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Uranium(III) Complexes with Bulky Aryloxide Ligands Featuring Metal−Arene Interactions and Their Reactivity Toward Nitrous Oxide

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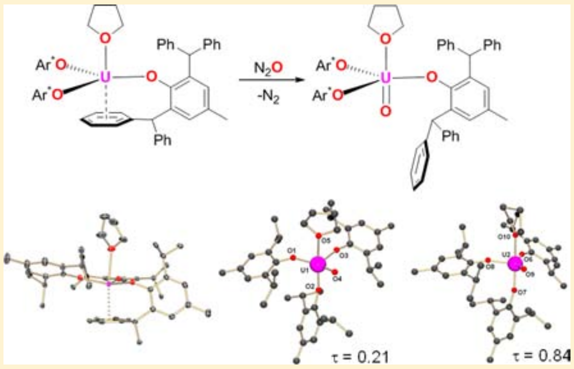
Supporting Information

ABSTRACT: We report the synthesis and use of an easy-to-prepare, bulky, and robust aryloxide ligand starting from inexpensive precursor materials. Based on this aryloxide ligand, two reactive, coordinatively unsaturated U(III) complexes were prepared that are masked by a metal−arene interaction via δ-backbonding. Depending on solvent and uranium starting material, both a tetrahydrofuran (THF)-bound and Lewis-base-free U(III) precursor can easily be prepared on the multigram scale. The reaction of these trivalent uranium species with nitrous oxide, N_2O, was studied and an X-ray diffraction (XRD) study on single crystals of the product revealed the formation of a five-coordinate U(V) oxo complex with two different molecular geometries, namely, square pyramidal and trigonal bipyramidal.

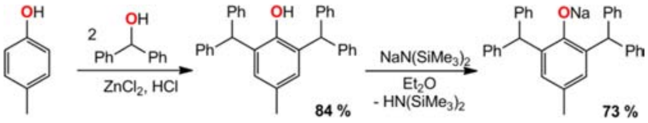


INTRODUCTION

The use of bulky aryloxide and alkoxide ligands for the stabilization of unsaturated homoleptic metal complexes are widespread in coordination chemistry.[2−7] Rothwell et al., for example, harnessed the bulky nature of aryloxide ligands coupled to intramolecular metal−arene interactions to synthesize reactive species, such as the mononuclear W(II) species, $[W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OAr)(PMe_2Ph)]$ (OAr = 2,3,5,6-tetraphenylphenoxide), which can undergo up to four-electron redox chemistry at a single metal center.[8,9] Although aryloxide ligands, such as HO-2,6-^{i}Pr$_2$-C$_6$H$_3$ have been widely used for uranium chemistry, likely because of their commercial availability, the small size of these ligands lead to dimerization via U−arene interactions.[10−15] Similarly, sterically demanding siloxide ligands such as HOSi^{t}Bu$_3$ have been employed for small molecule activation.[16] Research in our laboratory has focused on sterically encumbering tacn-,[17] N-,[18] and mesityl-anchored[19] aryloxide chelating ligands; these ligands provide suitable protection around the U(III) centers; however, steric flexibility at the primary coordination sphere is restricted because of the tethered nature of tripodal ligands. Therefore, we sought a supporting ligand with additional flexibility but without compromising the steric hindrance, a requirement needed to protect a large ion such as U(III).

Herein, we describe the facile multigram synthesis of a novel monoanionic aryloxide ligand, HOAr* (with Ar* = 2,6-Ph$_2$-C$_6$H$_4$-Me, 2,6-bis(diphenylmethyl)-4-methylphenyl) (Scheme 1), that provides steric protection, by forming the corresponding $[(Ar^*O)_3U(THF)]$ (**1**) and Lewis-base-free $[(Ar^*O)_3U]$ (**2**) complexes via convenient salt metathesis or alcoholysis reactions, respectively (Scheme 2). Both complexes **1** and **2** (Figure 1) feature a metal−(η^6-arene) interaction, which is fundamentally interesting since d and f valence orbitals are capable of engaging in covalent interactions, and have been demonstrated to influence the electronic structure of the overall system.[19−24] We also demonstrate the reactive nature of these masked U(III) systems by the activation of nitrous oxide at ambient temperature and pressure to produce a terminal U(V)-oxo.

