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Reduction of CO₂ and CS₂ with U(III) Metallocene Aryloxides

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Supporting Information Placeholder

ABSTRACT: The reactivity of two metallocene aryloxide U(III) complexes, [(C₅Me₅)₂U(O-R)], R = 4-^tBuC₆H₄, **1**; R = 2,6-ⁱBu₂-4-CH₃C₆H₂ (BHT), **3**, with CO₂ and CS₂ has been investigated. The reaction of **1** with CO₂ produces a bridging oxo complex with loss of CO, [(C₅Me₅)₂(4-^tBuC₆H₄-O)U]₂(μ₂-O), **4**, while **3** with CO₂ results in reductive disproportionation to form the bridging carbonate species, [(C₅Me₅)₂(BHT)U]₂(μ₂-κ²:η¹-CO₃), **5**. The difference in reactivity can be attributed by the steric properties of the ligand since reaction of **2** with an oxo-delivering agent yields the U(V) terminal oxo complex, [(C₅Me₅)₂(BHT)U=O], **6**. Reduction of CS₂ to form a bridging (CS₂)²⁻ ligand, [(C₅Me₅)₂(^tBuC₆H₄-O)U]₂(μ₂-CS₂), **7**, is observed with **1**, while reaction of **3** with CS₂ also produces a bridging (CS₂)²⁻ reduced ligand complex, followed by C-H bond activation of a methyl group from one (C₅Me₅)¹⁻ ring, [(C₅Me₅)₂(BHT)U{μ₂-C(H)S₂}U(C₅Me₄CH₂)(C₅Me₅(BHT))], **8**. All compounds were characterized by NMR and IR spectroscopy, and their solid-state structures determined by X-ray crystallography.

INTRODUCTION

Small molecule activation by molecular complexes offers the opportunity to study these transformations in a controlled, stoichiometric fashion. These investigations can then lead to prospects in advancing our understanding of functionalizing these substrates, and therefore new approaches not previously considered.¹⁻³ Specifically, CO and CO₂ are C₁ feedstock molecules, and strategies on their functionalization and conversion to desirable commodity chemicals is of interest.⁴ In addition, the more reactive congener of CO₂, CS₂,^{5,6} is easier for synthetic reactions, and can provide relevant insight into CO₂ manipulation.

The reductive capability, electropositive and oxophilic nature of U(III) complexes creates a favorable situation for small molecule activation,^{7,8} which has been well-established with CO₂ and CS₂. Carbon dioxide can undergo reductive disproportionation or reductive coupling. Reductive disproportionation can result in the formation of either carbonate⁹⁻¹⁴ or oxo¹⁴⁻²⁰ complexes with release of carbon monoxide. With f elements, reductive coupling to oxalate is less common,^{21,22} and there is only one report of CO₂ reduction by one electron.²³ There are some reports of CO₂ functionalization involving both reductive chemistry of U(III) as well as insertion into a U-N bond.^{24,25} With respect to CS₂, reductive coupling to produce tetrathiooxalate,^{20,26,27} disproportionation to yield CS and S²⁻,²⁸ or reduction to CS₂²⁻,^{12,29} are the modes of reduction previously observed. There is one report of a Eu(II) complex that forms a trithiocarbonate moiety;³⁰ however, CS₃²⁻ can be obtained through insertion of CS₂ into a diuranium complex with bridging sulfide ligand.²⁸ All of these transformations are two-electron processes, which are relatively facile with one or more U(III) metal centers.

The steric properties of the ligands surrounding f element complexes are inversely related to their reactivity. Less sterically crowded complexes are typically more reactive but can also be

unselective, leading to product mixtures. For example, the Meyer group has beautifully illustrated this by tailoring the steric properties of tacn-³¹⁻³³ or cyclen-based³⁴ aryloxides to isolate unprecedented chemical and structural moieties. In addition, Cloke and co-workers have demonstrated the differences in steric properties of the heteroleptic ligand environment³⁵ can lead to changes in CO₂ reactivity, which is particularly pronounced with their decorated cyclooctatetrenyl and cyclopentadienyl ligands.^{9,22}

Herein, we examine two U(III) metallocenes ligated by aryloxides with different steric properties. We chose these molecules, (C₅Me₅)₂U(O-R), R = 4-^tBuC₆H₄ and 2,6-ⁱBu₂-4-CH₃C₆H₂ (BHT), since the reactivity should occur only at the metal center, and not involve the metallocene or aryloxide. Herein, the activation of CO₂ and CS₂ is investigated to show the effect of steric properties of the aryloxide ligands.

