Uranium Siloxides

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Siloxides as Supporting Ligands in Uranium(III)-Mediated Small-Molecule Activation**

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Trivalent uranium compounds have been identified as excellent candidates for small-molecule activation,[1] and their potential use in catalytic cycles has been proposed.[2] Of particular current interest is their unprecedented reactivity with carbon dioxide,[3] which is both a major contributor to environmental concerns and an attractive potential low-cost source of carbon.[4] To date only two ligand systems for well-defined uranium-mediated carbon dioxide reduction have been reported. These ligand systems are based on highly encumbered polydentate aryl oxides[1b,d,5] or classic organometallic half-sandwich COT^R/Cp^R derivatives (COT^R and Cp^R are substituted cyclooctatetraenyl and cyclopentadienyl ligands).[6] Electron-rich homoleptic uranium(III) complexes of simple ligands, such as aryl oxides[1c] and silyl amides,[7] have shown useful reactivity with small molecules; however, their reaction with CO_2 led to multiple products. As ancillary ligands, siloxides (in particular, tris(*tert*-butoxy)siloxides) are characterized by their small size relative to that of silyl amides and aryl oxides[8] and their ability to adopt mono- or bidentate forms.[8,9] These properties often lead to increased reactivity and stability, which have been exploited in homogeneous catalysis.[10] They may thus provide an attractive alternative for the synthesis of highly reactive homoleptic U^{III} complexes. However, siloxides have not been used previously as supporting ligands in uranium-mediated reduction processes,[11] probably because the high reactivity of uranium(III) siloxide precursors makes their synthesis and handling challenging.

Herein we report a homoleptic siloxide complex of trivalent uranium, $[\{U(OSi(O\textit{t}Bu)_3)_2(\mu\text{-}OSi(O\textit{t}Bu)_3)\}_2]$ (**1**), and its reactivity towards CS_2, CO_2, and toluene. Whereas the reaction of **1** with CS_2 led to the two-electron reduction product $[\{U(OSi(O\textit{t}Bu)_3)_3\}_2\{\mu\text{-}\eta^2(C,S)\text{:}\eta^2(S,S)\text{-}CS_2\}]$ (**2**), CO_2 underwent reductive disproportionation in the presence of **1** to yield CO and a dimeric U^{IV}/U^{IV} carbonate complex. Moreover, the reaction of **1** with toluene afforded a diuranium inverted-sandwich complex.

When $[U\{N(SiMe_3)_2\}_3]$[12] was treated with tris-*tert*-butoxysilanol ($HOSi(O\textit{t}Bu)_3$, 3 equiv) in hexane at −40 °C, the uranium(III) complex $[U(OSi(O\textit{t}Bu)_3)_2(\mu\text{-}OSi(O\textit{t}Bu)_3)]_2$ (**1**) was obtained as a brown crystalline solid in 82 % yield. X-ray diffraction analysis of single crystals of **1** revealed a centrosymmetric dinuclear structure in which the two uranium centers are bridged by two siloxide ligands (Figure 1). Both uranium ions are coordinated in a distorted pentagonal-bipyramid geometry by the oxygen atoms of two terminal siloxide groups and two bridging bidentate siloxide ligands, and by a neutral *tert*-butoxy group of a bridging siloxide ligand. The U–U distance is 3.9862(2) Å. The measured U−O bond lengths for the terminal siloxides (mean U−O = 2.193(4) Å) lie in the range of typical U−O distances in uranium(III) alkoxide complexes.[1c,13] Longer U−O distances are observed, as expected, for the bridging siloxides (U1−O1 2.396(3), U1−O1A 2.549(3) Å) and for the neutral *tert*-butoxy group (2.540(2) Å). These distances are similar to those found for bridging siloxides in the rare reported examples of siloxide

