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# Double uranium oxo cations derived from uranyl by borane or silane reduction†

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A new type of double uranium oxo cation $[O–U–O–U–O]^{4+}$ is prepared by selective oxygen-atom abstraction from macrocyclic uranyl complexes using either boranes or silanes. A significant degree of multiple U=O bonding is evident throughout the $U_2O_3$ core, but either *trans-,cis-* or *trans-,trans-*OUOUO motifs can be isolated as boron- or silicon-capped oxo complexes. Further controlled deoxygenation of the borylated system is also possible.

Until recently, the oxo groups of the uranyl(VI) dication, $[UO_2]^{2+}$, which has a linear geometry and short, strong U–O bonds were considered to be very inert.[1] However, under anaerobic conditions, one electron reduction of uranyl compounds is now recognised to form uranyl(V) complexes that do not disproportionate, although the reactions rarely proceed further to lower U$^{IV}$ oxidation state.[2] Reduction reactions increase the oxo basicity, generating oxo-donor interactions to other Lewis acidic ions. This makes reduced uranium oxo compounds better models for the heavier, highly radioactive transuranic metal actinyl cations $[AnO_2]^{n+}$ (An = Np, Pu; n = 1, 2) for which clustering behaviour is problematic in PUREX separation processes for civil nuclear waste treatment.[3–6] Actinide oxo-bridges also facilitate electron-transfer reactions in environmental waste remediation,[7–9] enrich the coordination chemistry of actinides in minerals,[10] and can generate interesting electronic and magnetic structures.[11–13]

We originally reported reductive silylation as a route to the first covalent bond formation reaction of a molecular uranyl complex,[14] and, with others, have developed generic systems and rules that govern U$^{VI}$ to U$^{V}$ oxo-metalation,[15–19] *vs.* oxo-silylation.[20,21] Only very rarely does reduction to U$^{IV}$ occur, recently seen using oxophilic, highly reducing U$^{III}$ cations to form $[(UO_2I_4)\{UICl(py)_4\}_2]$, for example.[22] Also, exhaustive

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deoxygenation can convert simple uranyl salts to U$^{IV}$ halides when combinations of alkali metal and Group 1 alkyl reductants, and excesses of halosilanes are used.[23,24]

Here we show for the first time how simple diboranes are effective reagents for metal oxo-abstraction chemistry and how borane and silane-mediated uranyl reduction, oxo-functionalisation and abstraction, can afford a new $U_2O_3$ motif with *trans,-cis-* or *trans,-trans-*OUOUO linkages.

