

## Oxidation Chemistry of a Uranium(III) Aryloxyde

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The oxidation chemistry of the uranium(III) aryloxyde complex  $U(OAr)_3$  ( $OAr = 2,6\text{-di-}tert\text{-butylphenoxide}$ ) has been explored with a variety of one-electron oxidants. Oxidation of  $U(OAr)_3$  with either  $AgBF_4$  or  $AgPF_6$  produces the uranium(IV) fluoride  $FU(OAr)_3$ , **1**. The analogous chloride compound,  $ClU(OAr)_3$ , **2**, is prepared by reaction with either benzyl chloride or  $PCl_5$ . Oxidation by  $AgBr$ ,  $CBr_4$ , or  $PBr_5$  yields  $BrU(OAr)_3$ , **3**. Oxidation of  $U(OAr)_3$  by elemental iodine yields  $IU(OAr)_3$ , **4**. Compound **4** crystallizes in the space group  $P2_1/n$ , with unit cell dimensions  $a = 20.005(6) \text{ \AA}$ ,  $b = 10.228(4) \text{ \AA}$ ,  $c = 21.879(6) \text{ \AA}$ ,  $\beta = 115.30(2)^\circ$ ,  $V = 4047(2) \text{ \AA}^3$ , and  $Z = 4$ . Oxidation of  $U(OAr)_3$  with  $Cl_4$  (carbon tetraiodide) does not yield **4** but rather gives rise to  $I_2U(OAr)_2$ , **5**. Orthorhombic crystals of the THF adduct  $I_2U(OAr)_2(THF)$  were obtained from THF/hexane.  $I_2U(OAr)_2(THF)$  crystallizes in the space group  $Pbca$ , with unit cell dimensions  $a = 18.197(2) \text{ \AA}$ ,  $b = 17.866(2) \text{ \AA}$ ,  $c = 20.930(3) \text{ \AA}$ ,  $V = 6804.5(14) \text{ \AA}^3$ , and  $Z = 8$ . The chalcogenide-bridged compounds  $(ArO)_3U-O-U(OAr)_3$ , **6**, and  $(ArO)_3U-S-U(OAr)_3$ , **7**, can be prepared by reaction with a variety of chalcogen-donor reagents; reaction of the tris(aryloxyde)-uranium complex with  $N_2O$ ,  $NO$ ,  $Me_3NO$ , or  $pyNO$  yields compound **6**, while reaction with either  $COS$  or  $Ph_3P=S$  affords **7**. Compound **7** crystallizes as a diethyl ether solvate in the space group  $P\bar{1}$ , with unit cell dimensions  $a = 13.290(3) \text{ \AA}$ ,  $b = 13.744(4) \text{ \AA}$ ,  $c = 14.643(5) \text{ \AA}$ ,  $\alpha = 81.41(2)^\circ$ ,  $\beta = 65.36(2)^\circ$ ,  $\gamma = 67.58(2)^\circ$ ,  $V = 2247.4(11) \text{ \AA}^3$ , and  $Z = 1$ . Oxidation of  $U(OAr)_3$  by molecular oxygen does not result in the isolation of the oxo-bridged dinuclear species but in the formation of the known uranium(IV) compound  $U(OAr)_4$  by ligand redistribution.

## Introduction

Although the synthetic chemistry of the tetravalent oxidation state dominated early studies of the nonaqueous coordination chemistry of uranium, an increased number of investigations of the preparation and properties of complexes of uranium(III) have been made possible through the development of new synthetic precursors and the use of stabilizing bulky amide, aryloxyde, and alkyl ligands.<sup>2</sup> The preparation of these species has in turn permitted examination of the bonding and reaction chemistry of uranium(III) compounds.<sup>3,4</sup>

A broad range of ligand environments have been demonstrated to support the trivalent oxidation state, and structurally

characterized homoleptic uranium(III) compounds are increasingly common. It is now possible to systematically explore the effects of steric and electronic factors on reactivity patterns observed in low-valent organouranium chemistry. While these factors are largely understood for d-transition metal systems, the respective roles they play in the reactivity of related complexes of the actinides is less well understood. Molecular properties such as oxidation potential (and stability of ensuing oxidized products), Lewis base affinity, ligand lability, and molecularity are all likely to depend on the identity of these supporting ligands.

One reaction which may be used to probe the differences induced by different supporting ligand sets is simple oxidation of the metal center. While a limited number of reports have demonstrated two-electron oxidations can be effected in certain ligand systems, the dominant chemistry for uranium(III) is one-electron oxidation of the metal.<sup>4</sup> As an example, Finke and co-workers have shown that alkyl halides will oxidatively add to  $Cp^*_2UCl(THF)$  ( $Cp^* = C_5Me_5$ ) to form the uranium(IV) compounds  $Cp^*_2UCl(X)$  and  $Cp^*_2UCl(R)$ .<sup>4a,b</sup> Since that time, other groups have demonstrated the ability of halocarbons in effecting one-electron oxidation of  $U(III)$ .<sup>4c,5</sup> We have begun to explore comparable redox chemistry of uranium(III) in novel coordination environments, in an effort to understand the influence of ligand size and electronegativity on the stability of the resulting product.<sup>6</sup> To this end, we have initiated studies of the one-electron oxidation chemistry of the uranium(III) compound  $U(OAr)_3$  ( $OAr = 2,6\text{-di-}tert\text{-butylphenoxide}$ ).

## Experimental Section

All operations were performed using standard Schlenk techniques under UHP-grade argon or in a Vacuum Atmospheres drybox under

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helium. Tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), hexane, and toluene were dried and distilled under nitrogen from sodium benzophenone or Na-K alloy. Benzene-*d*<sub>6</sub>, methylene chloride, and benzyl chloride were dried over CaH<sub>2</sub>, vacuum transferred and freeze-pump-thawed three times prior to use. U(OAr)<sub>3</sub> was prepared by the literature method.<sup>2c</sup> The compounds AgBF<sub>4</sub>, AgPF<sub>6</sub>, CBr<sub>4</sub>, Cl<sub>4</sub>, HCl<sub>3</sub>, Me<sub>3</sub>NO (trimethylamine *N*-oxide) and pyNO (pyridine *N*-oxide) were purchased from Aldrich. Cl<sub>4</sub>, I<sub>2</sub>, Me<sub>3</sub>NO, and pyNO were sublimed prior to use. AgBr, PCl<sub>5</sub>, and PBr<sub>5</sub> were purchased from Strem and used without further purification. All gases were purchased from Matheson. The electrolyte, [Bu<sub>4</sub>N][BPh<sub>4</sub>] (Ph = C<sub>6</sub>H<sub>5</sub>), was purchased from Aldrich and recrystallized from acetone and dried under reduced pressure for 3 days.

<sup>1</sup>H NMR spectra (250.13 MHz) were measured on a Bruker AF250 spectrometer, with the chemical shifts (in ppm) reported relative to the protio impurity of the deuterated solvent. All spectra were recorded at 298 K unless indicated otherwise. Line widths were relatively sharp in all cases (3–26 Hz full width at half-height), as is common for tetravalent uranium complexes. Infrared spectra were obtained on a Bio-Rad FTS-40 infrared spectrometer as Nujol mulls on KBr plates. Elemental analyses were performed in our laboratories on a Perkin-Elmer 2400 CHN analyzer. The samples were prepared and sealed in aluminum capsules in the drybox prior to combustion.

**Electrochemistry.** Cyclic voltammetry experiments were carried out in an inert-atmosphere drybox with a PAR/EG & G Model 270 electrochemical analysis system. All measurements were conducted in THF solution utilizing 0.10 M [Bu<sub>4</sub>N][BPh<sub>4</sub>] (Ph = C<sub>6</sub>H<sub>5</sub>) as the supporting electrolyte. The working electrode was a gold disk, and the counter electrode was a silver wire. A silver wire, separated from the bulk solution by a fine-porosity fritted glass disk, was used as a pseudo-reference electrode. Solution resistance was compensated by electronic positive feedback. Potentials are referenced to the ferrocene/ferrocenium couple used as an internal standard. The measured half-wave potential (*E*<sub>1/2</sub>) for the ferrocene/ferrocenium internal standard is +0.705 V versus the pseudo-reference electrode at a scan rate of 0.20 V/s.

**Synthesis and Characterization. FU(OAr)<sub>3</sub> (1). A. With AgBF<sub>4</sub>.** To a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL of hexane was added 0.023 g (1.17 × 10<sup>-4</sup> mol) of AgBF<sub>4</sub> dissolved in 5 mL of THF. An immediate reaction took place, resulting in a color change from brown to a black suspension, with the formation of a precipitate of silver metal. The solution was stirred for *ca.* 5 min and filtered through Celite, yielding a yellow solution. After the filtrate was dried under reduced pressure, the residue was redissolved in a minimum volume of hexane and the resulting solution cooled to -40 °C. After 24 h, compound 1, FU(OAr)<sub>3</sub>, was isolated by filtration in 43% yield (0.044 g). The solid was recrystallized from hexane at -40 °C prior to analysis.

**B. With AgPF<sub>6</sub>.** Compound 1 was prepared in an identical manner from 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> and 0.029 g (1.15 × 10<sup>-4</sup> mol) of AgPF<sub>6</sub>. Isolated yield: 45% (0.046 g). The solid was recrystallized from hexane at -40 °C.

IR (cm<sup>-1</sup>): 1586 (m), 1403 (s), 1364 (w), 1305 (w), 1262 (m), 1217 (s), 1194 (s), 1122 (s), 1040 (w), 1010 (m), 961 (w), 919 (w), 882 (m), 859 (vs), 836 (w), 819 (vs), 796 (w), 751 (vs), 721 (m), 660 (vs), 630 (m), 586 (w), 545 (m), 512 (s), 445 (m). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 16.9 (s, 2H), 13.1 (s, 1H), -4.3 (s, 18H). Anal. Calcd for FUO<sub>3</sub>C<sub>42</sub>H<sub>63</sub>: C, 57.79; H, 7.28. Found: C, 57.27; H, 6.94.

**CIU(OAr)<sub>3</sub> (2). A. With Benzyl Chloride.** To a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL of hexane was added 0.012 g (1.19 × 10<sup>-4</sup> mol) of benzyl chloride. There was an immediate reaction, giving rise to a color change from brown to yellow. Removal of the solvent under reduced pressure resulted in the isolation of a yellow oil. The oil was redissolved in a minimum volume of Et<sub>2</sub>O, and the solution was cooled to -40 °C. After 24 h, compound 2 was isolated by filtration in 31% yield (0.032 g). The solid was recrystallized from Et<sub>2</sub>O at -40 °C prior to analysis.

**B. With PCl<sub>5</sub>.** A 0.100-g amount (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> was dissolved in 25 mL of THF and the solution was cooled to -40 °C. A second solution consisting of 0.012 g (5.76 × 10<sup>-5</sup> mol) of PCl<sub>5</sub> in 10 mL of THF was prepared and cooled to -40 °C. Addition of the PCl<sub>5</sub> solution to the tris(aryloxido)uranium complex caused an

immediate color change from brown to yellow. Removal of the solvent under reduced pressure resulted in the isolation of a yellow oil. The residue was redissolved in hexane and filtered through Celite. The yellow filtrate was concentrated and cooled to -40 °C. After 24 h, compound 2 was isolated by filtration in 42% yield (0.044 g).