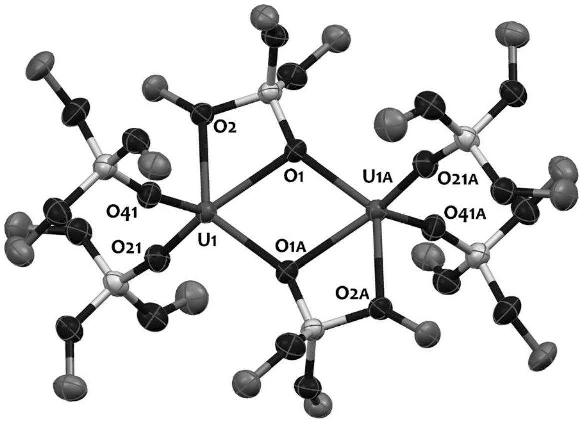

Figure 1. Ellipsoid plot (50% probability) for $[\{U(OSi(O\textit{t}Bu)_3)_2(\mu\text{-}OSi(O\textit{t}Bu)_3)\}_2]$ (**1**) crystallized from hexane. Hydrogen atoms and methyl groups were omitted for clarity.

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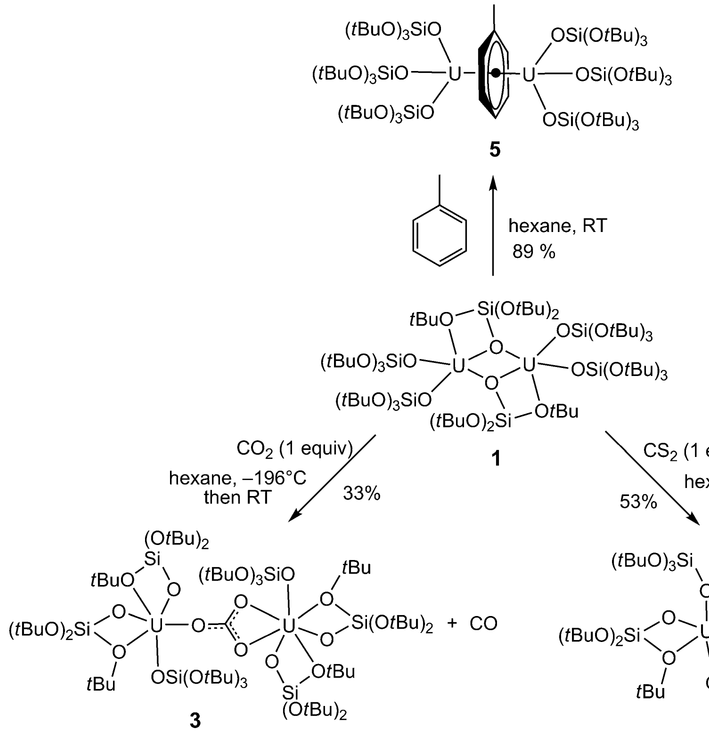
complexes of Ln^{III}.[14] In the isostructural Sm^{III} complex, the Sm–O distances for the bridging siloxides are longer, and those for the neutral *tert*-butoxy group shorter. These differences are probably simply due to the larger size of the Sm^{III} ion, which results in longer distances for the bridging siloxides and a stronger interaction with the neutral *tert*-butoxy group. In spite of the highly reducing character of U^{III} in such a strongly electron-donating environment, complex **1** was sufficiently stable in organic solvents (a few hours at room temperature) for us to investigate its reactivity. This stability provided by siloxide coordination with respect to the disproportionation reaction and cleavage by solvents[1g,15] is quite remarkable and is attributed to the bulk of the siloxide and to the multiple binding modes, as such siloxide ligands can readily become η^2 ligands. To investigate the potential of this new U^{III} precursor in reductive chemistry, we explored its reaction with the C1 substrates CS_2 and CO_2, and with toluene.

The addition of a stoichiometric amount of carbon disulfide to the trivalent uranium complex **1** in hexane (Scheme 1) resulted in an immediate color change of the solution from brown to yellow. NMR spectroscopic studies of the reaction mixture showed that a reaction product was formed selectively even in the presence of excess CS_2. The highly soluble product could be isolated in analytically pure form from a saturated solution in hexane in 53% yield. Crystallization from toluene yielded crystals of $[\{U(OSi(OtBu)_3)_3\}_2\{\mu\text{-}\eta^2(C,S):\eta^2(S,S)\text{-}CS_2\}]$ (**2**) suitable for X-ray diffraction studies. X-ray diffraction analysis showed the presence of a uranium(IV) dimer that featured a reduced bridging CS_2^{2-} group in a rare[16] $\mu\text{-}\eta^2(C,S1):\eta^2(S1,S2)$ binding mode (Scheme 1).