Scheme 1. Synthesis of the Ligands HOAr* and NaOAr*



RESULTS AND DISCUSSION

The synthesis of the free phenol HOAr* (with Ar* = 2,6-Ph$_2$-C$_6$H$_4$-Me, 2,6-bis(diphenylmethyl)-4-methylphenyl) (Scheme

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Scheme 2. Synthesis of U(III) Complexes 1 and 2

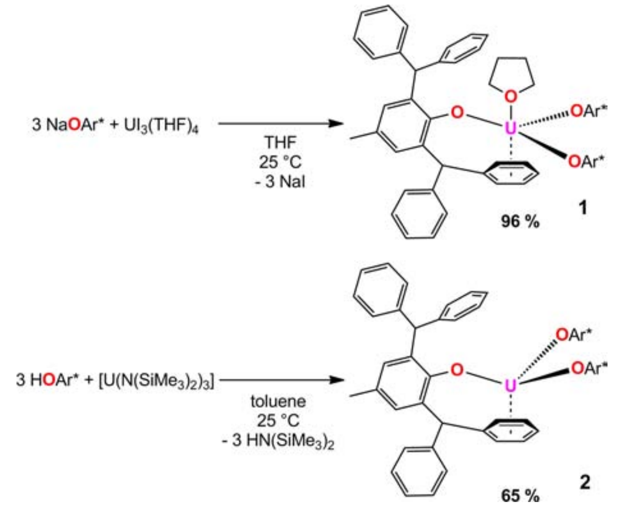


Table 1. Selected Bond Distances for 1 and 2 in Å

structural parameter	1	2
$U{-}O_{avg.}$	2.221(2)	2.158(2)
$C{-}O_{avg.}$	1.342(3)	1.357(3)
$U{-}C_{arene}$	2.964(3)	2.853(3)
$U{-}Ar_{centroid}$	2.614	2.484
$U{-}O_{THF}$	2.554 (2)	
$U_{out\text{-}of\text{-}plane\ shift}$	0.339(1)	0.987(1)

1) involves an adopted protocol from the aniline analogue recently reported by Markó et al.[25] This protocol allows for rapid and solvent-free conditions that afford the aryl alcohol in multigram quantities with high yield (85%) and of high purity. In addition, such protocol is highly modular and therefore permits various functional groups to be installed in the *p*-aryl position of the phenol. Formation of the corresponding sodium salt, NaOAr*, was readily accomplished by treatment of the phenol with $NaN(SiMe_3)_2$ in diethyl ether, leading to a yellow suspension, which can be filtered to afford pure product in ~75% isolated yield (Scheme 1). Straightforward salt metathesis reaction of NaOAr* (3 equiv) and $UI_3(THF)_4$ in tetrahydrofuran (THF) provided dark-brown solids of $[(Ar^*O)_3U(THF)]$ (**1**) in ~95% isolated yield (Scheme 2). Single-crystals for an X-ray diffraction (XRD) study were obtained from a saturated benzene solution at room temperature. The solid state structure revealed a U(III) center confined in a trigonal bipyramidal geometry, in which the axial positions feature a U1−(η^6-arene) interaction with a distance of 2.614 Å between the U(III) center and the centroid and an average $U{-}C_{arene}$ distance of 2.964(3) Å, as well as one molecule THF with U1−O4 = 2.554(2) Å that is weakly coordinated to the U(III) center (Table 1). The coordinated arene functionality in **1** is virtually unactivated based on the average C−C bond distance of 1.396(3) Å compared to longer C−C bond distances of 1.438(13) Å observed in $[\{Ar[R]\text{-}N)_2)U\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_7H_8)]$ (Ar = 3,5-C_6H_3-Me_2).[26] The equatorial sites are occupied by three aryloxide ligands with an average U1−aryloxide bond distance of 2.221(2) Å. The U1−O−C(ipso) angles are different for all three aryloxide ligands. While U1−O2−C(ipso) and U1−O3−C(ipso) are slightly comparable at 171.4(2)° and 163.0(2)°, respectively, U1−O1−C(ipso) is considerably more bent at 142.2(2)° with respect to the latter angles. This significant bending of the ligand is required for the phenyl group to situate itself in proper proximity and orientation to participate in U−arene δ-backbonding. Aside from the coordinated THF, complex **1** closely resembles the mononuclear, mesityl-anchored tripodal U(III) complex $[((^{t\text{-}Bu}ArO)_3mes)U]$;[1] therefore, prompting us to pursue the isolation of a potentially more reactive precursor, namely, the Lewis-base free analogue of **1**. Accordingly, coordinating solvents were strictly avoided throughout the reaction, and treatment of $[(Me_3Si)_2N)_3U]$ with 3 equiv of HOAr* in benzene produced analytically pure, dark brown solids in 65% isolated yield (Scheme 2).[27] An XRD study on single crystals obtained from a saturated benzene solution at room temperature clearly shows the absence of a coordinated THF ligand, while the U−(η^6-arene) feature observed in **1** is retained. To our surprise, other phenyl groups did not participate in metal−arene interactions. The structure of $[(Ar^*O)_3U]$ (**2**) can be described as adopting a distorted tetrahedral geometry with $U1{-}O_{avg}$ = 2.158(2) Å and an average U1−(η^6-arene) bond distance of 2.853(3) Å, which is slightly longer compared to **1**, although the $U{-}Ar_{centroid}$ distance is shorter in **2** (2.484 Å) compared to **1** (2.614 Å). The solid state structures of both **1** and **2** exhibit flanking aryl groups above and below the O1−O2−O3 plane; and thus, in **1** and **2** one side of the U1 center is blocked via the U1−(η^6-arene) interaction, while **1** additionally shows a bound THF *trans* to the U−arene interaction. Complex **2**, however,

