Halide Effects in the Synthesis of Mixed Uranium(IV) Aryloxide−Halide Compounds

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Several uranium(IV) aryloxide and mixed aryloxide−halide compounds of the formula $UX_{4-z}(OAr)_z$ (X = Cl, Br, I; OAr = 2,6-di-*tert*-butylphenoxide; $z = 2, 3, 4$) have been prepared by the reaction of KOAr with the appropriate uranium tetrahalide in tetrahydrofuran (THF). The complex $UI_4(CH_3CN)_4$ reacts with 2 equiv of KOAr in THF to yield the compound $I_2U(OAr)_2$ (**1**). The utility of this reaction is limited by the instability of $UI_4(CH_3CN)_4$ in THF, however, and isolated yields of the THF adduct of **1** do not exceed 50%. In contrast, $UBr_4(CH_3CN)_4$ is stable in THF solution and reacts with 2 equiv of KOAr to yield the dibromide, $Br_2U(OAr)_2$(THF) (**4·**THF), in 77% yield. Under identical reaction conditions, UCl_4 reacts to yield the complex $[K(THF)_4][UCl_3(OAr)_2]$ (**5**) in 68% yield. The uranium center in compound **5** is coordinated by two trans aryloxide ligands and three chloride ligands in a trigonal bipyramidal arrangement. Two chloride ligands of each unit are also coordinated to a potassium ion, forming an infinite chain in the lattice. Compounds **1** and **5** will further react with 1 equiv of KOAr to yield the compounds $XU(OAr)_3$ (**2**, X = I; **6**, X = Cl). Both $UI_4(CH_3CN)_4$ and UCl_4 will react with a 4.2 equiv of KOAr to yield the previously characterized compound $U(OAr)_4$ (**3**). The stability of the mixed aryloxide−halide uranium complexes toward ligand redistribution reactions has been investigated.

Introduction

The coordination and organometallic chemistry of uranium is marked by the accessibility of a multiplicity of oxidation states.[2] This variability in oxidation states permits multiple electron-transfer chemistry, which can be of use in effecting chemical transformations at the metal center, provided one employs ancillary ligands which are tolerant of changes in the oxidation state of the uranium. An example of such a ligand set is the bis(pentamethylcyclopentadienyl) framework, which is known to stabilize uranium complexes in all oxidation states from +3 to +6.[3−5] It is desirable to identify other such redox-tolerant ligand sets, to permit synthetic variations of both the electronic and steric constraints at the metal center. One possible candidate ancillary ligand is the 2,6-disubstituted aryloxide ligand. This ligand has been successfully introduced at both U(III) and U(IV) to generate neutral homoleptic complexes.[6] Further, the reactivity of these complexes is similar to that observed for better known uranium coordination environments. The one-electron oxidation chemistry of the compound $U(OAr)_3$ (OAr = 2,6-di-*tert*-butylphenoxide) has been investigated and been shown to be analogous to that of the uranium(III) compounds Cp_3U and $U[N(SiMe_3)_2]_3$[7] (e.g., $U(OAr)_3$ is oxidized by a suitable halide source to yield the uranium(IV) compounds of the formula $XU(OAr)_3$, where X = F, Cl, Br, I).[8]

To further develop the chemistry of aryloxide groups as ancillary ligands in organouranium chemistry, it is necessary to investigate alternative routes for the preparation of mixed aryloxide−halide compounds of uranium(IV). The preparations of the aryloxide compounds $U(OAr')_4$ (OAr′ = 2,6-diisopropylphenoxide), $[Li(THF)_4][U(OAr')_5]$, and $ClU(OAr'')_3$ (OAr″ = 2,4,6-tri-*tert*-butylphenoxide) have been reported by Lappert and co-workers from UCl_4 and the lithium salt of the aryloxide,[6a,9] but this work has yet to be extended to other uranium halides or aryloxide salts.

There are several factors to be probed in developing preparative routes to mixed aryloxide−halide complexes. The first of these is the comparative utility of the heavier halides of uranium as reagents. Given the difficulty of reported syntheses of UCl_4,[10] it is of significant interest to examine the applicability of other, more readily prepared tetravalent uranium halide reagents. Another goal of these investigations is to develop general routes for the preparation of the compounds $X_2U(OAr)_2$ (X = Cl, Br, I). These compounds have an ancillary ligand set most directly analogous to the bis(pentamethylcyclopentadienyl) framework which has been so successfully employed in uranium organo-

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metallic chemistry. The complex $I_2U(OAr)_2$ has been prepared by direct oxidation of $U(OAr)_3$,[8] but the chloride and bromide complexes cannot be prepared by analogous routes. Finally, it is important to assess the susceptibility of the aryloxide framework to ligand redistribution, a process documented for sterically unsaturated uranium cyclopentadienide compounds.[11] In this contribution, we report on these alternative routes for the synthesis of mixed aryloxide−halide compounds, and on the stability of mixed aryloxide−halide compounds of uranium with regard to ligand redistribution.

