Å, which is \textasciitilde0.07 Å shorter than the U–O bond lengths for the terminal boroxines in \textsuperscript{1m} (mean 2.196 Å). Similarly, the average B–O distance is 1.345 Å which is slightly shorter than complex \textsuperscript{1m} (mean 1.351 Å). Moreover, the mean U–O–B angle is 176.0°, and this is less bent than the terminal boroxine in \textsuperscript{1m} (mean 171.6°). Complex \textsuperscript{6m} has a nearly square pyramidal coordination geometry. The metallacycle formed from the [OBOBO]\textsuperscript{5–} unit has similarities with early metal complexes such as \textit{(\textit{η}²-catechol-\textit{µ}-catecholborate),ThCl(C₂H₄O₂)₂C₂H₄O₃} that are coordinated by alternating catechol and catecholborate groups in a hexaexo trianionic macrocyclic structure, observed for Zr, Nd, Sm, U and Th centres.\textsuperscript{52,53} For the boroxine ligand, the U–O bond distances are 2.193(4) Å and 2.191(4) Å. The B–O distances range from 1.342(9)–1.370(9) Å, which are in the same range as previously reported for main group boroxines. The six-membered ring unit has internal angles close to 120°, except for the O₄–U–O₅ bond which is much smaller, being only 77.40(16)°. The boroxine ligands have similar U–O and B–O bond lengths (U–O\textsubscript{avg} 2.172 Å, B–O\textsubscript{avg} 1.316 Å) to the terminal boroxines in \textsuperscript{1m} (mean U–O 2.196 Å, B–O 1.345 Å).
B–O 1.351 Å). Finally, the U–O–B angles for the boroxides range from 155.2(4)° to 168.7(4)°, which are significantly more bent than for the terminal boroxides in UIII (mean 171.6°).

Elemental sulfur

The reactivity of chalcogens and chalcogenides with actinide complexes has gained attention recently. Of particular interest is the potential of the metal–ligand bonding in these more polarisable systems to advance our understanding of the degree of covalency in uranium–ligand bonds, as this can provide insights into better separation of actinides from lanthanides in spent nuclear fuel. Addition of 0.5 equivalents of S₈ to a stirring solution of [U(OBMes₂)₃]₂⁺ leads to the formation of [[(OBMes₂)₃U]₂[μ-η⁵-η⁴-S₂]₂] (7m), which contains two independent bridging S₂ units. There is only one other example in the literature of a uranium complex featuring two bridging S₂ units, [[[AdArO]₃N][U][μ-η⁵-η⁴-S₂]₂] (5m). The ¹H NMR spectrum contains a set of resonances corresponding to the OBMes₂ ligand, indicating one ligand environment. Mass spectrometric analysis shows the molecular ion at m/z = 1033.56 that corresponds to the [M]+ fragment, [[(OBMes₂)₃U][μ-η⁵-η⁴-S₂]₂]+. Translucent red crystals of the sulfurbridged complex 7m suitable for XRD analysis were grown from a concentrated toluene solution.

Fig. 5 shows the molecular structure of 7m, confirming the formation of a uranium dimer with two S₂ units. Each uranium ion has a distorted pentagonal bipyramidal coordination geometry. The S₁η⁵-⁴S₂ bond length is 2.050(2) Å, which is a typical value for a S–S single bond, and comparable to H₂S₂ with a S–S bond length of 2.055 Å. The S–S distance between the two units is 3.491 Å, excluding the possibility of a S₄⁺ unit.

Thus, although one would normally anticipate a U⁴⁺ formal oxidation state product to form from the reduction of sulfur, here the U⁴⁺ assignment appears more appropriate. The ligands are both identified as bridging persulfido (S₂⁻), giving a formal U⁴⁺ oxidation state for 7m by comparison of the U–E bonds. Previously reported uranium persulfido S₂⁻ complexes show S–S distances from 2.050 Å to 2.103 Å. Previously reported transition metal supersulfido S₂⁻ complexes show S–S distances from 1.944 to 2.023 Å. Furthermore, the U–O_avg bond length is 2.078 Å, which is significantly shorter than the U–O bond lengths for the terminal boroxides in U¹m (mean 2.196 Å), and in 2m (mean 2.119 Å), also suggesting a formal oxidation state of +5 is most likely. Moreover, the B–O average distance is 1.359 Å, which is slightly longer than for complexes 1m and 2m (mean 1.351 Å and 1.356 Å respectively). The U–O–B angle of 165(3)° is much more bent than for the terminal boroxide ligands in 1m (mean 171.6°), which is reasonable if more electron density from the O atoms are being distributed into a backdonation from the uranium centres to the sulfido ligands.