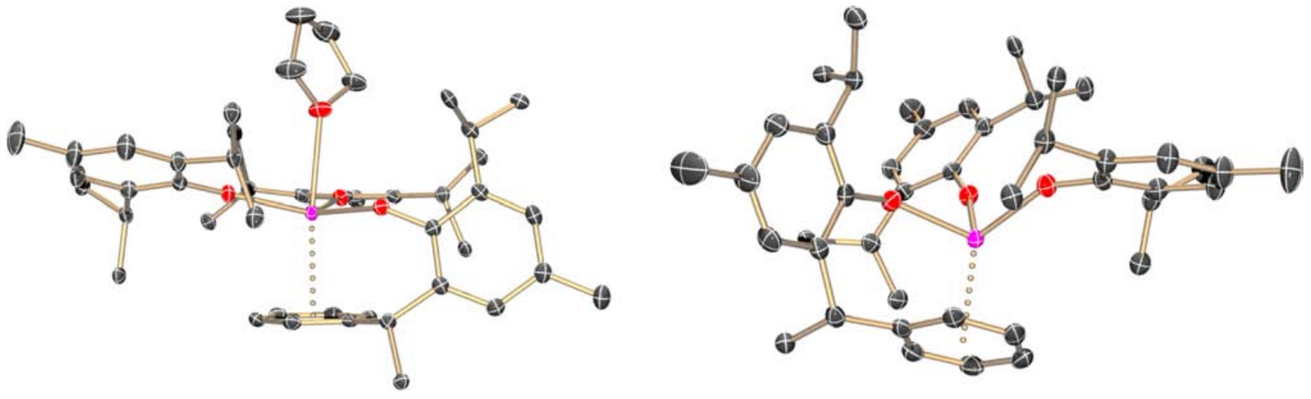


Figure 1. Molecular structures of **1** (left) and **2** (right) are shown with thermal ellipsoids at 50% probability level. Hydrogen atoms, some phenyl groups not bound to uranium, and co-crystallized solvent molecules have been omitted for clarity.

possesses an open coordination site *trans* to the U—arene moiety that is readily available for substrate binding and activation chemistry, while this coordination site is taken by THF in **1**.

Despite the coordinated THF ligand in **1**, characterization of **1** and **2** by ^{1}H NMR and UV/vis spectroscopy indicate that these complexes have similar dynamic behavior in solution. For instance, ^{1}H NMR (25 °C, C_6D_6) spectroscopy for both **1** and **2** display five resonances between 4–12 ppm. ^{1}H NMR spectra of **1** show no indication of free THF, which would result in sharp resonances, and resonances for the coordinated THF ligand in **1** cannot be observed; it is likely that the THF signals are paramagnetically shifted and broadened beyond detection. In this context, it is noteworthy to mention that there is no sign of THF loss in **1** even under dynamic vacuum (as confirmed by elemental analysis). Therefore rapid exchange of the bound THF in benzene solution is quite unlikely. UV/vis spectroscopy further supports the closely related nature of trivalent **1** and **2** and shows several Laporte-allowed metal-centered $5f^3$ to $5f^26d^1$ transitions for both complexes in the same visible light region (492 nm, ε = 1040 (**1**)/ 1400 (**2**); 671 nm, ε = 600 (**1**)/ 780(**2**); 798 nm, ε = 670 (**1**)/ 900 (**2**)) (Figure 2). While the UV/vis spectra of our tacn-anchored and N-anchored U(III) complexes show few but very intense absorptions at ~500 nm,[28,29] the UV/vis spectra of **1** and **2** show a striking similarity to the spectrum of [((${}^{t\text{-Bu}}$ArO)$_3$mes)U], for which the metal—arene interaction was established by DFT calculations.[1] All three compounds show medium intensity absorption bands in the range from 450 to 900 nm that seem to be characteristic for U(III) complexes experiencing a δ-backbonding interaction.

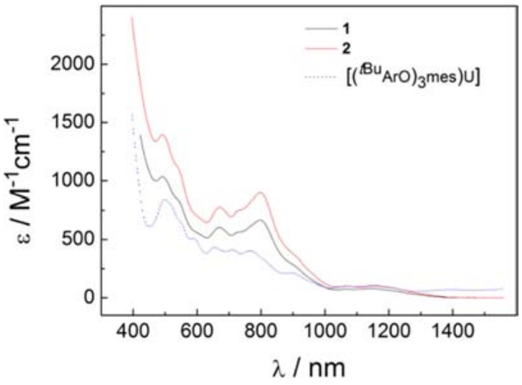


Figure 2. UV/vis spectrum of complexes **1**, **2**, and, for comparison, [((${}^{t\text{-Bu}}$ArO)$_3$mes)U][1] recorded in toluene.