RESULTS AND DISCUSSION

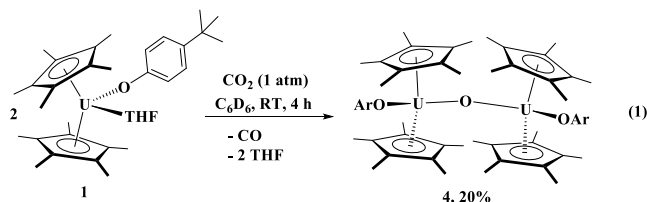
Reaction of [(C₅Me₅)₂UI(THF)] with K(O-4-^tBuC₆H₄) yields the corresponding U(III) aryloxide, [(C₅Me₅)₂U(O-4-^tBuC₆H₄)(THF)], **1**. The (C₅Me₅)¹⁻ resonance for **1** is located at -7.72 ppm in the ¹H NMR spectrum, which is consistent with the overall trend of more donating substituents on the aryl group shifting the (C₅Me₅)¹⁻ resonance downfield as compared to other U(III) metallocene complexes, Table 1. Complex **1** contains one THF molecule to complete the coordination sphere and, due to the lesser steric properties of the para-*tert*-butyl aryloxide, the U(IV), (C₅Me₅)₂U(O-4-^tBuC₆H₄)₂, **2**, is consistently observed in the ¹H NMR spectrum of **1** and subsequent reactions. We note that the amount of impurity is not enough to influence the combustion analysis. Complex **2** was synthesized independently from the reaction of (C₅Me₅)₂UCl₂ with two equivalents of K(O-4-^tBuC₆H₄). The aryloxide with greater steric properties, (C₅Me₅)₂U(O-2,6-ⁱBu₂-4-MeC₆H₂), **3**, has recently been reported,

and its $(C_5Me_5)^{-1}H$ NMR resonance does not follow the trend, but **3** does not have a THF molecule coordinated, so the comparison is not exact.

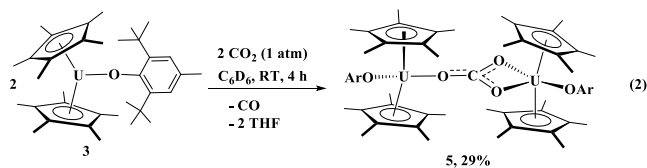
Table 1. Comparison of $(C_5Me_5)^{-1}H$ NMR resonances in U(III) metallocene complexes.

Compound	$(C_5Me_5)^{-1}H$ NMR resonance (ppm)
$(C_5Me_5)_2U(O-4-tBuC_6H_4)(THF)$, 1	-7.72
$(C_5Me_5)_2U(O-2,4,6-Me_3C_6H_2)(THF)$	-4.03
$(C_5Me_5)_2U(O-2,6-Pr_2C_6H_3)(THF)$	-3.87
$(C_5Me_5)_2U(O-2,6-tBu_2-4-MeC_6H_2)$, 3	-8.69

Each U(III) complex was treated with CO_2 . Both **1**, eq 1, and **3**, eq 2, showed an immediately color change from dark green to red, indicative of an oxidation to U(IV). The $(C_5Me_5)^{-1}$ resonance also shows a downfield shift from -7.72 ppm to -1.71 ppm in the case of the reaction of **1**, and a resonance at 0.10 ppm for the product of **3** with CO_2 , eq 1.



