Aryloxide anions can form outer sphere complexes with metals as electropositive as uranium[†]

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A uranium complex containing an outer sphere aryloxide anion is formed by the proteolytic cleavage of the methyl group in the monomethyl uranium metallocene, $(C_5Me_5)_2[^iPrNC(Me)N^iPr]UMe$, by 2,6-di-*tert*-butyl-4-methyl phenol.

The coordination chemistry of uranium is of considerable importance due to the use of uranium as a nuclear fuel¹ and the control of its speciation in nuclear waste streams.² Recent studies have shown that the secondary coordination sphere of uranium, as well as other actinides, plays a critical role in overall speciation.³ The coordination chemistry of uranium with oxygen-donor ligands is of particular interest since actinides are oxophilic and oxygen-donor ligands are prevalent in waste streams and in the environment.

Recent studies of uranium metallocenes in sterically crowded coordination environments have generated metallocene amidinate complexes like $(C_5Me_5)_2[^{i}PrNC(Me)N^{i}Pr-\kappa^2N,N']UMe$, 1, that contain a single hydrocarbyl ligand.⁴ Mono-methyl 1 is unusual compared to its dimethyl metallocene precursor, $(C_5Me_5)_2UMe_2$, in that the methyl group in 1 is much less reactive. For example, in contrast to $(C_5Me_5)_2UMe_2$, the U–Me bond in 1 does not react with $HC \equiv CPh$ or $HNPh_2$ or H_2 , even at 80 psi.⁵ In efforts to find reagents that would cleave the methyl group, aryl alcohols were studied and found to form a product that contained an outer sphere aryloxide anion. This was unexpected with a metal as electropositive as uranium.⁶

Complex 1 does not react with 2,6-di-*tert*-butyl-4-methyl phenol, ArOH, in toluene at room temperature, but upon heating to 85 °C for 1 h, the maroon complex $\{(C_5Me_5)_2[^iPrNC(Me)N^iPr]U\}^{1+}\{Me^tBu_2C_6H_2O\cdots HOC_6H_2'Bu_2-Me\}^{1-}$, 2, is formed according to eqn (1). The presence of methane was identified by ¹H NMR spectroscopy in a reaction in a sealed NMR tube. The reaction of 1 with one equiv. of the aryl alcohol gave lower yields of 2.‡

The structure of 2 was determined by X-ray diffraction and the data revealed a metallocene amidinate uranium cation complex, Fig. 1, with an outer sphere aryloxide anion hydrogen bonded to an aryl alcohol as shown in Fig. 2. To our knowledge, this is the first example of an outer sphere aryloxide metal complex. Aryloxide anions that do not coordinate to a metal *via* the oxygen-donor atom have been



Fig. 1 Thermal ellipsoid plot of the cation $\{(C_5Me_5)_2[^{i}PrNC(Me)-N^{i}Pr-\kappa^2N,N']U\}^{1+}$, in **2**, shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. U(1)–Cnt(C_5Me_5) = 2.433, 2.455 Å, U(1)–N(1) = 2.331(1) Å, U(1)–N(2) = 2.344(1) Å, U(1)–C(21) = 2.749(2) Å, Cnt(C_5Me_5)–U(1)–Cnt(C_5Me_5) = 137.7°, Cnt(C_5Me_5)–U(1)–N(1) = 105.9°, 109.0°, Cnt(C_5Me_5)–U(1)–N(2) = 109.6°, 108.8°, N(1)–U(1)–N(2) = 57.86(7)°.



Fig. 2 Thermal ellipsoid plot of the hydrogen bonding between the outer sphere aryloxide and aryl alcohol in **2** is shown at the 50% probability level. O(1)–C(29) = 1.370(3) Å, O(2)–C(44) = 1.302(3) Å, O(1)–H(1) = 0.762 Å, O(2)···H(1) = 1.810 Å.

crystallographically characterized in the past. However, these involve either a transition metal that coordinates the ligand *via* the phenyl ring, *e.g.* $(C_8H_{12})Rh(\eta^6-ArO)(HOAr)^7$ or



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complexes that contain no metal, *e.g.* $[(Ph_3PMe)^{1+}(OC_6H_3Ph_2-2,6)^{1-}]_2$,⁸ $[(Ph_3PEt)^{1+}(OAr)^{1-}]_{\infty}$,⁸ and the $[C_3(NMes)_2H]^{1+}$ imidazolium salt of $[(OAr)]^{1-}$.⁹ Hydrogen bonding with aryloxide ligands is observed in the latter three cases, but only in the rhodium complex does this involve interaction with an aryl alcohol as in **2**.