The binding energy of the THF molecule in **1** is estimated to be 63 kJ/mol with the dispersion-corrected density-functional method used. A major part of this binding energy indeed appears to derive from dispersion interactions because the interaction energy is diminished to only 6 kJ/mol without dispersion correction. Hence, the calculations suggest only a very weak electronic interaction with the uranium center.

In both **1** and **2**, one of the peripheral phenyl rings is bound in a η^6 fashion to the U(III) center. A brief analysis of the electronic structure reveals a δ-type interaction that is mediated by two singly occupied molecular orbitals shown in Figure 3 for complex **1**. The interaction can be described in terms of the U f atomic orbitals with antibonding π orbitals of the phenyl ring (two nodal planes). A similar bonding interaction has been described in [((${}^{t\text{-Bu}}$ArO)$_3$mes)U].[1] We note that we have not been able to find a situation with two η^6 phenyl-U interactions (i.e., a sandwich-type coordination of U) in the calculations.

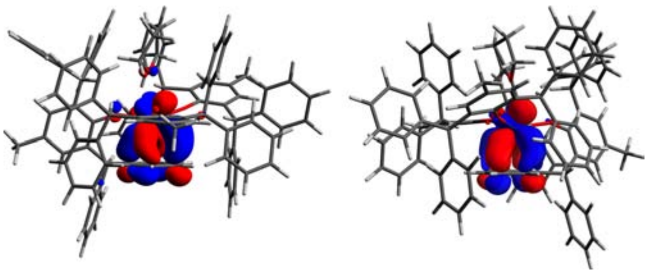
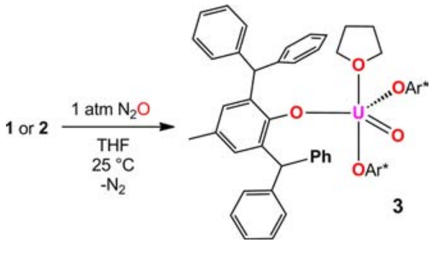


Figure 3. Graphical representation of singly occupied orbitals HOMO-1 (left) and HOMO-2 (right) in **1** according to the density functional calculations.

It is interesting to further quantify the interactions of the coordinated phenyl and the THF with U(III) in compounds like **1** and **2**. To this end, we have calculated the corresponding binding energies in the model system [(MeO)$_3$U(η^6-C_6H_6)(THF)], where the coordinating phenyl ring has been replaced by benzene and the aryloxide ligands (Ar*O$^-$) in **1** and **2** have been truncated to methoxide (MeO$^-$). In this simplified system, the benzene and THF dissociation energies are calculated to be 109 and 41 kJ/mol, respectively. Hence, the benzene ligand is bound more strongly to the U center than the THF ligand. The *trans* effect brings about a reduction in binding energies by approximately 30 kJ/mol for both ligands and as expected, the binding energies of the ligands are higher in the absence of another ligand in the *trans* position. This can be gathered from the calculated binding energies of benzene or THF to bare U(OMe)$_3$, which amounts to 139 kJ/mol (benzene) and 70 kJ/mol (THF), respectively. Further details on the calculations on **1** and **2** and the model systems can be found in the Supporting Information.

The reactivity of complexes **1** and **2** was probed in an oxygen-atom transfer reaction. Treating either **1** or **2** with an atmosphere of N_2O in THF solution yields, after removal of volatiles, red-orange solids that could be crystallized by vapor diffusion of hexane into a concentrated benzene solution and identified as U(V) terminal oxo complex [(Ar*O)$_3$(THF)U(O)] (**3**) (Scheme 3). It should be noted that terminal mono-oxo complexes of uranium(V) are quite a rare class of compounds that can generally be obtained via two-electron oxidation of uranium(III) with an oxygen atom transfer reagent, such as Me$_3$NO,[30,31] TEMPO,[31] py-NO,[32] O_2,[33,34] or via multiple bond metathesis of uranium(V) imido complexes with CO_2 with concomitant formation of isocyanate.[35] Nitrous oxide, N_2O, has been used as an oxidant for U(III) before; however, with one exception,[36] only bridging μ-oxo complexes could be obtained.[28,37,38] In fact, because of its stability and

Scheme 3. Synthesis of U(V)-oxo 3 from Precursor 1 or 2



poor ligand properties,[39−41] reactions with N_2O rarely lead to terminal metal oxo species; and thus, there are only very few examples reported in the literature.[42−50]