Scheme 1. Reduction of CO_2, CS_2, and toluene by complex **1**.

The most important feature of this structure (Figure 2) is the geometry of the coordinated carbon disulfide. The CS_2^{2-} ligand binds the two crystallographically equivalent U^{IV} centers, which are 5.406(2) Å apart, in a $\mu\text{-}\eta^2(C,S1):\eta^2(S1,S2)$ fashion. Both uranium ions are six-coordinate centers with four coordination sites occupied by the two oxygen atoms of two terminal siloxides and two oxygen atoms of a bidentate siloxide ligand. The mean $U–O_{siloxide}$ distance of 2.11(5) Å and the $U–O_{tBu}$ distance of 2.642(3) Å are in the range of previously reported uranium(IV) alkoxide U–O distances.[1c,17] The bond-valence sums calculated by using the Brown parameters[18] are in agreement with a +IV oxidation state for the uranium centers in **2** (see the Supporting Information). The structure is centrosymmetric with the CS_2^{2-} unit disordered across the symmetry center with an occupancy factor of 0.5. Unlike free CS_2 (C–S = 1.560(3) Å),[19] the CS_2 ligand in **2** is strongly asymmetrical: the C1S–S1 bond (1.748(11) Å) is significantly longer than the C1S–S2 bond (1.594(12) Å). Furthermore, the S1-C1S-S2 angle of 131.6(8)° deviates significantly from linearity. These structural data are in agreement with those reported for CS_2 complexes of transition metals and suggest the presence of a reduced CS_2 species.[20] The mean U–S distance (2.85(2) Å) and the U–C distance (2.546(13) Å)

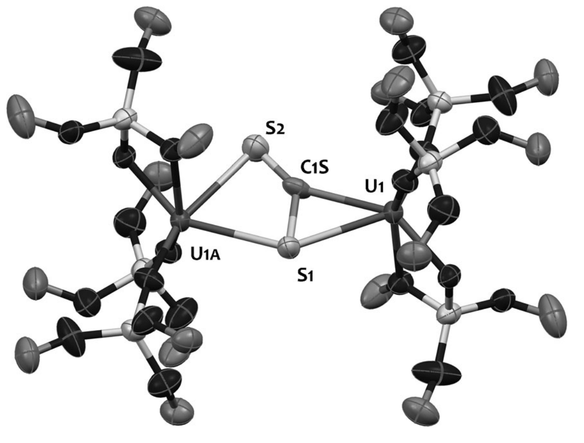


Figure 2. Ellipsoid plot (50% probability) for $[\{U(OSi(OtBu)_3)_3\}_2\{\mu\text{-}\eta^2(C,S):\eta^2(S,S)\text{-}CS_2\}]$ (**2**) crystallized from toluene. Hydrogen atoms, methyl groups, solvent molecules, and disorder were omitted for clarity.

compare well with those found in the single previous example of a CS_2 uranium(IV) complex, reported by Andersen and co-workers (U–S 2.792(3), U–C 2.53(2) Å).[20] However, the coordination mode of CS_2 was significantly different in their U^{IV}/U^{IV} dimer $[\{(RC_5H_4)_3U\}_2\{\mu\text{-}\eta^1:\eta^2\text{-}CS_2\}]$ obtained by the reduction of CS_2 by a U^{III} complex $[(RC_5H_4)_3U]$: the C–S bonds were also highly asymmetrical, but the η^2-C–S bond was shorter (1.426(2) Å) than the η^1-C–S bond (1.83(2) Å).

Recently, Meyer and co-workers reported the formation of a mixture of a trithiocarbonate and a tetrathiooxalate in the one- and two-electron reduction of CS_2 by the trivalent uranium complex $[((^{Ad}ArO)_3N)U(dme)]$ of a multidentate phenolate.[21] DFT studies indicated the CS_2^{2-}-bridged U^{IV}/U^{IV} dimer as the most reasonable intermediate in the formation of the final products.[21] However, this intermediate was not observed experimentally. To gain further insight into the reactivity of the siloxide complex **1** with CS_2, we carried out DFT calculations (see the Supporting Information) by using methodology previously developed during studies of the reaction of U^{III} with heteroallenes.[21,22]

The computed Gibbs free energy profile for the reactivity of CS_2 (see the Supporting Information) indicates that the experimentally observed bimetallic CS_2 adduct **2** is the most stable product. Any further reactions of the bimetallic complex **2** to yield sulfide, thiocarbonate, or tetrathiooxalate complexes are either thermodynamically or kinetically unfavorable, which explains the experimental observation of the complex **2** as the only product. This stability is probably the result of combined electronic and steric factors introduced by the electron-rich, bulky siloxide ligands.