IR (cm<sup>-1</sup>): 1605 (w), 1402 (m), 1363 (w), 1312 (w), 1263 (m), 1209 (s), 1186 (vs), 1117 (s), 1108 (sh), 1010 (w), 932 (w), 884 (w), 856 (vs), 819 (vs), 793 (m), 746 (vs), 725 (w), 658 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 17.0 (s, 2H), 12.5 (s, 1H), -4.8 (s, 18H). Anal. Calcd for CIUO<sub>3</sub>C<sub>42</sub>H<sub>63</sub>: C, 56.72; H, 7.14. Found: C, 56.89; H, 7.13.

**BrU(OAr)<sub>3</sub> (3). A. With AgBr.** To a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL of THF was added 0.022 g (1.17 × 10<sup>-4</sup> mol) of AgBr. The mixture was permitted to stir for *ca.* 3 h, resulting in a color change from brown to yellow with the formation of a precipitate of silver metal. The mixture was filtered through Celite, and the filtrate was taken to dryness under reduced pressure. The residue was redissolved in a minimum volume of hexane, and the solution was cooled to -40 °C. After 24 h, compound 3, BrU(OAr)<sub>3</sub>, was isolated by filtration in 48% yield (0.052 g). The solid was recrystallized from hexane solution at -40 °C prior to analysis.

**B. With CBr<sub>4</sub>.** To a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL of THF was added 0.039 g (1.87 × 10<sup>-4</sup> mol) of CBr<sub>4</sub>. The solution was permitted to stir for *ca.* 60 min, resulting in a color change from brown to yellow. The solution was filtered through Celite, and the filtrate was taken to dryness. The residue was redissolved in a minimum volume of hexane and the solution cooled to -40 °C. After 24 h, compound 3 was isolated by filtration in 58% yield (0.063 g).

**C. With PBr<sub>5</sub>.** To a stirred solution of 0.160 g (1.87 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in *ca.* 25 mL of hexane was added 0.025 g (5.85 × 10<sup>-5</sup> mol) of PBr<sub>5</sub> in 5 mL of THF. The solution was permitted to stir for *ca.* 3 h, resulting in a color change from brown to yellow. The solvent was removed under reduced pressure, the residue was redissolved in hexane, and the solution was filtered through Celite. The yellow filtrate was concentrated and the resulting solution cooled to -40 °C. After 24 h compound 3 was isolated by filtration in 48% yield (0.052 g).

IR (cm<sup>-1</sup>): 1582 (w), 1399 (m), 1365 (w), 1313 (w), 1261 (m), 1207 (m), 1177 (vs), 1118 (m), 1109 (m), 1040 (w), 1005 (m), 924 (w), 884 (w), 852 (vs), 832 (w), 817 (vs), 791 (m), 747 (vs), 654 (vs), 545 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 17.0 (s, 2H), 12.3 (s, 1H), -4.7 (s, 18H). Anal. Calcd for BrUO<sub>3</sub>C<sub>42</sub>H<sub>63</sub>: C, 54.02; H, 6.80. Found: C, 54.23; H, 6.57.

**IU(OAr)<sub>3</sub> (4). A. With I<sub>2</sub>.** To a stirred solution of 0.250 g (2.93 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 35 mL of hexane was added 0.038 g (2.99 × 10<sup>-4</sup> mol of I) of I<sub>2</sub>. The solution was permitted to stir for *ca.* 90 min, resulting in a color change from brown to yellow. The solution was concentrated under reduced pressure and subsequently cooled to -40 °C. After 24 h, filtration through a medium-porosity frit and drying under reduced pressure resulted in the isolation of a yellow solid. Additional crops were isolated from the mother liquors. The combined yield of 4 was 70% (0.201 g). Compound 4 was recrystallized from hexane at -40 °C prior to analysis.

**B. With HCl<sub>3</sub>.** To a stirred solution of 0.250 g (2.93 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 35 mL of hexane was added 0.115 g (2.92 × 10<sup>-4</sup> mol of I) of HCl<sub>3</sub>. The solution was permitted to stir for *ca.* 3 h, resulting in a color change from brown to yellow. The solution was filtered through Celite, and the filtrate was concentrated under reduced pressure and subsequently cooled to -40 °C. After 24 h, the product was isolated by filtration and dried under reduced pressure. The product, IU(OAr)<sub>3</sub>, 4, was isolated in 72% yield (0.208 g). Compound 4 was recrystallized from hexane at -40 °C.

IR (cm<sup>-1</sup>): 1578 (w), 1403 (vs), 1387 (w), 1375 (w), 1361 (w), 1258 (s), 1218 (sh), 1202 (w), 1184 (vs, broad), 1112 (vs), 1026 (w), 911 (w), 885 (m), 861 (vs), 818 (vs), 793 (s), 750 (vs), 723 (w), 660 (vs), 558 (m), 544 (m). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 16.5 (singlet, 2 H), 11.6 (singlet, 1H), -3.9 (singlet, 18H) ppm. Anal. Calcd for IUO<sub>3</sub>C<sub>42</sub>H<sub>63</sub>: C, 51.43; H, 6.47. Found: C, 51.89; H, 6.87.

**I<sub>2</sub>U(OAr)<sub>2</sub> (5).** To a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL of hexane was added 0.061 g (1.17 × 10<sup>-4</sup> mol) of Cl<sub>4</sub>. The solution was permitted to stir for *ca.* 2 h, resulting in the formation of a yellow precipitate in a yellow colored solution. The solution was filtered through a medium frit, and the yellow precipitate

Table 1. Crystallographic Parameters for the Compounds 4, 5 • THF, and 7

|   | IU(OAr) <sub>3</sub> (4)  | I <sub>2</sub> U(OAr) <sub>2</sub> (THF) (5 • THF)              | (ArO) <sub>3</sub> USU(OAr) <sub>3</sub> (7)                    |
|---|---|---|---|
| empirical formula                         | C <sub>42</sub> H <sub>63</sub> I <sub>3</sub> O <sub>3</sub> U | C <sub>32</sub> H <sub>50</sub> I <sub>2</sub> O <sub>3</sub> U | C <sub>92</sub> H <sub>146</sub> O <sub>8</sub> SU <sub>2</sub> |
| space group                               | <i>P2<sub>1</sub>/n</i>   | <i>Pbca</i>   | <i>P1</i>   |
| temp (°C)                                 | -70   | -70   | -70   |
| <i>a</i> (Å)                              | 20.004(6)   | 18.197(2)   | 13.290(3)   |
| <i>b</i> (Å)                              | 10.228(4)   | 17.866(2)   | 13.744(4)   |
| <i>c</i> (Å)                              | 21.879(2)   | 20.930(3)   | 14.643(5)   |
| $\alpha$ (deg)                            | 90.0  | 90.0  | 81.41(2)  |
| $\beta$ (deg)                             | 115.30(2)   | 90.0  | 65.36(2)  |
| $\gamma$ (deg)                            | 90.0  | 90.0  | 67.58(2)  |
| <i>V</i> (Å <sup>3</sup> )                | 4047(2)   | 6804.5(14)  | 2247.4(11)  |
| <i>Z</i>                                  | 4   | 8   | 1   |
| $\rho_{\text{calc}}$ (g/cm <sup>3</sup> ) | 1.610   | 1.903   | 1.395   |
| radiation ( $\lambda$ (Å))                | Mo K $\alpha$ (0.710 73)  | Mo K $\alpha$ (0.710 73)  | Mo K $\alpha$ (0.710 73)  |
| <i>fw</i>                                 | 980.9   | 974.6   | 1888.2  |
| $\mu$ (mm <sup>-1</sup> )                 | 4.808   | 6.614   | 3.673   |
| range (deg)                               | 3.0–45.0  | 2.0–50.0  | 3.0–45.0  |
| scan type                                 | $2\theta-\theta$  | $2\theta-\theta$  | $2\theta-\theta$  |
| <i>R</i> <sup>a</sup>                     | 5.34  | 5.84  | 5.46  |
| <i>R</i> <sub>w</sub> <sup>a</sup>        | 7.34  | 6.54  | 7.48  |

$$^a R = \sum |F_o - F_c| / \sum F_o; R_w = \sum \sqrt{w} |F_o - F_c| / \sum \sqrt{w} F_o.$$

was washed with copious amounts of hexane and dried under reduced pressure. The product, I<sub>2</sub>U(OAr)<sub>2</sub>, **5**, was isolated in 55% yield (0.058 g).

IR (cm<sup>-1</sup>): 1586 (w), 1403 (s), 1380 (w), 1375 (w), 1268 (m), 1212 (s), 1182 (vs), 1121 (vs), 1113 (s), 998 (m), 922 (w), 878 (m), 862 (vs), 822 (vs), 797 (s), 749 (vs), 726 (w), 665 (s), 556 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 26.4 (singlet, 2 H), 18.3 (singlet, 1 H), -9.3 (singlet, 18 H) ppm. Anal. Calcd for I<sub>2</sub>UO<sub>2</sub>C<sub>28</sub>H<sub>42</sub>: C, 37.26; H, 4.69. Found: C, 37.60; H, 5.07.

[(ArO)<sub>3</sub>U]<sub>2</sub>( $\mu$ -O) (**6**). **A. With N<sub>2</sub>O.** A flask containing a solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> dissolved in 30 mL of hexane was attached to a calibrated volume addition tube (7.3 mL). The tube and the reaction flask were evacuated and the addition tube was charged with 300 Torr (1.18 × 10<sup>-4</sup> mol) of N<sub>2</sub>O. Exposure of the hexane solution to the N<sub>2</sub>O resulted in a color change from brown to yellow within ca. 15 min. The solution was permitted to stir for 6 h, and the volume of solvent was then reduced to approximately 10 mL. The solution was then cooled to -40 °C. After 24 h, a yellow precipitate was collected by filtration. Additional crops were isolated by concentration of the mother liquors. The combined yield of compound **6**, (ArO)<sub>3</sub>U-O-U(OAr)<sub>3</sub>, was 53% (0.053 g). The solid was recrystallized from hexane solution at -40 °C.

**B. With NO.** A flask containing a solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> dissolved in 30 mL of toluene was attached to a calibrated volume addition tube (7.3 mL). The tube and the reaction flask were evacuated, and the addition tube was charged with 300 Torr (1.18 × 10<sup>-4</sup> mol) of NO, purified by fractional distillation. Exposure of the toluene solution to the NO resulted in a slow color change. The solution was permitted to stir for 4 h, resulting in a red solution free of precipitate. The solvent was removed under reduced pressure, and the residue was further dried under vacuum for 1 h. The residue was dissolved in a minimum volume of hexane and cooled to -40 °C. After 24 h a precipitate was collected by filtration. Additional crops were isolated by concentration of the mother liquors. The combined yield of compound **6**, (ArO)<sub>3</sub>U-O-U(OAr)<sub>3</sub>, was 53% (0.053 g). The solid was recrystallized from hexane solution at -40 °C.

**C. With Me<sub>3</sub>NO.** Me<sub>3</sub>NO (0.005 g, 6.65 × 10<sup>-5</sup> mol) was added to a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL of hexane. The solution was permitted to stir for ca. 3 h, resulting in a color change from brown to orange. The solvent was removed under reduced pressure, and the resulting tacky residue was further dried under vacuum for ca. 3 h. The residue was redissolved in a minimum volume of hexane, and the solution was cooled to -40 °C. After 24 h the solution was filtered, and the collected solid was dried under reduced pressure. Compound **6** was isolated in 36% yield (0.036 g).