The dinuclear uranyl(VI) complex $[\{UO_2(py)\}_2(L^A)]$ (**1**; py = pyridine) reacts with two equivalents of the diborane $B_2pin_2$ (pin = pinacolate) at 80 °C in pyridine to yield the new paramagnetic complex $[(py)(pinBO)UOU(OBpin)(py)(L^A)]$ **2** (Scheme 1, and ESI†). Both $[U^{VI}O_2]^{2+}$ ions in **1** have undergone U$^{VI}$→U$^{IV}$ reduction and borylation, and a single oxo-atom abstraction, resulting in extrusion of O(Bpin)$_2$. The O(Bpin)$_2$ byproduct gives rise to singlets at 23 and 16 ppm in the $^{11}B$ NMR spectrum of the reaction solution, in which the highest frequency chemical shift is attributed to the pyridine adduct of OB(pin)$_2$ (see Fig. S16 and S18, ESI†), and accurately identified *via* an independent synthesis of O(Bpin)$_2$ from B$_2$pin$_2$ and Me$_3$N=O in pyridine (see ESI†). In spite of the strength of B–O bonds, diboranes have only rarely been used to deoxygenate molecules, such as pyridine-oxides and phosphine-oxides,[25,26] *o*-nitrostyrenes,[27] and CO$_2$.[28] To our knowledge, this is the first example of their use to deoxygenate a metal complex. Reactions of uranyl with hydrosilanes such as HSiEt$_3$ can produce oxo-silylated U$^{V}$-OSiR$_3$ products such as $[U(OSiR_3)_2(I)_2(PDI)]$, (PDI is a redox non-innocent pyridinediimine),[29] usually requiring a strong Lewis acid activator such as B(C$_6$F$_5$)$_3$, *e.g.* to form the intermediate $[U(OB\{C_6F_5\}_3)(OSiR_3)(dbm)_2(THF)]$ (dbm = $O$C(Ph)CHC(Ph)$O$),[30] and deoxygenation usually requires more aggressive reagents such as halosilanes.[24,29] Complex **1** also reacts with HBpin, forming **2**, H$_2$ and O(Bpin)$_2$. However, this reaction requires an excess of HBpin (10 equiv.) and elevated temperatures (125 °C).
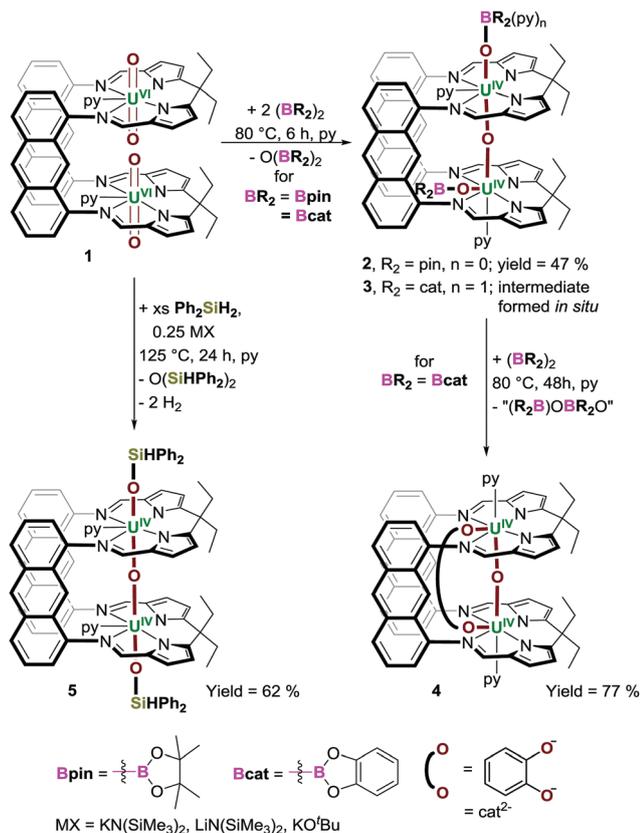
Resonances in the $^1H$ NMR spectra of **2** range from +29 to −41 ppm and a significant reduction in the asymmetric OUO stretching frequency is observed, from 912 cm$^{-1}$ for the uranyl group in **1**[31] to 566 cm$^{-1}$ in **2**. Complex **1** also reacts with the

Scheme 1 Diborane or silane-mediated deoxygenation of co-axial uranyl dications to form the new tetracations [OUOUO]$^{4+}$ **2**, **3**, and **5**, with either *trans*,-*cis*- (for boron) or *trans*,-*trans*- (for silicon) geometry, and the further deoxygenation of **3** to afford the UOU-containing **4**.



Fig. 1 Solid-state structures of **2·2toluene** (a) and **3·THF** (b). Displacement ellipsoids are drawn with 50% probability, and carbon atoms of L$^A$ and U-coordinated solvent molecules drawn wireframe. For clarity, hydrogen atoms, lattice solvent, and lower-fractional occupancy disorder components of the OBpin ligand (B(1)), and L$^A$ ethyl groups of **2·2toluene** are omitted.

diborane B$_2$cat$_2$ (cat = catecholate) at 80 °C in pyridine, forming a catecholboroxy-analogue of **2**, [(py){(py)catBO}UOU(OBcat)(py)(L$^A$)] **3**. Similarly to the formation of **2**, **3** is the product of U$^{VI}$→U$^{IV}$ reductive borylation of both U centres, and O-atom extrusion forming O(Bcat)$_2$ which was identified by $^{11}$B NMR spectroscopy (singlets at 15 and 9 ppm, Fig. S23 and S25, ESI†); the highest frequency singlet is due to the pyridine adduct of O(Bcat)$_2$ (verified *via* an independent synthesis from B$_2$cat$_2$ and Me$_3$N=O in pyridine, see ESI†). Whereas complex **2** can be isolated cleanly on a preparative scale, **3** transforms slowly into the new catecholate-bridged complex [(py)UOU(μ-O$_2$C$_6$H$_4$)(py)(L$^A$)] **4** which is the product of loss of both boroxy ligands and the addition of a catecholate ligand, [C$_6$H$_4$O$_2$]$^{2-}$, that bridges the two U$^{IV}$ centres (Scheme 1); upon the addition of a third equivalent of B$_2$cat$_2$ and heating for 48 h at 80 °C, **3** is converted exclusively into **4** in 77% yield. Only very small quantities of **3** have been isolated cleanly by fractional crystallisation. Complexes **3** and **4** may also be obtained from **1** and HBcat and, as with the formation of **2** from HBpin, these reactions require an excess of HBcat (10 equiv.).