The interesting reactivity of the siloxide complex **1** with CS_2 incited us to investigate the reaction with carbon dioxide. The treatment of a dark-brown suspension of the trivalent uranium complex **1** in hexane with CO_2 (1 equiv) for 6 h resulted in a slow color change accompanied by CO evolution to yield a light-green solution. The presence of free CO was identified by ^{13}C NMR spectroscopy and by the trapping of CO with vanadocene (see the Supporting Information). Volatile species were removed in vacuo, and the resulting green residue was recrystallized from toluene at −40 °C to afford the dinuclear uranium(IV) carbonate complex $[\{U(OSi(OtBu)_3)_3\}_2\{\mu\text{-}\eta^1:\eta^2\text{-}CO_3\}]$ (**3**) in 33 % yield (Scheme 1). Monitoring of the reaction with a stoichiometric amount of CO_2 by ^1H NMR spectroscopy showed the presence of only one additional product (minor at first), which was identified by X-ray diffraction studies as the U^{IV} complex $[U(OSi(OtBu)_3)_4]$ (**4**; see the Supporting Information). The ^1H NMR spectrum of the reaction mixture after 6 h showed that all of the starting complex **1** had been transformed into the complexes **3** and **4** in a 2.5:1 ratio. ^1H NMR spectroscopic studies of a solution of complex **3** in toluene over longer periods of time (1–3 days) showed that complex **3** decomposes in the presence or absence of CO_2 to yield **4**. These results indicate that complex **3** undergoes slow ligand redistribution to afford complex **4**, a process which also requires the formation of a unidentified uranium(IV) carbonate complex.

Complex **3** has a dimeric structure in which a carbonate anion bridges two uranium(IV) centers in a μ-η^1:η^2 fashion at a U–U distance of 6.2600(2) Å (Figure 3). Each uranium atom is coordinated by a terminal siloxide oxygen atom, with a U–O mean distance of 2.09(1) Å, and by the two siloxide oxygen atoms (U–O = 2.18(1) Å) and two *tert*-butoxy oxygen atoms (U–O = 2.67(6) Å) of two siloxide ligands coordinated in a bidentate fashion. These distances are in the range of previously reported uranium(IV) alkoxide U–O distances.[1c,17] The bridging carbonate ligand binds the two uranium centers in a μ-η^1:η^2 fashion with a shorter distance for the η^1-bound carbonate oxygen atom (U1–O121 = 2.25(2) Å) and two equivalent longer distances for the remaining carbonate oxygen atoms (U2–O122 = U2–O123 = 2.404(2) Å). The C–O distances observed within the carbonate unit in **3** are nearly equivalent, with a mean C–O value of 1.28(1) Å. A similar carbonate binding mode with comparable U–O and U–U distances was found in the dimeric uranium(IV) carbonate complexes $[(\eta\text{-}Cp^R)\{\eta\text{-}C_8H_6(SiiPr_3\text{-}1,4)_2\}U]_2[\mu\text{-}\eta^1:\eta^2\text{-}CO_3]$ and $[(^{Ad}ArO)_3N)U(\mu\text{-}\eta^1:\eta^2\text{-}CO_3^{2-})]$ obtained by the research groups of Cloke[6] and Meyer,[5] respectively, from the reaction of the corresponding U^{III} complexes with CO_2.