**D. With pyNO.** pyNO (0.007 g, 7.36 × 10<sup>-5</sup> mol) was added to a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 25 mL toluene. The solution was permitted to stir for ca. 60 min, resulting in

a color change from brown to yellow. The solvent was removed by reduced pressure, and the resulting tacky residue was further dried under reduced pressure for ca. 3 h. The residue was redissolved in a minimum hexane, and the solution was cooled to -40 °C. After 24 h the solution was filtered, and the collected solid was dried under reduced pressure. Compound **6** was isolated in 60% yield (0.061 g).

IR (cm<sup>-1</sup>): 1580 (vw), 1403 (s), 1266 (m), 1232 (sh), 1211 (s), 1190 (s), 1120 (s), 877 (w), 856 (vs), 821 (s), 794 (m), 747 (vs), 726 (w), 660 (s), 580 (s), 540 (m), 446 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 14.3 (singlet, 2 H), 12.3 (singlet, 1 H), -11.3 (br s, 18 H) ppm. Anal. Calcd for U<sub>2</sub>O<sub>7</sub>C<sub>84</sub>H<sub>126</sub>: C, 58.52; H, 7.37. Found: C, 57.99; H, 6.63.

[(ArO)<sub>3</sub>U]<sub>2</sub>( $\mu$ -S) (**7**). **A. With COS.** A flask containing a solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> dissolved in 30 mL of hexane was attached to a calibrated volume addition tube (7.3 mL). The tube and the reaction flask were evacuated, and the addition tube was charged with 300 Torr (1.18 × 10<sup>-4</sup> mol) of COS. Exposure of the hexane solution to the COS resulted in a color change from brown to yellow in ca. 5 min. The solution was permitted to stir for 6 h, and the volume was reduced to 10 mL. The solution was cooled to -40 °C. After 24 h, a yellow precipitate was collected by filtration. Additional crops were isolated by concentration of the mother liquors. The combined yield of compound **7**, (ArO)<sub>3</sub>U-S-U(OAr)<sub>3</sub>, was 49% (0.050 g). The solid was recrystallized from hexane solution at -40 °C.

**B. With Ph<sub>3</sub>P=S.** To a stirred solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> in 20 mL toluene was added 0.018 g (5.95 × 10<sup>-5</sup> mol) of Ph<sub>3</sub>P=S. The solution was permitted to stir for approximately 3 h, and the solvent was removed under reduced pressure. The residue was redissolved in 40 mL of hexane, and the mixture was filtered through Celite. The Celite was washed with additional quantities of hexane until the filtrate was clear. The volume of the hexane filtrate was reduced to 20 mL, and the solution was cooled to -40 °C. After 24 h, a yellow precipitate was collected by filtration. Compound **7** was isolated in 41% yield (0.042 g).

IR (cm<sup>-1</sup>): 1580 (w), 1404 (s), 1266 (m), 1212 (m), 1190 (s), 1119 (s), 873 (sh), 857 (vs), 821 (s), 795 (m), 753 (s), 724 (m), 661 (s), 542 (w), 448 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 15.8 (singlet, 2 H), 12.2 (singlet, 1 H), -9.2 (br s, 18 H) ppm. Anal. Calcd for U<sub>2</sub>SO<sub>6</sub>C<sub>84</sub>H<sub>126</sub>: C, 57.98; H, 7.30. Found: C, 57.99; H, 7.03.

U(OAr)<sub>4</sub> (**8**). A flask containing a solution of 0.100 g (1.17 × 10<sup>-4</sup> mol) of U(OAr)<sub>3</sub> dissolved in 30 mL of hexane was attached to a calibrated volume addition tube (7.3 mL). The tube and the reaction flask were evacuated and the addition tube was charged with 150 Torr (5.90 × 10<sup>-5</sup> mol) of O<sub>2</sub> passed through a column of Drierite. Exposure to O<sub>2</sub> caused the solution to turn dark and opaque within several minutes. The solution was permitted to stir for 6 h before the solution was concentrated to one-half its original volume. The solution was then filtered through a medium frit to remove an insoluble black solid. The filtrate was dried under vacuum to yield 0.043 g U(OAr)<sub>4</sub> (35%).

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for  $\text{IU}(\text{OAr})_3$  (**4**)

| Distances    |           |              |           |
|--------------|-----------|--------------|-----------|
| U—I          | 3.011(2)  | U—O(2)       | 2.102(8)  |
| U—O(1)       | 2.092(8)  | O(1)—C(11)   | 1.377(14) |
| U—O(3)       | 2.114(11) | O(3)—C(31)   | 1.363(19) |
| O(2)—C(21)   | 1.400(14) |              |           |
| Angles       |           |              |           |
| I—U—O(1)     | 109.8(3)  | I—U—O(2)     | 103.0(3)  |
| I—U—O(3)     | 111.4(2)  | O(2)—U—O(3)  | 110.1(4)  |
| O(1)—U—O(3)  | 102.9(4)  | U—O(2)—C(21) | 159.8(7)  |
| O(1)—U—O(2)  | 119.8(3)  |              |           |
| U—O(1)—C(11) | 169.8(11) |              |           |
| U—O(3)—C(31) | 169.7(6)  |              |           |

Compound **8** was identified by comparison of the  $^1\text{H}$  NMR and IR spectra with those from an authentic sample.<sup>7</sup>

**Crystal Structure Determinations.**  $\text{IU}(\text{OAr})_3$ . Crystallization of **4** from a concentrated hexane solution at  $-40^\circ\text{C}$  resulted in the formation of gold blocks. The crystals were examined in mineral oil under an argon stream. A block of dimensions  $0.13\text{ mm} \times 0.25\text{ mm} \times 0.34\text{ mm}$  was selected, mounted on a glass fiber with Apiezon "H" grease, and transferred to the goniostat cooled to  $-70^\circ\text{C}$ . Data were collected on a Siemens R3m/V diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Cell constants and an orientation matrix were obtained by least-squares refinement. A variable scan rate of  $1.50\text{--}14.65^\circ/\text{min}$  in  $\omega$  was employed for data collection. A total of 5845 reflections were collected ( $0 \leq h \leq 21$ ,  $0 \leq k \leq 11$ ,  $-23 \leq l \leq 21$ ) in the range  $3.00^\circ < 2\theta < 45.00^\circ$  with 5275 being unique ( $R_{\text{int}} = 6.35\%$ ). A series of high  $\chi$  (above  $80^\circ$ ) reflections were scanned to provide the basis for an empirical absorption correction that ranged from 0.3022 to 0.7788. No crystal decay was evident during data collection.

The cell was uniquely determined by the systematic absences to be  $P2_1/n$ . The uranium atom position was determined from direct methods. All remaining non-hydrogen atoms were located in succeeding difference Fourier maps and were refined anisotropically. The final residuals for the full-matrix least-squares refinement were  $R = 5.34$ ,  $R_w = 7.34$ , and  $\text{GOF} = 1.45$  based on 424 refined parameters. All calculations were carried out using the SHELXTL PLUS software provided by Siemens Analytical X-Ray Corp. Crystallographic parameters, bond distances, and bond angles for **4** are provided in Tables 1–3.

$\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$ . Orange, hexagonal prisms were grown by slow diffusion of hexane into a concentrated THF solution of **5** at  $-40^\circ\text{C}$ . The crystals were examined in mineral oil under an argon stream. A block of dimensions  $0.15\text{ mm} \times 0.15\text{ mm} \times 0.20\text{ mm}$  was selected, mounted on a glass fiber with Apiezon "H" grease, and transferred to the goniostat cooled to  $-70^\circ\text{C}$ . Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range of  $25^\circ < 2\theta < 36^\circ$ . A variable scan rate of  $1.50\text{--}5.50^\circ/\text{min}$  in  $\omega$  was employed for data collection. A total of 8821 reflections were collected ( $0 \leq h \leq 21$ ,  $0 \leq k \leq 21$ ,  $-24 \leq l \leq 6$ ) in the range  $2.00^\circ < 2\theta < 50.00^\circ$  with 5967 being unique ( $R_{\text{int}} = 3.46\%$ ). A single  $\chi$  reflection of  $88^\circ$  was scanned to provide the basis for an empirical absorption correction that ranged from 0.75 to 1.00. No crystal decay was evident during data collection.

The cell was uniquely determined by the systematic absences to be  $Pbca$ . The uranium atom was located by Patterson methods. All remaining non-hydrogen atoms were located in succeeding difference Fourier maps and were refined anisotropically. Hydrogen atoms were placed in idealized positions; they were included in structure factor calculations but were not refined. The final residuals for the full-matrix least-squares refinement were  $R = 5.84$ ,  $R_w = 6.54$ , and  $\text{GOF} = 1.97$  based on 353 refined parameters. All calculations were carried out using the SHELXTL PLUS software provided by Siemens Analytical. Crystallographic parameters, bond distances, and bond angles for  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  are provided in Tables 1, 4, and 5.

**Table 3.** Fractional Coordinates and Equivalent Isotropic Displacement Coefficients<sup>a</sup> for  $\text{IU}(\text{OAr})_3$  (**4**)