Experimental Section

All operations were performed using standard Schlenk techniques under UHP grade argon or in a Vacuum Atmospheres drybox under helium. Tetrahydrofuran (THF), diethyl ether (Et_2O), hexane, dimethoxyethane (dme), and toluene were dried and distilled under nitrogen from either sodium benzophenone or Na−K alloy. Benzene-d_6 was dried over CaH_2, vacuum transferred, and freeze−pump−thawed three times before use. THF-d_8 was dried over Na−K/benzophenone, vacuum transferred, and freeze−pump−thawed three times before use.

The uranium(IV) halides $UI_4(CH_3CN)_4$, $UBr_4(CH_3CN)_4$, and UCl_4 were prepared by literature methods.[10,12] Unless otherwise indicated, we will designate 2,6-di-*tert*-butylphenoxide as OAr throughout this paper. The compounds $XU(OAr)_3$ (X = Cl, Br, I), $I_2U(OAr)_2$, and $U(OAr)_4$ were independently prepared by alternate methods for direct spectroscopic characterization by infrared and ^{1}H NMR.[6,8] Potassium 2,6-di-*tert*-butylphenoxide (KOAr) was synthesized from 2,6-di-*tert*-butylphenol and potassium hydride.[13]

^{1}H NMR spectra (250.13 MHz) were measured on a Bruker AF250 MHz 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 for all compounds (3−15 Hz full width at half-height), unless otherwise noted. Infrared spectra were obtained on a Bio-Rad FTS-40 infrared spectrometer in Nujol on KBr plates. Elemental analysis 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.

Synthesis and Characterization. $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2I_2(THF)$ (1·THF). A solution containing 0.108 g (4.42×10^{-4} mol) of KOAr in 20 mL of THF was added dropwise to a stirred solution of 0.200 g (2.20×10^{-4} mol) of $UI_4(CH_3CN)_4$ in 25 mL of THF over a 10 min period. The solution was stirred for ca. 20 min, by which time the reaction mixture was opaque. The solvent was removed from the reaction mixture in vacuo. The resulting brown oil was redissolved in a solution of 10 mL of toluene and 1 mL of hexane and filtered through Celite. The filtrate was concentrated to dryness to produce an orange solid; this was redissolved in a minimum volume of THF, layered with hexane, and cooled to −40 °C. After several days an orange precipitate was collected by filtration. Additional batches were collected from the mother liquor by layering with more hexane. The combined isolated yield of $I_2U(OAr)_2(THF)$, **1**·THF, from all batches was 50% (0.11 g). The compound could be desolvated under dynamic vacuum to yield $I_2U(OAr)_2$ (**1**).

$U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3I$ (2). A solution of 0.040 g (1.64×10^{-4} mol) of KOAr in 10 mL of THF was added to a stirred solution of 0.150 g (1.66×10^{-4} mol) of **1** in 20 mL of THF dropwise over a 10 min period. A precipitate was observed to form and the solution became more yellow. The solution was permitted to stir for ca. 2 h, at which time the THF solvent was removed in vacuo. The resulting residue was redissolved with 20 mL of hexane, permitted to stir for a period of time, and finally filtered through Celite. The filtrate was concentrated under reduced pressure and cooled to −40 °C. Pure $IU(OAr)_3$, **2**, was isolated by filtration in 88% yield (0.14 g).

$U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2Br_2(THF)$ (4). A solution of 0.068 g (2.78×10^{-4} mol) of KOAr in 10 mL of THF was added to a stirred solution of 0.100 g (1.39×10^{-4} mol) of $UBr_4(CH_3CN)_4$ in 20 mL of THF dropwise over a 10 min period. The solution was stirred for ca. 8 h, by which time the solution was opaque due to the formation of a precipitate. The THF solvent was removed under reduced pressure, and the residue was extracted with 10 mL of a 2:1 toluene/hexane solution and filtered through Celite. This solution was again dried to yield a yellow solid. The solid was redissolved in 5 mL of hexane with a small amount of THF added and the solution was cooled to −40 °C, producing a golden yellow solid. Filtration yielded 0.094 g of solid $Br_2U(OAr)_2(THF)$, **4**·THF (77%). The compound could be desolvated under dynamic vacuum to yield $Br_2U(OAr)_2$ (**4**).

Data for 4. IR (cm^{-1} in Nujol): 1582 (vw), 1406 (s), 1364 (sh), 1306 (w), 1266 (m), 1219 (sh), 1206 (m), 1186 (vs), 1118 (s), 1092 (sh), 1034 (vw), 1000 (m), 958 (vw), 926 (w), 881 (m), 862 (vs), 830 (sh), 820 (vs), 794 (s), 749 (vs), 723 (m), 667 (vs), 631 (w), 548 (w), 451 (w). NMR: (C_6D_6) 28.5 (4 H), 20.1 (2 H), −6.2 (36 H) ppm. Anal. Calcd for $UBr_2O_2C_{28}H_{42}$: C, 41.6; H, 5.24. Found: C, 41.15; H, 5.20.

Data for **4**·THF. ^{1}H NMR: (C_6D_6) 28.5 (s, 4 H), 20.1 (s, 2 H), 13.0 (br s, 4 H), 6.5 (br s, 4 H), −6.2 (s, 36 H) ppm. Anal. Calcd for $UBr_2O_3C_{32}H_{50}$: C, 44.46; H, 5.83. Found: C, 44.72; H, 5.76.