DCC, N₅V–dicyclohexylcarbodiimide

The direct reaction of carbodiimides such as (DCC = N₅V–dicyclohexylcarbodiimide) with uranium was first reported in 2009. The aim of these reactions was to insert a carbodiimide into a U–C ligand bond in order to increase the steric crowding in organouranium complexes. Since then, several examples of insertion of carbodiimides into metal–ligand σ-bonds have been reported, as well as further reactivity towards small molecules with these ligands. Moreover, reactions of carbodiimides have also led to the formation of metallacycles that...
have unique structural properties and possible applications in catalysis.\textsuperscript{81–84}

\[
\begin{align*}
\text{1/2 [U(OBMes\textsubscript{2})\textsubscript{3}]_{2} + 2 DCC} & \Rightarrow \text{[U(OBMes\textsubscript{2})\textsubscript{3}]_{2} \text{Cy}} \text{N} \equiv \text{N Cy} \\
\text{C\textsubscript{6}H\textsubscript{11} - CNCy} & \Rightarrow \text{[U(OBMes\textsubscript{2})\textsubscript{3}]_{2} \text{Cy}} \text{N} \equiv \text{N Cy} \\
\text{8m} & \Rightarrow \text{8m}
\end{align*}
\]

Dropwise addition of a toluene solution of DCC to a dark purple toluene solution of 1\textsubscript{m} produced a green solution from which [U(\eta\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(\eta\textsuperscript{2}-bipy)] to [U(\eta\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(\eta\textsuperscript{2}-N(Cy)C(\text{-}N Cy)N(Cy))] via extrusion of CyNC from a coordinated DCC ligand then a 2 + 2 addition to the transiently formed UV\textsubscript{5} metallacycle to extrusion of the carbodiimide has been coupled by the reducing U centre to form the rearranged cyclohexyl-substituted guanidinate ligand via loss of cyclo-hexyls daytime. This presumably occurs similarly to the procedure reported for the reaction that converts [U(\eta\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(\eta\textsuperscript{2}-bipy)] to [U(\eta\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(\eta\textsuperscript{2}-N(Cy)C(\text{-}N Cy)N(Cy))] via extrusion of CyNC from a coordinated DCC ligand then a 2 + 2 addition to the transiently formed U\textsuperscript{5}Cy group.\textsuperscript{81} The fact that this forms from the U\textsuperscript{5} product again supports the stabilising effect of this ligand on the higher formal oxidation states of uranium.

Reactions of 1\textsuperscript{t} with CO and CO\textsubscript{2}

In contrast to 1\textsuperscript{m}, the bulkier 1\textsuperscript{t} reduces both CO and CO\textsubscript{2}; reaction with the former affording the known oxidation product 2\textsuperscript{t}, and the latter affording a bridging carbonate 9\textsuperscript{t}, although the yields are moderate and minimal respectively, Scheme 4.

Exposure of a degassed purple-brown solution of 1\textsuperscript{t} in cyclopentane to a 1 atm pressure of CO\textsubscript{2} results in the immediate formation of a green solution. Colourless crystals can be obtained upon allowing the solution to stand at room temperature overnight. The single crystals collected were of sufficient quality to obtain connectivity information by single crystal XRD analysis to identify the product as [\textmu\textsubscript{3}-CO\textsubscript{3}][U(OBTrip\textsubscript{2})\textsubscript{3}] (9\textsuperscript{t}). The solid-state structure is reminiscent of other bimetallic carbonate-bridged uranium(\textnu) complexes,\textsuperscript{85,86} with a disordered bridging carbonate linking the uranium centres with distorted trigonal bipyramidal geometries. The boroxide ligands are staggered along the U\textsubscript{1}-C\textsubscript{1}-U\textsubscript{1A} axis to minimise the steric interactions of the ligands. The formation of carbonate bridged bimetallic uranium(\textnu) complexes has been postulated to proceed via a terminal uranium(\textnu) oxo.\textsuperscript{87,88}

Comparatively, exposure of 1\textsuperscript{t} solutions to a CO atmosphere only results in decomposition to the homoleptic U(\textnu) boroxide complex 2\textsuperscript{t} and no CO containing products could be identified.