|        | $10^4x$ | $10^4y$   | $10^4z$ | $10^3U(\text{eq}) (\text{\AA}^2)$ |
|--------|---------|-----------|---------|-----------------------------------|
| U      | 2792(1) | 2658(1)   | 5070(1) | 19(1)                             |
| I      | 2972(1) | 4944(1)   | 4286(1) | 35(1)                             |
| O(1)   | 3830(5) | 1981(8)   | 5753(4) | 21(3)                             |
| O(2)   | 2078(4) | 1411(8)   | 4306(4) | 18(3)                             |
| O(3)   | 2295(4) | 3233(9)   | 5709(4) | 23(3)                             |
| C(11)  | 4473(7) | 1595(13)  | 6289(7) | 23(5)                             |
| C(12)  | 4562(8) | 282(14)   | 6477(7) | 29(5)                             |
| C(13)  | 5182(7) | -28(12)   | 7075(7) | 22(4)                             |
| C(14)  | 5700(9) | 878(15)   | 7442(8) | 37(5)                             |
| C(15)  | 5608(8) | 2164(14)  | 7221(7) | 30(5)                             |
| C(16)  | 5002(7) | 2554(12)  | 6642(7) | 20(4)                             |
| C(121) | 4062(9) | -895(13)  | 6098(7) | 31(5)                             |
| C(122) | 4515(8) | -1666(14) | 5799(8) | 32(5)                             |
| C(123) | 3328(8) | -564(15)  | 5496(8) | 41(5)                             |
| C(124) | 3921(8) | 1767(15)  | 6589(8) | 36(5)                             |
| C(161) | 4942(7) | 3955(13)  | 6383(7) | 26(5)                             |
| C(162) | 4925(9) | 3940(17)  | 5672(8) | 44(5)                             |
| C(163) | 5601(9) | 4806(15)  | 6837(9) | 47(5)                             |
| C(164) | 4271(8) | 4639(14)  | 6401(7) | 30(5)                             |
| C(21)  | 1810(6) | 280(12)   | 3917(7) | 18(4)                             |
| C(22)  | 2252(7) | -356(14)  | 3665(7) | 26(5)                             |
| C(23)  | 1981(8) | -1587(15) | 3375(8) | 37(5)                             |
| C(24)  | 1360(9) | -2127(14) | 3341(8) | 38(5)                             |
| C(25)  | 897(8)  | -1411(14) | 3530(7) | 33(5)                             |
| C(26)  | 1112(7) | -153(13)  | 3943(6) | 21(4)                             |
| C(221) | 2963(7) | 154(15)   | 3594(8) | 34(5)                             |
| C(222) | 2731(9) | 439(18)   | 2844(7) | 49(5)                             |
| C(223) | 3309(8) | 1379(15)  | 3980(9) | 41(5)                             |
| C(224) | 3546(7) | -920(16)  | 3838(7) | 39(5)                             |
| C(261) | 565(7)  | 619(13)   | 4028(7) | 24(5)                             |
| C(262) | -169(7) | -75(15)   | 3819(8) | 36(5)                             |
| C(263) | 407(8)  | 1919(14)  | 3641(8) | 36(5)                             |
| C(264) | 886(8)  | 833(15)   | 4790(7) | 36(5)                             |
| C(31)  | 1860(6) | 3601(12)  | 6018(7) | 17(4)                             |
| C(32)  | 1873(7) | 2881(12)  | 6571(6) | 20(4)                             |
| C(33)  | 1355(7) | 3216(14)  | 6815(7) | 27(5)                             |
| C(34)  | 849(7)  | 4208(13)  | 6553(7) | 25(5)                             |
| C(35)  | 891(8)  | 4961(13)  | 6040(6) | 26(5)                             |
| C(36)  | 1384(7) | 4705(14)  | 5773(7) | 24(4)                             |
| C(321) | 2451(8) | 1799(15)  | 6947(7) | 27(5)                             |
| C(322) | 2396(9) | 1370(16)  | 7587(8) | 39(5)                             |
| C(323) | 2274(8) | 576(15)   | 6493(9) | 44(5)                             |
| C(324) | 3230(8) | 2296(16)  | 7139(8) | 47(5)                             |
| C(361) | 1428(7) | 5631(13)  | 5220(7) | 23(4)                             |
| C(362) | 924(9)  | 6802(14)  | 5103(8) | 38(5)                             |
| C(363) | 2206(7) | 6225(16)  | 5493(8) | 36(5)                             |
| C(364) | 1195(7) | 4940(14)  | 4535(7) | 29(5)                             |

$$^a U(\text{eq}) = \frac{1}{3}[U_{11} + U_{22} + U_{33}].$$

**Table 4.** Selected Bond Distances (Å) and Bond Angles (deg) for  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  (**5** · THF)

| Distances      |           |                 |           |
|----------------|-----------|-----------------|-----------|
| U(1)—I(1)      | 2.982(1)  | U(1)—I(2)       | 3.025(1)  |
| U(1)—O(1)      | 2.080(8)  | U(1)—O(2)       | 2.073(9)  |
| U(1)—O(3)      | 2.473(9)  |                 |           |
| O(1)—C(1)      | 1.392(16) | O(2)—C(15)      | 1.372(15) |
| Angles         |           |                 |           |
| I(1)—U(1)—I(2) | 98.3(1)   | I(1)—U(1)—O(1)  | 92.5(2)   |
| I(2)—U(1)—O(1) | 113.7(2)  | I(2)—U(1)—O(2)  | 141.0(2)  |
| I(2)—U(1)—O(2) | 112.5(2)  | O(1)—U(1)—O(2)  | 96.2(3)   |
| I(1)—U(1)—O(3) | 87.5(2)   | I(2)—U(1)—O(3)  | 74.8(2)   |
| O(1)—U(1)—O(3) | 171.4(3)  | O(2)—U(1)—O(3)  | 78.5(3)   |
| U(1)—O(1)—C(1) | 172.6(8)  | U(1)—O(2)—C(15) | 166.2(8)  |

$(\text{ArO})_3\text{U—S—U}(\text{OAr})_3 \cdot 2\text{Et}_2\text{O}$ . Crystallization of **7** from a concentrated hexane/ether solution at  $-40^\circ\text{C}$  resulted in the formation of golden prisms. The crystals were examined in mineral oil under an argon stream. A block of dimensions  $0.29\text{ mm} \times 0.33\text{ mm} \times 0.45\text{ mm}$  was selected, mounted on a glass fiber with Apiezon "H" grease, and transferred to the goniostat cooled to  $-70^\circ\text{C}$ . Data were collected on a Siemens R3m/V diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Cell constants and an orientation matrix

(7) Van Der Sluys, W. G.; Sattelberger, A. P.; Streib, W. E.; Huffman, J. C. *Polyhedron* **1989**, *8*, 1247.

**Table 5.** Fractional Coordinates and Equivalent Isotropic Displacement Coefficients<sup>a</sup> for U<sub>2</sub>(OAr)<sub>2</sub>(THF) (5 • THF)

|       | 10 <sup>4</sup> x | 10 <sup>4</sup> y | 10 <sup>4</sup> z | 10 <sup>3</sup> U(eq) (Å <sup>2</sup> ) |
|-------|-------------------|-------------------|-------------------|---|
| U     | 382(1)            | 1712(1)           | 1266(1)           | 16(1)                                   |
| I(1)  | 39(1)             | 1238(1)           | -67(1)            | 27(1)                                   |
| I(2)  | -1044(1)          | 2512(1)           | 1560(1)           | 28(1)                                   |
| O(1)  | 1219(5)           | 2422(5)           | 965(4)            | 18(3)                                   |
| C(1)  | 1710(8)           | 2943(8)           | 716(6)            | 23(4)                                   |
| C(2)  | 2412(7)           | 2709(7)           | 526(5)            | 18(4)                                   |
| C(3)  | 2871(8)           | 3229(8)           | 225(6)            | 26(4)                                   |
| C(4)  | 2630(8)           | 3964(8)           | 150(7)            | 28(5)                                   |
| C(5)  | 1949(7)           | 4199(7)           | 352(6)            | 20(4)                                   |
| C(6)  | 1472(7)           | 3693(7)           | 651(6)            | 17(4)                                   |
| C(7)  | 2715(8)           | 1919(8)           | 638(7)            | 27(4)                                   |
| C(8)  | 3512(9)           | 1846(9)           | 422(9)            | 46(6)                                   |
| C(9)  | 2672(8)           | 1697(9)           | 1326(6)           | 28(4)                                   |
| C(10) | 2291(8)           | 1356(8)           | 216(6)            | 28(5)                                   |
| C(11) | 719(8)            | 3972(7)           | 870(6)            | 22(4)                                   |
| C(12) | 599(8)            | 3812(7)           | 1586(7)           | 28(5)                                   |
| C(13) | 128(8)            | 3648(8)           | 455(7)            | 27(4)                                   |
| C(14) | 650(9)            | 4828(7)           | 802(7)            | 29(5)                                   |
| O(2)  | 910(5)            | 1337(5)           | 2083(4)           | 22(3)                                   |
| C(15) | 1182(6)           | 928(7)            | 2585(6)           | 18(4)                                   |
| C(16) | 1298(7)           | 152(7)            | 2518(6)           | 19(4)                                   |
| C(17) | 1431(8)           | -277(7)           | 3061(6)           | 25(4)                                   |
| C(18) | 1507(8)           | 83(9)             | 3658(7)           | 32(5)                                   |
| C(19) | 1441(8)           | 847(8)            | 3708(6)           | 27(4)                                   |
| C(20) | 1275(7)           | 1298(8)           | 3173(7)           | 26(4)                                   |
| C(21) | 1314(7)           | -322(8)           | 1894(6)           | 22(4)                                   |
| C(22) | 730(9)            | -925(8)           | 1908(7)           | 33(5)                                   |
| C(23) | 2067(8)           | -707(8)           | 1846(7)           | 30(5)                                   |
| C(24) | 1217(8)           | 92(8)             | 1269(7)           | 20(4)                                   |
| C(25) | 1221(9)           | 2139(8)           | 3236(7)           | 35(5)                                   |
| C(26) | 421(8)            | 2412(9)           | 3156(8)           | 41(6)                                   |
| C(27) | 1740(8)           | 2553(9)           | 2779(8)           | 38(5)                                   |
| C(28) | 1479(10)          | 2412(9)           | 3906(7)           | 42(6)                                   |
| O(3)  | -468(5)           | 722(5)            | 1634(4)           | 25(3)                                   |
| C(29) | -1033(9)          | 354(9)            | 1250(8)           | 39(5)                                   |
| C(30) | -1476(1)          | -90(11)           | 1733(9)           | 51(7)                                   |
| C(31) | -1461(9)          | 433(12)           | 2310(9)           | 58(7)                                   |
| C(32) | -690(9)           | 690(10)           | 2314(7)           | 40(5)                                   |

$$^a U(\text{eq}) = \frac{1}{3}[U_{11} + U_{22} + U_{33}].$$

were obtained by least-squares refinement. The cell was determined to be triclinic. A variable scan rate of 1.50–14.65°/min in  $\omega$  was employed for data collection. A total of 5985 reflections were collected ( $0 \leq h \leq 12$ ,  $-13 \leq k \leq 14$ ,  $-14 \leq l \leq 15$ ) in the range  $3.00^\circ < 2\theta < 45.00^\circ$  with 5679 being unique ( $R_{\text{int}} = 1.52\%$ ). A series of high  $\chi$  (above  $80^\circ$ ) reflections were scanned to provide the basis for an empirical absorption correction that ranged from 0.72 to 1.00. No crystal decay was evident during data collection.

The choice of space group P1 was verified by satisfactory solution of the structure. The uranium atom position was determined from direct methods. All remaining non-hydrogen atoms were located in succeeding difference Fourier maps and were refined anisotropically. The final residuals for the full-matrix least-squares refinement were  $R = 5.46$ ,  $R_w = 7.48$ , and  $\text{GOF} = 1.93$  based on 441 refined parameters. All calculations were carried out using the SHELXTL PLUS software provided by Siemens Analytical. Crystallographic parameters, bond distances, and bond angles for **7** are provided in Tables 1, 6, and 7.

## Results and Discussion

**Electrochemistry of U(OAr)<sub>3</sub>.** Despite interest in the ability of low-valent organoactinide and -lanthanide species to reduce a wide variety of substrates, reports of the electrochemistry of uranium(III) compounds are relatively rare.<sup>8</sup> The products of electrochemical oxidation are generally unstable. The compound  $\text{Cp}^*_2\text{UCl}(\text{THF})$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) is reported to display a single oxidation wave at  $E_{\text{pa}} = -0.71$  V in THF (versus SCE).