The aryloxide anion was characterized in several ways. The hydrogen of the alcohol hydrogen bonded to the aryloxide anion was located and refined in the crystallographic analysis. Aryloxide resonances at 7.05, 2.24, and 1.38 ppm in the ¹H NMR spectrum are nearly identical to those of the protonated ligand, but no resonance for the alcohol proton is observed. The fact that these resonances are not shifted by the paramagnetic uranium center is consistent with the solid state structure that shows the aryloxide as an outer sphere ligand.

The infrared spectrum of **2** is also consistent with the presence of an aryl alcohol–aryloxide unit. A characteristic hydrogen bonded OH absorption is seen at 3650 cm^{-1} . This is shifted from the normal OH stretching frequency of 3630 cm^{-1} in the free aryl alcohol.

The 1.370(3) Å C(29)–O(1) bond distance in the ${ArO \cdots HOAr}^{1-}$ anion in 2 is indicative of a C-O single bond¹⁰ and is close to the analogs of 1.383(3) Å in ArOH,¹¹ 1.381(3) Å in 2,6-di-tert-butyl-4-phenyl phenol,¹² and 1.387(1) Å in 2,6-di-tert-butyl phenol.¹³ The C(29)–O(1) bond in 2 also compares well to the 1.382(6) Å C-O bond distance for the aryl alcohol that is hydrogen bonded to an aryloxide in $(C_8H_{12})Rh(\eta^6-ArO)(HOAr)^7$ and the 1.379(4) Å C–O distance in the 2,6-di-*tert*-butyl phenol in $MoO_2(OC_6H_3-2,6^{-t}Bu_2)_2$. HO-2,6-^tBu₂C₆H₃.¹⁴ The 1.302(3) Å C(44)–O(2) length in 2 is shorter than C(29)-O(1) and the 1.345(6) Å length in the lithiated salt [Li(OAr)(OEt₂)]₂,¹⁵ but it is very close to the 1.306(2) Å length in $[C_3(NMes)_2H]^{1+}[(OAr)]^{1-.9}$ The hydrogen bond length of 1.810(3) Å in 2 is shorter than the 1.935(5) and 1.998(3) Å distances in $[(Ph_3PMe)^{1+}(OC_6H_3Ph_2-2,6)^{1-}]_2$ and $[(Ph_3PEt)^{1+}(OAr)^{1-}]_{\infty}$, respectively,⁸ which involve multiple hydrogen bonds to the oxygen atoms.

The structure of the {(C_5Me_5)₂[^{*i*}PrNC(Me)N^{*i*}Pr- $\kappa^2 N, N'$]U}¹⁺ cation is similar to that of **1** except that the (C_5Me_5 ring centroid)–U–(C_5Me_5 ring centroid) angle has opened up to 137.7° in **2** compared to 130.9° in **1**. A similar situation is found with [(C_5Me_5)₂ThMe][B(C_6F_5)₄]¹⁶ and (C_5Me_5)₂ThMe₂¹⁷ which have 140.1° and 133.9° angles, respectively. Since the cation in **2** has one less ligand than **1**, shorter U-ligand distances are expected. Indeed, the 2.433 and 2.455 Å U–(C_5Me_5 ring centroid) bond distances in **2** are shorter than the 2.527 and 2.538 Å values in **1**. Similarly, the U–N bond distances of 2.331(1) and 2.344(1) Å in **2** are shorter than the 2.461(2) and 2.453(2) Å lengths in **1**. However, the shortening is more than the 0.05 Å difference in the ionic radii of 8- and 9-coordinate U⁴⁺.¹⁸

The isolation of a structure for **2** with an outer sphere aryloxide anion can be explained using steric arguments. The $\{(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']\}^{3-}$ metallocene amidinate ligand set apparently does not allow another ligand as large as $(OAr)^{1-}$ to coordinate to the U⁴⁺ center. This is consistent with the limited reactivity of the methyl group in **1**: although a group as small as methyl can coordinate to U⁴⁺ along with two $(C_5Me_5)^{1-}$ ligands and an amidinate, it is sterically

protected. Hence, when there is sufficient steric bulk around uranium from other ligands, it is possible to have anionic oxygen-donor atom ligands that exist as outer sphere ions.