The structure of each product was determined by X-ray crystallography, Figure 1 and 2. The structure of the product with the smaller aryloxo, $(O-4-tBuC_6H_4)^{-}$, is a bridging oxo, $[(C_5Me_5)_2(O-4-tBuC_6H_4)U]_2(\mu_2-O)$, **4**, while, in the case of the larger BHT ligand, the product is a carbonate bridged dinuclear complex, $[(C_5Me_5)_2(BHT)U]_2(\kappa_2;\mu_1-CO_3)$, **5**, eq 2.



The U-O(oxo) distances of 2.1323(5) and 2.148(4) Å in **4** are comparable to other bridging uranium(IV) metallocene oxo complexes. For example, the U-O bond lengths in $[(Me_3SiC_5H_4)_3U(\mu_2-O)]$,¹⁸ $[\{(C_5H_5)_3U\}_2(\mu_2-O)]$,³⁶ and $[(C_5Me_5)(C_5Me_4H)(OTf)U]_2(\mu_2-O)$ ³⁷ with bond lengths of 2.1053(2), 2.0881(4), and 2.13(2) Å. The U-O-U bond angle is 170.8(3)° with U-O-C(ipso) angle of 161.4(4)°.

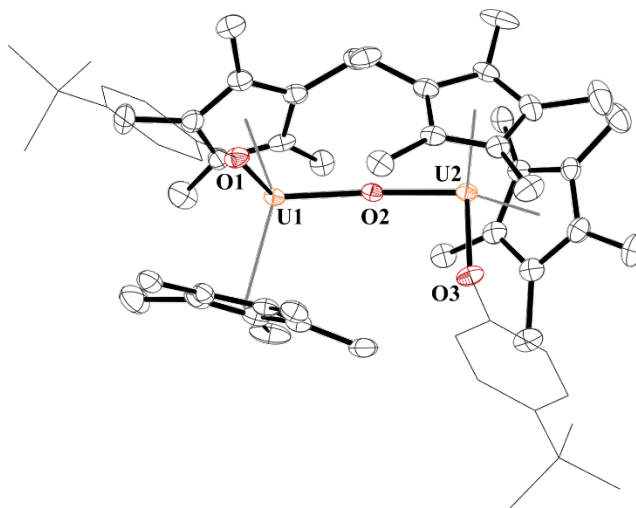


Figure 1. Thermal ellipsoid plot of **4** shown at the 50% probability level. The hydrogen atoms have been omitted and the $4-tBuC_6H_4$ part of aryloxo ligand in wireframe for clarity.

Complex **5** is the result of the reductive disproportionation of CO_2 into CO and CO_3^{2-} . Each BHT ligand in **5** are on opposite sides of the molecule from each other. The U-O(aryloxo) bond distances are 2.128(6) and 2.181(6) Å, while the U-O length bonded η^1 to U1 is 2.264(6) Å and chelating oxygen distances to U2 are 2.435(6) and 2.423(7) Å. The U-O-C(ipso) bond angles for each BHT ligand is 167.3(5)° with respect to U1 and 158.8(5)° for U2. All the C-O bond distances in the carbonate moiety are similar at 1.289(10), 1.311(11) and 1.272(11) Å.

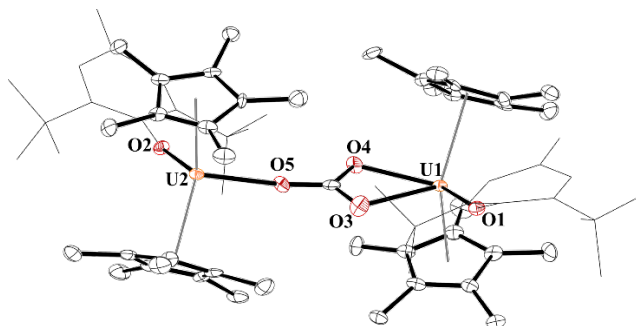
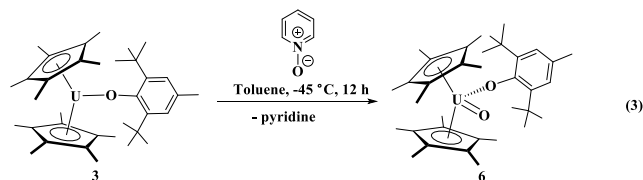


Figure 2. Thermal ellipsoid plot of **5** shown at the 50% probability level. The hydrogen atoms have been omitted and the BHT ligand in wireframe for clarity.