An X-ray diffraction study on single crystals of **2** obtained from slow evaporation of a toluene solution at room temperature (Fig. 1a) shows it comprises two exogenous boroxide ligands and that one *endo*-oxo atom has be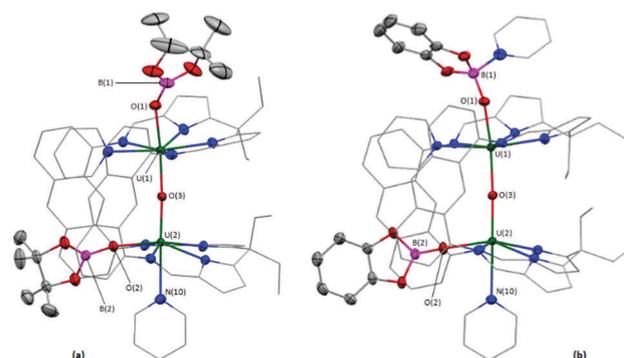en eliminated, with the remaining forming a fused U$^{IV}$–O–U$^{IV}$ core that is essentially linear (U(1)–O$_{endo}$–U(2) = 176.2(1)°). The U–O$_{exo}$ bond lengths are significantly longer than the U–O$_{endo}$ bonds; the U(1)–O(1) and U(2)–O(2) bond lengths are 2.161(2) and 2.172(2) Å, respectively, whereas the U(1)–O(3) and U(2)–O(3) bond lengths are 2.139(2) and 2.112(2) Å, respectively. Of greatest interest is that one reduced OUO dication retains the *trans*-(pinB)OUO geometry (O(1)–U(1)–O(3) = 169.05(8)°), but the other has rearranged to a *cis*-OUO configuration with a O(2)–U(2)–O(3) angle of 96.51(7)°. The *trans*,-*cis*-configurations of **2** and **3** are retained in solution – the $^{11}$B NMR spectrum of **2** shows two resonances at 475 and 221 ppm (496 and 126 ppm for **3**), and two sets of Bpin–CH$_3$ resonances are seen in the $^1$H NMR spectra of **2**.

X-ray quality crystals of **3·THF** were obtained by diffusion of hexanes vapour into a THF solution of a dried, crude reaction product mixture containing *ca.* 90% **3**, Fig. 1b. The core is similar to **2**, Fig. 1a, possessing axial and equatorial boroxides; the O(1)–U(1)–O(3) and O(2)–U(2)–O(3) bond angles are 170.7(1) and 99.2(1)°, respectively. However, the catBO-ligand that is axially coordinated to U(1) in **3** contains an additional pyridine donor, hampering direct comparison with **2** and resulting in a relative contraction of the U–O$_{exo}$ bond length in the py-solvated half of the structure, (U(1)–O(1) = 2.092(2) Å; U(2)–O(2) = 2.219(2) Å), and elongation of the B–O$_{exo}$ bond lengths (B(1)–O(1) = 1.400(5) Å; B(2)–O(2) = 1.315(5) Å) and of the U–O$_{endo}$ (U(1)–O(3) = 2.176(2) Å; U(2)–O(3) = 2.068(2) Å), presumably as a result of the lower Lewis acidity of B(1) than B(2).

The formation of **4** could occur *via* the extrusion of two equivalents of [OBcat], which would presumably form an insoluble boroxide polymer. Both complexes **3** and **4** have paramagnetically shifted $^1$H NMR spectra (resonances ranging from *ca.* +70 to −60 ppm), and the FTIR spectrum of reaction solutions that contain predominantly **3** has bands at 580 and 531 cm$^{-1}$, which are tentatively assigned as OUO stretches by comparison with **2**.