**Table 6.** Selected Bond Distances (Å) and Bond Angles (deg) for (ArO)<sub>3</sub>U–S–U(OAr)<sub>3</sub> (7)

| Distances      |           |                |           |
|----------------|-----------|----------------|-----------|
| U–S            | 2.588(1)  |                |           |
| U–O(1)         | 2.079(9)  | U–O(2)         | 2.125(8)  |
| U–O(3)         | 2.119(6)  | O(1)–C(1)      | 1.409(15) |
| O(2)–C(15)     | 1.393(14) | O(3)–C(29)     | 1.396(12) |
| Angles         |           |                |           |
| S–U(1)–O(1)    | 123.2(2)  | S–U(1)–O(2)    | 92.1(2)   |
| S–U(1)–O(3)    | 95.7(2)   |                |           |
| O(1)–U(1)–O(2) | 95.9(3)   | O(2)–U(1)–O(3) | 156.2(4)  |
| U(1)–S–U(1A)   | 180.0(1)  |                |           |
| U–O(1)–C(1)    | 171.8(5)  | U–O(2)–C(15)   | 173.8(8)  |
| U–O(3)–C(29)   | 171.8(6)  |                |           |

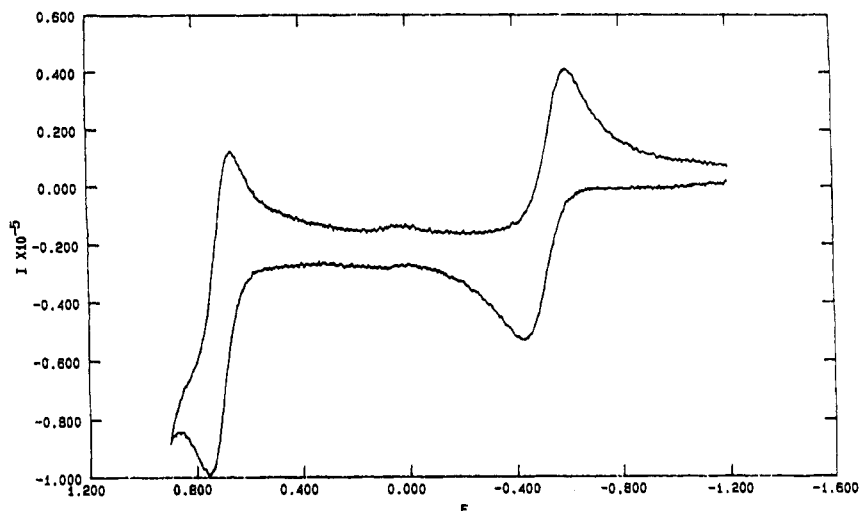
**Table 7.** Fractional Coordinates and Equivalent Isotropic Displacement Coefficients<sup>a</sup> for (ArO)<sub>3</sub>U–S–U(OAr)<sub>3</sub> (7)

|       | 10 <sup>4</sup> x | 10 <sup>4</sup> y | 10 <sup>4</sup> z | 10 <sup>3</sup> U(eq) (Å <sup>2</sup> ) |
|-------|-------------------|-------------------|-------------------|---|
| U(1)  | 965(1)            | 466(1)            | 3135(1)           | 35(1)                                   |
| S     | 0                 | 0                 | 5000              | 45(2)                                   |
| O(1)  | 1722(6)           | 1622(6)           | 2677(5)           | 41(3)                                   |
| O(2)  | -704(7)           | 1437(6)           | 3103(5)           | 43(4)                                   |
| O(3)  | 2541(7)           | -875(6)           | 2792(5)           | 44(4)                                   |
| C(1)  | 2390(9)           | 2287(8)           | 2303(8)           | 39(5)                                   |
| C(2)  | 2550(10)          | 2789(8)           | 2970(8)           | 41(5)                                   |
| C(3)  | 3289(12)          | 3378(10)          | 2521(10)          | 57(7)                                   |
| C(4)  | 3831(13)          | 3471(11)          | 1492(10)          | 65(8)                                   |
| C(5)  | 3603(12)          | 2995(10)          | 881(10)           | 57(7)                                   |
| C(6)  | 2868(11)          | 2403(9)           | 1245(8)           | 45(6)                                   |
| C(7)  | 2006(11)          | 2805(9)           | 4123(9)           | 50(6)                                   |
| C(8)  | 2972(12)          | 2443(10)          | 4535(9)           | 60(7)                                   |
| C(9)  | 1242(11)          | 2105(11)          | 4621(8)           | 55(6)                                   |
| C(10) | 1189(13)          | 3935(11)          | 4487(11)          | 73(8)                                   |
| C(11) | 2593(11)          | 1933(9)           | 527(8)            | 48(6)                                   |
| C(12) | 3083(13)          | 745(9)            | 530(9)            | 61(7)                                   |
| C(13) | 1275(11)          | 2369(11)          | 771(9)            | 59(7)                                   |
| C(14) | 3201(13)          | 2227(12)          | -581(8)           | 72(8)                                   |
| C(15) | -1823(8)          | 1972(8)           | 3087(8)           | 38(5)                                   |
| C(16) | -2519(10)         | 2955(9)           | 3561(8)           | 48(6)                                   |
| C(17) | -3618(13)         | 3411(12)          | 3545(12)          | 70(8)                                   |
| C(18) | -4041(14)         | 2944(16)          | 3071(14)          | 91(10)                                  |
| C(19) | -3317(15)         | 1944(15)          | 2608(12)          | 76(10)                                  |
| C(20) | -2203(12)         | 1449(11)          | 2598(9)           | 53(7)                                   |
| C(21) | -2108(10)         | 3539(9)           | 4068(9)           | 50(6)                                   |
| C(22) | -984(10)          | 3717(9)           | 3310(9)           | 49(6)                                   |
| C(23) | -3042(12)         | 4644(10)          | 4462(11)          | 73(7)                                   |
| C(24) | -1930(11)         | 2933(10)          | 4987(8)           | 57(6)                                   |
| C(25) | -1468(13)         | 361(12)           | 2119(9)           | 62(8)                                   |
| C(26) | -2069(16)         | 51(15)            | 1571(11)          | 91(11)                                  |
| C(27) | -1400(15)         | -462(12)          | 2956(10)          | 78(9)                                   |
| C(28) | -232(14)          | 298(14)           | 1331(9)           | 81(9)                                   |
| C(29) | 3492(10)          | -1816(8)          | 2693(8)           | 44(5)                                   |
| C(30) | 4366(10)          | -1898(9)          | 3048(7)           | 42(5)                                   |
| C(31) | 5213(11)          | -2899(10)         | 2985(9)           | 58(6)                                   |
| C(32) | 5229(14)          | -3752(10)         | 2576(10)          | 72(8)                                   |
| C(33) | 4430(14)          | -3642(11)         | 2193(10)          | 67(8)                                   |
| C(34) | 3516(11)          | -2672(9)          | 2238(8)           | 51(6)                                   |
| C(35) | 4387(11)          | -986(10)          | 3489(8)           | 50(6)                                   |
| C(36) | 3326(11)          | -658(10)          | 4499(8)           | 53(6)                                   |
| C(37) | 4413(9)           | -76(9)            | 2737(8)           | 50(5)                                   |
| C(38) | 5470(12)          | -1282(11)         | 3726(10)          | 63(7)                                   |
| C(39) | 2645(14)          | -2615(10)         | 1804(10)          | 68(8)                                   |
| C(40) | 2697(16)          | -1825(12)         | 933(11)           | 88(10)                                  |
| C(41) | 2910(19)          | -3655(12)         | 1339(14)          | 109(13)                                 |
| C(42) | 1412(15)          | -2363(16)         | 2617(13)          | 103(12)                                 |
| O(1') | 9557(8)           | 3648(7)           | -826(7)           | 68(3)                                   |
| C(1') | 8076(17)          | 3710(14)          | 823(14)           | 96(5)                                   |
| C(2') | 8629(14)          | 4358(12)          | -18(12)           | 76(4)                                   |
| C(3') | 10142(14)         | 4204(12)          | -1657(12)         | 78(4)                                   |
| C(4') | 11135(15)         | 3418(13)          | -2439(13)         | 86(5)                                   |

$$^a U(\text{eq}) = \frac{1}{3}[U_{11} + U_{22} + U_{33}].$$

This oxidation is irreversible, presumably owing to the reactivity of the ensuing coordinatively unsaturated cation. This hypothesis is supported by the observation that the related tetravalent

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**Figure 1.** Cyclic Voltammogram of  $U(OAr)_3$  in THF solvent with ferrocene as an internal standard. The scan rate is 0.20 V/s.

compound  $Cp^*_2UCl_2$  displays a reversible one-electron reduction wave at  $E_{1/2} = -1.30$  V vs SCE in  $CH_3CN$  with no apparent loss of chloride ion.<sup>8a</sup>

Preliminary to studying the chemical reactivity of the homoleptic aryloxy complexes of uranium(III), we have investigated the electrochemical behavior of  $U(OAr)_3$  by cyclic voltammetry. Figure 1 shows the cyclic voltammogram of  $U(OAr)_3$  (2 mM in tetrahydrofuran with  $[Bu_4N][BPh_4]$  supporting electrolyte). A very accessible redox couple is observed, assigned as a reversible one-electron oxidation of  $U(OAr)_3$ . The reversibility of the redox process was judged by the ratio of  $i_{p,a}/i_{p,c}$ . The anodic current peak occurs at  $-0.431$  V, and the cathodic current peak of this couple is observed at  $-0.597$  V, yielding a measured half-wave potential ( $E_{1/2}$ ) of  $-0.514$  V (versus the pseudo-reference electrode) at a scan rate of 0.20 V/s. The  $E_{1/2}$  value for  $U(OAr)_3$  relative to the ferrocene/ferrocenium internal standard is  $-1.22$  V. These values displayed little deviation with scan rate. The  $\Delta E_p$  for this wave is 0.166 V, which is almost twice as large as the  $\Delta E_p$  of 0.088 V observed for the ferrocene/ferrocenium internal standard, and is suggestive of a kinetically controlled electron-transfer process. The reversibility of the oxidation and the retarded rate of electron-transfer point to steric stabilization of the tetravalent product by the bulky aryloxy ligands.

Variation of the ligand environment has a considerable effect on the oxidation potential for the U(III/IV) couple. The compound  $Cp_3U(THF)$  is reported to undergo an irreversible oxidation at  $+0.32$  V in THF (versus cobaltocene/cobaltocenium).<sup>8b</sup> We have observed a similar one-electron oxidation process for the compound  $U[N(SiMe_3)_2]_3$  at  $-1.24$  V in THF (versus the ferrocene/ferrocenium internal standard in 0.1M  $[Bu_4N][BPh_4]$  supporting electrolyte in THF solvent).<sup>9</sup> Direct comparison between the strong donor ligands suggests that the bis(trimethylsilyl)amide ligand is a slightly better donor than the aryloxy, thus rendering  $U[N(SiMe_3)_2]_3$  easier to oxidize than  $U(OAr)_3$ .