$[K(THF)_4][UCl_3(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2]$ (5). A solution of 0.258 g (1.06×10^{-3} mol) of KOAr in 10 mL of THF was added to a stirred solution of 0.200 g (5.27×10^{-4} mol) of UCl_4 in 20 mL of THF dropwise over a 10 min period. The solution was permitted to stir for 15 h. The mixture was filtered through Celite, and the filtrate was reduced to less than 10 mL in volume and layered with hexane. The mixture was cooled to −40 °C. After several days, dull yellow needles were observed. The solid was isolated, washed with hexane, and dried under vacuum. This yielded 0.385 g $[K(THF)_4][UCl_3(OAr)_2]$, **5**, in 68% yield. Although stable upon isolation, solid **5** is susceptible to loss of THF over time.

IR (cm^{-1} in Nujol): 1582 (vw), 1403 (s), 1370 (sh), 1308 (w), 1265 (m), 1211 (s), 1189 (s), 1122 (s), 1056 (m), 1039 (w), 1016 (w), 1005 (w), 920 (w), 881 (w), 859 (vs), 821 (s), 796 (m), 749 (s), 727 (w), 661 (s), 560 (sh), 549 (w), 460 (sh), 449 (m). ^{1}H NMR: (C_6D_6) 30.6 (s, 2 H), 21.8 (s, 1 H), 10.0 (br s, THF), 2.7 (br s, THF), −3.8 (s, 18 H) ppm. Anal. Calcd for $KUCl_3O_6C_{44}H_{74}$: C, 48.82; H, 6.89. Found: C, 48.23; H, 7.17.

$U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3Cl$ (6). A solution of 0.023 g (9.41×10^{-5} mol) of KOAr in 10 mL of THF was added to a stirred solution of 0.100 g (9.24×10^{-5} mol) of **5** in 20 mL of THF dropwise over a 10 min period. The solution was permitted to stir for 4 h, at which time the solution was concentrated to dryness. The resulting residue was extracted with 20 mL of hexane. The mixture was permitted to stir and was then filtered through Celite. The solvent was removed in vacuo to obtain a yellow solid. Recrystallization from a concentrated Et_2O solution at −40 °C yielded 0.072 g of $ClU(OAr)_3$, **6**, in 88% yield.

$U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ (3). Synthesis from 2. A solution of 0.027 g (1.10×10^{-4} mol) of KOAr in 10 mL of THF was added to a stirred solution of 0.100 g (1.02×10^{-4} mol) of **2** in 20 mL of THF dropwise over a 10 min period. A precipitate was observed to form as the solution became darker. The solution was permitted to stir for 4 h, at which time the solvent was removed under reduced pressure. The resulting residue was dissolved in toluene and filtered through Celite. The solvent was removed in vacuo to yield a golden solid; recrystallization from hexane at −40 °C yielded 0.092 g of $U(OAr)_4$, **3** (85%).

Synthesis from $UI_4(CH_3CN)_4$. A solution of 0.124 g (5.07×10^{-4} mol) of KOAr in 10 mL THF was added to a stirred solution of 0.110 g (1.21×10^{-4} mol) of $UI_4(CH_3CN)_4$ in 20 mL of THF dropwise over a 10 min period. The solution was permitted to stir for 15 h, at which time the solvent was removed by vacuum to yield a tacky oil. The oil was redissolved in toluene, filtered through Celite, and concentrated to dryness. The residue was redissolved in a minimum of hexane, and the solution was cooled to −40 °C. After several days, compound **3** was isolated by filtration in 54% yield (0.069 g).

Synthesis from 6. A solution containing 0.027 g (1.10×10^{-4} mol) of KOAr in 10 mL of THF was added to a stirred solution of 0.100 g (1.12×10^{-4} mol) of **6** in 20 mL of THF dropwise over a 10 min

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Table 1. Crystallographic Parameters for $K(THF)_4[UCl_3(OAr)_2]$ (**5**)

empirical formula	$C_{44}H_{74}Cl_3KO_6U$
space group	$P\bar{1}$
temp (°C)	−70
a (Å)	11.007(2)
b (Å)	12.538(3)
c (Å)	19.704(4)
α (deg)	75.33(3)
β (deg)	83.59(3)
γ (deg)	70.33(3)
V (Å$^{3)}$	2576.1(9)
Z	2
ρ_{calc} (g/cm^3)	1.452
radiation (λ (Å))	Mo Kα (0.710 73)
fw	1082.51
μ (mm^{-1})	3.56
range (scan type)	3.0−45.0° ($\omega-2\theta$)
R^a	4.25
$R_w{}^a$	6.11

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

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[K(THF)_4][UCl_3(OAr)_2]$ (**5**)