While the reasoning for the difference in reactivity seemed obvious due to the differences in steric properties, we wanted to probe the possibility of forming a bridging oxo with the BHT ligand. Therefore, the reaction of **2** with the oxo delivering agent, pyridine-*N*-oxide was conducted, eq 3. The reaction immediately turned from dark green to dark brown. The solid-state structure, as



determined by X-ray crystallography, revealed a terminal oxo complex, $(C_5Me_5)_2(2,6-tBu_2-4-MeC_6H_2)U=O$, **6**. Therefore, the

mechanism in the formation of the carbonate is unlikely the result of a bridging oxo intermediate, like complex **4**, followed by insertion of CO₂, which has been observed previously.¹⁰

The electronic structure of **6** was interrogated by variable temperature magnetic susceptibility to confirm the oxidation state (Figures S16 and S17). The value of μ_{eff} determined from χT extrapolated to 0 K is 1.34 μ_{B} , which is typical of U(V). The U-O(oxo) bond distance of 1.855(3) Å, is within the range for U(V) terminal oxo complexes,³⁸ with a U-O(aryloxo) length of 2.134(2) Å.

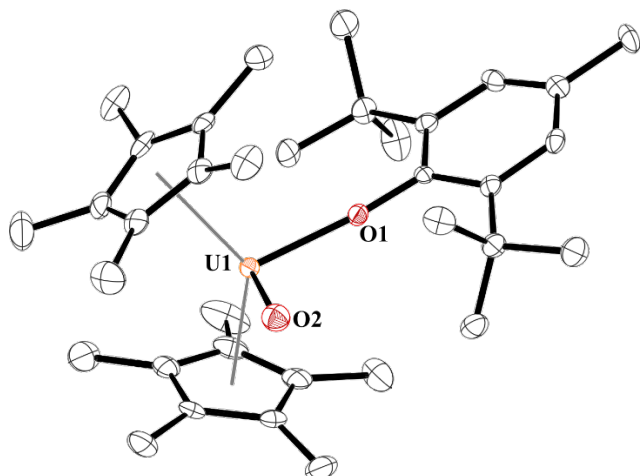


Figure 3. Thermal ellipsoid plot of **6** shown at the 50% probability level. The hydrogen atoms have been omitted and for clarity.

Next, we turned to the reactivity of **1** and **2** with CS₂. In the case of the reaction with **1**, the ¹H NMR spectrum features two (C₅Me₅)¹⁻ resonances at -4.41 and -2.47 ppm, and two ¹Bu resonances at 7.20 and 9.83 ppm, indicating an asymmetric ligand environment. The solid-state structure was hampered by disorder due to twinning, but the connectivity showed a bridging (CS₂)²⁻ ligand between uranium centers. The U-S bond distances of 2.94(1) and 2.926(5) Å compare well to the 2.913(2) and 2.910(2) Å in [$\{((^{\text{Ad}}\text{ArO})_3\text{N})\text{U}\}_2(\mu-\kappa^2:\kappa^2\text{-CS}_2\text{Se})$], (^{Ad}ArO)₃N = tris(2-oxy-3-adamantyl-5-methylbenzyl)amine.¹⁵ However, U(IV)-S bond distances with κ^2 -(S,S) ligands are typically ~ 2.80-2.90 Å.³⁹⁻⁴¹ The U-C61 bond distance in **7** is 2.44(2) Å is similar to U-C(methyl) bonds. For example, the U-C(methyl) bond distances in (C₅Me₅)₂U(CH₃)₂ is 2.424(7) and 2.414(7) Å.⁴²