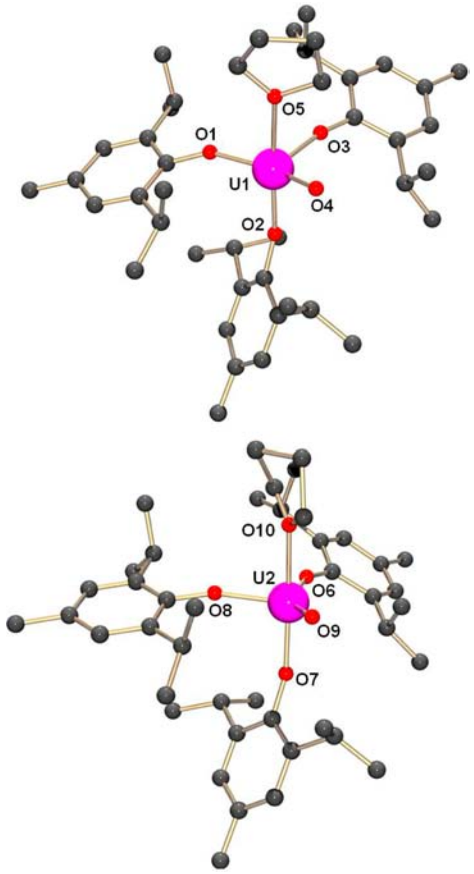


Figure 4. Molecular structures of **3A** (top) and **3B** (bottom) as balls and sticks representation (see Supporting Information for different views and ORTEP representations). Hydrogen atoms and flanking phenyl groups were omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 3A and 3B

structural parameter	3A	3B
$U_{1,2}{=}O_{4,9}$	1.842(8)	1.818(12)
$U_{1,2}{-}O_{1,8}$	2.103(9)	2.141(9)
$U_{1,2}{-}O_{3,6}$	2.127(8)	2.072(8)
$U_{1,2}{-}O_{2,7}$	2.129(8)	2.130(8)
$U_{1,2}{-}O_{THF}$	2.434(8)	2.398(10)
$O_{4,9}{-}U_{1,2}{-}O_{1,8}$	160.6(4)	119.6(5)
$O_{4,9}{-}U_{1,2}{-}O_{3,6}$	98.5(4)	143.0(5)
$O_{1,8}{-}U_{1,2}{-}O_{3,6}$	99.7(3)	95.5(3)
$O{-}U_1{-}O_{avg.,square\text{-}plane}$	89.8	

An XRD study on red prism-shaped single crystals revealed two crystallographically independent but chemically equivalent molecules of the complex in the asymmetric unit ($Z = 2$). Interestingly, the solid-state structures of compounds **3A** and **3B** show remarkable differences, with regards not only to their bond lengths and angles but also to their general coordination geometries as well (Figure 4). Compound **3A** adopts a distorted square-pyramidal geometry with two aryloxide ligands, the coordinated THF, and the terminal oxo ligand in the square plane and another axial aryloxide ligand. The U1−O4 bond distance of 1.842(8) Å (Table 2) compares well with those found for U(V) oxo complexes reported in the literature (1.842−1.859 Å).[31,32,35] Noteworthy, **3A** has two almost identical $U{-}O_{ArO}$ bond lengths (U1−O2, 2.129(8) Å and U1−O3, 2.127(8) Å); however, the bond distance for U1−O1 of 2.103(9) Å, the one bound *trans* to the mono-oxo ligand, is slightly shorter compared to the other two bond lengths. This observation clearly can be attributed to the inverse trans influence (ITI).[51,52] The average bond angle for the O−U−O angles of the square plane is 89.8°, which is well in agreement with a uranium center coordinated in a square-pyramidal fashion. In contrast, **3B** features a distorted trigonal-bipyramidal coordination geometry with two aryloxide ligands and the mono-oxo moiety in the trigonal plane and the coordinated THF as well as another aryloxide ligand in the axial positions. The U2−O9 bond distance of 1.818(12) Å is short compared to previous reports but is still well within the range of a U(V) oxo bond distance (vide supra). Interestingly, the bond distance in **3B** is even shorter than the respective bond in **3A**, which has an aryloxide ligand trans to the mono-oxo group. In addition to these geometric features, **3B** has three different $U{-}O_{ArO}$ bond lengths (U2−O6, 2.072(8); U2−O7, 2.130(8), and U2−O8, 2.141(9) Å). Both observations may be attributed to the steric pressure imposed by the flanking diphenyl groups of the aryloxide ligand, which should be higher in a trigonal-bipyramidal coordination geometry. The Addison parameter (τ) is an indicator of the degree of distortion from trigonal-bipyramidal and square-pyramidal geometry[53] and is 0.21 for **3A** and 0.84 for **3B**, which is in good agreement with the description of **3A** as square-pyramidal and **3B** as trigonal-bipyramidal. ^1H NMR spectroscopic data shows five strongly broadened signals between 0−9 ppm, indicating that both complexes **3A** and **3B** can interchange in solution.