Distances			
U(1)−Cl(1)	2.667(3)		
U(1)−Cl(2)	2.595(3)	U(1)−Cl(3)	2.636(3)
U(1)−O(1)	2.122(6)	U(1)−O(2)	2.123(6)
K(1)−Cl(1)	3.174(4)		
K(1)−Cl(3A)	3.213(4)		
K(1)−O(3)	2.694(7)	K(1)−O(4)	2.687(11)
K(1)−O(5)	2.684(9)	K(1)−O(6)	2.709(8)
O(1)−C(1)	1.366(12)	O(2)−C(15)	1.388(9)
Angles			
Cl(1)−U(1)−Cl(2)	134.4(1)	Cl(1)−U(1)−Cl(3)	132.6(1)
Cl(2)−U(1)−Cl(3)	93.0(1)		
Cl(1)−U(1)−O(1)	83.5(2)	Cl(2)−U(1)−O(1)	93.4(2)
Cl(3)−U(1)−O(1)	96.2(2)	Cl(1)−U(1)−O(2)	83.6(2)
Cl(2)−U(1)−O(2)	95.6(2)	Cl(3)−U(1)−O(2)	92.7(2)
O(1)−U(1)−O(2)	167.0(3)		
Cl(1)−K(1)−O(3)	80.0(2)	Cl(1)−K(1)−O(4)	79.5(3)
O(3)−K(1)−O(4)	90.3(3)	Cl(1)−K(1)−O(5)	101.2(2)
O(3)−K(1)−O(5)	82.1(2)	O(4)−K(1)−O(5)	172.3(3)
Cl(1)−K(1)−O(6)	103.1(3)	O(3)−K(1)−O(6)	172.9(3)
O(4)−K(1)−O(6)	84.1(3)	O(5)−K(1)−O(6)	103.0(3)
Cl(1) −K(1)−Cl(3A)	153.9(1)	Cl(1)−K(1)- Cl(3A)	79.1(2)
U(1)−Cl(1)−K(1)	156.7(1)	U(1)−Cl(3)−K(1A)	130.4(1)

period. The yellow solution was permitted to stir for 4 h, at which time the solvent was removed by vacuum. The resulting residue was extracted with toluene, and the solution was filtered through Celite. The filtrate was concentrated to dryness to yield a golden solid. Recrystallization from hexane at −40 °C yielded 0.089 g of $U(OAr)_4$, **3** in 76% yield.

Synthesis from UCl_4. A solution of 0.270 g (1.10 × 10^{-3} mol) of KOAr dissolved in 20 mL of THF was added to a stirred solution of 0.100 g (2.63 × 10^{-4} mol) of UCl_4 in 30 mL THF dropwise over a 10 min period. The solution was permitted to stir for 12 h, at which time the solvent was removed by vacuum to yield a tacky residue. The residue was extracted with toluene, and the solution was filtered through Celite. The filtrate was concentrated to dryness; recrystallization from hexane at −40 °C yielded **3** in 91% yield (0.25 g).

Ligand Redistribution Studies. In a representative procedure, a 5 mm NMR tube attached to a J. Young valve was loaded with 0.010 g (1.10 × 10^{-5} mol) of $UI_4(CH_3CN)_4$ and 0.011 g (1.04 × 10^{-5} mol) of $U(OAr)_4$. The solids were dissolved in a sufficient quantity of THF-d_8 or C_6D_6 (approximately 2 mL). The valve was closed, and the mixture was monitored by ^{1}H NMR spectroscopy. These experiments were carried out at 25 and 60 °C.

Crystal Structure Determination of $K(THF)_4[UCl_3(OAr)_2]$. Crystallization of **5** was accomplished by slow diffusion of hexane into a concentrated THF solution of the compound at −40 °C. The crystals were manipulated in mineral oil under an argon stream. A portion of a yellow-brown needle of dimensions 0.30 mm × 0.32 mm × 0.40 mm was selected, mounted on a glass fiber with Apiezon "H" grease, and transferred to the goniostat cooled to −70 °C. Data were collected on the Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants and an orientation matrix were obtained by least-squares refinement from 25 reflections. The cell was determined to be triclinic. The data were collected in $\omega-2\theta$ scan mode. A series of high χ (above 80°) reflections were scanned to provide the basis for an empirical absorption correction. No crystal decay was evident during data collection.

The solution of the data was accomplished by direct methods in the space group $P\bar{1}$. 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 = 4.25 and R_w = 6.11, and the GOF = 1.30 based on 496 refined parameters. All calculations were carried out using the SHELXTL PLUS software provided by Siemens Analytical. Crystallographic parameters, bond distances, and bond angles for **5** are provided in Tables 1 and 2.

Results and Discussion

In the course of developing synthetic routes to a series of mixed uranium aryloxide−halide compounds, we have examined the metathesis reactions of tetravalent uranium chloride, bromide, and iodide precursors. The only reported well-characterized tetravalent uranium iodide complex available for study is $UI_4(CH_3CN)_4$.[12] This complex was expected to yield clean products in metathesis reactions by analogy with the known chemistry of the trivalent analogue $UI_3(THF)_3$.[14] The tetravalent iodide is isolated as an orange solid from the reaction of uranium metal and elemental iodine in acetonitrile and is freely soluble in THF. It has limited thermal stability, however, and will decompose in THF solvent to yield a haloalkoxide complex arising from the ring opening of tetrahydrofuran.[15] In the solid state, $UI_4(CH_3CN)_4$ appears to decompose over several months in an inert atmosphere drybox, presumably by the loss of I_2. The instability of $UI_4(CH_3CN)_4$ in THF contrasts with the stability of the related thorium complex $ThI_4(THF)_4$, which has been successfully employed as a reagent in methathesis reactions in THF.[16]

Addition of 2 equiv of KOAr to a THF solution of $UI_4(CH_3CN)_4$ yields the compound $I_2U(OAr)_2(THF)$, **1**·THF, in 50% yield. The yield of **1**·THF by this route is lower than that previously reported for the reaction of $U(OAr)_3$ with carbon tetraiodide.[8] The reaction is also not as selective, and repeated recrystallizations of the product are necessary to generate analytically pure **1**·THF. It is possible that impurities are introduced which are products of the ring opening of THF, although the yield of the desired product is still moderate even when freshly prepared $UI_4(CH_3CN)_4$ is employed. Attempts to carry out the synthesis of **1** in other solvents have not been successful.