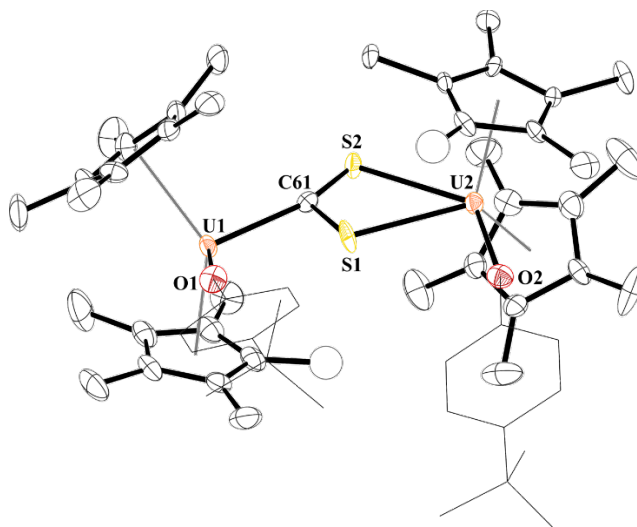


Figure 4. Thermal ellipsoid plot of **7** shown at the 50% probability level. The hydrogen atoms have been omitted and the 4-^tBuC₆H₄ part of aryloxo ligand in wireframe for clarity.

The reaction of **3** with CS₂ showed a more complicated ¹H NMR spectrum. The solid-state structure was determined by X-ray crystallography to be [(C₅Me₅)₂(BHT)U{ μ -C(H)S₂}U(C₅Me₄CH₂)(C₅Me₅)(BHT)]₂, **8**, Figure 5. Complex **8** is result of a C-H bond activation occurring at the carbene carbon of a (CS₂)²⁻ bridging ligand like that observed in **7**. When this reaction is kept at low temperature, a more symmetric ¹H NMR spectrum is obtained, indicating that the C-H bond activation takes places upon warming. Three resonances integrated to 15 protons each were observed at 1.48, 4.23, and 5.24 ppm, which correspond to the unperturbed three (C₅Me₅)¹⁻ ligands. The U-O bond distances of 2.127(7) and 2.141(7) Å are . The U-S bond lengths of 2.619(3) and 2.648(3) Å are similar to those found for U(IV) thiolate complexes. For comparison, the U-S distances in (C₅Me₅)₂U(SPh)₂ is 2.7060(14) and 2.7101(14) Å,⁴³ 2.6845(7) and 2.6967(7) Å in (C₅Me₄H)₂U(SPh)₂,⁴⁴ and 2.639(3) Å in (C₅Me₅)₂U(SMe)₂.⁴⁵ Metalation of a methyl group in (C₅Me₅)¹⁻ ring has been observed previously,⁴⁶⁻⁴⁹ but they are typically bound to the actinide center that (C₅Me₅)¹⁻ is coordinated, called tuck-in, or to another metal center, called tuck-over. In this case, as well as the C-H bond activation observed in the formation of transient nitrides,⁵⁰⁻⁵² the uranium center is bonded to the byproduct of the reactive organic fragment after C-H bond activation. In this case, we were able to trap the probable intermediate in complex **7**.

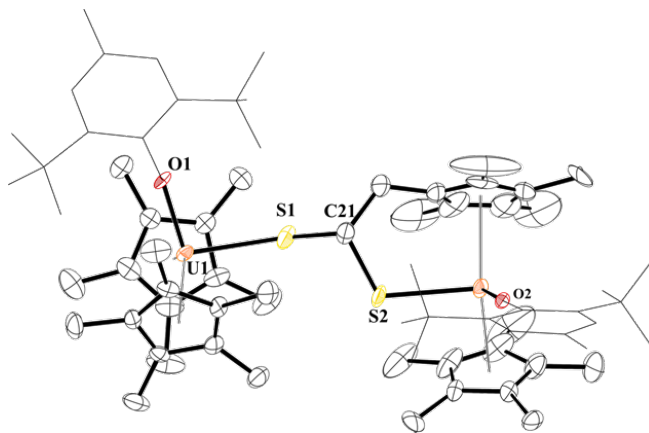


Figure 5. Thermal ellipsoid plot of **8** shown at the 50% probability level. The hydrogen atoms have been omitted and the BHT ligand in wireframe for clarity. COOL!