Variable temperature (2−300 K) direct current (dc) magnetic susceptibility measurements were performed for **1**, **2**, and **3** to probe the uranium ion's formal oxidation state and electronic structures (Figure 5). Superconducting Quantum Interference Device (SQUID) magnetization data for **1** and **2** are similar to each other, and both complexes exhibit highly temperature dependent magnetic moments, μ_{eff}, of 2.37 (**1**) and 2.52 μ_B (**2**) at 300 K, which gradually decrease with decreasing temperature to μ_{eff} = 1.21 (**1**) and 1.27 μ_B (**2**) at 2 K. Complex **3** has a magnetic moment of 1.96 μ_B at 300 K that is reduced to

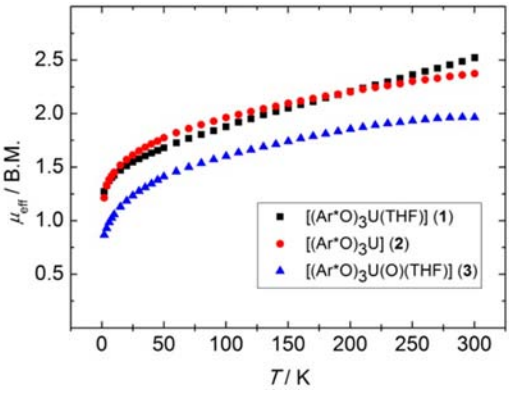


Figure 5. Temperature-dependent SQUID magnetization data of compounds **1**, **2** (top), and **3** (bottom). Data were corrected for underlying diamagnetism. Reproducibility was checked by three independently synthesized and measured samples for each compound (see Supporting Information).

μ_{eff} = 0.86 at 2 K, which is typically observed for uranium(V) complexes.[35,54,55]

■ CONCLUSION

In summary, we report the convenient and multigram synthesis of a new, sterically encumbering aryloxide ligand and present its ligand properties in coordination complexes of uranium. Single-crystal XRD studies on the homoleptic U(III) tris(aryloxide) and its THF-coordinated derivative revealed U−arene interaction via δ-backbonding in both complexes. In addition, the coordinated ligand features diphenyl groups that act as a "picket fence" above and below the plane of the U(III) center. In a preliminary reactivity study it is shown that both U(III) complexes, the THF-coordinated and the coordinatively unsaturated species, react with N_2O to form a U(V) complex with a terminal oxo ligand. The XRD study on single crystals of this five-coordinate oxo complex revealed two independent molecules per unit cell, which exhibit distinct molecular geometries, namely, a square pyramidal and trigonal bipyramidal, but that are interchanging in solution at room temperature, which is indicated by ^{1}H NMR spectroscopy. This observation emphasizes the ligand's flexibility to accommodate different geometries while, at the same time, the substantial steric bulk protects the reactive species from bimolecular decomposition reactions and can mask a low-valent U(III) ion. Accordingly, we are actively exploring the potential of this system for further small molecule activation chemistry.

■ EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. The glovebox is equipped with a −35 °C freezer. Solvents were purified using a two-column solid-state purification system (Glass Contour System, Irvine, CA), transferred to the glovebox without exposure to air, and stored over molecular sieves and sodium (where appropriate). NMR solvents were obtained packaged under argon and stored over activated molecular sieves and sodium (where appropriate) prior to use. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. All other chemicals were used as received from Sigma-Aldrich unless otherwise stated. Precursor complexes [(UI$_3$(dioxane)$_{1.5}$] and [U(N(SiMe$_3$)$_2$)$_3$] were prepared as described by Kiplinger et al.[56]

^{1}H NMR spectra were recorded on a JEOL ECX 400 or 270 instrument at a probe temperature of 23 °C. ^{1}H and ^{13}C NMR spectra are reported with reference to solvent resonances of C_6D_6 at 7.16 ppm and 128.0 ppm, respectively. Electronic absorption spectra were recorded from 400 to 1800 nm (Shimadzu (UV-3101PC)) in the indicated solvent. Results from elemental analysis were obtained from the Analytical Laboratories at the Friedrich-Alexander-University Erlangen-Nürnberg (Erlangen, Germany) on Euro EA 3000. XRD data were collected on a Bruker Smart APEX 2 diffractometer under a stream of N_2 (g) at 100 K for **1** and **3** and on a Bruker-Nonius Kappa CCD system under a stream of N_2 (g) at 150 K for **2**. Magnetism data of crystalline powdered samples (20−30 mg) were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe (2−300 K for **1**, **2**, and **3**). Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment ($\chi_{\mathrm{dia}} = -988.77 \times 10^6$ cm^3 mol^{-1} (**1**), -928.33×10^6 cm^3 mol^{-1} (**2**), -964.97×10^6 cm^3 mol^{-1} (**3**)) by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw).[57]