Mixed aryloxide−iodide complexes are more effective reagents in subsequent metathesis reactions, and the compound $I_2U(OAr)_2$ will react with 1 equiv of KOAr in THF to yield the trisaryloxide compound $IU(OAr)_3$,[8] **2**, in 88% yield. It is important that the KOAr solution be added to the $I_2U(OAr)_2$

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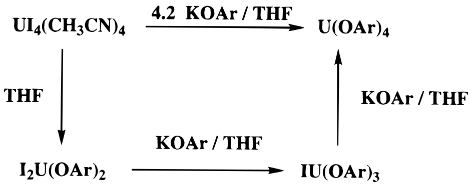
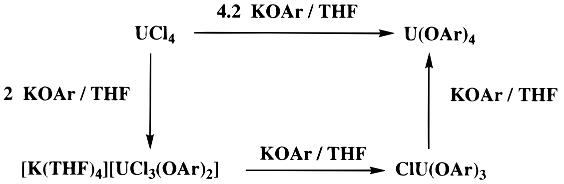
Scheme 1. Synthesis of Uranium Iodide−Aryloxide Compounds



Scheme 2. Synthesis of Uranium Chloride−Aryloxide Compounds



solution slowly in order to avoid formation of $U(OAr)_4$, **3**. Attempts to prepare **2** from $UI_4(CH_3CN)_4$ and 3 equiv of KOAr have resulted in low yields of the desired product. This difference in the effectiveness of $UI_4(CH_3CN)_4$ and mixed aryloxide−iodide complexes as precursors in metathesis reactions is again demonstrated in the synthesis of $U(OAr)_4$, **3**. This compound can be prepared by two routes as depicted in Scheme 1. The first is the addition of KOAr to **2**, which generates **3** in 85% yield. An alternative route for the preparation of **3** utilizes the reaction of $UI_4(CH_3CN)_4$ with a slight excess (4.2 equiv) of KOAr. The isolated yield of the latter route is only 54%.

Unlike $UI_4(CH_3CN)_4$, $UBr_4(CH_3CN)_4$ is stable in THF solvent; there is no evidence of reduction or solvent activation in solutions maintained for 1−2 days. The synthesis of the mixed bromide−aryloxide complex $Br_2U(OAr)_2(THF)$, **4**·THF, is readily accomplished in 77% yield from $UBr_4(CH_3CN)_4$ (eq 1). The ^1H NMR does not indicate the formation of any other bromide−aryloxide compounds, including a possible "ate" complex (vide infra), or the trisaryloxide $BrU(OAr)_3$.[8]

$$UBr_4(CH_3CN)_4 + 2KOAr \xrightarrow{THF} Br_2U(OAr)_2 + 2KBr \quad (1)$$

The dibromide, $Br_2U(OAr)_2$, **4**, is very similar to **1** in its physical and chemical properties. Like **1**, compound **4** can be isolated from solution as a stable THF adduct.[8] Solid isolated from the THF/hexane recrystallization analyzes as the adduct $Br_2U(OAr)_2$·THF. The ^1H NMR of this material is identical to **4**, except for the presence of broad resonances assigned to coordinated THF (observed at 13.0 and 6.5 ppm in C_6D_6). These resonances sharpen upon cooling the sample. Additionally, the aryloxide resonances show little deviation in chemical shift between the THF-free compound **4** and **4**·THF. Upon exposure to dynamic vacuum, the THF-coordinated material readily loses THF to generate the base-free dibromide **4**.

By comparison, the use of UCl_4 in related metathesis reactions is well documented. Lappert and co-workers prepared a variety of substituted aryloxide complexes of the U(IV) by reaction of the tetrachloride with the lithium salts of the aryloxide anion.[9] We have examined a series of metathesis reactions with the potassium salt of 2,6-di-*tert*-butylphenoxide analogous to those carried out with $UI_4(CH_3CN)_4$ in order to examine the product compositions and yields (Scheme 2).

In contrast to the reactions of $UX_4(CH_3CN)_4$ (X = Br, I), addition of 2 equiv of KOAr to a THF solution of UCl_4 does not yield the neutral bis(aryloxide) dichloride complex, but rather the "ate" complex $[K(THF)_4][UCl_3(OAr)_2]$, **5**, isolated as yellow-brown needles in 68% yield. The infrared spectrum of **5** is remarkably similar to the spectrum of compounds **1** and **4**, with the added appearance of weak stretches at 1056, 1016, and 1005 cm^{-1} assigned to coordinated THF ligands.[17] The solid is soluble in THF, benzene, and toluene, and the ^1H NMR in C_6D_6 reveals only one set of aryloxide resonances. The single-crystal X-ray structure determination of **5** has been undertaken in order to determine the structural features associated with "ate" complexation (Figure 1).