CONCLUSION

In summary, the reductive reactivity of CO₂ and CS₂ have been investigated with two heteroleptic U(III) complexes with varying steric properties. In each case, the steric properties caused different products to form with a bridging O²⁻ and (CS₂)²⁻ using the smaller aryloxoide, O-4-^tBuC₆H₄, and (CO₃)²⁻ and [C(H)(C₅Me₄CH₂)S₂]²⁻ with the larger BHT ligated complex. This demonstrates the capability of this ligand environment to afford new U(III) complexes as well as serve as a scaffold for uranium-mediated small molecule activation. We are currently investigating further reactivity with these ligand frameworks.

EXPERIMENTAL SECTION

General considerations. All syntheses were carried out under an N₂ atmosphere using glovebox and Schlenk techniques unless otherwise stated. All non-deuterated solvents used were dried by passing through a solvent purification system (MBraun, USA), and stored over sieves, and potassium metal for aromatic and aliphatic solvents, or calcium hydride for ethereal solvents. (C₅Me₅)₂UI(THF), (C₅Me₅)₂UCl₂, and (C₅Me₅)₂U(O-2,6-^tBu₂-4-MeC₆H₂), **3**, were prepared accordingly to their literature procedures. Carbon disulfide was purified by distillation of off calcium hydride. Benzene-*d*₆ and THF-*d*₈ (Cambridge Isotope Laboratories) were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. All ¹H spectra were taken on 600 MHz or 300 MHz Bruker spectrometers. All NMR chemical shifts are reported in ppm. ¹H NMR chemical shifts were referenced internally to the residual solvent peaks. IR were taken on a Nicolet Summit Pro FTIR spectrometer with, using a KBr pellet. Elemental analysis was performed on a Carlo Erba 1108 elemental analyzer, outfitted with an A/D converter for analysis using Eager Xperience software.

Synthesis of [(C₅Me₅)₂U(O-4-^tBuC₆H₄)(THF)], **1.** To vial containing (C₅Me₅)₂UI(THF) (416 mg, 0.588 mmol), ca. 10 mL of THF which was passed through a filter plug of potassium graphite and diatomaceous earth. In a separate vial a solution of potassium *p*-*tert*-butyl-phenoxide, (133 mg, 0.705 mmol) in 7 mL of THF, was passed through a plug of potassium graphite and diatomaceous earth. The phenolate solution was added dropwise to the (C₅Me₅)₂UI(THF) solution, which results in the formation of a grey powder, while the solution remains green. After one hour the solvent is removed under reduced pressure and is replaced with 10 mL of toluene. The solution is filtered, and the filtrate is stored at -45 °C, which results in green crystals of **1**, 75 mg, 18%. ¹H NMR (C₆D₆, 298 K): δ -38.36 (bs, 4H, THF), -14.85 (bs, 4H, THF), -7.72 (s, 30H, C₅(CH₃)₅), -1.28 (s, 2H, *o*-Ar-H), 0.88 (s, 9H, *p*-Ar-C(CH₃)₃), 7.00 (s, 2H, *m*-Ar-H). IR (KBr, cm⁻¹): 2961 (s), 2911 (s), 2860 (m), 1599 (m), 1505 (s), 1442 (bm), 1384 (s), 1260 (s), 1174 (m), 1064 (m), 922 (m), 871 (m), 835 (m), 680 (w), 478 (w). Anal. Calcd. (found) for C₃₄H₅₁O₂U, C 55.96 (55.51%), H 7.04 (6.82%).