Synthesis of HOAr [Ar* = 2,6-Ph$_2$-C$_6$H$_4$-4-Me].* In a 250 mL round-bottom flask was charged *p*-cresol (7.92 g, 73.2 mmol), diphenylmethanol (27.0 g, 146.5 mmol), and a large stirring bar. The reaction flask was heated to 140 °C to produce a melt followed by the addition of a solution of HCl/ZnCl$_2$ (2.22 mL, 73.2 mmol HCl; 37 mmol of ZnCl$_2$ (5.20 g)) dropwise via a glass pipet. After stirring for 0.5 h, the reaction mixture solidified, and the reaction was allowed to proceed for an additional 2 h to ensure completion. The reaction flask was cooled to room temperature, and the crude solids extracted into CH$_2$Cl$_2$ and washed once with water and twice with brine. All volatiles were removed by rotary evaporator, and cold MeOH (50 mL) was added to precipitate clean white solids of the product. Yield = 84% (27 g, 61.2 mmol). ^{1}H NMR (25 °C, 270 MHz, CDCl$_3$): δ = 7.32−7.26 (m, 12H, Ar-*H*), 7.26−7.09 (m, 8H, Ar-*H*), 6.50 (s, 2H, Ar-*H*), 5.67 (s, 2H, C*H*(Ph)$_2$), 4.43 (s, 1H, O*H*), 2.07 (s, 3H, Me). ^{13}C NMR (25 °C, 67.8 MHz, CDCl$_3$): δ 149.05 (Ar), 142.79 (Ar), 130.77 (Ar), 129.33 (Ar), 128.46 (Ar), 126.57 (Ar), 51.05 (Ph$_2$CH), 20.97 (Me). Anal. Calcd for $C_{33}H_{28}O$: C, 89.96; H, 6.41. Found: C, 89.83; H, 6.15.

Synthesis of NaOAr.* To a white suspension of HOAr* (5.00 g, 11.3 mmol) in diethyl ether (200 mL) at room temperature was added a solid portion of NaN(SiMe$_3$)$_2$ (2.18 g, 11.9 mmol) over 15 min to produce a homogeneous yellow solution. The mixture was allowed to proceed for 12 h to give a faint yellow suspension. Subsequently, the faint yellow solids were collected by vacuum filtration, and any residual solvent was removed in vacuo. Yield = 73%. ^{1}H NMR (25 °C, 270 MHz, C$_6$D$_6$): δ = 7.17−6.80 (m, 20H, Ar-*H*), 6.67 (s, 2H, Ar-*H*), 5.47 (s, 2H, C*H*(Ph)$_2$), 2.06 (s, 3H, Me). ^{13}C NMR (25 °C, 67.8 MHz, C$_6$D$_6$): δ 146.77 (Ar), 131.35 (Ar), 129.57 (Ar), 129.38 (Ar), 125.94 (Ar), 54.07 (Ph$_2$CH), 20.98 (Me).

*Synthesis of [(Ar*O)$_3$U(THF)] (**1**).* A 20 mL scintillation vial was charged with a magnetic stirring bar and UI$_3$(THF)$_4$ (1.00 g, 1.10 mmol) in 8 mL of THF. To this dark blue homogeneous solution was slowly added solid NaOAr* (1.53 g, 3.3 mmol) with a spatula. The reaction mixture quickly became dark red, and the reaction was allowed to proceed overnight. The suspension was filtered through a medium porosity frit containing Celite, and all volatiles were removed from the filtrate. The brown crude product was dissolved in benzene and filtered again over Celite and washed with benzene until washing is clear. The residual solvent was removed in vacuo to give a brown solid. Yield: 1.72 g (1.06 mmol, 96%). ^{1}H NMR (25 °C, 270 MHz, C$_6$D$_6$): δ = 11.49, 6.53, 5.83, 4.67, 4.17. IR (KBr pellet, cm^{-1}): 3057 (m), 3024 (m), 2918 (w), 2860 (w), 1598 (m), 1492 (s), 1442 (s), 1288 (w), 1265 (m), 1249 (m), 1209 (m), 1132 (m), 1076 (w), 1029 (m), 914 (w), 862 (m), 842 (m), 759 (w), 750 (w), 702 (s), 678 (m), 621 (w), 603 (m), 563 (w), 532 (w). Anal. Calcd. for $C_{103}H_{89}O_4U$: C, 75.95; H, 5.51. Found: C, 75.91; H, 5.49.

*Synthesis of [(Ar*O)$_3$U] (**2**).* A 20 mL scintillation vial equipped with a magnetic stirring bar was charged with [U(N[SiMe$_3$])$_3$] (525.9 mg, 0.73 mmol) in 5 mL of benzene. To this solution was added dropwise a benzene (3 mL) solution of HOAr* (966.5 mg, 2.19 mmol), and the reaction was allowed to proceed overnight. The resulting brown solution was filtered, washed with 2 mL of benzene, and filtered again through a medium porosity frit. The residual solvent was removed in vacuo to give pure **2**. Yield: 736 mg (0.47 mmol, 65%). ^{1}H NMR (25 °C, 270 MHz, C$_6$D$_6$): δ = 10.91, 8.46, 6.09, 5.77, 4.78, 4.12. IR (KBr pellet, cm^{-1}): 3057 (m), 3024 (m), 2918 (w), 2860 (w), 1598 (m), 1492 (s), 1442 (s), 1288 (w), 1265 (m), 1249 (m), 1209 (m), 1132 (m), 1076 (w), 1029 (m), 914 (w), 862 (m), 842 (m), 759 (w), 750 (w), 702 (s), 678 (m), 621 (w), 603 (m), 563 (w), 532 (w). Anal. Calcd for $C_{99}H_{81}O_3U$: C, 76.38; H, 5.24. Found: C, 76.20; H, 5.09.