Formation of complexes [U(OBMes\textsubscript{2})N\textsubscript{3}] 11\textsuperscript{m} and [U(OBTrip\textsubscript{2})N\textsubscript{3}] 11\textsuperscript{t}

As mentioned previously, any traces of the metallacycle [UN\textsubscript{2}{[k\textsuperscript{2}-N(SiMe\textsubscript{2}CH\textsubscript{3})]}\textsubscript{2}] in the synthesis of complexes 1\textsuperscript{m} and 1\textsuperscript{t} leads to the formation of complexes [UN\textsubscript{2}{[OBMes\textsubscript{2}] (11\textsuperscript{m})}] and [UN\textsubscript{2}{[OBTrip\textsubscript{2}] (11\textsuperscript{t})]. Moreover, an alternative synthesis for complex 11\textsuperscript{m} is achieved by addition of just one equivalent of HOBMes\textsubscript{2} to an orange-brown solution of the uranium metallacycle [UN\textsubscript{2}{[k\textsuperscript{2}-N(SiMe\textsubscript{2}CH\textsubscript{3})]}], which provides a brown solution from which [UN\textsubscript{3}{[OBMes\textsubscript{2}]} (11\textsuperscript{m})] can be isolated as brown solids (Scheme 5). Formation of complex 11\textsuperscript{m} was confirmed by \textsuperscript{1}H and \textsuperscript{29}Si spectroscopies, elemental analysis and single crystal XRD analysis.

The \textsuperscript{1}H NMR spectrum shows a paramagnetically shifted resonance at \textasciitilde-6.56 ppm, which corresponds to the methyl groups in the tris(silylamide) ligand, and three smaller sets of resonances for the boroxide ligand. Moreover, the \textsuperscript{29}Si NMR resonances shift from \textasciitilde-74.46 and \textasciitilde-81.84 ppm for the uranium metallacycle to \textasciitilde-131.74 ppm for complex 11\textsuperscript{m}.

Single crystal XRD analysis revealed that the solid-state structure of complexes 11\textsuperscript{m} and 11\textsuperscript{t} have a distorted tetrahedral coordination environment where the uranium centre is coordinated by one terminal boroxide ligand and three silylamide groups (Fig. 6). Crystals of complex 11\textsuperscript{m} suitable for

\[
\begin{align*}
\text{[UN\textsubscript{2}{[k\textsuperscript{2}-N(SiMe\textsubscript{2}CH\textsubscript{3})]} \text{HOBMes\textsubscript{2}} \text{C\textsubscript{6}H\textsubscript{11}} & \Rightarrow \text{[U(OBMes\textsubscript{2})N\textsubscript{3}] + H(N(SiMe\textsubscript{3}))} \\
\text{11\textsuperscript{m}} & \Rightarrow \text{11\textsuperscript{m}}
\end{align*}
\]

Scheme 5  Synthesis of heteroleptic complex 11\textsuperscript{m}.

![Fig. 6 Solid-state structure of (a) 11\textsuperscript{m} and (b) 11\textsuperscript{t}. Mesityl and trisopropylphenyl ligands are depicted as capped sticks and wireframe for clarity. Hydrogen atoms are omitted. The thermal ellipsoids are displayed at 50% probability.](https://example.com/fig6.png)