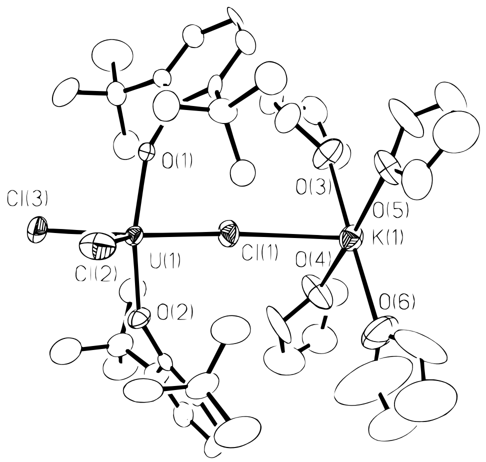


Figure 1. ORTEP drawing of $[K(THF)_4][UCl_3(OAr)_2]$ (**5**) with the atomic numbering scheme. The hydrogen atoms are omitted for clarity.

The uranium atom lies in the center of an approximate trigonal bipyramid of oxygen and chlorine atoms, with the aryloxide groups oriented trans in the axial positions. The O(1)−U−O(2) angle is slightly bent at 167.0(3)°. The overall geometry for **5** is similar to that very briefly reported by Lappert et al. for the structurally characterized compound $[U(OAr'')_2Cl_2(\mu\text{-}Cl)Li(THF)_3]$ (OAr″ = 2,4,6-tri-*tert*-butylphenoxide).[9b] This compound is may be considered also to have a trigonal bypyramidal arrangments of ligands about the uranium center, but with a cis disposition of the aryloxide ligands (the O−U−O angle is reported to be 158°). For comparison, the five-coordinate uranium(IV) compound $I_2U(OAr)_2(THF)$[8] also has a trigonal bypyramidal arrangment of ligands about the uranium center, but with a cis disposition of the aryloxide ligands. The uranium−oxygen (aryloxide) distances in **5** are identical (U−O(1) = 2.122(6) Å, U−O(2) = 2.123(6) Å). These distances are within the range observed for a variety of four- and five-coordinate uranium(IV) aryloxide complexes (2.07−2.19 Å).[6,8,9] The U−O−C(ipso) angles of the aryloxide ligands (U−O(1)−C(1); 154.7(5)°, and U−O(2)−C(15); 153.2(7)°) are similar to that in the tetrakisaryloxide complex $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ (154.0(6)°), and more bent than is commonly found in other actinide aryloxide complexes[6,8,9] except in those cases where "ate" complexation involves an interaction beween the aryloxide oxygen and the cation.[18]

The three chloride atoms lie in the equitorial plane of the pentagonal bipyramid. The U−Cl distances are not equivalent (U−Cl(1) = 2.667(4) Å, U−Cl(2) = 2.595(3) Å, and U−Cl(3) = 2.636(3) Å. The lengthening of the U−Cl(1) and U−Cl(3) distances is attributed to the interaction with the potassium (vide infra). In $UCl_4(THF)_3$, the average U−Cl distance is 2.595(2)

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(17) (a) Deacon, G. B., Tuong, T. D. *Polyhedron* **1988**, *7*, 249. (b) Lewis, J.; Miller, J. R.; Richards, R. L.; Thompson, A. *J. Chem. Soc.* **1965**, 5850.

(18) Barnhart, D. M.; Burns, C. J.; Sauer, N. N.; Watkin, J. G. *Inorg. Chem.* **1995**, *34*, 4079.

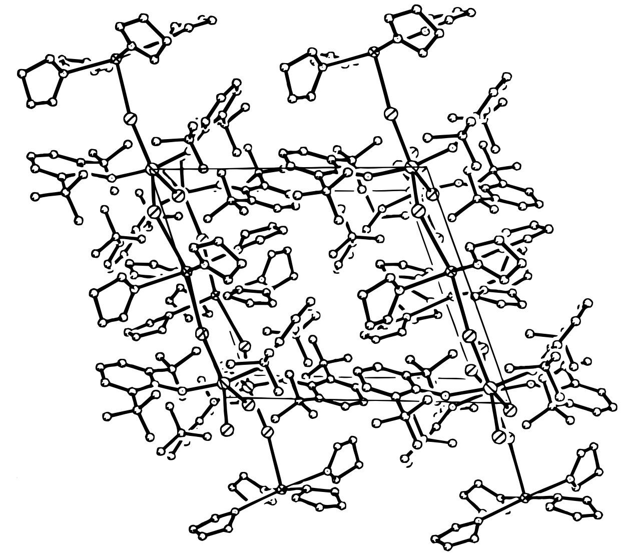

Figure 2. Packing diagram for $[K(THF)_4][UCl_3(OAr)_2]$ (**5**) illustrating the infinite chain produced by the bridging potassium atoms.