This steric argument is supported by the reaction of **1** with a smaller aryl alcohol. In contrast to eqn (1), phenol reacts immediately at room temperature with **1** to form an orange solution. The ¹H NMR spectrum and the unit cell of orange crystals grown from this solution were identical to that of the previously reported (C_5Me_5)₂U(OPh)₂, **3**, eqn (2).¹⁸ Whether this reaction is done with one equiv. of phenol or at -35 °C, only **3** was observed. Resonances for methane and the protonated amidinate ligand were observed by ¹H NMR spectroscopy.



In conclusion, the protonation of the methyl group in **1** with a large aryl alcohol leads to the formation of an outer sphere aryloxide that is hydrogen bonded to its protonated counterpart. With appropriate steric manipulation, in this case using the $\{(C_5Me_5)_2['PrNC(Me)N'Pr-\kappa^2N,N']\}^{3-}$ ligand set, outer sphere aryloxide complexes will result even in the presence of large, highly charged, electropositive metal ions like U⁴⁺.

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Notes and references

‡ Synthesis of2. In a glovebox, 2,6-di-tert-butyl-4-methyl phenol (150 mg, 0.681 mmol) was added to a stirred solution of 1 (223 mg, 0.335 mmol) in toluene (8 mL). When the solution was heated to 85 °C, the color turned from yellow-brown to red. After 1 h, the solvent was removed to generate 2 as a maroon powder (175 mg, 60%). Crystals suitable for X-ray crystallography were grown from a saturated solution of pentane–toluene at -35 °C. ¹H NMR (C₆D₆, 298 K): δ 7.05 (s, 2H, C₆H₂), 4.14 (s, 6H, CHMe₂), 2.24 (s, 3H, Me), 1.38 (s, 18H, CMe₃), -1.65 (s, 30H, C₅Me₅), -8.14 (s, 6H, CHMe₂). ¹³C NMR (C₆D₆, 298 K): δ 155.3 (C₅H₂), 136.9 (C₅H₂), 130.8 (C₅H₂), 126.3 (C₅H₂), 37.2 (C₅H₂), 31.0 (^{*i*}Bu), 25.8 (Me). IR (KBr): 3650m, 3279w, 2965s, 2903s, 2858s, 2722m, 1637m, 1556m, 1440s, 1414s, 1378s, 1311s, 1194s, 1118m, 1017m, 805m cm⁻¹. Anal. calcd for C58H94N2O2U: C, 63.95; H, 8.70; N, 2.57%. Found: C, 64.14; H, 8.48; N, 2.39%. When the reaction was done in a sealed J-Young tube, the presence of methane was observed in the ¹H NMR spectrum (δ 0.14 ppm). Crystallographic data for 2: C₅₈H₉₄N₂O₂U·2.5C₇H₈, M = 1319.72, monoclinic, space group $P2_1/n$, a = 13.8613(5) Å, b =21.4698(7) Å, c = 23.4715(8) Å, $\beta = 101.00^{\circ}$, V = 6856.7(4) Å³, Z = 4, T = 103(2) K, $\mu = 2.412$ mm⁻¹, 90.785 reflections measured on a Bruker CCD diffractometer, 19 175 unique ($R_{int} = 0.0303$) which were used in all calculations. The final R_1 was 0.0280 $(I > 2.0\sigma(I))$ and wR_2 (all data, 0.72 Å) was 0.0687. The APEX2²⁰ program package was used to determine the unit-cell parameters and for data collection (20 seconds per frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT²¹ and SADABS²² to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL²³ program. The diffraction symmetry was 2/mand the systematic absences were consistent with the orthorhombic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Synthesis of3. In a glovebox,

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