(a) (b)
XRD analysis are obtained from a concentrated toluene solution. The average U–N_avg bond length is 2.268 Å, which is ~0.03 Å shorter than that of the previously reported complex [U(N(SiMe3)4)]_3, which is reasonable if more electron density is being distributed to the boroxide ligand and more electron density is being pulled from the tris(silylamide) ligands, thus decreasing the U–N bond length. The B–O_avg is 1.365(4) Å, which is longer than the B–O_avg bond length in complex 1\textsuperscript{m} (mean 1.351 Å). Moreover, the N–U–N angles are 105.00(8)°, 113.72(8)° and 116.96(9)°, which are in the same range as for [U(N(SiMe3)4)]_3. The U–O distance is 2.1559(18) Å, which is slightly shorter than the U–O distance in the terminal boroxides for complex 1\textsuperscript{m} (U–O_avg is 2.196 Å) but longer than the U–O_avg for 2\textsuperscript{m} (2.144 Å). The U–O–B angle is 167.23(19)°, which is in the same range as U–O–B angles for the terminal boroxides in complex 1 (mean 171.6°). Colourless crystals of complex 11\textsuperscript{m} suitable for X-ray diffraction analysis were obtained from a concentrated benzene solution upon standing at room temperature. The U–O distance amounts to 2.167(3) Å, which is longer than that of OB(Mes)_2-coordinating analogue 11\textsuperscript{m}. The mean U–N bond length is 2.272(3) Å, which is longer than complex 11\textsuperscript{m} and the previously reported [U(N(SiMe3)4)]_3.\textsuperscript{10} Bond length of B–O (1.365(5) Å) is essentially the same as that of U(m) complex 2\textsuperscript{t} (1.364(7) Å). Bond angle of U–O–B is 169.8(3)°, which is in the same range as the U–O–B angle in complex 11\textsuperscript{m}.

Conclusions

Diaryl boroxide ligands are capable ligands for both U\textsuperscript{III} and U\textsuperscript{IV} cations but the U\textsuperscript{III} complexes are particularly air-sensitive and decompose readily to di

Experimental section

[U(OBMe\textsubscript{2})\textsubscript{3}]\textsubscript{2} (1\textsuperscript{m})

A Schlenk flask was charged with [U(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{3}] (1.08 g, 1.5 mmol) and HOBMe\textsubscript{2} (1.20 g, 4.5 mmol, 3 eq.) and a stir bar. The reaction mixture was dissolved in toluene (40 mL) to yield a purple solution, which was allowed to stir at room temperature for 4 hours. Volatiles were removed by evaporation to dryness. The residue was washed with cold hexane (–78 °C, 4 mL) and recrystallized from hexane providing dark purple block crystals suitable for single-crystal X-ray crystallography. Yield: 634 mg, 41%.

1\textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): δ\textsubscript{H} 8.29 (Ar- H terminal Mes, 16H); 7.20 (o-CH\textsubscript{3} terminal Mes, 48H); 2.53 (p-CH\textsubscript{3} terminal Mes, 24H); –3.71 (o-CH\textsubscript{3} bridging Mes, 12H); –9.20 (Ar-H and p-CH\textsubscript{3} bridging Mes, 20H); –15.13 (o-CH\textsubscript{3} bridging Mes, 12H).

1\textsuperscript{11}B NMR (160.46 MHz, C\textsubscript{6}D\textsubscript{6}): δ\textsubscript{B} 73.65 (OBMes). The latter is a tentative assignment. The sample analysed was dissolved in single crystals, but this resonance is close to that of hydrolysed ligand so it may be the other resonance is not observed in the window.

MS (APPI): m/z = 1033 ([M\textsuperscript{+}][U(OBMe\textsubscript{2})\textsubscript{3}]) C\textsubscript{54}H\textsubscript{66}B\textsubscript{3}O\textsubscript{3}U\textsuperscript{+} [M\textsuperscript{+}] requires 1033.5799, found 1033.5675 (+12.4 ppm).

FTIR (cm\textsuperscript{-1}): 3612, 2728, 1721, 1608, 1552, 1280, 1228, 1176, 1151, 1081, 1029, 960, 928, 847, 745, 672.

Anal. calc for C\textsubscript{104}H\textsubscript{132}B\textsubscript{6}O\textsubscript{6}U\textsubscript{2}: C, 62.75 H, 6.44 N, 0.00%. Found: C, 62.63 H, 6.47 N, 0.00%.