Å.[19] The Cl−U−Cl angles in **5** deviate from the ideal 120° expected for the equatorial groups of a trigonal bipyramidal molecule. While angles Cl(1)−U−Cl(2) and Cl(1)−U−Cl(3) are 134.4(1) and 132.6(1)°, respectively, the Cl(2)−U−Cl(3) angle is significantly smaller at 93.0(1)°. This angle is similar to the 98.3(1)° found for the I−U−I angle observed in $I_2U(OAr)_2(THF)$.[8]

While the compound $[U(OAr'')_2Cl_2(\mu\text{-}Cl)Li(THF)_3]$ (OAr″ = 2,4,6-tri-*tert*-butylphenoxide)[9b] exists in isolated ion pairs in the solid state, the packing diagram for **5** shows that the compound forms an infinite chain in the solid state through the interactions between the potassium and the chloride atoms (Figure 2). The potassium atom lies in a distorted octahedral geometry, with axial chloride groups that connect two different uranium centers, forming a repeating section in the chain. The Cl(1)−K−Cl(3a) angle is 153.9(1)°, and the K−Cl(1) distance is 3.174(4) Å. The octahedral coordination sphere about potassium is completed by four THF molecules. The K−O(THF) distances vary from 2.684(9) to 2.709(8) Å, and the O−K−O angles are found to vary from 82.1(2) to 103.3(3)°. Oligomerization via bridging chloride has been observed in the compound $[(C_5Me_5)_2CeCl_2K(THF)]_n$.[20] However, the potassium atom in this compound is five coordinate, with a single THF occupying the coordination sphere (K−O(THF) = 2.70(1) Å). The K−Cl distances for $[(C_5Me_5)_2CeCl_2K(THF)]_n$ vary from 3.077(3) to 3.157(3) Å. Clark and co-workers have recently shown that a number of lanthanide aryloxide compounds (aryloxide = 2,6-diisopropylphenoxide) possess solid-state structures where the potassium atom interacts with the aryl rings or the aryloxide oxygen atoms.[21] This possible interaction is clearly not observed in **5**. The other five-coordinate potassium "ate" complex of interest is the uranium(III) compound $\{[K(THF)_2]_2[U(NHAr')_5]\}\cdot THF$ (Ar′ = 2,6-diisopropylphenyl), where the solid-state structure indicates $\eta^6-\pi$ interactions between the arene ring and the potassium.[22]

Compound **5** reacts with 1 equiv of KOAr in THF to yield the trisaryloxide compound $ClU(OAr)_3$, **6**, in 88% yield. It is again important that the KOAr solution be added slowly to the $[K(THF)_4][UCl_3(OAr)_2]$ solution in order to avoid formation of $U(OAr)_4$, **3**, which is observed to be an impurity in the reaction product.

The tetrakisaryloxide $U(OAr)_4$, **3**, can also be prepared by two routes. The first is the addition of KOAr to $ClU(OAr)_3$, **6**, which yields $U(OAr)_4$ in 76% isolated yield. The alternative route utilizes reaction of UCl_4 with a slight excess KOAr. The isolated yield of the latter route is 91% isolated yield.

Ligand Redistribution Studies. An additional factor to explore in evaluating the use of aryloxide ligands as ancillary ligands in uranium organometallic chemistry is the susceptibility of this ligand environment to engage in redistribution reactions (i.e. halide−aryloxide exchange resulting in the formation of an equilibrium mixture of compounds $U(OAr)_xX_y$). Steric bulk in the ancillary ligand set can be used to inhibit these reactions, however. For instance, the bis(pentamethylcyclopentadienyl)-actinide framework has been employed extensively to stabilize dihalide complexes of uranium and thorium against the ligand redistribution problems which plague the unsubstituted cyclopentadienyl analogues.[10] It is unclear from previous work with uranium whether 2,6-disubstituted aryloxide ligands are sufficiently bulky to inhibit these reactions. The ability of bis(aryloxide) uranium diiodide and dibromide to form base adducts with THF, and for the dichloride to form a five-coordinate "ate" complex demonstrates that this framework is certainly less sterically saturated than $(C_5Me_5)_2UCl_2$. Aryloxide ligand redistribution has been reported to occur in certain reactions; for example, the oxidation of $U(OAr)_3$ with O_2 yielded the uranium(IV) compound $U(OAr)_4$.[8] The isolation and characterization of the bis(aryloxide) compounds **1** and **3**, however, suggests that these compounds are not readily susceptible to ligand exchange.

To gauge the lability of the aryloxide group in these uranium halide−aryloxide compounds, a series of experiments have been conducted to look for possible redistribution. Initial experiments were carried out using mixtures of UCl_4 and $U(OAr)_4$, $UBr_4(CH_3CN)_4$ and $U(OAr)_4$, and $UI_4(CH_3CN)_4$ and $U(OAr)_4$ (eq 2). These experiments were performed in THF-d_8. For the homoleptic uranium(IV) halides UX_4 (X = Cl, Br, I), there is no

$$UX_4 + U(OAr)_4 \rightarrow \quad (X = Cl, Br, I) \quad XU(OAr)_3 + X_2U(OAr)_2 + X_3U(OAr) \qquad (2)$$

evidence of aryloxide scrambling with $U(OAr)_4$ to form mixed products $UX_y(OAr)_{4-y}$ (X = Cl, Br, I; $y = 1-4$),[23] either at room temperature or elevated temperatures (prolonged heating at 60 °C eventually results in decomposition of the samples).