Independent Synthesis of (C₅Me₅)₂U(O-4-^tBuC₆H₄)₂, **2.** (C₅Me₅)₂UCl₂ (426 mg, 0.736 mmol) was dissolved in 10 mL of toluene and added to excess KO-4-^tBuC₆H₄, at room temperature. The solution turned from dark red to orange color, while stirring overnight. The solution was filtered and crystallized at -45 °C;

orange crystals of the product were recovered the next day (177 mg, 0.218 mmol, 30%). ¹H NMR (C₆D₆, 298 K): δ -12.10 (4H, d, *o*-Ar-H), -0.86 (18H, Ar-C(CH₃)₃), 2.28 (4H, d, Ar-H), 2.88 (30H, C₅(CH₃)₅). IR (KBr, cm⁻¹): 2962 (s), 2905 (m), 2863 (m), 1599 (w), 1505 (s), 1384 (m), 1252 (s), 1174 (m), 1063 (w), 871 (m), 832 (m), 693 (w), 539 (w). Anal. Calcd. (found) for C₄₀H₅₆O₂U, C 59.54 (59.24%), H 6.99 (7.16%).

Synthesis of [(C₅Me₅)₂(4-^tBuC₆H₄-O)U]₂(μ₂-O), **4.** To a frozen solution of degassed toluene and **1** (0.147 g, 0.202 mmol), excess carbon dioxide was added (~1 atm, 50 mL). The solution was allowed to warm to room temperature and stir overnight. The volume of the solution was reduced under reduced pressure and crystallized at -16° C to yield red crystals of **3** (27 mg, 0.020 mmol, 20%). ¹H NMR (C₆D₆, 298 K): δ -1.71 (60H, C₅(CH₃)₅), 4.42 (9H, Ar-C(CH₃)₃), 7.57 (4H, Ar-H), 14.53 (4H, Ar-H). IR (KBr, cm⁻¹): 2963 (s), 2908 (s), 2859 (m), 1599 (m), 1505 (s), 1441 (bm), 1384 (s), 1257 (s), 1174 (m), 1065 (m), 933 (w), 834 (m), 692 (w), 538 (w). Anal. Calcd. (found) for C₆₀H₈₆O₃U₂, C 54.15 (53.96%), H 6.51 (6.29%).

Synthesis of [(C₅Me₅)₂(BHT)U]₂(μ₂-κ²:η¹-CO₃), **5.** To a solution of **2** (29 mg, 0.040 mmol) in C₆D₆, 1.1 equivalents of carbon dioxide were condensed. The solution was warmed to room temperature and allowed to sit overnight. The resulting red solution was pumped to dryness and crystallized from a saturated toluene solution at -45° C, yielding red crystals of **4** (11 mg, 0.0071 mmol, 29%). ¹H NMR (THF-*d*₈, 315 K): δ -6.76 (9H, Ar-C(CH₃)₃), -0.28 (3H, Ar-CH₃), 0.06 (9H, Ar-C(CH₃)₃), 0.10 (bs, 30H, C₅(CH₃)₅), 0.14 (30H, C₅(CH₃)₅), 5.33 (3H, Ar-CH₃), 7.51 (1H, Ar-H), 11.96 (9H, Ar-C(CH₃)₃), 13.55 (1H, Ar-H), 22.13 (1H, Ar-H), 26.16 (1H, Ar-H), 29.76 (9H, Ar-C(CH₃)₃). IR (KBr, cm⁻¹): 2958 (m), 2907 (bm), 2861 (m), 1431 (m), 1396 (s), 1385 (s), 1260 (m), 1185 (m), 1112 (m), 1062 (m), 802 (m), 531 (w). Anal. Calcd. (found) for C₇₁H₁₀₈O₅U₂, C 56.19 (55.81%), H 7.17 (7.17%).

Synthesis of [(C₅Me₅)₂(BHT)U=O], **6.** A 5 mL toluene solution of pyridine-*N*-oxide (28.0 mg, 0.295 mmol), at -45 °C, was slowly added to a stirring toluene (10 mL) of **2** (214 mg, 0.295 mmol) solution, also at -45 °C. The solution quickly turned a darker shade of brown and was allowed to stir overnight. Volatiles were removed from the solution under vacuum and rinsed with 3 mL pentane. The black powder was crystallized in toluene, by layering with hexamethyldisiloxane at -45 °C, yielding black blocks (54 mg, 0.072 mmol, 25%). ¹H NMR (C₆D₆, 298 K): δ -7.93 (9H, Ar-C(CH₃)₃), 3.98 (3H, Ar-CH₃), 5.45 (30H, C₅(CH₃)₅), 6.08 (1H, Ar-H), 11.27 (1H, Ar-H), 19.77 (9H, Ar-C(CH₃)₃). IR (KBr, cm⁻¹): 2960 (m), 2914 (m), 2861 (m), 1618 (wb), 1421 (w), 1390 (m), 1385 (s), 1262 (s), 1120 (s), 1089 (m), 1034 (s), 828 (m), 809 (m), 644 (m), 472 (m). Anal. Calcd. (found) for C₃₅H₅₃O₂U, C 56.52 (56.56%), H 7.18 (7.48%).