[U(OBMe\textsubscript{2})\textsubscript{3}]\textsubscript{2} (2\textsuperscript{m})

A toluene solution (1.5 mL) of NaOBMe\textsubscript{2} (115 mg, 0.4 mmol, 4 eq.) was added dropwise over 10 min to a solution of Ui(dioxane)\textsubscript{2} (92 mg, 0.1 mmol) in toluene (1.5 mL) in a 7 cm\textsuperscript{3} vial with stirring for 18 hours. The reaction was centrifuged and filtered. Colourless plates suitable for single-crystal X-ray crystallography were grown from slow diffusion of hexanes into the reaction mixture. Yield: 16.7 mg, 12%.

1\textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): δ\textsubscript{H} 6.71 (Ar-H Mes, 16H); 2.15 (o-CH\textsubscript{3} Mes, 48H); 1.99 (p-CH\textsubscript{3} Mes, 24H). 1\textsuperscript{11}B NMR (160.46 MHz, C\textsubscript{6}D\textsubscript{6}): not observed in the window +130---130 ppm.
MS (APPI): m/z = 1299 ([M]⁺ [U(OBMes₂)₃]). C₇₂H₈₈B₂O₄U [M⁺] requires 1298.7563, found 1298.7595 (−3.2 ppm).

[U(OBTrip₂)₃]₂ (1t) [U(OBTrip₂)₄] (2t)

HOBTrip₂ (104 mg, 0.24 mmol) and UN⁺ (72 mg, 0.1 mmol) were dissolved in benzene (0.8 mL) in a 7 mL vial. The resulting dark red solution was stored at room temperature for 60 h during which time U(OBTrip₂)₃ (2t) crystallised as dark red crystals which can be isolated and washed with benzene (0.3 mL × 3). A second crop of 2t was isolated from the mother liquor to give a yield of 25% of 2t (30 mg, 0.02 mmol). Complex 1t (39 mg, 0.013 mmol, 32% yield) was isolated after removal of volatiles from the mother liquor.

Characterization of complex 1t:

1H NMR (500 MHz, C₆D₆): δ 8.10 (br-s, 12H, Ar-H), 2.90 (br-s, 18H, CH), 1.45 (br-s, 108H, Me). 11B NMR (160.46 MHz, C₆D₆): not observed in the window of 230–40 ppm. Repeated submissions of samples for elemental analysis did not yield reasonable data.

Characterization of complex 2t:

1H NMR (500 MHz, C₆D₆): δ 44.14 (s, 3H, Ar-H), 17.87 (s, 3H, Ar-H), 10.66 (s, 4H, Ar-H), 8.86 (s, 6Ar-H + 4 CH), 7.41 (s, 8H, CH), 6.74 (s, 4H, CH), 4.78 (s, 4H, CH), 4.13 (s, 12H, CH), 1.49 (m, 24H, CH₂), 1.24 (s, 24H, CH₂), 0.52 (d, j = 6 Hz, 12H, CH), 0.25 (d, j = 6 Hz, 12H, CH), 0.02 (d, j = 6 Hz, 9H, CH₃), −1.34 (s, 3H, CH₃), −3.43 (s, 12H, CH), −4.29 (s, 12H, CH), −13.75 (s, 12H, CH), −16.19 (s, 9H, CH), −18.40 (s, 3H, CH). 11B NMR (160.46 MHz, C₆D₆): no obvious resonance in the range of 230–40 ppm. Repeated submissions of samples for elemental analysis did not yield reasonable data.

[U(OBTrip₂)(OEt₂)] (1t·OEt₂)

A solution of HOBTrip₂ (326 mg, 0.75 mmol) in Et₂O (1 mL) was added dropwise to solution of UN⁺ (216 mg, 0.3 mmol) in Et₂O (1 mL) in a 7 mL vial. The resulting dark red solution was stirred at room temperature for 0.5 h, which was left at −30 °C for a further ca. 60 h. A brown precipitate was separated and washed with Et₂O (0.5 mL × 3) as complex 1t·OEt₂ (46 mg, 0.029 mmol) as dark red crystals. The isolated yield is low due to the very high solubility of the product.

1H NMR (500 MHz, C₆D₆): δ 8.94 (br, 12H, Ar-H), 3.56 (br-s, 18H, CH), 1.73 (br-s, 108H, Me). 11B NMR (160.46 MHz, C₆D₆): not observed in the window +130−130 ppm. No reasonable elemental analysis data were obtained despite repeated trials.