In the solid-state (Fig. 2a), **4** has crystallographically imposed mirror symmetry, with the central oxygen atom of the complex (O(3)) positioned on the mirror plane. It possesses a short U(1)–O(3) bond length of 2.090(2) Å and U(1)–O(1)/O(1′) bonds to the
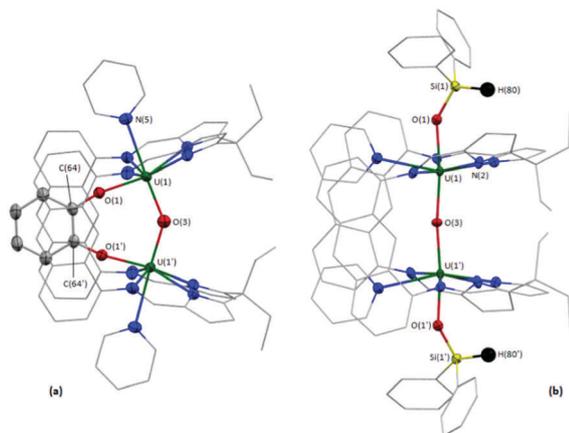
Fig. 2 Solid-state structures of **4·5.5THF** (a) and **5·py** (b). Displacement ellipsoids are drawn at 50% probability, and carbon atoms of L^A, U-coordinated solvent and SiPh_2 groups drawn wireframe. For clarity, hydrogen atoms (except for H(80) and H(80′) of **5·py**), the 50% occupancy disorder of the methyl carbon atom C(8) of **4·5.5THF**, and lattice solvent are omitted. Atoms with a prime (′) character in the atom labels are located at equivalent positions: ($x$, 1/2 − $y$, $z$) for **4·5.5THF** (a) and (1 − $x$, $y$, 3/2 − $z$) for **5·py** (b).

bridging catecholate ligand of 2.128(3) Å which, combined with the C(64)–O(1) bond length of 1.340(6) Å, indicate two U^IV centres and a dianionic catecholate ligand.[32] The U–O_{endo}–U angle in **4** (142.3(3)°) is significantly more acute than that in **2** and **3**, resulting in a close approach of the two U centres (3.956 Å in **4** versus 4.248 and 4.243 Å in **2** and **3**, respectively).

It was envisaged that **1** could react with other p-block reactants aside from diboranes, driven by the formation of strong new O–E bonds (E = p-block element). While **1** does not react with phosphines and stannanes (HPPh_2, P_2Ph_4, HSnPh_3, Sn_2Me_6, Sn_2Ph_6), it reacts with the silane Ph_2SiH_2 over 24 h at 125 °C to form [(py)(HPh_2SiO)UOU(OSiPh_2H)(py)(L^A)] (**5**; Scheme 1).[33] Complex **1** also reacts with PhSiH_3, Si_2Me_6, Ph_3SiH and Si_2Ph_2Me_4. Reactions with the former two silanes lead to the formation of unidentified, insoluble precipitates, whereas the latter two resulted in decomposition into [UO_2(py)(H_2L^A)] and unidentified uranyl-containing species.

Complex **5** is a siloxy-analogue of **2** and **3** and is only formed in the presence of a catalytic amount (25 mol%) of an alkali-metal salt such as KN(SiMe_3)_2, LiN(SiMe_3)_2 or KO^tBu, which is suggestive of a hypervalent silicate facilitating bond homolysis. The simple Lewis acids such as BF_3(OEt_2) or B(C_6F_5)_3 do not catalyse these reactions (see ESI†). The formation of **5** likely occurs in an analogous fashion to **2** and **3**, but with Si–H bond homolysis driven by the formation of strong Si–O bonds, and release of H_2 and O(SiPh_2H)_2 as reaction by-products. Indeed, when monitoring the reaction by ^{1}H NMR spectroscopy, H_2 was observed (4.31 ppm in d_5-pyridine) although it was not possible to identify Si-containing by-products in the ^{29}Si NMR spectrum, so these may be undergoing further condensation/catenation reactions.

The chemical shifts in the ^{1}H NMR spectrum of paramagnetic **5** span +64 to −41 ppm, and no obvious high-frequency asymmetric OUO stretch is found in the FTIR spectrum, consistent with a U^IV

formal oxidation state. The *trans-,trans*-symmetry of this silyl-capped ion is retained in the solution, but may be enforced by an inability of the large silyl-groups to fit between the anthracenyl spacers of L^A.