**Synthesis and Characterization of the compounds  $XU(OAr)_3$  ( $X = F, Cl, Br, I$ ).** Given the accessibility of the U(III)/U(IV) couple for  $U(OAr)_3$ , oxidation in the presence of a suitable halide source should readily provide a convenient route for the preparation of the uranium(IV) compounds  $XU(OAr)_3$  ( $X = F, Cl, Br, I$ ). Previous workers have shown that it is possible to prepare  $Cp_3UX$  ( $Cp = C_5H_5, MeC_5H_4$ ;  $X = F, Cl$ )

by the chemical oxidation of  $Cp_3U(THF)$  and a halide source.<sup>5,10</sup> In some instances, oxidation of the trivalent uranium metallocene to the tetravalent compound occurs with a concomitant ligand redistribution reaction, which can give rise to unexpected by-products.<sup>11</sup>

In the presence of  $AgBF_4$ , the uranium(III) aryloxy  $U(OAr)_3$  is oxidized to the uranium(IV) compound  $FU(OAr)_3$  (**1**) in 43% isolated yield (eq 1). The reaction is rapid and is quantitative



as determined by  $^1H$  NMR. The aryloxy resonances for the *tert*-butyl group and the meta and para protons on the phenyl ring are shifted and sharpened from the resonances of the starting uranium(III) compound, consistent with tetravalent uranium.<sup>2c,4e</sup> Compound **1** is similarly prepared in comparable yield with  $AgPF_6$ . With  $AgF$  under identical conditions, a similar oxidation reaction is observed, but the transformation is slow, and there is evidence by  $^1H$  NMR for the production of  $U(OAr)_4$  (**8**) as a minor impurity. Abstraction of fluoride from salts such as  $AgBF_4$  and  $AgPF_6$  has been previously observed in the oxidation of the uranium(V) organoimido complexes  $[(Me_3Si)_2N]_3UNR$  ( $R = C_6H_5, SiMe_3$ ); UV spectra and electrochemical data suggest that fluoride abstraction can occur prior to oxidation in these systems.<sup>12,13</sup> The strong Lewis acidity of uranium is evident in reactions of this type. Other examples of interest with regard to uranium(III) oxidations with a suitable fluoride source are the preparation of  $Cp'_3UF$  ( $Cp' = CH_3C_5H_4$ ) from  $Cp'_3U(THF)$  and  $PF_3$ , as well as the oxidation of  $U[N(SiMe_3)_2]_3$  with  $AgF$  to yield  $FU[N(SiMe_3)_2]_3$ .<sup>10,14</sup>

Isolated **1** is a light green-apple green solid that is soluble in nonpolar organic solvents. The infrared spectrum of **1** displays a strong absorption at  $512\text{ cm}^{-1}$  that is assigned to U–F stretch, in comparison to the values of 467 and  $509\text{ cm}^{-1}$  previously reported for  $(MeC_5H_4)_3UF$  and  $FU[N(SiMe_3)_2]_3$ .<sup>10,14</sup>

Lappert and co-workers have previously reported the synthesis of  $ClU(OAr')_3$  ( $OAr' = 2,4,6$ -tri-*tert*-butylphenoxide) in 55%

(10) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics*, **1988**, *7*, 1329.

(11) (a) Brennan, J. G. Ph.D. Dissertation, University of California, 1986. (b) Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics*, **1990**, *9*, 1623.

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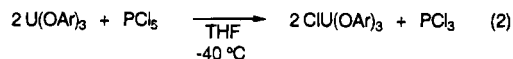
(13) Burns, C. J.; Smith, W. H.; Sattelberger, A. P. Unpublished results.

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(9) Burns, C. J. Unpublished results.

yield from  $\text{UCl}_4$ .<sup>15</sup> For the 2,6-di-*tert*-butylphenoxide system, the monochloride  $\text{ClU}(\text{OAr})_3$  (**2**) can be prepared by oxidation of  $\text{U}(\text{OAr})_3$  with benzyl chloride in 31% isolated yield in a synthetic scheme identical to that employed by Finke in the atom abstraction reactions of  $\text{Cp}^*\text{UCl}(\text{THF})$ .<sup>4a,b</sup>  $^1\text{H}$  NMR spectra of the crude reaction suggest that a minor amount (< 10%) of the compound  $(\text{benzyl})\text{U}(\text{OAr})_3$  is formed.<sup>16</sup> Ephritikhine and co-workers have previously reported that the oxidation of  $\text{Cp}_3\text{U}(\text{THF})$  with benzyl chloride yields an equimolar mixture of  $\text{Cp}_3\text{UCl}$  and  $\text{Cp}_3\text{U}(\text{benzyl})$ .<sup>4c,5</sup> We have observed similar chloride abstraction with either neopentyl chloride or methylene chloride to form compound **2** in moderate yields.

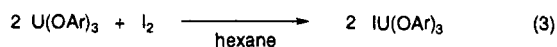
The chloro aryloxide compound,  $\text{ClU}(\text{OAr})_3$  (**2**), can also be prepared from  $\text{PCl}_5$ , as indicated in eq 2. Compound **2** is very



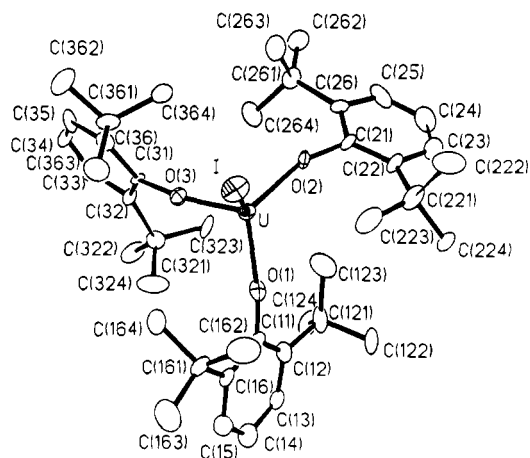
soluble in nonpolar solvents such as hexane but can be isolated as a yellow solid from a concentrated solution at  $-40^\circ \text{C}$  in 42% yield. It reacts further with additional  $\text{PCl}_5$  to form an as yet uncharacterized uranium-aryloxide compound that has solubility properties similar to those observed for **2**.<sup>17</sup>

The preparation of  $\text{BrU}(\text{OAr})_3$  (**3**) has been carried out using a variety of reagents. Oxidation reactions with  $\text{AgBr}$ ,  $\text{CBr}_4$ , and  $\text{PBr}_5$  are quantitative by  $^1\text{H}$  NMR. The oxidation of  $\text{U}(\text{OAr})_3$  with  $\text{Br}_2$  will also produce the bromide **3**; however, even trace amounts of water and oxygen easily result in the formation of the uranium(IV) compound  $\text{U}(\text{OAr})_4$  (**8**) at the expense of compound **3**. Precedent exists for the use of saturated halocarbons in d-transition metal oxidation systems. For example, Rothwell has previously employed  $\text{CBr}_4$  in the oxidation of  $\text{Ti}(\text{OAr})_3$ .<sup>18</sup> Although previous work on the oxidation of  $\text{UI}_3(\text{THF})_4$  with  $\text{CBr}_4$  in THF solvent resulted in the isolation of an alkoxide product resulting from ring opening of the tetrahydrofuran;<sup>19</sup> similar studies with  $\text{U}(\text{OAr})_3$  and  $\text{CBr}_4$  in THF solvent failed to provide any evidence for the formation of a ring-opened product.

The iodide analog, **4**, can be isolated in 70% yield using  $\text{I}_2$  as the oxidant (eq 3). Other reagents such as  $\text{HCl}_3$  and  $\text{C}_2\text{I}_4$



also form  $\text{IU}(\text{OAr})_3$  in comparable yields. As in the case of the bromide, this method has been previously employed by Rothwell in the oxidation of  $\text{Ti}(\text{OAr})_3$ .<sup>18</sup> Compound **4** has been structurally characterized (Figure 2). The ORTEP drawing indicates that the compound is monomeric, with the uranium tetrahedrally coordinated by the iodide and three oxygen atoms of the aryloxide group. The uranium-iodine bond distance for compound **4** is found to be 3.011(2) Å. This distance is comparable with other structurally characterized uranium(IV) compounds containing a uranium-iodine bond. In the recently prepared compound  $\text{UI}_2[\text{O}(\text{CH}_2)_4\text{I}]_2(\text{tppo})_2$  ( $\text{tppo}$  = triphenylphosphine oxide), a U-I distance of 3.011(1) Å is



**Figure 2.** ORTEP drawing of  $\text{IU}(\text{OAr})_3$  (**4**) with the atomic numbering scheme. The hydrogen atoms are omitted for clarity.

observed.<sup>19</sup> Additionally, the U-I distance in **4** is comparable to the U-I distances of 2.996(3) and 3.027(3) Å observed in the octahedral complex  $\text{trans-UL}_4(\text{tmu})_2$  ( $\text{tmu}$  = tetramethylurea) but is shorter than those observed in the U(IV) dimer  $\text{U}_2\text{L}_4(\text{O-}i\text{-Pr})_4(\text{HO-}i\text{-Pr})_2$  (3.034(3) and 3.050(3) Å).<sup>20</sup> In addition, slightly longer U-I distances are observed in  $\text{Cp}_3\text{UI}$  and  $(\text{indenyl})_3\text{UI}$ , 3.059(2) and 3.041(1) Å, respectively.<sup>21</sup>

The uranium-oxygen distances in compound **4** vary from 2.092(8) to 2.114(11) Å. For comparison, the compound  $\text{U}(\text{OAr})_3(\text{NET}_2)$  possesses U-O bond distances of 2.140(4), 2.143(4), and 2.146(4) Å, and the compound  $\text{U}(\text{OAr})[\text{N}(\text{SiMe}_3)_2]_3$  has a U-O distance of 2.145 Å.<sup>15,22</sup> The tetrakis(aryloxide)  $\text{U}(\text{OAr})_4$ , **8** ( $\text{Ar}$  = 2,6-di-*tert*-butylphenoxide), is reported to have a U-O distance of 2.135(4) Å.<sup>22</sup> The U-O distances in these structurally characterized tetravalent uranium aryloxide compounds are slightly longer than what is observed in **4**.

The I-U-O angles in **4** vary from 103.0(2) to 111.4(2)°, consistent with the tetrahedral geometry about the uranium coordination sphere. The U-O-C(ipso) angles are not equal, with the U-O(1)-C(11) and U-O(3)-C(31) angles measured to be 169.8(11) and 169.7(6)°, and the U-O(2)-C(21) angle to be 159.8(7)°. The smaller U-O-C(ipso) angle is similar to angles observed in the compounds  $\text{U}(\text{OAr})[\text{N}(\text{SiMe}_3)_2]_3$  and  $\text{U}(\text{OAr})_4$  (**8**).<sup>22</sup>

Compound **4** is analogous to the titanium compound  $\text{Ti}(\text{OAr})_3\text{I}$  ( $\text{OAr}$  = 2,6-di-*tert*-butylphenoxide) prepared by Rothwell and co-workers.<sup>18</sup> In  $\text{Ti}(\text{OAr})_3\text{I}$ , the planes of the aryloxide groups lie at an angle of 24° to the Ti-I axis, orienting in a propeller configuration in order to reduce the steric interactions of the *tert*-butyl groups. In addition, the short Ti-O distance and almost linear Ti-O-Ar angle reflect a certain amount of Ti-O  $\pi$  bonding that is possible at the electron-deficient,  $d^0$  metal center. Similar structural parameters were observed in the isomorphous compound  $\text{Hf}(\text{OAr})_3\text{Cl}$ .<sup>18</sup>

(15) Hitchcock, P. B.; Lappert, M. F.; Singh, A.; Taylor, R. G.; Brown, D. *J. Chem. Soc., Chem. Commun.* **1983**, 561.

(16) The assignment of  $(\text{benzyl})\text{U}(\text{OAr})_3$  was made by preparation of an authentic sample. Preliminary work on the synthesis and characterization uranium hydrocarbyl aryloxides has been presented. McKee, S. D.; Avens, L. R.; Burns, C. J. Actinides-93 International Conference, Santa Fe, NM, September 19-24, 1993. Abstract P-3.