A similar experiment was performed using the mixtures $Br_2U(OAr)_2/U(OAr)_4$ and $I_2U(OAr)_2/U(OAr)_4$ in either C_6D_6 of THF-d_8 (eq 3). There does not appear to be any reaction between

$$X_2U(OAr)_2 + U(OAr)_4 \rightarrow \quad (X = Br, I) \quad XU(OAr)_3 + X_2U(OAr)_2 + X_3U(OAr) \qquad (3)$$

the dihalide complexes and uranium tetrakisaryloxide, although the monohalide species may be formed by other means. At

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[19] Van Der Sluys, W. G.; Berg, J. M.; Barnhart, D.; Sauer, N. N. *Inorg. Chim. Acta* **1993**, *204*, 251.

[20] Evans, W. J.; Olofson, J. M.; Zhang, H.; Atwood, J. L. *Organometallics* **1988**, *7*, 629.

[21] Clark, D. L.; Huffman, J. C.; Watkin, J. G. *Inorg. Chem.* **1992**, *31*, 1554.

[22] Nelson, J. E.; Clark, D. L.; Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1992**, *31*, 1973.

[23] Preliminary crossover experiments between $UI_3(THF)_4$ and $U(OAr)_3$ in THF-d_8 also show that there is no crossover reaction to form compounds of the formula $UI_{3-x}(OAr)_x$.

room temperature, there is no evidence by NMR for the formation of $IU(OAr)_3$ (or $BrU(OAr)_3$) over a 24 h period. However, $IU(OAr)_3$ and $BrU(OAr)_3$ are formed when these experiments are carried out at elevated temperatures due to the thermal instability of the dihalide (eq 4).

$$I_2U(OAr)_2 \xrightarrow{60\ ^\circ C} IU(OAr)_3 \tag{4}$$

The diiodide decomposes most readily; conversion of $Br_2U(OAr)_2$ to $BrU(OAr)_3$ is significantly slower. The presence of $U(OAr)_4$ does not alter the rate of formation of the monohalide products. Other mixed iodide−aryloxide complexes should be formed in the redistribution reaction in eq 4, but they are not observed by ^1H NMR in solution. Prolonged heating at the elevated temperature leads to complete sample decomposition.

In an effort to explore the possibility of halide exchange, an experiment was conducted in which compounds **1** and **4** were allowed to react at room temperature (eq 5). By NMR, there

$$I_2U(OAr)_2 + Br_2U(OAr)_2 \rightarrow IBrU(OAr)_2 \tag{5}$$

is no evidence to support any formation of the mixed halide $IBrU(OAr)_2$. The absence of detectable halide exchange contrasts with the observation that this process occurs readily in UX_4L_2 compounds.[24]

Conclusions

We have examined the utility of uranium(IV) chloride, bromide, and iodide halides in metathesis reactions for the production of mixed halide−aryloxide complexes. The choice of halide precursor plays a role both in the nature and the yield of the isolated product. While $I_2U(OAr)_2$ can be prepared from $UI_4(CH_3CN)_4$, the thermal stability problems of the halide in THF complicate the use of the tetraiodide as an efficient starting material. The use of either $UBr_4(CH_3CN)_4$ and UCl_4 in metathesis reactions leads to the clean formation of mixed halide−aryloxide products, but the product identity can be a function of the starting material. For instance, reaction of $UBr_4(CH_3CN)_4$ with 2 equiv of potassium aryloxide generates the neutral complex $Br_2U(OAr)_2$, while the analogous reaction with UCl_4 yields only the "ate" complex $[K(THF)_4][UCl_3(OAr)_2]$. This distinction may not be significant in subsequent reactivity, however; preliminary experiments suggest that compound **5** serves as a "$Cl_2U(OAr)_2$" synthetic equivalent in both metathesis reactions and in reactions with strongly coordinating Lewis bases.

We have also examined the susceptibility of these complexes to ligand redistribution. Neither aryloxide nor halide exchange is observed. It is conceivable that ligand redistribution in all mixed uranium aryloxide−halide is inhibited to some degree by the steric bulk of the 2,6-di-*tert*-butyl phenoxide ligand. This contention is not supported, however, by the observation that redistribution does not occur even in complexes that are coordinatively unsaturated. In related high-valent uranium aryloxide chemistry, we have seen a similar lack of redistribution chemistry, even though structures have been isolated which demonstrate that bulky aryloxide groups can bridge metal centers.[25] We are currently exploring the role of steric hindrance with smaller aryloxide groups. If in fact there is an electronic origin to the kinetic stability of these species toward redistribution, the aryloxide supporting ligand sets investigated here could be attractive substitutes to carbocyclic ligands in organouranium chemistry.

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Supporting Information Available: Tables listing the complete sets of positional and equivalent isotropic thermal parameters of the non-hydrogen atoms, bond lengths and angles, hydrogen coordinates and isotropic thermal parameters, and anisotropic thermal parameters for compound **5** are available (19 pages). Ordering information is given on any current masthead page.

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[24] Avens, L. R.; Burns, C. J.; McKee, S. D. Unpublished results.

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