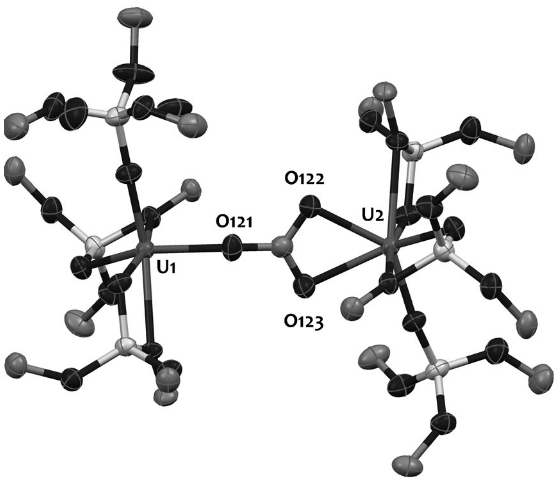


Figure 3. Ellipsoid plot (50% probability) for $[\{U(OSi(OtBu)_3)_3\}_2\{\mu\text{-}\eta^1:\eta^2\text{-}CO_3\}]$ (**3**) crystallized from toluene. Hydrogen atoms and methyl groups were omitted for clarity.

The slow transformation of **1** into the carbonate complex **3** was accompanied by CO formation, and no other reaction intermediates were observed. We computed the Gibbs free energy profile of the reaction between complex **1** and CO_2 (Figure 4). Two pathways were considered, namely, the formation of an oxo intermediate and the concerted one-electron reduction of two molecules of CO_2.[23] In both cases, the reaction involves the preliminary formation of a highly stable bimetallic $(CO_2)^{2-}$ complex. The concerted pathway was found to be the most favorable kinetically with an overall energy barrier of 14.5 kcal mol^{-1}, whereas the overall energy barrier for the oxo pathway is 23.8 kcal mol^{-1}. Such a reaction mechanism has never been proposed previously for reactions of U^{III} complexes. The only reaction mechanism proposed to date involved the formation of an oxo intermediate.[23] The oxo pathway is probably prevented in our system by the

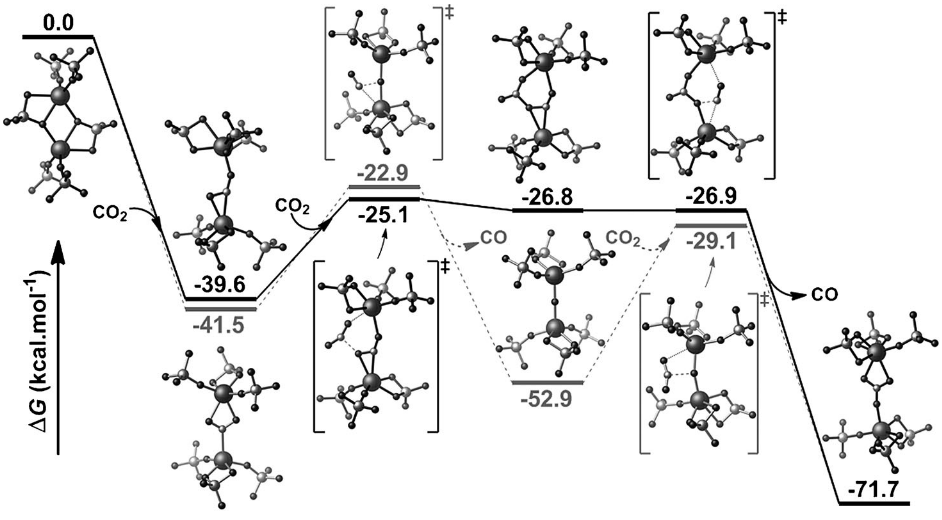


Figure 4. Gibbs free energy computed profile for the reactivity of CO$_2$ with the uranium complex **1**. The values are given in kcal mol^{-1}.

coordination environment provided by the siloxides, which can act as bidentate ligands. The concerted mechanism involves the reaction of a CO$_2$ molecule with the bimetallic complex to yield a transient six-membered-ring intermediate. From this intermediate, the spontaneous release of CO (energy barrier: 0.1 kcal mol^{-1}) leads to the formation of the observed carbonate complex.

The reactivity of **1** contrasts with that reported for simple uranium tris(aryl oxide)s with carbon dioxide, in which case no carbonate adducts were isolated, and multiple reduction and insertion products were identified.[1c] This different reactivity can be ascribed to the different electronic and steric properties of the siloxide supporting ligand. Thus, siloxides could be very useful as alternative ancillary ligands in U^{III}-mediated redox chemistry.