The solid-state structure of the pyridine solvate of **5·py** (see the ESI† for the THF solvate) was obtained. **5·py** possesses crystallographically imposed two-fold symmetry, with the central oxygen O(3) positioned on the two-fold axis, and shows a near linear U–O–U bond angle of 173.1(2)° (Fig. 2b), similar to **2** and **3**. However, in contrast to the B-capped compounds, the *exo*-oxosiloxides both remain *trans* with nearly linear O(1)–U(1)–O(3) and O(1′)–U(1′)–O(3) angles (172.09(9)°). The U(1)–O(1) and U(1)/U(1′)–O(3) bond lengths are 2.142(2) and 2.1486(3) Å, in good agreement with the R_2BO–U bond lengths in **2** and **3**, and with the U–O bond lengths in **4**.

The U–O bond lengths in **2–5** range from 2.068(2)–2.219(2) Å, which are significantly elongated relative to the U–O bond length anticipated for [U^{VI}O_2]^{2+} (shorter than 1.80 Å) and [U^VO_2]^+ complexes (~1.85–1.95 Å),[34,35] and are similar to those in the [U^{IV}O_2] complexes [(Ph_2HSiO)_2UCl_2(OPPh_3)_2] (2.120(5) Å),[23] [(Me_3SiO)_2UI_2(bipy)_2] (2.084(4) Å; bipy = 4,4′-bipyridine),[36] [Cp_2Co][{(C_6F_5)_3BO}{Me_3SiO}U(^{Ar}acnac)_2] (U–O(siloxy) = 2.173(8) Å; Ar = C_6H_3-3,5-^tBu_2),[37] [(UO_2I_4){DyI(py)_5}_2] (2.058(3) and 2.068(3) Å), [(UO_2I_4){UICl(py)_4}_2] (2.166(5) Å)[22] and [(Cp_2ClTiO)_2UCl(L)] (2.062(7) and 2.066(7) Å; L = a monoanionic acyclic diimino-dipyrrin ligand),[2] all of which derive from U^{VI}→U^{IV} reductive functionalisation of the uranyl(vi) ion. Furthermore, the average U–N_{pyrrolide/imine} bond length in complexes **2–5** is 2.548 Å, which is longer than those see in uranyl(v)– (2.525 Å)[14–16,19,20] and uranyl(vi)–pacman complexes (2.487 Å).[12,15]

The reductive deoxygenation of **1** by the diborane is a new reaction type and a mechanism would likely involve reaction at the most accessible *exo*-oxo ligands, with B–B bond homolysis forming U^V–OBR_2 and releasing BR_2 which can either abstract H atoms from solvent, or react with the other uranyl *exo*-oxo. This will result in a reduced, U^V intermediate [R_2BOU^V(O)_2-U^VOBR_2]^{4+} ion with elongated U^V=O_{endo} bonds that now have greater oxo-basicity, facilitating the electron transfer required for one *endo*-oxo to form a covalent μ-oxo-bridge between the two U centres. The proposed di(boroxide),di(μ-oxo) intermediate is an analogue of the [Me_3SiOU(μ-O)_2UOSiMe_3]^{4+} core seen previously.[21] The catecholate dianion in Bcat enables a further deoxygenation by the B atoms resulting in the conversion of **3** to **4**. The reaction of **1** with Ph_2SiH_2 presumably involves activation of the oxo group as a Lewis base through hypervalent silicate formation.[20,38]

Significantly, the use of a large spacer in the compartmental macrocycle L^A to enforce proximal co-linearity in uranyl(vi) coordination[31] has enabled the first reductive fusion of two uranyl dications into a single, double-uranium containing cation, and the diboranes B_2pin_2 and B_2cat_2 have been shown for the first time to be capable oxo-atom abstraction reagents; this latter feature should have a widespread utility for the deoxygenation of d-block metal oxo complexes. Both borane and silane reagents have allowed an unusually high degree of uranyl reduction, with the [OUOUO]^{4+} core existing in either *trans-,trans*-linear, or *trans-,cis*-bent conformation. The reaction

that transforms complex **3** into the catechol-bridged diuranium(IV) complex **4** suggests that further reaction chemistry of these dinuclear uranium complexes will be possible. Work is in progress to explore the level of electronic coupling between the metal centres in all of these complexes, and to explore whether analogous oxo-ion fusion chemistry is possible for the actinyl cations of neptunium and plutonium, $[AnO_2]^{n+}$.

## Conflicts of interest

There are no conflicts to declare.

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