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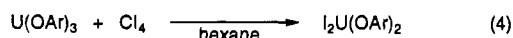
(21) (a) Ryan, R. R.; Penneman, R. A.; Kanellakopoulos, B. *J. Am. Chem. Soc.* **1975**, *97*, 4258. (b) Wong, C. H.; Yen, T. M.; Lee, T. Y. *Acta Crystallogr.* **1965**, *18*, 340. (c) Spirlet, M. R.; Rebizant, J.; Apostolidis, A.; Andreetti, G. D. *Acta Crystallogr.* **1989**, *C45*, 739. (d) Rebizant, J.; Spirlet, M. R.; Apostolidis, C.; Kanellakopoulos, B. *Acta Crystallogr.* **1991**, *C47*, 854. (e) Rebizant, J.; Spirlet, M. R.; Van Den Bossche, G.; Goffart, J. *Acta Crystallogr.* **1988**, *C44*, 1710.

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The complete propeller arrangement for the aryloxy groups is not observed in **4**. As shown in the ORTEP (Figure 2), two of the aryl ring planes lie roughly parallel to the U—I axis. However, the third aryl ring consisting of C(21)—C(26) is almost perpendicular to the U—I axis. Due to the longer U—O bond distances in **4** relative to the titanium and hafnium systems and the steric congestion of the *tert*-butyl groups, the aryloxides of **4** are able to adopt a configuration other than a propeller arrangement. The molecular structure of  $\text{U}(\text{OAr})_3(\text{NEt}_2)$  is similar to **4** in the relative disposition of the aryloxy groups about the metal center.<sup>15</sup>

**Synthesis and Characterization of  $\text{I}_2\text{U}(\text{OAr})_2$ .** Given the reactivity of  $\text{CBr}_4$  in the formation of **3**, it was believed that  $\text{Cl}_4$  (carbon tetraiodide) would be a suitable oxidant to form **4**. However, when the reaction was carried out in the presence of 1 equiv  $\text{Cl}_4$ , an unexpected product was isolated (eq 4). The



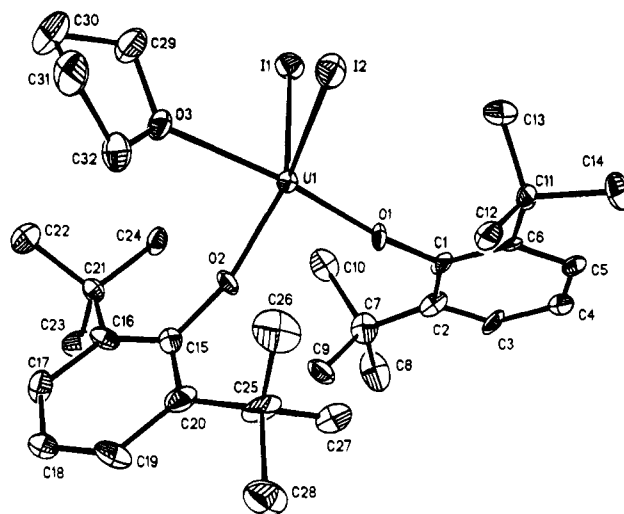
oxidation, carried out under conditions identical to the  $\text{I}_2$  reaction in hexane, produced the hexane insoluble uranium(IV) compound  $\text{I}_2\text{U}(\text{OAr})_2$  (**5**) in 55% yield. The  $^1\text{H}$  NMR of the filtrate indicates minor amounts of  $\text{IU}(\text{OAr})_3$  (**4**) and  $\text{U}(\text{OAr})_4$  (**8**) are produced, as well as some 2,6-di-*tert*-butylphenol. Experiments suggest that this transformation is not due to an impurity in the  $\text{Cl}_4$ .<sup>23</sup> We speculate that the reaction in eq 4 proceeds via the intermediacy of compound **4**. Whereas **4** will not react with  $\text{HCl}_3$  to form **5**, excess  $\text{I}_2$  will slowly convert **4** into **5**. In addition, **4** will react with  $\text{Cl}_4$  to form **5** in quantitative yield by  $^1\text{H}$  NMR. Furthermore, it is possible to synthesize **5** in either  $\text{Et}_2\text{O}$  or THF solvent in comparable yields from  $\text{U}(\text{OAr})_3$  and  $\text{Cl}_4$ .

Compounds **5** and **4** may readily be distinguished in solution by the chemical shifts for the various protons on the aryloxy ring. The resonances of the aryloxy ring protons are shifted downfield in **5** versus **4** (26.4 versus 16.5 ppm and 18.3 versus 11.6 ppm). Conversely, the *tert*-butyl resonance for **5** is shifted upfield from the value observed for **4** (−9.3 versus −3.9 ppm).

The nuclearity of compound **5** has not been determined. A related mixed aryloxy—halide complex,  $\text{Cl}_2\text{U}(\text{OAr}')_2$  ( $\text{OAr}' = 2,6\text{-di-}i\text{-tert-butyl-4-methylphenoxide}$ ), has been reported to be an oligomer, but neither structural information or solution data are available.<sup>15,24</sup>

Unlike  $\text{IU}(\text{OAr})_3$ ,  $\text{I}_2\text{U}(\text{OAr})_2$  is insoluble in organic solvents such as hexane and  $\text{Et}_2\text{O}$  but is very soluble in toluene and THF. Strongly coordinating bases yield base adducts, such as the THF adduct,  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$ . Experiments with  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  indicate that the THF adduct is not stable at room temperature and readily loses THF under dynamic vacuum. Crystals of  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  were obtained from THF/hexane. The molecular structure of this adduct was determined by single-crystal X-ray diffraction. The ORTEP drawing of the THF adduct is illustrated in Figure 3.

The compound is monomeric, with the uranium in the center of a distorted trigonal bipyramidal environment. The I(1)—U—I(2) angle is  $98.3(1)^\circ$ , and the U—I(1) and U—I(2) distances are 2.982(1) and 3.025(1) Å, respectively. These U—I distances are comparable to the U—I distance of 3.011(2) Å observed in  $\text{IU}(\text{OAr})_3$  (vide supra). Lappert and co-workers have structur-



**Figure 3.** ORTEP drawing of  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  (**5**·THF) with the atomic numbering scheme. The hydrogen atoms are omitted for clarity.

ally characterized the compound  $\text{Cp}''_2\text{UI}_2$  ( $\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3\text{-}(\text{TMS})_2$ ) and observe a I—U—I angle of  $105.4(8)^\circ$  and a U—I distance of 2.953(2) Å.<sup>24</sup> The axial uranium—oxygen distance in  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  (U—O(1)) is 2.080(8) Å, and the equatorial uranium—oxygen distance (U—O(2)) is 2.073(9) Å. These U—O(aryloxy) distances are identical within error and slightly shorter than those observed in  $\text{IU}(\text{OAr})_3$ . The U—O(3) distance for the bound THF is 2.473(9) Å. Both the uranium—oxygen distances for the THF and the aryloxy are comparable to distances reported for other structurally characterized uranium(IV) compounds.<sup>19,20,25</sup>

The O(1)—U—O(2) angle of the *cis* aryloxy moieties is  $96.2(3)^\circ$ . The *cis* orientation for the aryloxy groups is in direct contrast with the five coordinate uranium(IV) compound  $[\text{K}(\text{THF})_4][\text{UCl}_3(\text{OAr})_2]$ , where the aryloxy groups are in a *trans* disposition.<sup>26</sup> Steric interactions between the *tert*-butyl groups on the aryloxy would be minimized significantly in  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  if the aryloxy groups were in a *trans* disposition. However, with the adoption of the *cis* geometry, any steric interactions between the *tert*-butyl groups are minimized by the roughly perpendicular orientation of the aryloxy ring planes so as to allow the *tert*-butyl groups to lie together in a propeller-type arrangement. This orientation of the aryloxy groups in  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  is similar to  $\text{Ta}(\text{OAr})_2\text{-Cl}_3$  ( $\text{OAr} = 2,6\text{-di-}i\text{-tert-butylphenoxide}$ ).<sup>27</sup> In the tantalum example, the aryloxy groups also adopt a *cis* arrangement with the O—Ta—O angle reported to be  $104.2(2)^\circ$ .

The O(1)—U—I(1) and O(1)—U—I(2) angles in  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  are  $92.5(2)$  and  $113.7(2)^\circ$ , respectively, reflecting the distortion from a true trigonal bipyramidal geometry. The axial ligands are nearly linear, reflected by the O(1)—U—O(3) angle of  $171.4(3)^\circ$ . In  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  the uranium—aryloxy—ipso carbon angles U—O(1)—C(1) and U—O(2)—C(15) are  $172.6(8)$  and  $166.2(8)^\circ$ , respectively. The U—O—C<sub>ipso</sub> angle is  $154.0(6)^\circ$  in the tetrakis(aryloxy) complex **8**.<sup>22</sup>

The bis(pentamethylcyclopentadienyl)actinide framework has been employed extensively to stabilize dihalide complexes of uranium and thorium against the ligand redistribution problems

(23) Experiments indicate that the use of unpurified  $\text{Cl}_4$  (Aldrich 95%) produces the same product in comparable yields as material that has been purified by sublimation. As discussed in the text, reactions of the tris(aryloxy) compound with possible decomposition products of  $\text{Cl}_4$  ( $\text{CHI}_3$ ,  $\text{C}_2\text{L}_4$ ,  $\text{I}_2$ ) produce only the monoiodo complex.

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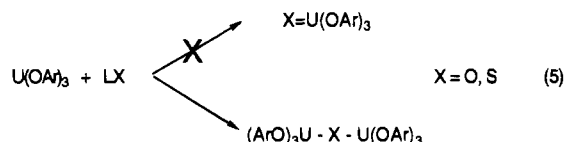
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which plague the unsubstituted cyclopentadienyl analogs.<sup>28</sup> The ability of bis(aryloxy)uranium diiodide to form base adducts demonstrates that this framework is less sterically saturated than  $(\text{Me}_3\text{C}_5)_2\text{UCl}_2$ , and yet the complex is not readily susceptible to ligand exchange. The possibility of ligand arrangement in the bis(aryloxy)- and tris(aryloxy)-halide systems is under investigation.<sup>26</sup>

**Synthesis and Characterization of  $[(\text{ArO})_3\text{U}]_2-\mu\text{-X}$  ( $\text{X} = \text{O}, \text{S}$ ).** Reaction of  $\text{U}(\text{OAr})_3$  with a suitable chalcogenide source results in formation of a uranium(IV) chalcogenide-bridged complex compound of the form  $(\text{OAr})_3\text{U}-\text{X}-\text{U}(\text{OAr})_3$  ( $\text{X} = \text{O}, \text{S}$ ; eq 5). Similar chalcogenide-bridged complexes of uranium(IV) are known for both the  $\text{Cp}_3\text{U}$  and  $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$  systems.<sup>3e,14,29</sup>



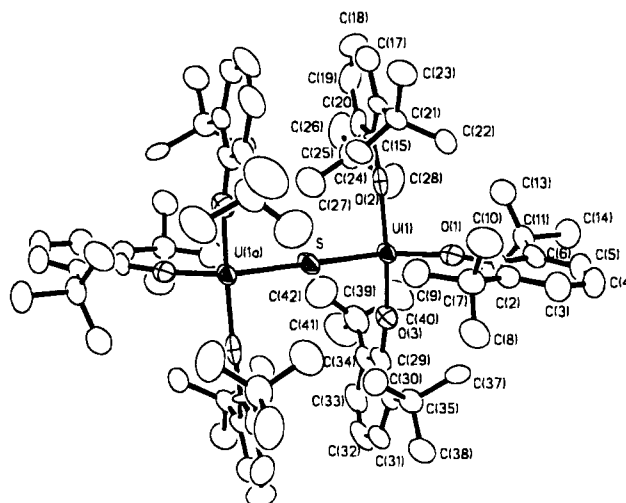
The complex  $(\text{ArO})_3\text{U}-\text{O}-\text{U}(\text{OAr})_3$  (**6**) can be synthesized from a variety of oxidants such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{Me}_3\text{NO}$ , and  $\text{pyNO}$ . Excess reagent leads to the formation of intractable solids or, in some instances, the formation of  $\text{U}(\text{OAr})_4$ , **8**, as an impurity. It is also possible to prepare **6** by the oxidation of  $\text{U}(\text{OAr})_3$  with iodosobenzene, but the major component of the reaction mixture is **4**.