As a further indication of the high reactivity and interesting properties of uranium(III) siloxide complexes in uranium-mediated small-molecule activation, the inverted-sandwich complex [{U(OSi(O*t*Bu)$_3$)$_3$(μ-η^6:η^6-toluene)}$_2$] (**5**) was isolated from the reaction of **1** with excess toluene in hexane. The X-ray crystal structure of this complex shows the presence of two identical U(OSi(O*t*Bu)$_3$)$_3$ units bridged by a toluene molecule in a μ-η^6:η^6 symmetrical fashion (Figure 5). The C–C distance for the bridging toluene molecule was determined to be 1.432(3) Å, which is slightly longer (ca. 0.04 Å) than that found in free toluene and similar to that found in other systems containing reduced arenes.[7b,24] The mean U–C bond distance (2.692(3) Å) is considerably shorter than those found in U^{III} complexes of neutral arenes (ca. 2.93 Å).[13,25] The U–O(siloxide) distances are also significantly shorter (2.117(2) Å) than those found in complex **1** and suggest the presence of a U^{IV} ion. Thus, complex **5** is best described as a U^{IV} complex of a dianionic toluene ligand resulting from the reduction of toluene by the U^{III} siloxide complex. However, the presence of a U^{V} complex with a tetraanionic arene cannot be ruled out without further studies. Complex **5** is a new example of a diuranium inverted-sandwich complex and should provide important information on the bonding in these systems, which include previously isolated complexes of U^{III} with a neutral arene,[26] U^{III} with a dianionic arene,[7b,24,26] and U^{V} with a tetra-anionic arene.[27]

Arene complexes of actinides are attractive targets, as they can further our understanding of the involvement of f orbitals in actinide bonding[26a] and potentially show useful magnetic properties[24] and reactivity.[26c] However, such complexes remain rare. Recently reported inverted-sandwich complexes of diuranium were formed through the reduction of uranium complexes with potassium metal or similar reducing agents or through U^{III} disproportionation.[26c] The unprecedented formation of complex **5** from the reduction of toluene in the absence of a strong reducing agent (potassium) demonstrates the novel reactivity of the low-valent uranium complex **1**.

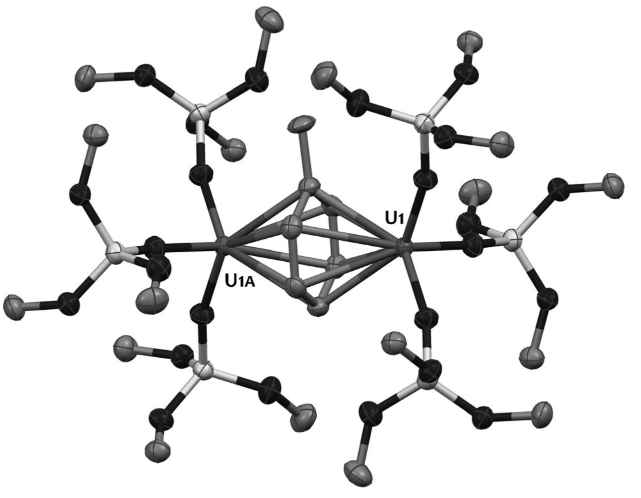


Figure 5. Ellipsoid plot (50% probability) for [{U(OSi(O*t*Bu)$_3$)$_3$(μ-η^6,η^6-toluene)}$_2$] (**5**) crystallized from hexane/toluene. Hydrogen atoms, siloxide methyl groups, and disorder were omitted for clarity.

In conclusion, we have described the synthesis of a well-defined siloxide complex of trivalent uranium, and we have demonstrated that siloxides can act as very efficient supporting ligands in uranium-mediated reductive transformations. The reaction of complex **1** with the heteroallenes CS$_2$ and CO$_2$ led to the isolation of a rare CS$_2$ sandwich complex of uranium and to the reductive disproportionation of CO$_2$ to carbonate and CO. Complex **1** also promoted the spontaneous reduction of toluene to give a new diuranium inverted-sandwich complex. The overall electron-releasing properties and steric bulk of the R$_3$SiO$^-$ groups can be tuned readily by the suitable choice of substituents, and when R = O*t*Bu, this siloxy ligand is even adaptable in its binding mode (η^1/η^2).

This successful synthesis of the first U^{III} siloxide complex will open up new possibilities in uranium chemistry.

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