*Synthesis of [(Ar*O)$_3$U(O)(THF)] (**3**).* A 20 mL scintillation vial was charged with a magnetic stirring bar and **1** (200 mg, 0.13 mmol) in 3 mL of THF. This solution was fitted with a balloon containing N_2O. After 3−4 min, the reaction mixture turned deep red and was stirred for another 30 min. The volatiles were removed, and the red precipitate was dried in vacuo. Yield: 201 mg (0.13 mmol, 100%). ^{1}H NMR (25 °C, 270 MHz, C$_6$D$_6$): δ = 6.72, 3.44, 2.76, 1.27, 0.97. IR (KBr pellet, cm^{-1}): 3057 (m), 3024 (m), 2958 (m), 2902 (w), 2864 (w), 1599 (m), 1493 (s), 1443 (s), 1288 (w), 1261 (m), 1211 (m), 1184 (m), 1134 (m), 1116(w), 1076 (w), 1029 (m), 916 (w), 862 (m), 844 (m), 760 (w), 743 (w), 702 (s), 682 (m), 621 (w), 603 (m), 563 (w), 534 (w). Anal. Calcd for $C_{99}H_{81}O_3U$: C, 75.21; H, 5.45. Found: C, 75.24; H, 5.56.

X-ray Crystal Structure Determinations. CCDC-919929 (for **1**), CCDC-919930 (for **2**), and CCDC-919931 (for **3A** and **3B**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. Fax: ++44−1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic Details. Black blocks of **1** were grown by slow diffusion of *n*-hexane into a concentrated benzene solution containing a drop of THF, brown prisms of **2** were grown by further concentrating a benzene solution through slow diffusion into 1,2,3,4-tetrahydronaphthalene, and orange plates of **3** were grown from slow diffusion of *n*-hexane into a concentrated benzene solution at room temperature. Crystals were coated with isobutylene oil on a microscope slide. Intensity data were collected using Mo*Kα* radiation (λ = 0.71073 Å, graphite monochromator) either at 100 K on a Bruker Smart APEX 2 diffractometer for compounds **1** and **3** or at 150 K on a Bruker-Nonius KappaCCD for **2**. Data were corrected for Lorentz and polarization effects; semiempirical absorption corrections were performed on the basis of multiple scans using SADABS.[58] All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL NT 6.12.[59] All hydrogen atoms were placed in positions of optimized geometry; their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of 1.2 or 1.5.

Compound **1** crystallized with half a molecule of benzene per formula unit. This disordered solvent molecule was situated on a crystallographic inversion center. SIMU and ISOR restraints were applied in the refinement of the disordered benzene.

Compound **2** crystallized with seven molecules of benzene per formula unit. SIMU restraints were applied for two of the solvate molecules (C301−C306 and C501−C506).

For compound **3**, the crystal under study turned out to be a twin with the twin element being a 179.5° rotation about the real (1 0 0) axis. Twin treatment was carried out using CELL_NOW[60] and TWINABS[61] resulting in a corresponding HKLF 5 file used for the refinement. A significant drop in R values from wR_2 = 0.36 to wR_2 = 0.18 (R1 = 0.15 before to R1 = 0.09 after) was achieved. The asymmetric unit of the unit cell contained two independent molecules of the complex and a total of 3.5 molecules of C_6H_6 and 0.5 molecules of C_6H_{14}. The two by only 50% occupied solvent molecules shared a common crystallographic site. SIMU, ISOR, and some DFIX restraints were applied in the refinement.

Density Functional Calculations. DFT calculations have been performed using the Turbomole[62,63] program package with the exchange-correlation functional by Becke and Perdew (BP)[64,65] and the multipole-accelerated resolution-of-the-identity technique.[66,67] The inability of the chosen functional to describe van der Waals dispersion interactions has been corrected with the third-generation correction scheme due to Grimme et al.,[68] unless noted otherwise. For the full systems, the SV(P) basis set has been used on all atoms except U and the O and C atoms which directly interact with the U center. On these atoms, the TZVPP (triple-ζ plus polarization) basis set was used. For the smaller model system, the TZVPP basis set has been used for all atoms. All basis sets have been taken from the Turbomole library,[69,70] which implies a scalar-relativistic Stuttgart small-core (60 core electron) effective core potential on U,[71,72] and no pseudopotentials on the other atoms. All energies include zero-point vibrational corrections. The complexes have been calculated as spin-quartets; spin contamination was found to be negligible. The orbital plots (Figure 3) have been prepared with the Avogadro program using a contour value of 0.025.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic, crystallographic, and spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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