Synthesis of [(C₅Me₅)₂(^tBuC₆H₄-O)U]₂(μ₂-κ²:η¹-CS₂), **7.** To a -45° C toluene solution of **1** (33 mg, 0.046 mmol) a few drops of freshly distilled CS₂ was added. The solution immediately turned dark red, and after 5 minutes of stirring had its volatiles removed under reduced pressure. Recrystallization from diethyl ether resulted in 16 mg (0.011 mmol 50%) dark red crystalline product. ¹H NMR (C₆D₆, 298 K): δ -4.41 (30H, C₅(CH₃)₅), -2.47 (30H, C₅(CH₃)₅), 7.20 (9H, C(CH₃)₃), 9.83 (9H, C(CH₃)₃), 21.23 (2H, ArH), 28.74 (2H, ArH), 29.22 (2H, ArH), 42.50 (2H, ArH). IR (KBr, cm⁻¹): 2961 (s), 2907 (mb), 2857 (m), 1600 (m), 1505 (s), 1438 (m), 1385 (m), 1259 (s), 1174 (m), 1065 (m), 1020 (m), 875

(m), 833 (m), 696 (w), 539 (w). Anal. Calcd. (found) for $C_{61}H_{86}S_2O_2U_2$, C 52.65 (52.37%), H 6.23 (6.21%).

Synthesis of $[(C_5Me_5)_2(BHT)U\{\mu_2-C(H)S_2U(C_5Me_4CH_2)(C_5Me_5)(BHT)\}]$, **8.** To a $-45^\circ C$ toluene solution of $(C_5Me_5)_2U(BHT)$ (94 mg, 0.13 mmol) a few drops of freshly distilled CS_2 was added. The solution immediately turned dark red and was allowed to stir overnight at room temperature. Volatiles were removed from the solution and the resulting red product was recrystallized in diethyl ether, to yield red crystals of (22.3 mg, 0.0145 mmol, 23%). 1H NMR (C_6D_6 , 298 K): δ -49.56 (1H, S-CH-S), -38.98 (3H, C_5-CH_3), -16.42 (3H C_5-CH_3), -14.87 (9H Ar-C(CH_3)₃), -12.70 (9H Ar-C(CH_3)₃), -5.37 (9H Ar-C(CH_3)₃), -0.61 (3H, C_5-CH_3), 1.48 (15H, $C_5(CH_3)_5$), 4.23 (15H, $C_5(CH_3)_5$), 5.24 (15H, $C_5(CH_3)_5$), 7.24 (9H Ar-C(CH_3)₃), 11.40 (3H, Ar- CH_3), 12.97 (3H, Ar- CH_3), 18.47 (1H, Ar-H), 20.53 (1H, Ar-H), 20.88 (2H, $C_5-CH_2-C(H)S_2$), 21.01 (1H, Ar-H), 25.65 (1H, Ar-H), 45.39 (3H C_5-CH_3). IR (KBr, cm^{-1}): 2956 (s) 2906 (s) 2865 (m) 1422 (m) 1411 (s), 1385 (s) 1260 (m), 1209 (m), 1195 (m) 1115 (s), 1020 (w), 824 (s), 810 (s), 736 (w), 535 (w). Anal. Calcd. (found) for $C_{71}H_{108}O_2U_2S_2$, C 55.60 (55.48%), H 7.10 (7.18%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

Any additional relevant notes should be placed here.

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