[U(OBMes₂)₃(OPPh₃)₂] (5m and 6m)

[U(OBMes₂)₃(µ-OBMes₂)]₂ (25 mg, 0.012 mmol) and OPPh₃ (7 mg, 0.024 mmol, 2 eq.) were placed in a Young NMR tube. The tube's contents were dissolved in C₆D₆ (0.4 mL). 1H NMR confirmed the formation of [U(OBMes₂)₃(OPPh₃)₂] (5m). Co-crystals of 5m and the side product [U(OBMes₂)₃(µ-OBMes₂)] (6m) suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a concentrated benzene solution of [U(OBMes₂)₃(OPPh₃)₂]. Yield: 23 mg, 60%.

1H NMR (500 MHz, C₆D₆): δ 6.90 (Ar-H, Mes, 12H); 6.46 (p-Ph H, 6H); 5.92 (p-Ph H, 12H); 3.64 (p-CH₃, Mes, 36H); 2.85 (m-Ph H, 12H). 11B NMR (160.46 MHz, C₆D₆): δ 8 in the window +130−130 ppm.

31P NMR (202 MHz, C₆D₆): δ 17.83 (OPPh₃).

MS (APPI): m/z = 1589 ([M]⁺ [U(OBMes₂)₃(OPPh₃)₂]). C₉₀H₁₀₀B₂O₄P₂U⁺ [M⁺] requires 1589.7520, found 1589.7520 (−0.0 ppm).

[U(OBMes₂)₃(µ²-OBMes₂)S₂] (7m)

To a magnetically stirred, dark purple solution of [U(OBMes₂)₃(µ-OBMes₂)] (165 mg, 0.08 mmol) in 2 mL of toluene in a 7 cm³ vial was added elemental sulfur (10 mg,
A solution of N,N'-dicyclohexylcarbodiimide [(DCC = \eta^2 \cdot N(Cy)C (=NCy)(Cy)]; Cy = C6H11] (10 mg, 0.048 mmol, 2 eq.) in benzene (1 mL) was added dropwise to a stirring benzene solution of [U(OBMes2)2(µ-OBMes2)]2 (50 mg, 0.024 mmol) in a 7 cm³ vial. The solution turned green immediately and was allowed to stir for 18 hours. The solution was then filtered and evaporated to dryness. ²⁷H NMR spectroscopy confirmed the formation of the title compound. Yield: 22 mg, 69%.

[(U(OBTrip2)N)(µ-CO3)] (11t)

Complex U(OBTrip2)N₃⁻⁷⁻ was also isolated as a side product in 5% yield from the synthesis of U²⁺/O₂⁻ as a brown precipitate, and washed with Et₂O (0.5 mL × 3) in low yield (46 mg, 0.04 mmol, 5% yield based on HOBTrip₂). Colourless crystals of 11t suitable for X-ray diffraction analysis were obtained from concentrated benzene solution upon standing at room temperature. Local code P10803.

¹H NMR (500 MHz, C₆D₆): δ = 13.73 (s, 3H, CH₃), 12.48 (s, 3H, CH₃), 11.15 (s, 2H, CH), 9.66 (s, 1H, CH), 9.06 (s, 1H, CH), 7.64 (s, 2H, CH), 7.32 (s, 1H, CH), 6.75 (t, 1H, Ar-H), 6.48 (t, 1H, CH), 3.89 (s, 3H, CH₃), 3.08 (s, 3H, CH₃), 2.92 (s, 3H, CH₃), 2.16 (s, 3H, CH₃), 1.76 (s, 3H, CH₃), −4.75 (s, 1H, CH), −6.63 (s, 1H, CH), −10.39 (s, 1H, CH), −10.52 (s, 1H, CH), −11.02 (s, 1H, CH), −11.32 (s, 1H, CH). There is restricted rotation of the CH₃ groups at room temperature on the ¹H NMR timescale. ¹³B NMR (160.46 MHz, C₆D₆): 109.74 (O–B–Ar).

Conflicts of interest

There are no conflicts to declare.

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