The analogous compound  $\text{Cp}''_3\text{U}-\text{O}-\text{UCp}''_3$  ( $\text{Cp}'' = \text{Me}_3\text{-SiC}_5\text{H}_4$ ) has recently been synthesized from either  $\text{N}_2\text{O}$  or  $\text{CO}_2$ .<sup>29</sup> Evans has reported the synthesis of  $[\text{Cp}^*_2\text{Sm}]_2-\mu\text{-O}$  using a variety of oxygen sources, including propylene oxide.<sup>30</sup> While we have observed reactivity between  $\text{U}(\text{OAr})_3$  and either propylene oxide or  $\text{CO}_2$ , the product(s) isolated are not the oxo-bridged compound **6**. Complete characterization of these reactions is still under investigation.

The  $^1\text{H}$  NMR spectrum of **6** indicates only one type of aryloxy group is present in solution. The infrared spectrum clearly shows the presence of a strong band at  $580\text{ cm}^{-1}$ , which is assigned to the  $\text{U}-\text{O}-\text{U}$  stretch by analogy to the assignment of the  $\text{U}-\text{O}-\text{U}$  stretch in  $[\text{Cp}'_3\text{U}]_2(\mu\text{-O})$  to a band at  $610\text{ cm}^{-1}$ .<sup>11,31</sup>

The analogous sulfido-bridged compound,  $(\text{ArO})_3\text{U}-\text{S}-\text{U}(\text{OAr})_3$  (**7**), can be prepared by reaction of the tris(aryloxy) complex with either an excess of  $\text{COS}$  or 1 molar equiv of  $\text{Ph}_3\text{P}=\text{S}$ . As expected, the reaction of  $\text{U}(\text{OAr})_3$  with  $\text{Ph}_3\text{P}=\text{O}$  does not form the oxo-bridged species but rather the adduct  $(\text{Ph}_3\text{P}=\text{O})\text{U}(\text{OAr})_3$ .<sup>32</sup> As has been previously discussed, this difference in reactivity between  $\text{Ph}_3\text{P}=\text{O}$  and  $\text{Ph}_3\text{P}=\text{S}$  is due to the difference in bond strengths between the  $\text{P}=\text{O}$  and the  $\text{P}=\text{S}$  bond.<sup>4e</sup> Other reagents have been observed to yield **7** as the major component in a mixture of products, including reaction with elemental sulfur and sulfur dioxide. These reactions are under further investigation.

The molecular structure of compound **7** has been determined by X-ray crystallography. Compound **7** crystallizes as a diethyl



**Figure 4.** ORTEP drawing of  $(\text{ArO})_3\text{U}-\text{S}-\text{U}(\text{OAr})_3$  (**7**) with the atomic numbering scheme. The hydrogen atoms are omitted for clarity.

ether solvate in the space group  $\text{P}\bar{1}$ . The ORTEP diagram (Figure 4) clearly establishes the assignment as a sulfido-bridged compound.

The most important structural features of the complex are the linear  $\text{U}-\text{S}-\text{U}$  angle and the  $\text{U}-\text{S}$  distance of  $2.588(1)\text{ \AA}$ . The compound  $\text{Cp}'_3\text{U}-\text{S}-\text{UCp}'_3$  ( $\text{Cp}' = \text{CH}_3\text{C}_5\text{H}_4$ ) possess a slightly bent  $\text{U}-\text{S}-\text{U}$  angle ( $164.9(4)^\circ$ ) and an average  $\text{U}-\text{S}$  distance of  $2.60(1)\text{ \AA}$ .<sup>4e</sup> The  $\text{U}-\text{S}$  distance in **7** is somewhat shorter than the  $2.696(3)\text{ \AA}$  distance observed in the uranium(IV) thiolate complex  $\text{U}(\text{SAr})[\text{N}(\text{SiMe}_3)_2]_3$  ( $\text{SAr} = \text{S-2,6-di-tert-butylphenyl}$ ).<sup>33</sup>

In compound **7**, the sulfur atom is located on a crystallographic inversion center. The uranium atom is four coordinate, surrounded by a single sulfur and three oxygen atoms of the aryloxy ligands. The  $\text{U}-\text{O}(1)$  distance of  $2.079(9)\text{ \AA}$  is slightly shorter than the  $\text{U}-\text{O}(2)$  and  $-\text{O}(3)$  distances of  $2.125(8)$  and  $2.119(6)\text{ \AA}$ . These distances are comparable to the  $\text{U}-\text{O}$  distances observed in  $\text{IU}(\text{OAr})_3$  and  $\text{I}_2\text{U}(\text{OAr})_2(\text{THF})$  (vide supra). However, there are significant deviations in the  $\text{S}-\text{U}-\text{O}$  and  $\text{O}-\text{U}-\text{O}$  bond angles in compound **7** when compared to the tetrahedral geometry observed in compound **4**. The  $\text{S}-\text{U}-\text{O}(1)$  angle is  $123.2(2)^\circ$ , but the  $\text{S}-\text{U}-\text{O}(2)$  and  $\text{S}-\text{U}-\text{O}(3)$  angles are  $92.1(2)$  and  $95.7(2)^\circ$ , respectively. Furthermore, the  $\text{O}(1)-\text{U}-\text{O}(2)$  and  $\text{O}(1)-\text{U}-\text{O}(3)$  angles are  $95.9(3)$  and  $98.5(3)^\circ$ , respectively, whereas the  $\text{O}(2)-\text{U}-\text{O}(3)$  angle is  $156.2(4)^\circ$ . The orientations of the aryloxy rings are significantly different than observed in compound **4** (compare Figures 2 and 4). As was apparent in **4**, the aryloxy groups of **7** do not form a propeller orientation about the  $\text{U}-\text{S}$  bond but rather orient in a way to reduce *tert*-butyl interactions between the aryloxides. An interesting aspect about the orientation adopted by the aryloxy groups containing oxygen atoms  $\text{O}(1)$ ,  $\text{O}(2)$ , and  $\text{O}(3)$  is the position of the *tert*-butyl methyl groups. The orientation is such that the "open" face opposite the  $\text{U}-\text{O}(1)$  vector is occupied by these methyl groups. A similar feature is reported by Rothwell in  $\text{Ta}(\text{OAr})_2\text{Cl}_3$ .<sup>27</sup> The  $\text{U}-\text{O}-\text{C}(\text{ipso})$  bond lengths and distances do not show any significant deviation from those observed in **4**.

In general,  $\text{U}(\text{OAr})_3$  reacts like other well-characterized trivalent uranium congeners in that the observed oxidation reaction with chalcogenide-based compounds results in the formal one-electron oxidation to uranium(IV). The charge balance of the  $\text{X}^{2-}$  ligand ( $\text{X} = \text{O}, \text{S}$ ) is maintained by formation

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of the chalcogenide bridge, at the expense of formation of a mononuclear uranium(V) compound.

One possible synthetic route to form the desired uranium(V) compound  $O=U(OAr)_3$  was the reaction of  $U(OAr)_3$  with molecular oxygen. Exposure of oxygen to a hexane solution of  $U(OAr)_3$  causes the solution to darken in color and to become opaque over time. Filtration of the reaction mixture removes an insoluble black solid and an orange colored filtrate. The uranium(IV) compound,  $U(OAr)_4$  (**8**), was isolated in 35%. Excess oxygen will reduce the amount of **8** produced. We have followed this reaction by  $^1H$  NMR in benzene- $d_6$ , and while there is a broad resonance at  $-5$  ppm assigned to the *tert*-butyl group of an intermediate, the identity of this intermediate is uncertain.

Ligand redistribution reactions have been observed in uranium(VI) oxo/alkoxide compounds, with the formation of insoluble uranium oxides the driving force for the reaction.<sup>34</sup> Reactions of  $(Me_3SiC_5H_4)_3U$  with  $O_2$  have been reported to yield ligand redistribution, resulting in formation of  $(Me_3SiC_5H_4)_4U$  in low yield.<sup>11</sup> Similar redistribution is observed with  $U-[N(SiMe_3)_2]_3$ .<sup>14</sup> In contrast to the uranium systems studied, reactions for a number of lanthanide compounds with oxygen have been shown to yield peroxo-bridged systems.<sup>35</sup>

## Conclusions

Despite the variability in oxidation potential which may be inferred by ancillary ligands, the redox chemistry of  $U(OAr)_3$  is decidedly similar to that reported for other uranium(III) compounds. Oxidation in the presence of a suitable halide source results in the formation of the uranium(IV) compound  $XU(OAr)_3$  ( $X = F, Cl, Br, I$ ). Similarly, oxidation in the presence of a suitable chalcogenide source forms the bridged binuclear uranium(IV) compounds  $[(ArO)_3U]_2-\mu-X$  ( $X = O, S$ ).

These oxidative preparative routes have not yet succeeded in producing pentavalent uranium halide- or chalcogenide-containing complexes. We are currently exploring other means of accessing these systems. Variation of the aryloxy substituent (and the attendant electronic and steric factors) will also permit further exploration of the redox and coordinative stability of actinide aryloxy complexes.<sup>36</sup>

While these investigations have not uncovered significant systematic differences in the redox chemistry of  $Cp_3U$ ,  $U-[N(SiMe_3)_2]_3$ , and  $U(OAr)_3$ , suitable routes have been developed for the synthesis of mixed halide-aryloxy complexes (such as  $IU(OAr)_3$  and  $I_2U(OAr)_2$ ). These complexes do not appear to demonstrate facile ligand distribution at room temperature and can serve as precursors in further metathesis reactions. This will permit further elucidation of the similarities and differences between cyclopentadienyl-based uranium(IV) compounds (e.g.,  $Cp_3UL$  and  $Cp^*_2UL_2$ ) and aryloxy-based uranium(IV) compounds, particularly in terms of the synthesis and reaction chemistry of uranium  $\sigma$ -bonded systems.<sup>16</sup> Such studies will allow us to better understand the electronic and steric factors that these ligand sets introduce into observed reactivity.

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**Supplementary Material Available:** ORTEP figures and tables providing hydrogen coordinates and isotropic displacement information, anisotropic displacement parameters, and bond lengths and bond angles for compounds **4**, **5** · THF, and **7** (21 pages). Ordering information is given on any current masthead page.

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